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

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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
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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\textsubscript{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\textsubscript{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

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 \( \text{•OH} \) 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
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.

<table>
<thead>
<tr>
<th>Process Stage</th>
<th>Parameters</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Filtration area</td>
<td>0.0055 m²</td>
</tr>
<tr>
<td></td>
<td>Pore size</td>
<td>100 nm</td>
</tr>
<tr>
<td></td>
<td>Filtration mode</td>
<td>Dead end</td>
</tr>
<tr>
<td></td>
<td>Pump flow rate</td>
<td>15 mL.min⁻¹</td>
</tr>
<tr>
<td></td>
<td>Flux</td>
<td>180 L.m⁻².h⁻¹</td>
</tr>
<tr>
<td></td>
<td>Backwash frequency</td>
<td>30 min</td>
</tr>
<tr>
<td></td>
<td>Backwash pressure</td>
<td>4 bar</td>
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<tr>
<td>Ozone</td>
<td>Gas flow rate</td>
<td>1.4 L.min⁻¹</td>
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<tr>
<td></td>
<td>Mass concentration</td>
<td>0.11 g.L⁻¹</td>
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<tr>
<td></td>
<td>Production rate</td>
<td>13.05 g.L⁻¹</td>
</tr>
<tr>
<td>BAC</td>
<td>Empty bed contact time</td>
<td>20 min</td>
</tr>
<tr>
<td></td>
<td>Flow rate</td>
<td>15 mL.min⁻¹</td>
</tr>
<tr>
<td></td>
<td>BET surface area of particles</td>
<td>502 m².g⁻¹</td>
</tr>
<tr>
<td></td>
<td>Depth of bed</td>
<td>180 mm</td>
</tr>
</tbody>
</table>

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),
\[ P_{T=20} = P_{abs} \times \frac{\mu_{T=20}}{\mu_{T}} \]  

(1)

\[ \mu_{T} = 1.784 - (0.0575 \times T) + (0.0011 \times T^2) - (10^{-5} \times T^3) \]  

(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 \( \mu_{T} \) 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
which were already temperature corrected using Equation 1 and 2, were used to calculate permeability or specific flux (L.m\(^{-2}\).h\(^{-1}\).kPa\(^{-1}\)) using Equation 3. The normalised permeability, \(J'_s\) was then calculated by dividing \(J/\Delta P\) by the initial or clean membrane condition as shown in Equation 4.

\[
J_s = \frac{J}{\Delta P} \quad (3)
\]

\[
J'_s = \left(\frac{J}{\Delta P}\right) \frac{V_s}{\left(\frac{J}{\Delta P}\right)_0} \quad (4)
\]

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

\[
UMFI = \frac{j'_s^{-1} - 1}{V_s} \quad (5)
\]

If the endpoint chosen was at the completion of the filtration cycle, the UMFI calculated represents the total fouling rate (UMFI\(_T\)) observed in this cycle. In multi-cycle filtration, hydraulically irreversible fouling refers to the fouling that cannot be reversed by backwashing with deionised water. Hydraulically irreversible fouling potentials were
evaluated by UMFIₐ, which was calculated by selecting the endpoint at the beginning of subsequent filtration cycle. Hydraulically reversible fouling potentials UMFIₐ were obtained by subtracting UMFIₐ from UMFIₚ (Huang et al. 2009).

### 2.4 Analytical method

The SE UVA₂₅₄, DOC, colour and constituent molecular weight distribution were determined before and after different treatments. The UVA₂₅₄ 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 KH₂PO₄ + 10 mM Na₂HPO₄) 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).
The fluorescence excitation (Ex) and emission (Em) wavelengths of 280 nm/352 nm (Ex/Em) were used for detection of protein-like compounds, and 330 nm/425 nm (Ex/Em) for detection of humic substances. Polystyrene sulphonate (PSS) molecular weight standards of 3420, 4600, 6200, 15650 and 39000 Da were used to calibrate the LC column.

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

### 3 Results and Discussion

#### 3.1 Raw water characterization

The characteristics of the raw SE used in these experiments is compared to those in the literature in Table 2. The pH, UVA\(_{254}\), conductivity and COD values of the sample were found to be very similar to literature values. The colour, turbidity and the total dissolved solid (TDS) of the sample were found to be lower than the literature values. However, the DOC of the sample was found to be higher than the literature values. The dissimilarity is due to the different types of secondary treatment in different treatment plants.
Table 2: Characteristics of SE used in this work, and comparison to other studies reported in literature.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
<th>Other studies</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.7-7.9</td>
<td>7.3 (Zheng et al. 2010), 7.8 (Kalkan et al. 2011), 7.4-8 (Pramanik et al. 2016)</td>
</tr>
<tr>
<td>UVA&lt;sub&gt;254&lt;/sub&gt;, cm&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>0.218±0.02</td>
<td>0.14 (Zhu et al. 2012), 0.22 (Kalkan et al. 2011), 0.34 (Nguyen and Roddick 2010)</td>
</tr>
<tr>
<td>Turbidity, NTU</td>
<td>0.9±0.1</td>
<td>7.3 (Zhu et al. 2012), 1.5 (Zheng et al. 2010)</td>
</tr>
<tr>
<td>Conductivity, µS cm&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>1665±35</td>
<td>1065 (Nguyen and Roddick 2010), 1620-1950 (Pramanik et al. 2016)</td>
</tr>
<tr>
<td>Total dissolved solid (TDS), mg.L&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>883±5</td>
<td>1038 (Fan et al. 2008)</td>
</tr>
<tr>
<td>Dissolved organic carbon (DOC), mg.L&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>13±0.5</td>
<td>11.7 (Zheng et al. 2010), 11.4 (Kalkan et al. 2011)</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD), mg.L&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>27.9±1</td>
<td>27 (Fan et al. 2008), 52.5 (Wang et al. 2008)</td>
</tr>
</tbody>
</table>

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

![EEM of SE feed solution.](image)

**Figure 2:** EEM of SE feed solution.

### 3.2 Effect of pre-treatment options on feedwater quality

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

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

The removal of DOC by ozonation was low (7%) but ozonation effectively removed 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.
distribution of the ceramic membrane (Ishizaki et al. 1998). As ceramic membranes have higher proportions of smaller pores and less larger pores, greater quantity of high MW biopolymers can be rejected by CMF.

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

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

In the O3+BAC+CMF process, samples taken after the ozonation stage showed that this stage removed a high proportion of biopolymers and HS (100% and 83% respectively).
Samples taken after the BAC stage, however, exhibited lower removals (75% and 66% respectively), indicating that the BAC is adding biopolymers and HS to the process stream. These increases can be attributed to the chemical oxidation and release by the ozone of the adsorbed material and biofilms on the BAC. Ceramic filtration after O3+BAC pre-treatment then removes most of the biopolymers (96%) but does not 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).

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

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

The low fouling nature of the ozone treated water can be seen from the total fouling index data (UMFI_T, Figure 7(b)) and the reversible (UMFI_R) and irreversible (UMFI_I) fouling index data (Figure 8). The UMFI_T for the raw water was found to increase in a linear fashion from 0.14 m^2.L^-1 to 0.73 m^2.L^-1. The BAC and ozone-BAC pre-treated feedwater were found to exhibit a slower increase to 0.34 m^2.L^-1. The UMFI_T of the ozone pre-treated feedwater, however, exhibited a very low increase from 0.02 to 0.03 m^2.L^-1. This can be attributed to the removal of biopolymers and HS (see Table 3). Ozone was found to improve the permeability of ceramic membrane in other studies using ozone combined with ceramic membranes to treat SE (Alpatova et al. 2013, Guo et al. 2014, Karnik et al. 2005, Kim et al. 2008).
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
biopolymers and would logically accumulate on the surface. Laine et al. showed that high MW biopolymers are known to be the major component of the cake layer (Laine et al. 1989). Pore fouling can also occur from materials that pass through the membrane (Polyakov and Zydney 2013).

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

Comparison of Figure 8(b) and Figure 8(d) shows that irreversible fouling is strongly increased after O3+BAC pre-treatment. Nguyen et al. investigated the effect of ozonation followed by BAC filtration on the characteristics and UF performance of activated sludge effluent. Irreversible fouling in their study was reduced after ozonation while BAC filtration did not cause any further decrease in this type of fouling (Nguyen and Roddick 2010). It was identified in a previous study that some microorganisms can be released due to sloughing of the biomass and transport on granular activated carbon fines (Gottinger et al. 2011). Moreover, when drinking water is treated by O3+BAC process, microbial degradation can result in membrane clogging and reduce membrane flux (Jin et al. 2013). It was also observed in another study that ozonation might lyse algae, releasing polymeric substances from algal cell wall (Plummer and Edzwald 2001). In this study, it is therefore possible that the broken pieces of biopolymers created by ozonation were captured at the 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 strengthened 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.
Figure 8: Reversible fouling (UMFI_r) and irreversible fouling (UMFI_i) with a. Raw feedwater; b. BAC pre-treatment; c. O3 pre-treatment; d. O3+BAC pre-treatment.

4 Conclusions

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

BAC pre-treatment improved the overall permeability of the ceramic membranes and the quality of the resulting permeate, primarily due to removal of a large proportion of biopolymer component (~60%) which fouls the membrane by reversible cake layer formation. BAC treatment also removed a large proportion of the humic substances
(~50%), but the net effect was associated with 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

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflection-Fourier transform infrared</td>
</tr>
<tr>
<td>BAC</td>
<td>Biological activated carbon</td>
</tr>
<tr>
<td>BDOC</td>
<td>Biodegradable dissolved organic carbon</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>BOD</td>
<td>Biological oxygen demand</td>
</tr>
<tr>
<td>CMF</td>
<td>Ceramic membrane filtration</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>DBP</td>
<td>Disinfection byproduct</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>DOM</td>
<td>Dissolved organic matter</td>
</tr>
<tr>
<td>EBCT</td>
<td>Empty bed contact time</td>
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<tr>
<td>EEM</td>
<td>Excitation-emission matrix</td>
</tr>
<tr>
<td>Em</td>
<td>Emission</td>
</tr>
<tr>
<td>Ex</td>
<td>Excitation</td>
</tr>
<tr>
<td>HPLC-SEC</td>
<td>High performance liquid chromatography – size exclusion</td>
</tr>
<tr>
<td>LC</td>
<td>Liquid Chromatography</td>
</tr>
<tr>
<td>MF</td>
<td>Microfiltration</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural organic matter</td>
</tr>
<tr>
<td>PDA</td>
<td>Photodiode array detector</td>
</tr>
<tr>
<td>PVDFI</td>
<td>Polyvinylidenefluoride</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse osmosis</td>
</tr>
<tr>
<td>TDS</td>
<td>Total dissolved solid</td>
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540  TMP: Trans-membrane pressure
541  TOC: Total organic carbon
542  UF: Ultrafiltration
543  UMFI: Unified membrane fouling index
544  UMFI_I: Hydraulically irreversible fouling potential
545  UMFI_R: Reversible fouling potential
546  UMFI_T: Total fouling index
547  UV: Ultra violate

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of DBP precursors, dicloxacillin and ceftazidime. Separation and Purification Technology 107, 179-186.


Gaulinger, S. (2007) Coagulation Pre-Treatment for Microfiltration with Ceramic Membranes, TECHNEAU.


Secondary effluent treatment by MF ceramic membrane

Normalized permeability

Time (min)

- Raw feed
- BAC
- O3
- O3+BAC