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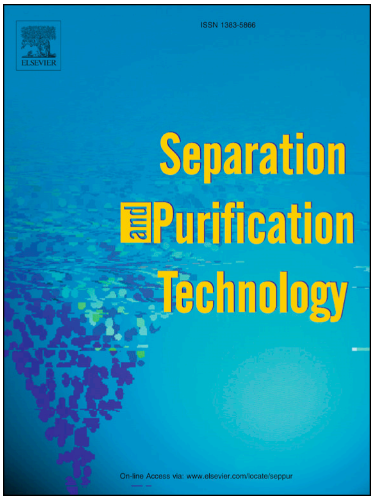

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Comparison of the effects of ozone, biological activated carbon (BAC) filtration and combined ozone-BAC pre-treatments on the microfiltration of secondary effluent

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ABSTRACT

The effects of ozonation (O_3), biological activated carbon (BAC) filtration and combined O_3 and BAC (O_3-BAC) pre-treatments on the microfiltration (MF) treatment of secondary effluent using a polyvinylidene fluoride (PVDF) membrane were studied. The permeability of the membrane was quantified and compared to the removal of humic substances (HS), biopolymers (BPs), dissolved organic carbon (DOC), absorbance at 254 nm (UVA_{254}), and colour by these pre-treatments. The apparent molecular weight distribution (AMWD) was determined to further characterise the secondary effluent before and after each treatment. The unified membrane fouling indices (UMFI) after O_3, BAC and the O_3-BAC pre-treatments were also determined to evaluate the relative effectiveness of different pre-treatments on fouling reduction. The overall removal of colour and UVA_{254} in the MF of the O_3 pre-treated secondary effluent was found to be 83% and 52% respectively, compared to 75% and 47% respectively for MF with BAC pre-treatment and 38% and 14% respectively without pre-treatment. The O_3-BAC pre-treatment yielded the highest normalized permeability after 100 minutes of operation (0.76) and the lowest UMFI (1×10^{-3} m^2/L). This result indicates that the O_3-BAC pre-treatment could reduce the frequency of chemical cleaning and may extend the membrane lifetime.

Keywords: ozone, BAC filtration, PVDF membrane, secondary effluent.

1 Introduction

Population growth and climatic changes are placing increasing pressure on our fresh water resources. The reclamation and reuse of biologically treated secondary effluent wastewater for irrigation purposes can be one of the most effective ways for preserving our limited resources of fresh water [1]. This effluent, however, cannot be reused directly as it contains concentrations of dissolved and macromolecular organic substances, inorganic compounds and pathogens that may pose risks to human health and the environment [2]. Further treatment to mitigate these risks is required before secondary effluent is used for irrigation in agriculture.

Low pressure membrane technologies (*e.g.*, microfiltration (MF) and ultrafiltration (UF) membranes) are becoming popular for the treatment of wastewater due to their superb efficacy and small footprint, with good reliability in operation and low cost [3-6]. These processes can be used for the required pathogen reduction, but the efficiency and performance of these processes can be severely decreased by fouling from wastewater constituents. Fouling results from the deposition of particles or compounds on the external surface, at the pore openings or within its pores, and increases the operational costs due to added cleaning and operational procedures [7-10]. Several pre-treatment options, such as ozonation, coagulation, biological activated carbon (BAC) filtration, powdered activated carbon, anion exchange or slow sand filtration [11] can be coupled with filtration to reduce fouling and improve performance.

Ozone oxidizes electron-rich compounds containing carbon-carbon double bonds and aromatic alcohols [12]. The loss of aromaticity and depolymerization results in a strong and rapid decrease in color, odor, taste and UV absorbance at 254 nm (UVA_{254}) in drinking water production. It also reduces the high apparent molecular weight fraction of natural organic matter. UVA_{254} represents the existence of unsaturated carbon bonds including aromatic compounds. These aromatic compounds are generally recalcitrant to biodegradation and a decrease in UVA_{254} often results in an increase in biodegradability [13, 14]. Ozone treatment has also been applied to secondary effluent [15]. Paraskeva *et al.* (1998) found that ozone removed biological oxygen demand (BOD), chemical oxygen demand (COD) and color and increased the dissolved oxygen (DO) concentration in secondary effluent [16]. The increased biodegradability by ozonation, however, can be removed by subsequent BAC filtration [17, 18].

The removal of contaminants using BAC filtration can be attributed to the adsorption on the activated carbon [19] and biodegradation due to microbial activity [20-22]. Thus organic matters like micro-pollutants and halogenated hydrocarbons, and taste and odour compounds can be removed by BAC [23]. Moreover the BAC does not require disposal of spent carbons as they can be used over several reactivation cycles [24]. The flux of MF and UF can be markedly increased by BAC filtration as it can remove very high molecular weight substances such as biopolymer (BPs) through biodegradation and adsorption of those molecules on the biofilm [11, 25, 26].

When BAC is combined with the ozonation process, this results in higher reduction of biological regrowth potential and better removal of degradation by-product precursors [27, 28]. Ozone transforms larger molecules of dissolved organic matter into smaller molecules, consequently increasing their biodegradability [29, 30]. As the biodegradable dissolved organic carbon produced in the ozonation process can be removed by a following BAC treatment, combined ozonation and BAC treatment is suggested for the drinking water treatment by several studies [17, 24, 28, 31-39].

Moreover, it has already been reported in a study [40] that the O_3-BAC has the lowest capital and operational cost compared to other pre-treatment options.

BAC treatment in combination with ozonation has also been used in wastewater treatment [41]. Wang *et al.* (2008) investigated the degradation characteristics of domestic wastewater secondary effluent by a combined ozonation and BAC process and found the removal efficiencies of COD, NH_3–N, total organic carbon (TOC), UVA_{254} and colour of the secondary effluent reached 58, 90, 25, 75 and 90% respectively [42]. In another study conducted by Reungoat *et al.* (2011), a combination of ozonation and BAC filtration was found to achieve 50% removal of DOC, more than 90% removal of a wide range of trace organic chemicals (TrOCs), 70% removal of non-specific toxicity and more than 95% reduction of estrogenicity [43].

Although ozonation followed by BAC treatment (O_3-BAC) seems to be an effective treatment process, the effect of this treatment train on the performance of MF has not been well established. Nguyen *et al.* (2010) investigated the effect of O_3-BAC on the UF performance of a highly coloured activated sludge effluent [18]. It was reported that the fouling of 0.05 µm polyvinylidene fluoride (PVDF) membrane was reduced after ozonation due to partial oxidation of the membrane foulants. Further improvement in UF after BAC was attributed to the reduction in suspended solids level in ozonated effluent. Farr *et al.* (2007) reported a comparative study of drinking water treatment using O_3-BAC-membrane and membrane-O_3-BAC processes [44]. The O_3-BAC-membrane process was found as the ideal configuration by removing 90% of the micropollutants from Lake Ontario water prior to ultrafiltration membrane treatment. Another study investigated the effect of O_3-BAC pre-treatment prior to ultrafiltration processes treating surface water from Lake Ontario [45]. It was concluded that ozone pre-treatment increased the active biomass in the BAC column and improved permeability of 0.02 µm PVDF membrane.

In our previous study, the effect of O_3-BAC on MF using a ceramic membrane was investigated for the treatment of secondary effluent and it was found that ozone pre-treatment improved flux through the ceramic membrane [46]. This study is aimed to compare the effect of O_3-BAC treatment on a PVDF membrane for the treatment of secondary effluent with our previous study with a similar pore sized (0.01 µm) ceramic membrane. More over, the individual impact of ozonation, BAC filtration pre-treatments were compared with the combined O_3-BAC pre-treatment using a PVDF microfiltration membrane.

2 Materials and methods

2.1 Raw water

Secondary effluent was collected from Melbourne Water’s Western Treatment Plant (WTP), Werribee, Victoria, Australia, where more than 50% of Melbourne’s sewage is treated by a series of lagoons and activated sludge plants. The sample was collected from the maturation lagoon overflow of WTP before the UV disinfection and chlorination. The sample was stored at 4°C. Prior to all tests, the stored sample was warmed to room temperature (22±1°C) and pre-filtered by 10 µm paper filters (Advantec 5A) in order to remove the particulate matters from it.

2.2 Experimental equipment

Figure 1 represents a schematic of the experimental equipment. Ozone was generated using an A2Z ozone generator. Pure oxygen was supplied into the generator at a flow rate of 2 L (NTP)/min. The generated ozone was injected in the feed sample at a flow rate of 1.4 L(NTP)/min. The BAC particles (Acticarb BAC GA1000N) were obtained from an operating ozone – BAC system in Castlemaine water reclamation plant, Castlemaine, Australia [47]. A BAC column with a height of 180 mm and diameter of 50 mm was used in this test. Prior to packing the BAC column, the activated carbon particles (BET surface area of 502 m^2/g, 30 Å pore size) were manually inoculated with the secondary effluent. The sample were fed into the BAC column at a flow rate of 15 mL/min. The BAC column had an empty bed contact time (EBCT) of 20 min. In order to reduce physical clogging of the media, the column was backwashed for 15 minutes every 10 days.

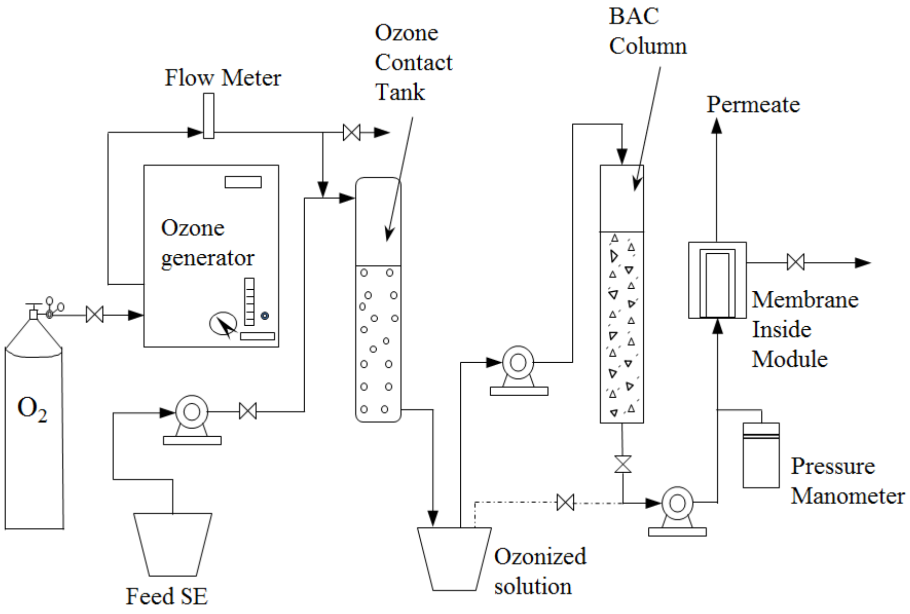


Figure 1: *Ozone-BAC-Polymeric membrane filtration rig.*

A single hollow fibre membrane filtration apparatus with 100 nm hydrophilic PVDF membrane was used to treat the secondary effluent. The membrane element had dimensions of 0.65 mm outer diameter and 0.48 mm inner diameter. The length of the membrane was 90 cm and the total filtration surface area was 1.84×10^{-3} m^2. Stainless steel fittings (Swagelok) and high pressure tubes were used for connecting the membrane equipment together. The membrane feed solution was pumped using a low speed piston pump (Fluid Metering, Inc, QG 150) at a flow rate of 2 mL/min. A digital manometer (TPI 665) was used to monitor pressure. The specification of the ozone generator, BAC column and polymeric membrane, and the operating conditions used in this study are shown in Table 1.

Table 1: Operating conditions of different treatment steps, microfiltration (MF), Ozonation (O_3) and biological activated carbon (BAC).

Treatment Step	Parameters	Conditions
MF	Filtration area	0.00184 m^2
	Pore size	100 nm
	Filtration mode	Dead end
	Pump flow rate	2 mL/min
	Flux	65 $L \cdot m^{-2} \cdot h^{-1}$
O_3	Gas flow rate	1.4 L/min
	Mass concentration	0.11 g/L
	Production rate	13.05 g/L
BAC	Empty bed contact time	20 min
	Flow rate	15 mL/min
	BET surface area of particles	502 m^2/g
	Pore size	30 Å
	Depth of bed	180 mm

2.3 Experimental procedure

The secondary effluent was fed to the PVDF membrane in four different arrangements: membrane only (MF); BAC followed by membrane (BAC-MF); ozone followed by membrane (O_3-MF); and ozone followed by BAC then followed by membrane (O_3-BAC-MF). The membrane was operated in outside-in mode in a conventional pressurized configuration using a direct filtration (dead-end) mode. Each filtration was conducted for at least two hours. The rise in pressure was temperature corrected to a reference temperature of 20°C using Equation 1 and Equation 2 [48],

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

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

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. The water quality parameters before and after each filtration steps were measured by collecting samples at each step. The measured residual ozone was always 0.3 ~ 0.8 mg/L prior to BAC column or polymeric membrane intake. This was controlled by keeping the ozonated secondary effluent at rest for at least 30 minutes prior to BAC or polymeric membrane filtration.

Fouling potential of the MF polymeric membranes were quantified using the unified membrane fouling indices (UMFI). The temperature corrected (using Equation 1 and 2) TMP data points were used to calculate permeability or specific flux ($L.m^{-2}.h^{-1}.kPa^{-1}$)

using Equation 3 [46]. The normalised permeability, J'_s was then calculated using Equation 4.

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

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

Where J is the membrane flux ($L.m^{-2}.h^{-1}$), J_s is the membrane permeability ($L.m^{-2}.h^{-1}.kPa^{-1}$), V_s is the specific volume ($L.m^{-2}$). To determine the UMFI experimentally, the normalized specific flux was obtained at given specific permeate volume. The procedure is described in in elsewhere [49]. The UMFI was calculated by dividing the difference in $1/J'_s$ by the difference in V_s measured between the starting of a filtration cycle to a particular endpoint as shown in Equation 5.

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

The calculated UMFI in Equation 5 represents the total fouling rate ($UMFI_T$) of a filtration cycle if the endpoint selected was at the completion of that filtration cycle [49].

2.4 Analytical method

The quality of secondary effluent samples before and after different treatments were analysed for UVA_{254}, DOC, colour and molecular weight distribution. A HACH spectrophotometer (DR 5000) with a 1 cm quartz cell was used to measure the UVA_{254}. A SHIMADZU Total Organic Carbon Analyzer (TOC-VCSH) equipped with an auto-sampler was used to measure the DOC. All samples were filtered through 0.45 µm membrane filter prior to the DOC analysis. A HACH spectrophotometer (DR 5000) with a 10 cm quartz cell was used to measure the colour of the sample. A Perkin-Elmer LS-55 Fluorescence Spectrometer was used to measure the excitation-emission spectrums of the sample water. The spectrometer used a xenon excitation source. Scans were carried out from 200 nm to 550 nm at increments of 5 nm. A total 70 numbers of scans/sample was conducted in the spectrometer. Molecular weight distributions of the wastewater components by Liquid Chromatography (LC) analyses were performed with a PDA and fluorescence detector in series. The method is described in detail in elsewhere [46].

The Indigo Method [50] was used to determine the concentrations of dissolved ozone in the experimental reaction solutions. The principle is that the indigo reagent will be decolorized by ozone and 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. After reaction of indigo reagent and the sample, the residual ozone at the sample was measured by subtracting the absorbance of indigo trisulfonate from that of an ozone free blank. A DR 5000 spectrophotometer (HACH) was used to measure the absorbance at 600 nm.

3 Results and discussions

3.1 Raw water characterization

The characteristics of the secondary effluent used in this work are shown in Table 2 [46].

Table 2: Characteristics of secondary effluent used in this work.

Parameters	Values
pH	7.7-7.9
UVA_{254}, cm^{-1}	0.218±0.02
Colour, Pt-Co	35-37
Turbidity, NTU	0.9±0.1
Conductivity, µS/cm	1665±35
Total dissolved solid (TDS), ppm	883±5
Dissolved organic carbon (DOC), mg/L	13±0.5
Chemical oxygen demand (COD), mg/L	27.9±1

The fluorescence excitation-emission spectrums of the secondary effluent used in this study were analysed elsewhere [46]. It was observed that, the secondary effluent exhibited at least two peak locations (280 nm/352 nm and 330 nm/425 nm, Ex/Em). Based on the analysis [46], the peak location with excitation and emission wavelengths of 280 and 352 nm was selected for detecting protein-like substances and the peak location with excitation and emission wavelengths of 330 and 425 nm was selected for detecting fulvic-like humic substances.

3.2 Effect of BAC, ozonation, or membrane treatment on secondary effluent

Figure 2 shows the average individual removal percentages of DOC, UVA_{254} and colour by MF, BAC filtration and ozone treatment (O_3). It is evident from Figure 2 that both BAC and O_3 were effective for removal of colour and UVA_{254} absorbance compared to the MF treatment. This removal can be attributed to the oxidative degradation of coloured compounds in the secondary effluent (*i.e.*, compounds with conjugated carbon-carbon double bonds or aromatic rings, particularly humic substance (HS) to more colourless materials, and to the adsorption and biodegradation of coloured organic compounds by BAC filtration. This confirms the ability of ozone treatment to improve the aesthetics of treated water [18, 51-53]. However, with respect to DOC removal, ozone treatment showed no substantial beneficial effects. The significant UVA_{254} reduction (47%) by BAC filtration can generally be attributed to the removal of HS [11]. The DOC reduction was generally low (less than 14%). These results are similar to those found in other studies. Li *et al.* (2005) studied two parallel BAC filters to treat secondary effluent and observed an average DOC removal efficiency of 14% [54].

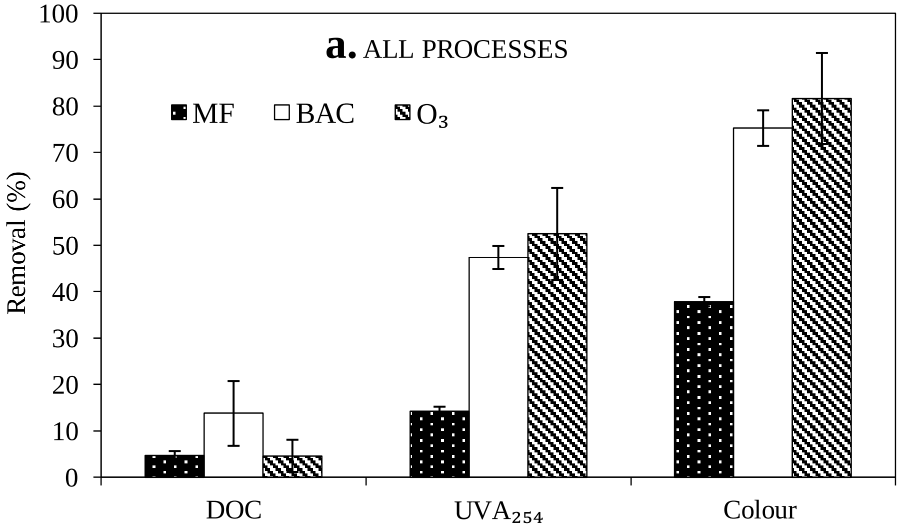


Figure 2: *Removal of DOC, UVA_{254} and colour of secondary effluent by MF, BAC, and O_3 (Temperature: 22±1°C).*

3.3 Effect of different pre-treatment options on MF treatment of secondary effluent

Figure 3a shows the removal percentages of DOC, UVA_{254} and colour from secondary effluent by the MF alone, BAC-MF, O_3-MF and O_3-BAC-MF options. Overall, the O_3-MF option was the most efficient in removing UVA_{254} (60%) and colour (91%). All the treatment options yielded poor DOC removal efficiency.

Figure 3b shows the removal percentages of DOC, UVA_{254} and colour from secondary effluent by the unit contribution of each stage in the BAC-MF option. BAC pre-treatment removed 44% of UVA_{254} and the polymeric membrane did not further reduce the UVA_{254}. The DOC and colour removal by BAC filtration was 7% and 74% respectively. Kirists *et al.* (2001) observed a 4% reduction of DOC by BAC filtration of Lake Michigan water (LMW), obtained from the crib of the South Water Production Plant (Chicago, IL) [55]. Pramanik *et al.* (2014) studied the BAC filtration as a pre-treatment for reducing the organic fouling of a MF membrane in the treatment of secondary effluent and found the reduction in colour by BAC filtration was 78% [11].

Figure 3c shows the removal percentages of DOC, UVA_{254} and colour by the O_3-MF treatment option. The reduction of DOC by ozonation was low (7%), however, ozonation effectively reduced UVA_{254} (59%) and colour (85%) as observed by others before. The addition of a membrane process did not improve DOC removal over that by ozonation. Previous investigations have shown that ozonation was highly effective in breaking unsaturated bonds, causing rapid decolorization of wastewater. However, this decolourisation is due to the oxidation of electron-rich compounds containing carbon-

carbon double bonds and aromatic alcohols [12]. The carbon content as measured by DOC thus remains largely unaltered by this treatment. This data is similar to that in previous studies [56]. Dow *et al.* (2013) investigated the performance of ceramic MF membrane to treat secondary effluent with ozone and/or coagulation pre-treatment [51] and found that ozone reduced DOC, colour and UVA_{254} by 5%, 52% and 85% respectively.

Figure 3d represents the removal percentages of DOC, UVA_{254} and colour by the O_3-BAC-MF option. The negative value in the removal percentages of UVA_{254} for the ozonized secondary effluent through BAC filtration was due to the increase in UVA_{254}. The rises in the UVA_{254} may be due to the release of UVA_{254} compounds from the BAC filtration column. This was determined by Bridgeman *et al.* (2014) using carbon isotopes analysis, where a new source of organic carbon was added during the water treatment processes, for example, from biofilms or from the abrasion of filter media [57]. Li *et al.* (2017) also observed that the BAC bed might release certain highly polar or high molecular weight compounds while tracking changes in composition and amount of dissolved organic matter throughout drinking water treatment plants [58]. Again, 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 compared to when BAC is used without ozone (Figure 3b).

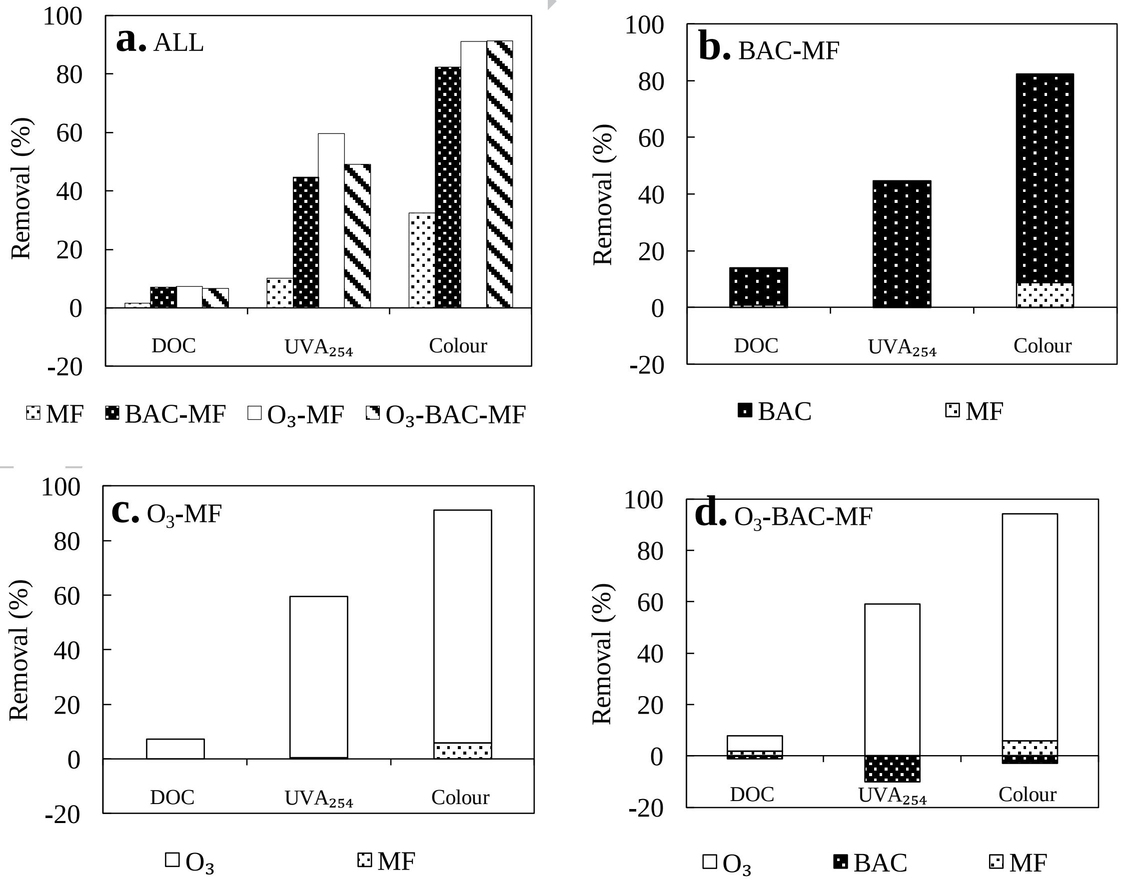


Figure 3: *Removal of DOC, UVA_{254} and colour of secondary effluent by* ***a.*** *all four sequences using polymeric membrane; unit contribution for each stages of*

b. *BAC-MF;* ***c.*** *O_3-MF;* ***d.*** *O_3-BAC-MF system (Temperature: 22±1°C); Flux: 180 L·m^{-2}·h^{-1}).*

Figures 4(a-d) represent the fluorescence spectrum at 280 nm/352 nm (Ex/Em) for the secondary effluent with different treatment options. The fluorescence spectrum at 280 nm/352 nm (Ex/Em) in Figures 4(a-d) was selected for protein like substances. A small peak is observed for the secondary effluent at approximately 43 kDa (Figures 4(a-d)). Generally, the BPs have a molecular weight (MW) range of greater than 20 kDa [18, 59]. Moreover, Myat et al. (2012) observed a peak at 50 kDa (fluorescence spectrum at 278 nm/304 nm (Ex/Em)) and attributed this to protein like BPs [60]. The peak detected at 43 kDa can thus, be attributed to BPs. The removal of BPs by the different process steps, calculated from the peak areas in Figures 4 are shown in Table 3.

Figures 5(a-d) represent the fluorescence spectrum at 330 nm/425 nm (Ex/Em) for the secondary effluent with different treatment options. The fluorescence spectrum at 330 nm/425 nm (Ex/Em) in Figures 5(a-d) was selected for fulvic-like HS. In Figures 5(a-d), multiple peaks are observed in the range of 0 to 5000 Da. Generally, the HS are ranged from 0 to 5000 Da [61]. The peaks observed in Figures 5(a-d) are thus, indicating the presence of HS in the secondary effluent. The removal of HS by the different process steps, calculated from the peak areas in Figures 5, are shown in Table 3.

As shown in Figure 4a, the BPs detected at 280 nm/352 nm (Ex/Em) were significantly removed by the MF (98% removed, Table 3) where, HS (Figure 5a) detected at 330 nm/425 nm (Ex/Em) were only slightly removed by the membrane (only 8% removed, Table 3). Pramanik *et al.* (2015) found that BPs were rejected more (20%) than HS (10%) using a 0.1 µm hydrophilic PVDF membrane [25]. In our previous work with a similar pore sized ceramic membrane [46], the removal of BPs and HS by the ceramic membrane were almost similar (97% removal of BPs and 7% removal of HS) to the removals by a PVDF membrane in this study.

In the BAC-MF process, a partial reduction of BPs (63%) (Figure 4b) and HS (49%) (Figure 5b) was observed by BAC filtration. The high MW BPs are expected to be biodegraded by microorganisms formed in the BAC and the HS to be adsorbed by the activated carbon of the BAC [11, 26]. A previous study has shown that the BAC treatment leads to the reduction in the fluorescent organic matter in all regions due to the adsorption and breakdown of fluorescent molecules [62]. Following the BAC, MF effectively removed BPs but resulted in little additional removal to HS. A similar trend on the removal of BPs and HS was observed by our previous study using tubular ceramic membrane [46]. Pramanik *et al.* (2016) also studied the effect of BAC pre-treatment in the 0.1 µm hydrophilic PVDF membrane MF of biologically treated secondary effluent and found that high MW BPs and HS were retained by the membrane [26].

In the O_3-MF process (Figure 4c), a significant amount of BPs were removed by ozonation. This was found in previous studies [63]. The removal effect of ozone is attributed to the transformation of BPs into smaller compounds [64]. However, ozonation also reduced significant quantity of HS (Figure 5c) which was observed in previous studies [65]. The significant removal of this fraction is believed to be due to the high aromaticity of HS [66]. Following ozonation, an increase in BPs and HS quantity were observed for the O_3-MF option. This could be the result of ozone oxidation of biopolymers and HS that are adsorbed in the membrane equipment, resulting in their liberation. In our previous study with a similar pore sized ceramic membrane [46], the removal of BPs after ceramic membrane filtration was lower (86%) than that of after ozonation (100%). This was attributed to the combination of some of the degraded biopolymer components to form larger MW species while forced through the ceramic membrane pores [67].

In the O_3-BAC-MF process (Figure 4d), BPs and HS were removed significantly by the ozonation. A slight increase in the BP (17%) and clear increase in the HS quantities (34%) were observed in the BAC effluent. Biopolymers were reduced by the subsequent MF and the HS remained unchanged. This can be attributed to the order of the process stages. The presence of ozone prior to BAC filtration is expected to oxidize the BAC particles and thus release adsorbed BP and HS, decreasing removal in the BAC effluent. This may be due to the break-through of some turbidity particles, or it may be caused by the aged biofilm fragments and/or powdered carbon particles in the BAC bed. A similar trend on the removal of BPs and HS were observed in our previous study conducted using a 100 nm ceramic membrane [46]. It should be noted that chemical oxidation is not harmful to the BAC process. Indeed, it is often practiced to regenerate the BAC. Regeneration in BAC is a process of increasing the adsorptive capacity of the carbon by chemical oxidation of adsorbed material, steam to drive off the adsorbed material, solvents and biological conversion [20].

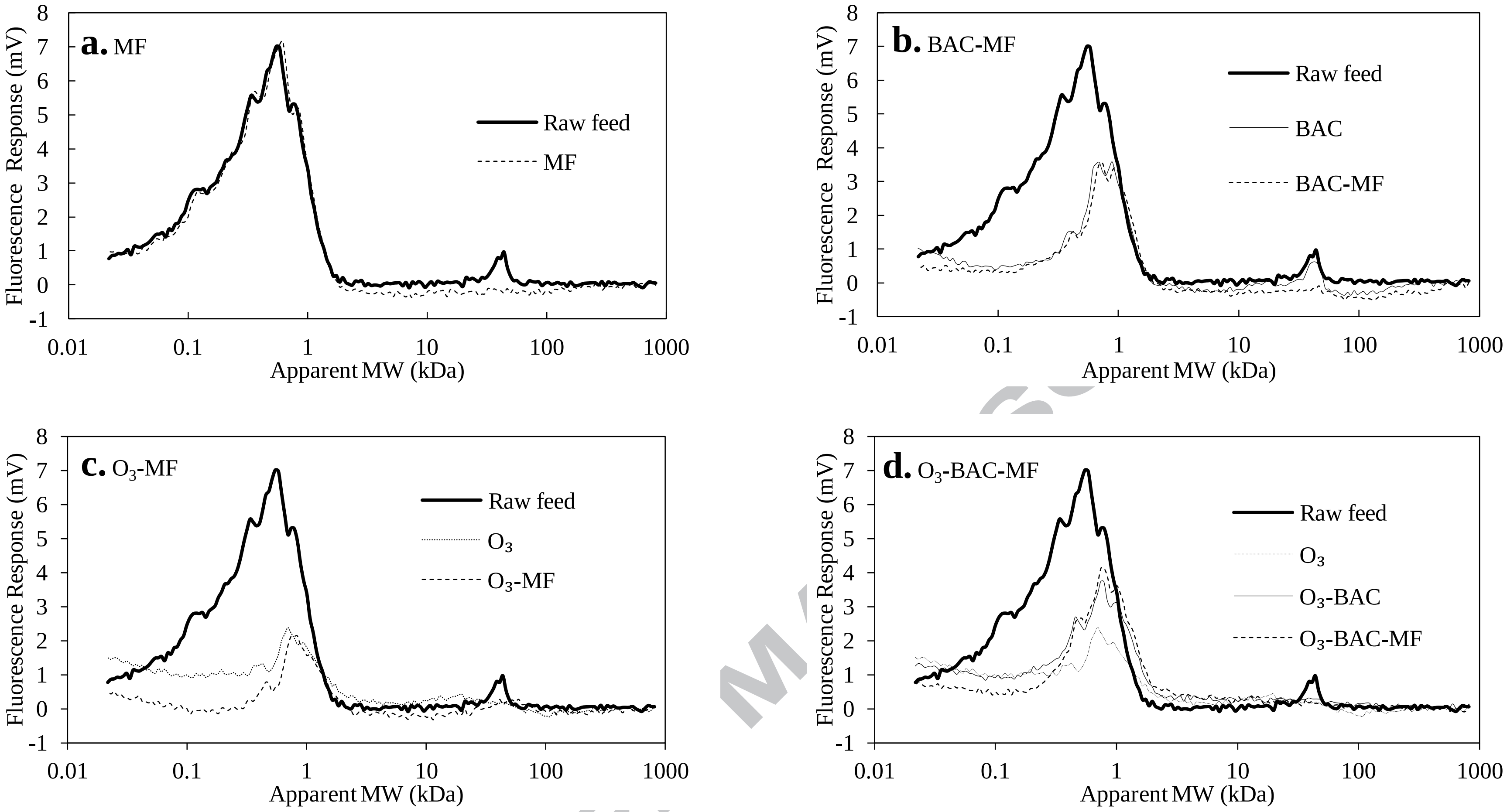


Figure 4: *Fluorescence spectrum at 280 nm/352 nm (ex/em) for secondary effluent treated by* ***a.*** *MF alone;* ***b.*** *BAC-MF;* ***c.*** *O_3-MF;* ***d.*** *O_3-BAC-MF system (Flux: 180 L·m^{-2}·h^{-1}; Temperature: 22±1°C).*

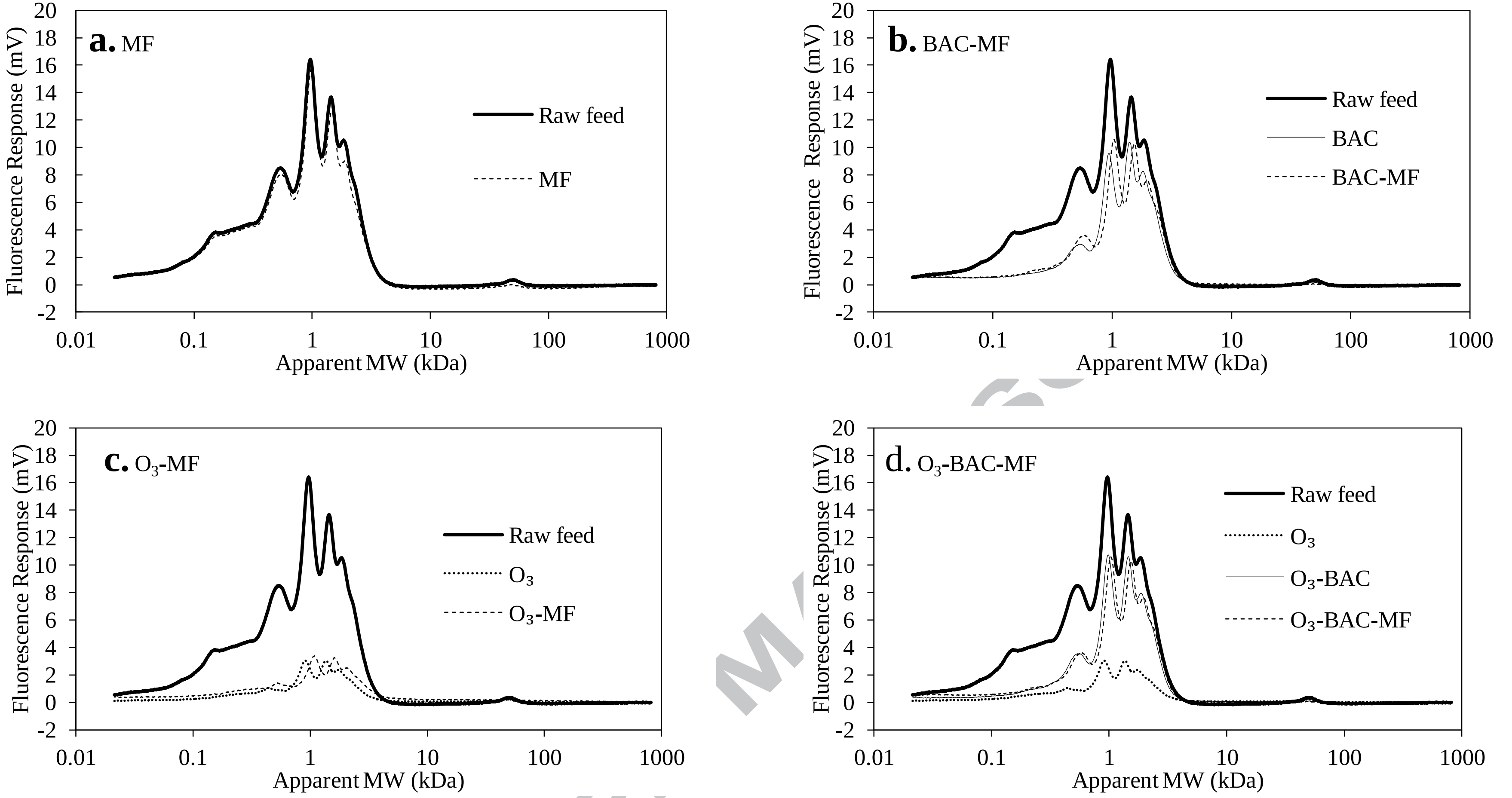


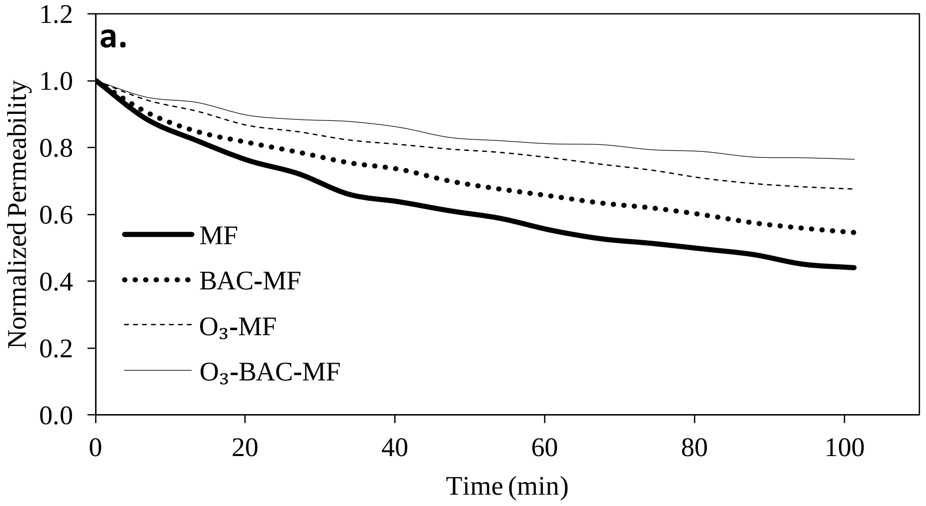
***Figure 5:** Fluorescence spectrum at 330 nm/425 nm (ex/em) for secondary effluent treated by **a.** MF alone; **b.** BAC-MF; **c.** O_3-MF; **d.** O_3-BAC-MF system (Flux: 180 $L \cdot m^{-2} \cdot h^{-1}$; Temperature: 22±1°C).*

Table 3: BPs and HS removal (%) relative to the feed water quality during different treatment steps (calculated by peak area from Figures 4 and 5).

Process	Process Step	BPs Removal (%) (40 kDa-45 kDa) Ex/Em : 280/352 nm	HS Removal (%) (0.1 kDa-5.5kDa) Ex/Em : 330/425 nm
MF	MF	98	8
BAC-MF	BAC	63	49
	BAC + MF	99	51
O_3-MF	O_3	100	82
	O_3 + MF	98	77
O_3-BAC-MF	O_3	100	82
	O_3 + BAC	83	58
	O_3 + BAC + MF	100	57

3.4 Effect of different pre-treatment options on the membrane permeability

One of the major challenges of membrane filtration processes is to minimise fouling in order to maintain a high membrane permeability. Figures 6a represent the normalized permeability with time after an initial stabilisation period of approximately 20 minutes. Figure 6b represents the unified membrane fouling index. It can generally be seen that pre-treatment of the secondary effluent gives rise to higher permeability. The most effective option was the O_3-BAC-MF option. This increased the permeability after 100 minutes of operation from 0.44 (no pre-treatment) to 0.76. The O_3 treatment on its own was more effective than BAC pre-treatment on its own. The O_3-MF treatment only increased the permeability at 100 minutes to 0.67, while the BAC-MF treatment increased permeability to 0.55. The fouling index (Figure 6b) for MF without pre-treatment was 4 times that of the most effective treatment (O_3-BAC-MF).



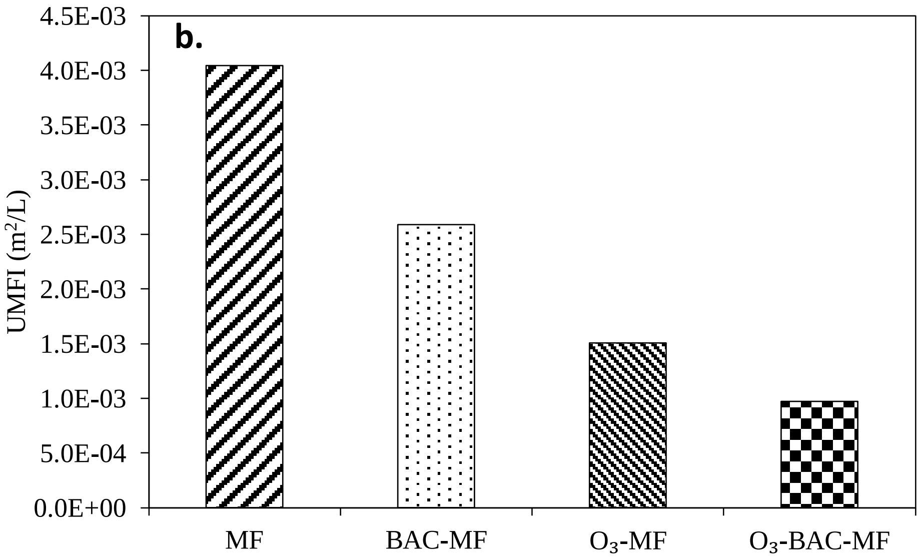


Figure 6: a. *Normalized permeability with time and* ***b.*** *unified membrane fouling index (UMFI) during treatment of secondary effluent by MF, BAC-MF, O_3-MF and O_3-BAC-MF system (Flux: 180 $L\cdot m^{-2}\cdot h^{-1}$; Temperature: 22±1°C).*

Fouling due to BP cake layer formation on the membrane surface was found in other studies [11, 68]. Fouling can also occur from smaller materials, such as HS, that pass through the membrane [69]. Laine *et al.* (1989) showed that high MW BPs are the major component of the cake layer in the filtration of feedwaters containing these constituents [70].

The increase in permeability resulting from BAC pre-treatment can be attributed to the reduction of BPs (63%) and HS (49%) associated with this process (see Table 3). Similar results were found in a previous study where BAC pre-treatment improved the flux of a 0.1 µm poly-vinylidene fluoride membrane by removing organic foulants from the biologically treated secondary effluent [11].

Ozonation pre-treatment (O_3) was found to result in better normalized permeability (0.67) than the BAC pre-treatment (0.55). This can be attributed to the higher removal of BPs (100%) and HS (82%) than the BAC pre-treatment (63% and 49% respectively). The effectiveness of ozone in the improvement of permeability of membranes is well known [52, 71-73]. Generally high MW compounds are most reactive with ozone [74, 75]. Ozonation transformed the higher MW BPs into smaller compounds [64]. Ozone is also known to decompose the HS into low MW substances [12, 76, 77]. Previous studies show that ozonation could also alter the surface charge (or zeta potential) and flocculation of organic particles in water and wastewater [78]. Changes in particle size and zeta potential may cause changes in the cake permeability in MF and therefore improve the membrane flux.

The correlation between high membrane permeability and high BP and HS removal in the membrane process feed stream seen in the BAC-MF and O_3-MF option is not evident for the O_3-BAC-MF option. This system exhibited the highest normalized permeability (0.76), despite the poorer feedwater quality than the other two systems involving pre-treatment (see Table 3). The ozone treatment initially improved the quality of secondary effluent by reducing significant amount of BPs (100%) and HS (82%), but the following BAC treatment worsened the quality of the feedwater to the membrane (83% BP removal, 58% HS removal). The higher permeability for the O_3-BAC-MF system than for the O_3-MF system (see Figure 6a) suggests that the released BPs, HS components and breakdown products from the action of ozone on the BAC have low fouling properties, and somehow mildly decrease the overall fouling properties of the secondary effluent. The mechanism of this mild decrease in the overall fouling properties of the secondary effluent is not known but may involve decreased interaction between BP and HS units, resulting in reduced caking on the membrane. However, in our previous study with a 0.1 µm ceramic membrane, the inclusion of BAC between ozone and ceramic membrane (O_3-BAC-CMF) was detrimental, which resulted in poorer permeability in O_3-BAC-CMF system than the O_3-CMF system. The poorer permeability in the O_3-BAC-CMF system was attributed to the chemical oxidation effect on the BAC biofilm and adsorbed components, which led to formation of foulants on the membrane surface. The difference in behaviour between PVDF and the ceramic membrane may be attributed to the difference in pore size distribution and/or to specific foulant-ceramic membrane interactions.

This study focused mainly on the effects of ozonation and BAC filtration on the flux and rejection behaviour of MF membranes treating secondary effluent. This study also uncovered some interesting findings while confirmed some previous works. It is observed that the O_3-BAC pre-treatment allows the microfiltration PVDF membrane to be operated with a more stable permeability condition compared to the no pre-treatment option, BAC filtration and O_3 pre-treatment option. The flux improvement implies that the combined pre-treatment would significantly reduce membrane fouling, thereby lowering the energy requirement for the membrane filtration process. Such a hybrid treatment train (O_3-BAC-MF) may be suitable for the upgrade of conventional wastewater treatment plants in dealing with micro-polluted water sources for better supply of reclaimed water. The overall UMFI for the combined O_3-BAC pre-treatment was reduced to 24% to the no pre-treatment option. This is similar to a study conducted by Nguyen *et al.* (2010) where the combined O_3-BAC pre-treatment was found to reduce overall UMFI by 51%. However, the O_3-MF treatment was found to be the most efficient option in removing DOC, UVA_{254} and colour. The effectiveness of O_3 in removing DOC, UVA_{254} and colour was found in previous study as well [51]. The release of fouling components from the BAC bed was observed in previous studies [57, 58] however, their lower fouling potential in microfiltration PVDF membrane was unknown.

The finding from this study is useful for water treatment industries in providing evidence of superior performance when locating BAC columns after O_3 treatment process despite of the released microbial fouling components from BAC beds. The full high flux effect from ozone however is well known to occur in conjunction with coagulation, which has been dosed just after the injection of ozone in site trials by others. Further, the study was limited to single filtration cycle. Therefore further work could consider a continuous process of several filtration cycles with subsequent backwashing. This could also be undertaken using a pilot scale filtration system, particularly which includes coagulation.

4 Conclusions

This study has shown that O_3 or BAC pre-treatment can results in beneficial membrane permeability increases in the MF treatment of secondary effluent using a 100 nm pore size polyvinylidene fluoride (PVDF) membrane. Individually, these treatments removed approximately 50% of UV_{254} and 80% of the colour from the secondary effluent feed. BAC treatment was found to remove 63% of BP and 49% of the HS component content, while O_3 treatment was found to remove 100% of the BP and 82% HS components. The resulting normalised unified membrane fouling index values after BAC treatment (2.5×10^{-3} m^2/L) or O_3 treatment (1.5×10^{-3} m^2/L) were considerably lower than without treatment (4×10^{-3} m^2/L).

The combined sequential use of O_3 and BAC pre-treatment was found to result in higher membrane permeability than that observed with individual O_3 or BAC pre-treatments, despite the lower removal of BPs and HS by the combined O_3-BAC process. The poorer feed quality was attributed to the order of the process stages. The ozone oxidation process ahead of BAC filtration removed a high quantity of the BPs and HS (100% and 82% respectively) but liberated adsorbed BP and HS components from the BAC. The liberated BPs has lower fouling properties than the BPs originally found in the secondary effluent. The fouling index for O_3-BAC-MF system was one quarter of that resulting from MF without pre-treatment.

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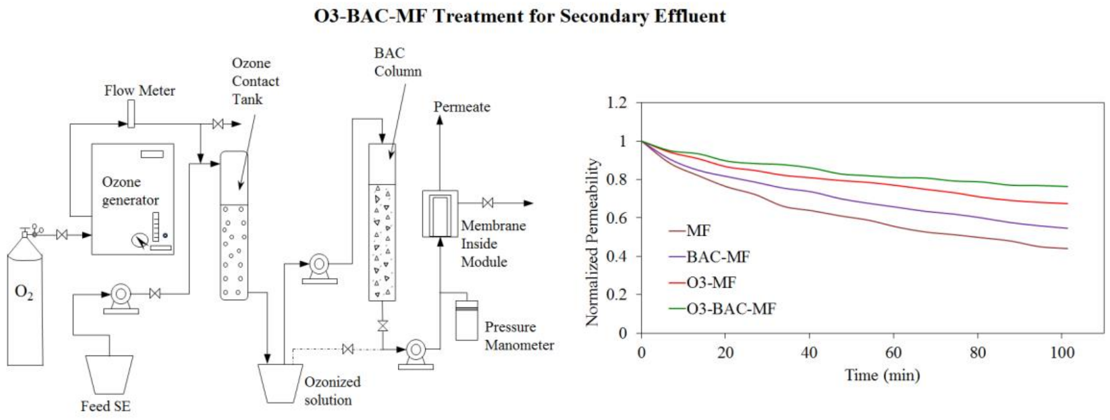
Graphical abstract



Comparison of the effects of ozone, biological activated carbon (BAC) filtration and combined ozone-BAC pre-treatments on the microfiltration of secondary effluent

Highlights

- Sequential use of O_3 and BAC pre-treatment resulted in higher membrane permeability
- O_3-BAC removed BP (100%) and HS (82%) but liberated adsorbed BP and HS from BAC
- Fouling index for O_3-BAC-MF system was one quarter of that resulting from MF
- O_3-BAC pre-treatment could reduce the frequency of chemical cleaning