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Variability and limits of the unified membrane fouling index: application to the reduction of low-pressure membrane fouling by ozonation and biofiltration

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ABSTRACT

The impacts of ozone (0–8 $\mathrm{mg\,O_3\,L^{-1}}$) and filtration with biological activated carbon on membrane fouling by surface waters were investigated using three low-pressure membranes (two ceramics—UF or MF—and one polymeric—UF). The unified membrane fouling index (UMFI) was used to quantify the reversibility and irreversibility of membrane fouling. Minimum UMFI were calculated and repeatability assays were performed in order to evaluate the analytical detection limit and the precision of the method, respectively. The lowest ozone dose tested (1 $\mathrm{mg\,O_3\,L^{-1}}$) reduced the total fouling by 44, 63, and 41% for the polymeric membrane, the UF ceramic membrane, and the MF ceramic membrane, respectively. Further increase of the dose led to minor or no improvement, except for the ceramic MF membrane. For the ceramic membranes, a similar trend to that observed for total fouling was observed for hydraulically irreversible fouling. For the polymeric membrane, the hydraulically and chemically irreversible fouling were too low to be measured. Although biofiltration reduced the average dissolved organic carbon and turbidity by 25 and 50%, respectively, no significant fouling reduction was observed. The results indicate that irreversible fouling measurements are highly variable and most of the time below the analytical detection limit.

Keywords: Drinking water; Membrane; Fouling; Ozonation; Biological activated carbon; Microfiltration; Ultrafiltration; Unified membrane fouling index; Ceramic

1. Introduction

Fouling has been recognized as the main challenge to the expansion of membrane filtration in the water purification industry [1]. Over the last decade, fouling during low pressure membrane filtration of surface waters has been extensively investigated. Natural organic matter (NOM) has been acknowledged to be the most important contributor to fouling for these types of waters. However, the exact mechanisms responsible for fouling remain poorly understood and are both source-water and membrane material dependent [2].

Pretreatment can reduce the extent of fouling. Of the numerous potential pretreatment alternatives, oxidation and biofiltration have been shown to be promising methods to improve membrane permeability [3–6]. Ozonation reduces NOM molecular weight (MW) and hydrophobicity, typically leading to fouling

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reduction [7]. Biological activated carbon (BAC) filtration reduces the concentrations of biopolymers, a key component of NOM that contributes to membrane fouling [8–10]. Integrated systems using ozone followed by BAC filtration as a means to control biodegradable organic material [11] and further reduce membrane fouling [12] have been successfully implemented.

Several membrane fouling indices have been proposed to quantify membrane fouling. Those indices include the silt density index (SDI, ASTM D4189–95) and the membrane fouling index (MFI) which gives the fouling potential of the feed water [13]. However, they do not provide the fouling potential of a specific combination of water and membrane operational conditions. Recently, the Unified Membrane Fouling Index (UMFI) was developed to quantitatively compare membrane fouling for a given type of water regardless of the membrane operational conditions [14,15]. It has been suggested that the UMFI can differentiate hydraulically and chemically reversible fouling from irreversible fouling [16]. Huang et al. [17] attributed the variability of fouling to the combination of water and membrane properties. It was noted that irreversible fouling evaluations using UMFI presented a higher variability. According to Nguyen et al.[16], total fouling (irreversible + reversible) is influenced by the type of membrane, hydraulically irreversible fouling by both the type of membrane and the source-water characteristics and chemically irreversible fouling only by the source-water characteristics. However, the detection limit of UMFI and the precision have never been addressed. This may explain the variability in reported irreversible fouling measurements using the UMFI. In addition, no study has evaluated the impact of ozone and biological filtration of surface waters using the UMFI concept.

The main objective of the present study was to assess the impact of ozonation and BAC filtration on the reduction of fouling. Fouling was evaluated using UMFI assays for three different membrane materials (polymeric and ceramic) and for types (ultrafiltration and microfiltration). In addition, this work presents an evaluation of the detection limit of the UMFI assays.

2. Materials and methods

2.1. Raw water characteristics and pretreatment conditions

The project was conducted using raw waters from L'Assomption River (Repentigny, Qc, Can), a source water highly impacted by agricultural activities. The raw water had a significant total organic carbon (TOC) (4.6–7.0 $\mathrm{mg\,C\,L^{-1}}$), variable turbidity and contained traces of iron and manganese (0–150 $\mathrm{\mu g\,L^{-1}}$).

Seven raw water samples (600 L) were collected from January to July 2011. Samples were warmed to room temperature for 24 h prior to use for each of the fouling experiments. A volume of 200 L was used for direct filtration assays (without any pre-treatment). The remaining 400 L was divided into two batches of 200 L, which were ozonated at two different doses.

The impact of adding a BAC filter after pre-ozonation and prior to membrane filtration was tested on two occasions in July. Raw waters (600 L) were collected onsite and used to feed a lab-scale pilot unit (Fig. 1). Influent waters ($Q = 1\,\mathrm{L\,min^{-1}}$) were ozonated at variable doses in a serpentine contactor with an hydraulic retention time of 10 min. Ozone transfer took place in a vertical column designed to achieve more than 90%. Ozone doses presented in the discussion that follows refer to transferred doses (i.e. corrected for ozone in the off-gas). For the range of transferred ozone doses investigated (0–8 $\mathrm{mg\,O_3\,L^{-1}}$), no dissolved ozone residuals were measured at the end of the contactor. Ozonated waters were gravity fed to a BAC (Picabiol, wood-base, $D_{10} = 0.85\,\mathrm{mm}$) filter, which had an empty bed contact time of 11 min (velocity = 7.4 $\mathrm{m\,h^{-1}}$). The BAC media (exhausted in adsorption) were collected from a full-scale industrial filter 24 h before the assays, backwashed with unchlorinated waters following its placement in the pilot filter, and operated at 0.4 $\mathrm{m\,h^{-1}}$ for 15 h before sampling. After the increase in flowrate, BAC filtrate was monitored to insure that the filter produced stable water in terms of turbidity. Treated water samples were stored at 4°C in the dark for a maximum of two days before being used to perform UMFI tests.

2.2. UMFI methodology

Three commercial membranes were tested. Table 1 summarizes their characteristics and their operating conditions. A clean-in-place (CIP) procedure was performed for each membrane before their first use. Dissolved organic carbon (DOC) measurements of the backwashed water were performed to ensure complete removal of storage solution. All membranes were operated in the dead-end, inside-out configuration. Membranes were operated at manufacturer recommended permeate flux which is membrane-dependent. When not in use, the membranes were stored in a 0.2% $NaHSO_3$ solution.

Before each UMFI assay, the modules were rinsed with deionized water (DI) water in order to remove the 0.2% $NaHSO_3$ storage solution. Waters to be tested

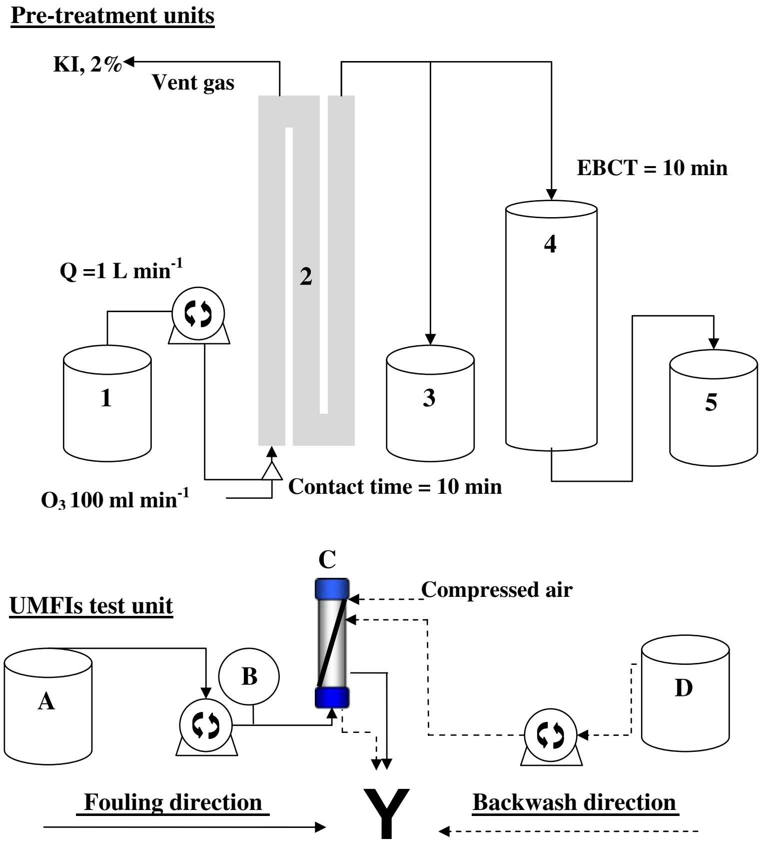

Fig. 1. Pre-treatment units for ozonation and BAC filtration of raw water.
Notes: (top): 1. Raw water; 2. Ozone contactors (10 min contact time); 3. Ozonated water; 4. BAC filter (EBCT = 10 min); 5. BAC filtrate. Water samples were then used as feed water for membrane filtration (bottom): A. Water sample; B. Pressure probe; C. Membrane module (inside/out mode); D. Deionized water for backwash.

were brought at room temperature and fed to the module using a peristaltic pump (Masterflex, Cole Parmer). Transmembrane pressure (PX 409-USB, Omega) and temperature (UTC-USB, Omega) were monitored continuously during the test. The UMFI assay was conducted until a specific volume of 200 L m^{-2} was reached or a minimum filtration time of two hours. At this point, backwash and CIP procedures were performed according to the manufacturers' recommendations. Backwash and CIP procedures are described in detail in Table 1.

2.3. UMFI calculations

The relationship presented in Eq. (1) was used to evaluate the UMFI [15].

$$\frac{1}{J'_{\mathrm{S}}} = 1 + (\mathrm{UMFI}) \times V_{\mathrm{S}} \tag{1}$$

where J'_{S} is the normalized specific flux (unitless), UMFI is an estimate of the extent of fouling (m^2 L^{-1}), and V_{S} (L m^{-2}) is the specific permeate volume. Total fouling (UMFI$_{\mathrm{T}}$) was calculated by using data from the entire filtration cycle. Using the procedure described in greater detail by Huang et al. [15], hydraulically irreversible fouling index (UMFI$_{\mathrm{R}}$) and chemically irreversible fouling index (UMFI$_{\mathrm{C}}$) were also calculated using data collected after the hydraulic backwash and after the CIP procedure, respectively. Consequently, total fouling (UMFI$_{\mathrm{T}}$) was fractionated in reversible and irreversible fouling as described in Eq. (2).

$$\underbrace{UMFI_T}_{\text{Total}} = \underbrace{\boxed{UMFI_T - UMFI_R}}_{\substack{UMFI_{HR}:\\ \text{Hydraulically}\\ \text{reversible}}} + \underbrace{\boxed{UMFI_R - UMFI_C}}_{\substack{UMFI_{CR}:\\ \text{Chemically}\\ \text{reversible}}} + \underbrace{UMFI_C}_{\substack{\text{Chemically}\\ \text{irreversible}}} \tag{2}$$

2.4. UMFI analytical detection limit

The UMFI is a fairly new concept and, consequently, no information has yet been provided on the

Table 1
Membrane characteristics and operating conditions

Membrane type	Polymeric	Ceramic	
Suppliers	X-flow (Norit, ND)	CERAMEM (Veolia Water, FR)	
Name	UF_PES	UF_Si	MF_Ti
Materials[a]	Polyethersulfone and polyvinylpyrrolidone	Silicon carbide	Titanium dioxide
Nominal pore size[b] (μm)	0.025	0.005	0.1
Membrane area (m^2)	0.04	0.13	0.13
Permeate flux ($Lm^{-2}h^{-1}$)	50	100	200
Initial specificflux[c] ($Lm^{-2}h^{-1}bar^{-1}$)	597 (6)	263 (2)	981 (14)
Backwash	Forward flush: DI water (50 lmh) + air (0.03 $Nm^3\ h^{-1}$) for 30 s Backwash : DI water (200 Lmh) for 30 s	Backwash: DI water (200 lmh) for 1 min Compressed air at 620 kPa for 5 s	Backwash : DI water (400 lmh) for 1 min Compressed air at 620 kPa for 5 s
CIP	1L of NaOCl 0.2% at pH 12 (NaOH 20%), soaked for 5 min 1L of HCl 1%,	Citric acid 0.5%, circulated in close loop for 30 min DI water at pH 12 (NaOH 20%) and Alconox® 0.01%, circulated in close loop for 30 min NaOCl 0.5% at pH 12 (NaOH) and Alconox® 0.1%, circulated in close loop for 45 min	
Storage	Sodium bisulfite 0.2%, refreshed every month		

[a] Membranes are characterized by manufacturer as being hydrophilic, however no quantitative chemical surface characteristics were provided.
[b] According to the membrane suppliers.
[c] Numbers in parentheses represent standard error.

method detection limit (MDL). The concept of MDL, as defined in Standard Methods [18], is not directly applicable to the UMFI as it would require performing in parallel seven UMFI assays using standardized water with respect to fouling. Alternatively, it was decided to derive the minimum detectable UMFI (termed $UMFI_{MIN}$) analytically using the precision of the analytical equipment needed to perform this assay. The $UMFI_{MIN}$ corresponds to the smallest permeability loss that can be detected with the experimental set-up. This value can be calculated using Eq. (3).

$$UMFI_{MIN} = \frac{\frac{J_{S_0}}{J_{S_0}-\Delta J_{S_0}} - 1}{V_S} \tag{3}$$

where J_{S_0} is the initial specific flux ($L\,m^{-2}\,h^{-1}\,bar^{-1}$), ΔJ_{S_0}, the loss in specific flux ($L\,m^{-2}\,h^{-1}\,bar^{-1}$), and V_s, the specific volume filtered ($L\,m^{-2}$). It can be noted that the $UMFI_{MIN}$ is influenced by membrane permeability and the cumulative permeate volume filtered. The $UMFI_{MIN}$ will therefore vary from one membrane type to another and will also be lower for longer assays due to the expected increase in specific volume. The $UMFI_{MIN}$ was calculated using data from fouling assays using DI water.

The value of was derived using the law of propagation of errors as presented in Eq. (4). The specific flux (J_{S_0}) can be calculated using Eq. (5).

$$\Delta J_{S_0} = J_{S_0} \times \sqrt{\left(\frac{\Delta V}{V}\right)^2 + \left(\frac{\Delta t}{t}\right)^2 + \left(\frac{\Delta S}{s}\right)^2 + \left(\frac{\Delta P_0}{P_0}\right)^2} \tag{4}$$

$$J_{S_0} = \frac{J_0}{P_0} = \frac{Q}{S \times P_0} = \frac{V}{t \times S \times P_0} \tag{5}$$

where V (L) represents the filtrate volume of water during the time t (h), S represents the membrane surface (m^2), Q represents the membrane debit (L h^{-1}), and P_0 represents the initial transmembrane pressure (bar).

2.5. Repeatability of the UMFI

The $UMFI_{MIN}$ is the lowest value that can be detected using a given experimental setup. However, this does not provide information on the experimental variability inherent to any laboratory procedure. For each membrane material, the precision of the method was evaluated by performing six replicate UMFI assays using the same water. The specific permeate volume of each replicate was 100 L m^{-2}. The repeatability of the methodology (i.e. precision) was defined by the coefficient of variation (cv) which is equal to the standard deviation/arithmetic mean (expressed in %). As UMFI assays are rarely run in duplicate due to the volume of water needed for the procedure, knowing the precision of the method will help deciding if differences in UMFI following various pre-treatment conditions are statistically significant or not.

2.6. Water quality analysis

2.6.1. General characterization

Turbidity, pH, UV absorbance (UVA_{254}), and DOC were measured using, respectively, a Hach 2100 N Turbidimeter, a Fisher Scientific AB15 pH-meter, a Cary 100 Scan spectrophotometer, and a Sievers 5310C TOC analyzer. Gas-phase ozone measurements were performed according to Standard Methods 2350E while dissolved ozone analysis was done according to Standard Methods 4,500 O_3 B [18]. Particle counts were measured using a dynamic particle analyzer (DPA 4100, Brightwell Technologies Inc.).

2.6.2. Apparent MW distribution

Apparent molecular weight distribution (AMWD) were determined using high-performance, size exclusion liquid chromatography (HPLC-SEC). HPLC-SEC analyses were performed on a Waters 2695 Separation Module HPLC system equipped with a Waters 2998 Photodiode Array Detector set at 260 nm. The carrier (0.7 mL min^{-1}) solvent consisted of 0.02 M phosphate buffer (Laboratory grade, Fisher Scientific), at pH 6.8 and adjusted with sodium chloride (Certified A.C.S, Fisher Scientific) to yield a final ionic strength of 0.1 M. AMW was correlated to the retention time by performing a calibration curve with Polystyrene Sulfonate Standards (American Polymer Standards Corporation) with defined MWs of 1100, 4000, 5000, and 7000 Da.

3. Results and discussion

3.1. UMFI variability

Three sources of variability were investigated: experimental variability (method repeatability), seasonal variability of the source water, and the impact of membrane materials.

3.1.1. $UMFI_{MIN}$ and repeatability

Repeatability tests were performed over 72 h using a unique batch of water. For each type of fouling, cumulative frequency distributions of the 18 experiments (6 replicates for each three membranes) are plotted on Fig. 2 for all data (Fig. 2a) and each individual membrane type (Fig. 2b–d). The total, hydraulically irreversible, and chemically irreversible fouling are considered in the analysis. The $UMFI_{MIN}$ derived from assays on DI waters are included as a reference. For a given membrane, the $UMFI_{MIN}$ could be precisely measured (i.e. exhibited a low cv). The variability in the $UMFI_{MIN}$ that was observed (4–5%) was attributed to minor variations in permeate flux (1%), and initial transmembrane pressure (4–7%). According to Standard Methods (1030 C) [18], a MDL can be calculated using the standard deviation and a 99% confidence level. As expected, the MDL calculated using this approach yields values 3–15 times higher than the $UMFI_{MIN}$ depending on the membrane type. This is consistent with Standard Methods statement that the MDL is approximately four times the instrument detection level.

The cumulative distribution for each membrane demonstrated distinct trends when comparing the ceramic and polymeric membranes. As presented in Fig. 2b, the polymeric membranes (UF_PES) had the lowest precision (i.e. the highest cv) for the total fouling ($UMFI_T$ with a cv of 43%) and the hydraulically irreversible fouling ($UMFI_R$ with a cv of 113%). The majority of the hydraulically and chemically irreversible fouling were actually below $UMFI_{MIN}$, suggesting that no irreversible fouling could be detected during the tests. On the other hand, fouling index estimates for both the ceramic membranes were more precise (Fig. 2c and d). For both ceramic membranes, the precision of the total fouling and the hydraulically irreversible fouling was 16–19% and 23–27%, respectively. Most of the chemically irreversible fouling for the ceramic membranes was below their $UMFI_{MIN}$. A paired *t*-test indicated that for both ceramic membranes the chemically irreversible fouling was not statistically different than the $UMFI_{MIN}$ ($p < 0.05$).

The greater precision obtained with ceramic membranes than for the polymeric membrane is most likely a consequence of their higher operating fluxes for the ceramic membrane, as the extent of fouling is positively correlated to the permeate flux. The $UMFI_T$ monitored for the polymeric membrane (UF_PES) were on average two times greater than their $UMFI_{MIN}$, while it was 32 times greater for the UF ceramic membrane (UF_Si) and 17 times greater for the MF ceramic membrane (MF_Ti). The precision of the UMFI for the polymeric membranes could be improved by increasing specific volume filtered.

Results of the present study suggest that measuring irreversible fouling in a single filtration cycle is not relevant. As suggested by Nguyen et al. [16], irreversible fouling should be studied in multiple cycle filtrations and over at least a few days for a good assessment of long-term membrane performance. However, this would require a larger volume of water and automation of the filtration cycles, two constraints which are not compatible with a laboratory procedure but which can be done at pilot-scale.

3.1.2. Seasonal variability

Seasonal variability was investigated by computing values of $UMFI_{MIN}$, $UMFI_T$, $UMFI_R$, and $UMFI_C$ on raw waters collected at different times of the year. For each type of fouling, cumulative probability frequency distributions of the 39 assays (three membranes × 13 raw waters) are plotted in Fig. 3 for all data (Fig. 3a) and each individual membrane type (Fig. 3b–d).

UMFI measurements varied over several orders of magnitude at different times of the year (Fig. 3a): 5E−04 to 3E−02 $m^2 L^{-1}$ for $UMFI_T$, 4E−04 to 7E−03 $m^2 L^{-1}$ for $UMFI_R$, and 1E−04 to 4E−03 $m^2 L^{-1}$for $UMFI_C$. The MF ceramic membrane (MF_Ti) was the most affected by seasonal variations of water quality ($UMFI_T$ with a cv of 82%), which could be explained by its higher filtration flux (200 lmh). Although improved UMFI measurements are obtained using a higher flux, the latter may also increase fouling variability [19]. The UF polymeric membrane (UF_PES, $UMFI_T$ with a cv of 67%) and the UF ceramic membrane (UF_Si, $UMFI_T$ with a cv of 48%) were less affected by seasonal variations of water quality.

Among the water quality characteristics recorded by the water utility, the turbidity (cv = 114%, max = 87 NTU) and the true color (cv = 86%, max = 157 CU) had the highest variability. Their highest values were observed during the snowmelt period (April). This period also corresponded to the highest fouling event for all three membranes. Compared to a stable winter condition (March as a reference, $p = 0{,}125$), total

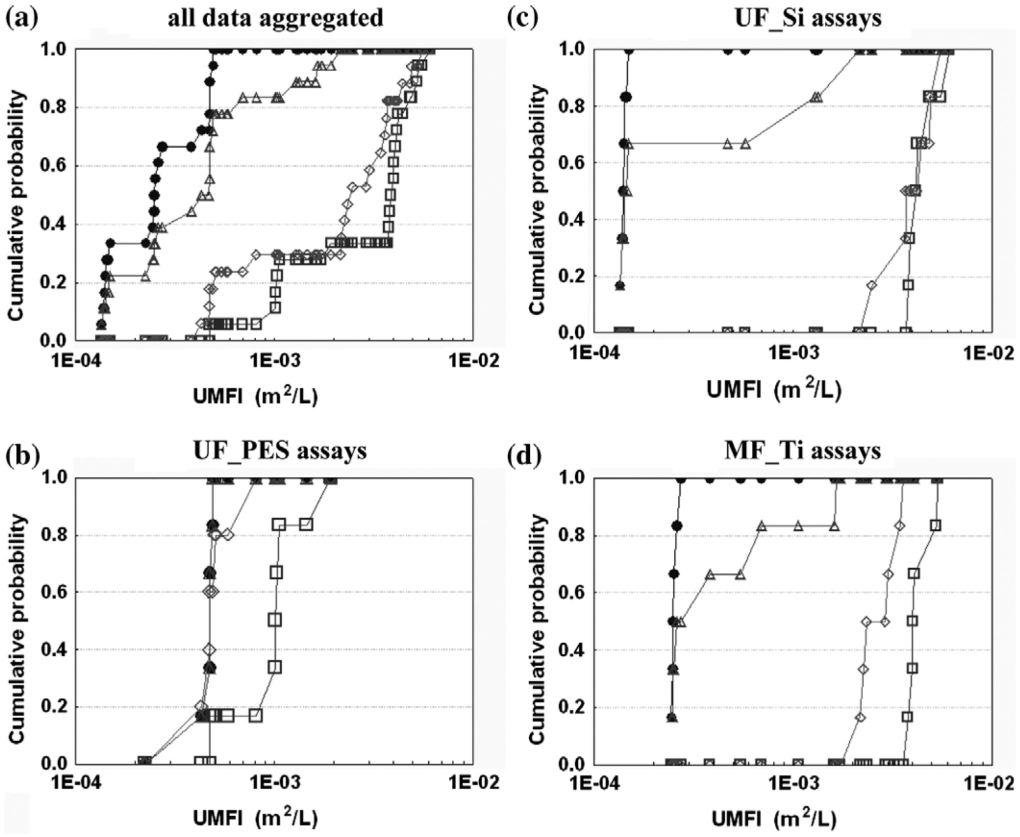

Fig. 2. Repeatability assays: cumulative probability distribution of UMFI for six replicates performed on the same raw water (or DI water in the case of $UMFI_{MIN}$).
Notes: $UMFI_{MIN}$ (closed circles), $UMFI_T$ (open squares), $UMFI_R$ (open diamonds), and $UMFI_C$ (open triangles).

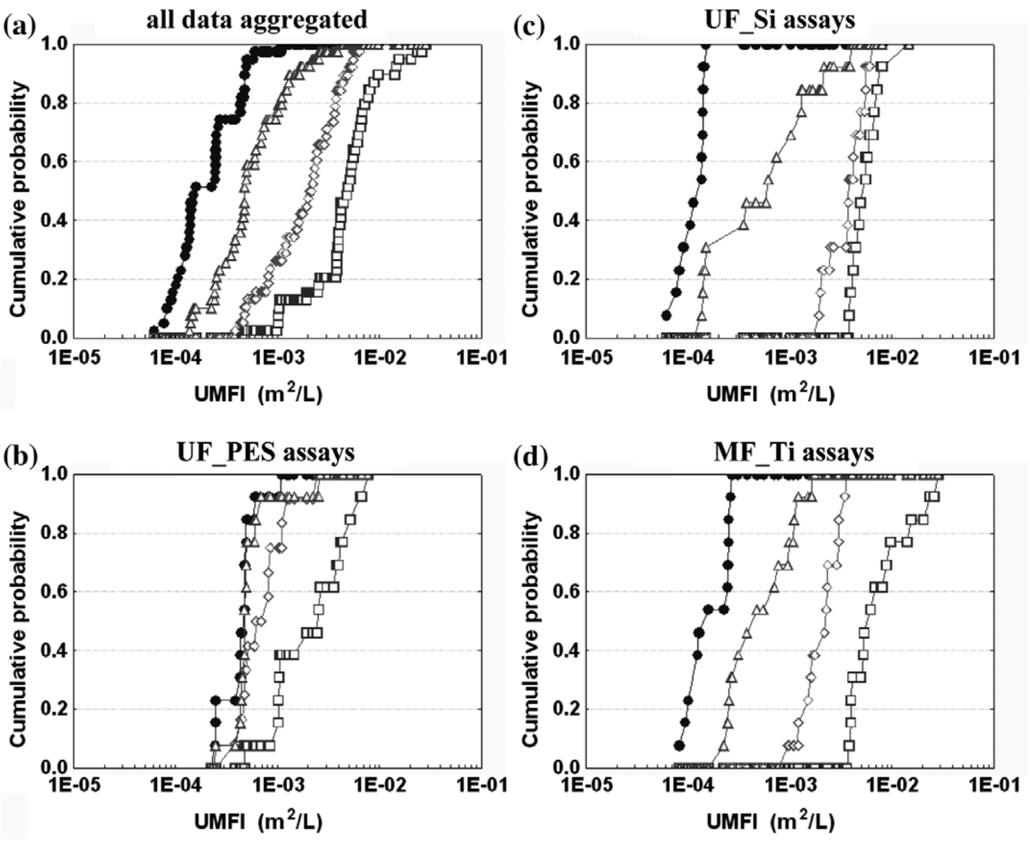

Fig. 3. Seasonal variability: cumulative probability distribution of UMFI in raw waters.
Notes: $UMFI_{MIN}$ (closed circles), $UMFI_T$ (open squares), $UMFI_R$ (open diamond), and $UMFI_C$ (open triangle).

fouling ($UMFI_T$) during that period increased by 209, 164, and 319% for the polymeric membrane (UF_PES), the UF ceramic membrane (UF_Si), and the MF ceramic membrane (MF_Ti), respectively. This observation showed that precaution must be taken when measuring fouling potential of raw waters.

3.1.3. Impact of membrane materials

For the same set of data as that used for the analysis of seasonal variations (13 raw water samples), average fouling index estimates, grouped by type of UMFI and membrane, are provided in Fig. 4. The polymeric membrane (UF_PES, 50 lmh) had the lowest $UMFI_T$, and most of its fouling was reversible ($UMFI_{HR}/UMFI_T$, $UMFI_R/UMFI_T$, and $UMFI_C/UMFI_T$ of 67, 33, and 20%, respectively). The UF ceramic membrane (UF_Si, 100 lmh) had a higher $UMFI_T$, and most of the fouling was hydraulically irreversible ($UMFI_{HR}/UMFI_T$, $UMFI_R/UMFI_T$, and $UMFI_C/UMFI_T$ of 43, 64, and 16%). The MF ceramic membrane (MF_Ti, 200 lmh) had the highest $UMFI_{T,}$ and most of the fouling was reversible ($UMFI_{HR}/UMFI_T$, $UMFI_R/UMFI_T$, and $UMFI_C/UMFI_T$ of 77, 23, and 7%). From this dataset, the $UMFI_T$ appears dependent on the operating flux. This finding is consistent with that of

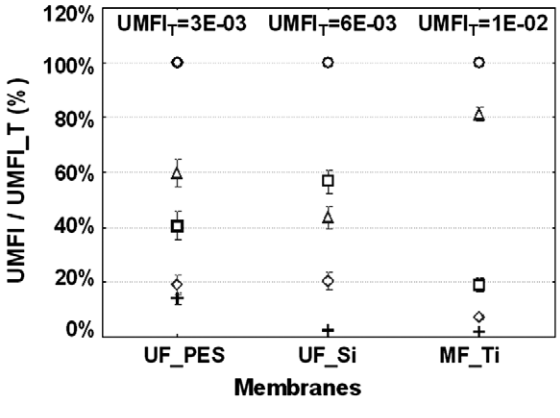

Fig. 4. Impact of membrane materials on fouling fractions. Notes: $UMFI_T$ (circles) = reference = 100%, $UMFI_R$ (squares), $UMFI_R$ (diamonds), $UMFI_{HR}$ (triangles), and $UMFI_{MIN}$ (cross). Values obtained in 39 fouling experiments of 13 raw waters. Whiskers represent standard errors. Fouling fractions are given as the percentage of total fouling $UMFI_T$.

Huang et al. [17]. According to their analysis, permeate, and backwash fluxes influenced the extent of total and hydraulically irreversible fouling. This observation might also explain the higher reversible fouling observed on MF_Ti as opposed to UF_Si. The former was operated at a higher backwash flux than UF_Si (400 vs. 200 lmh). Further research would be needed to evaluate the impact of membrane chemistry, hydrodynamic condition, and membrane pore size on irreversible fouling of ceramic membranes.

3.2. *Fouling reduction by pre-treatments*

Ozone dose between 0 and 8 mg O_3 L^{-1} was investigated from January to July, 2011. On two occasions in July, a pre-treatment consisting of a pre-ozonation (5 mg O_3 L^{-1}) followed by BAC filter was studied.

3.2.1. *Water characteristics*

The characteristics of raw water, ozonated water, and BAC filtrate are shown in Table 2. A dose of 5 mg O_3 L^{-1} (0.9 mg O_3/mg C) resulted in reductions of 42% for UVA_{254} ($p < 0.05$) and 7% for DOC ($p = 0.17$). The reduction in specific $UVA_{254\,nm}$ (SUVA = UVA_{254}/DOC) of 61% ($p < 0.05$) is likely due to the reduction of the hydrophobic fraction of DOC, as ozone has been shown to destroy C=C and C–O functional groups of aromatic and phenolic compounds which adsorb UV at 254 nm [20]. BAC filtration did not significantly affect the UVA_{254} ($p = 0.36$), but reduced the DOC concentration by 25% ($p < 0.05$). The reduction in DOC was likely due to biodegradation as the BAC had been exhausted in adsorption.

Size exclusion chromatography (SEC) with UV detection at 260 nm was used to gain insight into the effect of ozonation and BAC filtration on NOM characteristics (Fig. 5). Ozonation reduced the UV absorbance for low MW organics (<350 Da), building blocks (350–500 Da), and humic substances (1–20 kDa). The UV absorbance of higher MW organic material (>20 kDa) was not significantly affected by ozonation. Considering that ozonation did not affect the DOC concentration, the SEC results suggest that ozonation preferentially reacted with the lower MW hydrophobic fraction of DOC to generate degradation products with fewer C=C and C–O functional groups. Ozonation had a greater impact than BAC filtration on reducing the $UVA_{260\text{ nm}}$. This is consistent with studies by other authors who have indicated that the hydrophobic fraction of DOC is resistant to microbial degradation [21]. SEC with organic carbon detection would have been necessary to observe the breakdown products and the removal of biopolymers which do not extensively adsorb at 260 nm.

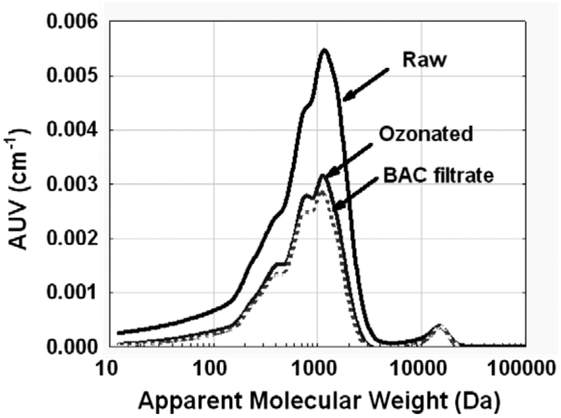

Fig. 5. Effects of ozonation and BAC filtration on AMWD: UVA response (at 260 nm) in cm^{-1} vs. MW in Da.

3.2.2. *Reduction of fouling by ozonation*

The ozone dose had a significant impact on total fouling ($p < 0.05$) as shown in Fig. 6a. The greatest effect was observed with the lowest ozone dose considered (1 mg L^{-1}). At an ozone dose of 1 mg L^{-1}, the $UMFI_T$ decreased by 44, 63, and 41% for the polymeric membrane (UF_PES), the UF ceramic membrane (UF_Si), and the MF ceramic membrane (MF_Ti), respectively. Further increasing the ozone dose did not further reduce the $UMFI_T$ for either UF membranes (PES and Si). Song et al. [6] also observed

Table 2
Characteristics of raw water, ozonated, and BAC filtrate

Parameters		Raw		Ozonated		BAC filtrate	
		4 July	24 July	4 July	24 July	4 July	24 July
pH	–	6.7	7.2	7.0	7.4	6.7	6.8
DOC	(mg L^{-1})	5.7	4.9	5.3	4.6	4.2	3.8
UV_{254}	(cm^{-1})	0.17	0.15	0.10	0.07	0.08	0.07
SUVA	(m^{-1} mg^{-1} L)	3.0	3.0	1.9	1.4	1.9	1.8
Turbidity	(NTU)	8.7	15	10.9	16.0	4.7	9.8

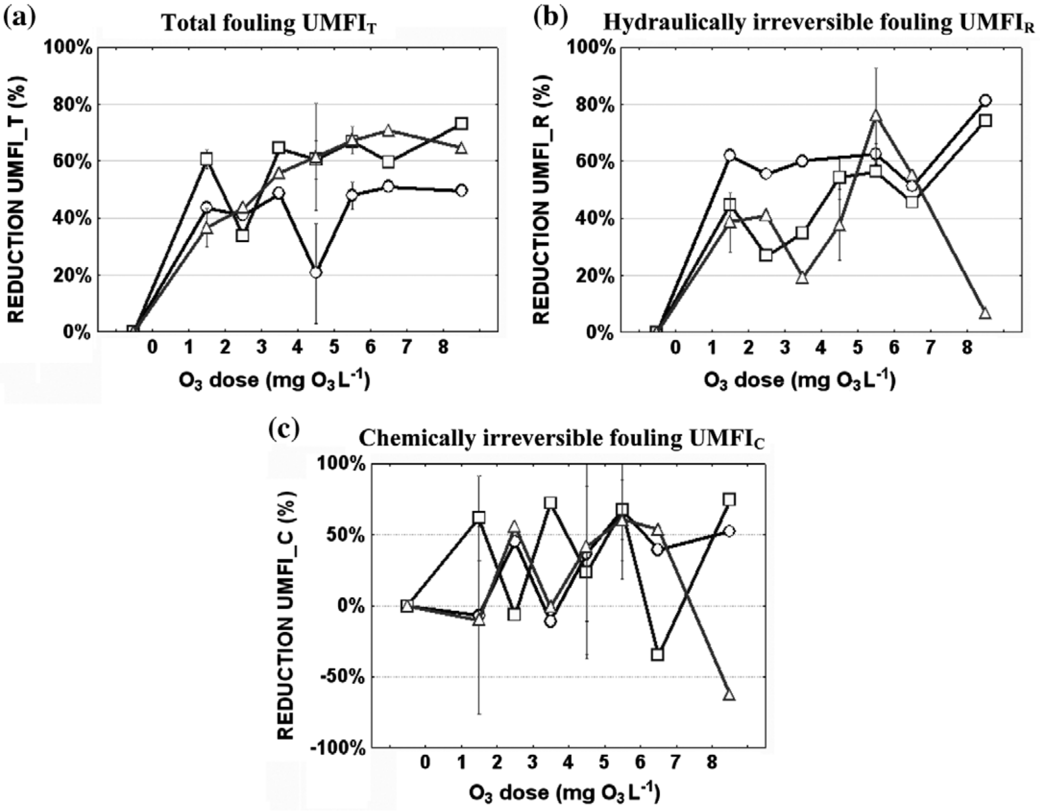

Fig. 6. Impact of ozone on fouling reduction for the three membranes investigated.
Notes: UF_PES (circles), UF_Si (squares), and MF_Ti (triangles) for increasing ozone dosages. Whiskers show standard error on replicates performed over the six-month study.

an optimal ozone dosage of $1.5\,\mathrm{mg\,O_3\,L^{-1}}$ for a MF PVDF membrane (range tested: 0.5–$3\,\mathrm{mg\text{-}O_3\,L^{-1}}$). Ozone oxidation was found to change the composition and hydrophobicity of organic matter [20], thus affecting membrane permeability. On the other hand, further increasing the ozone dose further reduced $\mathrm{UMFI_T}$ for the MF membrane (MF_Ti). At a dose of $8\,\mathrm{mg\,L^{-1}}$ for the MF membrane, the $\mathrm{UMFI_T}$ decreased by 65%.

For the ceramic membranes, a similar trend to that observed for total fouling was observed for hydraulically irreversible fouling (Fig. 6b). However, no statistically significant trends could be observed for the polymeric membrane (UF_PES), as the $\mathrm{UMFI_R}$ observed for UF_PES was generally less than the $\mathrm{UMFI_{MIN}}$. Similarly, no statistically significant trends could be noted for chemically irreversible ($\mathrm{UMFI_C}$) fouling for all membranes as the $\mathrm{UMFI_C}$ were less than the $\mathrm{UMFI_{MIN}}$ (Fig. 6c).

3.2.3. Reduction of fouling by BAC filtration

The impact of a sequential ozonation followed by BAC filtration on fouling was also investigated (Fig. 7). The absolute (Fig. 7a) $\mathrm{UMFI_T}$ and relative reductions compared to raw waters (Fig. 7b) are provided for each membrane and water types. Pre-ozonation ($5\,\mathrm{mg\,L^{-1}}$) reduced the $\mathrm{UMFI_T}$ by 36% for the polymeric membrane (UF_PES), while a higher reduction in the $\mathrm{UMFI_T}$ ($\approx$60%) was observed for the ceramic membranes. The addition of a BAC filter after ozonation did not lead to a further reduction in the $\mathrm{UMFI_T}$ any of the membranes.

The role of biofiltration for reducing membrane fouling has been investigated by many authors. Previous studies have indicated that BAC filtration may reduce fouling, a phenomenon linked with a reduction of the total suspended solids level [22]. However, these previous studies focused on the use of biofiltration for wastewater treatment, rather than for the treatment of raw drinking water sources. Huck and Sozanski [23] emphasized that the performance of BAC was mostly related to its ability to reduce biopolymers and colloidal matter. Such performance may be impacted by BAC filter design (e.g. Empty bed time contact [EBCT]). A reduction in membrane fouling with BAC filtration is not always achieved as demonstrated by Xiong [24] for low pressure membranes and Kim et al. (2007) [25] for nanofiltration. In the present study, the

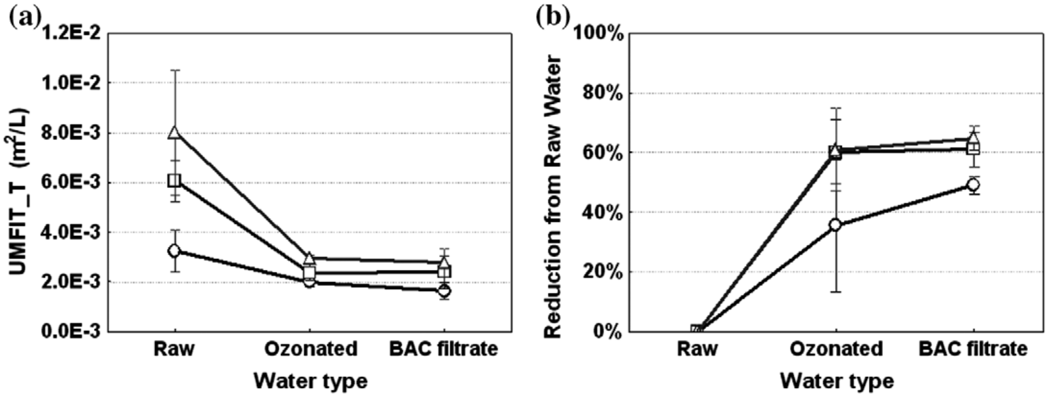

Fig. 7. Reductions of total fouling ($UMFI_T$) for the three membranes.
Notes: UF_PES (circles), UF_Si (squares), and MF_Ti (triangle) — as a function of water type. Raw water was ozonated at 5.5 +/-0.2 mg O_3 L^{-1}. EBCT of BAC was 11 min. Whiskers show standard errors.

BAC filter achieved moderate turbidity removal (40–60%) and substantial DOC removal ($p < 0.05$) as the latter was reduced from 5.3 to 4.2 mg L^{-1}. However, the effect of BAC filtration on $UMFI_T$ was not statistically significant. One potential explanation for the lack of fouling reduction might be related to the fact that waters had been pre-ozonated before BAC filtration. Hallé et al. (2009) [9] observed significant reduction of fouling by the use of biological filter prior to membrane filtration, a gain that was attributed to the lowering of the biopolymers. However, the influent water used in their study was not ozonated. In the present study, the HPLC-SEC analysis supports the idea that ozonation (0.9 mg O_3/mg C) modified the AMWD more extensively than BAC filtration. Although no biopolymer data are available, we can expect that content of the NOM would also have been impacted by this level of ozonation.

Note that only the impact of BAC on the $UMFI_T$ was tested. Therefore, we cannot disregard the hypothesis that hydraulically and chemically irreversible fouling may have been reduced by BAC filtration. In all cases, the interactions between ozonation and BAC filtration should be the topic of further investigations.

4. Summary and conclusion

The following conclusions were derived from this study.

(1) The chemically irreversible fouling ($UMFI_C$) was too low to be adequately quantified with the UMFI procedure. Irreversible fouling should be measured on multiple filtration cycles and over a longer period for better assessment of membrane performance.

(2) Permeate and backwash fluxes may have influenced the extent of total and hydraulically irreversible fouling. Further research would be needed to evaluate the impact of membrane chemistry, hydrodynamic condition, and membrane pore size on irreversible fouling of ceramic membranes.

(3) Ozonation reduced the UVA_{260nm} of low MW organics (< 350 Da), building blocks (350–500 Da), and humic substances (1–20 kDa). The SEC results suggest that ozonation preferentially reacted with the lower MW hydrophobic fraction of DOC to generate degradation products with fewer C=C and C–O functional groups.

(4) At an ozone dose of 1 mg L^{-1}, the $UMFI_T$ decreased by 44, 63, and 41% for the polymeric membrane (UF_PES), the UF ceramic membrane (UF_Si), and the MF ceramic membrane (MF_Ti), respectively. Increasing the ozone dose beyond 1 mg L^{-1} did not lead to significant additional reductions in fouling, except for the MF_Ti membrane.

(5) For the ceramic membranes, a similar trend to that observed for total fouling was observed for hydraulically irreversible fouling. However, no statistically significant trends could be observed for the polymeric membrane as the hydraulically and chemically irreversible fouling were too low.

(6) Even though BAC filtration removed on average 50% of the turbidity and 25% of DOC, the effect of BAC filtration compared to ozonation on total fouling was not statistically significant. However, we cannot disregard the hypothesis that hydraulically

and chemically irreversible fouling may be reduced by BAC filtration.

Further studies are warranted in order to assess correctly the interdependence of ozonation and BAC filtration on membrane performance.

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List of symbols

J_{S_0} — initial specific flux, L m^{-2} h^{-1} bar^{-1}
J_0 — initial membrane flux, L m^{-2} h^{-1}
P_0 — initial transmembrane pressure, bar
$Q = V/t$ — filtrate flow, L h^{-1}
S — membrane surface area, m^2
J'_S — normalized specific flux, unitless
V_S — membrane surface flux, L m^{-2}
$UMFI_T$ — unified membrane fouling index for total fouling, m^2 L^{-1}
$UMFI_R$ — unified membrane fouling index for hydraulic irreversible fouling, m^2 L^{-1}
$UMFI_C$ — unified membrane fouling index for chemically irreversible fouling, m^2 L^{-1}
$UMFI_{HR}$ — unified membrane fouling index for hydraulic reversible fouling, m^2 L^{-1}
$UMFI_{CR}$ — unified membrane fouling index for chemically reversible fouling, m^2 L^{-1}
cv — coefficient of variation, %

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