Removal of assimilable organic carbon and biodegradable dissolved organic carbon by reverse osmosis and nanofiltration membranes

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Abstract

The main objective of this study was to evaluate the effectiveness of reverse osmosis (RO) and nanofiltration (NF), under various solution chemistries, on bacterial regrowth potential as quantified by assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC). The bench-scale experiments, using tap groundwater spiked with acetate as organic carbon, revealed that AOC removals by RO/NF membranes were strongly dependent on charge repulsion. AOC removals were greater at conditions of low ionic strength and low hardness, and were slightly higher at high pH values. BDOC removals by NF membrane also increased with decreasing hardness and ionic strength, and increasing pH. However, the RO membrane showed less dependence on feed solution chemistry for BDOC removal, suggesting that BDOC removal was determined by the combined effect of both size exclusion and charge repulsion. The bench-scale observations were compared to a full-scale drinking water treatment plant that used nanofiltration as a primary treatment process. From full-scale operation, it was observed that nanofiltration was a very effective means to reduce BDOC, but conversely, did not reject the bulk of raw water AOC. The high BDOC rejection by NF membranes at full scale can be explained by size exclusion, since a significant fraction of BDOC in raw surficial ground water consists of compounds, such as humic and fulvic acids, which are larger than the pores of NF membranes. The insignificant AOC rejection observed in the full-scale system was probably due to the low pH, high hardness, and high ionic strength (TDS) of the raw groundwater combined with acid addition during pretreatment. These solution environments repress the electrostatic interaction between charged organic compounds and membranes, allowing passage of small molecular weight compounds and thus reducing AOC rejection. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Assimilable organic carbon (AOC); Reverse osmosis (RO); Water treatment; Organic separation; Biostability

1. Introduction

Bacterial proliferation in a drinking water distribution system is a major concern because of the degradation of the distribution water quality, the acceleration of pipe corrosion, and other undesirable effects. For bacterial growth to occur, various nutrient sources must be present. In particular, organic compounds, either dissolved or particulate, provide energy and carbon sources for heterotrophic bacteria to produce new cellular materials. The organic carbon in water supplies is mainly composed of humic and fulvic acids, carbohydrates, proteins, and carboxylic acids. In many distribution systems, it is assumed that the level of biodegradable organic matter (BOM) is the limiting nutrient for bacterial growth [1], although

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a small number of studies suggest that phosphorus may be limiting for some systems [2,3]. Thus, BOM concentration, often measured as assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC), provides a good indicator for the bacterial regrowth potential of the treated water. Further, AOC has actually been correlated with bacterial counts in water distribution systems [4,5].

Membrane filtration offers a versatile treatment alternative to improve the biological stability of the finished water. Especially, reverse osmosis (RO) and nanofiltration (NF) technologies, mainly because of their small pore sizes, have a great potential to remove biodegradable organic substances from source waters and consequently reduce the potential for bacterial growth in the distribution system. However, systematic studies concerning AOC or BDOC removal by membranes are rarely found in the literature. The few existing studies [6–9] showed that RO and NF were effective in rejecting higher molecular weight compounds (e.g. humic acids) typically quantified as DOC and BDOC. However, the lower molecular weight compounds typically quantified as AOC (e.g. acetic acid and amino acids) were rejected to varying degrees depending on the membrane material and probably the solution environment.

This paper addresses the effectiveness of RO and NF processes, as a drinking water technology, for the removal of AOC as well as BDOC. In this research a series of well-controlled, bench-scale filtration, experiments were performed at various feed solution chemistries using commercial thin-film composite polyamidic NF and cellulosic RO membranes. In addition, the electrokinetic properties of the membranes were carefully characterized and related to the performance in order to elucidate fundamental mechanisms of AOC and BDOC removal by RO/NF membranes. Lastly, full-scale NF membrane performance data collected from Palm Beach County Water Utilities District (PBCWUD) was compared to the bench scale test results.

2. Background

2.1. Biodegradable dissolved organic carbon

The BDOC content represents the fraction of dissolved organic carbon (DOC) that is assimilated and/or mineralized by a heterotrophic flora [10]. The inoculum for the test consists of environmental bacteria, suspended or alternately fixed on a support, such as sand or porous beads. BDOC is the difference between initial DOC of the water sample and the minimum DOC observed during the incubation period of 28 days for suspended indigenous bacteria or 5–7 days for bacteria attached to sand [11]. Joret et al. [12] reported that BDOC values represent 10–30% of the total dissolved organic carbon content of drinking water. Block et al. [13] showed that an absence of biodegradable organics after water treatment was essential for limiting bacterial regrowth. Servais et al. [14] suggested that a BDOC concentration of 0.16 mg/l or less in the finished water was required for the desired biological stability, which corresponds to no BDOC consumption within the distribution system. More recently, Volk et al. [11] determined a value of 0.15 mg/l at 20°C and 0.30 mg/l at 15°C for achieving biological stability in distribution systems of Paris suburbs. Additionally, coliform occurrences were related to the existence of BDOC content more than 0.10–0.15 mg/l in their study [11].

2.2. Assimilable organic carbon

AOC refers to a fraction of the total organic carbon (TOC) which can be utilized by two specific strains of bacteria, resulting in an increase in biomass concentration that is quantified. AOC typically comprises just a small fraction (0.1–9.0%) of the TOC. The inoculum for the AOC bioassay can be composed of a mixture of pure bacterial strains cultivated in laboratory conditions (*Pseudomonas fluorescens* P17 and *Spirillum* NOX) [11], or mixtures of environmental bacteria [12] characterized by a great nutritional versatility, or mixtures of bacteria that utilize groups of specific compounds [13]. Bacterial growth is monitored in the water samples by colony counts, and the average growth (N_{avg}) observed during the incubation is converted into AOC units (μg/l as acetate-carbon) by using a growth yield of the bacteria from calibration curves derived from standard concentrations of organic compounds (acetate or oxalate). A significant correlation exists between the AOC concentration and the density of heterotrophic bacteria in distribution water supplies [13,15]. Van der Kooij [15] showed that heterotrophic bacteria in a non-chlorinated system did

not increase when AOC levels were lower than 10 μg/l. LeChevallier et al. [5], on the other hand, suggested that the regrowth might be limited by AOC levels less than 50–100 μg/l in a system maintaining a disinfectant residual.

The AOC concentration may be regarded as a measure of the biological stability of the water with respect to heterotrophic growth, while the quotient AOC/BDOC may be regarded as an indication of the relative biological stability of the biodegradable organic compounds present in drinking water [5]. Studies performed by Van der Kooij [4] suggested that BDOC could not be used to predict the level of regrowth because no significant correlation was found between this parameter and the counts of heterotrophic bacteria. Moreover, since the detection limit of 0.1 mg/l is used in the BDOC bioassay, significant AOC changes on the order of μg/l as acetate-carbon are not usually detectable by BDOC analysis. Therefore, AOC and BDOC bioassays should be used together to supplement each other's information.

2.3. Removal of BOM by membrane filtration

Organic removal by membrane filtration has been a topic of many investigations. Clair et al. [9] used reverse osmosis membranes (FilmTec FT30 composite brackish water desalination, Dow Chemical, Germany), previously used by Lynch and Smith [16], to treat surface water with a DOC range of 8.1–22.3 mg/l. The membrane permeate contained 0.3–0.43 mg/l of DOC (96–98% reduction), which were similar results to those obtained by Lynch and Smith [16]. More recently, Cho et al. [17] studied the natural organic matter (NOM) rejection using ultrafiltration polyamide thin film composite (TFC) membranes (MWCO=8000 Da) as well as regenerated cellulose membranes (MWCO=3000 Da). It was shown that despite the large pores of UF membranes, the significant fractions of DOC were removed after membrane filtration, however, the degree of DOC removal was strongly affected by feed solution chemistry. DOC rejection decreased significantly as calcium concentration increased, decreased less significantly as pH decreased, and was nearly unaffected by changes in ionic strength. Based on these observations, they concluded that DOC removal was determined by several mechanisms including charge repulsion, size exclusion, and

hydrophobic interaction. However, BDOC and AOC removals were not determined in these studies.

Sibille et al. [6] performed studies using groundwater from the city of Auvers s/Oise, France, which was treated via ozonation followed by biological granular activated carbon filtration and nanofiltration in order to investigate the effects of membrane treatment on biological regrowth potential using NF membranes. The results of the experiments were that nanofiltration produced a considerable gain in potable water quality by decreasing the bacterial counts (from 820 to 340 cfu/ml), DOC (from 1.6 to 1.4 mg/l) and BDOC (from 0.35 to 0.25 mg/l). However, nanofiltration membranes let through to the permeate a low concentration of biodegradable organic matter (BDOC=0.25 mg/l) that might have still had a significant fraction of AOC in it. Unfortunately, AOC was not measured.

Noble et al. [7] determined AOC removals by three different schemes: (1) coagulation, flocculation and granular activated carbon (GAC), (2) conventional potable water treatment (i.e. coagulation, flocculation, and sand–anthracite), and (3) NF using sulfonated polyesther sulfide membranes with a molecular weight cutoff of 1000 Da (Nitto Denko NTR 7450, Hydranautics, San Diego, CA). The raw groundwater contained TOC=11 mg/l and AOC averaging 362 μg as acetate-C/l. For GAC columns, the effluent TOC was 1.6 mg/l and the AOC of the effluent water was 202 μg as acetate-C/l; a considerable reduction, but the effluent still contained a high AOC concentration. The high AOC of the GAC effluent was probably due to carbon fines from the column present in the effluent water. When sand–anthracite columns (both dual and monomedium) were used, the effluent TOC was 1.3 mg/l and AOC was 54 μg as acetate-C/l, which was much lower than the influent AOC probably due to the addition of ferric chloride for coagulation and the absence of carbon fines in the effluent. Finally, it was determined that when nanofiltration was used, there was a significant reduction in permeate TOC (0.63 mg/l) but no significant difference between AOC values of the influent and the permeate (AOC=334 μg as acetate-C/l), which meant that membrane filtration did not produce biologically stable water.

Finally, Agbekodo et al. [8] treated water from the River Oise at the Méry-sur-Oise Plant (France) by nanofiltration using FilmTec NF70 (Dow Chemical, Germany) membranes. The treatment process

consisted of clarification and sand-filtration, followed by the addition of sulfuric acid to drop the pH to 6.5, 10 and 5 μm filters, and a three-stage nanofiltration process. The raw water DOC ranged between 4 and 7 mg/l while the permeate DOC was constant at 0.15 mg/l. Of the permeate DOC, 60% was composed of amino acids, 18% of sugars, 15% of fatty-aromatic acids, and 7% of aldehydes. The BDOC (concentration not stated) composition was 63% amino acids, 22% sugars, 10% fatty-aromatic acids, and 5% aldehydes. In the study, it was concluded that amino acids passed through the nanofiltration membranes, and they are usually readily available to bacteria (AOC-forming compounds). Thus, different researchers observed that even though membrane filtration considerably reduces the DOC of the permeate water, it might let through a significant portion of the raw water AOC and BDOC through.

3. Experimental

3.1. Raw water quality

The laboratory tap water (chlorinated groundwater) at the University of Central Florida was used for the bench-scale raw water matrix. The raw water samples were withdrawn after a 5 min flushing period, and care was taken not to contaminate the raw water matrix. The average composition over the period of the studies of the UCF laboratory tap water is given in Table 1. The raw water was spiked with organics

Table 1
University of Central Florida Laboratory Tap Water Quality[a]

Parameter	Average concentration
Alkalinity	120±31 mg/l as $CaCO_3$
Hardness	190±38 mg/l as $CaCO_3$
Total dissolved solids (TDS)	160±15 mg/l
Ionic strength ($IS=2.5\times10^{-5}\times TDS$)	4×10^{-3}
pH	7.50–8.00
Turbidity	0.25 NTU
Heterotrophic plate count (HPC)	0–5 cfu/ml
AOC	55.6±29.95 μg as acetate-C/l background
BDOC	0.22±0.11 mg/l background
DOC	1.92±0.087 mg/l background
Chemical addition	0.2 mg/l sodium acetate

[a] Source: experimental analysis over the period of study.

(0.2 mg/l acetate as carbon) to determine the retention of AOC and the low molecular weight fraction of BDOC. Final concentrations of AOC and BDOC were approximately 257 μg/l as acetate-C and 0.42 mg/l, respectively. In addition, NaCl ($0–10^{-1}$ M) and $CaCl_2$ ($0–0.25\times10^{-1}$ M) were added to the raw water matrix to evaluate the effects of ionic strength and divalent cation concentrations (i.e. hardness) on the retention of organic matter by the membrane. Finally, the pH of the raw water was varied from 5.5 to 7.5 using HCl in order to assess its effect on the removal of AOC and BDOC.

3.2. Membranes used

The membranes used in this project were manufactured by Fluid Systems (San Diego, CA), and they were CA-SD and TFC-S for RO and NF membranes, respectively. The CA-SD membrane is a cellulose acetate blend RO membrane (MWCO≤100 Da) typically used for industrial, municipal, ground, and surface water applications where chlorination is desired. This membrane is capable of producing 348 l/m-day (28 gfd) water at 2.9 MPa (420 psi; typical operating pressure range 1.7–3.1 MPa (250–450 psi)) with 95.5% chloride ion rejection on 2000 mg/l NaCl solution at 25°C and pH 5.7. The CA-SD membranes were kept wet and stored in a dark area away from light at a cool temperature (5–10°C). Then they were rinsed with feed water at low pressure (<0.41 MPa or 60 psi) for a short time before starting the evaluation. This membrane was tested as flat sheets at operating pressures of 1.0–1.2 MPa (150–180 psi).

The TFCS is a thin film composite NF membrane (i.e. polyester fabric substrate, porous polysulfone support, and a cross-linked aromatic polyamide rejecting surface) with MWCO of 200 Da. The water and salt transport coefficients for this membrane are 2.2×10^{-6} g/cm^2 s atm and 1.8×10^{-6} cm/s, respectively. Ideal operating pressure ranges from 0.3 to 1.2 MPa (50–150 psi) with an optimum pressure of 0.54 MPa (80 psi). At this optimum pressure, the membranes have a capability of producing 186 l/m-day (15 gfd) water with 80% chloride rejection for a 500 mg/l NaCl solution, at 10% recovery, 25°C, and pH 7.5. TFC-S membranes were stored and prepared following the same procedure as CA-SD membranes. The TFCS membrane was tested as
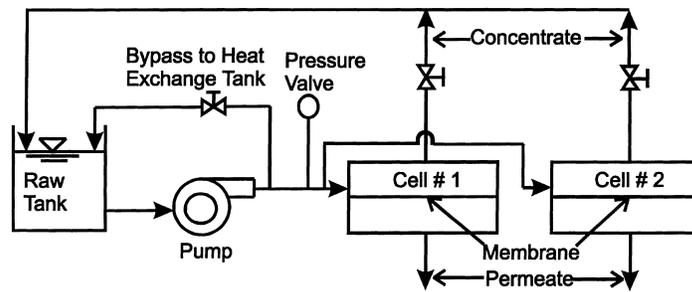
Fig. 1. Flat sheet membrane cell testing unit.

flat sheets at a pressure of 0.54 MPa (80 psi) in this study.

3.3. Flat sheet membrane filtration tests

Experiments were conducted using a circular flat sheet membrane test unit as shown in Fig. 1. The cell unit contained two cells, each with 81.3 cm² (12.6 sq. in.) active membrane area. In this cell configuration, the feed water was fed to the cell through the side inlet, and the concentrate and the permeate were collected from the center of top and bottom of the cell, respectively. As a result, the flow pattern inside the cell was not clearly defined and the tangential flow velocity was not determined. Feed flow of approximately 1.14 l/min (0.3 gpm) per cell was supplied by a single 250 W (1/3 hp) pump. In order to adjust the flow rate, distilled water was run through the membranes for the first 4 h for stabilization. During this period, flow meters were used to adjust the flow to each cell, and flow rates were measured hourly until the end of the experiment.

The flat sheet membranes were handled according to manufacturer instructions. Each membrane film was evaluated at a single set of operating conditions of approximately 37.8–75.7 l/day (10–20 gfd) flux and 1–5% recovery. Each film was discarded after one experiment, but each experiment was duplicated. Temperature was maintained at ambient conditions ($\cong 22 \pm 3°C$) by closed loop recirculation of a side stream of the feed water in a continuously fed bath for heat exchange. Each experiment was continued until 1 l of permeate had been collected for analysis, approximately 24 h. Flows for 10–20 gfd flux and 1% recovery were 2.5–3.5 ml/min permeate and

345 ml/min concentrate. Samples for UV-254 analysis were withdrawn every 1–2 h to monitor any changes in organic carbon rejection with operation time. With respect to AOC and BDOC, because of the quantity of sample required for analysis (approximately 1 l), it was unfeasible to take periodic samples. Also, there was an initial attempt to use distilled water to determine leakage, but the microbial flora used in both bioassays needed water with more electrolytes to prevent cell lysis.

3.4. Experimental design

A total of 24 different experiments were designed for this study. Each experiment was duplicated for reproducibility. The independent parameters used were membrane type (TFC-S or CA-SD), pH (5.5 or 7.5), hardness (0.0019–0.0269 M), and ionic strength (0.0040–0.1040 M) or TDS (160–4160 mg/l). The tap water contained approximately 0.0019 M of hardness and 0.0040 M of ionic strength and was designated as Solution A. The Solutions B–F were made to determine the effect of hardness and ionic strength on AOC/BDOC removal (Table 2).

3.5. Statistical analysis

The statistical analysis was performed using SPSS Student Version 9.0 (SPSS Inc., Chicago, IL). Experiments were performed varying membrane type (TFC-S or CA-SD), pH (5.5 or 7.5), ionic strength (0.0040–0.1040 M) or TDS (160–4160 mg/l), and hardness (190–2690 mg/l as $CaCO_3$). In order to standardize and compare the different parameters, they were transformed using Eq. (1), so that values would

Table 2
Experimental design details

Solution	A	B	C	D	E	F
Chemical addition	N/A	0.001 M NaCl	0.0005 M CaCl$_2$	0.001 M NaCl, 0.0005 M CaCl$_2$	0.025 M CaCl$_2$	0.1 M NaCl
Hardness (M)	0.0019	0.0019	0.0024	0.0024	0.0269	0.0019
Ionic strength	0.0040	0.0050	0.0053	0.0063	0.0665	0.1040

be unitless and fall between -1 and $+1$. The independent variable membrane type was assigned a value of $x=-1$ for CA-SD and $x=+1$ for TFC-S membranes, while pH was also transformed, so pH=5.5 corresponded to $x=-1$ and pH=7.5 corresponded to $x=+1$.

$$x_{i1} = \frac{\varepsilon_{i1} - [\max(\varepsilon_{i1}) + \min(\varepsilon_{i1})]/2}{[\max(\varepsilon_{i1}) + \min(\varepsilon_{i1})]/2} \qquad (1)$$

where x_{i1} is the transformed value and ε_{i1} is the original value.

The model parameters were considered significant by the magnitude of their p-values. All the analysis was performed using the logarithm base 10 of removal (delta) values (i.e. raw−permeate). The logarithm transformations of the dependent variables (i.e. AOC and BDOC) were used after residual analysis showed that the data was subject to multiplicative errors. When the variance is a function of its mean, the least squares assumption of homoscedasticity (i.e. constant variance for all levels of the independent variables) can be satisfied by transforming the dependent variable. This transformation is called variance stabilizing [18]. In the case of multiplicative distributions, the logarithm of the independent variable has approximately constant variance.

A total of 30 different models that either did not involve interactions (main effects only) or involved interactions (two-, three-, or four-level) were tested. The preferred models were chosen based on the highest coefficient of determination (R^2) and lowest mean square error (MSE). Even though third- and fourth-order interaction models were tested, simpler models (i.e. first- and second-order interactions) were favored if R^2 and MSE values were within 10% even if the simpler models contained the lower R^2 and MSE.

Since both compounds added to lower the pH from 7.5 to 5.5 (HCl) and compounds added to increase the hardness (CaCl$_2$) increase ionic strength, a correlation

matrix using Pearson's product moment correlation coefficient (r) was made. The Pearson's coefficient is a measure of the strength of the linear relationship between variables, and the greater the value of the coefficient, the greater the correlation between the variables. Table 3 shows the correlation matrix for the independent variables: membrane type, pH, ionic strength, and hardness. From the table, it was observed that neither membrane type nor pH correlated with any of the other parameters. On the other hand, ionic strength and hardness correlated with a Pearson's coefficient of 0.386 (p-value=0.063, not significant at 95% confidence), which implied a weak correlation. Correlation does not imply causality, but determines that the correlated variables are confounded with each other; therefore, their effects are dependent on each other. After confounding was determined, the chosen models were re-tested by excluding ionic strength from the independent variables and observing the effects of this removal on the coefficients of hardness. Fortunately, the removal of ionic strength did not alter the coefficients of hardness by more than 20%. Therefore, the confounding effects between hardness and ionic strength were not strong.

Table 3
Correlation matrix for the transformed independent variables[a]

Correlation matrix		MT	pH$_t$	IS$_t$	H_t
MT	Pearson correlation	1.000	0.000	0.000	0.000
	Significant (two-tailed)	<0.0001	1.000	1.000	1.000
pH$_t$	Pearson correlation	0.000	1.000	0.000	0.000
	Significant (two-tailed)	1.000	<0.0001	1.000	1.000
IS$_t$	Pearson correlation	0.000	0.000	1.000	0.386
	Significant (two-tailed)	1.000	1.000	<0.0001	0.063
H_t	Pearson correlation	0.000	0.000	0.386	1.000
	Significant (two-tailed)	1.000	1.000	0.063	<0.0001

[a] Independent variables are membrane type (MT), pH, ionic strength (IS), and hardness (H) using Pearson's correlation coefficients.

3.6. Zeta potential experiments

In order to assess changes in membrane surface charge at various solution chemistries, membrane surface zeta potentials were determined using a streaming potential analyzer (BI-EKA, Brookhaven Ins., Holtsville, NY). The zeta potential of the membrane surface was calculated from the measured streaming potentials using the Helmholtz–Smoluchowski equation [19]. The pH titration was first performed at a background electrolyte concentration of 10^{-2} M NaCl to determine the isoelectric point of the membrane. In addition, the divalent cation (Ca^{2+}) concentration was varied from 10^{-4} to 5×10^{-2} M at two different pH values: 5.5 and 7.5. The solution chemistries chosen for zeta-potential experiments were similar to those of feed waters used in the flat sheet membrane filtration tests. The matrix solution was distilled deionized water with 10^{-2} M NaCl as electrolyte background. For pH titrations, HCl and NaOH were added to vary the pH from 4 to 10. For calcium titrations, $CaCl_2$ was added to vary the calcium concentration from 0 to 0.05 M.

3.7. Full scale membrane water treatment plant

The NF membrane plant studied treated raw water from the Biscayne Aquifer (FL) that is a shallow, surficial aquifer, with significant surface influence and some salt-water intrusion. The characteristics of this raw water are summarized in Table 4. This plant utilizes a 32:16 NF membrane array, made of TFCS spiral-wound elements designed to reject

Table 4
Average water quality in the Biscayne aquifer[a]

Parameter	1-Year average values
Dissolved oxygen	<1–2 mg/l
pH	7.0
Alkalinity	219 mg/l as $CaCO_3$
Total hardness	249 mg/l as $CaCO_3$
Color	32 PCU
Ammonia-nitrogen	1.20 mg/l
Sulfate (SO_4)	20 mg/l
Total dissolved solids (TDS)	200 mg/l
Heterotrophic plate counts	214 cfu/ml
Coliform occurrences	0

[a] Source: Eugenia P. Carey, Regulatory Compliance Manager for Palm Beach County Board of County Commissioners Water Utilities Department.

95% of hardness and 85% of chlorides at normal operating conditions. The NF plant was designed for 35.2×10^6 l/day (9.3 MGD), but operated at an average of 29.5×10^6 l/day (7.8 MGD) during the study. Before static cartridge filters, 140 mg/l of sulfuric acid and 2 mg/l of antiscalant were added to reduce scaling. The water then passed through cartridge filters and the NF array. The membrane-filtered water was disinfected by adding 4 mg/l of chlorine and 1.3 mg/l of ammonia. The water was then aerated and 45 mg/l of sodium hydroxide was added for pH adjustment.

The sampling point was located immediately after the membranes and prior to post-membrane chemical additions. Sample collection was performed by following a guideline outlined in Standard Methods procedure # 9060A [20]. The procedure requires the addition of a 10% sodium thiosulfate ($Na_2S_2O_3$) solution to neutralize the chlorine residual in the samples. Kaplan and Bott [21] found that the addition of thiosulfate did not significantly stimulate the growth of P17 or NOX, thus having no effect on AOC concentrations. Sample storage was implemented according to procedure 9060B after collection.

3.8. Reagent water and glassware

Water for the preparation of all solutions was ultra-pure water of equivalent quality to that produced by a Milli-Q-UV plus system (Millipore Corp.). The water quality met or exceeded the Type I reagent water specifications provided in Table 1080:I of Standard Methods [20]. Purified water used for microbiological testing met the quality criteria specified in Table 9020:I of Standard Methods [20]. Laboratory chemicals were American Chemical Society reagent grade or higher purity. Glassware was cleaned in a sink employing a detergent wash, an acid wash, and several distilled water rinses. The glassware was then muffled at 550°C for 4 h to remove any organic contamination. All glassware used for microbiological testing was autoclaved prior to use. Silicon/PTFE septa were pretreated by heating in a 100 mg/l sodium persulfate solution for 30 min without allowing it to boil.

3.9. AOC bioassay

AOC was measured using the rapid method of LeChevallier et al. [22], except that plate counts were

used to enumerate bacteria rather that ATP fluorescence, in conjunction with Standard Methods [20] procedure # 9217 and the method of Van der Kooij [23]. The procedure used is outlined in great detail in Escobar and Randall [24]. Quality control for the AOC bioassay was performed using blank controls, $100 \, \mu g/l$ sodium acetate standards, and duplicate samples. The $100 \, \mu g/l$ sodium acetate standards inoculated with P17 produced an average AOC of $93.80 \pm 20.00 \, \mu g/l$ as acetate-C, while for NOX, they produced an average AOC of $77.20 \pm 12.53 \, \mu g/l$ as acetate-C. Experimental yield values from acetate standards for P17, $4.08 \pm 0.81 \times 10^6$ cfu/μg acetate-C, and NOX, $9.26 \pm 1.50 \times 10^6$ cfu/μg acetate-C, compared reasonably well with the literature values as specified in Standard Methods, 4.1×10^6 and 1.2×10^7 cfu/μg acetate-C for P17 and NOX, respectively. No controls were made to assess the effect of the thiosulfate (used to neutralize chlorine residual) since it has been determined not to affect AOC concentration [21] and is included in the Standard Method [20]. The method detection limit (MDL) for

the AOC bioassay was determined to be $57 \, \mu g$ as acetate-C/l via replicate analysis.

3.10. BDOC analysis

The procedure for BDOC determination followed the technique using sand fixed bacteria [24,25]. The MDL for BDOC was determined to be 0.15 mg/l.

4. Results and discussion

4.1. Membrane surface charge

Fig. 2 shows zeta potential (i.e. membrane surface charge) versus pH with background electrolyte solutions of 10^{-2} M of NaCl for both TFC-S and CA-SD membranes. From Fig. 2, it was observed that both membranes were more negative at higher pH than at lower pH values. This was attributed to the higher degree of deprotonation of membrane surface functional groups, such as carboxyl, at high pH. The drop in the
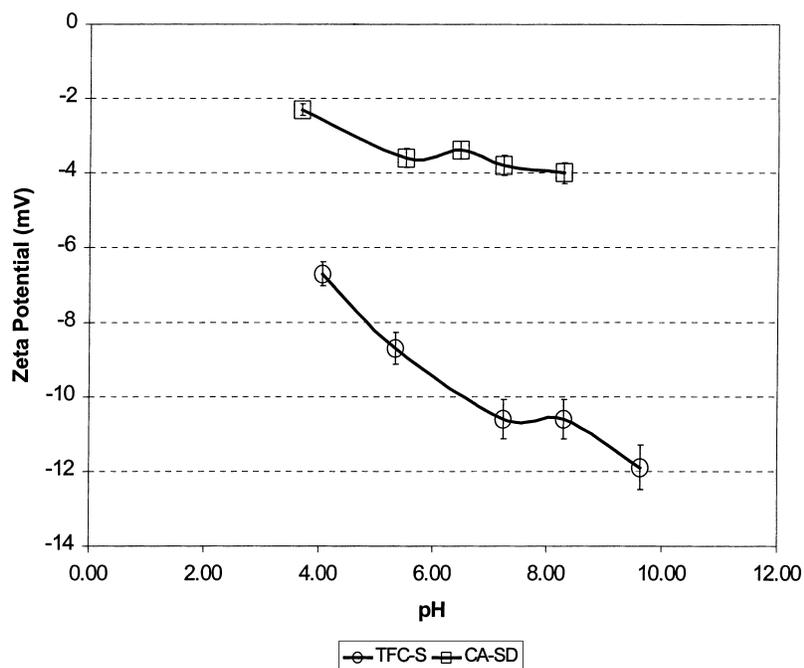

Fig. 2. Effect of pH on surface zeta potentials of TFC-S and CA-SD membranes (background electrolyte solution of 10^{-2} M of NaCl).
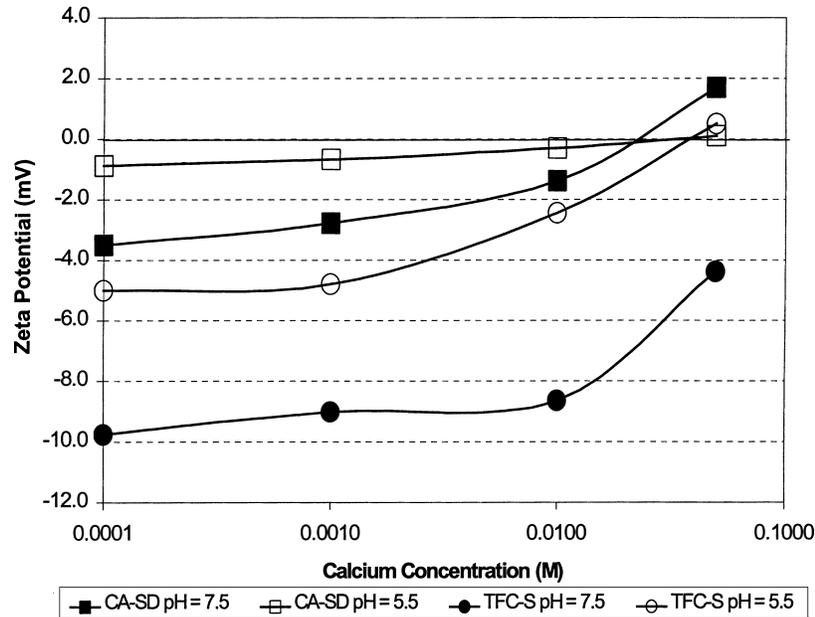
Fig. 3. Effect of calcium concentration on surface zeta potentials of TFC-S and CA-SD membranes (background electrolyte solution of 10^{-2} M of NaCl).

negative charge as a function of pH was more pronounced for the TFC-S membranes than for CA-SD membranes, which was expected since cellulose acetate membranes possess less ionizable functional groups, and as a result, are not as negatively charged as TFC-S membranes.

Fig. 3 shows the titration curves for both membranes when calcium ions were added to a solution with an electrolyte background of 10^{-2} M of NaCl. From this figure, it is observed that the addition of calcium significantly decreased the negative charge of the membranes. For the TFC-S membranes, when calcium concentration was increased up to 0.05 M, the absolute value of the negative charge decreased by approximately 6 mV at both pH 5.5 and 7.5. Similarly, for the CA-SD membranes, when calcium was added, the drop in the absolute value of the charge was not as strong. But it was still noticeable at 1.2 and 5.0 mV for a solution with pH 5.5 and 7.5, respectively; thus, it became either closer to zero or slightly positive. This observation can be explained by effective masking of the initially negative membrane surface charge by divalent cations. In addition, specific adsorption of divalent cations to membrane surface functional

groups may contribute to the neutralization of the negative charge of the membrane. Similar trends were reported by Hong and Elimelech [26].

4.2. AOC relative removals

Figs. 4 and 5 show the relative AOC removal, defined as (feed−permeate)/feed, for both CA-SD and TFC-S membranes at pH values of 7.5 and 5.5, respectively. The AOC of the raw water was $55.6 \pm 29.95 \, \mu g/l$ as acetate-C, and the raw water was spiked with $200 \, \mu g/l$ as acetate-C, so the feed AOC was approximately $256 \, \mu g/l$ as acetate-C. It should be noted that since the detection limit for the AOC bioassay was $57 \, \mu g/l$ as acetate-C, it might not be possible to differentiate between AOC removals in the range of 80–100%, particularly accounting for precision between duplicate samples. From both figures, at low concentrations of hardness and ionic strength (Solutions A–D), there was no significant difference between TFC-S and CA-SD membranes although TFC-S was a looser NF membrane. The rejection was greater than 90% for all cases at pH=7.5 and greater than 75% at pH=5.5. High AOC rejections may not
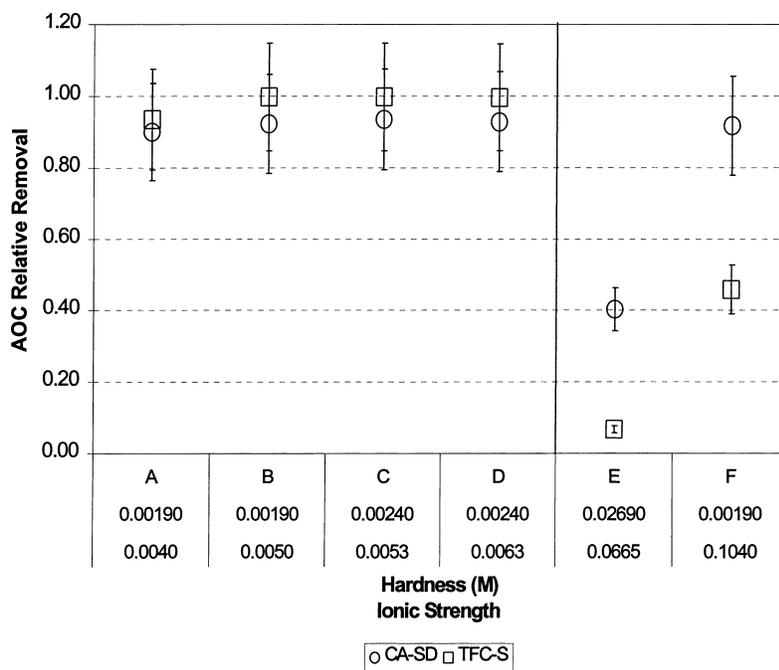
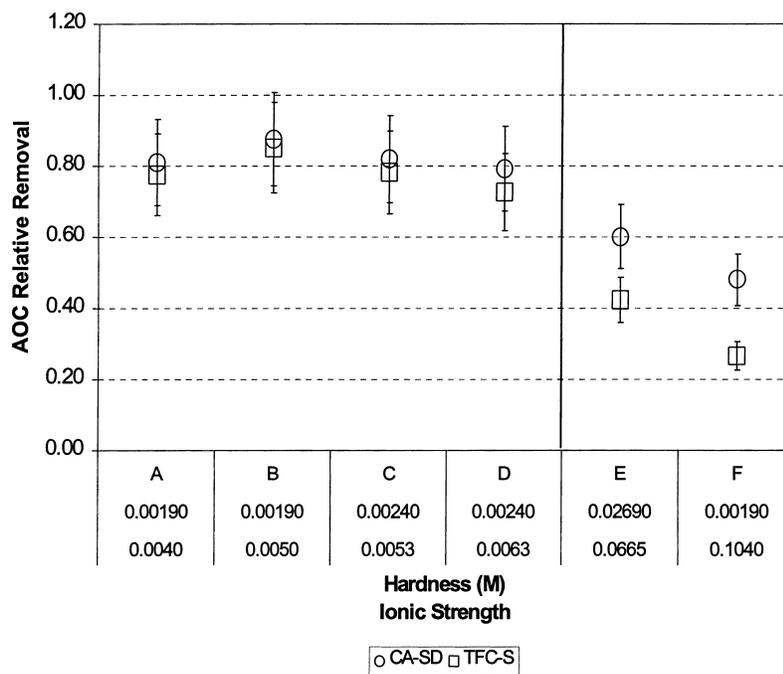Fig. 4. AOC relative removal (1−permeate/feed) by CA-SD and TFC-S membranes at pH=7.5.

Fig. 5. AOC relative removal (1−permeate/feed) by CA-SD and TFC-S membranes at pH=5.5.

be explained simply by size exclusion, since the significant fractions of AOC compounds (mainly acetate) were small enough to pass through both membranes (note that the MWCOs of TFC-S and CA-SD are 200 and 100 Da, respectively). This observation suggested that the main mechanism of AOC removal by both RO and NF membranes was probably charge repulsion.

In order to further verify the importance of charge repulsion, solution hardness and ionic strength were increased by adding $CaCl_2$ (Solution E) and NaCl (Solution F). At higher concentrations of hardness and ionic strength, the rejection of AOC was significantly reduced for both membranes. As divalent cation (Ca^{2+}) concentration increased (Solution E), AOC removals were reduced to 40% CA-SD and 7% TFC-S at pH 7.5, and 60% CA-SD and 42% TFC-S at pH 5.5. The increase in ionic strength by NaCl addition alone (Solution F) also affected AOC removal significantly with an exception of CA-SD membrane at pH 7.5 (46% TFC-S at pH 7.5, and 48% CA-SD and 27% TFC-S at pH 5.5). This exception was probably due to analytical error since the trend of decreasing raw water AOC was observed during the analysis of this sample. No other samples showed similar trends. The decrease in AOC removals can be explained by the reduced charge repulsion at high hardness and ionic strength. As hardness and ionic strength increased, the charges of the membranes and AOC compounds were more effectively screened (Fig. 3), leading to smaller charge repulsion between them, and thus a significant reduction in AOC rejection. It should be also noted that the decrease in AOC rejection was much more pronounced with TFC-S than CA-SD membranes. This is not surprising since TFC-S membranes were more negatively charged than CA-SD membranes (Fig. 2), and thus were more affected by charge masking due to increasing hardness and ionic strength.

From both Figs. 4 and 5, AOC relative removals by both membranes were slightly better at pH=7.5 than at pH=5.5. This observation can be attributable to greater electrostatic repulsion between the membranes and AOC compounds at higher pH values. As solution pH increased, the membranes and AOC compounds became more negatively charged due to the dissociation of their functional groups (Fig. 2). At pH 7.5, the main form of AOC compounds, acetic acids (pK_a=4.74) were almost completely dissociated, while at pH 5.5, only 85% of acetic acids were

deprotonated to acetate ions. Membrane functional groups were also more dissociated with increasing pH. As a result, the charge repulsion between the membranes and AOC compounds became more significant at higher pH. Lastly, it should be noted that the observed pH effect on AOC rejection was not as striking as hardness and ionic strength because of the small pH range tested.

The effect of hardness on AOC removal was somewhat different at pH 7.5 and 5.5 (Solution E). The reduction in AOC removal at pH 5.5 was not as drastic as at pH 7.5. It is hypothesized that at low pH, AOC compounds as well as membrane functional groups are more protonated (more neutrally charged), and as a result, much less membrane functional groups and AOC compounds were available for interacting with hardness (Ca^{2+}), explaining the reduced effect of hardness shown in Fig. 5 (Solution E). In addition, a decrease in membrane pore size due to reduced electrostatic repulsion between pore functional groups might be partially responsible for minimizing hardness effect at low pH. The reduced membrane pore size with decreasing pH was supported by a decrease in permeate flow rate for Solution E as pH decreased from 7.5 to 5.5. For TFC-S membranes operating at a pressure of 80 psi, the permeate flow rate at pH of 7.5 was 3.2 ml/min, while it was 2.7 ml/min at pH of 5.5. Likewise, for CA-SD membranes operating at a pressure of 180 psi, the permeate flow rates were 1.8 and 1.3 ml/min at pH=7.5 and 5.5, respectively.

4.3. BDOC relative removals

While AOC compounds are mainly composed of small, highly-charged organic carbon compounds such as acetate, BDOC compounds are (especially in natural waters) composed of both AOC compounds as well as larger, more heterogeneous compounds such as humic and fulvic acids. The BDOC compounds in testing solutions used in bench-scale experiments (i.e. tap water spike with acetate) are a blend of the acetate added and the organics originated from tap water. The BDOC compounds from tap water are presumed to be a mixture of heterogeneous organic substances with various size and charge characteristics. Thus, the rejection mechanism of BDOC compounds was expected to be more complicated than that of AOC compounds.
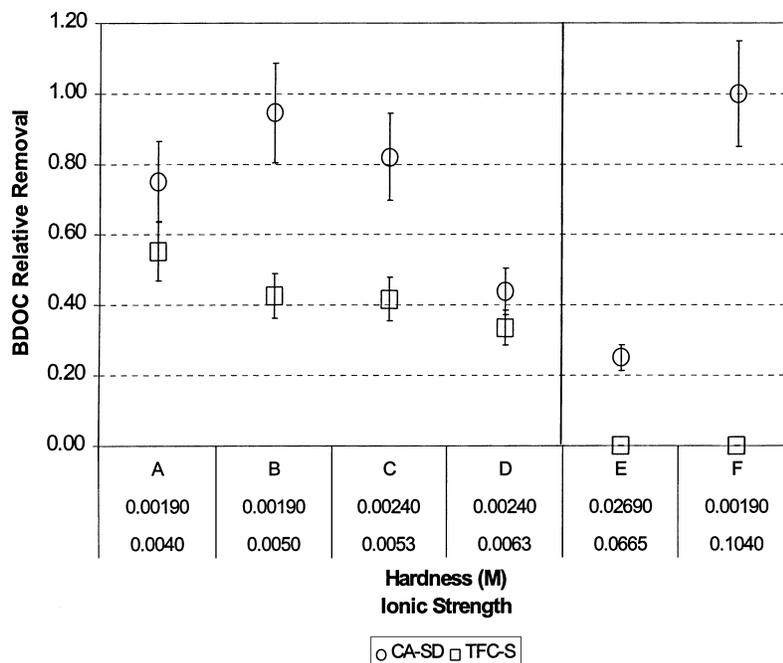
Fig. 6. BDOC relative removal (1−permeate/feed) by CA-SD and TFC-S membranes at pH=7.5.

The relative BDOC removal, presented in Fig. 6 (pH=7.5) and Fig. 7 (pH=5.5), showed indeed a more complex relationship, which probably implied that charge repulsion as well as size exclusion played major roles in BDOC removal by RO and NF membranes. Both figures showed that BDOC rejection at conditions of low hardness and ionic strength (Solutions A–D) was higher when CA-SD membranes (44–95% at pH=7.5, and 37–66% at pH=5.5) were used than TFC-S membranes (34–55% at pH=7.5, and 31–54% at pH=5.5), indicating that the membranes with the smaller MWCO rejected a greater portion of the BDOC. It is important to note that the BDOC of the raw water was 0.22 ± 0.11 mg/l and the spike was 0.2 mg/l as acetate, so the feed water BDOC concentration was 0.42 ± 0.11 mg/l. Since the detection limit for BDOC was determined to be 0.15 mg/l, separations in the range of 70–100% were not differentiated.

In addition to size exclusion, experimental results showed that charge repulsion was also important in BDOC removal. This was evidenced by the dependence of BDOC rejection on feed solution chemistry.

Figs. 6 and 7 showed that under the solution environment of low hardness and ionic strength (Solutions A–D), higher BDOC rejections were observed at pH=7.5 than pH=5.5 for both membranes. At pH=7.5, charge repulsion became stronger due to the ionization of functional groups of the membranes and BDOC compounds, resulting in greater BDOC removals. This finding suggested that the rejection of small charged BDOC compounds (e.g. the acetate added) by NF and RO membranes were strongly dependent on charge repulsion.

For TFC-S membranes, BDOC removals decreased significantly (no detectable rejection) as the hardness increased (Solution E) at both pH 7.5 and 5.5. The rejection of BDOC compounds was also greatly reduced when the ionic strength was increased by adding NaCl (Solution F). The membranes and BDOC substances were less negatively charged at higher hardness and ionic strength due to enhanced charge masking. Consequently, a decrease in electrostatic repulsion between the membranes and BDOC compounds caused BDOC rejection by TFC-S membranes to drop to below detection limit. It should be noted that the experiments
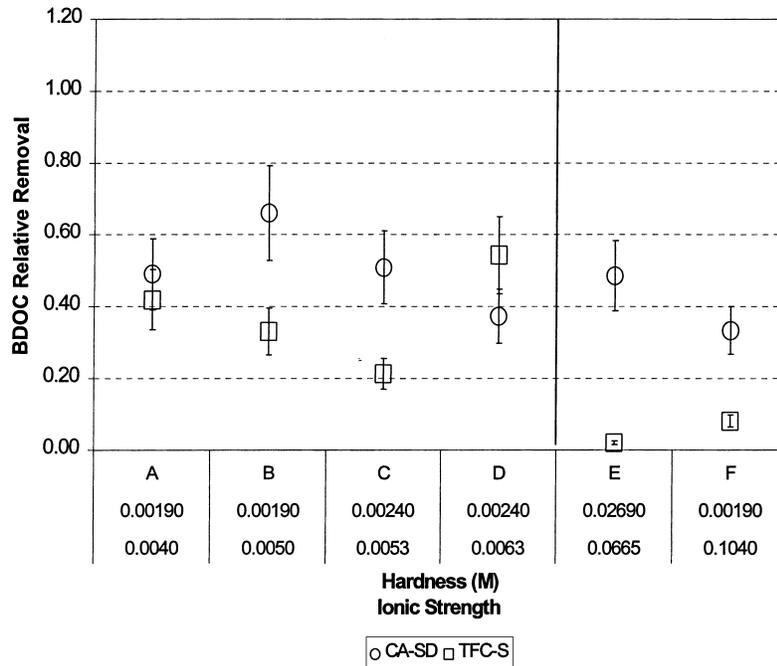
Fig. 7. BDOC relative removal (1−permeate/feed) by CA-SD and TFC-S membranes at pH=5.5.

showing 0% rejection of BDOC correspond to small but detectable AOC rejections. The 0% signifies that BDOC rejection was below detection limits (approximately 0.15 mg/l) for the assay, while the more sensitive AOC assay still showed removals.

The BDOC removal by CA-SD membrane, on the other hand, showed less dependence on hardness and ionic strength. At pH 7.5, increasing hardness caused BDOC rejection to decrease (Solution E). However, increasing ionic strength by NaCl alone did not significantly affect BDOC rejection (Solution F). The reason for the observed high BDOC rejection was that the raw water BDOC and the BDOC removed were equal, but were both below the method detection limit (0.15 mg/l), where relative removals can only be measured as either 0 or 100%. Conversely, at pH 5.5, increasing hardness and ionic strength caused no significant decrease in BDOC rejection by CA-SD membranes. This probably occurred because CA-SD membrane and BDOC compounds were less negatively charged at pH 5.5, and consequently charge repulsion was not as important as size exclusion, especially for tighter RO membranes. Based on

experimental observations, it is concluded that BDOC removal by RO and NF membranes was determined by the combined effect of size exclusion and charge repulsion.

A decrease in flow rate was indeed observed with Solution F (1.59 ml/min) and Solution E (2.26 ml/min) as compared to conditions of minimal ionic strength and hardness (Solution A: 5.28 ml/min). However, unlike pH, the reduced permeate flow is believed to be largely due to an increase in osmotic pressure with increasing ionic strength and/or hardness. Concentration polarization during operation also increases osmotic pressure, causing a further decrease in permeate flow.

4.4. Statistical analysis

A regression analysis was performed on the 24 duplicated experiments. The actual removals (i.e. feed−permeate) were used in the statistical analysis to minimize carry-over bias (raw water values accounted for twice in relative removals). Regarding AOC removal, the model that maximized fit and predictability at 95% confidence, and minimized error

included the membrane type (MT), the transformed ionic strength (IS), and the transformed hardness (H), all unitless, as shown in Eq. (2)

$$\log(\text{AOC removed}) = 2.08 - 0.088\,\text{MT} \\ -0.12\,\text{IS} - 0.27H \qquad (2)$$

This model displayed an adjusted $R^2 = 0.71$ and mean square of error (MSE) of 0.0287.

From the statistical model, it was determined that hardness, ionic strength and membrane type were significant in the prediction of AOC removals. As hardness and ionic strength increase, the membrane surface charge becomes less negative and charge repulsion decreases, so the role of size exclusion in rejection becomes increasingly important, which would explain the importance of membrane type in the model. Since the CA-SD membranes had lower MWCO than TFC-S membranes, rejection was better when CA-SD membranes were used.

From the model, the independent variable pH was found to be less significant at 95% confidence level in the prediction of AOC removals. Experimental data shown in Figs. 4 and 5 also indicated that the effect of pH on AOC relative removal was relatively small compared to hardness and ionic strength. The pK_a for acetate, the main component of AOC, is 4.74; that is, below this pH value, the predominant form is acetic acid, while above is acetate. Since the pH values tested (5.5 and 7.5) were above the pK_a, the majority of AOC compounds at both pH are in the form of acetate and consequently the pH effect was not observed as clearly as hardness and ionic strength.

BDOC removal was affected by the transformed independent variables ionic strength (IS), hardness (H), pH, and membrane type (MT), and their interactions at a 95% confidence level, as shown in Eq. (3)

$$\log(\text{BDOC removed}) \\ = -1.08 - 0.43\,\text{MT} - 0.36\,\text{pH} - 0.91H \\ -0.13(\text{MT})(\text{IS}) \\ -0.23(\text{MT})(H) - 0.32(\text{pH})(H) \qquad (3)$$

This adjusted R^2 was 0.98 and the MSE was 0.0135.

In natural waters, BDOC-forming compounds are mainly humic and fulvic acids (large organic carbon molecules) as well as AOC compounds (e.g. acetate,

propionate). For this reason, BDOC-forming compounds are more heterogeneous than AOC-forming compounds, so their rejection is expected to be more complex than the rejection of AOC compounds. The model suggests that all independent parameters tested were significant and related to each other, implying that BDOC removal was largely governed by the combined effect of several mechanisms, such as charge repulsion, size exclusion, and possibly hydrophobic interactions [16].

4.5. Comparison of nanofiltration between full-scale and bench-scale

Full-scale NF membrane plant operating data was collected over approximately 12 months starting from September 1997. Figs. 8 and 9 show the monthly AOC and BDOC concentrations of raw and NF filtered waters during this sampling period. The quality of the water obtained from the surficial Biscayne aquifer showed a high variation. This was attributed to the rainfall occurring on the surface in February, March, and particularly in July. All of the maximum source water values for AOC, and BDOC occurred during the month of July, coinciding with a period of heavy rainfall, 4.60 in., following a drought, when only 0.02 in. of rain fell. Differences in the aquifer raw water were visible and occurred at the other plants operated by PBCWUD also. Color, odor, and other customer complaints were also the highest during this period.

The year-average AOC concentrations were 141 and 147 µg/l as acetate-C for the raw water and nanofiltration effluent, respectively. There was no significant difference between the raw water and the nanofiltrate, suggesting that nanofiltration did not significantly remove AOC from the raw water. In fact, the average effluent AOC concentrations increased slightly compared to the raw water AOC. This may be due to the addition of antiscalant and low purity acid (relative to the low detection levels of the AOC bioassay), which may have contained carbon-compound impurities. AOC contribution from chemical feeds has been seen and documented previously [27,28].

The poor AOC rejection observed in the full-scale system were consistent with the hypothesis that charge repulsion was the main mechanism for AOC removal by NF membranes. In general, compounds quantified as AOC are from the fraction of BDOC composed of
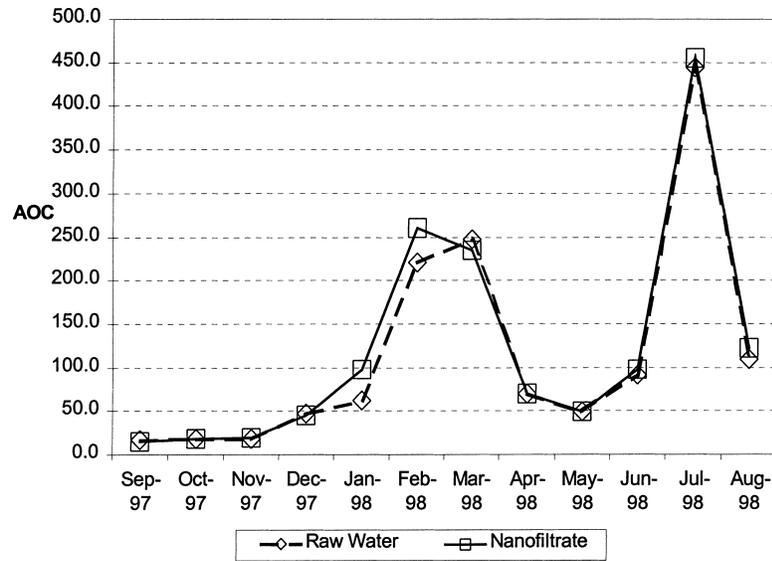
Fig. 8. Monthly AOC concentrations (μg acetate-C/l) for raw water and nanofiltrate.

smaller, highly charged organic substances. Most of these organic compounds are small enough to pass through NF membranes, and thus, their retention by NF membranes is mainly governed by electrostatic repulsion. It is also expected that AOC would be removed poorly at feed solution environments, which repress electrostatic interactions between the membranes and charged organic compounds. This is typically the case with a membrane treating groundwater, which would have (after pretreatment) low pH, high ionic strength, and high hardness. In fact, these solution chemistries were present at the full-scale plant
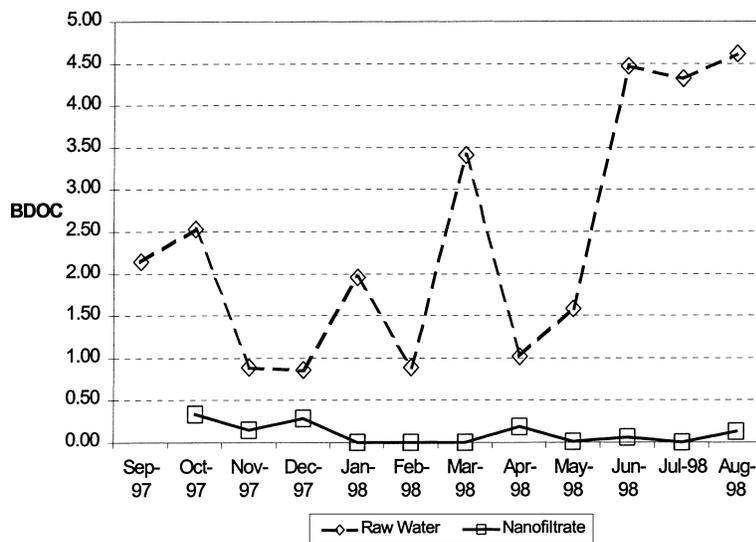

Fig. 9. Monthly BDOC concentrations (μg/l) for raw water and nanofiltrate.

studied and are easily created in typical full-scale operation with multi-stage high recovery systems, explaining the observed low AOC rejection.

In contrast to the AOC observations, monthly BDOC data showed that nanofiltration removed approximately 97% of the raw water BDOC. Average BDOC concentrations were 2.80 and 0.10 mg/l for the raw water and nanofiltration effluent, respectively. In addition, unlike AOC, the BDOC of nanofiltrate did not change with raw water BDOC, indicating that the main mechanism of BDOC removal by NF membranes was size exclusion. In natural waters, BDOC-forming compounds typically consist of large organic macromolecules such as humic and fulvic acids (unlike the bench scale experiments where BDOC had a disproportionate fraction of acetate). Thus, it is not surprising that BDOC was significantly removed by the full-scale TFC-S NF membrane which had a molecular cut off of 200 Da.

5. Conclusions

- Bench-scale studies and streaming potential analysis of both RO and NF membranes suggested that AOC rejection was a function of charge repulsion between the membrane surface and the AOC compounds.
- Increased hardness, ionic strength, or hydrogen ions were shown to mask the negative surface charge of the membrane. Charge masking due to increased hardness and ionic strength, or lower pH resulted in significant reductions in the removal of AOC and the low molecular weight fraction of BDOC.
- Full-scale nanofiltration removed the bulk of the raw water BDOC but virtually all of the AOC passed through. BDOC was probably rejected due to size exclusion, while AOC could not be rejected in the absence of significant charge repulsion.
- High raw water hardness and ionic strength in groundwater treatment, combined with acid addition to prevent scaling/fouling, results in a solution chemistry which allows compounds that are not sieved out (e.g. low molecular weight AOC compounds) to pass almost unhindered through NF membranes and a significant fraction may also pass through RO membranes. This has significant implications for the biostability of membrane treated

drinking water since AOC has been correlated with increased bacterial populations in water distribution systems, especially in the absence of or at low chlorine residuals.

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