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MEMBRANES FOR THE CONTROL OF NATURAL ORGANIC MATTER FROM SURFACE WATERS

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Abstract—A range of nanofiltration (NF) modules was evaluated to determine rejection of disinfection by-product (DBP) precursors from low turbidity surface waters. Dissolved organic carbon (DOC), trihalomethane formation potential (THMFP), haloacetic acid formation potential (HAAFP), and chloral hydrate formation potential (CHFP) rejections averaged 90, 97, 94, and 86%, respectively. Rejections of bromide ion, an inorganic precursor, ranged from 40–80%. Pretreatment using microfiltration (MF) alone before NF provided some removal of turbidity but not enough to maintain the initial flux and recovery of the NF unit. NF runs were sustained over 30 days; however, some adverse changes in operational conditions were observed, and significant pressure increases were necessary to maintain flux. Precursor rejections by NF following MF varied little over time frames of up to 30 days. MF was only moderately effective in particle removals, with virtually no DBP precursor removal provided by MF. Ultrafiltration (UF) alone did not exhibit significant changes in operational conditions over a 30-day time frame; however, only modest precursor (<30% DOC) removal was observed. © 2000 Elsevier Science Ltd. All rights reserved

Key words—nanofiltration, NOM, disinfection byproducts, microfiltration

Abbreviations—BDOC, biodegradable organic carbon; BRW, Boulder Reservoir Water; CHFP, chloral hydrate formation potential; Dalton, indicative of membrane pore size (1000 daltons ≈ 0.1 μm); DBP, disinfection byproducts; DE, diatomaceous earth; EPA, Environmental Protection Agency; EPM, electrophoretic mobility; HAAFP, haloacetic acid formation potential; HPC, heterotrophic plate count; LSI, Langelier saturation index; MWCO, molecular weight cutoff; MTBE, methyl *tert*-butyl ether; NF, nanofiltration; NOM, natural organic matter; RO, reverse osmosis; SLW, Silver lake water; THM, trihalomethanes; TOC, total organic carbon; TOXHP, total organic halde formation potential; TPN, total particle count; UVA, ultraviolet absorbance at 254 nm

INTRODUCTION

In potable water treatment, there is much interest in the use of membranes as total treatment systems for the removal of DBP precursors, particles (turbidity), and microorganisms, with the potential use of free chlorine as a post-disinfectant. The major deterrent to more widespread use of membranes is the requirement for (often extensive) pretreatment. Most success with minimal pretreatment has been with groundwaters containing low levels of turbidity; less work has been done with low-turbidity surface waters. Little is known about differences in the nature of turbidity in surface waters versus groundwaters. General criteria to minimize colloidal/mineral fouling generally include low levels of particles/colloids and undersaturation with respect to precipitates such as CaCO₃. Specific criteria are given in terms of feed-water turbidity (<2 NTU), pH (≈7.0), silt density index (SDI < 3), and Langelier saturation index (LSI < 0).

A potential major role for membranes in surface water treatment is the removal of disinfection by-product (DBP) precursors, comprising part of the pool of natural organic matter (NOM). Chlorination DBPs of regulatory interest includes trihalomethanes (THMs), haloacetic acids (HAAs), and possibly chloral hydrate (CH). Membranes within the category of nanofilters (NF), in particular, have great potential in this endeavor based on their molecular weight cutoff (MWCO) of ᵃ100–500 daltons. Ideally, minimal pretreatment for a surface water prior to NF would consist of (i) scale control, if necessary (depending on pH and LSI), by addition

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of acid and/or an antiscalant and (ii) cartridge filtration or microfiltration (MF) for particle/colloid removal. Ultrafiltration (UF) is another viable approach for particle removal, with some modest precursor removal possible.

The primary objective of our work was to extend the experience in DBP precursor removal by membranes with minimal pretreatment, into the realm of low-turbidity surface waters. The literature survey reveals that there has been much experience in minimal pretreatment of groundwaters (Fu, 1994). Champlin and Hendricks (1995) reported on direct NF treatment of low-turbidity surface waters without pretreatment; serious flux decline and fouling were observed after one week of operation. Otherwise, the work reported for surface waters has involved more extensive pretreatment (Taylor *et al.*, 1990a), including coagulation/filtration. Besides precursor rejection, a key issue is sustainability of long-term operation; in other words, maintenance of operating conditions for long periods of time with only infrequent membrane cleaning required.

In this study, pilot-scale evaluations of individual membrane modules have been performed according to two tiers, short-term and long-term testing. The focus has been on low-turbidity surface waters which potentially require minimal pretreatment, with the primary objective of DBP precursor removal. An emphasis has been placed on nanofilters (NF), with microfilters (MF) and ultrafilters (UF) considered as potential pretreatment steps before NF. The Tier I work was intended to define short-term precursor rejection efficiencies while the Tier II work was intended to elucidate potential fouling behavior over longer time frames (30 days).

BACKGROUND

Other studies (Taylor *et al.*, 1987, 1989a, b, 1990a, 1992; Amy *et al.*, 1990; Dykes and Conlon, 1989; Jacangelo *et al.*, 1989a; Taylor, 1991, 1992; Tan and Amy, 1991; Tan and Sudak, 1992; Amy et al., 1993; Siddiqui, 2000) have shown that effective DBP precursor reductions can be achieved by membrane separation. While much potential has been shown by nanofiltration (Conlon *et al.*, 1989), ultrafiltration without pretreatment has shown only limited potential (Laine *et al.*, 1992).

Pilot studies have shown nanofiltration to be very effective in removing THM precursors (Jacangelo *et al.*, 1989a, b). Taylor *et al.* (1987) tested membranes ranging in molecular weight cutoffs (MWCOs) from 100 to 40,000 daltons with high-color groundwaters from Florida and found that sustainable operation was possible with minimal pretreatment. They found that a reverse osmosis membrane (MWCO = 100 daltons) was not significantly more effective in removing THMFP precursors (98% reduction) than a nanofilter (MWCO = 400 daltons, 96% reduction), but required 60% greater pressure

and produced a 50% lower flux. Amy *et al.* (1990) conducted bench, pilot, and full scale studies of nanofiltration for treating Colorado River water and observed a 65–70% reduction in THMFP. These low rejections were attributed to the very low molecular weight character of precursors in this source water (i.e., a significant amount of precursors with MW $\leq$ 500 daltons). Conlon *et al.* (1989) reported results for two small nanofiltration plants which achieved reductions of THMFP of 91 and 99%, and reductions of TOXFP (organic halide) of 97 and >99% at 75% recovery. Edwards *et al.* (1988) conducted a pilot scale test of nanofiltration for treatment of water from a Florida river and observed a 95% reduction in THMFP. Tan and Sudak (1992) tested four nanofilters for treatment of a highly colored groundwater from southern California and observed reductions of THMFP ranging from 97 to 99%.

Clark *et al.* (1992) summarized the literature data on DOC rejections as a function of MWCO, and found little difference between MWCOs of 100–300 daltons. Eriksson (1988) reported sucrose (MW = 342 daltons) rejection of 98% for four different nanofilters. The membranes evaluated, all purportedly having a negative surface charge, achieved slightly lower TOC rejections (<94%) with a groundwater source, presumably due to the negative character of humic substances comprising part of the TOC.

Taylor *et al.* (1990a) demonstrated effective DBP precursor control using nanofiltration on a surface water, although fouling was observed and attributed to inadequate pretreatment. Odegaard and Thorsen (1989) effectively treated a colored surface water with membranes having MWCOs ranging from 800 to 1000 daltons. Cadotte *et al.* (1988) reported greater than 90% rejections of TOC and THMFP with a NF membrane. Fronk *et al.* (1990a, b) summarized a number of studies that used RO and NF membranes to remove synthetic and natural organics from water. Dykes and Conlon (1989) summarized the use of nanofiltration in Florida, where much of the work has been done on the evaluation of nanofilters for DBP control. Taylor *et al.* (1989a, b) discussed the application of membranes for potable water treatment and presented cost and performance data for a nanofilter pilot plant. Taylor (1990b) also presented performance data on the rejection of synthetic organic chemicals by nanofilters. Tan and Amy (1991) compared ozonation versus nanofiltration for the removal of color and reduction of DBPs, and found membranes to be significantly more effective in reducing DBP formation potentials.

Laine *et al.* (1994) discussed pretreatment issues and the potential role for preceding nanofiltration (NF) with ultrafiltration (UF) as a pretreatment step to remove particulate matter and large molecular size precursors; they found that higher MWCO

UF-membranes (e.g., 100,000 daltons) are only effective for particles whereas lower MWCO UF-membranes (e.g., 10,000 to 50,000 daltons) may provide some limited precursor removal. Laine *et al.* (1990) found that, without some kind of chemical pretreatment, UF is not effective in removing NOM, with DOC removals of less than 20%. Jacangelo *et al.* (1989b) discussed microfiltration (MF) as a pretreatment option and noted that this process is capable of removing particles and colloids in the range of 0.05–2 μm, either in a dead end or cross-flow mode. Taylor *et al.* (1992) used a MF membrane with an effective pore size of 0.2 μm for pretreatment of a surface water.

EXPERIMENTAL METHODS

Membrane testing unit and protocols

The membrane-testing apparatus permitted continuous evaluation of candidate membranes under recommended operating conditions of pressure, flux, and recovery. The module consisted of a high pressure pump, pressure vessels to hold spiral-wound membranes, and associated pressure gauges, flow meters, valves and tubing (Fig. 1). This apparatus permitted single-stage evaluation of an individual (40-inch by 2.5-inch) NF element.

Tier I evaluations were based on an "equilibration" time of 1 h, after which samples were taken for analytical characterization. In Tier I testing, the NF modules were preceded by cartridge filters (5 μm followed by 1 μm). Each membrane was evaluated individually and operated under a standard set of conditions consisting of a feed flow of approximately 3 gpm, a single stage recovery of

approximately 10%, and a variable pressure of between 80 and 125 psi according to manufacturers' recommendations. A decision was made to not include recovery as an experimental variable; the selection of 10% recovery was arbitrary and somewhat below that normally employed for low-recovery elements such as those studied. Depending on removal mechanism (sieving or diffusion), recovery may affect the degree of precursor rejection. A total of six nanofiltration membranes were evaluated according to the Tier I protocol.

Tier II evaluations were performed over a 30-day period with periodic samples taken over this time frame for analytical characterization. Operational conditions monitored included instantaneous flux, inlet and permeate pressure, and recovery. Given the choice of two modes of operational testing; constant pressure/declining flux vs constant flux/increasing pressure; we chose the latter. Constant flux was maintained by changing the feed flow rate, translating into pressure adjustments to compensate for variations in flux and recovery. In our work, we did not consistently monitor transmembrane pressure, only inlet and permeate pressure. Permeate pressures were found to correspond to atmospheric pressure. Typically. the pressure drop across a NF membrane (inlet minus reject pressure) is less than 10 psi (Jacangelo *et al.*, 1994). Four nanofilter membranes were evaluated according to the Tier II approach, with microfiltration pretreatment.

Candidate membranes tested

Four membrane manufacturers were contacted with solicitations for candidate NF and UF membranes for DBP precursor rejection. A total of seven spiral-wound (40-inch by 2.5-inch) NF modules were obtained, as summarized in Table 1. All of the molecular weight cutoffs (MWCOs) are manufacturer-specified. Five of the NF elements; NF-1, NF-2, NF-3, NF-4, and NF-7; were tested according to the Tier I protocol.
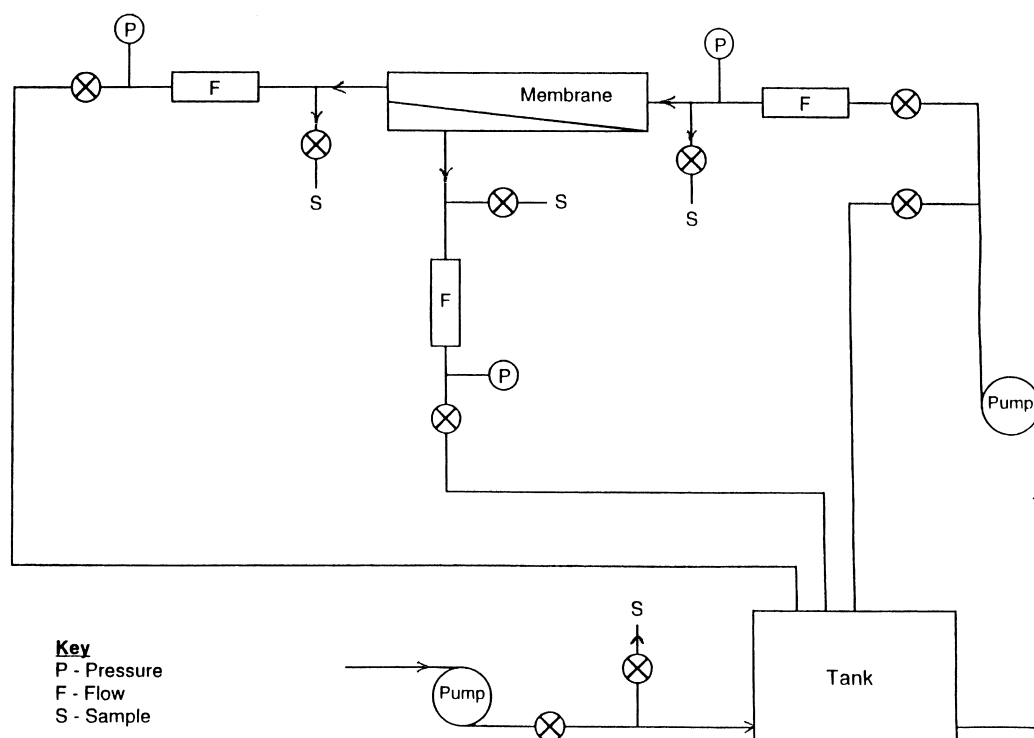

Fig. 1. Membrane element testing unit.

Table 1. Summary of membranes tested[a]

Membrane	Manufacturers specifications					Testing conditions		
	Material[b]	Configuration[c]	MWCO, daltons	Pressure range (psi)	Module area (ft²)	Initial inlet pressure (psi)	Initial product flux[d] (gpm/ft²)	Initial specification product (gpm/ft²-psi)
NF-1[e]	TFC	SR	200	< 250	23	80	0.0091	0.000114
NF-2[f]	TFC	SR	300	< 600	23	80	0.0061	0.000076
NF-3[g]	PVC derivative	SR	200–300	< 225	20	N/A	N/A	N/A
NF-4[h]	TFC	SR	100–150	70–400	21	N/A	N/A	N/A
NF-5[i]	TFC	SR	100–150	70–400	21	120	0.0124	0.000103
NF-6[j]	Polyamide TFC	SR	300	< 200	24	120	0.0071	0.000059
NF-7[k]	TFC	SR	500	< 200	24	N/A	N/A	N/A
UF[l]	TFC	SR	60,000	< 70	16	55	0.137	0.0025
MF[m]	Polyester textile	Cross-flow	0.1 μm	< 60	75	30	0.133	0.0044

[a]N/A = not applicable (short term evaluation).
[b]TFC = thin-film composite.
[c]SR = spiral-wound 2.5 × 40 inch elements except MF.
[d]Based on target recovery of approximately 10%.
[e]Filmtec NF70.
[f]Filmtec NF45.
[g]Hydranautics PVD1.
[h]Desal 5.
[i]Desal DL254.
[j]Osmonics MX07.
[k]Osmonics BQ01.
[l]Osmonics 192-PT3.
[m]Exxflow VS-70-10.

Four NF elements; NF-1, NF-2, NF-5 (similar to NF-4), and NF-6; were evaluated in Tier II testing with pretreatment by microfiltration (MF, Table 1). We employed a MF unit (cross-flow with a rated capacity of 10–15 gpm and a recovery of >95%; rated @ 0.1 μm) to evaluate as pretreatment before NF. The MF module was operated at 10 gpm with a split stream fed into each of two of the aforementioned NF modules. During Tier II testing, operational conditions were monitored over time, including flux, pressure, and recovery.

In addition to evaluating the MF/NF combination, ultrafiltration (UF) and microfiltration (MF) alone (UF, Table 1) were evaluated in Tier II testing to determine their ability to provide both operational sustainability and precursor removal.

Description of MF technology

Exxflow® microfiltration builds a dynamic filtration layer from the natural precipitate solids present in the water to be treated. As this water is pumped into the tubes, it escapes through the porous textile tube walls, leaving the solids deposited on the inside of the tube walls.
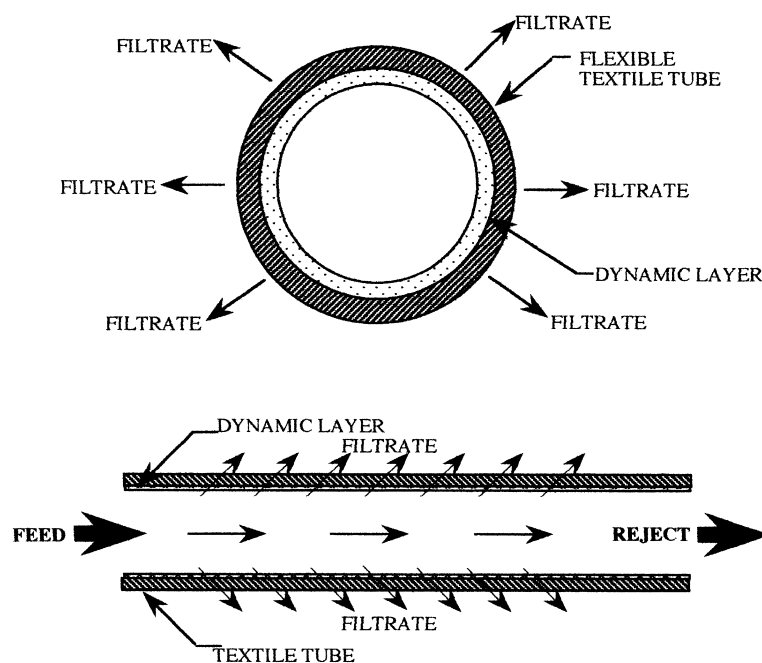

Fig. 2. Cross and longitudinal sectional view of Exxflow tubular MF membrane system.

These solids create a layer which becomes a membrane, the thickness of which is controlled by the flow of liquid along the tube; the faster the flow, the thinner the membrane, and visa versa (Fig. 2).

Analytical characterization

Feed-water and product-water samples were taken for analytical characterization according to the protocols described below.

Total Organic Carbon (TOC) was measured using a Shimadzu TOC-5000 analyzer. Dissolved Organic Carbon (DOC) was determined on 0.45 μm-filtered samples using the same instrument. UV absorbance at 254 nm (UVA) measurements were made with a Shimadzu UV-160 spectrophotometer on 0.45 μm-filtered samples. Specific absorbance was calculated as the ratio of UVA to DOC. Fluorescence measurements were performed at an excitation wavelength of 320 nm and an emission wavelength of 420 nm employing a Hitachi F-3010 spectrofluorimeter with 0.45-μm filtered samples. Low molecular weight (< 500 daltons) DOC and UVA were determined by ultrafiltration (UF) using an Amicon stirred cell with Amicon YCO5 membranes. Non-humic DOC and UVA were estimated by XAD-8 resin adsorption (humic = XAD-8 adsorbable; non-humic = non-adsorbable).

A Hewlett Packard 5890 GC/ECD (gas chromatograph with an electron capture detector) was used to measure chlorination DBPs. Chlorination conditions were based on a Cl_2/DOC of 3 mg/mg, a pH of 7.0, a temperature of 20°C, and a reaction time of 24 h. Trihalomethanes (THMFP) and chloral hydrate (CHFP) were measured using EPA Method 551 (liquid–liquid extraction with MTBE); haloacetic acids (HAAFP, summation of 5 species) were measured using EPA Method 552 (extraction with MTBE, derivatization with diazomethane).

Turbidity was measured using a Hach 2100 turbidimeter. Particle size distribution (PSD) from 0.5 to 25 μm was determined with a Met-One optical particle counter, providing an estimate of total particle number (TPN). Particle electrophoretic mobility (EPM, an index of surface charge) was determined using a Brookhaven Zeta Plus instrument.

Bromide ion was determined with a Dionex DX-300 ion chromatograph, based on EPA Method 300 with an AS9-SC column. Conductivity, pH, hardness, and alkalinity were measured according to Standard Methods for the Examination of Water and Wastewater (1988).

Source waters

As source waters, we selected several Colorado surface waters from mountain watersheds which are characterized by consistently low turbidity. General characteristics include: turbidity <1–5 NTU; DOC = 3 to 5 mg/l; low bromide; pH = 7; low sulfate; negative LSI; and SDI < 3. Low seasonal variability was observed with the exception of DOC where elevated levels were found during spring runoff (i.e., snowmelt). Specifically, we examined the following sources: (i) Silver Lake (SLW); (ii) Barker Reser-

voir (BLW); (iii) Boulder Reservoir (BRW) corresponding to raw/untreated water entering a conventional treatment plant; (iv) chemically-pretreated (27 mg/l alum) Boulder Reservoir (BRW-F) corresponding to sand-filtered water (before disinfection) from a conventional treatment plant; and (v) selected sources with bromide ion spikes.

Testing programs

In Tier-I testing, pretreatment consisted of cartridge filtration through a sequential 5.0 μm and 1.0 μm series, except for using chemically-pretreated water in one set of experiments. Raw-water turbidities of 5.2 and 1.6 NTU were reduced to 4.1 and 0.8 NTU for Silver Lake and Barker Reservoir, respectively, by cartridge filtration. The Boulder Reservoir (raw water) exhibited a negative LSI and a SDI of less than 3.0; based on its favorable LSI, no acid addition took place. The turbidity after cartridge filtration was 0.7 NTU for the raw feed-water, compared to 0.1 NTU for the chemically-pretreated feed-water. Chemical pretreatment consisted of alum coagulation followed by sedimentation and filtration.

In Tier-II testing, either the Silver Lake or Boulder Reservoir raw Source water was pretreated by MF before NF.

RESULTS AND DISCUSSION

Tier-I (short-term) testing results

Table 2 summarizes important feed-water characteristics (after cartridge filtration) for each of the source waters evaluated, including DOC (bulk and fractions) and spectrophotometric properties. Typical NF results for elements NF-1 through NF-4 are summarized in Table 3, including product-water characteristics derived from two feed-waters not chemically pretreated, raw waters from Barker Reservoir and Silver Lake. Generally, more variability was observed in precursor levels among the various feed waters compared to the various product waters. Product waters derived from each of the four membranes shown were quite similar in quality regardless of feed-water source. Table 3 also shows product-water results derived from raw vs chemically pretreated feed waters derived from Boulder Reservoir. Generally, only slight differences were observed in product water qualities derived from raw versus chemically-pretreated feed waters, indicating that the fraction of precursors removed by chemical pretreatment were also effectively removed by NF. Thus, the only motivation for con-

Table 2. Summary of feed water characteristics[a]

Parameter	SLW	BLW	BRW	BRW-F[b]
Turbidity (NTU)	4.2	0.8	0.75	0.12
TPN: 0.5–25 μm ($\sharp$/ml)	8000	9000	7000	N/A
DOC (mg/l)	3.7	2.0	3.2	1.5
< 0.5 K DOC (mg/l)	0.8	0.6	0.7	0.7
Non-humic DOC (mg/l)	1.3	0.85	1.4	0.6
UVA (cm^{-1})	0.230	0.060	0.080	0.030
Specific UVA (cm^{-1}/(mg/l))	0.062	0.030	0.025	0.030

[a]N/A = not analyzed.
[b]Chemically pre-treated and sand filtered.

Table 3. Summary of tier-I short-term testing

Source	Membrane	Permeate Charact.			Permeate DBPFPs		
		DOC (mg/l)	UVA (cm^{-1})	Fluor. Inten.	THMF (μg/l)	CHFP (μg/l)	HAAF (μg/l)
SLW-Raw		3.82	0.241	140	240	12	245
SLW-Perm.	NF-1	0.21	0.002	2.7	4.5	2.0	6.1
SLW-Perm.	NF-2	0.22	0.002	2.3	2.2	0.5	3.2
SLW-Perm.	NF-3	0.38	0.001	1.8	2.7	0.7	6.5
SLW-Perm.	c♯ NF-4	0.23	0.003	2.7	3.0	2.2	4.8
SLW-Perm.	Avg.	0.26	0.002	2.4	3.1	1.4	5.2
SLW-Perm.	Avg. %Rem.	93	99	98	98	88	99
BLW-Raw		2.21	0.065	50	75	6.5	80
BLW-Perm.	NF-1	0.31	0.002	2.3	4.2	1.9	7.5
BLW-Perm.	NF-2	0.32	0.003	2.5	2.5	1.7	5.7
BLW-Perm.	NF-3	0.21	0.001	2.4	2.5	1.5	3.0
BLW-Perm.	NF-4	0.25	0.002	2.6	2.4	1.5	4.2
BLW-Perm.	Avg.	0.27	0.002	2.5	2.9	1.6	5.2
BLW-Perm.	Avg. %Rem.	87	97	95	96	75	94
BRW-Raw		3.21	0.091	145	45	15	92
BRW-Perm.	NF-1	0.25	0.004	4.2	2.5	0.8	2.8
BRW-Perm.	NF-2	0.33	0.003	3.8	2.0	0.8	8.2
BRW-Perm.	NF-3	0.30	0.003	3.2	1.0	0.5	3.2
SLW-Perm.	NF-4	0.21	0.001	4.7	2.1	0.3	3.3
BRW-Perm.	Avg.	0.27	0.002	3.9	1.9	0.6	4.4
BRW-Perm.	Avg. %Rem.	92	98	97	96	96	95
BRW/F-Raw		1.55	0.045	20	15	2.0	40
BRW/F-Perm.	NF-1	0.18	0.008	9.0	1.7	1.1	3.8
BRW/F-Perm.	NF-2	0.22	0.006	5.0	1.2	2.2	3.0
BRW/F-Perm.	NF-3	0.22	0.001	2.4	2.2	2.3	3.8
BRW/F-Perm.	NF-4	0.19	0.004	5.0	3.1	3.8	8.5
BRW/F-Perm.	Avg.	0.21	0.005	5.3	2.1	2.4	4.8
BRW/F-Perm.	Avg. %Rem.	86	89	74	86	100[a]	88

sidering chemical pretreatment is for turbidity/particle removals before membrane treatment.

Based on the overall results derived from membranes NF-1 through NF-4 (MWCO < 300 daltons), DOC removals of 84–98% were observed, with an average of 90%. In all cases, the permeate DOC was reduced to below the raw-water < 500-daltons-DOC. Thus, a stirred-cell UF evaluation using a 500 dalton UF filter appears to have merit as an index for potential precursor removal by NF modules with MWCO < 500 daltons. For membrane NF-7 (MWCO = 500 daltons), the permeate DOC was only reduced by 40%; this particular membrane, based on its MWCO, is on the borderline between NF and UF membranes.

Based on all NF membranes and source waters, the following changes in spectrophotometric parameters were observed: (i) significant reductions in both UVA and fluorescence and (ii) reductions in specific absorbance (ratio of UVA/DOC). Reductions in specific absorbance indirectly suggest the preferential removal of humic and/or larger molecular weight DOC, over non-humic and/or lower molecular weight DOC. Corresponding reductions in fluorescence further suggest reductions in humic precursors. On the other hand, the lower levels of product-water bulk DOC compared to levels of feed-water non-humic DOC indirectly suggest some reductions in non-humic NOM. Based on XAD-8 resin adsorption, product-water DOCs included both humic and non-humic fractions of NOM at significantly lower levels than the corresponding feed-waters. These humic and non-humic fractions correspond to hydrophobic and hydrophilic fractions of NOM. While we did not characterize the membranes according to hydrophobicity, it is noteworthy that the different membranes were apparently capable of removing both hydrophobic and hydrophilic NOM. The removal of both hydrophobic and hydrophilic NOM suggests sieving as a removal mechanism.

Significant reductions in DBPFPs were observed with elements NF-1 through NF-4: (i) THMFP reductions ranged from 95 to 99%, with an average of 97%; (ii) CHFP reductions from 64 to 95%, with an average of 86%; and (iii) HAAFP reductions from 78 to 97%, with an average of 94%. The differences in rejection among membranes NF-1 through NF-4 were relatively small. Membrane NF-7 was much less effective, providing reductions of 79, 75, and 72%, respectively. Overall, there appeared to be a slight preferential removal of THM over HAA precursors, suggesting that lower molecular weight and/or non-humic DOC may be more influential in HAA formation.

The source waters contained very low levels of ambient bromide (< 10 μg/l); in several Tier I experiments, source waters were spiked with bromide. In these experiments, bromide rejections ranged from about 40 to 80%; this result has significant implications for the formation of brominated DBPs upon post-disinfection. Even though bromide is removed, the higher removal of DOC results in an elevated ratio of Br/DOC

which, in turn, favors the formation of brominated DBPS. Nevertheless, the formation of all THM and HAA species was reduced by NF, with reductions in brominated species less than strictly chlorinated species.

Good particulate removals were achieved with product-water turbidities generally <0.05 NTU. While pretreatment was not an objective of Tier-I testing, it is noteworthy that there was little difference between turbidities and particles counts in 5 μm vs 1 μm cartridge filtrates; larger reductions were observed between raw-waters and 5 μm filtrates.

Tier-II (long-term) testing results

Four of the five NF elements tested under Tier I conditions (NF-1 through NF-4) provided generally comparable rejections and specific productivities ((gpm/ft^2)/psi); a decision was made to advance the NF-1 and NF-2 elements into the Tier II testing, augmented by the NF-5 (a new version of NF-4) and NF-6 elements.
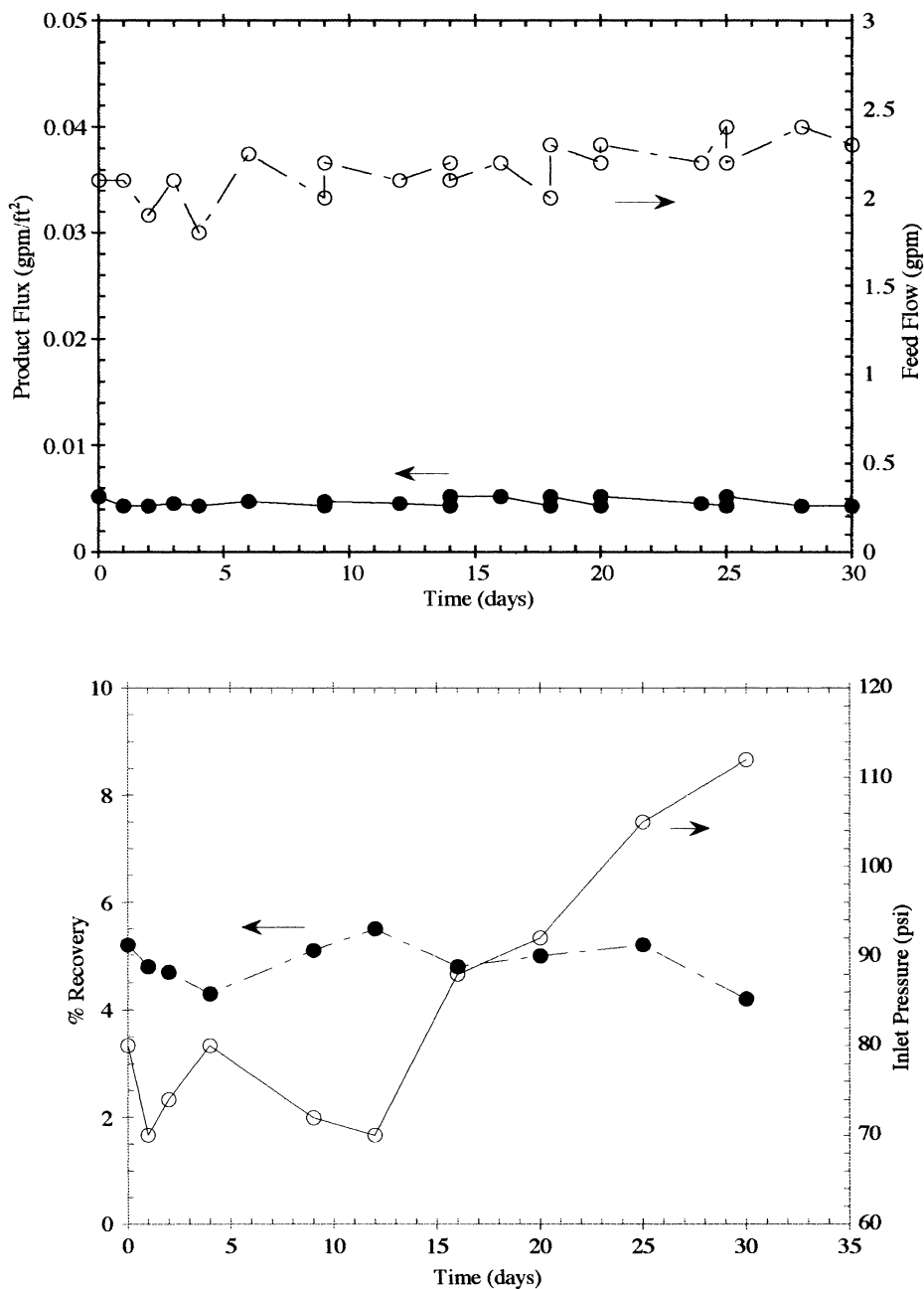
Fig. 3. Feed flow, product flow, recovery, and operating pressure vs time: Silver Lake Source; NF-2 module after MF.

The Silver Lake source was used as a feed water over a 30-day period for elements NF-1 and NF-2, following pretreatment through the MF unit. Hereafter, in these long-term tests, the feed water corresponds to the water applied to NF after MF pretreatment. Generally, flux and recovery were fairly constant over the 30-day period, although significant pressure increases were necessary (Fig. 3). As shown in Figs 3 and 4, significant pressure increases were necessary after about 20 days of operation, indicative of fouling. Product water precursor levels were fairly constant over time (Fig. 4),

with precursor rejections comparable to those observed in short-term (Tier I) tests.

The Boulder reservoir source was used to evaluate elements NF-5 and NF-6 after MF pretreatment over 30-day time frames. These results are shown in Figs 5 and 6. In both cases, after some variable operational conditions over the first 2 or 3 days, operational conditions stabilized thereafter with fairly constant conditions. Compared to the results shown in Figs 3 and 4, there appears to be less evidence of fouling for these two NF elements. Partial but incomplete flux recovery was observed when these two NF modules were cleaned after 30 days with a
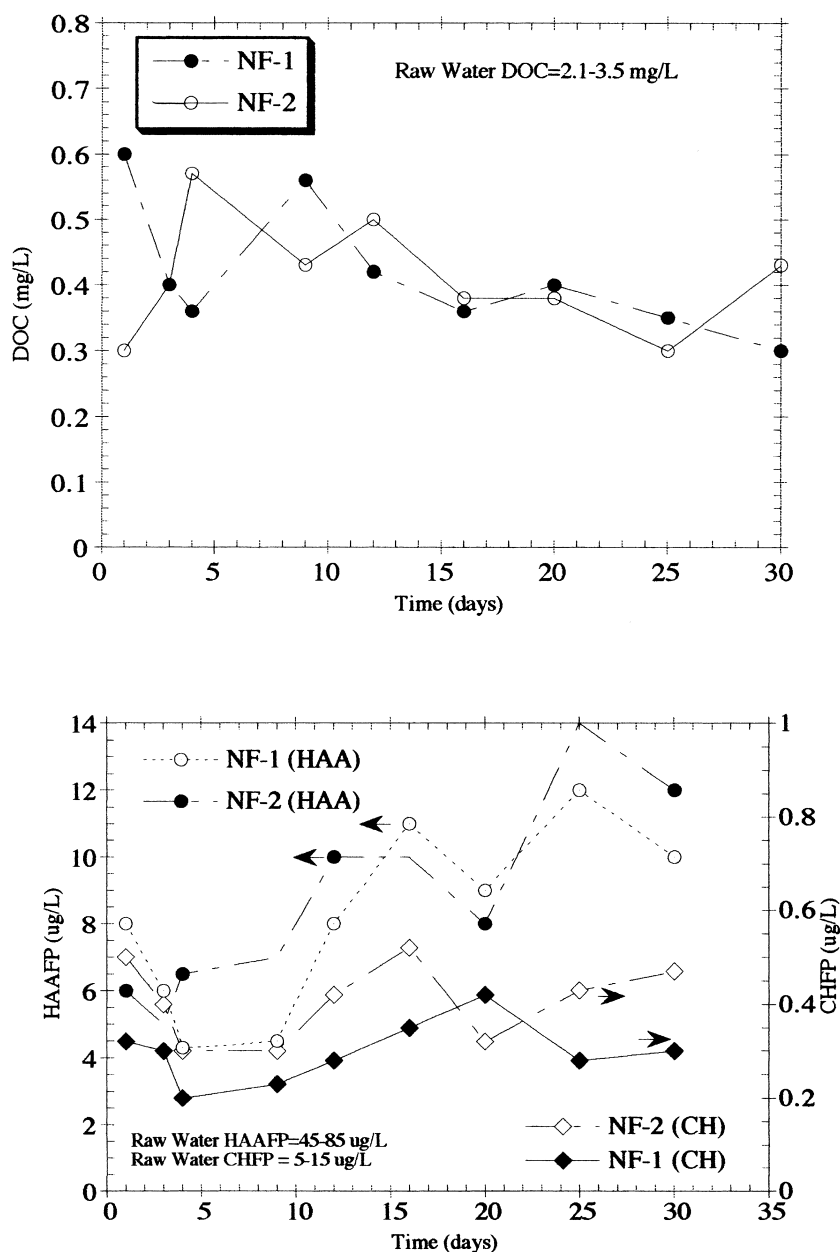

Fig. 4. DOC, CHFP, and HAAFP vs time: SLW.

pH 12 sodium dodecyl sulfate (0.1%) solution, recommended for control of colloidal fouling. While this cleaning strategy was primarily intended to rectify colloidal fouling, some NOM fouling may have occurred. Figure 7 highlights the associated precursor rejections achieved as a function of time; it is particularly noteworthy that variations in feed water quality had little influence on final product-water levels achieved.

The overall operational conditions associated with Tier II testing of NF elements can be summarized as follows. Over short (day to day) time scales, the various flows and inlet pressures decreased. Decreases in feed-flow rate and inlet pressure required near-daily maintenance of the inlet pressure at the initial value. Over the long-term (30 days) duration of the tests, product flux was sustained and/or flux decline was minimized by increasing inlet pressure through an increase in feed flow. For NF-1 and NF-2, flux was generally maintained at the expense of increased inlet pressure beyond the initial value. For NF-5 and NF-6, flux decline occurred as inlet pressure was adjusted back to the initial value; this behavior indicates a decrease in the water mass transfer coefficient caused by associated fouling. Based on LSI values and solubility calculations, it is unlikely that inorganic salts precipitated, and thus colloidal fouling was most likely. All of the four elements tested were prone to fouling and required pretreatment
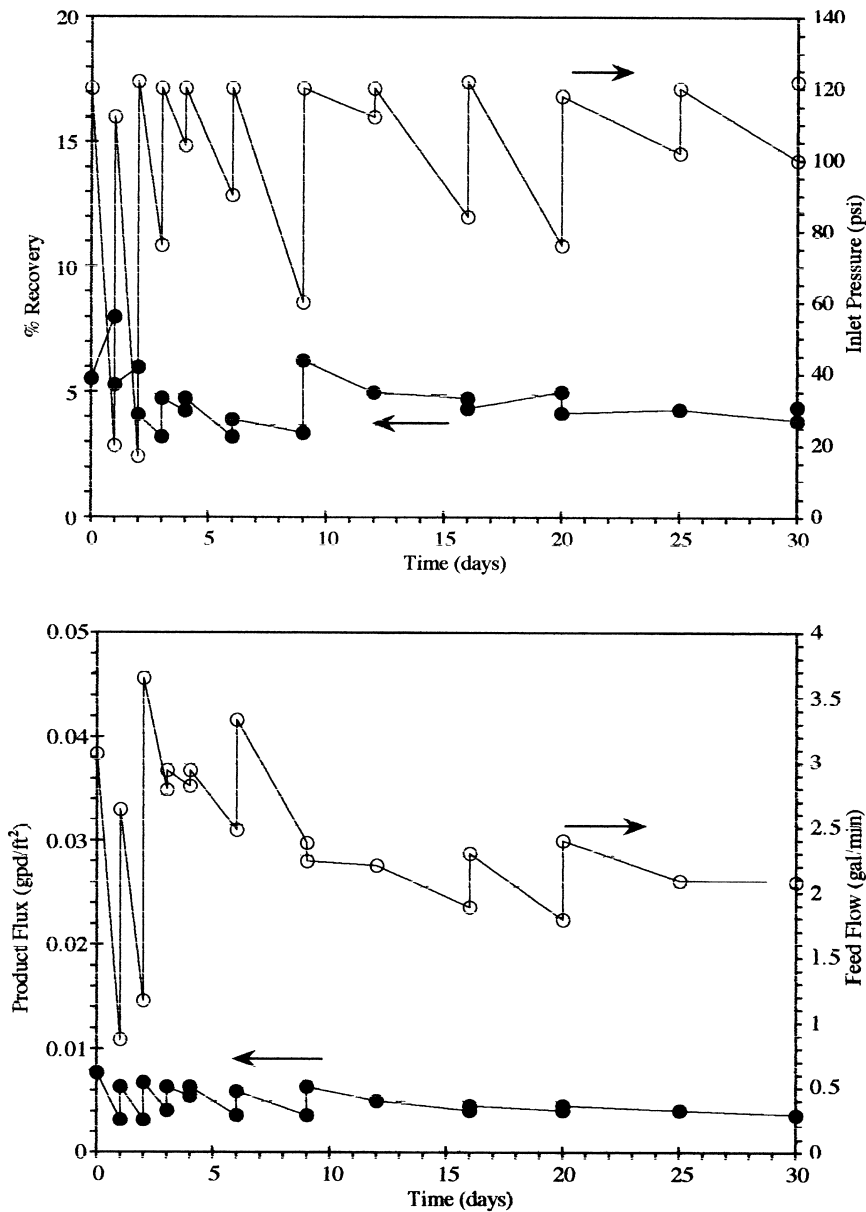

Fig. 5. Feed flow, product flow, recovery, and operating pressure vs time; BRW; NF-5 after MF.

beyond that afforded by the MF unit employed. None of the elements provided a clear advantage in terms of specific productivity (Table 1).

Ultrafiltration results

Results for the UF module alone are shown in Fig. 8; little change in operational conditions (and thus little evidence of fouling) were observed over 30 days. The% recovery of feed water ranged from 50 to 62 for operational pressure of ≈ 55 psi. DOC removal ranged from 25 to 32% and total article count reduction ranged from 70 to 96%. The results portray to the effectiveness of UF as a pre-filter. UF reduced THMFP and HAAFP by 50 and 32%, respectively.

Microfiltration results

MF was, at most, only moderately effective in removal of particles (Table 4) but virtually ineffective in precursor removal (Fig. 9). The evaluation of UF was performed to determine its ability to both remove particles, thus elucidating its potential role in pretreatment (Table 4), and precursors; some, but modest, precursor rejection was observed (Fig. 10). Cartridge filtration alone before NF did not prove to be a logistically viable option in the long-term Tier II tests; clogging of the cartridge filters occurred within 12–18 h time frames, with the 5 μm filters being most problematical (this may be
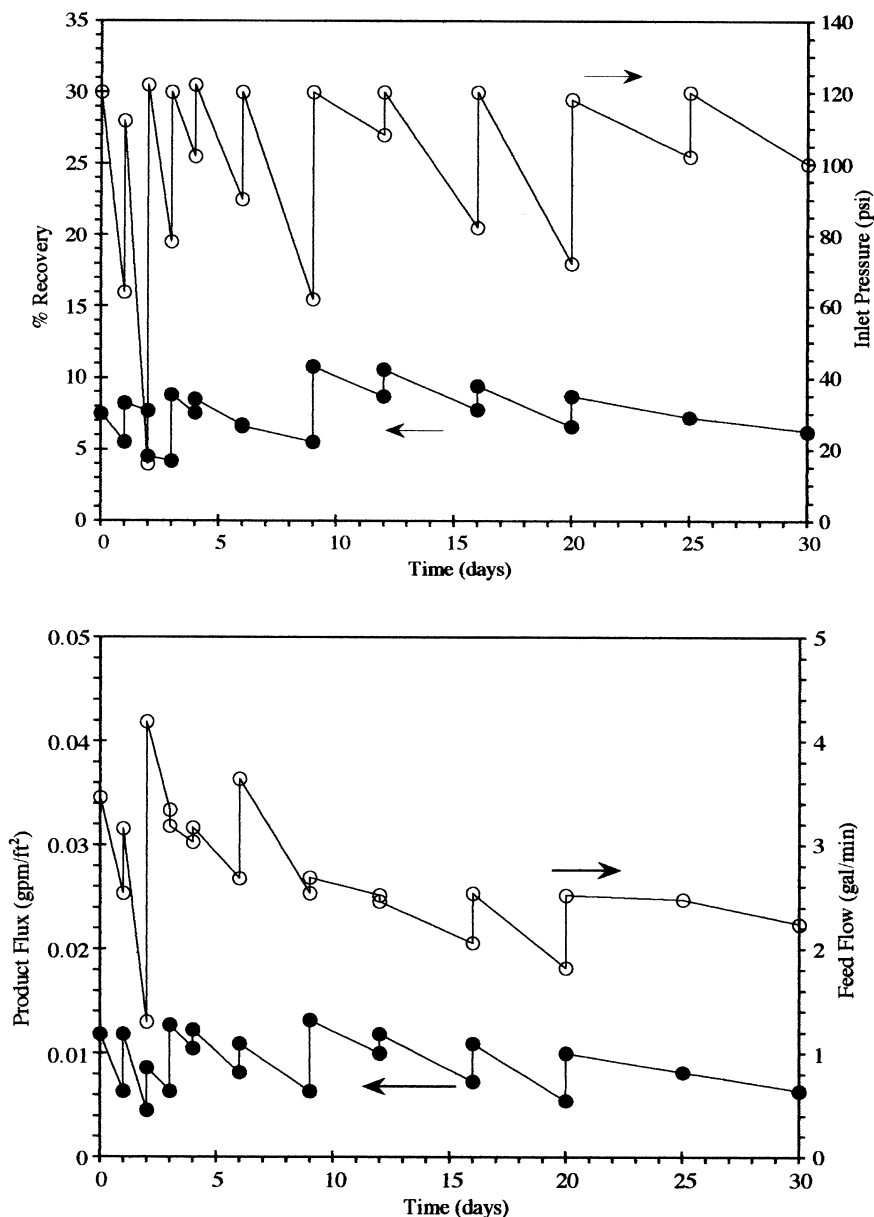

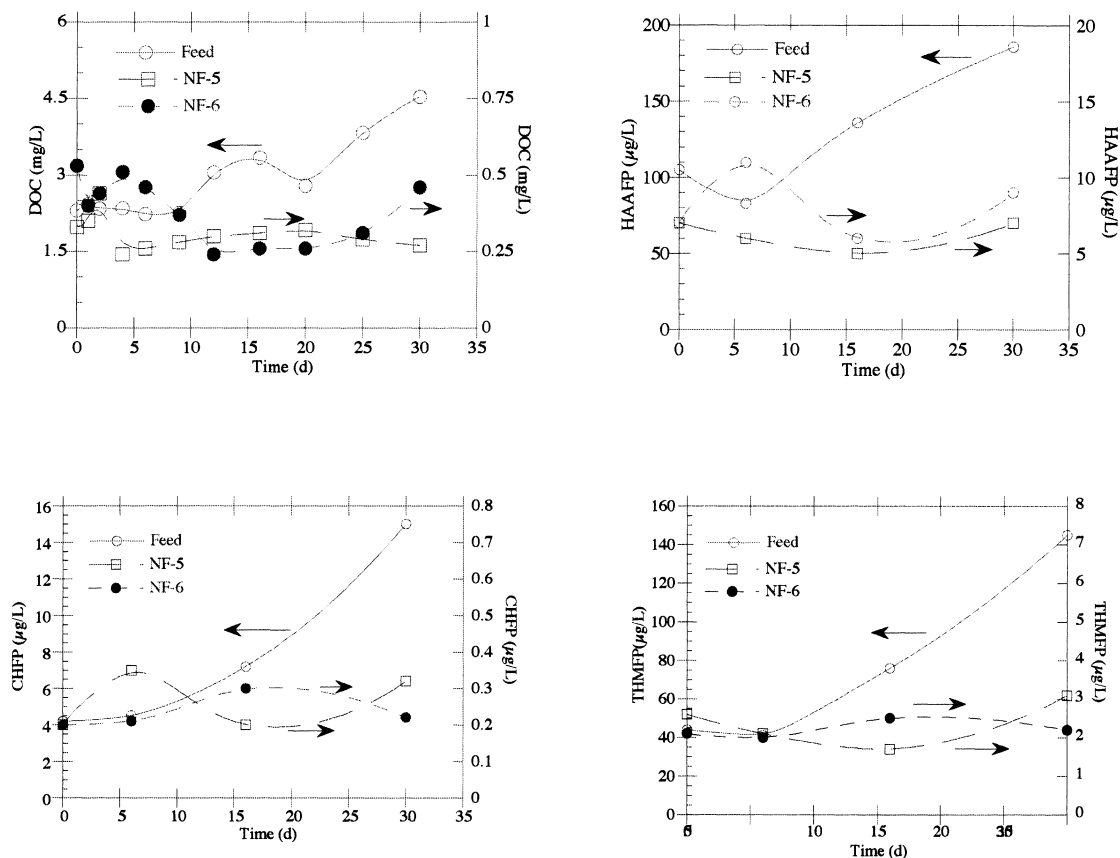Fig. 6. Feed flow, product flow, recovery, and operating pressure vs time: BRW, NF-6 after MF.

Fig. 7. Effect of feed water quality on product water quality: DOC, HAAFP, CHFP, and THMFP.

simply due to the fact that 5 μm filters were first in line).

The selected cross-flow MF unit ostensibly removes all particles and colloids down to 0.1 μm, according to the manufacturer. However, we consistently observed supramicron (>1 μm) particles in MF permeates. This particular MF unit is a *textile* membrane developed for higher turbidity source waters which "condition" the membrane; the manufacturer even suggested that diatomaceous earth (DE) may be used for conditioning. Figure 10 shows the MF performance in rejecting turbidity and particles over a 30-day period when raw-water

turbidities were relatively low, and during a different 8-day period when raw-water turbidities reached significantly higher levels; the conditioning provided by the higher turbidity levels is apparent.

To assess this MF unit under somewhat more optimal conditions, we evaluated DE conditioning. In this evaluation, we spiked the feed water with model particles; alumina (number average size of approximately 5 μm) particles as supramicron and fluorescent microspheres (151 and 24 nm) as submicron particles, The submicron microspheres were polystyrene latex impregnated with fluorescent dyes (Interfacial Dynamics Corp.,

Table 4. Source, feed and product waters: turbidity, particle counts, and particle mobility[a]

Source	Total TPN (♯/ml)	0.5–1 μm TPN (♯/ml)	1–5 μm TPN (♯/ml)	5–25 μm TPN (♯/ml)	EPM (μ/s)/(V/cm)	Turbidity (NTU)	Conduct. (umhos/cm)
SLW-Raw	13,300	2710	6770	3890	−1.0	0.97	21
SLW-MF	7900	1970	4600	1330	−1.0	0.78	25
SLW-UF	498	100	316	82	−0.7	0.22	17
SLW-NF-2	N/A	N/A	N/A	N/A	N/A	0.11	N/A
BRW	14,000–106,000	2800–21,000	7100–54,100	4000–30,000	−1.0	1.0–7.2	N/A
BRW-MF	11,000–53,000	2500–11,200	5300–27,000	3200–15,000	−1.0	1.0–4.2	N/A
BRW-UF	4300–12,600	780–5600	2400–3700	1100–3100	N/A	0.5–1.0	N/A
BRW-NF-2	N/A	N/A	N/A	N/A	N/A	0.05–0.13	N/A

[a]N/A = not analyzed.
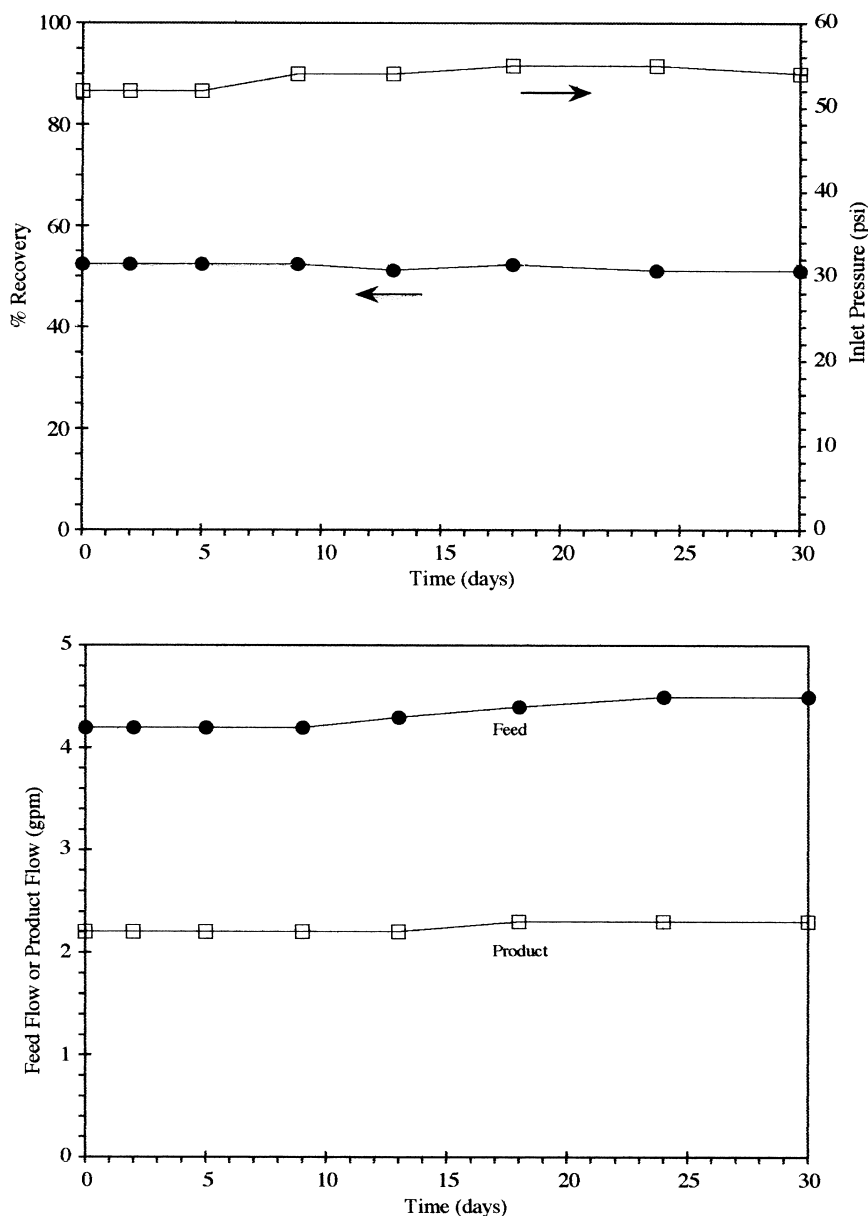
Fig. 8. Feed flow, product flow, recovery, and operating pressure vs time: BRW, UF alone.

Portland, OR). The 5.0 μm alumina particles were detected by particle counting. Two configurations of the MF membrane were tested: (1) the uncoated MF membrane; and (2) the membrane coated by diatomaceous earth (DE), which acts as "artificial turbidity". The MF membrane was coated with DE by adding 1 kg of DE to 20 l of raw water and recirculating the suspension through the membrane for 30 min prior to adding the microspheres. The MF membrane was actually designed for use in highly turbid waters containing colloids/particles that would coat the membrane on their own. The alumina results are shown in Fig. 11, showing the model particles measured in the product and reject streams.

While DE improved particle rejection, the unit still allowed the passage of some supramicron particles along with most of the submicron particles. The uncoated MF membrane allowed the passage of nearly 100% of the submicron microspheres and approximately 80% of the alumina particles. The DE-coated MF allowed the passage of only 18% of the 24 nm microspheres, 35% of the ~150 nm microspheres, and 10% of the 5 μm alumina particles. Hence, the diatomaceous earth effectively increased the filtering efficiency of the MF membrane. It is not clear, however, whether the particles were removed by physical filtration or by adsorption to the diatomaceous earth layer coating the membrane.
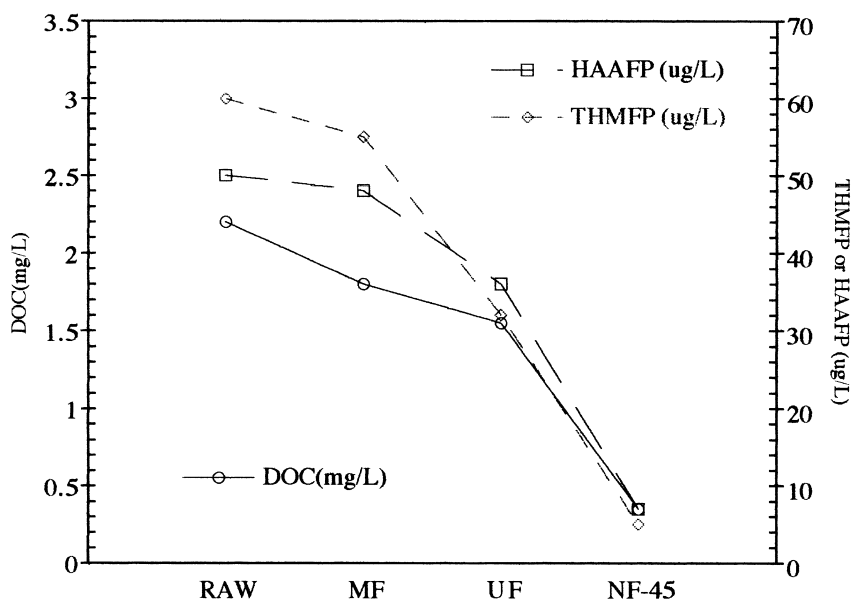
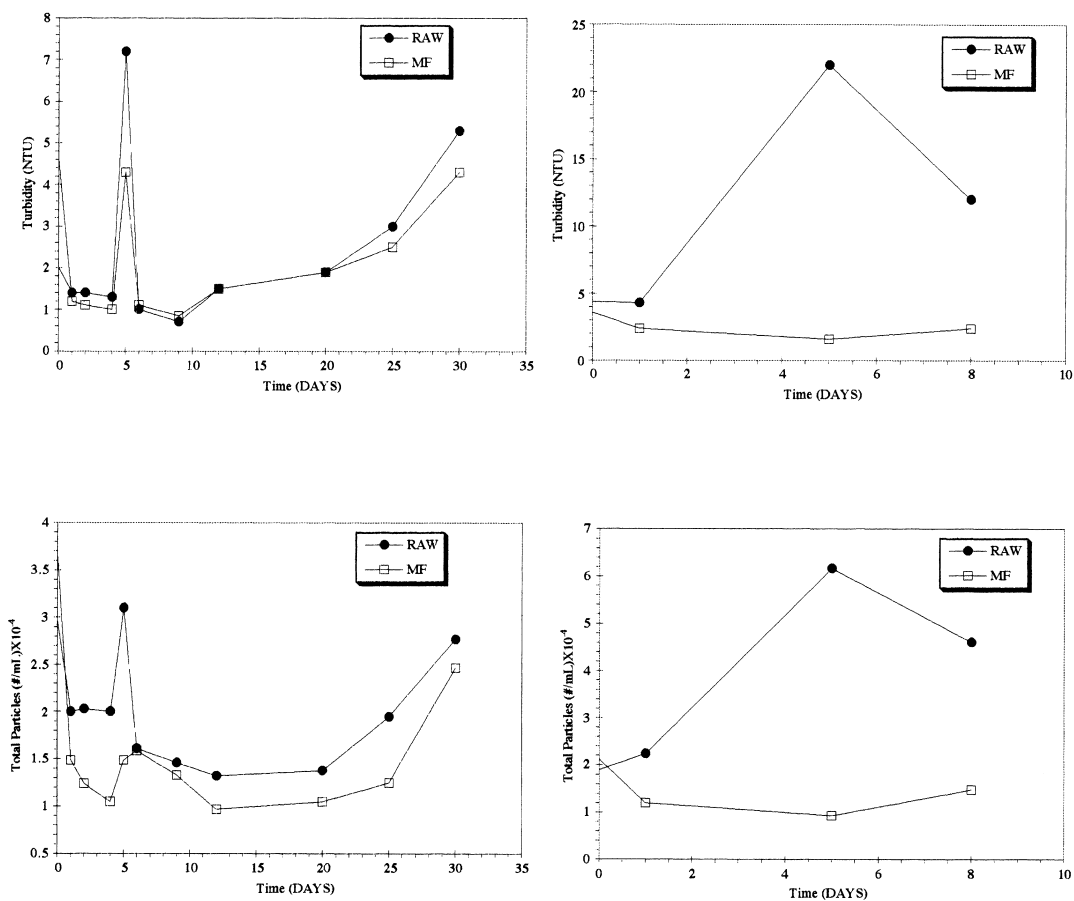Fig. 9. DOC, THMFP, HAAFP vs treatment (SLW): RAW, MF, UF, and NF.

Fig. 10. Turbidity and total particle numbers vs time for 30-day and 8-day MF tests.
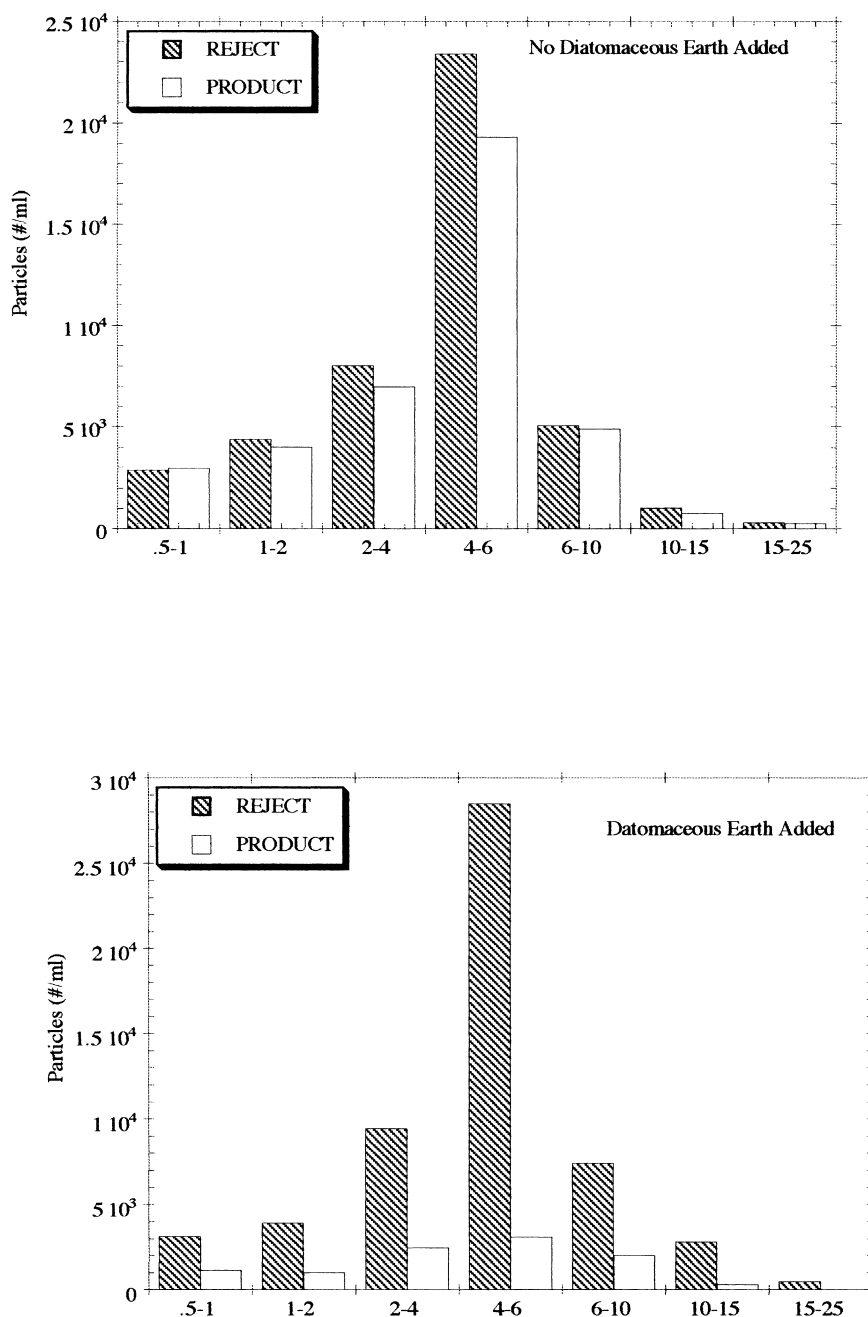
Fig. 11. MF rejections of alumina (supramicron) particles with and without diatomaceous earth.

MF reduced DOC by less than 6% and the formation of THMs and HAAs was reduced by 7 and <1%, respectively. MF was effective in particle count removal ranging from 20 to 40%. It is anticipated that this MF configuration will provide enhanced particle removal at relatively higher treatment flows. While the MF unit employed herein did not provide adequate pretreatment, other hollow-fiber MF (and UF) membranes developed/being developed may provide better pretreatment (Jacangelo *et al.*, 1994; Jacangelo, 1995; Yoo *et al.*, 1995).

Microbial removal

Limited work was done to address peripheral issues of membrane treatment such as rejection of biodegradable NOM, as measured by biodegradable dissolved organic carbon (BDOC); and microbe rejection, as measured by heterotrophic plate counts (HPC) and total coliform (TC) tests. The Silver Lake source contained 0.6 mg/l of BDOC; MF reduced this slightly to 0.4 mg/l, with further reduction to 0.2 mg/l achieved by NF. These results
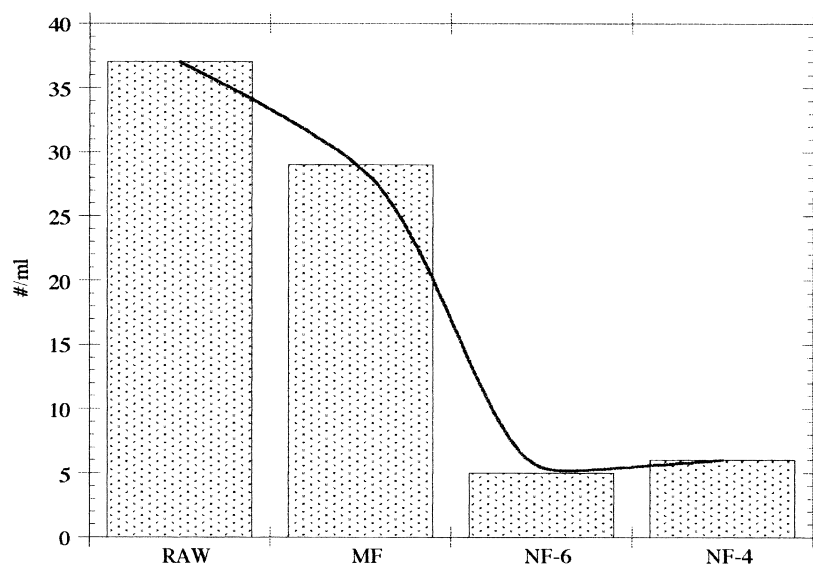
Fig. 12. HPC vs treatment (SLW): RAW, MF, and NF.

are similar to removals reported by Siddiqui *et al.* (1997).This same source water exhibited a TC density of 310/100 ml, with MF providing a reduction to 160/ml, and NF product waters showing non-detectable levels (Fig. 12). The raw-water HPC was reduced from 3700/100 ml to 2900/100 ml by MF and to 500/100 ml by NF. The HPC results from NF may be due to unavoidable bacterial growth occurring in the permeate line, as opposed to the NF membrane passing bacteria.

Comparative evaluation

Table 5. summarizes the comparative evaluation of NF, UF, and MF for the control of NOM from surface waters. The use of NF alone is problematic in view of high particle counts encountered in surface waters. The integration of UF or MF with NF is an alternative for high particle count surface waters.

CONCLUSIONS

1. NF is effective for reducing NOM and the formation of DBPs. However, in view of high particle counts in surface waters, NF alone, is not appropriate and can incur serious operational problems such as rapid fouling, increased pressure requirements, and reduced recoveries.
2. The incorporation of MF (of the type employed in this research) can potentially lengthen the NF membrane life and aid in the removal of *Giadia* and *Cryptosporidium*. The use of polymers and coagulants upstream of MF does not pose any operational problems but in fact enhances the removal of particles by tightening the sheet membranes inside the MF module.
3. Membrane treatment of low-turbidity surface waters by nanofiltration requires pretreatment for particle/colloid removal. However, options other than chemical pretreatment exist, most notably microfiltration, or possibly ultrafiltration. Nanofiltration run lengths of up to 30-days were sustainable with pretreatment by MF for some NF modules; for others, significant fouling was observed after about 20 days. More work is

Table 5. Comparative evaluation of UF, MF, and NF for surface waters

Parameter	UF	MF	NF
NOM control	0–30%	< 10%	> 80%
Particle removal	70–90% removal of suspended, colloidal contaminants	20–40%	> 95%
DBP Control	50% THM; 32% HAA	none	> 80%
Clogging	problems with surface water	no clogging; particles in raw water enhance removal efficiency over time	pre-treatment required
Cleaning requirements	required	backwashing required	cyclic cleaning required
Operational problems	none too severe	filling such as diatomaceous earth improves removal	fouling, clogging
Chemical pretreatment	In-line coagulant addition is applicable	In-line coagulant addition is applicable	In-line coagulant addition will clog membranes

needed to evaluate other MF modules more appropriate to low-turbidity sources, and to address reversible versus irreversible fouling of NF and associated element cleaning strategies. With resolution of fouling issues, optimization of such a system, MF followed by NF, can readily meet both turbidity and DBP regulations.

4. UF is effective as a pretreatment filter and to remove particles that can potentially clog NF membranes. UF membranes also shown to remove DBP precursors up to 30% and addition of organic polymers and chemical coagulants upstream of UF enhances NOM removal.

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