

Experimental evaluations of a pilot nanofiltration system with respect to NOM and BOM removals and stable permeability with appropriate pre-treatments: a case study in Korea

Won-Young Ahn, Seong-Keun Yim, Byung-Yong Son, Geon Tae Kim, Hyowon Ahn, Dongjoo Lee, Sangyoun Lee, Boksoon Kwon and Jaeweon Cho

ABSTRACT

A pilot-scale nanofiltration (NF) membrane system, operated at the Bansong water treatment plant of Changwon City in Korea for more than 1.5 years, was evaluated and compared with a pilot-scale granular activated carbon (GAC) and full-scale conventional treatment (CT) processes, in terms of the removal efficiencies of disinfection by-products (DBPs) formation potential and biodegradable organic matter (BOM). Nakdong river surface water (dissolved organic carbon (DOC)=2.5–6.3 mg l⁻¹) was utilized as the water source. The membrane system was also evaluated with respect to membrane permeability (along with flux decline) and flux recovery by chemical cleaning, along with the demonstration of pre-treatment alternative (combinations of conventional processes and microfiltration (MF) membrane) effects on NF membrane performance. Two different NF membranes, from the same manufacturer, were tested in this study: one with high permeability and low salt removal capability (ESNA I), and the other with low permeability and high salt removal capability (ESNA II). The former membrane exhibited consistent NOM removal behaviour (greater than 75% based on DOC and stable permeabilities, when operated with pre-treatment of the MF membrane), while the latter membrane exhibited less stable performance in terms of NOM removal and permeability, even with chemical cleaning. Overall, the NF membrane exhibited very stable efficiencies of haloacetic acids formation potential and biodegradable dissolved organic carbon removals, in comparison with both CT processes and GAC.

Key words | biodegradable organic matter (BOM), membrane permeability, natural organic matter (NOM), NF membrane

Won-Young Ahn
Seong-Keun Yim
Geon Tae Kim
R&D Center,
Kolon Engineering and Construction,
207-2 Mabuk-Ri,
Guseong-Myun, Yongin,
Korea

Byung-Yong Son
Hyowon Ahn
Dongjoo Lee
Korea Water Resources Corporation,
(KOWACO),
San 6-2,
Yeonchuk-dong, Daedeok-gu,
Daejeon 306-711,
Korea

Sangyoun Lee
Boksoon Kwon
Jaeweon Cho (corresponding author)
Department of Environmental Science and
Engineering,
K-JIST,
Oryong-dong 1,
Gwangju 500-712,
Korea
Tel.: 82-62-970-2443
Fax: 82-62-970-2434
E-mail: jwcho@kjist.ac.kr

INTRODUCTION

Chemical coagulation, sedimentation and rapid sand filtration were major drinking water treatment processes in Korea until the phenol leaching accident in the Nakdong River in 1992. After that accident, the necessity for advanced drinking water treatment processes (DWTP) increased, and the government decided to apply them to some domestic DWTPs. The Korean Ministry of Environment planned to retrofit DWTPs with ozone oxidation and

activated carbon adsorption processes between 1994 and 2005. The total treatment volume is 3,869,000 m³ day⁻¹, which is 14% of the total drinking water production in Korea (*Water Supply Statistics 2000* 2001). The major target compounds of the advanced treatment plants are those that affect taste or odour, colour, ammonia nitrogen, detergents, pesticides, herbicides and other trace toxic organic materials.

Membrane filtration is an effective process for the removal of the above compounds without any chemical treatment processes, especially when the disinfection by-products (DBPs) formation potential should be reduced. For the minimization of DBPs formation, NOM concentrations should be minimized prior to chlorination; nanofiltration (NF), and possibly tight-ultrafiltration (UF) membranes (with a molecular weight cut-off (MWCO) of less than 1,000 mass units) can be used for this purpose. Various studies on NOM removal and DBPs minimization by membrane processes have been performed with bench- and pilot-scale membrane units (Cho *et al.* 1999; Chellam 2000; Siddiqui *et al.* 2000; Glucina *et al.* 2000), as well as an actual membrane plant (Ventresque *et al.* 2000). With all of these tests, NF membranes (MWCO ranging from 150 to 1,000 mass units) proved to be very effective in the removal of NOM for the minimization of the formation of DBPs, and were not influenced significantly by factors such as NOM characters; for example: TOC levels, humic content as identified by specific UV absorbance values, pH, and ionic strength.

In the studies conducted with bench-scale membrane units, optimum chemical and operating conditions, such as pH, ionic strength, specific flux and cross-flow velocity, for stable membrane permeation product and minimum membrane fouling were rigorously investigated due to their ease of control (Braghetta & DiGiano 1997; Hong & Elimelech 1997; Cho *et al.* 2000). Escobar *et al.* (2000) reported that biodegradable organic matter removal, especially assimilable organic carbon (AOC), even by NF membranes, could be influenced by the ionic strength of feed water.

The effects of pre-treatment alternatives on membrane processes were mostly evaluated by various studies conducted with relatively large pilot-scale membrane units and actual treatment plants (Siddiqui *et al.* 2000; Glucina *et al.* 2000; Ventresque *et al.* 2000). Tight-NF (MWCO ranging from 150 to 500) membranes were used to treat a variety of NOM source waters exhibiting a wide range of NOM characters in terms of TOC (2.0~4.7 mg l⁻¹) and Specific UV absorbance at 254 nm (SUVA) (2.5~6.2 mg l⁻¹-m; indicating relative aromaticity/humic properties of NOM), along with the evaluation of different pre-treatment alternatives, including the conventional

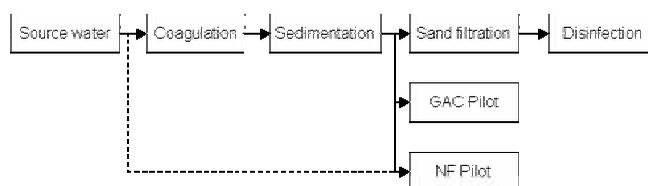


Figure 1 | Flow diagram of conventional treatment processes and pilot systems: coagulation with alum at a concentration of 40–60 mg l⁻¹, sedimentation with a hydraulic residence time of 2.0 h, GAC filtration (Calgon F820 with an effective diameter of 1.15 mm and a uniformity coefficient of 1.47, empty bed contact time=12 min).

process train (coagulation, sedimentation and either sand filtration or GAC), UF membrane and MF filters. Successful attempts for various pre-treatment alternatives for NF membrane processes have been reported. Both the UF membrane, with MWCO of 100,000 mass units, and the conventional process train (coagulation with alum sulfate and clarifier with powder activated carbon (PAC)) were effective in providing stable permeation production for tight-NF membrane plants with MWCO of 180 mass units (Glucina *et al.* 2000).

A cross-flow type of MF membrane was also shown to be effective for the pre-treatment of NF membrane processes, but a cartridge MF filter exhibited significant

Table 1 | Specifications of MF and NF membranes

	MF	NF
Code	CP-20	ESNA (2.5" × 40")
Manufacturer	Toray	Hydranautics
Membrane type	Hollow fibre	Spiral wound
Pore size	0.01 μm	MWCO of 250 mass units; (i) ESNA I with a higher permeability and minimum salt rejection of 50%*, and (ii) ESNA II with a lower permeability and minimum salt rejection of 70%*
Material	Polyacrylonitrile	Composite polyamide
Surface area	12 m ²	2.6 m ²

*Minimum salt rejection values for both ESNA membranes are provided by the manufacturer.

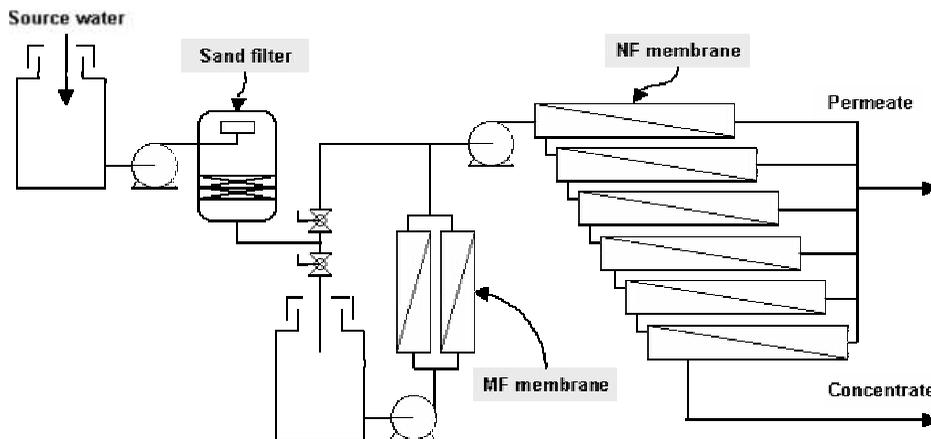


Figure 2 | Configuration of pilot-scale cascade system (with a system recovery ranging from 70 to 75%) of NF membrane.

clogging problems (Siddiqui *et al.* 2000). Many alternatives were used for pre-treatment at the Mery-sur-Oise NF plant, which has a capacity of $140,000 \text{ m}^3 \text{ day}^{-1}$, which included an ozonation process, coagulation with poly-aluminium chloride and polyelectrolyte, dual-layer filters with anthracite and sand, and a $6 \mu\text{m}$ cartridge MF filter (Ventresque *et al.* 2000). All of the processes mentioned above provide fairly high NOM removal, at least 80% with respect to TOC, and TOC of treated waters ranges between 0.1 and 0.5 mg l^{-1} , suggesting that the NF membrane

seems not to be significantly influenced, in terms of NOM removal, by the chemical properties of NOM included in water sources.

The objectives of this study were to evaluate a nanofiltration (NF) pilot system, located at a DWTP in Korea, against existing conventional treatment processes and GAC, with respect to the removal of NOM and biodegradable organic matter (BOM), and to determine optimum pre-treatment alternative combinations for obtaining stable permeation production.

Table 2 | Different operating phases of NF pilot system

Phase	Period	Influent water	Pre-treatment	Membrane type	Cleaning date
I	10 May 2000–24 July 2000	Sedimented	Sand + MF	ESNA I	12 July 2000
II	3 Aug 2000–11 Aug 2000	Raw	Sand + MF	ESNA I	
III	12 Aug 2000–2 Oct 2000	Raw	Sand + MF	RO	
IV	14 Oct 2000–5 Mar 2001	Sedimented	Sand	ESNA II	7–8 Dec 2000
V	8 Mar 2001–2 Apr 2001	Sedimented	Sand	ESNA II'	
VI	9 Apr 2001–12 July 2001	Sedimented	Sand + MF'	ESNA II'	3–4 Apr 2001
VII	13 July 2001–20 Dec 2001	Sedimented	Sand + MF'	ESNA II'	

Note: ESNA II' and MF': new membrane elements replaced.

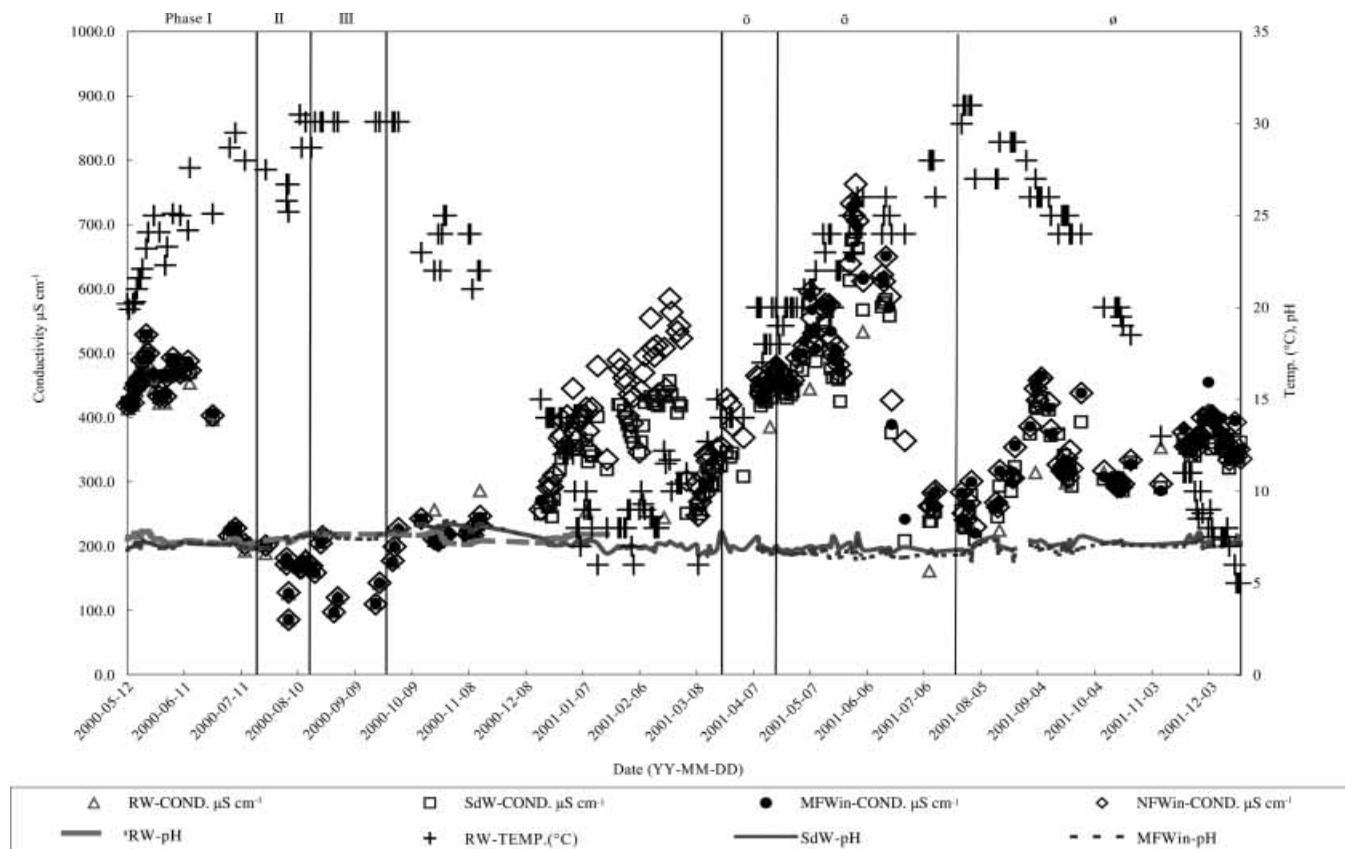


Figure 3 | Variations of conductivity, temperature and pH; RW: raw water, SdW: sedimented water, MFWin: influent to MF membrane, NFWin: influent to NF membrane (i.e. effluent of MF membrane).

METHODS AND MATERIALS

Pilot plant descriptions

An NF pilot plant was built at the existing conventional DWTP located in the City of Bansomg, to evaluate the removal efficiencies of NOM and haloacetic acids formation potential (HAAFP; sum of five compounds), and to establish an appropriate system combination with pre-treatments. There was also a GAC pilot plant (with a capacity of $13.0 \text{ m}^3 \text{ day}^{-1}$; each $0.3 \text{ m} \times 0.3 \text{ m} \times 1.2 \text{ m}$ (effective GAC depth), sand filter depth 25 cm) at the same location, which was compared with the NF pilot system in terms of NOM and DBPs formation removal. Conventional treatment processes comprise coagulation/sedimentation (chemical precipitation), sand filtration

and disinfection processes. Influent water was introduced after the sedimentation process into both the NF membrane and GAC, except for periods used to test the NF system without any pre-treatment, as shown in Figure 1.

The specifications of the MF and NF membranes tested are listed in Table 1, and the configuration of the NF pilot system is depicted in Figure 2. The cascade type NF pilot system includes a sand filter, a hollow-fibre type back-washable MF membrane for pre-treatment and a spiral wound type NF membrane process. Six NF membrane modules were installed in series; the system recovery ratio ranges from 70 to 75%.

Several different operating conditions were tested to determine an optimum pre-treatment alternative combination for the NF membrane. Table 2 lists all of the tested operating phases. From phases I through IV, different

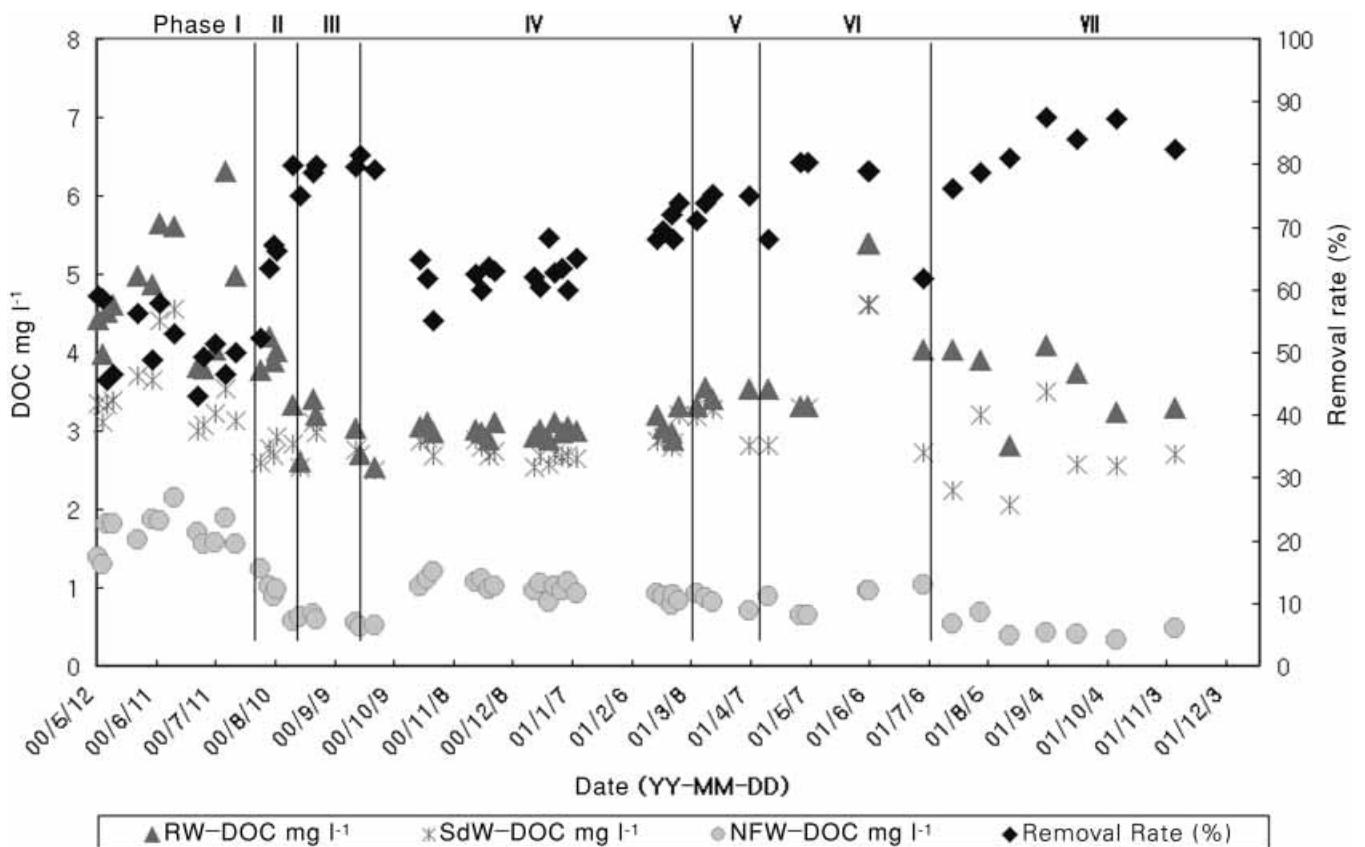


Figure 4 | Trends in DOC concentrations of raw water, sedimented water and NF membrane treated samples against time. Percentage removals are calculated using DOC values of membrane influent (i.e. sedimented water) and membrane treated samples (RW: raw water, SdW: sedimented water, NFW: NF permeate sample).

combinations of pre-treatment processes and influent conditions were evaluated. The phase I experiment was started with pre-treatment with both chemical precipitation (with alum) and the MF membrane. In the second phase, chemical precipitation was not used as a pre-treatment alternative so that only the MF membrane was used. Phase III contained the same pre-treatment as the second phase, except for a different type of membrane (i.e. reverse osmosis membrane with a MWCO of 150 mass units). The ESNA I membranes (with a higher permeability) were replaced with the ESNA II membranes (with a lower permeability) after phase IV. Quantitative analyses of the pre-treatment efficiency of the MF membrane were performed, under controlled operating conditions, during phases V (without MF membrane) and VI (with MF membrane). The membrane system (for phase

Table 3 | Characteristics of the Nakdong River water and its NOM

	Minimum	Average	Maximum	Standard deviation
pH	6.91	7.47	7.93	0.229
Conductivity ($\mu\text{S}/\text{cm}$)	160	300	533	90.29
Temperature* ($^{\circ}\text{C}$)	1	14	31	9.103
DOC (mg l^{-1})	2.54	3.67	6.32	0.846
UVA ₂₅₄ (cm^{-1})	0.048	0.080	0.146	0.015
SUVA ($\text{l mg}^{-1} \text{m}^{-1}$)	1.54	2.13	4.28	0.476
HAAFP ($\mu\text{g l}^{-1}$)	55.0	105.3	156.6	25.87

*Temperature is annually averaged for the period between 2000.12.20–2001.12.20.

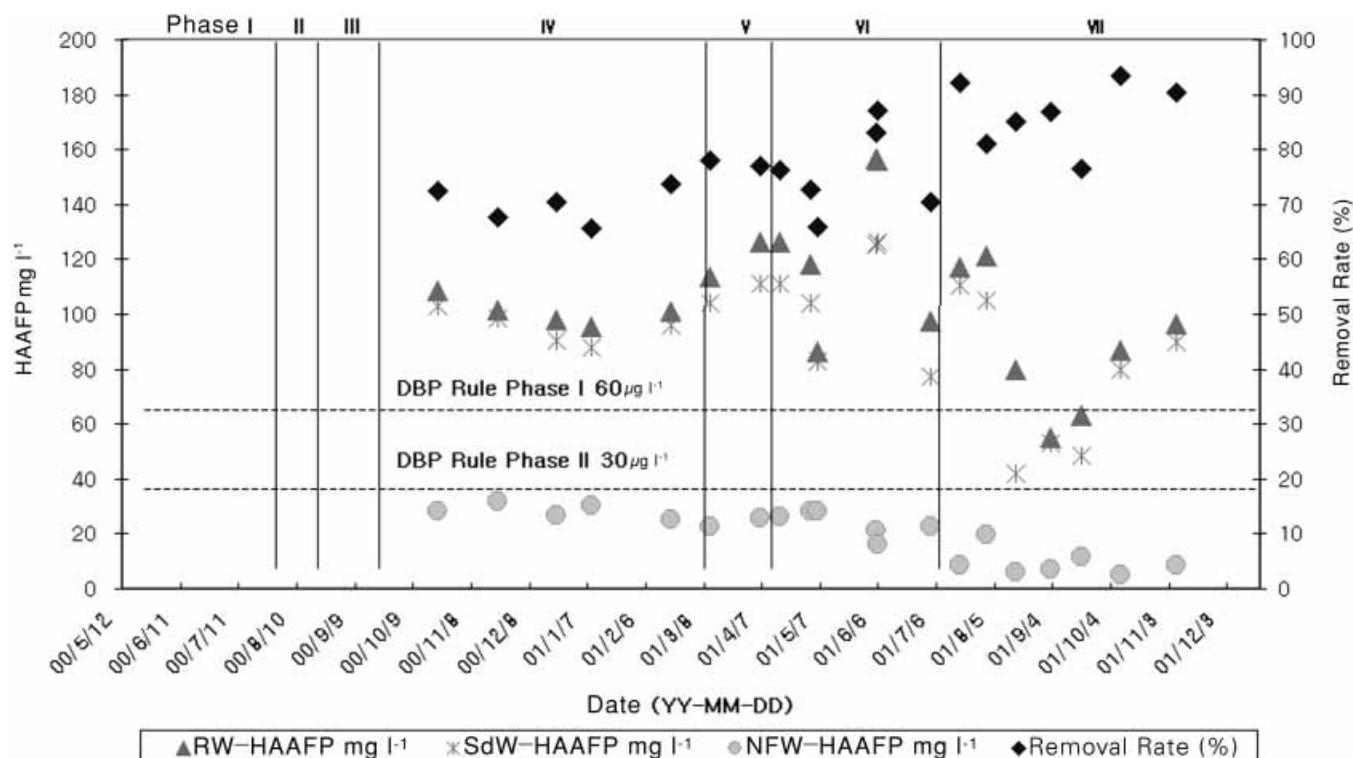


Figure 5 | Trends in HAAFP concentrations of raw water, sedimented water and NF membrane treated samples against time. Percentage removals are calculated using HAAFP values of membrane influent (i.e. sedimented water) and membrane treated samples (RW: raw water, SdW: sedimented water, NFW: NF permeate sample).

VII) with optimized processes is being used to evaluate membrane performance in terms of NOM removal and permeability trends.

Characteristics of influent water

The Nakdong River (source for the treatment plant) exhibited seasonal variations in conductivity, temperature and DOC values, as shown in Figures 3 and 4. Conductivity and DOC levels decrease and increase during the rainy summer season (July–August), respectively. Phases II and III, and the early periods of phases IV and VII represented higher temperatures and lower conductivities compared with other periods. The water characteristics of the Nakdong River are listed in Table 3. As based on SUVA, NOM included in the source water can be characterized to exhibit relatively hydrophilic properties.

NOM, haloacetic acids and biodegradable organic carbon analyses

High pressure size exclusion chromatography (HPSEC), with a protein-pak column (with a separation range of 1,000 to 30,000 mass units, as indicated by the manufacturer), was used to determine the molecular weight (MW) distribution of the NOM, with a 200 μ l sample loop and a UV spectrophotometric detector (Younglin, Korea). Eluent for the HPSEC comprised pure water (treated by an RO membrane and ion-exchange mixed beds), phosphate buffered to pH 6.8, and adjusted with NaCl to provide an ionic strength of 0.1 M (Chin *et al.* 1994). Standard solutions for construction of a MW calibration curve were made with sodium polystyrene sulfonates (PSS) (1.8 K, 4.6 K, 8.0 K and 18.0 K); acetone (MW = 58 mass units) and salicylic acid (MW = 138 mass units) were used to confirm the lower range of the calibration

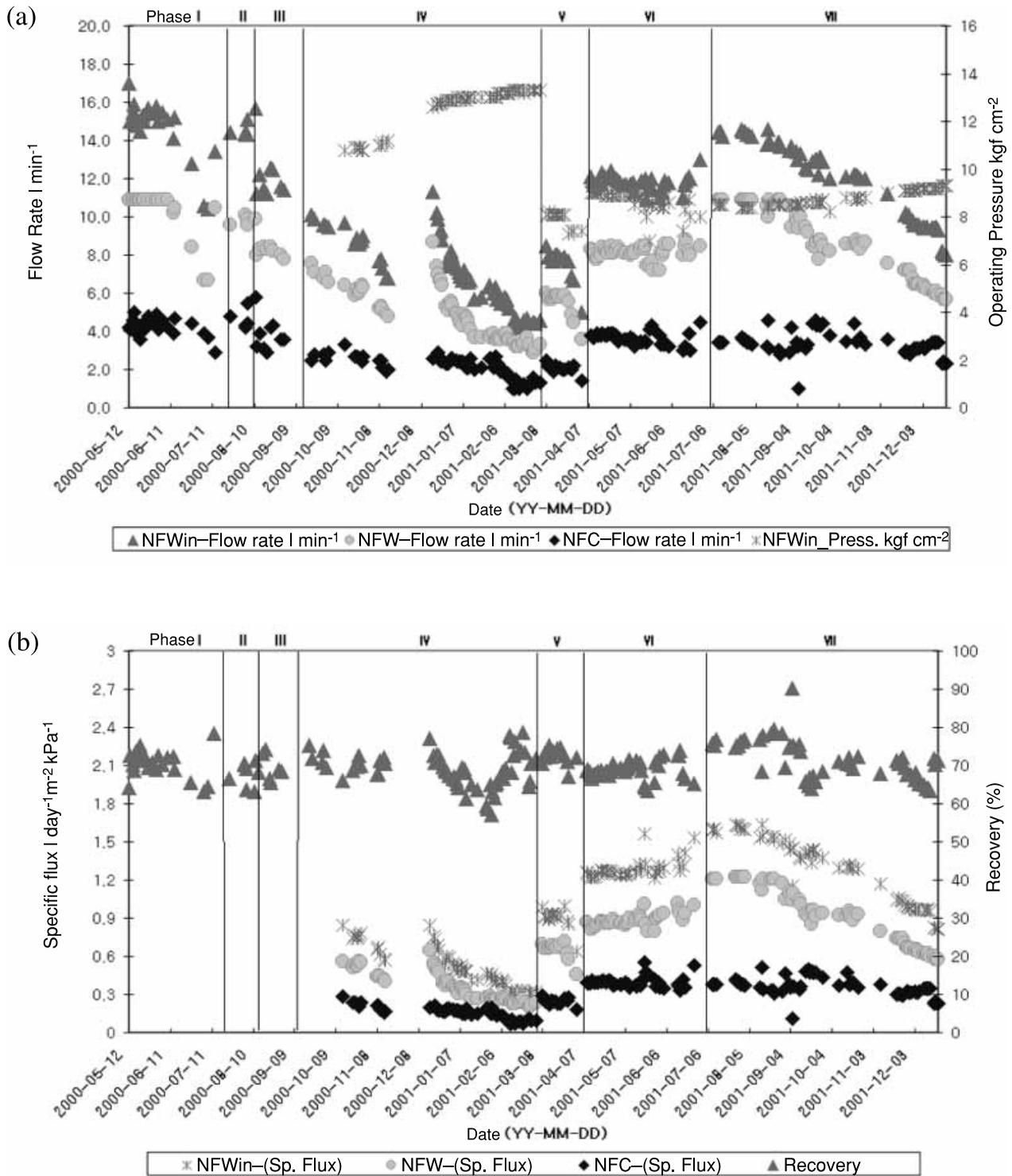


Figure 6 | Permeability (a) in terms of flow rate and (b) in terms of specific flux, operating transmembrane pressure ((pressure at feed side+pressure at retentate side)/2–pressure at permeate side) and system recovery (total flow rate of permeate (i.e. membrane treated water volume)/feed flow rate) of NF membrane against time (NFWin: influent to NF membrane, NFW: NF permeate sample, NFC: concentrated sample of NF membrane).

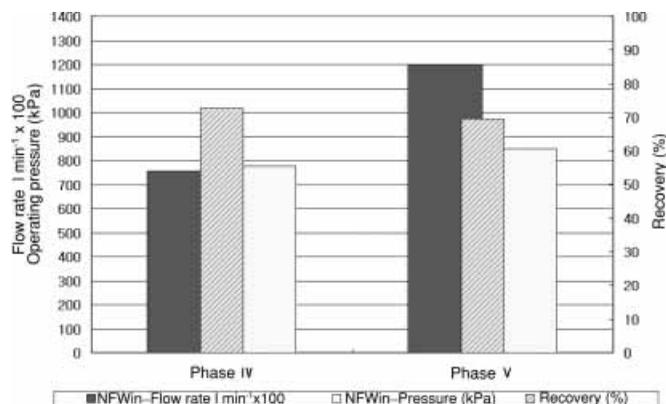


Figure 7 | Clean water permeability in terms of flow rate (LPM), operating transmembrane pressure and system recovery of NF membrane at phases IV versus V.

curve. XAD-8 and XAD-4 resins (Supelco, USA) were used for fractionating NOM into hydrophobic, transphilic and hydrophilic NOM components; isolated NOM components were used for their mass fraction calculation (hydrophobic vs. transphilic vs. hydrophilic).

Raw and treated samples were chlorinated using a concentrated HOCl solution, with a chlorine dosage level based on three times the dissolved organic carbon (DOC) concentration and 7.5 times the NH_4^+ concentration. Chlorinated samples were incubated at 20°C for 72 h (the residual chlorine concentration was between 0.8 and 1.0 mg l^{-1} for all samples) and the HAA formation potential (HAAFP) was measured using a modified EPA 552 micro-extraction method with diazo methane addition (for esterification). HAAs were measured using GC (HP 5890 Series II Plus) with an auto sampler (HP 6890 Series) and ECD detector.

BDOC measurements were performed using sand media (Jumunjin sand with an average diameter of 0.5 mm and a uniformity coefficient of 1.7) attached with bacteria acclimated with the natural source water for approximately 30 days. Bacteria-attached sand (200 g) was placed in a 1-l brown bottle (i.e. organic free incubator) and a 600 ml sample was added to the bottles. BDOC tests were conducted without aeration and incubated at $20 \pm 2^\circ\text{C}$ until the DOC level of the sample reached a minimum value; the difference between initial and final DOC values is the BDOC of the sample.

RESULTS AND DISCUSSION

Removal efficiencies of NOM and HAAs formation potentials

The NF membrane pilot test was performed over 1.5 years to evaluate long-term NOM removal efficiencies. Various trends in DOC values of the raw water, sedimented water (i.e. NF membrane influent water) and NF treated water are represented in Figure 4, along with NOM removal efficiency for the NF membrane. The average DOC values of the influent and NF membrane treated water were 3.67 mg l^{-1} and 1.02 mg l^{-1} , respectively. The average percentages of NOM removed by the NF membrane were 50.9, 62.3, 79.1, 64.4, 73.9, 74.7 and 82.5 for phases I–VII, respectively. As expected, the NF membrane with the lower permeability exhibited somewhat higher NOM removal efficiencies (phases IV–VII) than the NF membrane with higher permeability, and exhibited similar performance, in terms of NOM removal, to the RO membrane tested in this work. Even with the same NF membrane, the percentage of NOM removal seems to be influenced by the different pre-treatment alternatives (see phases IV–VII in Figure 4). The average HAAFP of influent and treated waters were 105.3 $\mu\text{g l}^{-1}$ and 20.1 $\mu\text{g l}^{-1}$, respectively. As shown in Figure 5, almost all of the HAAFP values of treated waters were below 30 $\mu\text{g l}^{-1}$, which is the suggested level according to the second phase of the D/DBP rule of the US EPA. Similarly to NOM removal trends, HAAFP removal seems to be affected by the different pre-treatment alternatives (with versus without MF membrane in phases IV–VII).

Pre-treatment effect on NF permeability and flux decline

The stability of the NF membrane permeability was strongly influenced by the pre-treatment process alternatives (see Figure 6). Experiments were conducted with various combinations of pre-treatment alternatives, including chemical precipitation, sand filtration and the MF membrane, to determine appropriate pre-treatment processes in terms of the permeability of the NF membrane. In phase I, the NF pilot system was operated with

Table 4 | NOM molecular weights of raw and treated waters

	Raw	SdW	GFW	NFW (with ESNA II)
Weight-average molecular weight (Mw)	1,795	1,542	1,045	642
Number-average molecular weight (Mn)	907	650	561	294
Polydispersivity (Mw/Mn)	2.0	2.4	1.9	2.2

SdW: water treated by sedimentation; GFW: GAC carbon treated water; NFW: permeate water by NF membrane.

all of the pre-treatment alternatives indicated above. In this period, the NF membrane exhibited stable performance, in terms of permeability, for 1 month without any chemical cleaning. The flux was substantially reduced, thus a chemical cleaning was conducted on 12 July 2001, which recovered the membrane's permeability.

In the second phase, chemical precipitation was omitted to demonstrate its effect on the performance of the NF membrane. Chemical precipitation can be used to remove suspended solids and some dissolved organic materials. Without chemical precipitation, the NF membrane exhibited normal operating performance, in terms of permeability, but the MF membrane was severely fouled and could not be operated any longer. In the first two phases, the NF membrane (ESNA I with a higher permeability and a lower salt removal capability) did not exhibit the anticipated high NOM removals, and therefore was replaced by a different type of NF membrane (ESNA II with a lower permeability and a higher salt removal capability), and used for phases IV through VII. In the third phase (i.e. a transition period from ESNA I to ESNA II), an RO

membrane (or tight NF membrane with a MWCO of 150) was tested for comparison with NF membranes. For phase IV, chemical precipitation and sand filtration, as pre-treatment processes, were used without an MF membrane. The permeability of the NF membrane decreased throughout the period. To recover the permeability of the NF membrane, chemical cleaning was conducted on 7 December 2000, but the recovered flux declined immediately following cleaning. Thus, the flux decline was believed to be due to the fouling of the spiral wound NF membrane module.

Experiments performed in phases I through IV indicate that pre-treatment with the MF membrane is an essential process for stable permeation production for NF membranes, regardless of the inclusion of the chemical precipitation process. Accordingly, both chemical precipitation and the MF membrane were included as pre-treatment processes, and a sand filtration process was introduced as a guard filter before the MF membrane. The only difference between phases IV and V was the membrane status (i.e. old and new); they exhibited different clean water permeabilities with almost the same transmembrane pressure (see Figure 7).

In phases V and VI, the effects of pre-treatment with an MF membrane on permeation production were quantitatively demonstrated. Under the same operating conditions, with a recovery ratio of 70% and a transmembrane pressure of 8 kgf cm⁻², the NF membrane flux, in the presence of an MF membrane, increased by 38.6% (i.e. from 0.66 to 0.91 l day⁻¹ m⁻² kPa⁻¹), compared with the flux without an MF membrane. In the last phase, long-term membrane operation was started with optimum

Table 5 | NOM compositions (%) of raw and treated waters

NOM	Raw	SdW	GFW	NFW (with ESNA II)
Hydrophobic	35.7	34.3	19.4	29.8
Transphilic	25.0	21.7	9.9	19.7
Hydrophilic	39.4	44.0	70.7	50.5

Table 6 | NOM removal behaviours by different processes

Date	CT*		GAC		NF		% Removal		
	Influent	Effluent	Influent	Effluent	Influent	Effluent	CT	GAC	NF
(a) based on DOC (unit: mg l ⁻¹)									
6 Apr 2001	3.53	2.37	2.81	0.65	2.81	0.70	32.9	76.8	75.2
2 May 2001	3.32	2.60	3.29	1.39	3.29	0.65	21.7	57.8	80.2
5 Jun 2001	5.39	4.19	4.61	2.15	4.61	0.97	22.3	53.4	79.0
2 July 2001	4.03	2.93	2.73	1.77	2.73	0.67	27.3	35.2	75.5
1 Aug 2001	3.90	3.20	3.20	1.78	3.20	0.68	17.9	44.0	78.8
3 Sep 2001	4.10	3.50	3.50	1.80	3.50	0.44	14.6	48.6	87.4
9 Oct 2001	3.25	2.55	2.55	1.85	2.55	0.92	21.5	27.5	63.9
7 Nov 2001	3.30	2.70	2.70	2.10	2.70	0.48	18.2	22.2	82.2
19 Dec 2001	3.50	3.00	3.00	2.50	3.00	0.60	14.3	16.7	80.0
(b) based on UVA ₂₅₄ (unit: cm ⁻¹)									
6 Apr 2001	0.0740	0.0460	0.0550	0.0030	0.0550	0.0040	37.8	94.5	92.7
2 May 2001	0.0670	0.0470	0.0380	0.0080	0.0380	0.0030	29.9	78.9	92.1
5 Jun 2001	0.0880	0.0650	0.0520	0.0160	0.0520	0.0030	26.1	69.2	94.2
2 July 2001	0.0740	0.0510	0.0320	0.0170	0.0320	0.0040	31.1	46.9	87.5
1 Aug 2001	0.0660	0.0270	0.0270	0.0130	0.027	0.0010	59.1	51.9	96.3
3 Sep 2001	0.066	0.033	0.033	0.012	0.033	0.000	50.0	63.6	100.0
9 Oct 2001	0.050	0.024	0.024	0.018	0.024	0.003	52.0	25.0	87.5
7 Nov 2001	0.069	0.0407	0.0407	0.0355	0.0407	0.0016	41.0	12.8	96.1
19 Dec 2001	0.056	0.036	0.036	0.028	0.036	0.009	35.7	22.2	75.0

*CT: conventional treatment.

pre-treatment and operating conditions. Despite a rapidly decreased temperature, relatively stable permeabilities for the NF membranes were produced, with relatively small increases of transmembrane pressure, in contrast to phase IV.

NOM removal analyses

To evaluate NOM removal behaviour, by conventional and advanced treatment processes, the characteristics of NOM in Nakdong River water (i.e. raw water) and treated

Table 7 | HAAFP5 removal behaviours (unit: mg l⁻¹)

Date	CT		GAC		NF		% Removal		
	Influent	Effluent	Influent	Effluent	Influent	Effluent	CT	GAC	NF
6 Apr 2001	126.1	110.8	111.3	41.4	111.3	25.7	12.1	62.8	76.9
2 May 2001	118.3	104.1	112.8	47.4	104.1	28.4	12.0	58.0	72.7
5 Jun 2001	156.6	145.1	125.1	36.9	125.1	21.1	7.3	70.5	83.1
2 July 2001	97.3	87.3	77.2	17.0	77.2	15.8	10.3	78.0	79.5
1 Aug 2001	121.0	105.0	105.0	23.1	105.1	19.9	13.2	78.0	81.1
3 Sep 2001	55.0	53.2	53.2	11.6	53.2	7.0	3.3	78.2	86.8
9 Oct 2001	87.0	79.6	79.6	19.3	79.6	5.3	8.5	75.8	93.3
7 Nov 2001	81.1	75.0	75.0	31.0	75.0	3.0	7.5	58.7	96.0
19 Dec 2001	64.3	52.2	52.2	33.5	52.2	6.8	18.8	35.8	86.9

water samples were analysed for molecular mass and relative hydrophobicity. The samples were collected following the different treatment processes, including coagulation/sedimentation, granular activated carbon (GAC) adsorption and NF membrane filtration with the same influent water. As listed in Tables 4 and 5, NOM contained in raw water had a weight-average molecular weight of 1,800 mass units, and comprised 36% hydrophobic, 25% transphilic and 39% hydrophilic NOM constituents. The properties of the NOM contained in treated waters exhibit different characteristics according to the treatment process. The treated water from the conventional process had almost the same NOM properties as raw water, but GAC- and NF-treated waters showed lower average molecular weights of 1,000 and 600 mass units, respectively, and smaller hydrophobic fractions.

NOM was removed by the NF membrane, with a minimum removal of 64% based on the DOC. Initially, the GAC and NF membranes exhibited a similar percentage for NOM removal, but the NF membrane exhibited much higher NOM removal trends over time, compared with the GAC process (see Table 6). NOM removal, based on UV absorbance at 254 nm (UVA₂₅₄), was also monitored to investigate relative removal characteristics of humic and

aromatic NOM constituents. As shown in Table 6(b), the humic/aromatic NOM fractions were preferentially removed compared with bulk NOM for almost all cases (i.e. in contrast to removal based on DOC).

To investigate the removal behaviours of DBPs formation potential by the different processes, HAAFP was analysed (see Table 7 and Figure 8). The NF membrane and GAC exhibited HAAFP removal values greater than

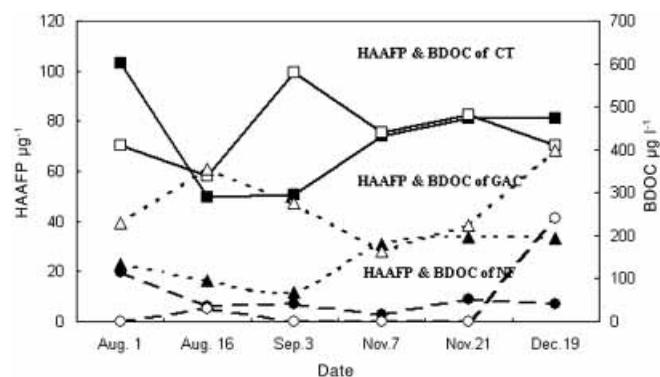


Figure 8 | Trends of HAAFP and BDOC values treated by conventional treatment (CT) processes, GAC and NF membrane: closed and open symbols indicate HAAFP and BDOC values, respectively.

Table 8 | The bases of cost analyses

	LPRO*	NF (ESNA II)	Reference
Operating pressure (kgf cm ⁻²)	13.6	9	—
Power cost (kWh)	53.3	53.3	KEPCO**; Industry (Gab type), 7 Nov 2001
Recovery (%)	75	75	—
Salt rejection (%)	90	70	—
Pump efficiency (%)	85	85	Calder Ltd, 1989

*Low pressure RO: FILMTEC TW30HP-4040 module with a NaCl rejection of 95–98% and a typical operating pressure of 15 kgf cm⁻².

**Korea Electric Power Corporation.

Table 9 | Comparison of operating costs of NF and LPRO

	LPRO	NF (ESNA II)
Energy (Won* ton ⁻¹)	32	23
Membrane replacement (Won ton ⁻¹)	57	57
Labour (Won ton ⁻¹)	32	32
Spare parts (Won ton ⁻¹)	8	8
Chemicals (Won ton ⁻¹)	15	15
Microfiltration (Won ton ⁻¹)	8	8
Depreciation cost (Won ton ⁻¹)	54	54
Total operating cost (Won ton ⁻¹)	206	197

*1 US dollar=1,154.50 Won (Korea exchange bank, 29 March 2004).

72 and 35%, respectively. From the perspectives of BDOC, GAC did not provide a consistent BDOC removal, and demonstrated similar efficiencies to the CT processes. However, the NF membrane gave reasonably low HAAFP and BDOC values.

Cost analyses

To evaluate the NF membrane system, with respect to operating and maintenance costs, a typical low-pressure

reverse osmosis (LPRO; FILMTEC TW30HP-4040 module with a NaCl rejection of 95–98% and a typical operating pressure of 15 kgf cm⁻²) process and the NF membrane (i.e. ESNA II) were compared. The stability of the treatment efficiency for the LPRO membrane is preferred, but involves higher operating costs compared with the NF membrane. The calculation method was cited in the membrane handbook (Ho & Sirkar 1992) and the calculations are summarized in Table 8. As shown in Table 9, the energy cost can be reduced by 30% compared with LPRO. If advanced treatments with membrane processes were adopted at the Bansomg DWTP, it seems that the NF membrane process would be enough to provide quality water at reasonably low operating and maintenance costs.

CONCLUSIONS

A pilot-scale NF membrane unit was evaluated in terms of the removals of NOM, DBPs precursors and BDOC, compared with GAC filtration and conventional treatment processes. It was shown that an NF membrane with a lower permeability was very effective for the removal of NOM (75–80%), HAAFP (73–83%) and BDOC (not detected for almost all NF treated samples) compared with another NF membrane with a higher permeability. Moreover, the latter membrane exhibited significant flux decline, even with pre-treatments. Optimization of combined pre-treatment alternatives was also determined to obtain stable membrane permeation without significant flux decline; the MF membrane alternative was found to be an essential pre-treatment in reducing significant flux decline of NF membranes. A long-term pilot test is being performed.

ACKNOWLEDGEMENTS

This work was supported by the Korea Science and Engineering Foundation (KOSEF) through the ADEMRC at K-JIST, and also supported by a grant (code 4-1-1) from

the Sustainable Water Resources Research Center of 21st Century Frontier Research Program. The study was also partly supported by the K-JIST through the project 'Remediation technology of acid mine drainage and contaminated soils in the metal mining areas'.

REFERENCES

- Braghetta, A. & DiGiano, F.A. 1997 Nanofiltration of natural organic matter: pH and ionic strength effects. *J. Environ. Engng, ASCE* **123**, 628–641.
- Chellam, S. 2000 Effects of nanofiltration on trihalomethane and haloacetic acid precursor removal and speciation in waters containing low concentrations of bromide ion. *Environ. Sci. Technol.* **34**, 1813–1820.
- Chin, Y., Aiken, G. & O'Loughlin, E. 1994 Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. *Environ. Sci. Technol.* **28**, 1853–1858.
- Cho, J., Amy, G. & Pellegrino, J. 1999 Membrane filtration of natural organic matter: initial comparison of rejection and flux decline characteristics with ultrafiltration and nanofiltration membranes. *Wat. Res.* **33**, 2517–2526.
- Cho, J., Amy, G. & Pellegrino, J. 2000 Membrane filtration of natural organic matter: comparison of flux decline, NOM rejection, and foulants during filtration with three UF membranes. *Desalination* **127**, 283–298.
- Escobar, I.C., Hong, S. & Randall, A.A. 2000 Removal of assimilable organic carbon and biodegradable dissolved organic carbon by reverse osmosis and nanofiltration membranes. *J. Membrane Sci.* **175**, 1–17.
- Glucina, K., Alvarez, A. & Laíné, J.M. 2000 Assessment of an integrated membrane system for surface water treatment. *Desalination* **132**, 73–82.
- Ho, W.S. & Sirkar, K.K. 1992 *Membrane Handbook 1992*. Kluwer Academic Publishers, Boston. pp. 361–366.
- Hong, S. & Elimelech, M. 1997 Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *J. Membrane Sci.* **132**, 159–181.
- Siddiqui, M., Amy, G., Ryan, J. & Odem, W. 2000 Membranes for the control of natural organic matter from surface waters. *Wat. Res.* **34**, 3355–3370.
- Ventresque, C., Gisclon, V., Bablon, G. & Chagneau, G. 2000 An outstanding feat of modern technology: the Mery-sur-Oise nanofiltration treatment plant (340,000 m³/d). *Desalination* **131**, 1–16.
- Water Supply Statistics 2000 2001 Water Supply Statistics 2000*. The Ministry of Environment of Korea, Seoul, Korea.

First received 30 September 2002; accepted in revised form 28 May 2003