

## Foulants analyses for NF membranes with different feed waters: coagulation/sedimentation and sand filtration treated waters

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### Abstract

Two different NF membranes were operated to remove natural organic matter (NOM) originating from Dongbok Lake in Korea. Coagulation/sedimentation and sand filtration treated waters as membrane feed waters were used. The tested NF membranes were autopsied to compare the fouling propensity from different feed waters using pure water and a NaOH solution. Organic/inorganic foulants onto membrane surface were analyzed in terms of molecular weight (MW) distribution, structure, and IR analysis, and fouled membranes were also characterized in terms of pore size distribution, surface charge, and SEM–EDS analysis. Polysaccharides and/or *N*-acetyl aminosugar groups with MW ranging from 30,000 to 50,000 g/mol were identified using HP-SEC and IR analysis. Inorganic foulants (i.e., Si and Al) were also fouled onto the membrane surface and/or pores, and it is effectively removed by caustic cleaning, not pure water. Caustic cleaning was proven to be effective to remove both fouled NF membranes as a basis of flux recovery, and it could efficiently desorb the hydrophobic NOM constituents or protein-like substances from the relatively hydrophilic and less negatively charged NF membranes.

**Keywords:** Nanofiltration; Natural organic matter (NOM); Organic/inorganic foulants; Coagulation/sedimentation; Sand filtration

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## 1. Introduction

Nanofiltration (NF) is gradually considering as an advanced water treatment process to control natural organic matter (NOM), endocrine disruptor compounds (EDCs), and pharmaceutical in the surface water [1–2]. It is also cost-effective process for seawater desalination on behalf of reverse osmosis (RO) membrane [3]. However, membrane fouling can reduce the membrane performances with respect to permeability, removal efficiency, and cost. Various physicochemical foulants such as microorganisms, particle, ion, and organic/inorganic compounds were reported in the previous works [4–6]. Membrane fouling can be divided into two categories in terms of reversible and irreversible. Reversible fouling (i.e., cake layer formation) is controlled from hydraulic cleaning by adjusting the crossflow velocity. Meanwhile, irreversible fouling (i.e., adsorption and/or chemical interaction) is controlled from chemical cleaning with acidic/alkaline agents. Cleaning efficiency was affected by various factors: agents, temperature, trans-membrane pressure, cleaning agent concentration, and duration time [7–8]. As increase the temperature, the cleaning efficiency can be improved. The efficient cleaning agents are also dependent on foulant characteristics. Generally, organic foulants were effectively removed by alkaline agents due to ionization and charge repulsion. Meanwhile, inorganic foulants were removed by acidic agents due to solubility.

The objective of this study is to compare two different nanofiltration membranes with different pore size distribution, surface charge, and hydrophobicity, with respect to organic (NOM and microorganisms related substances) fouling. For this, two different NF membranes were tested, which are made of the same material (meta phenylene diamine, MPD) but contain different chemical properties such as the surface charge and surface hydrophobicity. Foulants characteristics from a pilot-scale nanofiltration using different feed waters, coagulation/sedimentation and sand filtration treated water, were investigated.

## 2. Materials and methods

### 2.1. Membrane properties

Two different NF membranes were tested in this study; RF membrane (Saehan, Korea) is slightly lower negative charged and slightly lower contact angle (i.e., hydrophilic) than NF90 membrane (Filmtec, US) (see both Table 1 and Fig. 1). The zeta potential and contact angle of tested membranes were measured by the electrophoresis measurement method and both sessile drop and captive bubble methods [9–10]. Polystyrene latex with diameter of 520 nm which was coated with hydroxyl propyl cellulose (HPC) was used for the mobility measurement in terms of the membrane surface charge, using a commercialized apparatus (ELS-8000, OTSUKA,

Table 1  
Membrane properties

Code	Manufacturer	Material	MWCO	Zeta potential at pH 7.0	Contact angle (°)
RF	Saehan, Korea	Polyamide TFC*	550	–23.0	39.0
NF90	Filmtec, USA	Polyamide TFC*	200	–30.0	49.0

\*Both membranes are meta phenylene diamine (MPD) based thin-film-composite (TFC).

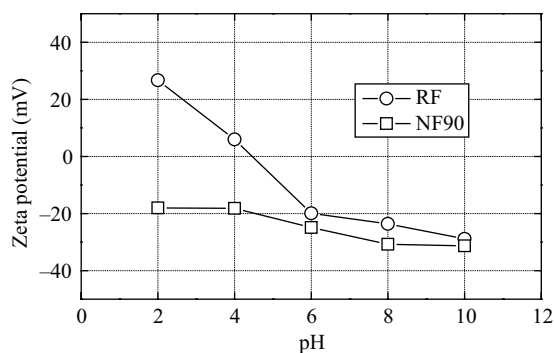


Fig. 1. Zeta potential trends as function of pH.

Japan). The pore size distributions of the NF membranes were also measured by the fractional rejection method, as shown in Table 1. A mixture of various polyethylene glycols (PEG) with a range of molecular weights (MW) were used, and MW distributions of the PEG included in both membrane feed and permeate solutions were determined by the HP size exclusion chromatography (SEC) method. Then, the fractional rejections of the PEG and corresponding pore size distributions for both membranes were determined [11]. As shown in Table 1, the RF membrane exhibits larger pore size distribution than the NF90 membrane, but both the membranes can be categorized as tight-NF membrane as this study was focused in the removal of natural organic matter (NOM) containing molecular weights mostly higher than 1000 g/mol.

Table 2  
Characterizations of NOM included in membrane feed solution

Feed	DOC (mg/L)	SUVA (L/mg-m)	pH	Conductivity ( $\mu$ S)	BDOC%
Feed1 <sup>a</sup>	1.8	0.8	6.9	65.0	13.0
Feed2 <sup>b</sup>	1.5	1.0	7.0	68.0	–

<sup>a</sup>Represents coagulation/sedimentation water (2003.2–2004.4).

<sup>b</sup>Represents sand filtration treated water (2004.10–2005.4).

## 2.2. Water characteristics

A pilot-scale test unit was set up at a drinking water treatment plant in Gwangju City, Korea. The filtration system was equipped with two 2540 modules (i.e., RF and NF90). The Dongbok reservoir water was used as influent for the pilot unit after either alum coagulation/sedimentation (without removing residual chlorine) or sand filtration (with removing residual chlorine) treated water. Characteristics of the NOM in the feed water were listed in Table 2; the NOM exhibits relatively hydrophilicity based on specific UV absorbance ( $=\text{UVA}_{254}/\text{DOC}$ ). Biodegradable organic carbon (BDOC) was estimated using a sand media attached with bacteria which were acclimated using the source water for more than 2 months.

The NOM structure was investigated using XAD-8/4 resin method. As listed in Table 3, both NOM in the feed water exhibits lower hydrophobicity (23.5 and 33.0%) and that in the membrane treated samples exhibit even much higher hydrophilicity. Thus, hydrophobic NOM fraction was envisioned to be removed by the two membranes.

## 3. Results and discussion

The changes in membrane properties, in terms of MWCO values and surface charge (i.e., zeta potential), were investigated (see Table 4 and Fig. 2). The MWCO values for both membranes by a coagulation/sedimentation treated

Table 3  
Structural analysis of various NOM using XAD-8/4 resins

	Samples	Hydrophobic	Transphilic	Hydrophilic
Feed1	Feed NOM	23.5	10.1	66.4
	NOM in RF permeate	5.7	4.3	90.0
	NOM in NF90 permeate	6.7	7.5	85.8
Feed2	Feed NOM	33.0	12.0	55.0
	NOM in RF permeate	5.2	7.4	87.4
	NOM in NF90 permeate	5.8	6.3	87.9

Table 4  
MWCO values of fouled NF membranes against the clean membranes

	RF		NF90	
	Clean	Fouled	Clean	Fouled
Feed1	550	570	200	380
Feed2	550	265	200	200

water slightly increased due to oxidation of membrane polymer by residual chlorine. In the case of sand filtration treated water, the MWCO were slightly reduced than the corresponding clean membranes due to accumulation of foulants on membrane surface. However, the zeta potentials and IR spectra for the tested membranes were substantially changed from the

corresponding clean membranes (see Figs. 2–3). Even though the surface charge trends of the two different clean NF membranes in terms of zeta potential are somewhat different, they exhibited similar trends as function of pH after fouling, as shown in Fig. 2. The FTIR spectra of the fouled NF membranes exhibited significantly different peaks (Fig. 3). A distinct wide peak around  $1045\text{ cm}^{-1}$  was found from all foulants by eluting pure water regardless of the membrane properties. This peak was identified as polysaccharide and/or *N*-acetyl aminosugar groups, which may be fractured-cell originated or extra-cellular polymeric substances [12–13]. Foulants by pure water also exhibits protein and methyl peaks around 1650 (amide I) and 1390. Meanwhile, foulants by 0.05 N NaOH exhibits high intensity around 570 (silica) and 1650

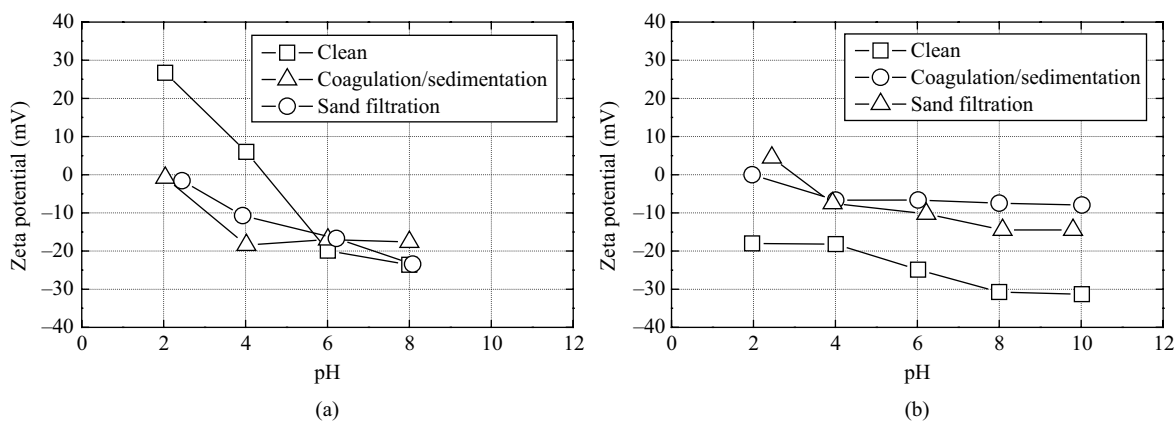


Fig. 2. Zeta potential trends against pH for the fouled NF membranes: (a) RF; (b) NF90.

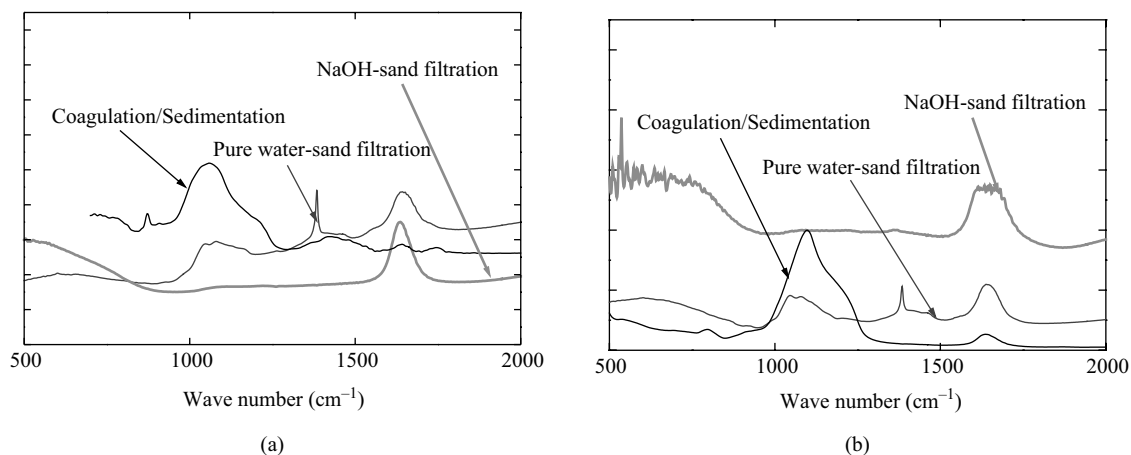


Fig. 3. IR spectra of fouled NF membranes: (a) RF; (b) NF90.

(amidel). Thus, we could identify indicatively that the major organic foulants on nanofiltration were composed of *N*-acetyl aminosugars and polysaccharides. The molecular weight (MW) distribution of foulants from sand filtration treated water was measured using HP-SEC method coupling with UV and fluoresce (FL) detector. Detailed descriptions were reported elsewhere [14]. As shown in Fig. 4, foulants from NaOH solution had relatively higher than those of pure water. The MW values ranging from 30,000 to 50,000 g/mol were identified

using fluorescence (FL) detector (protein-like substance). As shown in Fig. 5, the inorganic foulants were silica and aluminum ions from scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS). The inorganic foulants (Si, and Al) were removed after NaOH cleaning.

Various different cleaning agents for coagulation/sedimentation treated water were evaluated to recover reduced flux of fouled membranes. As shown in Fig. 6, caustic cleaning with 0.05 M NaOH was the most efficient of all other agents

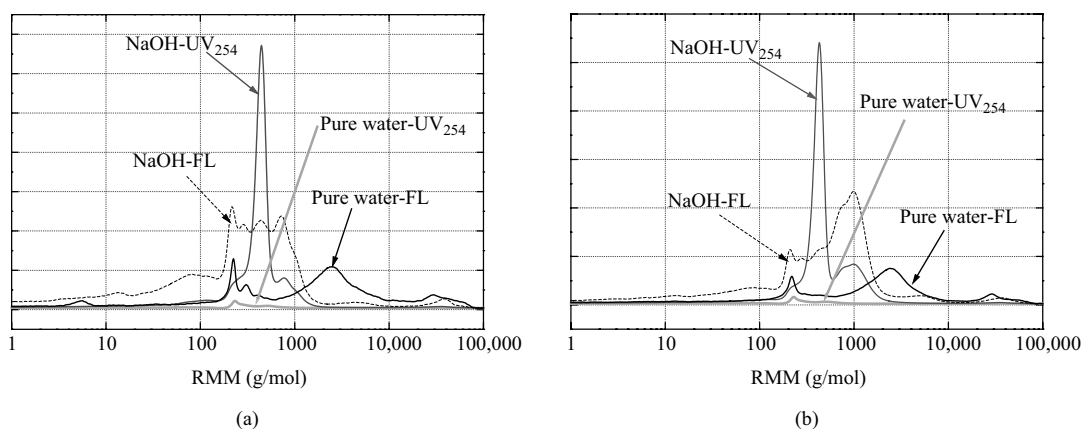


Fig. 4. MW distributions of foulants using different eluting solutions: (a) RF; (b) NF90.

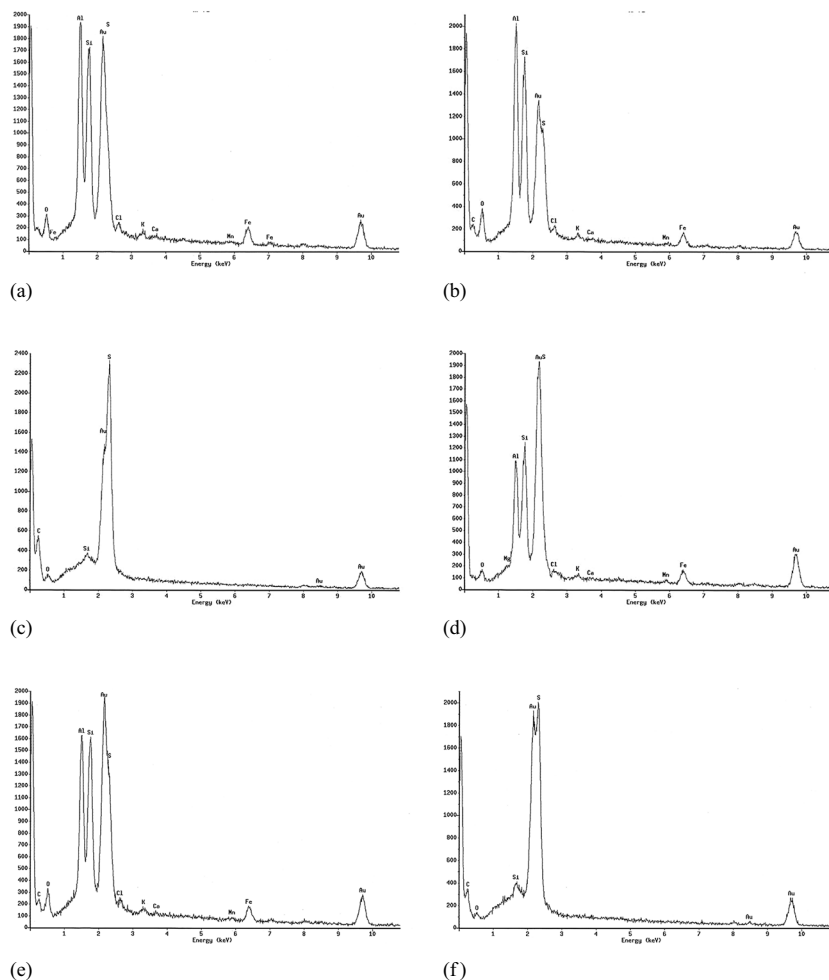


Fig. 5. SEM-EDS analysis; RF ((a)–(c)) and NF90 membrane ((d)–(f)): (a) fouled; (b) pure water; (c) NaOH; (d) fouled; (e) pure water; (f) NaOH.

including hydraulic, acidic, and surfactants [both sodium dodecyl sulfate (SDS) and EDTA] cleanings. The cleaning efficiency in Fig. 6 implies the ratio of recovered flux after a certain cleaning to that after hydraulic cleaning with pure water; the cleaning efficiency of 2.0 and 0.7, for examples, represent twice higher (e.g., caustic cleaning for NF90) and even lower (e.g., SDS cleaning for NF90) efficiencies compared to pure water cleaning, respectively.

As based on the results presented in Fig. 6, pure water (as a reference) and caustic cleanings

were selected to desorb organic foulants from the NOM fouled NF membranes. The desorbed foulants were characterized in terms of SUVA and structural analysis by XAD-8/4 resins (see Table 5). It was observed from the two different NF membranes that (1) the hydrophilic NOM fraction for sand filtration treated water substantially increased compared to the feed solution for both membranes, and (2) the hydrophobic and hydrophilic NOM constituents were more effectively removed from the RF and NF90 membranes by caustic and pure water cleaning,

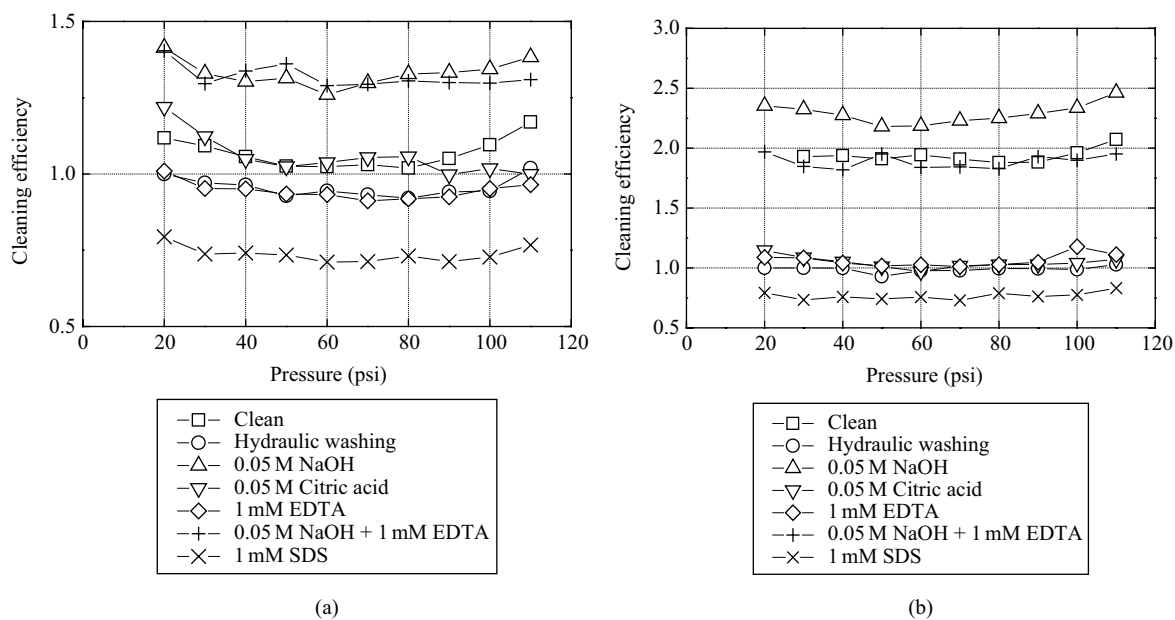


Fig. 6. Cleaning efficiencies of the fouled membranes with different cleaning agents: pressure conversion, 1 atm=14.7 psi: (a) RF; (b) NF90.

Table 5  
Foulants analyses

		RF			NF90				
		SUVA (L/mg-m)	Structure (%)			SUVA (L/mg-m)	Structure (%)		
			HP	TL	HL		HP	TL	HL
Coagulation/sedimentation	Feed	0.7–0.9	24	10	66	0.7–0.9	24	10	66
	Pure water	1.4	30	24	46	0.8	21	22	57
	0.05 N NaOH	1.7	37	13	50	1.9	23	13	64
Sand filtration	Feed	0.9–1.1	33	12	55	0.9–1.1	33	12	55
	Pure water	0.06	10	12	78	0.08	11	10	79
	0.05 N NaOH	0.9	9	8	83	1.4	14	14	72

respectively, from the perspective of NOM fraction (as characterized with XAD-8/4 resins).

#### 4. Conclusions

Two different NF membranes were evaluated in terms of organic/inorganic fouling; both are the same material-based TFC membranes but

exhibit different pore size distributions, surface charge, and contact angle. After a certain period of pilot-scale tests at the drinking water treatment plant, the two different NF membranes exhibited similar behaviors with respect to pore size distribution and surface charge. Both the fouled NF membranes by eluting pure water exhibited also very similar IR spectra, especially

a large and wide polysaccharide and/or *N*-acetyl aminosugar groups. From HP-SEC results, the higher MW values of foulants ranging from 30,000 to 50,000 g/mol were identified using FL detector. Caustic cleaning was proven to be effective to remove both fouled NF membranes as a basis of flux recovery, and it could efficiently desorb the hydrophobic NOM constituents or protein-like substances from the relatively hydrophilic and less negatively-charged NF membranes, in terms of NOM fraction, as compared to feed water. Inorganic foulants (i.e., Si and Al) were also fouled onto the membrane surface and/or pores and it is effectively removed by caustic cleaning, not pure water.

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