

Effects of sodium hydroxide cleaning on polyvinylidene fluoride fouled with humic water

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Abstract. This study investigated effects of NaOH cleaning on the intrinsic permeability of polyvinylidene fluoride (PVDF) membranes and flux recoveries and membrane resistances under various conditions encountered during ultrafiltration in water treatment plants. The NaOH cleaning using 10,000 mg/L NaOH led to discoloration of PVDF membranes and had little effect on water flux. The NaOH cleaning was efficient in removing the fouling layer caused by humic water. However, long filtration induced a fouling layer that was not removed easily by NaOH cleaning. The lower temperature during filtration yielded rapid increases in transmembrane pressure and decreases in NaOH cleaning efficiency. The alkaline cleaning of PVDF changed the membrane properties such as the hydrophobicity and morphology. Foulant properties, operational conditions such as temperature, and chemical agents should be considered for cleaning strategies for PVDF applied in water treatment.

Keywords: NaOH cleaning; PVDF; ultrafiltration; flux recovery; resistance

1. Introduction

Low-pressure membrane processes such as microfiltration (MF) and ultrafiltration (UF) have been widely installed in water treatment plants. The membrane material frequently applied to the low-pressure membrane processes in recent years is polyvinylidene fluoride (PVDF), which shows higher mechanical strength, thermal stability, and chemical resistance than other polymeric materials such as polysulfone and polyethersulfone. In addition, the raw material of PVDF has great solubility on solvent, making it easy to build a porous structure, which is advantageous for commercialization. However, the high hydrophobicity of PVDF may make it susceptible to fouling due to organic adsorption on the membrane surface (Hashim *et al.* 2011, Cha and Chi 2011). Several studies attempted to develop composite PVDF membranes for improvement of water production and fouling tendency using titanium dioxide nanoparticle or fibrillar mineral such as attapulgite (Tavakolmoghadam *et al.* 2016, Zhang *et al.* 2016)

Decrease in water flux, i.e., membrane fouling, is the main problem in the membrane processes.

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Membrane foulants are typically particulates, organic matter, inorganic ions, and microbial products. In both MF and UF, organic fouling by natural organic matter has been recognized as the most troublesome type of fouling. Application of rigorous pretreatment and enhanced backwashing often reduces the organic fouling in the membrane processes, but has not been able to prevent the decline of water flux of the membrane (i.e., fouling) that eventually occurs in the membrane (Lee *et al.* 2007, Kweon *et al.* 2012, Arhin *et al.* 2016).

Periodic chemical cleaning is recommended to remove fouling by natural organic matter. Foulants in feed water lower water permeation by blocking the water path in the membrane pores, making a cake layer on the membrane surface, or being adsorbed on the membrane during filtration, in the case of organic foulants.

For organic fouling, an alkaline solution, especially sodium hydroxide (NaOH), is typically used to remove foulants from membrane surfaces. NaOH has been used as a cleaning agent in membrane processes for skim milk production, bovine serum albumin filtration, sweet whey production, whey protein concentrate filtration, and surface water treatment (Regula *et al.* 2014). Zondervan and Roffel (2007) revealed that NaOH showed the best cleaning performance for ultrafiltration membranes made from polysulfone among other cleaning agents. The main cleaning mechanism was reported to be hydrolysis and solubilization (Porcelli and Judd 2010). Blanpain-Avet *et al.* (2004) reported that the removal of the majority of the fouling layer occurred in approximately 12 min for species that were loosely bound and easily solubilized by NaOH.

However, the increases in hydrophobicity after NaOH cleaning have been reported to lower the permeability of membranes manufactured from regenerated cellulose and fluoropolymers. Hashim *et al.* (2011) also revealed several negative effects of NaOH on PVDF membranes including degradation, polymer modification, and discoloration. Liu *et al.* (2011) showed that gradual hydrolysis of the ester linkages and dissolution of the upper surface of PVDF occurred in 1 N lithium hydroxide.

This study investigated the effects of NaOH cleaning on the intrinsic permeability of PVDF membranes using low- and high-concentration alkaline solutions applied in water treatment plants in usual operation. In addition, the effects of NaOH cleaning on flux recovery and the changes in the resistances of the fouling layer were evaluated in terms of filtration duration and temperature when humic water was filtered.

2. Materials and methods

2.1 Membranes

A hollow-fiber-type membrane module (Zeeweed 500, GE/Zenon, Canada) was obtained from GE/Zenon Company. The material was PVDF and the pore size was 0.04 μm . The fibers were cut to 25 cm long to fabricate a module. The module with a single fiber connected to a tube for suction has a membrane area of 14.92 cm^2 . The detailed specifications of the module are summarized in Table 1.

2.2 Feed waters

Ultrafiltration was performed using distilled/deionized (DI) water and humic acid water. The DI water was produced using Classic UV MK2 (ELGA, UK). The DI water was also used to

Table 1 Specifications of PVDF membrane used in this study

Properties	Specification
Material	Polyvinylidene Fluoride (PVDF)
Nominal pore size	0.04 μ m
Surface properties	Non-ionic & hydrophilic
Fiber diameter	1.9 mm OD/0.8 mm ID
Flow path	Outside-in
Transmembrane pressure	-90 to 90 kPa
Max. operation temperature	40°C (104°F)
Operation pH range	5.0-9.5

Table 2 Characteristics of the humic water in this study

Parameter (Unit)	Range
pH	6.92 - 7.0
Turbidity (NTU)	3.10 - 3.34
DOC (mg/L)	4.20 - 4.36
UV ₂₅₄ (cm ⁻¹)	0.376 - 0.396
Specific UV absorbance (L/mg·m)	8.95 - 9.10

measure clean water flux, rinse the membrane after chemical cleaning, and evaluate the efficiency of recovery by the chemical cleaning. Humic acid sodium salt (Sigma-Aldrich, USA) was purchased and 0.5 g of the salt was stirred in 1 L of DI water for 24 h. The humic water was filtered through a GF/C filter and diluted to a dissolved organic carbon (DOC) concentration of 4.2 mg/L. The key properties of the feed water are shown Table 2.

2.3 Membrane filtration

A module was immersed in the feed tank and a high-performance pump (GTS100, Green Tech, Seoul, Korea) was used to induce permeation under negative pressure. A gang stirrer was used to mix the feed water. A schematic diagram of the filtration apparatus is shown in Fig. 1.

Membrane fouling was monitored using changes in transmembrane pressure (TMP). A pressure transducer (ZSE40AF-01-R, SMC, Japan) was installed in the permeate line. The electric signal from the pressure transducer was recorded by a computer through a LabVIEW USB device (National Instruments, Hungary).

Filtration began with clean water flux (CWF) measurement using the DI water. The membrane intrinsic resistance was obtained from the clean water flux at the beginning of each filtration. After the feed water was filtered for either 8 or 24 h, NaOH cleaning or DI water cleaning was performed. Filtration and cleaning were performed six times and the recovery of water flux was evaluated comparing flux after each cleaning with the clean water flux. The equation to calculate flux recovery is as follows.

$$\text{Flux Recovery} = \frac{J_{\alpha}}{J_0}$$

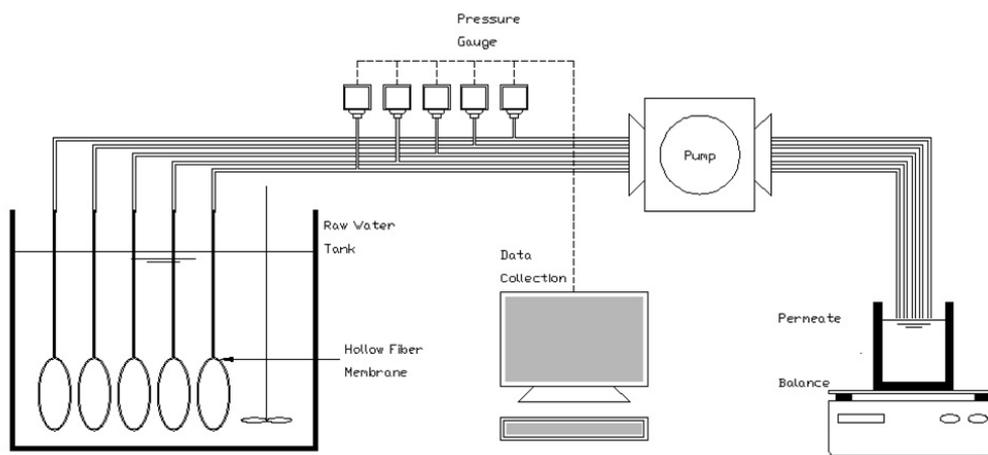


Fig. 1 Schematic diagram of the filtration apparatus

where J_{α} : flux at the α^{th} cycle of filtration and cleaning and J_0 : clean water flux measured at the beginning of the experiments.

The flux was calculated by dividing permeate water volume by operating time and membrane surface area. The water mass was collected during filtration using a balance with an electronic signal device. Each experiment used a virgin membrane after cleaning with DI water and soaking overnight.

2.4 Cleaning procedure

Fouled membranes were transferred to a 1 L beaker containing sodium hydroxide (93%, Duksan, Korea) cleaning solution. The cleaning was performed for 4 h with a concentration of 150 mg/L for normal operations and 24 h with a concentration of 10,000 mg/L for the experiment on the effects of a high-strength cleaning agent. A stir plate mixing at 350 rpm was used to facilitate the cleaning. After the cleaning, the membrane was washed sufficiently using DI water and used for the next filtration.

2.5 Surface analysis

The surface roughness and hydrophobic property of fouled and cleaned membranes were analyzed using atomic force microscopy (AFM) and contact angle (CA) measurements.

AFM (XE-100, Park Systems, Korea) was employed to scan surface areas of $10 \times 10 \mu\text{m}$ using non-contact mode, which utilizes a relatively small force, i.e., 0.01-0.1 nN, and is beneficial for soft specimens such as surfaces fouled with organic matter. For the analysis, the hollow fiber was cut in the middle and dried in an oven for 24 h.

Membrane surface roughness was quantified as root mean square (RMS) roughness, which is the RMS deviation of the peaks and valleys from the mean plane. The approaching force ranged from 4.0 to 6.0 N/m with a scan speed of 0.7 line/s and scan area of $10 \times 10 \mu\text{m}$. Scanned images were analyzed using SPIP software (Surface Imaging Systems, Herzogenrath, Germany). Each image was flattened into the baseline prior to roughness analyses (Vrijenhoek *et al.* 2001).

Contact angle measurements were performed with a Drop Shape Analyzer 100 (Kruss, Germany). The left and right contact angle measurements were averaged and recorded as an equilibrium contact angle. Ten measurements were carried out for each membrane. The reported values are the averages of three equilibrium contact angles.

2.6 Water quality

Characterization of water samples was performed by measuring turbidity, pH, DOC concentration, and ultraviolet absorbance at 254 nm (UV_{254}) prior to experiments. Specific ultraviolet absorbance (SUVA) values that indicate the hydrophilic or hydrophobic characters of natural organic matter (NOM) indirectly were also determined based on the DOC concentration. A Hach 2100N turbidimeter (Hach, Loveland, CO, USA) was used to measure turbidity and a StablCal[®] Calibration Set was used for calibration. A pH meter (Orion 5STAR, Thermo, USA) equipped with an electrode (Orion 8102BNUWP, Thermo, USA) was used to measure hydrogen concentrations. DOC was measured using a Sievers 5310C Laboratory Total Organic Carbon Analyzer (GE Analytical Instruments, Inc., Boulder, CO, USA) equipped with a 900 Autosampler System (Ionics Instruments, Boulder, CO, USA). Potassium hydrogen phthalate (Junsei Chemical Co., Ltd., Tokyo, Japan) was used as an external standard. DOC measurements were made after filtering samples through pre-rinsed 0.45- μm membrane syringe filters (Millipore, USA). UV absorbance measurements were made using Hellma[®] precision cells composed of synthetic quartz glass and a UV-Visible spectrophotometer (GENESYS 10 UV, Thermo, USA).

3. Results and discussion

3.1 Changes in membrane resistances caused by NaOH cleaning

The changes in TMP were recorded for six cycles of DI water filtration and alkaline cleaning. The ultrafiltration of DI water was performed with a constant flux of 20 LMH for 8 h at ambient temperature. During the cleaning, the concentration of the NaOH solution was either 150 mg/L with 4 h of soaking, i.e., the normal condition, or 10,000 mg/L with 24 h of soaking, i.e., the harsh condition. The changes in membrane resistances were calculated using Eq. (1)

$$J_{\alpha} = \frac{\Delta P}{\mu \cdot (R_m + R_{che,\alpha})} \quad (1)$$

where J_{α} is the flux during the α^{th} cycle of filtration, ΔP is the transmembrane pressure, μ is the water viscosity, R_m is the membrane intrinsic resistance, and $R_{che,\alpha}$ is the membrane resistance, if any, exhibited by after α^{th} cycle of NaOH cleaning.

The suction pressure was maintained at around 10 kPa during filtration since only DI water used for filtration. The changes in resistances were presumably attributed to aging of the PVDF membrane due to NaOH cleaning. The changes in the resistances caused by NaOH cleaning were between 0.02×10^{12} and $0.15 \times 10^{12} \text{ m}^{-1}$ for the normal condition and between 0.09×10^{12} and $0.14 \times 10^{12} \text{ m}^{-1}$ for the harsh condition. For comparison, the DI water cleaning was applied for the same number of cleaning as the NaOH cleaning. The changes in resistances by the DI water cleaning were ranged from $0.01 \times 10^{12} \text{ m}^{-1}$ to $0.07 \times 10^{12} \text{ m}^{-1}$, which were less than the changes by NaOH cleaning.

The variation in TMP caused by alkaline cleaning under either the normal or harsh condition was infinitesimal, although the color of the membrane changed from white to light brown and the magnitude of the decreases in resistance became great with repeated cleaning under the harsh condition. Numerous researchers have noted that degradation, surface modification, and discoloration of PVDF occurred at high NaOH concentrations with prolonged exposure (Ross *et al.* 2000, Hashim *et al.* 2011). Ross *et al.* (2000) revealed that chemical reactions such as defluorination and oxygenation and formation of a conjugated carbon double bond structure occurred in a PVDF membrane in a 12 M NaOH solution with a pH of 14 at 80°C. Hashim *et al.* (2011) also showed that PVDF became black and brittle at an alkaline concentration of 10 g/L with more than 3 h of exposure. Park (2008) cleaned PVDF membranes using 5,000 mg/L NaOCl and 1 M NaOH for 10 d and found increases in flux and decreases in turbidity removal, indicating deterioration of membrane integrity. However, Abdulla *et al.* (2012) reported a contrary result, revealing that a membrane exposed to a NaOH solution with a pH of 12 at 40°C for more than 4 months did not show any deterioration caused by aging. The changes in resistance and discoloration of the PVDF membrane cleaned under the harsh condition in this study implied that some degradation of the membrane occurred, but the degree of degradation was limited since there was little variation in TMP.

AFM was used to evaluate changes in the surface structure of the membrane after NaOH cleaning under the harsh condition (Table 3). AFM uses a sharp probe to build a map of the height of the sample's surface, i.e., morphology. The most frequently used parameter from an AFM image is the roughness, which is the RMS roughness (Al-Anezi *et al.* 2008). The average roughness (R_a) of a DI-water-cleaned membrane was 34.5 nm, and that increased to 51.0 nm after NaOH cleaning under the harsh condition. Since there was no foulant and the membrane was exposed only to NaOH, the increased roughness value indicated that the surface morphology was modified by NaOH cleaning, although the flux and the membrane resistance were varied infinitesimally. In addition, contact angles of the membranes after cleaning were measured to determine the extent of surface property alteration caused by alkaline cleaning as shown in Table 3. The contact angle has been used to describe the hydrophobic or hydrophilic character of membranes: the lower the contact angle, the more hydrophilic the membrane could be. The contact angle also increased after NaOH cleaning under the harsh condition. The increased hydrophobicity after NaOH cleaning corresponded with the results of Hashim *et al.* (2008).

3.2 Cleaning effects of NaOH on PVDF fouled by humic acids

Humic acid with 4 mg/L of DOC was filtered for 8 h and the cleaning using either distilled water or NaOH was performed for 4 h. The variation in TMP during the filtration was recorded and the specific flux was evaluated as shown in Fig. 2 for DI water cleaning and in Fig. 3 for NaOH cleaning.

Table 3 Roughness and contact angle changes of the membrane caused by NaOH cleaning under the harsh condition

	R_a (nm)	Contact angle (°)
DI cleaning	34.5	72.07
NaOH cleaning	51.0	76.21

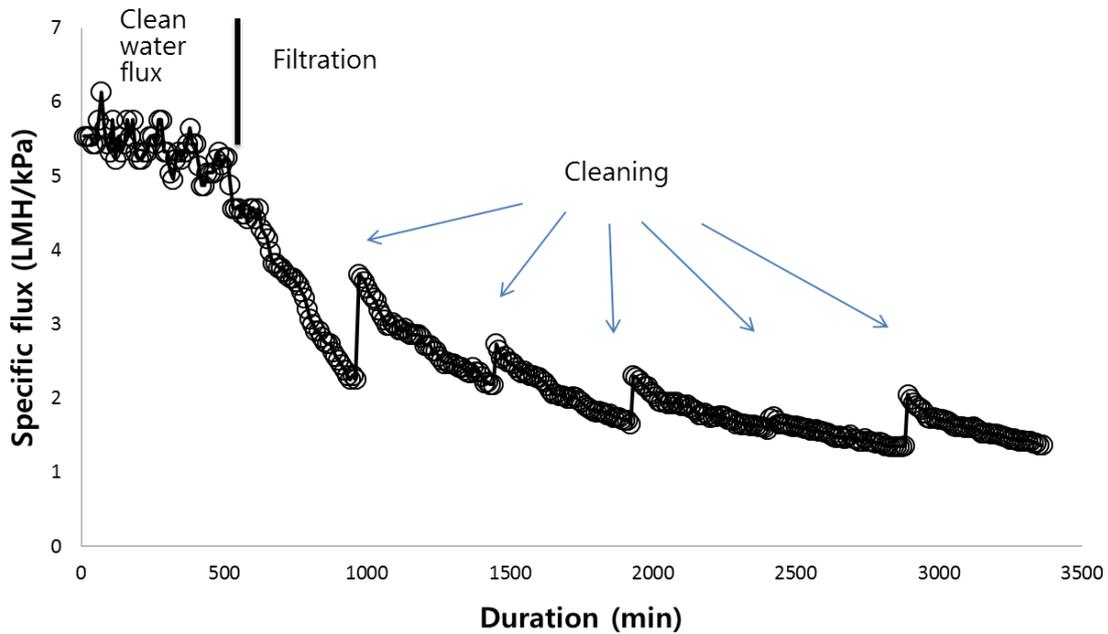


Fig. 2 Decrease in the specific flux during six cycles of filtration of humic acid solution and cleaning by distilled water

As shown in Fig. 2, the specific flux of humic acid filtration was initially approximately $5.7 \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{kPa})$ and decreased gradually as the filtration was repeated. At the sixth cycle, the specific flux was only $2.0 \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{kPa})$. Since there were no chemicals during the cleaning, the foulants accumulated on the membrane surface and the flux decrease became severe, and little flux recovery was shown after the DI water cleaning. Compared to the DI water cleaning, the NaOH cleaning led to great flux recovery (Fig. 3). The initial specific flux was $5.0 \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{kPa})$ and was reduced to $1.5 \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{kPa})$ after the first filtration. The flux was restored almost to the initial value after the first NaOH cleaning while the TMP was not reached to the value measured for the clean water flux, which gave the higher specific flux after the NaOH cleaning. The flux decline was substantially rapid during the later cycle of humic water filtration and the flux at the end of each cycle of the filtration reached $1.5 \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{kPa})$. The NaOH cleaning was effective in restoring the water flux of a membrane fouled with humic acid. The cleaning performances generally depend on complicated interactions of the membrane material, nature of foulants, cleaning conditions, and cleaning agent properties. The results of the specific flux decline behaviors from NaOH cleaning showed that NaOH reacted substantially with humic acids deposited on the PVDF membrane surfaces.

In addition, the CWF was obtained after the cleaning. The comparison between the CWF of the virgin membrane with the flux after cleaning was defined as the flux recovery. There are two main types of hydraulic parameters for characterizing cleanliness, i.e., parameters related to flux and parameters related to resistance. The most frequently used parameter has been the flux recovery (Regula *et al.* 2014). If the flux recovery is more than 95%, then the cleaning protocol is generally acceptable for the application (Field *et al.* 2008). The flux recovery results showed that NaOH cleaning was effective in terms of cleanliness (Fig. 4).

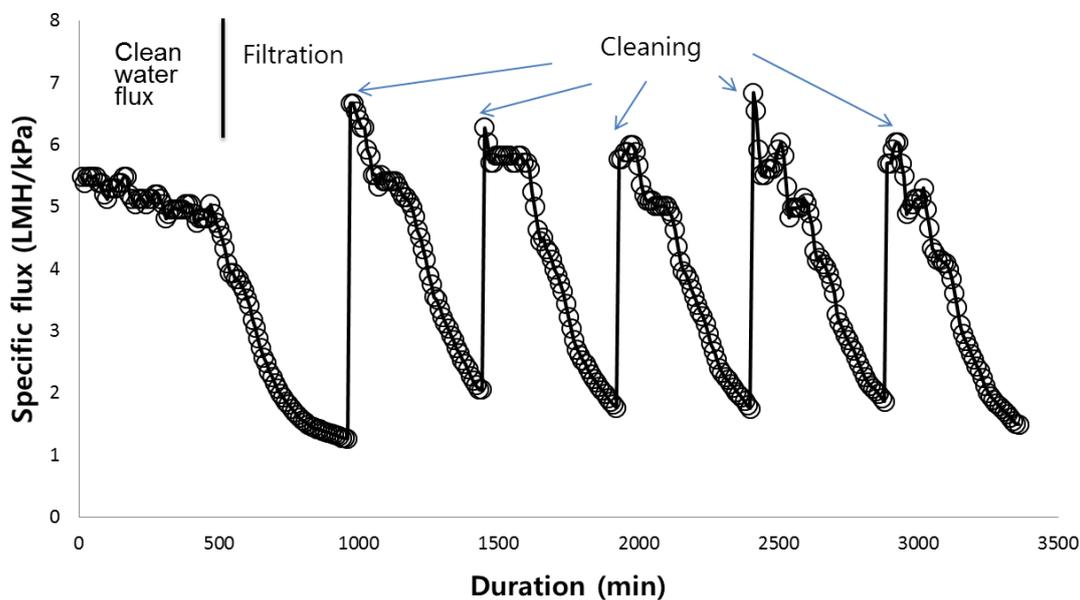


Fig. 3 Decrease in the specific flux during six cycles of filtration of humic acid solution and cleaning by NaOH solution

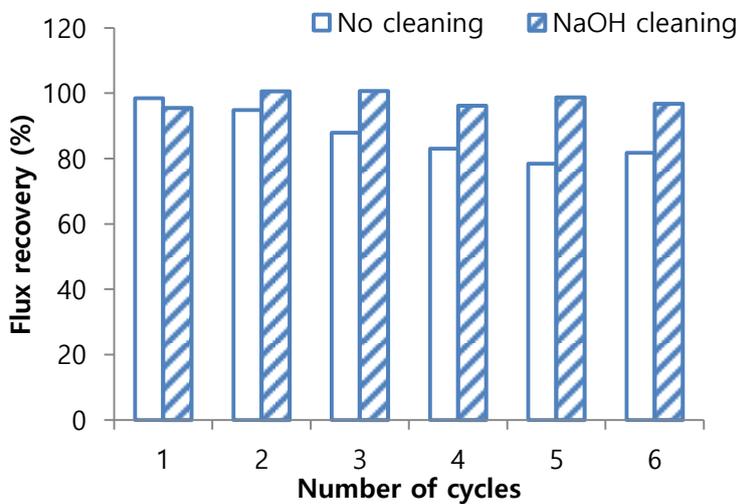


Fig. 4 Flux recovery during six cycles of filtration of humic acid solution and cleaning with (a) distilled water and (b) NaOH solution

3.3 Effects of filtration time on NaOH cleaning efficiency

The filtration time was extended from 8 h to 24 h to evaluate the efficiency of NaOH cleaning for heavily fouled membranes. The flux recoveries are compared in Fig. 5. The flux recovery caused by NaOH for membranes fouled with humic acid for 8 h ranged from 95.5% to 100.7%,

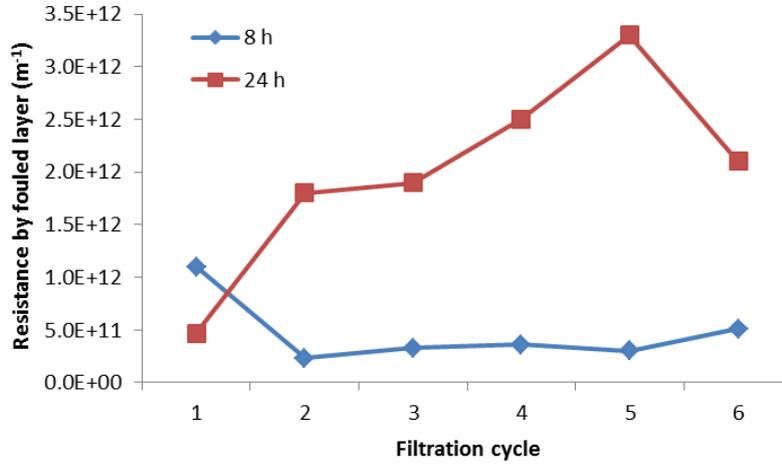


Fig. 5 Effects of filtration duration on efficiency of NaOH cleaning

indicating that most of the foulants were detached during the NaOH cleaning process. However, the flux recovery caused by NaOH for the membranes fouled for 24 h was substantially low compared to those after 8 h of filtration. After the second cycle, the flux recovered to almost 95%. After the third cycle, only 70% of the initial flux was recovered, indicating that severe fouling occurred and the NaOH cleaning was not effective in removing the foulants. In addition, the resistances produced by the foulants were evaluated using Eq. (2)

$$J_{\alpha} = \frac{\Delta P}{\mu \cdot (R_m + R_{f,\alpha})} \tag{2}$$

where J_{α} is the flux during the α^{th} cycle of filtration, ΔP is the transmembrane pressure, μ is the water viscosity, R_m is the membrane intrinsic resistance, and $R_{f,\alpha}$ is the membrane resistance, if any, exhibited by a fouled layer even after the α^{th} cycle of NaOH cleaning.

The resistances caused by the fouled layer increased greatly with repeated filtration for 24 h even after the NaOH cleaning. The resistances of the membranes fouled for 8 h were in the range of $0.5 \times 10^{12} \text{ m}^{-1}$ to $1.0 \times 10^{12} \text{ m}^{-1}$, whereas those of membranes fouled for 24 h were in the range of 0.5×10^{12} to $3.5 \times 10^{12} \text{ m}^{-1}$. In addition, the resistances increased after the second filtration and the highest value was obtained in a later cycle of filtration. Field *et al.* (2008) pointed out that the first few cycles of filtration and cleaning could lead to misunderstandings of cleaning efficiency, especially for UF membranes. The resistances of fouled membranes increased abruptly after the seventh cycle of operations in their study. The authors recommended that operations should be conducted for long periods to understand properly the effects of cleaning.

The results implied that there was a threshold value for cleaning efficiency; beyond this value, irreversible fouling would occur even if the cleaning agent was effective in removing the particular foulants. Therefore, a proper cleaning strategy in a cleaning interval is necessary to maintain adequate water flux values.

3.4 Effects of filtration temperature on NaOH cleaning efficiency

Key cleaning design parameters include cleaning agent concentration, temperature, chemical-

enhanced backflush rate, and cleaning exposure time. Extent of fouling during filtration also determines efficiency of cleaning. Increased temperatures induce low viscosity of water thus increased water flow through membrane pore during filtration and elevated mass transfer by increasing diffusive mass transfer during cleaning. Foulant solubility and NOM reactivity increased at higher temperatures, which helped in adsorption of NOM during filtration and facilitated cleaning the organic fouling layer. The temperature limits were also established owing to the membrane integrity determined by the potting ingredients used in the module rather than the membrane material itself (Porcelli and Judd 2010). Regula *et al.* (2014) pointed out that cleaning with caustic soda has an optimal efficacy at 50°C. There have been many studies on the effects of high temperatures on the aging of PVDF membranes caused by cleaning. Little research has been performed to understand the effects of low temperatures during filtration on fouling and cleaning efficacy. The temperature can affect the balance of the chemical reaction, the solubility of foulants, and the reactivity of compounds produced during the cleaning process.

Fig. 6 shows the variations in TMP during ultrafiltration of humic water at 10°C and 20°C; 10°C is the usual water temperature during winter in water treatment plants in Seoul, Korea. The TMP increases were very rapid and steep for ultrafiltration at 10°C compared to those at 20°C until the fourth cycle of filtration. In addition, the NaOH cleaning could significantly restore the TMP; thus, the TMPs at the beginning of the each filtration were maintained at 15 kPa for the four cycles of filtration. However, at the fifth cycle of filtration, the pattern of the TMP increase and the

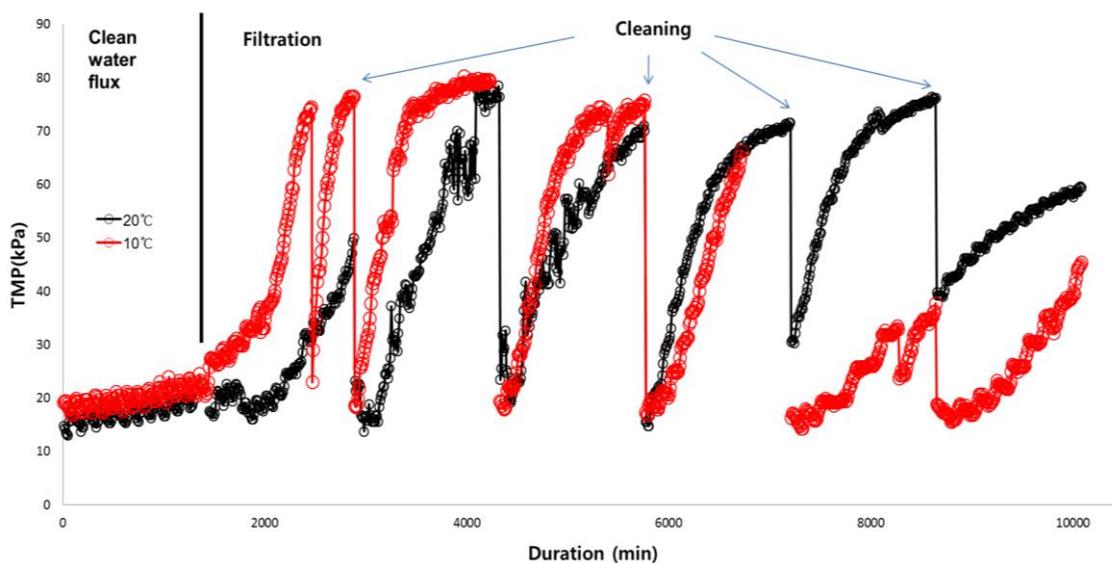


Fig. 6 Effects of filtration temperature on variation in TMP and efficacy of NaOH cleaning

Table 4 Changes in contact angle after filtration and cleaning at different temperatures

Cleaning agent	Temperature	Contact angle (°)
DI Water	20°C	72.07
NaOH	20°C	69.14
NaOH	10°C	64.67

TMP recovery were tremendously different for the two temperatures. For the filtration at 20°C, the TMP could not reach the initial value after NaOH cleaning while the pattern was similar to that of the previous filtration. For the filtration at 10°C, the TMP could be restored to the initial value after the NaOH cleaning; however, the TMP increase was dampened. For the earlier cycle of operation, the low temperature seemed to increase the fouling. Kim (2014) also noted that the membrane resistance was not altered by temperature during filtration and decreased with increasing temperature in experiments involving tap water cleaning of a membrane fouled by humic water. A higher temperature during filtration may induce greater interaction between humic water and membrane surfaces or a greater fouling layer on the membrane surfaces. A temperature lower than 10°C needs to be applied for a better understanding of the effects of temperature on the filtration and cleaning.

The contact angle after filtration of humic water and cleaning by NaOH was measured and is shown in Table 4. The contact angle showed that the membrane became more hydrophilic after the filtration and cleaning. Compared to the results after NaOH cleaning alone (Table 3), the fouling layer caused by humic water produced more hydrophilic properties on the membrane surfaces. The contact angle after the filtration at 10°C showed that the surface became more hydrophilic, which may explain the reduced TMP increases at the fifth and sixth cycles of filtration at the lower temperature.

4. Conclusions

The effects of chemical cleaning by NaOH on PVDF membranes fouled with humic water were investigated. The parameters included chemical agent concentration, cleaning duration, foulant properties, filtration time, and temperature during filtration.

- Discoloration of PVDF was observed at the NaOH concentration of 10,000 mg/L while the flux was fully restored. More frequent application of NaOH cleaning with the high concentration may lead to the deterioration of the membrane structure.
- NaOH cleaning was effective in restoring the flux of the membranes fouled by humic water. However, the longer filtration time (i.e., 24 h), compared to filtration for 8 h, produced a fouling layer that was difficult to remove via the NaOH cleaning.
- The temperature during filtration led to differences in TMP increase patterns and recovery rate caused by NaOH cleaning. The filtration at 10°C seemingly resulted in a more hydrophilic layer of foulants; thus, the NaOH cleaning was effective in restoring the TMP, although the rapid TMP increases were observed at the earlier stages of filtration and cleaning.
- More research on various factors of cleaning including solution properties such as pH and foulant compositions, operating conditions such as duration and temperature, and chemical agent properties such as concentration and reactivity is needed to understand the complicated interactions between foulants and chemical agents during cleaning processes.

Acknowledgments

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