

Consecutive chemical cleanings of hollow fiber ultrafiltration membranes from a pilot-scale surface water treatment plant

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(Received December 17, 2020, Revised March 4, 2021, Accepted April 13, 2021)

Abstract. The effects of the order of chemical cleaning protocols on the removal of hollow fiber ultrafiltration (HUF) membrane foulants, and restoration of membrane surface properties, were identified through autopsies of fouled HUF membrane modules from a pilot-scale surface water treatment system (Hongcheon-gun, Kangwon province, Republic of Korea). Quantitative and qualitative differences in the extracted HUF membrane foulants were found to depend on the types of chemical cleaning protocols applied, the consecutive cleaning protocol II (CP II; 0.1 N NaOH → 0.1 N HCl; the sum of DOC = 215.19 mgC m⁻²; the sum of TN = 17.82 mg N m⁻²; the sum of metals = 25.14 mg m⁻²) extracted both organic and inorganic foulants from HUF membrane surfaces more effectively than consecutive cleaning protocol I (CP I: 0.1 N HCl → 0.1 N NaOH; the sum of DOC = 189.89 mg C m⁻²; the sum of TN = 13.66 mg N m⁻²; the sum of metals = 9.95 mg m⁻²). Furthermore, the surface morphological characteristics of the cleaned HUF membrane using CP II were relatively similar to the virgin membrane surface compared to those of the cleaned HUF membrane using CP I. These findings demonstrated that the sequential coupling of two different chemical cleaning protocols played critical roles in removing organic and inorganic foulants from the fouled HUF membrane surfaces and restoration of membrane surface elementary composition potentially related to HUF membrane performances.

Keywords: consecutive chemical cleaning; membrane autopsy; membrane fouling; pilot-scale surface water treatment plant; ultrafiltration

1. Introduction

Rapid population growth, industrialization, and urbanization can significantly deteriorate surface water quality (Alam *et al.* 2007). This phenomenon has raised global drives towards stringent environmental regulation, demand for clean and safe water, and alternative water treatment technology (Zularisam *et al.* 2006). Ultrafiltration (UF) membranes have been accepted as the most promising technology for surface water treatment due to their high efficiency in particulate matter removal and potable water quality enhancement, combined with their relative cost-effectiveness, compared to reverse osmosis membranes or nanofiltration (Tian *et al.* 2010). Moreover, UF membranes, alone or combined with conventional water treatment processes, including coagulation, flocculation, and adsorption, effectively remove microorganisms in

surface waters (Fiksdal and Leiknes 2006). Although UF membranes have recently attracted great interest and are widely applied to water treatment, membrane fouling still remains a significant obstruction in hollow fiber UF (HUF) membrane applications due to the resulting productivity reduction (Xing *et al.* 2018).

Various materials in surface water are potential UF membrane foulants, including particulate, inorganic, and dissolved organic matter (DOM) (Zularisam *et al.* 2006). Among these, DOM has been investigated as one of the problematic materials of the UF membrane foulants due to particulate and soluble components complexation with DOM (i.e., humic-like substances, proteins, and polysaccharides) (Chu *et al.* 2017). Thus, the presence and concentration of potential foulants in surface water have played critical roles in governing the UF membrane fouling mechanisms.

Membrane fouling occurs due to pore blockage, charge interaction, and hydrophobic (HPO) interactions based on feed water DOM characteristics (Lee *et al.* 2001, Haan *et al.* 2018). Furthermore, hydrophilic (HPI) DOM—which includes amino acids, polysaccharides, and sugars—has a higher molecular weight (MW) than HPO DOM (i.e.,

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humic-like substance), which can increase membrane surface fouling potential (Jarusutthirak *et al.* 2002). The HPO DOM, including negatively charged carboxylic and phenolic functional groups, may contribute considerably to the formation of fouling layers on the negatively charged membrane surfaces, owing to their repulsive electrostatic interactions (Chon *et al.* 2012).

Physical or chemical cleaning methods have been used to remove UF membrane fouling. Physical cleaning methods, including air sparging, backwashing, flushing, and vibration, are performed regularly during UF membrane operations and mitigate most reversible membrane fouling (Aguiar *et al.* 2018). These methods are less likely to degrade the UF membrane and/or reduce its lifetime than chemical cleaning methods, though UF membrane operational efficiency may be reduced as more irreversible fouling is deposited on the UF membrane surface (Kimura *et al.* 2004). Chemical cleaning methods alleviate the fouling layer structure through a reaction between the cleaning solutions and the UF membrane fouling layer, which then facilitates the mechanical removal of the fouling layer.

Several chemical cleaning solutions are used either separately and/or in combination to reduce UF membrane fouling and are commonly classified as being acidic, basic, and oxidant solution formats (Sohrabi *et al.* 2011, Said *et al.*, 2014). Acid cleaning solutions (e.g., HCl, H₂SO₄) are used to remove multivalent metal ions by hydrolysis. Base cleaning solutions (e.g., NaOH) promotes the reduction of DOM (i.e., carboxylic and phenolic functional groups, polysaccharides, and proteins) due to increasing the solubility and electrostatic repulsion. Oxidant solution (e.g., NaOCl) with base cleaning solution at high pH conditions encourages the degradation of DOM functional groups (i.e., carboxyl, ketonic, and aldehyde groups) (Porcelli and Judd 2010). Optimal chemical cleaning solutions must be selected, depending on the identification of the foulant type(s) and the chemical resistance of the UF membrane, because some combinations of chemical cleaning solutions and UF membrane component materials can result in irreversible damage to the membrane, reducing its performance and operational lifetime (Wei *et al.* 2010). Several studies have identified the influences of the chemical cleaning solution types and chemical cleaning sequence on the UF membrane fouling layer cleaning efficiencies (Tian *et al.* 2010, Kimura *et al.* 2004, Gao *et al.* 2011, Zondervan *et al.* 2008). For instance, the oxidizing (NaOCl) and base (NaOH) chemical cleaning solutions were more effective in recovering the membrane performance due to reducing the irreversible fouling compared to the other chemical cleaning solutions (Kimura *et al.* 2004, Gao *et al.* 2011). Tian *et al.* have found the synergistic effects of the consecutive chemical cleaning with NaOH and ethanol for the elimination of PVC membrane foulants (Tian *et al.* 2010). Additionally, Zondervan *et al.* have demonstrated that the chemical cleaning sequence model could effectively govern the membrane fouling (Zondervan *et al.* 2008). However, the fundamental understanding of chemical cleaning efficiencies on surface water treatment plant (SWTP) UF membranes remains

incomplete because there have been no in-depth studies on the effects of two different, but consecutively applied, chemical cleaning protocols used to remove foulants from HUF membrane surfaces in a pilot-scale SWTP.

The main objective of the study was to identify the effects of consecutive chemical cleaning protocols on the extraction of both organic and inorganic foulants from HUF membrane surfaces in a pilot-scale SWTP. The two consecutive chemical cleaning protocols were tested on fouled HUF membranes collected from a pilot-scale SWTP in Hongcheon-gun (Kangwon province, Republic of Korea). Of the two cleaning agents employed, one was acidic (0.1 N HCl), and another basic (0.1 N NaOH), and the tested combination were: (i) consecutive chemical cleaning protocol I (CP I; 0.1 N HCl → 0.1 N NaOH), and (ii) consecutive chemical cleaning protocol II (CP II; 0.1 N NaOH → 0.1 N HCl). Removal of HUF membrane foulants using these protocols related to DOM properties in the feed and treated waters was examined in terms of quantitative and qualitative differences, using various analysis methods. HUF membrane surface characteristic changes were also investigated through membrane autopsies.

2. Materials and methods

2.1 Configuration of a pilot-scale SWTP using HUF membranes

A pilot-scale SWTP was installed near the Hongcheon River (Hongcheon-gun, Kangwon province, Republic of Korea) involving sedimentation and HUF membrane processes (Fig. 1). The feed water was taken from the Hongcheon river, a major drinking water source in Hongcheon-gun. The feed water was then employed to remove the high-density particles through a sedimentation process and treated by five HUF membrane modules (Cleanfil®-70R, Kolon Industries, Seoul, Republic of Korea; nominal pore size = 0.1 µm; effective surface area/module = 70 m²), which were operated in dead-end mode. The HUF membrane characteristics are summarized in Table 1.

2.2 Consecutive chemical cleaning protocols

Two different consecutive chemical cleaning protocols, using 0.1 N HCl (acidic cleaning solution) and 0.1 N NaOH (basic cleaning solution), were used to extract foulants from

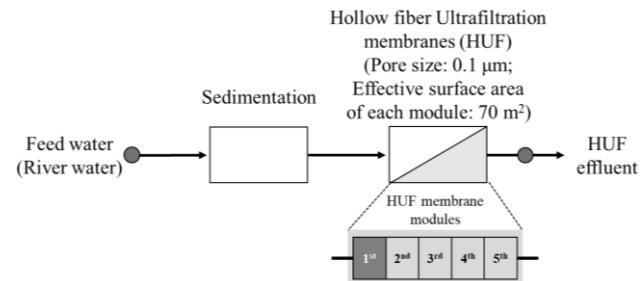


Fig. 1 Schematic of a pilot-scale SWTP using HUF membranes

Table 1 Characteristics of the HUF membranes

Type	HUF membrane
Manufacturer	Kolon Industries
Membrane code	Cleanfil®-P70R
Membrane material	Polyvinylidene fluoride
Dimension (ID / OD) (mm)	0.8 / 2.0 ^a
Effective surface area of each module (m ²)	70 ^a
Nominal pore size (μm)	0.1 ^a

^a Data supplied by the manufacturer

the HUF membranes of the pilot-scale SWTP: (i) CP I (0.1 N HCl → 0.1 N NaOH), and (ii) CP II (0.1 N NaOH → 0.1 N HCl). Seventeen coupons of the fouled HUF membranes (1st HUF membrane module, the effective surface area of each coupon: 0.000942 m²) were soaked in 0.5 L of each cleaning solution for 6 hours in the order of each cleaning protocol with moderate stirring to extract the foulants at 20 ± 1.0 °C. The pH of the foulant samples extracted from the HUF membranes was adjusted, using HCl and NaOH solutions, to a pH range of 5.5 – 6.5, and then filtered using glass fiber filters (GF/F; nominal pore size: 0.7 μm, Whatman, Clifton, NJ, USA) before refrigeration at 4°C until required for analysis.

2.3 Sample collection

2.3.1 Feed water and treated water samples

Feed water and HUF effluent samples were collected from the pilot-scale SWTP, to examine the extraction of bulk organic and inorganic matter from the feed and treated waters. All water samples were pre-treated using GF/F and stored in a refrigerator at 4°C until required for analysis.

2.3.2 Fouled and cleaned HUF membrane samples

Fouled HUF membranes were collected from the 1st HUF membrane module in the pilot-scale SWTP, cleaned using the two different consecutive chemical cleaning protocols—CP I and CP II—and then stored in a desiccator at room temperature. The physicochemical characteristics of the fouled and cleaned HUF membranes were investigated through several analytical methods to estimate the effects of the differences in the order of the chemical cleaning protocols.

2.4 Analytical methods

Portable pH and conductivity meters (Thermo Scientific Orion 3-Star plus, Waltham, MA, USA) were used to measure water sample pH and conductivity. Dissolved organic carbon (DOC) and total nitrogen (TN) concentrations in the water and foulant samples were quantified using a total organic carbon analyzer (TOC-VCPh, Shimadzu, Kyoto, Japan), coupled to a TN analyzer (TNM-1, Shimadzu, Kyoto, Japan). A UV/Vis spectrophotometer measured UV absorbance at 254 nm (UVA₂₅₄) (UV-1280, Shimadzu, Kyoto, Japan) with a 1 cm quartz cuvette (Hellma, Müllheim, Germany) to identify DOM aromatic hydrocarbon constituents in water and foulant

samples. Specific UV absorbance (SUVA) was calculated as the ratio of UVA₂₅₄ to DOC. Inductively coupled plasma-mass spectrometry (ICP-MS; NexION, Perkin Elmer, Waltham, MA, USA) was used to quantify inorganic constituents in water and foulant samples. All measurements were conducted in triplicate, and standard deviations were calculated to confirm reproducibility. DOM three-dimensional fluorescence excitation-emission matrices (3D FEEM) and MW distributions were measured using fluorescence spectroscopy (RF-6000, Shimadzu, Kyoto, Japan), and high-performance, size-exclusion chromatography (HPSEC; eluent composition = 96 mM NaCl + 2.4 mM NaH₂PO₄ + 1.6 mM Na₂HPO₄, flow rate = 0.7 mL min⁻¹). The HPSEC was equipped with a Protein-Pak 125 column (Waters, Milford, MA, USA) for UVA detection at 254 nm (SPD-10AVP, Shimadzu, Kyoto, Japan), and fluorescence detection at an excitation (EX) wavelength of 278 nm and an emission (EM) wavelength of 353 nm (RF-10AXL, Shimadzu, Kyoto, Japan), respectively (Chon *et al.* 2013a). A field emission electron microscope (FE-SEM; S-4300, Hitachi, Tokyo, Japan), coupled to an energy dispersive X-ray (EDX) spectrometer (EMAX, Horiba, Kyoto, Japan) was used to examine the differences in surface morphological features and variations in the inorganic constituents in the fouled and cleaned HUF membranes. Fouled and cleaned HUF membrane preparations were coated with platinum for FE-SEM / EDX analyses (Leica EM ACE 600, Leica-microsystems, Germany).

2.5 Statistical analysis

The statistical analysis was occurred using SigmaPlot (Version 12.5, Systat Software, Inc, CA, USA). Student's T-test was performed to examine differences among independent groups. The p-value of ≤ 0.05 was considered a statistically significant difference. Unless otherwise stated, the results (i.e., mean ± standard deviation) in the manuscript represented the triplicate analysis.

3. Results and discussion

3.1 Water characteristics

Variations in pH, conductivity, DOC, UVA₂₅₄, SUVA, and TN, and the concentrations of metal ions in the feed water and water treated using HUF membranes in the pilot-scale SWTP are listed in Table 2. The HUF membranes considerably reduced the pH ($p = 0.0098$), conductivity ($p < 0.05$), DOC ($p < 0.05$), UVA₂₅₄ ($p < 0.05$), and TN ($p = 0.034$) in the feed water. The HUF membrane process effectively removed DOC (removal efficiency = 56.0%), UVA₂₅₄ (removal efficiency = 54.2%), and TN (removal efficiency = 36.5%) from the feed water, while it was not efficient for the reduction of pH (removal efficiency = 10.3%) and conductivity (removal efficiency = 17.3%). Based on the low SUVA values (< 1), it was identified that the feed water DOM consisted mostly of HPI DOM fractions (Chon *et al.* 2013a), and significant SUVA value changes were not found after HUF membrane

Table 2 The changes in the water quality parameters through the pilot-scale SWTP using the HUF membranes ($n = 3$)

	Conditions	Feed water	HUF effluent
	pH	7.67 (± 0.01)	6.88 (± 0.02)
	Conductivity ($\mu\text{S cm}^{-1}$)	316.67 (± 1.17)	261.77 (± 1.34)
Bulk parameters	DOC (mgC L^{-1}) ^a	3.73 (± 0.12)	1.64 (± 0.04)
	UVA ₂₅₄ (cm^{-1})	0.024 (± 0.001)	0.011 (± 0.001)
	SUVA ($\text{L mg}^{-1} \text{m}^{-1}$)	0.64 (± 0.02)	0.67 (± 0.03)
	TN (mgN L^{-1}) ^a	1.67 (± 0.004)	1.06 (± 0.04)
Metals	Al ($\mu\text{g L}^{-1}$)	7.45 (± 1.00)	4.32 (± 0.95)
	Ca (mg L^{-1})	51.73 (± 1.70)	50.58 (± 1.63)
	Cu ($\mu\text{g L}^{-1}$)	2.92 (± 0.40)	2.67 (± 0.65)
	Fe ($\mu\text{g L}^{-1}$)	9.66 (± 0.22)	7.60 (± 0.29)
	Mg (mg L^{-1})	5.17 (± 0.31)	5.08 (± 0.53)
	Mn ($\mu\text{g L}^{-1}$)	0.34 (± 0.08)	0.19 (± 0.03)

^an = 2

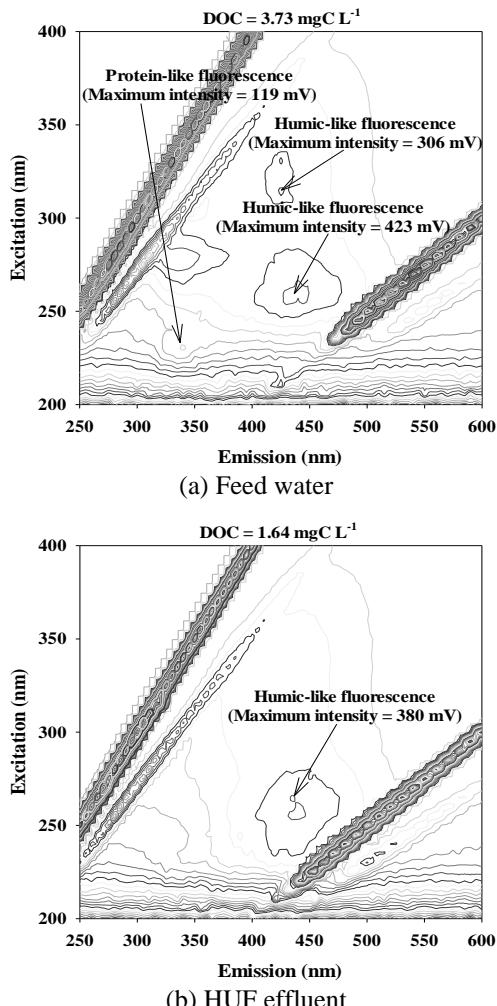


Fig. 2 3D FEEM for DOM in the feed water and HUF effluent through the pilot-scale SWTP using HUF membranes

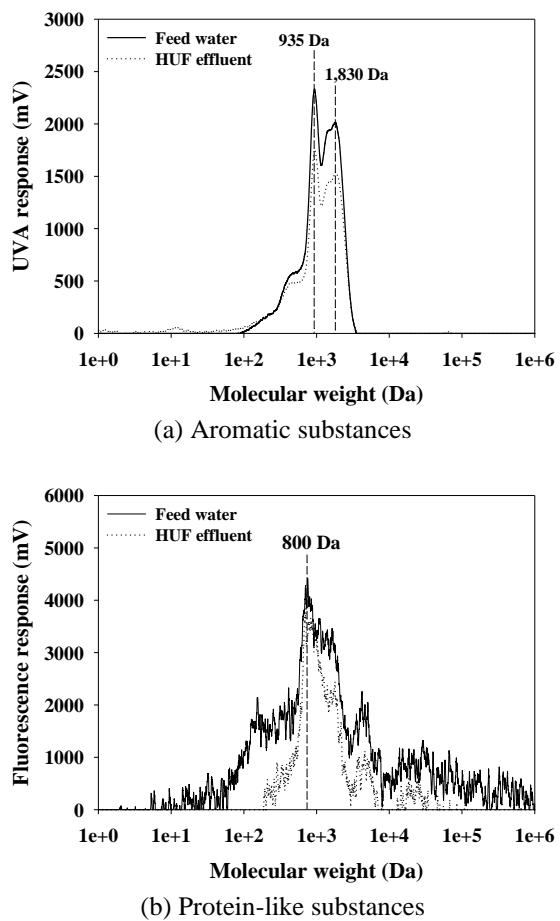


Fig. 3 MW distribution of DOM in the feed water and HUF effluent from the pilot-scale SWTP using HUF membranes

treatment. The HUF membranes were able to remove most metals from the feed water to a significant extent. These results support the conclusion that some of the multivalent metal complexes in the feed water HPO DOM fractions were possibly contributed to the formation of fouling layers on the HUF membrane surfaces (Lee *et al.* 2020).

3.2 DOM characteristics

Changes to the 3D FEEM of DOM in the feed and treated waters of the pilot-scale SWTP using HUF membranes are shown in Fig. 2. The two pairs of fluorescence peaks observed at $\text{Ex} = 260\text{--}320\text{ nm}$ and $\text{Em} = 400\text{--}460\text{ nm}$ represented humic-like substances, and fluorescence peaks at $\text{Ex} = 230\text{--}290\text{ nm}$ and $\text{Em} = 320\text{--}360\text{ nm}$ represented protein-like substances (Lee *et al.* 2020, Leenheer and Croué 2003). Maximum fluorescence peaks observed for the feed water were associated with the humic-like fluorophore (maximum intensity = 423 mV, at $\text{Ex} = 270\text{ nm} / \text{Em} = 440\text{ nm}$, and maximum intensity = 306 mV at $\text{Ex} = 320\text{ nm} / \text{Em} = 420\text{ nm}$), and the protein-like fluorophore (maximum intensity = 119 mV, at $\text{Ex} = 240\text{ nm} / \text{Em} = 340\text{ nm}$). The humic-like fluorophore was significantly reduced by the HUF membranes (maximum intensity = 380 mV at $\text{Ex} = 270\text{ nm} / \text{Em} = 440\text{ nm}$), and no

Table 3 Organic and inorganic constituents of HUF membrane foulants extracted using two different consecutive chemical cleaning protocols ($n = 3$)

Conditions	CP I (0.1 N HCl → 0.1 N NaOH)			CP II (0.1 N NaOH → 0.1 N HCl)		
	CP I - A	CP I - B	Sum	CP II - B	CP II - A	Sum
Bulk parameters	DOC (mgC m^{-2}) ^a	66.75 (± 2.69)	123.14 (± 10.18)	189.89	166.64 (± 4.37)	48.55 (± 0.20)
	UVA ₂₅₄ (cm^{-1})	0.016 (± 0.0004)	0.16 (± 0.001)		0.16 (± 0.001)	0.018 (± 0.001)
	SUVA ($\text{L mg}^{-1} \text{m}^{-1}$)	0.75	4.06		3.00	1.16
	TN (mgN m^{-2}) ^a	6.82 (± 0.22)	6.84 (± 0.89)	13.66	12.89 (± 1.12)	4.93 (± 0.60)
Metals	Al ($\mu\text{g m}^{-2}$)	917.95 (± 9.96)	921.07 (± 5.83)	1839.02	1739.10 (± 37.47)	396.53 (± 6.25)
	Ca (mg m^{-2})	6.85 (± 0.95)	N.D.	6.85	10.57 (± 0.81)	3.33 (± 0.46)
	Cu ($\mu\text{g m}^{-2}$)	21.86 (± 6.24)	21.85 (± 5.31)	43.71	28.10 (± 2.56)	34.34 (± 2.81)
	Fe ($\mu\text{g m}^{-2}$)	53.08 (± 2.81)	140.50 (± 6.25)	193.58	227.93 (± 7.56)	49.96 (± 4.68)
	Mg (mg m^{-2})	0.91 (± 0.28)	N.D.	0.91	7.71 (± 0.80)	0.81 (± 0.24)
	Mn ($\mu\text{g m}^{-2}$)	106.16 (± 5.62)	12.49 (± 2.49)	118.65	103.03 (± 3.12)	143.63 (± 9.91)
						246.66

^a n = 2, N.D. = Not detected

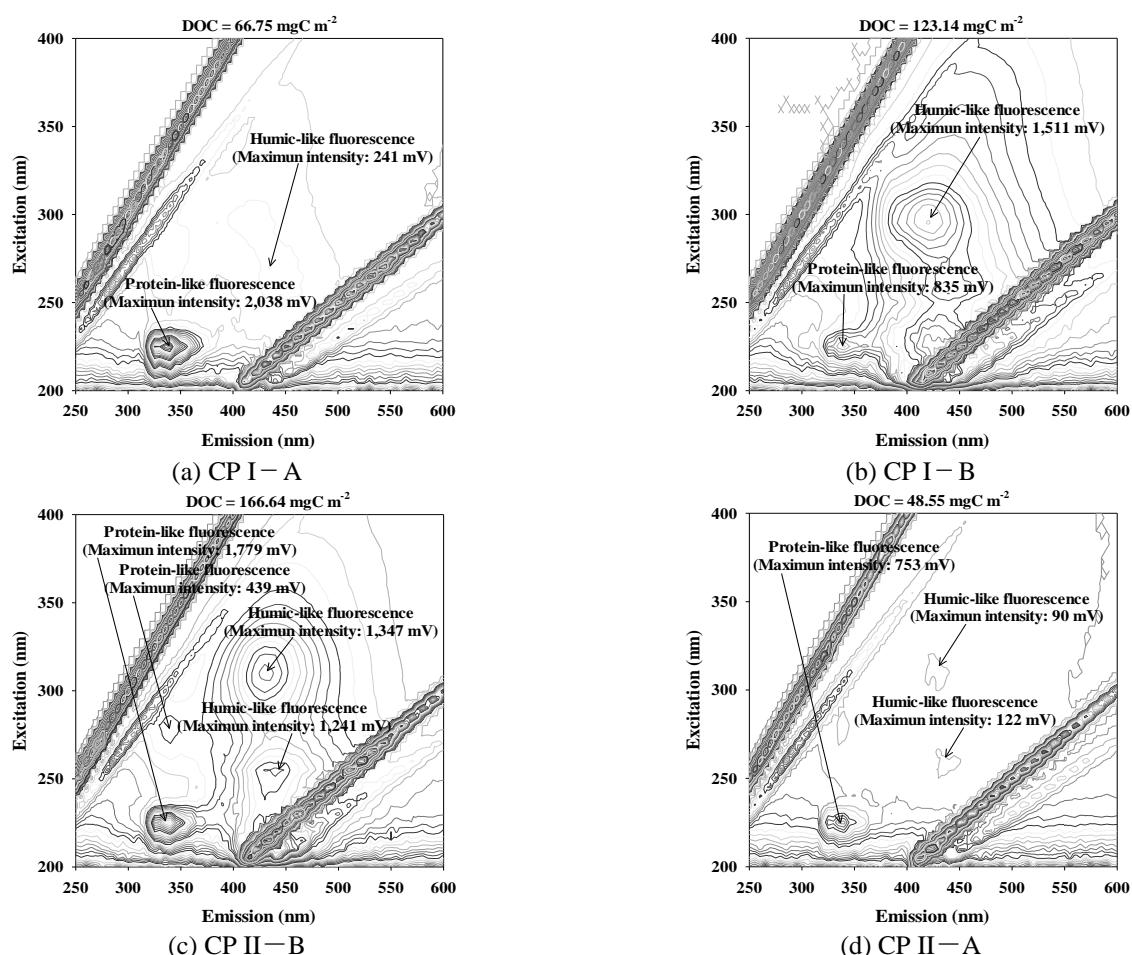


Fig. 4 Effects of the differences in the order of consecutive chemical cleaning protocols on the fluorescence properties of extracted HUF membrane foulants

remarkable protein-like fluorophore was found in the HUF effluent. These findings suggested that DOM differences between the feed water and HUF effluent samples were due to DOC removal by the HUF membranes in the pilot-scale SWTP.

The MW distribution for aromatic and protein-like substances of DOM in the feed water and HUF effluent samples from the pilot-scale SWTP is shown in Fig. 3. The aromatic substances were found to consist mainly of 935 daltons (Da) and 1,830 Da of low MW fractions, which were found to have decreased considerably after HUF membrane treatment. These results showed that the HUF membranes could effectively eliminate HPO DOM low MW fractions (i.e., humic-like substance) from the feed water (Zhou *et al.* 2017). The protein-like DOM in the feed water and HUF effluent samples consisted solely of the low MW fraction (800 Da), and the intensity of protein-like DOM in the feed water was slightly reduced by the HUF membranes. These results showed that aromatic and protein-like DOM could lead to fouling layer formation on membrane surfaces during operating the pilot-scale SWTP using the HUF membranes.

3.3 Quantitative and qualitative differences in extracted HUF membrane foulants using two different consecutive chemical cleaning protocols

3.3.1 Quantitative analysis of extracted HUF membrane foulants

The quantitative changes in the extracted HUF membrane foulants, such as DOC, TN, and metals, achieved using two different consecutive chemical cleaning protocols, are shown in Table 3. Irrespective of the chemical cleaning protocol sequence, the basic cleaning solution was more effective in extracting organic foulants from HUF membrane surfaces, in terms of DOC (CP I–B = 123.14 ± 10.18 mgC m⁻², CP II–B = 166.64 ± 4.37 mg C m⁻²; CP I–A = 66.75 ± 2.69 mg C m⁻², CP II–A = 48.55 ± 0.20 mgC m⁻²) and TN (CP I–B = 6.84 ± 0.89 mgN m⁻², CP II–B = 12.89 ± 1.12 mg N m⁻²; CP I–A = 6.82 ± 0.22 mg N m⁻², CP II–A = 4.93 ± 0.60 mg N m⁻²). Furthermore, the HUF membrane foulants extracted using the basic cleaning solution presented much higher SUVA values than those extracted using the acidic cleaning solution due to the preferential extraction of HPO DOM fractions (i.e., humic-like substance) from HUF membrane surfaces (Lee *et al.* 2001). The efficiency of metals extraction from the HUF membrane surfaces, including Al, Ca, Cu, Fe, Mg, and Mn, were strongly dependent on the type of chemical cleaning solution applied. These results showed that multivalent metals complexed with the HPO DOM fractions could contribute to the formation of irreversible fouling layers on HUF membrane surfaces (Chon *et al.* 2013b). Even though each chemical cleaning solution exhibited similar extraction trends for the HUF membrane foulants, the total foulant amount extracted using CP II (the sum of DOC = 215.19 mgC m⁻²; the sum of TN = 17.82 mg N m⁻²; the sum of metals = 25.14 mg m⁻²) was significantly more than that extracted using CP I (the sum of DOC = 189.89 mg C m⁻²; the sum of TN = 13.66 mg N m⁻²; the sum of

metals = 9.95 mg m⁻²). A possible explanation for these findings might be that CP II was more effective for extracting organic and inorganic foulants from the HUF membranes as the basic cleaning solution (i.e., 0.1 N NaOH) promoted DOM dissolution, which enhanced cleaning solution mass transfer to HUF membrane surfaces (Hao *et al.* 2011).

3.3.2 Qualitative analysis of extracted HUF membrane foulants

Differences in the fluorescence characteristics of HUF membrane foulants extracted using two different consecutive chemical cleaning protocols are shown in Fig. 4. Changes in the types of chemical cleaning solutions significantly influenced the extraction patterns of the organic foulants (humic-like substances and protein-like substances) from the HUF membrane surfaces. The basic cleaning solution effectively extracted both humic-like (CP I–B: the maximum intensity = 1,511 mV at Ex = 290 nm/Em = 420 nm; CP II–B: the maximum intensity = 1,347 mV at Ex = 310 nm/Em = 420 nm and maximum intensity = 1,241 mV at Ex = 260 nm/Em = 440 nm) and protein-like fluorophores (CP I–B: maximum intensity = 835 mV at Ex = 230 nm/Em = 340 nm; CP II–B: maximum intensity = 1,779 mV at Ex = 230 nm/Em = 340 nm and maximum intensity = 439 mV at Ex = 280 nm/Em = 340 nm). In contrast, the acidic cleaning solution was relatively efficient in detaching protein-like fluorophores (CP I–A: maximum intensity = 2,038 mV at Ex = 230 nm/Em = 340 nm; CP II–A: maximum intensity = 753 mV at Ex = 230 nm/Em = 340 nm) rather than the humic-like fluorophores (CP I–A: maximum intensity = 241 mV at Ex = 270 nm/Em = 420 nm; CP II–A: maximum intensity = 122 mV at Ex = 260 nm/Em = 430 nm and maximum intensity = 90 mV at Ex = 320 nm/Em = 420 nm) from membrane surfaces. Organic foulant extraction efficiencies were nevertheless improved when the extracted HUF membranes were cleaned using the basic solution as the first sample in the consecutive chemical cleaning protocols (the sum of DOC extraction from the HUF membrane foulants using CP II = 215.19 mg C m⁻² > the sum of DOC extraction from the HUF membrane foulants using CP I = 189.89 mg C m⁻²). These results implied that hydroxide ions (from 0.1 N NaOH) helped organic fouling layers to loosen which promoted acidic cleaning solution infiltration into the organic fouling layers (Ang *et al.* 2011).

Changes in the MW characteristics of the HUF membrane foulants extracted using two different consecutive chemical cleaning protocols are illustrated in Fig. 5. The aromatic substances of the extracted HUF membrane foulants were mainly composed of both the low MW (790–2,250 Da) and high MW (18,300 Da) fractions by the CP I and the low MW (770–2,130 Da) fractions by the CP II. Both CP I and CP II extracted aromatic substances with low MW related to humic-like substances (500–5,000 Da) efficiently from the HUF membrane surfaces (Her *et al.* 2007). However, the highest UVA response of the aromatic substances in the extracted HUF membrane foulants using CP II–B (UVA response at 1,210 Da = 33,650 mV) was much higher than

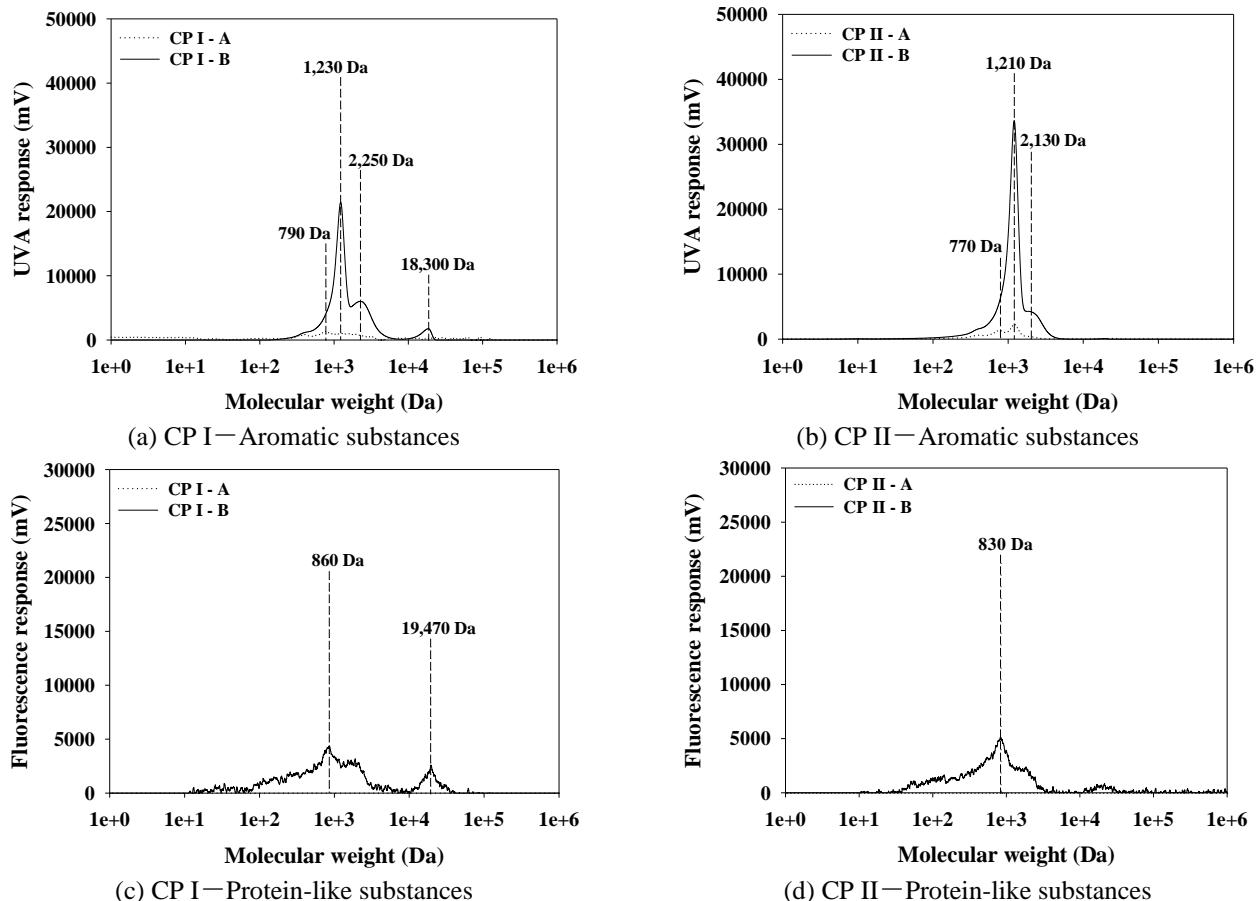


Fig. 5 Effects of differences in the order of the consecutive chemical cleaning protocols used on the MW distributions of the extracted HUF membrane foulants

Table 4 Differences in the EDX elemental analyses for the virgin, fouled, and cleaned HUF membranes using two different consecutive chemical cleaning protocols

Element	Atomic %				
	Virgin HUF	Fouled HUF	Cleaned HUF	Cleaned HUF	
			with CP I	with CP II	
HUF membrane	C	65.94	75.95	68.95	66.67
	F	34.06	24.05	31.05	33.33
	Totals	100	100	100	100

that of the CP I-B (UVA response at 1,230 Da = 21,420 mV). Concerning protein-like substances, the extracted HUF membrane foulants consisted primarily of low MW (the highest fluorescence response at 860 Da = 4,350 mV) and high MW (19,470 Da) fractions by CP I-B and the low MW (the highest fluorescence response at 830 Da = 5,120 mV) fractions by CP II-B. A distinctive fluorescence response was not found for the HUF membrane foulants extracted using either CP I-A or CP II-A. These observations indicated that the order of the consecutive chemical cleaning protocols could play a key role in extraction efficiencies for removing aromatic and protein-like substances from fouled HUF membranes (Aguiar *et al.* 2018).

3.4 Difference in surface morphologies of fouled and cleaned HUF membranes after using two different consecutive chemical cleaning protocols

The effect of changing the order of the chemical cleaning protocols on membrane surface morphologies are compared in Fig. 6. The surface of the virgin HUF membrane was relatively clean and homogeneous (Fig. 6 (a)), while precipitation of DOM and inorganic matter complexed with HPO DOM fractions (i.e., humic-like substances) induced pore size reduction on the surfaces of the fouled HUF membrane (Fig. 6 (b)) (Lee *et al.* 2020). These findings are in good agreement with the patterns of increasing transmembrane pressure (TMP) and decreasing permeate flux in the pilot-scale SWTP using the HUF membranes (Fig. 7). Both of the applied consecutive chemical cleaning protocols were able to remove organic and inorganic matter fouling layers from the membrane surfaces efficiently, leaving just a few inorganic precipitates to be seen on the cleaned HUF membrane surfaces (Fig. 6 (c) and 6 (d)). Although similar recovery patterns were found for the differences in the EDX elemental analysis of the fouled HUF membranes, after two different consecutive chemical cleaning protocols, the HUF membrane cleaned with CP II showed a relatively high percentage of F atom (related to the composite membrane components) compared with that cleaned using CP I (Table 4). These observations

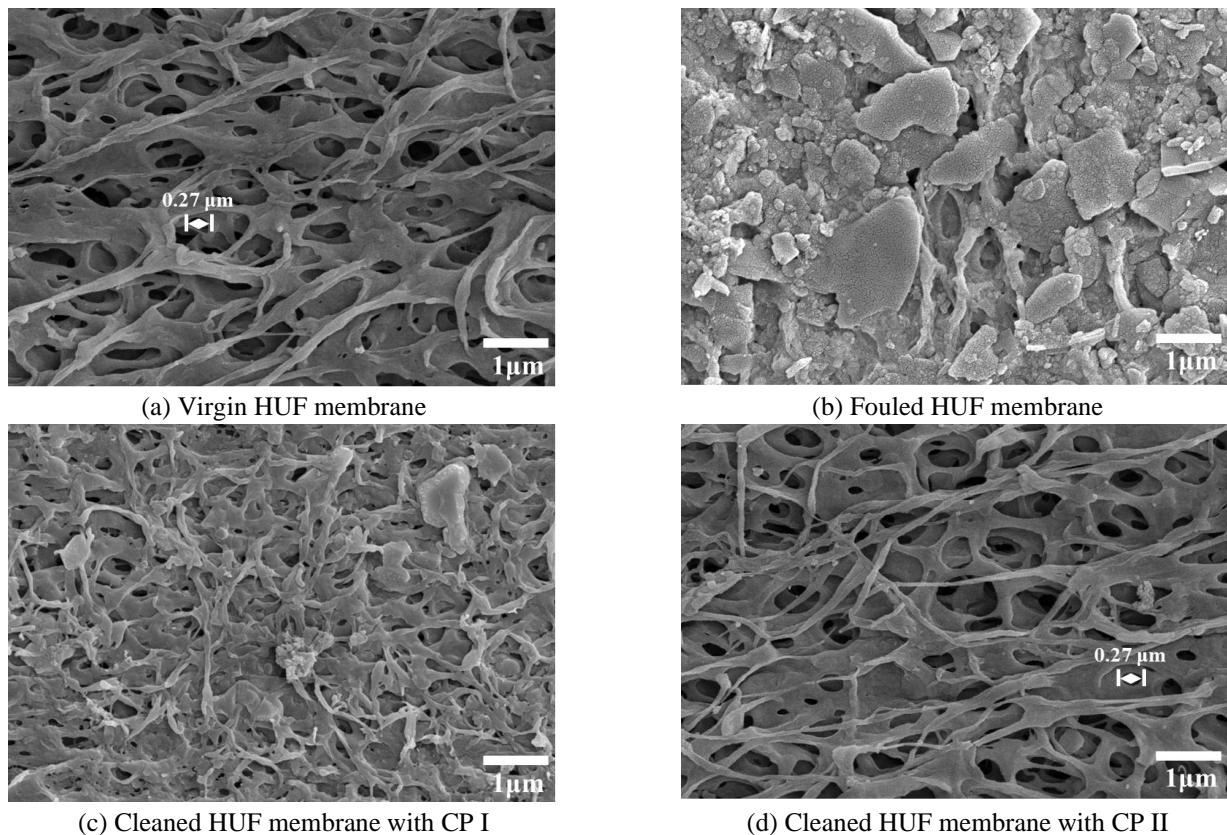


Fig. 6 The distinctions in the FE-SEM images of the virgin, fouled, and cleaned HUF membranes using two different consecutive chemical cleaning protocols

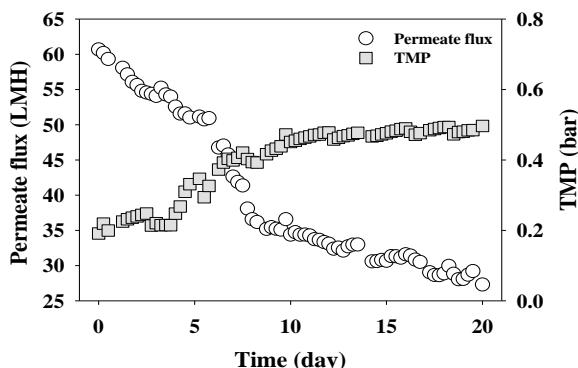


Fig. 7 TMP and permeate flux of the HUF membrane used in the pilot-scale SWTP

suggested that the order of the chemical cleaning protocols governed the extraction efficiency of organic and inorganic foulants from HUF membrane surfaces and might be facilitated the recovery of HUF membrane performance (i.e., transmembrane pressure and permeate flux) during the operation of the pilot-scale SWTP.

4. Conclusions

The properties of HUF membrane foulants extracted using two different consecutive chemical cleaning protocols (CP I: 0.1 N HCl → 0.1 N NaOH; CP II: 0.1 N NaOH → 0.1 N HCl), and the recovery of HUF membrane surface

characteristics, were examined through autopsies of fouled HUF membrane modules from a pilot-scale SWTP in Hongcheon-gun (Kangwon province, Republic of Korea). Extraction efficiencies for organic and inorganic foulants were quite different, depending on the type of chemical cleaning protocols used. The UF membrane foulants extracted using CP II (the sum of DOC = 215.19 mgC m⁻²; the sum of TN = 17.82 mg N m⁻²; the sum of metals = 25.14 mg m⁻²) comprised a higher concentration of organic and inorganic substances than those extracted using CP I (the sum of DOC = 189.89 mg C m⁻²; the sum of TN = 13.66 mg N m⁻²; the sum of metals = 9.95 mg m⁻²). These findings implied that hydroxide ions (found in the basic cleaning solution) loosened the fouling layers, facilitated infiltration by the subsequent acidic cleaning solution into the organic and inorganic membrane surface fouling layers. Although organic foulants based on humic-like and protein-like substances were effectively extracted from HUF membrane surfaces using both CP I and CP II, the surface compositional characteristics of the cleaned HUF membrane using CP II were relatively closer to the virgin membrane surface compared to those of the cleaned HUF membrane using CP I. These observations indicated that the sequential coupling of two different chemical cleaning solutions governed both extractions of the organic and inorganic foulants from the HUF membrane surfaces and restoration of membrane surface elementary composition potentially associated with HUF membrane performance during the pilot-scale SWTP operations.

Acknowledgments

This work was supported by Korea Environment Industry & Technology Institute (KEITI) through Aquatic Ecosystem Conservation Research Program, funded by Korea Ministry of Environment (MOE)(RE202001312).

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