



An autopsy study of hollow fiber and multibore ultrafiltration membranes from a pilot-scale ultra high-recovery filtration system for surface water treatment

Yong-Gu Lee^a, Jaegwan Shin^b, Seung Joon Kim^c, Kyung Hwa Cho^d, Paul Westerhoff^e,
Hojung Rho^{f,*}, Kangmin Chon^{a,b,**}

^a Department of Environmental Engineering, College of Art, Culture, and Engineering, Kangwon National University, 1 Kangwondaehak-gil, Chuncheon-si, Gangwon-do 24341, Republic of Korea

^b Department of Integrated Energy and Infrastem, Kangwon National University, Kangwondaehak-gil, 1, Chuncheon-si, Gangwon-do 24341, Republic of Korea

^c Technology Research Laboratory, Kolon Global Corporation, 11 Kolon-ro, Gwacheon-si, Gyeonggi-do 13837, Republic of Korea

^d School of Urban and Environmental Engineering, Ulsan National Institute of Science and Technology, Ulsan 44919, Republic of Korea

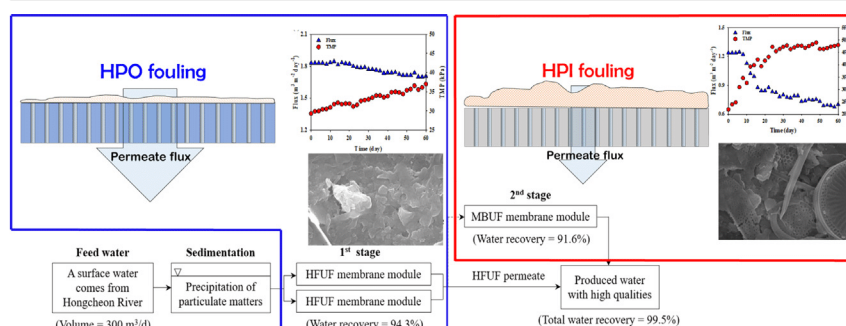
^e Nanosystems Engineering Research Center for Nanotechnology-enabled Water Treatment, School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, AZ 85287-5306, USA

^f Department of Environment Research, Korea Institute of Civil Engineering and Building Technology, 283 Goyang-Daero, Ilsanseo-Gu, Goyang-si, Gyeonggi-do 10223, Republic of Korea

HIGHLIGHTS

- A pilot-scale ultra high-recovery filtration system achieves $\geq 99.5\%$ total water recovery.
- HPO DOM predominantly contributes to formation of HFUF membrane fouling.
- HPI DOM primarily governs fouling mechanisms of MBUF membranes.
- Alkaline cleaning agents can be effective to recover performance of MBUF membranes.
- Membrane composite materials play a key role in fouling behaviors of UF membranes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Huu Hao Ngo

Keywords:

Dissolved organic matter
Hollow fiber ultrafiltration membranes
Membrane autopsy
Multibore ultrafiltration membranes
Pilot-scale ultra high-recovery membrane filtration system

ABSTRACT

The organic fouling characteristics of hollow fiber ultrafiltration (HFUF) and multibore ultrafiltration (MBUF) membranes from long-term ultrafiltration (UF) membrane systems were systemically investigated in this study. The objective was to obtain insights into the fouling behavior of dissolved organic matter (DOM) in a pilot-scale ultra-high-recovery membrane filtration system (p-UHMS) used for surface water treatment. The pilot system consisted of a series of two different UF membranes (1st stage: polyvinylidene fluoride (PVDF) HFUF and 2nd stage: polyethersulfone (PES) MBUF). It was designed to feed the HFUF concentrate to the MBUF membranes to achieve $\geq 99.5\%$ total water recovery for surface water treatment, as these advances might enhance the production efficiencies of drinking water. The experimental results confirmed that hydrophobic DOM controlled the formation of HFUF membrane organic fouling, whereas hydrophilic DOM, including polysaccharide-like and protein-like matter, promoted MBUF membrane fouling. These opposing trends were attributed to the hydrophilic characteristics of the MBUF membrane surfaces (contact angle: PVDF = $90\text{--}130^\circ$ and PES $\leq 80^\circ$), which reduced the hydrophobic interactions between the UF membrane surfaces and foulants. The performance declines of the MBUF membrane due to fouling layer formation was considerably severer than those of the HFUF membrane, decreasing total permeate water in the p-UHMS. Moreover, the quantity of the desorbed MBUF membrane foulants via 0.1 N NaOH was roughly 7.2 times larger than that of the desorbed HFUF

* Corresponding author.

** Correspondence to: K. Chon, Department of Environmental Engineering, College of Art, Culture, and Engineering, Kangwon National University, 1 Kangwondaehak-gil, Chuncheon-si, Gangwon-do 24341, Republic of Korea.

E-mail addresses: hrho@kict.re.kr (H. Rho), kchon@kangwon.ac.kr (K. Chon).

<http://dx.doi.org/10.1016/j.scitotenv.2022.161311>

Received 12 June 2022; Received in revised form 28 November 2022; Accepted 27 December 2022

Available online 2 January 2023

0048-9697/© 2023 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

membrane foulants through 0.1 N NaOH, indicating that alkaline-based cleaning agent could much more efficiently recover the performance of the fouled MBUF membranes. Hence, adequate cleaning strategies using alkaline-based agent for the MBUF membrane appeared to be essential for preventing the performance deterioration of the p-UHMS.

1. Introduction

The protection of surface water resources associated with drinking water production has become a major challenge worldwide, particularly in highly populated areas (e.g., cities). Owing to the reduced availability of freshwater further aggravated by climate change, drinking water production has gained significant attention recently (Chon et al., 2020; Delpla et al., 2009). Surface water contains various contaminants, including microorganisms, organic and inorganic matter, and particulate matter, which pose potential hazards to human health (Chigor et al., 2012). Therefore, coagulation/flocculation, disinfection, sedimentation, and sand filtration are widely used to prevent aesthetic problems (i.e., color, taste, and odor) and water-borne diseases in drinking water treatment plants (DWTPs) (Aboubaraka et al., 2017; Khan et al., 2013). However, meeting drinking water quality standards using conventional water treatment techniques has become increasingly challenging because of the discharge of various organic chemicals and heavy metals into water bodies (i.e., lakes and rivers). The problem is induced by rapid industrialization, urbanization, and population growth, which gradually deteriorate surface water quality, affect drinking water security, and increase the treatment costs of drinking water (Chon et al., 2012b; Cunha et al., 2016; Yoo et al., 2018).

Ultrafiltration (UF) membrane processes have been increasingly recognized as well-established techniques for surface water treatment because of the development of practical and economically feasible membrane composite materials and fabrication technologies (Tian et al., 2013). UF membranes have several advantages over conventional drinking water treatment processes because they can efficiently eliminate pathogenic microbes, viruses, colloidal matter, and particulate matter from surface water (Peter-Varbanets et al., 2009). However, UF membrane processes require a high-recovery water product using a series of UF membranes (e.g., 1st stage: polyvinylidene fluoride (PVDF) membranes, 2nd stage: polyethersulfone (PES) membranes) to minimize the environmental and economic impacts associated with the concentrates generated from the operations. Nevertheless, membrane fouling is a crucial concern, hindering the extensive usage of UF membranes for drinking water production (Laabs et al., 2006; Peiris et al., 2010). Based on the adhesive force between membrane surfaces and foulants, membrane fouling can be classified into two categories: (i) hydraulically reversible and (ii) hydraulically irreversible fouling (Chon and Cho, 2016). Hydraulically reversible fouling, which occurs when foulants are loosely bound to the membrane surfaces and may be readily removed by permeate back-flushing, reduces permeate fluxes. In contrast, hydraulically irreversible fouling, which occurs when foulants are strongly bound to the membranes and can be eliminated only via chemical cleaning, affects operating and management costs as well as membrane lifetime (Huang et al., 2007; Peiris et al., 2011; Peldszus et al., 2011; Raffin et al., 2011). Therefore, potential foulants and their fouling behaviors must be thoroughly identified to optimize back-flushing, pretreatment, and cleaning strategies to mitigate membrane fouling (Chon and Cho, 2016).

Dissolved organic matter (DOM) in surface water, including carbohydrates, humic substances, lipids, and proteins, along with particulates and biofilm growth, are the primary foulants during the treatment of surface water using UF membranes (Kimura et al., 2004; Tian et al., 2018). The fouling behaviors of DOM in membrane processes may be significantly affected by their physiochemical properties, including charge density (functional group composition), size (molecular weight), and structure (hydrophobicity and hydrophilicity) (Chon and Cho, 2016; Her et al., 2008). The diagnosis of fouled membranes from the pilot- and/or real-scale validations via autopsy methods of membranes can provide crucial information for the types of foulants and their fouling behaviors, which are associated with the variations in the quality of feed water and the

characteristics of DOM, depending on the pre-treatments and operational conditions (Chon and Cho, 2016; Chon et al., 2012a; Lee et al., 2020). Hence, it is necessary to characterize DOM thoroughly using various analytical techniques to improve our understanding of membrane fouling mechanisms (Chon et al., 2012a; Her et al., 2002). Therefore, many studies have investigated the relationship between the structural and functional properties of DOM and their fouling characteristics, even though rigorous characterization of DOM is expensive, labor-intensive, and time-consuming (Guigui et al., 2001; Leenheer and Croué, 2003; Tian et al., 2018). However, most of the previous studies have mainly focused on single-stage UF membrane processes with relatively low recovery rates (85–95 %) (Mierzwa et al., 2012; Reissmann and Uhl, 2006) and on short-term lab-scale recirculating UF membrane systems, which are not representative of pilot-scale and real-scale DWTPs (Chon and Cho, 2016; Mierzwa et al., 2012). Previous studies on surface water treatment have not reported the interactions between the surfaces of UF membranes and DOM in a pilot-scale ultra-high-recovery membrane filtration system (p-UHMS; recovery rate $\geq 99\%$) consisting of two types of UF membranes (1st stage: polyvinylidene fluoride (PVDF) and 2nd stage: polyethersulfone (PES)) in series. The limited studies have provided valuable insights into DOM autopsies of fouled UF membranes used in the pilot- and real-scale DWTPs, as pilot-and/or real-scale processes involve high operational costs and long-term operations (Chew et al., 2016; Yu et al., 2020).

The main objective of this study was to examine the fouling characteristics of hollow fiber ultrafiltration (HFUF) and multibore ultrafiltration (MBUF) membranes from a p-UHMS comprising of two serially connected UF membranes (1st stage: HFUF membranes; 2nd stage: MBUF membranes) during the treatment of surface waters. This system was designed to feed the MBUF membrane with the HFUF concentrate (i.e., MBUF feed) to achieve $\geq 99.5\%$ total water recovery. Properties of DOM in the collected water samples (i.d., feed and permeate) through two serially connected UF membranes, and the characteristics of foulants desorbed from the HFUF and MBUF membrane surfaces with three kinds of cleaning agents (i.e., 0.1 N sodium hydroxide (NaOH), 0.1 N hydrochloric acid (HCl), and deionized (DI) water) were thoroughly examined by numerous analytical manners. The correlations of the observed membrane fouling behaviors with the surface features and morphologies were confirmed by membrane autopsies. Thus, this study provides new insights into the foulants and fouling mechanisms associated with HFUF and MBUF membranes in p-UHMSs used for surface water treatment.

2. Materials and methods

2.1. Configuration of the pilot-scale ultra-high-recovery membrane filtration system

A p-UHMS for treating surface waters located at Hongcheon-gun (Kangwon province, Republic of Korea), consisting of sedimentation and HFUF and MBUF membrane processes, was operated for approximately 2 months (5th October 2017–5th December 2017) (Fig. 1). Feed water, collected from Hongcheon River near the p-UHMS, was passed through a reservoir to remove high-density particles (e.g., sand and gravel) and treated using a sedimentation process and five HFUF membrane modules (nominal pore size = $0.1\ \mu\text{m}$, effective surface area of each module = $70\ \text{m}^2$, and mean water recovery rate = 94.3% ; Cleanfil®-70R, Kolon Industries, Gyeonggi Province, Republic of Korea). The HFUF concentrate was further treated using a MBUF membrane module (nominal pore size = $0.02\ \mu\text{m}$, effective surface area of each module = $60\ \text{m}^2$, and mean water recovery rate = 91.6% ; dizzer® XL 0.9 MB 60 WR, Inge GmbH, Greifenberg, Germany) to increase the overall water recovery rate of the membrane filtration system to $\geq 99.5\%$ and decrease the turbidity to 79.4% .

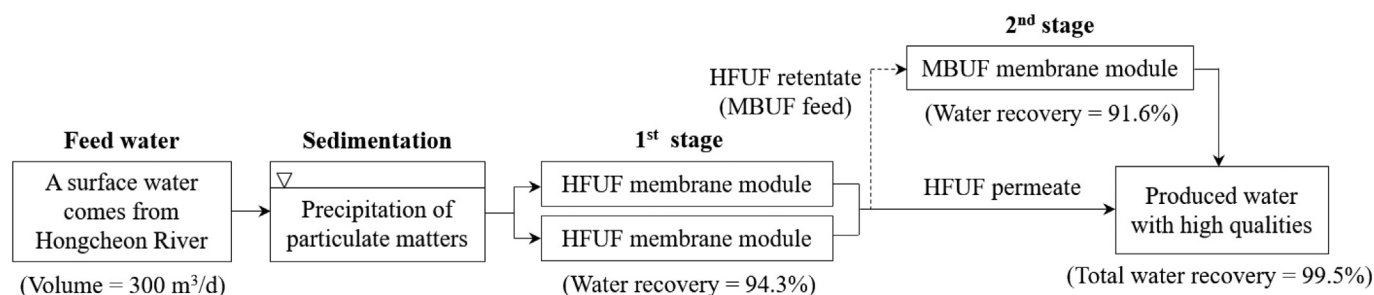


Fig. 1. The schematic diagram of the pilot-scale ultra high-recovery membrane filtration system (p-UHMS) consists of the sedimentation, HFUF and MBUF membranes for surface water treatment.

The characteristics of the two UF membrane types are summarized in Table 1. The MBUF membrane houses seven channels (diameter = 0.9 mm) in the polymer matrix, whereas the HFUF membrane has a single channel (diameter = 0.8 mm).

2.2. Preparation of samples

2.2.1. Water samples for DOM characterization

The water samples, including the HFUF feed (water from Hongcheon River after the sedimentation process), HFUF permeate (effluent from the HFUF process), MBUF feed (concentrate of the HFUF membrane), and MBUF permeate (effluent from the MBUF process), were collected from the p-UHMS to analyze the rejection behaviors of organic and inorganic matter. The collected water samples were pre-treated with glass fiber filters (GF/F; nominal pore size = 0.7 μm ; Whatman, Clifton, NJ, USA) and refrigerated (4 $^{\circ}\text{C}$) until further analysis to evaluate the elimination of organic, inorganic, and ionic substances and the change in DOM characteristics.

2.2.2. Extraction of the foulant from UF membranes

The foulants were desorbed from the fouled HFUF and MBUF membranes using DI water, 0.1 N HCl (acidic), and 0.1 N NaOH (alkaline). The alkaline cleaning agent generally promotes detachment of membrane foulants such as weakly acidic organic matter (e.g., carboxylic and phenolic functional groups), proteins, and polysaccharides. The acidic cleaning agent was used to desorb polyvalent metal species (e.g., salts and metal hydroxides) from fouled membrane surfaces (Porcelli and Judd, 2010). Fifty-five fouled HFUF membrane coupons (the surface area of coupons: 0.0207 m^2) and seven fouled MBUF membrane coupons (the surface area of coupons: 0.0207 m^2) were moderately stirred in 500 mL of each cleaning agent for 6 h at room temperature to desorb the foulants according to their physicochemical properties. The foulants desorbed from the HFUF and MBUF membrane surfaces using DI water, acidic, and alkaline cleaning agents were indicated as HFUF-DI and MBUF-DI, HFUF-A and MBUF-A, and HFUF-B and MBUF-B, respectively. Prior to the analysis, the pH of the desorbed foulant samples from the HFUF and MBUF membranes was

adjusted between 5.5 and 6.5 using NaOH or HCl solutions, and the samples were pre-treated via GF/F and stored at 4 $^{\circ}\text{C}$.

2.2.3. HFUF and MBUF membranes

The virgin HFUF and MBUF membranes were washed multiple times with DI water and immersed in DI water for 48 h to eliminate coating materials on the membrane surfaces. The rinsed virgin, fouled, and cleaned (i.e., after extraction of membrane foulants via DI water (cleaned HFUF-DI and cleaned MBUF-DI), acid-based cleaning agent (cleaned HFUF-A and cleaned MBUF-A), and alkaline-based cleaning agent (cleaned HFUF-B and cleaned MBUF-B)) were placed to the dry condition in a sealed desiccator for 72 h. Their morphological features and elemental compositions were investigated to establish the change in the fouling behaviors of the p-UHMS used for treating surface water.

2.2.4. Physicochemical analyses

The amounts of dissolved organic carbon (DOC) and total nitrogen (TN) were determined with a Shimadzu total organic carbon/TN analyzer (TOC-V_{CPH}/TNM-1, Kyoto, Japan). The aromatic constituents of DOM and desorbed membrane foulants were quantified using a Shimadzu ultraviolet-visible (UV-vis) spectrophotometer (UV-1280, Kyoto, Japan) at a 254 nm wavelength (UVA₂₅₄), and the specific ultraviolet absorbance (SUVA) values were estimated as the ratio of UVA₂₅₄ to DOC $\times 100$ (L/mg-m) (Chon et al., 2012b). Perkin Elmer inductively coupled plasma-mass spectrometry (NexION, MA, USA) and Dionex ion chromatography (ICS-5000, CA, USA) were used to quantify inorganic materials in the collected water and foulant samples. High-performance size-exclusion chromatography (HPSEC) coupled to a Protein-Pak 125 column (Waters, MA, USA), Shimadzu UVA/fluorescence detectors (SPD-10AVP/RF-10AXL, Kyoto, Japan) and Shimadzu fluorescence spectroscopy (RF-6000, Kyoto, Japan) were used to examine the molecular weight (MW) distribution and 3-dimensional excitation-emission matrix (EEM) fluorescence spectroscopy of DOM and desorbed HFUF and MBUF membrane foulants, respectively (Rho et al., 2019). The functional groups of the HFUF and MBUF membrane foulants desorbed were analyzed by Perkin Elmer fourier transform infrared (FTIR) spectroscopy (Frontier, MA, USA), coupled with a ZnSe attenuated total reflection optical crystal (Chon et al., 2013). Hitachi field-emission scanning electron microscopy (FE-SEM; S-4300, Tokyo, Japan), equipped with a Horiba energy-dispersive X-ray (EDX) spectroscopy (7200-H, Kyoto, Japan), was employed to investigate the surface morphological characteristics and elemental composition of the virgin, fouled, and cleaned HFUF and MBUF membranes. The relative hydrophobicity/hydrophilicity of the desorbed foulants from HFUF and MBUF membranes was examined via a resin fractionation technique using Amberlite XAD-4 and Supelrite DAX-8 resins (Supelco, PA, USA).

Table 1

The physicochemical features of the HFUF and MBUF membranes.

	HFUF	MBUF
Manufacturer	Kolon Industries	Inge GmbH
Membrane code	Cleanfil®-P70R	Dizzer® XL
Composite material	Polyvinylidene fluoride	Polyethersulfone
Outer diameter (mm)	2.0	4.0
Inner diameter (mm)	0.8	0.9
Nominal pore size (μm)	0.1	0.02
Effective surface area of each module (m^2)	70	60
Tensile strength (kg/fiber)	>25	N.A.

N.A.: not available.

3. Results and discussion

3.1. Water quality parameters

The characteristics of water quality of the feed and treated surface water samples were monitored during the 60-days of the p-UHMS operation to

assess their impacts on the fouling characteristics of the HFUF and MBUF membranes used to treat surface water (Table 2). Although the HFUF and MBUF membranes did not effectively reduce the conductivity of the water (HFUF = 4.4 % and MBUF = 3.3 %), they could sufficiently eliminate the turbidity from the HFUF and MBUF feed with removal efficiencies of 76.7 % and 98.3 %, respectively. The DOC and TN concentrations in the HFUF feed downstream of the HFUF membranes did not change significantly, with removal efficiencies of 8.3 % and 6.7 %, respectively, whereas approximately 28.6 % of DOC and 13.3 % of TN in the MBUF feed were removed through the MBUF membranes. These findings imply that the differences between the nominal pore sizes of the HFUF (0.1 μm) and MBUF (0.02 μm) membranes affected the removal efficiencies of bulk water contaminants (i.e., DOC and TN) (Nguyen et al., 2009). Despite the low reduction of DOC concentrations in HFUF feed water, the SUVA value of the HFUF membranes (removal efficiency of SUVA = 18.2 %) decreased to a greater extent than that of the MBUF membranes (removal efficiency of SUVA = 13.3 %). The preferential elimination of hydrophobic (HPO) DOM constituents through the HFUF membranes indicated that humic-like components could more readily foul the HFUF membrane surfaces than the MBUF membrane surfaces because of their relative hydrophobicity (contact angle = 115° (PVDF) > 59° (PES)) (Gray et al., 2007). Most of the inorganic matter were not efficiently removed by the HFUF and MBUF membranes due to their inherent pore sizes (HFUF = 0.1 μm and MBUF = 0.02 μm). However, the concentrations of some polyvalent metal species (i.e., Zn, Fe, Ca, and Mg) decreased, and they could form complexes with high-MW DOM, acting as potential fouling layers in polymeric membranes used in water treatment utilities (Chon and Cho, 2016; Chon et al., 2012a).

3.2. DOM characteristics

Although only approximately 10 % of the DOC was removed across the UF systems, similar to the changes in SUVA, large changes in DOM fluorescence were observed. Fig. 2 shows that two pairs of fluorescent chromophores detected in the HFUF feed were related to protein-like fluorophore (PLF) (maximum response = 226 mV and Ex/Em = 280 nm/340 nm) and humic-like fluorophore (HLF) (maximum response = 375 mV and Ex/Em = 260 nm/430 nm) (Peldszus et al., 2011). Downstream of the HFUF membranes, the PLF disappeared completely, and the intensity of the HLF (maximum response = 302 mV, Ex/Em = 260 nm/440 nm) significantly decreased. Similar but more pronounced patterns were observed for the removal of DOM via MBUF membranes. The MBUF feed also had two pairs of fluorescence peaks at Ex/Em = 230 nm/330 nm (PLF, maximum

response = 237 mV) and Ex/Em = 270 nm/440 nm (HLF, maximum response = 394 mV), whereas the MBUF permeate presented a comparatively weak peak indicative of the HLF at Ex/Em = 260 nm/430 nm (maximum response = 289 mV). These results agree with the removal of DOC from the p-UHMS used to treat surface water. Compared to the HFUF membranes, because the MBUF membranes enhanced the removal of DOM associated with the formation of organic fouling layers on their surfaces, the MBUF membranes showed a more significant decrease in flux than the HFUF membranes during the 60-day operation of the p-UHMS (Huang et al., 2000) (see Section 3.5).

The differences in the MW distribution of DOM (i.e., aromatic and protein-like components) in the HFUF feed, HFUF permeate, MBUF feed, and MBUF permeate via the p-UHMS are presented in Fig. 3. The aromatic components of DOM in the HFUF feed predominantly consisted of low-MW fractions (960 and 1870 Da), with a maximum UVA response (2178 mV) for 960 Da, and its size-exclusion chromatogram with UVA detection almost overlapped with that of DOM in the MBUF feed (major MW fractions: 960 Da and 1870 Da). However, an insignificant reduction was found in the UVA response of DOM in the HFUF permeate (UVA response at 960 Da = 2132 mV and at 1870 Da = 1966 mV), whereas the UVA response of low-MW aromatic components in the HFUF feed decreased considerably after treatment with the MBUF membranes (UVA response at 960 Da = 1724 mV and at 1870 Da = 1519 mV). The protein-like components of DOM in the HFUF and MBUF feeds also contained low MW fractions in the range of 780 Da (fluorescence response of HFUF feed = 5826 mV, fluorescence response of MBUF feed = 5163 mV) and 1420 Da (fluorescence response of HFUF feed = 3148 mV, fluorescence response of MBUF feed = 3139 mV), and their fluorescence responses slightly decreased for the HFUF (fluorescence response at 780 Da = 4541 mV, fluorescence response at 1420 Da = 3064 mV) or MBUF membranes (fluorescence response at 780 Da = 3742 mV, fluorescence response at 1420 Da = 2803 mV). The greater reduction in the UVA and fluorescence responses of DOM in the MBUF permeate than that in the HFUF permeate indicates that sieving effects were responsible for the removal of aromatic and protein-like DOM components in the tested p-UHMS (nominal pore size: MBUF (0.02 μm) > HFUF (0.1 μm)) (Nguyen et al., 2009).

3.3. Characterization of desorbed UF membrane foulants

3.3.1. Organic and inorganic constituents of the desorbed HFUF and MBUF membrane foulants

The bulk parameters of the desorbed HFUF and MBUF membrane foulants via three kinds of cleaning agents are listed in Table 3. The fouling deposits on the HFUF and MBUF membrane surfaces were more efficiently extracted using the alkaline cleaning agent (i.e., 0.1 N NaOH, DOC: HFUF-B = 76.5 mg C/m², MBUF-B = 552.4 mg C/m²) than DI water (DOC: HFUF-DI = 29.0 mg C/m², MBUF-B = 38.5 mg C/m²), and the acid-based cleaning agent (i.e., 0.1 N HCl, DOC: HFUF-A = 41.5 mg C/m², MBUF-A = 46.0 mg C/m²). Surprisingly, the desorbed MBUF membrane organic foulant with an alkaline-based cleaning agent was nearly 7.2 times higher than that of the HFUF membrane organic foulant. Based on the fact that HFUF membrane surfaces have a relatively HPO character compared to MBUF membrane surfaces, these findings imply that relatively HPI DOM played a significant role in MBUF membrane organic fouling layer formation. Since the total quantities of the DOC from the desorbed HFUF and MBUF membrane foulants with acid- and alkaline-based cleaning agents (DOC proportion: HFUF-A = 28.2 %, HFUF-B = 52.0 %, MBUF-A = 7.2 %, MBUF-B = 86.7 %) was much larger than those of the desorbed foulants from HFUF and MBUF membranes via DI water (DOC proportion: HFUF-DI = 19.7 %, MBUF-DI = 6.0 %), it may be concluded that irreversible fouling mainly controlled the formation of HFUF and MBUF membrane organic fouling layers in the surface water treatment processes (Peldszus et al., 2011). Moreover, similar to the reduction of the SUVA values by the HFUF (removal efficiency of SUVA = 18.2 %) and MBUF membranes (removal efficiency of SUVA = 13.3 %), the desorbed MBUF membrane

Table 2

The bulk water parameters of the collected water samples from the p-UHMS for surface water treatment (n = 6).

	HFUF feed	HFUF permeate	MBUF feed	MBUF permeate
pH	7.2 (± 0.2)	7.3 (± 0.04)	7.3 (± 0.01)	7.3 (± 0.01)
Conductivity ($\mu\text{S}/\text{cm}$)	275.7 (± 0.4)	263.3 (± 0.3)	276.2 (± 0.3)	267.2 (± 0.2)
Turbidity (NTU)	0.3 (± 0.2)	0.07 (± 0.01)	4.1 (± 1.7)	0.07 (± 0.01)
DOC (mgC/L)	1.6 (± 0.1)	1.5 (± 0.07)	2.1 (± 0.05)	1.5 (± 0.03)
UVA ₂₅₄ (cm ⁻¹)	0.04 (± 0.007)	0.03 (± 0.002)	0.03 (± 0.003)	0.02 (± 0.002)
SUVA (L/mg·m)	2.2 (± 0.04)	1.8 (± 0.03)	1.5 (± 0.02)	1.3 (± 0.02)
TN (mgN/L)	1.5 (± 0.1)	1.4 (± 0.1)	1.5 (± 0.05)	1.3 (± 0.01)
Al ($\mu\text{g}/\text{L}$)	5.1 (± 0.6)	5.0 (± 0.3)	5.4 (± 0.4)	4.9 (± 0.6)
Ca (mg/L)	49.3 (± 2.0)	48.7 (± 2.9)	50.7 (± 2.2)	49.8 (± 3.1)
Cu ($\mu\text{g}/\text{L}$)	1.8 (± 0.4)	1.3 (± 0.1)	2.6 (± 0.1)	2.1 (± 0.4)
Fe ($\mu\text{g}/\text{L}$)	8.7 (± 0.8)	6.9 (± 0.4)	12.3 (± 1.4)	8.5 (± 0.4)
Mg (mg/L)	5.1 (± 0.3)	5.0 (± 0.4)	5.1 (± 0.2)	5.0 (± 0.2)
Mn ($\mu\text{g}/\text{L}$)	0.4 (± 0.06)	0.3 (± 0.04)	0.6 (± 0.07)	0.5 (± 0.05)
Ni ($\mu\text{g}/\text{L}$)	0.7 (± 0.1)	0.6 (± 0.06)	0.6 (± 0.07)	0.5 (± 0.04)
Pb ($\mu\text{g}/\text{L}$)	0.1 (± 0.04)	0.0 (± 0.004)	0.0 (± 0.001)	0.0 (± 0.003)
Zn ($\mu\text{g}/\text{L}$)	33.2 (± 0.4)	6.1 (± 0.7)	16.8 (± 0.8)	9.0 (± 0.2)

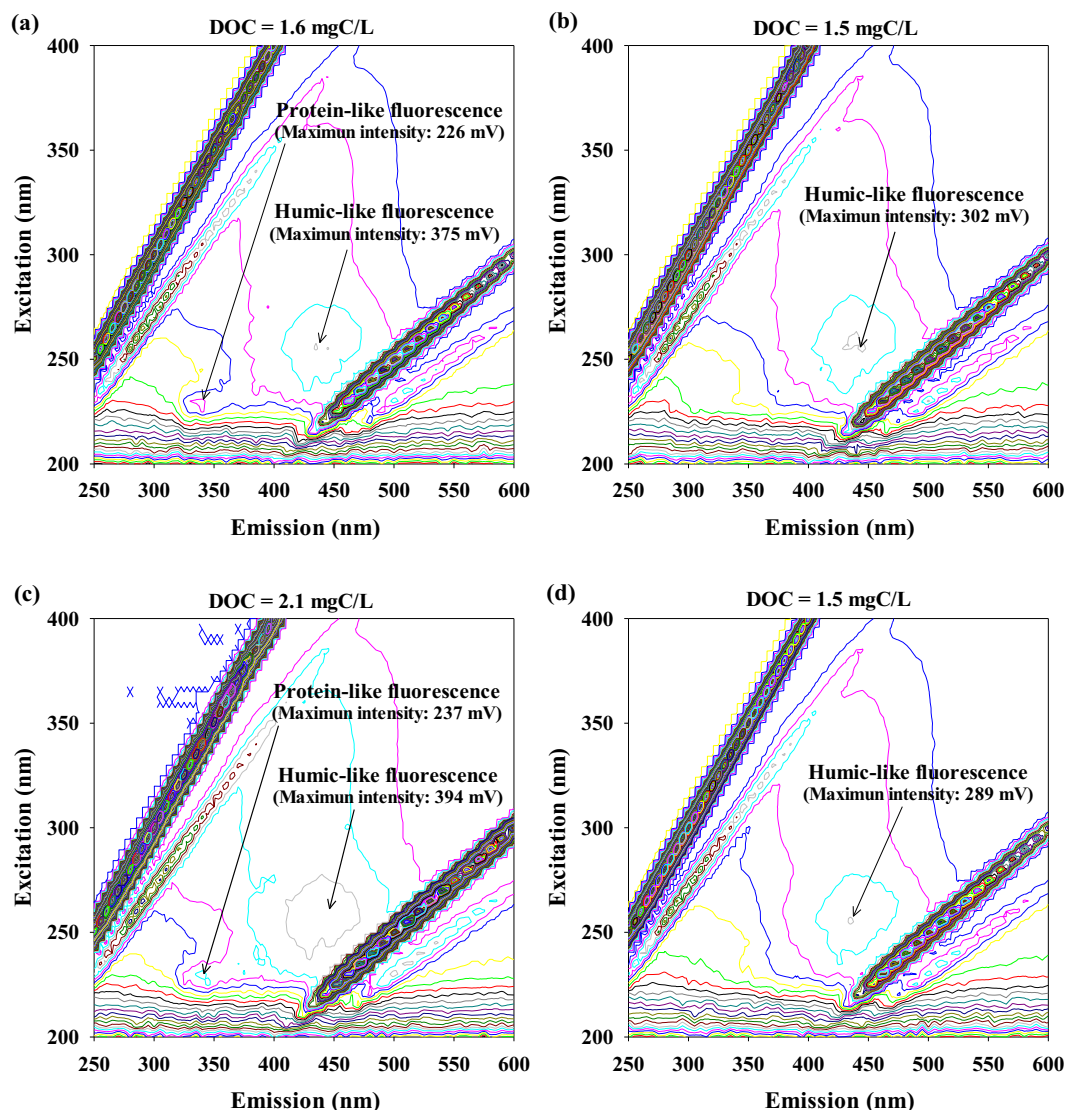


Fig. 2. The 3D FEEM of DOM in the collected water samples: (a) HFUF feed, (b) HFUF permeate, (c) MBUF feed, and (d) MBUF permeate.

foulants showed slightly lower SUVA values ($0.8\text{--}2.0\text{ L mg}^{-1}\text{ m}^{-1}$) compared to the desorbed HFUF membrane foulants ($0.9\text{--}2.2\text{ L mg}^{-1}\text{ m}^{-1}$). These results also imply that the relatively HPI DOM components contributed to the formation of organic fouling layers on the MBUF membrane surfaces due to less HPO-HPO interactions.

The inorganic matter in the foulants desorbed from the desorbed HFUF and MBUF membranes using the three types of cleaning agents are listed in Table 3. Polyvalent metal species, including Ca (molar ratio of the HFUF feed and membrane foulant = 1:0.01 and molar ratio of the MBUF feed and membrane foulant = 1:0.07), Fe (the molar ratio of the HFUF feed and HFUF membrane foulant = 1:8.6; the molar ratio of the MBUF feed and MBUF membrane foulant = 1:44.4), Mg (the molar ratio of the HFUF feed and HFUF membrane foulant = 1:0.05; the molar ratio of the MBUF feed and MBUF membrane foulant = 1:0.5), and Zn (the molar ratio of the HFUF feed and HFUF membrane foulant = 1:2.6; the molar ratio of the MBUF feed and MBUF membrane foulant = 1:16.9), were found to be the most abundant inorganic matter in the foulants desorbed from the HFUF and MBUF membranes. This clearly shows that the MW of the metal-DOM complexes significantly increased the inorganic fouling layers on the HFUF and MBUF membrane surfaces (Chon and Cho, 2016). The quantity of desorbed inorganic matter from the HFUF and MBUF membrane fouling layers was in the order HFUF-B > HFUF-A > HFUF-DI and MBUF-B > MBUF-A > MBUF-DI. This finding confirmed that most of the inorganic

matter deposited on the HFUF and MBUF membrane surfaces were inorganic colloids bound to DOM (Howe and Clark, 2002). The elemental composition of the virgin, fouled, and cleaned HFUF and MBUF membrane surfaces was investigated by EDX spectroscopy (Table 4). The C, O, and F or S contents in association with the composite materials were primarily found for the virgin HFUF (C = 55.0 %, O = 7.4 %, F = 36.3 %, Pt = 1.3 %) and MBUF (C = 75.6 %, O = 12.2 %, S = 11.5 %, Pt = 0.7 %) membrane surfaces. For the fouled HFUF and MBUF membranes, the O contents in relation to DOM (O of fouled HFUF = 62.1 %; O of fouled MBUF = 60.9 %) were much greater than the C and F or S contents, and a few inorganic materials, including Al, Ca, Cu, Fe, Mg, Mn, Ni, Pb, and Zn, might be newly detected because of the metal-DOM complexes adsorption on the HFUF and MBUF membrane surfaces (Lee et al., 2020). As expected, the reduction rates of the O contents were directly proportional to the decreases of inorganic contents in the cleaned HFUF and MBUF membrane surfaces, which support the assumption that organic and inorganic fouling occurred simultaneously in the UF membrane processes during the treatment of surface waters (Chon and Cho, 2016; Howe and Clark, 2002).

3.3.2. Characteristics of fluorescence spectra and MW on the desorbed HFUF and MBUF membrane foulants

The fluorescence properties of the desorbed foulants from HFUF and MBUF membranes in the p-UHMS, using 0.1 N NaOH, 0.1 N HCl, and DI

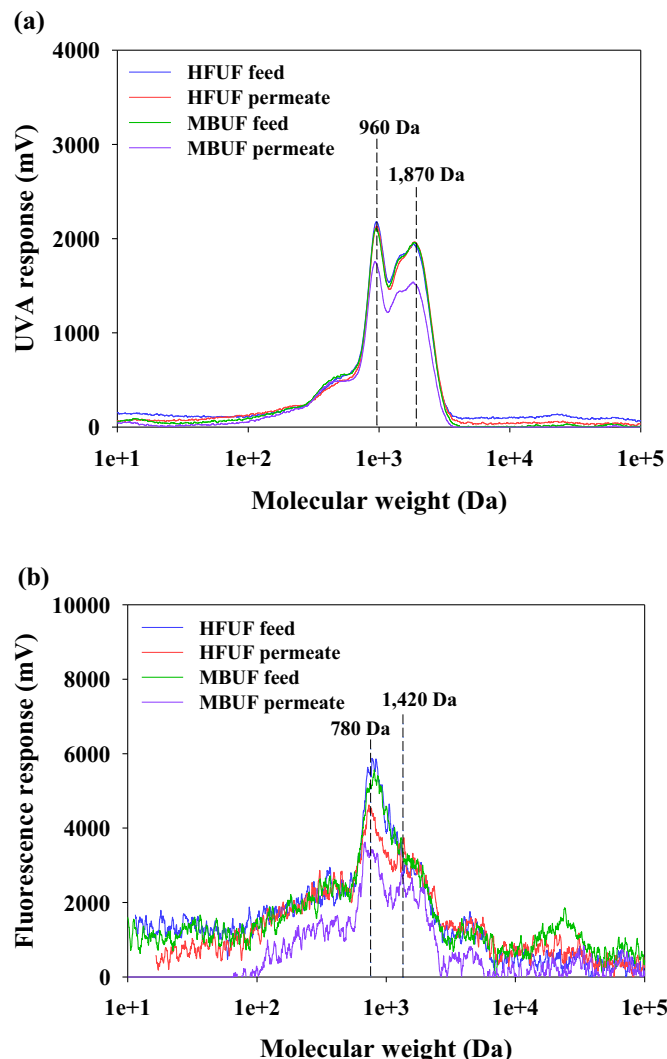


Fig. 3. The DOM MW distribution in the collected water samples: (a) aromatic components and (b) protein-like components.

water, are presented in Table 5. The desorbed foulants from the HFUF membranes (DOC: HFUF-DI = 28.5 mg C/m², HFUF-A = 42.7 mg C/m², and HFUF-B = 72.3 mg C/m²) showed two pairs of fluorophores at Ex/Em = 310–330 nm/410–440 nm (HLF) and 210–220 nm/325–340 nm (PLF). In contrast, three different fluorophores were detected in the desorbed MBUF membrane foulants (DOC: MBUF-DI = 41.8 mg C/m², MBUF-A = 47.1 mg C/m², and MBUF-B = 525.0 mg C/m²) at Ex/Em =

Table 4

The elemental composition of the virgin, fouled, and cleaned HFUF and MBUF membrane surfaces.

	Element	Atomic %				
		Virgin HFUF	Fouled HFUF	Cleaned HFUF-DI	Cleaned HFUF-A	Cleaned HFUF-B
HFUF membrane	C	55.0	29.2	35.2	43.5	49.4
	O	7.4	62.1	54.1	37.9	17.2
	F	36.3	2.0	6.2	15.2	32.4
	N	N.D.	N.D.	N.D.	N.D.	N.D.
	Al	N.D.	1.8	1.1	0.7	0.2
	Ca	N.D.	0.3	0.2	0.1	0.02
	Cu	N.D.	0.3	0.2	0.2	0.05
	Fe	N.D.	2.1	1.5	1.2	0.01
	Mg	N.D.	1.0	0.5	0.3	0.07
	Mn	N.D.	0.1	0.08	0.02	0.01
	Ni	N.D.	0.03	0.03	0.02	0.01
	Pb	N.D.	0.02	0.02	0.01	0.01
	Pt	1.3	0.8	0.7	0.8	0.8
	Zn	N.D.	0.3	0.2	0.1	0.1
	Element	Atomic %				
		Virgin MBUF	Fouled MBUF	Cleaned MBUF-DI	Cleaned MBUF-A	Cleaned MBUF-B
MBUF membrane	C	75.6	23.0	36.2	57.8	65.1
	O	12.2	60.9	47.0	30.3	23.9
	S	11.5	0.2	4.9	7.5	8.6
	N	N.D.	N.D.	N.D.	N.D.	N.D.
	Al	N.D.	2.5	1.6	0.8	0.3
	Ca	N.D.	0.6	0.2	0.1	0.05
	Cu	N.D.	0.2	0.1	0.07	0.06
	Fe	N.D.	10.1	8.6	2.3	1.0
	Mg	N.D.	1.2	0.5	0.3	0.1
	Mn	N.D.	0.4	0.3	0.2	0.1
	Ni	N.D.	0.1	0.04	0.02	0.01
	Pb	N.D.	0.02	0.01	0.01	0.01
	Pt	0.7	0.5	0.4	0.5	0.6
	Zn	N.D.	0.3	0.2	0.1	0.08

N.D. = not detected.

315–330 nm/410–440 nm (HLF), 225–255 nm/320–345 nm (PLF), and 275–280 nm/315–320 nm (PLF) (Chon et al., 2013). Furthermore, the maximum intensities of the HLF (162–2275 mV) and PLF (399–1899 mV) in the desorbed foulants from the MBUF membranes were considerably greater than those in the desorbed foulants from the HFUF membranes (the maximum intensity of HLF = 64–338 mV, the maximum intensity of PLF = 176–375 mV). These findings demonstrate that DOM fractions, such as humic-like and protein-like components, principal contributing factors to the formation of HFUF and MBUF membrane organic fouling layers, and their contributions were further noticeable to the MBUF membranes compared to the HFUF membranes because of the relative abundances of DOM in the MBUF feed (DOC of HFUF = 1.6 mg C/L, DOC of MBUF = 2.1 mg C/L).

Table 3

The organic and inorganic materials of the desorbed HFUF and MBUF membrane foulants in the p-UHMS for surface water treatment (n = 3).

Conditions	HFUF-DI	HFUF-A	HFUF-B	MBUF-DI	MBUF-A	MBUF-B
DOC (mg C/m ²)	29.0 (±0.6)	41.5 (±0.6)	76.5 (±1.2)	38.5 (±1.2)	46.0 (±0.7)	552.4 (±1.6)
UVA ₂₅₄ (cm ⁻¹)	0.009 (±0.001)	0.02 (±0.001)	0.05 (±0.001)	0.01 (±0.001)	0.02 (±0.001)	0.45 (±0.001)
SUVA (L/mg·m)	0.9 (±0.006)	1.1 (±0.005)	2.2 (±0.001)	0.8 (±0.001)	0.9 (±0.001)	2.0 (±0.002)
TN (mgN/m)	3.7 (±0.1)	7.6 (±0.2)	9.8 (±0.3)	76.9 (±0.1)	75.1 (±0.6)	106.7 (±0.7)
DOC fraction (%)	19.7	28.2	52.0	6.0	7.2	86.7
Al (μg/m ²)	6.9 (±0.5)	9.6 (±0.7)	32.9 (±1.6)	170.9 (±2.4)	673.2 (±3.6)	1118.7 (±5.9)
Ca (mg/m ²)	2.2 (±0.1)	3.3 (±0.1)	8.3 (±0.3)	12.2 (±0.5)	22.5 (±0.9)	52.8 (±2.8)
Cu (μg/m ²)	15.7 (±0.6)	25.1 (±1.5)	41.7 (±2.6)	80.2 (±3.2)	295.4 (±5.8)	835.8 (±6.7)
Fe (μg/m ²)	40.2 (±1.3)	172.5 (±5.5)	1593.8 (±5.1)	66.5 (±2.7)	328.0 (±5.3)	12,802.2 (±13.6)
Mg (mg/m ²)	1.6 (±0.05)	2.0 (±0.06)	2.3 (±0.07)	7.5 (±0.3)	13.3 (±0.5)	38.5 (±1.5)
Mn (μg/m ²)	93.6 (±0.7)	184.1 (±5.9)	273.5 (±8.7)	239.2 (±1.3)	391.8 (±7.7)	1084.2 (±4.5)
Ni (μg/m ²)	4.4 (±0.1)	5.3 (±0.2)	6.5 (±0.2)	5.6 (±0.3)	13.3 (±0.5)	26.9 (±1.1)
Pb (μg/m ²)	1.5 (±0.05)	2.1 (±0.1)	2.6 (±0.1)	2.5 (±0.2)	6.4 (±0.3)	8.4 (±0.4)
Zn (μg/m ²)	125.4 (±1.0)	614.8 (±2.9)	1349.8 (±4.5)	199.8 (±1.8)	1770.6 (±7.3)	4878.2 (±19.9)

Table 5

The desorbed foulant fluorophores from HFUF and MBUF membranes in the p-UHMS for surface water treatment.

	DOC (mgC/m ²)	Type of compounds	Peak	Ex (nm)	Em (nm)	Intensity (mV)
HFUF-DI	29.0	Humic-like fluorophore	I	330	410	64
		Protein-like fluorophore	II	210	340	176
HFUF-A	41.5	Humic-like fluorophore	I	320	410	178
		Protein-like fluorophore	II	220	325	206
HFUF-B	76.5	Humic-like fluorophore	I	310	440	338
		Protein-like fluorophore	II	220	330	375
MBUF-DI	38.5	Humic-like fluorophore	I	320	410	162
		Protein-like fluorophore	II	275	315	399
MBUF-A	46.0	Humic-like fluorophore	I	320	410	177
		Protein-like fluorophore	II	255	345	433
MBUF-B	552.4	Humic-like fluorophore	I	315	440	2275
		Protein-like fluorophore	II	225	320	648
			III	280	320	1899

The MW distributions of the foulants desorbed from the HFUF and MBUF membranes via the three cleaning agents determined using UVA and fluorescence detectors are shown in Fig. 4. A more robust UVA response was observed for the desorbed HFUF membrane foulants at 1220 Da (23,105 mV), whereas the desorbed MBUF membrane foulants contained low MW (810–2430 Da) and high MW (19,550 Da) components, with the highest UVA response at 2430 Da (29,736 mV). Similar patterns were also detected in the MW distribution of protein-like components in the foulants desorbed from the HFUF and MBUF membranes. The desorbed HFUF membrane foulants primarily comprised low-MW fractions

(880–2080 Da), and the MW distribution of protein-like components in the foulants desorbed from the MBUF membranes ranged from 830 to 19,470 Da. DOM in the MW range of 500–5000 Da is indicative of humic-like components (i.e., HPO DOM), and DOM with MW > 10,000 Da is associated with biopolymers (i.e., HPI DOM), including amino sugars and protein-like and polysaccharide-like components (Her et al., 2007; Jarusutthirak et al., 2002). Based on the abovementioned results, we postulate that HPO DOM with low MW (i.e., humic-like components) in the HFUF feed readily fouled the HFUF membrane surfaces because of their HPO nature (high hydrophobicity of polyvinylidene fluoride).

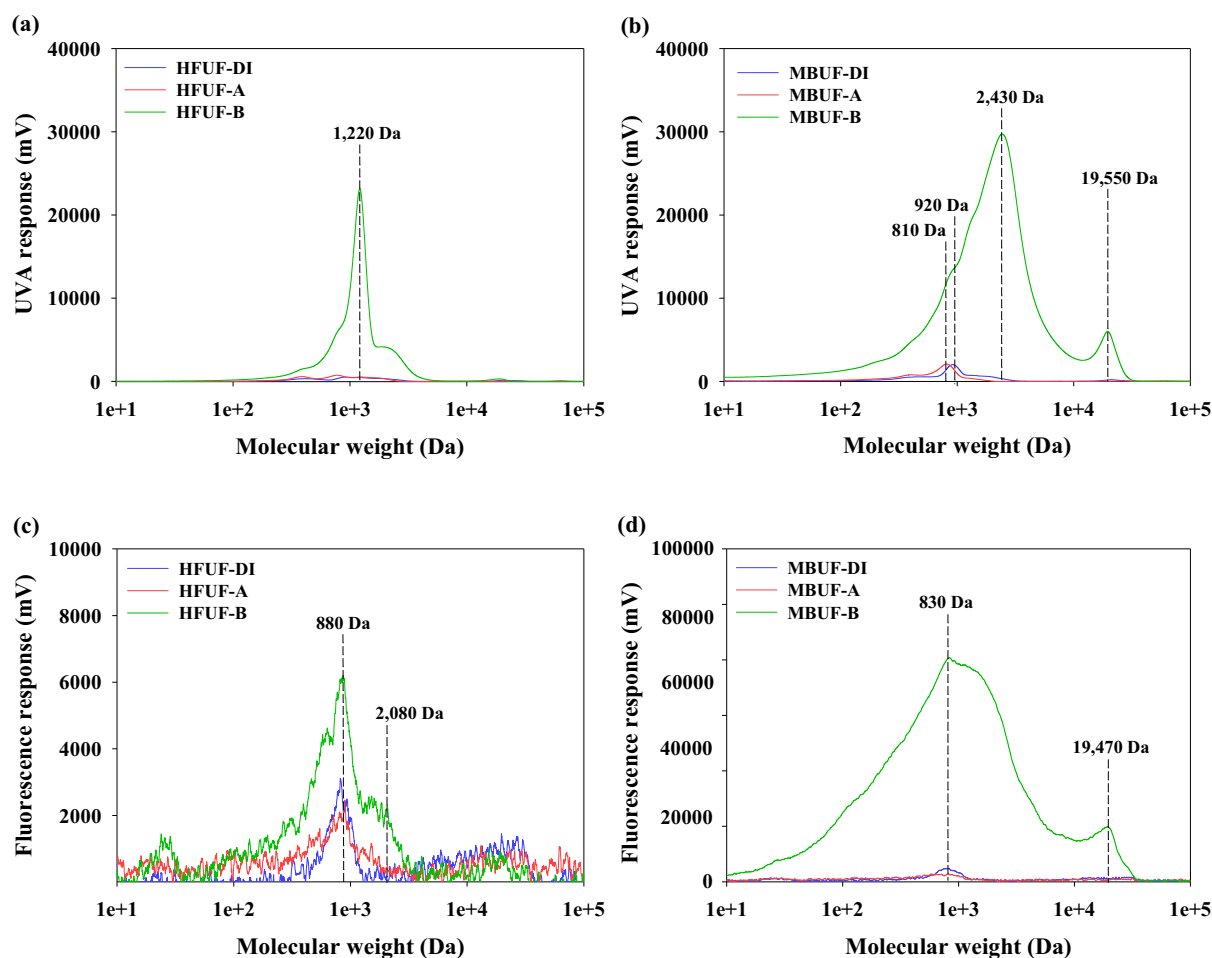


Fig. 4. The MW distribution of the desorbed HFUF and MBUF membrane foulants in the p-UHMS for surface water treatment using three kinds of cleaning agents: (a)–(b) aromatic components and (c)–(d) protein-like components.

Furthermore, HPI DOM residuals (e.g., amino sugars, polysaccharide-like, and protein-like components) with high MWs concentrated in the MBUF feed (i.e., HFUF concentrate) exhibited a high fouling tendency for relatively HPI MBUF membrane surfaces.

3.3.3. FTIR spectra and relative hydrophobicity/hydrophilicity of the desorbed HFUF and MBUF membrane foulants

The FTIR spectra of desorbed foulants from HFUF and MBUF membranes via three different cleaning agents in the p-UHMS are depicted in Fig. 5. Although the functional groups of the desorbed HFUF and MBUF membrane foulants were almost identical, the infrared (IR) response intensities were substantially different. The desorbed foulants from the HFUF and MBUF membranes exhibited IR responses associated with amide stretching vibrations (N—H stretch) derived from the release of polypeptides (i.e., protein-like components) via cell lysis of microorganisms (wavelength ranges = $3500\text{--}3300\text{ cm}^{-1}$, $1680\text{--}1630\text{ cm}^{-1}$, and $850\text{--}750\text{ cm}^{-1}$) and alcohol stretching vibrations (C—O stretch) from polysaccharide-like components (wavelength range = $1125\text{--}1090\text{ cm}^{-1}$) (Lee et al., 2020). A relatively weak IR response attributed to carboxylic acid stretching vibrations (O—H stretch) in relation to humic-like components was also detected for the desorbed foulants from the HFUF membranes in the range of $1440\text{--}1395\text{ cm}^{-1}$. The desorbed foulants from the MBUF membranes had a relatively strong IR response in the range of $1410\text{--}1310\text{ cm}^{-1}$ due to the alcohol stretching vibrations (OH stretch),

which were indicative of polysaccharide-like components (Chon et al., 2012a). These results support the hypothesis that HPO DOM (e.g., humic-like components) govern the formation of HFUF membrane organic fouling, and the deposition of HPI DOM (e.g., amino sugars, polysaccharide-like components, and protein-like components) onto MBUF membrane surfaces might induce severe membrane fouling in p-UHMSs during the treatment of surface water.

As shown in Fig. 6, the HFUF and MBUF membrane foulants desorbed via the alkaline cleaning agent were fractionated using the resin fractionation method into three categories: (i) HPO fractions (adsorbed onto DAX-8 resins), (ii) HPI fractions (not adsorbed onto either DAX-8 or XAD-4 resins), and (iii) transphilic (TPI) fractions (adsorbed onto XAD-4 resins) (Zularisam et al., 2007). The desorbed HFUF and MBUF membrane foulants with the alkaline-based cleaning agent mainly consisted of HPO and HPI components. However, the HPO components of the desorbed foulants from the HFUF membranes using the alkaline-based cleaning agent (HPO fractions = 51.9 %, HPI fractions = 42.1 %, TPI fractions = 6.0 %) were substantially significant compared with those of the desorbed MBUF membrane foulants via the alkaline-based cleaning agent (HPO fractions = 37.2 %, HPI fractions = 44.8 %, TPI fractions = 18.0 %), consistent with the results obtained from the characterization of the desorbed HFUF and MBUF membrane foulants (i.e., SUVA, fluorescence, MW characteristics, and functional group composition). Therefore, these findings strongly support the hypothesis that the differences in the HPO nature of the serially connected polymeric UF membranes might considerably affect the formation of DOM fouling layers in the p-UHMS used to treat surface water (total water recovery rate $\geq 99.5\%$).

3.4. Surface morphological features of the virgin, fouled, and cleaned HFUF and MBUF membranes

FE-SEM is employed to identify the difference in surface morphologies of the virgin, fouled, and cleaned HFUF and MBUF membranes with three kinds of cleaning agents (Fig. 7). Despite the passive pretreatment of surface water using only sedimentation, the HFUF membrane surfaces were generally not affected by biofouling (Fig. 7c). However, the pore sizes of the fouled HFUF membranes decreased considerably due to the precipitation of DOM and metal complexes with negatively charged DOM (e.g., humic-like components) (Chon and Cho, 2016). In contrast, the attachment of microorganisms was prevalent in the fouled MBUF membranes, resulting from the development of gel-like layers promoted by the precipitation of HPI DOM (e.g., amino sugars, polysaccharide-like components, and protein-like components) on the MBUF membrane surfaces. This enhanced the mechanical strength of microbial biofilms via the formation of hydrogen bonds

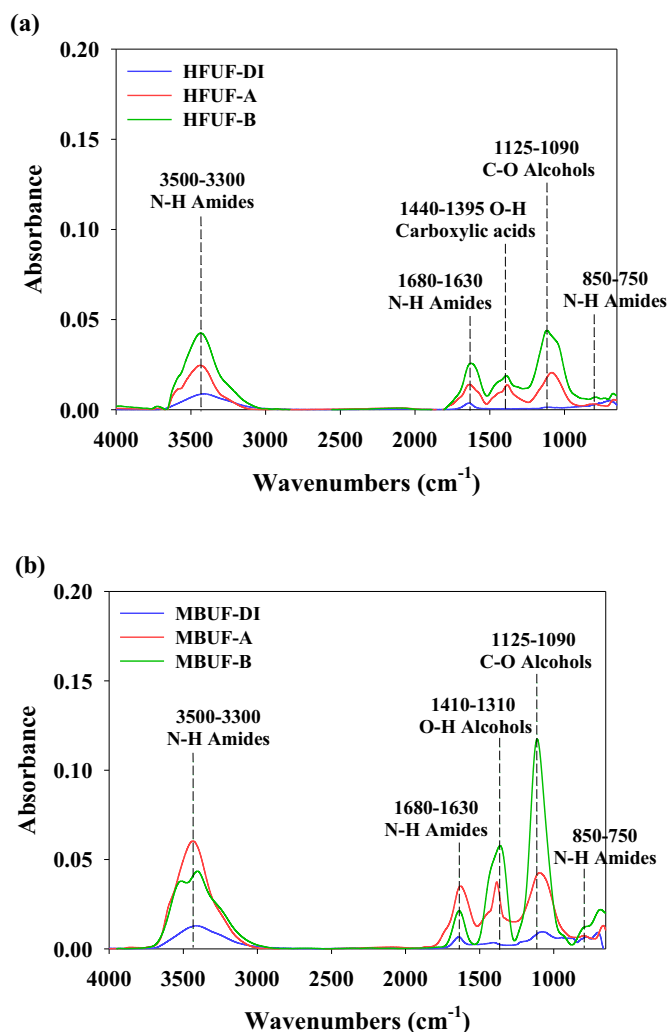


Fig. 5. The FTIR spectra of the desorbed (a) HFUF and (b) MBUF membrane foulants in the p-UHMS for surface water treatment using three kinds of cleaning agents.

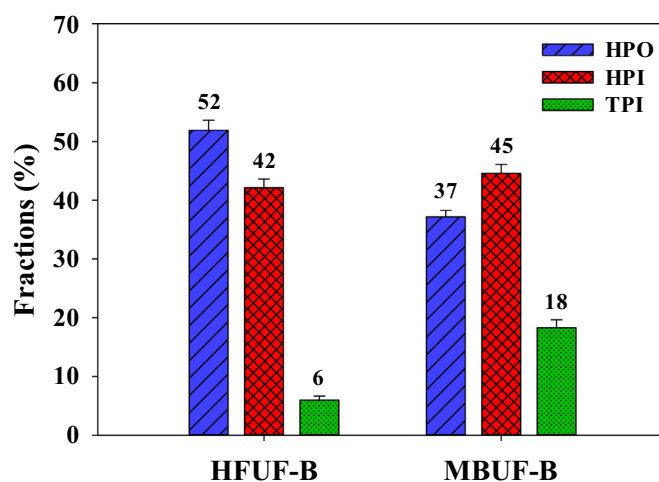


Fig. 6. The relative hydrophobicity/hydrophilicity of the desorbed HFUF and MBUF membrane foulants in the p-UHMS for surface water treatment.

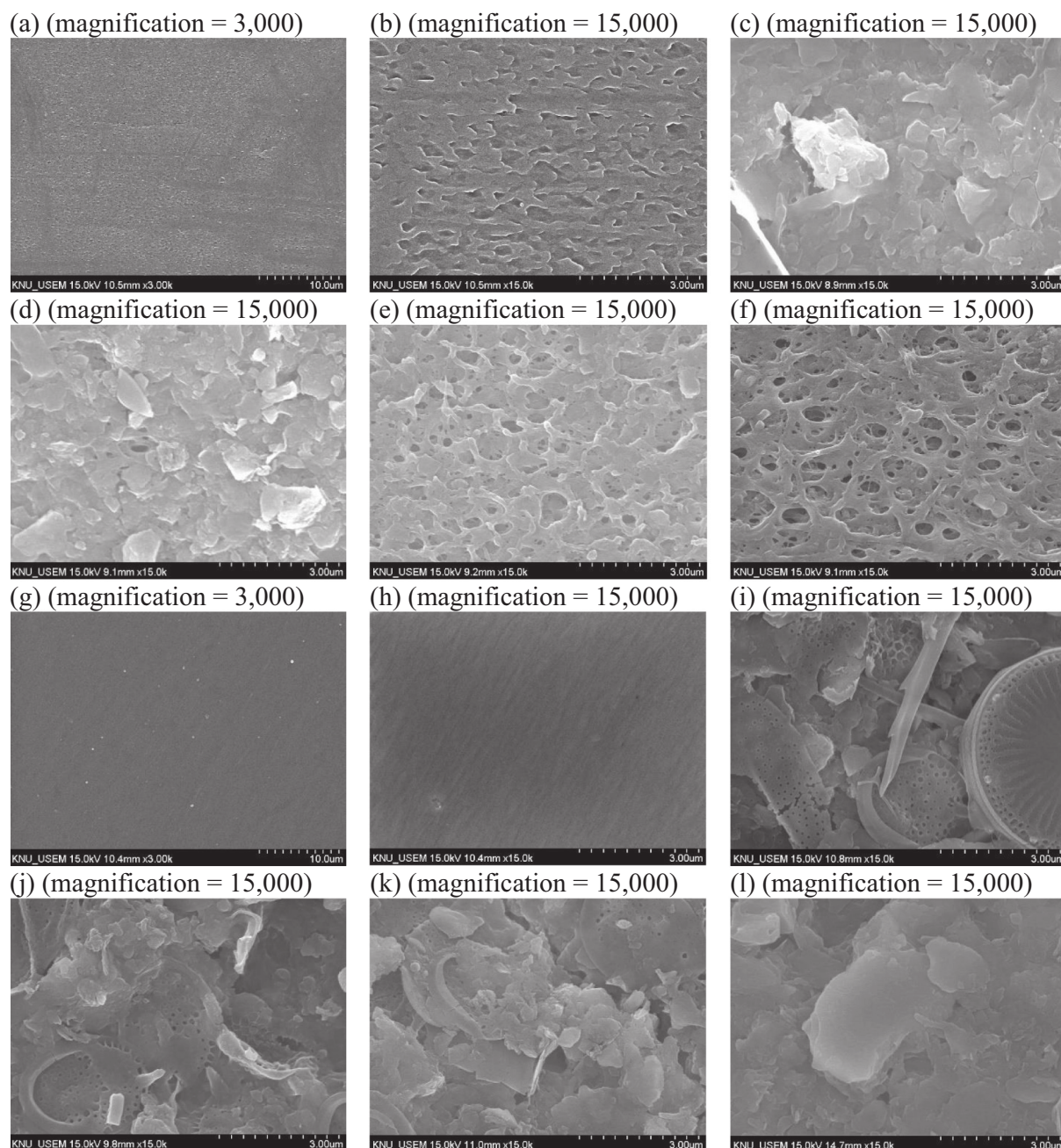


Fig. 7. The field emission scanning electron microscope images of (a)–(b) virgin HFUF, (c) fouled HFUF, cleaned HFUF membranes with (d) DI water, (e) acid-, and (f) alkaline-based cleaning agents, (g)–(h) virgin MBUF, (i) fouled MBUF, cleaned MBUF membranes with (j) DI water, (k) acid-, and (l) alkaline-based cleaning agents.

and van der Waals forces (dispersion) (Fig. 7i) (Herzberg et al., 2010). Moreover, pore blocking resulting from the deposition of DOM and particulate matter was more significant in the MBUF membranes than in the HFUF membranes, probably due to the higher contents of DOM and particulate matter in the MBUF feed (DOC: HFUF feed = 1.6 mg C/L and MBUF feed = 2.1 mg C/L; turbidity: HFUF feed = 0.3 NTU and MBUF feed = 4.1 NTU) (Chae et al., 2009). A rough surface with dense fouling layers was observed on the HFUF and MBUF membranes after cleaning with DI water (Fig. 7d and j). However, the deposition of microorganisms, DOM, and particulate matter was not predominant in the HFUF and MBUF membranes with the acidic cleaning agent (Fig. 7e and k). Furthermore, the surfaces of the fouled HFUF and MBUF membranes became considerably smoother after cleaning with the alkaline cleaning agent compared with the other cleaning agents (Fig. 7f and l). These results indicate that the

alkaline cleaning agents could efficiently eliminate biofouling as well as organic and inorganic fouling of the HFUF and MBUF membranes utilized in the p-UHMS during surface water treatment with total water recovery rate $\geq 99.5\%$.

3.5. Fouling behaviors of the HFUF and MBUF membranes

Temporal changes in the permeate flux and transmembrane pressure (TMP) of the HFUF and MBUF membranes are shown in Fig. 8. Although the HPO and HPI DOM contents were found to be the primary causes of irreversible fouling in both the HFUF and MBUF membranes, their fouling behaviors varied substantially depending on the quality of the feed water and membrane composite materials. During the 60-day operation of the p-UHMS, the TMP value of the HFUF membranes was constantly

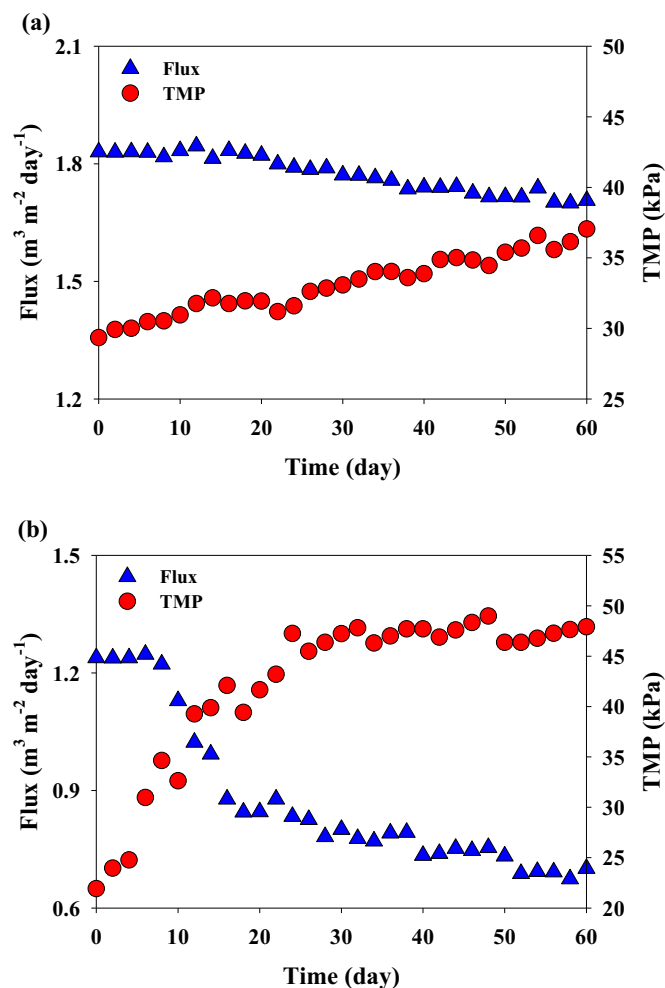


Fig. 8. The permeate flux and TMP profiles of the (a) HFUF and (b) MBUF membranes during the operating periods of the p-UHMS for surface water treatment.

incremented (29.3 kPa $\rightarrow$ 37.0 kPa) to maintain a constant permeate flux (permeate flux: 1.7–1.8 $\text{m}^3/\text{m}^2\cdot\text{d}$). In contrast, considerable variations occurred simultaneously in both the permeate flux and TMP of the MBUF membranes (permeate flux = 1.2 to 0.7 $\text{m}^3/\text{m}^2\cdot\text{d}$; TMP = 21.9 to 48.0 kPa). These results suggest that deposition of HPI DOM (e.g., amino sugars, protein-like, and polysaccharide-like components) onto the relatively HPI MBUF membrane surfaces (composite material: PES) could hinder the membrane performance (i.e., permeate flux and TMP) more significantly than deposition of HPO DOM (e.g., humic-like components) on the relatively HPO HFUF membrane surfaces (composite material: PVDF) (Jeon et al., 2016). Hence, an adequate pre-treatment procedure (e.g., adsorption using activated carbon) capable of lowering the HPI DOM contents in surface waters may be essential for preventing the deterioration of the MBUF membrane performance in the p-UHMS used for treating surface water (Nam et al., 2014).

4. Conclusions

The membrane autopsies of the HFUF (composite material: PVDF) and MBUF (composite material: PES) membranes provided valuable information about the fouling behaviors of DOM in a long-term p-UHMS used to treat surface water. Changes in the characteristics of the feed and permeate waters of the HFUF and MBUF membranes were systemically investigated to determine the organic foulant characteristics and membrane performance (i.e., permeate flux and TMP). The analytical results confirmed

that HPO DOM with low MW (i.e., humic-like components) in the HFUF feed readily fouled the HFUF membrane surfaces because of their HPO nature. Moreover, HPI DOM residuals (e.g., amino sugars, protein-like, and polysaccharide-like components) with high MWs concentrated in the MBUF feed (i.e., HFUF concentrate) showed a high fouling tendency for relatively HPI MBUF membrane surfaces. These results indicate that the UF membrane fouling behaviors were influenced by the physicochemical interactions between the UF membrane surfaces and DOM (which depended on the membrane composite material), rather than the interactions between DOM and DOM on the UF membrane surfaces. Moreover, the adhesion of HPI DOM onto the relatively HPI MBUF membrane surfaces could deteriorate the performance of the membrane more significantly than the adsorption of HPO DOM onto the relatively HPO HFUF membrane surfaces (TMP of HFUF = 29.3 kPa $\rightarrow$ 37.0 kPa; TMP of MBUF = 21.9 kPa $\rightarrow$ 48.0 kPa; permeate flux of HFUF = 1.7 $\text{m}^3/\text{m}^2\cdot\text{d} \rightarrow$ 1.8 $\text{m}^3/\text{m}^2\cdot\text{d}$; permeate flux of MBUF = 1.2 $\text{m}^3/\text{m}^2\cdot\text{d} \rightarrow$ 0.7 $\text{m}^3/\text{m}^2\cdot\text{d}$). Therefore, the membrane composite materials selected after considering the interactions between the UF membrane surfaces and foulants contributes to governing membrane fouling and economical membrane processes in the p-UHMS for surface water treatment (total water recovery rate $\geq$ 99.5 %).

Credit authorship contribution statement

Yong-Gu Lee: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft. **Jaegwan Shin and Seung Joon Kim:** Experimental assistance. **Kyung Hwa Cho and Paul Westerhoff:** Review & Editing. **Hojung Rho:** Writing – review & editing, Data analysis. **Kangmin Chon:** Resources, Writing – review & editing, Supervision.

Data availability

The authors do not have permission to share data.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by Korea Environment Industry & Technology Institute (KEITI) through Project for developing innovative drinking water and wastewater technologies funded by Korea Ministry of Environment (MOE) (RE202201776).

References

- Aboubaraka, A.E., Aboelfetoh, E.F., Ebeid, E.-Z.M., 2017. Coagulation effectiveness of graphene oxide for the removal of turbidity from raw surface water. *Chemosphere* 181, 738–746.
- Chae, S.-R., Yamamura, H., Choi, B., Watanabe, Y., 2009. Fouling characteristics of pressurized and submerged PVDF (polyvinylidene fluoride) microfiltration membranes in a pilot-scale drinking water treatment system under low and high turbidity conditions. *Desalination* 244, 215–226.
- Chew, C.M., Aroua, M.K., Hussain, M.A., Ismail, W.M.Z.W., 2016. Evaluation of ultrafiltration and conventional water treatment systems for sustainable development: an industrial scale case study. *J. Clean. Prod.* 112, 3152–3163.
- Chigor, V.N., Umoh, V.J., Okuofu, C.A., Ameh, J.B., Igbinosa, E.O., Okoh, A.I., 2012. Water quality assessment: surface water sources used for drinking and irrigation in Zaria, Nigeria are a public health hazard. *Environ. Monit. Assess.* 184, 3389–3400.
- Chon, K., Cho, J., 2016. Fouling behavior of dissolved organic matter in nanofiltration membranes from a pilot-scale drinking water treatment plant: an autopsy study. *Chem. Eng. J.* 295, 268–277.
- Chon, K., Cho, J., Shon, H.K., 2013. Fouling characteristics of a membrane bioreactor and nanofiltration hybrid system for municipal wastewater reclamation. *Bioresour. Technol.* 130, 239–247.
- Chon, K., Jeong, N., Rho, H., Nam, J.-Y., Jwa, E., Cho, J., 2020. Fouling characteristics of dissolved organic matter in fresh water and seawater compartments of reverse electro-dialysis under natural water conditions. *Desalination* 496, 114478.

- Chon, K., Kim, S.J., Moon, J., Cho, J., 2012a. Combined coagulation-disk filtration process as a pretreatment of ultrafiltration and reverse osmosis membrane for wastewater reclamation: an autopsy study of a pilot plant. *Water Res.* 46, 1803–1816.
- Chon, K., KyongShon, H., Cho, J., 2012b. Membrane bioreactor and nanofiltration hybrid system for reclamation of municipal wastewater: removal of nutrients, organic matter and micropollutants. *Bioresour. Technol.* 122, 181–188.
- Cunha, D.G.F., Sabogal-Paz, L.P., Dodds, W.K., 2016. Land use influence on raw surface water quality and treatment costs for drinking supply in São Paulo State (Brazil). *Ecol. Eng.* 94, 516–524.
- Delpla, I., Jung, A.-V., Baures, E., Clement, M., Thomas, O., 2009. Impacts of climate change on surface water quality in relation to drinking water production. *Environ. Int.* 35, 1225–1233.
- Gray, S.R., Ritchie, C., Tran, T., Bolto, B., 2007. Effect of NOM characteristics and membrane type on microfiltration performance. *Water Res.* 41, 3833–3841.
- Guigui, C., Bonnelye, V., Durand-Bourlier, L., Rouch, J., Aptel, P., 2001. Combination of coagulation and ultrafiltration for drinking water production: impact of process configuration and module design. *Water Sci. Technol. Water Supply* 1, 107–118.
- Her, N., Amy, G., Chung, J., Yoon, J., Yoon, Y., 2008. Characterizing dissolved organic matter and evaluating associated nanofiltration membrane fouling. *Chemosphere* 70, 495–502.
- Her, N., Amy, G., Foss, D., Cho, J., Yoon, Y., Kosenka, P., 2002. Optimization of method for detecting and characterizing NOM by HPLC – size exclusion chromatography with UV and on-line DOC detection. *Environ. Sci. Technol.* 36, 1069–1076.
- Her, N., Amy, G., Plottu-Pecheux, A., Yoon, Y., 2007. Identification of nanofiltration membrane foulants. *Water Res.* 41, 3936–3947.
- Herzberg, M., Berry, D., Raskin, L., 2010. Impact of microfiltration treatment of secondary wastewater effluent on biofouling of reverse osmosis membranes. *Water Res.* 44, 167–176.
- Howe, K.J., Clark, M.M., 2002. Fouling of microfiltration and ultrafiltration membranes by natural waters. *Environ. Sci. Technol.* 36, 3571–3576.
- Huang, H., Lee, N., Young, T., Gary, A., Lozier, J.C., Jacangelo, J.G., 2007. Natural organic matter fouling of low-pressure, hollow-fiber membranes: effects of NOM source and hydrodynamic conditions. *Water Res.* 41, 3823–3832.
- Huang, J., Takizawa, S., Fujita, K., 2000. Pilot-plant study of a high recovery membrane filtration process for drinking water treatment. *Water Sci. Technol.* 41, 77–84.
- Jarusutthirak, C., Amy, G., Croué, J.-P., 2002. Fouling characteristics of wastewater effluent organic matter (EfOM) isolates on NF and UF membranes. *Desalination* 145, 247–255.
- Jeon, S., Rajabzadeh, S., Okamura, R., Ishigami, T., Hasegawa, S., Kato, N., et al., 2016. The effect of membrane material and surface pore size on the fouling properties of submerged membranes. *Water* 8, 602.
- Khan, S., Shahnaz, M., Jehan, N., Rehman, S., Shah, M.T., Din, I., 2013. Drinking water quality and human health risk in Charsadda district, Pakistan. *J. Clean. Prod.* 60, 93–101.
- Kimura, K., Hane, Y., Watanabe, Y., Amy, G., Ohkuma, N., 2004. Irreversible membrane fouling during ultrafiltration of surface water. *Water Res.* 38, 3431–3441.
- Laabs, C.N., Amy, G.L., Jekel, M., 2006. Understanding the size and character of fouling-causing substances from effluent organic matter (EfOM) in low-pressure membrane filtration. *Environ. Sci. Technol.* 40, 4495–4499.
- Lee, Y.-G., Kim, S., Shin, J., Rho, H., Lee, Y., Kim, Y.M., et al., 2020. Fouling behavior of marine organic matter in reverse osmosis membranes of a real-scale seawater desalination plant in South Korea. *Desalination* 485, 114305.
- Leenheer, J.A., Croué, J.-P., 2003. Peer reviewed: characterizing aquatic dissolved organic matter. *Environ. Sci. Technol.* 37, 18A–26A.
- Mierzwa, J.C., da Silva, M.C.C., Veras, L.R.V., Subtil, E.L., Rodrigues, R., Li, T., et al., 2012. Enhancing spiral-wound ultrafiltration performance for direct drinking water treatment through operational procedures improvement: a feasible option for the Sao Paulo Metropolitan Region. *Desalination* 307, 68–75.
- Nam, S.-W., Choi, D.-J., Kim, S.-K., Her, N., Zoh, K.-D., 2014. Adsorption characteristics of selected hydrophilic and hydrophobic micropollutants in water using activated carbon. *J. Hazard. Mater.* 270, 144–152.
- Nguyen, T., Fan, L., Roddick, F., Harris, J., 2009. A comparative study of microfiltration and ultrafiltration of activated sludge-lagoon effluent. *Desalination* 236, 208–215.
- Peiris, R.H., Budman, H., Moresoli, C., Legge, R.L., 2011. Development of a species specific fouling index using principal component analysis of fluorescence excitation–emission matrices for the ultrafiltration of natural water and drinking water production. *J. Membr. Sci.* 378, 257–264.
- Peiris, R.H., Hallé, C., Budman, H., Moresoli, C., Peldszus, S., Huck, P.M., et al., 2010. Identifying fouling events in a membrane-based drinking water treatment process using principal component analysis of fluorescence excitation–emission matrices. *Water Res.* 44, 185–194.
- Peldszus, S., Hallé, C., Peiris, R.H., Hamouda, M., Jin, X., Legge, R.L., et al., 2011. Reversible and irreversible low-pressure membrane foulants in drinking water treatment: identification by principal component analysis of fluorescence EEM and mitigation by biofiltration pretreatment. *Water Res.* 45, 5161–5170.
- Peter-Varbanets, M., Zurbrugg, C., Swartz, C., Pronk, W., 2009. Decentralized systems for potable water and the potential of membrane technology. *Water Res.* 43, 245–265.
- Porcelli, N., Judd, S., 2010. Chemical cleaning of potable water membranes: a review. *Sep. Purif. Technol.* 71, 137–143.
- Raffin, M., Germain, E., Judd, S., 2011. Optimisation of MF membrane cleaning protocol in an Indirect Potable Reuse (IPR) scheme. *Sep. Purif. Technol.* 80, 452–458.
- Reissmann, F.G., Uhl, W., 2006. Ultrafiltration for the reuse of spent filter backwash water from drinking water treatment. *Desalination* 198, 225–235.
- Rho, H., Chon, K., Cho, J., 2019. An autopsy study of a fouled reverse osmosis membrane used for ultrapure water production. *Water* 11, 1116.
- Tian, J.-y., Ernst, M., Cui, F., Jekel, M., 2013. Correlations of relevant membrane foulants with UF membrane fouling in different waters. *Water Res.* 47, 1218–1228.
- Tian, J., Wu, C., Yu, H., Gao, S., Li, G., Cui, F., et al., 2018. Applying ultraviolet/persulfate (UV/PS) pre-oxidation for controlling ultrafiltration membrane fouling by natural organic matter (NOM) in surface water. *Water Res.* 132, 190–199.
- Yoo, S.S., Chu, K.H., Choi, I.-H., Mang, J.S., Ko, K.B., 2018. Operating cost reduction of UF membrane filtration process for drinking water treatment attributed to chemical cleaning optimization. *J. Environ. Manag.* 206, 1126–1134.
- Yu, H., Li, X., Chang, H., Zhou, Z., Zhang, T., Yang, Y., et al., 2020. Performance of hollow fiber ultrafiltration membrane in a full-scale drinking water treatment plant in China: a systematic evaluation during 7-year operation. *J. Membr. Sci.* 613, 118469.
- Zularisam, A., Ismail, A., Salim, M., Sakinah, M., Ozaki, H., 2007. The effects of natural organic matter (NOM) fractions on fouling characteristics and flux recovery of ultrafiltration membranes. *Desalination* 212, 191–208.