Characterization of organic foulants in pressure retarded osmosis membrane using fluorescence excitation-emission and PARAFAC

Sookhyun Nam[1], Jae-Wuk Koo[1], Eunju Kim[1], Seong-Nam Nam[2], Tae-Mun Hwang [1,*]

[1]Korea Institute of Civil Engineering and Building Technology

[2]Department of Civil and Environmental Engineering, Chung-Ang University, 84 Heukseok-ro, Dongjak-gu, Seoul 06974, Republic of Korea

[*]Corresponding author: Tel. +82-31- 910-0741; Fax +82-31- 910-0291;
Email: taemun@kict.re.kr

Abstract

The pressure retarded osmosis (PRO) process is the next generation seawater desalination technology and is considered as eco-friendly and economic renewable energy. As such, there have been active studies of means of efficient cleaning to restore membrane performance degraded due to the reversible membrane fouling that inevitably occurs after prolonged operation. Due to the fact that fouling occurs differently in each type of pretreatment process involved in the PRO, it is important to understand the type of organic matter that causes fouling in each of the PRO pretreatment processes. In this study, the composition of dissolved organic matter (DOM) was characterized and assessed among the membrane bioreactor (MBR), ultrafiltration (UF), activated carbon/sand filter (AC/S) and low pressure reverse osmosis (LPRO) processes as PRO pretreatments using a fluorescence excitation-emission matrix (F-EEM) coupled with parallel factor analysis (PARAFAC), and a liquid chromatography-organic carbon detector (LC-OCD) technique. By analyzing the correlation between power density and total organic carbon (TOC) in feed water of PRO, it was found that there was an

extremely high correlation between PRO power density and TOC. The major components could be summarized microbial humic-like fluorescence, humic and fulvic substances (C1), terrestrial humic-like fluorescence in high nutrient and wastewater influenced environments (C2) and tryptophan-like substances (C3).

Keywords: *PRO, Pressure retarded osmosis , Pretreatment, F-EEM, PARAFAC*

1. Introduction

Seawater desalination is a method of securing a stable supply of water resources that is unaffected by climate changes. It is a typical application in the Middle Eastern Region but more recently markets have expanded into the North America, Australia, South America, Southeast Asia, China and Europe. However, the importance of conserving energy use in the desalination process has been highlighted in recent years [1]. The reverse osmosis (RO) process is rapidly growing for desalination as it can obtain the water resource with relatively low energy compared to existing distillation type seawater desalination process. Current RO process technology has been developed to its maximum level; ways of combining the PRO process to RO process are being studied for lowering the operating energy. PRO processes involve technologies that use the osmotic energy differences between two solutions (high density saline solution, low density saline solution) to produce energy [2, 3]. It is necessary to introduce pretreatment processes that prevent foulants from developing during the application of feed water such as wasteswater effluent when designing PRO processes. Mega-ton water system project in Japan has developed the sustainable desalination. The aims of the Mega-ton water system project are energy reduction, water production cost reduction and low

environmental impact. One of the projects is the SWRO and PRO hybrid system which used the concentrated SWRO brine as a draw solution and the treated sewage as a feed solution. One of the key results is that they could obtain enough positive net output power through removing low pressure RO system as a PRO pretreatment or higher membrane performance [4, 5, 6]. Understanding the major foulants associated with the membrane process plays an important role in deciding upon filtration and cleaning strategy. Liquid chromatography with organic carbon detection (LC-OCD) or fluorescence excitation-emission matrix (EEM) spectroscopy is used for the purposes of determining the major organic substances in water [7, 8]. These techniques help to analyze major foulants of a membrane such as extracellular polymetric substances (EPS)-like and soluble microbial products (SMP) that are hydrophilic and have high-molecular weight [9]. Recently, cases of applying three-dimensional fluorescence EEMs to the analysis of DOM have been on the rise [10, 11]. However, as it is difficult to perform quantitative interpretations using EEM, the PARAFAC was performed. Recent organic matter EEM analysis methods involve multivariate data analysis [12] such as Principal Component Analysis (PCA) or Partial Least Squares (PLS) regression, or multi-way data analysis using PARAFAC [13]. The PCA has been used in fluorescence EEMs to evaluate pretreatment feed water and assess fouling of the UF and NF processes [14]. EEM-PARAFAC analysis is appropriate for the organic matter monitoring of drinking water plants and water recycling plants [15]. EEM-PARAFAC can also be used to explain changes in organic matter of the treated water in fractional components, and F-EEM is used to determine DOM removal efficiency in the water treatment process [16]. The aim of this study is to investigate the influence of concentrations and composition of DOM which is treated by MBR, UF, LPRO and

AC/S filter process in terms of PRO membrane performance and fouling. A lab-scale PRO device was used to evaluate the changes in foulants during each of the pretreatment processes. Major foulants were analyzed using EEM-PARAFAC by analyzing fractional changes of components. Through PARAFAC analysis, the component score changes of each process were observed and their correlation with fluorescent intensity, UV254 of the samples, and DOC were reviewed [17].

2. Materials and Methods

2.1 Lab scale PRO test device

In this study, as shown in Fig. 1, a cross-flow experimental setup was used. The operating method for the PRO was AL-DS (draw solution is contacted at active layer of membrane). The PRO membrane cell for the flat-sheet membrane was made of SUS (Steel Use Stainless), and has an effective membrane area of 0.064 m^2 (0.08 m length×0.08 m width). The applied pressure in the draw solution (DS) and pressure resistance in the feed solution (FS) were monitored using an electronic pressure gauge (GR200 graphic recorder, Hanyoung nux, Korea). To measure water flux and power density, an electronic scale (Ranger 7000, Ohaus, USA) was placed under the FS container and decrease in the water amount was recorded. The operational mode consisted of having the PRO membrane arranged so that its active layer faces the draw solution, and having the draw solution flow and feed water flow within the membrane cell form a counter current. The water flux was calculated based on the weight changes of the water. A chiller (RW-0525G, Jeiotech, Korea) was used to maintain a stable temperature (at 20 ^{o}C for both DS and FS). By using a booster pump (Hyosung, Korea), pressure conditions were controlled. DS was made from NaCl (SAMCHUN, Korea) to

maintain 1.2 M, which is same concentration of the brine from SWRO process in SWRO-PRO hybrid process. In theory, maximum power density can be achieved at 25~30 bars when applying PRO operations using a NaCl solution having a density of 1.2 M. The operational pressure of the draw solution was set at 15 bars and the flow of the feed solution and draw solution was set to be the same at 1.0 L/min. In order to make use of a draw solution similar to the RO brine concentration, a NaCl 1.2 M solution was used. Flow rate of both FS and DS were fixed at 1 LPM, and FS and DS volume were maintained as constant (2 L).

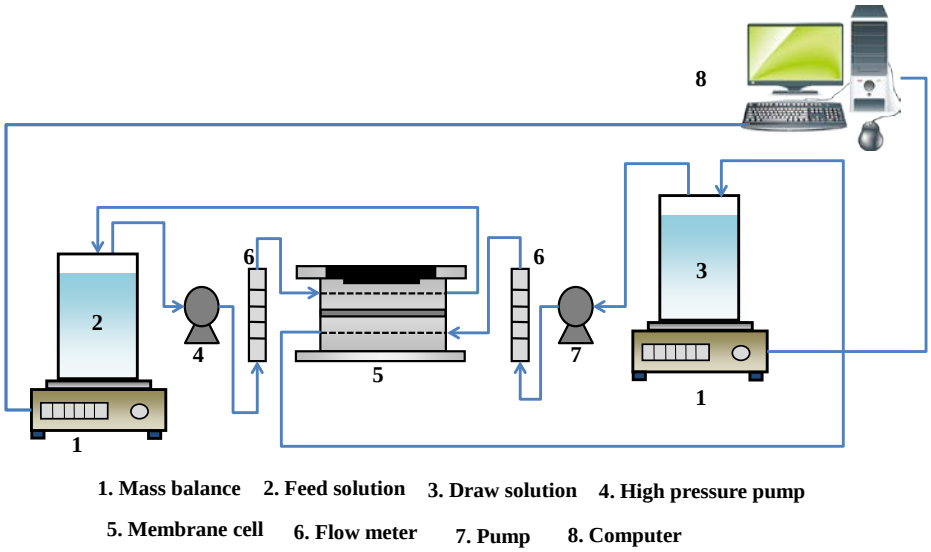


Fig. 1 Schematic of the lab scale PRO system.

2.2 Analytical methods

All samples were filtered (0.45 μm cellulose acetate) prior to analysis. The feed and permeate samples of all the process were analyzed using fluorescence F-EEM and its data was collected. The collected data was applied to PARAFAC modeling analysis. DOC of each sample was measured using a total organic carbon analyzer (Shimadzu TOC-V_{CPH}, Japan) and ultraviolet absorbance at 254 nm (UV254) was measured using

a UV/Vis spectrophotometer (DR 5000, HACH, USA). T-N, T-P were analyzed using a multi-parameter water quality analyzer (SYNCA 3ch, Germany). The fluorescence spectroscopy (AQUALOG, Horiba, Japan) was used for the EEM analysis. Fluorescence EEMs and absorbance spectra were analyzed using an excitation wavelength of 250-550 nm at intervals of 2 nm and an emission wavelength of 250-800 nm at intervals of 2.33 nm using medium gain and an integration time of 0.5 s. All EEMs were corrected and normalized according to published methods [18]. All sample, were corrected for Rayleigh scatter, and inner-filter effects using the Aqualog software. EEMs were blank subtracted to minimize Raman scattering, inner filter corrected following Lakowicz (2006) [19] and normalized [20]. To analyze DOM, the liquid chromatography organic carbon detection (LC-OCD) system manufactured by DOC-LABOR DR HUBER was used. The system consists of an auto-injector, size exclusion chromatography TSK-HW-50S column(250 mm×20 mm, Toso, Japan), and thin film reactor (TFR) that oxidizes components divided from the column into CO_2 and UV254 detector, non- dispersive infrared (NDIR) detector.

2.3 PARAFAC modeling

PARAFAC is a method used to analyze EEM data, where currently, 3D-PARAFAC models are widely in use. Under ideal conditions where EEMs independently follow the Beer's Law, each EEM presents a fluorescence from the underlying fluorescence; based on this principle, under ideal conditions in which Beer's law is applicable, the method of analyzing EEMs by presenting them three-dimensionally is referred to as 3D-PARAFAC modeling. The general principle of 3D-PARAFAC modeling involves the division of EEM data into three mode, *a*, *b*, and *c*, to undertake a three-dimensional

analysis. The following equation represents 3D-PARAFAC modeling [21, 22].

$$X_{ijk} = \sum_{f=1}^{F} a_{if} b_{if} c_{kf} + \varepsilon_{ijk}\,,\ i = 1,2 \ldots I; j = 1,2 \ldots J; k = 1,2 \ldots K; \quad (1)$$

Where x_{ijk} is one element of the three-way data array with dimensions *I*, *J* and *K*. x_{ijk} refers to the emission wavelength j, excitation wavelength k, and fluorescence intensity measured from sample *i*. The created model is based on parameters *a*, *b*, and *c*. This represents the concentration, emission spectra, and excitation spectra for each component. The component scores represent the relative density of the representative organic matter of the components. F refers to the number of components. Excitation and emission loadings present the characteristics of the excitation and emission spectra [23, 17]. Fluorescence EEM data were analyzed using the PARAFAC algorithm within the Eigenvector Inc. Solo Package (AQUALOG, Horiba, Japan). PARAFAC analysis was undertaken through modeling based on 70 EEM fluorescence data. The number of fluorescence components was determined by validating ANOVA, core consistency diagnostics, and half-split analyses. The maximum fluorescence intensities (F_{max}) of each substance represents the relative intensities of the substance concerned in the sample, and the excitation and emission loading values present the characteristics of the excitation and emission spectra.

3. Results and Discussions

3.1 Power density and flux decline

PRO processes use the osmotic energy differences between two solutions (high density

saline solution, low density saline solution) to produce energy. The PRO technology examined in this study relates to a technology that combines the use of wastewater and seawater. In this study makes use of effluents from wastewater treatment facilities or processed water from wastewater treatment facilities as PRO process feed water, and RO concentrate of a seawater desalination system as draw solution. The power can be produced per unit membrane area (i.e., power density) in PRO process is equal to the product of the water flux and the hydraulic pressure differential across the membrane. [24].

$$W = J_w \Delta P = A(\Delta\pi - \Delta P)\Delta P \quad (2)$$

where W is power density (W/m^2); Jw is the water flux ($Lm^{-2}\cdot h^{-1}$); A is the water permeability coefficient; $\Delta\pi$ is the osmotic pressure; and ΔP is the hydraulic pressure.

This equation describes the diffusive transport of water through PRO membrane. The power density is proportional with the product of the hydraulic pressure and water flux across the membrane. As shown the equation (2), the osmotic pressure is converted into mechanical energy. In ideal conditions, the hydraulic pressure increases during decreasing the water flux, unless ΔP is reached at zero ($\Delta P = \Delta\pi$, the flux reversal point). The maximum power density increases until ΔP is reached at $\Delta\pi/2$ and then decreases by the flux reversal flux.

$$W_{max} = A\frac{\Delta\pi^2}{4} \quad (3)$$

This study examined the influence of organic matters contents in water on PRO power densities. UF treated water, LPRO treated water and LPRO concentrate were mixed to control organic matter concentration. The feed solution was prepared to have TOC between the range of 1 mg/L ~ 10 mg/L. Fig 2 shows the dependence of the maximum power density on the TOC of the feed water. As indicated in Fig. 2, a high correlation as found between PRO power densities and TOC. This indicates that organic matters can be a major parameter on PRO performance.

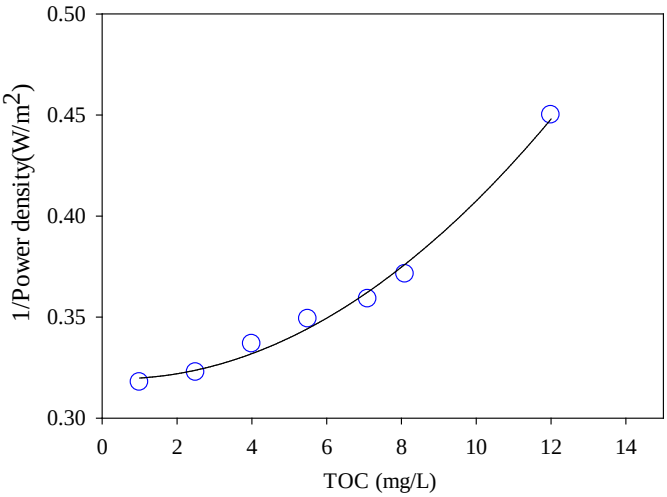


Fig. 2 Value of 1/power density by TOC concentration at DS 15 bars.

The four different feed waters were used for the experiments. The have different degree of pretreatment. The sewage treatement plant effluent is used as untreated feed water. This was taken from Ilsan-si sewage treatement plant in Republic of Korea. These waters were pretreated using ultrafiltration (UF) membrane, AC/S consisted with activated carbon and sand, low pressure reverse osmosis (LPRO). MBR treated water is

also taken from same plant. UF and MBR membrane (MR-MHP07A, LG Corporation, Korea) used in the experiment was a hollow fiber type polyvinylidene difluoride (PVDF) based membrane having a pore size of 0.1 μm. RO membrane (RE2540-BN, Toray Chemical, Korea) used. Table 1 shows the water quality of the pretreated water for PRO feed solution. As shown in the Fig. 3, the four different feed waters were compared with the normalized flux decline. Fig. 3 shows the effect of pretreatment on the flux decline of PRO system, four different waters were used as the feed waters. As shown in the Table 1, the turbidity of the all samples was not different. On the other hand, the DOC and UV254 absorbance of the UF and MBR were higher than that of the AC/S and LPRO. These show that the concentration of organic matters is higher in the UF and MBR treated water. It took approximately 10 hours for the J/J0 of the UF pretreated water to decrease to 0.6 and more than approximately 20 hours for the J/J0 of the AC/S pretreated water to decrease to 0.6. UF pretreated water showed 3 times faster membrane contamination rate than AC/S pretreated water. These results show that the organic matters in feed water are closely related to the power density and flux decline rate.

3.2 F-EEM analysis

Fig. 4 presents the F-EEM contour plots of the UF, MBR, AC/S and LPRO treated waters. The main foulants of the UF process showed various functional groups, has various molecular sizes and are composed of a complex mixture of humic and fulvic acids, proteins. Detailed information about all target analytes used in this study was shown in Table 2 [25]. The organic matter properties of the UF and MBR process included fulvic and humic-like fluorophores (λ_{ex}=250-260 nm and λ_{em}=380-480 nm;

Region III), humic-like fluorophores (λ_{ex}=330–350 nm and λ_{em}=420–480 nm; Region IV), and tryptophan-like fluorophores (λ_{ex}=270–280 nm and λ_{em}=320–350 nm; Region II). The organic matter properties of the AC/S and LPRO process removed most Region III and Region IV properties and mostly included tryptophan-like fluorophores (λ_{ex}=270–280 nm and λ_{em}= 320–350 nm; Region II).

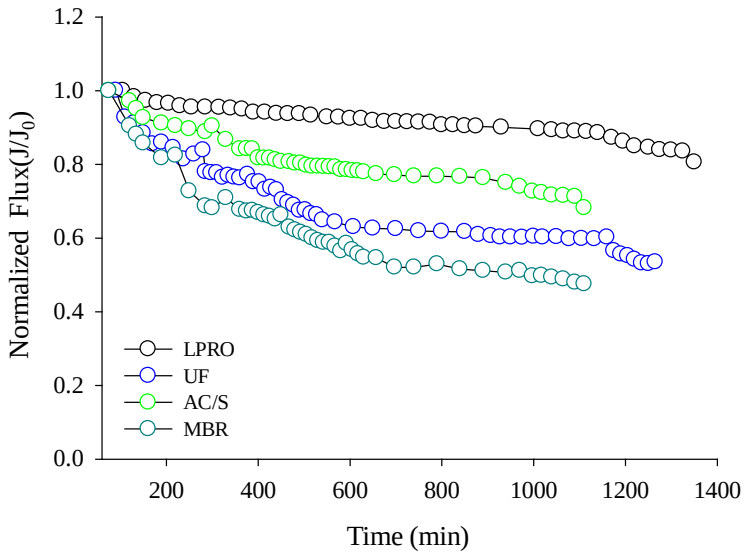


Fig. 3 Change in normalized flux over time according to PRO pretreatment processes.

Table 1 Average water quality and removal efficiencies for raw water and pretreated water.

Parameters	Feed water	Pre-treated water			
		UF	AC/S	MBR	LPRO
Total Coliform (No./mL)	2280±10	0±1	0±1	0±1	0±0
Turbidity (NTU)	8.06±2.00	0.065±0.004	0.090±0.005	0.090±0.005	0.040±0.001
UV254 (cm^{-1})	0.115±0.002	0.109±0.001	0.011±0.002	0.111±0.002	0.004±0.001
TDS (mg/L)	524±5	523±5	520±5	520±5	80±5
pH	6.88±0.2	6.89±0.2	6.89±0.2	6.89±0.2	6.87±0.2
TOC (mg/L)	7.63±0.3	6.73±0.3	0.78±0.3	7.23±0.3	0.40±0.1
DOC (mg/L)	7.36±0.3	6.62±0.3	0.72±0.3	6.88±0.3	0.40±0.1
Color (pt)	29±2	27±2	10±2	28±2	1±0
T-N (mg/L)	9.94±0.1	9.03±0.1	2.03±0.1	8.03±0.1	1.03±0.2
T-P (mg/L)	0.37±0.05	0.34±0.05	0.30±0.05	0.24±0.05	0.05±0.1

Table 2 Fluorescence regions and excitation-emission wavelength boundaries (Previously identified).

Region	Ex/Em	Description
I	270–280 / 300–320	aromatic proteins, tyrosine-like substances
II	270–280 / 320–350	aromatic proteins, tryptophan-like substances
III	250–260 / 380–480	fulvic-like and humic-like substances
IV	330–350 / 420–480	humic-like substances

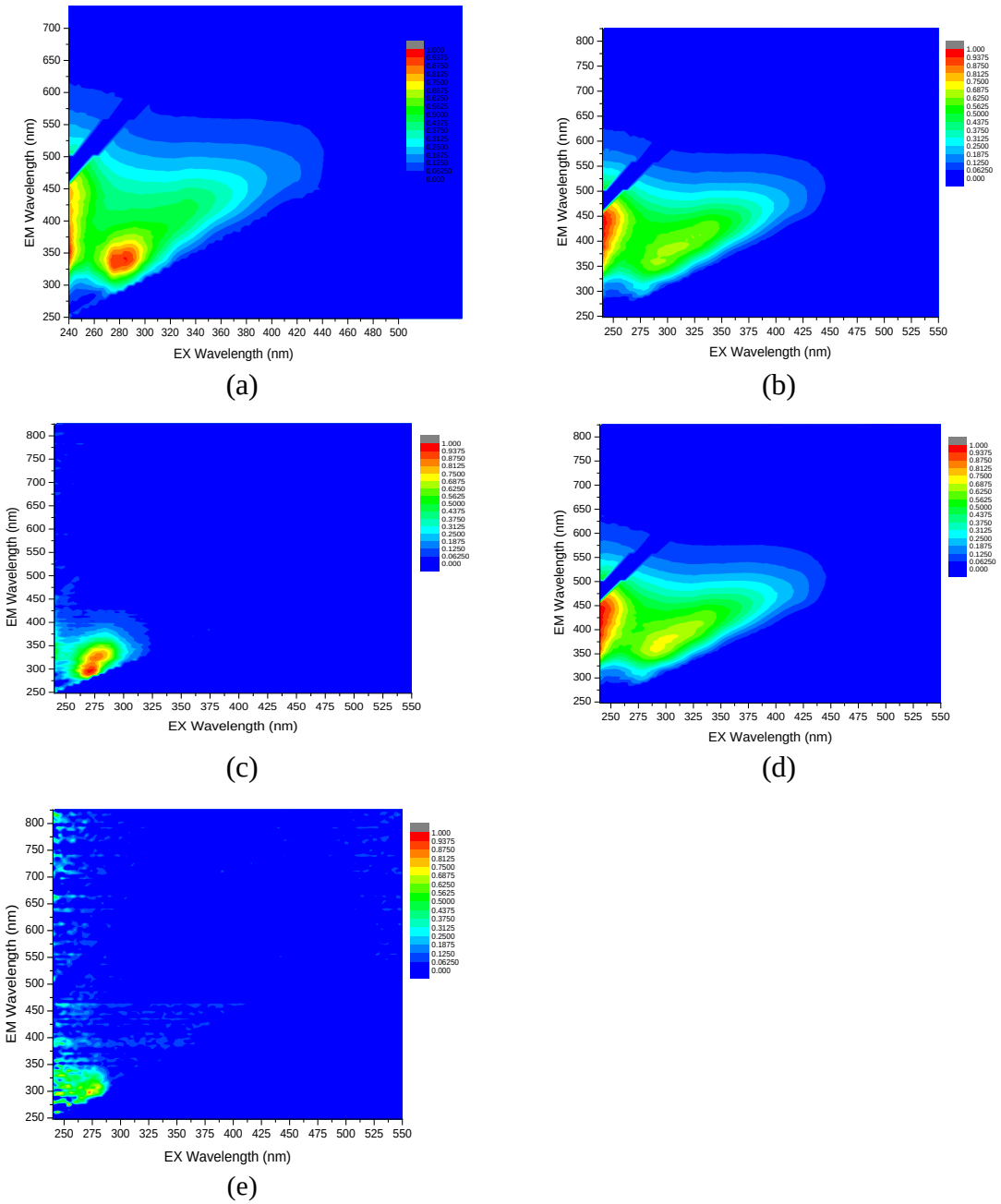


Fig. 4 3-EEM fluorescence spectra of (a) feed water (b) UF (c) AC/S (d) MBR (e) LPRO

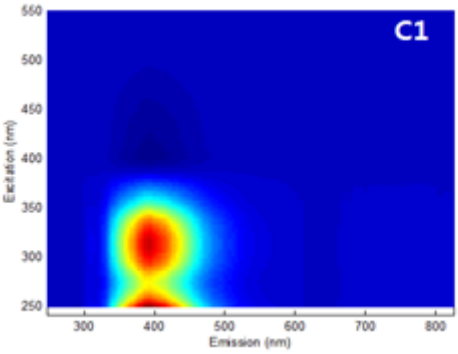
3.3 PARAFAC Components

70 EEM samples after the PRO pretreatment were analyzed. 3 components were determined through PARAFAC analysis. Data outliers were removed for the purpose of not only validating the model using the split-half method but also in order to facilitate

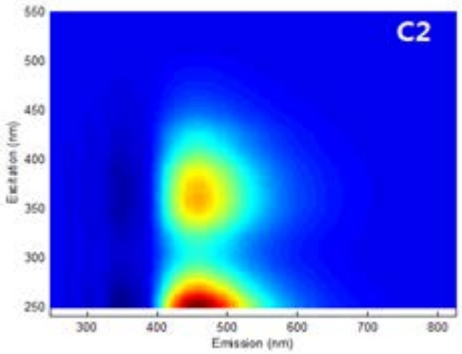
the modeling process. The model accounted for 97.3 % of the entire variance, the split-half validation match was 98.6 % and the core consistency was 94 %. Fig. 5 presents the excitation and emission wavelengths of the main peak. Table 3 presents the excitation and emission wavelengths of the main peaks of the three components, and also presents an explanation of similar components reported in other studies. A comparison of the components of this study to the components of other studies indicated that PRO pre-treated water includes humic-like fluorophores and protein-like fluorophores. A comparison of the C1 and C2 components of this study to other studies indicated that the C1 and C2 components were humic-like fluorophores that occurred terrestrially or anthropogenically. The C3 components can be explained as tryptophan-like (protein-like) fluorophores. The created model was split-half validated. For the purposes of evaluating the quantitative changes of F-EEMs of the pre-treated water of the PRO pretreatment process, PARAFAC analyses were applied to all samples and the concentration loadings of major components were analyzed.

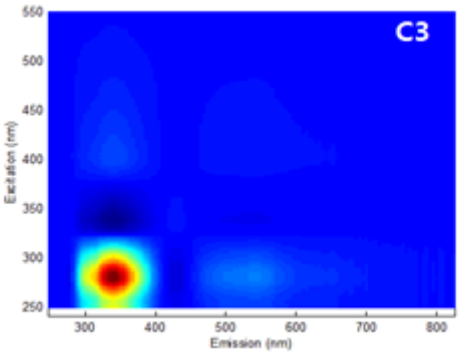
Table 3 Spectral characteristics of the three components that were identified by PARAFAC analysis in this study, and comparison with previously identified components.

Components	Ex/Em	Description	Reference
Component 1	250(325)/400	Microbial humic-like fluorescence, humic and fulvic substances	C4: (250)325/416 [26] C6: <250(320)/400 [27] G2: 250(320)/400 [28]
Component 2	250(350)/450	Terrestrial humic-like fluorescence in high nutrient and wastewater influenced environments	C1: <250(370)/464 [31] C4: 250(340)/438 [29] C4: 250(360)/440 [30] C8:<260(355)434 [30] C2: (250,340)/430 [31]
Component 3	280/330	Tryptophan-like substances(protein-like)	C4: 275/306 [32] C7: 280/344 [30] C8: 275/360 [32] C6:250(290)356 [34] peak B: 275/310 [35]



(a) Component 1





(b) Component –2 (c) Component –3

Fig. 5 Contour plots of three components identified from the PARAFAC model.

3.4 PARAFAC component changes according to each process

Fig. 6 presents the maximum fluorescence intensities (F_{max}) of the UF, AC/S, MBR and LPRO of PRO pretreatment processes. Following validation of the 3-component model, the maximum fluorescence intensities (F_{max}) of each process were calculated. F_{max} represents the relative intensities of each component. Analysis of the PRO pretreatment process feed water indicated that the humic and fulvic component, C1, had the highest F_{max} value at 14.57; the terrestrial humic-like component, C2, had an F_{max} value of 11.56; and the protein-like component, C3, had an F_{max} value of 6.95. In the UF PRO pretreatment process, the humic and fulvic component, C1, had the highest F_{max} value at

14.48; the terrestrial humic-like component, C2, had an F_{max} value of 11.63; and the tryptophan-like (protein-like) component, C3, had an F_{max} value of 6.87. There are little change of organic matter properties between UF and MBR process. In case of AC/S process, the humic and fulvic component, C1, had an F_{max} value at 0.64; the terrestrial humic-like component, C2, had an F_{max} value of 0.66; and the protein-like component, C3, had an F_{max} value of 5.05. C1 and C2 components were almost removed completely in AC/S and LPRO processes, whereas protein-like components were removed comparatively less than the C1 and C2 components. However, without prior knowledge of each component, their relative concentrations could not be properly explained, and thus they were compared to the LC-OCD analysis results [24, 37].

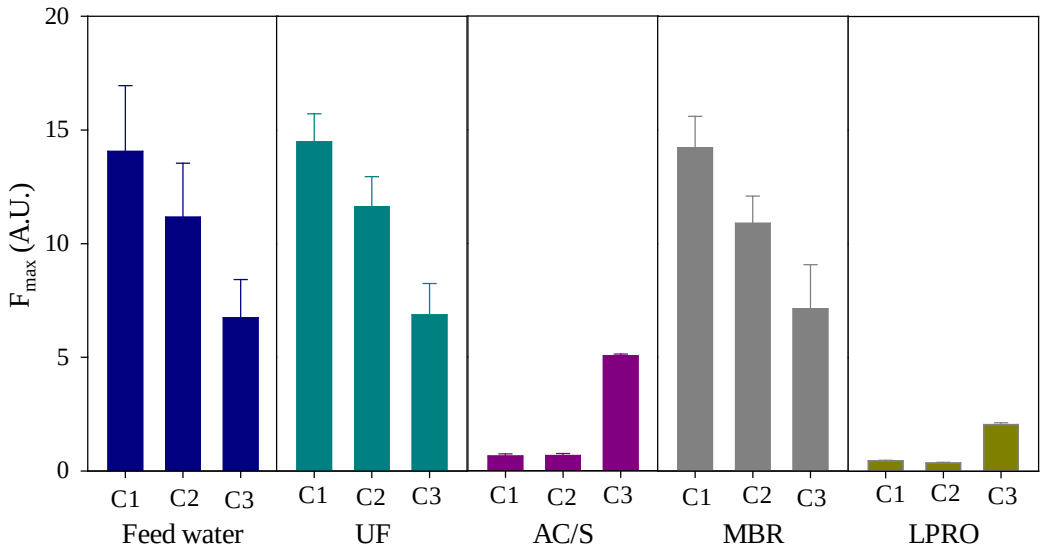


Fig. 6 Maximum fluorescence intensities (F_{max}) of PARAFAC components across UF-, AC/S, MBR and LPRO.

3.5 Liquid chromatography with organic carbon detection (LC-OCD)

The DOM chromatogram measured by LC-OCD represents characteristics of molecular weight distribution in samples. The first peak involves a series of biopolymer peak with organic colloid and protein, consisting of more than 20,000 g/mol of molecular weight. The second and third peaks represent humic materials and building blocks (polycarboxylic acid), which show a range of molecular weight from ~1,000 g/mol to 350~500 g/mol, respectively. The fourth peak has organic acid of low molecular weight as its main component. The fifth also has low molecular weight of neutrals and amphiphilic species (amino acid, alcohol, aldehyde, ketone, and others) with less than 350 g/mol as the main components. In this study, all samples were analyzed as having TOC of approximately 2 mg/L. Table 4 presents the DOC percentages of each substance of the samples.

Table 4 Percentage (%) and concentration (mg/L) of DOC for each substance of the samples.

Fractions	Feed water	UF	AC/S	MBR	LPRO
Humics	26.7(0.59)	24.8(0.53)	-	24.9(0.58)	-
Building Blocks	26.3(0.58)	29.0(0.62)	1.4(0.013)	26.2(0.61)	-
LMW acids	-	-	0.8(0.007)	-	0.8(0.002)
Neutrals	34.4(0.76)	41.1(0.89)	96.4(0.89)	42.2(0.99)	98.7(0.35)
Biopolymers	9.3(0.21)	5.1(0.11)	1.4(0.013)	6.7(0.16)	0.5(0.002)

The chromatogram of the secondary wastewater effluent used as feed water of the PRO pretreatment process indicated that neutrals constituted the highest portion of total DOC

at 34.4 %, humic substances constituted 26.7 %, building blocks constituted 26.3 %, and biopolymers constituted 9.3 %. The chromatogram of the PRO pretreatment UF process indicated that humic substances constituted 24.8 % of total DOC, building blocks constituted 29.0 %, neutrals constituted 41.1 %, and biopolymers constituted 5.1 %. As indicated in Fig. 7, the PRO membrane fouling substances were understood to be humic substances, building blocks, neutrals and biopolymers. In the UF process, humic substances and biopolymers were slightly removed, whereas building blocks and neutrals stayed at almost the same levels as in the feed water. The chromatogram of the DMF process indicated that most of the substances (96.4 %) were LMW neutrals, and that humic substances and building blocks were removed almost completely.

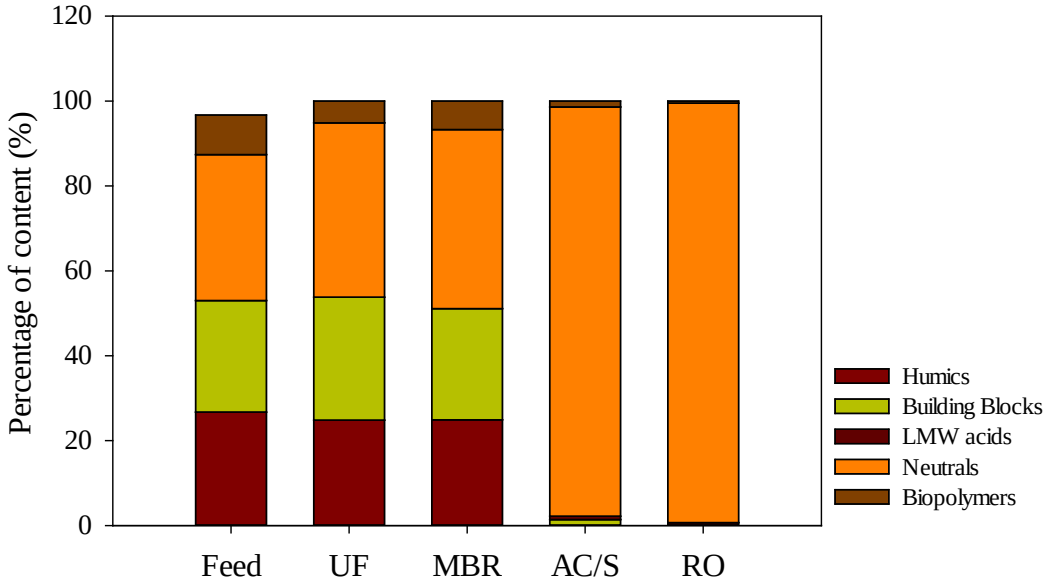


Fig. 7 LC-OCD chromatograms of the feed water, UF, MBR, AC/S, LPRO

3.6 Correlations

PRO pretreatment samples were used to determine correlation coefficients. Fig. 8 presents the results of a correlation analysis of the three PARAFAC components against SUVA, and F_{max}. The definition of SUVA is; SUVA=100×[UV254(cm^{-1})] /[DOC(mg/L)]. Units are m^{-1}/mg/L. The atomicity of DOC could be explained with SUVA. SUVA is the absorbance of ultraviolet light in a water sample at a 254 nm wavelength that is normalized for DOC concentration. The aromatic character of DOC could be explained with SUVA. C1 can be explained humic and fulvic substances, C2 can be explained relatively lower molecular weight and aromaticity AND C3 can be explained tryptophan-like (protein-like) substances. The C1 components can be correlated with SUVA (R^2=0.63). The C2 components can be correlated with SUVA (R^2=0.61). Both of which showed the existence of significant correlations ($p < 0.01$). But, C3 was negatively correlated with SUVA (R^2=0.52). Through this, it was judged that F_{max} values could be used as an online monitoring tool to characterize organic matters in water.

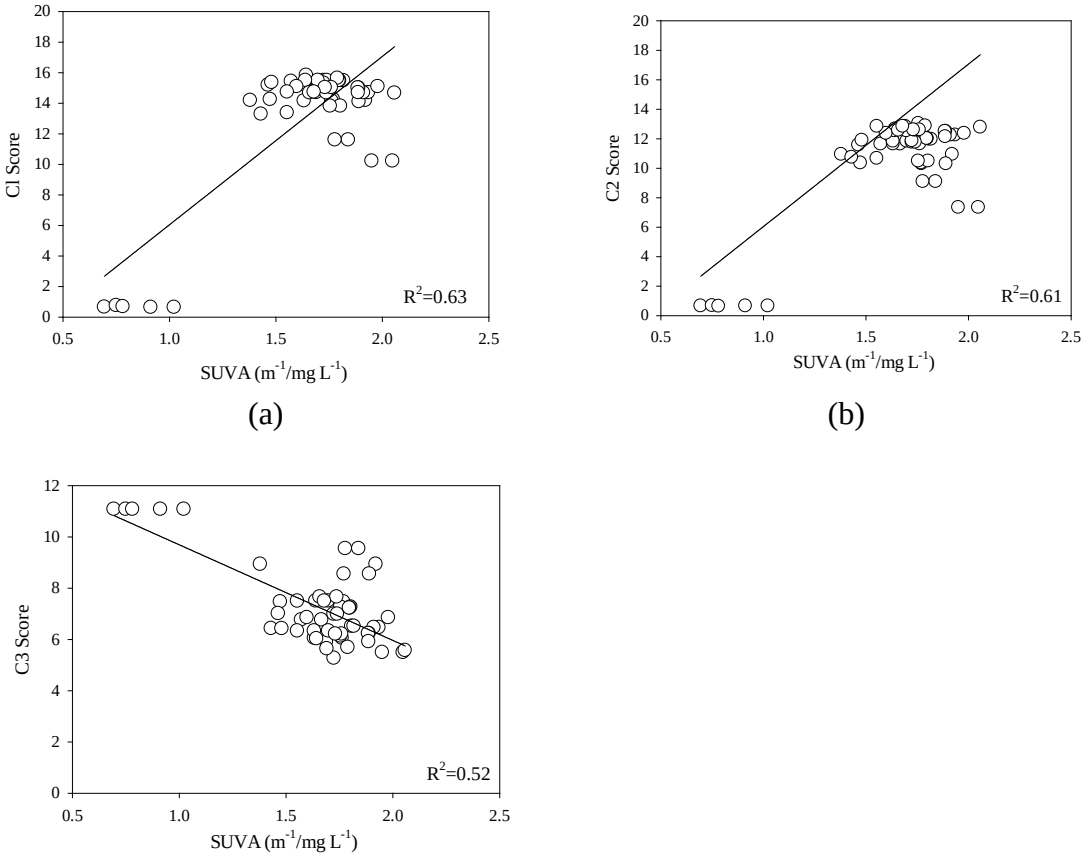


Fig. 8 Regressions between SUVA and (a) F_{max} of humic and fulvic-like component C1 and (b) F_{max} of humic-like component C2 (C) F_{max} of protein-like component C3.

4. Conclusions

The following conclusions were reached through performing this study, which was based on the results of a property analysis of organic matter that affects PRO process membrane fouling found by undertaking F-EEM, PARAFAC, and LC-OCD analysis of PRO pretreatment process water samples.

1) There was an extremely high correlation between PRO power densities and feed

water organic matter.

2) The results of fluorescence EEM analysis to analyze the properties of organic matter in wastewater effluent indicated the existence of a tryptophan-like (protein-like) peak, a characteristic property of an aromatic protein, and the existence of fulvic and humic peak.

3) Given that flux reduction occurred less in the PRO measurement results of AC/S filtered water than UF-treated water, a process that removes fulvic and humic peaks, factors that produce fouling in the PRO process, needs to be prioritized. Also, for processes that can reduce foulants more effectively than AC/S processes, pretreatment technologies that can affect biodegradable low molecular structure substances having protein-like (tryptophan) peaks need to be considered.

4) Using the database acquired from EEM measurements to perform PARAFAC modeling, 3 major peaks indicating humic and fulvic components, terrestrial humic-like components, and protein-like (tryptophan) components could be identified. Using these findings, major peak changes of the PRO pretreatment processes could be analyzed.

5) LC-OCD analysis results indicated that the main foulants of PRO membrane were understood to be humic substances, building blocks, neutrals and biopolymers.

6) EEM-PARAFAC modeling and LC-OCD analysis methods can be used to find useful tool to monitor the effect of organic matter foulant on the PRO membrane.

References

[1] N. Ghaffour, T.M. Missimer and G.L. Amy, Technical review and evaluation of the economics of water desalination: Current and future challenges for better water supply sustainability, Desalination 309 (2013) 197–207.

[2] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: Principles, applications, and recent developments, J. Membr. Sci. 281 (2006) 70–87.

[3] S. Loeb, Large-scale power production by pressure-retarded osmosis, using river water and sea water passing through spiral modules, Desalination 143 (2002) 115–122.

[4] M. Kurihara, M. Hanakawa, Mega-ton Water System: Japanese national research and development project on seawater desalination and wastewater reclamation, Desalination 308(2) (2012) 131–137.

[5] A. Tanioka, Preface to the special issue on “Pressure Retarded Osmosis in Megaton Water System Project”, Desalination, 389 (2016) 15–17.

[6] H. Sakai, 2015, Energy Recovery by PRO Systems JDA/ Megaton Project/PRO System, IDA conference, APDA & JDA Joint Forum.

[7] R.K. Henderson, N. Subhi, A. Antony, S.J. Khan, K.R. Murphy, G.L. Leslie, V. Chen, R.M. Stuetz, P. Le-Clech, Evaluation of effluent organic matter fouling in ultrafiltration treatment using advanced organic characterisation techniques, J. Membr. Sci. 328 (2011) 50–59.

[8] Tian, Jia-yu, Ernst, Mathias, Cui, Fuyi, Jekel, Martin, Correlation of relevant membrane foulants with UF membrane fouling in different waters, Water Res., 47 (2013) 1218–1228.

[9] L. Fan, T. Nguyen, F.A. Roddick, J.L. Hariis, Low-pressure membrane filtration of secondary effluent in water reuse: pre-treatment for fouling reduction, J. Membr. Sci. 320 (2008) 135–142.

[10] J. Chen, E.J. LeBoeuf, S. Dai, B. Gu, Fluorescence spectroscopic studies of natural organic matter fractions, Chemosphere, 50(5) (2003) 639–647.

[11] S.S. Kavurmaci, N.C. Birben, A. Tomruk, M. Bekbolet, Characterization of organic matter in natural waters by EEM fluorescence properties, DWT 57 (2016) 2428–2436.

[12] T. Persson, M. Wedborg, Multivariate evaluation of the fluorescence of aquatic organic matter, Anal. Chim. Acta. 434(2) (2001) 179–192.

[13] C.A. Stedman, S. Markager, R. Bro, Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy, Mar., Chem. 82 (2003) 239–254.

[14] R.H. Peris, C. Halle, H. Budman, C. Moresoli, S. Peldszus, P.M. Huck, R.L. Legge, Identifying fouling events in a membrane-based drinking water treatment process using principal component analysis of fluorescence excitation-emission matrices, Water Res. 44 (2010) 185–194.

[15] H. Yu, F. Qu, H. Chang, S. Chao, X.L.G. Aou, H. Liang, Understanding ultrafiltration membrane fouling by soluble microbial product and effluent organic matter using fluorescence excitation-emission matrix coupled with parallel factor analysis, Int. Biodeterior. & Biodegrad. 102 (2015) 56–63.

[16] M. Bieroza, A. Baker, J. Bridgeman, Exploratory analysis of excitation-emission matrix fluorescence spectra with self organizing maps as a basis for determination of organic matter removal efficiency at water treatment works, J. Geoephys. Res. (2009b) 114.

[17] S.A. Baghoth, S.K. Sharma, G.L. Amy, Tracking natural organic matter (NOM) in a drinking water treatment plant using fluorescence excitation-emission matrices and PARAFAC, Water Res. 45 (2011) 797–809.

[18] K.R. Murphy, K.D. Butler, R.G.M. Spencer, C.A. Stedmon, J.R. Boehme, G.R. Aiken, Measurement of dissolved organic matter fluorescence in aquatic environments: an inter-laboratory comparison, Environ. Sci. Technol. 44 (2010) 9405–9412.

[19] T. Larsson, M.D. Wedborg, Turner Correction of inner-filter effect in fluorescence excitation-emission matrix spectrometry using Raman scatter, Analytica. Chimica. Acta. 583 (2007) 357–363.

[20] A.J. Lawaetz, C.A. Stedmon, Fluorescence intensity calibration using the Raman Scatter peak of water, Appl. Spectrosc. 63 (2009) 936–940.

[21] C.A. Stedmon, R. Bro, Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial, Limnol. Oceanogr. Meth. 6(2008) 572–579.

[22] R. Bro, PARAFAC, Tutorial and applications, Chemom. Intell. Lab. Syst. 38 (1997) 149–171.

[23] H. Yu, F. Qu, H. Liang, Z.S. Han, J. Ma, S. Shao, H. Chang, G. Li, Understanding ultrafiltration membrane fouling by extracellular organic matter of Microcystis aeruginosa using fluorescence excitation–emission matrix coupled with parallel factor analysis, Desalination 337 (2014) 67–75.

[24] A. Achilli, T.Y. Cath, A.E. Childress, M. Elimelech, Power generation with pressure retarded osmosis: An experimental and theoretical investigation, J. Membr. Sci. 343 (2009) 42–52.

[25] J.A. Leenheer, J.P. Croue, Characterizing aquatic dissolved organic matter, Environmental Science & Technology 37 (2003) 18a–26a.

[26] C.A. Stedmon, S. Markager, Resolving the variability in dissolved organic matter fluorescence in a temperate estuary and its catchment using PARAFAC analysis, Limnol. Oceanogr. 50(2) (2005a) 686–697.

[27] K.R. Murphy, A. Hambly, S. Singh, R.K. Henderson, A. Baker, R. Stuetz, S. J. Khan, Organic matter fluorescence in municipal water recycling schemes: toward a unified PARAFAC model, Environ. Sci. Technol. 45 (2011) 2909–2916.

[28] H. Xu, H. Cai, G. Yu, H. Jiang Insights into extracellular polymeric substances of cyanobacterium Microcystis aeruginosa using fractionation procedure and parallel factor analysis, Water Res. 47 (2013) 2005–2014.

[29] K.R. Murphy, C.A. Stedmon, T.D. Waite, G.M. Ruiz, Distinguishing between terrestrial and autochthonous organic matter sources in marine environments using fluorescence spectroscopy, Mar. Chem. 108(1-2) (2008) 40–58.

[30] G.H. Yu, P. J. He, L.M. Shao, Novel insights into sludge dewaterability by fluorescence excitation–emission matrix combined with parallel factor analysis, Water Res. 44 (2010) 797–806.

[31] C.A. Stedmon, S. Markager, Tracing the production and degradation of autochthonous fractions of dissolved organic matter using fluorescence analysis, Limnol. Oceanogr. 50(5) (2005b) 1415–1426.

[32] R.M. Cory, D.M. McKnight, Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. Environ, Sci. Technol. 39 (2005) 8142–8149.

[33] P. Kowalczuk, W.J. Cooper, M.J. Durako, A.E. Kahn, M. Gonsior, H. Young, Characterization of dissolved organic matter fluorescence in the South Atlantic Bight with use of PARAFAC model : Relationships between fluorescence and its components, absorption coefficients and organic carbon concentrations, Mar. Chem. 118 (2010) 22–36.

[34] P.G. Coble, Characterization of marine and terrestrial DOM in seawater using excitation emission matrix spectroscopy, Mar. Chem. 51 (1996) 325–346.

[35] S.A. Baghoth, M. Dignum, A. Grefte, J. Kroesbergen, G.L. Amy, Characterization of NOM in a drinking water treatment process train with no disinfectant residual, Water Sci. Technol.: Water Supply 9(4) (2009) 379–386.

5. Acknowledgements

This research was supported by a grant (code 17IFIP-B065893-05) from the Industrial Facilities & Infrastructure Research Program funded by the Ministry of Land, Infrastructure and Transport of the Korean government.