



Research Paper

Feasibility of membrane distillation process for potable water reuse: A barrier for dissolved organic matters and pharmaceuticals

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ABSTRACT

In this study, the feasibility of the membrane distillation (MD) process as a wastewater reclamation system for potable reuse was investigated. The flux was stably maintained at about 20 L/m²h (LMH) at ΔT 30 °C, compared to higher flux at ΔT 50 °C, which showed a rapid decrease in the flux due to severe fouling. MD produced excellent quality of potable water satisfied the drinking water standards of Korea from effluent of sewage treatment plant (ESTP). The fractions of the hydrophobic OC (HOC) and chromatographic DOC (CDOC) from LC-OCD analysis was firstly suggested to understand different organic transport during the MD process. The transport of organic matters across the MD membrane mitigated at low operation temperature and the transported organics in all the tested waters were mostly volatile low molecular weight organics, aromatic amino acids. All of thirteen selected pharmaceuticals were completely removed by MD, regardless of their properties. In order to retard the membrane fouling of the MD process, coagulation and filtration pre-treatments were applied. The pre-treatment process coupled MD process could successfully remove impurities including NH₄-N without severe membrane fouling. Moreover, coagulation pretreatment reduced transport of ammonia due to decrease in pH.

1. Introduction

Many countries and regions around the world face freshwater shortages due to population growth, industrialization, urbanization, water contamination, and climate change. (Kummu et al., 2016; Angelakis and Gikas, 2014; Scruggs and Thomson, 2017). To address water shortage problems, many countries are increasingly considering innovative water management strategies, including potable water reuse, which is the process of using treated wastewater for drinking water. The Orange County Water District in Southern California has operated Water Factory 21 (WF21), which employed RO-based advanced treatment processes to produce high quality reclaimed wastewater for direct injection to the drinking water aquifers since 1977 (Mills and Watson, 1994). Since 2008, the Groundwater Replenishment System (GWRS) has replaced WF21 to produce 265,000 m³/d of highly purified water using RO technology, and expanded its production to 490,000 m³/d in the

future (Markus, 2009). In Singapore, the Public Utilities Board (PUB) provides a total of 532,000 m³/d (about 30% of the Singapore's total water demand) from 4 NEWater plants and plans to increase to meet up to 55% of total water demand by 2060 (Lee and Tan, 2016). The most important potable reuse project in Australia is the Groundwater Replenishment Scheme (GWRS) operated by Water Corporation of Western Australia. The GWRS is designed to recharge important drinking water aquifers for the city of Perth. The GWRS currently has the capacity to recycle around 28,000,000 m³ of water per year. It is proposed that by 2060, the scheme could recycle 115,000,000 m³ per year (Khan and Anderson, 2018). In addition, several potable reuse projects has been also spreading all over the world (Van Houtte and Verbaudhede, 2013; Burgess et al., 2015; Rodriguez et al., 2009; Lazarova et al., 2001).

Reverse osmosis (RO) is currently being widely used in advanced wastewater reclamation systems for potable reuse, based on the

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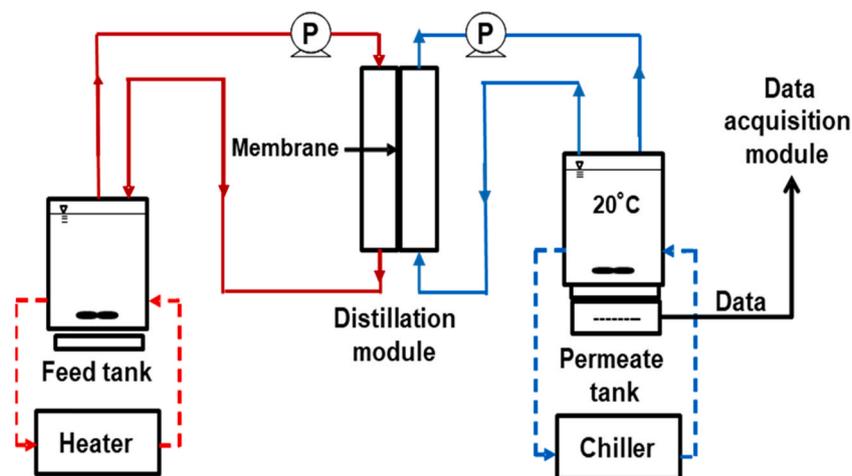


Fig. 1. Schematic diagram of the direct contact membrane distillation test system including the test module.

development of various pre-and post-treatment processes for RO, and RO's ability to produce high quality deionized water (Gündoğdu et al., 2019; Racar et al., 2017; Meng et al., 2018; Pype et al., 2016; Vourch et al., 2008). RO provides excellent treatment for a range of constituents, but it has issues of high energy consumption and membrane fouling. Furthermore, advanced wastewater reclamation systems for portable reuse have to be the critical need to provide quality assurance with respect to pathogens and micropollutants. However, emerging contaminants, especially low-molecular weight neutrally-charged compounds such as 1,4-dioxane and N-nitrosodimethylamine (NDMA) are frequently detected in RO permeate (Fujioka et al., 2012; Drewes et al., 2005; Wintgens et al., 2005). Therefore, it needs to be further addressed through process innovation and novel membrane process development.

Among the various candidate approaches, membrane distillation (MD) has attracted a great deal of attention, because of its low fouling potential and potential ability to use low-grade heat sources, such as solar power, geothermal energy or waste heat (Zhou et al., 2018; Chafidz et al., 2016; Guillen-Burrieza et al., 2014; Qtaishat and Banat, 2013; Sarbatly and Chiam, 2013; González et al., 2017). MD process is a hybrid membrane process that utilizes thermal energy. When a temperature difference across the membrane is maintained, vapor formation in the feed, transportation across the hydrophobic and porous (0.1–1 μm pore size) membrane, and condensation in the permeate occurs simultaneously. As a result, water vapor is transported across the membrane and non-volatile contents are rejected, theoretically at 100% (He et al., 2011; Camacho et al., 2013).

Recently, researchers have reported the transport of dissolved organics, which have the ability to deteriorate the quality of permeate water across MD membranes, from various water sources such as wastewater and seawater (Kim et al., 2015; Naidu et al., 2015a; Nguyen et al., 2017). Moreover, the variations in organic matter characteristics during the MD operation for wastewater reuse has not been studied yet.

In addition, studies have been conducted on fouling of the MD membrane (Wu et al., 2018; Tow et al., 2018; Warsinger et al., 2017; Tan et al., 2016; Gryta, 2008). Membrane fouling reduces the efficiency of the membrane distillation process and promotes membrane wetting. For this reason, there have been studies to alleviate the occurrence of membrane fouling using pretreatments such as coagulation, precision filtration, acidification and degasification (Cho et al., 2018; Sanmartino et al., 2017; Peng et al., 2015; Wang et al., 2008). However, no case study has been conducted to evaluate a necessity of the pre-treatment for MD process treating wastewater containing low salts and high organic matter.

The purpose of this study is to evaluate the feasibility of the MD process as a wastewater reclamation system for portable reuse and especially as a barrier for dissolved organic matters and emerging

contaminants. The MD performance of flux and removal rates for impurities including dissolved organic matter in effluent of sewage treatment plant (ESTP) was evaluated under two different feed temperature conditions through comparing with influent of water purification plant (IWPP). Dissolved organic matter transport across the MD membrane was analyzed using advanced organic matter characterization tools such as LC-OCD and F-EEM. The fate of selected pharmaceuticals was also investigated. A secondary purpose was to investigate the decline in flux produced by membrane fouling and the retardation of fouling by pre-treatment processes.

2. Materials and methods

2.1. Feed water and pharmaceuticals

In this study, effluent of sewage treatment plant (ESTP) in Korea was used as the feed water of the MD process, and influent of water purification plant (IWPP) in Korea was also used for comparison. All water samples were collected in September, while ESTP samples for the pre-treatment tests of the MD process were collected in November.

Thirteen pharmaceuticals (gemfibrozil, diclofenac, bezafibrate, ibuprofen, fenoprofen, naproxen, ketoprofen, clofibric acid, carbamazepine, phenacetin, acetaminophen, pentoxifylline, and caffeine) were spiked into the feed water at 2 $\mu\text{g}/\text{L}$. The physicochemical properties of selected pharmaceuticals are shown in Table S1. All pharmaceuticals in analytical grade were obtained from Sigma-Aldrich Korea (Gyeonggi-Do, Korea).

2.2. Experimental

2.2.1. Membrane

The MD experiments were carried out using a flat sheet type of hydrophobic PTFE membrane (FGLP 29325, Millipore, USA). The membrane was selected due to its high flux in a previous study (Kim et al., 2015). The specifications of the tested MD membrane are listed in Table S2.

2.2.2. MD module and operation

In this study, a direct contact membrane distillation configuration was used. The experiments were carried out at lab-scale with an effective membrane area of 0.0021 m^2 (3 cm \times 7 cm). The heights of the module channels on the feed and permeate sides were all 4 mm and the MD module was operated in counter current mode. The temperatures of the feed and permeate were 50 or 70, and 20 $^{\circ}\text{C}$, respectively. When the temperature difference between the feed and permeate water was 30 $^{\circ}\text{C}$, it was expressed as ΔT 30 $^{\circ}\text{C}$ (feed: 50 $^{\circ}\text{C}$, permeate: 20 $^{\circ}\text{C}$). Also, when

the temperature difference between the feed and permeate water was 50 °C, it was expressed as ΔT 50 °C (feed: 70 °C, permeate: 20 °C). The crossflow velocity of the feed and permeate water was identically at 0.14 m/sec. To maintain constant velocities of the feed and permeate, two gear pumps (WT3000-1 JA, Longer Pump, USA) were used. The volumes of the initial feed water tank were the same in all the experiments, 10 L, and the feed water was constantly stirred by magnetic stirrers. The volume of the permeate water tank was initially 0.5 L and filled with deionized water. The flux of the MD membrane was measured automatically at regular intervals with an electronic balance (GF-8000, AND, Japan) connected to a laptop. A schematic diagram of the MD system including the tested module is shown in Fig. 1.

2.2.3. Pre-treatment processes for MD process

The suggested pre-treatment processes for the MD tests were as follows: 1) filtration only with a GF/C membrane (Diameter 47 mm, Whatman, UK), 2) coagulation/flocculation using 20 ppm of PAC ($[Al_2(OH)_n C_{16-n}]$, 17% as Al_2O_3 , KG Chemicals, Korea) for 1 min for rapid mixing and 30 min for slow mixing and sedimentation for 1 h, and 3) GF/C membrane filtration after the coagulation/flocculation and sedimentation under the same experimental conditions. The filtered solution, supernatant after the sedimentation and the filtered supernatant were employed for the MD tests under given experimental conditions.

2.2.4. Experimental procedures

The MD performance (water quality (removal of impurities) and water quantity (flux variation)) of the collected two water samples from ESTP and IWTP were evaluated for 60 hrs under given temperature conditions (ΔT : 30 °C and ΔT : 50 °C). In order to mitigate the flux decline during MD operation under severe fouling conditions, three different pre-treatment processes (flocculation-sedimentation, filtration and filtration followed by flocculation-sedimentation) were applied to the MD process, which was operated for 48 hrs at high temperature differences (ΔT : 50 °C) using the secondary effluent from sewage treatment plant STP. All the collected water samples were directly introduced to the feed tank of the MD system, and each of the permeate at the end of the experiment was measured for the same target components.

2.3. Analytical methods

2.3.1. Water quality

The pH and electrical conductivity of the feed and permeate water were analyzed using a pH and conductivity meter (HQ40d, Hach, USA). Chemical oxygen demand (COD), total phosphorus (T-P), and NH_4-N were analyzed using a spectrophotometer (DU 730, Beckman-Coulter, USA). UV-254 absorbance was analyzed with a UV-visible spectrophotometer (UV-2450, Shimadzu, Japan) at a wavelength of 254 nm. Turbidity was analyzed with a turbidity meter (2100Q Portable turbidimeter, Hach, USA). Analysis of the total coliform, fecal coliform and suspended solids (SS) were carried out according to standard methods (American Public Health Association, 1999). Anions (NO_3-N , NO_2-N , chloride, PO_4-P and SO_4^{2-}) and cations (Ca, Mg, Fe, K, Na and Mn) were analyzed by ion chromatography (ICS-1000, Dionex, USA) and by ICP-OES (730 Series, Agilent, USA), respectively. Total organic carbon (TOC), dissolved organic carbon (DOC) and T-N were analyzed by the NPOC (Non-Purgeable Organic Carbon) method, using a TOC, T-N Analyzer (TOC-L, TNM-L, Shimadzu, Japan).

2.3.2. Dissolved organic matter characterization

In order to determine the organic characteristics of the feed and permeate in the MD process, two advanced organic matter characterization tools were employed. Fluorescence excitation emission matrix (F-EEM) was used to investigate fluorescent dissolved organic matter using a quartz cuvette (Hellma, USA) with F-EEM (LS50B, Perkin Elmer,

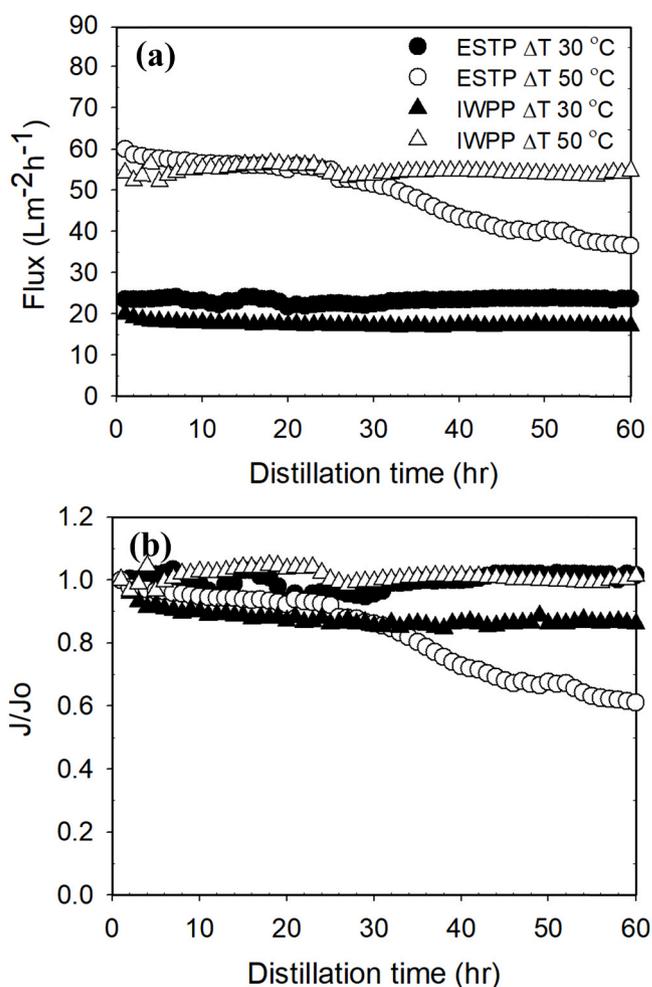


Fig. 2. Variations in the flux of the MD using ESTP and IWPP: (a) flux and (b) J/J_o .

USA). The wavelength was measured using excitation wavelengths ranging from 280 nm to 600 nm in 0.5 nm units and from 200 nm to 400 nm in 10 nm units. The humic-like (humic and fulvic) and amino acid-like (tyrosine and tryptophan) peaks could be detected in the following Ex and Em wavelengths (S1). In order to characterize the organic components based on the size of the organics, liquid chromatograph organic carbon detector (LC-OCD) (DOC-LABOR, Karlsruhe, Germany) was used to separate dissolved organic matter into biopolymers (> 20 kDa), humic substances (1–20 kDa), building blocks (300–500 Da), low molecular weight (LMW) acids (< 350 Da), and LMW neutrals (< 350 Da) according to their retention time sequence. The UV absorbance of DOC was measured with a 254 nm wavelength detector (WellChrom fixed wavelength detector K-200, Knauer, Germany). To prevent dilution by the increased volume of permeate water, the results of DOC concentration were converted to total mass (μg).

2.3.3. Pharmaceuticals

Samples for pharmaceutical measurements were collected in glass bottles and were shipped to TZW-DVGW Technologiezentrum Wasser (Karlsruhe, Germany) by international express delivery within one day of sampling. Cartridges filled with Bakerbon styrene-divinylbenzene (SDB-1, 200 mg) were used for enrichment of selected pharmaceuticals (Mallinckrodt Baker, The Netherlands), and solid phase extraction (SPE) was performed using an autotrace workstation (Caliper Life Sciences GmbH, Germany). High-performance liquid chromatography-electrospray ionization tandem mass spectrometry (HPLC-ESI-MS-MS) analyses were performed on an HPLC system 1100 (Agilent

Table 1

EDS analysis for the pristine, and tested membranes of ESTP and IWPP after 60 h of MD operation at ΔT 50 °C (Atomic %).

Elements (Atomic %)	Pristine	ESTP	IWPP
C	25.4	43.1	47.2
O		41.7	37.3
F	74.6	–	–
Al		1.4	4.0
Si		2.7	7.0
S		–	0.4
Ca		8.1	0.8

Technologies, Germany), equipped with an API 2000 triple quadrupole mass spectrometer (PE Sciex, Germany), using ESI under atmospheric pressure. The quantification limit was 20 ng/L for the thirteen pharmaceutical compounds selected in this study. Further details regarding the method can be found elsewhere (Sacher et al., 2008).

2.3.4. Membrane foulant analysis by SEM and EDS

The polytetrafluoroethylene (PTFE) membranes used in the experiments were stored and dried in a petri dish. Field emission scanning electron microscopy (FESEM; S-4200, Hitachi, JAPAN) was used to deliver the characteristics of membrane surface and energy dispersive spectrometry (EDS) attached to the SEM equipment was used for qualitative analysis of the fouling factor.

3. Results and discussion

3.1. Feasibility test of the MD process for portable reuse

3.1.1. Flux variations and fouling

The fluxes of the membrane distillation processes are shown in Fig. 2. The MD fluxes were maintained at 20 ± 3 L/m²h (LMH) at ΔT 30 °C for all the tested water samples. The initial flux at ΔT 50 °C was about 2.5 times higher than that at ΔT 30 °C. The MD flux for the IWPP was also maintained at 55 ± 6 LMH at ΔT 50 °C. However, the MD fluxes decreased to 35 ± 6 LMH with time for the ESTP at ΔT 50 °C. Generally, the flux of the MD process increased when the feed temperature increased due to increased vapor pressure at high temperature (Deshmukh and Elimelech, 2017).

In order to understand the MD fouling, SEM-EDS analyses were conducted for the ESTP and IWPP samples. As shown in Fig. S1, severe foulants were observed at the tested membrane surfaces compared to the pristine membrane. The degree of fouling was severer in ESTP than in IWPP. Dominant foulant of ESTP seems organic matter including cell debris but that of IWPP was inorganic colloidal particles. As shown in Fig. S1 (b) and (c), scalants were observed in both the ESTP and IWPP contacted membrane. The EDS results for the pristine and fouled membranes are listed in Table 1. The Ca, C and O elements increased significantly in both the fouled membranes, which can form CaCO₃ scaling. Other studies have also reported CaCO₃ scaling on MD membranes for wastewater and seawater desalination (Gryta, 2012; Laqbaqbi et al., 2017). Al and Si were also detected on both the fouled MD membranes but their level was higher for the IWPP than ESTP, which indicate that particulate fouling can also exist on the membrane surface. It indicated that particulate fouling induced by terrigenous colloidal particles in the feed water also occurred for the IWPP, in addition to CaCO₃ scaling. Severe membrane fouling occurred when the feed temperature was high (Fard et al., 2016) due to the reverse solubility of CaCO₃ scalant (Gryta, 2008) and protein denaturation by heat (Hou et al., 2017).

3.1.2. Water qualities for the feed and permeate of the MD test

The water qualities of the feed waters are shown in Table S3. ESTP showed the higher concentrations of almost all of the components except particulate. ESTP showed low particulates (suspended solids (SS):

Table 2

Results of LC-OCD analysis for the feed and permeate.

		Mass (μ g)			Removal rate (%)	
		Feed	Permeate		ΔT 30	ΔT 50
			ΔT 30	ΔT 50		
ESTP	HOC	1,446	166	214	88.5	85.2
	CDOC	16,314	307	1,120	98.1	93.1
	Bio-polymers	372	8	23	98.0	93.9
	Humic substances	5,442	–	–	100.0	100.0
	Building blocks	5,538	16	18	99.7	99.7
IWPP	LMW neutrals	4,950	272	1,072	94.5	78.3
	LMW acids	–	12	10	–	–
	HOC	12,816	293	744	97.7	94.2
	CDOC	11,586	259	728	97.8	93.7
	Bio-polymers	882	–	37	100.0	95.8
IWPP	Humic substances	8,928	–	–	100.0	100.0
	Building blocks	522	10	48	98.0	90.8
	LMW neutrals	1,488	175	423	88.3	71.6
	LMW acids	–	72	220	–	–

3.8 mg/L) but the increased amounts of organics (4.1 mg/L as TOC) compared to IWPP. It also showed higher values for the T-N (12.6 mg/L), T-P (0.4 mg/L) and for the measured numbers of microbes compared with the values in IWPP. While IWPP showed only higher in particulate (SS: 4.2 mg/L, turbidity: 3.4 NTU) compared to ESTP.

Most of the components in the permeates under the given experimental conditions were completely removed by the MD process except DOC and T-N (Table S4). Almost all of water quality parameters including microbes of pathogenic indicator were almost completely removed by the MD process except NH₄-N and organics. The highest electric conductivity of the MD permeate was low as 6.0 μ S/cm for all the MD tests. Detailed results for organic transport will be discussed in next chapter.

As shown in Table S4, the T-N is mainly composed of ammonia, nitrate and nitrite. The nitrate and nitrite in the feed solutions were completely removed by the MD process under the given experimental conditions, however, ammonia was transported across the MD membrane because ammonia is volatile at pH (6.63–7.85) in the feed waters (El-Bourawi et al., 2006). However, the level of transferred ammonia concentrations in all the MD permeates were also within the drinking water standards of Korea. Based on the treated water quality, it was concluded that the MD process can provide qualified water which is safe to be used for the drinking water in Korea.

3.2. Dissolved organic matters across the MD membrane

3.2.1. Dissolved organic matter characteristics

In order to understand dissolved organic matter transport across the MD membrane, advanced organic matter characterization tools were used. Table 2 shows the dissolved organic substances in the feed and permeate measured by LC-OCD according to their molecular weight and temperature differences. The dissolved organic matter fractions of feed water between the ESTP and IWPP was quite different according to the characteristics of water sources. For the ESTP, the proportion of building blocks and LMW neutrals having a relatively small molecular weight (< 500 Da) was greater than that of IWPP, whereas the IWPP had a higher portion of biopolymers and humic substrates with larger molecular weight (> 500 Da). In general, nature organic matter (NOM) showed higher average molecular weights (MW) than effluent organic matter (EfOM) (Wu et al., 2020). This difference can also be seen in the humic substances diagram (HS diagram) (Fig. S2). The HS diagram plots

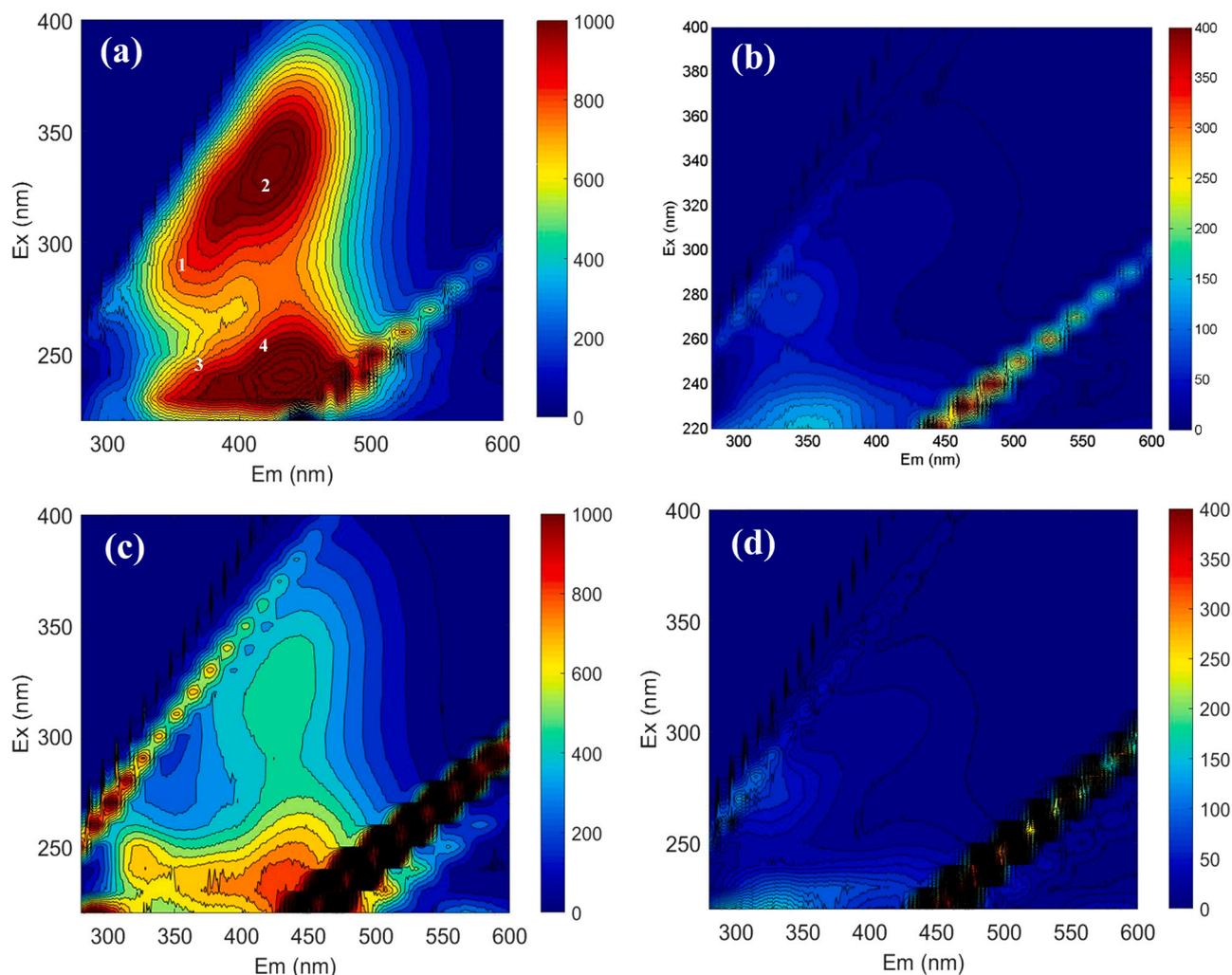


Fig. 3. Results of F-EEM analyses of feed and permeate at ΔT 50 °C (a, b: ESTP, c, d: IWPP).

the SAC/OC ratio (aromaticity) of the HS fraction against its nominal average MW (Mn-value), and gives information about the origin of HS (Huber et al., 2011). In the samples position in the HS diagram, the ESTP showed characteristics close to sewage fulvic acids (FA), on the other hand, IWPP showed characteristics close to pedogenic FA originated from surface water.

The removal rates at higher feed temperature (ΔT 50 °C) were relatively lower than those at ΔT 30 °C. The reason for the higher transport at high temperature is because the volatile substances have higher partial pressure at the higher temperature, which is the driving force in the MD process. The MD system used in this study removed > 99% of the humic substances, regardless of temperature difference (Table 2). Biopolymers and building blocks were detected in all permeates at trace levels (8–37 μg) in permeate tank (6 L), and their removal rates were in the range from 90.8% to 100%. A little fraction of biopolymers and building blocks can be volatile, and partial wetting of the MD membrane also results in organic transport at trace levels. These trends were maintained for all tested samples. However, the transportation of LMW neutrals and acids for the ESTP sample showed different trends than the IWPP sample. Only 10–12 μg of LMW acids were in the permeate of ESTP, otherwise 72–220 μg of LMW acids existed in the permeate of IWPP. However, LMW neutrals existed 272–1,072 and 175–423 μg for ESTP and IWPP, respectively. The percentages of LMW neutrals per total transported organics across the MD membranes at ΔT 50 °C were 95.7% and 58.1% for ESTP and IWPP, respectively. The ESTP samples mainly had volatile LMW neutrals, the

IWPP samples, however, had both volatile LMW neutrals and acids. Meanwhile, LMW acids were detected in the permeate, even though it was not contained in the feed water. The presence of LMW acids in the permeate is due to thermal disaggregation of humic substances. Humic substances could be thermally disaggregated to LMW organics in MD process (Naidu et al., 2015b). This thermal disaggregation of humic substances can also be seen in Fig. S3. In the LC-OCD chromatogram of the feed water, the peak corresponding to humic substances decreased, while the peaks corresponding to LMW organics (acids and neutrals) increased after heating at 70 °C. About 70% of humic substances were thermally disaggregated into building blocks, LMW acids and neutrals by heating.

In order to identify dissolved organic matter characteristics in the feed and permeate of the MD process, F-EEM analysis was conducted (Fig. 3). The dissolved organic matter characteristics of ESTP also differed from those of IWPP. In the IWPP sample, Peak 3 and 4, representing aromatic protein-like and fulvic acid-like organics were dominant. However, in ESTP, all the peaks appeared strongly. It is due to the difference in characteristics of the feed water sources, as explained in LC-OCD results. The high protein content in the dissolved organic matter is also an indication for EfOM (Huber et al., 2011). In the permeate samples, all the peaks except Peak 3 (aromatic protein-like) disappeared. This indicates that the humic acid-like and fulvic acid-like substances were completely rejected by the membranes, but volatile substances e.g. aromatic protein-like substances could pass through the membrane (Li et al., 2016).

Table 3
Removal efficiencies of selected CECs.

Compound	RO ^a	RO ^b	RO ^c	RO ^d	MD ^e
Gemfibrozil	98.8–98.9	100 ^g	98.4	96.9–100 ^f	100 ^g
Diclofenac	–	100 ^g	100 ^g	100 ^f	100 ^g
Bezafibrate	100 ^f	–	97.2	–	100 ^g
Ibuprofen	96.9–97.7	100 ^g	100 ^f	98.1–100 ^f	100 ^g
Fenoprofen	–	–	–	–	100 ^g
Naproxen	98.3–99.4	100 ^g	100 ^f	99.2–100 ^f	100 ^g
Ketoprofen	–	–	100 ^g	98.0–100 ^f	100 ^g
Clofibrac acid	–	–	73.3	100 ^f	100 ^g
Carbamazepine	–	–	99.1	94.8–99.1	100 ^g
Phenacetine	–	–	–	–	100 ^g
Acetaminophen	–	–	100 ^g	98.7–100 ^f	100 ^g
Pentoxifylline	–	90.2–100 ^g	–	–	100 ^g
Caffeine	99.5–99.9	83.3–100 ^g	–	–	100 ^g

^a Urtiaga et al., 2013

^b Snyder et al., 2007

^c Rodriguez-Mozaz et al., 2015

^d Al-Rifai et al., 2011

^e This study

^f Not detected

^g Below limit of quantification

Among the volatile organic acids in sewage, it has been reported that acetic acid included in volatile fatty acid (VFA) is the most important, and propionic, butyric and valeric acids are also abundant (75–90% of total acidity) (Tandoi et al., 2006). In this study, however, the most transported organic components were LMW neutrals and aromatic protein-like organics, as determined by LC-OCD and F-EEM, respectively. The VFA concentration could be low in the collected sample because VFA is usually formed from amino acids, sugars, and fatty acids during the fermentation in anaerobic digestion. The LMW neutrals were classified as alcohols, aldehydes, ketones, sugars and amino acids (Huber et al., 2011). In the case of the F-EEM, the aromatic protein-like substances were mainly amino acids. Therefore, the results of LC-OCD and F-EEM indicate that transported organic substances across the MD membrane could be aromatic protein-like and low molecular weight neutrals.

In the case of the river water, it was reported that 6% of the DOC were volatile and non-volatile fatty acids, and 0.05% of the DOC were free amino acids (Holland and Turekian, 2004). In this study, the DOC in the feed and permeate of IWPP were 2.5 and 0.6–0.8 mg/L (Tables S2 and S3). It showed that 24–32% of DOC were volatile organics. It was also reported that amino acids and sugars were high as 10–20% and 4–24% of DOC in lake where has autochthonous input by photosynthesis in shallow waters, respectively (Holland and Turekian, 2004).

3.2.2. HOC/CDOC ratio

The fractions of the hydrophobic OC (HOC) and chromatographic DOC (CDOC) were different depending on the feed and permeate solutions. The HOC/CDOC ratios of the feed solutions were 0.09 and 1.11 for the ESTP and IWPP, respectively. The feed solution collected from the cleaner surface water source (IWPP) and the concentrations of the HOC and CDOC were identical. Due to the relatively strong degradation of HOC (proteins) than CDOC (humics) by the microbial activity under environmental conditions (Park et al., 2018), the HOC/CDOC ratios of the ESTP samples could be lower than that of the IWPP sample.

HOC/CDOC ratios of the IWPP permeates were also different than those of the ESTP. HOC/CDOC ratios were maintained for the feed and permeate under different feed temperature conditions, which showed that the fractions of volatile substances in HOC and CDOC were similar. However, HOC/CDOC ratios from the ESTP and IWPP permeates increased from 0.19 to 0.54 and from 1.02 to 1.13 at ΔT 50 °C and at ΔT 30 °C, respectively. Based on the results of HOC/CDOC ratios of ESTP permeates, it could be concluded that the volatile fractions of CDOC in the ESTP are comparatively higher than that in the IWPP. Moreover,

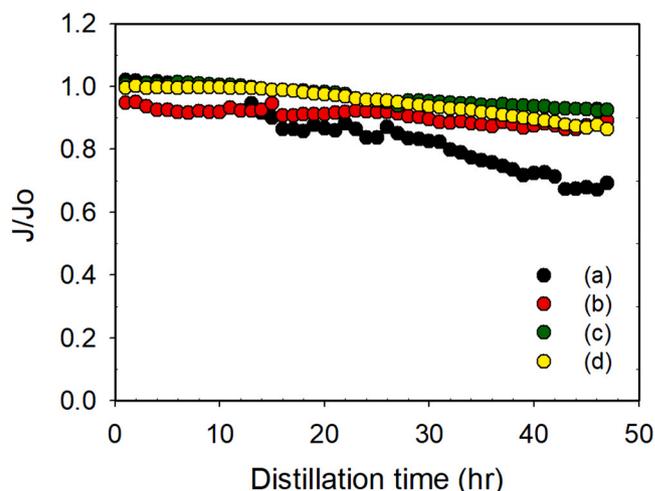


Fig. 4. Variations in flux according to the pre-treatment methods for ESTP (J/J0). ((a) Raw water, (b) GF/C filtering, (c) Flocculation and sedimentation and (d) GF/C filtering after the flocculation and sedimentation).

HOC/CDOC fraction decreased due to the increased transport of organics in CDOC, especially LMW neutrals. The ESTP sample had a relatively higher volatile organic fraction in HOC than the IWPP. Therefore, it can be concluded that the organic transport was enhanced at high feed temperature and the transportation of the organics across the MD membrane was affected by the organic characteristics of the water sources.

3.3. Pharmaceuticals rejection

All of 13 pharmaceuticals estimated were completely removed by MD (Table 3) and their concentration in the permeate were below the limit of quantification (0.02 µg/L). However, based on the references (Table 3), RO treatment could not achieve a complete removal for some pharmaceuticals depending on the compounds, though most of them were effectively removed. In particular, clofibrac acid and caffeine showed a relatively low removal efficiency of less than 90%. Wijekoon et al. (2014) reported that the transport of pharmaceuticals from the feed to the distillate solution depends on their volatility and pharmaceuticals with pK_H value higher than 9 (low volatility) were well removed by the MD process. As shown in Table S1, pK_H value were higher than 9 for all the pharmaceuticals selected in this study, except phenacetine. However, the removal efficiency of phenacetine was also 100%. It might be related with hydrophobicity of phenacetine. Unlike ionic pharmaceuticals that are classified their hydrophobicity based on log D, neutral pharmaceuticals are classified based on log K_{ow} value, in general. Phenacetine has a relatively high value of log K_{ow} (Table S1) with carbamazepine, which is classified as hydrophobic-neutral among neutral pharmaceuticals. High hydrophobicity of phenacetine tends to adsorb well to the hydrophobic membrane. The adsorption to the membrane might contribute to the removal in the short term and to the loss of pharmaceuticals. Naidu et al., (2017) reported a high loss of carbamazepine in MD processes. These hydrophobic compounds' losses caused by adsorption along with evaporation, in the long term, could contribute to retard the accumulation of compounds in the feed. Further study should be performed to characterize loss of pharmaceuticals including adsorption and evaporation in the long term. Taking all of the results together, the MD were successfully removed pharmaceuticals, which suggested that the MD can be a promising option to manage micropollutants for portable water reuse.

Table 4

EDS analysis results of the pretreatment test using the ESTP (Atomic %). ((A) Raw water, (B) GF/C filtering, (C) Flocculation and sedimentation, (D) GF/C filtering after flocculation and sedimentation).

Elements (Atomic %)	(A)	(B)	(C)	(D)
C	65.5	72.2	13.5	12.1
O	30.3	25.5	56.8	48.0
F	–	–	–	9.98
Al	0.4	0.3	23.9	24.2
Si	0.6	0.8	1.3	0.8
S	0.4	0.5	3.6	2.8
Ca	1.1	0.7	–	–

3.4. MD performance according to pre-treatments

3.4.1. Retardation of membrane fouling by the pre-treatment process

The MD fluxes for various pre-treatment processes are illustrated in Fig. 4. All the MD fluxes decreased with time, however, the reduction in flux due to fouling was retarded in the MD membrane processes when pre-treated feed solutions ($J/J_0 = 0.7$ for ESTP) were used. The significant flux decline ($J/J_0 = 0.7$) in the ESTP at 48 hr was mitigated when all of the pre-treatment methods were applied to the MD process ($J/J_0 = 0.87$ – 0.9). However, the decrease in flux patterns was almost similar among the three pre-treated cases.

In order to investigate foulants on the MD membrane surface, SEM analysis was also conducted for all the tested membranes. As shown in Fig. S4, it seems that the fouling on the membrane surface decreased in the order of coagulation + filtration > coagulation > filtration > no pre-treatment cases. The EDS result showed variations in the foulant on the membrane surface, as listed in Table 4. The EDS results were classified into two groups by coagulation process. The raw ESTP and GF/C filtered solutions showed almost the same element compositions on the fouled membrane surface. However, as shown in Fig. S4, clear flux retardation occurred when the GF/C filter was applied as a pre-treatment process. This can be explained, since the removal of particulates can retard the MD fouling. When the coagulant was applied, the element compositions on the membrane surface were also similar. 23.9–24.2% Al elements were detected from the attached coagulant on the membrane surface. Moreover, for the coagulation with GF/C filtration case, the element F was detected. Generally, EDS can detect element compositions on the membrane surface to a depth of 1–2 μm . Therefore, the detection of F at the membrane surface indicates that pristine PVDF membrane under the fouling layer was detected. It can be concluded that a thin fouling layer is formed when coagulation was applied with the GF/C filtration pre-treatment process.

3.4.2. Removal of impurities in MD process with pre-treatment

The water qualities of the feed and permeate waters after MD process with or without pre-treatments are shown in Tables S5 and S6. When the GF/C filter was employed ((B) and (D)), the turbidity and SS were significantly reduced from 1.6 to 0.2 NTU and from 3.5 to 4.5 mg/L to zero, respectively. Therefore, particulate fouling can be mitigated by

using simple GF/C filtration. By using the coagulation process ((C) and (D)), DOC was decreased from 4.8 to 3.4 mg/L.

When the coagulant was injected, the pH of the feed water was lowered from 6.6 to 4.7 (Table S5), which could limit ammonia transport across the membrane (Tun et al., 2016). Therefore, the $\text{NH}_3\text{-N}$ concentrations in the feed were decreased (Table S5) and no ammonia was transported across the MD membrane when coagulation was applied as the pre-treatment. (Table S6). Due to the coagulant addition, the electronic conductivities and Cl concentrations in the feeds significantly increased from 500 to 1,400 and from 70 to 400 (Table S5), respectively. However, the additional ions were successfully removed by the MD process.

The removed ions in the permeate by the MD process for water reuse could be provided by mixing the water sources such as groundwater or tap water. The mixing with other water sources with desalinated water could guarantee enough drinking water with a lower price and no more post treatment is required to increase alkalinity of the desalinated water.

3.4.3. Effect of the pre-treatment to the transport of dissolved organic matters

The LC-OCD result also supports the decrease in dissolved organic matters by the coagulation process, as shown in Table 5. Because filtration with a 0.45 μm pore filter is required for the all samples for the LC-OCD analysis, we were unable to determine the organic variation by filtration. The mass of HOC decreased from 11,400 μg to 5,280 μg and the concentration of CDOC decreased from 34,890 μg to 25,820 μg . In addition, the masses of bio-polymers and humic substances also decreased from 2,260 and 14,100 μg to 1,220 and 3,210 μg , respectively. On the other hand, the mass of building blocks and LMW neutrals increased from 10,390 and 8,130 μg to 11,010 and 10,380 μg , respectively. It could be considered that humic substrates were disaggregated into building blocks and LMW neutrals by the change in pH according to coagulant injection. And the mass of LMW acids was not detected in the feed water, but was detected in the permeate, as in the LC-OCD analysis for different water sources (Table 2). The organic mass (HOC: 11,400 μg , CDOC: 34,890 μg) of ESTP sampled in November was increased compared to that (HOC: 1,146 μg , CDOC: 16,314 μg) from September. However, when the mass (μg) of each organic was converted to concentration, the organic concentrations of HOC and CDOC from September and November were 1.1 and 3.5 mg/L and 0.1 and 1.6 mg/L, respectively. These variations can occur due to variations in wastewater input and seasonal variations of STP. In the permeate, when the coagulation with filtration was applied as the pre-treatment, the LMW neutrals were relatively lower (6.3–10%) in mass (8,717 μg) than those in other water samples (9,306–9,687 μg). This indicates that filtration can also remove small portions of organics as flocs.

The F-EEM results of the feed, pre-treated with coagulation and permeate water are shown in Fig. 5. The F-EEM result of the feed water from samples in November (Fig. 5(a)) was similar to those from September (Fig. 3(a)). As shown in Fig. 5(b), the intensity of all the peaks for the pretreated water decreased due to removal by coagulation, comparing to the feed water. The decreases of peak intensity for Peak 1,

Table 5

Mass of the dissolved organic fractions in the feed and permeate from the results of LC-OCD for the ESTP samples according to the pre-treatment methods.

	Mass (μg)						
	Feed		Permeate				
	Filtration	Coagulation with filtration	Raw	Filtration	Coagulation	Coagulation with filtration	
HOC	11,400	5,280	–	–	–	–	
CDOC	34,890	25,820	9,438	9,670	9,854	8,853	
Bio-polymers	2,260	1,220	–	–	–	–	
Humic substances	14,100	3,210	–	–	–	–	
Building blocks	10,390	11,010	49	66	49	33	
LMW neutrals	8,130	10,380	9,306	9,425	9,687	8,717	
LMW acids	–	–	84	179	119	103	

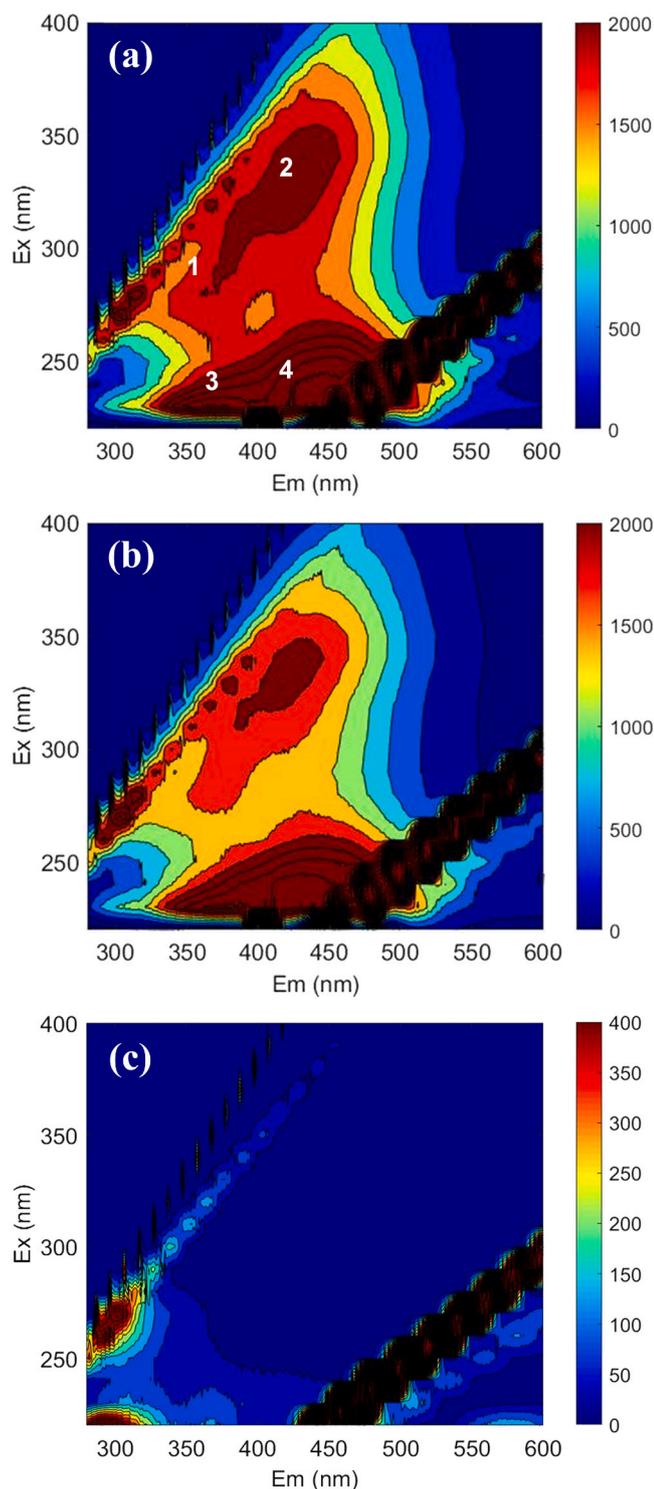


Fig. 5. Results of F-EEM analysis for (a) raw ESTP, (b) ESTP pretreated with flocculation and sedimentation, and (c) permeate.

2 and 3 were similar (about 15%) but that for Peak 4 (fulvic acid-like) was lower (9%) than the others. Coagulation is not very efficient in dissolved organic matter, especially in fulvic acids because they are hydrophilic and too low in molecular weight (Huber et al., 2011). In the pre-treated permeate sample (Fig. 5(c)), two strong peaks were detected. Compared to the F-EEM result from the permeate of ESTP (Fig. 3(b)), an additional strong peak was detected at the excitation wavelength (Ex) of about 220 at 240 nm, and a slight peak shift was observed near the emission wavelength (Em) of about 280–330 in the pre-treated permeate

sample. The substances in Peak 1 and 3 were classified as protein-like containing tryptophan and tyrosine, respectively (Westerhoff et al., 2003).

4. Conclusions

It is very important to maintain reliability in treated water quality and to maintain a treated water quality higher than a certain level when using effluent of STP as a potable water sources. The results of this study demonstrated that MD can be employed as an advanced wastewater reclamation system for portable water reuse. The results of this study also showed the following:

- (1) MD achieved the quality level required for drinking water, and produced excellent quality treated water from ESTP. When the feed water temperature was 50 °C and the flux was about 20 LMH, the system operated stably.
- (2) Most of dissolved organic matter was successfully rejected and only a few of LMW neutrals were primarily transported among the dissolved organic matter as determined by LC-OCD. F-EEM determined that aromatic protein-like substances appeared to produce the fluorescence intensity. These results showed that amino acids like tyrosine that are commonly found in nature are transmitted through the membrane.
- (3) All pharmaceuticals were removed so successfully that their concentrations in permeate were below the limit of quantification, regardless of their properties.
- (4) Membrane fouling occurred in various forms depending on water quality. Membrane fouling by organic matter had a greater effect than fouling by inorganic matter. Also, the higher the temperature difference, the higher the flux, but fouling caused by inorganic substances appeared to have a large effect.
- (5) The introduction of pretreatments improved the MD performance. When the both flocculation and sedimentation pretreatments were applied, the membrane fouling was successfully retarded. In addition, by injecting coagulant, the pH of the feed water was lowered, and the concentration of NH₄-N was reduced, and the fouling by organic substances was lowered.

Based on these results, MD can be applied as an advanced wastewater reclamation system for portable water reuse. The introduction of pre-treatment systems is expected to complement the performance of MD.

CRediT authorship contribution statement

Seongpil Jeong: Writing - original draft, Writing - review & editing. **Kyung Guen Song:** Conceptualization, Writing - original draft, Supervision, Writing - review & editing, Funding acquisition. **Junki Kim:** Investigation, Data curation, Visualization. **Jaewon Shin:** Investigation, Data curation, Visualization. **Sung Kyu Maeng:** Validation. **Joonhong Park:** Supervision.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2020.124499.

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