

Elsevier required licence: © <2019>.

This manuscript version is made available under the CC-BY-NC-ND 4.0 license

<http://creativecommons.org/licenses/by-nc-nd/4.0/>

The definitive publisher version is available online at

<https://www.sciencedirect.com/science/article/pii/S0959652619328793?via%3Dihub>

**The effects of naturally occurring operation factors on the removal mechanism of major
algae metabolized materials in forward osmosis process**

Sung-Ju Im^a, Ho Kyong Shon^b, In S. Kim^c, Am Jang^{a,*}

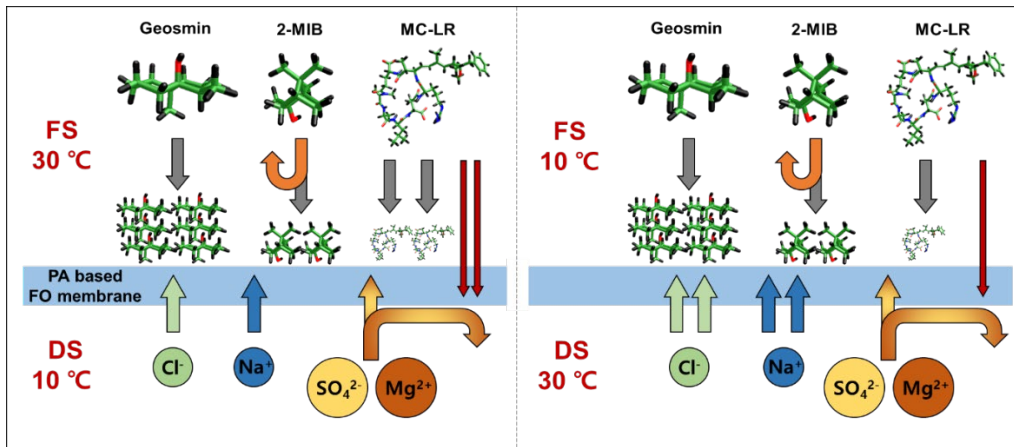
^aGraduate School of Water Resources, Sungkyunkwan University (SKKU), 2066, Seobu-ro,
Jangan-gu, Suwon-si, Gyeonggi-do 16419, Republic of Korea

^bCentre for Technology in Water and Wastewater, School of Civil and Environmental
Engineering, University of Technology Sydney, PO Box 123, 15 Broadway, Sydney, NSW,
2007, Australia

^cGlobal Desalination Research Center (GDRC), School of Earth Sciences and Environmental
Engineering, Gwangju Institute of Science and Technology, 123 Cheomdangwagi-ro, Buk-gu
Gwangju 61005, Republic of Korea

*Corresponding author: Tel.: +82-31-290-7526, Fax: +82-31-290-7549, E-mail:
amjang@skku.edu (Am Jang)

Abstract



This research investigated the removal mechanism of algae metabolized materials (geosmin, 2-methylisoborneol (2-MIB), and microcystin-leucine arginine (MC-LR)) according to the naturally occurring operation factors such as temperature (10, 20 and 30°C), transmembrane temperature (20°C: 10 vs. 30, 30 vs. 10°C) difference and valance of reverse salt flux (RSF) in forward osmosis membrane. Algae metabolized materials had high removal efficiency (94 ~ 99%) at all experimental conditions. According to the temperature difference, the absorption percentage of geosmin and 2-MIB on the FO membrane was 76, 75% and 75, 55%, respectively. However, adsorption percentage of toxin (MC-LR) materials were observed to be 11 and 85%, respectively. Temperature-dependent parameters such as water and solute viscosity & diffusivity, membrane intrinsic properties, have effects on the removal mechanism and rate. Consequently, the results from this research provide meaningful information on not only the removal of algae metabolized materials like micropollutants but also the water treatment process with consideration of the temperature conditions (temperature difference).

Keywords: Algae metabolized materials; forward osmosis; removal mechanism; transmembrane temperature.

Abbreviation

MC-LR	microcystin-leucine arginine
2-MIB	2-methylisoborneol
GS	geosmin
USEPA	United States Environmental Protection Agency
WHO	World health organization
T&O	Taste and odor
MF	micro filtration
UF	ultra-filtration
NF	nano-filtration
RO	reverse osmosis
PA	polyamide
TFC	thin film composite
FO	Forward osmosis
PS	polysulfone
PE	polyester

1. Introduction

During the algal blooming process, cyanobacteria can produce metabolized materials such as algal toxin, taste and odor (T&O) materials (**Fig. 1**). These metabolites are harmful to ecosystem, human health and life, and result in a decrease of water treatment efficiency and an increase of operation and maintenance cost. Among the algal metabolized materials, representative materials of algal toxin and T&O are microcystin-leucine arginine (MC-LR), geosmin and 2-methylisoborneol (2-MIB) respectively. MC-LR is major algal toxin formed by cyanobacteria. It remains inside the cell until cell is damaged or stressed (intracellular toxin) or lysed to the water bodies (extracellular toxin). MC-LR can act as the tumor promoter and cause cell deaths in human body because it can be attributed to their specific and irreversible inhibitions of the protein phosphatases [1, 2]. For this reason, World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) have placed MC-LR on the Drinking Water Contaminant Candidate List and recommended the concentration of MC-LR less than 1 µg/L [3]. Geosmin and 2-MIB are generated from bio-degradation and metabolism of cyanobacteria during the algal blooming. These materials are non-toxic and has no influence on the human health, however it can worsen the taste and cause the odor in the drinking water. Although there is no existing WHO regulation that regulates the standard concentration of drinking water, with the existence of T&O materials in the water with concentration higher than 10 ng/L, it is difficult to provide to end user (human). Therefore, T&O materials are managed by government as water quality observation categories (0.2 µg/L) in Republic of Korea [4-9]. For these reasons, controlling cyanobacteria metabolized materials is an emerging topic.

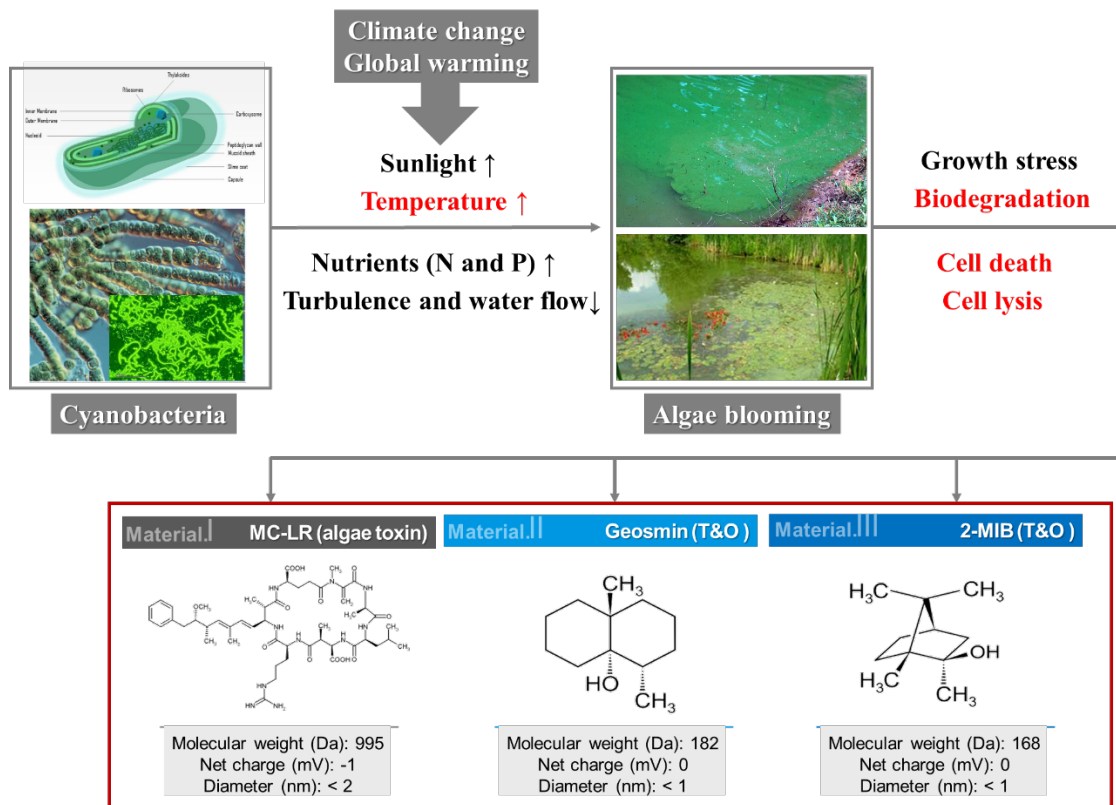


Fig. 1. Algae metabolized materials produced in water.

To treat algae metabolized materials, physicochemical processes such as coagulation/flocculation, sand filtration, activated carbon/adsorption and dual media filter, advanced oxidation processes including chlorination, ozonation, photo-fenton process and activated carbon/adsorption and oxidation hybrid process, and membrane processes such as micro filtration (MF), ultra-filtration (UF), nano-filtration (NF) and reverse osmosis (RO) have been suggested and applied [10-14]. However, these methods have some limitations to be used in drinking water production. For example, physicochemical processes require further treatment steps for removing residual metabolized materials to meet the standards. Advanced oxidation processes can also effectively treat algae metabolized materials, however,

disinfection byproducts are produced during the process by interacting with organic matters (not eco-friendly) [15, 16]. Additionally, because oxidation time and chemical dosage are directly associated with removal efficiency, high amount of chemical is needed (high operating cost and low cost-effectiveness) [4, 5, 17]. Among the processes, the MF and UF membrane technology shows relatively low rejection efficiency to algal metabolized materials. So, major limitations were technical and cost act as limit points at the same time. Therefore, it is necessary to treat the algal metabolized materials eco-friendly, simply, quickly and with low cost [4, 18, 19]. Forward osmosis (FO) process is an emerging technology in the water and wastewater treatment industries. This is driven by osmotic pressure difference between the feed (low concentration side) and the draw (high concentration side) solutions across the semi-permeable membrane. Filtration performance of FO membrane is similar with RO membrane (high rejection efficiency), but operation and maintenance cost is lower because driving force of FO is natural pressure (osmotic pressure difference) [13, 14, 20, 21]. Only few researches have been studied the treatment of algal metabolized materials by membranes [2, 4, 17-19, 22-27]. MC-LR was treated from algae blooming water using UF and NF membranes and T&O materials were removed by modified ceramic membrane.

This study applied the FO process for algal toxin and T&O materials and evaluated their performances at different temperature conditions. The effect of solution temperatures and their temperature differences were investigated because temperature is the major factor to trigger the algal blooming and temperature difference is one of inevitable parameters in FO membrane process [28]. Algae and bacterial bloom persist in water supplies that contain adequate levels of essential nutrients and water temperature between 15 to 30°C from the report of WHO guideline. In FO process, temperature and temperature difference is an important

factors due to temperature influence to mass transfer coefficient in FO process. Also, in real scale FO process face to temporal and spatial variation between feed solution and draw solution depending on the source [29]. Ultimately, study of removal mechanism of algal metabolized materials in the FO process will be able to make an effective treatment strategy, which was not suggested in the previous researches.

2. Materials and methods

2.1 Lab-scale FO experiment

This study used commercialized polyamide (PA) based thin film composite (TFC) FO membrane manufactured by Toray Chemical Korea Inc. (Seoul, Republic of Korea). PA based TFC FO membrane divided by three parts: 1) selective PA active layer, 2) interlayer formed by polysulfone (PS) and 3) porous substrate polyester (PE) support layer [30, 31]. An effective membrane area was 20.02 cm² (customized FO cell dimension: 77 mm × 26 mm). Experiment was conducted in FO mode (active layer facing feed solution). A schematic diagram of lab-scale FO system is presented in **Fig. 2**. The lab-scale FO system consists of two gear pumps (Longer Pump WT3000–1FA, China), an electric mass balance (AND GF-6000, NY, USA), and a magnetic stirrer (MISUNG SCIENTIFIC CO., LTD MS-300HS, Republic of Korea). Change in weight of draw solution was recorded every 5 min using an automatic program for obtaining the water flux. For stabilization of water permeation, water flux was calculated after first 10 min. Initial volumes of both feed solution (FS) and draw solution (DS) were 300 mL. Conductivity of feed solution was measured at predetermined time intervals by conductivity meter (Orion 4 Star, Thermo Scientific, Albany, USA) to determine reverse salt flux (RSF). The experiment was stopped after 3 hrs of operational time. To regulate the temperature of FS

and DS, chiller (CPT Inc., Republic of Korea) was connected to the FS and DS tank. Detailed operation conditions are depicted in **Table 1**.

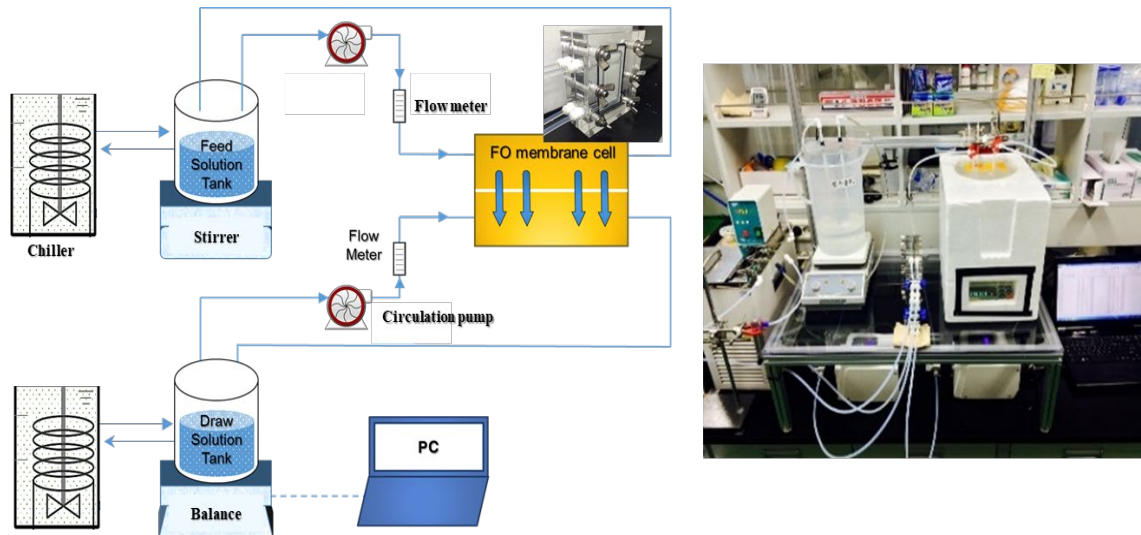


Fig. 2 Schematic diagram of lab-scale FO system.

Table 1 Operation conditions

		Value	Unit
Mode	FO mode		
Flow rate	FS and DS	600	mL/min
Temperature	FS and DS	10, 20, 30	°C
Temperature difference	FS - DS or DS - FS	20	°C
GS		3.5	mg/L
2-MIB		3.5	mg/L
MC-LR		5	µg/L

FS	DI water	10 - 30	$\mu\text{s}/\text{cm}$
DS	Synthetic seawater	48.6	ms/cm
	0.5 M NaCl solution		
Operating time		3	h

* we assume the significantly high concentration than normal concentration of the target algae metabolized materials are used in the experiment to mainly account for membrane adsorption after steady state saturation [32, 33].

According to the chemical formula (**Fig. S. 1**), the MC-LR has the carboxyl group composed of glutamic acid and methyl aspartic acid where amino group on arginine is representative hydrophilic. In addition, 3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid (ADDA) residue is indicate hydrophobic characteristic. Therefore, MC-LR is relatively negative in charge (-1) in wide range of pH values, from 3 to 12, due to the carboxyl group that gets dissociated. In more detail, $(\text{COOH})_2(\text{NH}_2^+)$ has +1 charge, $(\text{COO}^-)(\text{COOH})(\text{NH}_2^+)$ has neutral charge, $(\text{COO}^-)_2(\text{NH}_2^+)$ and $(\text{COO}^-)_2(\text{NH})$ has -1 and -2 charge, respectively [34]. Size and molecular weight of MC-LR are 3 nm and 900 - 1,100 Da, respectively [27, 35].

As shown in **Fig. S. 2**, geosmin (sesquiterpenes class) and 2-MIB (monoterpene class) are volatile materials and humans can recognize concentrations as low as 10 ng/L. Molecular weights of geosmin and 2-MIB are 182 and 168 Da, respectively. Net charge and diameter of geosmin and 2-MIB are neutral and lower than 1 nm, respectively [26, 36].

2.2 Analytical methods

2.2.1 Taste and odor (T&O) materials measured by GC/MS

2-MIB (purity: 99.5%) and geosmin (purity: >99%) standards were purchased from Wako Pure Chemical Industries, Ltd (Osaka, Japan). Liquid geosmin and crystallized 2-MIB standard chemicals were dissolved in methanol (Fisher Scientific, HP, USA). For adsorption kinetic analysis and step-feeding tests stock solution (20 mg/L) was prepared. To measure the geosmin and 2-MIB, they were extracted from FS and diluted DS in 10 mL volume of PTFE/silicone screw-cap amber glass vials. The fiber from solid-phase (micro) extraction was inserted into the vial and exposed to the headspace above the aqueous sample for 30 min in a water bath at 70°C. After the extraction, the fiber underwent GC-MS (GC: 6890N, MS: 5973 Network, Agilent Technologies, CA, USA) for thermal desorption and analysis. Helium was employed as a carrier gas at a constant column flow of 1 mL/min. The oven temperature started from 100°C. It was remained for 5 min and then increased to 280°C at 20°C/min. At 280°C it was held for 19 min.

2.2.2 Algal toxin material (MC-LR) measured by LC/MS

MC-LR in each sample was concentrated using Oasis HLB solid-phase extraction (SPE) cartridge (Waters, MA, USA). The cartridge was preconditioned with 7 mL dichloromethane and methanol (1:1, v/v), 7 mL methanol, and 7 mL Milli-Q water subsequently. The sample (200 mL) was acidified to pH 3 by adding 0.1M HCl and then loaded through the SPE cartridge at a flow rate of 2 mL/min using a vacuum pump. After loading the samples, the cartridge was eluted with 7 mL methanol followed by 7 mL dichloromethane and methanol

(1:1, v/v) at 2 mL/min. The extract was then evaporated under a gentle stream of nitrogen and reconstituted with 1 mL of methanol. After the SPE extraction, the MC-LR was analyzed by LC-MS 2020 (Shimadzu, Japan) equipped with an electrospray ionization (ESI) interface. A Phenomenex Kinetex 2.6 μm C8 column (50 \times 4.6 mm) was used as the chromatography column and was maintained at 40°C inside a column oven. The mixture of Milli-Q water buffered with 0.1% (v/v) formic acid and acetonitrile was used as mobile phase eluent at a flow rate of 0.5 mL/min. The following gradient program (in terms of the volume ratio of solvents, A:B) was used for chromatography: 0 min (90:10) \rightarrow 6 min (77:23) \rightarrow 15 min (55:45) \rightarrow 26 min (15:85) \rightarrow 35 min (90:10). High-purity nitrogen was used as both the nebulizing and drying gas at flow rates of 1.5 and 10 L/min, respectively.

2.3 Calculation

Water flux (**Eq. 1**) and RSF (**Eq. 2**) were determined by the following balance equations:

$$J_w = \frac{V_{t,2} - V_{t,1}}{At} \quad (1)$$

$$J_s = \frac{C_t V_t - C_o V_o}{At} \quad (2)$$

where, J_w : the water flux of a membrane (L/m²/h)

J_s : the RSF of a membrane (g/m²/h)

V_t : the volume of draw tank at time t

V_0 : the volume of draw tank at time 0

C_t : the concentration of the draw solute in the feed tank at time t

C_0 : the concentration of the draw solute in the feed tank at time 0

A: the membrane area (m^2)

t: operating time

The concentration of the draw solute in the feed tank was determined using predetermined calibration curve of NaCl where the conductivity was measured and converted to NaCl concentration.

Rejection efficiency was determined using the following equation **(Eq. 3)**:

$$R = \left(1 - \frac{C_p}{C_f}\right) \quad (3)$$

where, R is the rejection efficiency by a membrane (%), C_p is the concentration of the permeate at time t, and C_f is the concentration of the feed solution at time 0.

The adsorption mass on the FO membrane can be calculated as following equation **(Eq. 4)**:

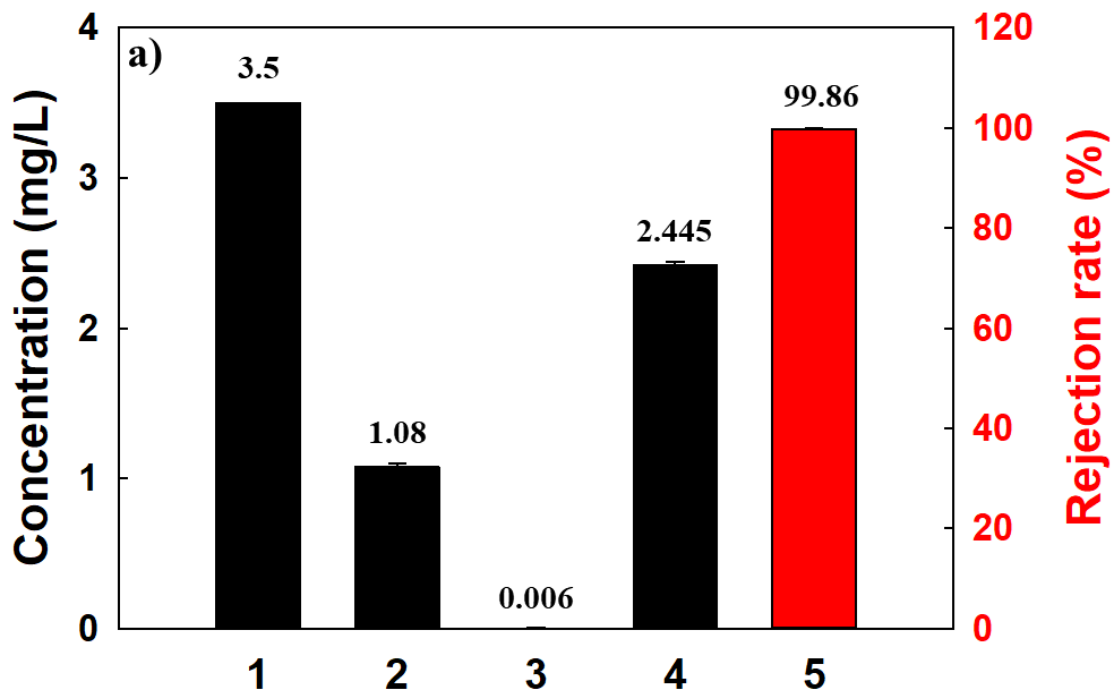
$$\text{Adsorption (ug/cm}^2\text{)} = \frac{C_{if}V_{if} - C_{ff}V_{ff} - C_{fd}V_{fd}}{A_m} \quad (4)$$

where C_{if} is the molar concentration in the initial FS, V_{if} is the volume of the initial FS. C_{ff} and V_{ff} is the molar concentration and volume in the final FS, C_{fd} and V_{fd} is the molar concentration and volume of the final FS, A_m is the effective membrane area of the FO cell.

3. Results and discussion

3.1 Rejection of algae metabolized materials

In this section, the experiments were conducted to determine the removal efficiency of algae metabolized materials using lab-scale FO process. Algae metabolized materials can be divided into two categories: One is taste and odor materials, and another one is toxin materials. In order to clarify the algae metabolized materials' removal mechanism by FO, the mass balance was made by measuring the concentration of initial FS, concentrated FS (CFS), diluted DS (DDS) and membrane surface.



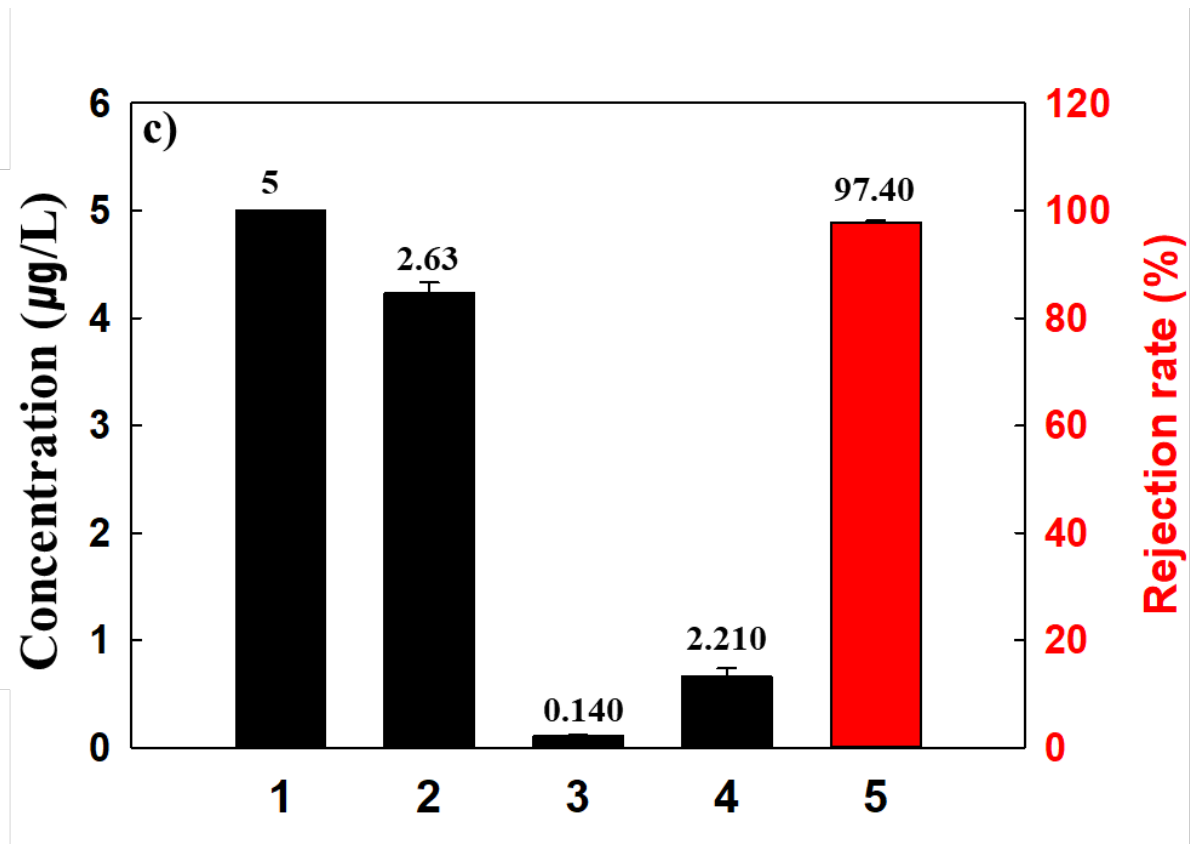
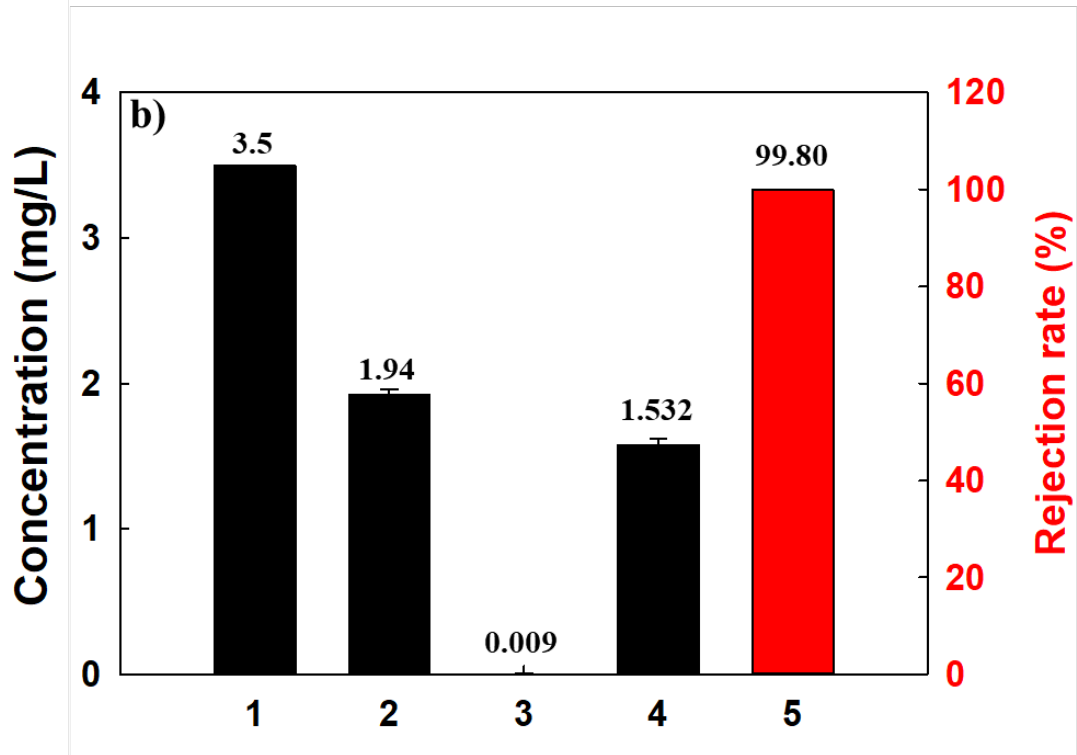


Fig. 3 Rejection of (a) geosmin, (b) 2-MIB and (c) MC-LR when Temp. of FS and DS was 20°C (1. FS; 2. CFS; 3. DDS; 4. Membrane; 5. Rejection)

Figs. 3a and **b** show the concentration of each part and rejection efficiency of the taste and odor materials in the FO process at constant temperature of 20°C. Both geosmin and 2-MIB (taste and odor materials) showed a high rejection efficiency of 99.86 ± 0.014 and 99.80 ± 0.014 %, respectively. In general, taste and odor materials are rejected by size exclusion, charge repulsion and adsorption onto the membrane [32, 34, 37]. Pore size and surface charge of PA based TFC FO membrane are around 0.42 nm and -17 mV, respectively (**S. 3**) [38]. The surface charge of taste and odor materials is nearly zero (0), and they can be approach easily approach to the membrane surface through the electro double layer on PA based TFC FO membrane and attached to the membrane surface. This means that the effect of charge repulsion to the taste and odor materials is negligible. Therefore, the adsorption onto the negatively charged membrane surface and the removal by size exclusion (geosmin and 2-MIB size is approximately 1 and 0.7 nm) are considered to be the main removal mechanisms of taste and odor materials in the FO process [26]. The geosmin concentration in FS was 3.50 mg/L but it was 1.08 ± 0.03 mg/L in CFS, and the adsorption amount on the membrane surface was 2.45 mg/L (0.122 mg/cm²). In the case of 2-MIB, the concentration of FS was also 3.50 mg/L, in the CFS it was 1.94 ± 0.02 mg/L, and the adsorption amount on the membrane surface was 1.53 mg/L (0.077 mg/cm²). Because these taste and odor materials, geosmin and 2-MIB, have different molecular structures and weights, rejection mechanism can be different between two compounds [22, 25]. The physico-chemical differences of taste and odor materials will be discuss in section 3.2. **Fig. 3c** shows the rejection efficiency of algal toxin material (MC-LR),

its concentration in FS, CFS, and DDS and on the membrane surface as well as water flux. MC-LR was also highly rejected by PA based TFC FO membrane with rejection efficiency greater than 97.4 %. PA based TFC FO membrane has relatively high removal efficiency for MC-LR, due to size exclusion, its surface charge, and fractionation. MC-LR has hydrophilic carboxyl group and hydrophobic 3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid (ADDA) residue. Therefore, MC-LR can adsorbed onto the PA based TFC FO membrane due to hydrophobic interaction since MC-LR is composed of amino acids possessing hydrophobic properties in aqueous media, especially the highly hydrophobic ADDA residue. In addition, surface charge of MC-LR is relatively negative (-1 mV) in wide range of pH values (from 3 to 12) due to the dissociation of carboxyl group and the size and molecular weight of MC-LR is 3 nm and 900 - 1,100 Da respectively [24, 27]. The adsorption amount on the surface of the membrane was about 44.5% ($2.21 \mu\text{g/L}$, $0.110 \mu\text{g/cm}^2$) of the FS concentration ($5 \mu\text{g/L}$). This suggests that the main removal mechanism of MC-LR is the adsorption, where hydrophobic interaction and hydrogen bonding are played key roles in the adsorption. Several previous researches suggested that electrostatic repulsion is the major removal mechanism in membrane processes such as UF, NF, RO and FO. Even though MC-LR is negatively charged in most pH levels, it is only weakly charged in solution phase. This means that, in the case of MC-LR removal, the effects of electrostatic repulsion is negligible. Additional considerations of rejection are surface architectural characteristics of the membrane (pore size, porosity, roughness, tortuosity, and thickness) and the FO performance, such as water flux and RSF. Water flux and RSF value depend on driving force called by osmotic pressure difference. High water flux means that large amount water molecules can pass through the FO membrane. At that time, contaminant also move to feed solution to draw solution side. Some previous studies prove the effects of water flux and RSF on rejection and fouling rate on

FO membrane [31, 39]. The results indicated that PA based TFC FO membrane is a safe barrier for MC-LR. As mentioned above, physico-chemical characteristics, morphology of membrane surface and operation conditions are the major factors that influence the removal of algae metabolized materials.

3.2 Effect of temperature

In the FO process, operation conditions are the dominant influential factors that determine water flux and RSF [20, 39]. Among the operation conditions, temperature is a governing factor for mass transfer coefficient and membrane properties such as structural parameters, water permeability, salt permeability, and concentration polarization (CP) effects [30, 31, 40]. In practical aspect, because FO used two water resources at different sides, temporal and spatial variations of temperature difference can affect the membrane performance significantly [22]. Therefore, in this section, in relation to one of the influencing factors, the algae metabolized materials removal efficiency was investigated according to the temperature difference of FS and DS and the transmembrane temperature difference.

3.2.1 Performance with temperature difference

Water flux and RSF values of PA based TFC FO membrane were significantly affected by FS and DS temperatures (**Fig. 4**). When the temperatures of FS and DS are equally increased from 10 to 30 °C, both water flux and RSF also increased. Water flux and RSF increased from 11.7 ± 6.3 to 27.9 ± 3.5 LMH and from 38.1 ± 0.32 to 55.5 ± 0.77 GMH, respectively. This may be due to the effects of temperature-dependent parameters, such as water permeability coefficient,

mass transfer coefficient, osmotic pressure, viscosity and solute diffusivity. These factors enhance the water permeability and mass transfer coefficient and reduce viscosity, resulting in increased water flux and RSF values. These results are in a good agreement with the results from the previous studies related to temperatures in membrane field [12, 40]. With these results, our research team could hypothesize that the membrane performance changes with respect to temperature due to the changes in membrane intrinsic properties of the solution that greatly depend on the temperature. Therefore, changes in physicochemical properties and membrane performance are expected to affect the removal mechanism of the algae metabolized materials [41].

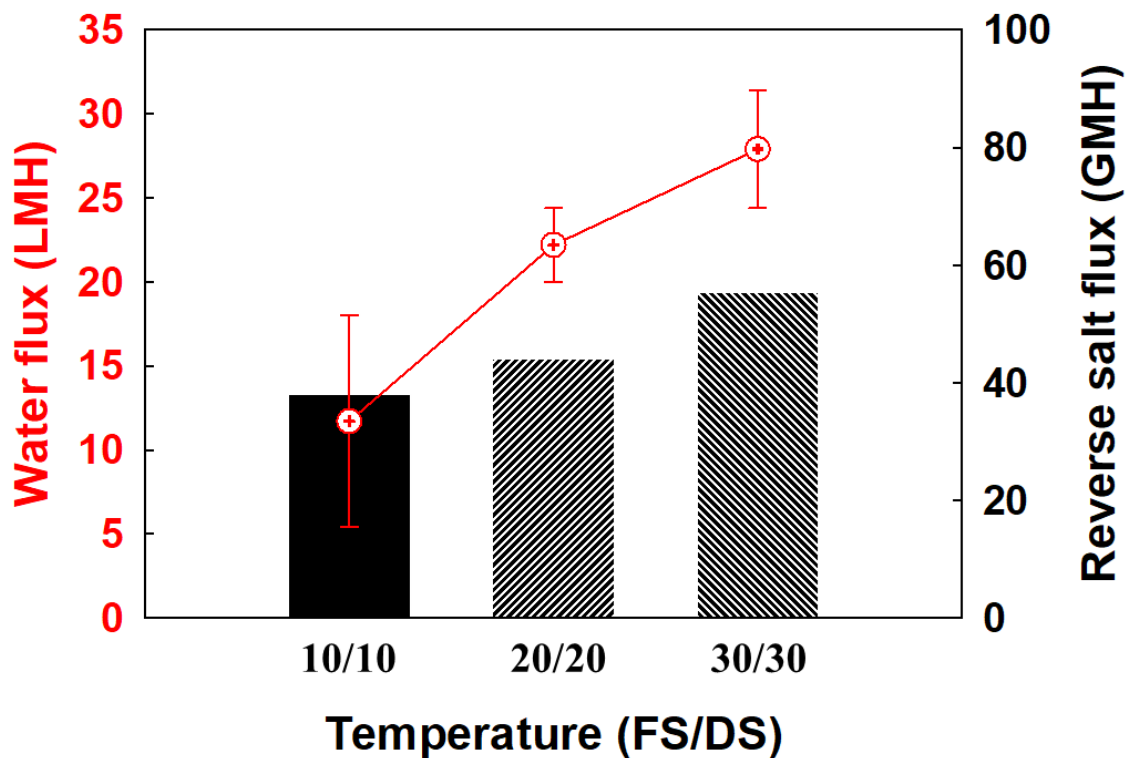


Fig. 4 Water flux and RSF of FO process depending on temperature

3.2.2 Rejection with temperature difference

Overall, the rejection efficiencies of taste and odor, and toxin materials generated from the algal metabolism were higher than 99% when the temperature of FS and DS were equally changed (**Table 2**). However, the major rejection mechanism of MC-LR, geosmin and 2-MIB were different. Depending on the physico-chemical properties of the materials, the amounts of materials in CFS and on membrane surface were different. For example, when the both solutions were at 10°C the geosmin had 1.07 ± 0.04 , and 2.42 mg/L (0.119 mg/cm^2) on the CFS and membrane surface, respectively. The 2-MIB had 1.92 ± 0.04 , and 1.53 mg/L (0.076 mg/cm^2) on the CFS and membrane surface, respectively and 4.24 ± 0.10 and 0.58 mg/L (0.029 mg/cm^2) on the CFS and membrane surface of the MC-LR. Based on these results, the main removal mechanism can be determined: whether it is size exclusion and adsorption, or the electrostatic repulsion. Between the algae metabolized materials and the FO membrane, depending on the functional group of the algae metabolized materials and the FO membrane surface, electrostatic repulsion and attraction occurs. A repulsion is a force that pushes two objects together, and attraction is a force that pulls two objects together. These concept was directly-opposed ideas. Therefore, we assume that the electrostatic repulsion was not act in adsorption phenomenon. As shown in **Table 2**, we analyzed algae metabolized materials in FS, CFS and DDS, and then calculated to adsorption rate. Depending on the concentration of the algae metabolized materials in each solution and the amount of adsorption on the surface of the FO membrane, the dominant action of the algae metabolized materials can be explained. Interestingly, as the temperature of FS and DS increased, the MC-LR concentration adsorbed or deposited on the membrane surface gradually increased. These results may be due to MC-LR, which was removed by electrostatic repulsion, was removed by size exclusion and adsorption. On the other

hand, in the case of the neutrally charged geosmin and 2-MIB, there was no change in the removal mechanism with the temperature change. MC-LR has a relatively negative surface charge in the solution phase. Therefore, it is expected that an increase in water permeability (driving force) with an increasing temperature on both sides offset the electrostatic repulsion force between the membrane surface and the MC-LR. However, geosmin and 2-MIB, which have relatively small size and molecular weight compared to MC-LR and have neutral charge, did not have a significant effect on the removal mechanism when temperatures on both sides were changed. Furthermore, geosmin has a lower solubility (0.051 g/L) and a higher k_{ow} (3.70) value compared to 2-MIB (0.45 g/L and 3.13, respectively). In other words, geosmin is more hydrophobic than 2-MIB, and therefore it has a very high possibility of hydrophobic-hydrophobic interaction with the membrane surface. Another reason can be explained by the chemical structures of algal metabolized materials. As the temperature of FS and DS equally increased except for 2-MIB, the adsorption and deposition rate on the membrane surface were increased: geosmin (68 – 70 – 75%), 2-MIB (44 – 44 – 42%) and MC-LR (12 – 44 – 76%) as shown in **Table 2**. MC-LR had a dramatic increase in the rate of adsorption and deposition on the membrane surface when the temperature in both sides were increased due to the molecular structural characteristics of MC-LR. For MC-LR, two negative monovalent and one positive monovalent are generated in the water phase (negative charge, -1). In other words, MC-LR has high possibility of attraction intermolecular force. However, both geosmin and 2-MIB have a neutral surface charge in water phase, and the intermolecular force between them is relatively lower than MC-LR. In addition, van der Waals force is acting between nonpolar and nonpolar materials, which is relatively weaker than the intermolecular force of polar materials. Therefore, MC-LR with high molecular weight and polarity has strong attraction between each molecules due to the increased water mobility with increased temperature in both sides. This resulted in

an increased ratio between adsorbed and deposited molecules. However, geosmin and 2-MIB are adsorbed and deposited on the membrane surface due to the van der Waals forces and the physicochemical properties of the membrane surface. In this case, a relatively low attraction force occurs between the materials as compared with the MC-LR. In addition, the difference in adsorption and deposition rate between geosmin and 2-MIB can be explained by the molecular structure of each substance. Geosmin has a flat molecular structure (without side chains) compared to 2-MIB (Fig. S.2). Therefore, geosmin has higher possibility of deposition/adsorption on the membrane surface than 2-MIB (side chain). Thus, the adsorption and deposition rates of geosmin and 2-MIB are different due to the molecular structural/morphological characteristics and the surface morphological characteristics of the membrane surface.

Table 2 Algae metabolized materials concentration of each solution at different temperature (FS=DS)

Temp. (FS/DS)	Type	FS (mg)	CFS (mg)	DDS (mg)	Membrane (mg) (mg/cm ²)	Deposition & Adsorption (%)	Rejection rate (%)
10/10	GS	3.5	1.07±0.04	0.007±0.002	2.423	68	99.87
					0.119		
	2-MIB	3.5	1.92±0.04	0.005±0.003	1.533	44	99.80
					0.077		

	MC-				0.576		
	LR	5	4.24±0.10	0.107±0.013	0.029	12	98.45
	GS	3.5	1.08±0.03	0.006±0.001	2.445	70	99.86
					0.122		
20/20	2-MIB	3.5	1.94±0.02	0.009±0.001	1.532	44	99.80
					0.077		
	MC-				2.210		
	LR	5	2.63±0.03	0.140±0.01	0.110	44	97.40
	GS	3.5	0.88±0.02	0.007±0.001	2.634	75	99.82
					0.132		
30/30	2-MIB	3.5	1.99±0.05	0.007±0.001	1.452	42	99.77
					0.723		
	MC-				3.800		
	LR	5	1.01±0.03	0.260±0.04	0.190	76	95.70

* FS: feed solution, CFS: concentrated feed solution, DDS: diluted draw solution.

3.2.3 Performance with transmembrane temperature difference

Generally, FO process required two difference water resources. One is low concentration sources, another is high concentration sources. Usually, low concentration sources were fed from wastewater, water reservoir, and lake. However, high concentration water resources were fed from sea water. Climate change affects all regions around the world. In particular summer and winter season can affect to the temperature of water resources. Average range of seawater

temperature was 10 to 15°C except for the Mediterranean ocean and region of the equator. In addition, since the occurrence of algae bloom at 25-30°C, transmembrane temperature experiment was essential.

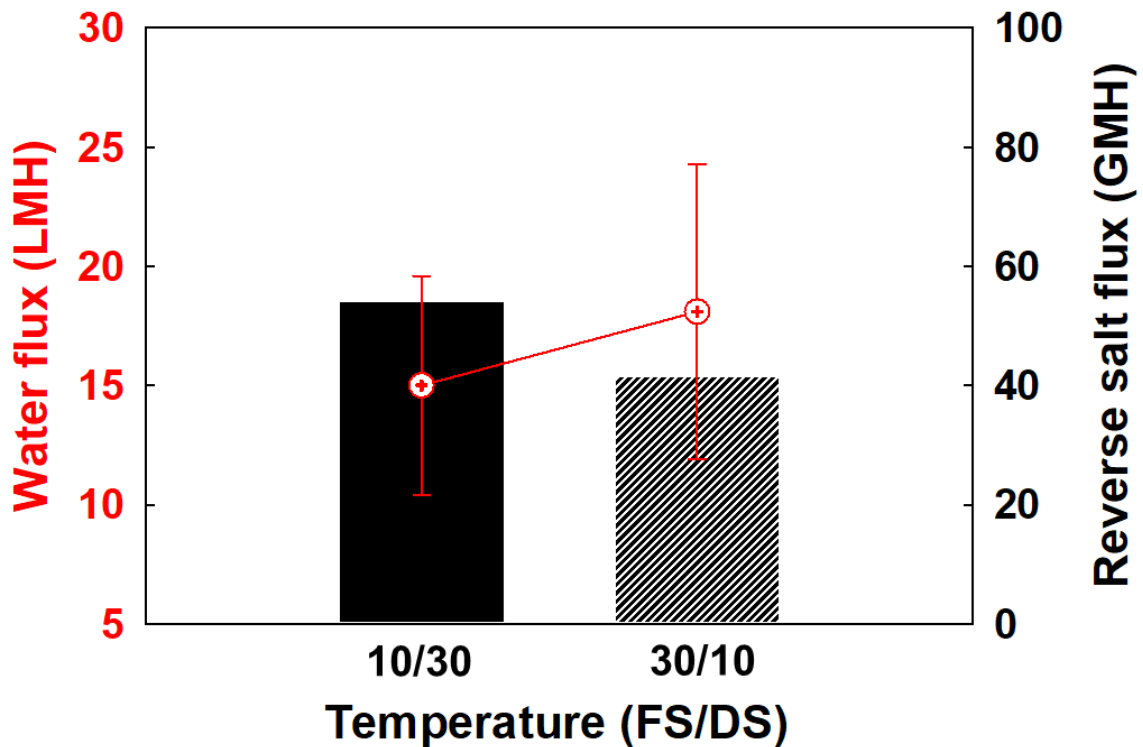


Fig. 5 Water flux and RSF of FO process depending on transmembrane temperature

Fig. 5 shows the water flux and RSF values when transmembrane temperature is 20°C and the temperature of FS and DS solution is changed to 10 and 30°C, respectively. The higher water flux (18.1±6.2 LMH) and lower RSF (41.5±2.0 GMH) were observed when FS temperature was higher than DS temperature (FS = 30°C and DS = 10°C). However, RSF value tendency was different. As illustrated in **Fig. 5**, at fixed temperature of FS and DS (10 and 30°C) it was resulted in the water flux and RSF values of 15.0±4.6 LMH and 54.2±5.7 GMH,

respectively. With high FS temperature, the diffusivity of water molecules increased and water molecules can hinder the solute flow. NaCl and MgSO₄ have different hydrate radius represented by nuclear charge (Na: 10.62, Mg: 11.61). Also, in water solution phase, those ions are surrounded with the water molecules, and the molecule radius of hydrated Mg²⁺ (0.30 nm) is larger than that of hydrated Na⁺ (0.18 nm) because Mg²⁺ can attract more water molecules [41]. In addition, viscosity decreased when temperature increased. The decrease in viscosity can enhance the water transporting kinetics through the membrane. The high DS temperature enhanced solute diffusivity and osmotic pressure resulted in the improvement of solute transporting kinetics in membrane surface. In addition, high RSF value can affect concentrated external concentration polarization (CECP) layer in active layer side. CECP layer directly influenced osmotic pressure on membrane surface thereby reduce osmotic pressure difference. From the results, the transmembrane temperature significantly affects the FO performance and the temperature of FS contributes to the FO performance more than the temperature of DS.

3.2.4 Rejection with transmembrane temperature difference

As shown in **Table 3**, the rejection efficiency of all algal metabolized materials according to the transmembrane temperature difference was higher than 93%. Geosmin and 2-MIB showed a high removal efficiency higher than 99% in the despite of the transmembrane temperature difference condition. However, the MC-LR showed 98.5% and 93.1% removal efficiency with different FS and DS temperature conditions: 10 and 30°C, and 30°C and 10°C conditions, respectively. It is relatively low rejection efficiency compared to the geosmin and 2-MIB contained FS. Interestingly, although there is no significant difference in the rejection efficiency with different temperature conditions of FS and DS, it has been observed that the

rejection mechanism of PA based TCF FO membrane are influenced by the temperature condition. In addition, it was expected that the changed water flux and RSF values in the FO have an impact on the rejection of algae metabolized although overall rejection efficiencies were not significantly affected.

Table 3 Algae metabolized materials concentration of each solution at transmembrane temperature (FS/DS) using NaCl as DS

Temp. (FS/DS)	Type	FS (mg)	CFS (mg)	DDS (mg)	Membrane (mg/cm ²)	Deposition & Rejection eff.	
						Adsorption (%)	Rejection (%)
10/30	GS	3.5	0.83±0.03	0.006±0.001	2.664 0.133	76	99.87
	2-MIB	3.5	1.06±0.06	0.005±0.005	2.435 0.122	69	99.74
	MC-LR	5	4.390±0.1 5	0.076±0.003	0.529 0.026	11.0	98.48
	GS	3.5	0.87±0.12	0.007±0.003	2.608 0.130	75	99.48
30/10	2-MIB	3.5	1.58±0.1	0.0055±0.001	1.915 0.096	55	99.80

MC-		0.627±0.0		4.026		
	5		0.347±0.091		80.5	93.06
LR		9		0.201		

* FS: feed solution, CFS: concentrated feed solution, DDS: diluted draw solution.

For both cases of transmembrane temperature, the adsorbed and deposited rate of the algae metabolized materials on the PA based TFC FO membrane were different from same temperature of FS and DS. Rejection efficiency and, adsorption and deposition rate of geosmin and 2-MIB were relatively similar with same temperature at both sides. However, when the temperature of FS is lower than DS (FS: 10°C and DS: 30°C) and the temperature of FS is higher than DS (FS: 30°C and DS: 10°C), the deposition and adsorption amounts of MC-LR are 0.529 and 4.026 µg, respectively. Transmembrane temperature difference does not have a significant effect on the rejection efficiency and mechanism. However, MC-LR was affected by transmembrane temperature difference significantly. When the DS temperature is 20°C higher than FS, it shows a higher rejection efficiency (98.5 > 93.1%) and a lower membrane deposition and adsorption rate (11 < 80%) compared to when FS temperature is higher than DS temperature. These results can be explained by the solution characteristics. As the DS temperature increases, the diffusion coefficient also increases, resulting in a high RSF. Solutes passing from the DS side to the FS side (called as RSF) inhibit the adsorption and deposition of the polar MC-LR on the membrane surface due to charge repulsion and increase the rejection rate. However, when the FS temperature is higher than the DS, the diffusion and activation coefficient of MC-LR both increase, which is a polar material that exist in the FS. As a result, the absorption and deposition rate of the polar MC-LR and the deposition rate are relatively increased.

3.2.5 Effect of RSF valance

Both transmembrane temperature difference between FS and DS and the effects of RSF were found to affect the rejection rate and rejection mechanism. For this reason, in this section we used MgSO_4 (divalent ion) as the draw solute to reduce the RSF value and maintain the water flux as that selected when using NaCl as the draw solute to determine the effect of RSF (Magnesium sulfate (MgSO_4) concentration was 2.5 M). As shown in **Fig. 6**, the water flux and RSF values were observed as follows (FS: 10, DS: 30 - Water flux: 14.0 ± 2.1 LMH, RSF: 23.1 ± 5.1 GMH / FS: 30, DS: 10 – Water flux: 17.5 ± 3.1 LMH, RSF: 19.0 ± 3.8 GMH). When divalent ion (MgSO_4) was used for draw solutes, relatively low RSF value was observed compare to the monovalent ion (NaCl) as draw solutes due to size of divalent ion low diffusion rate monovalent ion and effects of intensified size exclusion can acted ion shielding and nonspecific size reaction. Also, when FS temperature higher than DS, diffusivity of water molecule in FS was increased and viscosity was decreased, thereby increasing water flux and decreased RSF. This results were similar with previous studies and it was concluded that FO performance attributed by temperature was dependent on the properties of feed and draw solution. [30].

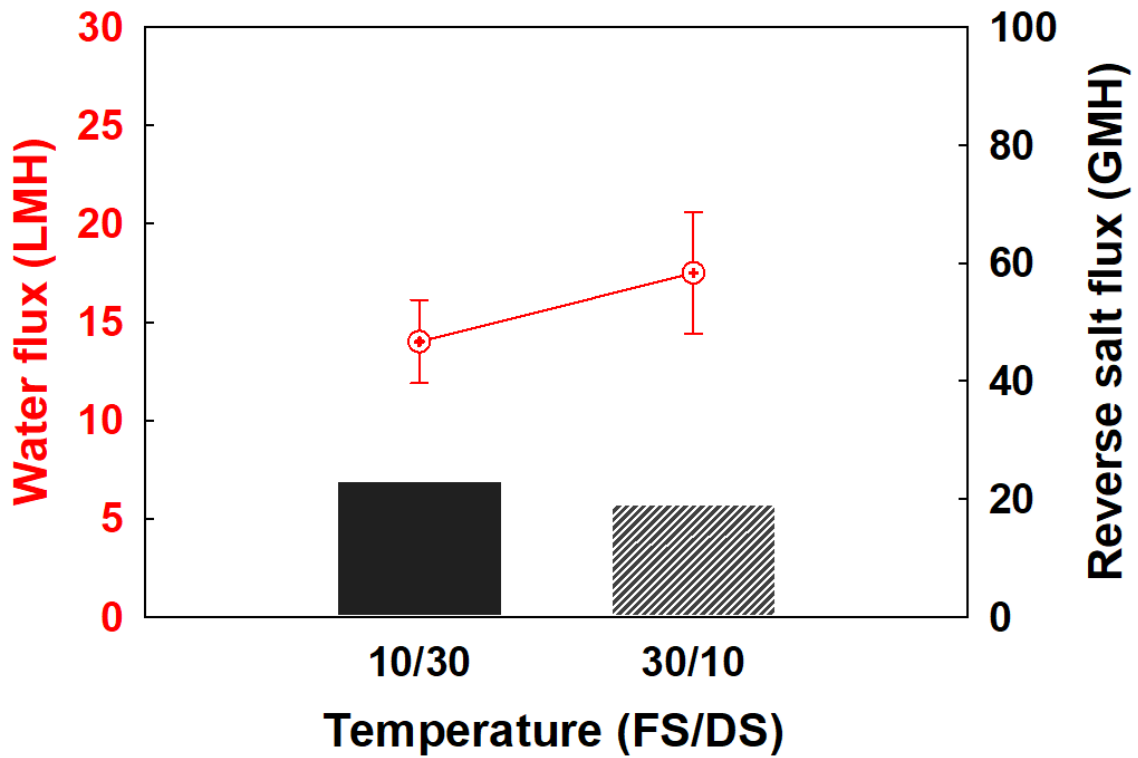


Fig. 6 Water flux and RSF of FO process depending on transmembrane temperature when draw solute using $MgSO_4$

Table 4 show the rejection efficiencies and concentrations of each solution of PA based TFC FO membranes using divalent ions ($MgSO_4$) as draw solute for removal of algal metabolized materials. For geosmin and 2-MIB, the effect of RSF is negligible for the rejection rate and rejection mechanism when FS temperature is lower than DS temperature (compared to **Table 3**). As mentioned in section 3.2.3, reverse draw solutes can affect to the membrane performance due to hydrated radius of solutes. For geosmin and 2-MIB, the rejection rate is similar to the case where the RSF value is higher and when the FS temperature is higher than the DS temperature due to the size of geosmin (0.91 nm) and 2-MIB (0.84 nm) was higher than

pore size of FO membrane (0.42 nm). However, the deposition and adsorption rates of the membrane surface increased by 15 and 25%, respectively. For MC-LR, the rejection rate and adsorption rate are observed to be 96.3% and 45.4%, respectively, when the FS temperature is lower than the DS temperature. Also, when the FS temperature is higher than the DS temperature, the removal rate and the adsorption rate were 94.8% and 50.8%, respectively. Compared with the use of monovalent ions as the draw solute, the rejection efficiency was reduced, and the adsorption and deposition rates were also significantly different. Interestingly, the major rejection mechanism was changed depending on the temperature and transmembrane temperature difference (effects of hydrated radius and membrane surface charge and RSF repulsion to surface deposition and adsorption). However, there was no significant difference in the rejection mechanism of MC-LR when divalent ions were used as draw solute.

Table 4 Algae metabolized materials concentration of each solution at transmembrane temperature (FS/DS) using MgSO₄ as DS

Temp. (FS/DS)	Type	FS (mg)	CFS (mg)	DDS (mg)	Membrane (mg) (mg/cm ²)	Deposition & Adsorption (%)	Rejection eff. (%)
10/30	GS	3.5	0.74±0.03	0.075±0.005	2.69	76.9	99.8
					0.134		
	2- MIB	3.5	1.36±0.04	0.075±0.002	2.07	59.1	99.8
					0.103		

	MC-				2.27		
	LR	5	2.55±0.05	0.18±0.06	0.113	45.4	96.3
	GS	3.5	0.31±0.04	0.021±0.001	3.17	90.6	99.5
					0.158		
30/10	2-				2.79		
	MIB	3.5	0.7±0.1	0.011±0.002	0.139	79.7	99.7
	MC-				2.54		
	LR	5	2.2±0.1	0.26±0.05	0.127	50.8	94.8

* FS: feed solution, CFS: concentrated feed solution, DDS: diluted draw solution.

3.3 Implications for FO operation

Main implication of algae metabolized materials rejection and rejection mechanism depending on temperature and transmembrane temperature difference was test-bed considered data base. This research results were applying operating conditions that can occur in actual process operating conditions that can occur in real plant when considering type of water resources, seasons, and regions. This result suggests the possibility of applying the FO process for not only purpose of treating and solving the algae blooming problems caused by the global warming effects but also emerging contaminants in wastewater. Depending on the temperature difference of each solution, the amount of RSF and draw solutes valance, the amount of algae metabolized materials deposited and /or adsorbed on the membrane surface is relatively dominant compare to the other rejection mechanisms. Therefore, to effective remove and/or control the algae metabolized materials, physicochemical properties of the membrane surface should be maintained similar to the virgin membrane through periodic physical cleaning and

back washing. In addition, if there is a temperature difference between FS and DS depending on the seasons or intake sites, it is necessary to carry out process operation considering both sides of temperature for maintain removal efficiency and performance. It is possible to suggest a major rejection mechanism according to various operating conditions and solution characteristics. Providing meaningful information not only the removal of algae metabolized materials but also the integrated with temperature (temperature difference) based water treatment process and the removal of micro pollutants and micro plastics.

4. Conclusions

In this study, evaluation of PA based TFC FO membrane performance according to the temperature and transmembrane temperature difference was evaluated. Overall rejection rate of algae metabolized materials was 93 ~ 99% and FO membrane is applicable for treating algae bloomed water. Changed water and solutes diffusivity, membrane surface morphology, solutes chemical properties and structural characteristics due to effects of temperature affected the rejection rate and rejection mechanism. The effect of molecular structure was more dominant compared to the temperature in geosmin and 2-MIB (neutral surface charge) rejection. However, in the case of MC-LR, the diffusivity and permeate flow velocity of polar material increased by temperature and polar materials interfacial attraction are removed from the PA-based TFC FO membrane. The removal efficiency of algae metabolized materials according to RSF value was not significantly affected, but the removal mechanism (electrostatics interaction and repulsion) was affected by the RSF. The results demonstrated that PA based TFC FO membrane can be applied to remove algae metabolized materials from the algae bloomed water. Consequently, important parameters (water flux, RSF value/valance and adsorption ratio)

depending on temperature and transmembrane temperature can providing useful information not only algae bloom water but also micro-plastic and micro-pollutants from various water resources.

Acknowledgement

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT, & Future Planning (2017R1A2B3009675).

References

- [1] J. Abraham, Y. Lin, A. RoyChowdhury, C. Christodoulatos, M. Conway, B. Smolinski, W. Braidia, Algae toxicological assessment and valorization of energetic-laden wastewater streams using *Scenedesmus obliquus*, *Journal of Cleaner Production*, 202 (2018) 838-845.
- [2] J. Eke, P. Wagh, I.C. Escobar, Ozonation, biofiltration and the role of membrane surface charge and hydrophobicity in removal and destruction of algal toxins at basic pH values, *Separation and Purification Technology*, 194 (2018) 56-63.
- [3] E.C. Wert, J.A. Korak, R.A. Trenholm, F.L. Rosario-Ortiz, Effect of oxidant exposure on the release of intracellular microcystin, MIB, and geosmin from three cyanobacteria species, *Water Res*, 52 (2014) 251-259.
- [4] M. Campinas, M.J. Rosa, Evaluation of cyanobacterial cells removal and lysis by ultrafiltration, *Separation and Purification Technology*, 70 (2010) 345-353.
- [5] H. Chen, J.M. Burke, T. Mosindy, P.M. Fedorak, E.E. Prepas, Cyanobacteria and

microcystin-LR in a complex lake system representing a range in trophic status: Lake of the Woods, Ontario, Canada, *Journal of Plankton Research*, 31 (2009) 993-1008.

[6] M.B. Dixon, Y. Richard, L. Ho, C.W. Chow, B.K. O'Neill, G. Newcombe, A coagulation-powdered activated carbon-ultrafiltration--multiple barrier approach for removing toxins from two Australian cyanobacterial blooms, *J Hazard Mater*, 186 (2011) 1553-1559.

[7] S.V.J.M. Dos, P.A.M.T. de, S.M. de Oliveira Azevedo, R.Y. Honda, B. Correa, Toxic cyanobacteria and microcystin concentrations in a public water supply reservoir in the Brazilian Amazonia region, *Toxicon*, 45 (2005) 901-909.

[8] J.A. Park, S.M. Jung, J.W. Choi, J.H. Kim, S. Hong, S.H. Lee, Mesoporous carbon for efficient removal of microcystin-LR in drinking water sources, Nak-Dong River, South Korea: Application to a field-scale drinking water treatment plant, *Chemosphere*, 193 (2018) 883-891.

[9] H.-Y. Shiu, M. Lee, P.-T. Chiueh, Water reclamation and sludge recycling scenarios for sustainable resource management in a wastewater treatment plant in Kinmen islands, Taiwan, *Journal of Cleaner Production*, 152 (2017) 369-378.

[10] M. Capocelli, M. Prisciandaro, V.Piemonte, D. Barba, A technical-economical approach to promote the Water Treatment & Reuse Processes, *Journal of Cleaner Production*, (2018).

[11] C.M. Chew, M.K. Aroua, M.A. Hussain, Advanced process control for ultrafiltration membrane water treatment system, *Journal of Cleaner Production*, 179 (2018) 63-80.

[12] S.J. Im, J. Choi, S. Jeong, A. Jang, New concept of pump-less forward osmosis (FO) and low-pressure membrane (LPM) process, *Sci Rep*, 7 (2017) 14569.

[13] S.J. Im, J. Choi, J.G. Lee, S. Jeong, A. Jang, Application of volume-retarded osmosis and low-pressure membrane hybrid process for water reclamation, *Chemosphere*, 194 (2018) 76-84.

[14] S.-J. Im, H. Rho, S. Jeong, A. Jang, Organic fouling characterization of a CTA-based

spiral-wound forward osmosis (SWFO) membrane used in wastewater reuse and seawater desalination, *Chemical Engineering Journal*, 336 (2018) 141-151.

[15] R.K. Singh, L. Philip, S. Ramanujam, Removal of 2,4-dichlorophenoxyacetic acid in aqueous solution by pulsed corona discharge treatment: Effect of different water constituents, degradation pathway and toxicity assay, *Chemosphere*, 184 (2017) 207-214.

[16] A. Dixit, A.J. Tirpude, A.K. Mungray, M. Chakraborty, Degradation of 2, 4 DCP by sequential biological–advanced oxidation process using UASB and UV/TiO₂/H₂O₂, *Desalination*, 272 (2011) 265-269.

[17] C. Teodosiu, A.-F. Gilca, G. Barjoveanu, S. Fiore, Emerging pollutants removal through advanced drinking water treatment: A review on processes and environmental performances assessment, *Journal of Cleaner Production*, 197 (2018) 1210-1221.

[18] S. Sorlini, F. Gialdini, C. Collivignarelli, Removal of cyanobacterial cells and Microcystin-LR from drinking water using a hollow fiber microfiltration pilot plant, *Desalination*, 309 (2013) 106-112.

[19] M. Campinas, M.J. Rosa, Removal of microcystins by PAC/UF, *Separation and Purification Technology*, 71 (2010) 114-120.

[20] S.-J. Im, S. Jeong, A. Jang, Feasibility evaluation of element scale forward osmosis for direct connection with reverse osmosis, *Journal of Membrane Science*, 549 (2018) 366-376.

[21] G. Naidu, S. Jeong, Y. Choi, M.H. Song, U. Oyunchuluun, S. Vigneswaran, Valuable rubidium extraction from potassium reduced seawater brine, *Journal of Cleaner Production*, 174 (2018) 1079-1088.

[22] V.S. Babu, M. Padaki, L.P. D'Souza, S. Déon, R. Geetha Balakrishna, A.F. Ismail, Effect of hydraulic coefficient on membrane performance for rejection of emerging contaminants, *Chemical Engineering Journal*, 334 (2018) 2392-2400.

- [23] F. Dixit, B. Barbeau, M. Mohseni, Characteristics of competitive uptake between Microcystin-LR and natural organic matter (NOM) fractions using strongly basic anion exchange resins, *Water Res*, 139 (2018) 74-82.
- [24] M.B. Dixon, C. Falconet, L. Ho, C.W. Chow, B.K. O'Neill, G. Newcombe, Removal of cyanobacterial metabolites by nanofiltration from two treated waters, *J Hazard Mater*, 188 (2011) 288-295.
- [25] A. Gijsbertsenabrahamse, W. Schmidt, I. Chorus, S. Heijman, Removal of cyanotoxins by ultrafiltration and nanofiltration, *Journal of Membrane Science*, 276 (2006) 252-259.
- [26] C. Kim, S.I. Lee, S. Hwang, M. Cho, H.-S. Kim, S.H. Noh, Removal of geosmin and 2-methylisoboneol (2-MIB) by membrane system combined with powdered activated carbon (PAC) for drinking water treatment, *Journal of Water Process Engineering*, 4 (2014) 91-98.
- [27] J. Lee, H.W. Walker, Mechanisms and factors influencing the removal of microcystin-LR by ultrafiltration membranes, *Journal of Membrane Science*, 320 (2008) 240-247.
- [28] A.H. Hawari, A. Al-Qahoumi, A. Ltaief, S. Zaidi, A. Altaee, Dilution of seawater using dewatered construction water in a hybrid forward osmosis system, *Journal of Cleaner Production*, 195 (2018) 365-373.
- [29] G. Amy, N. Ghaffour, Z. Li, L. Francis, R.V. Linares, T. Missimer, S. Lattemann, Membrane-based seawater desalination: Present and future prospects, *Desalination*, 401 (2017) 16-21.
- [30] M. Song, S.-J. Im, S. Jeong, A. Jang, Evaluation of an element-scale plate-type forward osmosis: Effect of structural parameters and operational conditions, *Desalination*, 430 (2018) 15-23.
- [31] M. Xie, W.E. Price, L.D. Nghiem, M. Elimelech, Effects of feed and draw solution temperature and transmembrane temperature difference on the rejection of trace organic

- contaminants by forward osmosis, *Journal of Membrane Science*, 438 (2013) 57-64.
- [32] Y.L. Liu, X.M. Wang, H.W. Yang, Y.F. Xie, Adsorption of pharmaceuticals onto isolated polyamide active layer of NF/RO membranes, *Chemosphere*, 200 (2018) 36-47.
- [33] R. Valladares Linares, V. Yangali-Quintanilla, Z. Li, G. Amy, Rejection of micropollutants by clean and fouled forward osmosis membrane, *Water Res*, 45 (2011) 6737-6744.
- [34] M.G. Antoniou, A.A. de la Cruz, D.D. Dionysiou, Cyanotoxins: New Generation of Water Contaminants, *Journal of Environmental Engineering*, 131 (2005) 1239-1243.
- [35] V.K. Sharma, T.M. Triantis, M.G. Antoniou, X. He, M. Pelaez, C. Han, W. Song, K.E. O'Shea, A.A. de la Cruz, T. Kaloudis, A. Hiskia, D.D. Dionysiou, Destruction of microcystins by conventional and advanced oxidation processes: A review, *Separation and Purification Technology*, 91 (2012) 3-17.
- [36] Y. Matsui, S. Nakao, A. Sakamoto, T. Taniguchi, L. Pan, T. Matsushita, N. Shirasaki, Adsorption capacities of activated carbons for geosmin and 2-methylisoborneol vary with activated carbon particle size: Effects of adsorbent and adsorbate characteristics, *Water Res*, 85 (2015) 95-102.
- [37] <Desalinating seawater and recovering waste water using hybrid forward and reverse osmosis at the pilot level.pdf>.
- [38] S.-J. Kim, S. Kook, B.E. O'Rourke, J. Lee, M. Hwang, Y. Kobayashi, R. Suzuki, I.S. Kim, Characterization of pore size distribution (PSD) in cellulose triacetate (CTA) and polyamide (PA) thin active layers by positron annihilation lifetime spectroscopy (PALS) and fractional rejection (FR) method, *Journal of Membrane Science*, 527 (2017) 143-151.
- [39] S. Zhao, L. Zou, Effects of working temperature on separation performance, membrane scaling and cleaning in forward osmosis desalination, *Desalination*, 278 (2011) 157-164.
- [40] S.-J. You, X.-H. Wang, M. Zhong, Y.-J. Zhong, C. Yu, N.-Q. Ren, Temperature as a factor

affecting transmembrane water flux in forward osmosis: Steady-state modeling and experimental validation, *Chemical Engineering Journal*, 198-199 (2012) 52-60.

[41] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, Comparison of the removal of hydrophobic trace organic contaminants by forward osmosis and reverse osmosis, *Water Res*, 46 (2012) 2683-2692.