



Development of a novel wastewater treatment system combined direct up-concentration using forward osmosis membrane and anaerobic membrane bioreactor

Onoda, Sosuke

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Doctoral Dissertation

Development of a novel wastewater treatment system
combined direct up-concentration using forward osmosis
membrane and anaerobic membrane bioreactor

正浸透膜による直接濃縮と嫌気性膜分離活性汚泥法を組み合わせた
新規下水処理システムの開発

July 2016

Graduate School of Engineering
Kobe University

Sosuke Onoda

Contents

Chapter I

General introduction

I.1	Role of wastewater treatment in water circulation	7
I.2	Energy problems and wastewater treatment	8
I.3	Current wastewater treatment technology (anaerobic biological treatment)	9
I.4	Anaerobic biological treatment and the challenges	14
I.5	Membrane filtration technology in water treatment	18
I.5.1	Membrane filtration	18
I.5.2	Classification of the separation membrane	19
I.5.3	Wastewater treatment system combined membrane filtration and biological treatment	22
(1)	Membrane bioreactors (MBRs)	22
(2)	Anaerobic membrane bioreactor (AnMBRs)	23
I.5.4	Forward osmosis membrane and the application	25
(1)	Forward osmosis	25
(2)	Theory of forward osmosis	26
(3)	Membrane fouling on forward osmosis membrane	30
(4)	Applications of the forward osmosis method to wastewater	

treatment and solution concentration	31
I.6 Wastewater treatment system combined direct up-concentration using FO membrane and AnMBR	33
I.7 Scope of this study	36
Reference	38

Chapter II

Direct up-concentration of wastewater by forward osmosis membrane and evaluation of the methane production potential of concentrated wastewater

II.1 Introduction	44
II.2 Experiment	48
II.2.1 Concentration of municipal wastewater using FO membrane	48
II.2.2 Batch methane fermentation test using concentrated municipal wastewater	50
II.2.3 Analytical methods	52
II.3 Calculation of material balance of organic matter during up-concentration using FO membrane	52
II.4 Results and discussion	53
II.4.1 Membrane fouling in hollow fiber FO membrane	53
II.4.2 Water qualities of permeate in DS side	55

II.4.3	Accumulation of organic matter in concentrated municipal wastewater	57
II.4.4	Material balance of organic matter during up-concentration using FO membrane	59
II.4.5	Batch methane fermentation test	61
II.5	Conclusions	62
	Reference	64

Chapter III

Rejection of nutrients contained in an anaerobic digestion effluent using a forward osmosis membrane

III.1	Introduction	67
III.2	Materials and methods	71
III.2.1	Feed and draw solutions	72
III.2.2	Forward osmosis filtration setup	73
III.2.3	Water quality analysis	74
III.2.4	Calculation	75
III.3	Results and discussion	76
III.3.1	FO experiment using the surrogate AnMBR effluent	76
III.3.2	Rejection of ammonium ions	77

III.3.3	FO membrane process as a post-treatment of the AnMBR	86
III.3.4	Treatment of concentrate discharged from FO membrane post-treatment	88
III.4	Conclusions	89
	Reference	91

Chapter IV

Characteristics of foulants of forward osmosis membranes used in municipal wastewater concentration processes

IV.1	Introduction	97
IV.2	Materials and methods	100
IV.2.1	Feed water and draw solution for FO membrane filtration	100
IV.2.2	Batch FO membrane filtration experiment	104
IV.2.3	Evaluation of membrane fouling after the batch FO membrane filtration experiment	105
IV.2.4	Characterization of foulants detached from membranes	106
IV.2.5	Analytical methods	106
IV.3	Results and discussion	107
IV.3.1	FO membrane fouling caused by each feed water	107
IV.3.2	Characteristics of foulants in FO membranes	110

IV.4 Conclusions	115
Reference	117
Supporting information	122

Chapter V

Evaluation of energy production of system combined direct up-concentrating municipal wastewater using a forward osmosis membrane and anaerobic membrane bioreactor

V.1 Introduction	123
V.2 Materials and methods	124
V.2.1 Calculation of operational energy of proposed system	124
V.2.2 Evaluation of effect of operational temperature for AnMBR performance (Lab-scale AnMBR)	126
V.2.3 Calculation of methane yield	129
V.3 Results and discussion	130
V.3.1 Calculation of operational energy of proposed system	130
V.3.2 Evaluation of effect of operational temperature for AnMBR performance (Lab-scale AnMBR)	133
V.3.3 Calculation of operational energy of proposed system based on performance of lab-scale AnMBR	135

V.4 Conclusions	136
Reference	138

Chapter VI

Conclusions

VI.1 Conclusions	140
VI.2 Perspectives	143
List of publications	145
Acknowledgement	146

Chapter I

General Introduction

I.1 Role of wastewater treatment in water circulation

Water is an important resource that is as old as the earth, and is essential to both human life and industrial activity. The circulation of water in the earth system affects the amount of water in rivers and aquifers, purifies water with contaminants, and plays a major role in watershed ecosystem conservation. Sometimes the water cycle brings disasters such as flooding or drought. Anthropogenic activities can have influences on the water cycle (Fig. I-1).

The water circulation system in Japan, including flood control, uses a variety of renewable energy sources. Water circulation systems have become ever more engineered. In these engineered systems, the sewer plays an important role as a cornerstone of public health. Wastewater discharged from domestic and industrial activities is not self-cleaned and must be treated to prevent pollution being discharged directly into rivers and streams. There is a fear that the deterioration of the city sanitary systems will lead to water quality deterioration at the source. By performing appropriate pollution treatment processes, wastewater treatment plants protect the natural waters of rivers, lakes, and oceans from pollution. Wastewater treatment therefore supports a sanitary living environment and industrial activities.

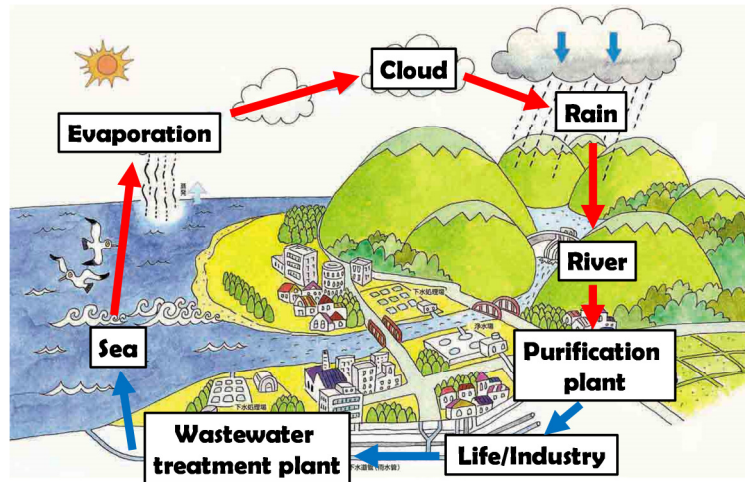


Fig. I-1 The terrestrial water cycle [1]

I.2 Energy problems and wastewater treatment

Due to rapid economic growth after World War II, sewer systems have been developed for aquatic ecosystem conservation and public health purposes. In 2015, the sewer penetration rate in Japan reached 77.6% [2]. In addition, due to an accumulation of experience and knowledge regarding wastewater treatment process, effluent water quality and operation stability have reached high levels.

On the other hand, with an increased focus on global energy and environmental issues, oil depletion, global warming, and risks from nuclear power generation, a conversion to safe and sustainable energy production methods is actively being sought. The Japanese Land, Infrastructure, and Transportation Ministry has announced the "New Sewer Vision" [3] (Fig. I-2). Their mission has been "to contribute to the creation of a sustainable society." Sewers today must move beyond the role of only "processing" sewage. They must begin to play an important role with respect to energy and environmental issues, as well.

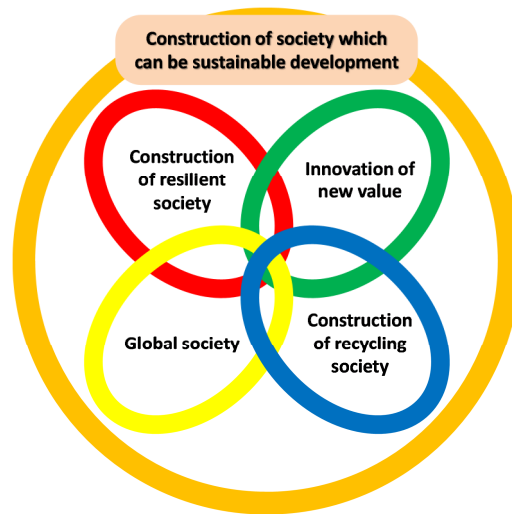


Fig. I-2 Construction of a sustainable society [3]

I.3 Current wastewater treatment technology (anaerobic biological treatment)

Wastewater treatment in Japan often use aerobic biological treatment, also called the activated sludge method [4]. In the activated sludge method, collections of microorganisms that decompose organic matter (the activated sludge) are introduced to wastewater. The activated sludge consumes dissolved oxygen and decomposes organic material in the wastewater to carbon dioxide, water, and intracellular growth, producing clear water. Activated sludge method is a technique that can be expanded on the methods reported in Refs [4, 5]. In the conventional activated sludge method [6] (Fig. I-3), sewage flows into the treatment plant. Large solid material is removed by a screen and first sedimentation tank. During this primary treatment, 30-40% of biochemical oxygen demand (BOD) and 50-60% of suspended solids (SS) are removed [7]. Effluent from the first sedimentation tank is next sent to a biological reactor and mixed with activated sludge. In the biological reactor, oxygen is supplied continuously and stirring further increases aeration. The resulting sludge mixture remains for a given time in the biological reactor, after which it is sent to a final sedimentation tank, where the solids

are separated from the mixture by gravity. Supernatant is discharged as treated water, and part of the settled solids are returned to the biological reactor as activated sludge. Excess sludge is disposed of.

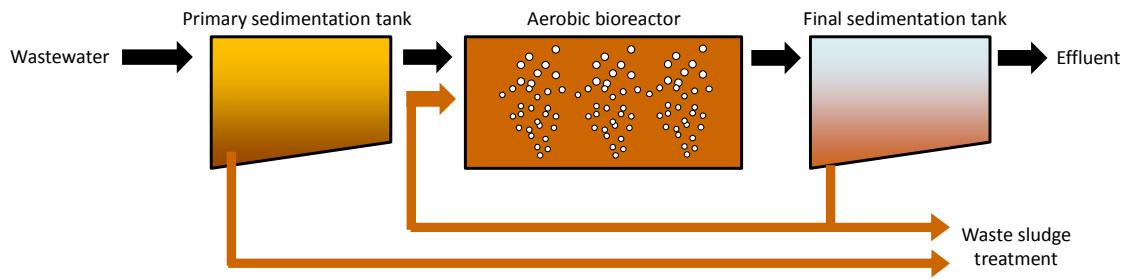


Fig. I-3 Schematic of the conventional activated sludge method

While the conventional activated sludge process described above is the most common method, variants have been developed depending on the target wastewater or operation scale. Two examples are the oxidation ditch process [8] and the step-feed method [9]. However, both of these methods are primarily intended for organic removal, and cannot remove nutrients such as nitrogen and phosphorus. If water containing excess nutrients is discharged into rivers and seas, eutrophication can occur. As the cause of blue-green algae and red tide, nitrogen and phosphorous must be removed (in addition to organic matter) during sewage treatment.

Sewage contains both organic nitrogen (in the form of proteins, amino acids, and urea), and inorganic nitrogen (in the form of ammonia and nitric acid). Organic nitrogen is converted to ammonium during biodegradation. In order to convert ammonia in wastewater to nitrogen gas for removal, two biological reactions are necessary. First, nitrification converts the ammonia to nitrite and nitrate, and then denitrification converts nitrate to nitrogen gas [10] (Fig. I-4). Since nitrification proceeds in aerobic conditions,

and denitrification proceeds in anaerobic conditions, these reactions must be performed in separate reactors.

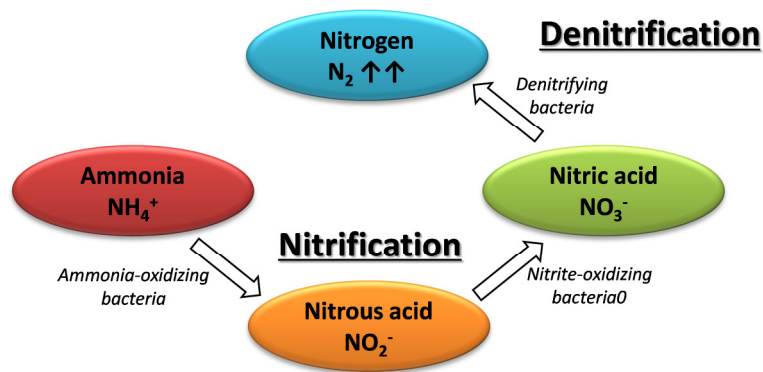


Fig. I-4 Biological nitrogen removal (nitrification and denitrification)

Phosphorus is removed through accumulation in the sludge by biological mechanisms, because gasification (as with carbon and nitrogen) is not possible [11, 12]. The typical biological phosphorus removal method is shown in Fig. I-5. The microorganisms used in this process are able to accumulate high concentrations of phosphorous through polyphosphate accumulation. In biological phosphorus removal processes, it is again necessary to have separate reactors aerobic conditions and anaerobic conditions. Polyphosphate accumulating bacteria release phosphorus in anaerobic conditions. When followed immediately by aerobic conditions, the bacteria then accumulate an even greater concentration than that released during anaerobic treatment. Removal of the bacteria mass results in a net reduction in phosphorous levels in the effluent.

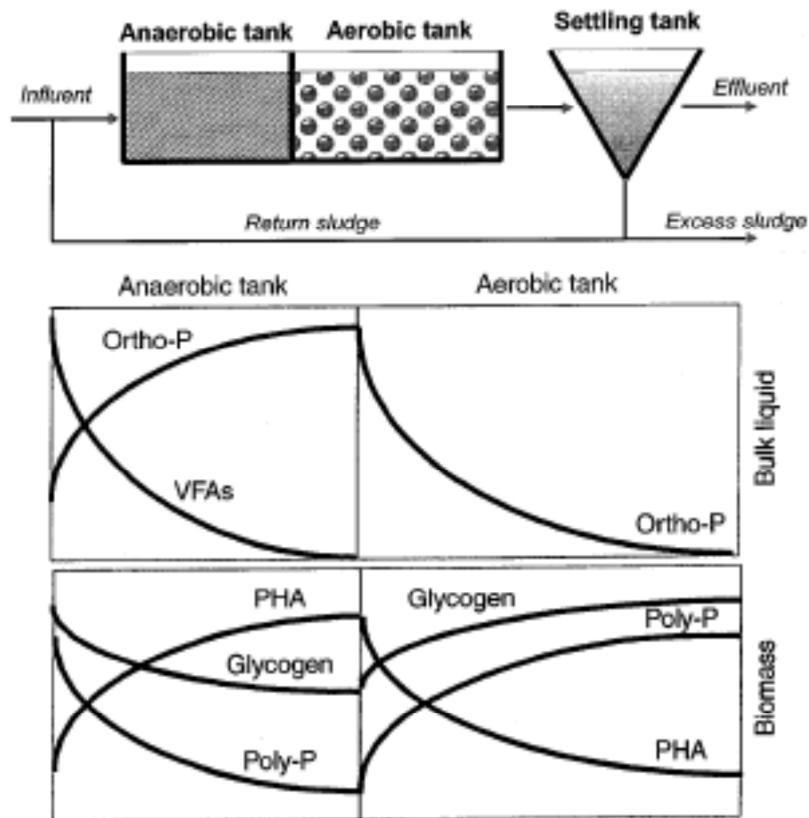


Fig. I-5 Biological phosphate removal process [13]

An activated sludge method combining biological nitrogen and phosphorus removal—the anaerobic-anoxic-oxic activated sludge process (A2O)—has also been developed [14] (Fig. I-6). In the anaerobic tank, phosphorus is released by microorganisms. Nitrate is converted to nitrogen gas in the anoxic tank. In the oxic tank, excessive phosphorus uptake occurs, leaving the phosphorus immobilized in the polyphosphate accumulating bacteria. The nitrification reaction also occurs in the oxic tank. Denitrification is accomplished by circulating part of the sludge from the oxic tank to the anoxic tank.

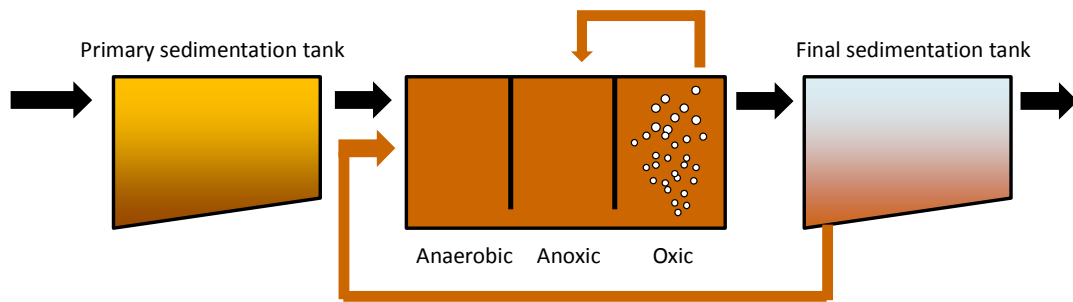


Fig. I-6 A2O method

As compared to the anaerobic treatment (which will be described later), aerobic sewage treatment produces higher quality effluent and has high technical reliability due to accumulated knowledge and experience. In aerobic treatment processes, it is necessary to keep dissolved oxygen concentrations in the sludge above a certain level in order to maintain microorganism activity. Oxygen is supplied to the microorganisms through various aeration processes, consuming large amounts of energy. Japan for Sustainability reported that 0.7% of the total energy consumption in Japan is due to sewage treatment [15], and more than 50% of this energy consumption is due to aeration processes [16]. Furthermore, a great deal of energy is consumed while processing the large amount of waste sludge generated [17]. Thus, aerobic sewage treatment is an energy-consuming system.

I.4 Anaerobic biological treatment and its challenges

In anaerobic biological treatment, the organic contaminants in the raw water are decomposed into methane and carbon dioxide by the metabolic action of anaerobic microorganisms through the stages of hydrolysis, acetogenesis, and methanogenesis [18] (Fig. I-7). First, polymer organic materials, such as proteins and carbohydrates, flow into the bioreactor and are decomposed into amino acids and sugars. These are then further degraded into volatile fatty acids (VFA) and lower alcohols such as butyric acid, propionic acid, and acetic acid by acid-producing bacteria. These acid products are finally converted into biogas (mainly composed of methane and carbon dioxide) by methane producing bacteria. When VFA is generated during the acid production phase, pH may become acidic. However, because methane generation progresses in parallel, pH is maintained at about 7.0-7.4 in proper operating conditions. The generated ammonia and organic acids are known to inhibit methanogenesis at high enough concentrations [19].

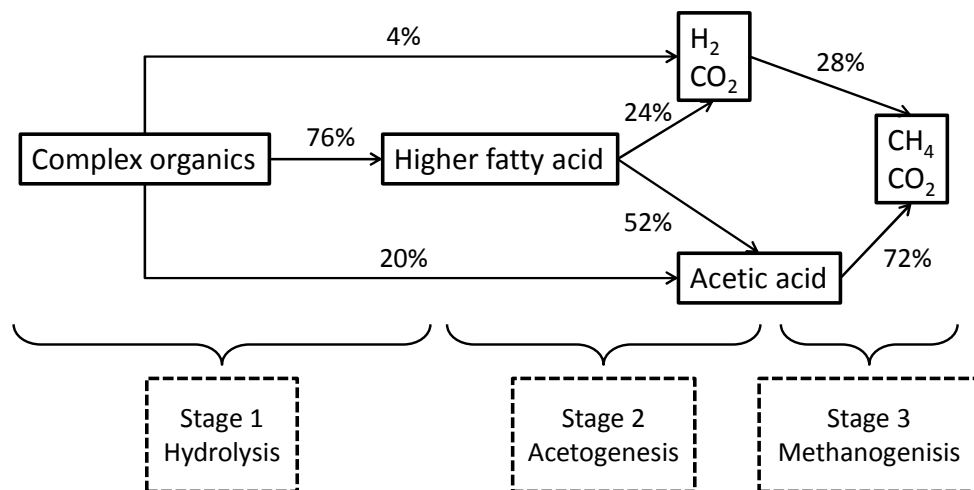


Fig. I-7 The degradation pathways of organic matter in anaerobic treatment [18]

Since aeration is not required for anaerobic processing, energy consumption is about half that of aerobic treatment. Organic matter in the raw sewage is converted into biogas composed mainly of methane and carbon dioxide, which can be purified to methane gas and utilized as fuel [20]. Because the bacterial cell yield of organic matter is low, anaerobic treatment has the further advantage of producing much less waste sludge, about 30% that of aerobic treatment [21]. On the other hand, the optimum temperature of anaerobic microorganisms is about 35 to 40°C, because a slow reaction rate below this range, reduces methane gas generation efficiency. It is therefore necessary to maintain the optimal temperature range by heating. The application of anaerobic treatment for wastewater with dilute organic matter concentrations is difficult from an economic point of view because the energy consumption required for heating is larger than the energy produced by methane fermentation [22]. Anaerobic treatment is therefore mainly applied to wastewater containing high concentrations of organic matter, such as that discharged from food plants. Anaerobic digestion of the waste sludge from aerobic wastewater treatment is another common choice. Generally, the organic materials concentration range for which anaerobic treatment can be applied is approximately 1500-2000 mg-COD/L [23]. Therefore, municipal wastewater, containing 250-800 mg-COD/L, is difficult to be treated anaerobically. Further, since anaerobic treatment does not always produce high quality effluent, post-treatment is sometimes required.

During anaerobic treatment, it is necessary to have high concentrations of methanogens with slow a growth rate in the bioreactor in order to achieve stable processing performance and high-load treatment. A high-load anaerobic treatment method (called the microbial immobilization method) has been put into practical use in

industrial wastewater treatment systems. Three processes (Up-flow anaerobic filter process, anaerobic fluidized bed process and up-flow anaerobic sludge blanket) are described below in details.

Up-flow anaerobic filter process (Fig. I-8 (a))

In the microbial immobilization method, wastewater comes in contact with a carrier, such as plastic or crushed stone, that is submerged in the reactor. An anaerobic biofilm forms on the surface of the carrier. There are many variations in size and type of carrier and water flow direction (up-flow or down-flow). By adding the carrier, the effective volume of the reactor is reduced, which may cause a blockage or foaming of the reaction vessel due to crystallization of inorganic materials in the mixed liquor suspension on the surface of the carrier.

Anaerobic fluidized bed process (Fig. I-8 (b))

An improved method utilizes sand (particle diameter 0.2-1.0 mm, anthracite, lightweight aggregate) suspended in the reactor. In this way, clogging problems are eliminated, and contact efficiency with the wastewater is high so that the substrate degrades well. On the other hand, there are some technical problems. This method is relatively difficult to scale up and requires energy for circulation of the carrier flow, which can increase operating costs. The biofilm peeling off due to friction between colliding particles and sand carrier washout can both decrease efficiency.

Up-flow anaerobic sludge blanket (UASB) process (Fig. I-8 (c))

The Up-flow Anaerobic Sludge Blanket (UASB) was developed by Lettinga et al.

in the 1970s [24]. In this method, granular sludge (particle diameter 0.2-1.0 mm) with good sedimentation properties is used in a typical bioreactor without carrier. The aggregation and agglomeration of the anaerobic bacteria allows for contaminant removal. High loads can be processed using UASB, since clogging of the reactor is not an issue. UASB is the most widely used treatment for high-concentration organic wastewater treatment, such as wastewater from food processing. The UASB tank has a raw water supply device at the bottom of the reactor, and a gas-solids separator at the top. Anaerobic treatment is performed by generating granular sludge, and uniform drainage is accomplished with up-flow from the bottom of the reactor.

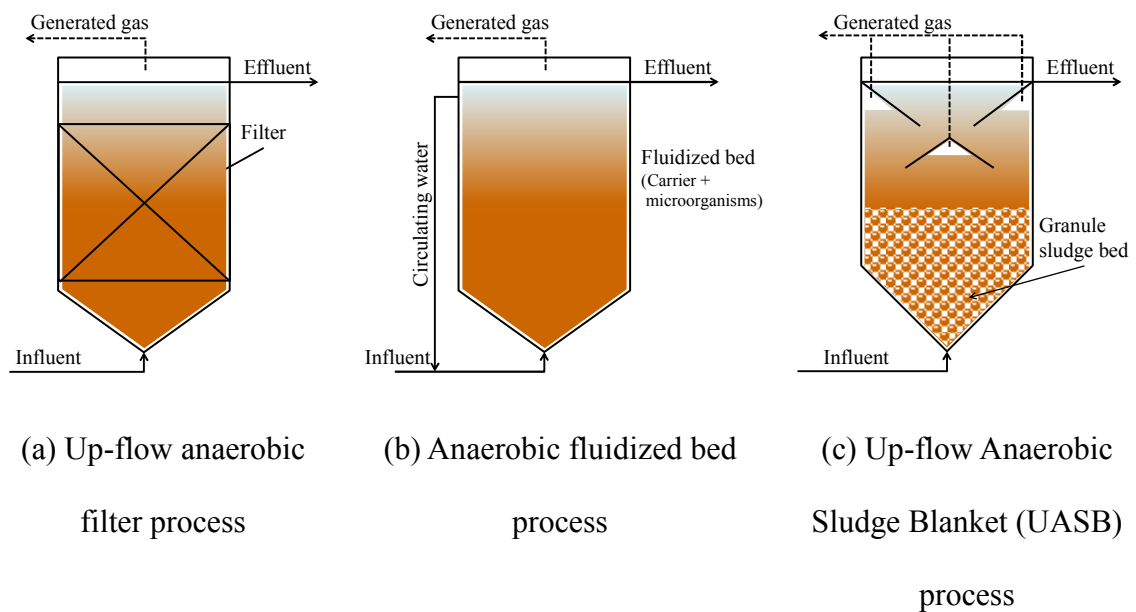


Fig. I-8 Anaerobic biological treatment systems [18]

I.5 Membrane filtration technology in water treatment

I.5.1 Membrane filtration

There are various technologies available to separate solid and solute impurities from the solutions. Sedimentation, distillation, extraction, and membrane separation are the most common methods. Membrane separation is a separation technology using a membrane, which purifies target materials by permeation through the membrane. There are two types of operations: dead-end and cross-flow filtration systems (Fig. I-9). In dead-end filtration, the filtration resistance increases easily due to rapid deposition of the separation target materials on the membrane surface. For this reason, in a constant-pressure filtration, the permeate flux decreases with time, while in a constant-flux filtration the operational pressure increases with time. This phenomenon is called as membrane fouling. Membrane fouling occurs in cross-flow filtration as well, however, eventually reaching a steady state where membrane permeation flux becomes a constant value determined by the feed-water flow-rate (the cross-flow velocity over the surface of the membrane).

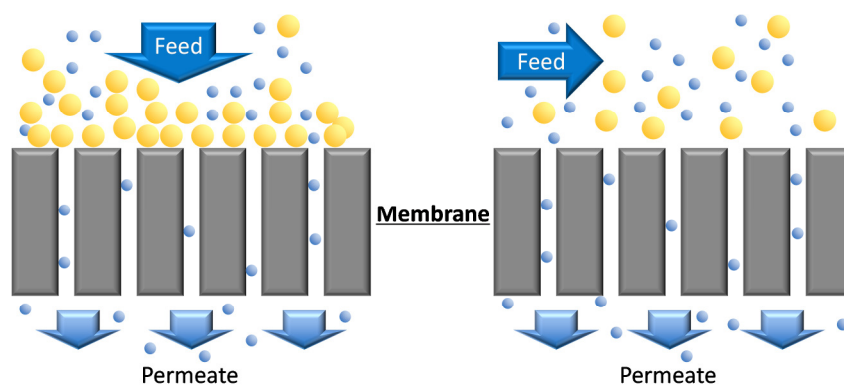


Fig. I-9 Two types of membrane filtration

(Left) Dead-end filtration (Right) Cross-flow filtration

I.5.2 Classification of separation membranes

Various types of separation membranes can be used, depending on the separation target materials. The type of each membrane, approximate pore size range, and typical applications are shown in Fig. I-10.

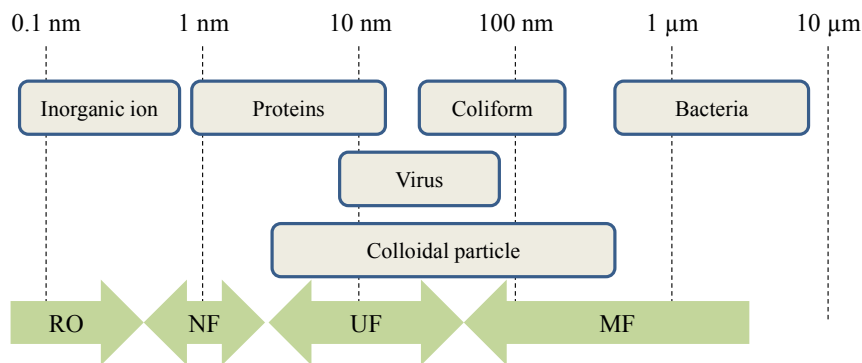


Fig. I-10 Classification of membrane, pore size and target materials for microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO)

(1) Microfiltration (MF) membranes

Microfiltration membranes have pore sizes larger than about 0.1 μm, and are mainly used for the separation of suspended particles. Although it can be used in dead-end and cross-flow filtration, the latter is more common. Many types of materials are used for MF membranes. Cellulose acetate-based material was used in the past, but due to low chlorine resistance, a synthetic polymer-based material has been adopted in recent years. Polyvinylidene difluoride (PVDF) and similar materials that have high chemical resistance are a common choice [25].

In the water treatment field, MF membranes are used for water purification treatment and in membrane bioreactors (explained below).

(2) Ultrafiltration (UF) membranes

Ultrafiltration membranes have smaller pores than those of microfiltration membranes, at approximately 100 nm to a few nm. Separation performance is classified by the molecular weight cutoff rather than the pore size. A molecular weight cutoff is the molecular weight at which more than 95% of the molecules will be rejected by the membrane. Although UF membranes can be used in either dead-end or cross-flow filtration, the latter is also more common by used. Similar to the MF membranes, chlorine resistance is an issue, and synthetic polymer-based material has become the common choice. Polysulfone-, polyacrylonitrile-, and polyethersulfone-based materials have all been put to practical use as UF membranes [25].

Typical applications for UF are water treatment and pre-treatment for reverse osmosis filtration processes.

(3) Reverse osmosis (RO) and Nanofiltration (NF) membranes

When a low concentration solution and a high concentration solution are separated by a semipermeable membrane, both solutions strive towards an equilibrium state. The water in the low concentration solution moves to the high concentration side through the semi-permeable membrane. This phenomenon is called *(forward) osmosis*. When osmosis has reached equilibrium, the pressure difference generated between both solutions (rise of water level) is called as *osmotic pressure*. When applying a pressure greater than the osmotic pressure to the high concentration side, the water permeates through the membrane from the high concentration side to the low concentration side. This phenomenon is called as *reverse osmosis* (Fig. I-11), and the membrane used in

this process is called as reverse osmosis membrane (RO membrane). A reverse osmosis membrane with higher water permeability and lower salt rejection is called as a nanofiltration membrane (NF membrane).

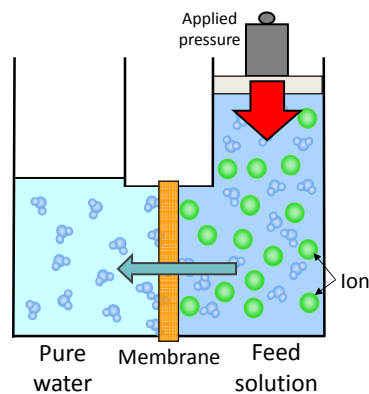


Fig. I-11 Schematic illustration of reverse osmosis

Reverse osmosis membranes can be classified into two types: cellulose acetate based and aromatic polyamide based membranes. The cellulose acetate based membrane has high chemical resistance, while the aromatic polyamide based membrane has high water permeability. The material for RO is therefore selected depending on raw water quality and operating conditions. Aromatic polyamide based material is typically used for NF membranes [25].

Common applications of RO membranes are for seawater desalination, wastewater desalination treatment, and ultrapure water production.

I.5.3 Wastewater treatment systems combining membrane filtration and biological treatment

(1) Membrane bioreactors (MBRs)

In aerobic treatment, including in the conventional activated sludge method described above, there are several operation problems. The effluent and activated sludge are separated by gravity settling in the final sedimentation tank, meaning that the size and concentration properties of the sludge change due to fluctuations in influent water quality and the flow rate of the wastewater feed. If operational conditions are not carefully managed, bulking can occur [26]. Bulking is a phenomenon wherein clear supernatant cannot be obtained and sludge is not well precipitated. If bulking occurs, the activated sludge in the sedimentation tank cannot be separated, and carry-over of activated sludge will occur. In a wastewater treatment plant, prevention of bulking is very important, and much of the maintenance cost is spent on this. Furthermore, since the final sedimentation tank requires a residence time of several hours in order to sufficiently precipitate the sludge, it occupies a large footprint, increasing implementation costs.

In order to resolve these problems, the membrane bioreactor (MBR) was developed (Fig. I-12). In MBR, the final sedimentation tank is not necessary since the treated water and sludge are separated by a membrane, and pure water can always be obtained. In the usual sedimentation, separation rates decrease with increasing sludge concentrations, and it is therefore necessary to keep the sludge concentration low. In MBR, however, since sludge is separated by the membrane, it is possible to operate at high sludge concentrations without worrying about the sludge settling [27].

MBR was first applied to sewage treatment in the United States in 1969 [28].

An MBR method where the membrane is submerged in the bioreactor was proposed in Japan by Yamamoto et al. in 1989 [29], and has been put into practical use [30]. Since the quality of MBR-treated water is high, reverse osmosis can be used after MBR process. This combination has been attracting attention in recent years as a technology suitable for water reclamation, in order to meet increasing water demand worldwide [31].

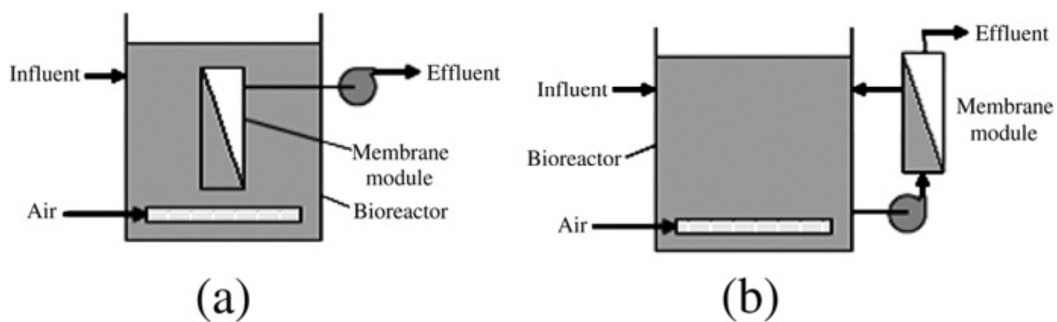


Fig. I-12 Schematic illustration of MBR [32]

(Left) Submerged MBR (Right) Sidestream MBR

(2) Anaerobic membrane bioreactors (AnMBRs)

The anaerobic membrane bioreactor (AnMBR) combines anaerobic biological treatment with membrane filtration [33] (Fig. I-13). As described above, during anaerobic treatment, retention of the anaerobic microorganisms is important due to their slow specific growth rate. In AnMBR, it is possible to have a high concentration of anaerobic microorganisms in the bioreactor due to the complete solid-liquid separation by the membrane. AnMBR also has the advantage of being able to maintain good fermentation conditions because inhibitors (i.e., VFA or ammonia) can be discharged while retaining sludge in the bioreactor [34]. Application of AnMBR is best for targeting raw materials that easily induce inhibition and require a long degradation time.

AnMBR has been applied to the treatment of high concentration organic wastewater such as liquor lees and alcohol fermentation drainage, but it has not yet been applied to municipal wastewater with a large volumetric flow and low concentration of organic matter [35]. The main reason for this is that there is not an economic advantage due to the need for large amounts of heating energy.

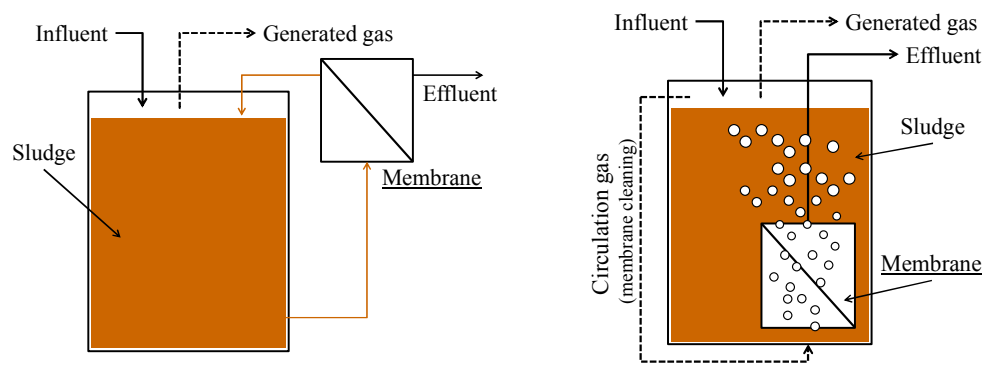


Fig. I-13 Anaerobic membrane bioreactor

(Left) Sidestream AnMBR (Right) Submerged AnMBR

I.5.4 Forward osmosis membranes and applications

(1) Forward osmosis

In addition to the above-mentioned membranes (MF, UF, NF, RO), the forward osmosis method has recently been attracting attention as a novel membrane filtration technology (Fig. I-14). Forward osmosis utilizes spontaneous water permeation through a membrane (FO membrane) caused by osmotic pressure differences between the low salt concentration solution (feed solution; FS) and high concentration solution (draw solution; DS). Since it does not need the application of mechanical pressure, the energy consumption for water permeation may ultimately drop to zero.

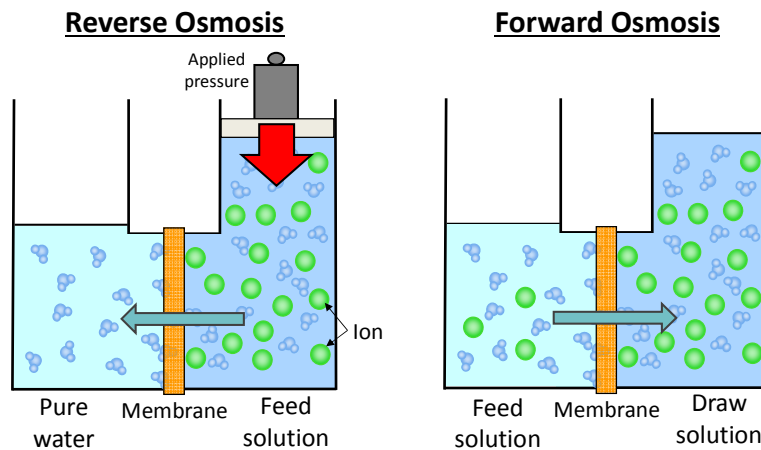


Fig. I-14 Forward osmosis process and reverse osmosis process

To obtain pure water by forward osmosis, it is necessary to separate water from the DS. Researchers are actively developing a draw solute that can be easily purified [36, 37 and 38]. However, a suitable draw solute that has high osmotic pressure generation and easy recovery has not yet been found. Thus, a process using natural DS, such as seawater with concentration [39] or osmotic power generation [40], will likely be commercialized.

(2) Theory of forward osmosis

The water flux in a forward osmosis process, J_W [L/(m²·h)], is calculated as:

$$J_W = A(\Delta\pi - \Delta P) \quad (\text{I-1})$$

where A is the coefficient of membrane water permeability, ΔP is the applied pressure [bar], and $\Delta\pi$ is the osmotic pressure difference [bar] between FS and DS in the vicinity of the membrane surface. The coefficient of membrane water permeability must be measured for each membrane using a reverse osmosis test with pure water.

Since mechanical pressure is not applied in forward osmosis, ΔP becomes zero. In forward osmosis, concentration polarization—where the effective osmotic pressure difference is much lower than the osmotic pressure difference between FS and DS—occurs. Internal and external concentration polarization must be considered separately [41]. The forward osmosis membrane can have a large influence on the internal concentration polarization. The internal concentration polarization occurs inside the supporting layer of the forward osmosis membrane, but does not occur in reverse osmosis (Fig. I-15). The FO membrane has a two-layer structure composed of the active layer (with dense structure) and the support layer (with porous structure). When the active layer faces the FS side (AL-FS) (Fig. I-15 (a)), the effective osmotic pressure decreases due to dilution of the DS with water that has permeated through the active layer from the FS side. When the active layer faces the DS side (AL-DS) (Fig. I-15 (b)), the effective osmotic pressure also decreases, due to the solute permeated from the DS side to the FS side remaining in the internal support layer. The magnitude of reduction in effective osmotic pressure due to internal concentration polarization is larger in AL-FS. However, in AL-DS, the porous supporting layer faces the FS side and membrane fouling becomes significant. The AL-FS mode is therefore preferred for

water treatment and solution concentration purposes [42].

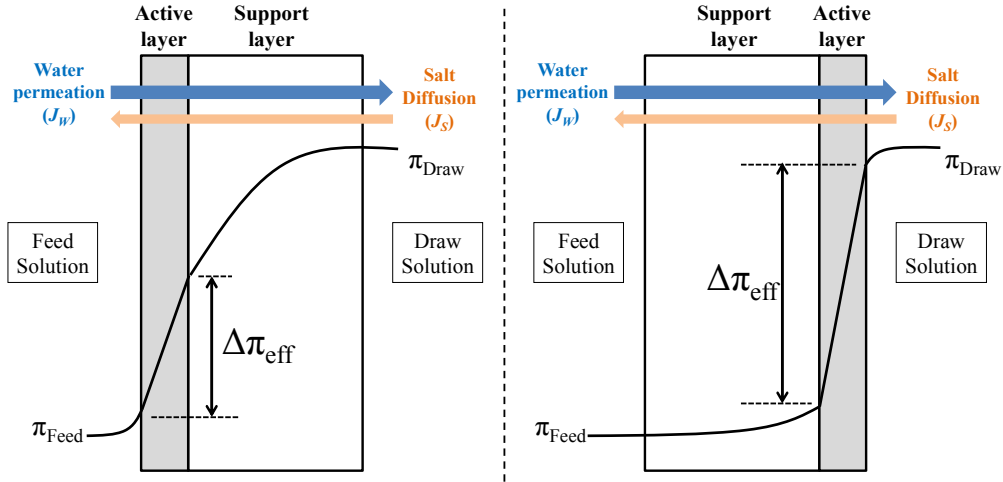


Fig. I-15 Schematic illustration of concentration polarization in FO membrane filtration. (a) AL-FS mode, (b) AL-DS mode [43]

The permeability theory of forward osmosis is based on the solution-diffusion model and mass balance [44]. In addition to the water membrane permeability coefficient, A , solute permeability in the active layer, B [$\text{mol}/(\text{m}^2 \cdot \text{h})$], can be measured with a reverse osmosis test using a salt solution and then calculated using equations (I-2), (I-3), and (I-4).

$$B = J_w \left(\frac{1-R}{R} \right) \exp \left(-\frac{J_w}{k_f} \right) \quad (\text{I-2})$$

$$R = 1 - \frac{C_p}{C_b} \quad (\text{I-3})$$

$$k_f = \frac{J_{\text{salt}}}{\ln \left[\frac{\Delta P}{\pi_b - \pi_p} \left(1 - \frac{J_{\text{salt}}}{J_w} \right) \right]} \quad (\text{I-4})$$

where R is salt rejection [unitless], C_p is the salt concentration of permeate [mol/L],

C_b is the salt concentration of feed water [mol/L], π_b is the osmotic pressure of feed water [bar], J_W is the permeate flux using pure water as feed water [L/(m²·h)], J_{salt} is the permeate flux using salt water as feed water [L/(m²·h)], and k_f is the mass transfer coefficient.

The structure parameter, S , indicates the difficulty of salt diffusion through the supporting layer and can be calculated using equation (I-5).

$$S = \frac{\tau t}{\varepsilon} \quad (I-5)$$

where τ is the tortuosity of the membrane porous support layer [unitless], t is the membrane thickness [μm], and ε is porosity of the porous support layer [unitless]. If the tortuosity of the support layer is smaller, the membrane is thinner, and the porosity is larger, then S becomes small, and the FO membrane becomes a high performance membrane with minimal impact from the internal concentration polarization.

The solute concentration at each position, taking the effect of internal concentration polarization into account, are shown in Fig. I-16 for AL-DS.

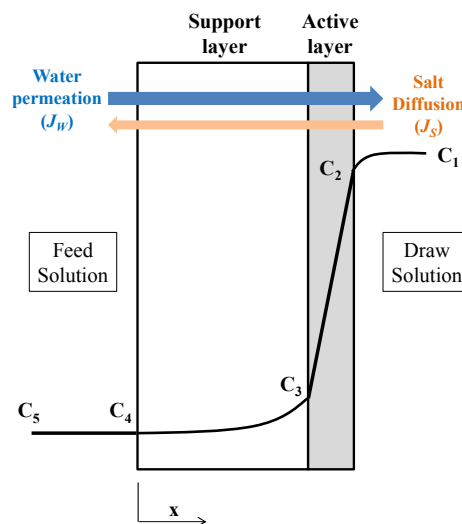


Fig. I-16 Concentration polarization in an FO membrane (AL-DS mode)

Applying mass balance to the internal membrane at steady state, the rate of reverse salt diffusion, J_S , can be calculated using equation (I-6).

$$J_S = D\varepsilon \frac{dC}{dx} - J_W C(x) \quad (\text{I-6})$$

where D is the diffusion coefficient of the solute. Equation (I-6) can be rewritten using the permeability of the solute through the active layer as:

$$J_S = B(C_2 - C_3) \quad (\text{I-7})$$

Setting equations (I-6) and (I-7) equal to each other, equation (I-8) can be obtained. (using the boundary condition $x=0$, $C=C_4$ and $x=\tau t$.)

$$\frac{J_W \tau t}{D\varepsilon} = \ln \left(\frac{J_W C_3 + B C_2 - B C_3}{J_W C_4 + B C_2 - B C_3} \right) \quad (\text{I-8})$$

Using the *van't Hoff* equation ($\pi = CRT/M$, π : osmotic pressure, C: molar concentration, R: gas constant, T: absolute temperature, and M: molecular weight), and the fact that the osmotic pressure is proportional to the concentration, equation (I-9) can be derived.

$$\frac{C_4}{C_2} = \frac{\pi_4}{\pi_2} \quad (\text{I-9})$$

Combining equations (I-8) and (I-9) gives equation (I-10) for the AL-DS mode:

$$J_W = \frac{D}{S} \ln \left(\frac{B + A\pi_2 - J_W}{A\pi_4 + B} \right) \quad (\text{I-10})$$

and equation (I-11) can be derived for the AL-FS mode:

$$J_W = \frac{D}{S} \ln \left(\frac{B + A\pi_2}{A\pi_4 + B + J_W} \right) \quad (\text{I-11})$$

As shown in equation (I-10) and (I-11), the water permeability in forward osmosis increases with the decrease of S .

(3) Membrane fouling on forward osmosis membrane

If the membrane filtration is continued with a constant driving force, gradually membrane pores are blocked by the filtration target materials (i.e. foulant), the water flux will decrease. This phenomenon is called as *membrane fouling*. Membrane fouling is very complex phenomenon which is affected by the water quality of feed water, the operational condition, the property of membrane (structure or material) and etc. Thus, although working on many researchers study, the detail mechanism has not been clear [25].

The membrane fouling which can be recovered by air scrubbing or wiping by sponge is called as reversible fouling, and which cannot be recovered is called as irreversible fouling. To recover the irreversible fouling, it needs the chemical cleaning. However, the chemical cleaning damages the membrane, because the cost increases and the adverse effect on the environment by the treatment and disposal of spent chemicals are concerned, the frequency of chemical cleaning must be minimized.

With continue to membrane filtration, the foulant including the feed water is accumulated on the feed side surface of the membrane. Here, in the case of the pressure driven membrane (i.e. MF, RO and etc.), the structure of foulant cake layer formed on the membrane is densely compacted. In contrast, in the case of the osmotic pressure driven membrane (i.e. FO), the foulant cake layer is loosely. Thus, this loose layer in FO can be recovered 80-100% by periodic rinse [45]. Also, there is the specific types of fouling in FO membrane which doesn't occur in the pressure-driven membrane

filtration process. It is called as *cake enhanced osmotic pressure* [46]. The schematic illustration of this phenomenon is shown in Fig. I-17. The salt leaked from DS side to feed side by salt back diffusion accumulate in the cake layer formed membrane surface. As a result, the salt concentration near the feed side of active layer is increased than the bulk, the effective osmotic pressure difference is reduced. This is the specific phenomenon of FO membrane filtration process which doesn't occur in RO membrane filtration process which the water and salt permeate the same direction.

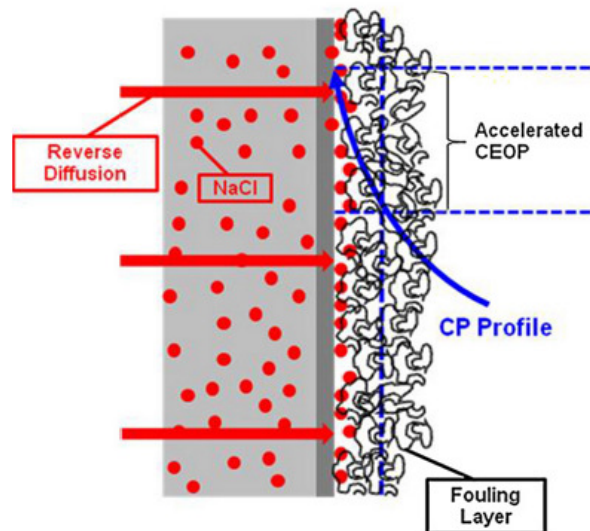


Fig. I-17 Schematic illustration of cake enhanced osmotic pressure [47]

(4) Applications of the forward osmosis method to wastewater treatment and solution concentration

Water harvesting from municipal wastewater

A system for harvesting pure water from municipal wastewater combines FO and membrane distillation (MD) (Fig. I-18). Xie et al. reported a water recovery of more than 80% and stable operation [48]. However, a heat source is needed to create the

temperature difference required in the MD operation. Only in rare situations where the waste heat from the sewage treatment can be utilized, the process may be commercialized.

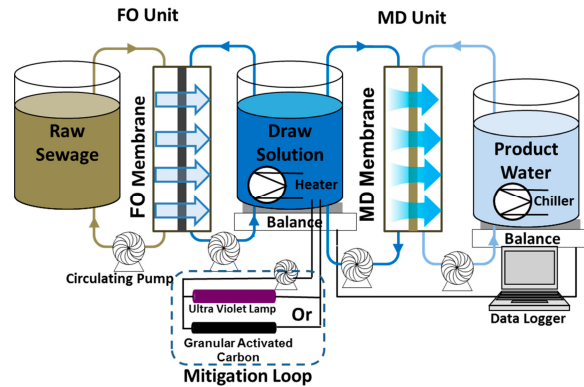


Fig. I-18 Schematic illustration of an FO-MD system [48]

Osmotic membrane bioreactors

Osmotic membrane bioreactors use FO followed by MBR [49] (Fig. I-19). The greatest advantage in this process is that the treated water quality is better than that from using an MF or UF membrane alone. In addition, the FO membrane is unlikely to experience fouling [49]. One disadvantage is the accumulation of salt diffused from the DS side, which adversely affects the biological reaction. Since the osmotic pressure difference is the driving force in the FO-MBR system, it is difficult to keep constant membrane permeation. The operating conditions of the bioreactor, such as retention time, would therefore be constantly changed, making consistent operation difficult.

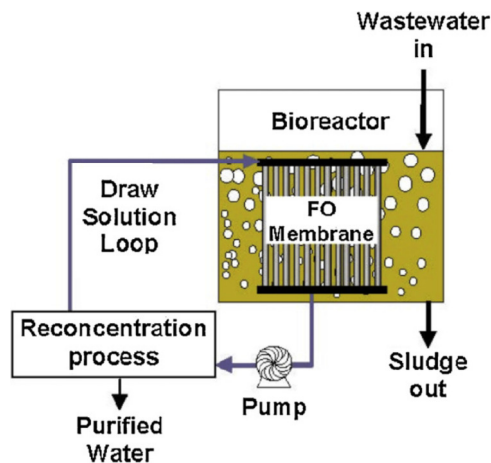


Fig. I-19 Schematic illustration of an osmotic membrane bioreactor [49]

Juice concentration

Applying FO to a solution concentration operation is relatively easy. Compared to conventional concentration methods, such as evaporation, FO can perform solution concentration without pressure or heat, thus maintaining quality of the end product. Petrotos et al. reported concentrating tomato juice using an FO process [50], and Babu et al. reported concentrating fruit juices using an FO process [51]. However, since salt diffused from the DS side would be mixed with the product (i.e., the concentrate), development of an FO membrane with lower salt leakage is quite important to commercialize this process.

I.6 Wastewater treatment system combined direct up-concentration using FO membrane and AnMBR

New technologies can help alleviate the energy problems associated with sewage treatment. The FO membrane, a new separation membrane, can be easily applied to solution concentration operations. Therefore, a novel wastewater treatment

system that combines AnMBR and direct condensation using an FO membrane proposed in this work to convert the current energy-consuming wastewater treatment systems to an energy-creating system.

The schematic illustration of the proposed system is shown in Fig. I-20. The largest particles in the influent wastewater are removed in the primary sedimentation tank. An FO membrane has been installed at the outlet of the primary sedimentation tank, and seawater is passed along the other side of the FO membrane. Osmotic pressure differences between the wastewater and seawater cause water to be drawn through the FO membrane from the wastewater to the seawater side, thus concentrating the wastewater. The diluted seawater is discharged to the sea. The concentrated wastewater next moves to the AnMBR. Here, due to a significant reduction in the quantity of wastewater, the heating energy required is much less. By converting organic matter in the concentrated sewage into biogas, the AnMBR accomplishes both removal of organic matter and energy production. Since the AnMBR does not have a mechanism for removing nutrients (i.e., nitrogen and phosphorus), post treatment for nutrient removal is necessary. For the post treatment system, the MAP (magnesium-ammonium-phosphate) system [52] for phosphorus recovery and a nitrification-denitrification MBR for nitrogen removal is proposed. In order to improve the recovery rate of the MAP, the phosphorus and nitrogen are first concentrated using FO.

There are some previous researches of AnMBR for wastewater treatment, but the concentrating wastewater prior AnMBR like the system proposed in this study is not done. In the case of no-concentration, the volume of the post-treatment for AnMBR effluent is almost same as inlet wastewater, it requires a relatively large-scale

post-treatment system. On the other hand, in the case of proposed system in this study, since the volume of AnMBR effluent is 1/10 ~ 1/20 times for inlet wastewater, the post-treatment system will become compact, and the energy consumption per inlet wastewater will be reduced.

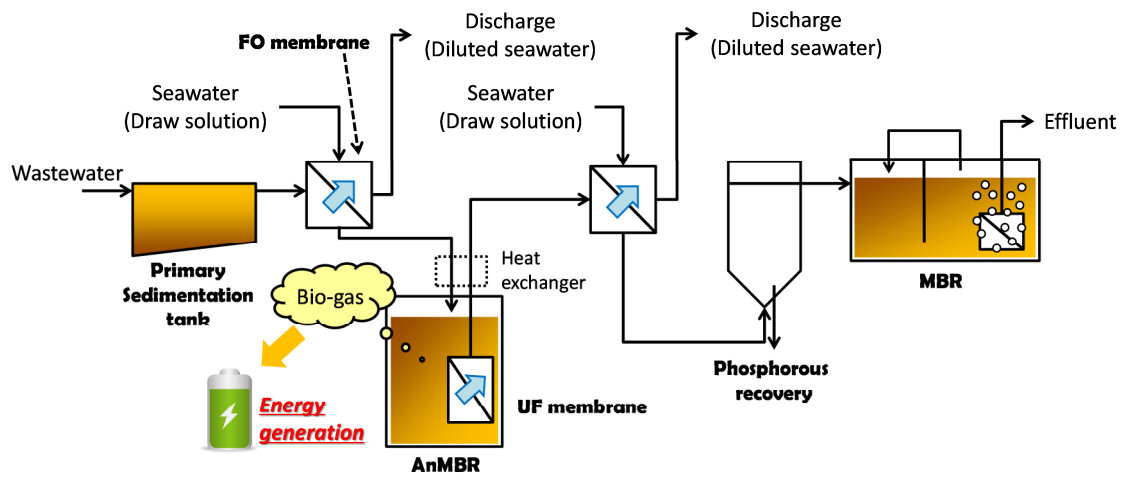


Fig. I-20 Schematic illustration of a novel wastewater treatment system combined direct up-concentration using FO membrane and AnMBR

I.7 Scope of this study

In this study, I propose a novel wastewater treatment system that combines AnMBR and direct condensation using an FO membrane, with the objective of evaluating the technical and economic feasibility.

A thesis outline is presented in Table I-1. **Chapter I** contains introduction and background. **Chapter II** contains an evaluation of the technical feasibility of directly concentrating wastewater using an FO membrane. The possibility of performing methane fermentation efficiently with the concentrated wastewater will also be explored. In this chapter, I evaluate the feasibility of applying the FO membrane. **Chapter III** contains an evaluation of nutrient rejection when concentrating the effluent from AnMBR with an FO membrane. **Chapter IV** contains an evaluation of the characteristics of membrane fouling on the FO membrane in the concentrating wastewater and of the AnMBR effluent using actual municipal wastewater. Although there are several similar reports that evaluate membrane fouling using surrogate wastewater, my study uses actual wastewater. Analysis of AnMBR effluent is necessary knowledge for future applications of FO membranes. **Chapter V** contains estimation of the energy produced from biogas obtained by the AnMBR and the overall energy consumption of the proposed system. Future challenges and operating conditions required to achieve an energy-producing wastewater treatment system are also clarified. Finally, **Chapter VI** contains a summary of this study with discussion and conclusions.

Table I-1 Thesis outline

Chapter	Contents
I	General introduction
II	Experimental evaluation of direct up-concentration of wastewater using forward osmosis membranes and the methane production potential of concentrated wastewater
III	Evaluation of nutrient rejection during concentration of the effluent from AnMBR by FO
IV	Characterization of FO membrane fouling during wastewater treatment of the AnMBR effluent
V	Estimation of energy consumption and production in the proposed system and clarification of future challenges
VI	Conclusions

Reference

- [1] The city of Hiroshima web site,
<http://www.city.hiroshima.lg.jp/www/contents/1324256478494/index.html>
- [2] Japan Sewage Works Association web site, <http://www.jswa.jp/rate/>
- [3] The vision of new sewer, <http://www.mlit.go.jp/common/001051257.pdf>
- [4] Metcalf, Eddy. Wastewater Engineering: Treatment Disposal and Reuse 3rd ed. New York, McGrawHill,1991.
- [5] Bitton G., Wastewater Microbiology. New York, Willey-Liss, 1994
- [6] Gray, Nick F., Activated sludge: theory and practice. Oxford University Press, 1990
- [7] Kubo M., Morisaki H., Kubota K., Imanaka T., Environmental microbiology.
Kagakudojin press, 2012
- [8] Mandt M. G. and Bell B. A., Oxidation ditches in wastewater treatment, Ann Arbor Science, Ann Arbor MI, 169 ,1982
- [9] Fillos J., Diyamandoglu V., Carrio L. A. and Robinson L, Full-scale evaluation of biological nitrogen removal in the step-feed activated sludge process. Water environment research, 68(2) (1996) 132-142
- [10] Kuai L. and Verstraete W., Ammonium removal by the oxygen-limited autotrophic nitrification-denitrification system. Appl. Environ. Microbiol., 64(11) (1998) 4500-4506.
- [11] Wada H., Industrial wastewater treatment technology. Tokyo Denki University Press, 2011
- [12] George T., Franklin L. B., and Stensel H. D., Wastewater engineering: treatment and reuse. Metcalf & Eddy, Inc., New York., 2003
- [13] Van Loosdrecht M. C. M., Hooijmans C. M., Brdjanovic D. and Heijnen, J. J.,

- Biological phosphate removal processes. *Appl. Environ. Microbiol.*, 48(3) (1997) 289-296.
- [14] Baeza J. A., Gabriel D. and Lafuente J. Effect of internal recycle on the nitrogen removal efficiency of an anaerobic/anoxic/oxic (A²/O) wastewater treatment plant (WWTP). *Process Biochem.*, 39(11) (2004) 1615-1624.
- [15] Japan for sustainability, Japanese municipalities targeting energy selfsufficiency at sewage treatment plants. *JFS Newsletter No. 71* (2008)
- [16] McCarty P. L., Bae J. and Kim J., Domestic wastewater treatment as a net energy producer—can this be achieved? *Environ. Sci. Technol.*, 45(17) (2011) 7100-7106.
- [17] Wei Y., Van Houten R. T., Borger A. R., Eikelboom D. H. and Fan Y., Minimization of excess sludge production for biological wastewater treatment. *Water Res.*, 37(18) (2003) 4453-4467.
- [18] Kataoka N., Characteristics and development chronology of anaerobic biotreatment technology. *Ebara newsletter*, No.229 (2010)
- [19] Niu Q., Qiao W., Qiang H., Hojo T. and Li Y. Y., Mesophilic methane fermentation of chicken manure at a wide range of ammonia concentration: Stability, inhibition and recovery. *Bioresour. Technol.*, 13 (2013) 358-367.
- [20] Smith A. L., Stadler L. B., Love N. G., Skerlos S. J. and Raskin L., Perspectives on anaerobic membrane bioreactor treatment of domestic wastewater: a critical review. *Bioresour. Technol.*, 122 (2012) 149-159.
- [21] Van Zyl P. J., Wentzel M. C., Ekama G. A. and Riedel K. J., Design and start-up of a high rate anaerobic membrane bioreactor for the treatment of a low pH, high strength, dissolved organic waste water. *Water Sci. Technol.*, 57(2)

(2008)

- [22] Watanabe R., Influence of temperature on treatment performance of synthetic sewage by anaerobic membrane bioreactor (AnMBR), *Journal of Japan Society on Water Environment*, 37(5) (2014)
- [23] Metcalf and Eddy, *Wastewater Engineering Treatment and Reuse*, 4th edition. McGraw-Hill, New York, 2003
- [24] Lettinga G. and Vinken J. N., Feasibility of the upflow anaerobic sludge blanket (UASB) process for the treatment of low-strength wastes. In *Proceedings of the 35th industrial waste conference*, May 13-15 1980, at Purdue University, Lafayette, Indiana, USA. School of Civil Engineering, Purdue Univ..
- [25] Nakao S., Watanabe Y., *New development of wastewater treatment technology using membrane*, CMC Publishing, 2004
- [26] Eikelboom, D. H., Filamentous organisms observed in activated sludge. *Water Res.*, 9(4) (1975) 365-388.
- [27] Shim J. K., Yoo I. K. and Lee Y. M., Design and operation considerations for wastewater treatment using a flat submerged membrane bioreactor. *Process Biochem.*, 38(2) (2002) 279-285.
- [28] C. W. Smith, D. Gregorio and R. M. Taleott, The use of ultrafiltration membrane for activated sludge separation, *Present. 24th Annu. Purdue Ind. Waste Conf.*, 24 , (1969) 1300–1310.
- [29] Yamamoto K., Hiasa M., Mahmood T. and Matsuo T., Direct solid-liquid separation using hollow fiber membrane in an activated sludge aeration tank. *Water Sci. Technol.*, 21(4-5) (1989) 43-54.
- [30] Atkinson S., Research studies predict strong growth for MBR markets. *Membrane*

Technology, 2006(2) (2006) 8-10.

- [31] Tao G., Kekre K., Wei Z., Lee T. C., Viswanath B. and Seah H., Membrane bioreactors for water reclamation. *Water Sci. Technol.*, 51(6-7) (2005) 431-440.
- [32] Mutamim N. S. A., Noor Z. Z., Hassan M. A. A. and Olsson G., Application of membrane bioreactor technology in treating high strength industrial wastewater: a performance review. *Desalination*, 305 (2012) 1-11.
- [33] Choo K. H. and Lee C. H., Membrane fouling mechanisms in the membrane-coupled anaerobic bioreactor. *Water Res.*, 30(8) (1996) 1771-1780.
- [34] Kanai M., Ferre V., Wakahara S., Yamamoto T. and Moro M., A novel combination of methane fermentation and MBR—Kubota Submerged Anaerobic Membrane Bioreactor process. *Desalination*, 250(3) (2010) 964-967.
- [35] Lin H., Chen J., Wang F., Ding L. and Hong H., Feasibility evaluation of submerged anaerobic membrane bioreactor for municipal secondary wastewater treatment. *Desalination*, 280(1) (2011) 120-126.
- [36] Y.C. Kim, S. Han, S. Hong, A feasibility study of magnetic separation of magnetic nanoparticle for forward osmosis, *Water Sci. Technol.* 64 (2) (2011) 469–476.
- [37] D. Li, X. Zhang, J. Yao, G.P. Simon and H. Wang, Stimuli-responsive polymer hydrogels as a new class of draw agent for forward osmosis desalination, *Chem. Commun.* 47 (6) (2011) 1710–1712.
- [38] Y. Cai, W. Shen, J. Wei, T.H. Chong, R. Wang, W.B. Krantz, A.G. Fane and X. Hu, Energy efficient desalination by forward osmosis using responsive ionic

- liquid draw solutes, *Environ. Sci. Water Res. Technol.* 1 (3) (2015) 341–347.
- [39] Yangali-Quintanilla V., Li Z., Valladares R., Li Q. and Amy G., Indirect desalination of Red Sea water with forward osmosis and low pressure reverse osmosis for water reuse. *Desalination*, 280(1) (2011) 160-166.
- [40] Achilli A., Cath T. Y. and Childress A. E., Power generation with pressure retarded osmosis: An experimental and theoretical investigation. *J. Membr. Sci.*, 343(1) (2009) 42-52.
- [41] Gray G. T., McCutcheon J. R. and Elimelech M., Internal concentration polarization in forward osmosis: role of membrane orientation. *Desalination*, 197(1) (2006) 1-8.
- [42] Zhao S., Zou L. and Mulcahy D., Effects of membrane orientation on process performance in forward osmosis applications. *J. Membr. Sci.*, 382(1) (2011) 308-315.
- [43] Cath T. Y., Childress A. E. and Elimelech M., Forward osmosis: principles, applications, and recent developments. *J. Membr. Sci.*, 281(1) (2006) 70-87.
- [44] McCutcheon, J. R. and Elimelech M., Modeling water flux in forward osmosis: implications for improved membrane design. *AIChE Journal*, 53(7) (2007) 1736-1744.
- [45] Kim Y., Elimelech M., Shon H. K. and Hong S., Combined organic and colloidal fouling in forward osmosis: fouling reversibility and the role of applied pressure. *J. Membr. Sci.*, 460 (2014) 206-212.
- [46] Hoek E. M. and Elimelech M., Cake-enhanced concentration polarization: a new fouling mechanism for salt-rejecting membranes. *Environ. Sci. Technol.*,

37(24) (2003) 5581-5588.

- [47] Lee S., Boo C., Elimelech M. and Hong S., Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO). *J. Membr. Sci.*, 365(1) (2010) 34-39.
- [48] Xie M., Nghiem L. D., Price W. E. and Elimelech M., A forward osmosis–membrane distillation hybrid process for direct sewer mining: system performance and limitations. *Environ. Sci. Technol.*, 47(23) (2013) 13486-13493.
- [49] Achilli A., Cath T. Y., Marchand E. A. and Childress A. E., The forward osmosis membrane bioreactor: a low fouling alternative to MBR processes. *Desalination*, 239(1) (2009) 10-21.
- [50] Petrotos K. B., Quantick P. and Petropakis H., A study of the direct osmotic concentration of tomato juice in tubular membrane–module configuration. I. The effect of certain basic process parameters on the process performance. *J. Membr. Sci.*, 150(1) (1998) 99-110.
- [51] Babu B. R., Rastogi N. K. and Raghavarao K. S. M. S., Effect of process parameters on transmembrane flux during direct osmosis. *J. Membr. Sci.*, 280(1) (2006) 185-194.
- [52] Wang J., Song Y., Yuan P., Peng J. and Fan M., Modeling the crystallization of magnesium ammonium phosphate for phosphorus recovery. *Chemosphere*, 65(7) (2006) 1182-1187.

Chapter II

Direct up-concentration of wastewater by forward osmosis membrane and evaluation of energy production of system comprised of concentrating wastewater and anaerobic treatment

II.1 Introduction

Wastewater treatment plays a very important role in public hygiene in a city. On the other hand, huge energy is devoted to the wastewater treatment. The amount of energy consumed in wastewater treatment is approximately 700 GWh in Japan, and this corresponds to 0.7 % of the total energy consumption in Japan [1]. Furthermore, it has been reported that its value becomes 3% in USA [2]. At present, aerobic biological treatment (e.g., conventional activated sludge process), in which organic matter contained in wastewater is converted into carbon dioxide and microbial cells under aerobic condition, is the primal choice for treating municipal wastewater. Many wastewater treatment plants based on conventional activated sludge process are in operation for more than several decades. As a result, considerable operational know-hows of the aerobic wastewater treatment processes have already been accumulated. In such aerobic wastewater treatment processes, aeration is essential for maintaining dissolved oxygen (DO) concentration in the bioreactor at certain level (e.g., more than 2 mg/L) [3] to keep the activity of aerobic microorganisms. However, aeration generally consumes huge energy. In general, 45-75% of total operation cost of aerobic biological wastewater treatment is consumed by aeration to the bioreactor [4]. Reducing the energy consumption associated with aeration is of critical importance for

improving sustainability of wastewater treatment.

On the other hand, in addition to aerobic treatment methods, organic matter can also be removed from wastewater under anaerobic conditions. In the anaerobic treatment, organic constituents contained in wastewater are converted to methane and carbon dioxide (sometimes referred as biogas) by the activities of anaerobic microorganisms [5]. Since aeration is not required in anaerobic treatment, energy consumption in anaerobic treatment is generally much lower than that in aerobic treatment. The additional advantages of applying anaerobic treatment are reduced sludge production and capability of producing methane gas which can be used as fuel. Since municipal wastewater contains plenty of organic matter which can be a source of methane generation, applying anaerobic treatment to municipal wastewater treatment would be an attractive choice for reducing the energy demand associated with wastewater treatment. According to the estimation made by McCarty et al., domestic wastewater treatment could be a net energy producer by applying full anaerobic treatment [2].

However, operation of anaerobic treatment is difficult for wastewater with low concentration. It was reported that raw water with chemical oxygen demand (COD_{Cr}) concentration of higher than 1500-2000 mg/L is preferable for anaerobic treatment [6]. On the other hand, typical COD_{Cr} concentration in municipal wastewater is in the range of 250-800 mg/L [6]. To perform anaerobic wastewater treatment efficiently, concentrating raw wastewater prior to introducing it into anaerobic bioreactor would be effective. Lateef et al. succeeded to concentrate real municipal wastewater with COD_{Cr} concentration of more than 6000 mg/L using microfiltration (MF) membrane [7]. Based on the COD_{Cr} concentration in the concentrated wastewater, they estimated that

producing 0.5 kWh of electricity per cubic meter of wastewater would be possible by applying anaerobic treatment to the concentrated wastewater. The study performed by Lateef et al. clearly indicated that membrane separation is one of the suitable technologies for enabling recovery of energy in a form of methane from municipal wastewater. However, the use of MF membrane would have several limitations. At first, the permeate of MF membrane could not be direct discharged into natural water body because some dissolved matters contained in wastewater are permeated through an MF membrane. This feature of MF membrane results in the requirement of some post-treatment to improve the quality of treated water. The other point is loss of organic matter into the treated water. Since approximately half of organic matter contained in municipal wastewater is in the form of dissolved state (i.e., could not be rejected by MF membrane), efficiency of recovering organic matter by MF membrane is thought to be limited. On the basis of the points mentioned above, it can be said that proper selection of membrane is essential for successful concentration of organic matter contained in municipal wastewater.

In this study, I focused on the application of forward osmosis (FO) membrane for concentrating organic matter contained in municipal wastewater. FO membrane filtration process is gaining attention owing to its unique character (i.e., applying hydraulic pressure is not required during the membrane filtration [8]). In FO membrane filtration process, water molecules contained in feed solution (FS) with relatively low osmotic pressure are spontaneously transported into draw solution (DS), which has an osmotic pressure higher than FS, on the basis of the osmotic pressure gradient. Since FO membrane generally has similar rejection capability to reverse osmosis (RO) membrane, almost all dissolved components are expected to be rejected by applying FO

membrane. This feature of FO membrane is thought to be a clear advantage of this technology from the view point of treated water quality, especially in the comparison with porous membranes (i.e., MF and ultrafiltration (UF) membranes). In addition, several researchers reported that FO membrane filtration process is one of the suitable technologies for concentrating products containing high organic matter or suspended solid concentrations [9, 10 and 11], because the structure of the fouling layer developed in FO membrane filtration process is more loose than RO membrane filtration process, and the recovery of membrane fouling is easier [12]. By applying direct FO membrane filtration, I will be able to achieve wastewater treatment and production of concentrated wastewater to be subjected to an anaerobic digester simultaneously. Gu et al. proposed anaerobic membrane bioreactor (AnMBR) system, in which an FO membrane is directly submerged in the anaerobic bioreactor [13]. In their study, however, elevated salt concentration in the bioreactor as a result of back-diffusion of salt from DS may cause inhibitory effect on the activity of microorganisms responsible for anaerobic treatment. The increase in salt concentration in the bioreactor would also result in decrease in the driving force of the FO membrane filtration (i.e., effective osmotic pressure difference between bioreactor and DS). Zhang et al. concentrated a municipal wastewater using FO membrane by more than 300% [14]. However, in this study, they did not evaluate whether the concentrate ratio obtained in this study is significant or not for anaerobic treatment.

Based on the backgrounds mentioned above, in this study, I investigated the performance of an FO membrane in concentrating real municipal wastewater in terms both of rejections of constituents contained in the wastewater and development of membrane fouling. The concentrate was subsequently subjected to a batch methane

fermentation test to evaluate the methane production potential of concentrated municipal wastewater.

II.2 Experiment

II.2.1 Concentration of municipal wastewater using FO membrane

In this experiment, effluent from primary sedimentation tank in Port Island wastewater treatment plant in Kobe city, Japan was used as feed water in an FO membrane filtration test. Characteristics of the wastewater used in this study are summarized in Table II-1. A schematic illustration of experimental apparatus is shown in Fig. II-1.

Table II-1 Water quality of effluent from primary sedimentation tank in Port Island wastewater treatment plant (Feed water of concentration test)

Item	Unit	Value
TOC	mg/L	88.5
CODcr	mg/L	300
PO ₄ -P	mg-P/L	4.2
NH ₄ -N	mg-N/L	34.0

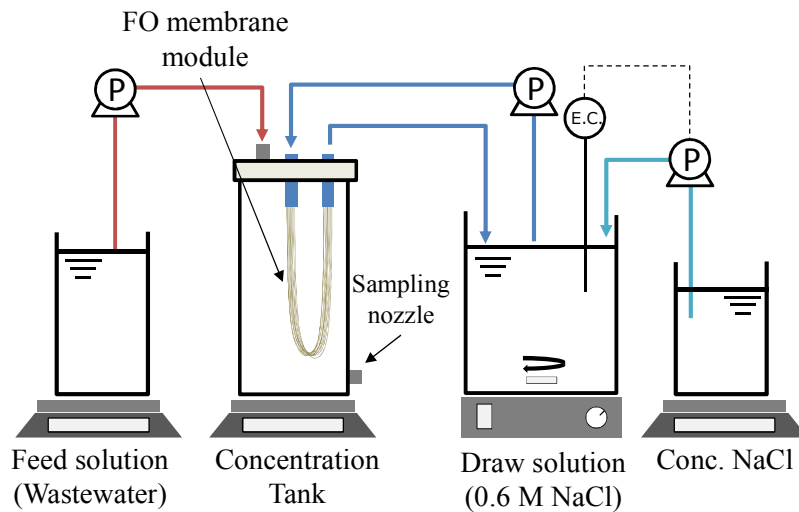


Fig. II-1 Schematic illustration of concentration system using hollow fiber FO membrane

Concentration tank, in which a small FO membrane module was directly submerged, was made of transparent acrylic resin and had an effective volume of 1500 mL. During experiment, concentration tank was hermetically-sealed. The FO membrane used in this experiment was asymmetric hollow fiber membrane made of cellulose triacetate (Toyobo, Osaka, Japan). This FO membrane has an active layer at outer surface. In a small FO membrane module used in this study, 350 fibers were bundled, resulted in a total effective membrane surface area of 0.0846 m². Membrane orientation was active layer facing feed solution (AL-FS). This is because that membrane fouling generally becomes less significant in this orientation [15]. 0.6 M NaCl solution was used as draw solution (DS) and the initial volume of DS was 2000 mL. The cross-flow velocity of DS in the hollow fiber was set to 5.5 cm/s. During the FO membrane filtration test, the salt concentration of the DS was adjusted at a constant by supplying a concentrated NaCl solution (approximately 4.0 M), based on the decrease in electrical conductivity using a

conductivity control device (CM-31P, Toa-DKK, Tokyo, Japan). The wastewater was added to the concentration tank using a peristaltic pump (MP-1000, Eyela, Tokyo, Japan). The feed pump was controlled by water level sensor to keep the water level at a constant position.

In the FO membrane filtration test mentioned above, flow rate of water across the FO membrane (Q) was evaluated from the rate of decrease in the mass of feed water in the feed water tank. The water flux J_W was calculated using the following equation:

$$J_W = \frac{Q}{A} = \frac{m_0 - m_t}{A \cdot t} \quad (\text{II-1})$$

where Q is the flow rate of FO membrane (g/h), A is the effective membrane surface area (m^2), t is the operation time (h), m_0 is the initial weight of feed tank (g) and m_t is the weight of feed tank at t (g). To maintain the water permeability of the FO membrane during the concentration operation, a simple physical cleaning by stirring strongly the inside condensation tank by a magnetic stirrer was carried out for every 22 hours. After physical cleaning, it was subjected to the pure water permeation test using a Milli-Q (as FS) and 0.6 M NaCl (as DS) for the assessment of degree of irreversible fouling.

II.2.2 Batch methane fermentation test using concentrated municipal wastewater

A batch methane fermentation test was carried out to evaluate the methane gas yield of concentrated wastewater. 0.4 L of anaerobically digested sludge collected from Higashinada wastewater treatment plant in Kobe city, Japan was placed in a conical flask. 0.4 L of concentrated wastewater was added to the flask, and then, the flask was hermetically-sealed. During the test, water temperature was kept at 40°C, and the mixture of digested sludge and concentrated wastewater was continuously agitated

using a magnetic stirrer. The biogas generated was collected in a gas holder and then the volume of gas generated was recorded. In order to subtract the gas generated from organic matter originally contained in the anaerobically digested sludge, a blank test was carried out using the exactly the same digested sludge collected at the same place and the same time. In the blank test, 0.4 L NaCl solution, which had a comparable electrical conductivity to the concentrated wastewater subjected to the batch methane fermentation test, was added to the anaerobically digested sludge instead of the concentrated wastewater. Experimental conditions except for the characteristics of the added liquid (i.e., concentrated wastewater and NaCl solution) were set to the same between the two flasks. Since NaCl solution added did not have any organic matter, which can be a source of methane generation, the gas generated in the blank flask can be considered as the one originated from organic matter originally contained in the anaerobically digested sludge. Therefore, the difference in the amount of biogas generated between the two flasks can be considered as the amount of biogas generated from the organic matter contained in the concentrated wastewater.

Based on the assumption that methane occupied 70% of the biogas generated [16], methane yield η_{CH_4} was calculated by the following equation:

$$\eta_{CH_4} = \frac{(V_1 - V_0) \cdot 0.7}{V_{mix} \cdot \{(C_1^{start} - C_1^{end}) - (C_0^{start} - C_0^{end})\}} \quad (II-2)$$

where η_{CH_4} is the methane yield ($m^3\text{-CH}_4/\text{kg-COD}_{Cr}$), V_1 is the volume of biogas generated from the digested sludge mixed with the concentrated wastewater (m^3), V_0 is the volume of biogas generated from blank (m^3), V_{mix} is the total volume of the digested sludge and concentrated wastewater (m^3), C_1^{start} and C_1^{end} are COD_{Cr} concentration of the digested sludge mixed with the concentrated wastewater at

start/end of the batch fermentation test ($\text{kg-COD}_{\text{Cr}}/\text{m}^3$) and C_o^{start} and C_o^{end} are COD_{Cr} concentration at start/end of the test of blank.

II.2.3 Analytical methods

The concentration of COD_{Cr} was determined by the chromium oxidation (DRB200, HACH, Colorado, USA). The concentrations of total organic carbon (TOC) and total inorganic carbon (TIC) were determined using a TOC analyzer (TOC-VCSH, Shimadzu, Kyoto, Japan). The concentration of phosphate ion $\text{PO}_4\text{-P}$ was determined by molybdenum blue method [17], and the concentration of ammonium ion was determined by the closed salicylate-chlorine method (HACH, Colorado, USA) using a HACH spectrometer (DR900).

II.3 Calculation of material balance of organic matter during up-concentration using FO membrane

The material balance on the organic matters which were feed to concentration tank during municipal wastewater concentration test was calculated by divided it into the following parts; accumulated in concentration tank, permeate the FO membrane, and lost due to some experimental limitations (e.g. mineralization by biodegradation, accumulation into a dead-space such as adherence to the inner wall of the concentration tank or loss at the time of physical cleaning). Each quantity was calculated by the following equation.

$$Q_{\text{Feed}}^{\text{TOC}} = C_{\text{waste}}^{\text{TOC}} \cdot \left(\sum V_{\text{permeate}} + V_{\text{tank}} \right) \quad (\text{II-3})$$

$$Q_{\text{accumulate}}^{\text{TOC}} = C_{\text{conc}}^{\text{TOC}} \cdot V_{\text{tank}} \quad (\text{II-4})$$

$$Q_{\text{permeate}}^{\text{TOC}} = \sum (C_{\text{permeate}}^{\text{TOC}} \cdot V_{\text{permeate}}) \quad (\text{II-5})$$

$$Q_{lost}^{TOC} = Q_{Feed}^{TOC} - Q_{accumulate}^{TOC} - Q_{permeate}^{TOC} \quad (II-6)$$

where Q_{Feed}^{TOC} is the quantity of the total organic carbon (TOC) which was feed to concentration tank during the concentration test (mg), C_{waste}^{TOC} is the TOC concentration of municipal wastewater (mg-C/L), $V_{permeate}$ is the volume of water that permeate the FO membrane measured by every 12 h during concentration test (L), V_{tank} is the volume of concentration tank (L), $Q_{accumulate}^{TOC}$ is the quantity of the TOC which was accumulate in the concentration tank (mg), C_{conc}^{TOC} is the TOC concentration of concentrated wastewater at end of the concentration test (mg-C/L), $Q_{permeate}^{TOC}$ is the quantity of the TOC which permeated the FO membrane (mg) and $C_{permeate}^{TOC}$ is the TOC concentration of the permeate that measured by every 12 h during concentration test (mg-C/L).

II.4 Results and discussion

II.4.1 Membrane fouling in hollow fiber FO membrane

Variation in water flux during concentration of wastewater using hollow fiber FO membrane module is shown in Fig. II-2. The closed plots show the water flux during the FO membrane filtration of wastewater, and the open plots show the water flux determined by filtering Milli-Q water after physical cleaning. Although the water flux in the FO filtration of wastewater was clearly decreased during the continuous filtration for 36 hours due to membrane fouling, most of the membrane fouling developed was reduced by the physical cleaning: the decrease in the Milli-Q water flux determined after physical cleaning was not pronounced throughout the experiment. This result indicates that the majority of the membrane fouling developed during the FO membrane of wastewater for 36 hours was physically reversible. This finding suggests

that a stable long-term operation of FO membrane filtration for concentrating municipal wastewater can be achieved by adopting appropriate physical cleaning during the filtration. In the pressure-driven membrane filtration processes, such as an MF membrane filtration, the foulant layer is compacted by mechanical pressure and deposited on the membrane surface, which increases the filtration resistance [12]. In contrast, in the FO membrane filtration process, compaction of fouling layer is expected to be less significant because of the absence of extensive hydraulic pressure. Therefore, it is difficult to consider compaction of fouling layer is a dominant factor to increase the filtration resistance in FO membrane filtration. One of the reasons for the FO flux decrease is the reduction of the effective osmotic pressure difference caused by NaCl leaked from the DS side. The leaked NaCl accumulates in cake layer on membrane surface formed by foulant and leads to “cake enhanced osmotic pressure” [18].

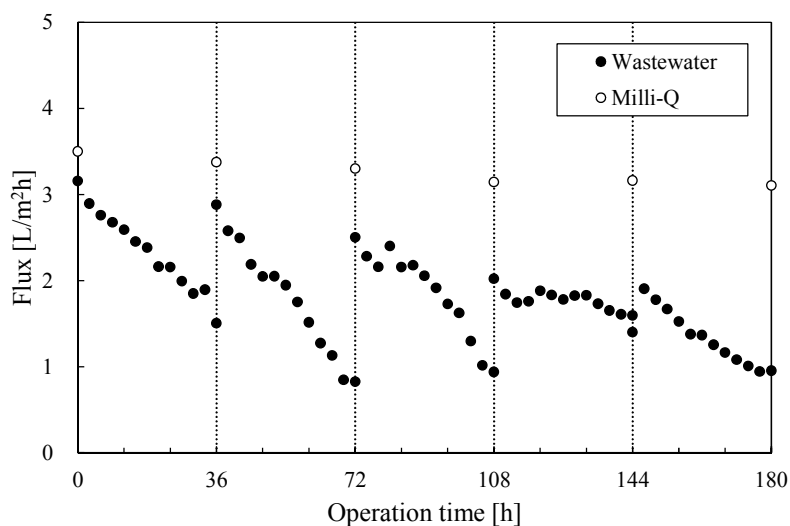


Fig. II-2 Variation in flux during concentration of municipal wastewater. The arrow shows the physical cleaning of membrane.

Although the membrane fouling can be almost completely reduced by physical

cleaning carried out in every 36 hours, water flux determined immediately after the implementation of physical cleaning was gradually decreased as number of cycle increased. The gradual decrease in water flux after the physical cleaning is explained by the decrease in the effective osmotic pressure difference between the feed wastewater and the DS. The potential causes of this decrease might be increase in the concentration of salts originally contained in the raw wastewater (final volumetric concentration ratio after 180 h operation was approximately 19 times) and diffusion of salts contained in the DS as a result of so-called reverse solute diffusion (i.e., the solute contained in a DS diffused into an FS based on a concentration gradient). To minimize the reduction in water flux during the up-concentration of municipal wastewater using FO membrane, the development of an FO membrane with low reverse solute flux from DS to FS is important. Incidentally, assuming as described below, in the case of 10000 m³/d scale wastewater treatment plant, the number of membrane modules will be 2823, and the footprint will be approximately 170 m².

- Average FO membrane permeate flux is 2 L/m²h.
- Volumetric concentration ratio of FO membrane is 20 times.
- FO membrane surface area is 70 m²/module.
- FO membrane module stacking is 5 stages.

II.4.2 Water qualities of permeate in DS side

The variations in water quality of permeate obtained during the concentration test using the FO membrane are shown in Fig. II-3. Here, I could not measure the COD_{Cr} concentration in the permeate because diluted DS including the permeate has high salt concentration. For this reason, I substitute TOC as an indicator of organic

matter. The initial TOC and phosphate ion concentrations of permeate were 11.5 mg-C/L and less than 0.1 mg-P/L, respectively. The rejections of TOC and phosphate ion were more than 90% and 98%, respectively. These results indicate that sufficient rejection for organic matter and phosphorus was accomplished by the FO membrane filtration alone.

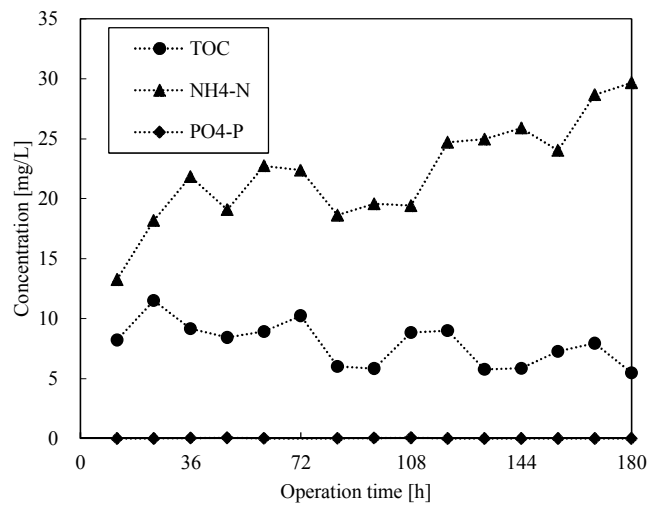


Fig. II-3 Variation in water quality of permeate in municipal wastewater concentration test.

In contrast, the concentration of ammonium ion exceeds the discharge standards of the total nitrogen in Hyogo prefecture, Japan (20 mg/L). In the concentration process using an FO membrane, the concentration of ammonium ion in the feed side of the FO membrane increases as the wastewater is concentrated. The gradual increase in the concentration of ammonium ion in the feed water resulted in the increase in that of permeate. At the end of this experiment, at which the wastewater was concentrated by 19 times based on volume, the concentration of ammonium ion in the permeate reached to 29.7 mg/L. To make the proposed process feasible, a significant

improvement in the rejection of ammonium ion by an FO membrane is essential. On the other hand, if ammonia rejection by an FO membrane is improved, the concentration of ammonia in the concentrated wastewater increases. High concentration of ammonia is known to inhibit the methane fermentation in the anaerobic treatment. In mesophilic methane fermentation, it is necessary to control the concentration of ammonium nitrogen to less than 2000 mg/L [19]. Considering the typical concentration of total nitrogen (most of nitrogen species including organic nitrogen are generally transformed into ammonium ion during anaerobic digestion) in municipal wastewater of 10-40 mg/L [20], more than 50-times concentration is required to increase the concentration of ammonium ion to a level at which methane fermentation is inhibited. On the other hand, as discussed later, the results obtained in this study indicate that 19-times concentration by an FO membrane is totally enough for achieving a wastewater treatment system with net energy production. Therefore, the elevated concentration of ammonium ion in the concentrated wastewater would not be problematic from the view point of efficiency of methane fermentation. Actually, the decrease in the ammonium ion concentration in the FO membrane permeate would be an more important topic, especially when a stringent discharge standard considering problems associated with eutrophication needs to be satisfied.

II.4.3 Accumulation of organic matter in concentrated municipal wastewater

Fig. II-4 shows the variation in the concentrations of TOC and TIC in the concentrated municipal wastewater during the up-concentration of municipal wastewater using the FO membrane. As can be seen in Fig. II-4, the concentration of total carbon (TC) (i.e. sum of TOC and TIC) was gradually increased. On the other hand,

the TIC per TC ratio increased from 0.3 at the beginning to 0.4 at the end of the experiment, indicating that a portion of organic matter rejected by the FO membrane was mineralized during the experiment. This result suggests that further improvement of concentrating organic matter is possible by reducing the time required for concentration.

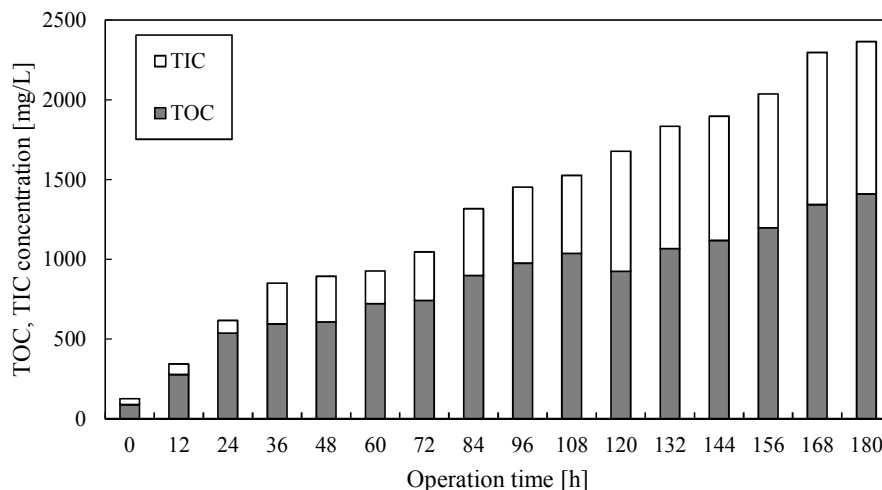


Fig. II-4 Variation in water quality of permeate in municipal wastewater concentration test.

With regard to COD_{Cr} , although it was not possible to accurately measure due to the inhibition by salt concentration of concentrated wastewater. However, if the COD_{Cr}/TOC ratio was kept constant during the concentration test, the COD_{Cr} concentration of concentrated wastewater at 180 h may be estimated around 4800 mg/L. (i.e. the concentrate factor about organic matter is approximately 16 times). This value is apparently higher than that required for efficient anaerobic treatment (i.e., 1500-2000 mg/L) [6]. The value of COD_{Cr} concentration achieved in the experiment in this study was higher than that reported by Zhang et al. (i.e., 1642.3 mg/L), and the results obtained in this study reinforce the findings obtained in Zhang et al. [14], which

suggested that applying pre-concentration using an FO membrane is highly possible to realize an anaerobic treatment in the main stream of wastewater treatment for potential energy production.

As mentioned above, there is still possibility for improving the accumulation of COD_{Cr} by minimizing the mineralization during the up-concentration of municipal wastewater using an FO membrane. To minimize the mineralization, the retention time of concentrated municipal wastewater in the concentration chamber should be as short as possible. In other words, it is important to draw the FO membrane permeate from the raw wastewater as quick as possible. In this study, the packing density of the FO membrane in the concentration chamber (i.e., membrane surface area available in a unit volume of the chamber) was arbitrary selected. Indeed, further increase in the surface area of the membrane installed in the chamber is possible. An appropriate selection of packing density of the FO membrane is apparently an important research topic in future. In addition, an effective membrane cleaning method for maintaining the membrane flux during the concentration should be investigated. In the experiment carried out in this study, although the development of physically irreversible fouling was marginal as shown in Fig. II-2, the membrane flux gradually decreased during the FO membrane filtration of the municipal wastewater. If an effective membrane cleaning method is applied during the FO membrane filtration, the membrane flux can be kept at higher level, which results in rapid withdrawal of the FO membrane permeate from the municipal wastewater.

II.4.4 Material balance of organic matter during up-concentration using FO membrane

The material balance of organic matter determined at the end of up-concentration using the FO membrane is shown in Fig. II-5. Among the organic matter subjected to the up-concentration, the 84% was accumulated in the concentrate and 8% was lost into the permeate through the FO membrane. In addition to the fates of organic matter mentioned above, 8% of the organic matter was likely to be lost due to some experimental limitations (e.g. mineralization by biodegradation, accumulation into a dead-space such as adherence to the inner wall of the concentration tank or loss at the time of physical cleaning). In the study performed by Lateef et al., the fraction of organic matter that can be recovered through the concentration using an MF membrane was limited to slightly more than half of the organic matter introduced in the concentration chamber [7]. In the present study, apparently larger fraction of organic matter contained in the real municipal wastewater can be recovered through the up-concentration of wastewater using an FO membrane. This difference could be attributed to the difference in the type of membrane used for concentrating wastewater. Generally, an FO membrane has a rejection capability of almost equal to that of the reverse osmosis (RO) membrane. Therefore, rejection of dissolved organic matter by the FO membrane is expected to be much higher than that by the MF membrane. Such increased rejection of organic matter by the FO membrane filtration would make this process suitable for pretreatment of anaerobic treatment for producing methane gas.

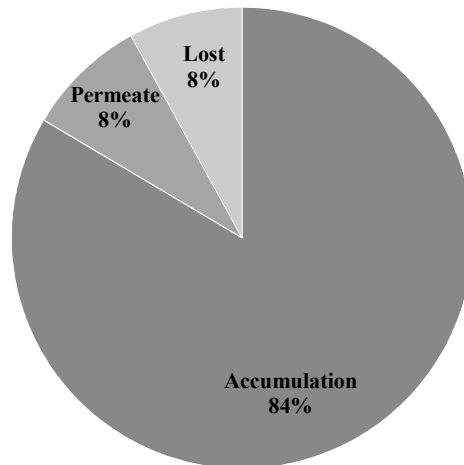


Fig. II-5 Material balance of organic matter during concentration of municipal wastewater by FO membrane

With regard to the organic matter mineralized by biodegradation during the up-concentration of the municipal wastewater, significant mineralization reduction can be expected by decreasing the retention time in the concentration tank (approximately 10 h in the experiment carried out in this study). Since the concentration chamber used in this study was arbitrary constructed, it is expected that there is still possibility for increasing the packing density of the membrane further. By increasing packing density of FO membrane in the concentration chamber, the volume of water filtrated through the FO membrane in a unit time increases, which results in the decrease in the retention time in the concentration chamber.

II.4.5 Batch methane fermentation test

The concentrated wastewater used in this test is different from the concentrated wastewater obtained in FO membrane filtration test from the mentioned above. The COD_{Cr} concentration of the concentrated wastewater used in this test was 2600 mg/L.

The biogas which is generated in blank test is originated from the organic matter contained in seed sludge (i.e., digested sludge collected from a full-scale anaerobic digester). Therefore, the difference between the volume of biogas generated in the blank test and the batch fermentation test in which the concentrated municipal wastewater was the volume of biogas originated from the organic matter contained in the concentrated wastewater. In the result of the methane fermentation test, the volume of biogas from the reactor which was fed 0.4 L concentrated wastewater is 0.3 L, from the blank reactor is 0.1 L. On the basis of the assumption mentioned above, the volume of biogas originated from 0.4 L of the concentrated municipal wastewater was estimated to be 0.2 L. In addition, the amount of removal COD_{Cr} at the end of operation is 0.64 g- COD_{Cr} (removal rate of COD_{Cr} was 0.62). Taking into above, the methane yield from the organic matter contained in the concentrated municipal wastewater was calculated to be 0.22 $\text{m}^3\text{-CH}_4/\text{kg-COD}_{\text{Cr_rem}}$ (assuming the methane occupied 70% of the biogas produced [21]). This value is in almost agreement with the methane yields in the anaerobic fermentation of the organic matter contained in municipal wastewater reported in previous studies [22, 23]. As mentioned above, it is possible that biogas generation by methane fermentation with using concentrated wastewater.

II.5 Conclusions

I estimated the energy balance of a wastewater treatment system comprised of the up-concentration of municipal wastewater by the FO membrane and anaerobic fermentation of the concentrated wastewater. The results of concentration test revealed that more than 16 times concentration of organic carbon contained in real municipal wastewater was possible by using the hollow fiber FO membrane. The methane yield

from the concentrated organic matter was $0.22 \text{ m}^3\text{-CH}_4/\text{kg-COD}_{\text{Cr_rem}}$. The result suggested that biogas generation by methane fermentation with using concentrated wastewater is possible.

Reference

- [1] Japan for sustainability, 2008. Japanese municipalities targeting energy self-sufficiency at sewage treatment plants. JFS Newsletter No. 71.
- [2] McCarty P. L., Bae J., Kim J., 2011. Domestic wastewater treatment as a net energyproducer – can this be achieved? *Environ. Sci. Technol.* 45, 7100–7106.
- [3] Parker D. S., Merrill M. S., 1976. Oxygen and air activated sludge: another view. *Journal (Water Pollution Control Federation)* 2511-2528.
- [4] Reardon D.J., 1995. Turning down the power. *Civ. Eng.* 65 (8), 54–56.
- [5] Heijnen J. J., Mulder A., Enger W., and Hoeks F., 1989. Review on the application of anaerobic fluidized bed reactors in waste-water treatment. *Chem. Eng. J.* 41 (3), B37-B50.
- [6] Metcalf, Eddy, 2003. *Wastewater Engineering Treatment and Reuse*, 4th edition. McGraw-Hill, New York.
- [7] Lateef S. K., Soh B. Z., and Kimura K., 2013. Direct membrane filtration of municipal wastewater with chemically enhanced backwash for recovery of organic matter. *Bioresour. Technol.* 150, 149-155.
- [8] Cath T. Y., Childress A. E., and Elimelech M., 2006. Forward osmosis: principles, applications, and recent developments. *J. Membr. Sci.*, 281 (1), 70-87.
- [9] Petrotos K. B., Quantick P., and Petropakis H., 1998. A study of the direct osmotic concentration of tomato juice in tubular membrane–module configuration. I. The effect of certain basic process parameters on the process performance. *J. Membr. Sci.* 150 (1), 99-110.
- [10] Garcia-Castello E. M., McCutcheon J. R., and Elimelech M., 2009. Performance

- evaluation of sucrose concentration using forward osmosis. *J. Membr. Sci.* 338, 61–66.
- [11] Babu B.R., Rastogi N.K., and Raghavaro K.S.M.S., 2006. Effect of process parameters on transmembrane flux during direct osmosis. *J. Membr. Sci.* 280, 185–194.
- [12] Lee S., Boo C., Elimelech M., and Hong S., 2010. Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO). *J. Membr. Sci.* 365 (1), 34-39.
- [13] Gu Y., Chen L., Ng J. W., Lee C., Chang V. W. C., and Tang C. Y., 2015. Development of anaerobic osmotic membrane bioreactor for low-strength wastewater treatment at mesophilic condition. *J. Membr. Sci.* 490, 197-208.
- [14] Zhang X., Ning Z., Wang D. K., and da Costa J. C. D., 2014. Processing municipal wastewaters by forward osmosis using CTA membrane. *J. Membr. Sci.* 468, 269-275.
- [15] Zhao S., Zou L., and Mulcahy D., 2011. Effects of membrane orientation on process performance in forward osmosis applications. *J. Membr. Sci.* 382 (1), 308-315.
- [16] Smith A. L., Stadler L. B., Love N. G., Skerlos S. J., and Raskin L., 2012. Perspectives on anaerobic membrane bioreactor treatment of domestic wastewater: a critical review. *Bioresour. Technol.* 122, 149-159.
- [17] Menzel D. W., Corwin N., 1965. The measurement of total phosphorus in seawater based on the liberation of organically bound fractions by persulfate oxidation. *Limnology and oceanography* 10 (2), 280-282.
- [18] Hoek E. M., Elimelech M., 2003. Cake-enhanced concentration polarization: a new

fouling mechanism for salt-rejecting membranes. *Environ. Sci. Technol.* 37 (24), 5581-5588.

[19] Belhadj S., Joute Y., El Bari H., Serrano A., Gil A., Siles J. Á., Chica A. F., and Martín M. Á., 2014. Evaluation of the Anaerobic Co-Digestion of Sewage Sludge and Tomato Waste at Mesophilic Temperature. *Appl. Biochem. Biotechnol.* 172 (8), 3862-3874.

[20] Kimura K., Nishisako R., Miyoshi T., Shimada R., and Watanabe Y., 2008. Baffled membrane bioreactor (BMBR) for efficient nutrient removal from municipal wastewater. *Water Res.* 42 (3), 625-632.

[21] Lettinga G., De Man, A., Van der Last A. R. M., Wiegant W., Van Knippenberg K., Frijns J., and Van Buuren J. C. L., 1993. Anaerobic treatment of domestic sewage and wastewater. *Water Sci. Technol.* 27 (9), 67-73.

[22] Saddoud A., Ellouze M., Dhouib A., and Sayadi S., 2007. Anaerobic membrane bioreactor treatment of domestic wastewater in Tunisia. *Desalination*, 207 (1), 205-215.

[23] Martinez-Sosa D., Helmreich B., Netter T., Paris S., Bischof F., and Horn H., 2011. Anaerobic submerged membrane bioreactor (AnSMBR) for municipal wastewater treatment under mesophilic and psychrophilic temperature conditions. *Bioresour. Technol.* 102 (22), 10377-10385.

Chapter III

Rejection of nutrients contained in an anaerobic digestion effluent using a forward osmosis membrane

III.1 Introduction

In chapter II, throughout the fundamental experiment, it was suggested that direct up-concentration of wastewater using FO membrane and biogas generation by methane fermentation using concentrated wastewater are possible. In this chapter, the objective is obtaining the knowledge for improving rejection of nutrients (especially ammonia) on FO membrane, one of the most important subjects for commercializing of proposed system.

Wastewater treatment is an essential part of maintaining public health and water quality surrounding a city. However, treating wastewater generally consumes a lot of energy [1]. From the viewpoint of sustainability, the development of wastewater treatment technologies that consume less energy is of great importance. Aerobic treatments, such as the conventional activated sludge treatment process, are the most-preferred method of treatment of municipal wastewater. In these processes, the concentration of organic constituents is relatively low. Owing to the familiarity of the operation and maintenance of aerobic wastewater treatment technologies, its technical reliability is sufficiently high. However, the removal of organic constituents with the help of aerobic microorganisms consumes a lot of energy for the aeration of bioreactor

to maintain dissolved oxygen (DO) concentration above a certain level. In general, 45–75% of the total operating costs of aerobic treatment processes are attributed to costs associated with aeration [2].

Recently, anaerobic wastewater treatment is gaining much attention in the field of municipal wastewater treatment [3, 4]. In anaerobic treatment, the organic content of wastewater is converted into methane and carbon dioxide by anaerobic microorganisms [5, 6]. In anaerobic treatment processes, aeration is not required, resulting in substantial reduction in energy consumption as compared to aerobic treatment processes. The additional advantages of anaerobic treatment include considerably less sludge production and energy recovery through the collection of biogas-containing methane generated during the treatment [7]. Therefore, anaerobic treatment for municipal wastewater would allow us to construct energy-independent or even producing wastewater treatment systems [8-10]. However, the growth rates of anaerobic microorganisms are generally low, indicating that the possibility of washout of microorganisms involved in anaerobic treatment is high. Therefore, membrane separation is used in anaerobic wastewater treatment (i.e., anaerobic membrane bioreactor; AnMBR), since the membrane retains the anaerobic microorganisms. Recently, many researchers reported that an AnMBR can be successfully applied for the removal of organic constituents from municipal wastewater [11, 12]. However, since an AnMBR does not have pathways for the removal of nitrogen and phosphorus, implementation of some post-treatment processes are necessary [13]. Post-treatment

processes would increase the operation and maintenance costs of the whole treatment system. The development of low-cost and effective post-treatment techniques for the effective removal of nutrients in the effluent of an AnMBR would expand the possibility for the application of an AnMBR to municipal wastewater treatment. For this purpose, I focused on a forward osmosis (FO) membrane filtration process for polishing the AnMBR effluent.

Recently, FO has attracted attention as a low-energy membrane separation process [14]. In an FO membrane filtration process, water is spontaneously transferred across a semi-permeable membrane from the feed solution (FS) with lower osmotic pressure to draw solution (DS) with high osmotic pressure governed by the difference in osmotic pressure. Since the skin layer of an FO membrane is almost comparable to that of a reverse osmosis (RO) membrane, effective removal of the nutrients that may remain in the AnMBR effluent (e.g., ammonium and phosphate ions) by the FO membrane can be expected. However, in RO membrane filtrations [15], rejections of ions would differ depending on the ion species. In addition, the operating condition of the FO membrane process and property of membrane surface would also affect the degree of rejection [16, 17]. Gaining such fundamental knowledge is necessary in designing a wastewater treatment system based on AnMBR and FO membrane filtration processes.

Recently, several researchers reported that 70~80% rejection of ammonium ion and almost complete rejection of phosphate ion can be achieved by FO membrane

installed in AnMBR (i.e., anaerobic osmotic membrane bioreactor) [18]. Similar or more efficient rejections of these nutrients were also reported in osmotic membrane bioreactor (OMBR) operated under aerobic conditions [19, 20]. However, when an FO membrane filtration process is incorporated in anaerobic wastewater treatment systems as a form of osmotic membrane bioreactor, in which FO membrane is utilized for withdrawing water molecules from a bioreactor, depending on operating conditions, accumulation of salts and potential toxicants may adversely affect the performance of microorganisms contained in bioreactor. On this basis, placing FO membrane filtration process outside the anaerobic bioreactor would also be reasonable selection. OMBRs used in the previous studies [19, 20] were operated with mixed liquor suspension (MLSS) concentrations of 5.5-7.0 g/L. Since the existence of suspended solids may alter ion profiles in the vicinity of membrane surface, it is still unclear whether the findings obtained in the previous studies mentioned above can be directly applied to operations of FO membrane applied to a post-treatment of AnMBR. To obtain knowledge that can be used for designing post-treatment process of AnMBR using an FO membrane, rejections of nutrients contained in feed water without suspended solids need to be investigated.

Valladares Linares et al. investigated the rejection of ammonium ion in both AL-FS and AL-DS orientations [21]. However, in their study, the effects of operating conditions of FO membrane other than membrane orientation on the rejection of ammonium ion were not investigated. On the basis of the information mentioned above,

it can be said that limited information is currently available on the rejection of the nutrients by the FO membrane used as a post-treatment of effluent of AnMBR. Current understanding on nutrient rejection by FO membranes is still limited.

In this study, I investigated the potential of the FO membrane filtration process as a post-treatment technique of an AnMBR. To simulate AnMBR effluent, diluted anaerobic digestion sludge from full scale sewage treatment plant was prepared. Firstly, the rejection of ammonium and phosphate ions was evaluated using a surrogate AnMBR effluent comprising the supernatant of the real anaerobic digester. Subsequently, the effects of the operating conditions of the FO membrane (e.g., membrane orientation, solute concentration in DS, and solute species in DS) on rejection of nutrients were also investigated using artificial solutions prepared in my laboratory. On the basis of the experimental data obtained in this study, factors affecting the rejection of ammonium and phosphate ions are discussed.

III.2 Materials and Methods

III.2.1 Feed and draw solutions

A surrogate AnMBR effluent and artificial solutions prepared with commercially available chemical reagents were used as the FS. The surrogate AnMBR effluent has been prepared using anaerobically digested sludge obtained from the Higashinada Sewage Treatment Plant in Kobe, Japan. The anaerobic digester at the facility was fed with excess sludge generated from real municipal wastewater in Kobe

City. To simulate the AnMBR effluent, suspended solids in the sludge collected were removed by centrifugation (15000 rpm, 3 min) followed by membrane filtration using polytetrafluoroethylene (PTFE) membrane with a nominal pore size of 0.22 μm . To adjust the nitrogen concentration to the typical concentration of the AnMBR effluent [22], the filtrate was diluted 50-fold by an aerobic MBR effluent obtained from the pilot-scale MBR operated at the Port Island Sewage Treatment Plant in Kobe, Japan. An aerobic MBR effluent was selected as the diluent to keep the salt concentration at the same level as real wastewater. Artificial solutions have been prepared to evaluate factors affecting the rejection of ammonium and phosphate ions. The sources of ammonium and phosphate ions in these solutions were NH_4Cl and NaH_2PO_4 , respectively, and 0.6 M NaCl solution was used as the DS. The salt concentration in the DS was selected in the simulation of the typical salt concentration of seawater. To evaluate the effect of variation in the solute species in the DS on the rejections of target nutrients, the draw solutions contained NaNO_3 , LiCl , glucose, and MgSO_4 were also used in the FO filtration tests. The detailed compositions of FS and DS are summarized in Table 1. In the solute concentration designated in Table III-1, the water fluxes in the FO membrane filtration were almost the same (approximately 8 $\text{L}/\text{m}^2/\text{h}$ in initial water flux).

Table III-1 Feed and draw solution using experiments

	Solute	Concentration
Feed solution		8.8 mg-C/L
	Surrogate AnMBR effluent	28.2 mg-N/L
		7.1 mg-P/L
	NH ₃ Cl	10, 30 mg-N/L
	NaH ₂ PO ₄	5.0 mg-P/L
Draw solution	NaCl	0.6 M
	NaNO ₃	0.6 M
	LiCl	0.6 M
	Glucose	1.2 M
	MgSO ₄	1.2 M

III.2.2 Forward osmosis filtration set-up

A schematic representation of the lab-scale FO filtration unit used in this work is depicted in Fig. III-1. The filtration experiment was continued for 10 h. A cellulose-based flat-sheet asymmetric membrane (CTA-ES, Hydration Technology Innovations (HTI), Albany, OR, USA) was used in the FO filtration tests. The effective membrane surface area in the FO filtration unit was 29.75 cm². The cross-flow velocity was set at 13.84 m/h using a tubing pump (MP-1000, Eyela, Tokyo, Japan). A counter-flow pattern was selected because stable osmotic pressure difference between FS and DS can be generated in this arrangement [23]. The initial volumes of FS and DS

were 1 L. To evaluate the effect of membrane orientation on the rejection of ammonium and phosphate ions, the FO filtration test was carried out under two conditions: active layer facing FS (AL-FS) and active layer facing DS (AL-DS). The DS tank was located on an electronic balance (FX-5000i, A&D, Tokyo, Japan), and the change of weight was measured every 10 min. The FO membrane filtration was continued for 10 h. Since the focus of this study is evaluating rejections of nutrients by an FO membrane which is currently available in the market, alteration of membrane properties should be avoided as much as possible. Therefore, I decided to perform short-term FO operation in this study. In order to confirm the reproducibility, the experiments were performed three times under each condition.

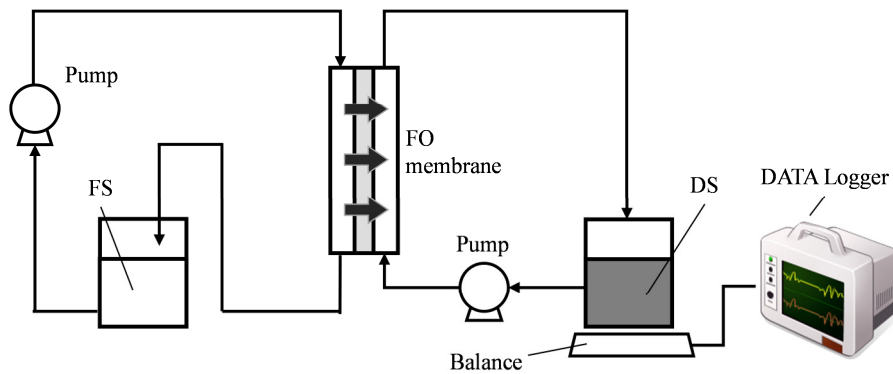


Fig. III-1 Schematic representation of the lab-scale FO filtration unit

III.2.3 Water quality analysis

Concentrations of ammonium, lithium, and magnesium ions were determined by an ion chromatograph (HIC-SP, Shimadzu, Kyoto, Japan) equipped with a cation

analysis column (Shim-pack IC-C4, Shimadzu, Kyoto, Japan). The glucose concentration was evaluated as the total organic carbon (TOC) concentration determined using a TOC analyzer (TOC-VCSH, Shimadzu, Kyoto, Japan). The phosphate ion concentration was determined by the molybdenum blue method [24].

III.2.4 Calculation

The rejection of any dissolved components (ammonium and phosphate ions in this study) is calculated by following equation:

$$R_{solute} (\%) = \left(1 - \frac{J_{solute}/J_w}{C_{FS-solute}}\right) \times 100 \quad (\text{III-1})$$

where J_w is the water flux across the FO membrane [L/m²/h], J_{solute} is the flux of ammonium or phosphate ion across the FO membrane [mmol/m²/h], $C_{FS-solute}$ is the initial ammonium or phosphate ion concentration in the FS [mol/L].

J_w and J_{solute} are calculated by the following equations:

$$J_w = \frac{V}{S \cdot t} \quad (\text{III-2})$$

$$J_{solute} = \frac{C_{FS-solute} \cdot V_0 - C_{FS-solute}' \cdot (V_0 - V)}{S \cdot t} \quad (\text{III-3})$$

where V is the volume of water transferred [L], V_0 is the initial volume of the FS [L] (1 L), S is the effective membrane surface area [m²] (0.002975 m²), t is the operating time [h] (10 h), $C_{FS-solute}'$ is the final concentration of ammonium or phosphate ion [mol/L].

The reverse solute flux from the DS to FS J_s [mmol/m²/h] is calculated by the following equation:

$$J_s = \frac{C_{FS'}(V_0 - V)}{S \cdot t} \quad (\text{III-4})$$

where $C_{FS'}$ is the final draw solute concentration in the FS [mol/L].

III.3 Results and discussion

III.3.1 FO experiment using the surrogate AnMBR effluent

Rejection of ammonium and phosphate ions in the FO filtration test, using a surrogate AnMBR effluent as FS, is shown in Fig. III-2. About 10-15% of flux decline was observed while 10 h filtration using both surrogate AnMBR effluent. Irrespective of the membrane orientation, more than 95% of phosphate ions were rejected by the FO membrane. This result suggests that FO membrane filtration is a suitable technique for removing phosphorus from the AnMBR effluent. On the other hand, rejection of ammonium ions by the FO membrane was relatively poor, and was significantly dependent upon membrane orientation: 48% in the AL-FS orientation and 59% in AL-DS the orientation. Considering the typical nitrogen concentration in the AnMBR effluent (around 30 mg-N/L [22]), a further improvement in the process through increased ammonium ion rejections is clearly necessary. As shown in Fig. III-2, the rejection of ammonium ions by FO membrane depends heavily on its operating conditions; therefore, selection of appropriate operating conditions is a crucial factor in FO membrane filtration process. Further, to be able to select appropriate operating conditions, an understanding of the factors affecting the rejection of ammonium ions is important. Therefore, I investigated the effect of key parameters, i.e., ammonium

concentration in FS, solute concentration, and species in DS, on the rejection of ammonium ions.

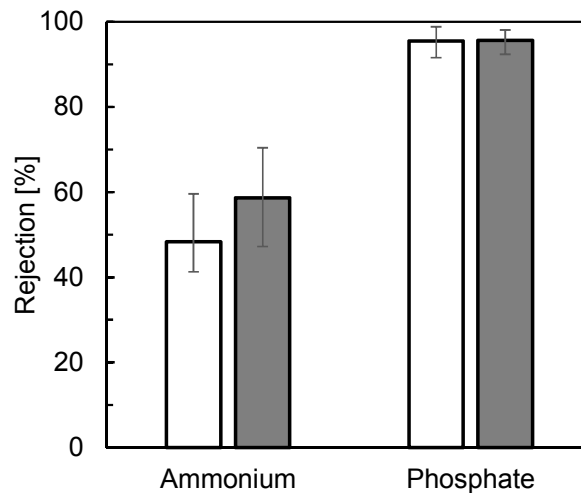


Fig. III-2 Rejection of ammonium and phosphate ions using the surrogate AnMBR effluent. 0.6 M NaCl solution was used as the draw solution. White bars represent the result in AL-FS and gray bars represent the result in AL-DS.

III.3.2 Rejection of ammonium ions

Effect of FS concentration on the rejection of ammonium ion and reverse solute flux

To investigate the effect of ammonium concentration in FS on the rejection of ammonium ions by FO membrane, filtration tests using artificial FS with different ammonium concentrations were conducted. In addition, in the experiment using artificial feed solution, during the FO operation, water flux decreased approximately 10-15%. There is not clear difference of degree of water flux decline between artificial feed solutions and surrogate AnMBR effluent, it can be said that development of

membrane fouling was negligible in all of the experiments carried out in this study. Rather, the decreases in water fluxes were likely to be attributed to dilution of DS. The results are shown in Fig. III-3.

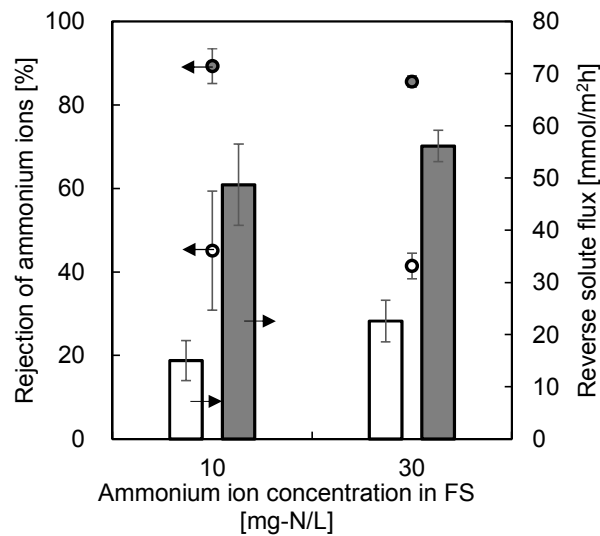


Fig. III-3 Rejection of ammonium ions, and reverse solute flux at different FS concentrations. 0.6 M NaCl solution was used as the draw solution. Circles represent rejection of ammonium ions and bars represent reverse solute flux. White bars and circles represent the results in AL-FS and gray bars and circles represent the results in AL-DS.

For each different ammonium ion concentration, the FO membrane demonstrated relatively high rejection of ammonium ions with the AL-DS orientation, whereas the rejection decreased sharply when it had the AL-FS orientation. This trend was generally in accordance with that obtained in the experiment using the surrogate AnMBR effluent

(Fig. III-2), suggesting that the experiment using artificial solutions partially reproduced the phenomenon exhibited by the experiment that used the surrogate AnMBR effluent.

The results presented in Fig. III-3 revealed that the rejection of ammonium ions for the AL-DS orientation is consistently higher than that in the AL-FS orientation, irrespective of the ammonium ion concentration in FS. One of the possible reasons for the higher rejection of ammonium ions in the AL-DS orientation might be due to a high water flux; the water flux typically becomes higher when an FO membrane is operated with the AL-DS orientation [25]. The increase in water flux is likely to have a positive effect on the apparent rejections because the proportion of water among the molecules transported from FS to DS increases. In other words, even flux of ammonium ion is constant, if the water flux increases, ammonia concentration of permeate decreases, and rejection of ammonium ion is higher (refer to equation (III-1) and (III-3)). This phenomenon also occurs in RO membrane [26]. To investigate whether the mechanism mentioned above was involved in the increased ammonium rejections observed in the experiment with AL-DS orientation, we calculated the flux of ammonium ion across the FO membrane based on the data obtained in the FO membrane filtration test.

Water flux across the FO membrane and flux of ammonium determined in the FO filtration tests carried out at different FS concentrations are shown in Figs. III-4 (a) and III-4 (b), respectively. As shown in Fig. III-4 (a), water flux across the FO membrane recorded with the AL-DS orientation was slightly higher than that recorded with the AL-FS orientation for all different FS concentrations. This trend is in

accordance with the previous findings [27], according to which the difference in water flux is thought to be caused by the difference in effective osmotic pressure achieved for the FO operation with the AL-DS and AL-FS orientations due to the effect of internal concentration polarization [28]. However, the difference in water flux associated with the difference in FO membrane orientation was not substantial enough to explain the large difference in the rejection of ammonium ions, as shown in Fig. III-3. This in turn suggests the possibility of other mechanisms being involved in the increased rejection of ammonium ions in FO filtration with AL-DS orientation. With regard to the changes in ammonium ion concentration in FS, the results presented in Fig. III-4 (b) revealed that the flux of ammonium ion clearly decreased when the FO membrane was operated with the AL-DS orientation. This result indicates that the improvement in the rejection of ammonium ions with the AL-DS orientation is mainly attributed to the reduction in ammonium flux rather than the increased water flux. On the basis of the findings stated above, the investigation on factors affecting flux of ammonium ion would be important for improving rejection of ammonium ion. This will be discussed in the following sections.

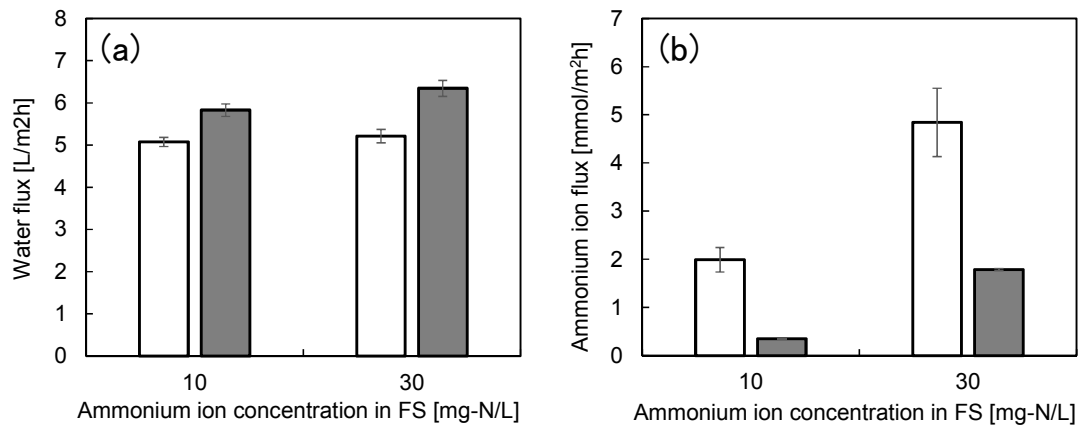


Fig. III-4 Water flux and ammonium ion flux at different FS concentration (DS: 0.6 M NaCl). (a) comparison of water flux (b) comparison of ammonium ion flux. 0.6 M NaCl solution was used as the draw solution. White bars represent the result in AL-FS and gray bars represent the result in AL-DS.

The reverse solute flux from the DS to FS is also presented in Fig. III-3. As can be observed, reverse salt diffusion was apparently more pronounced in the FO operation with the AL-DS orientation. Xie et al. reported that the rejection of selected organic micro pollutants by FO membrane increased as the reverse solute flux increased [16], which serves as a good explanation for the improved rejection of ammonium ions in my experiments with an AL-DS orientation. Therefore, I investigated the effect of reverse solute rejection on the rejection of ammonium ions by changing the solute concentration and species in DS. The results will be presented in the following sections.

Effect of solute concentration and species in the DS on rejection of ammonium ions

The degrees of flux of ammonium ion and reverse solute flux determined in the FO filtration test with different solute concentrations and solute species are shown in Figs. III-5, III-6 and III-7. With regard to the effect of solute concentration in the FS, flux of ammonium ion sharply decreased when the solute concentration of DS was set at 1.2 M. The decrease in flux of ammonium ion was particularly pronounced in the FO filtration with the AL-DS orientation. The trend in decrease in flux of ammonium ion is generally in accordance with the trend in increase in the degree of reverse solute flux; reverse solute flux increased as solute concentration in the DS increased and this propensity was particularly pronounced in the FO filtration process with the AL-DS orientation.

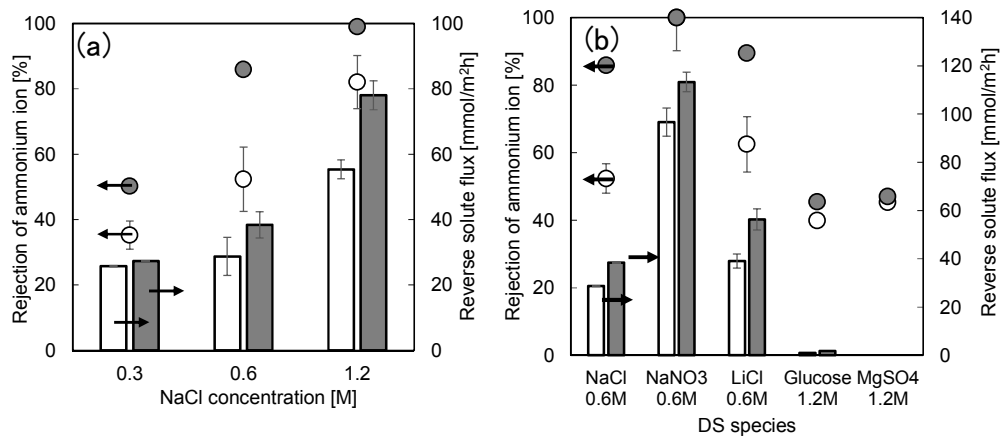


Fig. III-5 Relationship between rejection of ammonium ions and reverse solute flux. (a) different DS concentrations, (b) different solute of DS species. 30 mg-N/L NH₄Cl solution was used as the FS. Circles represent rejection of ammonium ions and bars represent reverse solute flux. White bars and circles represent the results

in AL-FS and gray bars and circles represent the results in AL-DS.

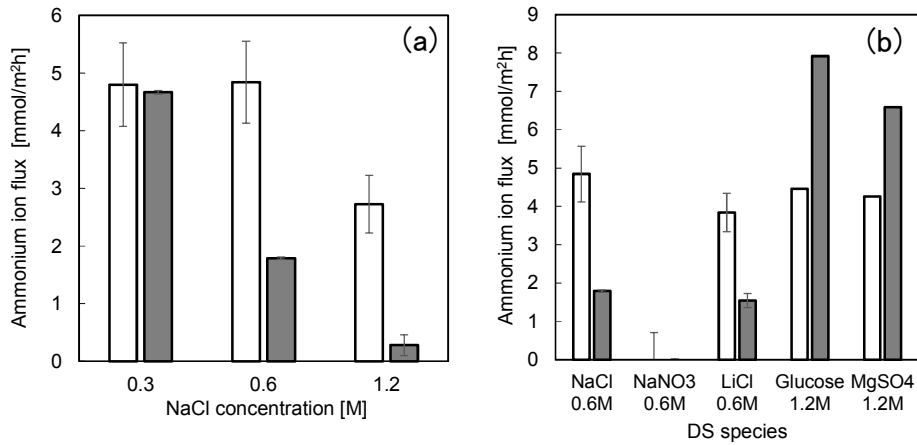


Fig. III-6 Comparison of ammonium ion flux.(a) different DS concentrations, (b) different solute of DS species. 30 mg-N/L NH₄Cl solution was used as the FS. White bars represent the result in AL-FS and gray bars represent the result in AL-DS.

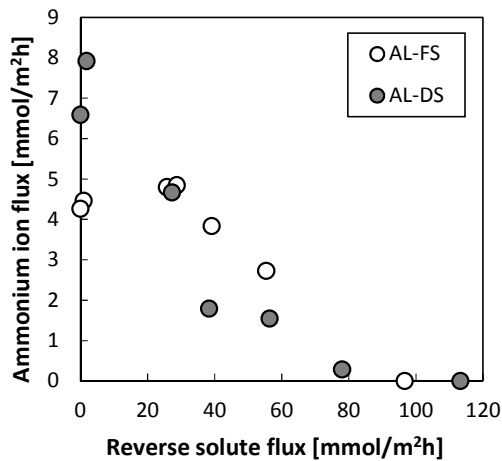


Fig. III-7 Relationship between reverse solute flux and ammonium ion flux in FO membrane filtration.

The relationship between flux of ammonium ion and reverse solute flux was

further confirmed in the FO filtration test using DSs containing different solute species (Figs. III-5 (b) and III-6 (b)). The reverse solute fluxes in AL-DS mode are higher than in AL-FS mode would be influence of internal concentration polarization. Sodium nitrate and lithium chloride exhibited higher degree of reverse solute flux. Rejection of ammonium ion was also high in the FO filtration process when a DS containing sodium nitrate and lithium chloride were used. In contrast, when the DS contained solutes with low reverse solute flux propensities, such as magnesium sulfate and glucose, the flux of ammonium ion was higher than that when the DS contained of sodium chloride. Based on the experimental results presented in Fig. III-6, the effect of the degree of reverse solute flux on the rejection of ammonium ion was likely to be different depending on membrane orientation; the rejection of ammonium ion in AL-DS mode of operation was much more sensitive than that in AL-FS mode of operation. The same trend can be observed clearly also in Fig. III-7. This fact implies that the rejection of ammonium ion is not directly affected by the degree of reverse solute flux. A possible explanation on the difference in sensitivity of rejection of ammonium ion to degree of reverse solute flux might be the difference in solute profile caused by the difference in membrane orientation. In AL-DS mode of operation, the solutes diffused from DS tend to be accumulated in the support layer of the FO membrane, whereas such solute would immediately be diffused into FS in AL-FS mode of operation. The elevated solute concentration created as a result of such accumulation may have some preventive effect for ions being transported (e.g., decrease in their activity). In previous report, it has been

reported that approximately 90% rejection of ammonium ion can be achieved in osmotic membrane bioreactor (OMBR) operated with AL-FS mode [19]. In OMBR, due to high suspended solid concentration, formation of sludge cake layer on the surface of FO membrane is likely to be much more significant than the FO membrane filtration experiments carried out in this study. Taking the fact that cake layer formation on the membrane surface also accelerates the accumulation of solute diffused from DS into consideration, the results obtained in this study is thought to be in agreement with the previous findings obtained in the investigation on OMBR.

These results, again, suggest that increasing reverse solute diffusion has a positive influence on ammonia removal by the FO membrane. A similar phenomenon has been reported in a previous study by Phillip et al. [28]. However, the detailed mechanism of this phenomenon is not clear. It is well-known that membrane surface properties such as surface charge affect rejection of ions by an FO membrane [29]. However, this might not be a good explanation on the difference in rejection of ammonium ion in each experiment carried out in this study. This is because that, in all of the experiments carried out in this study, pH values of both DS and FS were in the range of 5.5~8, which was apparently higher than the isoelectric point of cellulose acetate membranes [30, 31]. In addition, FO membranes made by CTA is known to have no functional group that dissociate under the pH range of the experiments carried out in this study [32]. On the basis of the discussion mentioned above, it is very likely that the difference in rejection of ammonium flux found in this study was not attributed to the

difference in membrane surface properties. Elucidating the dominant phenomena affecting rejection of ammonium ion is an important subject to be explored in terms of improvement in the membrane performance.

III.3.3 FO membrane process as a post-treatment of the AnMBR

The results obtained in this study revealed that FO membrane filtration process could be a suitable technique for the post-treatment of AnMBR. Taking typical concentrations of ammonium-nitrogen (approximately 30 mg/L) and phosphorus (3~4 mg/L) into consideration, the virtual concentrations of nitrogen and phosphorus in the permeate of the FO membrane (excluding the effect of dilution by DS) can be lowered up to around 10~15 mg/L for nitrogen (when operated with the AL-DS orientation) and less than 0.5 mg/L for phosphorus. The phosphorus concentration in the permeate was lower than the wastewater discharge standard in Europe (1 mg-P/L), but the nitrogen concentration in the permeate exceeded this standard (10 mg-N/L) in my experiments. In future, as the FO membrane performance improves, the nitrogen concentration in the permeate can also be lowered than the standard value.

Among the nutrients in the effluent of an AnMBR, phosphorus is likely to be removed well, irrespective of the operating conditions. On the other hand, the removal of ammonium ions will depend heavily on operating conditions of the FO membrane filtration process, suggesting that an FO membrane filtration unit intended to be used for post-treatment should be designed for maximizing the removal of ammonia rather

than phosphorus. On the basis of the above-mentioned results, increase in reverse solute flux from the DS to the FS is likely to have positive influence on the rejection of ammonium ions by the FO membrane. However, there might be several practical concerns regarding the AL-DS orientation, when actually designing the FO membrane filtration facility. Firstly, membrane fouling tends to be more significant when an FO membrane is operated with the AL-DS orientation [33]. Since the AnMBR effluent would typically have a high fouling potential, achieving stable FO membrane filtration with the AL-DS orientation is thought to be challenging. In addition, high reverse solute flux would also be a problem for effective operation of the FO membrane filtration process to be used as a post-treatment of AnMBR. Reverse solute flux results in an increase in the osmotic pressure of the FS, which in turn, reduces the effective osmotic pressure difference between the FS and the DS.

Based on the discussion above, further improvement in the FO membrane filtration process is needed for (1) improving the ammonium rejection with the AL-FS orientation, and (2) achieving stable FO filtration with the AL-DS orientation. One of the probable approaches for overcoming the above-mentioned issues would be to achieve improved membrane performance. Specifically, development of membranes with high rejection of ammonium ions with an AL-FS orientation or resistant to membrane fouling in the FO filtration process with the AL-DS orientation are important topics for future research. The findings obtained in this study would be useful for elucidating the mechanisms by which rejection of ammonium ion is affected, and

therefore, also useful for establishing countermeasures stated above.

III.3.4 Treatment of concentrate discharged from FO membrane post-treatment

Apart from the quality of treated water (i.e., permeate of FO membrane), an appropriate treatment of concentrate discharged from FO membrane filtration unit is of great importance for proposing wastewater treatment systems based on AnMBR and FO membrane filtration processes. The results obtained in this study suggested that the rejections of ammonium and phosphate ions are approximately 60% and 95%, respectively. Assuming that the concentrations of ammonium and phosphate ions in an effluent of AnMBR are 30 and 3.5 mg/L, respectively [22], concentrations of these ions in a concentrate from FO membrane filtration unit can be estimated as approximately 90 mg/L for ammonium ion and 15 mg/L for phosphate ion. Unfortunately, these concentrations may not be sufficiently high for recovering these nutrients through crystallization of magnesium ammonium phosphate [34]. For phosphorus recovery, the hydroxyapatite crystallization process could be applied, since this process functions successfully in solution containing phosphorus in relatively low concentration (e.g., 3.5 mg/L) [35] though controlling the scaling comprised of calcium phosphate would be an additional issue in this application. Recent advancement in phosphorus adsorbent [36, 37] may give us further opportunities for efficiently recovering phosphorus from concentrate discharged from FO membrane filtration units. On the other hand, recovering ammonia from an FO concentrate is likely to be more difficult. Taking into

account that the economic value of ammonia is smaller than that of phosphorus, it can be thought that ammonium-nitrogen needs to be “removed” rather than “recovered”. Thus, I will select the nitrification-denitrification MBR as the post treatment system after phosphorous recovery process. By applying the above two post-treatment processes, concentrate of FO membrane will be purified to water quality which can be discharged.

III.4 Conclusions

In this study, I investigated the possibility of applying an FO membrane filtration process for the post-treatment of an AnMBR. The results of an FO membrane filtration test using a surrogate AnMBR effluent prepared by supernatant obtained from a real anaerobic digester revealed that the FO membrane demonstrated excellent rejection of phosphate ions, whereas the rejection of ammonium ions was moderate and depended heavily on the orientation of the FO membrane. The flux of ammonium ions across the FO membrane decreased as the solute concentration in the FS increased. In the FO filtration experiment using the DS with a high solute concentration, the reverse solute flux from the DS to FS increased. The above-mentioned trend was particularly remarkable in the FO filtration with the AL-DS orientation, in which the reverse solute flux was higher than that in the other membrane orientation. The relationship between the degree of reverse solute flux and flux of ammonium ion was confirmed by the FO filtration test using different solute species in the DS. When lithium chloride, which had

a high reverse solute flux than sodium chloride, was used for preparing the DS, the flux of ammonium ion decreased. On the other hand, a higher flux of ammonium ion was observed in the FO filtration using the DS containing solutes with less reverse flux, such as magnesium sulfate or glucose. On the basis of the results obtained in this study, it can be concluded that reverse solute flux has a positive influence on the rejection of ammonium ions.

References

- [1] Wei Y., Van Houten R.T., Borger A.R., Eikelboom D.H. and Fan Y., Minimization of excess sludge production for biological wastewater treatment. *Water Res.*, 37 (2003) 4453–4467.
- [2] Rosso D., Stenstrom M. K. and Larsson L. E., Aeration of large-scale municipal wastewater treatment plants: State of the art, *Water Sci. Technol.*, 57 (2008) 973–978.
- [3] Bandara W.M.K.R.T.W., Kindaichi T., Satoh H., Sasakawa M., Nakahara Y., Takahashi M. and Okabe S., Anaerobic treatment of municipal wastewater at ambient temperature: Analysis of archaeal community structure and recovery of dissolved methane, *Water Res.*, 46 (2012) 5756–5764.
- [4] Latif M.A., Ghufuran R., Wahid Z.A. and Ahmad A., Integrated application of upflow anaerobic sludge blanket reactor for the treatment of wastewaters, *Water Res.*, 45 (2011) 4683–4699.
- [5] An Y., Wang Z., Wu Z., Yang D. and Zhou Q., Characterization of membrane foulants in an anaerobic non-woven fabric membrane bioreactor for municipal wastewater treatment, *Chem. Eng. J.*, 155 (2009) 709–715.
- [6] Skouteris G., Hermosilla D., Lopez P., Negro C. and Blanco A., Anaerobic membrane bioreactors for wastewater treatment: A review, *Chem. Eng. J.*, 198–199 (2012) 138–148.
- [7] Ho J. and Sung S., Anaerobic membrane bioreactor treatment of synthetic municipal

wastewater at ambient temperature, *Water Environ. Res.*, 81 (2009) 922–928.

[8] Heubeck S., de Vos R.M. and Craggs R., Potential contribution of the wastewater sector to energy supply, *Water Sci. Technol.*, 63 (2011) 1765–1771.

[9] Lin H., Chen J., Wang F., Ding L. and Hong H., Feasibility evaluation of submerged anaerobic membrane bioreactor for municipal secondary wastewater treatment, *Desalination*, 280 (2011) 120–126.

[10] Urban I., Weichgrebe D. and Rosenwinkel H., Anaerobic treatment of municipal wastewater using the UASB-technology, *Water Sci. Technol.*, 56 (2007) 37–44.

[11] Zhang X., Wang Z., Wu Z., Lu F., Tong J. and Zang L., Formation of dynamic membrane in an anaerobic membrane bioreactor for municipal wastewater treatment, *Chem. Eng. J.*, 165 (2010) 175–183.

[12] Baek S. H., Pagilla K. R. and Kim H. J., Lab-scale study of an anaerobic membrane bioreactor (AnMBR) for diluted municipal wastewater treatment, *Biotechnol. Bioproc. Eng.*, 15 (2010) 704–708.

[13] Chan Y. J., Chong M. F., Law C. L. and Hasell D. G., A review on anaerobic-aerobic treatment of industrial and municipal wastewater, *Chem. Eng. J.*, 155 (2009) 1–18.

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

- [15] van Voorthuizen E. M., Zwijnenburg A. and Wessling M., Nutrient removal by NF and RO membranes in a decentralized sanitation system, *Water Res.*, 39 (2005) 3657–3667.
- [16] Xie M., Nghiem L. D., Price W. E. and Elimelech M., Comparison of the removal of hydrophobic trace organic contaminants by forward osmosis and reverse osmosis, *Water Res.*, 46 (2012) 2683–2692.
- [17] Lu X., Boo C., Ma J., and Elimelech M, Bidirectional Diffusion of Ammonium and Sodium Cations in Forward Osmosis: Role of Membrane Active Layer Surface Chemistry and Charge, *Environ. Sci. Technol.*, 48 24 (2014) 14369-14376.
- [18] Gu Y., Chen L., Ng J. W., Lee C., Chang V. W. C., and Tang C. Y., Development of Anaerobic Osmotic Membrane Bioreactor for Low-Strength Wastewater Treatment at Mesophilic Condition, *J. Membr. Sci.*, 490 (2015) 197–208.
- [19] Achilli A., Cath T. Y., Marchand E. A., and Childress A. E, The forward osmosis membrane bioreactor: a low fouling alternative to MBR processes, *Desalination*, 239 1 (2009). 10-21.
- [20] Qiu G., and Ting Y. P., Short-term fouling propensity and flux behavior in an osmotic membrane bioreactor for wastewater treatment, *Desalination*, 332 1 (2014) 91-99.
- [21] Linares R. V., Li Z., Abu-Ghdaib M., Wei C. H., Amy G., and Vrouwenvelder J. S., Water harvesting from municipal wastewater via osmotic gradient: an

evaluation of process performance, *J. Membr. Sci.*, 447 (2013) 50-56.

- [22] Lin H., Peng W., Zhang M., Chen J., Hong H. and Zhang Y., A review on anaerobic membrane bioreactors: Applications, membrane fouling and future perspectives, *Desalination*, 314 (2013) 169–188.
- [23] Xiao D., Li W., Chou S., Wang R., and Tang C. Y., A modeling investigation on optimizing the design of forward osmosis hollow fiber modules, *J. Membr. Sci.*, 392 (2012) 76-87.
- [24] Menzel D. W., and Corwin N., The measurement of total phosphorus in seawater based on the liberation of organically bound fractions by persulfate oxidation, *Limnology and Oceanography*, 10 2 (1965), 280-282.
- [25] Zhao S., Zou L. and Mulcahy D., Effects of membrane orientation on process performance in forward osmosis applications, *J. Membr. Sci.*, 382 (2011) 308–315.
- [26] Wijmans J. G., and Baker R. W., The solution-diffusion model: a review, *J. Membr. Sci.*, 107 1 (1995) 1-21.
- [27] Zhao S. and Zou L., Relating solution physicochemical properties to internal concentration polarization in forward osmosis, *J. Membr. Sci.*, 379 (2011) 459–467.
- [28] Phillip W. A., Yong J. S. and Elimelech M., Reverse draw solute permeation in forward osmosis: modeling and experiments, *Environ. Sci. Technol.*, 44(13) (2010) 5170-5176.

- [29] Setiawan L., Wang R., Li K., and Fane A. G., Fabrication of novel poly (amide-imide) forward osmosis hollow fiber membranes with a positively charged nanofiltration-like selective layer, *J. Membr. Sci.*, 369 1 (2011) 196-205.
- [30] Elimelech M., Chen W. H., and Waypa J. J., Measuring the zeta (electrokinetic) potential of reverse osmosis membranes by a streaming potential analyzer, *Desalination*, 95 3 (1994) 269-286.
- [31] Childress A. E., and Elimelech M., Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes, *J. Membr. Sci.*, 119 2 (1996) 253-268.
- [32] Lu X., Boo C., Ma J., and Elimelech M., Bidirectional diffusion of ammonium and sodium cations in forward osmosis: Role of membrane active layer surface chemistry and charge, *Environ. Sci. Technol.*, 48 24 (2014) 14369-14376.
- [33] Mi B. and Elimelech M., Chemical and physical aspects of organic fouling of forward osmosis membranes, *J. Membr. Sci.*, 320 (2008) 292-302.
- [34] Wang J., Song Y., Yuan P., Peng J., and Fan M., Modeling the crystallization of magnesium ammonium phosphate for phosphorus recovery, *Chemosphere*, 65 7 (2006) 1182-1187.
- [35] Jang H., and Kang S. H., Phosphorus removal using cow bone in hydroxyapatite crystallization, *Water Res.*, 36 5 (2002), 1324-1330.
- [36] Meng S., Li Y., Zhang T., Chen J., Xu P., Song C. and Qiu L., Influences of environmental factors on Lanthanum/Aluminum-Modified Zeolite

Adsorbent (La/Al-ZA) for phosphorus adsorption from wastewater, *Water Air Soil Pollution*, 224 6 (2013) 1-8.

[37] Pitakteeratham N., Hafuka A., Satoh H., and Watanabe Y., High efficiency removal of phosphate from water by zirconium sulfate-surfactant micelle mesostructure immobilized on polymer matrix, *Water Res.*, 47 11 (2013) 3583-3590.

Chapter IV

Characteristics of foulants of forward osmosis membranes used in municipal wastewater concentration processes

IV.1. Introduction

Wastewater treatment systems are generally energy intensive; however, municipal wastewater contains significant amounts of valuable resources, such as organic matter, that can be used for producing methane gas (an energy source) and nitrogen and phosphorus (nutrients). If I could successfully recover these valuable resources, wastewater treatment could be transformed from an energy-consuming system to a resource-recovery system.

Anaerobic treatment is considered a core technology in the development of wastewater treatment systems. In such treatment, the organic matter contained in the wastewater can be converted to methane through the activities of microorganisms during anaerobic treatment. Recently, anaerobic membrane bioreactors (AnMBRs) have been attracting significant attention in both research and industry. Because particulate matter, including microorganisms, can be completely retained by the membrane (i.e., the microorganisms are not washed out from the reactor), it is expected that the reactor can achieve stable operation even under relatively high biomass concentrations [1]. However, the relatively low concentration of organic matter in municipal wastewater

may prevent the operation of an AnMBR at its optimal temperature (i.e., approximately 38°C), decreasing the treatment efficiency. In addition, because AnMBRs do not include a pathway for removing nutrients, such as nitrogen and phosphorus, post-treatment is needed to recover such nutrients.

The forward osmosis (FO) membrane filtration process might be a suitable means of overcoming the aforementioned problems with AnMBRs [2, 3]. In this process, the water to be treated is spontaneously transferred across a semipermeable membrane by the osmotic pressure gradient between the feed water and draw solution (DS). In the context of AnMBR, an FO membrane could be utilized to up-concentrate municipal wastewater prior to AnMBR or post-treatment for removing nutrients. Lateef et al. reported that the chemical oxygen demand (COD) could be increased to more than 6000 mg/L by applying direct membrane filtration by using a microfiltration (MF) membrane [4]. However, the dissolved organic matter, which cannot be retained by an MF membrane, remaining in the MF membrane effluent poses an operational issue, resulting in a loss of organic matter (i.e., a source of methane) and requiring intensive post-treatment to remove the organic matter contained in the effluent. Because FO membranes have a similar rejection capability as reverse osmosis (RO) membranes, applying FO membranes to concentrate municipal wastewater prior to anaerobic treatment may solve the problems associated with the release of organic matter into the effluent of the membrane-based concentration process. Zhang et al. achieved an approximately six-fold concentration of municipal wastewater (the final concentration

of COD in the concentrated wastewater was approximately 1600 mg/L) by using FO membrane filtration [5], which may be suitable for application in anaerobic treatment without extensive heating [6]. With regard to its application in post-treatment for removing nutrients, it has been reported that FO membranes can achieve the moderate ammonium nitrogen removal and almost complete phosphorus removal [7]. If these nutrients could be effectively retained by an FO membrane, the recovery of the concentrated nutrients would then be possible (e.g., by applying the magnesium ammonium phosphate (MAP) crystallization process) [8].

The implementation of the wastewater pre-concentration and AnMBR effluent post-treatment processes depend critically on controlling membrane fouling. In all membrane-based water treatment processes, the reduction in water permeability due to membrane fouling is a serious problem. Membrane fouling is believed to be less important in FO membrane filtration processes than in pressure-driven membrane systems (e.g., RO membranes) due to the absence of extreme hydraulic pressures [9]. In addition, the fouling of FO membranes is reported to be highly reversible [10]. However, most of the previous investigations into the fouling of FO membranes were conducted using artificial foulants (Aldrich humic acid (AHA), bovine serum albumin (BSA), and sodium alginate) [10-12]. Because such artificial foulants cannot represent the entire range of membrane fouling caused by the organic matter contained in actual wastewater [13], the current understanding of the fouling of FO membranes is extremely limited. To understand this process properly, the analysis of fundamental data obtained from FO

membrane filtration tests by using actual feed water (e.g., actual municipal wastewater or AnMBR effluent) is of critical importance.

Based on this background, I investigated the fouling of FO membranes caused by actual municipal wastewater and an effluent obtained from a bench-scale AnMBR operated using the same municipal wastewater as feed water. Upon the conclusion of the FO membrane filtration tests, the foulants were detached from the membranes to characterize the dominant types present. In addition, the validity of evaluating FO membrane fouling by using artificial foulants (i.e., AHA, BSA, and sodium alginate) was also investigated. Based on the data obtained from this study, the characteristics of organic matter that affect the development of the FO membrane fouling are discussed.

IV.2. Materials and Methods

IV.2.1. Feed water and draw solution for FO membrane filtration

The water quality data for the feed waters used in this study are shown in Table IV-1. Municipal wastewater was collected from the Port Island wastewater treatment plant in Kobe, Japan. The effluent from the primary sedimentation basin was used as the feed water in the FO membrane filtration test. The wastewater was subjected to coarse mesh (approximately 2 mm) filtration prior to the test. The effluent of an AnMBR was obtained from a bench-scale bioreactor operated at the Port Island wastewater treatment plant. This AnMBR was also fed with the effluent from the primary sedimentation basin. The hydraulic retention time (HRT) and organic loading rate of the AnMBR were 30 h

and 2.3×10^{-3} kg-COD_{Cr}/m³/day, respectively. During the continuous operation of the AnMBR, the mixed liquor suspension was not withdrawn from the reactor. The AnMBR was equipped with an ultrafiltration (UF) membrane made of hydrophilized polyvinyl chloride (PVC) with a nominal pore size of 0.04 μm (Sekisui Chemical, Osaka, Japan). The osmotic pressures of the municipal wastewater and AnMBR effluent were approximately 0.05 MPa. The osmotic pressure was measured using a Wescor 5600 vapor pressure osmometer (Wescor Inc., Logan, UT, USA).

Table IV-1 Water quality data for municipal wastewater, AnMBR effluent, and water containing artificial foulant

Feed water	TOC [mg-C/L]	Biopolymers [mg-C/L]	LC-OCD analysis			Electrical conductivity (after adding Na ₂ SO ₄) [mS/m]
			Humics + building blocks [mg-C/L]	LMW acids [mg-C/L]	LMW neutrals [mg-C/L]	
Municipal wastewater	97.1	5.2	18.7	14.7	10.3	113
AnMBR effluent	37.6	0.85	6.0	0.7	2.0	No data
AHA (300 mg/L)	98.1	0.6	86.3	0.0	0.0	112
BSA (200 mg/L)	103.3	85.9	8.3	0.0	0.0	113
Sodium alginate (335 mg/L)	93.2	91.3	0.0	0.4	0.0	120
Mixture <div style="border-left: 1px solid black; border-right: 1px solid black; border-bottom: 1px solid black; padding: 5px; display: inline-block;"> AHA : 240 mg/L BSA : 20 mg/L Alginate : 34 mg/L </div>	97.1	15.0	26.5	1.7	3.0	111

In addition to the municipal wastewater, solutions containing artificial foulants (AHA (Sigma-Aldrich, Germany), BSA (Sigma-Aldrich, Germany), and sodium alginate (Wako Pure Chemical Industries, Japan) and a mixture of all three (hereinafter referred to as the “mixture”) were also used in the investigation. The artificial feed waters were prepared by dissolving AHA, BSA, and sodium alginate in water at concentrations of 225 mg/L, 500 mg/L, and 200 mg/L, respectively. The "mixture" was prepared by dissolving the three artificial foulants in the same water so that the final concentration of AHA, BSA, and sodium alginate become 240 mg/L, 20 mg/L, and 34 mg/L, respectively. The experiment using the mixture was carried out to evaluate the extent of synergistic effects (i.e., the acceleration of membrane fouling caused by the interaction between multiple foulants) on the development of membrane fouling. All artificial feed waters had total organic carbon (TOC) concentrations of approximately 100 mg/L, which is almost equal to that of the municipal wastewater used. The TOC concentrations were determined using a TOC analyzer (TOC-V, Shimadzu, Kyoto, Japan). In the experiments using artificial feed waters, the osmotic pressure was adjusted to be equal to that of the municipal wastewater by adding Na₂SO₄. The LC-OCD chromatograms of each feed water are shown in Fig. IV-S1.

A 0.6 M NaCl solution was used as the DS. The salt concentration of the DS was selected to be similar to the typical concentration found in seawater. During the FO filtration test, the NaCl concentration was maintained by adding saturated NaCl solution to the DS tank according to the change in salt concentration (evaluated by monitoring

electrical conductivity).

IV.2.2. Batch FO membrane filtration experiment

The development of membrane fouling was evaluated by batch FO membrane filtration experiments. The schematic illustration of this experiment system is shown in Fig. IV-1. This experiment was carried out using a lab-scale cross-flow FO membrane filtration apparatus having an effective membrane surface area of 29.75 cm². A commercial cellulose triacetate FO membrane with an embedded support (CTA-ES, Hydration Technologies Inc., Albany, OR) was used. Both feed water and DS were circulated to the apparatus using a peristaltic pump (MP-2000, EYELA, Tokyo, Japan) in a counter-current direction, and both cross flow velocity of feed water and DS was 23.1 cm/min. Then, the water was recirculated to reservoir tanks. At the beginning of the experiment, the volumes of both feed water and DS were set at 2 L. All filtration tests were performed with the active layer of the membrane facing the feed solution (AL-FS) flow direction. This arrangement is thought to be the best one when treating feed water with a high fouling potential [14]. The water flux (J_w , L/m²h) was determined by measuring the reduction in the weight of the feed water. The filtration tests were carried out at room temperature (approximately 25 °C), and they were continued for 72 h.

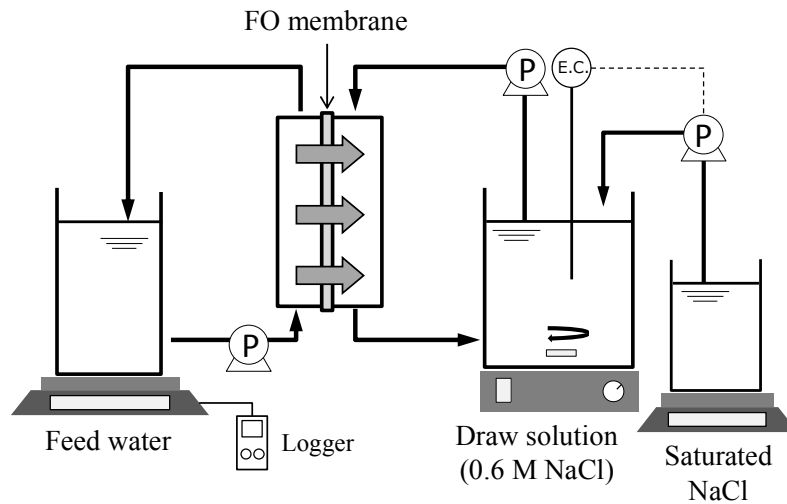


Fig. IV-1 Schematic illustration of the batch FO membrane filtration experiment system

IV.2.3. Evaluation of membrane fouling after the batch FO membrane filtration experiment

To evaluate the degree of membrane fouling incurred in the batch FO membrane filtration experiment, the water permeability of the fouled FO membrane was measured using Milli-Q water as feed water. At this time, if the FO membrane is slightly dirty, the Milli-Q FS will also be dirty because of its circulation, and the fouling cannot be accurately evaluated. Therefore, before the water permeability measurement, the loosely adhered dirt was rinsed by circulating Milli-Q water at the same cross-flow velocity as used in the batch FO membrane filtration experiment (23.1 cm/min) (defined as the "Milli-Q rinse" procedure). The feed was then replaced with new Milli-Q water, and water permeability was measured. I regarded this measurement as the water permeability after the filtration. In addition, the cross-flow velocity of the feed water

(Milli-Q) and DS were same as used in section IV.2.2. Following this initial stage, the membrane was removed from the apparatus and immersed in Milli-Q water in a tightly sealed container. The container was then shaken at 180 rpm for 30 min in a thermostatic shaker (NTS-400AL, EYELA, Tokyo, Japan) to detach the remaining tightly attached foulant layer. The water permeability was measured in the same manner as described above and was regarded as the water permeability of the membrane after physical cleaning.

IV.2.4. Characterization of foulants detached from membranes

By subjecting the Milli-Q used for the above-mentioned shaking cleaning to fluorescence excitation-emission matrix (EEM) and liquid chromatography with organic carbon detection (LC-OCD) analyses, foulant detached from the FO membrane were analyzed.

IV.2.5. Analytical methods

Fluorescence EEMs were generated using a fluorescence spectrophotometer equipped with a 150-W ozone-free xenon arc-lamp (Aqua log, Horiba, Kyoto, Japan). The interval of the excitation and emission wavelengths was 3 nm. The excitation and emission wavelengths between 220 nm and 880 nm were measured. The concentrations of biopolymers and humic substances were determined using an LC-OCD system (Model 8, DOC-LABOR, and Karlsruhe, Germany). The chromatographic column (250

mm × 20 mm, TSK HW 50S, 3000 theoretical plates, Toso, Japan). The chromatographic column is a weak cation exchange column on polymethacrylate basis. And the phosphate buffer of pH of 6.85 (2.5 g-KH₂PO₄/L + 1.5 g-Na₂HPO₄/L) was used as mobile phase.

IV.3. Results and Discussion

IV.3.1. FO membrane fouling caused by each feed water

Fig. IV-2 shows the changes in water flux during the batch FO membrane filtration tests using the municipal wastewater, effluent from the bench-scale AnMBR fed with the municipal wastewater, and the three solutions containing artificial foulants (i.e., AHA, BSA, and sodium alginate) and their mixture. As mentioned above, the TOC concentrations of the feed waters containing artificial foulants were adjusted to be equal to that of the municipal wastewater (i.e., 100 mg-C/L). Nevertheless, the flux decline caused by the municipal wastewater was apparently greater than that caused by the artificial feed solutions. The FO membrane filtration test using the artificial foulants mixture was carried out to evaluate the impact of the synergistic effect of several types of organic matter on the development of membrane fouling. In a previous investigation undertaken by Neemann et al., the occurrence of non-covalent interactions between BSA and sodium alginate resulted in an increase in the fouling potential of low-pressure membranes [15]. The results obtained from the present study indicate that such synergistic effects are not important in the fouling of FO membranes. In the case of the

AnMBR effluent, the TOC concentration (37.6 mg/L) was lower than that of the other feed waters examined in this study. However, the development of membrane fouling in the FO filtration test using the AnMBR effluent was much more significant than in those tests in which the feed waters were comprised of artificial organic compounds. The degree of membrane fouling caused by the AnMBR effluent was almost the same as that developed in the test using the municipal wastewater, suggesting that the organic matter contained in the AnMBR effluent has a much higher potential for causing fouling of the FO membrane used in this study.

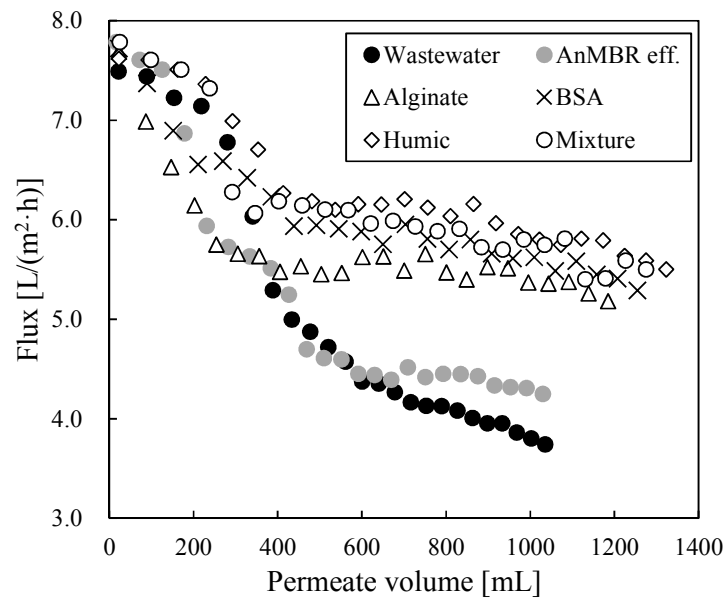


Fig. IV-2 Changes in water flux in the batch FO membrane filtration tests using various feed waters

The degrees of recovery in membrane water permeability achieved by Milli-Q

rinsing are described in Fig. IV-3. The vertical line in Fig. IV-3 is the normalized flux. This is the value obtained by dividing the water flux measured after the batch FO membrane filtration experiments, or after physical cleaning, by the water flux of a new FO membrane. Physically irreversible fouling was substantially developed in the FO filtration tests using the municipal wastewater, and the effluent obtained from the bench-scale MBR, as shown by the fact that water permeabilities could not be fully recovered by this method of cleaning. On the other hand, the water permeability of membranes was almost completely recovered by Milli-Q rinsing, where the solutions containing the artificial foulants (i.e., AHA, BSA, sodium alginate and their mixture) were used as the feed water. In many previous studies, the fouling of FO membranes has been reported to be highly reversible by physical cleaning, such as surface flushing [10, 16, 17]. However, in most previous studies, a feed water composed of artificial organic compounds was used [10, 16]. The results obtained in this study clearly indicate that the trend in the reversibility of FO membrane fouling found in previous studies was only limited to membrane fouling caused by artificial foulants. As indicated by the results obtained in this study, artificial foulants such as AHA, BSA, and sodium alginate were not capable of reproducing the entire range of membrane fouling developed in tests using the municipal wastewater. This study has shown that investigations of FO membrane fouling with surrogate wastewater are unable to obtain reliable results unless a suitable composition is chosen. To accurately investigate the development of this type of fouling, an FO membrane filtration test using actual municipal wastewater should be

performed.

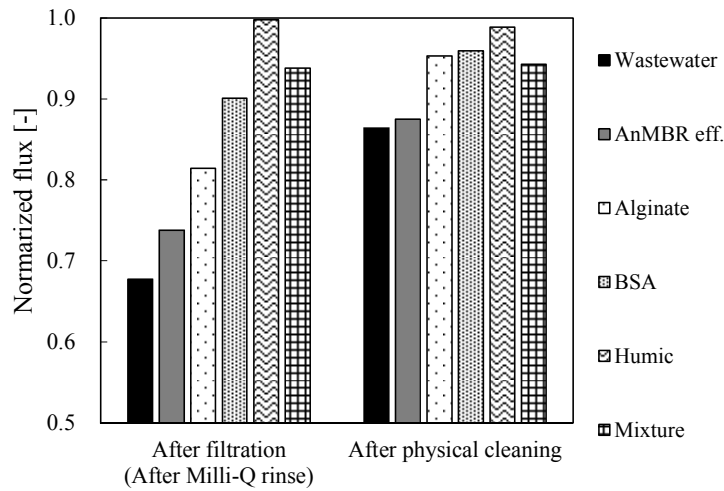


Fig. IV-3 Recoveries of membrane water permeabilities by physical cleaning (intensive shaking)

IV.3.2. Characteristics of foulants in FO membranes

Based on the results presented in the previous section, it can be concluded that, in evaluating the fouling mechanisms of FO membranes, information about the characteristics of the foulants in actual feed waters is of critical importance. In this study, the foulants accumulated on the FO membranes during the filtration tests using actual municipal wastewater were detached and characterized.

The important fractions of the organic matter causing the fouling were investigated using LC-OCD analysis. The biopolymer concentrations evaluated using this analysis has been recently considered to be one of the most important foulants in many types of membrane separation (e.g., river water filtration using low-pressure

membranes) [18, 19]. The results of the LC-OCD analysis of the organic matter contained in the feed water and the foulants detached from the membranes are presented in Fig. IV-4.

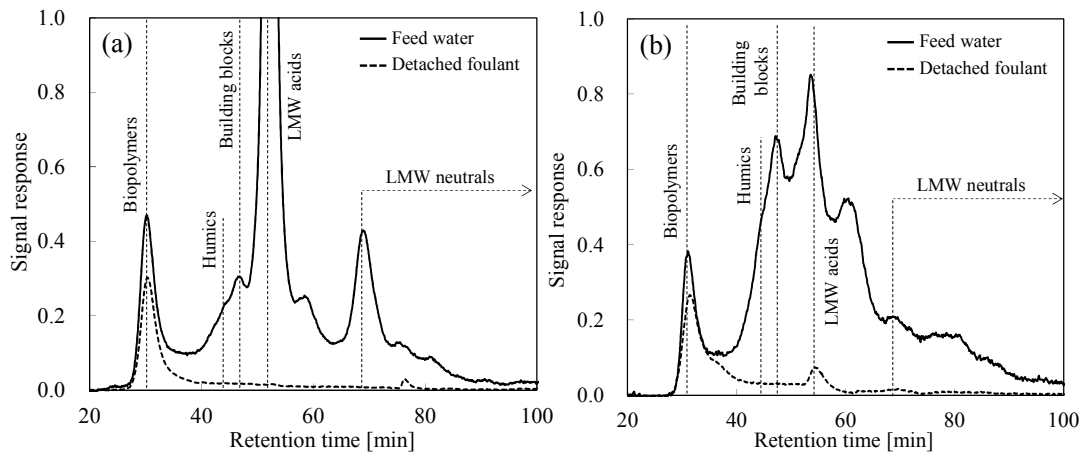


Fig. IV-4 Chromatograms obtained by the LC-OCD analysis of the organic matter contained in feed waters and foulants detached from membranes. (a) Municipal wastewater (b) AnMBR effluent.

As can be seen in the figure, the chromatogram obtained for the municipal wastewater and AnMBR effluent contained peaks associated with a broad range of organic matter, namely biopolymers (about 30 min), humic substances (about 45 min), building blocks (about 50 min), and low-molecular-weight (LMW) acids (about 58 min) and neutrals (about 70 min) [20]. In the chromatogram obtained for the feed water, the peak assigned to biopolymers was not prominent. In contrast, the peak assigned to biopolymers was predominant in the chromatogram obtained for the foulant detached from the

membranes, irrespective of the feed water used (i.e., both municipal wastewater and AnMBR effluent). In the LC-OCD chromatogram for the detached foulant, the peak assigned to humic substances, i.e., a peak located at approximately 45 min [20] was not clearly seen, indicating that hydrophobic organic matter was a minor component in the foulant that caused physically irreversible fouling of the FO membrane used in filtering the municipal wastewater and AnMBR effluent.

Fig. IV-5 shows the fluorescence EEM spectra obtained for the feed water and the foulants detached from the membranes at the end of the FO filtration test using the municipal wastewater. In the fluorescence EEM spectra, a peak located at the area of $Ex/Em = 275 \text{ nm}/350 \text{ nm}$ (Peak 1 in Fig. IV-5) can be attributed to protein-like substances contained in soluble microbial products (SMPs) [21]. Peaks that can be attributed to humic acid-like substances appear at the area of $Ex/Em = 350 \text{ nm}/425 \text{ nm}$ (Peak 2 in Fig. IV-5) [21]. In the spectra obtained for the municipal wastewater, in addition to the peak that can be attributed to protein-like substances, peaks that can be attributed to humic acid-like substances were also clearly seen (Fig. IV-5 (a)). On the other hand, only the peak that can be attributed to protein-like substances was prominently detected and the peaks that can be attributed to humic acid-like substances were not seen in the spectra determined for the foulants detached from the FO membrane used in filtering the municipal wastewater (Fig. IV-5 (b)). This result suggests that proteins contained in the SMP preferably attached to the FO membrane during the filtration tests. The importance of the protein-like substances in the

development of membrane fouling has also been reported in other membrane filtration processes [22, 23]. The results presented in Fig. IV-5 also indicate that the contribution of hydrophobic organic matter, such as humic substances, to the development of the fouling of the FO membrane was not pronounced. This result is generally in agreement with those obtained by LC-OCD analysis (Fig. IV-3), indicating that biopolymers are predominant in the foulants detached from the membranes since protein is one of the major components of biopolymers. Some researchers have used principal component analysis or the PARAFAC model to conduct a more detailed analysis of EEM data [24, 25]. Although such advanced statistical analyses were not implemented in this study, the results presented in Fig. IV-5 strongly suggests that organic macromolecules produced through the activity of microorganisms were the major contributors to membrane fouling during the FO membrane filtration tests.

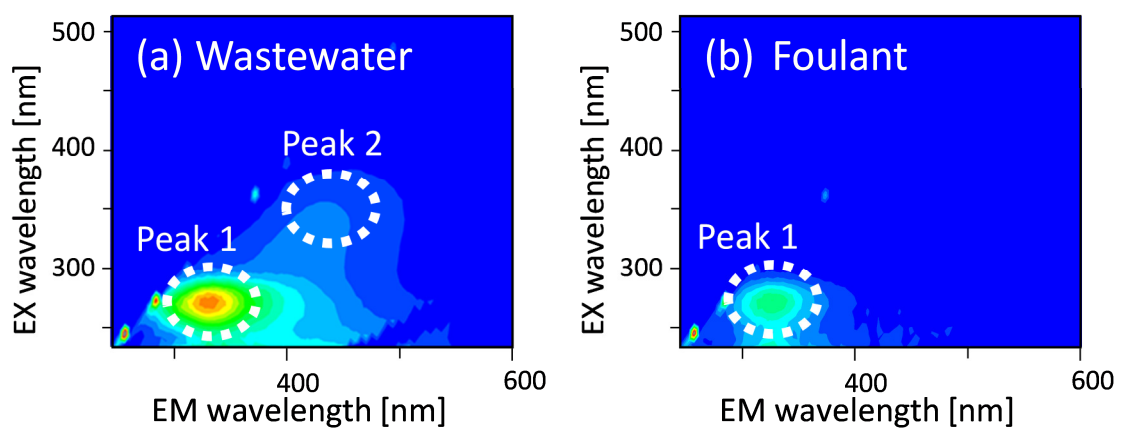


Fig. IV-5 Fluorescence EEM spectra obtained for municipal wastewater (a) and the foulant detached from the membrane (b).

As mentioned above, organic macromolecules produced through microbial activities are thought to be responsible for the fouling of FO membranes. Many researchers have reported that these organic substances cause severe fouling in various types of membrane filtration processes used for drinking water and wastewater treatment processes [18, 22-26]. Since the driving force in the FO membrane filtration process is completely different to that of other conventional membrane-based water treatment processes, where a gradient in hydraulic pressure is utilized, the characteristics of the dominant foulants in this process were also expected to be different. However, the dominant foulants in the FO membrane filtration process are likely to be similar to those of pressure-driven membrane filtration processes. To confirm this finding investigations into the characteristics of the foulants obtained at the end of long-term continuous-operation FO membrane filtration processes, operating under conditions that simulate practical applications, should be an important area of research.

Among the feed waters used in this study, the solutions containing artificial foulants (excepting that containing AHA) had much higher biopolymer concentrations than the real municipal wastewater, as revealed by the LC-OCD results. Based on the aforementioned finding that biopolymers are the dominant contributors to FO membrane fouling, these artificial solutions would be likely to cause more severe membrane fouling than real municipal wastewater. However, the results of the FO

membrane fouling test revealed that the membrane fouling caused by real municipal wastewater was more severe than the fouling caused by the artificial solutions, including the “mixture.” This discrepancy suggests that the potential for causing membrane fouling differs depending on the types and characteristics of the polysaccharides or proteins present. In such cases, the detailed characteristics of the polysaccharides or proteins, which have high fouling potentials, need to be investigated. Recent advances in analytical techniques for investigating the detailed characteristics of polysaccharides and proteins [27-29] may give opportunities to identify those that cause severe fouling in FO membrane filtration processes. Further study regarding these points is needed.

IV.4. Conclusions

The characteristics of organic compounds causing severe membrane fouling in the FO membrane filtration process were investigated. The comparison of FO membrane fouling by artificial foulants (i.e., AHA, BSA, and sodium alginate) and organic matter contained in actual municipal wastewater showed that the organic matter contained in the municipal wastewater had a much higher fouling potential than that of the artificial foulants. This suggests that the artificial foulants discussed above are not appropriate compounds for investigating the fouling of FO membranes. The foulants detached from the FO membranes used for filtering the municipal wastewater were characterized using fluorescence EEM and LC-OCD analyses. The results of these

analyses clearly indicate that biopolymer-like organic matter (organic macromolecules generated by microbial activities) was the dominant component in the detached foulant. Based on the results of this study, it can be concluded that, as in the cases of conventional pressure-driven membranes, hydrophilic organic macromolecules are important organic fractions contributing to the fouling of FO membranes, despite the significant difference in the driving force between the two processes.

References

- [1] Skouteris G., Hermosilla D., López P., Negro C. and Blanco Á., Anaerobic membrane bioreactors for wastewater treatment: a review, *Chem. Eng. J.*, 198 (2012) 138-148.
- [2] Chen L., Gu Y., Cao C., Zhang J., Ng J. W. and Tang C., Performance of a submerged anaerobic membrane bioreactor with forward osmosis membrane for low-strength wastewater treatment, *Water Res.*, 50 (2014) 114–123.
- [3] Ding Y., Tian Y., Li Z., Liu F. and You H., Characterization of organic membrane foulants in a forward osmosis membrane bioreactor treating anaerobic membrane bioreactor effluent, *Bioresour. Technol.*, 167 (2014) 137–143.
- [4] Lateef S.K., Soh B.Z. and Kimura K., Direct membrane filtration of municipal wastewater with chemically enhanced backwash for recovery of organic matter, *Bioresour. Technol.*, 150 (2013) 149–155.
- [5] Zhang X., Ning Z., Wang D.K. and Costa J.C.D., Processing municipal wastewaters by forward osmosis using CTA membrane, *J. Membr. Sci.*, 468 (2014) 269–275.
- [6] McCarty P.L., Bae J. and Kim J., Domestic wastewater treatment as a net energy producer—can this be achieved?, *Environ. Sci. Technol.*, 45(17) (2011) 7100–7106.
- [7] Onoda S., Masumori Y., Miyoshi T., Yasukawa M., Takahashi T. and Matsuyama H., Rejection of nutrients contained in an anaerobic digestion effluent 424 using

- a forward osmosis membrane, *Desalination and Water Treatment*, 57(34) (2016), 15748-15758..
- [8] Song Y., Yuan P., Zheng B., Peng J., Yuan F. and Gao Y., Nutrients removal and recovery by crystallization of magnesium ammonium phosphate from synthetic swine wastewater, *Chemosphere*, 69(2) (2007) 319–324.
- [9] Lee S., Boo C., Elimelech M. and Hong S., Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO), *J. Membr. Sci.*, 365(1) (2010) 34–39.
- [10] Mi B. and Elimelech M., Organic fouling of forward osmosis membranes: fouling reversibility and cleaning without chemical reagents, *J. Membr. Sci.*, 348(1) (2010) 337–345.
- [11] Tang C.Y., She Q., Lay W.C.L., Wang R. and Fane A.G., Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration, *J. Membr. Sci.*, 354(1) (2010) 123–133.
- [12] Motsa M.M., Mamba B.B., D'Haese A., Hoek E.M.V. and Verliefde A.R.D., Organic fouling in forward osmosis membranes: the role of feed solution chemistry and membrane structural properties, *J. Membr. Sci.*, 460 (2014) 99–109.
- [13] Yamamura H., Okimoto K., Kimura K. and Watanabe Y., Influence of calcium on the evolution of irreversible fouling in microfiltration/ultrafiltration

- membranes, *J. Water Sup. Res. Tech.-Aqua*, 56(6–7) (2007) 425–434.
- [14] Zhao S., Zou L. and Mulcahy D., Effects of membrane orientation on process performance in forward osmosis applications, *J. Membr. Sci.*, 382(1) (2011) 308-315.
- [15] Neemann F., Rosenberger S., Jefferson B. and McAdam E.J., Non-covalent protein–polysaccharide interactions and their influence on membrane fouling, *J. Membr. Sci.*, 446 (2013) 310–317.
- [16] Lee S., Boo C., Elimelech M. and Hong S., Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO), *J. Membr. Sci.*, 365(1) (2010) 34–39.
- [17] Li L.Z.Y., Yangali-Quintanilla V., Valladares-Linares R., Li Q., Zhan T. and Amy G., Flux patterns and membrane fouling propensity during desalination of seawater by forward osmosis, *Water Res.*, 46(1) (2012) 195–204.
- [18] Kimura K., Tanaka K. and Watanabe Y., Microfiltration of different surface waters with/without coagulation: clear correlations between membrane fouling and hydrophilic biopolymers, *Water Res.*, 49(1) (2014) 434–443.
- [19] Chen F., Peldszus S., Peiris R.H., Ruhl A.S., Mehrez R., Jekel M., Legge R.L. and Huck P. M., Pilot-scale investigation of drinking water ultrafiltration membrane fouling rates using advanced data analysis techniques, *Water Res.*, 48 (2014) 508–518.
- [20] Huber S.A., Balz A., Abert M. and Pronk W., Characterisation of aquatic humic

and non-humic matter with size-exclusion chromatography--organic carbon detection--organic nitrogen detection (LC-OCD-OND), *Water Res.*, 45(2) (2011) 879–885.

[21] Chen W., Westerhoff P., Leenheer J.A. and Booksh K., Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter, *Environ. Sci. Technol.*, 37(24) (2003) 5701–5710.

[22] Miyoshi T., Tsuyuhara T., Ogyu R., Kimura K. and Watanabe Y., Seasonal variation in membrane fouling in membrane bioreactors (MBRs) treating municipal wastewater, *Water Res.*, 43(20) (2009) 5109–5118.

[23] Peldszus S., Hallé C., Peiris R.H., Hamouda M., Jin X., Legge R.L., Budman H., Moresoli C. and Huck P.M., Reversible and irreversible low-pressure membrane foulants in drinking water treatment: identification by principal component analysis of fluorescence EEM and mitigation by biofiltration pretreatment, *Water Res.*, 45(16) (2011) 5161–5170.

[24] Peiris R.H., Hallé C., Budman H., Moresoli C., Peldszus S., Huck P.M. and Legge R.L., Identifying fouling events in a membrane-based drinking water treatment process using principal component analysis of fluorescence excitation-emission matrices, *Water Res.*, 44(1) (2010) 185-194.

[25] Murphy K.R., Hambly A., Singh S., Henderson R.K., Baker A., Stuetz R. and Khan S.J., Organic matter fluorescence in municipal water recycling schemes: toward a unified PARAFAC model, *Environ. Sci. Technol.*, 45(7) (2011)

2909-2916.

- [26] Zhao Y., Song L. and Ong S.L., Fouling behavior and foulant characteristics of reverse osmosis membranes for treated secondary effluent reclamation, *J. Membr. Sci.*, 349(1–2) (2010) 65–74.
- [27] Kimura K., Tanaka I., Nishimura S., Miyoshi R., Miyoshi T. and Watanabe Y., Further examination of polysaccharides causing membrane fouling in membrane bioreactors (MBRs): Application of lectin affinity chromatography and MALDI-TOF/MS, *Water Res.*, 46(17) (2012) 5725–5734.
- [28] Miyoshi T., Aizawa T., Kimura K. and Watanabe Y., Identification of proteins involved in membrane fouling in membrane bioreactors (MBRs) treating municipal wastewater, *Int. Biodeterior. Biodegrad.*, 75 (2012) 15–22.
- [29] Kimura K., Nishimura S., Miyoshi R., Hoque A., Miyoshi T. and Watanabe Y., Application of glyco-blotting for identification of structures of polysaccharides causing membrane fouling in a pilot-scale membrane bioreactor treating municipal wastewater, *Bioresour. Technol.*, 179 (2014) 180–186.

Supporting information

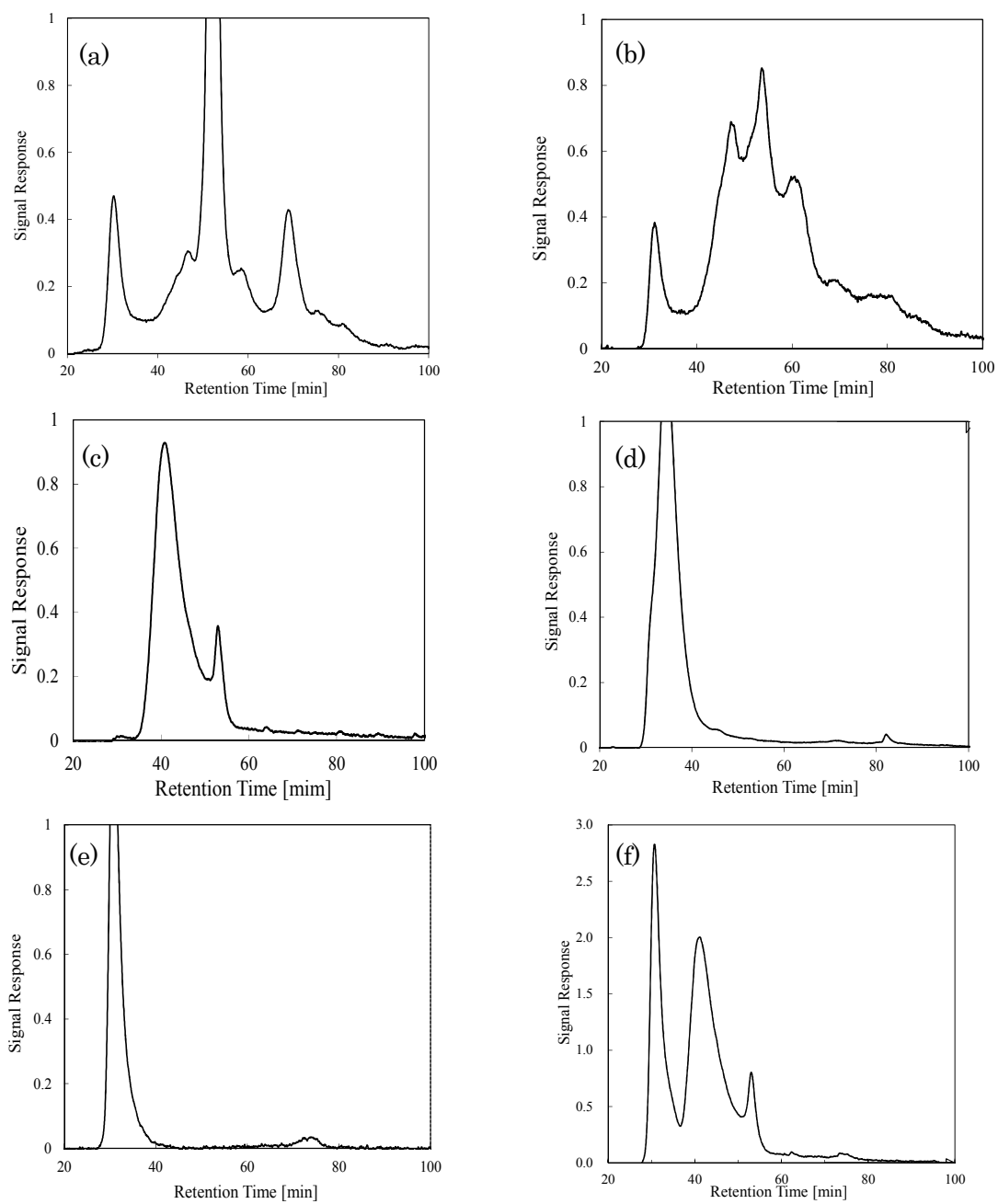


Fig. IV-S1 LC-OCD chromatograms of (a) municipal wastewater, (b) AnMBR effluent, and artificial solution [(c) AHA, (d) BSA, (e) sodium alginate, (f) mixture].

Chapter V

Evaluation of energy production of system comprised of direct up-concentrating municipal wastewater using a forward osmosis membrane and anaerobic membrane bioreactor

V.1 Introduction

In Chapter II, it was confirmed that the methane fermentation of the wastewater concentrated using FO membrane at 40°C of operation temperature is possible. In this chapter, the objective is picking out the operational condition of AnMBR for the proposed system becomes net energy production system. Specifically, first, I estimated the operational energy of overall of the proposed system based on actual measurement value obtained in Chapter II. After that, I evaluated experimentally the effect that the temperature of AnMBR which gives a great impact to the operational energy of overall the proposed system gives to the performance of organic matter removal, and by feedback the methane yield and organic matter removal efficiency to the estimation, I calculated the target operational temperature for the proposed system becomes net energy production system.

V.2 Materials and methods

V.2.1 Calculation of operational energy of proposed system

The proposed system, including the concentration of wastewater and the AnMBR, is schematically shown in Fig. I-20. The net energy generation— E_{net} —for treating a unit volume of municipal wastewater in the proposed system, was calculated by the following equation:

$$E_{net} = E_g - E_c \quad (\text{V-1})$$

where E_{net} is the net energy generation (kWh/m³), E_g is the energy generation (kWh/m³) and E_c is the energy consumption (kWh/m³).

The energy consumption (E_c) can be further divided into energy for operation (i.e., energy required for pumping etc.) and energy for heating (required for maintaining the temperature of the mixed liquor suspension during the anaerobic treatment). With regard to the operational energy, the energy consumption for operating the FO membrane filtration device and the AnMBR were assumed to be 0.1 kWh/m³ [1] and 0.06 kWh/m³ [2], respectively. For calculating the energy required for heating the anaerobic bioreactor, the following assumptions were made: the bioreactor is thermally insulated (i.e. negligible heat exchange with the outside) and heat is exchanged between the effluent and the influent of an AnMBR. Under the assumptions mentioned above, E_c was calculated by the following equation;

$$E_c = 0.1 + \frac{\{Cp \cdot (T_{An} - T'_{in}) + 0.06 + 0.1 + E_{c_Post}\}}{R_{FO}} \quad (\text{V-2})$$

when using the heat exchanger of the efficiency (η_{HEX}), equation V2 will be able to converted following equation;

$$E_c = 0.1 + \frac{Cp \left[T_{An} - \left\{ \left(\frac{T_{in} + T_{An}}{2} - T_{in} \right) \eta_{HEX} + T_{in} \right\} \right] + 0.06 + 0.1 + E_{c_Post}}{R_{FO}} \quad (V-3)$$

where Cp is the specific heat of water (kWh/m³/K), T_{An} is the operational temperature of AnMBR (K), T_{in} is the temperature of the influent in the heat exchanger (K), T'_{in} is the temperature of the influent in the AnMBR (i.e., the effluent of the heat exchanger) (K), η_{HEX} is the efficiency of the heat exchanger (-), E_{c_Post} is the energy consumption during post-treatment after AnMBR (kWh/m³) and R_{FO} is the volume basis concentration rate of wastewater by FO membrane (-). The post-treatment system after AnMBR and its energy consumption E_{c_Post} have been discussed later in this paper, based on the experimental results obtained.

The energy generated by the combustion of methane gas obtained from the anaerobic treatment E_g was calculated by the following equation:

$$E_g = \frac{C_{in} \cdot Rem_{AnMBR}^{COD} \cdot \eta_{CH_4} \cdot H_{CH_4} \cdot \eta_{CG}}{R_{FO}} \quad (V-4)$$

where C_{in} is the COD concentration of the influent of AnMBR (i.e. the concentrated wastewater; kg-COD/m³) and Rem_{AnMBR}^{COD} is removal efficiency of COD at AnMBR. In this study, the removal efficiency of COD from the batch methane fermentation test mentioned above was applied to Rem_{AnMBR}^{COD} . η_{CH_4} is the methane yield (m³-CH₄/kg-COD_{rem}), H_{CH_4} is the heat quantity of methane gas (kWh/m³-CH₄) and

η_{CG} is the energy conversion efficiency of methane gas (-). η_{CG} is approximately 0.5 in conventional thermal power generation processes, although, this efficiency can be increased up to approximately 0.8, when combined with an exhaust heat recovery system [3].

V.2.2 Evaluation of effect of operational temperature for AnMBR performance (Lab-scale AnMBR)

Materials

The effluent from primary sedimentation tank of Port Island wastewater treatment plant in Kobe city was used as feed water, and the anaerobic digestion sludge of Higasinada wastewater treatment plant was used as seed sludge. The composition of these samples were shown in Table V-1.

Table V-1 Water qualities of feed water and seed sludge of lab-scale AnMBR experiment

	Content	Value
Feed water	COD	421 mg/L
	NH ₄ -N	28 mg/L
	PO ₄ -P	2.6 mg/L
Seed sludge	MLSS	7400 mg/L
	MLVSS	5300 mg/L

Would otherwise, although the feed water should be used concentrated wastewater using FO membrane, since the production capacity of concentrated wastewater of FO membrane experiment system was not enough, the wastewater without concentration was used in this experiment. The important points in the difference between the case of using concentrated wastewater are concentration of organic matter and ammonia. Regard to organic matter, since the concentration is lower than concentrated wastewater, the removal efficiency was evaluated to be lower. And I believed that this is no problem because this evaluation is safety side. Regard to ammonia which is inhibitor for methane fermentation, similar to organic material, it is expected that the concentration is lower than concentrated wastewater. Namely, it will be underestimated the possibility of inhibition. However, assuming the volumetric concentration factor is 19 times and the rejection of ammonia on FO membrane is 100%, the ammonia concentration of concentrated wastewater will be approximately 600 mg/L. Typically, it reported that the inhibition of methane fermentation by ammonia occurs at the ammonia concentration higher than 2000 mg/L [4], for that reason, it is predicted that possibility of the methane fermentation inhibition occurring even in the case of using concentrated wastewater is low. Therefore, using the raw wastewater in this experiment would not be a big problem. However, I have to recognize that verification is needed in the future.

Set-up and operation of lab-scale AnMBR

The schematic illustration of the submerged AnMBR system used this

experiment was shown in Fig. V-1. A sealable glass container (effective volume of 2 L) was used as bioreactor. A pH meter (ION/pH METER IM-32P, Toa-DKK, Tokyo, Japan) and oxidation-reduction potential meter was provided on the bioreactor. Temperature of bioreactor was controlled by thermostatic bath (Thermal robo TR-1A, As One, Osaka, Japan). During operation, the suspension in bioreactor was stirred by magnetic stirrer (SA-501, Sansyo, Tokyo, Japan). The microfiltration membrane module (polyvinylidene difluoride hollow fiber membrane, pore size; 0.08 μm , surface area; 0.012 m^2) to separate the effluent and sludge was submerged in the bioreactor, and initial filtration flux was 0.3 $\text{m}^3/\text{m}^2/\text{d}$. Since the membrane fouling occurred, the hydraulic retention time in bioreactor varied between 15~30 hour. The organic matter concentration and methane yield were measured with 5h operation. Amount of biogas generation and methane concentration of biogas were measured by water replacement method and detecting tube (No. 2HH for CO_2 , Gastec Corporation, Japan). Here, I measured CO_2 concentration in biogas, and I assumed remainder methane gas. When I changed the operational temperature, various data was measured after acclimation period of 24h operation. The sludge extraction excepting sampling was not done. To control pH larger than 7.0, 0.1 M NaOH (reagent grade, Wako Pure Chemical Industries, Tokyo, Japan) solution was added during operation.

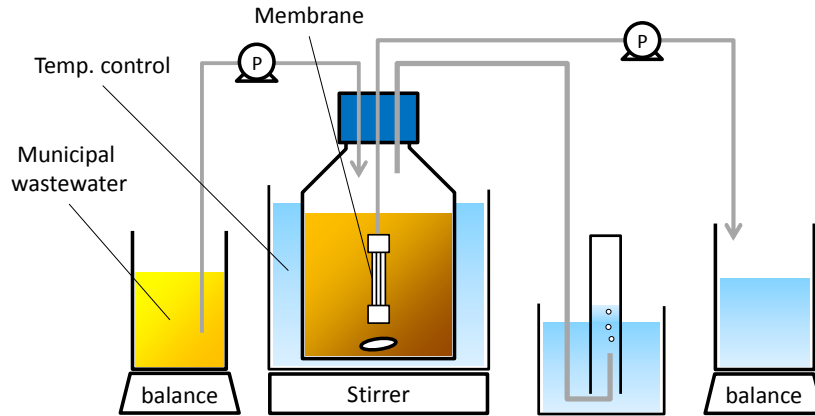


Fig. V-1 Schematic illustration of lab-scale AnMBR system

V.2.3 Calculation of methane yield

COD concentration of influent and effluent of lab-scale AnMBR was measured, and COD removal rate of lab-scale AnMBR (R_{AnMBR}^{COD} , kg-COD/kg-MLVSS/day) was calculated by following equation:

$$R_{AnMBR}^{COD} = \frac{(C_{in} - C_{eff}) \cdot Q}{C_{MLVSS} \cdot V \cdot T} \quad (V-5)$$

where C_{in} and C_{eff} are COD concentration of influent and effluent (kg/m^3) of AnMBR. Q is the quantity of influent (m^3). C_{MLVSS} is concentration of mixed liquor volatile suspended solids (MLVSS) in bioreactor (kg/m^3). V is the volume of bioreactor (m^3). T is the hydraulic retention time (day).

The methane gas yield η_{CH_4} ($\text{m}^3\text{-CH}_4/\text{kg-COD}_{rem}$) was calculated by following equation:

$$\eta_{CH_4} = \frac{(1 - C_{CO_2}) \cdot V_{Biogas}}{Q \cdot (C_{in} - C_{eff})} \quad (V-6)$$

where C_{CO_2} is concentration of CO_2 in biogas (-), V_{Biogas} is amount of biogas generation (m^3), Q is the quantity of influent (m^3).

V.3 Results and discussion

V.3.1 Calculation of operational energy of proposed system

Based on the energy generation potential of the concentrated wastewater obtained in the experiment described in the Chapter II, the energy balance of the wastewater treatment system involving the up-concentration of wastewater using an FO membrane and AnMBR was evaluated. The results are shown in Table V-2.

Table V-2 Energy balance of the system combining the wastewater concentration by the FO membrane and the anaerobic MBR. All energy values correspond to energy per 1 m³ of raw wastewater without concentration. The concentrate factor of wastewater by FO membrane was assumed to be 19 times as volume and 16 times as COD concentration. The AnMBR operational temperature was assumed to be 40°C

	Consumption [kWh/m ³]	Generation [kWh/m ³]
Concentration of wastewater by FO membrane	0.1	—
AnMBR (Operation)	0.0032	—
AnMBR (Heating)	0.79	—
Biogas power generation	—	0.33
Post-treatment (MAP and MBR)	0.017	
Total	0.91	0.33

In this estimation, the method for post-treatment after AnMBR should also be considered. Considering that the COD concentration of the concentrated wastewater was 4800 mg-COD/L and the removal ratio of COD obtained from the batch methane fermentation test was 0.62, the COD concentration of the effluent from the AnMBR would be approximately 1800 mg/L. The reduction in the concentrations of the ammonium and phosphate ions is expected to be negligible. As a result, the concentrations of these ions in the effluent of the AnMBR are expected to be the same as those in the concentrated wastewater (i.e., 130 mg/L for ammonium ions and 78

mg/L for phosphate ions). As the concentrations of COD, ammonium and phosphate ions exceed the discharge standards, applying appropriate post-treatment is indispensable. In this study, the magnesium ammonium phosphate (MAP) crystallization process [5] was selected for the recovery of phosphorous, while the anaerobic MBR process [6] was selected for the removal of nitrogen and organic matter. According to some previous publications, the energy consumption of MAP and MBR processes were reported to be 0.02 kWh/m³ [7] and 0.4 kWh/m³ [8], respectively. On this basis, the energy consumption for post-treatment (E_{C_Post}) is estimated to be 0.32 kWh/m³ (0.017 kwh/m³ of raw wastewater).

The energy consumption during the up-concentration of municipal wastewater using an FO membrane was assumed to be 0.1 kWh/m³ [1]. In the estimation, it was also assumed that the energy consumption of the AnMBR, excluding the energy required for heating, is 0.06 kWh/m³ (0.0032 kWh/m³ of raw wastewater) [2]. The other parameters required for calculating the energy consumption were assumed as follows: specific heat of water (C_p) as 1.16 kWh/m³/K, the temperature in the bioreactor of AnMBR (T_{An}) as 313 K, the temperature of the concentrated wastewater (T_{in}) as 293 K and the efficiency of heat exchanger (η_{HEX}) as 0.7 (-). The energy consumption of the proposed system (E_C) was estimated to be 0.91 kWh/m³ by using equation (V-3). Similarly, it was assumed that the COD concentration in a municipal wastewater (before concentration) is 300 mg-COD/L, the COD_{C_r} concentration in concentrated wastewater C_{in} is 4800 kg-COD/m³, the methane yield (η_{CH_4}) is 0.22 m³-CH₄/kg-COD_{rem}, the heat quantity of methane gas (H_{CH_4}) is 36 MJ/m³-CH₄ [9] and the energy conversion

efficiency from the combustion of methane gas (η_{CG}) is 0.8 (-). On the basis of the assumption mentioned above, the energy generated while treating a unit volume of wastewater by the proposed system (E_g) was estimated to be 0.33 kWh/m³ by using equation (V-4). Therefore, the net energy generation (E_{net}) was calculated to be -0.58 kWh/m³, by using equation (V-1).

Unfortunately, the net energy consumption of the proposed system was larger than the typical energy consumption of conventional activated sludge process (i.e., 0.2 kWh/m³ [10]). Therefore, it is necessary to reduce the net energy consumption of the proposed system.

V.3.2 Evaluation of effect of operational temperature for AnMBR performance (Lab-scale AnMBR)

Effect of fermentation temperature to COD removal rate and biogas generation rate of lab-scale AnMBR is shown in Fig. V-2.

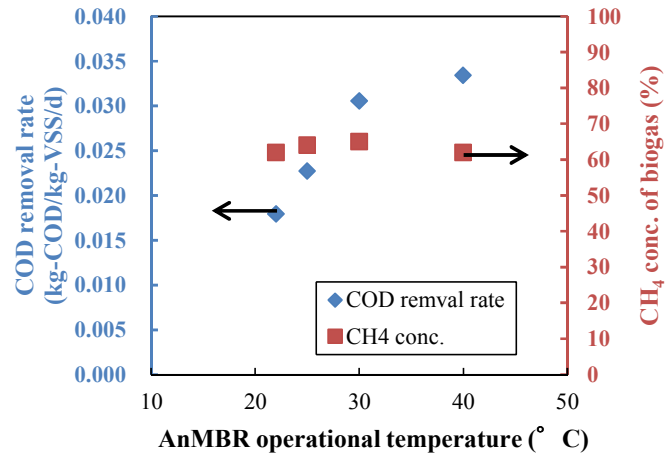


Fig. V-2 Effect of fermentation temperature to COD removal rate and methane concentration of biogas of lab-scale AnMBR

The COD removal rate was decreased with decreasing in the operational temperature. Cause of this is that the activity of microorganisms decreased with decreasing in the operational temperature. This result indicated that although longer retention time is necessary with lower operational temperature. On the other hand, methane concentration of biogas was not affected by operational temperature. The methane yield (η_{CH_4}) calculated using equation (V-6) were shown in Fig. V-3. The methane gas yield could be keep approximately constant value in either operational temperature. And range of these values is 0.21-0.23 m³-CH₄/kg-COD_{rem}, it is close with the typical range reported previous research (0.23-0.33 L-CH₄/g-COD_{rem}) [11, 12]. With the above, the possibility of achieving the enough organic matter removal and methane yield even at low operational temperature were indicated.

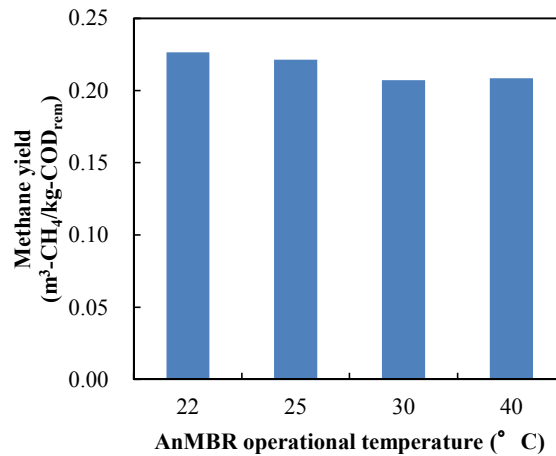


Fig. V-3 Effect of fermentation temperature to methane yield of lab-scale AnMBR

V.3.3 Calculation of operational energy of proposed system based on performance of lab-scale AnMBR

Effect of AnMBR operational temperature to energy balance of proposed system calculated based on above actual measured methane yield at 22-40°C is shown in Fig. V-4. It should be noted that, the estimation conditions other than the operating temperature of AnMBR are the same as described in V.3.1. It is shown clearly from Fig. V-4, since energy consumption E_c is susceptible to operational temperature than energy generation E_g , the magnitude relation were interchanged a certain operational temperature on the border. And its temperature was approximately 26°C. In other words, if it is possible to operating AnMBR at temperature lower than 26°C, the proposed system will be able to become net energy production system. Here, Watanabe et al. reported that they achieved 92% of COD removal efficiency at 15°C on the experiment

using artificial wastewater [13]. Although the verification for whether or not this can be achieved even in the case of using the actual municipal wastewater is necessary in the future, I'm expected to be enough possible.

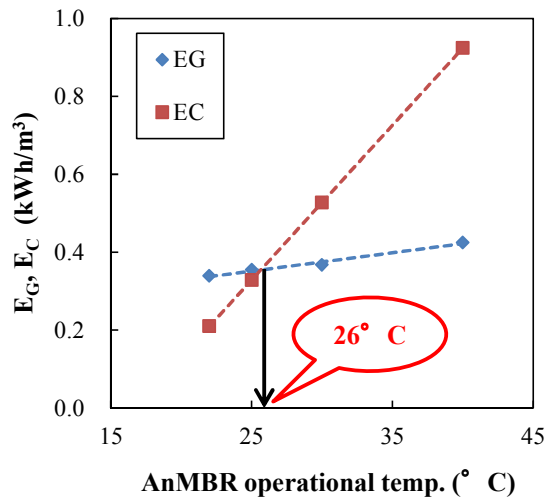


Fig. V-4 Effect of fermentation temperature to energy balance of proposed system

V.4 Conclusions

In this chapter, the operational condition of the system comprised of direct up-concentrating municipal wastewater using an FO membrane and AnMBR to become net energy production system was searched by experiments and calculations. In the lab-scale AnMBR experiment, it confirmed that COD removal efficiency and biogas generation amount was decreased with decreasing in operational temperature. By estimation based on this actual measured value, it was clear that if it is possible to

operating AnMBR at temperature lower than 26°C, the proposed system will be able to become net energy production system.

Reference

- [1] McGovern R. K., On the potential of forward osmosis to energetically outperform reverse osmosis desalination. *J. Membr. Sci.*, 469 (2014) 245-250.
- [2] Lin H., Chen J., Wang F., Ding L. and Hong H., Feasibility evaluation of submerged anaerobic membrane bioreactor for municipal secondary wastewater treatment. *Desalination*, 280(1) (2011) 120-126.
- [3] Zupančič G. D., Uranjek-Ževart N. and Roš M., Full-scale anaerobic co-digestion of organic waste and municipal sludge. *Biomass Bioenergy*, 32(2) (2008) 162–167.
- [4] Belhadj S., Joute Y., El Bari H., Serrano A., Gil A., Siles J. Á., Chica A. F., and Martín M. Á., 2014. Evaluation of the Anaerobic Co-Digestion of Sewage Sludge and Tomato Waste at Mesophilic Temperature. *Appl. Biochem. Biotechnol.* 172 (8), 3862-3874.
- [5] Wang J., Song Y., Yuan P., Peng J. and Fan M., Modeling the crystallization of magnesium ammonium phosphate for phosphorus recovery. *Chemosphere*, 65(7) (2006) 1182–1187.
- [6] Metcalf and Eddy, *Wastewater Engineering Treatment and Reuse*, 4th edition. McGraw-Hill (2003) New York.
- [7] Van Dijk J. C. and Braakensiek H., Phosphate removal by crystallization in a fluidized bed. *Water Sci. Technol.*, 17 (1984) 133–142.
- [8] Xiao K., Xu Y., Liang S., Lei T., Sun J., Wen X. and Huang X., *Engineering*

application of membrane bioreactor for wastewater treatment in China: Current state and future prospect. *Frontiers of Environmental Science & Engineering*, 8(6) (2014) 805–819.

- [9] Cuéllar A. D. and Webber M. E., Cow power: the energy and emissions benefits of converting manure to biogas. *Environ. Res., Letters* 3(3) (2008) 034002.
- [10] Gnirss R. and Dittrich J., Microfiltration of municipal wastewater for disinfection and advanced phosphorus removal: Results from trials with different small-scale pilot plants. *Water Environ. Res.*, (2000) 602-609.
- [11] Saddoud A., Ellouze M., Dhouib A. and Sayadi S., Anaerobic membrane bioreactor treatment of domestic wastewater in Tunisia. *Desalination*, 207(1) (2007), 205–215.
- [12] Martinez-Sosa D., Helmreich B., Netter T., Paris S., Bischof F. and Horn H., Anaerobic submerged membrane bioreactor (AnSMBR) for municipal wastewater treatment under mesophilic and psychrophilic temperature conditions. *Bioresour. Technol.*, 102(22) (2011) 10377-10385.
- [13] Watanabe R., Sugo T., Wakahara S., Li Y. Y., Influence of temperature on treatment performance of synthetic sewage by anaerobic membrane bioreactor (AnMBR), *Journal of Japan Society on Water Environment*, 37(5) (2104) 197–204.

Chapter VI

Conclusions

In this chapter, the results obtained in previous chapters are summarized as conclusion, and perspectives for further research are discussed.

VI.1 Conclusions

In this study, the system comprised of direct up-concentrating municipal wastewater using an FO membrane and AnMBR was proposed as a novel wastewater treatment system which can generate energy. By the various experiment, technical and economic possibility of applying this process was shown. The conclusions of this study are summarized below.

1. Direct up-concentration of wastewater by forward osmosis membrane and evaluation of energy production of system comprised of concentrating wastewater and anaerobic treatment

The technical feasibility of a wastewater treatment system comprised of the up-concentration of municipal wastewater by the FO membrane and anaerobic fermentation of the concentrated wastewater were estimated. The results obtained from concentration test revealed that more than 16 times concentration of organic carbon contained in real municipal wastewater was possible by using the hollow fiber FO membrane. The methane yield from the concentrated organic matter was $0.22 \text{ m}^3\text{-CH}_4/\text{kg-COD}_{\text{rem}}$. The obtained

results suggest that applying the FO membrane to concentration of municipal wastewater and operating the fermentation using concentrated wastewater by FO membrane are possible in technical point of view.

2. Rejection of nutrients contained in an anaerobic digestion effluent using a forward osmosis membrane

The possibility of applying an FO membrane filtration process for the post-treatment of an AnMBR was investigated. The results of an FO membrane filtration test using a surrogate AnMBR effluent prepared by supernatant obtained from a real anaerobic digester revealed that the FO membrane demonstrated excellent rejection of phosphate ions, whereas the rejection of ammonium ions was moderate and depended heavily on the orientation of the FO membrane. The flux of ammonium ions across the FO membrane decreased as the solute concentration in the DS increased. In the FO filtration experiment using the DS with a high solute concentration, the reverse solute flux from the DS to FS increased. The above-mentioned trend was particularly remarkable in the FO filtration with the AL-DS orientation, in which the reverse solute flux was higher than that in the other membrane orientation. The relationship between the degree of reverse solute flux and flux of ammonium ion was confirmed by the FO filtration test using different solute species in the DS. When lithium chloride, which had a high reverse solute flux than sodium chloride, was used for preparing the DS, the flux of ammonium ion decreased. On the other hand, a higher flux of ammonium ion was observed in the FO filtration using the DS containing solutes with less

reverse flux, such as magnesium sulfate or glucose. On the basis of the obtained results, it can be concluded that reverse solute flux has a positive influence on the rejection of ammonium ions. And this is an important information for improvement of the FO membrane and selection of operational condition of FO membrane in the future.

3. Characteristics of foulants of forward osmosis membranes used in municipal wastewater concentration processes

The characteristics of organic compounds causing severe membrane fouling in the FO membrane filtration process were investigated. The organic matter contained in the municipal wastewater had a much higher fouling potential than that of the artificial foulants. This suggests that the artificial foulants discussed above are not appropriate compounds for investigating the fouling of FO membranes. The results obtained from analysis of the foulants detached from the FO membranes clearly indicate that biopolymer-like organic matter (organic macromolecules generated by microbial activities) was the dominant component in the detached foulant. Based on the results of this study, it can be concluded that, as in the cases of conventional pressure-driven membranes, hydrophilic organic macromolecules are important organic fractions contributing to the fouling of FO membranes, despite the significant difference in the driving force between the two processes.

The knowledge obtained from this section is very important for selection of pre-treatment process prior FO membrane filtration and development of

low fouling FO membrane which will be necessary for commercialization of proposed system in the future.

4. Evaluation of energy production of system comprised of direct up-concentrating municipal wastewater using a forward osmosis membrane and anaerobic treatment

The operational condition for the system comprised of direct up-concentrating municipal wastewater using a forward osmosis membrane and anaerobic treatment become net energy generation system was simulated by the experiments and calculations. In lab-scale AnMBR experiment, it was confirmed that COD removal rate and amount of biogas generation decrease with decreasing of the operational temperature of AnMBR. By estimation based on the experimental values, if operating the AnMBR at lower than 26°C is possible, the proposed system will become net energy generation system.

The knowledge obtained in this section indicates a very important target value for the development which will be continued for commercialization of proposed system.

VI.2 Perspectives

In this study, the system comprised of direct up-concentrating municipal wastewater using a FO membrane and AnMBR could be evaluated technical and economic possibility of applying. However, in fact, still a lot of challenges for commercialization. Regard to the FO membrane, the challenges may be improvement of ammonia rejection, optimization of module structure and

establishment of the method of membrane cleaning. Regard to AnMBR, the corresponding to membrane fouling would be most important challenge. After these challenges have been solved in the lab-scale, the pilot-scale continuous experiment would be done. And finally, it would lead to commercialization, through the demonstration experiment with the inclusion of the municipality.

As described above, although there are some steps for commercialization of this proposed process, the conversion to the energy production system is one of the ultimate dreams in wastewater treatment field, and I aspire that the development is continued toward commercialization in the future.

List of publications

- Chapter II and V** **Sosuke Onoda**, Yuta Masumori, Taro Miyoshi, Masahiro Yasukawa, Tomoki Takahashi and Hideto Matsuyama, Direct up-concentration of wastewater using a forward osmosis membrane and evaluation of the energy production of the system involving concentrated wastewater and anaerobic treatment, *Desalination and Water Treatment*, *Submitting*
- Chapter III** **Sosuke Onoda**, Yuta Masumori, Taro Miyoshi, Masahiro Yasukawa, Tomoki Takahashi and Hideto Matsuyama, Rejection of nutrients contained in an anaerobic digestion effluent using a forward osmosis membrane, *Desalination and Water Treatment*, 57(34) (2016), 15748-15758.
- Chapter IV** **Sosuke Onoda**, Yuta Masumori, Taro Miyoshi, Masahiro Yasukawa, Tomoki Takahashi and Hideto Matsuyama, Characteristics of foulants of forward osmosis membranes used in municipal wastewater concentration processes, *Desalination and Water Treatment*, (2016) in press

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Sosuke Onoda

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“Development of a novel wastewater treatment system combined direct
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