


Recovering nutrients and rejecting trace organic compounds in human urine by a forward osmosis–membrane distillation (FO–MD) hybrid system

Chihiro Gau, Satoshi Sato, Daizhou Zhang, Yasuhiro Ishibashi and Jun Kobayashi *

Faculty of Environmental and Symbiotic Science, Prefectural University of Kumamoto, 3-1-100 Tsukide, Higashi-Ku, Kumamoto 862-8502, Japan

*Corresponding author. E-mail: jkobayashi@pu-kumamoto.ac.jp

 JK, 0000-0002-9198-0563

ABSTRACT

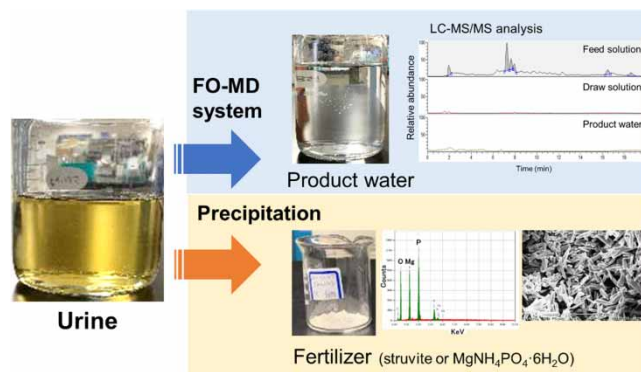
Urine is a major source of reclaimed water and fertilizer. Urine treatment involves two key processes: the recovery of nutrients and the rejection of trace organic compounds (TOCs). In this study, we investigated the rejection of TOCs and the recovery of nutrients in human urine using a seawater-driven forward osmosis and membrane distillation (FO–MD) hybrid system. Three 24 h experiments were conducted at draw solution temperatures of 30, 40, and 50 °C. The average rejection rates of cations, anions, and dissolved organic carbon were more than 93.7% and 79.5% in the FO–MD system and FO side, respectively. Ten types of TOCs were detected in the feed solution, whereas none were detected in the product water, indicating that the TOCs were completely rejected. The precipitates, i.e., the recovered nutrients in the FO side, were extremely close to magnesium ammonium phosphate (struvite, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), according to their electron microscopic images, elemental composition, and X-ray diffraction spectra, and it was estimated that approximately 85% of the nutrients in the feed solution were recovered. The rejection and recovery efficiencies were unaffected by the draw solution temperature. These results indicate the potential for the sustainable use of FO–MD-based treatments for human urine.

Key words: LC-MS/MS, reclaimed water, struvite, trace organic compounds, XRD

HIGHLIGHTS

- More than 93.7% of cations and anions in feed solution were rejected.
- Trace organic compounds were completely rejected in this system.
- Nutrients in feed solution were recovered as struvite.

GRAPHICAL ABSTRACT



NOMENCLATURE

A effective membrane area
 C_d chemical concentration in the draw solution

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY 4.0), which permits copying, adaptation and redistribution, provided the original work is properly cited (<http://creativecommons.org/licenses/by/4.0/>).

C_f	chemical concentration in the feed solution
CTA	cellulose triacetate
C_w	chemical concentration in the product water
DOC	dissolved organic carbon
DOM	dissolved organic matter
EC	electrical conductivity
ED	electrodialysis
EDS	energy dispersive X-ray spectroscopy
FO	forward osmosis
J_w	transmembrane water flux
LC-MS/MS	high-performance liquid chromatography with tandem mass spectrometry
MD	membrane distillation
SEM	scanning electron microscope
TICC	total ion current chromatogram
TOC	total organic carbon
TOrCs	trace organic compounds
XRD	X-ray diffraction
Δt	time interval
ΔV	total increased volume of permeate water

1. INTRODUCTION

As a means of addressing the increasing human population and climate change, reclaimed water is attracting attention as an alternative water resource. Technology using membranes, such as reverse osmosis (RO) and nanofiltration, has been widely applied to various wastewater, including municipal and industrial wastewater. However, this pressure-driven membrane process consumes high energy and tends to form fouling on the membrane.

Compared with the pressure-driven membrane process, forward osmosis (FO), which is an osmotically driven membrane process, has attracted attention because of lower energy consumption and membrane fouling (Zhao *et al.* 2012; Xue *et al.* 2015). An FO system has been utilized not only to concentrate water volume but also to recover nutrients, such as nitrogen and phosphorus, from municipal wastewater and urine (Xie *et al.* 2014; Zhang *et al.* 2014). Additionally, an FO system shows high rejection for harmful metals, including mercury and arsenic (Ge *et al.* 2016; Wu *et al.* 2017), and trace organic compounds (TOrCs), such as pharmaceuticals in wastewater (Hancock *et al.* 2011; Xie *et al.* 2012a, 2012b; Coday *et al.* 2014; Lutchmiah *et al.* 2014). However, in an FO system, the difference in osmotic pressure between the feed solution and draw solution gradually decreases with operation time because the draw solution is diluted by permeated water from the feed solution. Therefore, the integration of FO with other processes, including membrane distillation (MD) and electrodialysis (ED), has been applied recently. An FO–MD hybrid system can not only reconcentrate a diluted draw solution for sustainable process performance but also complement wastewater nutrient recovery with freshwater production (Xie *et al.* 2016).

There has been considerable attention to the recycling of urine worldwide (Larsen *et al.* 2021; Wald 2022). Among nutrient-rich water, including municipal wastewater, human urine is regarded as one of the best available resources for fertilizer because it contains 4.0–14 g L⁻¹ nitrogen, 0.35–2.5 g L⁻¹ phosphorus, and 0.75–2.6 g L⁻¹ potassium (Rose *et al.* 2015; Patel *et al.* 2020; Larsen *et al.* 2021). Particularly, using separated urine in an FO system is cost effective and environmentally friendly for nutrient recovery (Zhang *et al.* 2014). Nitrogen and phosphorus in wastewater are frequently recovered as magnesium ammonium phosphate (struvite, MgNH₄PO₄·6H₂O) by adding magnesium (Xie *et al.* 2014).

Several studies have examined recovering nutrients from wastewater and digested sludge using an FO–MD hybrid system (Xie *et al.* 2013a, 2014). Also, several studies have reported successful rejection of nitrogen and phosphorus using the FO–MD hybrid system for urine (Liu *et al.* 2016; Volpin *et al.* 2019). In the FO–RO hybrid system, the rejection of neutral and ionic TOrCs, such as pharmaceuticals in wastewater, has been studied in detail (Hancock *et al.* 2011; Holloway *et al.* 2014). However, a comprehensive analysis of TOrCs for human urine treatment using an FO–MD system has not been conducted, and little is known about the comprehensive rejection of TOrCs using an FO–MD system.

This study aims to evaluate the rejection of ions and TOrCs from feed solution to produce water and the production of struvite potential from human urine using a seawater-driven FO–MD hybrid system. This study comprehensively investigated TOrCs in urine using the full-scan mode of high-performance liquid chromatography with tandem mass spectrometry (LC-MS/MS). Seawater is abundant and low cost, and it has frequently been used as a draw solution, as well as a source

of NaCl (Xue *et al.* 2015). Therefore, seawater was chosen in this study as a draw solution from the viewpoint of sustainable and simple operation.

2. MATERIAL AND METHODS

2.1. Feed and draw solutions

Human urine (pooled from 13 normal donors, 991-03-P), which is a feed solution, was purchased from Lee Biosolutions, Inc. (MO, USA). The electrical conductivity (EC) and pH of the urine samples were 9.51 mS/cm and 6.14, respectively. Insoluble material in the urine samples after thawing was removed by a precombusted glass fiber filter (0.45 μm pore size, GF/B, Whatman[®], UK) at 450 °C for 2 h before the experiments. Synthetic seawater (Sealife, Nihonkaisui Co., Ltd, Tokyo, Japan) was used as a draw solution and adjusted 30% with distilled water. Table 1 lists the details of the content of urine (feed solution) and synthetic seawater (draw solution).

2.2. FO–MD system setup

Figure 1 shows a FO–MD system. A lab-scale FO–MD system is composed of an FO cell, a direct contact MD cell and thermostatic baths, peristaltic pumps, and digital balances. A flat sheet FO membrane of cellulose triacetate (CTA) (FTS H2O[™] flat sheet membrane), a flat sheet MD membrane of polytetrafluoroethylene (0.2 μm pore size, CF042), and an FO cell (CF042D-FO) were purchased from Sterlitech Corporation (WA, USA). The FO cell holds an FO membrane with an effective area of 34 cm². The MD cell is made of acrylic plastic and holds an MD membrane with an effective area of 37 cm². These membranes were used with an active layer facing the feed solution. Counter current crossflow circulation of each solution was applied by peristaltic pumps at a rate of 0.1 L min⁻¹. Thermostatic baths were used to adjust the water temperature in the draw solution and the distilled water in the MD system. The feed solution in the FO system and the distilled water (product water) in the MD system were weighed, and the changes in their weight were recorded by digital balances at regular time intervals for 24 h.

2.3. Experiment procedure

The initial water volume of each solution was as follows: the feed solution reservoir (1 L glass bottle) contained 0.5 L of the urine sample, the draw solution reservoir (2 L Erlenmeyer flask) contained 1 L of 30% synthetic seawater, and the product water reservoir (1 L glass bottle) contained 0.5 L of distilled water. The feed solution and the draw solution reservoirs were connected to the FO cell and the pump, and the draw solution and the product water reservoirs were connected to the MD cell and the pump. The water temperature of the feed solution was not adjusted, whereas that of the draw solution was

Table 1 | Content of the feed and draw solutions

	Feed solution (mg L ⁻¹)	Draw solution (mg L ⁻¹)
Ca ²⁺	65 ± 5.5	420 ± 28
K ⁺	1,100 ± 54	350 ± 27
Mg ²⁺	33 ± 2.8	1,300 ± 74
Na ⁺	14,400 ± 65	10,400 ± 1,030
NH ₄ ⁺	230 ± 24	0.46 ± 0.65
Br ⁻	18 ± 3.2	92 ± 21
Cl ⁻	1,800 ± 47	21,000 ± 4,900
F ⁻	36 ± 8.0	N.D.
PO ₄ ³⁻	850 ± 30	N.D.
NO ₂ ⁻	N.D.	N.D.
NO ₃ ⁻	38 ± 4.8	N.D.
SO ₄ ²⁻	750 ± 92	4,300 ± 2,300
DOC	4,600 ± 140	N.A.

Values show average and standard deviation ($n = 3$).

N.D., not detected; N.A., not analyzed.

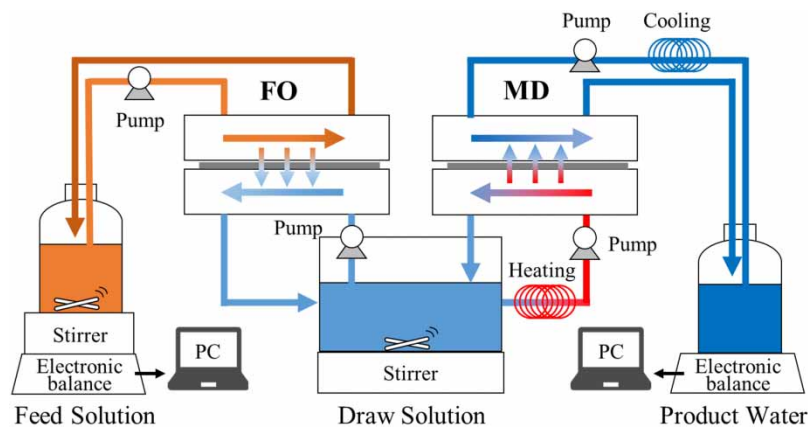


Figure 1 | Schematic diagram of the laboratory scale forward osmosis and membrane distillation (FO–MD) system.

adjusted at 30, 40, and 50 °C. These water temperatures were set to investigate the appropriate temperature for maintaining the stability and sustainability of the FO–MD system; that is, the temperature where the difference in flux between the feed and draw solutions and the draw solution and distilled water is at the minimum. The distilled water in the MD system was maintained at 20 °C. The experiments were conducted under three different temperatures of the draw solution for 24 h. For the feed solution, the pH and EC were measured at 6 h intervals. From the feed, draw, and product solutions, 5 mL of the samples were taken at 6 h intervals for chemical analysis.

2.4. Chemical analysis

Water temperature and pH were measured using a portable multisensor (D-73; Horiba, Ltd, Kyoto, Japan); EC was measured using a portable EC sensor (ES-71; Horiba, Ltd). Anions (Br^- , Cl^- , F^- , NO_2^- , NO_3^- , PO_4^{3-} , and SO_4^{2-}) and cations (Ca^{2+} , K^+ , Li^+ , Mg^{2+} , Na^+ , and NH_4^+) in the water samples were measured using an ion chromatograph (IC-2010, Tosoh Corporation, Tokyo, Japan). After filtration (GF/B, Whatman, UK), dissolved organic carbon (DOC) was analyzed using a total organic carbon (TOC) analyzer (TOC-L, Shimadzu, Kyoto, Japan). TOC in the draw solution could not be measured because of high salinity.

TOrCs were measured using an LC-MS/MS (Ultimate 3000/TSQ Quantum Access Max, Thermo Fisher Scientific) with a full scan mode (m/z 100–500). The water samples were filtered using a disposal filter (pore size 0.2 μm , Autovial[®] 5, Whatman[®], UK), and then 0.5 mL methanol was added to 0.5 mL of the filtered sample. An aliquot of 10 μL of the sample was injected onto a ZORBAX Eclipse Plus C-18 (2.1 mm i.d. \times 150 mm length, 3.5 μm ; Agilent Technologies, CA, USA) and separated using a mobile phase of 0.01% CH_3COOH and methanol at a flow rate of 0.2 mL min^{-1} at 40 °C.

2.5. Recovery of magnesium ammonium phosphate (struvite)

After the experiment, spontaneous precipitation of the feed solution was removed by filtration (GF/B, Whatman) in order not to mix with struvite. The recovery of struvite was according to the method of Xie *et al.* (2014). Magnesium chloride was added to the feed solution to achieve a mole ratio of 1:1.5 between PO_4^{3-} and Mg^{2+} . This solution was then adjusted at pH 9.5–9.6 by adding 1 M NaOH and filtered with a cellulose filter (No.7, Advantec Toyo Kaisha, Ltd, Tokyo, Japan). The residual precipitate on the filter was transferred to a glass beaker and dried in a desiccator. Particles of the precipitate were observed using a scanning electron microscope (SEM) (JCM-6000 NeoScope[™]) (JEOL Ltd, Tokyo, Japan) with 15 kV of acceleration voltage. Elements in the precipitate and in the fouling in the FO membrane were observed using energy-dispersive X-ray spectroscopy (EDS) (JED-2300, JEOL). These samples were sputter-coated with a thin layer of platinum by auto-fine coater (JEC-3000FC, JEOL). X-ray diffraction (XRD) analysis of precipitation was conducted using an XRD spectrometer (SmartLab-9KW, Rigaku, Tokyo). Standard material of struvite (purity >99.997%) for an XRD analysis was purchased from Sigma-Aldrich Co. (MO, USA).

2.6. Data analysis

The transmembrane water flux, J_w ($\text{L m}^{-2} \text{h}^{-1}$), of the FO and MD processes was calculated as follows:

$$J_w = \frac{\Delta V}{A \times \Delta t} \quad (1)$$

where ΔV (L) is the total increased volume of permeate water collected over a predetermined time interval Δt (h), and A (m^2) is the effective membrane area.

Rejection of cations, anions, and TORCs in the FO–MD system was determined from the difference in chemical concentration between the feed solution (C_f) and the product water (C_w) and is defined as follows:

$$\text{Rejection (\%)} = \left(1 - \frac{C_w}{C_f}\right) \times 100 \quad (2)$$

The precise rejection of chemicals in the FO process in the FO–MD system is difficult to evaluate because the draw solution is continuously distilled in the MD process. Therefore, we defined a rejection of cations, anions, and TORCs in the FO process as an apparent rejection. Apparent rejection in the FO process was determined from the difference in the chemical concentration between the feed solution (C_f) and the draw solution (C_d) and is defined as follows:

$$\text{Rejection (\%)} = \left(1 - \frac{C_d}{C_f}\right) \times 100 \quad (3)$$

3. RESULTS AND DISCUSSION

3.1. Water flux

The average water flux from the feed solution to the draw solution (FO side) for 24 h ranged from 3.0 to 3.4 $\text{L m}^{-2} \text{h}^{-1}$ (Figure 2). The water fluxes in this study were within the reported values in the studies that used an FO or FO–MD system (Xue *et al.* 2015; Liu *et al.* 2016) and were similar to the reported values in a study that used 1.0 M NaCl as the draw solution and human urine as the feed solution in an FO–MD hybrid system (Liu *et al.* 2016). Figure 3 shows the time trend of the water flux. Water fluxes for the FO side gradually decreased with operation time, whereas those for the MD side periodically fluctuated. These time trends of the water fluxes were probably affected by fouling on the FO membrane and water sampling for chemical analysis. Regarding the decline in the water flux for the FO side, the suspended matter was spontaneously formed in the feed solution with operation time, and the fouling may be made on the FO membrane surface. The standard deviation (SD) of water flux increased with an increase in the water temperature of the draw solution (Figure 2). The fouling was more severe with increasing water temperatures and probably resulted in the large SD of the water flux in the experiment at 50 °C of the draw solution. The water flux rapidly declined after 12 h due to severe

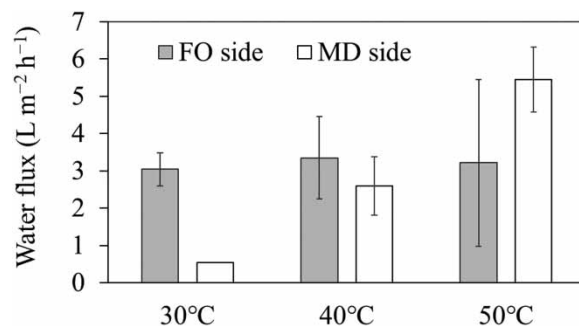


Figure 2 | Water flux in the FO side and MD side. Values of the y-axis indicate the average and SD of water flux. The values of the x-axis indicate the water temperature set in the draw solution. The FO side indicates water flux from the feed solution to the draw solution. The MD side indicates water flux from the draw solution to the product water.

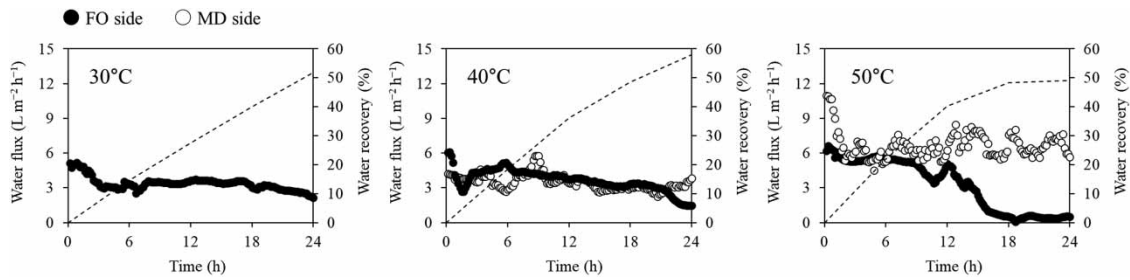


Figure 3 | Time trend of water flux in the FO side and MD side. Each point indicates a 60 min moving average of flux monitored at 10 min intervals. The FO side indicates the water flux from the feed solution to the draw solution. The MD side indicates water flux from the draw solution to the product water. The water flux of the MD side at 30 °C was not obtained because the balance was out of order. The dashed line shows the decreased volume of water (%) in the feed solution.

fouling on the membrane in the experiment at 50 °C of the draw solution. An EDS analysis of the FO membrane surface indicated that P, Ca, O, and C were the main elements. This result suggested that the fouling on the FO membrane is caused by the mixture of these elements. To estimate the composition of the mixture, chemical equilibrium was estimated by the Visual MINTEQ (Gustafsson 2018) using the measured concentrations of cations, anions, and DOC in the feed solution for the experiment at 50 °C, which observed an extreme decrease in the water flux. The estimated result suggested that $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (hydroxyapatite) is oversaturation under the final condition of pH (7.4) and water temperature (37.4 °C) in the feed solution after 24 h. Additionally, forming of Ca-dissolved organic matter (DOM) and Mg-DOM was also suggested.

The average water flux from the draw solution to the product water (MD side) increased from 0.5 (30 °C) to 5.4 $\text{L m}^{-2} \text{h}^{-1}$ (50 °C) with an increasing water temperature of the draw solution. The driving force of the MD is the difference in the water vapor pressure between the solutions; therefore, the water flux increased with increasing water temperature. The observed water fluxes at 40 and 50 °C were similar to the reported values in the MD process (Liu *et al.* 2016).

Comparing the water flux between the FO side and the MD side at each water temperature, the difference in the water flux was large at 30 and 50 °C, with the water flux at the FO side > than that at the MD side at 30 °C and the water flux at the MD side > than that at the FO side at 50 °C (Figure 2). The smallest difference in the water flux between the FO side and the MD side was observed at 40 °C, and this result implies that the suitable temperature of the draw solution was approximately 40 °C to operate stably in this FO–MD system. Although experiment conditions in the FO–MD system differed from those in this study, it has also been reported that a water transfer rate in an FO process with 1 M NaCl may be suitable for balancing a water temperature of 40 °C in a previous study (Liu *et al.* 2016).

3.2. Concentration ratio of nutrients in the feed solution in the FO system

Figure 4 shows the concentration ratios of representative cations and anions. Average concentration ratios of NH_4^+ , NO_3^- , and PO_4^{3-} for the experiments after 24 h were 2.3, 1.4, and 1.7, respectively. Furthermore, the concentration ratios of Ca^{2+} and Mg^{2+} were increased with operation time until 12–18 h but finally decreased to less than 1 (0.7–0.9) after 24 h. It was expected that the concentration ratio of each ion was to be approximately 2 when the water volume in the feed solution reached half. However, the concentration ratio of NH_4^+ slightly exceeded 2, and that of NO_3^- , PO_4^{3-} , Ca^{2+} , and Mg^{2+} was

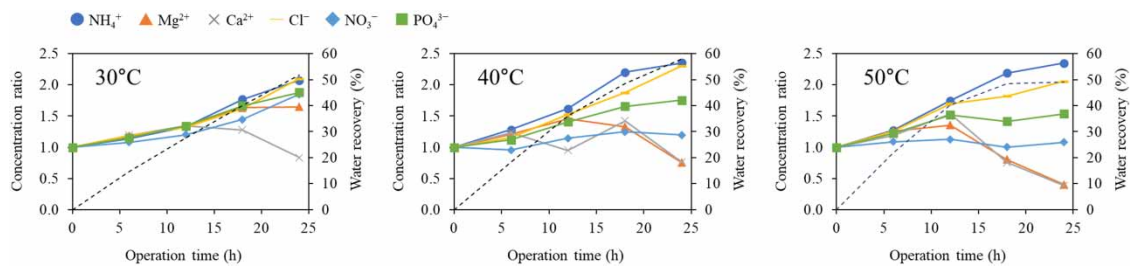


Figure 4 | Time trend of concentration ratio for representative cations and anions in the feed solution. The dashed line shows the decreased volume of water (%) in the feed solution.

less than 2. For an increase in ammonium, hydrolysis of urea by bacteria and free urease in the feed solution may occur with operation time (Udert *et al.* 2003a). For a decrease in concentration ratios of PO_4^{3-} , Ca^{2+} , and Mg^{2+} , spontaneous precipitation in fresh urine has been predicted to be dicalcium phosphate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) (Zhang *et al.* 2014). For hydrolyzed stale urine, a mixture of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) crystals and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) would mainly be the precipitate (Udert *et al.* 2003b; Zhang *et al.* 2014). The formation of these precipitations may be supported by decreasing the concentration ratios of Ca^{2+} and Mg^{2+} . Also, a remarkable decrease in the concentration ratios of Ca^{2+} and Mg^{2+} suggested absorption to the membrane surface by internal polarization because the zeta potential of CTA membranes shows a generally negative value (Xue *et al.* 2015).

3.3. Rejection of cations and anions

On the FO side, average apparent rejections of four ion species and DOC were obtained ranging from 79.5% (ammonium) to 100% (Table 2). Although the rejection of ammonium was lower than that of others, moderate rejection of ammonium in a FO system has been reported, and the rejection in this study was within the reported values in the laboratory- and pilot-scale experiments (Zhang *et al.* 2014; Xue *et al.* 2015; Wang *et al.* 2016; Li *et al.* 2018). The rejection of anions, such as NO_3^- and PO_4^{3-} and DOC (>99.4%), was higher than that of ammonium. This result was possibly due to electrostatic repulsion between membrane and solute molecules (Xue *et al.* 2015).

For the FO–MD system, rejections of each ion and DOC ranged from 93.7% to 100% (Table 2). The rejection of ammonium improved from 79.5% (on the FO side) to 93.7% (after combining the MD process). High rejection of these was also reported in a 120-h continuous experiment using an FO–MD system (Li *et al.* 2018). Rejections of bromide, chloride, and fluoride tended to be slightly lower (97.9–98.8%) than those of other ions. These halide anions are probably transferred from the draw solution (seawater) to the product water through the MD membrane.

3.4. Rejection of trace organic compounds

Ten peaks were detected in the feed solution by positive and negative ion modes (Figure 5 and Table 3). A mass spectrum of the 10 peaks ranging from 113 to 494 of molecular weight was obtained. However, the compositions and names of the chemicals could not be identified because of the lack of mass resolution of the LC-MS/MS. These 10 peaks were not detected in the draw solution and product water, and they were perfectly rejected in the FO side and FO–MD system. The high rejection of positively and negatively charged TORCs was consistent with the previous studies using the FO or FO–RO systems (Hancock *et al.* 2011; Xie *et al.* 2013a; Coday *et al.* 2014). The rejection of charged TORCs, such as pharmaceuticals in domestic wastewater, that are treated at the facility by a demonstration-scale sequencing batch membrane bioreactor system was greater than

Table 2 | Rejection of cations, anions, and DOC in the FO and FO–MD hybrid systems (%)

	FO side ^a	FO–MD ^a
Na^+	– ^b	99.8 ± 0.2
NH_4^{++}	79.5 ± 3.9	93.7 ± 2.2
Mg^{2+}	– ^b	99.2 ± 0.7
Ca^{2+}	– ^b	99.4 ± 0.6
K^+	– ^b	100.0
F^-	100.0	97.9 ± 2.3
Cl^-	– ^b	97.9 ± 2.9
Br^-	– ^b	98.8 ± 1.7
NO_3^-	100.0	100.0
PO_4^{2-}	100.0	100.0
SO_4^{2-}	– ^b	99.5 ± 0.8
DOC	– ^c	99.1 ± 0.9

^aData show average and standard deviation for all the experiments ($n = 3$).

^bRejection could not be calculated because of abundance in draw solution (seawater).

^cDOC in draw solution could not be measured because of high salinity.

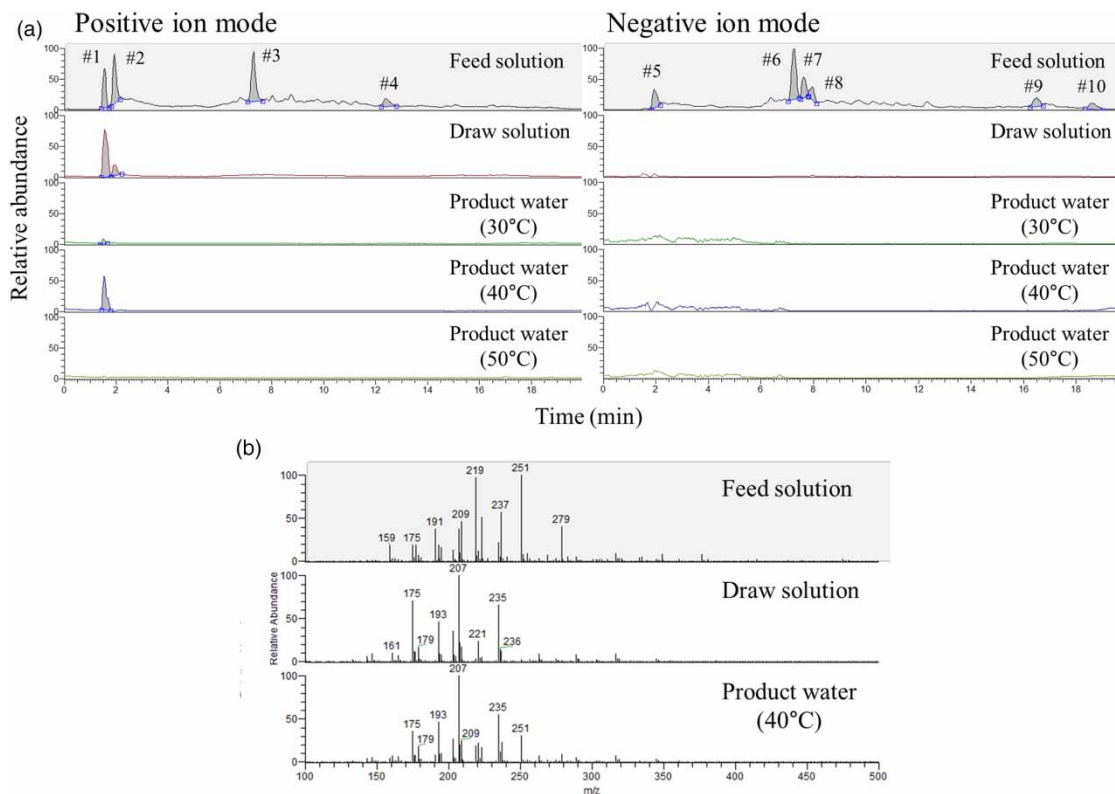


Figure 5 | Total ion current chromatogram (TIC) of trace organic compounds and mass spectra in each solution. (a) TIC of TOCs in each solution. (b) Mass spectrum of peak #1. The numbers assigned to the peaks in Figure 5(a) correspond to those in Table 3. The value in parenthesis for each product water indicates the water temperature set in the draw solution.

80 and 99% in a bench-scale FO experiment and a hybrid FO–RO process, respectively (Hancock *et al.* 2011). Rejection of negatively charged TOCs tends to increase because of enhanced electrostatic repulsion between the FO membrane and solutes (Xie *et al.* 2013a). Additionally, the formation of a larger hydrated layer around the ionic species may also affect the rejection of negatively charged TOCs (Holloway *et al.* 2014). The rejection of positively charged compounds follows

Table 3 | Rejection of trace organic compounds (TOCs) by the FO–MD system

	Retention time (min)	FO side	FO-MD	Estimated molecular weight
Positive ion mode				
#1	1.55	100	100	250
#2	1.93	100	100	113
#3	7.29	100	100	264
#4	12.39	100	100	278
Negative ion mode				
#5	1.93	100	100	182
#6	7.27	100	100	181
#7	7.66	100	100	188
#8	7.99	100	100	188 and 194 ^a
#9	16.58	100	100	174
#10	18.58	100	100	494

^aMolecular weight could not be specified because of possible coelution.

the general principle of size exclusion (Coday *et al.* 2014). The high rejection of positively charged TOrcs can be explained by a large hydrated radius of ionic species in an aqueous solution (Holloway *et al.* 2014). Such high rejection of TOrcs was also observed in a pilot-scale FO–RO system for 40 d (Hancock *et al.* 2011). In this pilot-scale experiment, TOrc rejection was greater than that observed in bench-scale experiments. This result was possibly due to membrane compaction, the establishment of a fouling layer, and optimized hydrodynamic conditions in the pilot-scale system (Hancock *et al.* 2011).

High rejection of TOrcs was observed regardless of the temperature of the experiment in this study. The rejection of charged TrOCs was higher than that of neutral TrOCs, and their rejection was insensitive to temperature variation (20–40 °C) in FO (Xie *et al.* 2013b). The rejection of TOrcs may be more affected by fouling on an FO than water temperature because membrane fouling increases electron repulsion, resulting in high rejection of negatively charged TOrcs (Coday *et al.* 2014). Since the fouling on the FO membrane was observed in the experiments at 40 and 50 °C in this study, the rejection of the TOrcs might be somewhat affected by the fouling.

Two peaks were detected in the positive ion mode in the feed at retention times of 1.55 and 1.93 min in the draw solution and product water in the experiments at 30 and 40 °C, respectively (Figure 5(a)). As a result of comparing mass spectra among the solutions, these peaks in the product water and draw solution were different from those in the feed solution (Figure 5(b)). This difference in the mass spectra suggested that these peaks originated from the draw solution, not from the feed solution. Therefore, these peaks were excluded from the calculation of the rejection.

The detected TOrcs in the feed solution could not be identified; nevertheless, these are possibly biodegradable chemicals, such as metabolites in urine. If the retained TOrcs in the feed solution are biodegradable chemicals, a biological wastewater treatment process may be applied to treat the feed solution.

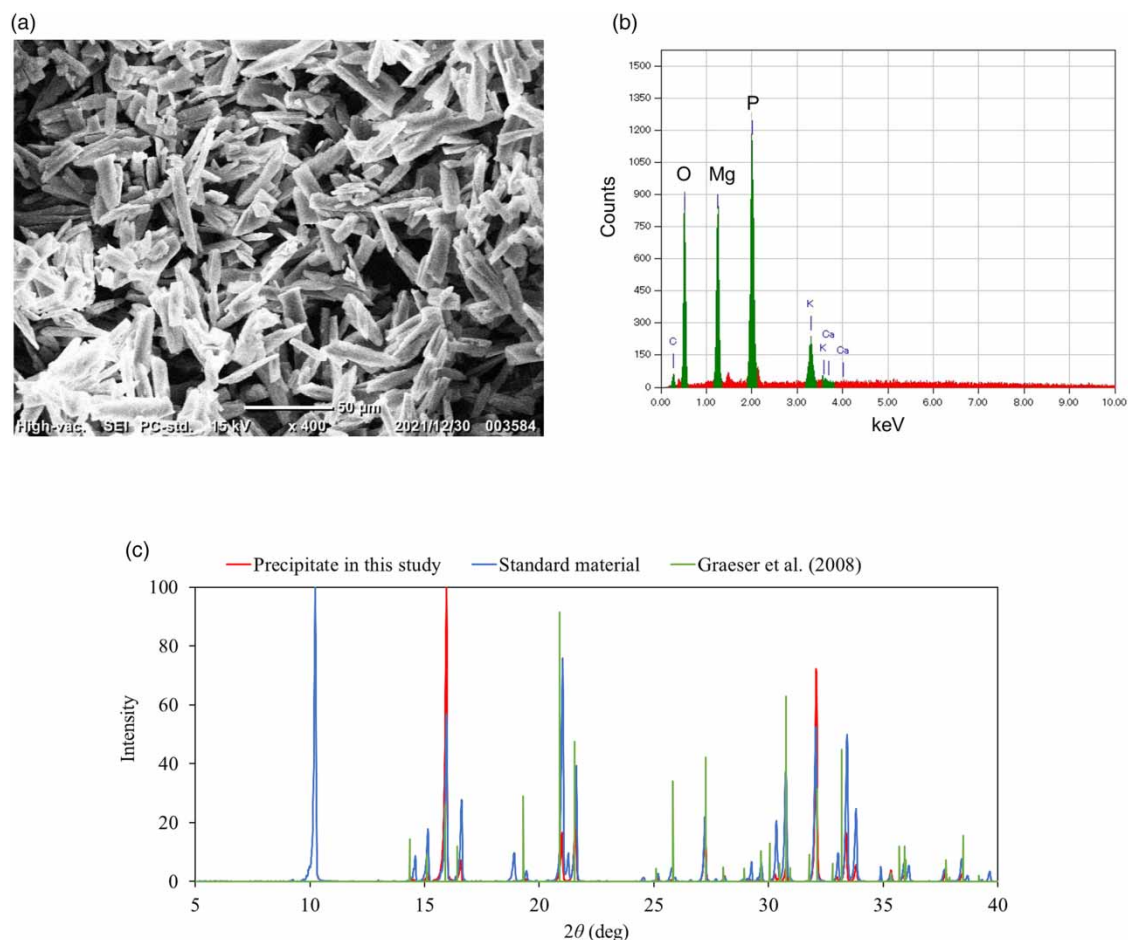


Figure 6 | Crystal structure analysis for the precipitate. (a) SEM image. (b) Detected elements by EDS. (c) XRD spectra^a. ^aCrystal structure data of struvite (Graeser *et al.* 2008) were obtained from the American Mineralogist Crystal Structure Database. The standard material of purity is >99.997%.

3.5. Recovery of struvite

Figure 6 shows SEM images and observed elements of the precipitate in the feed solution. The precipitate had an orthorhombic structure (Figure 6(a)). In the EDS analysis, three peaks of oxygen, magnesium, and phosphorus, which are the main elements composing struvite, were detected in the precipitate (Figure 6(b)). Nitrogen, which is another important element in struvite, could not be detected in this study because it is light, as well as in the previous study (Xie *et al.* 2014). Therefore, to determine the proportion of nitrogen, we examined this by comparing the mass of NH_4^+ in the feed solution before and after forming the precipitation. The mass of NH_4^+ in the feed solution decreased to approximately 20% after the experiments. This decrease suggests that approximately 80% of NH_4^+ had been consumed by forming the precipitate. Regarding the XRD spectrum of the precipitation, the main peaks were observed at 15.9, 21.5, and 32.1 2θ (deg). These peaks corresponded well with that of the standard material and the crystal structure of struvite (Graeser *et al.* 2008) stored in the American Mineralogist Crystal Structure Database (Downs & Hall-Wallace 2003) (Figure 6(c)). This result demonstrates that the precipitation obtained in this study was a struvite.

The average recovery rate of the struvite was 85% of the theoretical yield at the initial feed solution. Effective struvite precipitation could only be achieved when phosphorus concentration was above 100 mg L^{-1} (Xie *et al.* 2016), and in this study, the phosphorus concentration (approximately 830 mg L^{-1}) was enough to recover struvite effectively. The difference between the recovery rate and the theoretical yield of the struvite may imply that phosphorus was consumed by forming the precipitate and fouling on the FO membrane in the FO–MD experiments. To recover more amounts of struvite, using hydrolyzed stale urine may be helpful because ammonium increases by the hydrolysis of urea (Zhang *et al.* 2014).

4. CONCLUSION

In this study, the rejection of ions and TOrCs and the recovery of nutrients as struvite from human urine were investigated using a seawater-driven FO–MD hybrid system. More than 93.7% of the cations and anions in the feed solution were rejected by the FO–MD system. Furthermore, TOrCs in the feed solution were perfectly rejected regardless of the temperature of the experiment. Additionally, struvite was recovered from the concentrated feed solution. Thus, this study indicates the importance and potential of human urine as reclaimed water and fertilizer. Further evaluation of the quality of reclaimed water, nontarget analysis by a high-resolution LC-MS/MS, and gas chromatography/mass spectrometry would be needed.

In this study, the experiments were conducted at 30, 40, and 50 °C of the draw solution. The water flux was sensitive to the temperature, but the efficiencies of the rejections of the ions and TOrCs and the recovery of the struvite were not. From the viewpoint of sustainable operation, i.e., the smallest difference in the water flux between the FO and the MD systems, 40 °C is a favorable temperature for the draw solution in this system.

Thus, this study demonstrated the applicability of an FO–MD hybrid system for recovering nutrients and product water from urine. Furthermore, this hybrid system is useful for producing reclaimed water that minimizes chemicals, such as ammonium and TOrCs.

ACKNOWLEDGEMENTS

The authors thank Prof. Tetsuro Agusa and Yuki Imuta of the Prefectural University of Kumamoto for their valuable comments. The authors are grateful to Dr Yoshiro Ohgi of Kumamoto Industrial Research Institute, Japan, for the XRD analysis.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

- Coday, B. D., Yaffe, B. G. M., Xu, P. & Cath, T. Y. 2014 Rejection of trace organic compounds by forward osmosis membranes: a literature review. *Environmental Science and Technology* **48** (7), 3612–3624. doi: 10.1021/es4038676.
- Downs, R. T., Hall-Wallace, M. 2003 The American Mineralogist Crystal Structure Database. *American Mineralogist* **88**, 247–250.

- Ge, Q., Han, G. & Chung, T. S. 2016 Effective As (III) removal by a multi-charged hydroacid complex draw solute facilitated forward osmosis-membrane distillation (FO-MD) processes. *Environmental Science and Technology* **50** (5), 2363–2370. doi:10.1021/acs.est.5b05402.
- Graeser, S., Postl, W., Bojar, H. P., Berlepsch, P., Armbruster, T., Raber, T., Ettinger, K. & Walter, F. 2008 Struvite-(K), $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$, the potassium equivalent of struvite—a new mineral. *European Journal of Mineralogy* **20** (4), 629–633. doi:10.1127/0935-1221/2008/0020-1810.
- Gustafsson, J. P. 2018 *Visual MINTEQ Version 3.1*. Stockholm, Sweden. Available from: <https://vminteq.lwr.kth.se/>
- Hancock, N. T., Xu, P., Heil, D. M., Bellona, C. & Cath, T. Y. 2011 Comprehensive bench- and pilot-scale investigation of trace organic compounds rejection by forward osmosis. *Environmental Science and Technology* **45** (19), 8483–8490. doi:10.1021/es201654k.
- Holloway, R. W., Regnery, J., Nghiem, L. D. & Cath, T. Y. 2014 Removal of trace organic chemicals and performance of a novel hybrid ultrafiltration-osmotic membrane bioreactor. *Environmental Science and Technology* **48** (18), 10859–10868. doi:10.1021/es501051b.
- Larsen, T. A., Riechmann, M. E. & Udert, K. M. 2021 State of the art of urine treatment technologies: a critical review. *Water Res X* doi:10.1016/j.wroa.2021.100114.
- Li, J., Hou, D., Li, K., Zhang, Y., Wang, J. & Zhang, X. 2018 Domestic wastewater treatment by forward osmosis-membrane distillation (FO-MD) integrated system. *Water Science and Technology* **77** (5–6), 1514–1523. doi:10.2166/wst.2018.031.
- Liu, Q., Liu, C., Zhao, L., Ma, W., Liu, H. & Ma, J. 2016 Integrated forward osmosis-membrane distillation process for human urine treatment. *Water Research* **91**, 45–54. doi:10.1016/j.watres.2015.12.045.
- Lutchmiah, K., Verliefe, A. R. D., Roest, K., Rietveld, L. C. & Cornelissen, E. R. 2014 Forward osmosis for application in wastewater treatment: a review. *Water Research* **58**, 179–197. doi:10.1016/j.watres.2014.03.045.
- Patel, A., Mungray, A. A. & Mungray, A. K. 2020 Technologies for the recovery of nutrients, water and energy from human urine: a review. *Chemosphere* **259**, 127372. doi:10.1016/j.chemosphere.2020.127372.
- Rose, C., Parker, A., Jefferson, B. & Cartmell, E. 2015 The characterization of feces and urine: a review of the literature to inform advanced treatment technology. *Critical Reviews in Environmental Science and Technology* **45**, 1827–1879. doi:10.1080/10643389.2014.1000761.
- Udert, K. M., Larsen, T. A., Biebow, M. & Gujer, W. 2003a Urea hydrolysis and precipitation dynamics in a urine-collecting system. *Water Research* **37** (11), 2571–2582. doi:10.1016/S0043-1354(03)00065-4.
- Udert, K. M., Larsen, T. A. & Gujer, W. 2003b Estimating the precipitation potential in urine-collecting systems. *Water Research* **37** (11), 2667–2677. doi:10.1016/S0043-1354(03)00071-X.
- Volpin, F., Chekli, L., Phuntsho, S., Ghaffour, N., Vrouwenvelder, J. S. & Shon, H. K. 2019 Optimisation of a forward osmosis and membrane distillation hybrid system for the treatment of source-separated urine. *Separation and Purification Technology* **212**, 368–375. doi:10.1016/j.seppur.2018.11.003.
- Wald, C. 2022 The urine revolution: how recycling pee could help to save the world. *Nature* **602** (7896), 202–206. doi:10.1038/d41586-022-00338-6.
- Wang, Z., Zheng, J., Tang, J., Wang, X. & Wu, Z. 2016 A pilot-scale forward osmosis membrane system for concentrating low-strength municipal wastewater: performance and implications. *Scientific Reports* **6**, 21653. doi:10.1038/srep21653.
- Wu, C. Y., Chen, S. S., Zhang, D. Z. & Kobayashi, J. 2017 Hg removal and the effects of coexisting metals in forward osmosis and membrane distillation. *Water Science and Technology* **75** (11–12), 2622–2630. doi:10.2166/wst.2017.143.
- Xie, M., Nghiem, L. D., Price, W. E. & Elimelech, M. 2012a Comparison of the removal of hydrophobic trace organic contaminants by forward osmosis and reverse osmosis. *Water Research* **46** (8), 2683–2692. doi:10.1016/j.watres.2012.02.023.
- Xie, M., Price, W. E. & Nghiem, L. D. 2012b Rejection of pharmaceutically active compounds by forward osmosis: role of solution pH and membrane orientation. *Separation and Purification Technology* **93**, 107–114. doi:10.1016/j.seppur.2012.03.030.
- Xie, M., Nghiem, L. D., Price, W. E. & Elimelech, M. 2013a A forward osmosis-membrane distillation hybrid process for direct sewer mining: system performance and limitations. *Environmental Science and Technology* **47** (23), 13486–13493. doi:10.1021/es404056e.
- Xie, M., Price, W. E., Nghiem, L. D. & Elimelech, M. 2013b Effects of feed and draw solution temperature and transmembrane temperature difference on the rejection of trace organic contaminants by forward osmosis. *Journal of Membrane Science* **438**, 57–64. doi:10.1016/j.memsci.2013.03.031.
- Xie, M., Nghiem, L. D., Price, W. E. & Elimelech, M. 2014 Toward resource recovery from wastewater: extraction of phosphorus from digested sludge using a hybrid forward osmosis–membrane distillation process. *Environmental Science and Technology Letters* **1** (2), 191–195. doi:10.1021/ez400189z.
- Xie, M., Shon, H. K., Gray, S. R. & Elimelech, M. 2016 Membrane-based processes for wastewater nutrient recovery: technology, challenges, and future direction. *Water Research* **89**, 210–221. doi:10.1016/j.watres.2015.11.045.
- Xue, W., Tobino, T., Nakajima, F. & Yamamoto, K. 2015 Seawater-driven forward osmosis for enriching nitrogen and phosphorus in treated municipal wastewater: effect of membrane properties and feed solution chemistry. *Water Research* **69**, 120–130. doi:10.1016/j.watres.2014.11.007.
- Zhang, J., She, Q., Chang, V. W. C., Tang, C. Y. & Webster, R. D. 2014 Mining nutrients (N, K, P) from urban source-separated urine by forward osmosis dewatering. *Environmental Science and Technology* **48** (6), 3386–3394. doi:10.1021/es405266d.
- Zhao, S. F., Zou, L., Tang, C. Y. Y. & Mulcahy, D. 2012 Recent developments in forward osmosis: opportunities and challenges. *Journal of Membrane Science* **396**, 1–21. doi:10.1016/j.memsci.2011.12.023.

First received 20 June 2022; accepted in revised form 27 September 2022. Available online 3 October 2022