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Dewatering of source-separated human urine for nitrogen recovery by membrane distillation



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ABSTRACT

The nitrogen content of a synthetic ammonia wastewater was concentrated using direct contact membrane distillation (DCMD). The ratio of transferred ammonia to water (i.e., specific ammonia transfer: SAT) was controlled by operational conditions. With 20 °C on the permeate side, and a high temperature of 70 °C on the feed side, the process exhibited low SAT values for PTFE/PP (PTF045LDOA), PTFE/PP (TF-450), and PVDF (HVHP-14250) membranes. This was because the increase in water flux ($> 24 \text{ L/m}^2 \text{ h}$) was greater than that of ammonia transfer. A positive relationship between SAT and free ammonia concentration was identified under different total ammoniacal nitrogen concentration and pH. The acidification pretreatment to pH 5 led to further reduction in the SAT value (as low as $6.91 \times 10^{-5} \text{ g-N/g-H}_2\text{O}$). As a practical application, the dewatering process of source-separated human urine by DCMD required an additional filtration step to prevent fouling, but the filtration had an insignificant effect on the SAT. For the acidified and filtered source-separated human urine, total ammoniacal nitrogen was successfully concentrated with a low SAT value ($< 2.06 \times 10^{-3} \text{ g-N/g-H}_2\text{O}$).

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1. Introduction

The emission of nitrogen and other nutrients from sewerage systems currently causes severe eutrophication problems in public water bodies [1]. Ecological sanitation mitigates nutrient release in the water environment by treating nutrients in a safe manner in order to contribute to sustainable social and natural developments [2]. Human urine is the largest nutrient contributor to municipal wastewater [3]. The public health has been protected by hygienically stable disposal of human urine. A urine-diverting dry toilet for human urine has been implemented as an ecological sanitation technology. The human urine from the urine-separating toilet, i.e., source-separated human urine, allows it to be treated and applied on the farmland as fertilizer [4].

Source-separated human urine contains 3.5% organics (urea, creatinine, uric acid, etc.) and 1.5% inorganic salts (sodium, potassium, chloride, magnesium, calcium, ammonium, sulfates, phosphates, etc.), but it is highly diluted with approximately 95% water [5]. The TAN concentration of source-separated human

urine varies depending on population, age, physical activity, feeding habits, and water consumption [6]. The TAN concentrations reported for source-separated human urine from households, schools, and workplaces ranged from 1.80 to 2.61 g-N/L [3,7,8]. The valuable nutrient compounds exist in a ratio of 11:1:2 for nitrogen, phosphorous, and potassium [6]. This chemical composition makes source-separated human urine a preferable fertilizer capable of replacing 20–25% of commercial fertilizers, instead of releasing urine into domestic wastewater [9]. However, direct application of source-separated human urine as fertilizer, would be inconvenient, unpleasant, and unhygienic [6]. Source-separated human urine also causes increased pH by urease activity, and consequent production of ammonia in soil environments [7]. To avoid inappropriate application, there is demand for a concentrated, microbial-free fertilizing product in crystalline form, such as NH_4NO_3 . The major nitrogen fraction (NH_4^+) in source-separated human urine is produced by urease activity during storage, but biological nitrification is required to obtain the equal molar concentrations of NH_4^+ and NO_3^- . These NH_4NO_3 crystals can be produced from nitrified source-separated human urine by reduction of water content, evaporation, and crystallization [10].

Several processes (e.g., evaporation, freeze-thaw, and reverse osmosis) have been considered in finding an effective method to reduce the water content of human urine [8]. For example,

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significant water reduction was achieved by evaporation (> 96%) and the freeze–thaw process (~75%) [8,11]. However, these two processes required unacceptably intensive energy. In addition, the dissolved ammonia contained in source-separated human urine can easily be lost (evaporated) to the atmosphere during thermal evaporation [8,11]. In contrast, the dewatering process using reverse osmosis membranes is a relatively cost-effective way to reduce the water content and remove micro-pollutants from the produced water [10]. However, membrane processes are often hampered by fouling problems that lower membrane porosity, which results in decreased efficiency and increased operational cost. Therefore, a clear need exists for development of a novel, cost effective technique that also solves the fouling problem.

The membrane distillation (MD) process is a process driven by a vapor pressure gradient caused by temperature difference [12]. The MD process could be an effective dewatering process to concentrate the human urine because it requires less energy than evaporation and has a lower tendency for membrane fouling, compared with the reverse osmosis process. Moreover, the operational cost of the MD process can be lowered using waste heat generated by industrial plants or heat from solar thermal sources. In the MD system, the vapor molecules transfer through a microporous hydrophobic membrane, and non-volatile matter can be completely rejected, theoretically [13]. As a result, the MD process is able to condense the ammonia and nitrate contents on the feed side by dewatering. However, high ammonia concentration and the alkaline condition of source-separated human urine lead to high volatile free ammonia (FA) content and consequent significant ammonia transfer to the permeate through the hydrophobic pores of the MD membrane. For this reason, the MD application is limited to membrane-based ammonia stripping (condensing NH_4^+ on the permeate side) to recover ammonia from highly concentrated ammonia wastewater such as source-separated human urine or swine manure [14–17]. Therefore, the optimized conditions to concentrate ammonia on the feed side are not available in our best of knowledge. The main aim of this study was to select appropriate membrane material, and to find optimal conditions for the best dewatering performance and the least ammonia transfer to the permeate side in the MD system. The parameters (type of membrane, pH, temperature, and total ammoniacal nitrogen (TAN) concentration) were optimized using synthetic nitrogenous wastewater. Then, a setup providing optimal conditions was applied to processing source-separated human urine. In addition, the effects of acidification and pre-filtration on flux and ammonia transfer were evaluated using source-separated human urine.

2. Materials and methods

2.1. Materials

Flat sheet commercial membranes with mean pore size of $0.45 \mu\text{m}$ were applied in the DCMD system [PTFE/PP (PTF045LD0A, Pall, USA), PTFE/PP (TF-450, Pall, USA) and PVDF (HVHP-14250, Millipore, USA)]. To investigate FA transfer through the DCMD membrane, synthetic wastewater samples were prepared in different concentrations of ammonium chloride (Sigma-Aldrich, Germany) in deionized water. Source-separated human urine was collected from the Water Quality and Treatment Laboratory, School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST). The pH of synthetic wastewater (ammonium chloride solution) and source-separated human urine were adjusted using NaOH (10 mol/L) and HCl (11.3 mol/L). For the pre-filtration of source-separated human urine, a membrane filter paper ($1.2 \mu\text{m}$, GF/C, Whatman, UK) was

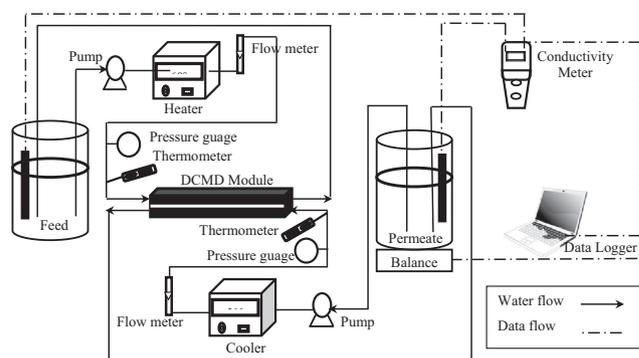


Fig. 1. Schematic diagram of experimental set-up for DCMD system.

used.

2.2. Experimental conditions

In this study, direct contact MD (DCMD) was applied to concentrate human urine because DCMD is the simplest structure capable of producing reasonable high flux, among the various MD configurations [12]. Schematic representation of the DCMD system is shown in Fig. 1. Feed and permeate streams were designed to flow counter-currently with gear pumps, and circulated to their reservoir tanks. The temperature of feed and permeate solutions was controlled by thermostatic water baths (WCR-P22, Daihan Scientific, Korea). The temperature sensors and pressure gauges were placed in front of the feed and permeate inlets of the membrane module. The flow rates were set to 2 L/min (i.e., a cross flow velocity of 31.75 cm/s) in both hot and cold streams, into symmetrical, rectangular channels 3-mm deep. The flat sheet hydrophobic membrane was located in a horizontal module, which was connected to the feed and permeate tanks. The effective membrane area was 0.003 m^2 (8.6 cm long and 3.5 cm wide).

The DCMD dewatering, using PTFE/PP (PTF045LD0A), PTFE/PP (TF-450) and PVDF (HVHP-14250) membranes, was conducted at feed temperatures of 40, 50, 60, and $70 \text{ }^\circ\text{C}$ and at a fixed permeate temperature of $20 \text{ }^\circ\text{C}$. The best membrane type was selected in terms of low FA transfer and high water flux. For the selected membrane, different pH conditions (5, 6, 7, 8, and 9) and TAN concentrations (0.465, 0.986, 1.945, 2.972, 3.972, and 4.940 g-N/L) were applied. Then, source-separated human urine processing was tested under the two conditions of initial pH 8.8 and acidified condition pH 6. Filtration pretreatment of acidified source-separated human urine was conducted using membrane filter paper of $1.2 \mu\text{m}$ pore size before the MD process. Water flux and ammonia enrichment on the feed side were evaluated for the acidified and filtered source-separated human urine. The concentrations of TAN, total nitrogen (TN), total phosphorus (TP), and total organic carbon (TOC) of all source-separated human urine samples are summarized in Table 1. The temperature on the feed and permeate sides were maintained at 60 and $20 \text{ }^\circ\text{C}$, respectively, if not noted otherwise.

2.3. Analysis

The samples were taken from both sides every 30 min for 2 h to measure the TAN concentration on the feed and permeate sides. The concentration of TAN was analyzed using a Kjeltac TAN analyzer (Auto 2300 system, FOSS, Denmark). The ammonium and FA concentrations were calculated based on the TAN concentration, pH and temperature, as follows:



Table 1
Characteristics of source-separated human urine samples and corresponding permeates.

Parameters	Units	Raw sample		Acidified sample		Acidified and filtered sample	
		Feed	Permeate	Feed	Permeate	Feed	Permeate
pH	–	8.8	9.9	6	9.8	6	9.9
TAN	g/L	5.9	1.2	5.7	0.1	5.6	0.1
TN	g/L	7.9	1.9	10.0	0.0	9.0	0.0
TP	g/L	1.1	0.1	1.0	0.1	1.1	0.1
TOC	g/L	1.0	0.2	1.0	0.2	1.1	0.2
Alkalinity	g/L as CaCO ₃	2.1	0.4	0.26	0.05	0.24	0.05
Conductivity	mS/cm	49.6	2.1	74.8	0.3	74.2	0.2



$$K_a = \frac{[\text{NH}_3] \cdot [\text{H}^+]}{[\text{NH}_4^+]} \quad (3)$$

$$K_b = \frac{[\text{NH}_4^+] \cdot [\text{OH}^-]}{[\text{NH}_3]} \quad (4)$$

$$pK_a = 0.09018 + \frac{2729.92}{T} = -\log_{10} K_a$$

(T[K]: Temperature of the solution) (5)

$$K_a \cdot K_b = 10^{-14} \quad (6)$$

as $[\text{NH}_3] + [\text{NH}_4^+] = [\text{TAN}]$,

$$K_a = \frac{[\text{NH}_3] \cdot [\text{H}^+]}{[\text{NH}_4^+]} \rightarrow [\text{NH}_4^+] = \frac{M \cdot [\text{H}^+]}{(K_a + [\text{H}^+])} \quad (7)$$

$$K_b = \frac{[\text{NH}_4^+] \cdot [\text{OH}^-]}{[\text{NH}_3]} \rightarrow [\text{NH}_3] = \frac{M \cdot [\text{OH}^-]}{(K_b + [\text{OH}^-])} \quad (8)$$

Based on the molar concentrations of ammonium and FA, the partial vapor pressures were calculated, as follows:

$$P_{v,i} = 10^{\left(A - \frac{B}{T+C}\right)} \quad (9)$$

$$pP_{v,i} = \frac{M_i}{M_T} \times P_{v,i} \quad (10)$$

where $P_{v,i}$ is the vapor pressure of the component i at temperature T . The A , B and C coefficients are listed in Table 2 according to the component [18,19]. The unit of the partial vapor pressure of water (mmHg) was converted to bar before further calculation. $pP_{v,i}$ is the partial vapor pressure of the component i (FA or water). M_i is the molar concentration of the component i and M_T is the molar concentration of the total components (the sum of ammonia and water).

Heat transfer resistance and the mass transfer coefficient of the membranes can be calculated ((Eqs. (11) and 12)).

Because the mass transfer resistance of the feed and permeate are generally negligible [20], the heat transfer resistance (R_m) was calculated to compare the water flux performances [21]. For the

simplified mass transfer coefficient, the conversion coefficient (α) was substituted to unit value because the operation conditions were the same for all three membranes [22].

$$R_m = \frac{\varepsilon \delta_m}{k_{air}} + \frac{(1-\varepsilon)\delta_m}{k_p} \quad (11)$$

R_m =heat transfer resistance

ε =membrane porosity

δ_m =thickness of the membrane

k_{air} =thermal conductivity of water vapor

k_m =thermal conductivity of the polymer

$$K = \frac{\varepsilon}{\delta_m} \alpha \quad (12)$$

K =mass transfer coefficient

ε =porosity

δ_m =membrane thickness

α =conversion coefficient

TN, TP, and NO₃-N were measured with commercial kits (26722-45, Hach, USA; 27426-45 Hach, USA; 26053-45, Hach, USA, respectively), and a UV-vis spectro-photometer (DR 5000-02, Hach, USA). Total suspended solid was measured from 10 mL water samples by filtering through a pre-weighted glass fiber filter (GF/C, Whatman, England) and drying at 105 °C for 24 h. For the volatile suspended solid (VSS) measurement, the filter was placed in a furnace at 550 °C for 20 min and the final weight was recorded. The data on permeation flux, and on the conductivity of feed and permeate, were monitored with an analytical balance (CUX6200H, CAS Corporation, Korea) and a portable conductivity meter (HQ40d, Hach, USA), respectively. Based on the ammonium concentration profile and water flux, the ammonia transfer in the DCMD system was evaluated using the SAT coefficient. The SAT coefficient can be expressed as follows:

$$\text{Specific Ammonia Transfer (SAT)} = \frac{\text{TAN}_{\text{transfer}}(\text{g})}{\text{H}_2\text{O}_{\text{transfer}}(\text{g})} \quad (13)$$

where $\text{TAN}_{\text{transfer}}$ is the transferred total ammoniacal nitrogen (TAN) and $\text{H}_2\text{O}_{\text{transfer}}$ is the transferred water. The SAT values were calculated after 2 h under the given experimental conditions. The pH of feed and permeate were measured using a portable pH meter (Accumet Research AR15, Fisher Scientific, USA).

3. Results and discussion

3.1. Selection of membrane type

The type of membrane used, is one of the important operational factors that determines the ammonia transfer [23–26] and permeate flux [27]. In this study, three types of membranes PTFE/PP (PTF045LD0A), PTFE/PP (TF-450), and PVDF (HVHP-14250) with the same pore size (0.45 μm) were used to evaluate the feasibility of ammonia enrichment in the feed solution. The initial TAN concentration of the feed solution was 1.22 ± 0.04 g-N/L. Temperature was set at 60 °C on the feed side and at 20 °C on the permeate side. An initial pH was adjusted to 9 in the feed side. The TAN concentration of the feed solutions increased to 1.40 ± 0.02 g-N/L within 2 h for the two membranes [PTFE/PP (PTF045LD0A) and PTFE/PP (TF-450)], while an insignificant change of the TAN concentration in the feed solution was observed for PVDF (HVHP-14250) (Fig. 2). Consistently lower SAT values of 2.05×10^{-3} and 2.63×10^{-3} g-N/g-H₂O were exhibited for the PTFE/PP (PTF045LD0A) and PTFE/PP (TF-450) membranes, respectively, than for the PVDF (HVHP-14250) membrane (7.64×10^{-3} g-N/g-H₂O).

Table 2
Coefficients for the calculation of vapor pressure.

	Unit of vapor pressure	A	B	C	Unit of temperature
FA	bar	6.67956	1002.71	–25.215	K
Water	mmHg	8.07131	1730.63	233.426	°C

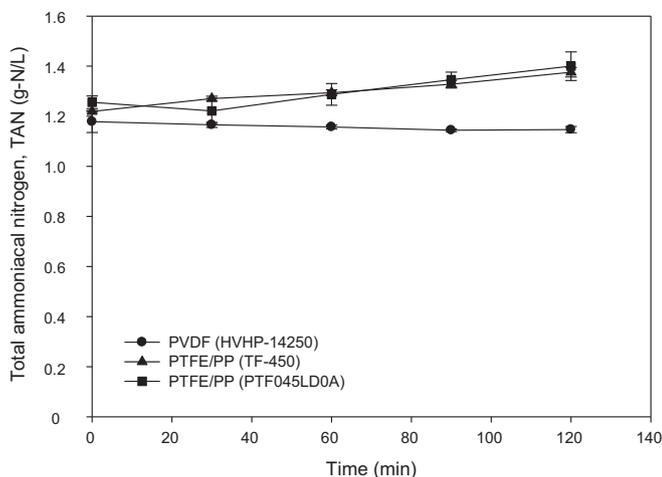


Fig. 2. Concentration of TAN in the effluent during DCMD operation with different membrane materials.

Vapor pressure is the driving force for the ammonia flux in the DCMD system. Thus, it was hypothesized that higher temperature would result in greater ammonia transfer and consequently higher SAT values. TAN concentration and water flux were quantified for the three hydrophobic membranes to calculate SAT values at different temperatures (40, 50, 60, and 70 °C) on the feed side. The water flux was exponentially increased with rising temperature (Fig. 3). In comparison of water flux among the three membranes, PTFE/PP (PTF045LD0A) exhibited the highest (65.84 LMH) at 70 °C of the feed solution. The others were 51.77 LMH for PTFE/PP (TF-450) and 24.00 LMH for PVDF (HVHP-14250), under the same conditions. Membrane properties such as membrane materials, membrane thickness, and membrane morphology (surface porosity, tortuosity, pore size, etc.) influenced water flux in the MD system [28]. In this study, the selection of a membrane for high flux in this MD application is a compromise between a low thermal conductivity, a thin structure and a high porosity (Table 3) [29–31]. Two PTFE membranes exhibited high fluxes due to its thin structure and high porosity. The most probable reason for the higher water flux of the thinner membrane, i.e., PTFE/PP (PTF045LD0A), is because of the reduced mass transfer resistance in a thinner structure [12]. The reason for the high water flux is also well described in our previous research under the same temperature conditions and similar module configuration, pipe

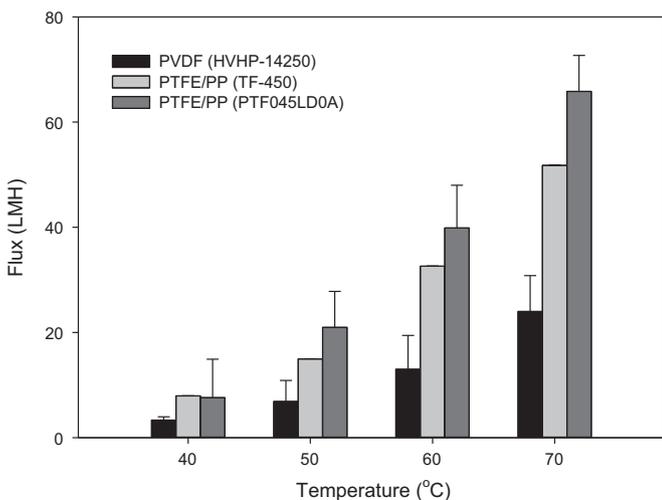


Fig. 3. Flux variation of PTF045LD0A, TF-450, and HVHP-14250 membranes at different temperatures.

lines and measuring devices [29]. For the PTFE/PP (TF-450), the highest porosity could be the main factor for high flux, in this study.

Taking account of these considerations, the heat transfer resistance and the simplified mass transfer coefficient were compared ((Eqs. (11) and (12)). The thermal conductivities of PTFE and PVDF were assumed by 0.25, and 0.18 W/m K based on the references (Table 3). The active layer thickness of the TF-450 membrane was assumed as the half the total membrane thickness. The active layer thickness of the PTF045LD0A membrane was 36 μm [29]. As a result, the heat transfer resistances of PTFE/PP (PTF045LD0A), PTFE/PP (TF-450) and PVDF (HVHP-14250) membranes were calculated by 0.0010, 0.0027 and 0.0042 W/K, respectively. The simplified mass transfer coefficient of PTFE/PP (PTF045LD0A), PTFE/PP (TF-450) and PVDF (HVHP-14250) membranes were calculated as 20,278, 8,989 and 5,357, respectively. Therefore, the resistance and the simplified mass transfer coefficient values are corresponded with the higher fluxes of PTFE/PP (PTF045LD0A) and PTFE/PP (TF-450). In addition, the selection of PTFE membranes as active layer material for MD applications can be the best option because PTFE has been proven to be an ideal material providing one of the highest hydrophobic characters among polymers, together with qualified chemical resistance and thermal stability [30].

The total amounts of transferred ammonia and acclimated water volume on the permeate side for the three membranes, increased as temperature rose from 40 to 70 °C (shown in Fig. 4a). However, the ratio of transferred ammonia (g of ammonia) to acclimated water (g of water) (i.e., the SAT value) was low at high temperature (Table S1). The low SAT values are attributed to a steeper increase in the acclimated water volume than that of ammonia at high temperature. As a result, low SAT values were found with high water flux (i.e., higher than 24 LMH in particular, see Fig. 4b). The PTFE/PP (PTF045LD0A) and PTFE/PP (TF-450) membranes were similar for the lower total amount of transferred ammonia, and higher volume of acclimated water. Although the PTFE/PP (TF-450) membrane resulted in a lower total amount of transferred ammonia in the range from 40 to 60 °C, its acclimated water volume was also lower than for the PTFE/PP (PTF045LD0A) membrane. Therefore, the PTFE/PP (PTF045LD0A) membrane gave a similar SAT value with that of the PTFE/PP (TF-450) membrane (Table S1).

The relationship between the water flux and the SAT value were significantly distinguishable between low flux (A) and high flux (B) regions in Fig. 4b. In region A, the PVDF (HVHP-14250) membrane exhibited a sensitive response of SAT values from 1.59×10^{-2} to 4.17×10^{-3} g-N/g-H₂O, with a water flux range from 3.02 to 24.00 LMH. PTFE/PP (PTF045LD0A) also showed relatively the same SAT values in region A. In contrast, PTFE/PP (TF-450) constantly showed the lowest SAT values. Previous study showed that thickness and pore size have significant roles on the ammonia transfer through hydrophobic membrane in the MD system [24]. In this study, the effect of pore size was ruled-out by using the same pore size. The thick structure of PTFE/PP (TF-450) resulted in the high resistance on the ammonia transfer, and consequently the water transfer was predominant over the entire temperature range of the feed side. In region B (of high flux: more than 24 LMH), the stable and minimal average SAT values exhibited for the PTFE/PP (PTF045LD0A) and PTFE/PP (TF-450) membranes, respectively, were $2.63\text{--}1.62 \times 10^{-3}$ g-N/g-H₂O.

At given high temperature, the MD membranes exhibit better water flux than ammonia flux. Note that selective gas transfer is generally made feasible with molecule-scale pores as a molecular sieve. In this regard, the larger MD pores (0.45 μm) had a negligible effect on selective gas transfer in this study. Moreover, The Knudsen–molecular diffusion model (dusty-gas model) of MD systems has the least interaction between gas molecules and the

Table 3
Properties of the tested membranes.

Membrane	Pore size (μm)	Material of active layer	Thermal conductivity (W/m K)	Thickness (μm)	LEP (kPa)	Porosity (%)	Reference
PTF045LD0A	0.45	PTFE	0.25	89	> 179	73	[29]
TF-450	0.45	PTFE	0.25	178	138	80	[29,30]
HVHP-14250	0.45	PVDF	0.18	140	105	75	[30,31]

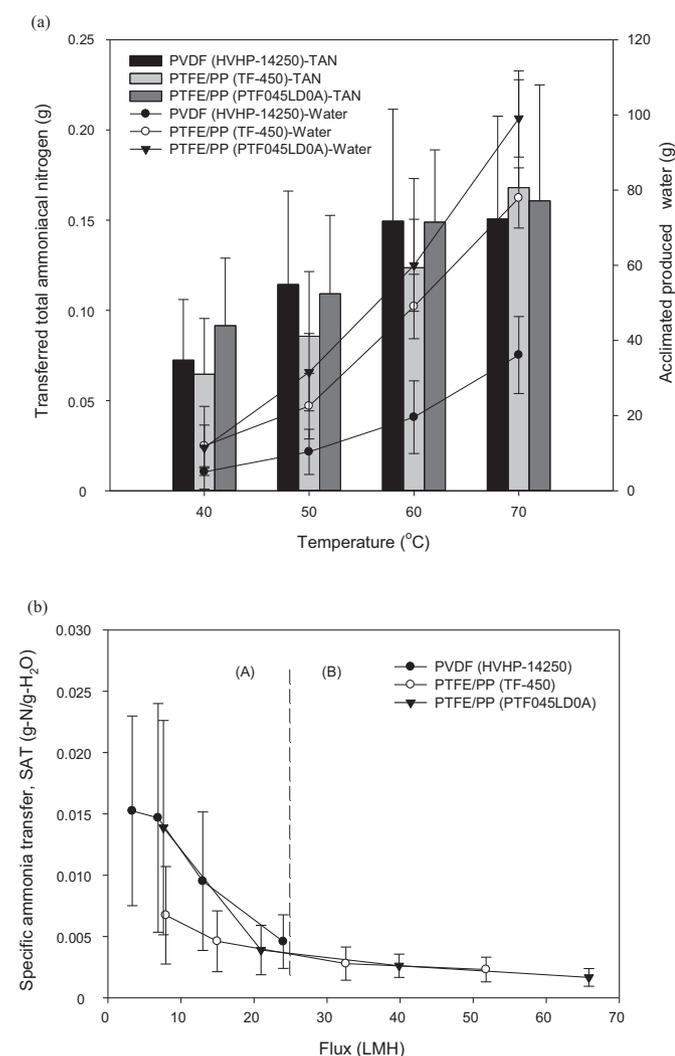


Fig. 4. (a) Ammonia and water transfer according to temperature of feed solution and (b) specific ammonia transfer according to water flux.

pore channels of the membrane surface [32]. In this study, the vapor pressure difference has major role in differentiating the SAT values. Generally, the vapor pressure of ammonia increases with the increase of temperature and ammonia concentration, in aqueous solution [33]. However, it is impossible to remove whole ammonia contents even in high temperature conditions due to the equilibrium between ammonia and ammonium ion. In aqueous phase, ammonia has the dissociate equilibrium ((Eqs. (1)–(4)). At a temperature of 40 $^{\circ}\text{C}$, the equilibrium constants towards NH_4^+ formation of 6.5×10^{-6} is larger than that towards ammonia formation of 1.5×10^{-9} , resulting in a difference of 4.2×10^3 times. The calculation of partial pressures of FA and water under 40 $^{\circ}\text{C}$ and pH 9 conditions with a TAN of 1.22 g-N/L resulted in a prevalent FA fraction of 61% due to the high pH. In final, the partial pressures of FA and water are 0.17 and 0.83 bar, respectively (Eqs. (9) and (10)). Therefore, it was concluded that the higher partial

pressure of water (compared to that of ammonia) was the major factor causing low SAT values at high temperature in this study. In a higher temperature of 70 $^{\circ}\text{C}$, the partial pressure of FA results in 0.13 bar, which is only a minor reduction, compared to that of 40 $^{\circ}\text{C}$. Therefore, the reason for a drastic change of the SAT in high temperatures should be described more clearly in terms of the selection mechanism between ammonia and water for the permeation in further study.

Water flux is the most critical factor determining dewatering performance [34]. In this regard, higher temperature is preferred to obtain high water-flux in dewatering systems using MD [28]. High temperature is also beneficial for providing a high gained output ratio value and better thermal efficiency [35–37]. In view of this, the water flux in high temperature was the only factor used to select the membrane type. Note that the stable and minimal SAT values are also available in high temperature conditions. Considering the highest flux of 65.84 LMH and the lowest SAT value of 1.62×10^{-3} g-N/g- H_2O at 70 $^{\circ}\text{C}$, the PTFE/PP (PTF045LD0A) membrane was selected as a membrane material suitable for recovering ammonia from source-separated human urine. In further experiments, the DCMD device was operated with a large temperature gap (60 and 20 $^{\circ}\text{C}$ for feed and permeate solutions, respectively). The feed solution temperature of 60 $^{\circ}\text{C}$ was selected, instead of 70 $^{\circ}\text{C}$, because the feed temperature should be within a certain range to prevent membrane fouling during urine purification. Even though increased feed temperature gave increased permeate flux, the improved permeation could cause solutes (organic and salt particles) to become hyper-saturated and to crystallize near or on the membrane surface [5].

3.2. Effects of nitrogen content on the SAT value

The highest TAN concentration found for source-separated human urine was 5.90 g-N/L in this study (Table 1). The pH of fresh human urine is about 6.2, but, after storage, it ranges from 8.7 to 9.1 [8]. Thus, the SAT values were investigated using a wider TAN range (from 0.465 to 4.940 g/L) at pH 9. The permeation flux was stable within the range 33.34–35.50 LMH, disregarding the TAN concentration in the feed solution. FA concentrations were in the range 0.39–4.14 g-N/L (Fig. 5a). The ammonia transfer depends on the partial pressure of free ammonia. As expected, the SAT values also increased linearly from 1.39×10^{-3} to 1.25×10^{-2} g-N/g- H_2O ($R^2=0.9710$) along with increased FA concentrations (Fig. 5b).

Nitrate, together with ammonium, is a valuable component for producing nitrogen fertilizer in the form of ammonium nitrate [7]. To verify possible effects of ionic interaction between ammonium and nitrate ions, on ammonia transfer, various concentrations of nitrate (from 0 to 2.50 g $\text{NO}_3\text{-N/L}$) were added to ammonia feed solution with a TAN of 1.12 ± 0.4 g/L. The results revealed no significant effects of nitrate concentration on flux and ammonia transfer (Fig. 6). Insignificant nitrate transfer through the MD membrane was observed as well (Table S2). Based on these results, it is expected that the ionic interaction is negligible comparing to the thermal driving force to keep ammonia partial pressure. However, there is limited information of the effects of ionic interaction on the partial vapor pressure of volatile compounds in an aqueous solution.

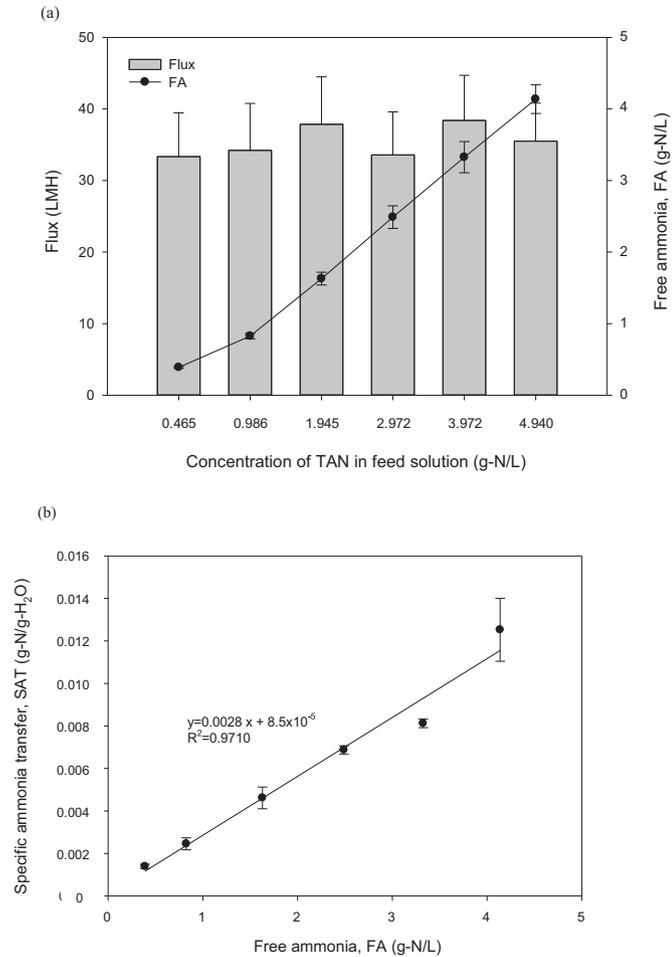


Fig. 5. (a) Flux and FA concentration as a function of initial TAN concentration and (b) SAT values depending on FA in feed solution according to TAN concentration.

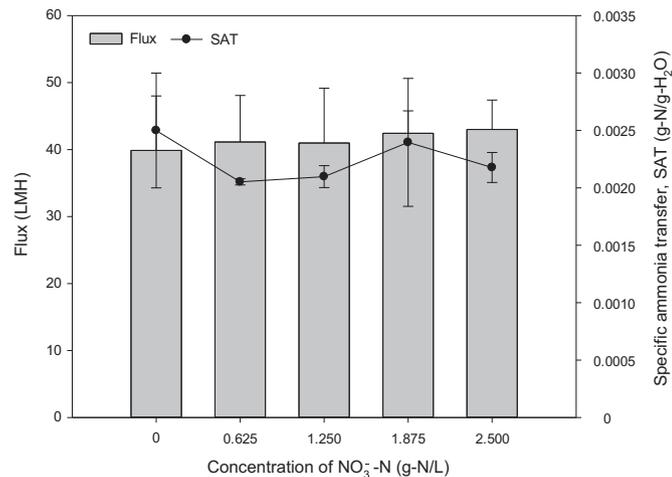


Fig. 6. Variation of flux and SAT values at different concentrations of NO₃-N (g/L) in feed solution at a fixed TAN concentration of 1.12 g-N/L.

3.3. Effects of acidification on the SAT value

SAT values were evaluated in different pH conditions using a fixed TAN concentration of 1.21 ± 0.08 g/L. The pH of the feed solution contributes to drastic change of the FA concentration (an exponential-like function), as shown in Fig. 7a. In the pH range 5–9, the calculated FA concentration increased from 7.07×10^{-4} to 1.10 g-N/L at 60 °C. According to Fig. 7a, the flux variation was

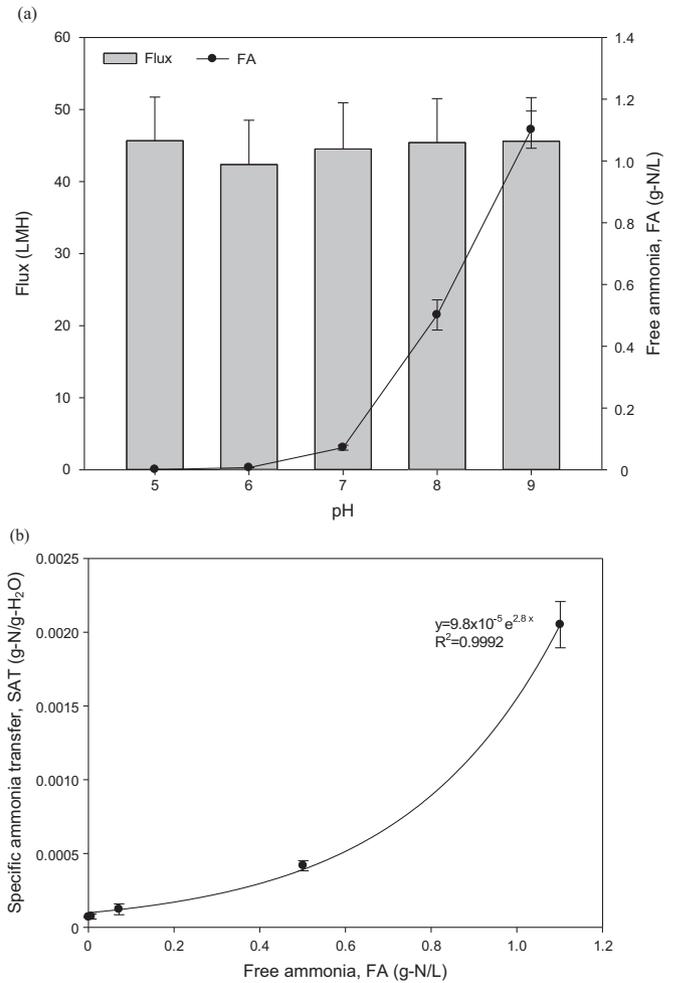


Fig. 7. (a) Flux and FA variations depend on pH and (b) SAT values as a function of FA.

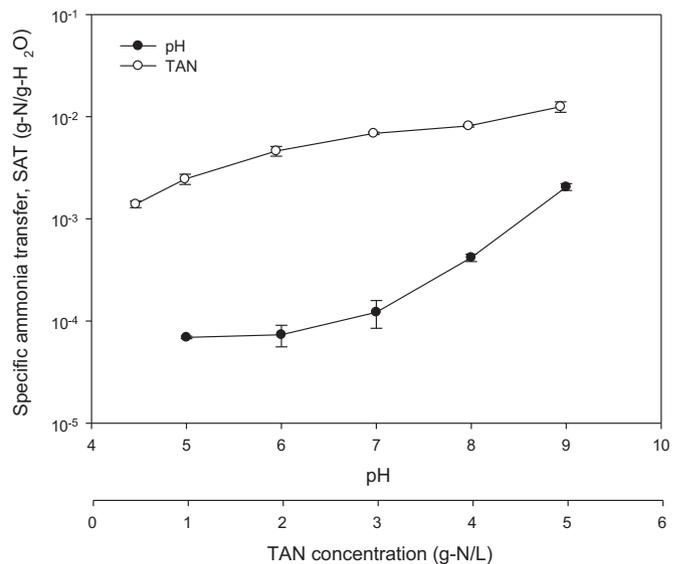


Fig. 8. The sensitivity analysis of SAT values according to TAN and pH.

45.66–45.60 LMH for pH values from 5 to 9. There was no significant change of the permeate flux at these pH values. The pH 9 (i.e., 1.10 g-FA/L) of Fig. 7b exhibited a SAT value of 2.05×10^{-3} g-N/g-H₂O which is consistent with the value of 2.45×10^{-3} g-N/g-H₂O at 0.88 g-FA/L, performed in the same conditions (see Fig. 5b).

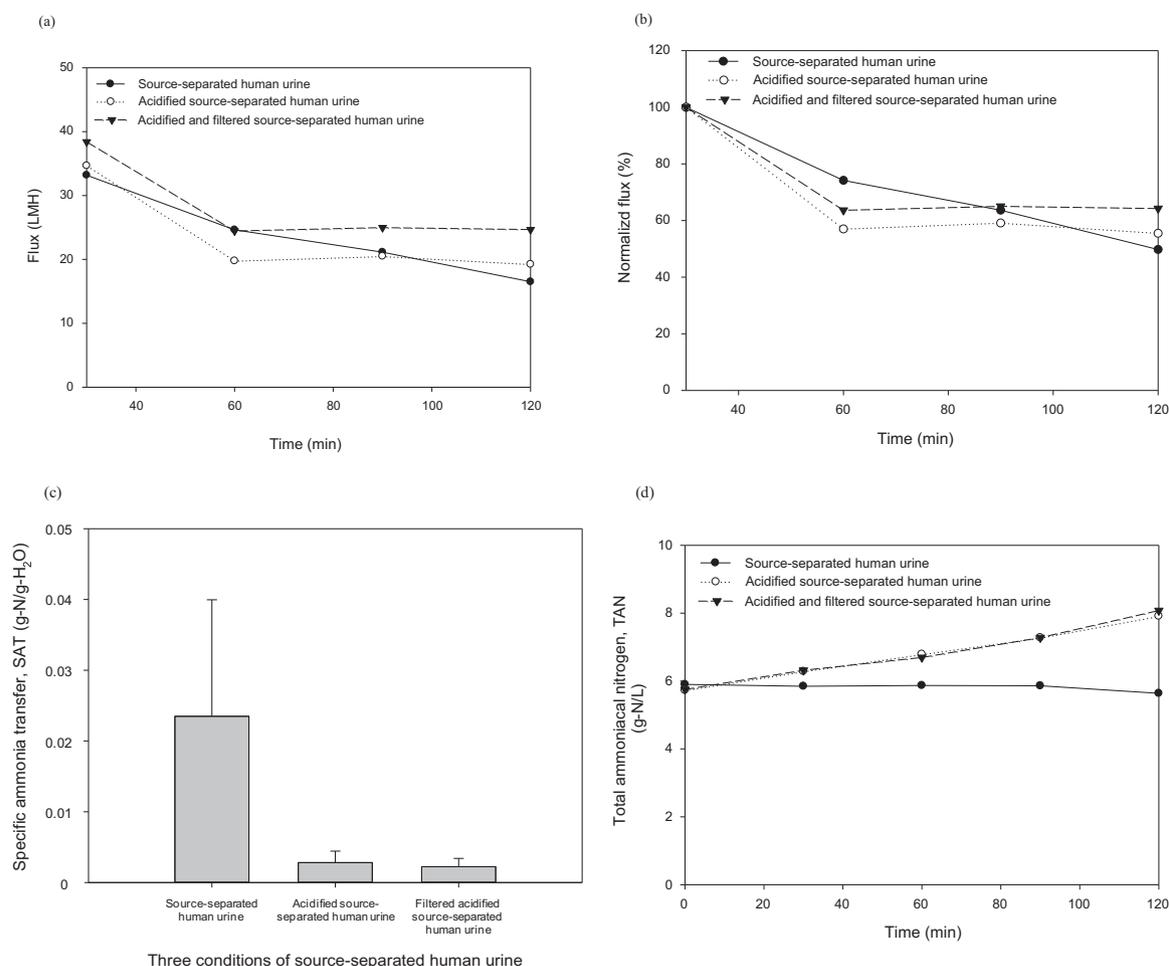


Fig. 9. (a) Flux variation, (b) normalized flux variation, (c) SAT (g-N/g-permeate) as a function of time and (d) TAN concentration in the feed solution (g-N/L).

However, the other pH conditions in Fig. 7b showed lower SAT values for corresponding FA concentrations, which followed an exponential function ($R^2=0.9992$). The SAT value for pH 5 was extremely low (6.91×10^{-5} g-N/g-H₂O). This implies that lowering the pH has a larger impact than TAN, and significantly reduces ammonia transfer in the MD system (Fig. 8). The reasons for the facilitated ammonia transfer by high pH and the stable SAT values at pH 5 and 6 are not clear. The relationship between pH and SAT values can be revealed only by understanding dynamic variation of pH and ammonia partial pressure during the operation, depending on various physicochemical conditions such as buffer capacity.

3.4. MD application to source-separated human urine

The DCMD system was operated to dewater source-separated human urine. All experiments were carried out with the PTFE/PP (PTF045LD0A) membrane as mentioned. The original pH of the stored source-separated human urine was 8.8. The acidification of source-separated human urine is a critical operational factor for preventing ammonia transfer through the MD membrane. Thus, source-separated human urine was acidified to pH 6 in order to get a low SAT value. The amount of 35–37% HCl added to 1 L of source-separated human urine (at initial pH 8.8), was 12.6 mL for pH 8; 35.7 mL for pH 7; 43.2 mL for pH 6; 44.8 mL for pH 5, and 46.2 mL for pH 4. As an additional pretreatment, filtration was done using a glass fiber paper of 1.2- μ m to prepare acidified and filtered source-separated human urine.

Source-separated human urine samples showed lower flux than that of the synthetic wastewater, and a sharp decrease in flux

occurred within 2 h due to significant fouling (Fig. 9a). The filtration pretreatment resulted in an increase in flux of 19.4% on average in comparison to acidified source-separated human urine. The higher flux of acidified and filtered source-separated human urine is attributed to the absence of VSS content (0 mg/L), compared to that of source-separated human urine (218 mg/L) (Table 1). The VSS is the major factor causing deposition on the membrane surface, and consequently, blocked pores [35]. However, in terms of normalized flux in Fig. 9b, acidification resulted in less significant benefit to prevent fouling, and the trend of flux decline was the same. This implies that major organic and inorganic foulants still remained in forms of sub- μ m-sized, colloidal particles or solutes.

Acidification resulted in significantly reduced SAT values (from 2.00×10^{-2} to 2.48×10^{-3} g-N/g-H₂O) during 2 h of operation (Fig. 9c). This was due to minimization of the FA concentration at pH 6. However, filtration resulted in insignificant difference in the average SAT values of 2.48×10^{-3} g-N/g-H₂O for acidified source-separated human urine and 2.06×10^{-3} g-N/g-H₂O for acidified and filtered source-separated human urine. The low SAT values resulted in successful acclimation of the TAN content in the human urine resource. The TAN concentrations in source-separated human urine samples gradually increased with time (Fig. 9d). In contrast, MD treatment of source-separated human urine without acidification resulted in failure of the enrichment of TAN contents.

The synthetic wastewater described in Section 3.2 showed successful enrichment of TAN content without acidification (i.e., at pH 9), even with a high concentration of TAN (up to 4.940 g/L). In

contrast, for the source-separated human urine, we failed to demonstrate TAN acclimation in the feed without acidification. As a result, SAT values between source-separated human urine and synthetic wastewater under the same conditions (TAN ~ 5.0 g/L, 60 °C, pH ~ 9), showed a large difference (2.00×10^{-2} and 1.25×10^{-3} g-N/g-H₂O, respectively). It can be speculated that the fouled layer on the membrane could block water molecules more easily than ammonia molecules due to the higher dipole moment of water.

4. Conclusions

PTFE/PP (PTF045LDOA), PTFE/PP (TF-450), and PVDF (HVHP-14250) membranes were tested for dewatering ammonia-rich synthetic wastewater in a DCMD system. The PTFE/PP (PTF045LDOA) membrane exhibited successful TAN enrichment in the feed solution, with the highest flux and lowest SAT values, at high temperature. Increase of the feed temperature from 40 to 70 °C facilitated the transfer of water and ammonia through the membrane. The SAT value was also reduced from 8.00×10^{-3} to 1.62×10^{-3} g-N/g-H₂O due to larger effects of temperature on water flux rather than on ammonia flux. The SAT value increased in proportion to the FA content, which is affected by the TAN concentration and pH. As an effective pretreatment, acidification from pH 9–5 resulted in the dramatic reduction of the SAT value from 2.05×10^{-3} to 6.91×10^{-5} g-N/g-H₂O. Acidification and filtration of the source-separated human urine prevented ammonia transfer and mitigated membrane fouling in the DCMD system. This indicates that the production of N-fertilizer from source-separated human urine is feasible by applying the MD system with a high-performance hydrophobic membrane.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.memsci.2016.04.004>.

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