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Optimisation of a forward osmosis and membrane distillation hybrid system for the treatment of source-separated urine

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Abstract

The high concentration of nitrogen, phosphorous and potassium in human urine makes it a suitable raw material for fertiliser production. However, urine is often diluted with a significant amount of flushing water which increases the costs for the downstream nutrients recovery process. Re-using the water and the nutrients in the urine is paramount for enhancing the sustainability of our waste management system. In this work, a combination of forward osmosis (FO) and membrane distillation (MD) was used to extract distilled water from human urine. FO was chosen as MD pre-treatment to increase the overall nitrogen rejection and to prevent wetting of the MD membrane. The goal of this investigation was to tune the FO and MD operating parameters to reduce the nitrogen transport to the MD permeate. Urine pH, draw solution (DS) salt concentration and operating pressure were varied as a means to enhance the FO performances. On the other hand, feed temperature, nitrogen concentration and membrane characteristics were investigated to optimise the MD process. With 2.5 M NaCl as DS commercial FO membranes achieved a water flux between $31.5 - 28.7 \text{ L.m}^{-2}.\text{h}^{-1}$ and a minimum nitrogen flux of 1.4 g.L^{-1} . An additional 33% reduction in the nitrogen transport was observed by applying minimal hydraulic pressure on the DS. However, this was also found to significantly reduce the net transmembrane water flux. Acidification of the feed was also beneficial for both FO and MD nitrogen rejection. Finally, we demonstrated that, by tuning the MD membrane porosity and thickness, higher MD permeate quality could be achieved. To conclude, the hybrid FO-MD process is expected to be an effective solution for the production of clean water and concentrated fertiliser from human urine. This double barrier separation process could be suitable for both water reclamation in space application and resource recovery in urban application.

Keywords: Forward osmosis, Membrane distillation, Human urine, Nitrogen rejection, fertiliser.

1 Introduction

Wastewater reuse is becoming one of the most sustainable solutions to the freshwater scarcity problem. Besides water, wastewater also contains valuable nutrients which can be extracted and reused to meet the increasingly growing fertiliser demand. However, recovering essential nutrients such as nitrogen (N) and phosphorous (P) from combined sewage is exceptionally costly due to its large volume and complex composition. To manage domestic wastewater more economically, source-separation of different streams (i.e. yellow, brown and grey waters) is becoming essential [1-3]. In municipal wastewater treatment plants (WWTPs), 80% of the N, 50% of the P and 55% of the potassium (K) come from human urine (i.e. yellow water) [4, 5]. These are all essential macronutrients for living organisms. However, if not adequately removed or recovered, the N and P in the urine can pose a serious environmental issue as they can lead to the eutrophication of the recipient water bodies as well as threatening the aquatic life by increasing NH_3 concentration [6, 7]. Additionally, as $64 \pm 27\%$ of the pharmaceuticals are excreted via urine, their concentration is about 2 - 3 times higher than the one in the combined sewage [8, 9]. Finally, the energy savings from reducing the load of urine-nitrogen to the WWTP can be significant. In fact, the energy requirements for removing the N from combined sewage is between $45 \text{ MJ Kg}_\text{N}^{-1}$ ($12.5 \text{ kWh Kg}_\text{N}^{-1}$, nitrification/denitrification) to $19 \text{ MJ Kg}_\text{N}^{-1}$ ($5.3 \text{ kWh Kg}_\text{N}^{-1}$, Sharon-Anammox) [10]. Given the average N and P production from urine (i.e., $11 \text{ g}_\text{N} \cdot \text{day}^{-1}$ and $1.1 \text{ g}_\text{P} \cdot \text{day}^{-1}$ per person) [10, 11] in a city like Sydney, with a population of about 5.37 million, every day about 640000 kWh of energy has to be used just to remove the N and P coming from the urine. With the current average Australian energy price of $0.21 \text{ USD} \cdot \text{kWh}^{-1}$, this value translates into a cost of about $137000 \text{ USD} \cdot \text{d}^{-1}$.

On the other hand, being able to produce fresh water from human urine has been of great interest for space applications as the reclaimed water is used by the crew member for drink, shower and oxygen production by water splitting [12, 13]. This is because the current commercial price for shipping 1 kg of water to the International Space Station (ISS) is of about \$10000 [12, 14-18]. As treating the wastewater on board, a spacecraft accounts for approximately half of the total life support payload, being able to improve the efficiency of the current processes is paramount [16]. In the terrestrial context, where the urine collected from urinals and source-separating toilets is often heavily diluted with tap water, optimising the urine dewatering could benefit the downstream nitrogen and phosphorus recovery. Concentrating urine 10 or more times, with minimal nutrients loss, could increase the economic viability N and P recovery via, e.g., stripping of ammonia and precipitation of struvite.

To sum up, being able to extract fresh water from urine would have several benefits ranging from (I)

increasing the water reuse in space applications to (II) minimising the wastewater treatment energy consumption of the wastewater treatment plant and (III) reducing the costs associated with the production of fertilisers from it.

In the last two decades, many efforts have been dedicated to the development and optimisation of different physico-chemical processes for the extraction of pure water from source-separated urine [4, 19]. These processes include (but are not limited to) reverse osmosis (RO), nanofiltration (NF), freeze/thaw concentration and evaporation [4, 15, 20]. Pressure-driven processes, i.e. RO and NF, show a promising approach for volume reduction and rejection of micropollutants while failing to better reject small uncharged compounds like urea and ammonia present in the wastewater [4, 20]. Besides, hydraulic pressure-driven NF/RO suffers from membrane fouling and scaling, and high operational costs [15, 21]. Finally, as the initial urine osmotic pressure is in the range of 10-22 bar, RO can concentrate it up to maximum 3-7 times [22]. For freeze-thaw, it was calculated that 1100 MJ m⁻³ of energy was necessary for a five-fold urine volume reduction. Finally, evaporation is the most straightforward technology for removing water from urine [4]. Despite its simple operation, this technology still suffers from ammonia volatilisation which can jeopardise the final permeate quality and reduce the amount of re-usable nitrogen [4, 23]. Urine acidification or partial nitrification was found to be an effective way to minimise the nitrogen losses during the evaporation process [4, 5]. However, the high buffer capacity of urine makes the acidification process costly while the biological oxidation of ammonia requires extensive aeration and process control to be stable [24, 25].

More recently, the combination of osmotically and thermally driven membrane processes including forward osmosis (FO) and membrane distillation (MD) has been investigated for the treatment of human urine [15, 16, 23, 26]. Although the number of studies is quite limited, initial results demonstrated the feasibility of recovering water and nutrients from source-separated urine. By using FO as MD pre-treatment, a higher quality and more stable MD permeate can be achieved due to the generally high rejection of commercially available FO membrane [27-32]. This hybridisation allowed for the purification of wastewater that generally challenging to treat by standalone MD, due to fouling/scaling and wetting problems, such as landfill leachate [30], oily wastewater [27, 29], digested sludge [28, 33] As(III) removal [34], wastewater reuse [35, 36] and desalination [37, 38].

When it comes to urine treatment via MD, the main issues were related to the permeation of ammonia gas to the produced water and the wetting of the MD membrane due to the presence of detergents in the urine collected from urinals [23]. For urine treatment, FO process is shown to have ease of operation and low fouling potential [26, 39]. However, if high urine concentration has to be achieved through dewatering, FO draw solution (DS) regeneration is deemed necessary. Otherwise,

the cost of DS will make the process prohibitive.

A hybrid FO - MD system for the treatment of human urine could provide a double barrier to increase the quality of the final permeate while regenerating DS for continuous operation. However, long-term experiments revealed that the accumulation of N-compounds with time in the DS remains one of the main limitations, especially when the by-product water from the urine treatment is to be used for drinking (e.g., during space exploration).

The objective of this study was to investigate and optimise the FO-MD hybrid system for the dewatering and concentration of source-separated urine. Based on the results obtained in the few available studies, emphasis was given on developing strategies to reduce the transport of nitrogen compounds to achieve final recycled water that can be used directly on-site (for toilet flushing and fertigation) [5, 25]. The ultimate goal is to develop a viable system that will contribute positively towards the sustainability of the food-water-energy nexus.

Figure 1: Schematic of a decentralised source-separated urine treatment system. Urine is osmotically concentrated by the FO system for subsequent nutrient recovery while the MD system is used to

reconcentrate the draw solution and produce distilled water. The recycled water from the FO-MD system can be used on-site for either flushing toilets or green wall irrigation.

2 Materials and Methods

2.1 Feed and draw solutions

Synthetic fresh urine (FU) and stored urine (SU) were used in this study as feed solutions (FS). Synthetic solutions were selected against real ones to make sure that the optimisation of the system was performed under controlled and stable conditions. Briefly, fresh urine represents the urine collected directly from the urinal with minimal storage time. In this case, the majority of the nitrogen is expected to be in the form of urea. Fresh urine is generally acidic (i.e., pH <6.5) due to the presence of organic acids such as oxalic acid in the urine [22, 40]. During storage under septic conditions, the urea hydrolyses to $\text{NH}_3/\text{NH}_4^+$ and carbonate hence causing an increase in the pH and chemical proprieties (Table 1) [41]. In this paper, this new solution is referred to as stored urine. The solutions were prepared according to the recipe of Udert et al. [42], and their primary characteristics are displayed in Table 1. FU contains mainly urea as a source of nitrogen and has an osmotic pressure of about 14 bar while SU contains nitrogen in the form of ammonia. As one mole of urea hydrolysis forming two moles of ammonia and one of carbonate, SU has higher osmotic pressure, close to 30 bar. The release of ammonia also increases the pH of stored urine over 8.5. Even though real urine collected from flushing urinals might have different dilution factors ranging from 1:1 to 1:100, only concentrated FU/SU urine was used as feed for the FO tests [40, 43]. This was chosen to have a conservative estimation of the water and nitrogen flux during FO operations. In fact, if urine is diluted, the FO water flux would likely increase, as the osmotic pressure difference ($\Delta\pi$) between feed and draw would decrease, while the nitrogen flux decrease as the ΔC_N between FS and DS will decrease (Fick's law on membrane diffusion rate: $J_N = D_N \cdot A \cdot \Delta C_N/x$).

Table 1: Characteristics of the fresh synthetic urine (FU) and stored urine (SU) used in this study.

Fresh Urine		Stored Urine	
Component	(g/L)	Component	(g/L)
Urea	16	NH_4 -Acetate	9.6
NaCl	0.18	NaCl	3.6
KCl	4.2	KCl	4.2
NH_4Cl	1.8	Na_2SO_4	2.3
Na_2SO_4	2.3	NaH_2PO_4	2.1
NaH_2PO_4	2.9	NH_4OH	13 mL
MgCl_2	0.37	NH_4HCO_3	21.4
CaCl_2	0.51		

NaOH	0.23		
Osmotic Pressure¹	13.7 bar	Osmotic Pressure¹	29.1 bar
pH	6.24	pH	8.87
Conductivity	14.6 mS/cm	Conductivity	23.2 mS/cm

¹ The osmotic pressure was calculated using OLI Studio Analyser (Version 9.5, OLI Systems Inc., USA).

The DS was prepared by dissolving sodium chloride (reagent grade, Sigma Aldrich, Australia) into deionised water at various concentrations ranging from 1 M (i.e. 47.4 bar – seawater RO desalination brine) to 2.5 M (i.e. 131.9 bar – produced water from Oil and Gas operations).

2.2 Forward osmosis and membrane distillation membranes

A commercial flat sheet polyamide (PA) thin-film composite (TFC) membrane from Toray Chemical Inc. (South Korea) was used in this study. The pure water permeability coefficient of the active layer (i.e. A value), as well as the salt rejection (R) and salt permeability coefficient (B) for urea, ammonium and ammonia in both FU and SU, were determined in RO mode at 10 bar applied pressure [44, 45]. The A value was calculated by dividing the average water flux (i.e. of 5 consecutive measurements taken at the 1-minute interval) by the applied pressure. The salt rejection was determined from the difference between the bulk feed concentration and the final permeate concentration after 1-hour operation. Finally, the B value was determined using the following equation:

$$B = \frac{1 - R}{R} (\Delta P - \Delta \pi) A \quad (1)$$

Where R is the salt rejection of the targeted compound, ΔP is the applied pressure (10 bar in this study), $\Delta \pi$ is the osmotic pressure of the targeted compound (i.e. urea, ammonia, ammonium) in either FU or SU and A is the pure water permeability coefficient. Table 2 shows the pure water permeability (A) and solute permeability (B) of the used membrane. The employed membrane showed both higher A value and lower B values compared to cellulose tri-acetate membrane used in a previous study [26].

Table 2 Pure water permeability (A) and solute permeability (B) of the employed membrane. The B value for urea, ammonium and ammonia in both FU and SU, was determined in RO mode at 10 bar pressure.

		TFC (This study)	CTA (Zhang et al. 2014)
A value (m/s.Pa)		1.54E-11	2.09E-12
	Urea - Fresh urine	2.21E-06	1.12E-05
B value (m/s)	NH ₃ - Fresh urine	6.82E-07	9.30E-06
	NH ₄ ⁺ - Fresh urine	1.97E-07	-

NH ₃ - Stored urine	7.09E-07	1.21E-06
NH ₄ ⁺ - Stored urine	2.05E-07	-

Table 3 Proprieties of the MD membranes employed. * The contact angle was based on a recent study with the same membranes [46].

Membrane material	PVDF (Polyvinylidene fluoride)	PTFE (polytetrafluoroethylene)
Manufacturer	Durapore®-GVHP	Fluoropore®-FGLP
Nominal Pore size	0.22 µm	0.22 µm
Thickness	125 µm	150 µm
Contact Angle*	131 ± 1°	146 ± 1°
Active layer porosity	75%	85%

Also, two different commercial membranes were tested for the MD process. The first was a polyvinylidene fluoride (PVDF) membrane (Durapore®-GVHP, pore size 0.22 µm, thickness 125 µm and porosity 75%) while the second was a polytetrafluoroethylene (PTFE) membrane (Fluoropore®-FGLP, pore size 0.22 µm, thickness 150 µm and porosity 85%). Both purchased from Merck Millipore (Table 3).

2.3 Bench-scale FO and MD systems

The performance of the FO and MD systems (i.e. water flux and solute transport across the membrane) was evaluated in a batch mode of operation whereby FO feed and draw solutions, and MD permeate solution was recirculated back to their respective tank. Both systems were operated under the counter-current flow mode. The membrane cell for both systems has two symmetric channels on each side (7.7 cm length, 2.6 cm width and 0.3 cm depth) with an active membrane area of 0.002 m². Gear pumps with variable speed (Cole Parmer, USA) were used to circulate the solutions from the tanks to the membrane cell and then back to the tanks. The DS tank for the FO system and the permeate tank for the MD system were placed on a digital scale connected to a computer. Weight measurements allowed for the determination of the transmembrane water flux. pH and conductivity probes (Hach, Germany) were connected to the feed tank of the FO system and to the permeate tank of the MD system to record the change of pH and conductivity in the FS and permeate solution.

The FO experiments were conducted under the active layer facing the FS mode (AL-FS). A new membrane was used for each new test and was stabilised with DI water on both sides for 30 minutes

before the start of the experiment. After stabilisation, both feed and draw solutions were replaced, and the water flux was measured continuously every 3 minutes. Tests were conducted at a cross-flow velocity of 8.5 cm/s at a constant temperature of 25°C maintained with a temperature controlled bath connected to a heating/chilling unit. To ensure comparable results, all the experiments were stopped after 5% urine concentration factor (which took approximately 120 minutes).

For the MD experiments, the direct contact MD (DCMD) configuration was chosen due to its higher performance (i.e. water flux) and relative ease of set up [47]. A new membrane was also used for each new experiment. The membrane cell was placed horizontally with the feed flowing on the top side. The feed temperature was varied from 40 to 60°C by a heating bath. Deionised water was used on the permeate side and kept at 25°C using a chiller. Both feed and permeate solutions were allowed to recirculate for about 30 minutes before starting the experiments to reach the targeted temperature. The cross-flow velocity on both sides was maintained at 8.5 cm/s.

2.4 Experimental protocol

2.4.1 Optimisation of the FO process

Optimisation of the FO process was carried out for both FU and SU solutions. The optimisation focused on reducing the transport of nitrogen compounds through the membrane. For FU, urea was the targeted nitrogen compounds while for SU, it was mainly ammonia. In fact, for the combined FO-MD system, NH_3 is the main issue if it accumulates in the DS side since NH_3 can pass through the MD membrane together with water vapour.

To reduce the transport of urea through the FO membrane, it was hypothesised that applying small hydraulic pressure on the DS could lessen the nitrogen diffusion to the FS. In fact, similarly to pressure assisted osmosis (PAO) [48] whereby pressure is applied on the feed side to increase the water flux and reduce the reverse salt flux from the DS; here, applying pressure on the DS would theoretically reduce the transport of salts from the feed to the draw solution. To test that, pressure (up to 2 bar) was applied on the DS side using a pressure valve connected to the DS outlet pipe (a pressure gauge was also installed to control more accurately the change in pressure). For experiments with stored urine, the pH was adjusted from initial pH (i.e. 8.87) down to pH 6, via the addition of the required stoichiometric amount of a 2 M HCl solution, to shift the equilibrium $\text{NH}_3/\text{NH}_4^+$ towards NH_4^+ (reaction 2) and thus reduce the concentration of NH_3 in the feed solution.

2.4.2 Optimisation of the MD process

Apart from testing different feed temperatures and MD membrane types, feed urine solutions with different dilution (1:1, 1:10 and 1:100) were tested to evaluate the effect of initial nitrogen compounds concentration on the quality of the final permeate. In fact, by using FO as a pre-treatment, nitrogen compounds will accumulate on the DS side which will affect the performance of the MD process. Also, both PTFE and PVDF based membranes were employed for the experiments and their performances evaluated. PVDF and PTFE are among the most widely used membranes for MD due to their hydrophobic nature and high thermal stability. The water droplet contact angle on a PTFE surface varies from 108° to 115° while for PVDF membrane was found to be 107° [49, 50].

2.5 Analytical methods

Samples were taken from the draw solution side in FO experiments and from the permeate side in MD experiments. The N-NH_4^+ concentration was measured using Merck cell test and spectrophotometer (Spectroquant NOVA 60; Merck, Germany) while NH_3/Urea were measured via spectrophotometer, at 340 nm wavelength, using Megazyme kit.

3 Results and discussion

The direct application of MD for the concentration of human urine is questionable as, in the majority of urine collection systems, real urine is mixed with detergents and surfactants. Surfactants can lower the surface tension of the membrane, thereby causing fouling and pore wetting which would jeopardise the whole process [51]. However, if FO is chosen as a “pre-treatment”, surfactants can be almost entirely removed (the rejection was found above 99.8%) [52], thereby providing an optimal solution for the MD process to work with. Additionally, FO should reduce the amount of ammoniacal nitrogen leaching to the MD feed which, in turns, would increase the quality of the MD permeate.

3.1 FO performances in dewatering fresh and stored urine

In this section, the FO water flux was measured using fresh or stored urine as FS and different NaCl concentration as DS. Afterwards the nitrogen transport, as $\text{NH}_3/\text{NH}_4^+/\text{Urea}$, through the membrane per litre of treated water was investigated. Figure 2 displays the achieved water flux when SU or FU is used. The higher water flux with FU was found to be due to its lower osmotic pressure compared to SU (i.e., 13.7 versus 29.1 bar). However, Figure 3 shows that FU also exhibits higher urea transport. This can be explained by looking at Table 2 and Eq. 3. It can be seen that the solute transport coefficient for urea is higher than both NH_3 and NH_4^+ . The low rejection of urea is due to the combination of low molecular weight, the absence of charge, high diffusivity ($D_{\text{urea}} = 1.32 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$) as well as a high concentration in the feed solution [53].

$$B_{\text{urea}} = 2.21 \cdot 10^{-6} \frac{\text{m}}{\text{s}} > B_{\text{NH}_3} = 7.09 \cdot 10^{-7} \frac{\text{m}}{\text{s}} > B_{\text{NH}_4^+} = 2.05 \cdot 10^{-7} \frac{\text{m}}{\text{s}} \quad (3)$$

Additionally, Figure 3 shows that the nitrogen flux decreases with the increase in DS concentration. A possible explanation can be given by looking at Eq. 4, where J_w is the water flux and B_N the permeability of the selected nitrogen compound [26]. Eq. 4 shows that the rejection is directly proportional to the water flux. In particular, if the water flux increases, so does the rejection.

$$R [\%] = J_w / (J_w + B_N) \quad (4)$$

$$\text{Nitrogen Transport } [g/L] = \frac{\frac{\Delta m_{N, \text{Draw}}}{A \cdot \Delta T}}{J_w} \quad (5)$$

Eq. 5 was then used to calculate the nitrogen flux depicted in Figure 3. Where, $\Delta m_{N, Draw}$ is the nitrogen mass increase in the draw solution, A the membrane area and ΔT the sampling time interval and $\bar{J}_W$ the average water flux between the samples.

$$R_N[\%] = \left(1 - \frac{m_{N, Draw}}{m_{N, Feed}} \right) * 100 \quad (6)$$

Eq. 6 was then used to calculate the nitrogen rejection as the ration between the mass of nitrogen in the draw $C_{N, Draw}$ and the initial mass of nitrogen in the feed $C_{N, Feed}$ [54].

To summarise, due to its lower osmotic pressure, FU exhibited a water flux on average 13% greater than the one of SU. On the other hand, it also exhibited higher nitrogen transport. Finally, as urea and NH_4^+ are non-volatile, they will accumulate in the draw solution over time. Therefore, DS purging/replenishment will be necessary.

Figure 2 Forward osmosis water flux using fresh or stored urine as feed, and NaCl at different concentrations as draw solution.

Figure 3 Nitrogen rejection (right axis) and transport from feed to draw per volume of treated water (left axis). For every draw concentration, the stacked column on the left refers to the fresh urine while the column on the right to the hydrolysed urine.

3.2 Optimisation of the FO process

3.2.1 Fresh urine: Effect of hydraulic pressure applied to the draw solution side

This section investigated the effect of DS pressure and FS pH on the transmembrane FO nitrogen flux. A 1.5 M NaCl was used as DS. This DS concentration was chosen to match the flux of FO with the one of MD. Applying pressure on the feed side (i.e., pressure assisted osmosis) was often found to decrease the reverse diffusion of ions from the DS to the FS [55]. Other studies explained this phenomenon as the effect of enhanced convective flux that drives the draw solutes away from the membrane due to back diffusion [56]. Here, the same principle was tested as a means to reduce the forward diffusion of urea to the DS. Specifically, pressures ranging from 0.5 to 2 bar were applied on the draw side and the forward flux of urea measured. It was found that the specific urea flux could be decreased by about 30% when a pressure of 2 bar is applied on the draw side. Nevertheless, the water flux was also found to drop by 42% (Fig. 4). Before deciding whether to apply back pressure on the system, the induced increase in the capital and operation costs (CAPEX and OPEX) caused by a higher required membrane surface area, should be calculated and benchmarked with the savings from lowering the reverse nitrogen diffusion. Additionally, the effect of long-term back pressure on the mechanical stability of the FO membrane should be investigated to assess that no permanent

damage (such as active layer delamination) occurs on the membrane.

To sum up, nitrogen rejection can be boosted by simply applying back pressure on the DS, the downside of that is that it would also decrease the effective driving force.

Figure 4 Water and urea flux as a function of transmembrane pressure exerted on the draw side. The operating conditions are also detailed in the picture.

3.2.2 Stored urine: Effect of feed solution pH

Urine acidification has been extensively investigated as a means to reduce the ammonia permeation in both FO and MD [23, 53, 57]. Lower pH would improve the nitrogen rejection of both FO and MD.

In fact, shifting the equilibrium $\text{NH}_3 \xrightleftharpoons{\text{pK}_a=9.25} \text{NH}_4^+$ to the ionic NH_4^+ would reduce the amount of uncharged NH_3 which is difficult to reject [58]. On the other hand, the charged nature of NH_4^+ causes its ionic radius to increase when hydrated, thereby enhancing its rejection as well. On the other hand, the rejection of uncharged NH_3 would be only regulated by size exclusion mechanism. The nitrogen rejection by MD would also increase when the pH of the urine is 7 or less as NH_4^+ is non-volatile while NH_3 is a gas with a boiling point of -33.3°C . However, it has to be noted that it would be preferable to acidify urine when it is fresh to prevent urea from hydrolysis. In fact, the high buffer capacity of hydrolysed urine would increase the required acid to reach pH neutralisation four times (i.e., about $230 \text{ mmol H}^+\cdot\text{L}^{-1}_{\text{urine}}$) [4].

Figure 5 (A) confirms the hypothesis of the effect of the pH on the nitrogen transport. With the decrease in the pH, the concentration of charged NH_4^+ ions in the urine increases thereby leading to a lower total nitrogen flux. However, the addition of acid (in this case HCl) also increases the salinity

of the urine and, therefore, its osmotic pressure. As a consequence, the FO water flux was also found to decrease with the decrease in the pH. In fact, the protonation of NH_3 is not expected to influence the FO flux as the diffusivity coefficients of NH_3 and NH_4^+ are very similar (i.e., $D_{\text{NH}_4^+} = 1.82 \cdot 10^{-9} \frac{\text{m}^2}{\text{s}} \sim D_{\text{NH}_3} = 2.07 \cdot 10^{-9} \frac{\text{m}^2}{\text{s}}$). The lowering of the FO water flux caused a slight increase in the nitrogen transport rate through the membrane as the nitrogen transport is the ratio between nitrogen flux ($\text{g}_\text{N} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) and water flux. Additionally, the stability of the polyamide active layer might be compromised under alkaline conditions due to hydrolysis via the direct nucleophilic addition of OH^- to the carbonyl group [59]. Therefore, operating under pH of 6-7 is also recommended from the membrane stability point of view.

Finally, at high pH membrane scaling might be more severe due to carbonates and phosphate precipitation of the membrane active layer. When real urine is used, the effect of pH in the co-precipitation of inorganic and organic foulants on the membrane should be further investigated.

It can be concluded that, despite the lower water flux, acidified stored urine is preferable to ensure a stable higher ammonium rejection.

Figure 5 Impact of feed acidification in the transport of nitrogen (A) and water (B) across the TFC-FO membrane. Figure (B) also displayed the calculated feed osmotic pressure as a function of the pH. The osmotic pressure of the solution was calculated using ROSA software (Version 9.1, Dow Filmtech, USA).

3.3 Optimisation of the MD process

3.3.1 Effect of feed temperature and membrane types on the water permeation

The optimal MD operation was studied to minimise the N transport in the permeate. In this section,

the water flux of the PVDF and PTFE commercial MD membranes was tested and compared. The membranes were tested at with 1.5 M NaCl as feed and having a temperature ranging from 40°C to 60°C. Afterwards, the optimal feed temperature was used to investigate the ammonia transport to the MD produced water. It can be seen that the ΔT between feed and permeate should be above 40°C, for PVDF, and above 30°C for PTFE for the MD to have the same FO water permeation rate (Figure 6). This can be also avoided by increasing the MD membrane area. Figure 6 also shows how the employed PTFE membranes achieved, on average, 35% higher water flux compared to PVDF membranes. One possible explanation is the higher porosity of PTFE over PVDF (i.e., 85% compared to 75%) and hydrophobicity (determined by contact angle) i.e., 146° compared to 131°. Similar results were found by Silva T. et al [46].

Figure 6 Water flux of PVDF and PTFE MD membranes using 1.5 M NaCl as DS and feed temperature of 40, 50 or 60°C. The permeate temperature was kept at 20°C.

3.3.2 Effect of feed solutes concentration on the permeate quality

Once the optimal ΔT between feed and permeate was determined, the mass transfer of nitrogen was measured as a function of ammonia concentration and membrane material. To do so, stored urine with different dilution factors (1:1, 1:10 and 1:100) were tested to evaluate the effect of initial nitrogen compounds concentration on the quality of the final permeate (as explained in section 2). New solutions were used for the MD tests to ensure a consistent feed for each replicate. Ammonia concentration, pH and temperature are the dominant factors in the ammonia permeation rate [23]. The NH_3 vapour pressure increases with the increase in NH_3 concentration and solution temperature. The pH, in particular, regulates the amount of NH_3 (gas) over NH_4^+ (liquid). High

concentrations of gaseous NH_3 would significantly increase the nitrogen transport to the produced water. Several studies have proven that ammonia transport can be minimised if the urine is acidified to pH below 6 [14, 15, 23]. In this study, the performance of PVDF and PTFE membranes was benchmarked in the harsh case scenario, i.e., high feed temperature, pH and concentration (Fig. 7).

Membrane pore size and thickness were found to be the dominant factors in the ammonia flux through the MD membrane. Membrane thickness is inversely proportional to the NH_3 mass transfer [23, 60]. In this case, the employed membranes have the same pore sizes, $0.22\ \mu\text{m}$, while the thickness of the PTFE membranes was higher than the PVDF ones. Therefore, it is expected that the NH_3 transfer would be lower when the PTFE membrane is used. Additionally, the higher water flux of PTFE would also lower the nitrogen to water transfer rate. Overall, if FO can reject >95% of the ammoniacal nitrogen, PTFE membrane is expected to ensure a low nitrogen concentration in the permeate.

Figure 7 Specific nitrogen flux from the urine solution ($T = 60^\circ\text{C}$, $\text{pH} = 8.87$) to the de-ionised water permeate ($T = 20^\circ\text{C}$) using PVDF or PTFE MD membranes. The feed solution consists of stored urine with dilution factor of 1:1, 1:10 and 1:100.

4 Conclusions

Production of water and marketable fertilisers from human urine is becoming increasingly necessary to ensure sustainable wastewater management. However, human urine is often heavily diluted which can jeopardise the nutrients recovery process. In this work, forward osmosis (FO) was used as a pre-treatment to membrane distillation (MD) to concentrate fresh urine (FU) and stored urine (SU) and produce distilled water. The FO pre-treatment step is expected to be necessary to prevent MD wetting due to the possible presence of surfactants and foulants in real urine. Operating parameters of both FO and MD processes were optimised to minimise the nitrogen leakage to the final MD permeate. With 2.5 M NaCl as draw solution (DS) commercial FO membranes achieved a water flux of 31.5 (FU) – 28.7 (SU) $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, a NH_4^+ flux of $0.1 \text{ gNH}_4^+\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, and NH_3 flux of $1.8 \text{ gNH}_3\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and an urea flux of $2.9 \text{ gUrea}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. Additionally, the application of moderate back pressure on the DS was able to reduce the nitrogen flux by up to 30%. This is expected to be due to the convective flux from the DS to the FS that drives the $\text{NH}_4^+/\text{NH}_3$ /urea solutes away from the membrane. However, this led also to the decrease in the water flux.

Additionally, further investigation should be done to assess the impact of high back pressure on the membrane stability, especially on the possibility of active layer delamination. During the recovery of the DS via MD, the use of PTFE membranes was found beneficial in reducing the nitrogen leakage to the permeate solution. The higher porosity and thickness of PTFE membranes over PVDF showed to achieve higher water flux and lower NH_3 flux. In particular, the thickness of the membrane was found to be inversely proportional to the NH_3 mass transfer.

Overall, the high nitrogen rejection of FO during SU filtration can significantly decrease the nitrogen leakage to the final permeate water during the MD process. This double barrier separation process could be suitable for both water reclamation in space application and resource recovery in urban application.

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References:

- [1] A.C. Alder, R.I. Eggen, M. Maurer, J. Lienert, Source Separation: Will We See a Paradigm Shift in Wastewater Handling? , *Environmental Science Technology*, 43 (2009) 6121-6125.
- [2] T.A. Larsen, W. Gujer, The concept of sustainable urban water management, in: *Water Science and Technology*, 1997, pp. 3-10.
- [3] T.A. Larsen, S. Hoffmann, C. Lüthi, B. Truffer, M. Maurer, Emerging solutions to the water challenges of an urbanizing world, *Science*, 352 (2016) 928-933.
- [4] M. Maurer, W. Pronk, T.A. Larsen, Treatment processes for source-separated urine, *Water Research*, 40 (2006) 3151-3166.
- [5] K.M. Udert, M. Wächter, Complete nutrient recovery from source-separated urine by nitrification and distillation, *Water Research*, 46 (2012) 453-464.
- [6] Z. Wang, K.M.Y. Leung, Effects of unionised ammonia on tropical freshwater organisms: Implications on temperate-to-tropic extrapolation and water quality guidelines, *Environmental Pollution*, 205 (2015) 240-249.
- [7] M. Kir, M. Topuz, M.C. Sunar, H. Topuz, Acute toxicity of ammonia in Meagre (*Argyrosomus regius* Asso, 1801) at different temperatures, *Aquaculture Research*, 47 (2016) 3593-3598.
- [8] R. Zhang, P. Sun, T.H. Boyer, L. Zhao, C.H. Huang, Degradation of pharmaceuticals and metabolite in synthetic human urine by UV, UV/H₂O₂, and UV/PDS, *Environmental Science and Technology*, 49 (2015) 3056-3066.
- [9] J. Lienert, T. Bürki, B.I. Escher, Reducing micropollutants with source control: Substance flow analysis of 212 pharmaceuticals in faeces and urine, in: *Water Science and Technology*, 2007, pp. 87-96.
- [10] M. Maurer, P. Schwegler, T.A. Larsen, Nutrients in urine: Energetic aspects of removal and recovery, in: *Water Science and Technology*, 2003, pp. 37-46.
- [11] AEMC, Final Report: 2013 Residential Electricity Price Trends, Australian Energy Market Commission (AEMC), (2013).
- [12] L.D. Harper, C.R. Neal, J. Poynter, J.D. Schalkwyk, D.R. Wingo, Life Support for a Low-Cost Lunar Settlement: No Showstoppers, *New Space*, 4 (2016) 40-49.
- [13] N.M. Samsonov, L.S. Bobe, V.M. Novikov, N.S. Farafonov, B.J. Pinsky, G.K. Abramov, M.S. Amiragov, V.B. Astafyev, V.G. Rifert, V.B. Filonenko, N.N. Protasov, J.E. Sinjak, Systems for Water Reclamation from Humidity Condensate and Urine for Space Station, *SAE Transactions*, 103 (1994) 1500-1507.
- [14] Z.P. Zhao, L. Xu, X. Shang, K. Chen, Water regeneration from human urine by vacuum membrane distillation and analysis of membrane fouling characteristics, *Separation and Purification Technology*, 118 (2013) 369-376.
- [15] Q. Liu, C. Liu, L. Zhao, W. Ma, H. Liu, J. Ma, Integrated forward osmosis-membrane distillation process for human urine treatment, *Water Research*, 91 (2016) 45-54.
- [16] T.Y. Cath, S. Gormly, E.G. Beaudry, M.T. Flynn, V.D. Adams, A.E. Childress, Membrane contactor processes for wastewater reclamation in space: Part I. Direct osmotic concentration as pretreatment for reverse osmosis, *Journal of Membrane Science*, 257 (2005) 85-98.
- [17] K.K. Tommerup M., Vogel J., Flynn M. and Shaw A., Testing Aquaporin Inside Membrane on the International Space Station, 46th International Conference on Environmental Systems, (2016).
- [18] S. Gormly, M. Flynn, A.S. Howe, Space Cargo Transport Bags Through Membrane Water Treatment Elements To Space Architecture Building Element: A Total Product Sustainability And Life Cycle Design Optimisation Experiment, *Journal of Green Building*, 7 (2012) 71-84.
- [19] K.M. Udert, C.A. Buckley, M. Wächter, C.S. McArdell, T. Kohn, L. Strande, H. Zöllig, A. Fumasoli, A. Oberson, B. Etter, Technologies for the treatment of source-separated urine in the eThekwin Municipality, *Water Sa*, 41 (2015) 212-221.
- [20] W. Pronk, H. Palmquist, M. Biebow, M. Boller, Nanofiltration for the separation of pharmaceuticals from nutrients in source-separated urine, *Water Research*, 40 (2006) 1405-1412.
- [21] G. Amy, N. Ghaffour, Z. Li, L. Francis, R.V. Linares, T. Missimer, S. Lattemann, Membrane-based seawater desalination: Present and future prospects, *Desalination*, 401 (2017) 16-21.
- [22] D. Putnam, Composition and Concentrative proprieties of human urine, NASA, WASHINGTON, United States, (1971).

- [23] L.L. Tun, D. Jeong, S. Jeong, K. Cho, S. Lee, H. Bae, Dewatering of source-separated human urine for nitrogen recovery by membrane distillation, *Journal of Membrane Science*, 512 (2016) 13-20.
- [24] K. Udert, C. Fux, M. Münster, T. Larsen, H. Siegrist, W. Gujer, Nitrification and autotrophic denitrification of source-separated urine, *Water Science and Technology*, 48 (2003) 119-130.
- [25] A. Fumasoli, B. Etter, B. Sterkele, E. Morgenroth, K.M. Udert, Operating a pilot-scale nitrification/distillation plant for complete nutrient recovery from urine, *Water Science and Technology*, 73 (2016) 215-222.
- [26] J. Zhang, Q. She, V.W.C. Chang, C.Y. Tang, R.D. Webster, Mining nutrients (N, K, P) from urban source-separated urine by forward osmosis dewatering, *Environmental Science and Technology*, 48 (2014) 3386-3394.
- [27] S. Zhang, P. Wang, X. Fu, T.-S. Chung, Sustainable water recovery from oily wastewater via forward osmosis-membrane distillation (FO-MD), *Water Research*, 52 (2014) 112-121.
- [28] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, 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 (2014) 191-195.
- [29] D. Lu, Q. Liu, Y. Zhao, H. Liu, J. Ma, Treatment and energy utilization of oily water via integrated ultrafiltration-forward osmosis-membrane distillation (UF-FO-MD) system, *Journal of Membrane Science*, 548 (2018) 275-287.
- [30] Y. Zhou, M. Huang, Q. Deng, T. Cai, Combination and performance of forward osmosis and membrane distillation (FO-MD) for treatment of high salinity landfill leachate, *Desalination*, 420 (2017) 99-105.
- [31] D. Zhao, P. Wang, Q. Zhao, N. Chen, X. Lu, Thermoresponsive copolymer-based draw solution for seawater desalination in a combined process of forward osmosis and membrane distillation, *Desalination*, 348 (2014) 26-32.
- [32] D. Zhao, S. Chen, C.X. Guo, Q. Zhao, X. Lu, Multi-functional forward osmosis draw solutes for seawater desalination, *Chinese Journal of Chemical Engineering*, 24 (2016) 23-30.
- [33] N.C. Nguyen, H.T. Nguyen, S.-T. Ho, S.-S. Chen, H.H. Ngo, W. Guo, S.S. Ray, H.-T. Hsu, Exploring high charge of phosphate as new draw solute in a forward osmosis-membrane distillation hybrid system for concentrating high-nutrient sludge, *Science of The Total Environment*, 557-558 (2016) 44-50.
- [34] Q. Ge, G. Han, T.-S. Chung, Effective As(III) Removal by A Multi-Charged Hydroacid Complex Draw Solute Facilitated Forward Osmosis-Membrane Distillation (FO-MD) Processes, *Environmental Science & Technology*, 50 (2016) 2363-2370.
- [35] T. Husnain, Y. Liu, R. Riffat, B. Mi, Integration of forward osmosis and membrane distillation for sustainable wastewater reuse, *Separation and Purification Technology*, 156 (2015) 424-431.
- [36] J. Li, D. Hou, K. Li, Y. Zhang, J. Wang, X. Zhang, Domestic wastewater treatment by forward osmosis-membrane distillation (FO-MD) integrated system, *Water Science and Technology*, 77 (2018) 1514-1523.
- [37] P. Wang, Y. Cui, Q. Ge, T. Fern Tew, T.-S. Chung, Evaluation of hydroacid complex in the forward osmosis-membrane distillation (FO-MD) system for desalination, *Journal of Membrane Science*, 494 (2015) 1-7.
- [38] W. Luo, H.V. Phan, G. Li, F.I. Hai, W.E. Price, M. Elimelech, L.D. Nghiem, An Osmotic Membrane Bioreactor-Membrane Distillation System for Simultaneous Wastewater Reuse and Seawater Desalination: Performance and Implications, *Environmental Science & Technology*, 51 (2017) 14311-14320.
- [39] F. Volpin, L. Chekli, S. Phuntsho, J. Cho, N. Ghaffour, J.S. Vrouwenvelder, H. Kyong Shon, Simultaneous phosphorous and nitrogen recovery from source-separated urine: A novel application for fertiliser drawn forward osmosis, *Chemosphere*, 203 (2018) 482-489.
- [40] K.M. Udert, T.A. Larsen, W. Gujer, Biologically induced precipitation in urine-collecting systems, *Water Science and Technology: Water Supply*, 3 (2003) 71-78.
- [41] D.G. Randall, V. Naidoo, Urine: the liquid gold of wastewater, *Journal of Environmental Chemical Engineering*, (2018).
- [42] K. Udert, T.A. Larsen, W. Gujer, Fate of major compounds in source-separated urine, *Water Sci. Technol.*, 54 (2006) 413-420.

- [43] X. Liu, Z. Hu, C. Zhu, G. Wen, X. Meng, J. Lu, Effect of contact to the atmosphere and dilution on phosphorus recovery from human urine through struvite formation, *Environmental Technology*, 35 (2014) 271-277.
- [44] T.Y. Cath, M. Elimelech, J.R. McCutcheon, R.L. McGinnis, A. Achilli, D. Anastasio, A.R. Brady, A.E. Childress, I.V. Farr, N.T. Hancock, J. Lampi, L.D. Nghiem, M. Xie, N.Y. Yip, Standard Methodology for Evaluating Membrane Performance in Osmotically Driven Membrane Processes, *Desalination*, 312 (2013) 31-38.
- [45] A. Tiraferri, N.Y. Yip, W.A. Phillip, J.D. Schiffman, M. Elimelech, Relating performance of thin-film composite forward osmosis membranes to support layer formation and structure, *Journal of Membrane Science*, 367 (2011) 340-352.
- [46] T.L.S. Silva, S. Morales-Torres, C.M.P. Esteves, A.R. Ribeiro, O.C. Nunes, J.L. Figueiredo, A.M.T. Silva, Desalination and removal of organic micropollutants and microorganisms by membrane distillation, *Desalination*, 437 (2018) 121-132.
- [47] J.-G. Lee, A.S. Alsaadi, A.M. Karam, L. Francis, S. Soukane, N. Ghaffour, Total water production capacity inversion phenomenon in multi-stage direct contact membrane distillation: A theoretical study, *Journal of Membrane Science*, 544 (2017) 126-134.
- [48] G. Blandin, A.R.D. Verliefde, C.Y. Tang, A.E. Childress, P. Le-Clech, Validation of assisted forward osmosis (AFO) process: Impact of hydraulic pressure, *Journal of Membrane Science*, 447 (2013) 1-11.
- [49] M. Tomaszewska, Preparation and properties of flat-sheet membranes from poly(vinylidene fluoride) for membrane distillation, *Desalination*, 104 (1996) 1-11.
- [50] J. Zhang, J.-D. Li, M. Duke, Z. Xie, S. Gray, Performance of asymmetric hollow fibre membranes in membrane distillation under various configurations and vacuum enhancement, *Journal of Membrane Science*, 362 (2010) 517-528.
- [51] N.G.P. Chew, S. Zhao, C.H. Loh, N. Permogorov, R. Wang, Surfactant effects on water recovery from produced water via direct-contact membrane distillation, *Journal of Membrane Science*, 528 (2017) 126-134.
- [52] P. Zhao, B. Gao, Q. Yue, H.K. Shon, The performance of forward osmosis process in treating the surfactant wastewater: The rejection of surfactant, water flux and physical cleaning effectiveness, *Chemical Engineering Journal*, 281 (2015) 688-695.
- [53] S. Lee, R.M. Lueptow, Membrane Rejection of Nitrogen Compounds, *Environmental Science & Technology*, 35 (2001) 3008-3018.
- [54] M. Xie, W. Luo, H. Guo, L.D. Nghiem, C.Y. Tang, S.R. Gray, Trace organic contaminant rejection by aquaporin forward osmosis membrane: Transport mechanisms and membrane stability, *Water Research*, 132 (2018) 90-98.
- [55] B.D. Coday, D.M. Heil, P. Xu, T.Y. Cath, Effects of Transmembrane Hydraulic Pressure on Performance of Forward Osmosis Membranes, *Environmental Science & Technology*, 47 (2013) 2386-2393.
- [56] S. Sahebi, S. Phuntsho, J. Eun Kim, S. Hong, H. Kyong Shon, Pressure assisted fertiliser drawn osmosis process to enhance final dilution of the fertiliser draw solution beyond osmotic equilibrium, *Journal of Membrane Science*, 481 (2015) 63-72.
- [57] T.Y. Cath, D. Adams, A.E. Childress, Membrane contactor processes for wastewater reclamation in space: II. Combined direct osmosis, osmotic distillation, and membrane distillation for treatment of metabolic wastewater, *Journal of Membrane Science*, 257 (2005) 111-119.
- [58] Y. Yoon, R.M. Lueptow, Removal of organic contaminants by RO and NF membranes, *Journal of Membrane Science*, 261 (2005) 76-86.
- [59] K.P. Lee, J. Zheng, G. Bargeman, A.J.B. Kemperman, N.E. Benes, pH stable thin film composite polyamine nanofiltration membranes by interfacial polymerisation, *Journal of Membrane Science*, 478 (2015) 75-84.
- [60] Z. Ding, L. Liu, Z. Li, R. Ma, Z. Yang, Experimental study of ammonia removal from water by membrane distillation (MD): The comparison of three configurations, *Journal of Membrane Science*, 286 (2006) 93-103.

Research highlights

- FO-MD hybrid system was successfully used for dewatering fresh and stored human urine;
- During FO, 2 bar hydraulic pressure on the draw side increased the nitrogen rejection by 33%;
- Feed acidification would increase both FO and MD nitrogen rejection;
- Ideally, MD membranes with high porosity and thickness are required to achieve high water flux and low ammonia transfer rate.