# Nitrogen Recovery from Human Urine

# by Membrane Processes

by

Hannah Ray

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Graduate Supervisory Committee:

Treavor Boyer, Chair
Francois Perreault
Shahnawaz Sinha

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# ABSTRACT

This dissertation investigated the use of membrane processes to selectively separate and concentrate nitrogen in human urine. The targeted nitrogen species to be recovered were urea from fresh human urine and unionized ammonia from hydrolyzed human urine. Chapter 1 investigated a novel two-step process of forward osmosis (FO) and membrane distillation (MD) to recover the urea in fresh human urine. Specifically, FO was used to selectively separate urea from the other components in urine and MD was used to concentrate the separated urea. The combined process was able to produce a product solution that had an average urea concentration that is 45–68% of the urea concentration found in the fresh urine with greater than 90% rejection of total organic carbon (TOC).

Chapter 2 determined the transport behavior of low molecular weight neutral nitrogen compounds in order to maximize ammonia recovery from real hydrolyzed human urine by FO. Novel strategic pH manipulation between the feed and the draw solution allowed for up to 86% recovery of ammonia by keeping the draw solution pH <6.5 and the feed solution pH >11. An economic analysis showed that ammonia recovery by FO has the potential to be much more economically favorable compared to ammonia air stripping or ion exchange if the proper draw solute is chosen.

Chapter 3 investigated the dead-end rejection of urea in fresh urine at varying pH and the rejection of unionized ammonia and the ammonium ion in hydrolyzed urine by reverse osmosis (RO), nanofiltration (NF), and microfiltration (MF). When these different membrane separation processes were compared, NF is found to be a promising

technology to recover up to 90% of ammonia from hydrolyzed urine with a high rejection of salts and organics.

Chapter 4 investigated the use of the RO and NF to recover ammonia from hydrolyzed human urine in a cross-flow system where both rejection and fouling experiments were performed. For both RO and NF, ammonia rejection was found to be 0% while still achieving high rejection of TOC and salts, and MF pretreatment greatly reduced the extent of fouling on the membrane surface.

To God who made this all possible

To my family and friends who made this all bearable

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# CHAPTER 1

# INTRODUCTION

Nitrogen (N) is an abundant compound found in the atmosphere and soils, and is required for the human body and plant growth[1]. Although N is necessary for many processes, it can also cause extensive damage in the environment. Consequently, the nutrient necessary for life will inherently destroy life in these areas. Chemical N fixation converts nonreactive N, $N_2$, to reactive N, defined as N that which is radiatively, photochemically, and biologically active on Earth [2]. Accumulation of reactive N in the environment, especially freshwater bodies, can cause eutrophication, toxic algal blooms, and hypoxic zones[3-5]. N pollution in the environment can be traced to many point and non-point sources such as landfills, industry waste disposal, and the greatest contributor, agricultural fertilizer runoff[4, 6]. A study of the Chesapeake Bay found that point sources contributed to roughly half the annual total nitrogen (TN) load to the Patuxent River, one of the Bay's three estuaries[5]. A specific point source of N pollution of concern is the discharge of treated wastewater[6]. Wastewater has been shown to account for 60% of the N inputs in smaller watersheds in Long Island due to the waste coming from New York City. Both Kaneohe Bay, Hawaii and Narragansett Bay, Rhode Island receive 40–80% of their N inputs from wastewater treatment plants[3]. Consequently, removal and/or recovery of the N from waste streams, such as wastewater, before it is sent back into the environment is critical. The current handling and treatment of wastewater could benefit from significant changes that not only improve N removal but strive for N recovery that

would turn a waste stream into a product. One such strategy for improved wastewater treatment is through urine diversion.

## Urine Chemistry and Diversion

The USEPA estimates that the average person produces 88 gallons of wastewater a day at home[7]. Wastewater (black water, yellow water, and gray water) is made up of a number of different nutrients such as N, phosphorus (P), and potassium (K). However, the bulk of these nutrients are attributed to one particular flow: urine. Urine constitutes 80% of the N and 50% of the P in wastewater but only 1% of the volumetric flow[8, 9]. Substantial energy and materials inputs are required at the wastewater treatment plants (WWTPs) to remove N and P from wastewater: 45 MJ/kg N for denitrification and 49 MJ/kg P for phosphate precipitation[10]. However, treatment can be insufficient causing N to accumulate where the wastewater effluent is discharged[3, 4, 6]. Therefore, urine is a small, nutrient dense solution that currently requires extensive energy to treat while still polluting the environment. Diversion and collection of urine separate from the rest of wastewater (urine diversion) will greatly reduce the nutrient concentrations at the WWTP and thus the energy and material requirements. Moreover, urine diversion can result in reduced N and P accumulation in areas of wastewater discharge with the added advantage of recovery of the nutrients in urine to produce products with economic profit.

Once the urine is collected, it will require treatment to remove or recover the nutrients. N is the most abundant nutrient in urine, which averages 11g N/cap/d[11], and coupled with N's industrial applications make it a desirable nutrient to target for recovery over the other nutrients present in urine. Urine has a unique chemistry that must be considered when choosing a specific treatment process. When urine is first excreted from

the body, the N is in the form of urea, the pH is 6, and calcium and magnesium are present[12]. This is referred to as fresh urine. However, the urea in urine undergoes spontaneous urea hydrolysis when it comes into contact with the urease enzyme. Urease is a ubiquitous plant, fungal, and bacterial enzyme present in most bathroom settings[13, 14]. Urea hydrolysis results in the transformation of urea into ammonia and bicarbonate, an elevation of the pH from 6 to 9, and the precipitation of struvite and hydroxyapatite[13-16]. After this occurs, the urine is referred to as hydrolyzed. Consequently, depending on the state of the urine, there are two different forms of N to recover from human urine: urea and ammonia.

Urea and ammonia are both critical compounds used in industry daily. Urea is a fertilizer used worldwide and is the main component in diesel exhaust fluid which is used to reduce the nitrous oxide emissions into N gas[17]. It is also used in the fabrication of resins and in many hand and face creams[18]. Ammonia is also widely used as a fertilizer. In addition, ammonia is used as a refrigerant for process cooling, in textile and pharmaceutical manufacturing, and in the production process of urea [19, 20]. Both N species are currently produced synthetically. Ammonia is first produced through the energy intensive Haber-Bosch process where N's triple bond must be broken [2, 19, 21]. Once ammonia is produced, it is mixed in large, pressurized reactors with carbon dioxide to create urea. The current energy requirements for ammonia production reach up to 12,000 kWh/ton-$NH_3$[19]. Recovery of urea and ammonia from urine could provide a natural, local source of these necessary compounds compared to the current energy intensive, synthetic production process and turn the current linear flow of N use into a circular flow (seen in Figure 1.1).

## Urine Treatment Processes

Numerous recovery processes have been implemented to recover N from urine. Struvite precipitation, nitrification, ion exchange, and ammonia air stripping are the most common and studied processes. Struvite precipitation, nitrification, and ion exchange all recover a charged species of N from urine. However, recovery of urea or ammonia will require advanced processes as recovery of low molecular weight neutral compounds is a more difficult task. Ammonia air stripping has been thoroughly studied in the context of urine and has proven to be effective but at the cost of high energy and chemical inputs ($21.65–24.24/$m^3$ for the most optimized scenarios) [22]. Urea recovery from urine had been an unstudied process until 2018. Urea's small size and uncharged nature as well as its thermolytic stability have made its removal/recovery ineffective. Recently, activated carbon was used as a recovery technique for the urea in synthetic human urine[23]. Activated carbon, while shown to be effective for urea adsorption in synthetic urine, could be problematic due to co-adsorption of pharmaceuticals which are present in real urine. Research has shown that the use of biochar on both synthetic and real urine is effective for up to 90% removal of the pharmaceuticals[24, 25]. Therefore, a recovery process that specifically targets the N in urine while leaving or rejecting the other components in urine is necessary.

Membrane technology is a continuously evolving area of study. The interest in membrane technology for uses other than clean water production is heightening. There is specific interest in both newer membrane processes, such as forward osmosis (FO) and membrane distillation (MD), as well as using more established membrane processes, such as reverse osmosis (RO) and nanofiltration (NF), in more advanced applications. FO and

MD are both low-pressure membrane processes that have the ability to run off of alternative energy sources such as waste heat or solar power[26, 27]. FO operates by using an osmotic pressure gradient between a feed solution and a concentrated draw solution to pull water across a semi-permeable membrane[26]. MD operates using a vapor pressure gradient created by a temperature difference to pull water from a feed solution, across a hydrophobic membrane, into a permeate solution[27]. RO and NF, unlike FO and MD, are high-pressure processes that use pressure to overcome the osmotic difference between the feed and permeate solution to push clean water through a semi-permeable membrane while rejecting unwanted compounds[28]. Urea and unionized ammonia, while not the target of membrane rejection studies, have been reported to have low rejection by membranes (<50%) due to their small size and uncharged nature lessening the ability of rejection by size exclusion or electrostatics[29, 30]. However, this apparent weakness of membrane processes can be used as a selective separation technique for low molecular weight neutral compounds such as urea and unionized ammonia by FO, RO, and NF. The process of N separation by RO and NF is straight forward, where larger unwanted compounds in urine such as salts, organic matter, and microbes are rejected by the membrane while urea or unionized ammonia are able to pass through into the permeate unrejected by the membrane. Through these processes, a pure N product is produced for greater industry application. FO is a similar process but requires the use of a draw solute to create the osmotic pressure difference needed for separation and thus produces a mixed solution of recovered N and the components included in the draw solute. Therefore, much consideration must be given to the draw solute so that it either adds value to the product or can be easily removed from the product. It is important to note that for typical

membrane operation, a high rejection of all constituents is desired. However, for this proposed system, a low rejection of N, either ammonia or urea depending on the condition, coupled with a high rejection of all other constituents is the desired outcome as this corresponds to a high N separation from urine. Lastly, MD can be used to further concentrate the recovered N with significant interest in recovered urea due to its stability in solution unlike ammonia. Therefore, this dissertation investigated the recovery of urea and ammonia by the aforementioned membrane processes.

## Research Questions and Hypotheses

The primary research questions and hypotheses addressed in this dissertation are:

**Research Question 1**

*Can urea be selectively recovered from human urine by forward osmosis and membrane distillation?*

**Hypothesis 1**

*The small size and uncharged nature of urea will allow for it to transfer across the membrane into the draw solution while the other components in urine are rejected.*

**Research Question 2**

*What is the transfer behavior of low molecular weight neutral compounds in an FO system and can that understanding be used to maximize ammonia recovery from hydrolyzed urine by FO?*

**Hypothesis 2**

*Low molecular weight neutral compounds will transfer to achieve concentration equilibrium, and thus by manipulating the pH of the feed and draw solutions to transform*

*ammonia that transfers across the membrane into ammonium, limitations from concentration equilibrium can be overcome.*

**Research Question 3**

*What is the percent rejection of N, specifically urea in fresh human urine and ammonia and ammonium in hydrolyzed human urine, by reverse osmosis and nanofiltration?*

**Hypothesis 3**

*Nanofiltration will have lower rejection of both urea and ammonia compared to reverse osmosis due to nanofiltration's larger pore size, and ammonia will have an overall lower rejection compared to urea regardless of membrane type due to the smaller size of ammonia.*

**Research Question 4**

*What is the percent rejection of ammonia and other constituents of concern in a cross-flow RO and NF system and what is the fouling behavior of the proposed systems with and without microfiltration used as a pretreatment?*

**Hypothesis 4**

*Similar ammonia rejection results will be seen in the cross-flow systems and microfiltration pretreatment will significantly reduce the amount of fouling both organic and bacteria in nature.*

## Organization of Dissertation

The goal of this dissertation was to selectively recover urea and ammonia from human urine through the use of membrane processes, specifically FO, RO, NF, and MD. Each following chapter pertains to work performed to both qualitatively and quantitatively accomplish the overall goal of this dissertation. Chapter 2, which is the subject of a paper published in *Environmental Science: Water Research & Technology*, focused on the demonstration that urea recovery from fresh urine was possible through applications of FO and MD and considered the effect of urine stabilization pre-treatment on the processes. Chapter 3, which is the subject of a paper published in *Environmental Science & Technology*, determined the transfer behavior of low molecular weight neutral compounds across the FO membrane in order to maximize ammonia recovery from real hydrolyzed human urine by FO through novel pH manipulation. Chapter 4, which is the subject of a paper published in the *Journal of Environmental Chemical Engineering*, determined the rejection of different reactive nitrogen species in both fresh and hydrolyzed human urine by RO and NF in a dead-end system. Chapter 5, which is the subject of a paper to be submitted to *Water Research*, confirmed the rejection properties of ammonia by RO and NF in a cross-flow system and assessed the fouling behavior of the two membrane systems in real hydrolyzed human urine. Lastly, Chapter 6 connects overarching conclusions from the interconnected work to help further the understanding of nitrogen recovery from human urine by membranes.

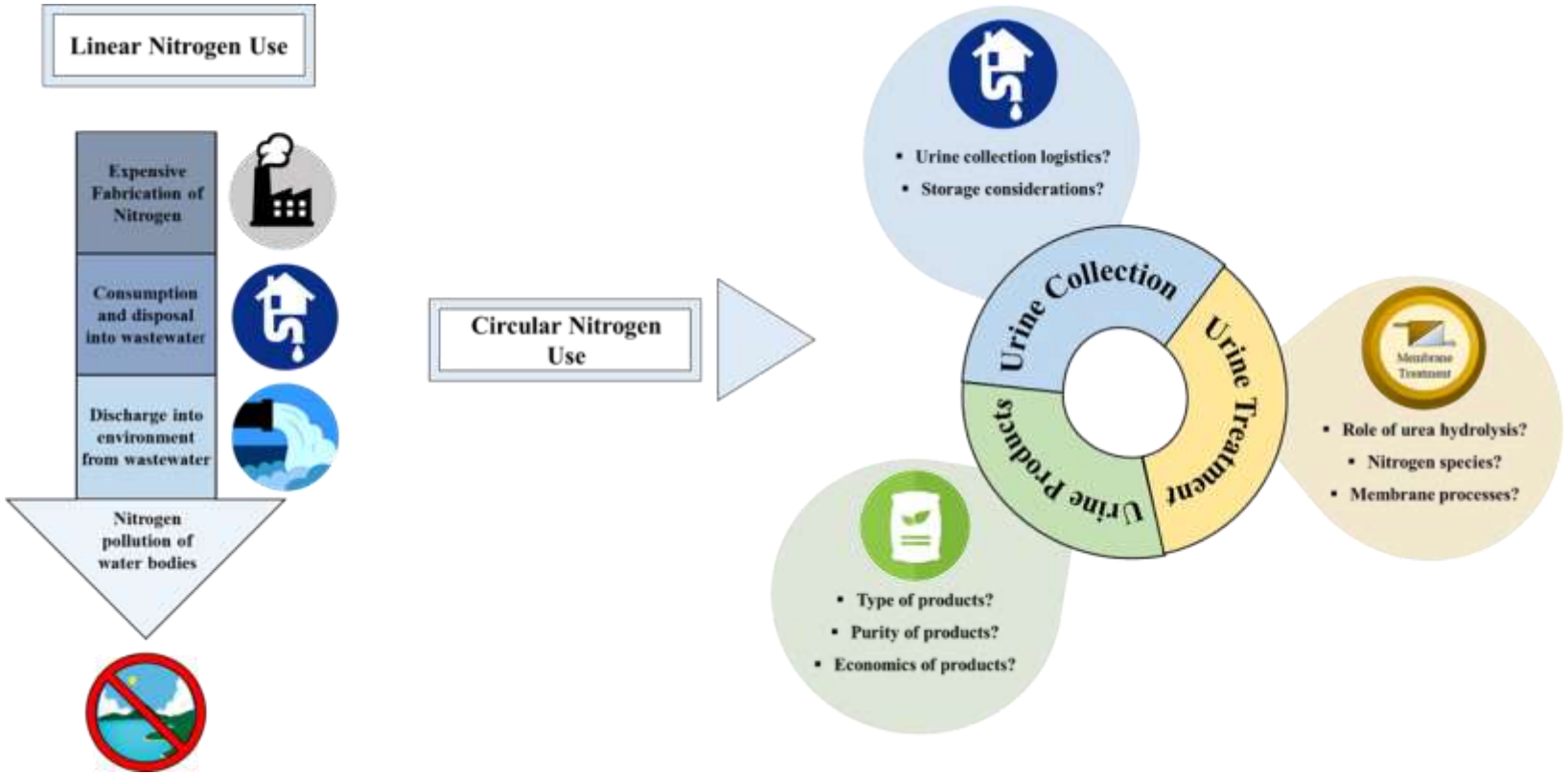

Linear Nitrogen Use
Expensive Fabrication of Nitrogen
Consumption and disposal into wastewater
Discharge into environment from wastewater
Nitrogen pollution of water bodies
Circular Nitrogen Use
Urine Collection
Urine Treatment
Urine Products
Urine collection logistics?
Storage considerations?
Role of urea hydrolysis?
Nitrogen species?
Membrane processes?
Type of products?
Purity of products?
Economics of products?

**Figure 1.1.** A visual representation of both the current flow of nitrogen use and a proposed enhanced flow for nitrogen use. The left side of the schematic shows the current linear flow of nitrogen through fabrication, consumption, discharge, and pollution which has significant environmental and economic consequences such as expensive fabrication and subsequent treatment in wastewater as well as eutrophication, toxic algal blooms resulting in reduced tourism in effected areas and increased expenses to further treat impacted waters. The right side of the schematic shows the proposed change to a circular flow of nitrogen through the collection and treatment of human urine and subsequent production of urine products. While the proposed circular flow may not completely close the gap of nitrogen use, it can effectively reduce environmental and economic consequences. Each step in the circular flow provides necessary questions that need to be answered for implementation of this proposed change which this dissertation sought to answer

# CHAPTER 2

# UREA RECOVERY FROM FRESH HUMAN URINE BY FORWARD OSMOSIS AND MEMBRANE DISTILLATION (FO-MD)

## Proof-of-concept for urea separation and concentration by FO-MD

Urea is a compound that has increased in demand by 100-fold in four decades since the 1960s; the world demand as of 2016 is 177 million tons [17, 21]. Urea is also a compound with many industrial uses such as fertilizer, diesel exhaust fluid, hand creams, deicing of streets and airports, and resin fabrication [21, 31]. Urea used for these applications is synthesized using a multistep process in which ammonia is first produced using the Haber-Bosch process and then mixed in pressurized reactors with carbon dioxide to form urea [21]. The current synthetic production process is highly energy intensive and requires space, resources, and high costs which can become problematic considering the current growth of urea demand worldwide[21, 32]. In addition, the current cradle to grave of urea handling is energy intensive: urea is created from ammonia, used for fertilizer, consumed by humans, excreted, hydrolyzed into ammonia in the sewers, and then extensive energy is used to remove the nitrogen by nitrification/denitrification at the wastewater treatment plant.

Urine, a waste stream, is comprised of, on average, 11 g/cap/day N [11]. Currently, urine, as part of comingled wastewater, is sent to wastewater treatment plants (WWTPs) where the nutrients in urine are treated as contaminants that must be removed to reduce nutrient loading, ecosystem disruption, and eutrophication problems in the environment [33, 34]. Diverting urine from the wastewater stream would significantly reduce the nitrogen and phosphorus concentrations entering the WWTP and, consequently, reduce treatment

costs because urine accounts for 80% of the nitrogen and 50% of the phosphorus in municipal wastewater [8, 34]. Urine diversion would also yield the added benefit of providing a renewable source of urea, which would transform a costly contaminant into an economic asset. As a first step, however, a feasible approach must be devised to separate urea from the other components in urine, and then concentrate the urea for industrial applications.

While research on urine diversion has increased, there is currently no established process for urea recovery from urine or any other liquid waste. Urine diversion research has mainly focused on recovery of phosphorus through struvite precipitation, and recovery of nitrogen in the form of ammonia or ammonium through air stripping, nitrification, ion exchange, or precipitation [33, 35]. Shifting the focus of nutrient recovery to urea could harness an abundant, natural source of urea and provide a renewable and local alternative to the current urea production process but, to achieve urea recovery, processes must be applied in the context of fresh urine. Indeed, when urine is initially excreted from the body, nitrogen is in the form of urea. However, when urea comes into contact with the urease enzyme, a ubiquitous bacterial, plant, and fungal enzyme, it hydrolyzes to form ammonia and bicarbonate [13, 36], which shifts the pH from 6 to 9 and causes the precipitation of struvite and hydroxyapatite (hard inorganic scales that can ruin bathroom fixtures and pipes). After hydrolysis occurs, urea can no longer be recovered. The urease enzyme, which catalyzes this reaction, is abundant in restrooms [16]. Consequently, urea hydrolysis often occurs soon after urine is excreted, making urea unavailable for recovery if urine is not immediately stabilized.

Urea stabilization is vital in urine diversion systems for both operational integrity and nutrient recovery. Urea stabilization is the inhibition of the catalysis functions of the urease enzyme to ensure urea hydrolysis does not occur. Urease activity can be inhibited by the addition of urease inhibitors such as metals (e.g., silver, zinc, or copper), thiols, or fluoride, or by changing the pH of the urine outside of the operating range of the enzyme [37-40]. Recent research has found that the addition of dilute acid such as acetic acid to lower the pH to 4–4.5, or the addition of a base such as calcium hydroxide to increase the pH above 11, can inhibit the hydrolysis reaction [39-44]. Therefore, daily addition of an acid or base to the urinal or urine-diverting toilet would stabilize the urea through the collection system to the point of treatment allowing for urea to be recovered if a treatment system able to efficiently recover urea can be developed.

Membrane processes have been employed in the past for removal of contaminants and concentration/reduction of volume of many different waste streams such as industrial wastewater, landfill leachate, desalination brine, and digested sludge [45-49]. Forward osmosis (FO) is a unique membrane process that utilizes a concentration gradient between the feed and draw solutions over a semi-permeable membrane to pull water out of the feed solution into the draw solution [26]. FO is also an advantageous membrane process due to its reduced fouling propensity and fouling reversibility attributed to the low-pressure operation [26, 50]. Therefore, for the treatment of high fouling feed waters, such as urine, FO is preferable to pressure-driven reverse osmosis (RO) separation. FO's low pressure operation also opens up opportunity for use of alternative energy sources such as waste heat or solar power which could significantly lower its operation costs in comparison to RO. However, urea is a small, uncharged compound [13, 30] and, due to its

small size and uncharged nature, is typically poorly rejected by desalination membranes, both RO and FO membranes, (<50%), which has severely limited the treatment options for urea recovery [29, 30].

This paper describes a proof-of-concept study for a two-step process of FO followed by membrane distillation (MD) to separate and concentrate urea while also considering the effects of urea stabilization. Urea's low rejection by FO membranes was used as a novel way to selectively separate urea from the other components (e.g. salts, trace organics). MD was then utilized to concentrate the separated urea. MD is a thermally-driven separation process that uses a hydrophobic membrane and temperature gradient to concentrate solutions at a low pressure [27]. Volpin et al. (2018) recently showed the effectiveness of FO for urea separation in fresh urine (50%) [51]. In addition, Volpin et al. (2019) investigated the ability of FO-MD on the concentration of ammonium in hydrolyzed urine [52]. MD as a standalone treatment of human urine has recently been investigated for water recovery and nutrient concentration through the concentration of urine as one solution[53, 54]. However, the use of FO-MD as a combined system for urea separation and concentration from human has not been investigated. In addition, the effect of urea stabilization is a key understanding for this hybrid process because of the effect pH can have on membrane operation and urine chemistry. Therefore, the goal of this research was to demonstrate that urea recovery from fresh urine was possible through applications of FO and MD and consider the effect of urine stabilization pre-treatment on the processes. The specific objectives were to: (1) evaluate the effect of urine pre-treatment on urea separation by FO, (2) evaluate the combined effect of urine pre-treatment and FO treatment on urea concentration by MD, and (3)

assess the FO-MD system performance and its implications. Bench-scale FO and MD membrane set-ups with real human urine were used to determine urea separation and concentration, respectively. An economic analysis of the combined FO-MD process was performed to further evaluate the system.

## Materials and Methods

### Fresh urine

Real fresh urine and synthetic fresh urine were both used for this project. Human urine collection was approved as exempt by the Arizona State University Institutional Review Board and informed consent was obtained for any experimentation with human subjects. Real fresh urine was collected from anonymous volunteers, both male and female adults at Arizona State University. The urine was collected using plastic collection trays, and all samples were combined before the start of the experiment. The urine was used within 48 h of collection and the pH was tested to ensure it was in the range for fresh urine reported in the literature (pH 6–6.5) [34, 55]. The synthetic fresh human urine used for experiments was prepared based on previous literature and is detailed in the Table A.1 [39]. The pH of the synthetic fresh urine was adjusted to 6 using sodium hydroxide.

### Acid and base addition chemicals

Acetic acid (ACS grade, Fisher Scientific) was added at a concentration of 26.4 meq/L to decrease the pH for urea stabilization. Calcium hydroxide (ACS grade, Fisher Scientific) and sodium hydroxide (ACS grade, Fisher Scientific) were also used for urea stabilization at concentrations of 5 g/L and 5.4 g/L respectively to increase the pH of the urine above 11.

**Forward osmosis and membrane distillation setups**

Semi-permeable FO membranes (Porifera) were used for all FO experiments. The FO experiments were operated with the active layer facing the feed solution. Hydrophobic GE Polyvinylidene difluoride (PVDF) 0.45 µm 300 mm x 4 m membranes (GE 10600023) were used for all MD experiments. Membrane cells were made by the ASU machine shop, and glass coils by the ASU glassblowing shop. Cole-Parmer flow pumps, tubing, and flow meters were used to circulate and monitor the flow of the solutions in the FO and MD systems. A Cole-Parmer chiller was used for both the FO and MD experiments, and a Cole-Palmer heated bath was used for all MD experiments. A Sartorius microbalance was used to track the increase in weight during the experiment to determine the flux of the FO and MD systems. WinWedge, a computer software, connected the balance to Microsoft Excel to log the data. pH and conductivity meters were used to take readings for all samples. Specific details on the materials can be found in the Appendix A.

**Forward osmosis experiments**

Four liters of fresh urine was used as the feed solution for all experiments. Two liters of 1 M NaCl was used as the draw solution for all experiments. Both the draw solution and feed solutions were circulated through chilled water at 18 °C. A cross-flow velocity of 0.00258 m/s was used for all experiments. The experiments were operated for 24 h. Forty milliliter samples were taken at 0, 1, 6, 12, and 24 h from the draw and feed solutions. Conductivity and pH readings were taken immediately, the samples were filtered through 0.45 µm filters, and then stored at 4 °C for further analysis. The samples

were analyzed for urea, TN, and TOC. The volume of the draw solution at the end of the experiment was measured and the solution was stored at 4 °C.

**Membrane distillation experiments**

The product draw solution from the FO experiment was used as the feed solution for the MD experiments. The volume of feed solution depended on the FO experiment but was in the range of 2100–2600 mL. One liter of DI water was used as the permeate solution. The experiment was run on a 45 °C temperature difference between the feed solution (65 °C) and the permeate solution (20 °C). To achieve this temperature difference, the chiller was set to 8 °C and the heater was set to 87 °C. A fiber and foil based radiant barrier was wrapped around the feed solution carboy for insulation. Before the start of the experiment, the feed and permeate solutions were circulated through the system with the membrane cell valves turned off, so the solution did not cross the membrane, for 15 min to achieve the necessary temperature difference by the start of the experiment. The MD experiments followed the same procedure as the FO experiments for sample collection and analysis.

**Cleaning procedure**

The membrane systems were cleaned immediately after each experiment using the following procedure: tap water rinse, 10% bleach for 15 min, tap water rinse, 5 mM EDTA for 15 min, tap water rinse, DI water with NaOH added to increase the pH to 11 for 15 min, tap water rinse, and three DI water rinses each for 10 min.

**Analytical methods**

All samples were filtered before analysis through 0.45 μm nylon syringe filters (Environmental Express). Urea was analyzed using a urea assay kit (Bioassay Systems,

DUR-100) and a BioTek Synergy H1 Hybrid Multi-Mode Reader plate reader following the procedure detailed in the assay manual. All samples were analyzed in triplicate to ensure precision. Urea results were confirmed through analysis of TN. TOC and TN were both analyzed using a Shimadzu TOC-L/TNM-L Analyzer. Fourier-transformed infrared (FTIR) spectra results were collected for each membrane using a Thermo Nicolet 6700 spectrometer. Further detail can be found in the SI.

**Data analysis**

Visual MINTEQ 3.1, a chemical equilibrium software, was used to determine saturation indices for the minerals produced by the elevated pH. The components of urine were entered at their appropriate concentrations at the elevated pH of 12.5. Saturation indices provided by the software were used to determine oversaturation of minerals and thermodynamically favorable precipitations that would occur within the solution. IBM SPSS Predictive Analytics was used to run One-Way ANOVA tests with Post-Hoc tests. The parameters chosen were descriptive for the One-Way ANOVA test and Tukey with an alpha value of 0.05 for the Post-Hoc test.

For the economic analysis, operating costs only were considered. FO operating costs were determined to be $\$1.15/m^3$ [56]. MD operating costs were determined to be $\$1.17/m^3$ [57]. Both FO and MD operating costs were based on previous economic analyses. It has been reported that the use of alternative energy for MD operation reduces the costs from $\$1.17/m^3$ to $\$0.5/m^3$ [58, 59]. The same ratio was then applied to the above FO operating cost. All chemical costs were based on prices from Alibaba[102] and reclaimed water prices were based on rates from the Pasco County rates in Florida. All calculations were made based on the treatment of 100 $m^3$ of urine.

## Results and Discussion

### Urea separation by forward osmosis

Five fresh urine pre-treatment conditions were used to understand the effect of urine pre-treatment (acid or base addition) on both FO and MD as separate membrane processes and as combined two-step process. The five urine conditions tested were real fresh urine, real fresh urine with acetic acid, real fresh urine with calcium hydroxide, real fresh urine with sodium hydroxide, and synthetic fresh urine with sodium hydroxide. To assess the membrane performance for each urine pre-treatment condition, both water flux and urea flux were evaluated. A more stable water flux indicates less fouling and the ability for increased operation over time. As determined by dead-end FO experiments, urea transfer across the membrane is dependent on concentration equilibrium of urea. However, increased water passage across the membrane can ensure a greater amount of urea separation in a certain time period. Fig. 2.1 (a) shows the average cumulative permeate volume results for urea separation by FO for the five fresh urine pre-treatment conditions performed in duplicate. Cumulative permeate volume vs. normalized flux allows for comparison of the membrane operation for different types of solutions and accounts for possible variations in membrane permeability. The real fresh urine condition (open squares) had the greatest amount of water passage throughout the 24 h, and the flux steadily declined over time due, presumably, to organic and biological fouling. The real fresh urine with acetic acid (yellow triangles) and the synthetic fresh urine with sodium hydroxide (black stars) had similar water passages over time. However, the synthetic fresh urine with sodium hydroxide had a much greater decline in flux than the real fresh urine with acetic acid. The real fresh urine with calcium hydroxide (blue circles) and real

fresh urine with sodium hydroxide (black diamonds) had similar low water passages and steep declines in flux over time. Each FO experiment was performed in duplicate. Figure A.1 shows the graphed comparison of the duplicate FO experiments for each condition.

Fig. 2.1 (b) shows the urea separation by FO for the five fresh urine pre-treatment conditions. The urea separation is represented by $C/C_{o,}$ because each real fresh urine pre-treatment condition used a different batch of collected urine. Fresh urine can vary greatly in urea concentration (9.3–23.3 g/L) [12]. Table 1.1 shows the average urea recovery percentages and Table A.4 shows the actual t = 0 h and t = 24 h urea concentrations for FO for each condition. The average urea separation for the real fresh urine (blue bar) and synthetic fresh urine with sodium hydroxide (pink bar) conditions were the greatest, at 20% and 21% respectively. The urea separation for the real fresh urine with acetic acid (red bar) was 15%. Real fresh urine with calcium hydroxide (green bar) and real fresh urine with sodium hydroxide (yellow bar) separated 12% and 11% of the urea. Therefore, for this system, the urea rejection by the FO membrane ranged from 79–89%.

It is important to note that for implementation of urine diversion, urine pre-treatment will be necessary, whether acid or base, for the operating integrity of the collection systems. Saetta and Boyer (2017) found that spontaneous hydrolysis of fresh urine was inevitable in a nonwater urinal setting [41]. Urea hydrolysis of urine results in the precipitation of hard minerals that ruin urine collection systems and plumbing [15, 16]. In addition, urine pre-treatment preserves the nitrogen in the form of urea for recovery. Therefore, positive results for the real fresh urine condition does not mean it is the favorable choice for operation, rather the real fresh urine condition results were used to further understand the acid and base conditions. Real fresh urine with acetic acid had

lower water passage compared to the real fresh urine condition but it was more effective in terms of water passage and flux decline in comparison to the real urine with base addition experiments. Chen et al. (2015) demonstrated that acetic acid can act as a metabolic signal for bacteria that stimulates biofilm formation [60]. Acetate is an easily available carbon source for microorganisms and has been used to enhance microbial growth in wastewater [61]. Thus, if biofouling was occurring on the membrane, which is highly likely due to the high organic material found in urine as well as high possibility for bacteria, the addition of acetic acid allowed for a hospitable environment for increased biofilm growth. Biofilm growth on the membrane hinders the water passage over time [62], which would also decrease the flux of urea across the membrane. Acetic acid is a favorable urine pre-treatment condition due to its ease of use, efficacy as a urea hydrolysis inhibitor, and cost effective nature [39]. Preliminary plate tests on the membrane surface for the fresh urine condition revealed high bacteria counts which confirms the presence and growth of bacteria in a 30 hr. time period. Figure A.3 shows pictures of the plates and their colony-forming unit counts. Implementation of a filtration pre-step to remove the larger organic material and bacteria that can build biofilms on the membranes could enhance the membrane operation and thus urea separation making it a more effective urine pre-treatment condition for FO.

The real fresh urine with calcium hydroxide and sodium hydroxide performed especially poor for FO with steep declines in flux, little water passage, and low urea separation (11% and 12% respectively) over the 24 h. One reason for the poor performance is that raising the pH of the fresh urine decreases the solubility of magnesium minerals which results in their supersaturation and precipitation out of

solution. A large amount of precipitation was observed in the urine immediately after the base was added. Visual MINTEQ 3.1 was used to confirm and Table A.2 shows the saturation indices for fresh urine at pH 12.5. Brucite, magnesium chloride, magnesium hydroxide, and magnesium phosphate are all supersaturated at a pH of 12.5. Precipitation of these minerals would build up on the membrane, hindering water passage and reducing the flux of both water and urea. The buildup of minerals on the membrane could also trap more organic material such as the many metabolites and proteins found in human urine. Monahan et al. (1995) found that whey proteins exhibited extensive irreversible protein unfolding at pH 9 and 11 at room temperature [63]. In addition, Meireles et al. (1991) reported that proteins such as albumin were not by nature foulants unless denaturation occurs [64]. It was also determined that long term fouling of ultrafiltration membranes was highly linked to protein denaturation [64]. Consequently, the proteins in human urine may have denatured at the high pH and further fouled the membrane.

The synthetic fresh urine with sodium hydroxide experiments were performed to determine whether the poor performance of the base addition experiments was due to the high pH which could have altered the membrane surface or the membrane fouling acerbated by the presence of organic material. The synthetic fresh urine with sodium hydroxide condition was chosen because of its high pH and lack of organic material and microorganism. Therefore, unlike the real fresh urine conditions which can experience inorganic fouling by scaling as well as organic fouling and biofouling, the synthetic fresh urine with sodium hydroxide can only experience inorganic scaling. Fig. 2.1 shows the synthetic fresh urine with sodium hydroxide passing a greater amount of water than the two real fresh urine with base addition conditions. However, the synthetic solution did

experience a steep drop in flux. This was most likely due to the inorganic scaling of the membrane due to the minerals that precipitated at the high pH. The synthetic fresh urine with sodium hydroxide condition did have higher separation of urea compared to the two real fresh urine with base conditions (21% vs. 11–12%). This supports the explanation that organic fouling of the membrane reduced the water and urea flux for the real fresh urine with base addition conditions.

Visual analysis of the FO membranes after 24 h of operation with fresh urine revealed membrane fouling in varying degree for all conditions, which was further characterized by FTIR analysis. Fig. 2.2 show a greater number of functional group peaks at higher intensities on the membrane surfaces for the real fresh urine with calcium hydroxide (green line) and real fresh urine with sodium hydroxide (yellow line) conditions than for the real fresh urine (blue line) and real fresh urine with acetic acid conditions (red line). There is a high number of intense peaks indicative of carbon-based compounds, such as C–H and C–OH. Presence of C–O with derivatives such as C–O–C suggest the presence of polysaccharides. Methyl C–H bending indicates that carboxylic acid groups are present on the membrane surface which is representative of many different organic materials in urine. The FTIR trends demonstrate that there is more organic material on the surface of the membrane for the real fresh urine with base conditions. Table A.3 shows the TOC content in the draw solution at t = 24 h. To understand how much organic matter passed through the FO membrane, the TOC content accounted for by the urea concentration at t = 24 h was calculated and subtracted from the total TOC content at t = 24 h. Consequently, the TOC concentrations shown in Table A.5 is that which is not accounted for by urea and can thus be attributed to organic matter that

transferred from the feed solution into the draw solution. For the real fresh urine with acid and base conditions, the TOC content ranged from 70–107 mg/L C. Moreover, for the acid addition, acetic acid will contribute to the TOC concentration and therefore the TOC not attributed to acetic acid will be even smaller than the reported concentrations which are already very small amounts (≤ 3% permeation). As seen in Table A.3, for all experiments, ≤ 6% of TOC transferred from the feed to the draw solution.

A statistical One-Way ANOVA test with a Tukey Post Hoc test and alpha value of 0.05 was performed on the FO urea separation percentages. Figure A.2 shows the grouping of statistical differences for each condition. The symbols a, b, and ab are used to differentiate the conditions with statistical differences and those without a statistical difference. The results determined there were two subsets denoted by a and b with one condition falling in both subsets which is denoted by ab. Conditions with the same symbol do not have a statistical difference while conditions with different symbols do have a statistical difference. The test determined that for synthetic fresh urine with sodium hydroxide (a), real fresh urine (a), and real fresh urine with acetic acid (ab), there was no statistical difference between the conditions for urea separation. For real fresh urine with acetic acid (ab), real fresh urine with calcium hydroxide (b), and real fresh urine with sodium hydroxide (b) there was also no statistical difference for urea separation. Both the synthetic fresh urine with sodium hydroxide (a) and real fresh urine (a) had a statistical difference from the real fresh urine with sodium hydroxide (b) and real fresh urine with calcium hydroxide (b). The common condition in the two subsets was the real fresh urine with acetic acid (ab) which did not have a statistical difference with any urine condition.

While the statistical results demonstrate the real fresh urine with base conditions as not having a statistical difference from the real fresh urine with acetic acid condition, this is for urea separation alone which cannot be the only factor considered for a membrane process. The base conditions had considerably more membrane fouling, which in a large-scale industrial system would require daily membrane cleaning as well as frequent membrane replacement which are costly and undesirable. However, the inorganic and organic fouling could be mitigated by a process that reduces the precipitates which caused inorganic fouling and also removes organic material in urine to reduce biofilm growth. Ouma et al. (2016) demonstrated that ultrafiltration of hydrolyzed urine was successful at reduction of suspended solids by 99% [65]. Lin (2017) found that at pH 10 NF90 nanofiltration membranes were able to reject >90% of the pharmaceuticals and personal care products tested in the presence of humic acid, alginate, and silica which represent biological, organic, and colloidal fouling [66]. pH 10 was found to be optimal in comparison to neutral or acidic pH [66]. Thus, a membrane filtration pre-treatment could be advantageous to remove particulates, organic material, and bacteria that could make the fresh urine with base conditions a competitive operating condition for FO.

For FO operation, the real fresh urine, synthetic fresh urine with sodium hydroxide, and real fresh urine with acetic acid had no statistical difference and were the most effective for urea separation. The synthetic fresh urine with sodium hydroxide performed well due to its lack of organic material, which is unrealistic, and the real fresh urine performed well due to its lack of addition of an acid or base for urea stabilization, which in a real world setting is critical. Therefore, when membrane performance such as water passage, flux decline, and fouling were considered, the real fresh urine with acetic

acid was the most effective choice for FO operation. Application of a membrane filtration step, such as ultrafiltration, could enhance the overall performance of both the acid and base conditions. The novel application of FO to separate urea from real fresh urine was achieved. Considering the range of industrial uses of urea, MD was evaluated as a urea concentration step following urea separation by FO.

**Urea concentration by membrane distillation**

Fig 2.3. (a) shows the cumulative permeate volume results for urea concentration by MD for the five fresh urine pre-treatment conditions. Of importance is that the solution that was applied to MD was the product draw solution from FO. This solution contained 1 M NaCl, the urea separated from the fresh urine condition during FO, and any other compounds in small amounts that could have permeated through the membrane. By the end of the FO experiments, the pH of the draw solutions resembled that of the fresh urine pre-treatment conditions. The pH of the draw solutions for the fresh urine condition, fresh urine with acid, and fresh urine with base were as follows: 6.5, 4.5, and 12.5.

The flux for each fresh urine condition remained relatively constant, unlike in FO, while the total water passage varied for each condition. The total water passage was highest for the fresh urine with base conditions, followed by the real fresh urine condition; the real fresh urine with acetic acid passed the least amount of water. The flux and water passage for the two real fresh urine with base conditions were more erratic than that of the real fresh urine and real fresh urine with acetic acid conditions. This can be explained by any change in temperature that could have occurred during the experiment. The temperature gradient is the driving force for MD. Thus, if the indoor temperature

changed overnight which had been observed, it could cause the flux to respond erratically. Fig. 2.3 (b) shows the results for urea concentration, by concentration factor, for MD. Concentration factor was chosen due to both the varying concentrations of urea in the initial urine batches as well as the varying urea separation percentages by FO. Representation of the data by the concentration factor of urea allows for comparison solely of the MD process without any bias from the FO process. Table 2.1 shows the average concentration factors and average final MD product concentrations for the five fresh urine pre-treatment conditions. For the real fresh urine, real fresh urine with acetic acid, real fresh urine with calcium hydroxide, real fresh urine with sodium hydroxide, and synthetic fresh urine with sodium hydroxide conditions, the average concentration factors of urea by MD at t = 24 h was 2.1, 1.9, 2.3, 3.3, and 2.1, respectively. Table A.4 details the urea recovery percentages for MD. For all fresh urine conditions, the average recovery percentages range from 77–92%. The statistical ANOVA test on the MD concentration factors of urea showed there was no statistical difference between any of the fresh urine conditions. As stated previously, membrane performance must also be considered to assess the overall operation of urea concentration by MD for a specific pre-treatment condition.

For the real fresh urine and real fresh urine with acetic acid conditions, a large amount of orange precipitate was observed within the system. The tubing, flow meters, and membranes all showed signs of the orange precipitate. The three fresh urine with base conditions did not show any signs of this precipitation. This can be explained by the high pH inhibiting the formation of organic fouling throughout the system. Basic/alkali solutions are used as MD chemical cleaners due to their effective ability at removing

organic fouling [67]. In addition, the salting out effect of organic material at high ionic strength solutions is another explanation for the precipitation [68, 69]. For the real fresh urine with base conditions, much of the organic material was trapped on the FO membranes causing their poor FO performance. As stated previously, urine contains many metabolites, proteins, and other organic material. Thus, those molecules could have been trapped on the thick fouling layer of the FO membrane and therefore were not in the MD feed solution for the base conditions. However, the real fresh urine and real fresh urine with acetic acid did not have as much organic material built up on their respective FO membranes, demonstrated by the FTIR results, and thus allowing the organic material such as small metabolites to pass through the membrane into the draw solution. MD reduced the feed solution volume greatly for all pre-treatment conditions, ~2200 mL to ~800 mL. This reduction in volume causes a considerable increase in ionic strength for the feed solution as it contains the 1 M NaCl used as the draw solute during FO. Organic molecules decrease in solubility as ionic strength increases [68, 69]. Therefore, as the ionic strength increased during the MD experiments for the real fresh urine and real fresh with acetic acid conditions, the organic compounds precipitated out of solution and caused the observed organic fouling. FTIR analysis of the MD membranes, Fig. 2.4, show the real fresh urine with base conditions having lower intensity peaks compared to the real fresh urine and real fresh urine with acetic acid. Future research which focuses on the transport of urinary metabolites and other smaller organic compounds through both the FO and MD processes could help identify the areas where improvement could alleviate the MD system fouling for the acid and fresh urine pre-treatment conditions. While the statistical test found no statistical difference between the conditions for concentration of urea, this

does not consider fouling of the system. The orange precipitation which occurred in the tubing, flow meters, and glass heating coils during operation of the real fresh urine and real fresh urine with acetic acid was irreversible. Therefore, for MD operation, MD of the draw solutions coming from FO of real fresh urine with base addition were the most optimized conditions for water passage, urea concentration, and reduced fouling.

**FO-MD system performance and implications**

Urine pre-treatment with acid and base had varying effects for each membrane process. Table 2.1 shows the overall performance of each condition with the last column showing the urea concentration in the final product compared with the initial concentration of urea in urine. For the real fresh urine, real fresh urine with acetic acid, real fresh urine with calcium hydroxide, real fresh urine with sodium hydroxide, and synthetic fresh urine with sodium hydroxide, this value was 61%, 45%, 45%, 65%, and 68%. Statistical tests on this value found no statistical difference between any of the fresh urine conditions. However, membrane operation (i.e., water passage, flux, and fouling) must be taken into account when assessing membrane system performance. Consequently, for FO operation, acid addition was the most optimal, yet for MD, base addition was the most optimal. While the two membrane processes did not converge on a single urine pre-treatment, implementation of a membrane filtration step to remove precipitates, organics, and bacteria could significantly enhance the base addition conditions during FO and the acid addition condition during MD. The results of this study show that FO-MD was effective for urea recovery.

Looking beyond the proof-of-concept evaluation of this work, the draw solute and pre-treatment require future research to understand the full potential of the combined

system. Sodium chloride, a common draw solute highly studied in the literature, was chosen for proof-of-concept understanding of the urea separation by FO. If a pure urea solution is the desired product, NaCl would hinder any future use of the urea. Therefore, for implementation of this combined membrane process (FO-MD), a more suitable draw solute should be investigated. Trimethaylamine-carbon dioxide, water-soluble magnetic nanoparticles, and water-soluble thermoresponsive nanoparticles have all been shown to be effective, advanced draw solutes [70-73]. The trimethaylamine-carbon dioxide can be removed through heating the solution which could occur during the MD process. The magnetic nanoparticles can be removed using a magnet. Both these options allow for reuse of the draw solute which reduces cost and waste. The implementation of these draw solutes into the FO membrane process could not only improve the purity of the urea product but also increase the water passage and thus the urea separation. Honer et al. (2017) developed a method to produce soluble urea fertilizer ionic cocrystals from calcium and magnesium minerals containing urea [74]. The fertilizer has nitrogen stabilization properties that allows for reduced nitrogen loss during fertilization [74, 75]. The use of magnesium or calcium as draw solutes would allow for high osmotic pressure, less reverse salt flux compared to sodium or chloride, and reduced costs compared to more advanced draw solutes. In addition, the urea product from MD containing calcium and/or magnesium could then be used to produce a fertilizer product by the aforementioned process.

Table 2.2 shows an economic analysis of each condition for the operation of the FO-MD system for urea and water recovery from the treatment of 100 $m^3$ of fresh human urine. The analysis considers the operation costs of FO and MD which includes the

electricity needed for the pumping, cooling, and heating. Additionally, the chemical input cost is also included in the total cost of operation. The analysis includes offsets from the produced urea and clean water which can be used for reclaimed water purposes. Two different scenarios are considered for the analysis: the current system total and an ideal system total which includes 50% FO urea recovery and reduced FO-MD operation costs due to alternative energy use. Volpin et al. (2018), Volpin et al. (2019), and Engelhardt et al. (2019) found that 50% rejection of urea and thus 50% separation was able to be achieved by an FO membrane [51, 56, 76]. Therefore, if the pre-treatment steps mentioned above are applied, 50% urea recovery is possible which would greatly affect the offset benefits. Alternative energy use such as solar power and waste heat are an active area of research for both FO and MD operation. Previous economic analyses have determined that alternative energy use has the potential to greatly reduce the energy requirements for operation. Calculations were performed to determine the FO urea recovery percentage necessary for each condition to breakeven with alternative energy use included.

The economic analysis showed that the operation of the FO-MD system with the current urea recovery rates produced a negative cost ranging from $143–238. However, if the urea recovery is increased to 50% for each condition and alternative energy use is included, the cost of operation changes from a negative cost to a profit ranging from $2.05–84.65. The breakeven FO urea recovery percentages ranged from 24–49% while the current recovery percentages ranged from 11–20%. Therefore, increasing the FO recovery percentages by even 10% can greatly affect the cost of operation. The fresh urine condition is the most profitable as it does not require a chemical input but, as discussed above, is not a condition that could be applied due to the necessity for urea

stabilization. The two base addition conditions are similar in costs and are the most profitable in terms of urea stabilization conditions. The acetic acid addition condition is the least profitable and that is due to the high industry cost of acetic acid in comparison to calcium hydroxide or sodium hydroxide. The economic analysis demonstrates that the choice of chemical for urea stabilization can affect not only the overall operation of the system but the overall profitability of the system and should be carefully considered when setting system parameters.

Therefore, while the current system is not profitable, increasing the FO recovery which has been thoroughly discussed above and the use of alternative energy which is an active research area has the potential to make this combined system profitable. This system does not include the additional offsets that come from the reduced wastewater treatment costs which has been estimated to be as high as $\$6.2/m^3$ [56]. This would produce an offset that is roughly 2–3 times more than the current system total costs. In addition, further treatment of the concentrated human urine can produce phosphorus and potassium products such as struvite and potash which are both fertilizer products with economic value.

## Conclusions

- This study assessed and confirmed the ability of FO to separate urea from human urine.
- Urea stabilization pre-treatment by acetic acid addition was determined to be the most effective FO operation condition for urea separation, increased flux, and reduced fouling.

- A high pH was determined to be the most effective parameter for MD operation and urea concentration due to the reduced fouling observed in the high pH environment.
- The combined membrane system of FO-MD was determined to be an effective process that separates and concentrates urea from human urine.
- The economic analysis of the current system shows an overall cost of $173–268. However, increasing the FO recovery to 50% and the use of alternative energy changes the cost to a profit ranging from $2–85. The most to least profitable for the fresh urine conditions is fresh urine > fresh urine with calcium hydroxide > fresh urine with sodium hydroxide > fresh urine with acetic acid.

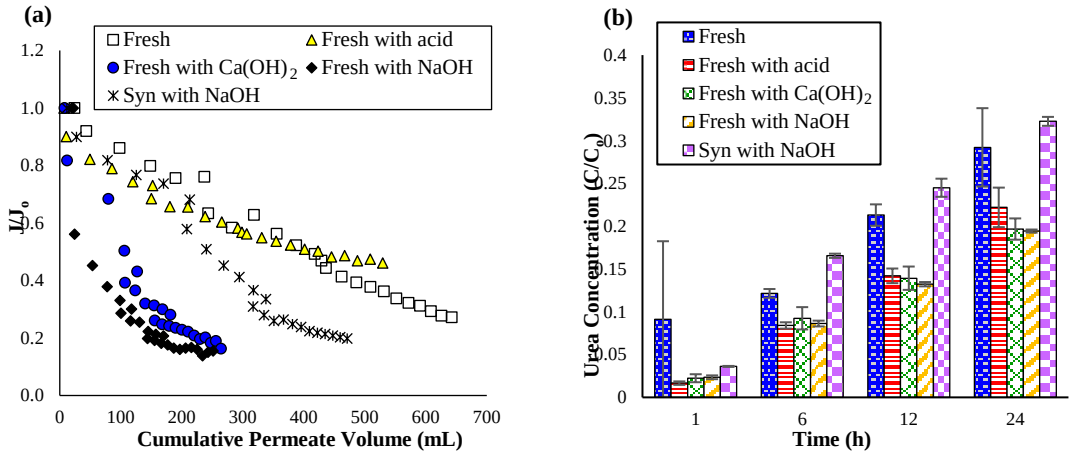



**Figure 2.1.** Forward osmosis operation and urea separation results for the 5 fresh urine conditions. (a) is the normalized water fluxes as a function of cumulative permeate volume (mL) for the forward osmosis experiments and are mean values from the duplicate runs. (b) is the urea separation and are mean values ± one standard deviation for duplicate runs. The experiment ran for 24 h.

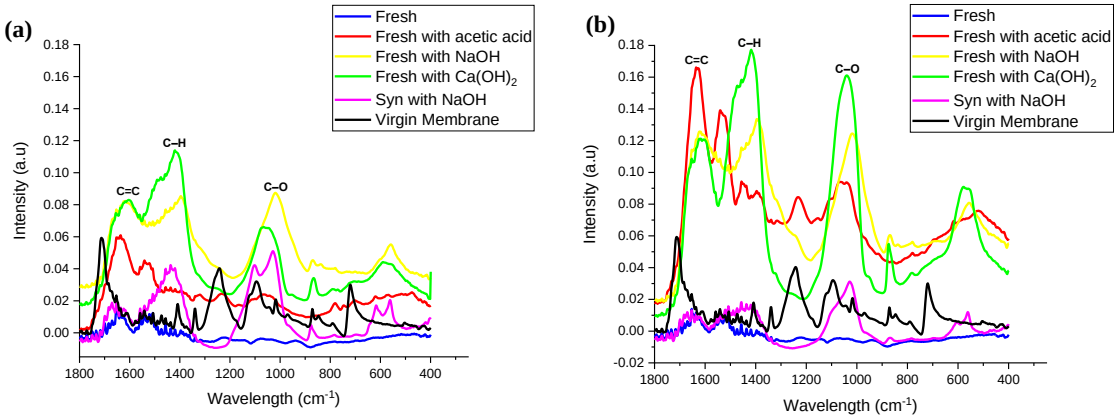



**Figure 2.2.** Fourier-transform infrared spectroscopy (FTIR) of the membrane surfaces for the 5 fresh urine conditions for the forward osmosis experiment(a) are the results for the first test and (b) are the results for the duplicate tests.

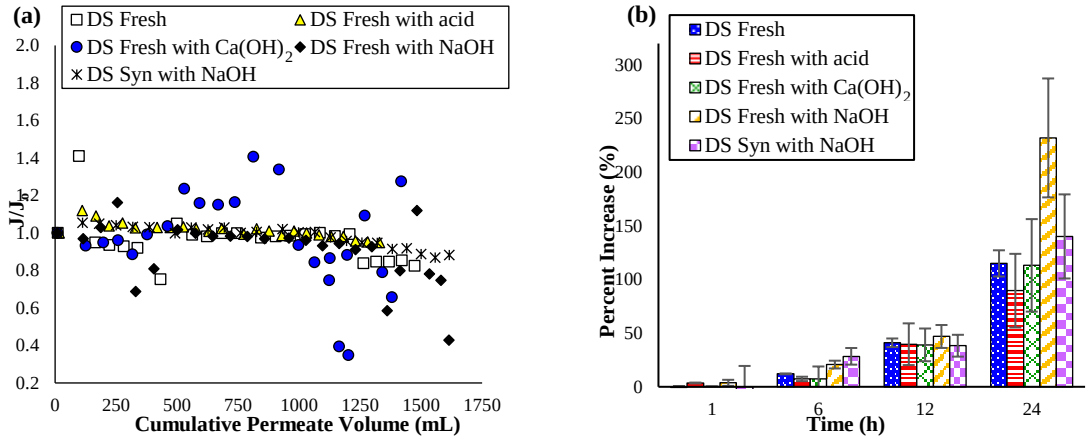



**Figure 2.3.** Membrane distillation operation and urea concentration results for the 5 fresh urine conditions. (a) is the normalized water fluxes as a function of cumulative permeate volume (mL) for the membrane distillation experiments and are mean values from the duplicate runs. (b) is the urea concentration factors and are mean values ± one standard deviation for duplicate runs. The experiment ran for 24 h.

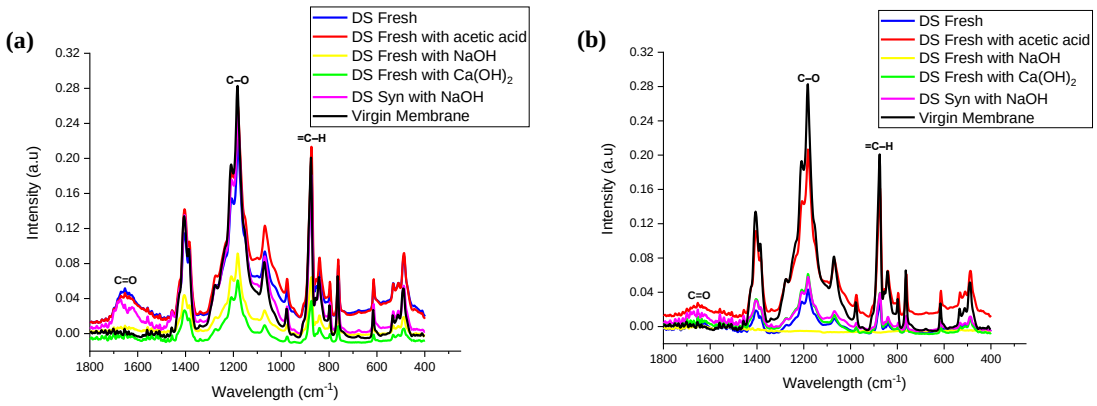



**Figure 2.4.** Fourier-transform infrared spectroscopy (FTIR) of the membrane surfaces for the 5 fresh urine conditions for the membrane distillation experiments. (a) are the results for the first test and (b) are the results for the duplicate tests.

**Table 2.1.** Percent recovery of urea for FO, average MD urea concentration factors, and the average final MD urea concentration when compared to initial urine urea concentration. Values are averages of the duplicate runs.

| Urea Recovery for FO and MD | | | |
|---|---|---|---|
| **Urine Condition** | **FO %Recovery** | **MD Concentration Factor** | **Final MD Concentration Compared to Urine (%)** |
| **Fresh** | 20 | 2.1 | 61 |
| **Fresh with acetic acid** | 15 | 1.9 | 45 |
| **Fresh with base ($Ca(OH)_2$)** | 12 | 2.3 | 45 |
| **Fresh with base (NaOH)** | 11 | 3.3 | 65 |
| **Synthetic fresh with base (NaOH)** | 21 | 2.1 | 68 |

**Table 2.2**. An economic analysis of the operating costs and benefits for urea recovery by FO-MD. Calculations were based on the treatment of 100 $m^3$ of urine. Amounts in red mean a net negative output while amounts in green mean a net positive output.



| Economic Analysis of FO-MD Operation | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Fresh Urine Condition** | **Chemical Addition** | **Chemical Amount** | **Chemical Cost** | **FO+MD Operation** | **Urea Production** | **Urea Cost** | **Water Production** | **Water Offset** | **Total** | **Breakeven FO %Recovery** | **50% FO Recovery + Alt. Energy** |
| 1 | - | - | - | $2.32/m³ | 1.3 kg/m³ | $0.35/kg | 0.31 m³ produced/m³ treated | $0.65/m³ | $172.85 | 24% | $84.65 |
| 2 | Acetic acid | 1.6 kg/m³ | $0.5/kg | $2.32/m³ | 0.88 kg/m³ | $0.35/kg | 0.27 m³ produced/m³ treated | $0.65/m³ | $268.05 | 49% | $2.05 |
| 3 | Calcium hydroxide | 5 kg/m³ | $0.17/kg | $2.32/m³ | 0.95 kg/m³ | $0.35/kg | 0.24 m³ produced/m³ treated | $0.65/m³ | $204.90 | 31% | $63.10 |
| 4 | Sodium hydroxide | 5.4 kg/m³ | $0.3/kg | $2.32/m³ | 0.75 kg/m³ | $0.35/kg | 0.34 m³ produced/m³ treated | $0.65/m³ | $217.40 | 33% | $56.60 |

# CHAPTER 3

# AMMONIA RECOVERY FROM HYDROLYZED HUMAN URINE BY FORWARD OSMOSIS WITH ACIDIFIED DRAW SOLUTION

## Use of potassium phosphate to separate ammonia from hydrolyzed urine

Ammonia is a critical compound in high demand due to its numerous industrial applications such as a fertilizer, plastic and adhesive manufacturing, refrigerant gas, and as a precursor compound in urea production [19, 77]. The Haber-Bosch process is the most common method for ammonia production which has extensive energy requirements of 12,000 kWh/ton-$NH_3$[19]. In addition to a high energy demand, ammonia is a major contaminant of surface and groundwater sources which can threaten water security[6]. While nonpoint sources such as agricultural and urban runoff are large contributors of ammonia pollution, wastewater effluent can be a significant point source polluter of ammonia in water bodies causing detrimental effects such as eutrophication and toxic algal blooms[3, 4, 6]. Therefore, there is a substantial need for new approaches to manage ammonia pollution. New technologies that are energy efficient as well as reduce ammonia discharge are strongly desired. This leads to a focus on recovery and reuse of untapped waste streams that are rich with ammonia. One such waste streams is human urine.

Human urine is a nitrogen dense waste stream, averaging 11 g N/person/day[11], that is currently sent to wastewater treatment plants (WWTPs) where energy demands of 45 MJ/kg N for nitrogen removal and 49 MJ/kg P for phosphorus removal are expended to reduce eutrophication effects downstream of wastewater discharge[10]. On average, urine constitutes 80% of the nitrogen and 50% of the phosphorus in wastewater while only

contributing 1% of the volumetric flow [8, 9]. However, even with nutrient removal techniques at the WWTP, ammonia ($NH_3$ and $NH_4^+$ depending on composition) contamination still occurs downstream of effluent discharge as the removal techniques are not completely effective. Therefore, diversion of urine from the rest of wastewater not only reduces the nutrients at the wastewater treatment plant, the energy needed to remove them, and their ability to end up in effluent discharge, but also adds the potential for recovery of the nutrients which can be an economic stimulus[10].

Human urine exists in two states, fresh and hydrolyzed which dictates the form of nitrogen able to be recovered. In fresh urine, the dominant form of nitrogen is urea. After contact with the ubiquitous urease enzyme, the urea is hydrolyzed into ammonia which becomes the dominant form of nitrogen and the urine is then considered hydrolyzed[13, 36]. Therefore, for ammonia recovery (both $NH_3$ and $NH_4^+$ which is dependent on the pH), the urine must be hydrolyzed. Current recovery methods for ammonia from urine include ammonia air stripping[78, 79], ammonium adsorption by ion exchange[80-82], or microbial fuel cells [33, 83, 84]. While previous research has shown each to be an effective recovery method, the draw backs of energy demand, chemical inputs, and scalability can hinder each from implementation. Membranes have been a successful process for treating water and wastewater for decades. Consequently, recent research has focused on the use of membranes for treatment of human urine. Membrane distillation[85-87], reverse osmosis (RO)[88], and nanofiltration (NF)[88] have shown positive results for ammonia recovery. As membrane research has advanced, forward osmosis (FO), a low-pressure membrane process, has emerged as a promising technology that can have a lower energy demand compared to other membrane processes such as RO and NF while still maintaining a high

rejection of salts, organics and other pollutants[50, 89-92]. FO operates using an osmotic pressure gradient to pull water from the feed solution into a concentrated draw solution [26, 50]. The most common use of FO has been for the concentration of high fouling solutions such as such as landfill leachate, RO brine, and municipal wastewater [45, 93].

In regards to FO's use on human urine, its main application has been for concentration of the nutrients in urine[30, 52, 94, 95]. As membranes are known to have low rejection of low molecular weight neutral compounds such as urea and ammonia ($NH_3$), most studies have focused on the use of FO on acidified hydrolyzed human urine so that the nitrogen is as ammonium ($NH_4^+$) and gets concentrated in the feed. Nikiema et al. (2017) found that the use of FO on unacidified hydrolyzed human urine for nutrient concentration caused high transfer of ammonia which was seen as a negative result[96]. In addition, recent research has shown that application of FO on fresh human urine has the ability to separate urea from the urine [51, 97]. Therefore, through the use of FO, the urea and ammonia ($NH_3$) in urine can transfer across the FO membrane while inorganic ions, pharmaceuticals, and organic compounds are readily rejected and retained in the urine[50, 98]. This study aimed to use the low rejection of ammonia ($NH_3$) as a benefit to selectively separate ammonia from hydrolyzed urine and retain it in the draw by transformation of ammonia ($NH_3$) into ammonium ($NH_4^+$) after separation through pH manipulation of the feed and draw solutions. For this to be achieved, an understanding of the transfer behavior of low molecular weight neutral compounds such as urea or ammonia must be established. In particular, it is necessary to understand how these compounds transfer across the FO membrane (i.e., does it move with water transfer by advection or is it independent of water transfer moving by diffusion only). As urea and ammonia ($NH_3$) are

not readily rejected by the membrane, an understanding of what drives separation is needed to guide the use of FO processes for enhanced ammonia recovery. The use of FO for selective ammonia recovery has not been studied, and moreover has the potential to provide a novel method for high ammonia recovery coupled with reduced energy demands.

Therefore, the goal of this research was to understand the transport of ammonia ($NH_3$) in order to maximize its recovery from real hydrolyzed human urine by FO through novel pH manipulation. The specific objectives were to: (1) determine the transfer behavior of low molecular weight neutral compounds across the FO membrane using urea as a model compound in a diffusion only system, (2) assess ammonia ($NH_3$) transfer in a cross-flow FO system, (3) use the understanding of the transfer behavior to enhance the FO system for ammonia ($NH_3$ and $NH_4^+$) recovery, and (4) perform an economic analysis of the ammonia recovery by the FO system in comparison to other nitrogen recovery processes from urine.

## Materials and Methods

### Human urine

Human urine collection was approved by the Arizona State University (ASU) Institutional Review Board. Real fresh urine was collected from anonymous volunteers. The further detail on the collection procedure can be found in Ray et al.[99]. The collected fresh human urine was stored for six months to allow for hydrolysis of the urea to occur and for safe handling as determined by the World Health Organization[100]. The hydrolyzed urine was then used for the cross-flow FO experiments. The initial real

hydrolyzed urine conditions can be found in Table B.1. The synthetic fresh human urine used for the dead-end FO experiments was prepared based on previous literature and is detailed in the Table B.2[34, 101].

**Chemical Additions**

Sodium hydroxide (NaOH, Fisher Scientific) was added to the real urine to raise the pH of the hydrolyzed urine to 11.5. Solutions of calcium chloride (CaCl2, Fisher Scientific) and urea (CH4N2O, Fisher Scientific) at 0.25 M were used for the dead-end FO experiments., which was chosen as 0.25 M is the urea concentration found in fresh urine and used in the synthetic urine recipe. Potassium phosphate monobasic (KH2PO4, Fisher Scientific) and sodium chloride (NaCl, Fisher Scientific) both at 1.5 M concentration were used as the draw solutes. The 1.5 M concentration for the draw solution was chosen based on a balance between the osmotic pressure for operation and amount of salt necessary to achieve the concentration.

**FO setups**

Polyamide thin-film composite FO membranes (Porifera Inc., Ca) were used for all experiments. This membrane was selected based on a previous FO study where urea was shown to pass through the membrane into the draw solution[97]. The FO experiments were operated with the active layer facing the feed solution. Membrane cells were made by the ASU machine shop, and glass coils by the ASU glassblowing shop. Cole-Parmer flow pumps, tubing, and flow meters were used to circulate and monitor the flow of the solutions. A Cole-Parmer chiller was used for all cross-flow experiments. A Sartorius microbalance was used to track the increase in weight during the experiment to determine the flux of the cross-flow systems. WinWedge, a computer software, connected the

balance to Microsoft Excel to log the data. pH and conductivity meters were used to take readings for all samples. Specific details on the materials can be found in the SI. Figure B.1 depicts the dead-end FO setup used for determination of urea transfer across the FO membrane. The setup was built using polyvinyl chloride pipes and pipe connectors.

**Urine Pretreatment**

One liter of hydrolyzed urine was first filtered through the microfiltration (MF) membranes and sent to waste to prime the filters. Two batches of 4 L of hydrolyze human urine was measured and the pH urine was adjusted to 11.5 with NaOH (25–41 mL/L of 10 N NaOH). NaOH was chosen over $Ca(OH)_2$ due to the precipitation of calcium minerals that occurs in the urine and its lower cost compared to KOH. The 8 L of urine were filtered by MF and stored at 4 °C for the start of the FO experiment. MF was chosen as the pretreatment as previous research showed precipitation as a cause for membrane fouling[97]. Further detail on the MF system can be found in the SI.

**Dead-end FO experiments**

Three conditions were used to determine the urea transfer. For all three conditions, 450 mL of solution was used on each side of the membrane and the active layer faced the solution containing urea. Condition 1 was synthetic fresh urine on one side of the membrane and DI water on the other side of the membrane. Condition 2 was synthetic fresh urine on one side of the membrane and 1 M NaCl on the other side of the membrane. Condition 3 was a solution containing both 0.25 M $CaCl_2$ and 0.25 M urea on one side of the membrane and 0.25 M $CaCl_2$ on the other side of the membrane. Measurements were taken at 0, 1, 2, 3, and 4 h for all three conditions. Measurements at 48 and 96 h were also taken for condition 3. Samples were analyzed for pH, conductivity,

urea, total organic carbon (TOC), and total nitrogen (TN) where TOC and TN measurements were used to confirm urea results. Further detail can be found in the SI.

**Cross-flow FO experiments**

Four liters of real hydrolyzed urine that was pretreated by MF and pH adjusted to 11.5 using NaOH was used as the feed solution for all experiments. Two liters of 1.5 M NaCl was used as the draw solution for condition 1 where the pH was adjusted to 11.5. Two liters of 1.5 M $KH_2PO_4$ that had a natural pH of 4.2 was used as the draw solution for condition 2. Both the draw solution and feed solution were circulated through chilled water at 18 °C to ensure the liquid does not heat up due to pumping and cause precipitation and/or volatilization problems. A cross-flow velocity of 0.0026 m/s was used for all experiments. The experiments were operated for 48 h. Conductivity probes were placed in the draw and feed solution bottles and measurements were taken every 5 minutes during the experiment and Table B.3 shows the initial and final conductivities for the NaCl and $KH_2PO_4$ draw solution conditions. Forty milliliter samples were taken at 0, 6, 12, 24, 36, and 48 h from the draw and feed solutions. pH readings were taken immediately, the samples were filtered through 0.45 μm pore filters, and then stored at 4 °C for further analysis. The samples were analyzed for ammonia, TN, TOC, $Cl^-$, $PO_4^{3-}$, $Na^+$, and $K^+$. Results referencing ammonia are defined as $NH_3 + NH_4^+$. The volume of the draw solution at the end of the experiment was recorded. The membrane system cleaning procedure can be found in the SI.

**Analytical methods**

All samples were filtered before analysis through 0.45 μm nylon syringe filters (Environmental Express). Urea was analyzed using a urea assay kit (Bioassay Systems,

DUR-100) and a BioTek Synergy H1 Hybrid Multi-Mode Reader plate reader following the procedure detailed in the assay manual. Three check standards were used for every plate reading for accuracy and performed in duplicate to ensure precision. All samples were analyzed in triplicate to ensure precision. A Lachat Quikchem 8500 Series 2 Flow Injection Analysis system (FIA) was used to determine the total ammonia nitrogen concentrations. Samples were run in duplicate and a check standard was used for accuracy. The pH and conductivity were recorded using an Orion Dual Star Multiparameter Meter, an Orion 9156BNWP Combination pH probe, and Orion Star A212 conductivity probe. TOC and TN were both analyzed using a Shimadzu TOC-L/TNM-L Analyzer. Further detail can be found in the SI.

**Economic analysis**

Forward osmosis capital and operating costs were both considered and were based on a previous economic analysis by Volpin et al.[56]. All chemical costs were based on prices from Alibaba accessed in July 2020[102].

## Results and Discussion

**Urea behavior in dead-end FO**

Urea was chosen as the model compound over ammonia to understand the transfer behavior due to its nonvolatile and pH independent behavior. The dead-end FO setup was an open system and therefore loss of ammonia to the atmosphere would have been inevitable and highly affected the results. Additionally, while urea can degrade at extreme conditions (pH > 13 and temperature > 177 °C)[103, 104], the pH stability of urea is advantageous as it does not change speciation based on pH unlike ammonia. Figure 1 is a schematic that summarizes the three conditions and depicts the movement of water and

urea for a visual understanding of the dead-end FO process. Figure 3.2 shows the urea concentration over time for the three conditions and measured numerical values can be found in Table B4 and B5. For condition 1: synthetic fresh urine and DI water, the water moved from the hypotonic (solution with a lower osmotic pressure) DI water solution across the FO membrane to the hypertonic (solution with a higher osmotic pressure) synthetic urine throughout the entire experiment as expected considering the osmotic pressure difference between the synthetic fresh urine and DI water (18.7 bar vs. 0 bar). The average water transfer rate was 4.8 $L/m^2/h$ (LMH). As seen in Figure 3.2 (a), there was an increase in urea concentration in the DI water solution for the entirety of the experiment. The average concentration of urea in the DI water at 4 h (522 mg/L) was small (~4%) in comparison to the concentration of urea in the synthetic urine at 4 h (14,222 mg/L). For condition 2: synthetic fresh urine and 1 M NaCl, the water moved from the hypotonic synthetic fresh urine to the hypertonic 1 M NaCl throughout the entire experiment. One molar NaCl has a greater osmotic pressure (48.7 bar) compared with synthetic fresh urine (18.7 bar). The average water transfer rate was 5.0 LMH. The concentration of urea increased over time in the 1 M NaCl solution and decreased in the synthetic fresh urine, as expected. Condition 3 was a 0.25 M $CaCl_2$ solution and a solution containing both 0.25 M $CaCl_2$ and 0.25 M of urea. $CaCl_2$ was chosen as issues of reverse salt flux would be reduced with $CaCl_2$ in comparison to NaCl. Reverse salt diffusion through the FO membrane would change the osmotic pressure and consequently the tonicity of the two solutions in the system. Because urea is not rejected by the FO membrane due to its small size and uncharged nature, it can move freely across the membrane between the two solutions and will not exert an effective osmotic pressure;

this is known as an ineffective osmole [105, 106]. Therefore, the two solutions are isotonic (equal osmotic pressures) which was demonstrated by no water movement over time. However, there was a transfer of urea from the $CaCl_2$ solution containing urea to the $CaCl_2$ without urea during the 96 h.

The driving force for urea transfer is a concentration gradient to achieve equilibrium done so by diffusion; however, water transfer increases the rate at which urea transfers across the membrane by advection. Therefore, both diffusion and advection are involved in the transfer of low molecular weight neutral compounds. When the water was moving from the synthetic urine to the 1 M NaCl in condition 2, the transfer of urea by both advection and diffusion was greater in the 4 h compared to the urea transfer from the synthetic urine to the DI water solution when water was moving against the urea transfer in condition 1 and diffusion was the only acting force on urea transfer. The normalized driving force, which is defined as $\dot{m}_{urea}/\Delta C_{urea}$ where $\dot{m}_{urea}$ is the mass transfer of urea and $\Delta C_{urea}$ is the change in urea concentration, was calculated for condition 1 and 2 to determine if the change in driving force was the reason for condition 2 having a greater urea transfer compared to condition 1. When the mass transfers were normalized by the driving force so that dilution or concentration of urea was accounted for, condition 2 still had a greater transfer of urea compared to condition 1. This is further emphasized by the condition 3 experiment, where the concentration gradient to achieve equilibrium was the only force acting on the urea transfer (no water transfer). After the initial 4 h, only ~6% of the urea had transferred across the membrane while, after 96 h of operation, the urea was close to equilibrium with ~50% of the urea transferred to the $CaCl_2$ solution. Therefore, the rate of urea transfer due solely to diffusion is small and requires a

significant amount of time for equilibrium to be achieved. But when transfer by diffusion is combined with advection, the rate is considerably increased. Lastly, because urea is not rejected by the FO membrane and dependent on concentration equilibrium, 50% recovery of low molecular weight neutral compounds is the theoretical maximum that could be separated in a batch system.

**Ammonia behavior in cross-flow FO**

Transfer of ammonia was investigated in cross-flow FO system to test if the previously determined neutral compound transfer behavior held true when there is water movement and low-pressure acting on the system. Figure 3.3 (a) shows the FO system flux vs. cumulative permeate volume over time. Flux (J) is defined as J = Q/A where Q is the flowrate and A is the membrane area. The normalized flux decreases over time as more water is passed through to the draw solution presumably due to fouling as well as reduction of the osmotic pressure due to dilution of the draw. Real human urine is a complex solution that contains many compounds ranging from salts and nutrients to pharmaceuticals and metabolites. Scaling due to the high concentration of salts and organic fouling due to high TOC content could both contribute to fouling of the membrane. A previous study on FO treatment of fresh human urine for urea recovery detected inorganic scaling, organic fouling, and biofouling on the FO membranes where conditions using high pH caused magnesium precipitation as well as possible urinary protein unfolding [97]. Therefore, pH adjustment causing precipitation followed by filtration, which was utilized in this study, would help reduce membrane scaling for long term operation. In the context of biofouling, MF would be expected to remove all of the bacteria and a small fraction of the viruses by attaching to bacteria biofilm. Additionally,

the high pH of the urine and presence of ammonia would be effective to inactivate many enteric organisms such as bacterial pathogens reducing the opportunity for biofouling[107, 108]. While fouling did occur due to the treatment of real human urine, the cumulative water passage and flux decline is comparable to other wastewater systems treated by FO such as Boo et al. and Xie et al. applied FO as part of a combined system for seawater desalination and digested sludge treatment, respectively[109, 110]. In both cases, the flux declines followed similar trends as the current results for the amount of water passed. Perreault et al. found that graphene oxide functionalization of thin film composite membranes (GO-TFC) for FO reduced the biofouling by 50% after 24 h when treating synthetic secondary wastewater augmented with *P. aeruginosa* [111]. Consequently, use of the GO-TFC could reduce the observed fouling, improve the flux, and thereby enhance the system overall. Additionally, the high pH of the solutions could also cause problems with membrane operation and therefore flux over time. As a high pH is necessary for the nitrogen to be as ammonia ($NH_3$) for recovery reasons, lowering the pH is undesirable. Figure 3.4 details the rejection of TOC and other various ions by the FO membrane to further asses the performance of the system. TOC rejection was found to be high, 96%, which shows the efficiency of the FO membrane at rejecting the numerous organic compounds found in human urine. This is in accordance with Liu et al. which found the treatment of fresh urine by FO to have 97% rejection of TOC and a diffusion rate of 0.7% in 2 h [94]. Hanckock et al. found that FO was able to reject up to 80% of trace organic compounds (TOrCs) that were charged while nonionic TOrCs rejection varied from 40–90% which also supports the higher diffusion of neutral compounds, such as ammonia, by FO membranes [89]. Additionally, the current FO system had high rejection of $Cl^-$, $PO_4^{3-}$

, and $Na^+$ which were all ≥ 91%. However, $K^+$ had a lowered rejection of 72% which is due to the smaller hydrated radius and higher permeability of $K^+$ in comparison to $Cl^-$, $PO_4^{3-}$, and $Na^+$ [30, 96, 112].

Figure 3.5 (a) shows the average concentration of ammonia in the feed and draw solutions over time for duplicate experiments. Results referencing ammonia are defined as $NH_3 + NH_4^+$ as ammonia was the target nitrogen compound tracked through the cross-flow system and the extent of urea hydrolysis was 77% leaving ammonia the dominant form of nitrogen in the urine. However, as the pH of both the draw solution and feed solution is 11.5, all the nitrogen should be as ammonia. The ammonia concentration starts out in the feed solution and slowly decreases over time while the concentration of ammonia in the draw solution increases over time. At 48 h the concentration of ammonia in the draw solution is close (within 15%) to the concentration of ammonia in the feed solution indicating that concentration equilibrium was reached. The dead-end FO experiments in the previous section showed that concentration equilibrium was reached around 96 h by an FO system that had no pressure or movement of water. Additionally, the previous results also determined that water movement in the direction of transfer increases the rate of transfer. Therefore, the movement of water from the feed solution to the draw solution and operation at a low-pressure allowed for concentration equilibrium to be reached by 48 h instead of 96 h. Consequently, the determination that concentration equilibrium is the driving factor for ammonia transfer with a 50% maximum recovery was confirmed in a real FO system. These results are in agreement with previous research that treated hydrolyzed human urine by FO and determined 40–35% of the ammonia passed through membrane and transferred into the draw solution [96]. The previous study

only ran the FO for 7 h and thus if the system was run for longer, equilibrium would have been able to be reached. Additionally, Volpin et al. treated synthetic fresh urine for urea recovery by both short- and long-term FO experiments and found that only 50% of the urea was recovered[51].

**Enhanced ammonia recovery via FO with pH manipulation**

It has been confirmed that the recovery of ammonia in the current FO system is limited to 50%. However, ammonia is a pH dependent nitrogen compound that can vary between ammonia ($NH_3$) at high pH and ammonium ($NH_4^+$) at low pH as determined by the $pK_a$ of ammonium ($pK_a = 9.24$). Ammonia is a low molecular weight neutral compound with low membrane rejection while ammonium is a positively charged ion with high membrane rejection due to its increased radius when hydrated and electrostatic nature [29, 93, 96, 99]. Therefore, for recovery of ammonia from hydrolyzed human urine greater than 50%, ammonia concentration equilibrium must not be reached and a high retention of ammonia in the draw solution must occur. This can be achieved by a novel process where pH is strategically manipulated to increase ammonia recovery. The pH of urine must be high (>11.5) so that all of the nitrogen is as ammonia ($NH_3$) and able to pass freely across the FO membrane so that it can be separated from the urine. If the urine was at an acidic pH, the nitrogen would be as ammonium ($NH_4^+$) and highly rejected by the FO membrane causing little nitrogen to be separated from the urine into the draw solution. Therefore, to achieve a recovery greater than 50%, the ammonia must be transformed to ammonium by an acidic draw solution (pH < 6.5) so that it will be retained in the draw solution due to the larger size and charge of the ammonium ion. Furthermore, as the ammonia transforms to ammonium, the concentration of ammonia in

the draw solution will decrease keeping equilibrium from being achieved and higher amounts of ammonia to be separated as ammonia concentration equilibrium drives separation. Thus, the FO system was operated with a $KH_2PO_4$ draw solution that has a natural pH of ~4.2 and real hydrolyzed human urine as the feed solution where the pH was adjusted to 11.5. In addition, $KH_2PO_4$ was chosen to recover ammonia as the recovered product will be a fertilizer product that contains nitrogen, phosphorus, and potassium (NPK) which are all necessary for plant growth.

Figure 3.3 (b) shows the FO system flux vs. cumulative permeate volume over time. The flux results followed a similar trend as the experiments where NaCl was used as the draw solute with the current draw solution condition transferring ~250 mL less of water. This is most likely due to the higher osmotic pressure of the NaCl draw solution compared to the $KH_2PO_4$ draw solution (68 vs. 64 bar). The normalized flux decreases over time as more water is passed through to the draw solution presumably due to fouling as in the NaCl experiments mentioned above. Additionally, dilution of the draw solution combined with loss of $K^+$ due to reverse salt flux would also reduce the flux over time. Figure 4 shows the rejection of TOC and various ions for the system. Similar to the condition with NaCl as the draw, the TOC rejection was 97% and rejection of $Cl^-$, $PO_4^{3-}$, and $Na^+$ were $\geq$ 92%. The rejection of $K^+$ was greater than 100% (186%) due to reverse salt flux of the $K^+$ in the concentrated $KH_2PO_4$ draw solution which diffused from the draw into the feed nearly doubling the concentration of $K^+$ in the feed. This phenomenon was observed by Kim et al. when potassium chloride was used as the draw solution to test the rejection of organic micropollutants by FO [113]. The use of a different draw solute such as a sodium phosphate solution may have less problems with reverse salt flux but would

be harmful to the soil and plant growth due to the high concentration of sodium necessary to be an adequate draw solution with a high enough osmotic pressure[114]. While reverse salt flux of $K^+$ is not necessarily harmful to the process as it only adds value to the concentrated human urine in the feed which could be further treated for nutrient recovery, it does reduce the osmotic pressure of the draw solution which reduces the water flux and thus reduces the ammonia transfer by advection. Wang et al. determined that the use of a double-skinned cellulose acetate membrane was able to reduce reverse salt flux transport of $MgCl_2$ while still producing high water flux for the FO system[115]. Emadzadeh et al. found that a TFC made with polysulfone–titanium dioxide nanocomposite substrates at 0.5 wt% embedded nanoparticles increased water permeability while reducing reverse salt flux[116]. Therefore, alteration of the current FO membrane could mitigate the $K^+$ reverse salt flux observed. As $K^+$ was able to reverse salt flux, movement of $H^+$ would be expected. The pH over time can be found in Figure B.3 (b) which shows that the pH of the urine was buffered enough to only lower by ~1 pH unit over the 48 h and the pH of the draw increased by ~2 pH units. While it is undesirable for the pH of either solution to alter over time, the minimal pH change was not expected to affect the ammonia recovery as the pH of the draw stayed below the $pK_a$ (9.24) and the pH of the urine stayed above the $pK_a$ which was necessary for the pH manipulation process.

Figure 3.5 (b) shows the average concentration of ammonia in the feed and draw solutions over time. The ammonia concentration starts out in the feed solution and decreases over time while the concentration of ammonia in the draw solution increases over time. However, unlike in the NaCl condition where all the nitrogen was as ammonia and the experiment reached concentration equilibrium by 48 h, the $KH_2PO_4$ condition

passed concentration equilibrium between 12 and 24 h. The ammonia concentration continued to increase in the draw solution where at 48 h, 78–86% of the ammonia had been recovered in the draw solution. Therefore, the change of ammonia in the feed solution into ammonium in the draw solution by strategic pH manipulation was able to pass the 50% recovery maximum as desired. The percent recovery of ammonia by FO is comparable to other ammonia recovery processes such as ammonia air stripping and ammonium absorption by ion exchange which have recovery efficiencies of 80–99% [22, 117]. Overall, the novel FO system had optimal ammonia recovery rates with high rejection of TOC and other ions.

**Economic analysis of ammonia recovery by FO**

An economic comparison was made between the current FO system for ammonia recovery and two highly researched ammonia recovery processes for human urine treatment: ammonia air stripping[78, 79] and ammonium adsorption by ion exchange[80-82]. A key factor of the current FO process is that it is highly versatile as the draw solute is the most significant variable for FO operation. The draw solution, a simple and easily made salt solution, can be tailored to the current market prices of salts and geographical locations. Market prices change for different salts due to demand and availability which can be highly dependent on geographical area. Therefore, the economic analysis considered three different scenarios where the draw solute was either changed or reduced in concentration to understand its effects on the overall economic output for this FO ammonia recovery system. Scenario 1 is the tested conditions in this work where a 1.5 M $KH_2PO_4$ draw solute was used. For Scenario 2, the draw solute concentration was reduced by half to 0.75 M $KH_2PO_4$. For Scenario 3, the draw solute was changed to 1.5

M $MgSO_4$. $MgSO_4$ is a cheaper salt compared to $KH_2PO_4$ that was used in a previous study for treatment of seawater by FO-NF where the draw solution was shown to be effective for operation[118]. Therefore, it was included in this assessment as an alternative draw solute.

The economic analysis considered the pretreatment of the hydrolyzed human urine by MF ($0.06/$m^3$ based on work by Chellam et al. [119]) and the pH adjustment with NaOH ($3.00/$m^3$ based on the required dose of NaOH to raise the pH given in the methods section and the price of NaOH, $0.3/kg[102]). The draw solutes ($KH_2PO_4$ and $MgSO_4$) and their amounts (2 L of either 1.5 M or 0.75 M depending on the condition) were determined as well as the capital and operating costs of the FO system ($1.65/$m^3$ based on work by Volpin et al.[56]). Offsets from the recovered products were also considered in the analysis. All chemical costs and product offsets were taken from Alibaba (accessed in July 2020). Table 3.1 shows the results for the economic analysis. The market values for each recovered product were assigned by the dominant components in the solution. Scenario 1 and 2 produce a draw solution product with high concentrations of potassium and phosphate and a low concentration, by comparison, of ammonium. The closet market product to this solution is a monopotassium phosphate solution as the P and K are more dominant than the N. For scenario 3, the closest market product to this solution is ammonium sulfate. Market values for these two products (monopotassium phosphate and ammonium sulfate) were used to acquire the product offset value. However, for scenario 1 and 2, the product may have a greater worth due to the added nitrogen requiring less supplementing of an additional nitrogen fertilizer for a plant's necessary NPK requirements.

Scenario 3 was the most cost effective scenario with a total cost of $2.55/m$^3$ of urine treated. This is due to the current low cost of magnesium sulfate. Scenario 1 and 2 had total costs of $31.47/m$^3$ and $17.51/m$^3$, respectively. Currently, potassium phosphate is a highly priced chemical and thus its use as the draw solute increased the cost drastically. However, the urine-derived product containing ammonium, potassium, and phosphate has a much greater market value than the Scenario 3 product containing ammonium, magnesium, and sulfate. Therefore, it is highly dependent on the needs of the user to determine what is of greatest value. Some users may need a higher quality product and thus the higher total cost may be less of a concern. Additional economic benefits such as reduced costs of downstream wastewater treatment and nutrient recovery from the concentrated urine were not considered in the economic analysis but would further reduce the cost of operation [56]. The draw solute is a key consideration which highly affects the overall process operation, recovered products, and costs. While not included in the full economic analysis, Table B.6 provides a comparison of various inorganic draw solutes and considerations for their use. While cost is an important factor, other considerations such as osmotic pressure, water flux, dissolved pH, reverse salt flux, and water solubility will affect the overall operation and thus should be included in the design process.

Table 3.3 shows the results for the economic comparison of the FO process with ammonia air stripping and ammonium adsorption by ion exchange. The total cost for each process is given along with the product offset. Ammonia air stripping is an effective ammonia recovery process that produces ammonium sulfate. However, the process has traditionally been known as an expensive process due to the necessary chemical inputs

and energy demands. A study on the optimization of ammonia air stripping found that for the most optimized scenario of increasing air flow rate and temperature instead of pH can reduce the cost to \$21.65–24.24/$m^3$ [22]. Ammonium adsorption by ion exchange is also an effective process for ammonium recovery but has the same issues with chemical input, brine disposal, and expensive resin costs. There is limited research on the economics of ammonium adsorption by ion exchange. One study, which looked solely at the performance and cost of the ion exchange materials, found that Dowex Mac 3 resins performed for 100 uses has an operating cost of \$7.50/$m^3$ [81]. An additional study determined the cost of the sulfuric acid regeneration solution to be \$4.20/$m^3$ [120]. However, there is limited data on the economics for the columns and pumping which would be expected to raise the total cost. Comparison of the 3 scenarios will give a better understanding of how the current FO process compares to widely established processes. For process costs alone, Scenario 3 is the most cost effective at a price of \$10.11/$m^3$. The ranking of lowest costs to highest for the 5 processes is: scenario 3 > ammonium adsorption by ion exchange > ammonia air stripping > scenario 2 > scenario 1. However, the process cost does not take into account the product offsets. Both scenario 1 and 2 produce products with market values that are three times greater than the product produced by scenario 3, ammonia air stripping, and ammonium absorption by ion exchange. While scenario 1 has a high process cost in comparison to the other processes, scenario 2 is comparable in cost to ammonia air stripping (\$35.31 vs. \$22.93). Additionally, considering the product offset of scenario 2 makes it a more competitive process in comparison to the ammonia air stripping.

This study provides key insights on a novel FO process for ammonia recovery from hydrolyzed urine. Determination of how low molecular weight neutral compounds transfer in FO systems allowed for tailored improvements for targeted ammonia recovery. Through strategic pH manipulation, the FO system proved to be an effective process with up to 86% recovery of ammonia with high rejection of TOC and other ions. Additionally, an economic analysis demonstrated the FO process to be highly competitive economically when magnesium sulfate is chosen as the draw solute. However, use of potassium phosphate produces a product with a higher market value. Thus, further research on the draw solute chemicals and concentration can be used to optimize the economics of the FO process. In addition, creating a cost-effective process that produces valuable products is expected to enhance user acceptance of urine diversion. For example, acceptance of urine diversion decreased with increasing cost for the process[66]. Hence, an economical urine diversion process would have multiple benefits to society.

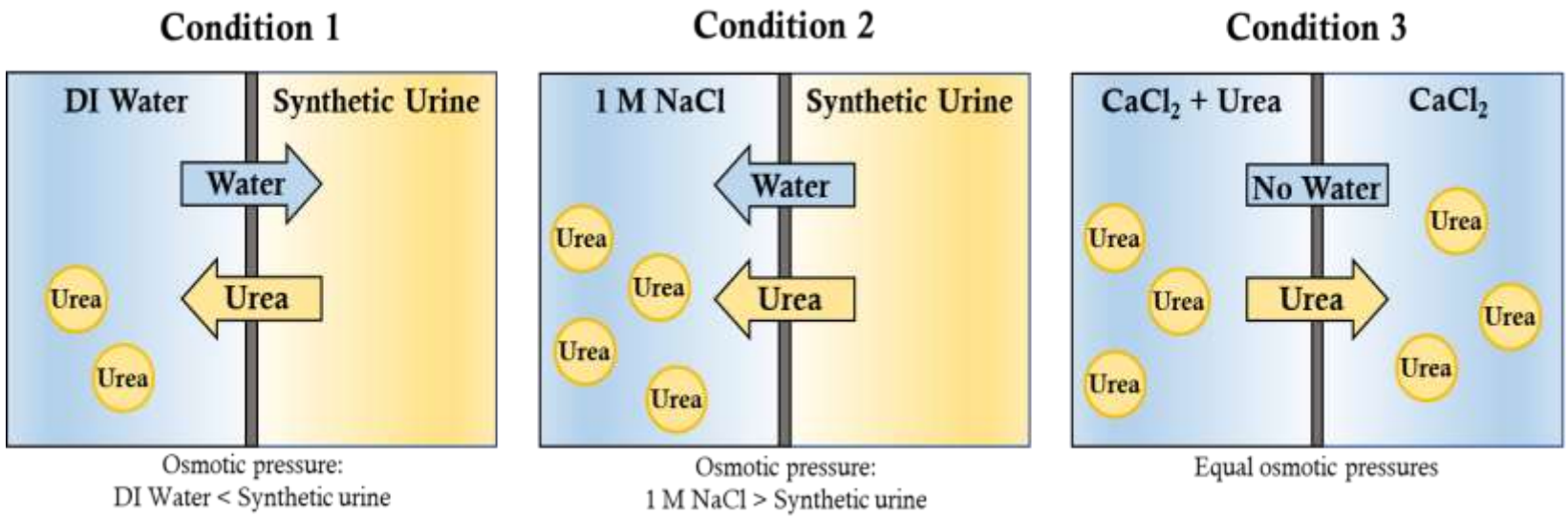



**Figure 3.1**. A schematic depicting the different conditions for the dead-end FO experiments to determine the transfer behavior of low molecular weight neutral compounds. Evaluation of the osmotic pressure gradient is given. Condition 1: urea transfer is going against water transfer. Condition 2: urea and water transfer are going in the same direction. Condition 3: there is no water transfer.

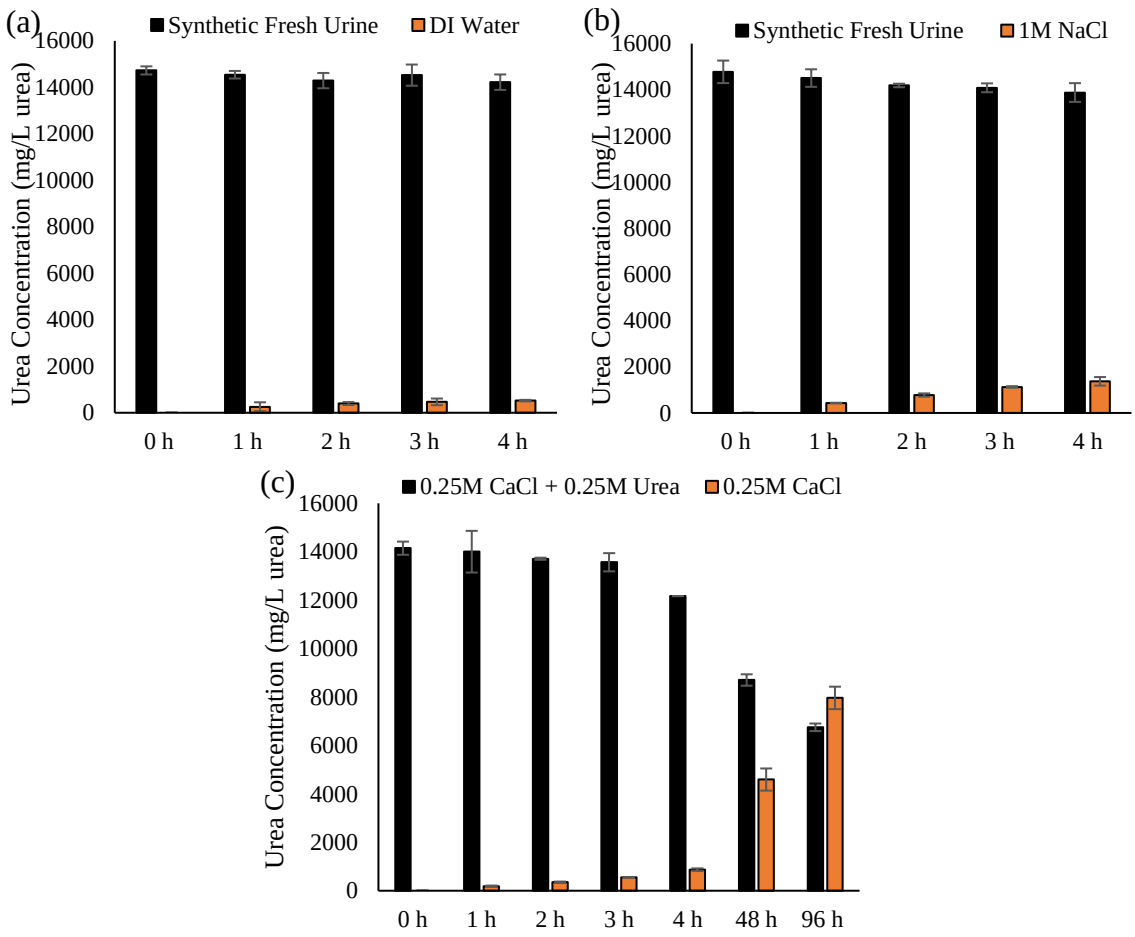



**Figure 3.2**. Depicts the dead-end FO evaluation of low molecular weight neutral compound transfer where urea was used as the model compound. The urea concentration over time for (a) condition 1: DI water and synthetic fresh urine, (b) condition 2: synthetic fresh urine and 1M NaCl, and (c) condition 3: 0.25M CaCl + 0.25M urea and 0.25 CaCl. Error bars represent +/- one standard deviation.

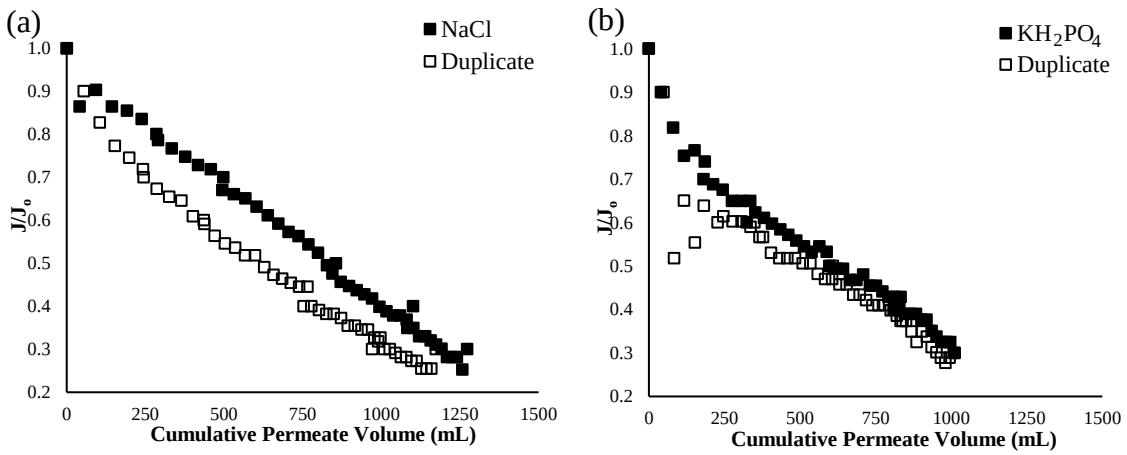



**Figure 3.3.** (a) represents normalized flux as a function of cumulative permeate volume for the forward osmosis experiment where 1.5 M NaCl draw solute was used and both feed and draw solutions had a pH of 11.5. (b) represents normalized flux as a function of cumulative permeate volume for the forward osmosis experiment where 1.5 M $KH_2PO_4$ draw solute was used. The feed solution had a pH of 11.5 and the draw solute had a pH of 4.2. The duplicate tests for each condition are graphed for comparison.

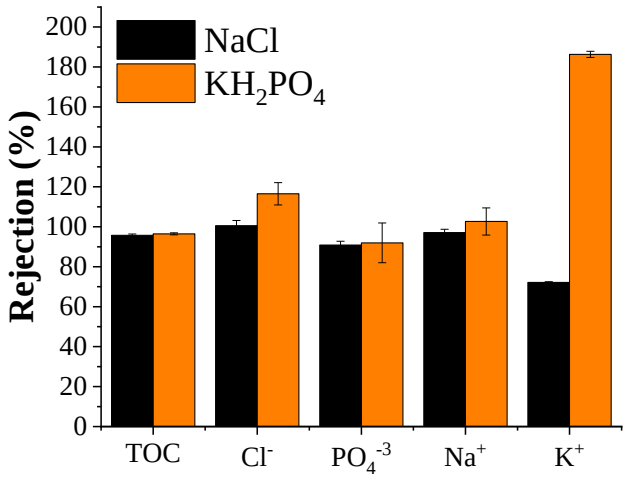



**Figure 3.4.** Shows the rejection of TOC and various ions by the cross-flow forward osmosis system for the two different conditions in real hydrolyzed human urine. Black bars represent the results for the NaCl as draw solution condition and orange bars represent the results for the $KH_2PO_4$ as draw solution condition. Error bars represent +/- one standard deviation.

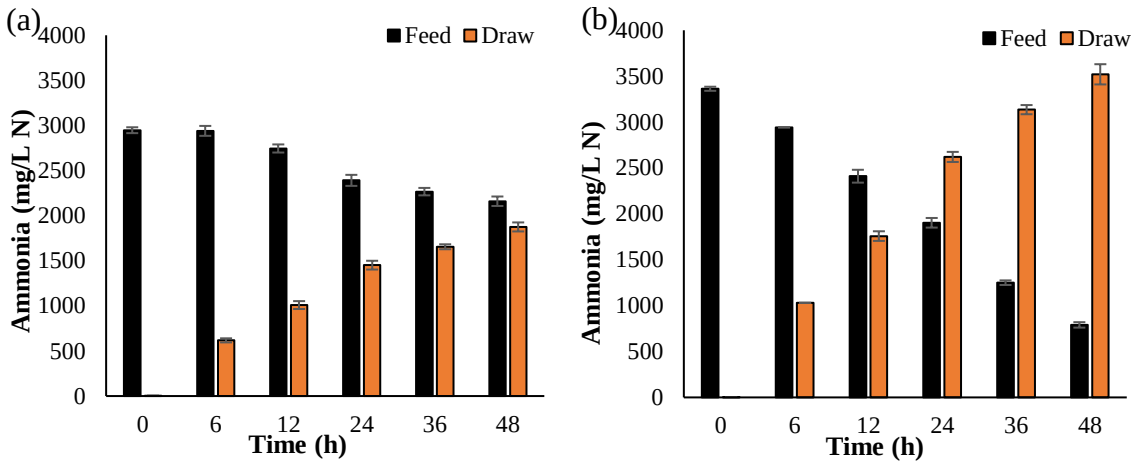



**Figure 3.5.** (a) represents ammonia concentration over time for the forward osmosis experiment where 1.5 M NaCl draw solute was used and both feed and draw solutions had a pH of 11.5. (b) represents the ammonia concentration over time for the forward osmosis experiment where 1.5 M $KH_2PO_4$ draw solute was used. The feed solution had a pH of 11.5 and the draw solute had a pH of 4.2. Black bars correspond to the ammonia in the feed solution and the orange bars correspond to the ammonia in the draw solution. The experiments were performed in duplicate and error bars represent +/- one standard deviation.

**Table 3.1.** Economic analysis of the three scenarios for ammonia recovery from hydrolyzed human urine by forward osmosis. Chemical prices were taken from Alibaba accessed in July 2020.



| Scenario | Pretreatment by MF + pH | Draw Solute | Amount of Draw Solute | Chemical Cost | FO Operation | Product | Production Rate | Total Process Cost | Product Offset | Balance |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $3.06/m$^3$ | $KH_2PO_4$ | 102 kg/m$^3$ | $0.6/kg | $1.65/m$^3$ | Ammonium Potassium Phosphate | 86.1 kg/m$^3$ | $65.91/m$^3$ | $0.4/kg | $31.47/m$^3$ |
| 2 | $3.06/m$^3$ | $KH_2PO_4$ | 51 kg/m$^3$ | $0.6/kg | $1.65/m$^3$ | Ammonium Potassium Phosphate | 44.5 kg/m$^3$ | $35.31/m$^3$ | $0.4/kg | $17.51/m$^3$ |
| 3 | $3.06/m$^3$ | $MgSO_4$ | 90 kg/m$^3$ | $0.06/kg | $1.65/m$^3$ | Ammonium Magnesium Sulfate | 63.0 kg/m$^3$ | $10.11/m$^3$ | $0.12/kg | $2.55/m$^3$ |

**Table 3.2.** Economic comparison of different ammonia recovery processes. For each ammonia recovery process, the total process cost and the offset coming from the recovered product is given.

| Nitrogen Recovery Process | Total Process Cost | Product Offset |
|---|---|---|
| Scenario 1 | $65.91/m$^3$ | $0.4/kg |
| Scenario 2 | $35.31/m$^3$ | $0.4/kg |
| Scenario 3 | $10.11/m$^3$ | $0.12/kg |
| Ammonia Air Stripping | $22.93/m$^3$ | $0.12/kg |
| Ammonium Ion Exchange | $11.70/m$^3$ | $0.12/kg |

# CHAPTER 4

# REJECTION OF NITROGEN SPECIES IN REAL FRESH AND HYDROLYZED HUMAN URINE BY REVERSE OSMOSIS AND NANOFILTRATION

## Urea, ammonia, and ammonium rejection by RO, NF, and MF

Although nitrogen is one of the most abundant elements, it is unavailable until it is fixed into a usable form. Fixation, through the Haber-Bausch process, produces unionized ammonia [2, 19, 21]. Unionized ammonia and the ammonium ion are largely used in fertilizer production. Unionized ammonia is also a cleaning agent, a refrigerator gas, and a precursor compound for urea production [19]. Urea, a nitrogen dense compound made from unionized ammonia and carbon dioxide, has many industrial uses such as a worldwide fertilizer, resin fabrication, and is the main component in diesel exhaust fluid which is used to reduce the nitrous oxide emissions coming from diesel engines [18]. Chemical nitrogen fixation converts nonreactive nitrogen, $N_2$, to reactive nitrogen, defined as nitrogen that which is radiatively, photochemically, and biologically active on Earth [2]. Production of reactive nitrogen compounds such as ammonia and urea first through the energy intensive Haber-Bosch process and then further fabrication is the main source of production worldwide despite the fact that many waste streams are rich with nitrogen available for recovery [2].

Wastewater is made up of valuable nutrients such as nitrogen, phosphorus, and potassium. Of these nutrients, total nitrogen influent concentrations range from 20 to 70 mg/L N [121]. At the wastewater treatment plant (WWTP), energy and materials are implemented to remove these nutrients, with specific concern for nitrogen and phosphorus due to their eutrophication properties [10]. One component of wastewater,

urine, is a small percent by volume but a large contributor of nitrogen. Urine constitutes 80% of the nitrogen and 50% of the phosphorus in wastewater by mass, while only accounting for 1% of the volumetric flow [8, 9]. Thus, urine is a small, nutrient dense waste stream responsible for a large portion of the energy and material requirements during wastewater treatment. Consequently, urine has potential for nitrogen recovery, but its unique chemistry must be considered.

Urine exists in two states: fresh and hydrolyzed. When urine is initially excreted from the body, the nitrogen is in the form of urea and the urine is considered fresh. After excretion, urea undergoes rapid hydrolysis due to contact with the ubiquitous urease enzyme [13, 36]. Hydrolysis transforms the urea into ammonia and bicarbonate [15]. After hydrolysis has occurred and the nitrogen is in the form of ammonia, the urine is considered hydrolyzed. The type of nitrogen recovery process is heavily dependent on the species of nitrogen and the chemistry of the urine. For recovery from hydrolyzed urine, struvite precipitation, ion exchange, and ammonia air stripping are common processes that have proven to effectively recover the nitrogen but at a high cost of energy and chemical input [22, 34, 35, 78, 79, 122-125]. Due to urea's rapid hydrolysis after excretion, and small, uncharged nature, recovery of nitrogen from fresh urine is more difficult. Research has determined addition of a dilute acid such as acetic acid or base such as sodium hydroxide can inhibit the hydrolysis reaction and stabilize the urea if urea recovery is the ultimate goal[40-42, 44, 126]. Because of the urease enzyme's functional pH of 7–8, lowering the pH to 5 or raising the pH above 11 alters the active sites of the enzyme and hinders its ability to hydrolyze the urea [36, 126]. In addition to urea stabilization, recent research has also found that selective separation of urea from fresh urine is possible through

implementation of low-pressure forward osmosis (FO) by utilizing the FO membrane's low rejection of urea [51, 56, 97]. Yet, concentration equilibrium can limit recovery to 50% for low-pressure systems due to urea and ammonia acting as ineffective osmoles [127].

High-pressure membrane processes such as reverse osmosis (RO) and nanofiltration (NF) have high rejection of salts and ions, such as $Cl^-$, $Na^+$, $Mg^{2+}$, $Ca^{2+}$, which has been thoroughly researched [128]. However, in the context of human urine, a feed solution with a high propensity for fouling, quantification of the rejection of smaller, uncharged compounds by RO and NF has yet to be thoroughly established. RO application on human urine has only been studied for the purpose of clean water production and nutrient concentration while NF of human urine has only been studied with the focus on the removal of pharmaceuticals and other micropollutants [33, 125, 129-131]. While previous research has studied the rejection of the ammonium ion in various feed solutions, not including human urine, unionized ammonia is seldom studied due to its small size and poor rejection, similar to the urea compound. Addressing this gap of knowledge on the rejection of the uncharged form of nitrogen by membranes is critical because selective urea and ammonia recovery may be achievable through the application of RO and NF by capitalizing on the low rejection of these compounds. Indeed, the low rejection of urea and ammonia allows for passage across the membrane into the permeate, while the membrane's high rejection of salts and other trace organic compounds keeps the rest of the compounds in urine on the feed side of the membrane, thus separating the nitrogen out of urine. Therefore, a low rejection of urea and unionized ammonia by the membrane processes is desired for nitrogen recovery. However, to accurately assess the potential of membrane-based separation for nitrogen recovery, the rejection of urea and

ammonia by membranes must be quantified with consideration of the unique chemistry of urine and the practical considerations associated with urine diversion processes such as urea stabilization.

The goal of this research was to determine the rejection of different reactive nitrogen species in both fresh and hydrolyzed human urine by membrane separation. This understanding of nitrogen transport in different membrane systems will enable the identification of urine treatment strategies that will allow for high nitrogen recovery. The specific objectives of this research were to (1) quantify the rejection of urea in fresh human urine by RO, NF, and MF and determine the effect of urea stabilization on urea rejection by varying the pH of the urine, (2) quantify the rejection of unionized ammonia and ammonium ion in hydrolyzed human urine by RO, NF, and MF by varying the pH of the urine, and (3) discuss the implications of nitrogen recovery from human urine by these membrane processes. Due to the composition of human urine, reference to fresh urine corresponds to urea rejection while reference to hydrolyzed urine corresponds to ammonia rejection. The term ammonia is used generally to refer to either ammonium ion or unionized ammonia depending on the corresponding pH. Because MF is intended for particle separation and not solute rejection, low nitrogen rejection by MF was used as a positive control to compare with nitrogen rejection by RO and NF.

## Materials and Methods

### Chemical additions

Acetic acid (CAS 64-19-7, Fisher Scientific) was added to the real urine to lower the pH (fresh urine to 5 and hydrolyzed urine to 6.5). Sodium hydroxide (CAS 1310-73-2, Fisher Scientific) was added to the real urine to raise the pH (fresh to 12.5 and

hydrolyzed urine to 11.5). Jack bean urease (CAS 9002-13-5, Sigma Aldrich) was added to the stored urine the day of the experiment at a concentration of 3 g/L to ensure complete hydrolysis.

**Membranes and setups**

All dead-end RO experiments used Filmtec flat sheet BW30 membranes. All dead-end NF experiments used DOW NF90 membranes. All MF experiments used the Sartorius Vivaflow 200 0.2 μm and a Cole-Parmer Masterflex L/S digital pump with an Easy-Load II pump head. The Sterlitech HP4750 High Pressure Stirred Cell was used for all dead-end RO and NF experiments.

**Urine collection, storage, and safe handling**

Both real fresh and hydrolyzed human urine were used for this project. Human urine collection was approved by the Arizona State University Institutional Review Board. Real fresh urine was collected from anonymous volunteers, both male and female, who fit the criteria: (1) 18 years or older and (2) not pregnant. A urine collection setup was used in both male and female bathrooms in the Biodesign Institute at Arizona State University. Collection setups utilized plastic collection trays for women and urinal collection tanks for men. Thorough directions with both words and pictures were taped to the wall for understanding on how to properly donate. All collection trays were used once and then bleach cleaned for the next collection event. Gloves were available if desired for the anonymous volunteers. The collection tanks were kept in secondary containment throughout the collection event. All samples were combined during the collection event to ensure anonymity. Fresh urine was used within 48 h of collection and the pH was tested to ensure it was in the range for fresh urine reported in the literature (pH 6–6.5).

The initial urine composition is detailed Tables C.1 and C.2. Collected fresh human urine was stored in the lab for six months to allow for hydrolysis of the urea to occur. Personal protection equipment of gloves, a lab coat, and splash glasses were used when handling urine for experiments. Bleach was readily available for disinfection and biological spill kits were kept in the lab. All pouring of urine was done in a chemical fume hood.

**Urine preparation**

For the fresh urine experiments, three urine conditions were used: fresh urine with acetic acid (pH ~5), fresh urine with sodium hydroxide (pH ~12.5), and fresh urine with no addition (pH ~6). Acetic acid was added to the fresh urine for the acid addition experiments at a concentration of 0.0264 M. Sodium hydroxide was added to the fresh urine for the base addition experiments at a concentration of 0.125 M.

For the hydrolyzed urine experiments, three urine conditions were used: hydrolyzed urine with acetic acid (pH ~6.5), hydrolyzed urine with sodium hydroxide (pH ~11.5), and hydrolyzed urine with no chemical addition (pH ~9). Acetic acid was added to the hydrolyzed urine for the acid addition experiments at a concentration of 0.111–0.130 M. Sodium hydroxide was added to the hydrolyzed urine for the base addition experiments at a concentration of 0.278 M.

**Dead-end reverse osmosis and nanofiltration of fresh and hydrolyzed urine**

The RO and NF membranes were pre-wetted in a 50% isopropanol/50% ultrapure water (ultrapure resistivity 18.2 Ω) solution for 30 min. The membranes were then transferred into ultrapure water for 10 min. After the 10 min were completed, the membranes were transferred to fresh ultrapure for an additional 10 min. Each experiment used 270 mL of fresh urine.

For both the fresh and hydrolyzed urine experiments, the pH and conductivity of the urine was recorded after the chemical additions were added. A 20 mL sample was filtered through 0.45 μm filter, and then stored at 4 °C for further analysis. The Sterlitech HP4750 High Pressure Stirred Cell was assembled with the primed membrane active-layer facing the feed solution and the urine solution was added. The increase in mass of the permeate was tracked using a Sartorius microbalance and timed throughout the experiment to determine the flux. A stir bar was used in the cell to provide agitation. The operating temperature was room temperature (22 °C). The pressure of the cell was slowly increased to 27.6 bar. The timer was started once the first drop of permeate passed through the cell. The experiment was stopped once 20 mL of permeate had passed through the cell for the fresh urine experiments and 30 mL for the hydrolyzed urine experiments. Therefore, all fresh urine experiments were had an 8% water recovery (permeate = 20 mL and feed = 250 mL) and the hydrolyzed urine experiments had a 12% water recovery (permeate = 30 mL and feed = 250 mL). All urine condition experiments were performed in duplicate. The pH and conductivity of the permeate was taken and the sample was then filtered and stored for analysis.

**Microfiltration of fresh and hydrolyzed urine**

The Sartorius Vivaflow 200 system was first rinsed with 1 L of ultrapure water with the retentate going to waste. Two hundred milliliters of urine was used for each experiment. The Vivaflow 200 was operated at a pressure of 2.25 bar with a flowrate of 275–375 mL/min. First, 100 mL of the urine was rinsed through the system with the retentate and permeate going to waste. The remaining 100 mL was then circulated

through the system until 50 mL of permeate was collected. Conductivity and pH readings were taken and then the sample was filtered and stored at for analysis.

All fresh urine experiment samples were analyzed for urea, total nitrogen (TN), total organic carbon (TOC), pH, and conductivity. All hydrolyzed urine experiment samples were analyzed for total ammonia nitrogen, TN, TOC, pH, and conductivity.

**Analytical Methods**

All samples were filtered before analysis through 0.45 μm nylon syringe filters (Environmental Express). Both urea and ammonia were measured directly. Urea was analyzed using a urea assay kit (Bioassay Systems, DUR-100) and a BioTek Synergy H1 Hybrid Multi-Mode Reader plate reader following the procedure detailed in the assay manual. A 1000 mg/L standard was used to increase the calibration curve from 500 to 1000 mg/L. Three check standards were used for every plate reading for accuracy and performed in duplicate to ensure precision. All samples were analyzed in triplicate to ensure precision. A Lachat Quikchem 8500 Series 2 Flow Injection Analysis system (FIA) was used to determine the total ammonia nitrogen concentrations. Samples were run in duplicate and a check standard was used for accuracy. Urea and ammonia results were confirmed through analysis of TN. TOC and TN were both analyzed using a Shimadzu Total Organic Carbon/Nitrogen Analyzer. Four check standards were used through each TOC/TN run. The pH and conductivity was recorded using an Orion Dual Star Multiparameter Meter, an Orion 9156BNWP Combination pH probe, and Orion Star A212 conductivity probe. The pH and conductivity were both calibrated following the instructions detailed in the pH probe and conductivity manuals.

**Data Analysis**

IBM SPSS Predictive Analytics was used to run Two-Way ANOVA tests with Post-Hoc tests. The parameters chosen were descriptive for the Two-Way ANOVA test and Bonferroni with an alpha value of 0.05 for the Post-Hoc test.

## Results and Discussion

### Urea rejection in fresh urine by RO, NF, and MF

Typically, high rejection percentages are preferred as they correspond to high retention of salts and unwanted constituents in the product water. However, since this work focused on nitrogen separation and recovery, a low nitrogen rejection and a high salt and TOC rejection is desired. A low nitrogen rejection means a high nitrogen recovery in the permeate product water while a low permeate conductivity means a high rejection of salts. Additionally, a high rejection of TOC corresponds to the rejection of low molecular weight organic compounds that are commonly found in urine. Therefore, a low nitrogen rejection and high rejection of salts and organic compounds means a high-purity nitrogen product free from contaminants. To confirm this approach, low nitrogen rejection by MF was used as a positive control to compare with nitrogen rejection by RO and NF.

Urea stabilization is a necessary process when considering the treatment of human urine for without it, spontaneous urea hydrolysis will occur during urine collection. Urea hydrolysis results in a pH increase causing the precipitation of struvite and hydroxyapatite, which are hard minerals that can ruin bathroom fixtures and piping and remove nutrients from solution [41, 125]. Passive dosing of a dilute acid or base at the collection devices would allow for stabilization of the urea through the collection system for urea recovery as well as maintaining the operating integrity of the piping system[40, 41].

Therefore, three fresh urine conditions were tested in duplicate. Fresh urine with no chemical addition, fresh urine with acetic acid addition, and fresh urine with sodium hydroxide addition were investigated to evaluate the urea rejection and the effect of urea stabilization on urea rejection by RO, NF, and MF. Fresh urine with no chemical addition was used for comparison with the acid and base additions but is not possible in a real urine system due to the aforementioned problems related to urea hydrolysis.

Figure 4.1 (a) shows the results for urea rejection by the three membrane processes at the three pH values. A Two-Way ANOVA statistical test and Bonferroni Post-Hoc with an alpha value of 0.05 was performed on the rejection and conductivity data which can be seen on the graph using the symbols a, b, ab, and c. It was determined that altering the pH for urea stabilization did not cause a statistical difference in urea rejection for both RO and MF experiments. The average rejection of urea for the RO and MF membranes were 57% and 3%, respectively. For NF, the average rejection of urea for pH 5, pH 6, and pH 12.5 were 56%, 55% and 42%, respectively. For NF, it was also determined there was no statistical difference between the urea rejection at pH 5 and pH 6 or the urea rejection at pH 6 and pH 12.5. However, there was a statistical difference between the urea rejection at pH 5 and pH 12.5. This suggests that addition of a base in comparison to an acid can lower the urea rejection by NF membranes by 10–15 percentage points. Increasing the pH to 12.5 is a drastic condition for membrane operation; however, a high pH was required in this research to investigate urea stabilization as shown in previous studies. The NF membrane operating pH as detailed by the supplier is 2–11. Operating above the specified pH can cause improper membrane function such as lowered rejection which can explain the slightly lower rejection of urea

by the NF membrane at pH 12.5. This is supported by conductivity measurements of the permeate. Figure 4.1 (b) shows the conductivity of the permeate solutions for each condition. Figure 4.2 (a), (c), and (e) show the difference in conductivity between the feed and permeate solutions for the fresh urine conditions by membrane type and Table 4.1 shows the percent reduction of conductivity. For the NF experiments, the conductivity of the permeate at pH 12.5 was statistically greater than the conductivity of the permeate at pH 6 and pH 5. Additionally, for NF experiments, the conductivity was reduced by 96–97% at pH 5 and pH 6. For pH 12.5, the conductivity was reduced by 79% for NF which was confirmed to have a significant difference. Previous literature has linked lowered rejection of uncharged organic compounds and increased permeate flux with elevated pH for membranes such as RO and NF [132-134]. The phenomenon was thought to be caused by an increase in the membrane's pore radii at the elevated pH. As the pH is increased, the acidic functional groups within the membrane experience electrostatic repulsion causing the pores to expand [132, 133]. This phenomenon is thought to occur only when ions are present in the feed solution [132, 135], such as it is the case with urine. Therefore, at pH 12.5, it is possible that the membrane rejection performance was lowered due to increased pore size allowing a greater amount of urea and other charged compounds, most likely monovalent ions, to pass through the membrane increasing the urea concentration and conductivity in the permeate. Use of ceramic membranes could mitigate this problem as they are known to withstand more harsh chemical inputs and have a higher pH operating range (2–14)[136, 137]. While in the past ceramic membranes have been more expensive, recent research has focused on reducing ceramic membrane costs by using low-cost, raw materials for fabrication which would make them a more

competitive choice for commercial water and wastewater treatment[137, 138]. TOC rejection, however, was not significantly affected by pH for any membrane tested, with ≥92% rejection for RO and NF and ≤5% for MF where the TOC contributed by urea was subtracted for the total permeate TOC and not considered so as to understand the membrane's performance for rejection of TOC that is not accounted for by urea.

Urea is an uncharged compound and therefore does not have electrostatic interactions to play a role in rejection. Urea is also a smaller compound with a molar mass of 60.06 g/mol which makes rejection by steric hindrance more difficult. Lee and Lueptow (2001) tested the rejection of nitrogen compounds by RO, low-pressure reverse osmosis (LPRO), and NF in deionized water solutions [29]. It was determined that urea had an average rejection of 52% for both RO and LPRO and NF had a urea rejection of 19% [29]. Yoon and Leuptow (2005) also showed the low rejection of urea by RO and NF (15–40%)[139]. In addition, Zhang et al., (2014) found that operation of an FO membrane in RO mode for the treatment of human urine had a urea rejection of 50% or lower [30]. This confirms that the current RO urea rejection results are consistent with previous literature. However, the lower NF results by the previous study (19% vs. 55%) can be accounted for by their use of NF45 membranes in comparison to NF90 which are characterized by a lower rejection due to the larger pore size of NF45 membranes. Additionally, Lee and Lueptow (2001) and Yoon and Leuptow (2005) tested the nitrogen rejection in DI water solutions which would create the environment for little to no organic fouling [29]. The current experiments were tested in real human urine which has a high organic content and a high concentration of other dissolved ions. Therefore, these results confirms previous research trends in a more complex solution.

There is limited published data on the rejection of urea or other organic compounds by MF as it is usually used as a pretreatment process for particle removal before NF or RO. The MF membrane used has a pore size of 0.2 μm. At this pore size, little to no dissolved compounds should be rejected, as its main purpose is the rejection of particulate matter. Figure 4.1 (a) shows that little urea was rejected by the MF membrane (3% for all MF conditions) and that the rejection was not affected by pH. In addition, the conductivity and TOC of the feed solution and the permeate solution were nearly identical, which can be seen in Figure 4.2 (a), (c), and (e) and Table 4.1. These results support the lack of rejection of any charged or uncharged dissolved compounds which was expected and indicate that MF would be a poor process for nitrogen separation. However, these results do show that MF would be an effective pretreatment process to remove particulate matter yet leave all dissolved compounds. This is especially important for treatment of human urine by membranes as fouling due to particulate matter will greatly reduce the effectiveness of the nitrogen recovery by the membranes, which Ray et al. (2019) demonstrated by through the use of fresh human urine and FO-MD [140]. Particulate matter caused extensive membrane fouling on the FO membrane surface reducing the overall urea recovery [140]. Additionally, for fresh urine conditions, coupling MF with the urea stabilization chemical additions can help reduce membrane scaling. Acid addition is a current technique for scale reduction and thus the acetic acid addition, which would have been added at the point of collection for urea stabilization, could help reduce the ability for calcium carbonate scale to form[141]. If acetic acid is not found to be effective due to its potential to stimulate biofilm growth, alternative acids could be used such as dilute citric acid or sulfuric acid [60, 126]. If a base were to be used for urea

stabilization, calcium and magnesium compounds will become supersaturated and precipitate due to the high pH which was observed by Ray et al (2019)[97]. Because the base, like the acid, will be added at the point of collection, the precipitation could be easily removed by MF before it is to be treated by NF or RO. Thus, the base addition would act as a precipitation pretreatment step in addition to a urea stabilization method.

**Ammonia and ammonium rejection in hydrolyzed urine by RO, NF, and MF**

Implementation of urea stabilization at the point of urine collection (bathroom fixtures) will ensure an effective urine collection process. However, Ray et al., (2018) determined that urea stabilization by acid addition was a reversible process where hydrolysis could be inhibited for a period of time but would then start to occur after a certain time [126]. Therefore, if the urine was collected and stored, hydrolysis would occur and nitrogen in the form of unionized ammonia or ammonium ion could be recovered, which may be desirable. Due to the pH dependence of the two nitrogen species in hydrolyzed urine and the desire to know the rejection of each nitrogen species in urine, three different hydrolyzed urine conditions were investigated: hydrolyzed urine with no chemical addition (pH 9), hydrolyzed urine with acetic acid addition (pH 6.5), and hydrolyzed urine with sodium hydroxide addition (pH 11.5). These three conditions were chosen because pH 9 is the buffered pH of hydrolyzed urine[33]. At pH 9, 70% of the nitrogen is as ammonium ion and 30% is as unionized ammonia. At pH 6.5, all of the nitrogen is in the form of ammonium ion. At pH 11.5, all of the nitrogen is in the form of unionized ammonia. The conditions were chosen based on calculations made using the $pK_a$ of ammonium (9.25) and equations developed by Emerson et al., (1975) to determine the necessary pH for the desired nitrogen speciation [142, 143]. Therefore, the three

conditions allowed for determination of rejection of nitrogen for both species separately as well as determination of the rejection of nitrogen when both species are present in urine and no chemical addition is made to the urine.

Figure 4.3 (a) shows the results for ammonia rejection for each hydrolyzed urine condition. The average ammonia rejection by MF was 3% as there was determined to be no statistical difference for MF nitrogen rejection based on pH and therefore no difference in rejection of unionized ammonia or the ammonium ion. There was no statistical difference in ammonia rejection between the RO and NF membranes at pH 6.5 and pH 9, when the dominant nitrogen species was the ammonium ion. For pH 6.5, the average ammonia rejection for the two membranes was 95%. For pH 9, the average ammonia rejection for the two membranes was 80%. However, at pH 11.5, when all the nitrogen was unionized ammonia, there was a clear statistical difference between the two membranes with RO rejecting 36% of the ammonia and NF rejecting 10% of the ammonia. In addition, there was no statistical difference between the NF rejection and MF rejection of ammonia, as unionized ammonia, at pH 11.5. Figure 4.3 (b) shows the conductivity of the permeate for each condition. Figure 4.2 (b), (d), and (f) show the difference in conductivity between the feed and permeate solutions for the hydrolyzed urine conditions by membrane type and Table 4.1 details the percent reduction of conductivity. Unlike at pH 12.5 for the fresh urine results, there was no significant difference in the conductivity of the permeate or in the percent reduction of conductivity for RO or NF at any pH. This can be explained by the higher pH for the fresh urine compared to the hydrolyzed urine (pH 12.5 vs. pH 11.5) as pH 11.5 is closer to the operating pH range detailed by the supplier (pH 2–11). In addition to a high reduction in

conductivity which accounts for charged ion rejection, both the RO and NF had a high rejection of TOC (≥93%) which would account for the rejection of low molecular weight neutrals and acids which are common organic compounds found in urine.

It can be concluded that RO rejected only 36% of unionized ammonia and NF rejected only 10% of the unionized ammonia. Like urea, unionized ammonia is small and uncharged which gives it a low rejection. However, unionized ammonia is even smaller than urea (18 g/mol vs. 60 g/mol). Thus, even less than 50% of the unionized ammonia was rejected. RO and NF rejected 93% of the ammonium ion without a statistical difference in rejection. This is an expected result for RO as RO membranes have tighter pores than NF allowing sufficient rejection of both monovalent and divalent ions by size exclusion and electrostatics. NF membranes, which tend to have a looser pore structure, have lower rejection of monovalent ions compared to divalent ions. Yet, both RO and NF had no statistical difference in rejection of nitrogen when the ammonium ion was the dominant nitrogen species. The membrane surface for both the RO and NF membranes is negatively charged which would cause rejection of co-ions in urine (such as $SO_4^{2-}$ and $PO_4^{3-}$) to be rejected due to charge repulsion. A counter-ion, such as $NH_4^+$, is then rejected by electroneutrality principles. It can be concluded that the ammonium ion is effectively rejected by the NF membrane by electrostatics, in particular, charge neutrality caused by the other ions in the urine solution. Lee and Lueptow (2001) found that both a BW30 RO membrane and a NF membrane had similar rejection of $NH_4^+$ (≈85%) in a synthetic wastewater solution [130]. Additionally, Lee and Leuptow (2001) found that RO and LRPO had greater than 90% rejection of ammonium carbonate, ammonium formate, and ammonium chloride while NF45 had greater than 75% rejection of ammonium

carbonate and much lower rejections of the other ammonium compounds due to their valency [29]. Minhalma and Pinho (2004) treated coke plant ammoniacal wastewaters by an HR-98-PP NF membrane and determined the rejection of ammonium to be 95% [144].

Consistent with the results for the fresh urine, MF had insignificant rejection of ammonia (3%) regardless of pH and thus nitrogen species. The unchanged conductivity and TOC of the feed and permeate solutions as also seen by the fresh urine MF results show that MF had little to no rejection of any dissolved compounds (≤12% of TOC). For hydrolyzed urine conditions, pretreatment of the urine by struvite precipitation followed by MF could reduce the membrane scaling during the NF or RO process by preventively removing the compounds that would cause scaling issues due to the concentration of the urine.

**Implications**

Figure 4.4 gives a conceptual overview of the important results. The different nitrogen species in urine and the effect of pH on the speciation of nitrogen can be seen. Additionally, the percent of nitrogen recovered are detailed for RO and NF at the three conditions. These results show the low rejection of urea (≈ 50% RO and NF) and unionized ammonia (36% RO and 10% NF) by pressurized membrane processes. While the low rejection of urea has been reported in literature, rejection of unionized ammonia by RO or NF in a real human urine solution has not been previously reported. This new knowledge has significant implications for nitrogen recovery from urine. Urea recovery from urine does not currently have an established method and is a difficult task due to its small size, uncharged nature, and stable vapor pressure. Conversely, ammonia recovery has been thoroughly studied through the processes of ion exchange for the ammonium

ion and ammonia air stripping for unionized ammonia but at a high cost with extensive chemical input. These results demonstrate that RO and NF have a unique ability to selectively separate urea and unionized ammonia from the other constituents in human urine shown by the high nitrogen permeation along with the high rejection of TOC and low permeate conductivity. Additionally, RO and NF are established membrane process used daily for water treatment purposes and point of use treatment. Operation and maintenance have been thoroughly investigated in the literature. Therefore, implementation of a RO or NF process would be an easy transition for operators as well as availability and accessibility of necessary products.

A statistically significant result from this work is the equal rejection of the ammonium ion (a monovalent ion) demonstrated by both RO and NF yet the unequal rejection of unionized ammonia by RO and NF (36% vs. 10%). There was additionally no statistical difference in the conductivities of the RO and NF permeate at pH 11.5 with NF rejecting 98% TOC. Therefore, it may be advantageous to use NF for unionized ammonia recovery compared to RO. Consideration will need to be given to the necessary purity of the product as RO may have an overall higher rejection of other constituents. Previous research has shown that NF was an effective membrane process for up to 92% retention of micropollutants and pharmaceuticals at the right conditions [129]. Ninety percent nitrogen recovery by NF would make for an efficient recovery process that could be operated at a lower pressure. Additionally, urea is a compound that can be synthesized from ammonia. Therefore, the recovery of ammonia from urine by NF could produce an ammonia product, or be used in the production of urea.

The vision for implementation of urine diversion with nitrogen recovery is that it would occur at the building level with specific interest in large commercial and institutional buildings where substantial volumes of urine would be generated, collected, and treated on-site. Saetta et al. (2019) determined that urea hydrolysis could be monitored and inhibited through the use of a cyber-physical system (CPS) which tracked the chemistry of the urine and took into account the building occupancy to make real-time decisions of dosing of acetic acid for urea stabilization[145]. Therefore, a CPS would be used to implement urea stabilization through dosing of acetic acid or sodium hydroxide. The stabilized urine would then be either treated for urea recovery by RO or NF soon after collection or, through reduced dosing and enhanced storage time, urea hydrolysis would occur in the storage tanks and the hydrolyzed urine could be treated for ammonia recovery by RO or NF. The form of nitrogen recovered would depend on the stakeholder's need and would determine the amount of storage needed for treatment.

The current study has determined the rejection of different nitrogen compounds by RO, NF, and MF in real human urine as well as the most effective conditions for nitrogen recovery. However, future research testing these conditions through larger scale, continuous flow RO and NF processes is needed to understand the extent of membrane fouling and key methods for its mitigation. Additionally, understanding the effect of key RO and NF parameters such as trans-membrane pressure and flux decline in a continuous flow system with real human urine will be necessary for future application of these membrane processes for nitrogen recovery.

## Conclusions

Urea and ammonia rejection by RO, NF, and MF was investigated in real fresh and hydrolyzed human urine. Selective separation of unionized ammonia in hydrolyzed urine by NF and RO was determined to be an effective process with 90% of unionized ammonia recovered by NF and 64% of unionized ammonia recovered by RO. For hydrolyzed urine, the optimal recovery conditions are a NF membrane at pH 11.5 which resulted in in 90% recovery of unionized ammonia, 86% reduction of conductivity, and 98% rejection of TOC. Additionally, NF separation for unionized ammonia recovery may be advantageous over RO due to its lower rejection of unionized ammonia yet high rejection of salts and TOC. In fresh urine, urea rejection by RO was 57% and not affected by adjusting the pH for urea stabilization. NF rejection of urea in fresh urine ranged from 42–56% with base addition decreasing the rejection of urea compared to acid addition. For fresh urine, the optimal recovery conditions are pH 6 or greater for RO and NF (RO and NF had no statistical difference at the pH values tested), which resulted in the greatest urea recovery and the lowest conductivity. For context, there is no established process for urea recovery from urine. Therefore, urea recoveries of approximately 50% are promising due to the lack of technology options.

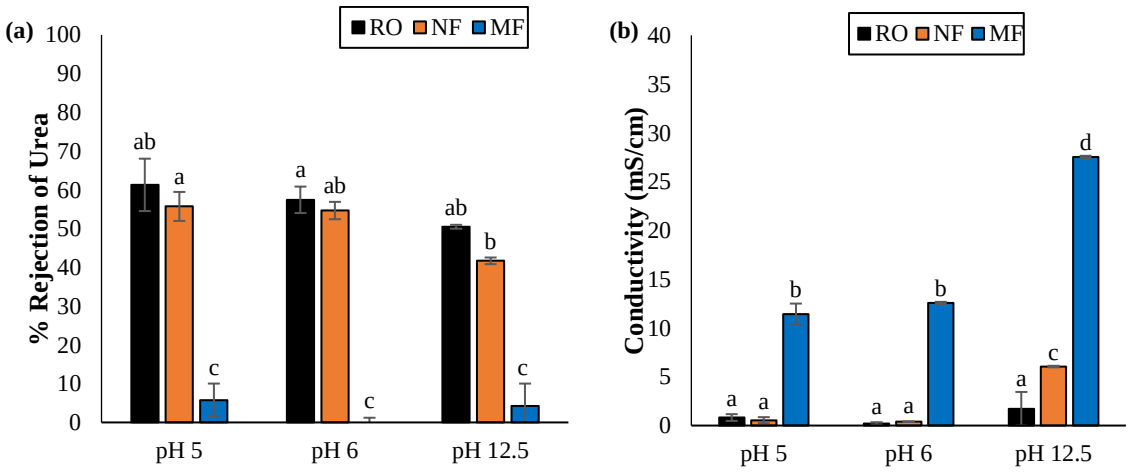



**Figure 4.1.** (a) Average urea rejection by RO, NF, and MF of real fresh human urine at three different pH values. (b) Average conductivity of the permeate solution by RO, NF, and MF of real fresh human urine at three different pH values. All experiments were performed in duplicate and error bars represent +/- one standard deviation. The statistical analysis of the rejection data determined three subgroups (a, b, and c) with three conditions falling in two subgroups (ab). The statistical analysis of the conductivity data determined four subgroups (a, b, c, and d). Conditions with one or more of the same symbols do not have a statistical difference while conditions with different symbols do have a statistical difference.

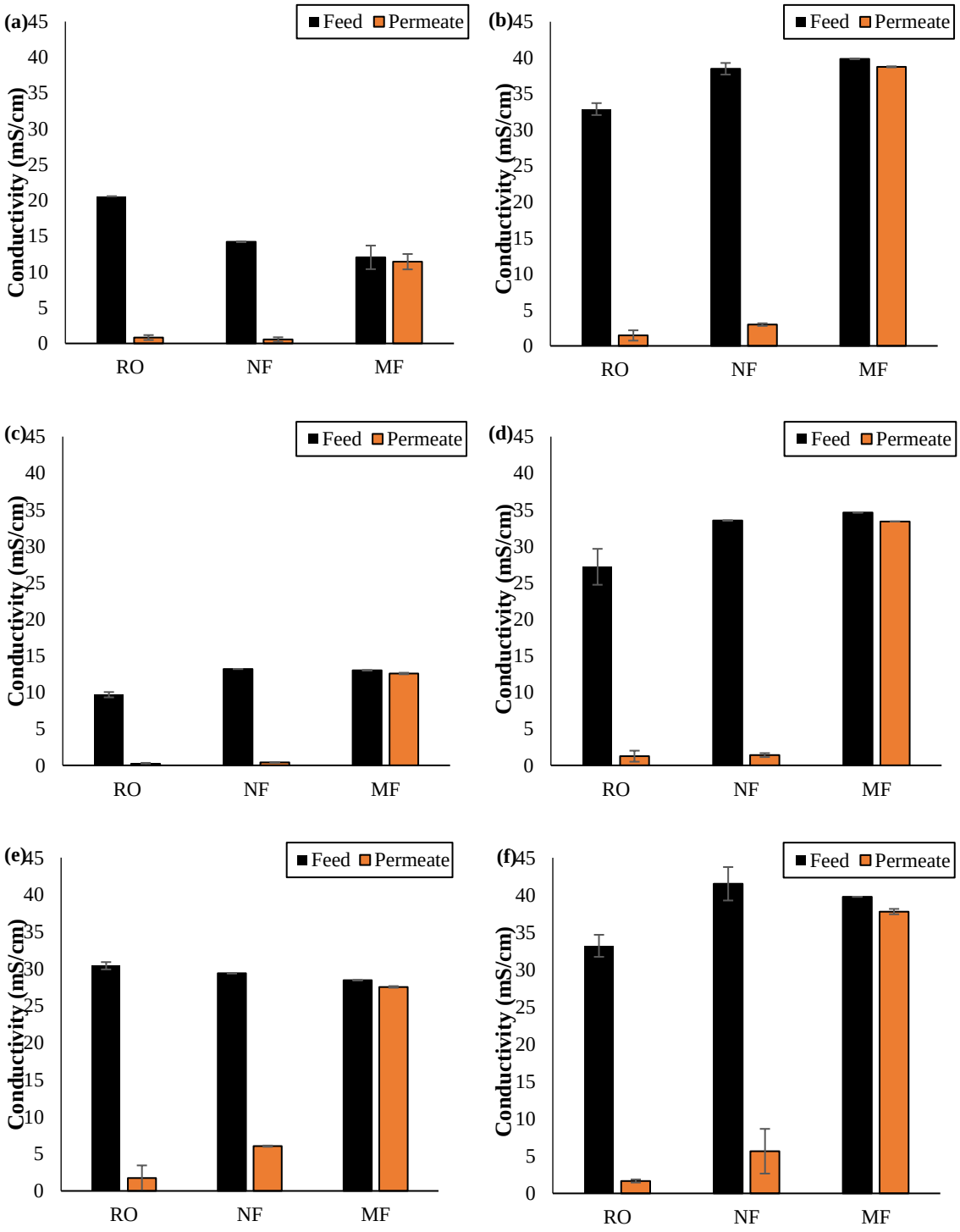



**Figure 4.2.** Comparison of feed and permeate conductivities for the three membrane types at each pH condition. The left column of subplots shows the fresh urine

conditions at (a) pH 5, (c) pH 6, and (e) pH 12.5. The right column of subplots shows the hydrolyzed urine conditions at (b) pH 6.5, (d) pH 9, and (f) pH 11.5. Experiments were performed in duplicate and error bars represent +/- one standard deviation.

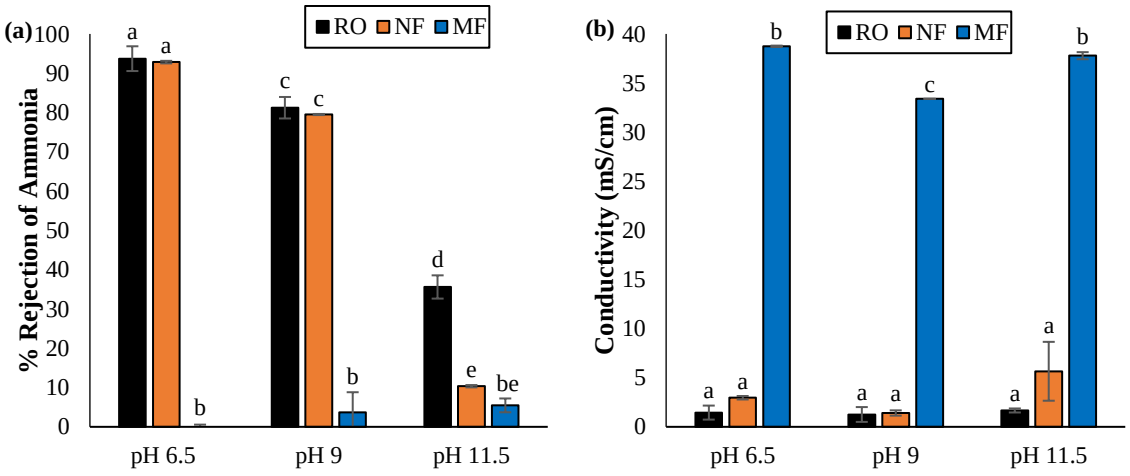



**Figure 4.3.** (a) Average ammonia rejection by RO, NF, and MF of real hydrolyzed human urine at three different pH values. (b) Average conductivity of the permeate solution by RO, NF, and MF of real hydrolyzed human urine at three different pH values. All experiments were performed in duplicate and error bars represent +/- one standard deviation. The statistical analysis of the rejection data determined five subgroups (a, b, c, d, and e) with one condition falling in two subgroups (be). The statistical analysis of the conductivity data determined three subgroups (a, b, and c). Conditions with one or more of the same symbols do not have a statistical difference while conditions with different symbols do have a statistical difference.

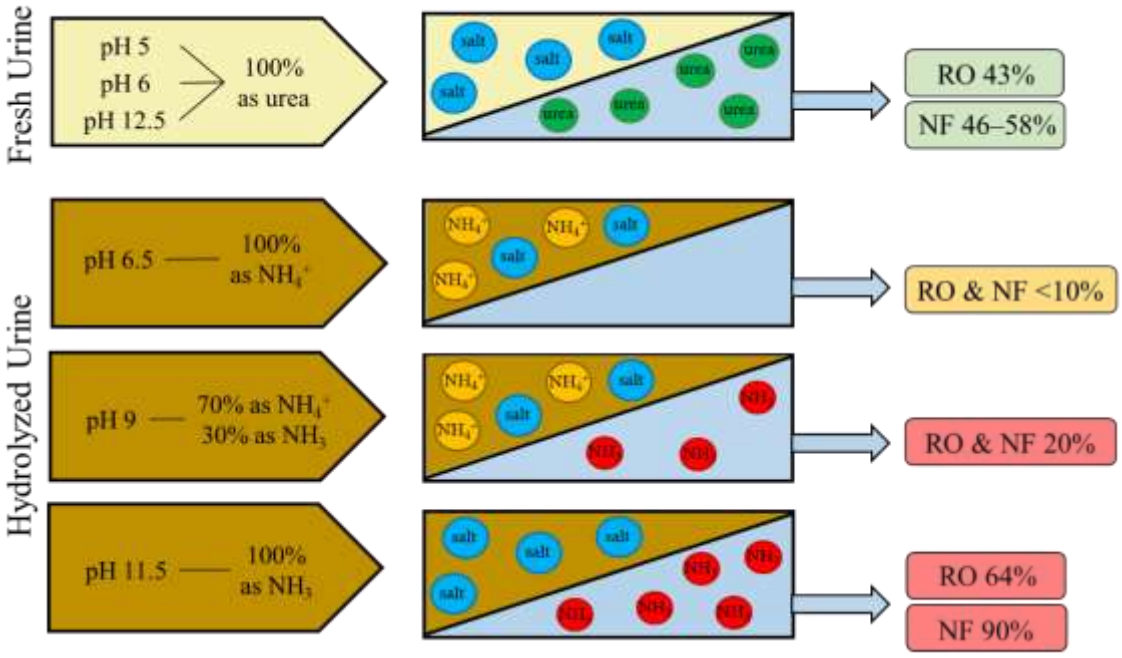



**Figure 4.4.** Graphical overview of the difference between fresh and hydrolyzed urine and the effect of pH on the nitrogen species in the urine. The "salt" compounds are used to show the movement of inorganic compounds that would be found in urine. The results for nitrogen recovery through separation by RO and NF, urea for fresh urine and ammonia for hydrolyzed urine, are given.

**Table 4.1.** Membrane performance characteristics for conductivity reduction and rejection of TOC. All reported values are averages for the duplicate experiments.

| Conductivity and TOC | | | | |
|---|---|---|---|---|
| **Membrane Type** | **Urine Type** | **pH** | **% Reduction of Conductivity** | **% Rejection of TOC** |
| RO | Fresh | 5 | 96 | 96 |
| | | 6 | 98 | 100 |
| | | 12.5 | 94 | 100 |
| | Hydrolyzed | 6.5 | 96 | 97 |
| | | 9 | 95 | 98 |
| | | 11.5 | 95 | 93 |
| NF | Fresh | 5 | 96 | 99 |
| | | 6 | 97 | 91 |
| | | 12.5 | 79 | 94 |
| | Hydrolyzed | 6.5 | 92 | 99 |
| | | 9 | 96 | 94 |
| | | 11.5 | 86 | 98 |
| MF | Fresh | 5 | 5 | 4 |
| | | 6 | 3 | 0 |
| | | 12.5 | 3 | 0 |
| | Hydrolyzed | 6.5 | 3 | 9 |
| | | 9 | 4 | 0 |
| | | 11.5 | 5 | 1 |

# CHAPTER 5

# AMMONIA RECOVERY AND FOULING MITIGATION OF HYDROLYZED HUMAN URINE TREATED BY NANOFILTRATION AND REVERSE OSMSOIS

## Ammonia Rejection and Fouling Behavior in Cross-flow RO and NF Systems

The global ammonia market is expected to reach a demand of USD 81 billion by 2025, over a 50% increase from 2017 [20]. The ammonia market is largely dominated by a need for nitrogen based fertilizers with a rising demand for "eco-friendly" refrigerants [20]. Other industry uses of ammonia include pharmaceutical production and textile manufacturing. Currently, ammonia is manufactured predominately via the Haber-Bosch process which requires 12,000 kWh/ton-$NH_3$ to combine gaseous hydrogen and nitrogen with an iron based catalyst at pressures above 100 bar and temperatures ~500°C [19, 146]. Consequently, 1–2% of the global energy use and 1.4% of the world's $CO_2$ emissions are due solely to ammonia production via the Haber-Bosch process, making ammonia the most energy-intensive and carbon emitting commodity chemical in the world [147]. In addition to the high energy demand of ammonia production, ammonia is also a considerable pollutant in the environment causing eutrophication and toxic algal bloom formation in freshwater bodies [3, 4, 6]. Ammonia pollution can be traced to many point and nonpoint sources, such as fertilizer runoff, confined animal feeding operations, and landfill leachate. One important and controllable point source of ammonia pollution is domestic wastewater [6]. To date, wastewater is sent to wastewater treatment plants (WWTPs) where it is treated for nitrogen and phosphorus removal and disinfection. However, current treatment techniques such as nitrification/denitrification do not provide pathways for nitrogen recovery as well as haven been demonstrated to allow excess

nitrogen to be discharged into waterbodies due to incomplete removal and accumulate having detrimental effects on both humans and the environment[4, 6]. In addition, biological nitrogen treatment techniques have been reported to release nitrous oxide, a harmful greenhouse gas, furthering the damage done for nitrogen removal by WWTPs [148]. Inventive, new ways of handling and treating wastewater, such as urine diversion, could have numerous benefits including ammonia recovery from urine which would reduce the demand of synthetically produced ammonia via the Haber-Bosch.

Human urine is a unique waste stream as it contributes only 1% of the volumetric flow of wastewater yet is responsible for 80% of the nitrogen and 50% of the phosphorus [8, 9]. Therefore, urine is a volumetrically small, nutrient dense waste stream that requires considerable energy at the WWTP and contributes to downstream pollution. Diversion of urine from the rest of wastewater would significantly reduce the nitrogen going into the WWTP as well as reduce the accumulation in the environment due to the discharge [10, 33]. In addition, the nitrogen in urine (~11 g N/person/day[11]) could be recovered and repurposed into industrial products in high demand. Urine's unique chemistry must be considered if nitrogen recovery is desired. Urine undergoes rapid change after excretion altering the form of nitrogen, pH, and salt concentrations. Fresh urine is characterized by a pH of 6, the presence of calcium and magnesium, and urea is the dominant form of nitrogen[15]. Once urine comes into contact with the ubiquitous urease enzyme (commonly found in bathrooms[149]), the urea is hydrolyzed into ammonia and bicarbonate, the pH rises to 9, and calcium and magnesium precipitate[13, 36]. Therefore, the urine must be hydrolyzed for ammonia recovery to be possible. In addition to urine chemistry,

processes efficient in terms of operation, ammonia recovery, and economically competitive must be determined.

The highly researched techniques for ammonia recovery from urine include ammonia air stripping[78, 79], adsorption by ion exchange[80-82], and microbial based fuel and electrolysis cells[10, 84, 150]. While each process has shown to be effective, not taking into account the current obstacles of energy demand, chemical costs, and scalability, the products produced from these processes are limited to ammonium sulfate. Production of a pure ammonia product would allow for greater application in industry beyond fertilizer such as meeting the rising demand for "eco-friendly" refrigerants, a pure ammonia solution used widely in industry for process cooling [151]. High pressure membrane processes such as reverse osmosis (RO) and nanofiltration (NF) are commonly used in water and wastewater treatment for production of clean water and volume reduction of waste streams due to their effective desalination properties and consistent performance [152, 153]. Research on the application of RO and NF on numerous waste streams has continued to expand with studies performed on the treatment of municipal, laundry, textile, coal, dairy, and carwash wastewater [153-163]. With regard to treatment of human urine, the research is limited. Ek et al. (2006) tested RO for concentration of hydrolyzed urine nutrients and found high rejection of phosphorous, potassium, and sulfur while nitrogen rejection varied based on pH (high rejection at low pH and low rejection at high pH)[164]. Pronk et al. (2006) found that NF was effective for rejection of 93% of pharmaceuticals in fresh urine but low rejection of urea and ammonia[129]. Ray et al. (2020) showed the effectiveness of RO and NF for selective ammonia separation from urine while still maintaining high rejection of TOC and salts[88]. Ammonia is a low

molecular weight neutral compound which reduces rejection by size exclusion and electrostatics allowing ammonia to pass through into the permeate. Separation of ammonia into the permeate by RO and NF allows for production of a pure ammonia solution. Ray et al. (2020) studied RO and NF by dead-end rejection tests to determine this novel ammonia separation [88]. While helpful for understanding solute rejection, dead-end studies do not consider the fouling of system which has the potential to highly alter solute rejection as the membrane fouls over time. Therefore, further research is required in cross-flow orientation to confirm the aforementioned results as well as to consider the effect that human urine, a feed solution with a high propensity for fouling, will have on a high pressure membrane process. Lastly, if the desire is to propose a new strategy for recovery of ammonia and reuse in products targeted for industry use, evaluation of the economic viability of the process and comparison with other established ammonia recovery processes are vital for application. Novelty and efficiency need to be coupled with economic feasibility.

Therefore, the goal of this research was to determine the ammonia rejection in hydrolyzed human urine and assess the fouling by cross-flow reverse osmosis and nanofiltration. The specific objectives were to (1) determine the ammonia rejection properties for RO and NF in a cross-flow system, (2) assess the fouling behavior of the RO and NF systems, (3) determine the impact microfiltration (MF) pretreatment has on fouling, and (4) perform a basic economic analysis of ammonia recovery by RO and NF compared to other ammonia recovery processes such as forward osmosis, ammonia air stripping, and ammonium adsorption by ion exchange.

## Materials and Methods

**Human Urine**

Human urine collection was approved by the Arizona State University (ASU) Institutional Review Board. Real fresh urine was collected from anonymous volunteers. The further detail on the collection procedure can be found in Ray et al.[99]. The collected fresh human urine was stored for six months to allow for hydrolysis of the urea to occur and for safe handling as determined by the World Health Organization[100]. The hydrolyzed urine was then used for the RO and NF experiments. The initial real hydrolyzed urine conditions can be found in Table D.1.

**RO and NF Setups**

RO experiments used Filmtec flat sheet BW30 membranes and NF experiments used DOW NF90 membranes both with active areas of 8.4 cm x 4.6 cm. The membranes were operated with active layer facing the feed solution and with polypropylene feed spacers (Conwed Plastics, 34 mils). The membrane system was comprised of 5 gal tank connected to a stainless steel Swagelok setup with a needle valve and pressure gauge used to control pressure. Inside the tank, a 3/8" x 50' stainless steel wort chiller (NY Brew Supply) was connected to the building cold water loop to chill the urine during experiments. A stainless steel membrane cell (5” x 3.8” x 2.5”) was made by the ASU machine shop. A Cole-Parmer flow meter (F-40375LN-6) and a Sensirion SLI-2000 flow meter (Staefa, Switzerland) were used to track the flow of the feed and the permeate, respectively.

**RO and NF Ammonia Rejection Experiments**

Hydrolyzed human urine was first pH adjusted to 11.1–11.2 using sodium hydroxide (25–41 mL/L of 10 N NaOH) and then filtered through the MF membranes.

More information on the urine pretreatment can be found in the SI. The RO and NF membranes were pre-wetted in a 50% isopropanol/50% ultrapure water (ultrapure resistivity 18.2 Ω) solution for 30 min. The membranes were then transferred into DI water for 10 min. Once completed, the membranes were transferred to fresh DI for an additional 10 min. For both RO and NF, the rejection experiments were operated at 375 psi, the cross-flow velocity was 37.8 cm/s, and the urine was kept at 20 °C. Ten liters of urine was used for each experiment. A t = 0 sample was taken after the urine had circulated through the system for 5 min to ensure complete mixing with the remaining DI water in the system as the systems could never be fully emptied. Once the system was started, the urine was circulated through the system until 50 mL of permeate was produced. Conductivity and pH measurements were immediately taken on the t = 0 and permeate samples. The samples were filtered through 0.45 μm pore filters and stored at 4 °C for further analysis. The samples were analyzed for ammonia, total nitrogen (TN), total organic carbon (TOC), $Cl^-$, $PO_4^{3-}$, $Na^+$, and $K^+$. Results referencing ammonia are defined as $NH_3 + NH_4^+$.

**RO and NF Fouling Experiments**

The fouling experiments were performed with 10 L of hydrolyzed human urine as the feed solution. Two different urine conditions were tested for both RO and NF: MF pretreated hydrolyzed urine and non-MF pretreated hydrolyzed urine. Therefore, depending on the condition, the urine was either pretreated by pH adjustment and MF in the manner previously stated or pretreated by pH adjustment alone. The membranes were prepared in the same manner as the rejection experiments. Prior to the fouling experiments, the membranes underwent a compaction period in DI water until the

permeate flux reached stable values (~4 h), after which the pretreated hydrolyzed human urine was added. Pressure, temperature, and crossflow velocity were held constant at 375 psi, 20 °C, and 37.8 cm/s, respectively. The permeate flow was returned to the reservoir to maintain a constant salt concentration. Fouling experiments were carried out for 24 h and the collected flux data was compiled into rolling averages of 20 data points.

**Analytical Methods**

All samples were filtered before analysis through 0.45 μm pore nylon syringe filters (Environmental Express). A Lachat Quikchem 8500 Series 2 Flow Injection Analysis system (FIA) was used to determine the total ammonia nitrogen concentrations and the permeate $Cl^-$ concentrations. Samples were run in duplicate and a check standard was used for accuracy. TOC and TN were both analyzed using a Shimadzu TOC-L/TNM-L Analyzer. Ion concentrations were measured by ion chromatography (Dionex ICS-1000) and inductively coupled plasma - optical emission spectrometer (Thermo iCAP6300). Scanning electron microscopy (SEM) analysis was done on the surface of the membranes and of the foulant collected from the tank by a JEOL JSM 6300 SEM. Fourier-transformed infrared (FTIR) spectra results were collected for each membrane using a Thermo Nicolet 6700 spectrometer Bruker IFS66V/S and PerkinElmer Frontier FTIR. The pH and conductivity were recorded using an Orion Dual Star Multiparameter Meter, an Orion 9156BNWP Combination pH probe, and Orion Star A212 conductivity probe. Further detail can be found in the SI.

**Data Analysis**

IBM SPSS Predictive Analytics was used to run Two-Way ANOVA tests with Post-Hoc tests. The parameters chosen were descriptive for the Two-Way ANOVA test and Bonferroni with an alpha value of 0.05 for the Post-Hoc test.

### Economic Analysis

RO and NF capital and operating costs were both considered and were based on a previous economic analysis by Mendret et al.[165]. The other ammonia recovery process costs and product offsets were based off an analysis summarized by Ray et al.[166]. All chemical costs were based on prices from Alibaba accessed in September 2020[102].

## Results and Discussion

### Ammonia and other compound rejection by RO and NF

Ammonia transfer was investigated in cross-flow RO and NF systems to test whether the previously determined low ammonia rejections by dead-end RO and NF hold true. Figure 5.1 shows the rejection of various compounds in real hydrolyzed human urine by RO and NF. Both RO and NF had ammonia rejections of 0% and less than 5% rejection of TN. The rejection of TOC was > 92% and the rejection of the multivalent $SO_4^{2-}$ and $PO_4^{3-}$ was > 97% for both RO and NF. The rejection of $Cl^-$, $Na^+$, and $K^+$ ranged from 91–97% for RO and 83–94% for NF. Notably, there was no statistical difference in rejection of $NH_3$, TN, TOC, $SO_4^{2-}$, $PO_4^{3-}$, $Na^+$, and $K^+$ for RO and NF. However, there was a statistical difference in rejection of $Cl^-$ between RO and NF. A high rejection of multivalent ions and TOC is expected as both RO and NF have a tight enough pore structure that should readily reject the larger compounds as well as the negatively charged membrane surface furthering rejection by electrostatic interactions. It is has been established that RO has superior rejection in terms of monovalent ion rejection which

explains the statistical difference in rejection of $Cl^-$, $Na^+$, and $K^+$. Yet, the rejection of $Na^+$ and $K^+$ by NF is above 93% showing a good rejection of two different monovalent ions for the membrane process. $Cl^-$ proved to have the lowest rejection in both the RO and NF systems with NF's rejection of $Cl^-$ being the lowest among all tested compounds, 83%. While the rejection of $Cl^-$ is lower for NF compared to RO, the rejection in comparison to other studies of NF rejection of $Cl^-$ is much higher. Studies such as Hilal et al. (2007) and Rautenbach and Linn (1996) who tested NF for seawater desalination and as a pretreatment for RO seawater treatment for scale reduction, respectively, found that NF had $Cl^-$ rejections ranging from 30–41% [167-169]. This can be explained by the chemistry of hydrolyzed human urine which is characterized by substantially less divalent anions, in particular $SO_4^{2-}$, than seawater (hydrolyzed urine = 960 ppm, seawater = 2800 ppm). Krieg et al. (2005) and Rautenbach and Linn (1995) theorized that the presence of the high valence $SO_4^{2-}$ drove more $Cl^-$ across the membrane, lowering the overall $Cl^-$ rejection [169, 170]. Therefore, the lack of high concentrations of $SO_4^{2-}$ allowed for greater rejection by the NF membrane which makes NF treatment of human urine more competitive as it can produce permeate with a quality closer to RO.

Ray et al. (2020) reported a BW30 RO membrane and a NF90 membrane, the same membranes used in this study, to have an ammonia rejection of 36% and 10%, respectively, when tested in dead-end orientation[88]. The lowered rejections determined by cross-flow orientation in this study can be explained by the pressure difference. Ray et al. operated the dead-end tests at 400 psi while this study operated at 375 psi which was the maximum pressure the system could operate at a steady pressure[88]. Grandison et al. (2002) who tested the rejection of different sugar solutions by NF in both dead-end and

cross-flow orientation found that increasing pressure increases rejection in particular for neutral compounds due to compaction[171]. Compaction of the membrane causes reduction of the pore sizes which is the most dominant rejection characteristic for neutral compounds[171]. Therefore, the lower operating pressure allowed for greater permeation of ammonia across the RO and NF membranes for the cross-flow orientation. The 0% rejection of ammonia by both RO and NF coupled with the high rejection of salts and TOC demonstrate that in terms of solute rejection and recovery, the membrane processes are highly effective towards ammonia.

**Fouling Behavior by RO and NF and the Role of MF Pretreatment**

Membrane fouling whether scaling, organic, or biofouling, will have significant effects on the overall operation of the membrane process. Reduced flux, lowered rejection of salts, and possible increase in ammonia rejection are consequences of membrane fouling that would reduce the effectiveness of the membrane process over time. In addition to membrane performance, fouling can require costly and frequent membrane cleaning and replacement which can greatly hinder application. Therefore, the fouling behavior of RO and NF for treatment of hydrolyzed human urine was investigated over 24 h. Furthermore, due to urine's high propensity for fouling, the use of a pretreatment such as MF to reduce the extent of fouling that could occur during the high-pressure RO and NF application was considered for this work. Consequently, both non-MF pretreated hydrolyzed human urine and MF pretreated hydrolyzed human urine were tested for RO and NF to understand the role that MF pretreatment has on the type and severity of fouling.

Figure 5.2 (a) shows the normalized flux over time for RO for both the MF pretreated and non-MF pretreated conditions. Over the 24 h, the flux for the non-MF pretreated urine decreased steadily as fouling occurred. The flux for the MF pretreated urine stayed fairly constant, not dropping below 0.8. Therefore, the MF pretreated had significant benefits for flux operation over the 24 h. Figure 5.2 (b) shows the same normalized flux over time for NF for the two MF conditions. Unlike with RO, the decrease in flux for the non-MF pretreated condition was minimal with little discrepancy between the non-MF and MF conditions. Thus, the flux for NF was not affected by the fouling that occurred, or at least to an extent that MF pretreatment had a noticeable effect. The experiments were performed in duplicate with the data reported in figure D.1.

SEM imaging of the membrane surfaces and of foulant grown in the tank during the non-MF RO experiments were performed after the conclusion of the 24 h fouling experiments to better characterize the type and severity of fouling. Figure 5.3 shows the SEM images for a virgin RO membrane, the MF pretreated RO membrane, and the non-MF pretreated RO membrane. The non-MF pretreated RO membrane was characterized by a dense fouling layer. Faint filament outlines can be seen in the dense fouling layer suggesting a compaction of bacteria and possible organic compounds. Due to the MF pretreatment, which greatly reduced the fouling density that occurred on the membrane surface, the SEM images of the MF pretreated RO membrane surface, figure 5.3 (c) and (d), allow for greater distinction of the fouling layer. The fouling is characterized by probable bacilli bacteria that range in size from 1 to 2 μm which further supports the assumption that the non-MF pretreated RO membrane experienced dense fouling due to bacteria and organic compounds. In addition to the bacteria, there are longer rod-shaped

structures that have sizes greater than 4 μm which would suggest the structure is not bacteria related. It is theorized to be fibers that dislodged from the MF filters that pretreated the urine. The dense fouling layer observed on the non-MF membrane surface has the appearance of extensive rod like structures layered together which would mean that the fouling layers between the two conditions are relatively the same, yet they differ in severity. That is due to the MF pretreatment which is effective for most bacteria removal. Degradation of the MF membrane over time due to the high operating pH, 11.2, could have allowed small amounts of bacteria through along with the fibers which is evident in the MF pretreated conditions where small amounts of bacteria are present on the membrane surface. Yet, the fouling layer is considerably less severe compared to the non-MF pretreated conditions. Figure 5.4 shows the SEM images for a virgin NF membrane, the MF pretreated NF membrane, and the non-MF pretreated NF membrane. The fouling observed on the NF membranes has the same characteristics as the RO conditions and would appear to be dominated by bacilli bacteria, organic compounds, and the theorized MF fibers. Furthermore, the trends seen by the RO conditions also hold true for NF operation. Figure 5.5 shows the SEM images of foulant that grew inside the tank (both on the sides and top of the tank, not in the liquid) for the non-MF pretreatment RO conditions. The foulant was prepped to preserve the structures of any biological components in the foulant. The images show the foulant to be dominated by bacilli and cocci bacteria. These images correlate well to the images of the membrane surface which were presumed to have dense layers of bacilli bacteria which has now been proved to have been present in the non-MF pretreated urine.

Figure 5.6 (a) shows the FTIR results for a virgin RO membrane, the MF pretreated RO membrane, and the non-MF pretreated RO membrane. The non-MF pretreated RO condition has extensive peak suppression which is indicative of a fouling layer that is dense enough to coat the membrane suppressing the intensity. Cho et al. (1998) demonstrated that fouled NF and UF fouled membranes with NOM had peak suppression[172]. This would support that the fouling layer is comprised of mostly compacted bacteria. There is still peak suppression exhibited by the MF pretreated RO condition, yet it is not as extensive which further justifies that MF does not alter the type of fouling that occurs but only reduces the extent of it. Figure 5.6 (b) shows the FTIR results for the NF membrane conditions. Unlike for the RO conditions, both the MF pretreated and non-MF pretreated exhibit very similar expressions and peak suppressions.

**Basic Economic Analysis of Ammonia Recovery from Urine by RO and NF**

An economic analysis was performed to determine the process costs and product offsets of ammonia recovery from human urine by RO and NF. The economic analysis also compared RO and NF with other established ammonia recovery processes from urine: ammonia air stripping, ammonia adsorption by ion exchange, and FO. The economic analysis of the RO and NF systems tested in the study considered the pretreatment of the hydrolyzed human urine by MF ($0.06/m$^3$ based on work by Chellam et al.[119]) and the pH adjustment with NaOH ($4.50/m$^3$ based on the required dose of 15 kg/m$^3$ NaOH to raise the pH and the price of NaOH, $0.3/kg[102]). Based on work by Mendret et al. (2019), which considered the economics of BW30 and NF90 membrane systems for water reuse applications, the RO and NF operation and maintenance costs for a system performing at 80% recovery were defined as $0.14/m$^3$ and $0.11/m$^3$,

respectively[165]. The annual capital costs for the RO and NF systems were defined as $0.014/m$^3$ and $0.016/m$^3$, respectively.[165] The product produced from the RO and NF systems is a water–ammonia solution and thus the product offset, $0.4/m$^3$, was determined by Alibaba prices for ammonia solutions. The process costs and product offsets for ammonia air stripping, ammonium adsorption by ion exchange, and FO are based on a previous economic analysis by Ray et al.[166].

Considering process cost alone, RO and NF are the most economically favorable processes at $4.69–4.72/m$^3$. The reduced cost for RO and NF is likely due to the lower chemical requirement necessary for operation compared to the other processes. FO has a high chemical requirement due to the draw solute concentration that is needed to establish an osmotic pressure difference as well as the chemical demand for pH adjustment. Ammonia air stripping has a chemical requirement for pH adjustment as well as an energy demand for temperature change. Ammonium adsorption by ion exchange requires chemical for regeneration as well as has a high cost for brine management and disposal. After RO and NF, FO, when magnesium sulfate is used as the draw solute (FO scenario 3), and ammonium adsorption by ion exchange have median process costs, $10.11–11.90/m$^3$ that are not highly unfavorable. Currently, this economic analysis shows that based on process costs alone and the tested parameters, FO, when potassium phosphate is used as the draw solute (FO scenarios 1 & 2), and ammonia air stripping have high process costs and are not competitive with the other processes.

The product offset coming from RO and NF has the highest value, $0.4/kg. An ammonia–water solution has diverse industry application as it can be used for production of different industry products (e.g., textiles, pharmaceuticals, refrigerant gas). The FO

scenarios 1 & 2 also produce a product with an offset of $0.4/kg due to the presence of phosphate in the fertilizer. The high product offset for FO scenarios 1 & 2 make the processes more economically competitive and depending on the stakeholder's product need, a desirable choice. FO scenario 3, ammonia air stripping, and ammonium adsorption by ion exchange produce an ammonium sulfate product which has a lower offset of $0.12/kg. Considering both the process costs and product offsets, RO and NF are highly competitive ammonia recovery processes for treating human urine with diverse industry application.

## Conclusions

This study investigated RO and NF for ammonia recovery from hydrolyzed human urine by quantifying the rejection of ammonia and various other compounds in urine in cross-flow orientation. In addition, the fouling behavior of the RO and NF systems was characterized and the efficacy of MF pretreatment for fouling reduction was determined. Ammonia rejections of 0% for both RO and NF along with high rejections of other salts and TOC further demonstrate the membrane processes to be effective ammonia recovery techniques. The stakeholder needs will determine the choice of RO or NF for application. For example, if the stakeholder needs the highest purity product possible, RO should be chosen over NF as NF had a lower rejection of monovalent ions, particularly $Cl^-$. An alternative to RO as well as to achieve an even higher purity product would be the use of a dual-stage NF system. Liu et al. (2013) determined that the use of a dual-stage NF system for seawater desalination was a feasible technology[173]. Therefore, operation of a dual stage NF system or dual stage system that utilizes an NF membrane

and a brackish water RO membrane could help with achieving a high quality pure ammonia product[173,174]. However, if purity of the product does not interfere with industrial application of the product, than use of NF would be an effective choice.

MF pretreatment had significant effects for both RO and NF operation. MF pretreatment preserved the flux of the RO membrane as well as preserved the integrity of the membrane surface for RO and NF. Extensive biofouling as well as minor inorganic fouling coming from the MF filter were identified on the surfaces of the membranes. Therefore, for long-term operation and preservation of the membrane, MF pretreatment is necessary. Both RO and NF experienced extensive bacteria growth on the membrane surface as well as in the feed tank. The severity of the bacteria growth was significantly reduced by MF pretreatment with very minimal growth occurring in the tank for the MF pretreated conditions. An economic analysis determined RO and NF to be competitive ammonia recovery processes in terms of both process cost, \$4.69–\$4.72/$m^3$, and product offset, \$0.4/kg, when compared with ammonia air stripping, ammonium adsorption by ion exchange, and FO having the lowest process cost and highest product offset value.

While this study investigated the fouling behavior over 24 h, future research concentrated on long-term operation of the membrane systems would provide more understanding on the flux over time and how fouling will affect its progression. In addition, research that tests different RO and NF membranes, such as SW30 or NF200, could produce even higher quality ammonia products [175]. Lastly, research which tests different membrane parameters such as lower pressure or higher cross-flow velocity would help identify the optimal conditions for operation and ammonia recovery and achieve not only the highest quality ammonia product but also determine the most

economically important parameters which can then be manipulated to find a balance between recovery and cost.

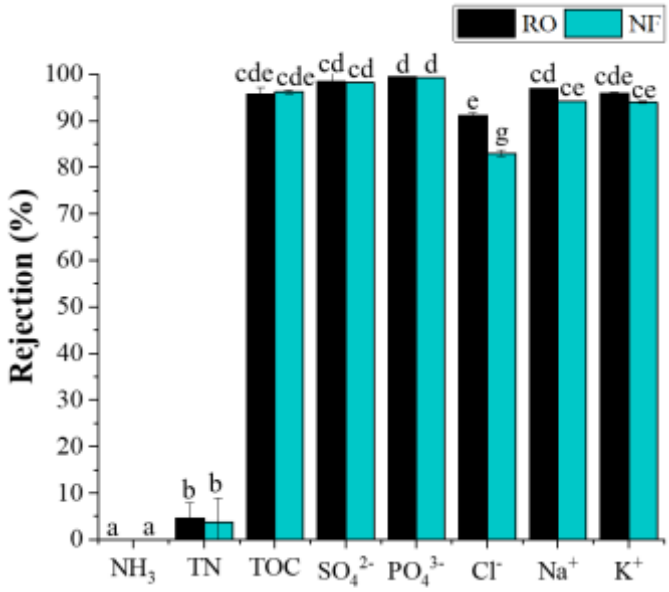



**Figure 5.1**. Rejection of various compounds in real hydrolyzed human urine by cross-flow reverse osmosis and nanofiltration. Conditions with one or more of the same symbols do not have a statistical difference while conditions with different symbols do have a statistical difference.

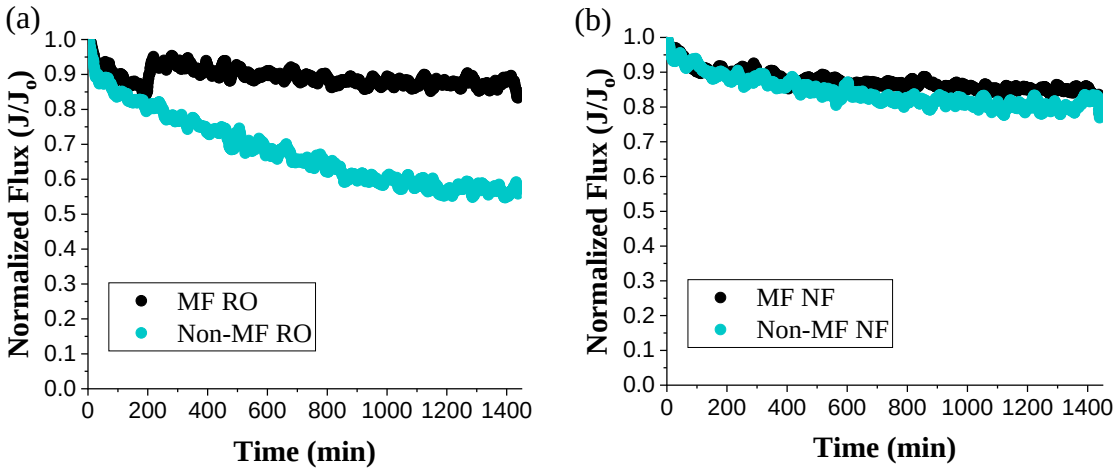



**Figure 5.2**. The normalized flux over time for the reverse osmosis and nanofiltration fouling experiments. (a) The normalized flux over time for the 2 reverse osmosis conditions to assess microfiltration as a pretreatment. (b) The normalized flux over time for the 2 nanofiltration conditions to assess microfiltration as a pretreatment.

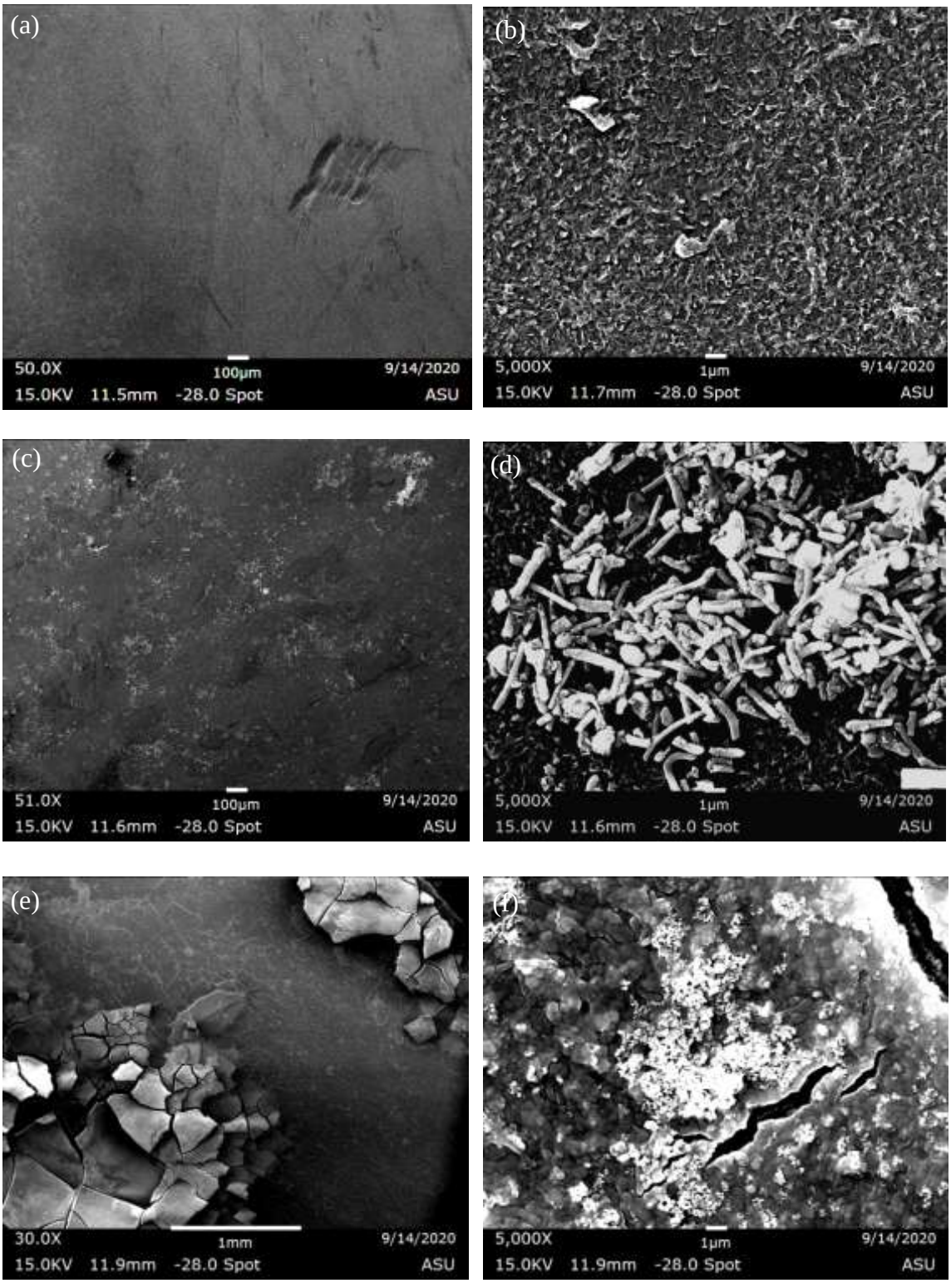
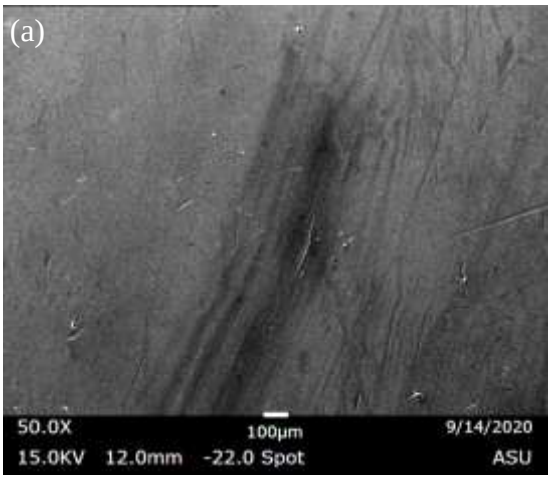

(a)
50.0X 100µm 9/14/2020
15.0KV 11.5mm -28.0 Spot ASU
(b)
5,000X 1µm 9/14/2020
15.0KV 11.7mm -28.0 Spot ASU
(c)
51.0X 100µm 9/14/2020
15.0KV 11.6mm -28.0 Spot ASU
(d)
5,000X 1µm 9/14/2020
15.0KV 11.6mm -28.0 Spot ASU
(e)
30.0X 1mm 9/14/2020
15.0KV 11.9mm -28.0 Spot ASU
(f)
5,000X 1µm 9/14/2020
15.0KV 11.9mm -28.0 Spot ASU

**Figure 5.3**. Scanning Electron Microscopy (SEM) images of the reverse osmosis membrane surface for the fouling tests. (a) control 50X, (b) control 5000X, (c) MF RO condition 50X, (d) MF RO condition 5000X, (e) Non-MF RO condition 30X, and (f) Non-MF RO condition 5000X.


(a)
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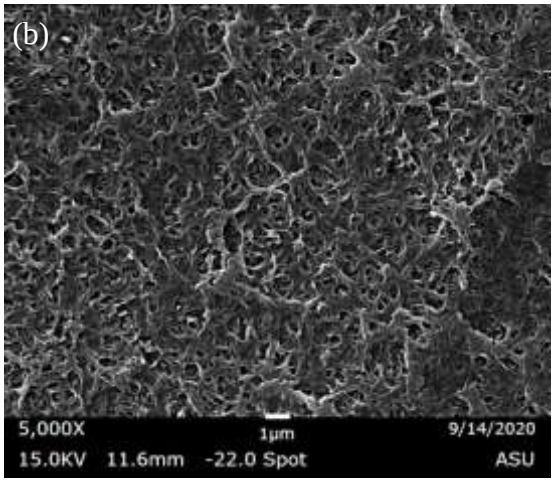
15.0KV 12.0mm -22.0 Spot ASU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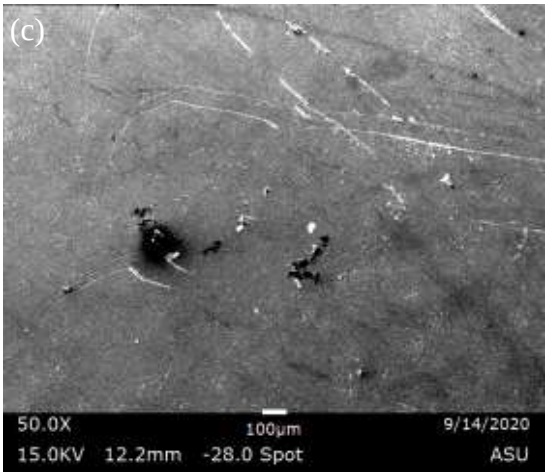
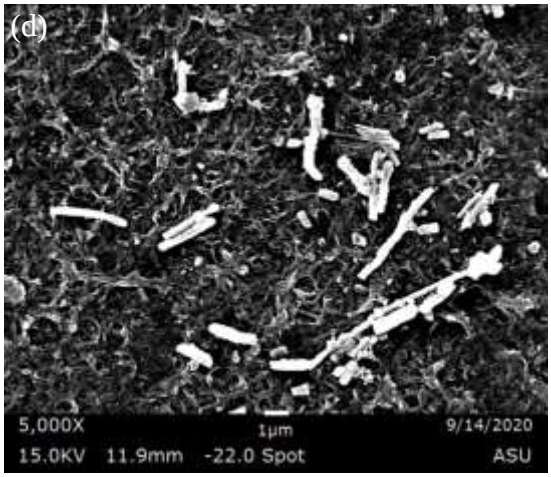

(c)
50.0X 100µm 9/14/2020
15.0KV 12.2mm -28.0 Spot ASU


(d)
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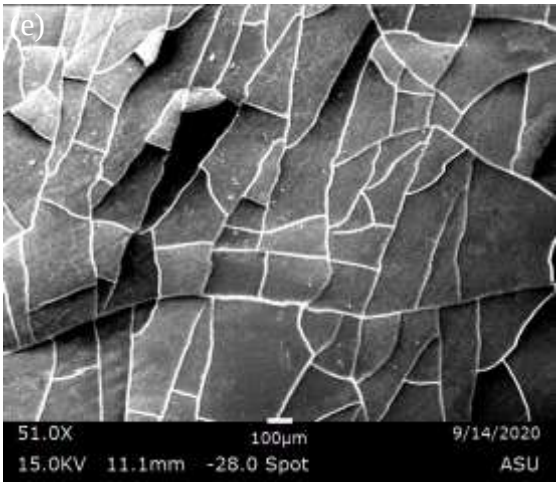
15.0KV 11.9mm -22.0 Spot ASU


(e)
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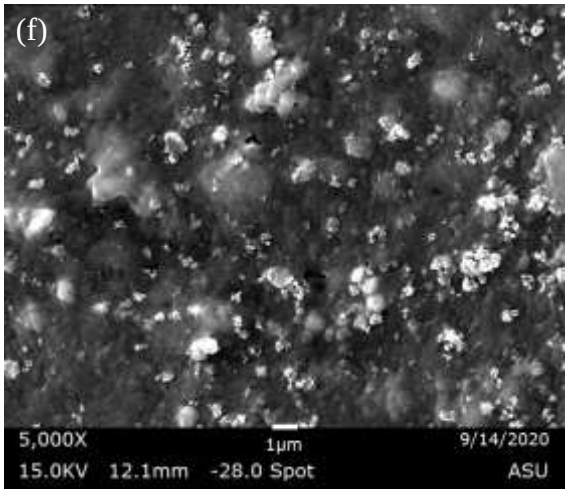
(f)
5,000X 1µm 9/14/2020
15.0KV 12.1mm -28.0 Spot ASU

**Figure 5.4**. Scanning Electron Microscopy (SEM) images of the nanofiltration membrane surface for the fouling tests. (a) control 50X, (b) control 5000X, (c) MF NF condition 50X, (d) MF NF condition 5000X, (e) Non-MF NF condition 50X, and (f) Non-MF NF condition 5000X.

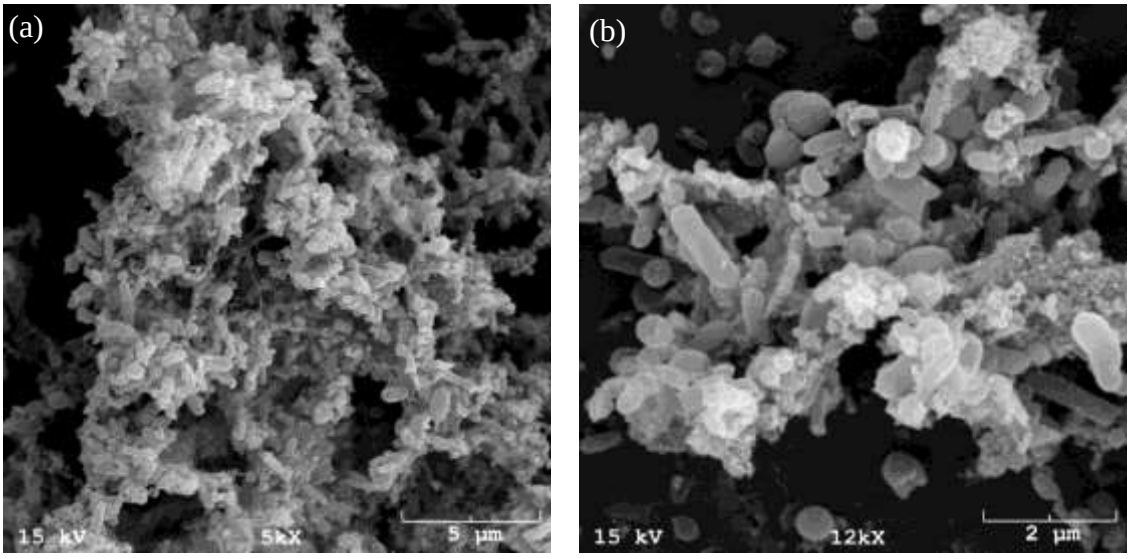


**Figure 5.5**. Scanning Electron Microscopy (SEM) images the foulant produced in the tank during the non-MF RO experiment. (a) 5000X and (b) 12000X.

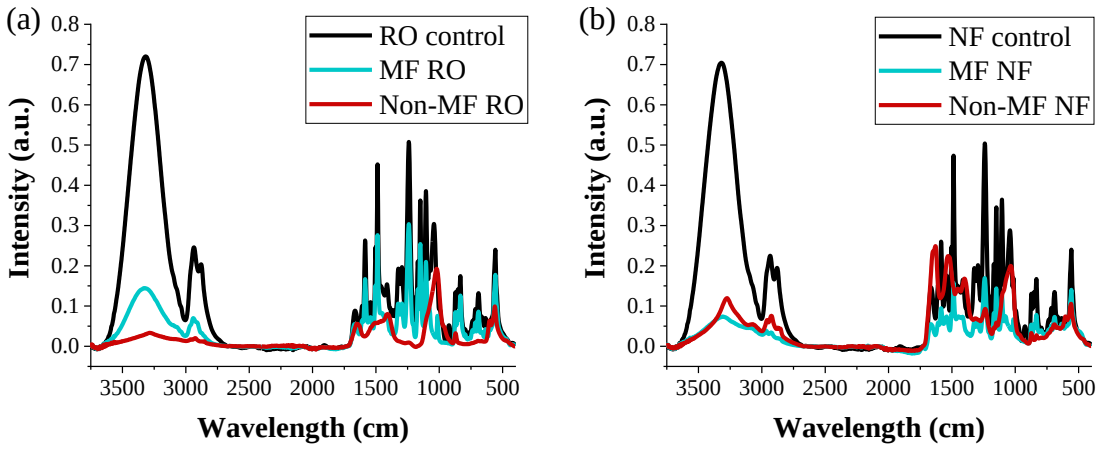


**Figure 5.6**. Fourier-transform infrared spectroscopy (FTIR) of the membrane surfaces for reverse osmosis and nanofiltration. (a) FTIR results for the 2 conditions and control membrane for reverse osmosis. (b) FTIR results for the 2 conditions and control membrane for nanofiltration.

**Table 5.1.** The initial urine composition for the reverse osmosis and nanofiltration compound rejection tests.

| Initial Urine Composition - Rejection Tests | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Membrane Process** | **Condition** | **pH** | **Conductivity (mS/cm)** | **Ammonia (mg/L N)** | **Total N (mg/L N)** | **TOC (mg/L C)** | **$PO_4^{3-}$ (mg/L $PO_4$)** | **$SO_4^{2-}$ (mg/L $SO_4$)** | **$Cl^-$ (mg/L)** | **$K^+$ (mg/L)** | **[a]$Na^+$ (mg/L)** |
| Reverse Osmosis | Test 1 | 11.14 | 40.06 | 3745 | 4582 | 1453 | 733 | 955 | 2974 | 1607 | 10182 |
| | Test 2 | 11.21 | 39.39 | 4330 | 4251 | 1551 | 661 | 998 | 2899 | 1521 | 9937 |
| Nanofiltration | Test 1 | 11.20 | 38.73 | 4375 | 4402 | 1466 | 688 | 925 | 2957 | 1522 | 9785 |
| | Test 2 | 11.21 | 40.28 | 4415 | 4212 | 1479 | 741 | 957 | 3171 | 1578 | 10211 |

[a]$Na^+$ concentrations are elevated due to NaOH addition for pH adjustment

**Table 5.2.** An economic analysis of ammonia recovery by RO and NF compared with other ammonia recovery processes from urine.

| Economic Comparison | | | |
|---|---|---|---|
| **Nitrogen Recovery Process** | **Process Cost[a]** | **Product Offset[a]** | **Product** |
| Reverse Osmosis | $4.72/m$^3$ | $0.4/kg | Pure Ammonia Solution |
| Nanofiltration | $4.69/m$^3$ | $0.4/kg | Pure Ammonia Solution |
| Forward Osmosis Scenario 1[b] | $65.91/m$^3$ | $0.4/kg | Ammonium Potassium Phosphate |
| Forward Osmosis Scenario 2[b] | $35.31/m$^3$ | $0.4/kg | Ammonium Potassium Phosphate |
| Forward Osmosis Scenario 3[b] | $10.11/m$^3$ | $0.12/kg | Ammonium Magnesium Sulfate |
| Ammonia Air Stripping | $22.93/m$^3$ | $0.12/kg | Ammonium Sulfate |
| Ammonium Ion Exchange | $11.90/m$^3$ | $0.12/kg | Ammonium Sulfate |

[a]All chemical costs were taken from Alibaba accessed in September 2020

[b]The scenario was based on work by Ray et al. (2020)

# CHAPTER 6

# CONCLUSIONS

## Conclusions

Nitrogen recovery from human urine is an alternative waste treatment and recovery process that not only reduces the accumulation of nitrogen in the environment but provides an alternative, natural, and local source of nitrogen with high versatility reducing the high demand for synthetically fabricated nitrogen through expensive and energy intensive processes. This work considered a number of different membrane processes for the selective recovery of two different nitrogen species, urea and ammonia. While each chapter assesses a separate process and nitrogen recovery technique, consideration of the collective work has produced notable conclusions that not only add new knowledge but can also inform future research.

The first notable conclusion is the role of pH. pH plays a significant role in terms of chemistry of the feed solution, membrane operation, and economic considerations. Human urine and pH are necessary considerations as it is a defining factor of the state of the urine (i.e. fresh vs. hydrolyzed) as well as a technique for ensuring the form of nitrogen that is present in the urine. Adjustment of the pH of urine whether through acid or base addition will inhibit the urea hydrolysis reaction ensuring the nitrogen stays in the form of urea keeping it available for recovery. If the urine has hydrolyzed, adjustment of the pH of the urine above 11 will ensure the nitrogen is complexly in the form of nitrogen for maximum recovery. Therefore, consideration must be given to what the desired end product is and determine how pH will need to be factored into the process, as it will be necessary. Operation at a consistently high pH (>11) can have negative effects on the

membrane process (e.g., flux and salt rejection). Yet, the high pH is necessary for ensuring the nitrogen is in the form of ammonia. Thus, determination of a balance of pH and membrane operation parameters must be determined. Economically, pH adjustment adds to the overall cost of the process. The high buffering capacity of hydrolyzed urine requires a substantial amount of base to be added to increase the pH above 11 to ensure maximum ammonia recovery (~18 g/L NaOH). In comparison, the buffering capacity of fresh urine is lower requiring less acid or base to be added for urea hydrolysis purposes (5.4g/L NaOH and 1.6 g/L acetic acid). Therefore, a pretreatment step such as pH requires total system consideration.

Another notable conclusion is the unequal recoveries of urea and ammonia. While urea and ammonia are both low molecular weight neutral compounds, the size difference makes a difference. The smaller molar volume of ammonia (24.85±0.02 $cm^3/mol$[176] vs. 43.13±0.78 $cm^3/mol$[176]) favors it for passage through the membrane allowing little to no rejection (0–36%). This work demonstrated the higher rejection of urea that can range from 45–80% depending on the membrane process which favors NF at pH 12.5 for the highest recovery. High-pressure RO and NF have higher recoveries and by extension lowered rejection of both nitrogen compounds compared to the low-pressure FO. This is most likely due to the high-pressure forcing passage through the membrane. Unlike in the low-pressure FO where lowered amounts of water passage are able to help transfer the urea through the membrane by advection and therefore relying more heavily on transfer by diffusion which was shown to be a considerably slow process.

Fouling must be given consideration when membrane processes are being studied even more so when the feed solution is human urine, a solution with high salts, TOC, and

microbial activity that will all affect the severity of fouling. Two main conclusions can be made from this work: (1) the type of urine (i.e. fresh vs. hydrolyzed) highly affects the type of fouling observed and the severity of it fouling and (2) MF pretreatment is vital for membrane integrity regardless of the membrane process. When treating fresh human urine by FO, the fouling was characterized by inorganic scaling due to precipitation that in turn exacerbated the organic fouling and biofouling. This is due to the presence of calcium and magnesium in fresh urine that readily precipitated out of solution especially in the conditions where a base was added to inhibit urea hydrolysis. Interestingly, the fouling observed by non-MF pretreated fresh urine and non-MF pretreated fresh urine with acid or base addition for FO operation was more extensive than the RO and NF fouling observed for hydrolyzed urine both pretreated by MF or untreated by MF. Furthermore, the fouling observed in fresh urine treated by FO, a process with a lower propensity for fouling in comparison to RO and NF which tend to have a higher degree of fouling due to compaction of the fouling layer, was the most significant overall. A possible explanation for this is that fresh urine is more biologically active while the long storage time and presence of ammonia in hydrolyzed urine allow for neutralization of much of the biological activity in fresh urine. Therefore, the chemistry of fresh urine (i.e. presence of $Ca^{2+}$ and $Mg^{2+}$ and biological activity) makes its fouling prosperity more severe than that of hydrolyzed urine. When treating hydrolyzed human urine where calcium and magnesium are not present, the scaling was minimal and biofouling, bacilli and cocci, and organic fouling were the main contributors to membrane fouling. The severity of the fouling was effectively reduced by MF pretreatment for the hydrolyzed urine treated by FO, RO, and NF. Therefore, pretreatment by MF is a necessary step for

preservation of the integrity of the membrane regardless of the type of membrane process.

Economic viability is just as necessary as sustainability and novelty. Understanding how the proposed treatment process fairs in comparison to similar treatment techniques is vital for its intended industry application. An economic analysis may not reveal the proposed process to be the most financially competitive process but it not only shows honest transparency but reveals the economically integral pieces of the treatment process that can be further studied and manipulated to produce more profitable outcomes. For this dissertation, each tested membrane process for nitrogen recovery also included an economic analysis that gave the process outcome as well as compared the process to other recovery techniques. FO has the potential to be an economically viable process but that is heavily dependent on the chosen draw solute that not only affects the costs but the produced product. For RO and NF, the economic analysis is much harder to determine due to the production of a pure ammonia product which makes its industry applications diverse and far-reaching. However, this also allows for greater diversification of application and clientele for this process. A basic economic analysis shows the process being an effective way for ammonia to be recovered and recycled into a product that has a present need in industry.

Chapter 1 and Figure 1.1 showed the current linear flow of nitrogen use and the proposed circular flow of nitrogen that this dissertation assessed. Figure 1.1 also pointed out the main considerations that need to be assessed for circular flow of nitrogen through treatment of human urine by membranes for nitrogen recovery to be possible: urine collection logistics, role of urea hydrolysis, pH adjustment, the types of products

produced, and the economics involved for each. Therefore, a valuable tool in the form of a decision tree was produced from this work. Figure 6.1, shows a summary decision tree for the use of membranes for nitrogen recovery from human urine which incorporates the main considerations mentioned above. The decision tree starts with the type of urine and breaks down the products that are able to be produced based on the chosen membrane process which is dependent on the type of nitrogen which is in turn dependent on the type of urine used. While the tree starts with the type of urine, the tree can be used from the bottom to top to determine the necessary conditions to produce a specific product depending on the needs of the stakeholder. The overall considerations that one would need to consider when planning a nitrogen recovery system using membranes are given in this figure and could be useful for future application endeavors.

## Future Work

This dissertation, while generating new insight into nitrogen recovery from membranes, has also revealed new areas for future research. The first area in need of future research is the application of RO and NF on MF-treated real fresh human urine for the recovery of urea. A pure urea solution would be an effective, lucrative product. While dead-end rejection of urea was determined to be ~50%, dead-end rejection data also showed RO has having 36% rejection of ammonia and yet the rejection in a cross-flow system was determined to be ~0%. Therefore, further research is warranted to determine if RO and NF are a viable process to recovery a pure ammonia product as well as the effect that acid or base addition for urea hydrolysis inhibition would have on the overall membrane processes.

Another area requiring more research is the testing of different types of membranes. For this dissertation, one FO, RO, and NF membrane were used. There are a number of different membranes that have differing properties that might make them a more suitable candidate for selective separation of urea and ammonia. An example is the Filmtec NF270 membrane which has shown lowered rejection of urea and other compounds in comparison studies with the Filmtec NF90 membrane which was used in this study. NF270 is considered a looser membrane in comparison to the tighter NF90. Another example is the Dow SW30 membrane, normally used for seawater, in comparison to the Dow BW30 membrane, normally used for brackish water, which was used in this study. Therefore, comparing the nitrogen rejection of these membranes may show a different membrane more favorable for selective separation, especially if the need for a pure solution is not as necessary. Thus, lowered rejection of nitrogen by other membranes along with lowered rejection of other compounds may not be problematic depending on the stakeholder's need.

In a similar manner as the membrane types, further research focused on the membrane operation properties such as flowrate and pressure could allow for maximum recoveries at a more economically favorable property such as reduced pressure. In the case of FO, the property of draw solute warrants further research. Experiments using differing salts that add value to the product as well as at differing concentrations to determine the lowest concentration that can achieve the highest nitrogen recovery. This is especially important as this dissertation determined that while advection coming from the water transfer produced from the osmotic pressure gradient helps with low molecular weight neutral compound transfer, transfer by diffusion is acting upon the system as well.

Furthermore, the greater amount of water transfer, the greater the dilution of the recovered ammonia. Therefore, determining the ideal draw solute concentration that allows for nitrogen transfer yet is the most economically favorable is necessary for future FO application.

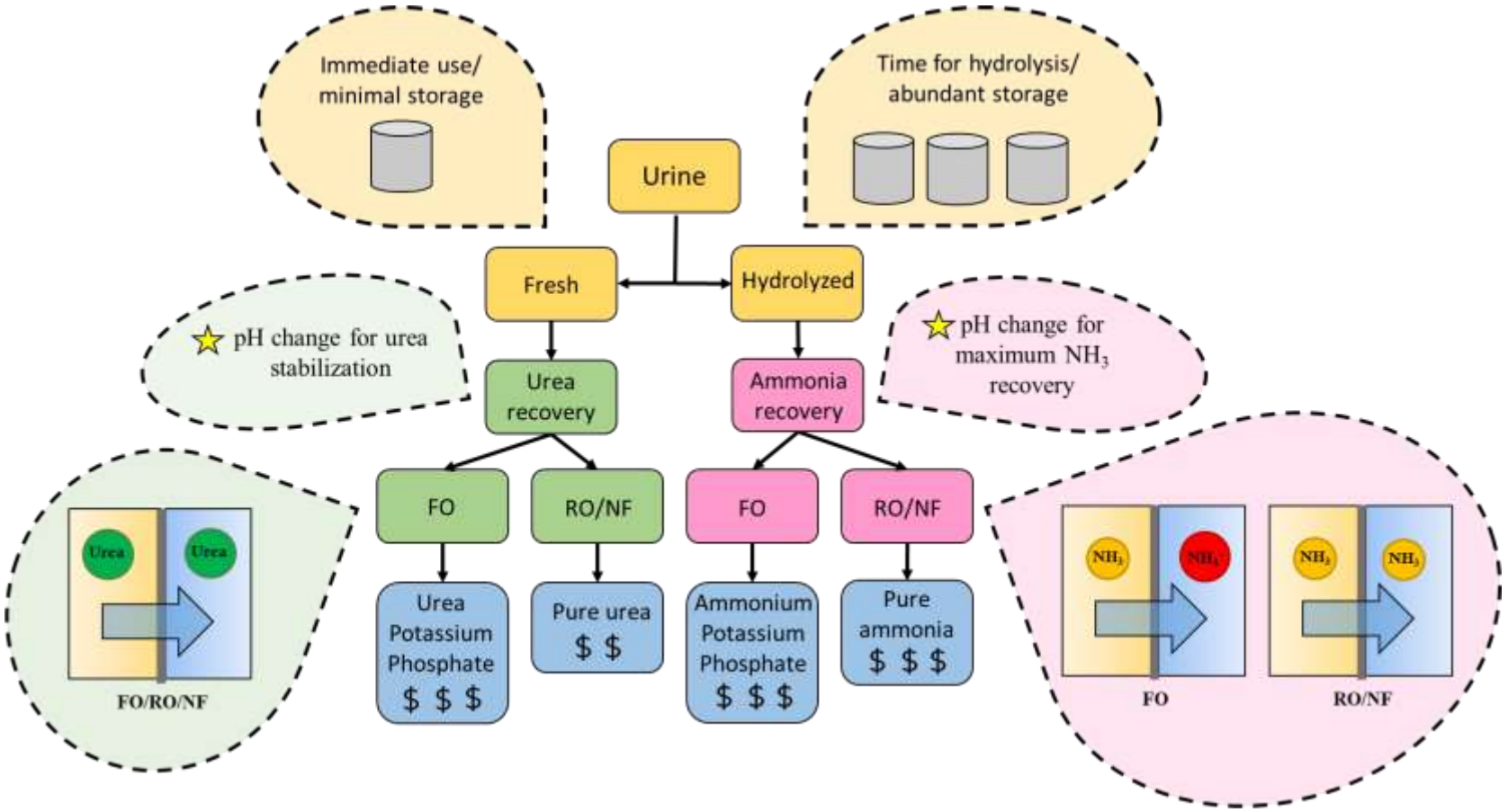
Immediate use/
minimal storage
Time for hydrolysis/
abundant storage
Urine
Fresh
Hydrolyzed
pH change for urea
stabilization
pH change for
maximum $NH_3$
recovery
Urea
recovery
Ammonia
recovery
FO
RO/NF
FO
RO/NF
Urea
Urea
FO/RO/NF
Urea
Potassium
Phosphate
$ $ $
Pure urea
$ $
Ammonium
Potassium
Phosphate
$ $ $
Pure
ammonia
$ $ $
$NH_3$
$NH_3$
$NH_3$
$NH_3$
FO
RO/NF

**Figure 6.1.** A summary decision tree for the use of membranes for nitrogen recovery from human urine. The decision tree flows as follows: type of human urine > type of nitrogen to be recovered > type of membrane process > type of product produced. Additional information is given for each step. The time and comparative storage needs, the reason for pH alteration, how the nitrogen is acting within the membrane process, and the comparative relative value of the different products produced. An important distinction should be made that while this schematic starts with the type of human urine and ends with the type of product produced, the decision tree can also be applied from bottom to top depending on the stakeholder needs. If one has a desired product, the decision tree will determine the necessary process and urine that will be required to produce that product.

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# APPENDIX A

# SUPPLEMENTARY INFORMATION FOR CHAPTER 2:

# UREA RECOVERY FROM FRESH HUMAN URINE BY FORWARD OSMOSIS AND MEMBRANE DISTILLATION (FO-MD)

## Materials and Methods

### Forward osmosis and membrane distillation set-ups

Cole-Parmer Acrylic In-Line Flowmeter, 1 GPM Water, 3/8" NPT (F) were used to monitor the flow of the solution in the FO and MD systems. Cole-Parmer console drive, 115 VAC, 50/60 Hz pumps were used to circulate the solutions in the system. Cole-Parmer Masterflex platinum-cured silicone tubing, L/S 17, was used throughout the FO and MD setup. A Cole-Parmer Polystat recirculator, 17 L/min, 250W cooling capacity, 115V 60 Hz chiller was used for the FO and MD experiments, and a Cole-Parmer Polystat Standard 6.5 L heated bath, 150 °C, 115VAC/60Hz was used for MD experiments. A Sartorius microbalance was used to track the increase in weight during the experiment to determine the flux of the FO and MD systems. WinWedge, a computer software, connected the balance to Microsoft Excel to log the data. pH and conductivity readings were taken for all samples using an Orion Dual Star Multiparameter Meter, an Orion 9156BNWP Combination pH probe, and Orion Star A212 conductivity probe.

### Analytical methods

Urea was analyzed using a urea assay kit (Bioassay Systems, DUR-100) and a BioTek Synergy H1 Hybrid Multi-Mode Reader plate reader following the procedure detailed in the assay manual. However, a 1000 mg/L standard was used to increase the calibration curve from 500 to 1000 mg/L. Three check standards were used for every plate reading: 800, 500, and 100 mg/L in duplicate to ensure accuracy. Total organic carbon (TOC) and TN were both analyzed using a Shimadzu Total Organic Carbon/Nitrogen Analyzer. Four check standards were used for each TOC/TN run: TN 5, TN 1, TOC 10, and TOC 5 mg/L.

**Table A.1**. The composition of the synthetic urine used for all synthetic urine experiments

| Synthetic fresh urine composition | |
|---|---|
| **Compound** | **Concentration (g/L)** |
| Urea | 15.0075 |
| NaCl | 2.5715 |
| $Na_2SO_4$ | 2.1305 |
| KCl | 2.982 |
| $MgCl_2 \cdot 6H_2O$ | 0.813 |
| $NaH_2PO_4$ | 2.3995 |
| $CaCl_2 \cdot 2H_2O$ | 0.588 |
| pH | 6 |

**Table A.2**. The saturation indices for magnesium minerals in synthetic urine at pH 12.5

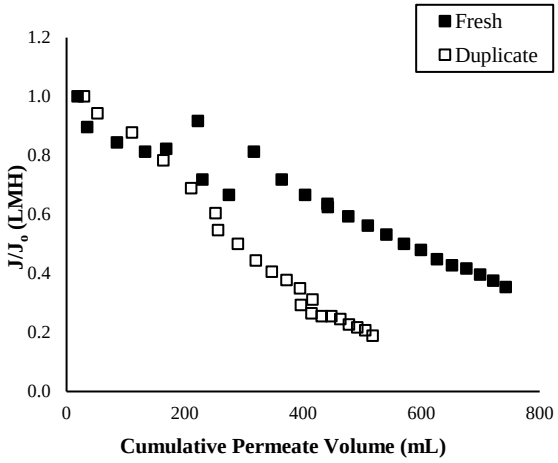
| Visual MINTEQ Saturation Indices | |
|---|---|
| **Mineral** | **Saturation index** |
| $Mg(OH)_2$ | 4.05 |
| $Mg(OH)_2$ active | 2.35 |
| $Mg_2(OH)_3Cl{:}4H_2O$ | 2.57 |
| $Mg_3(PO_4)_2$ | 3.89 |

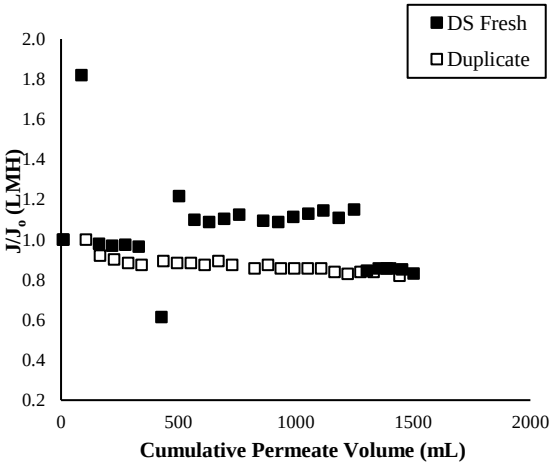
**Table A.3**. The TOC content in the FO draw solution at t = 24 h that is not accounted by the urea concentration. All units are mg/L C.

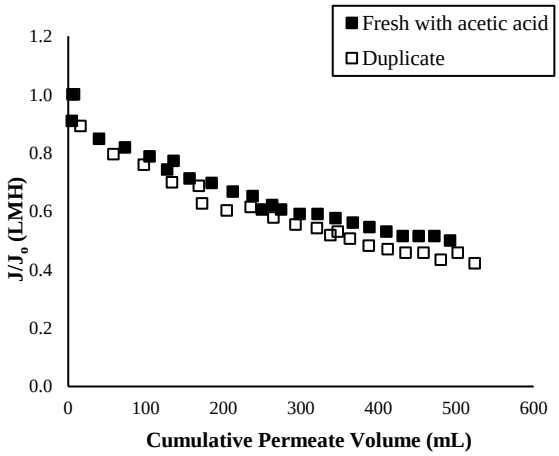
| Forward osmosis TOC content | | | |
|---|---|---|---|
| **Urine Condition** | **TOC in Draw at t = 24 h minus urea content** | **Duplicate Run** | **Average % Permeation of TOC** |
| **Fresh** | 391 | 43 | 6 |
| **Fresh with acid** | 100 | 85 | 3 |
| **Fresh with base ($Ca(OH)_2$)** | 107 | 70 | 2 |
| **Fresh with base (NaOH)** | 103 | 106 | 4 |
| **Synthetic fresh with base (NaOH)** | 24 | 35 | 5 |

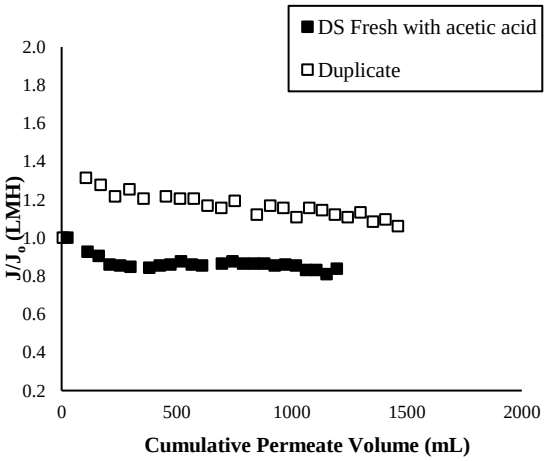
**Table A.4**. Urea concentrations and mass balance for forward osmosis and membrane distillation

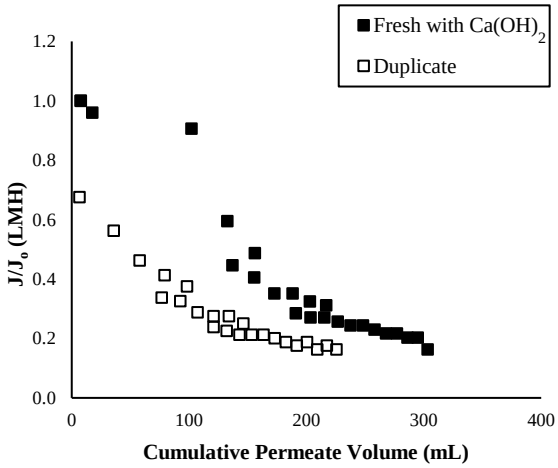
| Table A.4 - Urea Recovery for FO and MD | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Urine Condition | FO Initial Feed (mg/L urea) | FO Initial Feed (mg urea) | FO Product (mg/L urea) | FO Product (mg urea) | FO %Recovery | MD Initial Feed (mg urea) | MD Product (mg/L urea) | MD Product (mg urea) | MD %Recovery | Concentration Factor | Final MD Concentration Compared to Urine (%) |
| Fresh | 9027 | 36108 | 2930 | 8204 | 23 | 6711 | 5327 | 6179 | 92 | 1.8 | 59 |
| Duplicate | 6427 | 25710 | 1670 | 4459 | 17 | 4421 | 4004 | 4084 | 92 | 2.4 | 64 |
| Fresh with acetic acid | 8826 | 35304 | 1815 | 4792 | 14 | 4002 | 2711 | 3362 | 84 | 1.5 | 31 |
| Duplicate | 6170 | 24680 | 1471 | 4008 | 16 | 4101 | 3474 | 3682 | 90 | 2.4 | 60 |
| Fresh with base ($Ca(OH)_2$) | 10601 | 42404 | 2179 | 5230 | 12 | 5306 | 5877 | 3802 | 72 | 2.7 | 55 |
| Duplicate | 10834 | 43336 | 2036 | 4744 | 11 | 4467 | 3832 | 3698 | 83 | 1.9 | 35 |
| Fresh with base (NaOH) | 8137 | 32548 | 1571 | 3737 | 11 | 3483 | 5958 | 2985 | 86 | 3.8s | 73 |
| Duplicate | 7894 | 31576 | 1544 | 3629 | 11 | 3279 | 4466 | 3037 | 93 | 2.9 | 57 |
| Synthetic fresh with base (NaOH) | 13732 | 54928 | 4379 | 11385 | 21 | 8730 | 9786 | 6968 | 80 | 2.2 | 71 |
| Duplicate | 13108 | 52432 | 4277 | 11098 | 21 | 9506 | 8433 | 7421 | 78 | 2.0 | 64 |

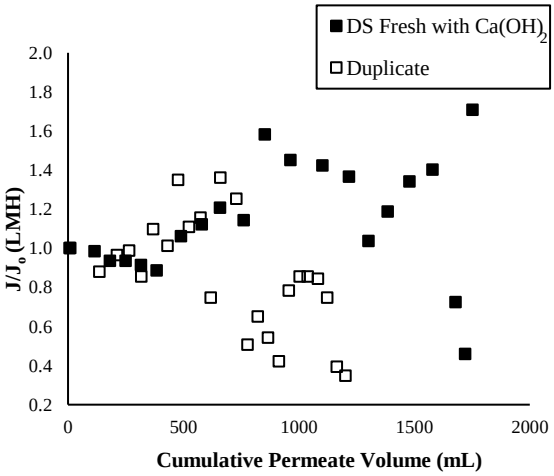

Fresh
Duplicate
J/J$_o$ (LMH)
Cumulative Permeate Volume (mL)


DS Fresh
Duplicate
J/J$_o$ (LMH)
Cumulative Permeate Volume (mL)


Fresh with acetic acid
Duplicate
J/J$_o$ (LMH)
Cumulative Permeate Volume (mL)


DS Fresh with acetic acid
Duplicate
J/J$_o$ (LMH)
Cumulative Permeate Volume (mL)


Fresh with Ca(OH)$_2$
Duplicate
J/J$_o$ (LMH)
Cumulative Permeate Volume (mL)


DS Fresh with Ca(OH)$_2$
Duplicate
J/J$_o$ (LMH)
Cumulative Permeate Volume (mL)

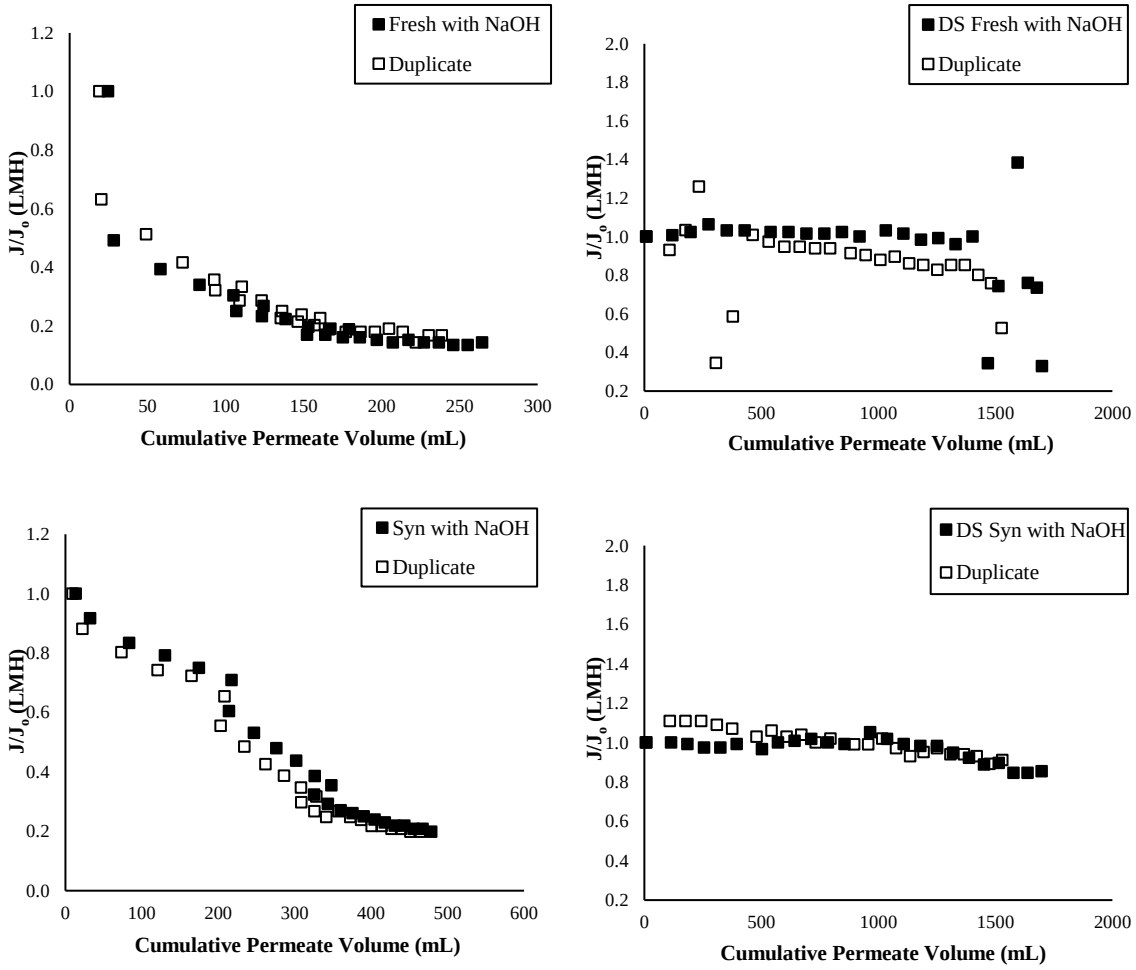



**Figure A.1.** Duplicate membrane comparisons for each urine condition. The left column is comparisons of FO duplicate experiments. The right column is comparisons of MD duplicate experiments.

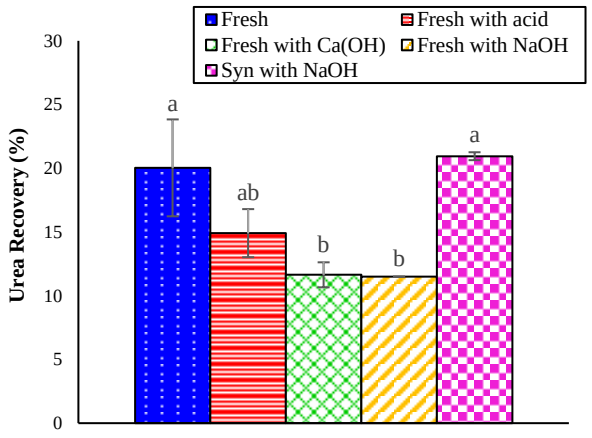
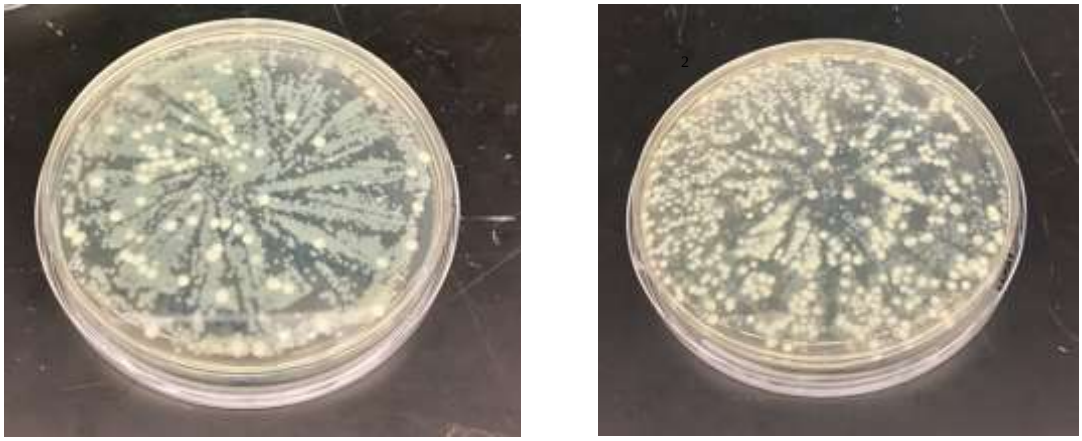



**Figure A.2.** Urea separation percentages by forward osmosis for each urine pre-treatment condition. The graph includes the statistical grouping coming from a One-Way ANOVA test on the separation percentages. The graphed data is mean values ± one standard deviation for duplicate runs for time 24 h.



1:100,000 = 8.26e9 CFU  1:10,000 = 5.28e9 CFU

**Figure A.3.** Spread plates for bacteria counts from the forward osmosis membrane surface for the real fresh urine condition after 30 hours of operation. Two different dilutions were performed. CFU stands for colony-forming unit.

# APPENDIX B

## SUPPLEMENTARY INFORMATION FOR CHAPTER 3:

## AMMONIA RECOVERY FROM HYDROLYZED HUMAN URINE BY FORWARD OSMOSIS WITH ACIDIFIED DRAW SOLUTION

## Materials and Methods

### Microfiltration Pretreatment

Spectrapure microfiltration (MF) systems were used to pretreat the urine. A 1 µm sediment filter cartridge (L-SF-MT-1-10) followed by a 0.2 µm ZetaZorb sediment filter cartridge (L-SF-ZZ-0.2ABS-10) were used to process the urine after the pH of the urine was altered. A dual position housings fitting mounting bracket (FA-2STA-10) with a Cole-Parmer Masterflex L/S digital pump with an Easy-Load II pump head were used. All filter diameters were 25.4 cm. The Spectrapure MF membranes were chosen as they were a local, commercially available, cost-effective option that should effectively remove suspended solids and bacteria based on the pore sizes.

### Forward osmosis and membrane distillation set-ups

Cole-Parmer Acrylic In-Line Flowmeter, 1 GPM Water, 3/8" NPT (F) were used to monitor the flow of the solution in the FO systems. Cole-Parmer console drive, 115 VAC, 50/60 Hz pumps were used to circulate the solutions in the system. Cole-Parmer Masterflex platinum-cured silicone tubing, L/S 17, was used throughout the FO setup. A Cole-Parmer Polystat recirculator, 17 L/min, 250W cooling capacity, 115V 60 Hz chiller was used for the FO experiments. A Sartorius microbalance was used to track the increase in weight during the experiment to determine the flux of the FO and MD systems. WinWedge, a computer software, connected the balance to Microsoft Excel to log the data. pH and conductivity readings were taken for all samples using an Orion Dual Star Multiparameter Meter, an Orion 9156BNWP Combination pH probe, and Orion Star A212 conductivity probe.

### Dead-end forward osmosis of fresh urine

The FO membranes were wetted in a 50% isopropanol/50% ultrapure water (resistivity 18.2 Ω) solution for 30 min. The membranes were then transferred into ultrapure water for 10 min. After the 10 min were completed, the membranes were transferred to fresh ultrapure for an additional 10 min. For all experiments, 450 mL of solution was used on each side of the membrane. Initial samples were taken from the bulk solutions. The solutions were then poured into membrane setup and the timer was started. The initial heights of the solutions were marked. At 1 h, the rise or fall of the solution was recorded using a measuring tape, and a 20 mL sample was taken from each side. The new liquid heights were marked.

Cleaning procedure

The membrane systems were cleaned immediately after each experiment using the following procedure: tap water rinse, 10% bleach for 15 min, tap water rinse, 5 mM EDTA for 15 min, tap water rinse, DI water with NaOH added to increase the pH to 11 for 15 min, tap water rinse, and three DI water rinses each for 10 min.

Analytical methods

For the urea analysis by assay kit, a 1000 mg/L standard was used to increase the calibration curve from 500 to 1000 mg/L. Three check standards were used for every plate reading: 800, 500, and 100 mg/L in duplicate to ensure accuracy. Ammonia and urea results were confirmed through analysis of Total Nitrogen (TN). Four check standards were used for each TOC/TN run: TN 5, TN 1, TOC 10, and TOC 5 mg/L. The criteria for accuracy was within 10% of check standards, and the criteria for precision was samples run in duplicate.

**Figure B.1.** Picture detailing the dead-end forward osmosis (FO) setup that was used for determination of urea transfer across the FO membrane.

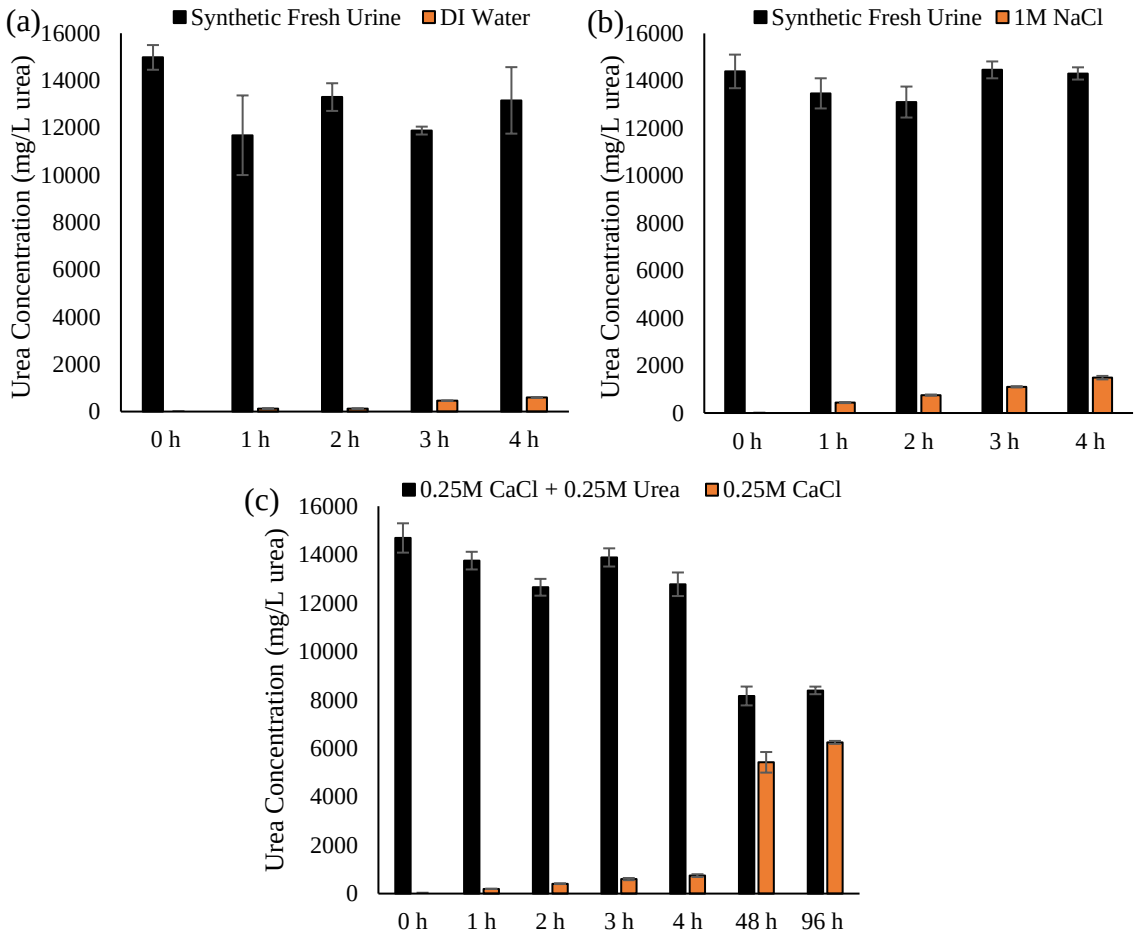



**Figure B.2**. Duplicate data for the dead-end FO evaluation of low molecular weight neutral compound transfer where urea was used as the model compound. The urea concentration over time for (a) condition 1: DI water and synthetic fresh urine, (b) condition 2: synthetic fresh urine and 1M NaCl, and (c) condition 3: 0.25M CaCl + 0.25M urea and 0.25 CaCl. Error bars represent +/- one standard deviation.

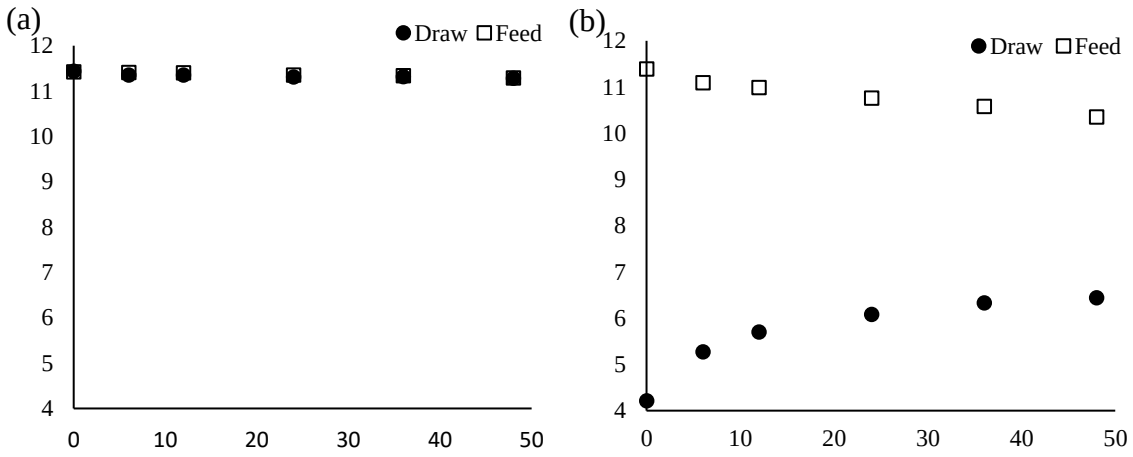



**Figure B.3**. The pH of both the feed and draw solutions over time. (a) NaCl draw solution condition where both the feed and draw solutions were pH adjusted to 11.5 which explains the overlap of the feed and draw data points. (b) $KH_2PO_4$ draw solution condition where the feed was pH adjusted to 11.5 and the draw had a natural starting pH of 4.2. The graphed values are averages for duplicate experiments.

**Table B.1**. The initial urine composition for the two real hydrolyzed urine scenarios. The table refers to the urine composition after pH adjustment and microfiltration.

| Initial Urine Composition | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Condition** | **Urine Type** | **pH** | **Conductivity (mS/cm)** | **Urea (mg/L urea)** | **[b]Urea (mg/L N)** | **Ammonia (mg/L N)** | **Total N (mg/L N)** | **TOC (mg/L C)** | **$PO_4^{3-}$ (mg/L $PO_4$)** | **$Cl^-$ (mg/L)** | **$K^+$ (mg/L)** | **[a]$Na^+$ (mg/L)** |
| NaCl Draw Solute | Urine t=0 | 11.45 | 30.74 | 2120 | 991 | 2980 | 4300 | 1990 | 521 | 2770 | 1110 | 7630 |
| | Duplicate | 11.42 | 32.69 | 2140 | 997 | 2920 | 4300 | 1940 | 536 | 2750 | 1120 | 7630 |
| $KH_2PO_4$ Draw Solute | Urine t=0 | 11.39 | 32.17 | - | - | 3340 | 3350 | 1230 | 895 | 2520 | 1090 | 8430 |
| | Duplicate | 11.32 | 32.20 | - | - | 3390 | 3380 | 1260 | 667 | 2500 | 1080 | 8260 |

[a]$Na^+$ concentrations are elevated due to NaOH addition for pH adjustment

[b]Urea was measured as mg/L urea and was then converted to mg/L N for extent of hydrolysis calculations

**Table B.2**. The composition of the synthetic urine used for all synthetic urine experiments

| Synthetic fresh urine composition | |
|---|---|
| **Compound** | **Concentration (g/L)** |
| Urea | 15.0075 |
| NaCl | 2.5715 |
| $Na_2SO_4$ | 2.1305 |
| KCl | 2.982 |
| $MgCl_2 \cdot 6H_2O$ | 0.813 |
| $NaH_2PO_4$ | 2.3995 |
| $CaCl_2 \cdot 2H_2O$ | 0.588 |
| pH[a] | 6 |

[a]The pH of the synthetic fresh urine was adjusted to 6 using sodium hydroxide

**Table B.3**. The initial (t = 0) and final (t = 48 h) conductivities for both the NaCl and $KH_2PO_4$ draw solution conditions for ammonia recovery by forward osmosis.

| Initial and Final Conductivity | | | | |
|---|---|---|---|---|
| **Condition** | **Solution t = 0 h** | **Conductivity (mS/cm)** | **Solution t = 48 h** | **Conductivity (mS/cm)** |
| NaCl Draw Solute | Urine | 30.74 | Urine | 46.14 |
| | Duplicate | 32.69 | Duplicate | 45.44 |
| | Draw | 124.1 | Draw | 79.63 |
| | Duplicate | 134.5 | Duplicate | 82.83 |
| $KH_2PO_4$ Draw Solute | Urine | 32.17 | Urine | 41.67 |
| | Duplicate | 32.20 | Duplicate | 41.69 |
| | Draw | 81.89 | Draw | 75.05 |
| | Duplicate | 81.93 | Duplicate | 75.61 |

**Table B.4.** The dead-end forward osmosis urea transfer data for the three different conditions. Figure 3.2 shows the results in graphed form. All units are mg/L of urea.

| Dead-end FO Urea Transport | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Condition** | **Solution** | **0 (h)** | **1 (h)** | **2 (h)** | **3 (h)** | **4 (h)** | **48 (h)** | **96 (h)** |
| **1: Urine – DI water** | Urine | 14700 | 14500 | 14300 | 14500 | 14200 | - | - |
| | DI water | - | 257 | 396 | 468 | 522 | - | - |
| **2: Urine - 1 M NaCl** | Urine | 14800 | 14500 | 14200 | 14000 | 13900 | - | - |
| | 1 M NaCl | - | 430 | 776 | 1130 | 1370 | - | - |
| **3: $CaCl_2$+urea - $CaCl_2$** | $CaCl_2$+urea | 14000 | 14000 | 13700 | 13 | 12200 | 8700 | 6700 |
| | $CaCl_2$ | - | 185 | 350 | 553 | 868 | 4590 | 7970 |

**Table B.5.** The duplicate dead-end forward osmosis urea transfer data for the three different conditions. Figure B.2 shows the results in graphed form All units are mg/L of urea.

| Duplicate Dead-end FO Urea Transport | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Condition** | **Solution** | **0 (h)** | **1 (h)** | **2 (h)** | **3 (h)** | **4 (h)** | **48 (h)** | **96 (h)** |
| **Urine - DI** | Urine | 1400 | 11700 | 13300 | 11900 | 13200 | - | - |
| | DI | - | 127 | 125 | 459 | 598 | - | - |
| **Urine - 1 M NaCl** | Urine | 14400 | 13500 | 13100 | 14500 | 14300 | - | - |
| | 1 M NaCl | - | 440 | 755 | 1100 | 1490 | - | - |
| **$CaCl_2$+urea - $CaCl_2$** | $CaCl_2$+urea | 14688 | 13800 | 12700 | 13900 | 12800 | 8200 | 8400 |
| | $CaCl_2$ | - | 196 | 410 | 600 | 742 | 5400 | 6200 |

**Table B.6.** A comparison of various draw solutes depicting their relative costs and considerations



| Comparison of Various Draw Solutes | | | | |
|---|---|---|---|---|
| **Draw Solute** | **Cost[a]** | **pH in Water** | **Solubility in Water** | **Considerations[b,c]** |
| $KH_2PO_4$ | $0.4/kg | 4.5 | 25g/100mL at 25 °C | High osmotic pressure, high reverse salt flux ($K^+$), low water solubility |
| $MgSO_4$ | $0.06/kg | 5.5–6.5 | 30g/100mL at 20 °C | low cost, low water solubility |
| $NH_4H_2PO_4$ | $0.6/kg | 3.8–4.4 | 40.4g/100mL at 25 °C | High osmotic pressure, high cost, low water flux |
| $(NH_4)_2SO_4$ | $0.12/kg | 5.5 | 76.4g/100mL at 25 °C | High osmotic pressure, high water solubility, low cost |
| $KNO_3$ | $0.6/kg | 6.2 | 35.7g/100mL at 25 °C | High cost, high reverse salt flux ($K^+$) |
| $NH_4NO_3$ | $0.2/kg | 5.25 | 213g/100mL at 25 °C | Low cost, high reverse salt flux ($NH_4^+$ and $NO_3^-$) |

[a]All costs were acquired from Alibaba accessed in July 2020
[b]Considerations were based on Shon et al. (2015)
[c]All comparisons are made only among the salts considered

# APPENDIX C

## SUPPLEMENTARY INFORMATION FOR CHAPTER 4:

## REJECTION OF NITROGEN SPECIES IN REAL FRESH AND HDYROLYZED HUMAN URINE BY REVERSE OSMOSIS AND NANOFILTRATION


**Figure C.1.** Depiction of the urine collection process in the Biodesign Institute's women's restroom.


**Figure C.2.** Depiction of the urine collection process in the Biodesign Institute's men's restroom.

**Table C.1.** Initial urine composition for the membrane experiments

| Initial Urine Composition | | | | | | | |
|---|---|---|---|---|---|---|---|
| Membrane Type | Urine Type | pH | Urea (mg/L urea) | Ammonia (mg/L N) | Total N (mg/L N) | Conductivity (mS/cm) | TOC (mg/L C) |
| RO | Fresh | 5 | 13376 | - | 6360 | 20.57 | 6395 |
| | | 6 | 6149 | - | 2338 | 9.93 | 4447 |
| | | 12.5 | 10667 | - | 5608 | 30.06 | 5008 |
| | Hydrolyzed | 6.5 | - | 3405 | 4692 | 33.46 | 5650 |
| | | 9 | - | 3670 | 4108 | 28.92 | 2737 |
| | | 11.5 | - | 3730 | 4159 | 34.24 | 2864 |
| NF | Fresh | 5 | 8053 | - | 4465 | 14.20 | 4554 |
| | | 6 | 8682 | - | 4613 | 13.19 | 4185 |
| | | 12.5 | 8131 | - | 4451 | 29.39 | 4332 |
| | Hydrolyzed | 6.5 | - | 4230 | 4260 | 37.90 | 6085 |
| | | 9 | - | 4515 | 4579 | 33.52 | 2587 |
| | | 11.5 | - | 4195 | 4478 | 39.93 | 2773 |
| MF | Fresh | 5 | 10785 | - | 5551 | 13.20 | 5321 |
| | | 6 | 10313 | - | 5434 | 13.01 | 4509 |
| | | 12.5 | 10137 | - | 5110 | 28.45 | 4150 |
| | Hydrolyzed | 6.5 | - | 4405 | 4112 | 39.84 | 5800 |
| | | 9 | - | 4510 | 4566 | 34.61 | 2923 |
| | | 11.5 | - | 4625 | 4413 | 39.77 | 2897 |

**Table C.2.** The initial urine composition for the duplicate membrane experiments

| Initial Urine Composition - Duplicate Run | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Membrane Type** | **Urine Type** | **pH** | **Urea (mg/L urea)** | **Ammonia (mg/L N)** | **Total N (mg/L N)** | **Conductivity (mS/cm)** | **TOC (mg/L C)** |
| RO | Fresh | 5 | 13376 | - | 6360 | 20.57 | 6395 |
| | | 6 | 4962 | - | 6475 | 9.41 | 1987 |
| | | 12.5 | 10617 | - | 5462 | 30.75 | 4956 |
| | Hydrolyzed | 6.5 | - | 3445 | 3833 | 32.29 | 5341 |
| | | 9 | - | 3070 | 3602 | 25.44 | 2829 |
| | | 11.5 | - | 3255 | 3348 | 32.15 | 2687 |
| NF | Fresh | 5 | 8013 | - | 3739 | 14.22 | 4972 |
| | | 6 | 8682 | - | 4613 | 13.19 | 4185 |
| | | 12.5 | 8131 | - | 4451 | 29.39 | 4332 |
| | Hydrolyzed | 6.5 | - | 4330 | 4275 | 37.90 | 6085 |
| | | 9 | - | 4515 | 4579 | 33.52 | 2587 |
| | | 11.5 | - | 4245 | 4535 | 39.93 | 2773 |
| MF | Fresh | 5 | 7276 | - | 3401 | 10.87 | 3171 |
| | | 6 | 10490 | - | 5434 | 13.01 | 4509 |
| | | 12.5 | 10137 | - | 5110 | 28.45 | 4150 |
| | Hydrolyzed | 6.5 | - | 4405 | 4112 | 39.84 | 5800 |
| | | 9 | - | 4510 | 4566 | 34.61 | 2923 |
| | | 11.5 | - | 4625 | 4413 | 39.77 | 2897 |

# APPENDIX D

## SUPPLEMENTARY INFORMATION FOR CHAPTER 5:

## AMMONIA RECOVERY AND FOULING MITIGATION OF HYDROLYZED HUMAN URINE TREATED BY NANOFILTRATION AND REVERSE OSMSOIS

## Materials and Methods

### Microfiltration Pretreatment.

Spectrapure microfiltration (MF) systems were used to pretreat the urine. A 1 µm sediment filter cartridge (L-SF-MT-1-10) followed by a 0.2 µm ZetaZorb sediment filter cartridge (L-SF-ZZ-0.2ABS-10) were used to process the urine after the pH of the urine was altered. A dual position housings fitting mounting bracket (FA-2STA-10) with a Cole-Parmer Masterflex L/S digital pump with an Easy-Load II pump head were used. All filter diameters were 25.4 cm. The Spectrapure MF membranes were chosen as they were a local, commercially available, cost-effective option that should effectively remove suspended solids and bacteria based on the pore sizes.

### Analytical methods.

Ammonia and urea results were confirmed through analysis of Total Nitrogen (TN). Four check standards were used for each TOC/TN run: TN 5, TN 1, TOC 10, and TOC 5 mg/L. The criteria for accuracy was within 10% of check standards, and the criteria for precision was samples run in duplicate.

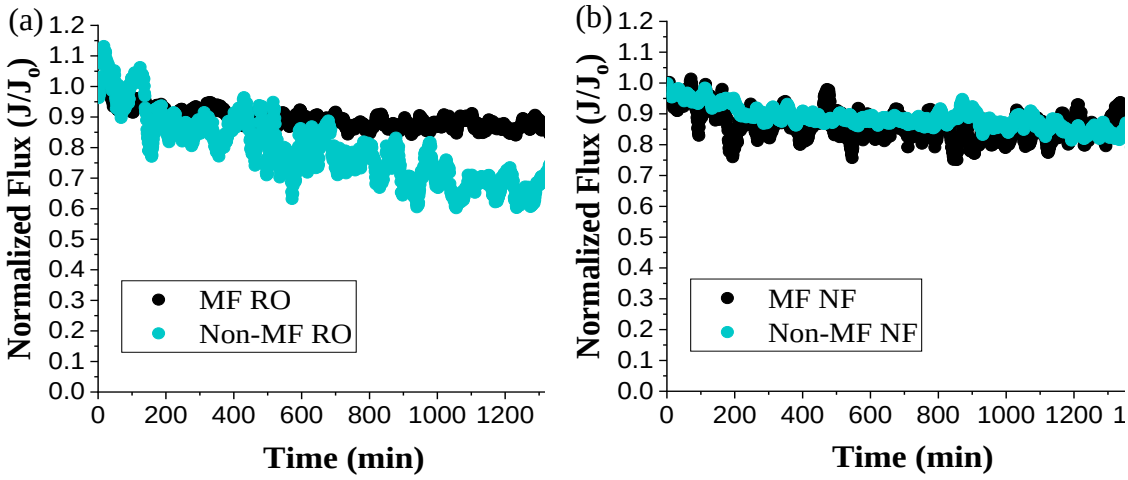



**Figure D.1**. The normalized flux over time for the duplicate reverse osmosis and nanofiltration fouling experiments. (a) The normalized flux over time for the 2 reverse osmosis conditions to assess microfiltration as a pretreatment. (b) The normalized flux over time for the 2 nanofiltration conditions to assess microfiltration as a pretreatment.

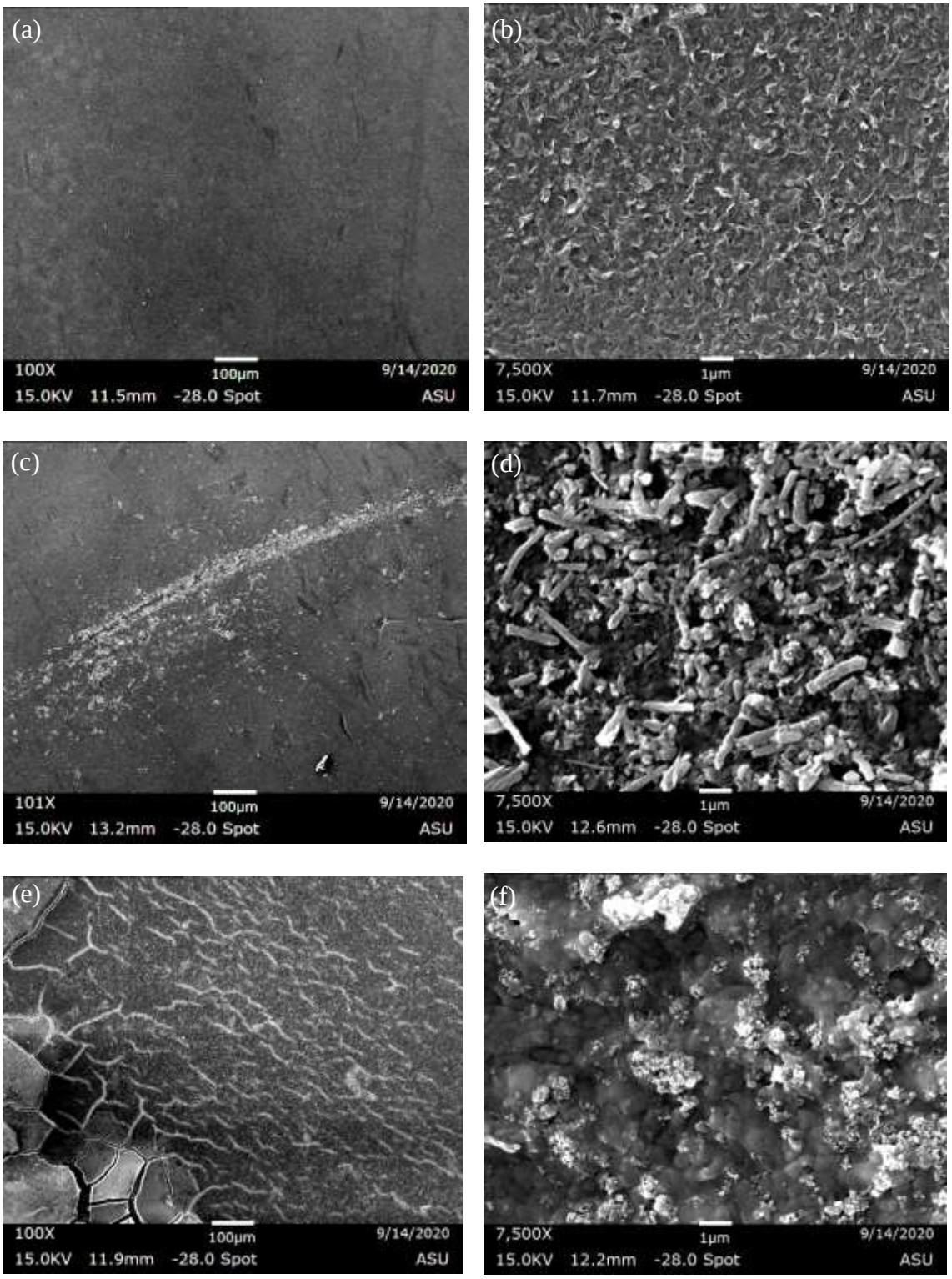

(a)
100X 100µm 9/14/2020
15.0KV 11.5mm -28.0 Spot ASU
(b)
7,500X 1µm 9/14/2020
15.0KV 11.7mm -28.0 Spot ASU
(c)
101X 100µm 9/14/2020
15.0KV 13.2mm -28.0 Spot ASU
(d)
7,500X 1µm 9/14/2020
15.0KV 12.6mm -28.0 Spot ASU
(e)
100X 100µm 9/14/2020
15.0KV 11.9mm -28.0 Spot ASU
(f)
7,500X 1µm 9/14/2020
15.0KV 12.2mm -28.0 Spot ASU

**Figure D.2**. Scanning Electron Microscopy (SEM) images of the reverse osmosis membrane surface for the duplicate fouling tests. (a) control 100X, (b) control 7500X, (c) MF RO condition 100X, (d) MF RO condition 7500X, (e) Non-MF RO condition 100X, and (f) Non-MF RO condition 7500X.

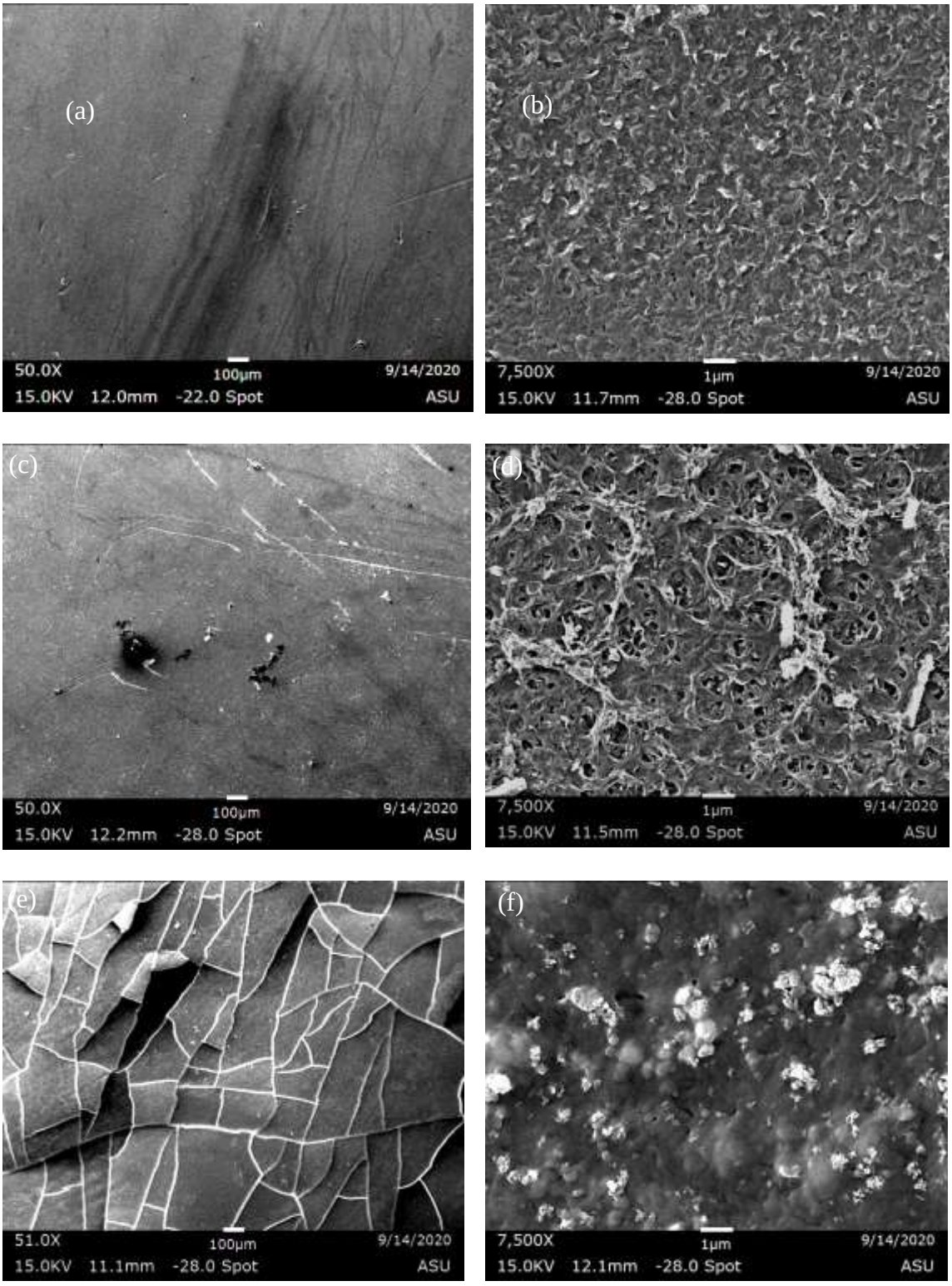

(a)
50.0X 100µm 9/14/2020
15.0KV 12.0mm -22.0 Spot ASU
(b)
7,500X 1µm 9/14/2020
15.0KV 11.7mm -28.0 Spot ASU
(c)
50.0X 100µm 9/14/2020
15.0KV 12.2mm -28.0 Spot ASU
(d)
7,500X 1µm 9/14/2020
15.0KV 11.5mm -28.0 Spot ASU
(e)
51.0X 100µm 9/14/2020
15.0KV 11.1mm -28.0 Spot ASU
(f)
7,500X 1µm 9/14/2020
15.0KV 12.1mm -28.0 Spot ASU

**Figure D.3**. Scanning Electron Microscopy (SEM) images of the nanofiltration membrane surface for the duplicate fouling tests. (a) control 50X, (b) control 7500X, (c) MF NF condition 50X, (d) MF NF condition 7500X, (e) Non-MF NF condition 50X, and (f) Non-MF NF condition 7500X.

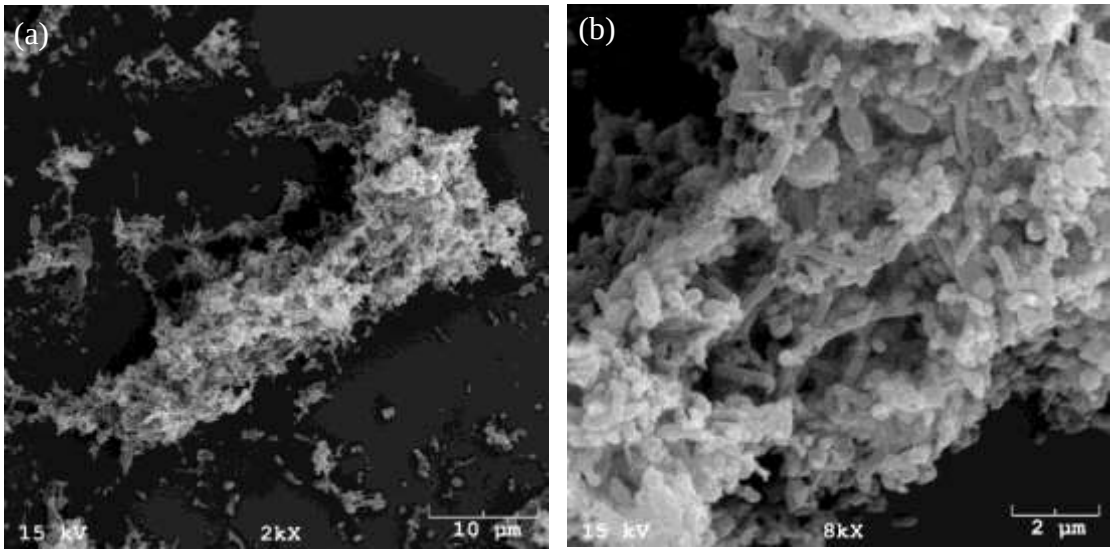



**Figure D.5**. Scanning Electron Microscopy (SEM) images of the foulant which grew in the tank during the duplicate non-MF RO experiment. (a) sample at 2000X and (b) sample at 8000X.

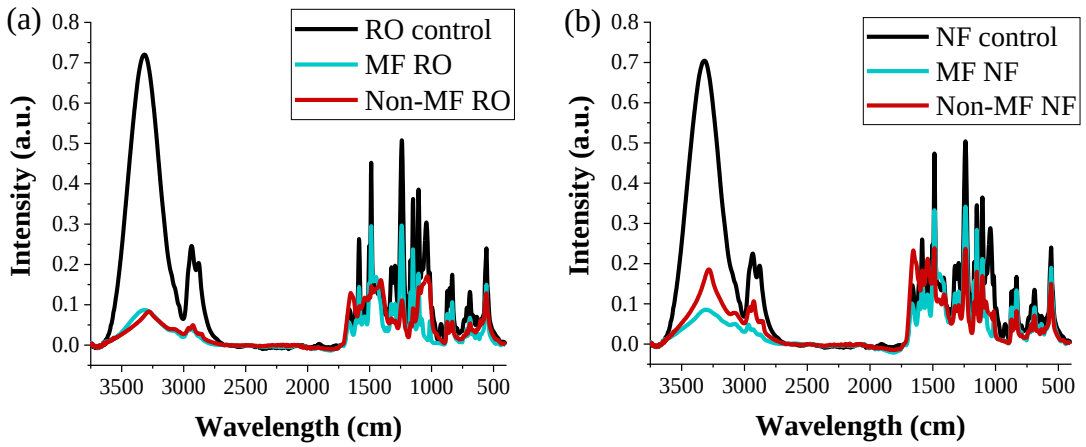



**Figure D.6**. Fourier-transform infrared spectroscopy (FTIR) of the membrane surfaces for the duplicate reverse osmosis and nanofiltration tests. (a) FTIR results for the 2 conditions and control membrane for reverse osmosis. (b) FTIR results for the 2 conditions and control membrane for nanofiltration.

# APPENDIX E

# INSTITUTIONAL REVIEW BOARD (IRB) APPROVAL FOR HUMAN SUBJECT TESTING

ASU Knowledge Enterprise Development

APPROVAL: EXPEDITED REVIEW

Treavor Boyer
Sustainable Engineering and the Built Environment, School of (SEBE)
-
thboyer@asu.edu

Dear Treavor Boyer:

On 12/6/2016 the ASU IRB reviewed the following protocol:

| | |
|---|---|
| Type of Review: | Initial Study |
| Title: | Nutrient Removal and Recovery from Source Separated Urine |
| Investigator: | Treavor Boyer |
| IRB ID: | STUDY00005328 |
| Category of review: | (3) Noninvasive biological specimens |
| Funding: | Name: Arizona State University (ASU) |
| Grant Title: | |
| Grant ID: | |
| Documents Reviewed: | • IRB Recruitment Email and Flyer.pdf, Category: Recruitment Materials;<br>• IRB Application Revised.docx, Category: IRB Protocol;<br>• Treavor Boyer CITI Training 10-30-15.pdf, Category: Non-ASU human subjects training (if taken within last 3 years to grandfather in);<br>• Daniella Saetta CITI Training 4-18-16.pdf, Category: Non-ASU human subjects training (if taken within last 3 years to grandfather in);<br>• Showing Changes, Category: Consent Form;<br>• Final Clean Version, Category: Consent Form;<br>• Point by Point Response Letter to Changes, Category: Other (to reflect anything not captured above); |

The IRB approved the protocol from 12/6/2016 to 12/5/2017 inclusive. Three weeks before 12/5/2017 you are to submit a completed Continuing Review application and required attachments to request continuing approval or closure.

If continuing review approval is not granted before the expiration date of 12/5/2017 approval of this protocol expires on that date. When consent is appropriate, you must use final, watermarked versions available under the "Documents" tab in ERA-IRB.

In conducting this protocol you are required to follow the requirements listed in the INVESTIGATOR MANUAL (HRP-103).

Sincerely,

IRB Administrator

cc: Hannah Ray
Neha Jagtap
Hannah Ray
Avni Solanki
Daniella Saetta

ASU Knowledge Enterprise Development

APPROVAL: MODIFICATION

Treavor Boyer
SEBE: Sustainable Engineering and the Built Environment, School of
-
thboyer@asu.edu

Dear Treavor Boyer:

On 2/14/2020 the ASU IRB reviewed the following protocol:

| | |
|---|---|
| Type of Review: | Continuing Review |
| Title: | Nutrient Removal and Recovery from Source Separated Urine |
| Investigator: | Treavor Boyer |
| IRB ID: | STUDY00005328 |
| Funding: | Name: Arizona State University (ASU) |
| Grant Title: | None |
| Grant ID: | None |
| Documents Reviewed: | • Final Clean Version, Category: Consent Form;<br>• Showing Changes, Category: Consent Form; |

The IRB approved the modification.

When consent is appropriate, you must use final, watermarked versions available under the "Documents" tab in ERA-IRB.

In conducting this protocol you are required to follow the requirements listed in the INVESTIGATOR MANUAL (HRP-103).

Sincerely,

IRB Administrator

cc: Daniella Saetta
Uranus Richard

Rebecca Dietz
Urusha Regmi
Angela Egan
Neha Jagtap
Hannah Ray
Lerys Del Moral
Michael Edgar
Daniella Saetta