Environmental Science
Water Research & Technology

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Journal:	*Environmental Science: Water Research & Technology*
Manuscript ID	EW-ART-08-2019-000720
Article Type:	Paper
Date Submitted by the Author:	22-Aug-2019
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Water Impact Statement

Urea is a critical compound used worldwide. However, synthetic fabrication of urea is energy intensive. Urea is the main component in human urine but there currently is not an established recovery method from urine. Diversion of urine and subsequent recovery of urea by forward osmosis and membrane distillation turns a waste into an economic product while also reducing water consumption.

Urea recovery from fresh human urine by forward osmosis and membrane distillation (FO-MD)

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Submitted to

Environmental Science: Water Research & Technology

21 August 2019

ABSTRACT

Urea is widely used as fertilizer and has other valuable uses such as diesel exhaust fluid and for resin fabrication. Human urine is a readily available and local source of urea that is overlooked due to the rapid hydrolysis of urea in fresh urine and wastewater, which makes its recovery challenging. Moreover, urea is a compound without an established method for recovery from urine or other waste streams. In this research, a novel two-step process of forward osmosis (FO) and membrane distillation (MD) was developed 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. Five pre-treatment conditions were investigated

for urea stabilization. For FO, fresh urine, fresh urine with acetic acid, fresh urine with calcium hydroxide, fresh urine with sodium hydroxide, and synthetic fresh urine with sodium hydroxide recovered 20%, 15%, 12%, 11%, and 21% of the urea in urine, respectively. MD was able to concentrate the product draw solutions from FO containing urea by a factor of 1.9 to 3.3. 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 TOC. The proof-of-concept study illustrated that FO-MD provides a technology platform for urea recovery from fresh human urine, which currently does not have an established method for recovery.

INTRODUCTION

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 [1, 2]. 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 [1, 3]. 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 [1]. 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[1, 4]. 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 [5]. 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 [6, 7]. 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 [7, 8]. 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 [6, 9]. 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 [10, 11], 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 [12]. 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 [13-16]. 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 [15-20]. 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 [21-25]. 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, 27]. 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 [11, 28] 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 [28, 29].

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 [30]. Volpin et al. (2018) recently showed the effectiveness of FO for urea separation in fresh urine (50%) [31]. In addition, Volpin et al. (2019) investigated the ability of FO-MD on the concentration of ammonium in hydrolyzed urine [32]. 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[33, 34]. 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) determine the transfer properties of urea across the FO membrane, (2) evaluate the effect of urine pre-treatment on urea separation by FO, and (3) evaluate the combined effect of urine pre-treatment and FO treatment on urea concentration by MD. Bench-scale FO and MD membrane set-ups with real human urine were used to evaluate urea separation and concentration, respectively. A bench-scale, dead-end FO set-up with synthetic human urine was used to understand urea transfer across the FO membrane.

MATERIALS AND METHODS

Materials

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) [7, 35]. The synthetic fresh human urine used for experiments was prepared based on previous literature and is detailed in the Table S1 [15]. 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 SI.

Experimental methods

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 $\$1.15/m^3$ [36]. MD operating costs were determined to be $\$1.17/m^3$ [37]. 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 $\$0.5/m^3$ [38, 39]. The

same ratio was then applied to the above FO operating cost. All chemical costs were based on prices from Alibaba 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. 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 S1 shows the graphed comparison of the duplicate FO experiments for each condition.

Fig. 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) [41]. Table 1 shows the average urea recovery percentages and Table S4 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 [17]. Urea hydrolysis of urine results in the precipitation of hard minerals that ruin urine collection systems and plumbing [12, 42]. 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 [43]. Acetate is an easily available carbon source for microorganisms and has been used to enhance microbial growth in wastewater [44]. 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 [45], 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 [15]. 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 S3 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 S2 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 [46]. In addition, Meireles et al. (1991) reported that proteins such as albumin were not by nature foulants unless denaturation occurs [47]. It was also determined that long term fouling of ultrafiltration membranes was highly linked to protein denaturation [47]. 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. 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 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 S3 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 S5 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 S3, 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 S2 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% [48]. 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 [49]. pH 10 was found to be optimal in comparison to neutral or acidic pH [49]. 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 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. 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 percent increase of urea allows for comparison solely of the MD process without any bias from the FO process. Table 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 S4 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 [50]. In addition, the salting out effect of organic material at high ionic strength solutions is another explanation for the precipitation [51, 52]. 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 [51, 52]. 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. 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 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 [53-56].

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 [57]. The fertilizer has nitrogen stabilization properties that allows for reduced nitrogen loss during fertilization [57, 58]. 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 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 [31, 36, 59]. 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 $\$6.2/m^3$ [36]. 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.

ACKNOWLEDGEMENTS

This publication is based upon work supported by the National Science Foundation, NSF CAREER grant CBET-1150790 and ASU Fulton Schools of Engineering start-up funding.

Supporting Information

Information regarding the methods and materials, a picture of the dead-end FO setup, synthetic urine recipe, and additional supporting tables and figures can all be found in the SI.

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FIGURES

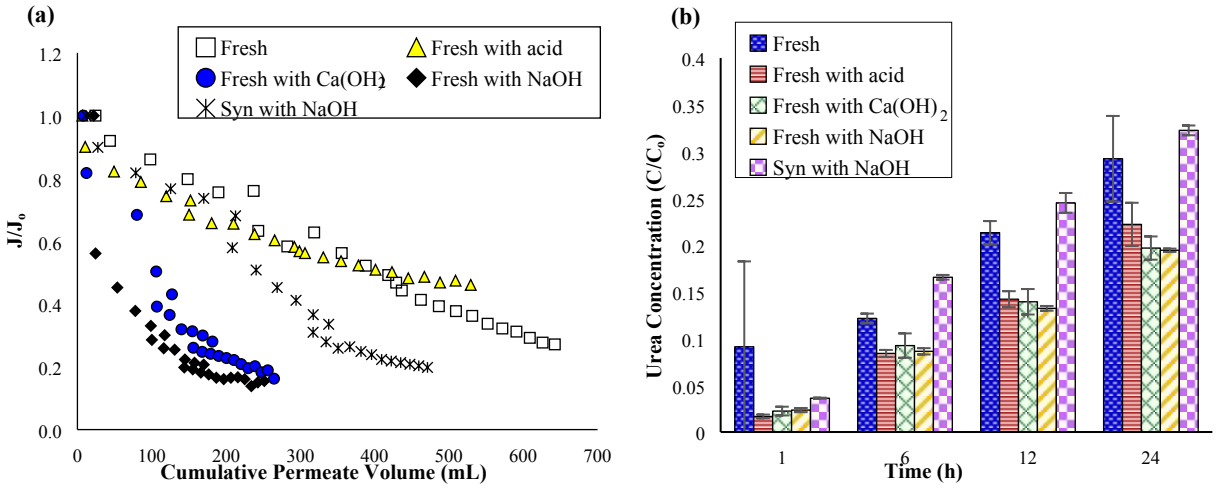


Figure 1. Forward osmosis operation and urea separation results for the 5 urine conditions. Part (a) is the normalized water fluxes as a function of cumulative permeate volume (mL) for the forward osmosis experiments and are mean values from the duplicate runs. Part (b) is the urea recovery and are mean values ± one standard deviation for duplicate runs. The experiment ran for 24 h.

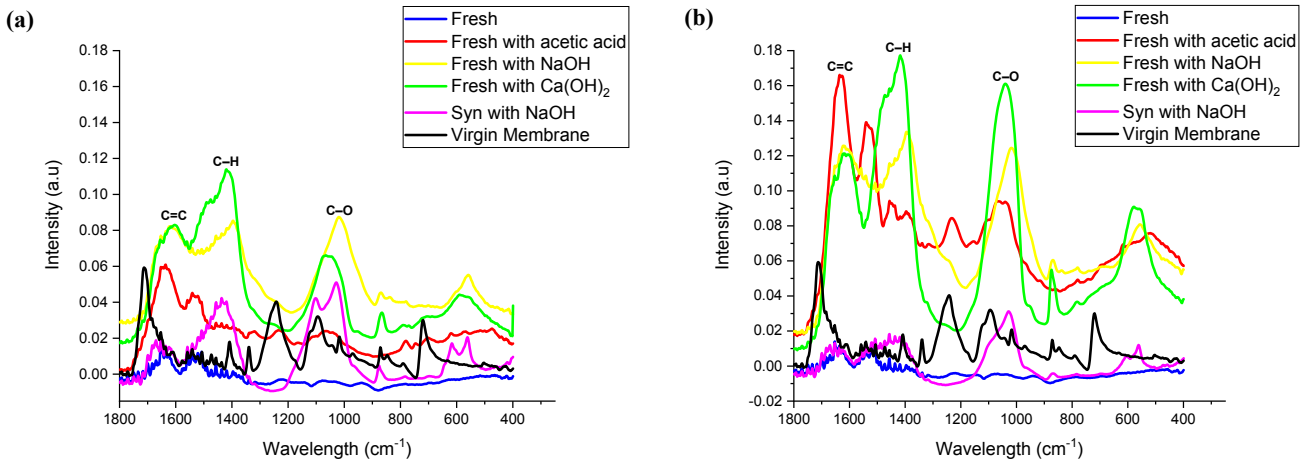


Figure 2. Fourier-transform infrared spectroscopy (FTIR) of the membrane surfaces for the 5 urine condition experiments for the forward osmosis experiments. Part (a) are the results for the first test and part (b) are the results for the duplicate tests.

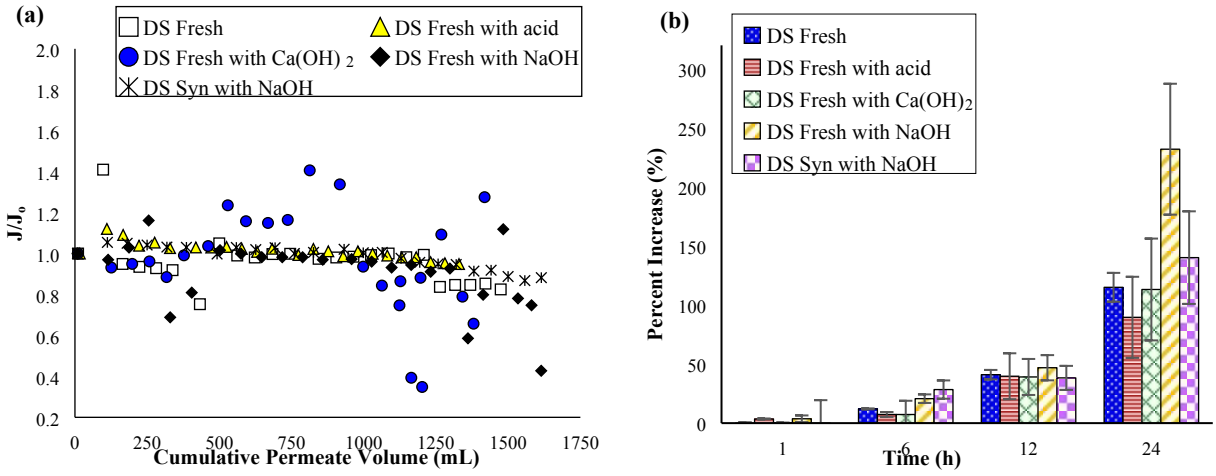


Figure 3. Membrane distillation operation and urea concentration results for the 5 urine conditions. Part (a) is the normalized water fluxes as a function of cumulative permeate volume (mL) for the membrane distillation experiments and are mean values from the duplicate runs. Part (b) is the urea recovery and are mean values ± one standard deviation for duplicate runs. The experiment ran for 24 h.

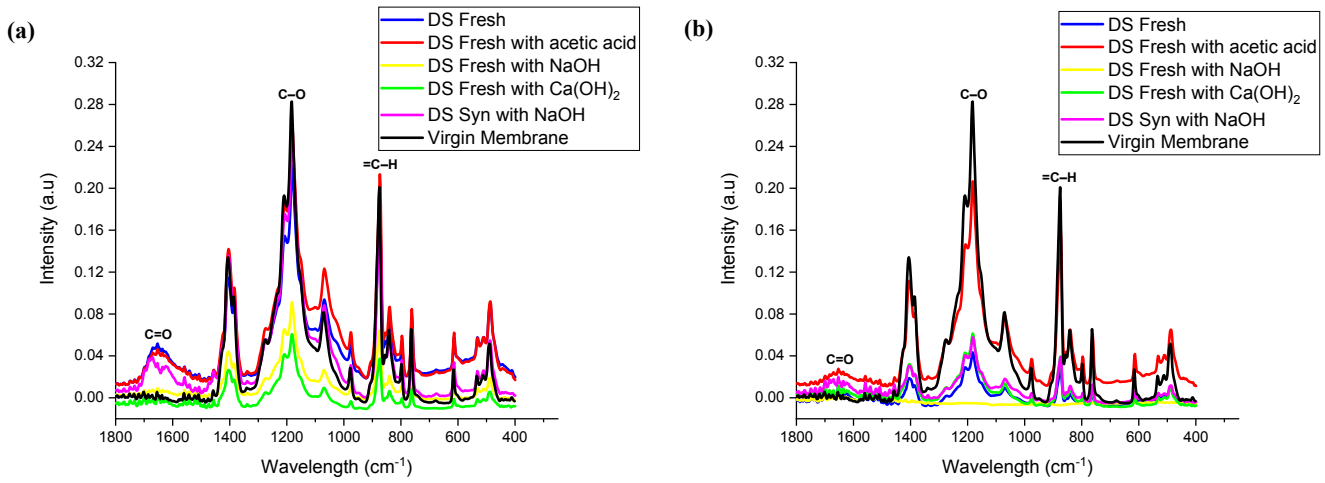


Figure 4. Fourier-transform infrared spectroscopy (FTIR) of the membrane surfaces for the 5 urine conditions for the membrane distillation experiments. Part (a) are the results for the first test and part (b) are the results for the duplicate tests.

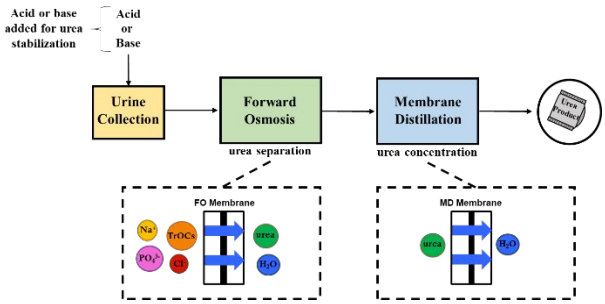
TABLES

Table 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: 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/m^3	1.3 kg/m^3	\$0.35/kg	0.31 m^3 produced/m^3 treated	\$0.65/m^3	\$172.85	24%	\$84.65
2	Acetic acid	1.6 kg/m^3	\$0.5/kg	\$2.32/m^3	0.88 kg/m^3	\$0.35/kg	0.27 m^3 produced/m^3 treated	\$0.65/m^3	\$268.05	49%	\$2.05
3	Calcium hydroxide	5 kg/m^3	\$0.17/kg	\$2.32/m^3	0.95 kg/m^3	\$0.35/kg	0.24 m^3 produced/m^3 treated	\$0.65/m^3	\$204.90	31%	\$63.10
4	Sodium hydroxide	5.4 kg/m^3	\$0.3/kg	\$2.32/m^3	0.75 kg/m^3	\$0.35/kg	0.34 m^3 produced/m^3 treated	\$0.65/m^3	\$217.40	33%	\$56.60


Acid or base added for urea stabilization
Acid or Base
Urine Collection
Forward Osmosis
Membrane Distillation
Urea Product
urea separation
urea concentration
FO Membrane
MD Membrane
Na+
TrOCs
PO4 3-
Cl-
urea
H2O