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Water Impact Statement

Ammonia is a vital compound used in many different industries. Diversion of human urine and subsequent ammonia recovery through reverse osmosis and nanofiltration turns a waste into an economic product. Furthermore, urine diversion as a process reduces water consumption at the toilet as well as protects precious water sources from nutrient pollution due to wastewater discharge.

Ammonia recovery and fouling mitigation of hydrolyzed human urine treated by nanofiltration and reverse osmosis

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Abstract

Ammonia is a critical compound due to the numerous industry products which rely on its production such as fertilizer, refrigerant gas, and textile manufacturing. Ammonia is also a pollutant in wastewater due mainly to the source of human urine. Urine diversion allows for treatment and recovery of the ammonia in urine. Reverse osmosis (RO) and nanofiltration (NF) are widely used and trusted water and wastewater treatment processes. Through novel selective separation, the ammonia in the urine can be recovered to produce an ammonia product with economic value. However, cross-flow RO and NF on real human urine for selective ammonia recovery has been untested. Therefore, this project investigated the use of RO and NF to recover ammonia from hydrolyzed human urine in a cross-flow system where both ammonia permeation and fouling experiments were performed. For both RO and NF, complete ammonia permeation (0% rejection) was observed while still achieving high rejection of total organic carbon (>92%) and salts (SO_4^{2-} and PO_4^{3-} were > 97% and 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^+ between RO and NF. Microfiltration pretreatment greatly reduced the extent of fouling on the membrane surface and was deemed necessary for long-term operation. An economic analysis showed that RO and NF systems had the lowest process cost, \$4.69–\$4.72/m^3, and highest product offset, \$0.4/kg, when compared with other ammonia recovery processes.

1. Introduction

The global ammonia market is expected to reach a demand of USD 81 billion by 2025, over a 50% increase from 2017 [1]. The ammonia market is largely dominated by a need for nitrogen based fertilizers with a rising demand for "eco-friendly" refrigerants [1]. 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 [2, 3]. 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 [4].

In addition to the high energy demand of ammonia production, ammonia is also a considerable pollutant in the environment causing eutrophication and harmful algal bloom formation in freshwater bodies [5-7]. 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 [5]. 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. In addition, these techniques allow excess nitrogen to be discharged into waterbodies due to incomplete removal which accumulates having detrimental effects on both humans and the environment [5, 6]. Biological nitrogen treatment techniques have been reported to release nitrous oxide, a harmful greenhouse gas, furthering the damage done for nitrogen removal by WWTPs [8]. Implementing new ways of handling and treating wastewater, such as urine diversion, could have numerous benefits, including ammonia recovery from urine to 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 [9, 10]. 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 [11, 12]. In addition, the nitrogen in urine (~11 g N/person/day [13]) could be recovered and repurposed into industrial products in high demand.

However, the chemistry of human urine 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 [14]. Once urine comes into contact with the ubiquitous, microbial urease enzyme[15], the urea is hydrolyzed into ammonia and bicarbonate, the pH rises to 9, and calcium and magnesium precipitate [16, 17]. 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 [18, 19], adsorption by ion exchange [20-22], and microbial based fuel and electrolysis cells [12, 23, 24]. 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 [25].

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 [26, 27]. Research on the application of RO and NF on numerous waste streams has continued to expand with studies performed on the treatment of municipal [28, 29], laundry [30], textile [31-33], coal [34], dairy [35, 36], and carwash [37] wastewater. 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) [38]. 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 [39]. However, those studies and past studies treating animal urine have solely looked at concentration of the urine which does not produce a product with high industry value.

Ray et al. (2020) showed the effectiveness of RO and NF for novel selective ammonia separation from urine while still maintaining high rejection of TOC and salts [40]. 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 [40]. While helpful for understanding solute rejection, dead-end studies do not consider the fouling of a 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. In addition, investigation of microfiltration (MF), a cost-effective pretreatment technique, will help future implementation. Previous research has studied the use of MF pretreatment for RO and NF treating seawater, surface water, and secondary wastewater effluent [41-45]. However, it has not been studied as a pretreatment in a urine-based system.

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.. Very few economic analyses have been performed on the use of RO and/or NF for wastewater treatment especially with regard to human urine and nitrogen recovery. Economic comparisons of different configurations for the use of RO and/or NF have been considered for different water reuse scenarios where the source water has very little comparison to the treatment of human urine [32, 46-50]. Other studies have considered the economics of nitrogen recovery from human urine but without regard to the use of RO and/or NF [51-53]. Therefore, there is gap in the economics research, and novelty and efficiency need to be coupled with economic feasibility

Therefore, the goal of this research was to determine the ammonia permeation in hydrolyzed human urine and assess the fouling by cross-flow RO and NF. The specific objectives were to (1) determine the ammonia permeation 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 of MF pretreatment 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.

2. Materials and Methods

2.1 Human Urine

Human urine collection was approved by the Arizona State University (ASU) Institutional Review Board (IRB) and informed consent was obtained for any experimentation with human subjects. Real fresh, undiluted urine was collected from anonymous volunteers, both male and female. Number of donors and ratio of male to female is not known due to anonymity requirements by the ASU IRB which granted the project's human urine collection. Further details on the collection procedure can be found in the SI. The collected fresh human urine was stored for six months to allow for complete hydrolysis of the urea to occur and for safe handling as determined by the World Health Organization [54]. The hydrolyzed urine was then used for the RO and NF experiments. The initial real hydrolyzed urine composition can be found in Table S1 and S2.

2.2 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 × 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" × 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” × 3.8” × 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. A picture of the RO and NF setup used for all experiments can be seen in Figure S1.

2.3 RO and NF Ammonia Permeation Experiments

Hydrolyzed human urine was first pH adjusted to 11.1–11.2 using sodium hydroxide (25–41 mL/L of 10 M NaOH) and then filtered through the MF membranes. pH 11.1–11.2 was chosen to ensure all the nitrogen would be in the form of unionized ammonia for permeation. 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, as this was enough volume needed for analysis and chemical rejection was all that was being considered in these experiments. The feed tank and the beaker collecting the permeate were sealed using a plastic top and parafilm, respectively, to reduce any loss of ammonia. 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 $NH_3 + NH_4^+$.

2.4 RO and NF Fouling Experiments

The fouling experiments were performed with 10 L of hydrolyzed human urine which was pH adjusted to 11.1–11.2 using sodium hydroxide (25–41 mL/L of 10 M NaOH) as the feed solution. Two different urine conditions were tested in duplicate 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. MF was chosen as a pretreatment as it designed to remove colloidal material and bacteria (>0.1–10 µm) both which contribute to membrane fouling. 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 so that the feed solution over time was representative of the urine and not a higher concentrated urine solution as a full-scale system would be operated flow through mode instead of batch mode where the feed solution has a consistent chemistry. Fouling experiments were carried out for 24 h and the collected flux data was compiled into rolling averages of 20 data points. Therefore, each flux data point represented a 20 min average. 24 h was chosen due to the satisfied flux decline (10%) seen in the experiments which is consistent with a flux decline a utility would allow before a clean-in-place would be necessary. Feed samples were collected and tested for pH, conductivity, TOC, TN, NH_3, SO_4^{2-}, PO_4^{3-}, Na^+, K^+, and Cl^-. Membrane coupons were also cut and saved for SEM analysis. Each of the four different test conditions (non-MF RO, MF RO, non-MF NF, and MF NF) were performed in duplicate, and thus 8 fouling experiments in total were completed. Consistent results between replicates showed the reliability of duplicate testing. The system was cleaned with 10% bleach which was circulated for 30 min. The system was then rinsed 3 times with tap water for complete removal of the bleach followed by 3 rinses of DI water each for 15 min.

2.5 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. For membrane analysis, a representative sample of the membrane’s surface was placed in a metal stub and adhered using double-sided carbon tape. The samples were sputter-coated with 10 nm of gold and platinum to avoid electrostatic charging during examination. Membrane morphology was evaluated using an SEM (ESEM-FEG XL-30, Philips Hitachi SU-70, Hillsboro, OR) at an acceleration voltage of 10 kV. For foulant analysis, dried samples were mounted on aluminum stubs and coated with 10-12 nm of gold-palladium using a Hummer II sputter coater (Technics, San Jose, CA). Imaging was done on a JSM 6300 SEM (JEOL USA, Peabody, MA) operated at 15 kV and images were captured with an IXRF Systems model 500 digital processer (IXRF System Inc., Austin, TX). Further information of the foulant sample processing can be found in the SI. 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.

2.6 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.

2.7 Economic Analysis

RO and NF capital and operating costs were both considered and were based on a previous economic analysis by Mendret et al. (2019) [50]. The other ammonia recovery process costs and product offsets were based off an analysis summarized by Ray et al. (2020) [52]. All chemical costs were based on prices from Alibaba accessed in September 2020 [55]. Further detail can be found in the SI.

3. Results and discussion

3.1 Ammonia and other compound permeation by RO and NF

Ammonia transfer was investigated in cross-flow RO and NF systems to test whether the previously determined high ammonia permeation by dead-end RO and NF held true [40]. Figure 1 shows the rejection of various compounds in real hydrolyzed human urine by RO and NF. Both RO and NF had complete permeation of ammonia (0% rejection) and less than 5% rejection of TN, respectively. 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^+ between RO and NF. However, there was a statistical difference in rejection of Cl^- between RO and NF. The permeate composition for each test can be found in Table S3.

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 has been established that RO has superior rejection in terms of monovalent ion rejection which explains the statistical difference in rejection of Cl^-. 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%. This can be explained by the hydrated radii as Na^+ (0.36 nm) has a larger hydrated radius compared to K^+ and Cl^- (both 0.33 nm) causing greater rejection of Na^+ [56]. In addition, while the hydrated radii of K^+ and Cl^- are the same, the concentration of Cl^- in the feed (~2900 ppm) is greater than the concentration of K^+ (~1500 ppm) creating a larger concentration gradient driving more Cl^- across the membrane into the permeate [57].

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% [58, 59]. 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) as well as less overall Cl^- (hydrolyzed urine ≈ 2900 ppm, seawater ≈ 19000 ppm). Krieg et al. (2005) and Rautenbach and Linn (1996) theorized that the presence of the high valence SO_4^{2-} drove more Cl^- across the membrane, lowering the overall Cl^- rejection [59, 60]. As mentioned above, the lower concentration of Cl^- in hydrolyzed human urine would have a lower concentration gradient, reducing the driving force of Cl^- across the membrane in comparison to seawater. Therefore, the lower concentrations of SO_4^{2-} and Cl^- 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 [40]. The higher permeation determined by cross-flow orientation in this study can be explained by the pressure difference and flux. Ray et al. (2020) 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 [40]. 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 [61]. Compaction of the membrane causes reduction of the pore sizes which is the most dominant rejection characteristic for neutral compounds [61]. In addition, the flux for the dead-end tests was substantially higher than the current cross-flow tests (16–18 LMH vs. 4–6 LMH) which can be explained by the difference in dead-end vs. cross-flow tests as well as the variability in urine batches. Therefore, the lower operating pressure and lower flux allowed for greater permeation of ammonia across the RO and NF membranes for the cross-flow orientation.

The lowered flux and thus salt rejection can be explained by the tangential flow of the cross-flow orientation compared with the stirred dead-end cell. Darunee et al. (2002) tested the flux and salt rejection of a constructed both a dead-end and cross-flow system and found that at high pressures, 300–400 psi, the salt rejection decreased for the cross-flow system, a phenomenon that was not reported for the dead-end cell [62]. This was attributed to the lower velocity of the cross-flow system as the dead-end cell acts as a system with high cross-flow velocity [62]. The complete permeation of ammonia (0% rejection) 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.

In addition to the recovered ammonia product, the feed solution which would have phosphorus and potassium in a more concentrated form due to their high rejection by the membrane could undergo subsequent treatment processes for complete nutrient recovery. Phosphorus adsorption to hybrid anion exchange (HAIX) would allow for targeted phosphorus recovery and evaporation would produce potash, a potassium product [20, 63]. Therefore, membrane treatment for ammonia recovery could be the first step in a full nutrient recovery process.

3.2 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 MF pretreatment to reduce the extent of fouling that could occur during the high-pressure RO and NF application was considered for this work as MF has the ability to reject colloidal material and bacteria (>0.1–10 µm) both which contribute to membrane fouling. Thus, the urine was pH adjusted and then MF was applied to the urine removing endogenous particulate matter, larger bacteria, and precipitates that could have formed due to the increase in pH. 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 2 (a) shows the normalized flux over time for RO for both the MF pretreated and non-MF pretreated conditions. The initial water flux for MF RO and non-MF RO were 5.1 and 4.3 LMH, respectively. 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 pretreatment had significant benefits for flux operation over the 24 h for RO operation. The operating pressure had slowly dropped and was adjusted back to 375 psi at 200 min which accounts for the sudden increase in flux. Figure 2 (b) shows the same normalized flux over time for NF for the two MF conditions. The initial water flux for MF NF and non-MF NF were 6.6 and 5.8 LMH, respectively. 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 as affected by the fouling that occurred, or at least to an extent that MF pretreatment had a noticeable effect. The difference in effect of the MF pretreatment on flux for RO and NF can be explained by the surface roughness between the two membrane types. Vrijenhoek et al. (2001) determined that colloidal fouling can be correlated to surface roughness where accumulation in the membrane "valleys" causes flux decline [64]. RO membranes have a rougher membrane surface (BW30 RMS = 38.1 nm [65]) compared to NF membranes (NF90 RMS = 27.8 nm [66]) causing the MF pretreatment, which removes colloids, to have a greater effect on the flux.

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 3 shows the SEM images for a virgin RO membrane, the MF pretreated RO membrane, and the non-MF pretreated RO membrane. The SEM images for the duplicate experiments can be found in Figure S2. 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 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. Jiang et al. (2017) reported SEM images of the different fouling types for RO membranes with the images of biofouling and organic fouling highly resembling the fouling seen in this study [67]. Scaling, which is usually characterized by sharp, crystalline structures as seen in the SEM images by Jiang et al. (2017) and Takizawa et al. (2018), was not identifiable on the membrane surface [67, 68]. Thus, biofouling and organic fouling were the dominate fouling mechanisms for the current RO system.

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. The longer fibers were theorized to be fibers that dislodged from the MF filters that pretreated the urine. Figure S3, which is SEM images of the MF filter, confirm that MF filter is characterized by the aforementioned long rod structures. 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. MF is not completely effective in its removal of all bacteria and thus small amounts of bacteria pass 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.

SEM imaging of the foulant that grew in the tank was performed to characterize the type of foulant (i.e., algae, bacteria, scaling) which would allow for a better understanding of what was occurring in the system. Figure 4 shows the SEM images for a virgin NF membrane, the MF pretreated NF membrane, and the non-MF pretreated NF membrane. The SEM images for the duplicate experiments can be found in Figure S4. 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 MF fibers. Furthermore, the trends seen by the RO conditions also hold true for NF operation.

Figure 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 SEM images for the duplicate experiments can be found in Figure S5. The images show the foulant to be dominated by bacilli and cocci bacteria. Krishnakumar (2016) and Salmiati et al. (2015) reported SEM images of known bacilli and cocci bacteria, respectively, confirming the characterization of the tank foulant [69, 70]. Additionally, the confirmed bacilli bacteria in the tank foulant correlate well to the images of the membrane surface which were presumed to be dense layers of bacilli bacteria. Thus, biofouling was not only dominate on the membrane surface but also in the tank.

Figure 6 (a) shows the FTIR results for a virgin RO membrane, the MF pretreated RO membrane, and the non-MF pretreated RO membrane. The FTIR results for the duplicate experiments can be found in Figure S6. 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 [71]. 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 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. Due to the lower system cross-flow velocity, 37.8 cm/s, and lower surface area of the flat sheet membrane, 38.6

cm^2, the water recovery during the fouling experiments was minimal, .03–.06%. Operation using spiral bound membranes or a flat sheet membrane with a higher surface area would increase the flux and water recovery seen by the system.

3.3 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. (1998) [72] and Viegas (2019) [73]) 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 [55]). Based on work by Mendret el 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 [50]. The annual capital costs for the RO and NF systems were defined as \$0.014/m^3 and \$0.016/m^3, respectively [50]. 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 [52]. Further details on the process cost derivations can be found in the SI.

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 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 to produce a variety of 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 makes 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.

4. Conclusions

This study investigated RO and NF for ammonia recovery from hydrolyzed human urine by quantifying the novel permeation 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. Complete ammonia permeation for both RO and NF along with high rejections of other salts (SO_4^{2-} and PO_4^{3-} were > 97% and Cl^-, Na^+, and K^+ ranged from 91–97% for RO and 83–94% for NF) and TOC (>92%) 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. (2014) determined that the use of a dual-stage NF system for seawater desalination was a feasible technology [74]. 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 purity ammonia product [75]. However, if purity of the product does not interfere with industrial application of the product, then use of NF would be an effective choice. Further treatment of the concentrated, nitrogen depleted urine would allow for valuable complete nutrient recovery through targeted phosphorus and potassium treatment processes such as HAIX and evaporation, respectively.

This study serves as the first investigation of MF pretreatment for a membrane system using human urine. The 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 and organic fouling as well as minor inorganic fouling coming from the MF filter were identified on the surfaces of the membranes. Therefore, for operation integrity 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.

While this study investigated the fouling behavior over 24 h, future research concentrated on long-term operation of the membrane systems would provide further understanding of the flux over time and how fouling will affect its progression. In this study, the permeate was returned to the feed so that concentration of the urine would not be a cause for fouling. However, future research on the concentrative effects of the urine is needed to understand long term operation. In addition, research that tests different RO and NF membranes, such as SW30 or NF200, could produce even higher quality ammonia products [76]. Lastly, research which tests different membrane parameters such as a lower operating pressure or a higher cross-flow velocity would help identify the optimal conditions for operation and ammonia recovery. Consequently, this would help achieve not only the highest quality ammonia product but also determine the most economically important parameters which could then be manipulated to find a balance between recovery and cost.

5. Author Contributions

Ray: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization, Project administration, Resources, Funding acquisition. **Perreault:** Conceptualization, Methodology, Validation, Resources, Writing - Review & Editing, Visualization. **Boyer:** Conceptualization, Methodology, Validation, Resources, Writing - Review & Editing, Visualization, Supervision, Funding acquisition.

6. Conflicts of Interest

There are no conflicts of interest to declare.

7. Acknowledgments

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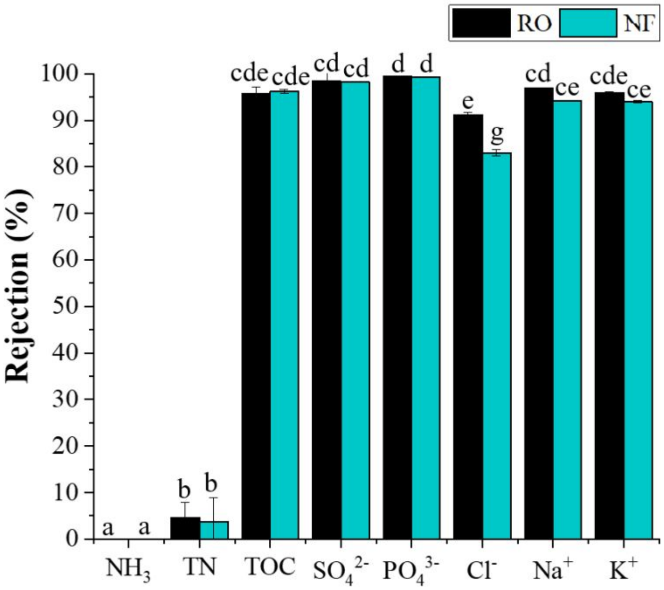


Figure 1. Rejection of various compounds in real hydrolyzed human urine by cross-flow reverse osmosis and nanofiltration. Conditions with one or more of the same symbols do not have a statistical difference while conditions with different symbols do have a statistical difference.

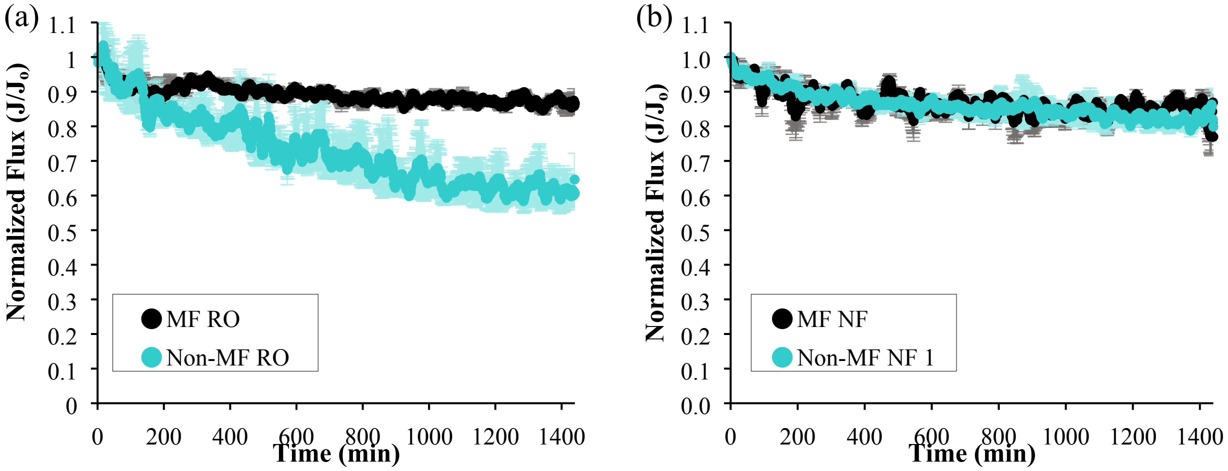
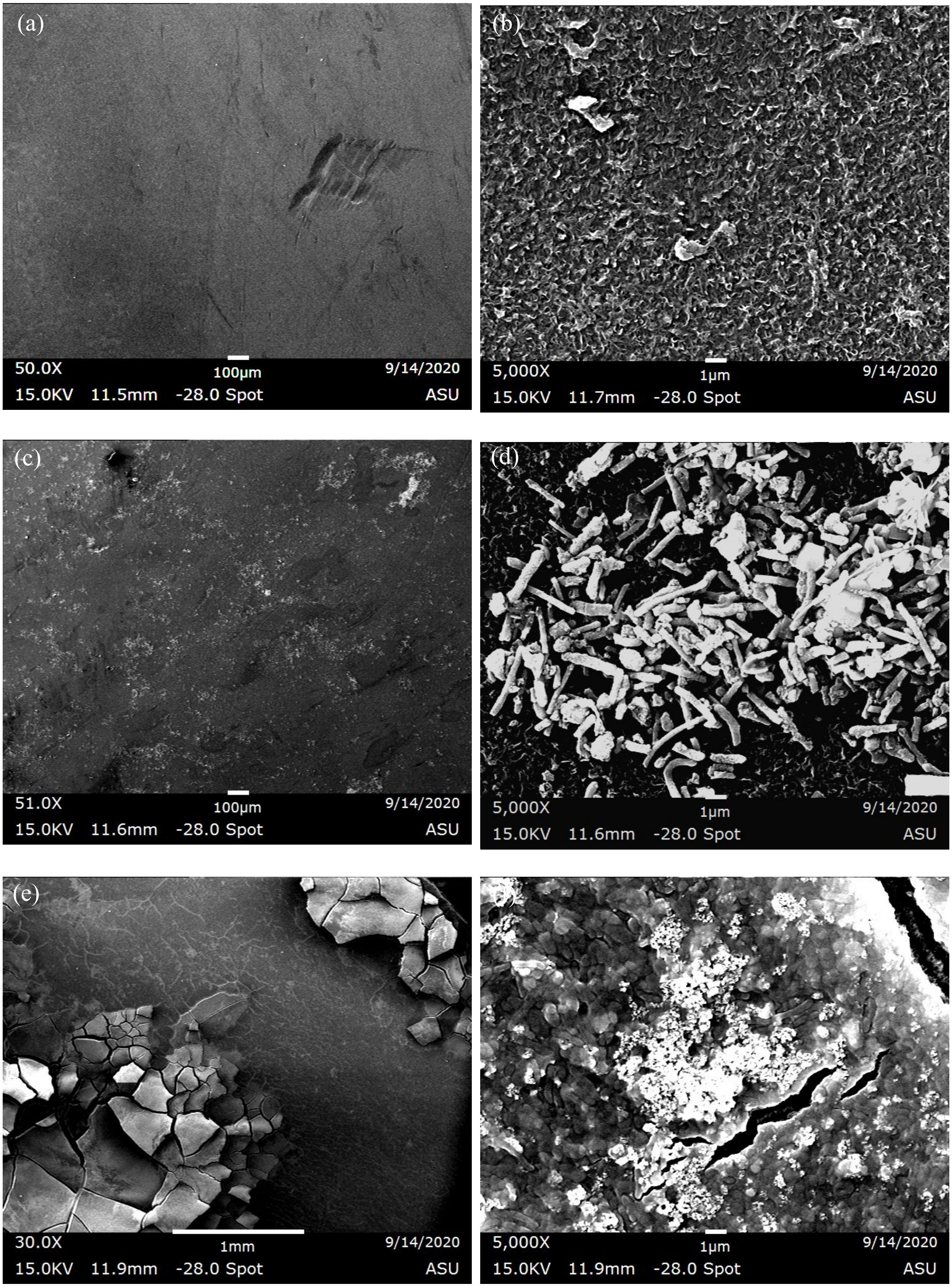


Figure 2. The average normalized flux over time for the reverse osmosis and nanofiltration fouling experiments. (a) The normalized flux over time for the 2 reverse osmosis conditions to assess microfiltration as a pretreatment. (b) The normalized flux over time for the 2 nanofiltration conditions to 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
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15.0KV 11.9mm -28.0 Spot
ASU
5,000X
1μm
9/14/2020
15.0KV 11.9mm -28.0 Spot
ASU

Figure 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.

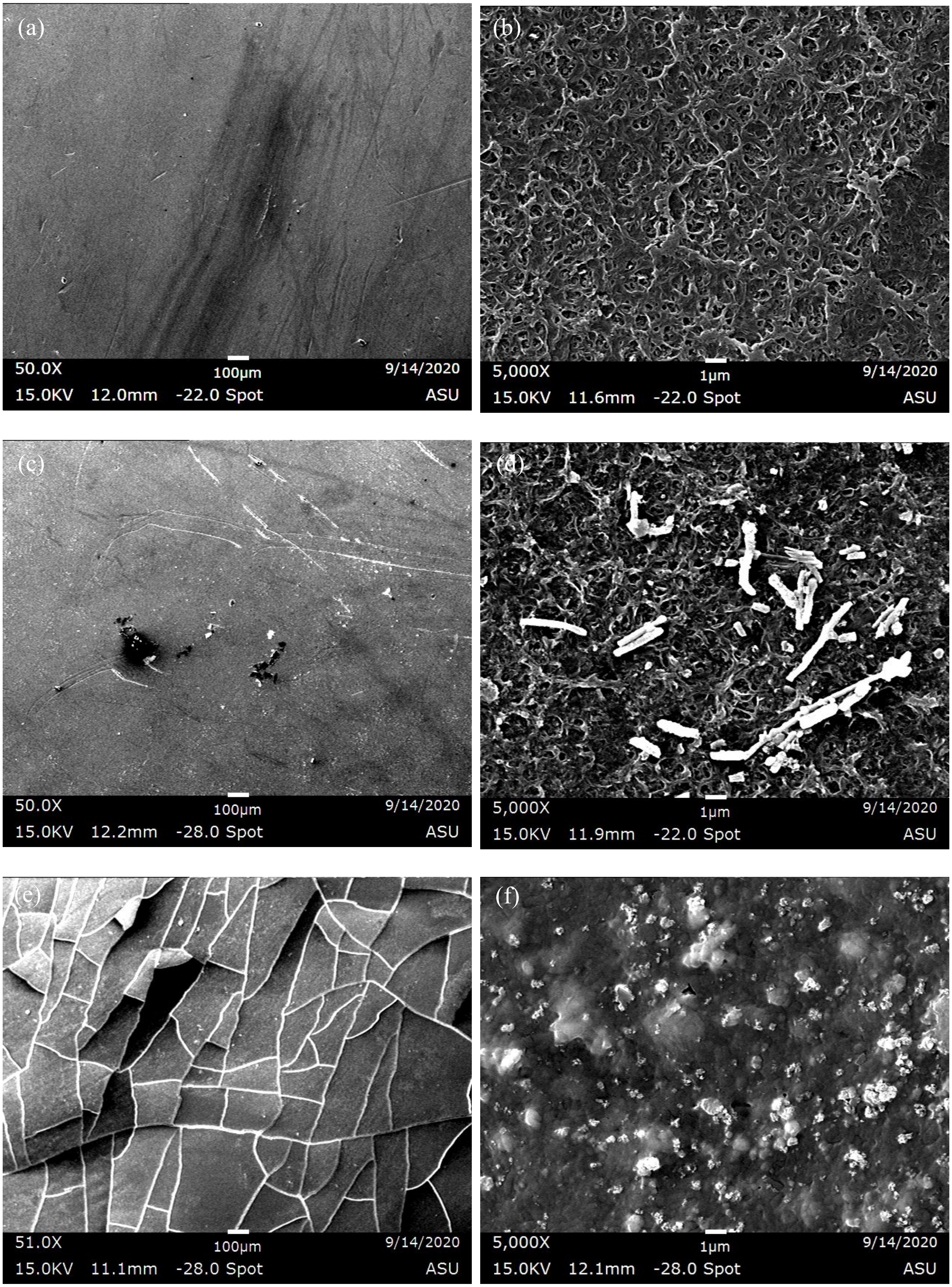

(a)
50.0X
100μm
9/14/2020
15.0KV 12.0mm -22.0 Spot
ASU
(b)
5,000X
1μm
9/14/2020
15.0KV 11.6mm -22.0 Spot
ASU
(c)
50.0X
100μm
9/14/2020
15.0KV 12.2mm -28.0 Spot
ASU
(d)
5,000X
1μm
9/14/2020
15.0KV 11.9mm -22.0 Spot
ASU
(e)
51.0X
100μm
9/14/2020
15.0KV 11.1mm -28.0 Spot
ASU
(f)
5,000X
1μm
9/14/2020
15.0KV 12.1mm -28.0 Spot
ASU

Figure 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.

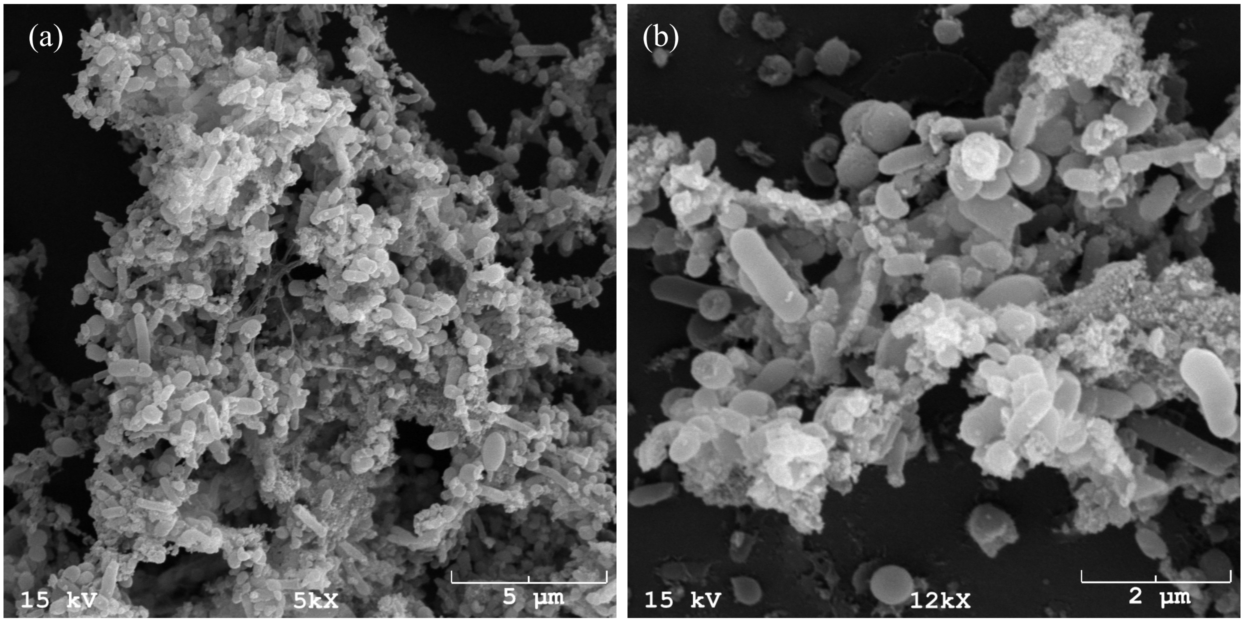


Figure 5. Scanning Electron Microscopy (SEM) images the foulant produced in the tank during the non-MF RO experiment. (a) 5000X and (b) 12000X.

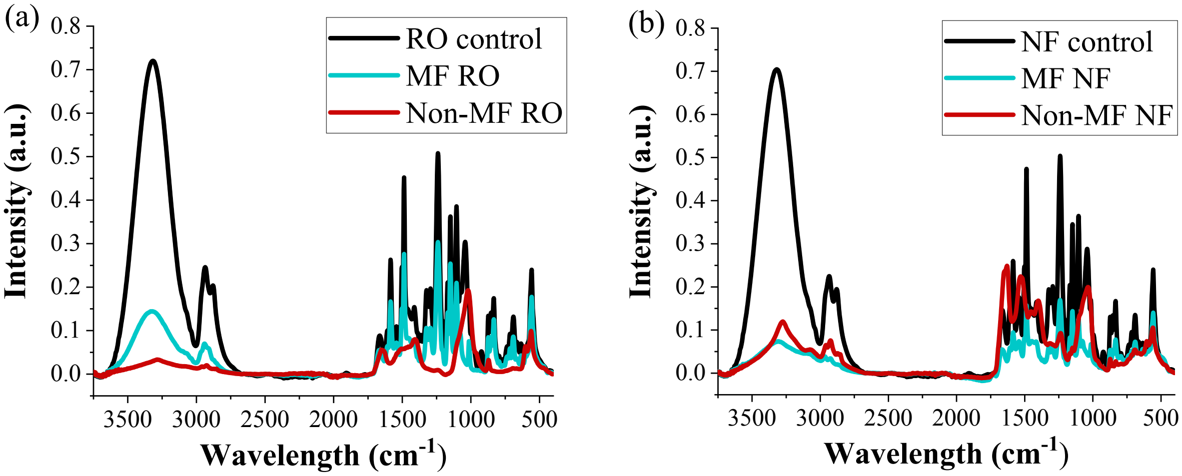
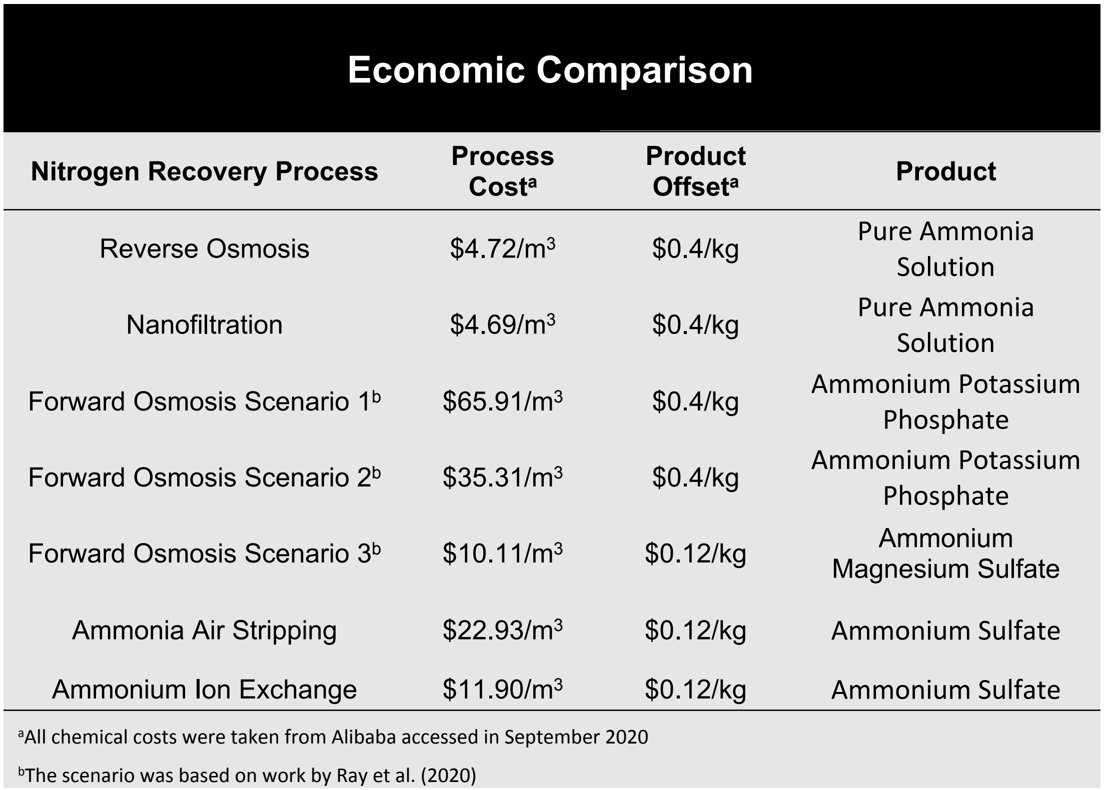


Figure 6. Fourier-transform infrared spectroscopy (FTIR) of the membrane surfaces for reverse osmosis and nanofiltration. (a) FTIR results for the 2 conditions and control membrane for reverse osmosis. (b) FTIR results for the 2 conditions and control membrane for nanofiltration.

Table 1. 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)