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Recovery of Urea from Human Urine Using Nanofiltration and Reverse Osmosis

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Cite This: https://doi.org/10.1021/acsestwater.2c00336
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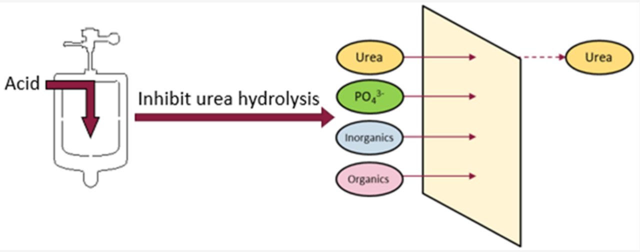
ABSTRACT: Urea is a high-production chemical with critical uses in agriculture, transportation, and air pollution control. Urine is a waste product that could supplement synthetic urea production. This study utilized reverse osmosis and nanofiltration (NF) separation to selectively recover urea from fresh human urine. Urea permeation experiments were conducted to determine the effects of urea stabilization via pH adjustment and membrane type on urea permeation and ion rejection. Fouling mitigation experiments were conducted to determine the efficacy of microfiltration pretreatment on reducing membrane fouling. Results showed that NF90 produced a purer urea product than did BW30, permeating 76% of the urea while rejecting 68% of the conductivity. NF270 permeated >95% of urea while rejecting up to 82% of the phosphorus, allowing for the separation of nitrogen and phosphorus in liquid streams. Urea stabilization did not reduce urea permeation or conductivity rejection, signifying the use of pH 5 as a suitable condition due to its ease of application. Microfiltration pretreatment of urine reduced foulant thickness and permeate flux loss.



KEYWORDS: *urine diversion, membrane fouling, microfiltration, urea stabilization, nitrogen recovery*

1. INTRODUCTION

Urea is a valuable chemical used in fertilizers and in diesel exhaust fluid (DEF), biocement, polymeric adhesives, and elastomers. Commercial urea is produced through the conversion of dinitrogen gas into ammonia (NH_3) via the Haber−Bosch process and the combination of NH_3 with carbon dioxide (CO_2) at high temperatures and pressures.[1,2] The production of urea is thus energy intensive and produces greenhouse gas emissions. Given concerns about the environmental impact of chemical production and transportation, more sustainable sources of urea would advance circular economy initiatives related to nitrogen (N) and fertilizer.[3,4]

Urine is a waste product that is produced at a rate of approximately 1.4 L person^{-1} day^{-1}, with a urea production rate of approximately 11 g of N person^{-1} day^{-1}.[5] Urine could be used to supplement urea production. The collection of urine for urea recovery would require diversion of urine from centralized wastewater treatment systems. Doing so would reduce the nutrient loads on wastewater treatment plants and increase operation efficiency, as literature has shown that urine contributes to 80% of the total nitrogen (TN) and 50% of the total phosphorus (TP) but only 1% of the total volumetric flow of wastewater.[6] Different urine treatment processes have been studied to recover N, including air stripping of NH_3 gas,[7−11] biological nitrification of NH_3,[12−14] and adsorption of ammonium (NH_4^+) onto ion exchange resins.[15−17] In these processes, NH_3/NH_4^+ is targeted because urine typically goes through urea hydrolysis. For example

$$(NH_2)_2CO + H_2O \rightarrow CO_2 + 2NH_3 \qquad (1)$$

where in the presence of the urease enzyme, urea rapidly hydrolyzes into NH_3 and CO_2.[18,19] Therefore, to recover urea from urine, inhibition of urea hydrolysis in fresh urine is necessary. Previous research has shown that pH adjustment of urine below pH 5 (e.g., using acetic acid) or above pH 12 {e.g., using sodium hydroxide (NaOH), calcium hydroxide [$Ca(OH)_2$], or magnesium hydroxide} can prevent the enzymatic urea hydrolysis reaction and allow for the recovery of urea.[19−21]

Membrane separation can be a suitable technology for the recovery of urea from fresh urine. A summary of the literature on the recovery of urea from fresh urine using membranes can be found in Table S1.[22−31] Membrane rejection occurs via two mechanisms: (1) electrostatic (Donnan) rejection, whereby charged molecules are rejected due to interactions with the

Special Issue: Resource Recovery and Recycling from Water Streams: Advanced Membrane Technologies and Case Studies

Received: July 26, 2022
Revised: September 6, 2022
Accepted: September 7, 2022

solution and charged membrane,[32,33] and size (steric) exclusion, whereby molecules larger than the pore size of the membranes cannot permeate through and are rejected.[34,35] Urea is not well rejected by membranes as it is both neutral and below the molecular weight cutoff (MWCO) of commercial membranes, even state-of-the-art desalination membranes (diameter of 2.6 Å, molecular weight of 60.06 g/mol).[26,27,30,31] Thus, the recent literature has aimed to increase the rejection of urea by membranes by modifying membrane active layers and applying heat treatment.[31] Other literature has aimed to use different membrane types and orientations to adsorb urea to membranes[24,28] or used different treatment processes to adsorb urea to different commercially available adsorbents, with variable success.[36−38] However, other constituents in urine, such as ions, endogenous organics, and pharmaceuticals, can be rejected well by membranes.[25−27,30,39] It thus is advantageous to allow urea to permeate through membranes to separate it from other urine constituents. Previous literature showed that forward osmosis membranes (FO) could be coupled with membrane distillation to recover urea in a low-pressure system.[26] However, while low-pressure systems require low energy input, recovery is often limited to 50% due to the concentration equilibrium.[40] Thus, pressure-driven membrane treatment orientations provide greater potential for urea recovery, as shown by literature values of urea recovery of >50%. Recent studies have shown that polyamide brackish-water reverse osmosis (RO) (i.e., BW30) or nanofiltration (NF) membranes (i.e., NF90) allow for urea permeation while rejecting other urine constituents.[27] However, these tests were performed in a dead-end orientation for proof-of-concept rejection profiles. In contrast, most industry-operated membrane systems are run in cross-flow orientation, which allows for slower flux decline due to membrane fouling, reduced membrane cleaning frequency, and longer membrane lifetimes.[41] Furthermore, cross-flow membrane systems have been shown to have higher rejection of contaminants due to decreased adsorption of contaminants to the membrane surface, decreasing their flux across the membrane.[42,43] While previous studies specifically used BW30 and NF90 membranes for urea recovery, literature suggests that NF270 could be a better candidate membrane, as NF270 has a low rejection of neutral organic compounds[44] but can reject multivalent ions.[33,45,46] A recent study evaluated urea recovery using cross-flow NF90 and NF270 but used only stabilized urine at high pH values and did not evaluate the economic potential of the process.[29] Commercial manufacturers of membranes specify pH operating conditions under which membranes can guarantee performance; for membranes such as BW30 and NF90, the pH ranges between 2 and 11. Given the need to prevent urea hydrolysis for urea recovery, use of a high-pH condition (i.e., pH 12) could have negative effects on long-term performance. Some previous literature has suggested that at high solution pH, acidic functional groups within the membrane active layer electrostatically repel each other, causing the pore size to increase and thus permeate flux to increase and rejection to decrease;[47,48] however, other literature suggests that neutral molecules do not experience the effects of solution pH unless ions exist in solution.[47,49,50] Therefore, there is a need to evaluate the effects of urea stabilization at low pH on urea separation by polyamide BW30, NF90, and NF270 membranes in a cross-flow orientation and to determine the product economic potential.

During urine treatment, membrane surfaces can build up a fouling layer that consists of organic constituents, microorganisms, and inorganic precipitates.[39] Urine stabilization via acetic acid has been shown to alter the microbiome of fresh urine during storage,[51] while the addition of NaOH or $Ca(OH)_2$ was shown to accelerate inorganic fouling in the separation of urea from fresh urine in FO.[26] Mitigation of organic fouling via disinfection/oxidation is likely not viable due to the high organic molecule concentration in urine, but physical pretreatment methods may be more feasible, such as sand filtration, microfiltration (MF), or ultrafiltration (UF).[52] Microfiltration may be a suitable option for pretreating stabilized fresh urine, as MF is commonly applied as pretreatment before RO/NF processes at municipal treatment plants.[53−57] Previous studies have shown that pretreatment of urine using MF successfully reduced fouling during cross-flow RO/NF treatment of hydrolyzed human urine, as many biological and inorganic constituents in hydrolyzed urine are larger than the pore size of microfilters.[39] However, previous studies on the membrane treatment of stabilized fresh urine did not evaluate fouling;[29,30] thus, the interplay between urine stabilization and fouling mitigation in fresh human urine has not been evaluated.

Thus, the goal of this research was to provide an improved understanding of the recovery of urea from fresh human urine using cross-flow membrane separation. The specific objectives of this research were (1) to investigate the role of pH adjustment in the recovery of urea using synthetic fresh urine (SFU), (2) to investigate the role of different commercial RO/NF membranes in the recovery of urea using SFU, (3) to demonstrate the efficacy of the RO/NF system for the recovery of urea using real fresh urine (RFU) pretreated with MF, (4) to investigate how MF pretreatment of RFU affects the fouling behavior of RO/NF membranes, and (5) to conduct a product analysis to illustrate the economic potential of the process.

2. MATERIALS AND METHODS

2.1. Fresh Human Urine. Synthetic fresh urine (SFU) and real fresh urine (RFU) were used in this study. Preparation of SFU was based on the method described in ref 26 as described in Tables S2 and S3, and samples were adjusted to pH 5, 6, and 12 using 10 M sodium hydroxide and concentrated (17.4 M) acetic acid. Real fresh urine was collected using a portable urinal setup designed for urine collection as shown in Figures S1−S3. Real fresh urine was adjusted to pH <5 using 2.5 M acetic acid and a control logic based on knowledge gained from the literature.[51] The concentrations of constituents in RFU are listed in Table S4. The donors ranged from 18 to 50 years of age. Only males were included in the study. Collection of human urine was approved by the Arizona State University Institutional Review Board. Additional details on SFU and RFU collection and preparation are provided in the Supporting Information.

2.2. RO/NF Membranes. Three commercial membranes were used in this study: a loose RO membrane, BW30 (Filmtec); a tight NF membrane, NF90 (Filmtec); and a loose NF membrane, NF270 (Filmtec). The specifications of these membranes, including salt rejection, flux, operating pH range, and material type, are listed in Table S5.[58] Additional details about the preparation of membranes and the membrane system are provided in the Supporting Information. Pictures of the membrane system and different components are shown in Figures S4−S7.

2.3. RO/NF Urea Permeation Experiments. Urea permeation experiments were conducted to determine the effect of different pH conditions and different commercial membranes on the permeation of urea and rejection of other urine constituents. Ten liters (2.6 gal) of SFU was added to the 5 gal feed tank, and the system was run at an operating pressure of 375 psi, a feed velocity of 37.8 cm/s (i.e., a volumetric flow rate of 1 L/min), and a temperature of 20 °C, as described in the literature.[39] A wetted membrane was loaded into the membrane cell with a polypropylene spacer (Conwed Plastics, 34 mm) placed between the feed flow and the active side of the membrane. A sample of the urine was taken before the experiment, and a time zero sample was taken after running the system for 10 min to ensure that any deionized (DI) water in the system leftover from cleaning was fully mixed into the urine. The system was run until at least 20 mL of permeate was collected, and the pH and conductivity of the undiluted urine, time zero, and permeate samples were measured. Samples were stored at 4 °C, and TN and total organic carbon (TOC) were measured on unfiltered samples. Samples were then filtered through nylon syringe filters with a pore size of 0.45 μm, and total ammonium nitrogen (TAN), chloride (Cl^-), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) were measured. Analytical methods can be found in section 1.4 of the Supporting Information. The TAN comprises both un-ionized (NH_3) and ionized ammonium (NH_4^+). Each condition was run in duplicate, and the experiment was repeated for each pH pretreatment condition and each membrane type for SFU experiments.

An "optimum" pH condition was selected on the basis of SFU permeation results and additional factors explained in the Results and Discussion. This optimum pH condition was then used for the RFU experiments, in which real urine was collected, adjusted to the optimum pH as described in section 2.1, and pumped through a two-stage MF unit (SpectraPure), which consisted of a 1 μm sediment filter (L-SF-MT-1-10) and a 0.2 μm ZetaZorb sediment filter (L-SF-ZZ-0.2ABS-10), using a Cole-Parmer Masterflex peristaltic pump at a rate of 1000 mL/min. Pictures of the MF unit and pump are shown in Figures S8 and S9, respectively. Ten liters of MF-pretreated RFU was added to the feed tank, and an undiluted urine sample, a time zero sample, and a permeate sample were all collected while running the system under the previous operating conditions. The pH and conductivity of samples were immediately measured, and samples were acidified with 12 M sulfuric acid (H_2SO_4) to a pH of <2 to prevent further hydrolysis. Unfiltered samples were analyzed for TN and TOC. Samples were then filtered through nylon syringe filters with a pore size of 0.45 μm, and samples were analyzed for TAN, Cl^-, PO_4^{3-}, Na^+, K^+, Ca^{2+}, and Mg^{2+}; SO_4^{2-} was measured for real urine samples, and acidification of samples with H_2SO_4 prevented accurate membrane rejections of SO_4^{2-} from being calculated. Analytical methods can be found in section 1.4 of the Supporting Information.

2.4. RO/NF Fouling Experiments. Fouling experiments were conducted to determine the effects of MF pretreatment on biological, organic, and inorganic fouling of the membranes. An "optimum" membrane was selected on the basis of RFU and SFU permeation results and additional factors explained in the Results and Discussion. This membrane was used for fouling experiments. A prewetted membrane was loaded into the membrane cell with a spacer between its active side and the feed flow. Ten liters of DI water was added to the feed tank, and the system was run under previous operating conditions until the permeate flow was stable (∼4 h), signifying that the membrane was fully compacted. The DI water was drained from the feed tank. RFU was collected and pretreated to the predetermined best pH, and 10 L of urine without MF pretreatment was added to the feed tank. The system was run for 24 h under the previous operating conditions, with the permeate looping back into the feed tank. Permeate flux data were measured every minute and reported in 20-data point rolling averages. After the experiment, membranes were extracted from the membrane cell, and a small portion of the active area was cut and fixed in a glutaraldehyde solution at 4 °C for at least 1 h; the contents of the fixative solution are listed in Table S6. After storage in the preservative, membranes were dehydrated using a series of incremented ethanol dilutions, from 0% to 100% ethanol in 20% increments, with each increment employed for at least 10 min. Membranes were then air-dried and analyzed using scanning electron microscopy (SEM) and Fourier-transform infrared (FTIR). Membranes were carbon-coated using graphite before SEM analysis. The experiment was performed in duplicate and repeated with urine that was pretreated with MF.

2.5. Product Analysis. A product analysis was conducted to illustrate different commercial products that could be created using recovered urea and to compare the costs of commercial urea products with the proposed membrane treatment process. Costs of commercial fertilizers were taken from Data Transmission Network/Progressive Farmer in February 2022.[59] Costs of DEF were taken from Discover DEF in March 2022.[60] Costs were converted into dollars per kilogram of nitrogen (N) for comparison. Other novel uses for urea were taken from the literature. Costs of acetic acid were taken from Alibaba in July 2022.[61] Costs of MF and NF processes were taken from the literature.[39,62,63]

2.6. Data Analysis. Rejection of a constituent via membrane separation was calculated as follows:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

where C_p is the permeate concentration and C_f is the feed concentration. The percent rejection was calculated by subtracting the feed (time zero) concentration by the permeate concentration. The percent permeation was calculated by subtracting the percent rejection from 100%.

TN is the combination of urea, NH_4^+, and NH_3, and TAN is the combination of NH_4^+ and NH_3. The concentration of urea was calculated as the difference between the TN and TAN concentrations.

The error was represented as the standard deviation. Error bars in figures show the standard deviation of duplicate experiments for urea permeation, ion rejection, and TOC rejection. Letters over data bars show statistical significance groups compared to each data point in a graph. Statistical significance was determined using two-factor analysis of variance tests and paired *t* tests.

3. RESULTS AND DISCUSSION

3.1. Evaluation of pH Conditions and Membrane Types for SFU. Three different pH conditions (i.e., pH 5, 6,

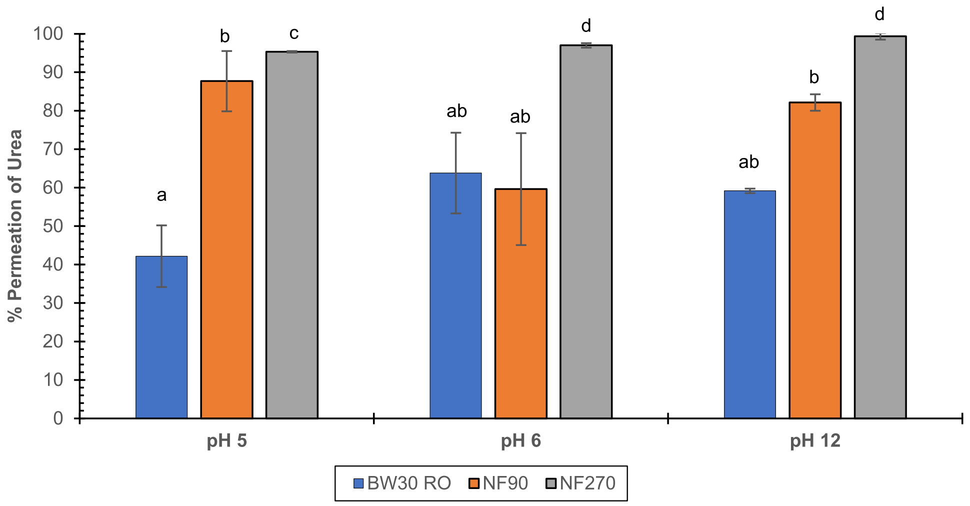


Figure 1. Urea permeation results for SFU experiments, across three pH pretreatment conditions and three membranes. Letters above bars show statistical significance groups.

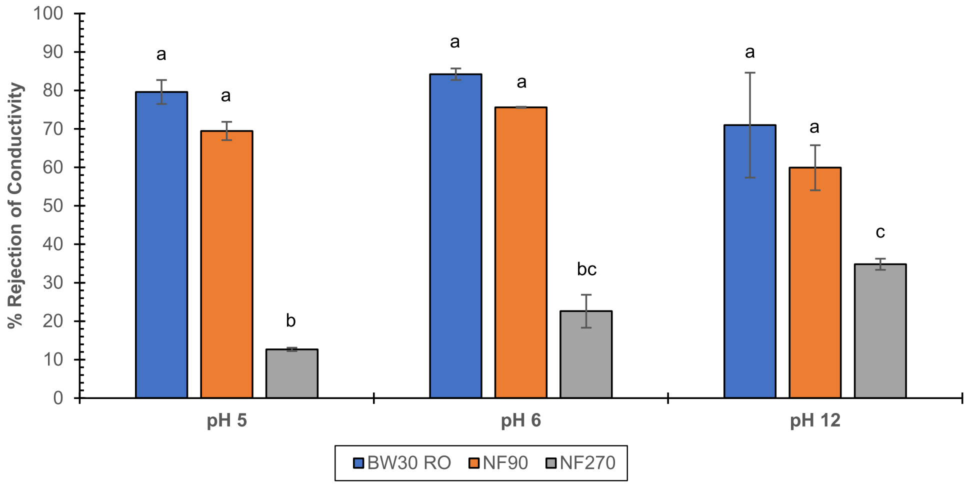


Figure 2. Conductivity rejection results for SFU experiments, across three pH pretreatment conditions and three membranes. Letters above bars show statistical significance groups.

and 12) were evaluated to determine the efficiency of applying urine stabilization via acid or base addition before membrane separation. Additionally, three different membrane types (i.e., BW30, NF90, and NF270) were evaluated to identify the effects of membrane type on the permeation of urea and rejection of other urine constituents. Figure 1 shows the permeation of urea for each of the pH conditions and membrane types. There were no statistical differences between each pH condition for BW30 and NF90. Only NF270 showed a statistically significant difference between the pH 5 condition and the pH 6 and 12 conditions, though all pH conditions for NF270 exhibited >95% urea permeation. Because urea is a neutral compound, electrostatic interactions, which would normally increase with an increase in pH as the ζ potential of the polyamide layer becomes more negative[32] and as free carboxylic groups on the membrane surface become ionized,[47,64] have minimal effects on urea permeation. There were significant differences between different membrane properties for all pH conditions. As the membrane pore size increased (i.e., increasing from BW30 to NF270), urea permeation increased for all pH conditions, signifying the importance of membrane pore size to the rejection of neutral compounds. BW30 had the lowest average permeation of urea of 55%; NF90 had an average permeation of 77%, and NF270 had the highest average permeation of urea of 97%. The low rejection of urea by NF270 was comparable to the results in the literature, where neutral, polar organic compounds were rejected poorly by NF270.[44] However, the rejection trends of BW30 and NF90 are different from what was found in the literature, in which BW30 and NF90 in a dead-end orientation exhibited no significant differences in urea rejection.[27] This may reflect the differences in the operating modes between dead-end and cross-flow filtration. It is well-documented that concentration polarization has a weaker effect during cross-flow separation, as horizontal flow can resuspend molecules on the surface, mitigating the flux loss of water across the membrane and maintaining the rejection profile.[65] Furthermore, the literature has shown the ability of urea to form hydration shells in water, i.e., where water can orient itself around urea molecules via dipole−dipole interactions,[66] which can cause increased rejection of constituents by membranes due to increased radii.[67] These hydration shells can be shed during membrane separation due to shear forces caused by the flow of bulk fluid near the membrane surface.[67] Due to the

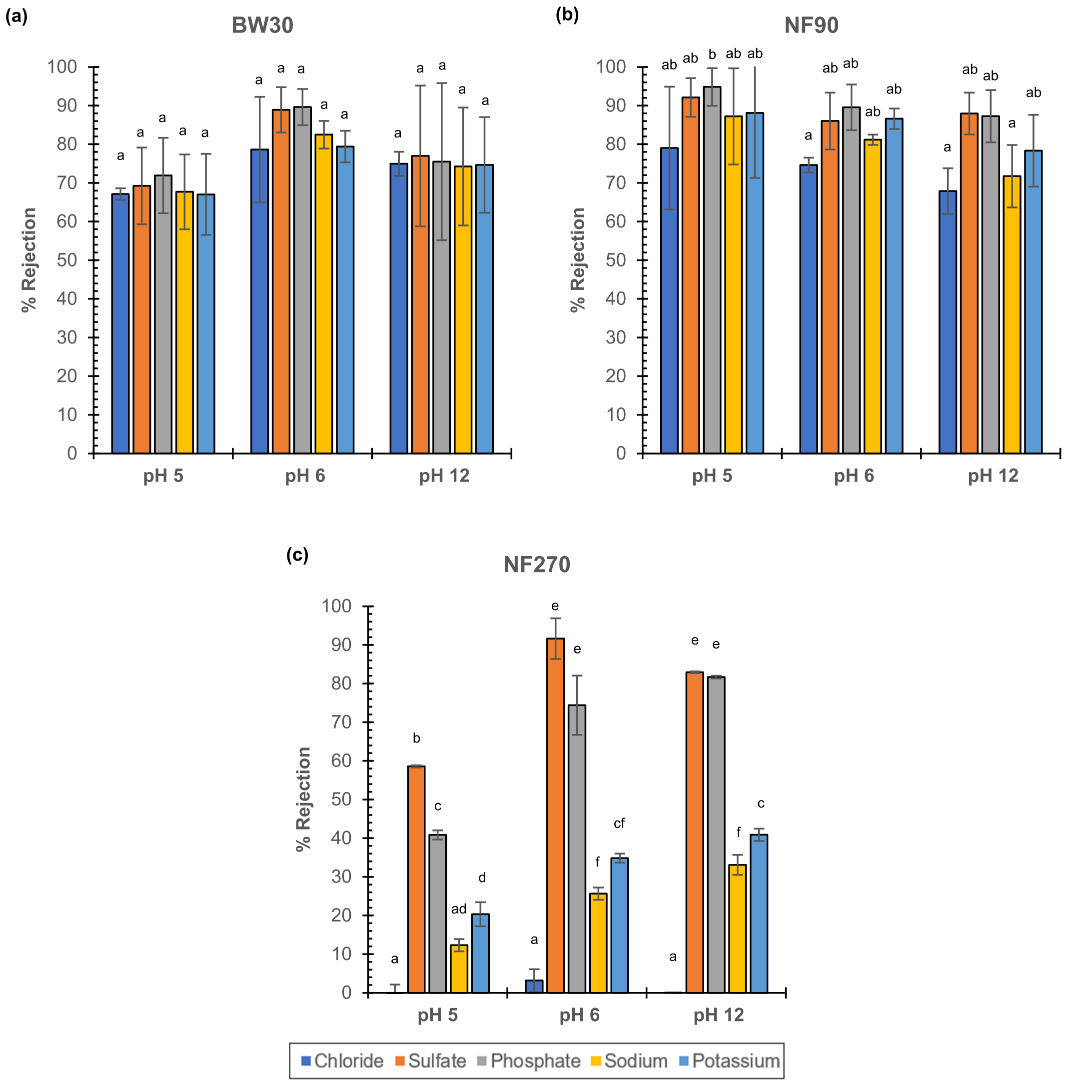


Figure 3. Specific ion rejection results for SFU experiments, across three pH pretreatment conditions and two membranes: (a) BW30, (b) NF90, and (c) NF270. Letters above bars show statistical significance groups.

different flow operations between dead-end and cross-flow filtration, a higher shear force is applied to hydration shells during dead-end filtration, shedding them with higher efficiency.[67] The formation of hydration shells around urea molecules also provides a justification for the lower than expected permeation based on the MWCO of NF membranes used in the study; urea (molecular weight of 60.06 g mol^{-1}) is below the MWCO of both NF90 and NF270 (between 180 and 340 g mol^{-1}[68]), so it would be expected that urea would be recovered well by these membranes. The significantly lower urea recovery of NF90 compared to that of NF270 can be explained by the membrane makeup of NF90 compared to that of NF270. NF90 consists of MPD-TMC, which has been shown to have a pore structure that is tighter than that of NF270s piperazine-TMC.[69] Thus, the tighter pore structure of NF90 inhibited the transport of urea through the membrane more than the structure of NF270 did, resulting in lower urea permeation. Notably, the literature found that polyamide membranes such as the three used in this study had higher rejections of neutral, polar compounds than membranes made with different materials, such as cellulose acetate.[22] Polyamide membranes were selected for this study due to their common application for full-scale water and wastewater treatment,[70] but it may be beneficial to test other membranes, such as cellulose acetate membranes, under different pH conditions that may permeate urea at higher efficiencies while rejecting other constituents at similar efficiencies.

Figure 2 shows the rejection of ions, measured by conductivity, for each of the pH conditions and membrane types. There were no statistical differences across different pH conditions for BW30 and NF90. For NF270, a higher pH resulted in higher rejection of ions. The literature has shown that an increase in solution pH increases the negative surface charge of the membrane.[32] While for BW30 and NF90, the pore size is sufficiently small that this surface charge difference has negligible effects, the larger pore size of NF270 resulted in fewer ions being rejected via steric hindrance and a more significant contribution of rejection via electrostatic interactions. Thus, the highly negative surface charge of NF270 at pH 12 allowed for a significant increase in ion rejection compared to that under lower-pH conditions. While the NF90 and BW30 membranes had comparable ion rejections, NF90 had a significantly higher permeation of urea (77% vs 55%). Thus, the NF90 membrane could be used to create a purer and

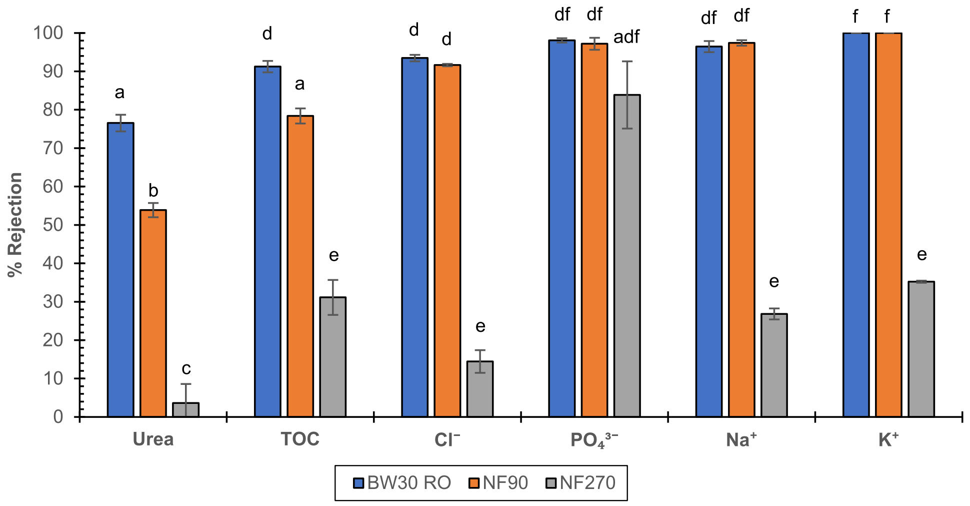


Figure 4. Rejection of different compounds by BW30, NF90, and NF270 from RFU at pH 5. Letters above bars show statistical significance groups.

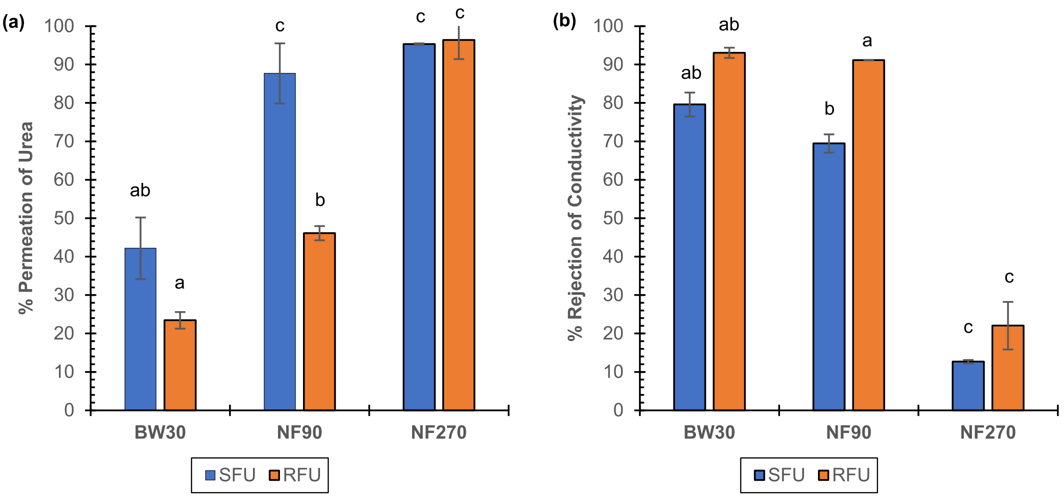


Figure 5. Comparison of SFU and RFU experiments for (a) urea permeation and (b) conductivity rejection. Letters above bars show statistical significance groups.

more concentrated urea product compared to that from the BW30 membrane. These results are different from the literature in a dead-end orientation, which showed that there were no significant differences in urea permeation or conductivity rejection.[27] Similar to urea, ions can form hydration shells that can be shed by shear forces, which are different for dead-end and cross-flow orientations.[67] Lastly, the NF270 membrane had low ion rejections for all three pH conditions. As stated above, the larger pore size resulted in lower rejection of all compounds.

Figure 3 shows the specific rejections of ions for (a) BW30, (b) NF90, and (c) NF270. No significant differences between specific ion rejections were seen for BW30. For NF90, most conditions had no significant differences besides a lower rejection of monovalent ions (i.e., Cl^- and Na^+) at pH 12 than PO_4^{3-} at pH 5. However, for NF270, the rejection of multivalent ions (i.e., SO_4^{2-} and PO_4^{3-}) was significantly higher than that of monovalent ions. The minimal significant differences between ions for BW30 and NF90 illustrate the importance of pore size for these membranes. While electrostatic interactions alone would result in greater rejection of multivalent ions, the pore sizes of BW30 and NF90 allow for high rejection of monovalent ions at rates comparable to those of multivalent ions. However, the larger pores of NF270 result in higher rejection of multivalent ions, with greater electronegativities and larger hydrated radii, than monovalent ions. NF270 membranes have been well-documented to have high rejection of multivalent anions[33,45,46] but low rejection of monovalent ions.[45,71−73] Given the high permeation of urea and rejection of multivalent ions, NF270 could be used for selective separation of urea and monovalent ions from multivalent ions. While other available methods for separating multivalent ions from urine (e.g., precipitation via pH adjustment[20]) may require additional chemical addition, mixing, and solid−liquid separation, NF270 can be applied with minimal additional steps to produce separate liquid streams of urea and multivalent ions. Notably, some urine treatment literature has the goal of recovering N and P in separate streams.[9,16] NF90 and NF270 are both valuable for different applications, with maximized operating efficiencies when using the pH 5 condition. This is because (a) pH 6 cannot be used in a real-world system, as urea stabilization is necessary for recovery of urea and to reduce operational challenges associated with urine collection,[19,74−76] and (b) pH 5 is preferred over pH 12, as pH 12 is greater than the commercially specified pH operating conditions, and high-pH

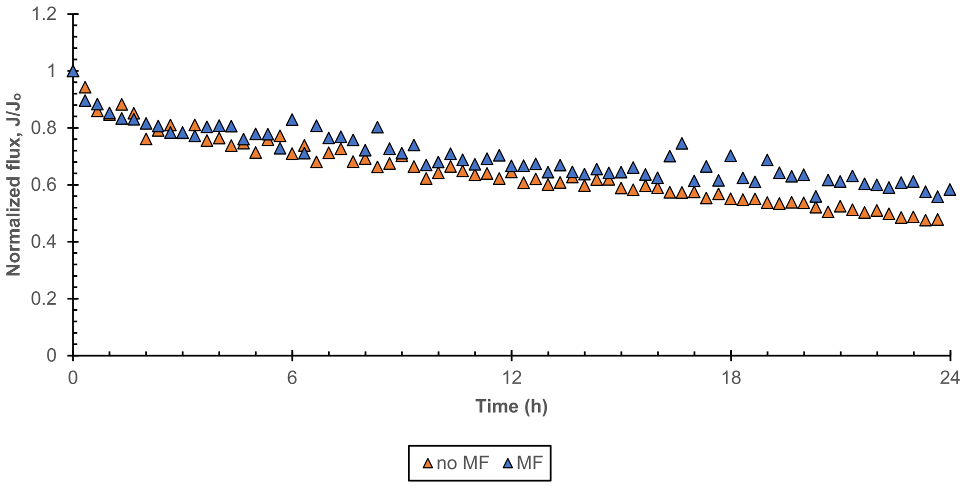


Figure 6. Permeate flux reduction over the 24 h period for experiments with and without MF pretreatment.

solutions have been shown to cause reduced membrane performance;[77] additionally, multivalent cations can precipitate at high pH, contributing to inorganic fouling of the membrane.

3.2. Comparison of RFU with SFU for Selected pH Conditions. Figure 4 shows the rejection of different compounds from RFU at pH 5 by the three membranes. NF90 had significantly lower rejection (higher permeation) of urea than did BW30 but no significant difference in rejection of ions compared to that of BW30. Furthermore, while NF90 had a significantly lower rejection of TOC (78%) than did BW30 (91%), this significant difference can be ascribed to urea permeation, which contributes to TOC. There was no statistical difference in TOC rejection between BW30 (95%) and NF90 (83%, but with large variances) when eliminating urea concentrations from the TOC concentrations. The TOC rejection includes microorganisms, proteins, metabolites such as creatinine, and other compounds commonly found in urine. NF270 exhibited similar trends in SFU experiments, with a high (>94%) permeation of urea but a low rejection of monovalent ions, each of which was significantly lower than those of BW30 and NF90. However, PO_4^{3-}, a multivalent ion, was rejected at >77% by NF270, and there was no significant difference in PO_4^{3-} rejection between each of the membranes. These results signify the efficacy of NF90 to produce a urea product in a real-world system. Furthermore, for applications in which separation of urea and PO_4^{3-} is desirable, NF270 could be used to produce two separate liquid streams that could undergo additional treatment to produce desirable N and P products, especially given the higher rejection of PO_4^{3-} from RFU by NF270. This additional treatment may include concentration steps, such as by membrane distillation,[26,30] or adsorption using ion exchange resins[78] or biochar[79] to remove impurities such as pharmaceuticals and other organics, which can produce higher-value liquid N and P products.

Figure 5 shows a comparison between SFU results and RFU results for the pH 5 condition. BW30 and NF270 exhibited no significant differences in urea permeation and ion rejection between SFU and RFU. NF90 had significantly higher urea permeation and lower ion rejection for SFU than for RFU. However, similar trends existed between SFU and RFU. NF90 had a higher urea permeation but comparable ion rejection compared to those of BW30, and NF270 had near-100% urea permeation but low ion rejection. The significant difference observed for NF90 suggests additional rejection of constituents due to organics existing in real urine (e.g., microorganisms, proteins, and metabolites) that interact with urea and ions. The literature has shown that proteins, which exist in RFU, have a negative charge at high pH and a positive charge at low pH.[80,81] The polarity of urea allows it to orient its nitrogen—hydrogen groups toward (away from) proteins for high (low)-pH solutions;[82] these interactions can allow for increased rejection of urea molecules due to the charged nature of proteins (i.e., Donnan exclusion) and the increased radii of protein—urea complexes (i.e., steric hindrance), especially when considering the formation of hydration shells around protein—urea complexes.[83] Similarly, charged proteins and ions can interact via electrostatic interactions,[84] resulting in increased ion rejection. Additionally, increased rejection of specific ionic species due to interactions with organic constituents may have increased the rejection of other ionic species, as retention of a cation requires the retention of an anion to maintain the charge neutrality of the solution.[85,86] However, these interactions produced a statistical difference for only NF90. As each of the three membranes studied has similar active layers but different pore sizes, it is plausible to suggest that membranes with overly large pores (i.e., NF270) will not have observable significant Donnan effects of charged proteins on the rejection of compounds (i.e., their radius of influence is not large enough), but RO membranes (i.e., BW30) have pores that are sufficiently small that the rejection of protein—urea complexes was not significantly greater than the rejection of urea—water hydration shells.

Given its significantly higher permeation of urea but comparable ion rejection compared to those of BW30, NF90 was selected for continued examination as a membrane for producing a urea product. As stated before, NF270 can be used for specific applications such as liquid fertilizers or applications in which separation of N and multivalent ions (especially PO_4^{3-}) in a nonprecipitated form is desired. Other treatment trains commonly applied for urine treatment have aimed to produce separate streams of N and P, such as stripping of NH_3 gas coupled with struvite precipitation;[9] further work is needed to characterize the economic feasibility of using NF270 to produce separate streams of N and P compared to these treatment trains.

3.3. Fouling Mitigation with MF Pretreatment. Fouling experiments were conducted to characterize fouling of membranes in a cross-flow orientation during treatment of

RFU and to determine if MF pretreatment can be a suitable mitigation strategy. The selected condition from sections 3.1 and 3.2 was used for fouling experiments (i.e., NF90, pH 5 RFU). Permeate flux reduction for MF and no-MF conditions over the 24 h period is shown in Figure 6. Duplicate results for permeate flux are shown in Figure S10. Pictures of the membranes after the 24 h period are shown in Figure S11. A thicker foulant was produced during the experiment without MF pretreatment. This corresponded to an average permeate flux reduction of 46% for experiments without MF pretreatment, compared to 40% for experiments with MF pretreatment. While a 6% difference in permeate flux reduction may seem minimal, current industry practice is to apply clean-in-place after a 10−15% loss of permeate flux.[87] When contextualized with the long-term operation of cross-flow RO/NF systems at scale (i.e., months), a reduction in fouling by 6% may help increase the operation time of membrane systems by multiple months. As MF pretreatment could reduce fouling and maintain a higher flux across the NF90 membrane, there are observable operational benefits of including MF pretreatment of urine before RO/NF treatment, especially given the variability in foulant concentrations that can cause unexpected operational concerns.

Fouled membranes were analyzed by FTIR and SEM, and the results are shown in Figures S12−S14. Notably, the gel-layer foulant was loosely attached to the membrane, resulting in detachment of the foulant during the preservation process. Even with the detachment, the results of FTIR analysis (Figure S12) still showed greater peak suppression (i.e., at 3300 cm^{-1}) for experiments with no MF pretreatment, signifying that the signal from the membrane was suppressed by the accumulation of a fouling layer on the surface. Upon comparison of SEM images of experiments with no MF pretreatment (Figure S13) and experiments with MF pretreatment (Figure S14), there appears to be a greater density of rod-shaped bacteria (i.e., lightly colored) covering the membrane surface (i.e., darker colored), which contributes to greater flux decline through cake/biofilm-enhanced concentration polarization[88,89] and electrostatic attraction of constituents to the negatively charged microbial surface. While microbial characterization was not performed to confirm the speciation of the microorganisms seen on the surface of the membrane, it was clear that rod- and sphere-shaped bacteria were the dominant types of microorganisms, which matches with the microbial results seen in the literature on urine treatment.[51] As one can visually confirm through SEM images, these microorganisms were much larger than the membrane pores and were thus rejected by NF90 at nearly 100%, resulting in increased foulant thickness. Other organic materials such as proteins, metabolites, and other biomolecules exist naturally in urine; this organic material appeared to coat the surface of some microorganisms, contributing to additional fouling of the membrane, but hydrophobic organic compounds with low molecular weights, such as uric acid, and other small compounds may have had low rejection due to their low affinity for water and their smaller hydrated radii.[36,90] The literature has shown low rejection of small proteins and amino acids by NF membranes, but manipulation of membrane properties, especially pore size and surface charge, can allow for better rejection of biomolecules.[91] In these scenarios, additional fouling could occur due to the buildup of biomolecules on the membrane surface, but the use of MF pretreatment could greatly benefit the operations of these systems, as smaller biomolecules that sorb to the surface of larger biomolecules, especially microorganisms, may be rejected by MF. In instances of significant biological fouling, ultrafiltration could be evaluated as a potential option due to its smaller pore size. MF as a pretreatment process before RO/NF is commonly applied at drinking water, wastewater, and desalination plants to produce high-quality water products for human consumption and potable reuse scenarios due to its benefits for performance and economic viability;[53−57] the precedent for this set of processes thus further reduces barriers to implementation of these treatment trains on a larger scale.

3.4. Product Analysis for Urine-Derived Urea. Urea recovered from RFU could be used for a variety of products, including different fertilizer formulations, DEF, urea-based resins, biocement, and synthetic polymers. A summary of commercially available urea-based products and comparable products (i.e., N−P fertilizers) is given in Table S7. As one can see, N−P fertilizers have more value than others due to the high value of PO_4^{3-}. Urea-based fertilizers have more value than NH_3/NH_4^+-based fertilizers, as urea can release N slowly to reduce runoff and/or leaching. DEF has the highest value of N-only products, as its urea purity is higher than that of urea fertilizers and it has a unique market, especially considering its requirement by law.

A product analysis of urine-derived urea was conducted to determine overall process costs and to compare the costs with commercially available product costs, as shown in Table 1. The product analysis considered pH adjustment using concentrated acetic acid [\$0.37/m^3 of urine, based on a conservative dose of 0.5 mL/L (0.53 kg/m^3) and the price of acetic acid, \$0.7/kg[61]], MF pretreatment (\$0.06/m^3[41] from the literature[63]), and NF90 or NF270 treatment. From the literature, the operation and maintenance costs of the NF90 and NF270 systems operating at 80% recovery were \$0.11/m^3 and \$0.1/m^3, respectively; the annual capital costs of the NF90 and NF270 systems were \$0.016/m^3 and \$0.017/m^3, respectively.[62] Using conservative estimates of the recovery of urea from NF90 (40%) and NF270 (80%), the costs of the overall processes for NF90 and NF270 were \$0.99/kg of N and \$0.49/kg of N, respectively. These processes are thus estimated to be cheaper than commercial products (e.g., urea fertilizer at \$2.21/kg of N[59]) and DEF (\$4.67/kg of N[60]), as shown in Table S7, signifying the potential of urine-derived urea to supplement the production of urea and urea-based products. However, producing DEF from urine may require the integration of other processes with membrane treatment and use of tighter membranes such as BW30 or even SW30 (a

Table 1. Economic Analysis of Urine-Derived Urea Processes

process	material used	cost per m^3 of urine	cumulative cost per kg of N	product
urea stabilization	acetic acid	\$0.37		
MF pretreatment	MF	\$0.06		
membrane treatment	NF90	\$0.13	\$0.99	urea in permeate, ions in concentrate
	NF270	\$0.12	\$0.49	urea and monovalent ions in permeate, multivalent ions (e.g., PO_4^{3-}) in concentrate

seawater membrane used for desalination) to reduce concentrations of monovalent ions.

While urea products like fertilizer and DEF have global markets, other urea-based products not commercially available could be valuable in the future. For example, urea-based ion exchange resins have been developed that have high selectivity for metals,[92,93] urine-recovered urea has been used for alternative biocementation processes such as microbially induced carbonate precipitation[94,95] and enzyme-induced carbonate precipitation,[96] and urea has been used as a building block for the production of synthetic elastomers[97,98] and urea−formaldehyde adhesive resins.[99] Many of these novel urea-based materials are only in experimental stages of development, but future production of these materials using urine-derived urea would advance circular economy initiatives.

4. CONCLUSION

This study examined the efficacy of the recovery of urea from fresh urine using membrane treatment. These are the major conclusions.

(1) NF membranes can be used to selectively permeate urea from urine, with different pore sizes allowing for different separation of urea and PO_4^{3-}. (2) Urea stabilization using acetic acid can be applied as a pretreatment condition for NF treatment without alteration of membrane rejection properties. (3) MF pretreatment of real urine can be applied to reduce fouling of membranes, sustaining their long-term operation. (4) NF treatment of pretreated urine has the economic potential to supplement urea production for applications such as fertilizers or DEF.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.2c00336.

Additional experimental background, methods, and results, including photographs of urine collection and membrane setups, tables of urine and membrane specifications, and summary tables of literature review and product analysis (PDF)

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CRediT: **Lucas Crane** formal analysis (lead), investigation (lead), methodology (equal), visualization (lead), writing-original draft (lead), writing-review & editing (equal); **Hannah Ray** conceptualization (supporting), methodology (equal), writing-review & editing (equal); **François Perreault** methodology (equal), writing-review & editing (equal); **Treavor H Boyer** conceptualization (lead), funding acquisition (lead), methodology (equal), writing-review & editing (lead).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Science and Technologies for Phosphorus Sustainability (STEPS) Center, a National Science Foundation Science and Technology Center (CBET-2019435).

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