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

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SUPPLEMENTAL MATERIALS

17 pages

6 figures

3 table

1. Materials and Methods

1.1 Urine collection, storage, and safe handling. Real fresh, undiluted urine was collected from anonymous volunteers, both male and female, who fit the criteria: (1) 18 years or older and (2) not pregnant. A urine collection setup was used in both male and female bathrooms in the Biodesign Institute at Arizona State University. Number of donors and ratio of male to female is not known due to anonymity requirements by the Institutional Review Board (IRB) which granted the project's human urine collection. Collection setups utilized plastic collection trays for women and urinal collection tanks for men. Thorough directions with both words and pictures were taped to the wall for understanding on how to properly donate. All collection trays were used once and then bleach cleaned for the next collection event. Gloves were available if desired for the anonymous volunteers. The collection tanks were kept in secondary containment throughout the collection event. All samples were combined during the collection event to ensure anonymity. Additional human urine was collected from the nonwater urinal system in the Biodesign Institute C building on Arizona State University campus. The urine was collected and subsequently mixed with the previously described fresh urine collected from donors. The collected human urine was stored in the lab for at least six months to allow for complete hydrolysis of the urea to occur. Personal protection equipment of gloves, a lab coat, and splash glasses were used when handling urine for experiments. Bleach was readily available for disinfection and biological spill kits were kept in the lab[1].

1.2 Microfiltration pretreatment

Spectrapure microfiltration (MF) systems were used to pretreat the urine. A 1 µm sediment filter cartridge (L-SF-MT-1-10) followed by a 0.2 µm ZetaZorb sediment filter cartridge (L-SF-ZZ-

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

1.3 Analytical methods

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

The RO feed tank foulant was collected and suspended in nanopure water. Cells were then collected by centrifugation (5,000×g, 1 min) and the pellet fixed in Karnovsky's fixative (2% paraformaldehyde, 2.5% glutaraldehyde in 0.2 M Sorenson's buffer, pH= 7.2) overnight at 4°C. The fixed cells were washed once with Dulbecco's Phosphate Buffered Saline (DPBS), adhered to poly-L-lysine coated coverslips, and then washed two additional times with DPBS. Secondary fixation was done with 1% OsO_4 in DPBS for 1h at room temperature, followed by three washes with DI water. Cells were dehydrated with an ascending series of ethanol solutions followed by critical-point drying using a CPD-020 unit (Balzers-Union, Principality of Liechtenstein) with liquid CO_2 as the transition fluid. The 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).

1.4 Economic Analysis

The RO and NF process costs were calculated by adding the following costs together: MF operating cost, pH adjustment with NaOH cost, the RO and NF operation and maintenance costs for a system performing at 80% recovery, and the annual capital costs for the RO and NF systems. All costs were taken from published studies (cited in the discussion text) besides the cost of the NaOH which was derived based on dose and prices taken from Alibaba. The actual derivation of the operating cost is defined as: \$0.06/m^3 + \$4.50/m^3 + \$0.14/m^3 for RO (\$0.11/m^3 for NF) + \$0.014/m^3 for RO (\$0.016/m^3 for NF) = \$4.72/m^3 for RO and \$4.69/m^3 for NF.

For the economic comparison, the total FO operating costs (\$10.11/m^3, \$35.31/m^3, and \$65.91/m^3) include: MF operating cost (\$0.06/m^3 based on work by Chellam et al. [2]), the cost of pH adjustment with NaOH (\$1.50/m^3 based on the required dose of NaOH to raise the pH given in the methods section and the price of NaOH, \$0.3/kg[3]), the cost of the draw solute, and the cost of FO operation (\$1.65/m^3 based on work by Volpin et al.[4]). The cost of the draw solute was derived based on chemical type (KH_2PO_4 and $MgSO_4$), dose (2 L of either 1.5 M or 0.75 M depending on the condition), and prices take from Alibaba. Full cost breakdowns for the FO system can be found in the economic assessment by Ray et al. [5]. The cost for ammonia air stripping was based on work by Liu et al. which determined the most optimized conditions resulted in an operating cost of \$21.65–24.24/m^3 [6]. The cost for ammonium adsorption by ion exchange (\$11.70/m^3) was derived from adding the cost of the ion exchange material (Dowex

Mac 3 resins performed for 100 = \$7.50/m^3 [7]) and the cost of sulfuric acid regeneration (\$4.20/m^3 [8]).

2. Figures and Tables

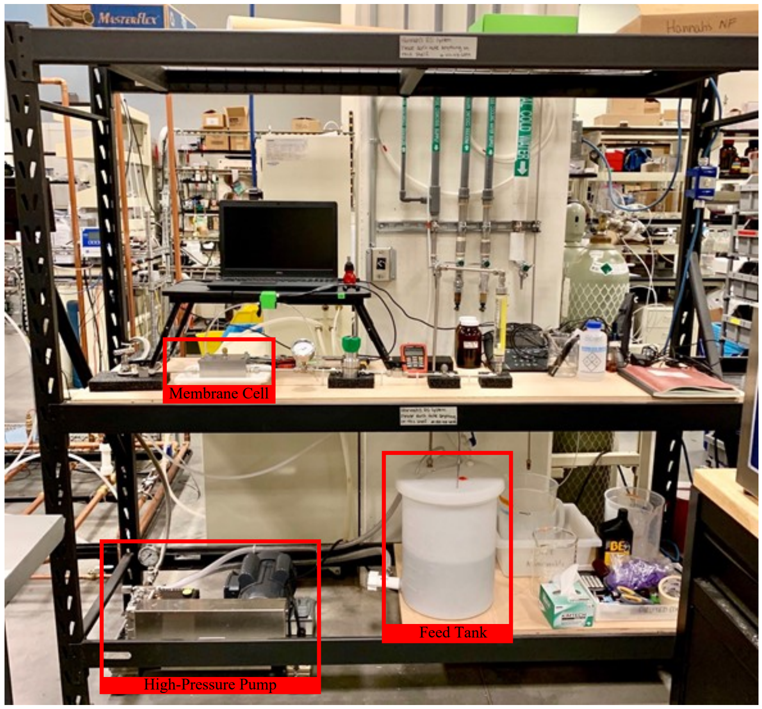


Figure S1. A picture of the RO and NF membrane setup used for all experiments,

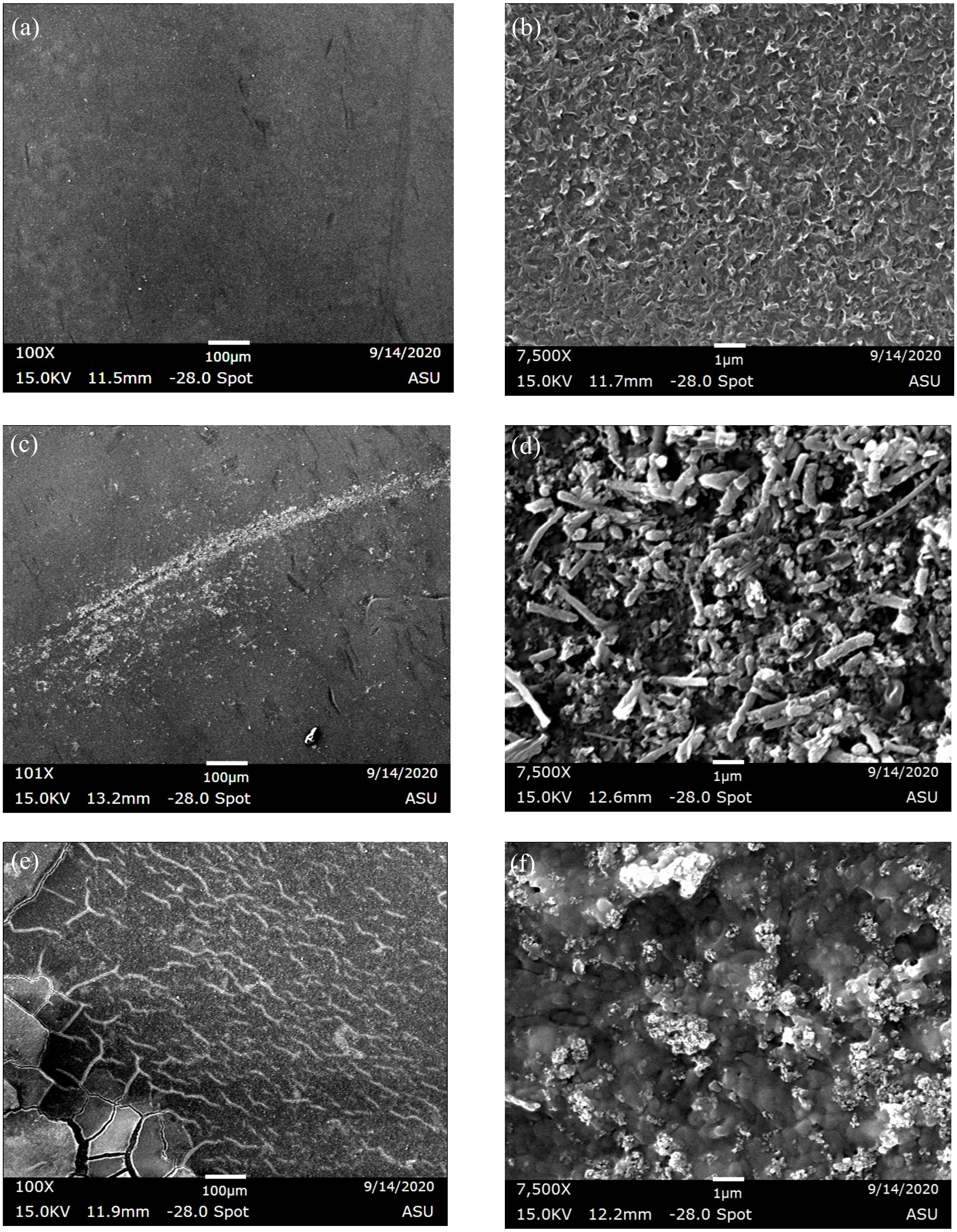
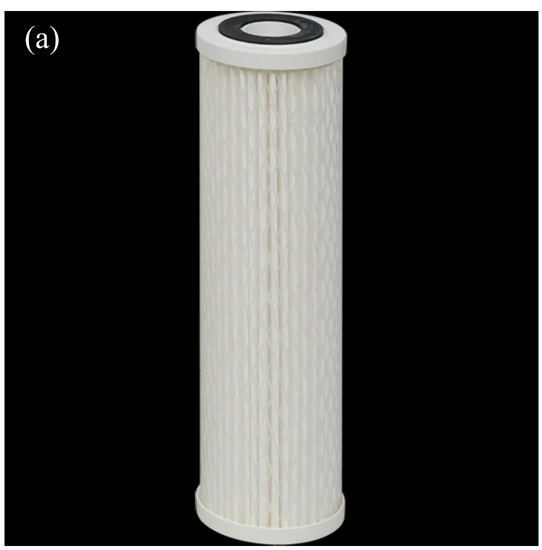


Figure S2. Scanning Electron Microscopy (SEM) images of the reverse osmosis membrane surface for the duplicate fouling tests. (a) control 100X, (b) control 7500X, (c) MF RO condition 100X, (d) MF

RO condition 7500X, (e) Non-MF RO condition 100X, and (f) Non-MF RO condition 7500X.



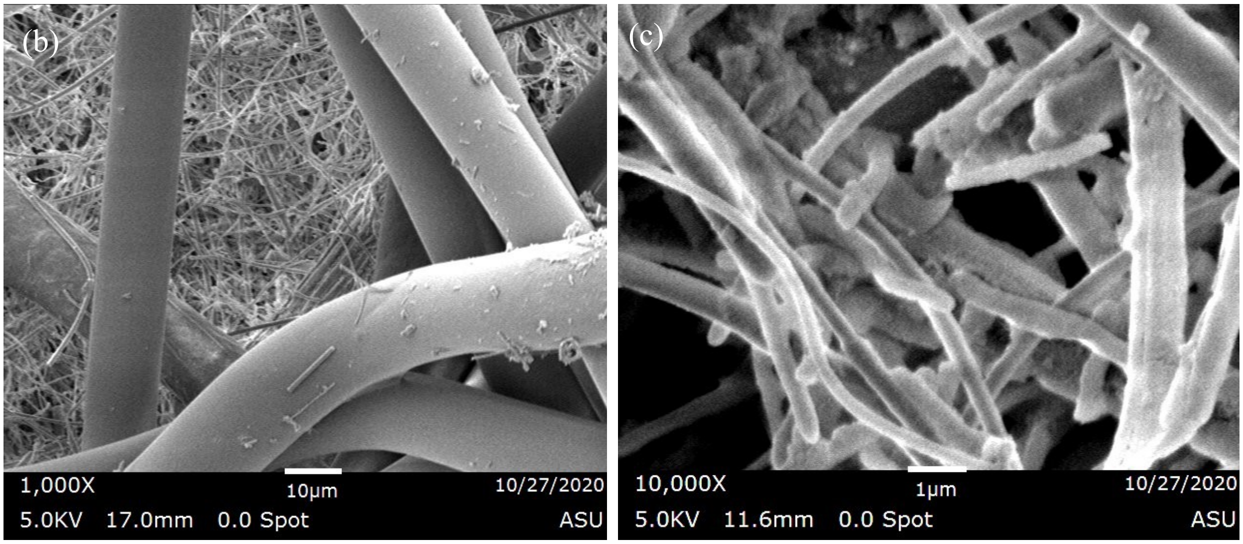
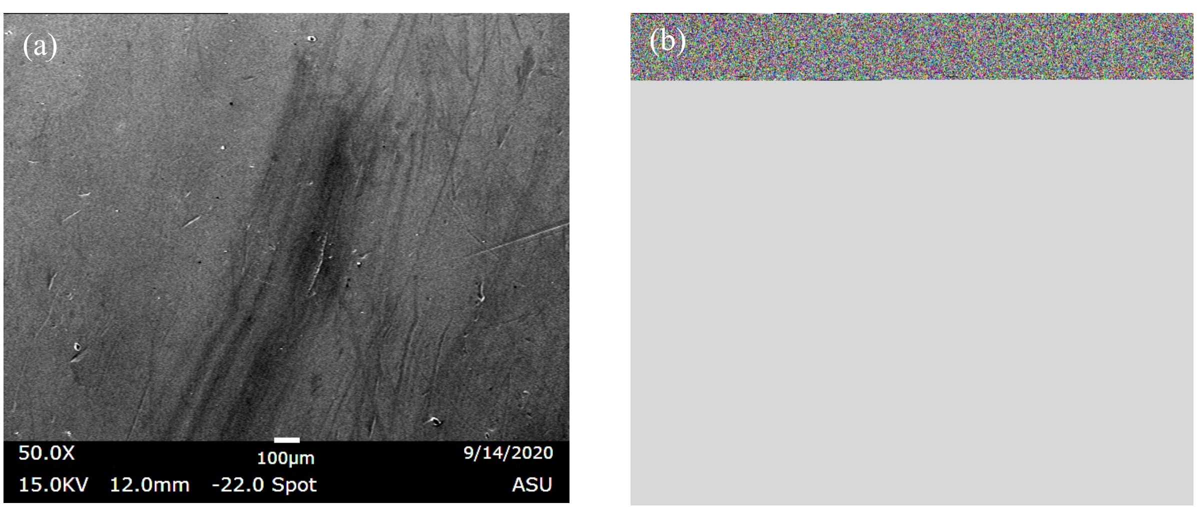


Figure S3. Scanning Electron Microscopy (SEM) images of microfiltration (MF) filter that was used to pretreat the hydrolyzed human urine. (a) the MF filter, (b) sample at 1000X, and (c) sample at 10,000X.



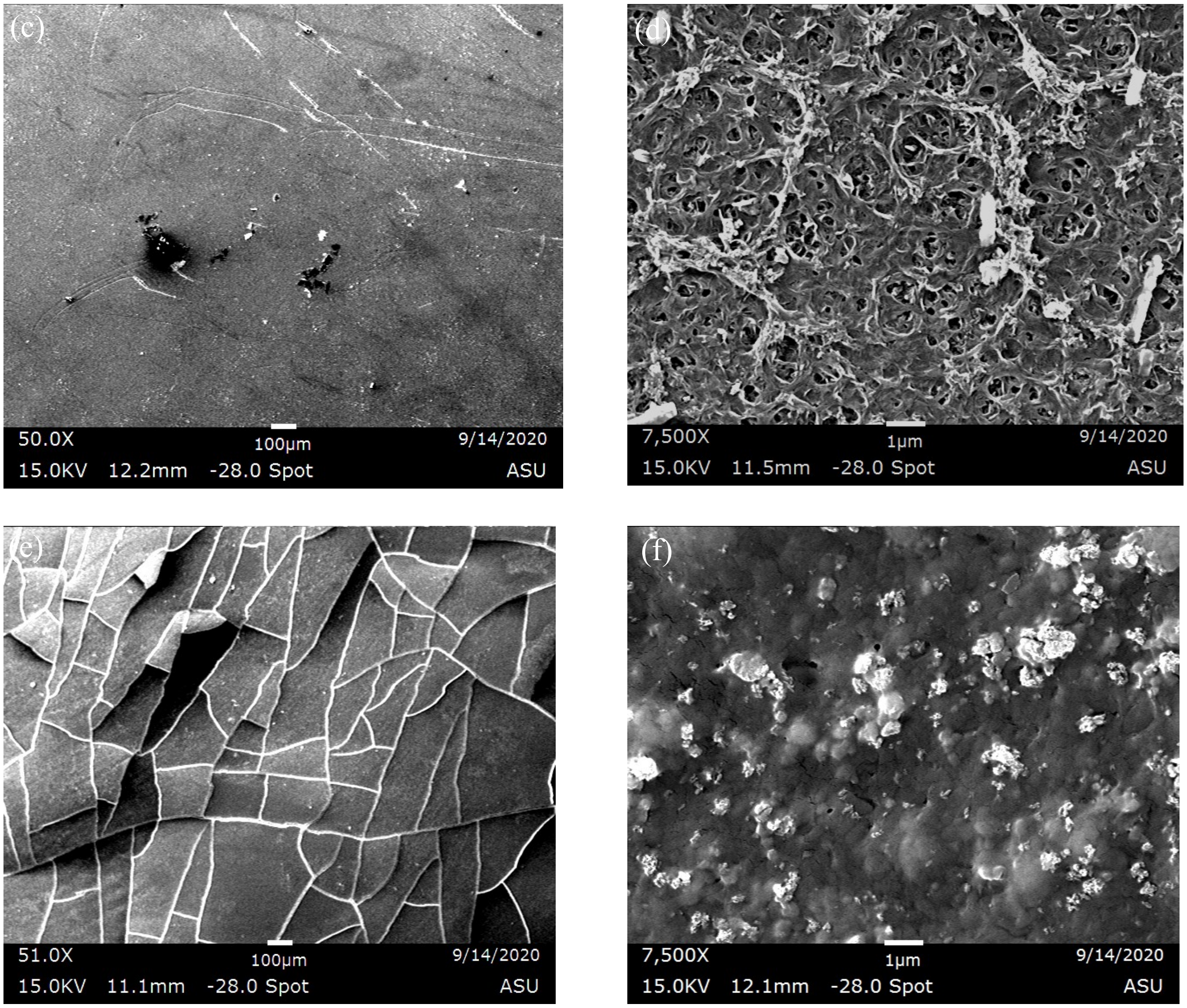


Figure S4. Scanning Electron Microscopy (SEM) images of the nanofiltration membrane surface for the duplicate fouling tests. (a) control 50X, (b) control 7500X, (c) MF NF condition 50X, (d) MF NF condition 7500X, (e) Non-MF NF condition 50X, and (f) Non-MF NF condition 7500X.

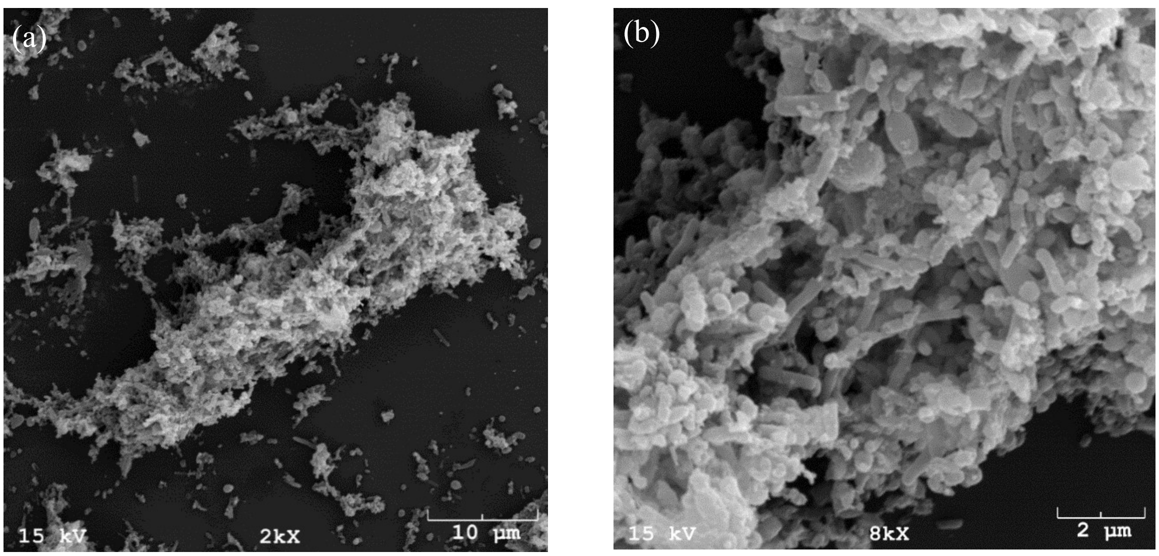


Figure S5. Scanning Electron Microscopy (SEM) images of the foulant which grew in the tank during the duplicate non-MF RO experiment. (a) sample at 2000X and (b) sample at 8000X.

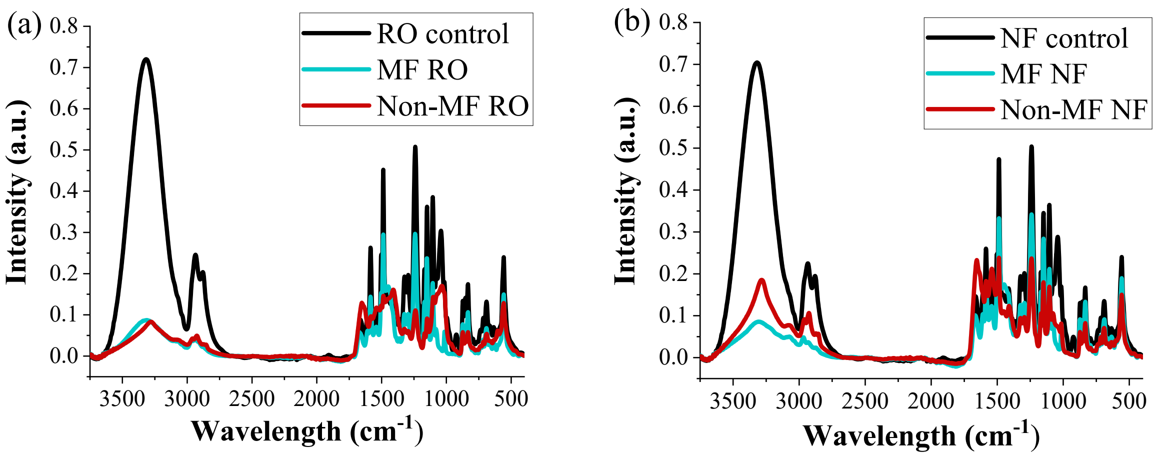


Figure S6. Fourier-transform infrared spectroscopy (FTIR) of the membrane surfaces for the duplicate reverse osmosis and nanofiltration tests. (a) FTIR results for the 2 conditions and control membrane for reverse osmosis. (b) FTIR results for the 2 conditions and control membrane for nanofiltration.

Table S1. The initial urine composition for the reverse os

Membrane Process	Condition	p
Reverse Osmosis	Test 1	11
	Test 2	11
Nanofiltration	Test 1	11
	Test 2	11

[a]Na^+ concentrations are elevated due to NaOH

Table S2. The initial urine composition for the reverse os

Initial Urine Composition - Fouling Tests

Membrane Process	Condition	pH	Conductivity (mS/cm)	Ammonia (mg/L N)	Total N (mg/L N)	TOC (mg/L C)	PO_4^{3-} (mg/L PO_4)	SO_4^{2-} (mg/L SO_4)	Cl^- (mg/L)	K^+ (mg/L)	a (m
Nanofiltration	Non-MF Pretreated	11.45	30.74	2980	4300	1990	521	521	2770	1110	7
	Duplicate	11.42	32.69	2920	4300	1940	536	536	2750	1120	7
	MF Pretreated	11.45	30.74	2980	4300	1990	521	521	2770	1110	7
	Duplicate	11.42	32.69	2920	4300	1940	536	536	2750	1120	7
Reverse Osmosis	Non-MF Pretreated	11.39	32.17	3340	3350	1230	895	895	2520	1090	8
	Duplicate	11.32	32.20	3390	3380	1260	667	667	2500	1080	8
	MF Pretreated	11.39	32.17	3340	3350	1230	895	895	2520	1090	8
	Duplicate	11.32	32.20	3390	3380	1260	667	667	2500	1080	8

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

Table S3. The permeate composition for the reverse osm

Permeate Composition - Rejection Tests

pH	Conductivity (mS/cm)	Ammonia (mg/L N)	Total N (mg/L N)	TOC (mg/L C)	PO_4^{3-} (mg/L PO_4)	SO_4^{2-} (mg/L SO_4)	Cl^- (mg/L)	K^+ (mg/L)	Na^+ (mg/L)
11.35	2.72	3870	4266	77	3.8	23	250	84	314
11.45	2.89	4420	4156	50	2.9	9	269	87	325
11.63	4.72	4540	4074	61	4.4	13	518	94	583
11.54	4.51	4515	4207	52	4.0	14	522	93	588

[illegible]ddition for pH adjustment

3. References

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