Supporting Information

Utilization of Bidirectional Cation Transport in Thin-Film Composite Membrane: Selective Removal and Reclamation of Ammonium from Synthetic Digested Sludge Centrate via Osmosis-Distillation Hybrid Membrane Process

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S1. Experimental Protocol for Selective Removal and Reclamation of Ammonium Nitrogen.

To demonstrate the bidirectional transport of monovalent cations in the TFC membrane, individual osmosis experiments were conducted using 50 mM NH₄Cl or DI water as feed solutions and NaHCO₃ with different concentrations ranging from 0.1 to 0.6 M as draw solutions. The selective permeability of the TFC membrane for different cations was investigated by measuring the ionic fluxes of synthetic centrate using 0.2 M NaHCO₃ as the draw solution. The impact of ammonium accumulation in the draw solution on the transport of ammonium in the TFC membrane was systematically investigated by adjusting the concentration of NH₄⁺–N in the draw solution. The water flux, J_w^{FO} , of the TFC membrane was calculated by the average of dividing the weight decrease of the feed solution by the time interval (5 min) and membrane area (6 cm²). The reverse and forward ion fluxes (J_s) were calculated by measuring the ionic concentration in the feed and draw solutions, respectively, as follows:

$$J_{s}A_{m}T = C_{T}V_{T} - C_{0}V_{0} \tag{1}$$

where C_0V_0 and C_TV_T are the initial and final amount of the specific ions in feed or draw solutions, respectively, *T* is the experimental time, and A_m is the membrane area.

The decreased chemical potential gradient of water and ammonium between the feed and draw solution in the osmosis unit led to a decrease in their driving forces, which inhibited the sustainability of the osmotic process. SGMD process was used to concentrate the draw solution and facilitate the removal of ammonium. The effect of draw solution concentration on the water flux of SGMD process (J_w^{SGMD}) was investigated using 0.1–0.6 M NaHCO₃ as the draw solution. The ammonium in the draw solution, which was transported by the TFC membrane, transformed to gaseous ammonia as the temperature increased to 60 °C,^{1, 2} and was then transported across the hydrophobic membrane and removed by the sweeping gas through the SGMD process. The ammonia fluxes of SGMD process were tested using 0.2 M NaHCO₃ containing different concentrations of NH₄Cl (i.e., 20–100 mg L⁻¹ NH₄⁺–N) as draw solutions.

The osmosis-distillation hybrid experiments were conducted using synthetic centrates as feed solutions and 0.2 M NaHCO₃ as draw solutions. The water fluxes (J_w^{FO} and J_w^{SGMD}) and cation (NH₄⁺, K⁺, Ca²⁺, Mg²⁺) transport fluxes in the osmosis and distillation units were tested to evaluate the stability and performance of the ODHM system. Considering the quantity of ammonium

removed by sampling, the actual removal rate of ammonium nitrogen in synthetic centrate (η_{NH4+}) was calculated as follows:

$$\eta_{\mathrm{NH}_4^+} = \frac{C_n^\theta - C_n}{C_n^\theta} \tag{2}$$

where n is the number of sampling times in the feed solution, C_n is the measured concentration of ammonium nitrogen in the feed solution, and C_n^{θ} is the theoretical concentration of ammonium nitrogen in feed solution with the assumption that there was no transportation of ammonium in TFC membrane. The C_n^{θ} was obtained using the following equation:

$$C_{n}^{\theta} = \frac{C_{0}V_{0} - \sum_{1}^{n-1} V_{n-1}^{\text{Sample}} C_{n-1}^{\theta}}{V_{0} - \sum_{1}^{n-1} V_{n-1}^{\text{Sample}} - \sum_{1}^{n} \Delta V_{n}^{\text{Water Flux}}}$$
(3)

where C_0 is the initial concentration of ammonium nitrogen in the feed solution, V_0 is the initial volume of the feed solution, $\Delta V_n^{\text{Water Flux}}$ is the volume of water that transported from feed to draw solution during the time interval between the *n*-th sampling and the (n-1)-th sampling, and V_{n-1}^{Sample} is the volume of the (n-1)-th sampling.

S2. Silver binding method

Areal densities of the carboxyl groups on the surface of the pristine and modified TFC membranes were quantified using a silver binding method as described in a previous study.³ Briefly, membranes were immersed twice for 10 min in 10 mL of 40 μ M silver nitrate at pH 7.0 to combine the silver ions and carboxyl groups. After binding, the membranes were soaked four times for 1 min in 10 mL of 1 μ M silver nitrate at pH 7.0 to rinse the residual silver nitrate. The membranes were then immersed in 5 mL of 1 % nitric acid for 30 min to release the bound silver ions. The concentrations of silver in the solution were quantified using inductively coupled plasma mass spectrometry (ICP-MS; 7700 Series, Agilent) to determine the ionized carboxyl group density ([*R-COO*⁻]) in TFC membranes, which is expressed as:

$$[R-COO^{-}] = \frac{C_{\mathrm{Ag}^{+}} V_{\mathrm{Ag}^{+}} N_{\mathrm{A}}}{A}$$

$$\tag{4}$$

where C_{Ag^+} is the concentration of silver ions, V_{Ag^+} is the volume of nitric acid, N_A is the Avogadro constant, and A is the surface area of the tested membrane (6 cm²).

S3. Supplemental Description of Analytical Methods

The samples taken from draw solution contained high concentrations of draw solutes, which were much higher than the concentrations of the tested ions (e.g., NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+}) that transported from the feed solution. Due to the intolerance of many analytical instruments to high concentrations of sodium and the background solutes may affect the accuracy of analytical results, dilution was required before measurement.

In this study, the concentration of NH_4^+ was measured with a UV-2550 spectrophotometer (Shimadzu, Japan) using Nessler reagent spectrophotometry method. The determination range of Nessler reagent spectrophotometry method for NH_4^+ –N is 0.025–2.0 mg L⁻¹, while the concentrations of NH_4^+ –N accumulated in the draw solution were 15–30 mg L⁻¹ after 1-h FO experiment when the draw solute (NaHCO₃) concentrations were 0.1–0.6 M. According to the fundamental of Nessler reagent spectrophotometry method, NaHCO₃ is not the interferent during the measurements of NH_4^+ –N.⁴ The concentration of NH_4^+ –N in the draw solution could therefore be accurately measured after appropriate dilution. Each sample would be diluted using DI water with series dilution factors to meet the determination range. The DI water was also analyzed as a blank sample and its influence was subtracted. A test was conducted to verify that NaHCO₃ did not interfere with the measurements of NH_4^+ –N in this study. Solutions were prepared with 0, 5, 10, 20, and 30 mg L⁻¹ NH₄–N using NH₄Cl in three different water matrixes, including DI water, 0.2 M NaHCO₃, and 0.6 M NaHCO₃. Results in Figure S2 revealed that the presence of NaHCO₃ in the concentration range of 0–0.6 M did not interfere with the NH₄–N measurements when using Nessler reagent spectrophotometry method.

The concentrations of K⁺, Ca²⁺, and Mg²⁺ were measured by ICP-OES (Optima 8000, PerkinElmer, USA). The concentrations of K⁺, Ca²⁺, and Mg²⁺ accumulated in the draw solutions after 6-h experiments were ~ 30, 3, and 1 mg L⁻¹, respectively, while the NaHCO₃ background concentration was 0.2 M (16.8 g L⁻¹) without considering dilution. As the manufacturer introduced, the optimum concentration of measured ions for the ICP-OES is below 10 ppm (RSD < 0.8 %) while the salinity of sample should below 1 wt% (1.68 wt% NaHCO₃ in our experiment). Therefore, the draw solution samples should be diluted before analyzed. An experiment was conducted to determine the diluted times and the possible influence of high concentrations of sodium on the detection of trace K⁺, Ca²⁺, and Mg²⁺ during ICP-OES analysis. In detail, 30 mg L⁻¹ K⁺, 3 mg L⁻¹

 Ca^{2+} , and 1 mg L⁻¹ Mg²⁺ were dosed into 0.2 M NaHCO₃ solution and DI water, respectively. Then, the 0.2 M NaHCO₃ solution that contained measured ions was diluted 10, 20, 50 times for measurements. As shown in Figure S3, the NaHCO₃ background concentration of up to 20 mM did not lead to significant analytical error, while the deviations were larger when NaHCO₃ background concentrations were 4 mM and 10 mM. It indicates that the NaHCO₃ background has minor effect on the accuracy of analytical results, while the over-dilution of samples could be the main reason of inaccuracy. Therefore, the dilution time of the samples was chosen at 10 when analyzing K⁺, Ca²⁺, and Mg²⁺ in the draw solution.

S4. Bidirectional transport of ions through the TFC membrane

Besides the cations transport, the anions in solutions (e.g., HCO_3^- , Cl^- , and OH^-) may diffuse through the membrane under the effects of Donnan equilibrium. As shown in Figure S4, when using 50 mM NH₄Cl as the feed solution and 0.2 M NaHCO₃ as the draw solution in the osmotic process, the forward fluxes of NH₄⁺ and Cl⁻ were 1.32 and 0.13 mol m⁻² h⁻¹, respectively, and the reverse fluxes of Na⁺ and HCO₃⁻ were 1.40 and 0.23 mol m⁻² h⁻¹, respectively. According to the variation of the solution pH, the forward flux of H⁺ was calculated at 0.51 mmol m⁻² h⁻¹. Regarding the charge balance, the net charge of the draw solution was ~ 0.02 mol m⁻² h⁻¹ (1.32 (+) + 0.13 (-) + 0.00051 (+) - 1.40 (+) - 0.23 (-)), thereby indicating a near electroneutral condition in the draw solution.



Figure S1. Schematic diagram of the lab-scale ODHM system for selective removal and reclamation of ammonium from synthetic centrate.



Figure S2. Measured NH_4^+ –N concentration by using Nessler reagent spectrophotometry method as a function of NH_4^+ -N dose with various concentration of $NaHCO_3$ as background.



Figure S3. Influence of NaHCO₃ background concentration on the measurement accuracy of K^+ , Ca^{2+} , and Mg^{2+} during ICP-OES analysis.



Figure S4. Fluxes of reverse and forward transported ions in osmotic process. The experiments were conducted for 1 hour using 50 mM NH₄Cl as feed solution and 0.2 M NaHCO₃ as draw solution. The volumes of feed and draw solutions were 0.5 L. The temperatures of feed and draw solutions were maintained at 30 ± 0.5 °C and 60 \pm 0.5 °C, respectively. The crossflow velocities were stable at 0.05 m/s. Error bars represent the standard deviation.



Figure S5. Specific salt flux (J_s/J_w) for NH₄⁺, K⁺, Ca²⁺, and Mg²⁺ of the TFC membrane. The experiments were conducted for 1 hour using a synthetic centrate as feed solution, and a 0.2 M NaHCO₃ solution as draw solution. The volumes of the synthetic centrate and NaHCO₃ solution were 0.5 L. The temperature of the synthetic centrate and draw solution was maintained at 30 ± 0.5 and 60 ± 0.5 °C. The crossflow velocity was 0.05 m/s. Error bars represent the standard deviation.



Figure S6. Conductivities (A) and pHs (B) of the feed and draw solutions as a function of experimental time in the treatment of synthetic centrate by ODHM process. (C) Water fluxes of FO and SGMD units as a function of experimental time during the experiments of ODHM process. (D) C_n^{θ} and C_n of the synthetic centrate during the experiments of ODHM process. (D) C_n^{θ} and C_n of the synthetic centrate during the experiments of ODHM process. (D) C_n^{θ} and C_n of the synthetic centrate during the experiments of ODHM process. The experiments were conducted for 5 hours using a synthetic centrate as feed solution, 0.2 M NaHCO₃ as draw solution, and DI water as absorption liquid for ammonia and water vapor from the sweeping gas. The temperature of the synthetic centrate, NaHCO₃ solution, sweeping gas, and DI water were maintained at 30 ± 0.5 °C, 60 ± 0.5 °C, 25 ± 0.5 °C, and 0 °C. The crossflow velocity of the synthetic centrate, draw solution, and sweeping gas was 0.05 m/s, 0.05 m/s, and 3 L/min. Error bars represent one standard deviation.



Figure S7. Specific salt flux (J_s/J_w) for NH₄⁺ of the TFC pristine and modified membranes. The conditions of experiments were same as that in Figure 4A. Error bars represent the standard deviation.

Tables

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Methods	Examples	Mechanisms	Performances	References
Biological	Combination of nitrification and denitrification	Aerobic activated sludge process was primarily applied to transform the ammonia to nitrite then nitrate (nitrification), and anoxic step allowed denitrifying bacteria to reduce nitrate to N ₂ (denitrification)	89.6% ammonium removal efficiency in the presence of organic carbon after 18 d treatment	5
treatment	Anaerobic ammonium oxidation process	Nitrite was utilized as electron acceptor to oxidize ammonium and produced gaseous nitrogen under anoxic conditions	Ammonium removal efficiency: 82–90%; Nitrogen removal capacity: 1.5–2.4 kg N m ⁻³ d ⁻¹	6
	Air stripping/absorption	Adjusted the pH and temperature to a certain range (pH: 9.4– 11.5; T: 46.5–75 °C); transported the ammonia from wastewater to air stream	Ammonia removal: 50–98 %	7
Chemical/physical extractions	Electrochemical treatment	Combination of electrodialysis and membrane stripping. The ammonium transported from anode to cathode under the applied potential, and reacted with electrochemically produced hydroxide ions to yield ammonia, then extracted to trap chamber	Ammonia removal: 70–98 %	8
	Zeolite materials	Using the selective ion-exchange capability of zeolite, combined with sequencing batch reactor to remove the ammonium	Ammonia removal: 68.5–70.9 %	9
	Struvite precipitation	Added excessive Mg^{2+} and $PO4^{3-}$ with adjustment of pH and temperature	Ammonia removal: 54.2–82.4%;	10
	Forward osmosis	Concentrated the centrate and extracted the ammonium by struvite precipitation	_	11
Membrane process	Membrane distillation	Ammonia wastewater at a relative low concentration (100 mg L ⁻¹); adjusted the pH and temperature to a certain range (pH: >11; T: 50–75 °C); extracted the ammonia by MD process	Ammonia removal: 28–97 %	12

Feed	Draw	Trial	Feed initial pH	Feed final pH	Feed pH difference	Draw initial pH	Draw final pH	Draw pH difference
	0.1 M NaHCO ₃	1	6.47	6.95	0.48	8.78	8.75	-0.03
		2	6.22	6.9	0.68	8.92	8.96	0.04
	0.2 M NaHCO ₃	1	6.15	7.79	1.64	9.02	8.95	-0.07
50 mM		2	6.76	7.6	0.84	8.92	8.98	0.06
NH ₄ Cl	0.4 M	1	6.28	7.81	1.53	9.12	8.97	-0.15
	NaHCO ₃	2	6.75	7.93	1.18	8.89	8.89	0
	0.6 M NaHCO ₃	1	6.29	7.92	1.63	8.95	8.92	-0.03
		2	6.63	7.83	1.2	8.92	8.96	0.04

Table S2. Composition and pH of the feed and draw solutions for the experiments in Figure 1B.

			Feed			Draw					
	NH4Cl (M)	NaCl (M)		NH4 ⁺ -N/(mg L ⁻¹)		NaHCO3	NH4HCO3	NH4 ⁺ -N/(mg L ⁻¹)			
			Target	Trial 1	Trial 2	(M)	(M)	Target	Trial 1	Trial 2	
1	0.043	0	600	572.71	586.65	0.2	0	0	0	0	
2	0.036	0.007	500	524.36	540.24	0.193	0.007	100	100.33	99.49	
3	0.029	0.014	400	415.67	430.44	0.186	0.014	200	204.84	214.17	
4	0.022	0.021	300	307.40	320.49	0.179	0.021	300	327.60	312.97	

 Table S3. Composition of the feed and draw solutions for the experiments in Figure 1E.

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