Supplementary Material

Hydrogel facilitates membrane superwetting for wastewater treatment and resource recovery

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1. Experimental

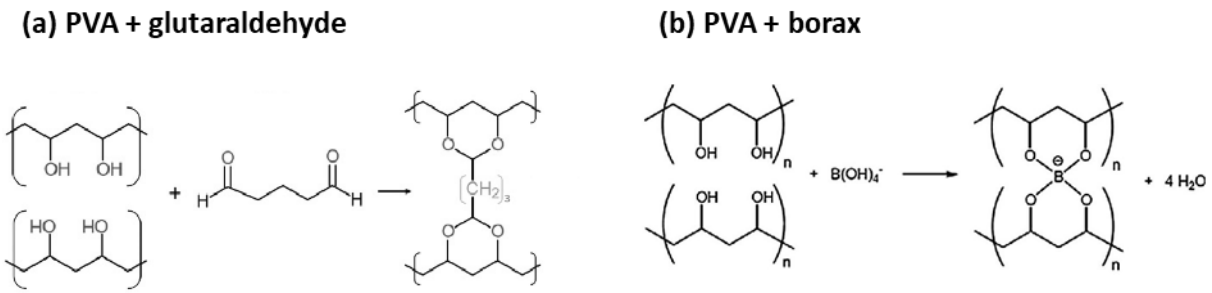
1.1. Materials

Cellulose triacetate (CTA, LT-35, 61% acetylation degree) and cellulose acetate (CA, LT-50, 55% acetylation degree) were obtained from Daicel Corporation (Japan). *N*-methyl-2-pyrrolidone (NMP, 99% standard content, Fujifilm Wako Pure Chemical Corporation, Ltd., Japan) was used as the solvent and ethylene glycol (EG, Fujifilm Wako Pure Chemical Corporation, Ltd.) and benzoic acid (Nacalai Tesque, Inc., Japan) were used as the pore-forming additives. A polyester (PET) nonwoven fabric (90HF, Awa Paper & Technological Company, Inc., Japan) was used as a support. Polyvinyl alcohol (PVA, Mw = 30,000–70,000, 87–90% hydrolyzed, Sigma-Aldrich, Japan), glutaraldehyde (GA, Sigma-Aldrich), hydrochloric acid (HCl, 2 mol/L, Fujifilm Wako Pure Chemical Corporation, Ltd.), acetone (99.8%, Fujifilm Wako Pure Chemical Corporation, Ltd.), and sodium tetraborate decahydrate (borax, Sigma-Aldrich) were used for the preparation of PVA hydrogel. Membrane performance was evaluated using sodium chloride (NaCl) and ammonium chloride (NH_4Cl), both purchased from Fujifilm Wako Pure Chemical Corporation, Ltd. Membrane fouling studies were conducted using the following model foulants: bovine serum albumin (BSA, Fujifilm Wako Pure Chemical Corporation, Ltd.), sodium alginate (SA, Sigma-Aldrich), humic acid (HA, sodium salt, Sigma-Aldrich), fluorescein isothiocyanate-conjugated bovine serum albumin (FITC-BSA, Sigma Aldrich), fluorescein isothiocyanate-conjugated lysozyme (FITC-Lys), *Escherichia coli* (*E. coli*, NBRC 3301, Biological Resource Center, National Institute of Technology and Evaluation, Japan). FITC-Lys was prepared by dissolving 0.01 g of Fluorescein-4-isothiocyanate (FITC-1, Dojindo, Japan) and 0.1 g of lysozyme (from egg white, FUJIFILM Wako Pure Chemical Corporation) into 100 mL $NaHPO_4^-$ buffer (pH = 8.6) and kept in a dark place at 25 °C for 3 hours, followed by dialysis in a phosphate buffered saline (PBS) solution with pH = 7.4 for 72 hours (Wang *et al.* 2021). *E. coli* was prepared in a tryptic soy broth medium (TSB, soybean casein digest medium, Oxoid, Thermo Fisher Scientific, Japan) A fluorescent stain SYTO9 (Thermo Fisher Scientific, USA) and GA were used for bacterial staining. All experiments used Milli-Q water (Milli-Q Ultrapure Water Solutions, Millipore Sigma, Japan). All materials were used as received and without further treatment.

1.2. Preparation of polyvinyl alcohol composite membrane

The cellulose based membrane support was first prepared using nonsolvent-induced phase separation. A polymer dope solution was prepared with the following composition: 41% CTA, 52.8% NMP, 5.9% EG, 0.3% benzoic acid (w/w). Another solution containing a 1:1 blend solution containing CTA and CA was prepared. The solutions were casted (thickness of 250 nm) onto a nonwoven PET fabric-lined glass plate. The nascent membrane was immersed in a coagulation bath containing 95% Milli-Q water, 0.75% EG, and 4.25% NMP (w/w) at 12 °C for 20 min and afterwards placed in water at 60 °C for 1 hour for thermal annealing.

The PVA hydrogel was prepared on top of the cellulose acetate-based membranes using two different crosslinking methods, using GA (Park *et al.* 2018) and borax (Wang *et al.* 2022). The mechanisms of the PVA hydrogel crosslinking using GA and borax are shown in Scheme S1. As shown in Scheme S1, PVA reacts with glutaraldehyde to form a water-insoluble acetal, whereas the condensation reaction of PVA with borax results in a water-insoluble acetal-like product, with the hydroxyl groups of PVA binding with a boron center. First, an aqueous solution containing 1% (w/w) PVA was prepared at 95 °C with constant stirring for 6 hours, and the solution was kept in an oven at 60 °C overnight. The PVA solution was poured onto the surface of the cellulose-based membrane, and placed in an oven at 60 °C for 1 hour. Excess PVA solution was removed using an air gun. For the first type of PVA hydrogel composite membrane, the PVA-immersed membrane was dried in the oven at 100 °C for 10 minutes and PVA crosslinking was done by immersing the membrane in a solution containing 50 mM GA and 20 mM HCl in Milli-Q water/acetone (1:1 v/v) at room temperature. After the crosslinking, the samples were cured at 100 °C for 10 minutes. The resultant membrane was denoted as CTA/CA-PVA-G. For the second type of PVA hydrogel composite membrane, the PVA-immersed membrane was directly immersed in a 1% (w/w) borax solution (aq.) for 1 hour at room temperature, and the membrane was denoted as CTA/CA-PVA-B. All prepared membranes were stored in Milli-Q water until further use.



Scheme S1. Crosslinking mechanisms of PVA with (a) glutaraldehyde (Long *et al.* 2019) and (b) sodium tetraborate (borax) (Dave and Nath 2018).

1.3. Membrane performance evaluation

Pure water permeability (PWP, A, L/m^2·h·bar) and solute permeability (B_{NaCl} and $B_{NH4\text{-}N}$, L/m^2·h) were determined using a cross-flow reverse osmosis (RO) system using Milli-Q water, 1000 mg/L NaCl, and 1000 mg/L NH_4-N (prepared from NH_4Cl) feed solutions, respectively, following the same parameters from our previous study (Zhang *et al.* 2021). A and B_{NaCl} values were calculated using equations reported in the same study.

The osmotic performance of the TFC membranes (water flux and NH_4^+ rejection) was evaluated using a laboratory-scale forward osmosis (FO) system (Gonzales *et al.* 2021a, Zhang *et al.* 2021), shown in Figure S1, with an effective membrane area of 4.5 cm^2. 1 L solutions of 100 mg/L NH_4^+ (prepared from NH_4Cl) and 3.5% (w/w) NaCl were used as FS and DS, respectively. The pH of all the FS containing NH_4Cl was adjusted to 7.0. During the FO tests conducted for 2 hours, the selective layer of the TFC membrane was facing the FS (AL-FS mode). The flow rates of both FS and DS were maintained at 300 mL/min, and transmembrane pressure (TMP) was kept at minimum. The mass changes of the FS were recorded using a top-loading balance (FX-3000i, A&D Company, Limited, Japan) connected to a computer. Water flux (J_w) was calculated using equations presented in previous study (Zhang *et al.* 2021), while ammonium rejection (R_{NH4}) was calculated from the permeating NH_4^+ into the DS, measured using an ammonia test kit (Hach Co., Japan). All tests were performed in triplicate, and statistical analysis (determination of mean and standard deviation) were performed.

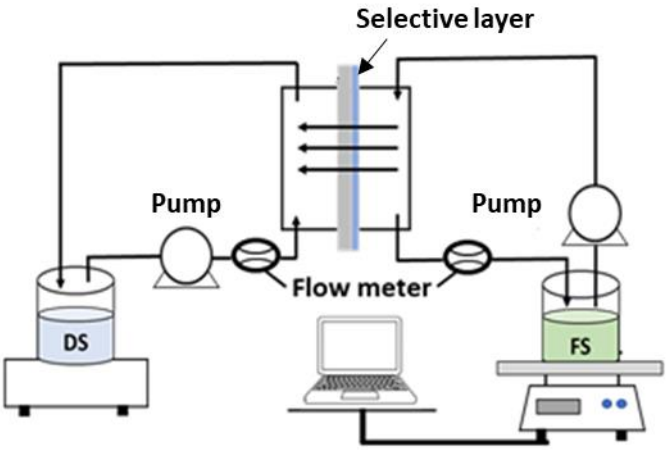


Figure S1. Schematic diagram of the laboratory-scale forward osmosis filtration setup. FS and DS refer to the feed solution and draw solution, respectively.

1.4. Membrane characterization

Membrane surface morphology was imaged using a field-emission scanning electron microscope (FE-SEM, JSF-7500F, JEOL, Japan). Surface chemical composition was determined using X-ray photoelectron spectroscope (XPS, JPS-9010 MC, JEOL, Japan) with AlKα X-rays and Fourier transform infrared-attenuated total reflectance detector (FTIR-ATR) spectroscope (Nicolet iS5 (FTIR)/ iD5 (ATR), Thermo Fisher Scientific, Japan). The membrane hydrophilicity was evaluated by water contact angle measurements using an optical contact angle goniometer (Drop Master 300, Kyowa Interface Science Co., Japan). The membrane surface roughness was evaluated using 3D laser scanning microscopy (VK-X3000, Keyence, Japan). The surface zeta potential of the TFC membranes was evaluated using an electrokinetic analyzer for solid surface analysis (SurPASS 3, Anton-Paar GmbH, Austria). Membrane characterization techniques were adapted from our previous studies (Gonzales *et al.* 2021b).

1.5. Membrane stability

The stability of the PVA coating was tested by immersion of the membrane in Milli-Q water for 30 days, followed by re-evaluation of water contact angle and intrinsic transport properties.

1.6. Membrane fouling evaluation

Fluorescent isothiocyanate-conjugated proteins (FITC-BSA and FITC-Lys) were used as model probes for evaluation of the organic fouling mitigation propensity of the membranes. The membrane samples were immersed in a PBS solution containing 20 mg/L of the fluorescent proteins. The membranes were placed in dark, agitating conditions (shaking rate of 100 rpm) at room temperature for 12 hours. The samples were rinsed using PBS solution to remove loosely-attached proteins. The membrane samples were then imaged using confocal laser scanning microscopy (CLSM, FV1000D, Olympus Corporation, Japan) and the images were analyzed using ImageJ (National Institute of Health, USA).

The antibacterial activity of the prepared membranes was evaluated by adhesion and cell viability of *E. coli*. First, a colony of *E. coli* taken from an agar dish was precultured in 20 mL of 30 g/L fresh tryptic soy broth (TSB) medium for 12 hours at 30 °C shaking at 120 rpm to reach a mid-exponential growth phase. The precultured bacterial suspension culture was diluted 50 times using TSB medium and cultured for 4 hours at 30 °C shaking at 120 rpm. Finally, the cultured bacterial suspension was diluted with TSB medium to an optical density of 0.05 at 450 nm (10^6–10^7 CFU/mL). The membranes (0.5 cm × 1.0 cm) were soaked in 2 mL of the bacterial suspension (pH ≒ 7) at 30 °C shaking at 120 rpm for 24 hours to test for the membrane bacterial adhesion property. The samples were rinsed twice with 0.85% (w/w) aqueous NaCl solution after incubation and stained by a LIVE/DEAD BacLight Bacterial Viability test kit (Life Technologies, Thermo Fisher Scientific). Then, to fix the stained bacteria, the membranes were immersed in a 2.5% (v/v) aqueous glutaraldehyde solution for 10 minutes, and kept in 0.85% (w/w) aqueous NaCl solution. CLSM was used to qualitatively evaluate the amount of attached live and dead bacterial cells.

Dynamic biofouling FO operation was also conducted similar to previous studies (Wang *et al.* 2021, Yang *et al.* 2021). *E. coli* was precultured in TSB medium at 30 °C for 12 hours, and afterwards, the precultured microorganism suspension was diluted further with TSB medium until a final optical density of 0.05 at 450 nm (10^6–10^7 CFU/mL), as measured by a spectrophotometer (V-650, Jasco, Japan). FO operation with Milli-Q water as FS and 3.5% (w/w) NaCl as DS was first performed for 1 hour, and the FS was replaced

with the *E. coli* suspension, and operation was resumed for 5 hours. Two 6 hour operation cycles were conducted. After the FO operation, the membrane samples were rinsed with 0.85% (w/w) NaCl solution (aq.) and stained with SYT09 for 20 minutes and fixed with 2.5% glutaraldehyde solution for 3 minutes. The membrane samples were then imaged using FE-SEM and confocal laser scanning microscopy (CLSM, FV1000D, Olympus Corp., Japan).

A model wastewater solution containing 500 mg/L each of BSA, SA, and HA was prepared. Using the comprehensive foulant solution as FS and 3.5% (w/w) NaCl as DS, the membranes were tested for fouling resistance for 8 hour operation, followed by 2 hour backwashing with Milli-Q water, and another 8 hour operation. The normalized water flux, or the ratio of the instantaneous and initial water flux values, were used to evaluate the fouling propensity and flux recovery.

1.7. Long term operation with industrial wastewater

Long-term FO operation was first conducted using a model wastewater containing 200 mg/L NH_4-N from NH_4Cl to show the long-term NH_4-N content enrichment without the influence of foulants and other inorganic substances. After that, long-term FO operation using real industrial wastewater obtained locally in Japan was conducted. Prior to FO operation, the wastewater was filtered through a 0.22 μm filter. The wastewater has a pH of 8.01, total dissolved solids of 477 mg/L, chemical oxygen demand of 555 mg/L, and NH_4^+ content of 130 mg/L. The pristine and amine-modified membranes were used to dewater the model and industrial wastewater and enrich the ammonium content. FO operation was conducted using the wastewater as FS until approximately 10% of the initial FS volume remains or until osmotic flow ceases to compare the membrane NH_4^+ enrichment performance.

2. Results and Discussion

2.1. Membrane fabrication and characterization

Initially, a flat sheet cellulose triacetate (CTA membrane) was prepared and used as the pristine membrane. The pristine CTA membrane exhibited a water contact angle of 54.8° and a pure water permeability of 0.61 $L/m^2 \cdot h \cdot bar$, as tested by RO filtration. To

improve the hydrophilicity and water permeability of the membrane, cellulose acetate (CA) was mixed with CTA at 1:1 w/w ratio. The CTA/CA blend membrane exhibited a water contact angle of 39.2° and pure water permeability of 0.89 L/m^2·h·bar (Figure S2), which were significant improvements from the pure CTA membrane.

The chosen modification strategy for fouling control of the CTA/CA membrane is polyvinyl alcohol coating. This was chosen due to its simplicity and scalability, as well as applicability for both flat sheet and hollow fiber membranes. To ensure stability of the coating, only crosslinking is required. Two crosslinking agents were chosen: glutaraldehyde (GA) and borax. GA introduces intramolecular crosslinks with the hydroxyl groups of PVA, forming water-stable acetal groups. Borax, on the other hand, is known to crosslink the chains of PVA by linking the oxygen atoms with the borate ions of borax. Known as a di-diol complexation, this reaction occurs when two diol units of PVA link with one borate ion. After this reaction, the polymer chains behave like a polyelectrolyte with electrostatic repulsions, resulting in network expansion (Lin *et al.* 2005).

For GA crosslinking, the pristine membrane was first immersed in 4% (w/w) PVA for 1 hour and then immersed afterwards in 50 mM GA for 1 h. and heated at 100 °C for 10 minutes. For borax crosslinking, 50 mL 4% (w/w) PVA and 5 mL 1% (w/w) borax were mixed together, and the membrane was immersed in the mixture for 1 hour at 70 °C. Modification resulted in lower water contact angle values of 18.2° and 20.9° for CTA/CA-PVA-G and CTA/CA-PVA-B, for samples crosslinked with GA and borax, respectively, indicating higher hydrophilicity. Also, the water contact angle became 0 within 10 seconds for both modified membranes.

The *A* values of the modified membranes were determined to be 0.71 L/m^2·h·bar (CTA/CA-PVA-G) and 0.79 (CTA/CA-PVA-B) L/m^2·h·bar, slightly lower than that of pristine CTA/CA (0.89 L m^{-2} h^{-1} bar^{-1}) (Figure S2(a)). The lower permeability was indicative of the presence of the coating on the membrane surface. The solute permeability coefficients (*B* value, Figure S2(a)) and solute rejection (Figure S2(b)) of the membranes were also determined against NaCl and NH_4Cl. Both PVA hydrogel composite membranes showed very low permeability of both salts, at around 0.2 L/m^2·h. These values corresponded with the NaCl and NH_4Cl rejection of the membranes, which

were all found to be higher than 95% (Figure S2(b)).

The forward osmosis (FO) performance of the membranes was evaluated. FO operation was performed using 100 mg/L NH_4^+ (from NH_4Cl) as the feed solution and 3.5% (w/w) NaCl as the draw solution. Consistent with the pure water permeability of the membranes, the CTA/CA membrane showed the highest water flux of 6.3 L/m^2·h. The modified membranes exhibited lower water flux values of 5.7 L/m^2·h (CTA/CA-PVA-G) and 5.4 L/m^2·h (CTA/CA-PVA-B). Similar performance was found for reverse NaCl flux, measured in terms of g/m^2·h: CTA/CA (4.1 g/m^2·h) > CTA/CA-PVA-G (2.9 g/m^2·h) > CTA/CA-PVA-B (1.8 g/m^2·h). The NH_4^+ flux of all membranes was found to be low, between 0.15–0.21 g/m^2·h.

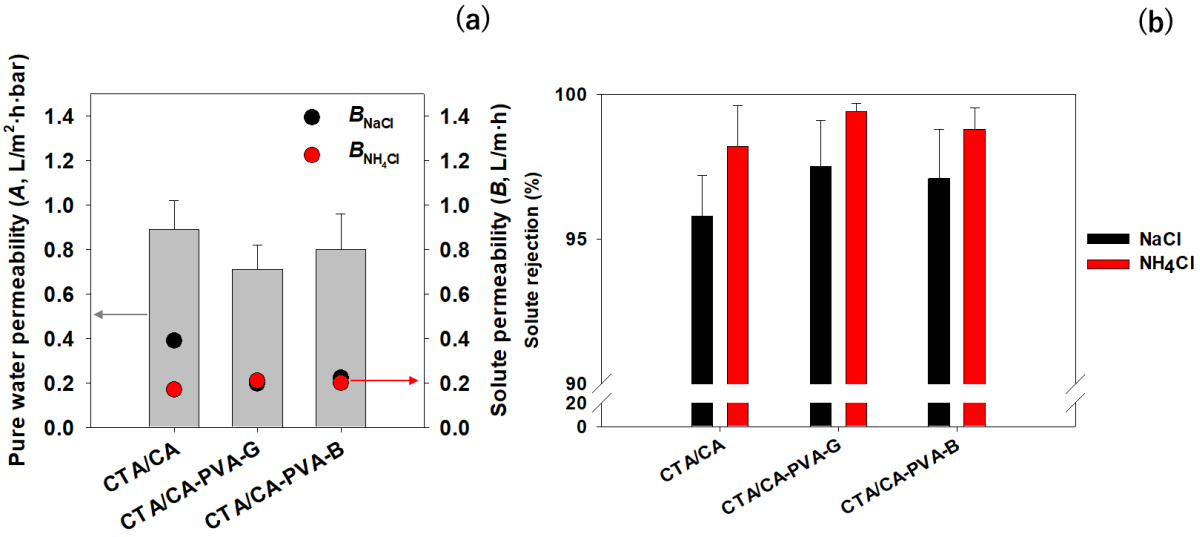


Figure S2. (a) Intrinsic transport properties (pure water permeability and solute permeability) of the pristine CTA/CA and PVA hydrogel composite membranes (CTA/CA-PVA-G and CTA/CA-PVA-B) and (b) Rejection values of the membranes against NaCl and NH_4Cl. (Feed solutions: Milli-Q water, 1000 mg/L NaCl, 1000 mg/L NH_4-N; Applied pressure: 10 bar)

The surface chemistry of the pristine CTA/CA and PVA hydrogel membranes was characterized by ATR-FTIR and XPS (Figure S3). As shown in Figure S3(a), all the membranes showed C—H stretching at around 2840–3000 cm^{-1}. The CTA/CA membrane showed stretching at 1221 cm^{-1} and 1720 cm^{-1} assigned to C=O and C—O—C from the

carboxylic ester groups of CTA and CA. The success of the preparation of the PVA hydrogel composite membranes was indicated by the presence of broad O—H stretching at around 3200–3550 cm^{-1}.

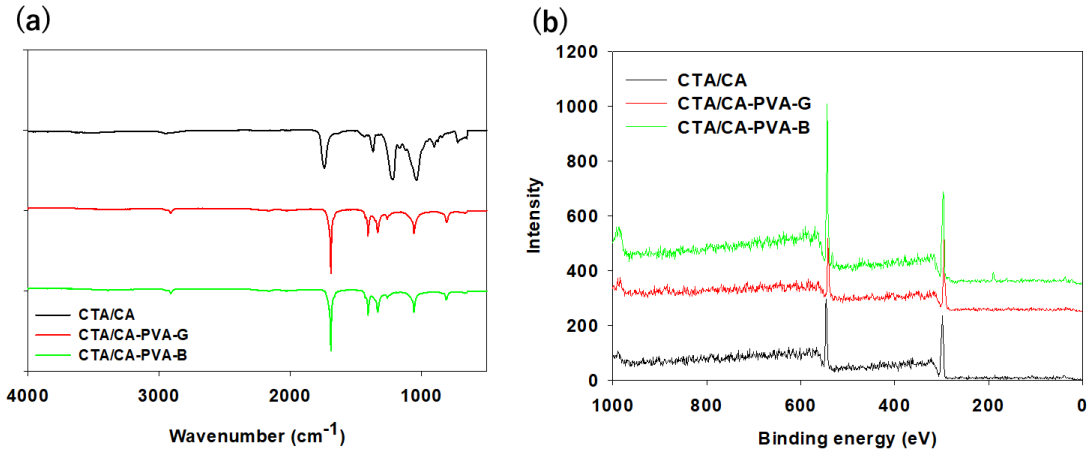


Figure S3. (a) FTIR and (b) XPS wide scan spectra of the pristine CTA/CA and PVA hydrogel composite membranes (CTA/CA-PVA-G and CTA/CA-PVA-B).

Table S1. Surface elemental composition of the pristine CTA/CA and PVA hydrogel composite membranes (CTA/CA-PVA-G and CTA/CA-PVA-B).

Membrane	C (%)	O (%)	B (%)	O/C ratio
CTA/CA	57.55	42.45	-	0.74
CTA/CA-PVA-G	68.32	31.68	-	0.46
CTA/CA-PVA-B	64.36	35.36	0.28	0.55

Figure S3(b) and Table S1 show the results of the XPS scanning of the CTA/CA and PVA hydrogel composite membranes. The wide-scan XPS spectra (Figure S3) show the dominant C and O peaks and the surface elemental composition are shown in Table S1. The change in O/C ratio of the membrane surface composition after the crosslinking of the PVA layer atop the CTA/CA membrane indicated the success of the preparation of the PVA hydrogel membranes regardless of crosslinking agent.

2.2. Osmotic performance

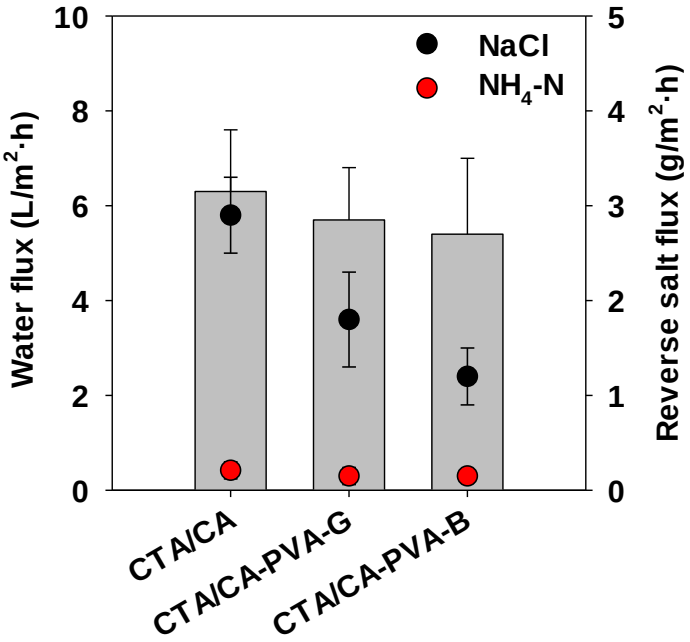


Figure S4. Water flux, reverse NaCl flux, and NH_4-N flux during forward osmosis operation. (Feed solution: 100 mg/L NH_4-N solution, Draw solution: 3.5% (w/w) NaCl, Flow rate: 300 mL/min)

The forward osmosis (FO) performance of the CTA/CA and PVA hydrogel composite membranes was evaluated using model wastewater containing 100 mg/L NH_4-N (from NH_4Cl) as feed solution and model seawater (3.5% (w/w) NaCl) as draw solution. As shown in Figure S4, the results of the FO tests agree with the intrinsic transport properties (Figure S2). The pristine CTA/CA membrane showed the highest water flux of 6.32 $L/m^2 \cdot h$, and due to the introduction of the hydrogel layers onto the composite membranes, the water flux values slightly decreased to 5.73 $L/m^2 \cdot h$ and 5.39 $L/m^2 \cdot h$ for CTA/CA-PVA-G and CTA/CA-PVA-B, respectively. Despite the hydrophilicity of the PVA hydrogel layer, the hydrogel introduction caused blockage of the pores and increased transport resistance during filtration operation. Due to the introduction of the thin dense PVA hydrogel layer on both CTA/CA-PVA-G and CTA/CA-PVA-B membranes, the selectivity of the membrane against NaCl increased. The pristine CTA/CA membrane exhibited a reverse NaCl flux of 4.12 $g/m^2 \cdot h$, while the PVA hydrogel membranes showed

lower reverse NaCl flux values of 2.87 g/m^2·h (CTA/CA-PVA-G) and 1.84 (CTA/CA-PVA-B) g/m^2·h. Using a 100 mg/L NH_4-N solution, all the membranes showed outstanding selectivity against NH_4-N, with all membranes demonstrating very low NH_4-N flux values of around 0.15 g/m^2·h to 0.21 g/m^2·h. These results show that the PVA hydrogel composite membranes were able to retain the high NH_4-N retention property of cellulose acetate-based membranes.

2.3. Stability of the PVA hydrogel layer

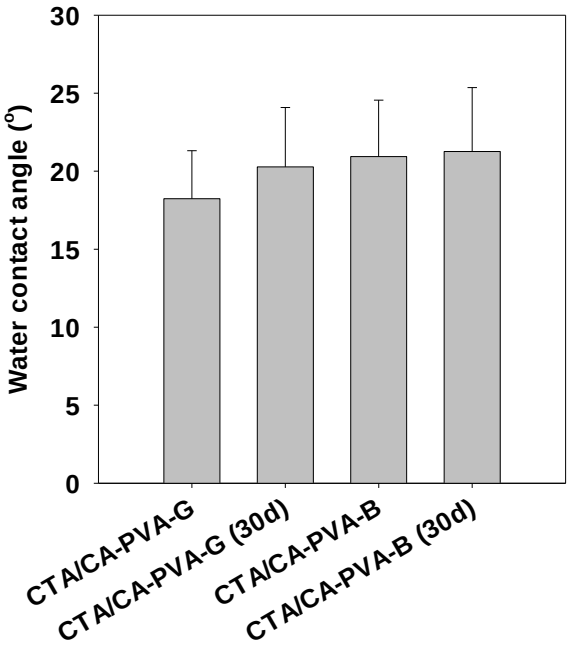


Figure S5. Water contact angle measurements of the PVA hydrogel composite membranes before and after immersion in Milli-Q water for 30 days.

Table S2. Water flux, reverse NaCl flux, and NH_4-N flux during forward osmosis operation. (Feed solution: 100 mg/L NH_4-N solution, Draw solution: 3.5% (w/w) NaCl, Flow rate: 300 mL/min) Membranes immersed in water for 30 days are denoted that CTA/CA-PVA-G/B-30d.

Membrane	Water flux ($L/m^2 \cdot h$)	NaCl flux ($g/m^2 \cdot h$)	NH_4-N flux ($g/m^2 \cdot h$)
CTA/CA-PVA-G	5.7	2.9	0.15
CTA/CA-PVA-G-30d	6.2	2.4	0.17
CTA/CA-PVA-B	5.4	1.8	0.15
CTA/CA-PVA-B-30d	5.7	2.7	0.12

The stability of the PVA hydrogel layer was tested by immersing the PVA hydrogel composite membranes in Milli-Q water for 30 days. The water contact angle measurements (Figure S5) and osmotic performance (Table S2) of the membranes after immersion in Milli-Q water were all comparable with those of the as-prepared PVA hydrogel membranes. It can be said that the crosslinked PVA coating is stable in aqueous systems.

2.4. Comparison with other NH_4-N-retaining forward osmosis membranes

The PVA hydrogel composite membranes prepared in this work were compared with other NH_4-N-retaining forward osmosis (FO) membranes in literature. Typically, polyamide (PA) thin film composite (TFC) membranes are used for the FO process; however, the PA selective layer has a negative charge brought about by the hydrolysis of the carboxyl groups. The negative surface charge of PA TFC membrane makes it unable to retain positively-charged species, such as NH_4-N, due to electrostatic interactions. Thus, most NH_4-N-retaining FO membranes in literature involves the surface modification of PA TFC membranes to either introduce positively-charged species onto the membrane surface or lessen the amount of unreacted carboxyl groups of the polyamide. These modifications all require additional modification and grafting steps, after the subsequent preparation of the membrane substrate and preparation of PA using interfacial polymerization. Modification procedures toward the enhancement of NH_4-N retention of

PA TFC membranes include chemical grafting with positively-charged substances, i.e., amines (Jafarinejad *et al.* 2019, Bao *et al.* 2021, Yao *et al.* 2022), secondary interfacial polymerization (Li *et al.* 2022), material incorporation (Engelhardt *et al.* 2019), and quaternization (Gonzales *et al.* 2022). All of these modifications on PA TFC membranes resulted in high NH_4-N retention, all over 94%, as shown in Table S3. Some of these membranes were also tested for fouling and applicability for the use of real wastewater. The PVA hydrogel composite membranes reported in this work, on the other hand, showed comparable pure water permeability (0.7–0.8 $L/m^2 \cdot h \cdot bar$) and high NH_4-N retention of over 97%. This work also demonstrated the outstanding fouling resistance of the PVA hydrogel composite membranes against a wide range of foulants, i.e., proteins, carbohydrates, humics, and bacteria, as well as applicability for the treatment of real industrial wastewater. These were achieved by only a simple immersion coating method and crosslinking of PVA, making this membrane preparation process not only facile and scalable, but also effective for wastewater treatment.

Table S3. Performance comparison with other NH_4-N-retaining membranes in literature.

Membrane	Pure water permeability ($L/m^2 \cdot h \cdot bar$)	NH_4-N rejection (%)	Fouling resistance	Reference
Polyethylenimine (PEI)-grafted polyamide (PA) thin film composite (TFC)	(No data)	~ 99	Tested using activated sludge	(Jafarinejad *et al.* 2019)
Aquaporin Inside (AQP HFFO)	(No data)	> 95.9	(Not tested)	(Engelhardt *et al.* 2019)
Ethylenediamine-grafted PA TFC	0.46	> 97.0	(Not tested	(Yao *et al.* 2022)
2-Aminoethanol-grafted PA TFC	0.55	> 97.0	(Not tested)	(Yao *et al.* 2022)
Secondary interfacial polymerization with tris-(2-aminoethyl)amine on PA TFC	0.32	94.7	(Not tested)	(Li *et al.* 2022)
PEI-grafted PA TFC	1.11	98.5	Organics and bacteria-resistant	(Gonzales *et al.* 2022)
Quaternized PA TFC	1.05	98.7	Organics and bacteria-resistant	(Gonzales *et al.* 2022)
Polyamidoamine-grafted PA TFC membrane	> 1.45	99.4	Tested using septic tank effluent	(Bao *et al.* 2021)
Glutaraldehyde-crosslinked polyvinyl	0.71	97.5	Organics and bacteria-resistant;	This work

alcohol (PVA) hydrogel composite		Tested using wastewater	
Borax-crosslinked PVA hydrogel composite	0.79	97.1	Organics and bacteria-resistant; Tested using wastewater	This work

References

Bao X, et al. (2021) Ammonium ultra-selective membranes for wastewater treatment and nutrient enrichment: Interplay of surface charge and hydrophilicity on fouling propensity and ammonium rejection. Water Res 190, 116678. https://doi.org/10.1016/j.watres.2020.116678

Dave HK, Nath K (2018) Synthesis, Characterization and Application of Disodium Tetraborate Cross-Linked Polyvinyl Alcohol Membranes for Pervaporation Dehydration of Ethylene Glycol. Acta Chim Slov 65 (4). https://doi.org/10.17344/acsi.2018.4581

Engelhardt S, et al. (2019) Urea and ammonium rejection by an aquaporin-based hollow fiber membrane. J Water Process Eng 32, 100903. https://doi.org/10.1016/j.jwpe.2019.100903

Gonzales RR, et al. (2022) Ammonium enrichment and recovery from synthetic and real industrial wastewater by amine-modified thin film composite forward osmosis membranes. Sep Purif Technol 297, 121534. https://doi.org/10.1016/j.seppur.2022.121534

Gonzales RR, et al. (2021a) Aliphatic polyketone-based thin film composite membrane with mussel-inspired polydopamine intermediate layer for high performance osmotic power generation. Desalination 516, 115222. https://doi.org/10.1016/j.desal.2021.115222

Gonzales RR, et al. (2021b) Facile development of comprehensively fouling-resistant reduced polyketone-based thin film composite forward osmosis membrane for treatment of oily wastewater. J Membr Sci 626, 119185. https://doi.org/10.1016/j.memsci.2021.119185

Jafarinejad S, et al. (2019) Concentrating ammonium in wastewater by forward osmosis using a surface modified nanofiltration membrane. Environ Sci Water Res Technol 5 (2), 246-255. https://doi.org/10.1039/C8EW00690C

Li J, et al. (2022) Surface modification of thin film composite forward osmosis membrane using tris(2-aminoethyl)amine for enhanced ammonium recovery. Desalination 541, 116002. https://doi.org/10.1016/j.desal.2022.116002

Lin H-L, et al. (2005) Light scattering and viscoelasticity study of poly(vinyl alcohol)–borax aqueous solutions and gels. Polymer 46 (15), 5541-5549. https://doi.org/10.1016/j.polymer.2005.04.074

Long J, et al. (2019) Controlled release of dexamethasone from poly(vinyl alcohol) hydrogel. Pharm Dev Technol 24 (7), 839-848. https://doi.org/10.1080/10837450.2019.1602632

Park MJ, et al. (2018) Hydrophilic polyvinyl alcohol coating on hydrophobic electrospun nanofiber membrane for high performance thin film composite forward osmosis membrane. Desalination 426, 50-59. https://doi.org/10.1016/j.desal.2017.10.042

Wang C, et al. (2022) Facile fabrication and characterization of high-performance Borax-PVA hydrogel. J Sol-Gel Sci Technol 101 (1), 103-113. https://doi.org/10.1007/s10971-021-05584-0

Wang S-Y, et al. (2021) Surface charge control of poly(methyl methacrylate-co-dimethyl aminoethyl methacrylate)-based membrane for improved fouling resistance. Sep Purif Technol 279, 119778. https://doi.org/10.1016/j.seppur.2021.119778

Yang Z, et al. (2021) Tailored thin film nanocomposite membrane incorporated with Noria for simultaneously overcoming the permeability-selectivity trade-off and the membrane fouling in nanofiltration process. J Membr Sci 640, 119863. https://doi.org/10.1016/j.memsci.2021.119863

Yao X, et al. (2022) Surface modification of FO membrane for improving ammoniacal nitrogen (NH4+-N) rejection: Investigating the factors influencing NH4+-N rejection. J Membr Sci 650, 120429. https://doi.org/10.1016/j.memsci.2022.120429

Zhang L, et al. (2021) In situ engineering of an ultrathin polyamphoteric layer on polyketone-based thin film composite forward osmosis membrane for comprehensive anti-fouling performance. Sep Purif Technol 272, 118922. https://doi.org/10.1016/j.seppur.2021.118922