Supporting Information (SI)

Hybrid Pressure Retarded Osmosis−Membrane Distillation (PRO−MD) Process for Osmotic Power and Clean Water Generation

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1. Materials and Methods

1.1 Pressure retarded osmosis (PRO)

Pressure retarded osmosis (PRO) is an osmotically driven membrane process between forward osmosis (FO) and reverse osmosis (RO), during which a hydraulic pressure difference (ΔP) lower than the osmotic pressure gradient ($\Delta\pi$) across the membrane is applied on the high-salinity draw solution.[1] Driven by $\Delta\pi$-ΔP, water spontaneously permeates from a low-salinity feed to the pressurized high-salinity draw solution through the semipermeable membrane. This continual water flux (J_w) consequently increases the volume of the pressurized water within the draw solution compartment and can be channeled to an energy recovery device such as turbine for electricity generation. In terms of energy production, membrane power density (W) is defined as the osmotic energy output per unit membrane area, which can be calculated by the product of ΔP and J_w as:[2,3]

$$W = J_w \times \Delta P \qquad \text{(S1)}$$

W is a major performance indicator of the PRO membrane since it determines the required amount of membrane area and the size of a PRO plant for a given capacity of energy production. Ideally, the theoretical maximum W can be obtained when ΔP is equal to the half of $\Delta\pi$:

$$W_{\max} = A\frac{\Delta\pi^2}{4} \qquad \text{(S2)}$$

Therefore, the W_{max} of a PRO membrane is directly proportional to membrane water permeability coefficient A and the square of $\Delta\pi$.

1.2 Materials

Radel® A polyethersulfone (PES, Solvay Advanced Polymer, L.L.C., GA), N-methyl-2-pyrrolidone (NMP, >99.5%, Merck), polyethylene glycol 400 (PEG, Mw = 400 g/mol, Sigma-

Aldrich) and deionized (DI) water were utilized in the capacity as the polymer, solvent and additive respectively for the spinning of the PES hollow fiber substrate. Polyvinylidene fluoride (PVDF) HSV#900 was purchased from Arkema Inc and used to fabricate the MD membrane. Polyvinylpyrrolidone (PVP) (average Mw = 360 kDa) was ordered from Sigma-Aldrich and utilized as the additive in PVDF dope solution. A mixture of glycerol (Industrial grade, Aik Moh Pains & Chemicals Pte. Ltd, Singapore) and deionized water (50/50 wt%) was used for post-treating the as-spun PES hollow fiber before drying and module fabrication. Trimesoyl chloride (TMC, >98%, Tokyo Chemical Industry, Co. Ltd., Japan), *m*-phenylenediamine (MPD, >99%, Sigma-Aldrich), sodium dodecyl sulphate (SDS, >97%, Fluka) and hexane (>99.9%, Fisher Chemicals) were the chemical agents to fabricate the polyamide selective layer via interfacial polymerization. Sodium chloride (NaCl) purchased from Merck was used for the membrane transport characterizations and separation performance tests. The deionized (DI) water was produced by a Milli-Q unit (Millipore) with a resistivity of 15 MΩ cm. The wastewater brine (WWBr) was collected from the Veolia NEWater plant in Kranji, Singapore, and directly used as the feed in PRO subsystem. The total organic carbon (TOC), chemical oxygen demand (COD), biochemical oxygen demand (BOD), total dissolved solids (TDS), total suspended solid (TSS), pH, and the concentrations of main ions of the WWBr were measured by Singapore Test Services (Singapore Test Services Pte Ltd, Singapore) and DOC-Labor (Dr. Huber, German) and tabulated in Table S1.

1.3 Fabrication of the PES-TFC PRO hollow fiber membrane and the PVDF flat sheet MD membrane

The PES hollow fiber substrate for the PES-TFC PRO membrane was firstly prepared via a dry-wet spinning process using the dual-layer spinneret coextrusion technology, as described in our previous work.[4] The as-spun PES hollow fibers were rinsed with tap water for 2 days to remove the residual solvent and additives. Subsequently, the membranes were soaked in a 50 wt% glycerol aqueous solution for 2 days and then dried in air at room temperature (about 23 °C) before storage.

After making the membrane module, a thin polyamide selective layer was formed on the inner surface (lumen side) of the PES hollow fiber substrate via interfacial polymerization between MPD and TMC monomers. Firstly, the 2 wt% MPD aqueous solution containing 0.1 wt% SDS was fed into the lumen side of hollow fibers for 5 min at a flow rate of 4.25 ml/min. The residual MPD droplets were then removed by purging a sweeping air for a period of several minutes using a compressed air gun. The second solution, a 0.15wt% TMC/hexane solution was brought into contact with the MPD saturated inner surface at a flow rate of 2.50 ml/min for 5 min to form a thin polyamide layer. The PES-TFC membranes were then purged with air for 15 sec to remove residual hexane and stored in deionized water for further characterizations.

The microporous PVDF flat-sheet membrane was prepared via nonsolvent induced phase separation (NIPS) method for the MD subsystem. A polymer dope solution of PVDF/PVP/NMP with a weight ratio of 12/8/80 (wt. %) was prepared at a temperature of 50 °C. The dope solution was allowed to degas and cool down for one day before casting onto a glass plate with a 150 μm thick casting knife gap. The as-casted membrane together with the glass plate was immediately immersed in a water coagulation bath. The formed PVDF membrane was rinsed with clean water for at least 3 days to remove the NMP solvent. Then, the membrane was washed with ethanol to remove the residual solvent and additive. Finally, the membranes were dried in a Freez-dryer (Martin Christ, Alpha 1-4 LD plus) after frozen in a fridge for 4 hours before further characterizations and performance tests.

1.4 Membrane Characterizations

Membrane morphology was observed by a field-emission scanning electron microscope (FESEM JEOL JSM-6700LV). Membrane samples for FESEM were firstly dried by a freeze dryer (ModulyoD, Thermo Electron Corporation, USA) and then prepared by immersing and fracturing the fiber in liquid nitrogen. Before testing, a thin layer of platinum was sputtered on the samples by a JEOL JFC-1100E ion sputtering coater.

The water contact angle of PVDF membrane was measured by a Rame-Hart Contact Angle Goniometer (model 100-22). Deionized water was dropped onto the membrane surface by a Gilmont micro-syringe. The contact angle was immediately measured once the droplet formed on the surface. At least 10 droplets were introduced and the average contact angle was reported to ensure the accuracy.

The average pore size and pore size distribution of the PVDF membrane was measured by a CFP-1500 AE capillary flow porometer (PMI, Vista, CA). The porosity, ε, of PVDF membrane was calculated by Eq. S3:

$$\varepsilon = \left(1 - \frac{m_{memb} / V_{memb}}{\rho_{mater}}\right) \times 100\% \qquad \text{(S3)}$$

where m_{memb} and V_{memb} are the weight and volume of a piece of membrane, while ρ_{mater} is the density of the membrane material. V_{memb} was obtained from the dimension of the piece of membrane; m_{memb} was measured by an accurate balance (A&D, GR-200); and ρ_{mater} was measured by a multi pycnometer (Quantachrome MVP-D160-E).

The pure water permeability, A, NaCl rejection, R, and salt permeability coefficient, B, of the PES-TFC hollow fiber membrane were measured via RO operation using the PRO setup. Before the tests, the PES-TFC membranes were pressurized from inside to out at 20 bar using deionized water for 30 min. After that, deionized water was pumped into the lumen side of the hollow fiber membranes at 2 bar, and the permeate from the shell side was collected and A in L m^{-2} h^{-1} bar^{-1} (abbreviated as LMH/bar) was calculated as:

$$A = \frac{\Delta V}{A_m \Delta t \Delta P} \tag{S4}$$

where ΔV (L) is the volumetric change of permeate collected over a period of Δt (h) during the test, A_m (m^2) is the effective permeation area, and ΔP (bar) is the transmembrane pressure difference.

The membrane rejection (R) to NaCl was obtained by using a 1000 ppm NaCl solution as the feed at 5 bar. The conductivities of permeate and feed were employed to calculate R:

$$R = (1 - \frac{Cd_p}{Cd_f}) \times 100\% \tag{S5}$$

where Cd_f and Cd_p refer to the conductivity of the feed and permeate, respectively. Salt permeability B in L m^{-2} h^{-1} (abbreviated as LMH) was then calculated using equation:[5]

$$\frac{1-R_s}{R_s} = \frac{B}{A(\Delta P - \Delta \pi)} \tag{S6}$$

where ΔP and $\Delta \pi$ are the pressure difference and osmotic pressure gradient across the membrane, respectively.

The water flux in FO and PRO processes could be modeled by the following equations.[6,7]

For the FO mode (selective layer against the feed solution):

$$J_w = \frac{1}{K_m} \ln \frac{A\pi_{D,b} + B}{A\pi_{F,m} + J_w + B} \tag{S7}$$

For the PRO mode (selective layer against the draw solution):

$$J_w = \frac{1}{K_m} \ln \frac{A\pi_{D,m} - J_w + B}{A\pi_{F,b} + B} \tag{S8}$$

where $\pi_{D,b}$ and $\pi_{F,b}$ refer to the bulk osmotic pressures in the respective draw and feed solutions, $\pi_{D,m}$ and $\pi_{F,m}$ are the corresponding osmotic pressures on membrane surfaces in the draw and feed solutions. The relationship among solute diffusion resistivity within the porous layer K_m, diffusivity D_s, membrane structural parameter S, membrane tortuosity τ, membrane thickness l and membrane porosity ε can be represented as follows:

$$K_m = \frac{S}{D_s} = \frac{l\tau}{\varepsilon D_s} \tag{S9}$$

2. PRO Subsystem and Experiments

As illustrated in Fig. S1, a lab-scale counter-current flow PRO subsystem was used for osmotic power generation.[3,8] A high-pressure hydra cell pump was used to channel and pressurize the draw solution and a pressure relief valve after the membrane module and a needle valve prior to the module were installed to adjust the hydrostatic pressure and the cross-flow rate. Digital pressure transmitters and flow meters were mounted to aid monitoring of key process parameters. The feed solution was recirculated by a variable speed peristaltic pump (Cole-Palmer, Vernon Hills, IL).

The PRO tests were carried out under the PRO mode where the active layer of the membrane was always facing the high salinity draw solution. The draw solution was pumped to the lumen side of the membrane and the feed was pumped to the shell side. A hydraulic pressure was applied on the draw solution and rapidly increased to the predetermined values at an interval of 5 bar while the feed was maintained at atmospheric pressure. The water permeation flux, J_w in L m^{-2} h^{-1} (abbreviated as LMH) was calculated from the volumetric change of the feed solution.

$$J_w = \frac{\Delta V_f}{A_m \Delta t} \tag{S10}$$

where ΔV_f (L) is the volumetric change of feed solution over a period of Δt (h) and A_m (m^2) is the effective membrane area.

The salt concentration in the feed water was determined from the conductivity measurement using a conductivity-concentration calibration curve. The reverse salt flux, salt reverse-diffusion from the draw solution into the feed, J_s in g m^{-2} h^{-1} (abbreviated as gMH), was thereafter determined from the increase of the feed conductivity:

$$J_s = \frac{\Delta(C_f V_f)}{A_m \Delta t} \tag{S11}$$

where C_f and V_f are the salt concentration and volume of the feed, respectively. The theoretically osmotic power density, W in W/m^2 was calculated from:

$$W = \frac{J_w \Delta P}{36} \tag{S12}$$

The water recovery rate, R_e, was calculated as:

$$R_e = \frac{\Delta V_f}{V_{f,i}} \times 100\% \tag{S13}$$

where $V_{f,i}$ (L) is the initial volume of the feed solution and ΔV_f is the change of feed water.

2. MD Subsystem and Experiments

A vacuum membrane distillation (VMD) subsystem was applied for producing clean water and regenerating the PRO draw solution using the fabricated PVDF membrane. Fig. S2 shows the schematic drawing of the lab scale VMD setup. The membrane was placed in the stainless steel tube and the diluted PRO draw solutions were used as the feed. The feed solution temperature was controlled by a heat exchanger at the designated value. The feed could be circulated to the steel tube by a rotary pump. On the other hand, the permeate side of the membrane was connected to a vacuum pump, and the permeate samples were collected by cold traps immersed in liquid nitrogen. The system was stabilized for half an hour before the collection of samples at an interval of 20 minutes. The samples were weighted by an accurate balance (A&D, GR-200). The samples' salinity were analyzed by a conductivity meter Lab 960 m (0−500 ms cm^{-1} ± 0.1 μs cm^{-1}, SCHOOT instrument). Finally, the permeation flux and salt rejection for each of the feed composition and feed temperature were calculated in a way similar to Eq. S10 and Eq. S5.

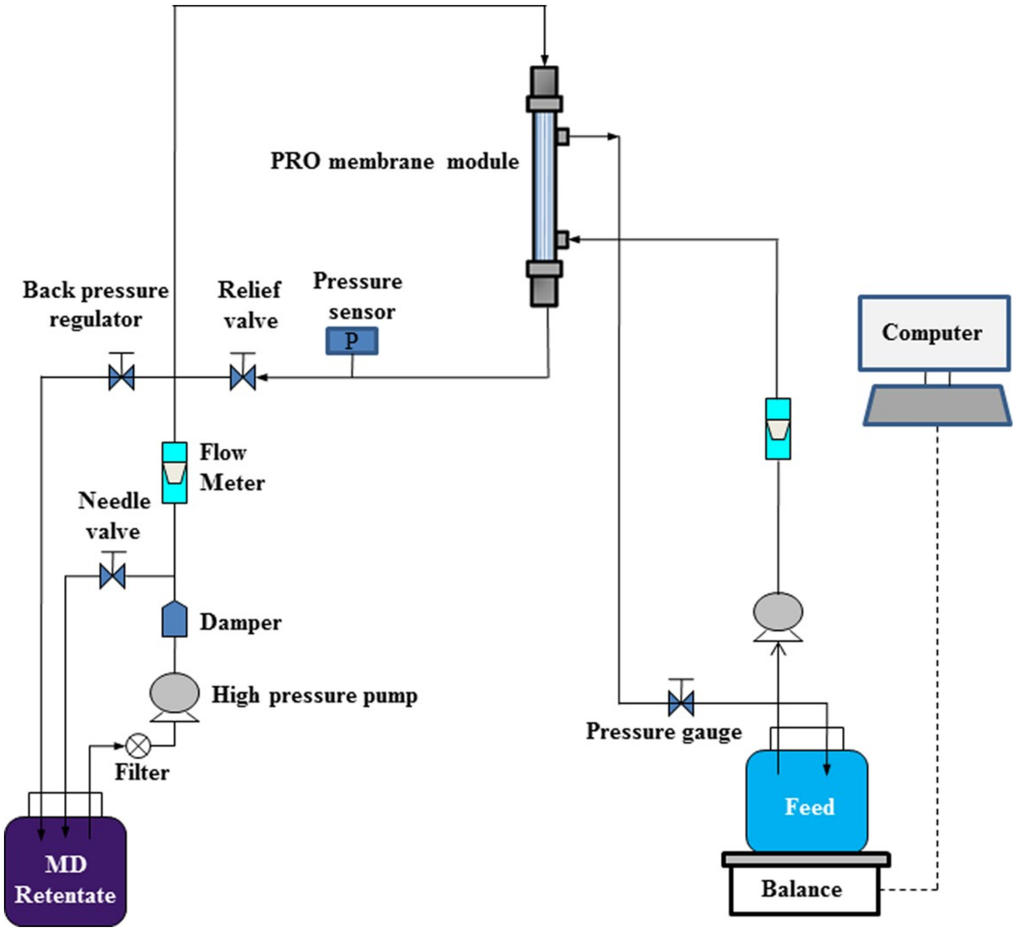

Fig. S1 Schematic diagram of the lab-scale PRO subsystem

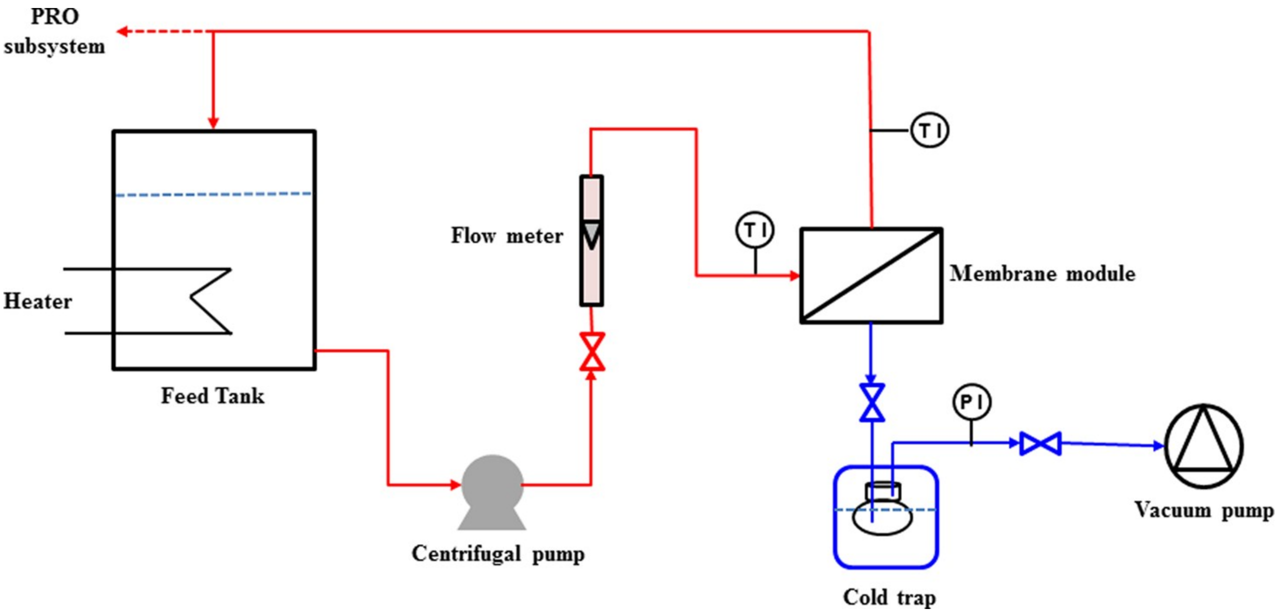

Fig. S2 Schematic diagram of the lab-scale VMD subsystem

Table S1 TOC and ion concentrations of the wastewater brine (WWBr) from NEWater plant

Sample	TOC	pH	BOD	COD	TSS	TDS	Cl^-	PO_4^{3-}	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	Fe^{2+}/Fe^{3+}	unit
WWBr	22.59	7.4	7.3	190	<1	1100	220	46	210	98.4	38.1	89.0	9.9	0.3	ppm

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