Supporting information

Understanding roughness – fouling relationship in reverse osmosis: Mechanism and implications

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Supporting Information Includes:

- 8 pages of supporting methods
- 14 figures
- 1 pages of references
1. Materials

N-methyl-2-pyrroldione (NMP, >99.5%, Merck), polyethylene glycol (PEG, Mw 400, Sigma Aldrich), polyethersulfone (PES) and polyester nonwoven (type: E055094-74B) were used in support membrane preparation. M-Phenylenediamine (MPD, > 98%, TCI), trimesoyl chloride (TMC, > 98%, Sigma Aldrich), sodium dodecyl sulfate (SDS, > 99%, Sigma Aldrich), sodium hydroxide (NaOH, > 99%, Sigma Aldrich) and hexane (> 99%, Merck) were employed for interfacial polymerization. Sodium chloride (NaCl, > 99%, Merck), alginate (Sigma Aldrich), BSA (> 97%, Sigma Aldrich), humic acid (Sigma Aldrich), calcium chloride (CaCl$_2$, > 93%, Sigma Aldrich), sodium sulphate (Na$_2$SO$_4$, > 99.5%, Sinopharm chemical), citric acid (> 99.5%, Sigma Aldrich), phosphate buffered solution (PBS, ultrapure grade), glutaraldehyde (25 wt. % solution in water, Acros Organics), Staphylococcus epidermidis (S. epidermidis, ATCC 12228), Escherichia coli (E. coli, ATCC 25922) were used to evaluate the reverse osmosis or fouling performances of the membranes. PBS-stabilized 5 nm gold nanoparticles (GNPs, Sigma Aldrich) were applied to investigate the water flux distribution on membrane surfaces.

2. Membrane surface characterization

The membrane surface morphology was examined with field emission scanning electron microscopy (FESEM, JEOL JSM-6700). The membrane was first dried in a freeze-dryer and then coated with platinum by Cressington sputter coater ion 208 HR. The membrane surface roughness was measured with atomic force microscope (AFM, Agilent Technologies, Santa Clara, CA) under tapping mode. The AFM images were processed with NanoScope Analysis 1.50.
Surface charge properties were analyzed with a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria). The experiments were conducted by streaming potential measurements using a 0.01 M NaCl solution. The pH of the solution was adjusted by 0.1 M HCl to pH 2.2 and then increased slowly to pH 11 through the addition of a 0.1 M NaOH solution. The water contact angle as well as the surface energy of the membranes were measured with a goniometer (VCA Optima, AST Products Inc.) at 22.5 °C.

The elemental compositions on membrane surfaces were characterized using X-ray photoelectron spectroscopy (XPS, Kratos AXIS UltraDLD, Kratos Analytical Ltd., England) equipped with a monochromatized AlKα X-ray source (1486.71 eV, 5 mA, 15 kV). A Vision Procession software was used to determine the atomic concentrations.

3. **Static and crossflow foulant attachment tests**

BSA, *E. coli* and *S. epidermidis* were used for static and crossflow foulant attachment tests. For static bacteria attachment tests, the membranes were first rinsed with phosphate-buffered saline (PBS) for three times. Then, each membrane was immersed in 0.75 ml of *E. coli* or *S. epidermidis* suspensions (10⁸ cfu/ml in PBS) and incubated at 37 °C overnight. After the incubation, the membranes were taken out, rinsed with PBS for three times, and then immersed in 2.5 wt. % glutaraldehyde solution at 4 °C overnight. The number of bacteria on membrane surfaces was quantified using FESEM.

The static BSA attachment tests were conducted following previous study.¹ The membranes were first immersed in methanol overnight and then washed with DI water for three times. The cleaned membranes were fixed in the dead-end cell with the selective layer facing protein solution (4.5 g/L BSA in 1× PBS buffer) for 24 h. The fouled membranes were first rinsed with PBS solution for three times and then DI water for three times. Then, the
membranes were cut into small pieces with same size, immersed in 1.5 mL 0.5 wt. % SDS solution and shaken by a shaking machine at 60 rpm for 24 h to desorb the attached BSA molecules. A micro BCA protein assay kit (#23225, Pierce Biotechnology, IL, US) was used to determine the protein concentration in the SDS solution. The protein concentrations were obtained from three samples and averaged for each membrane.

The crossflow attachment tests were conducted in similar ways except that foulants were fed in the crossflow mode by a pump at the flow rate of 0.2 L·min⁻¹.

4. Measurement of water and salt transport properties

The permeance of each membrane was determined by dividing the permeate volume with the membrane area (S, 13.2 cm²), filtration time and transmembrane pressure (ΔP) according to the following equation:

\[ A = \frac{V}{St\Delta P} \]  
\[ \text{(S1)} \]

The rejection rate of salts was calculated from following equation, where \( C_p \) and \( C_f \) correspond to salt concentrations in the permeate and feed solutions, respectively:

\[ R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \]
\[ \text{(S2)} \]

The salt concentrations were obtained by conductivity measurement.

5. Membrane cleaning tests
The membranes were cleaned by physical flushing and chemical cleaning, and recovered flux were measured. The permeance after fouling test ($A_b$) was first tested with 1000 ppm sodium chloride solution. After that, the membranes were first cleaned with DI water for 30 minutes at the flow rate of 3.75 cm/s. The permeability after cleaning with water ($A_a$) was recorded to investigate the reversibility of fouling process. Then, the membranes were washed with citric acid (pH = 3) and sodium hydroxide (pH = 10), each for 15 min. Finally, the membrane permeability was tested again ($A_c$). The water flux recovery after cleaning process was calculated as followed:

$$\text{Water Flux Recovery} = \frac{A_c - A_a}{A_b - A_a}$$  \hspace{1cm} (S3)

6. **Membrane porosity and pore size characterization**

The membrane porosity was measured through water uptake tests based on the following equation,$^2$

$$\varepsilon = \frac{(w_{\text{wet}} - w_{\text{dry}})/\rho_{\text{water}}}{(w_{\text{wet}} - w_{\text{dry}})/\rho_{\text{water}} + w_{\text{dry}}/\rho_{\text{polymer}}}$$  \hspace{1cm} (S4)

where $\varepsilon$ is the membrane porosity, $w_{\text{wet}}$ and $w_{\text{dry}}$ are the weight of wet membrane and dry membrane and $\rho_{\text{water}}$ and $\rho_{\text{polymer}}$ are the density of water and polymer, respectively.

The pore size is measured based on Guerout–Elford–Ferry equation,$^3$

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) + 8\eta l A}{\varepsilon}}$$  \hspace{1cm} (S5)

where $\eta$ is the viscosity of water ($8.9 \times 10^{-4}$ Pa·s), $l$ is the membrane thickness (150 μm), $A$ is the permeability of support membrane ($214.63 \pm 22.65$ L·m$^{-2}$·h$^{-1}$·bar$^{-1}$). The operational pressure was 2 bar. Based on these equations, the porosity and pore size are estimated to be
0.754 (±0.004) and 36.67 (±1.95) nm, respectively. These data were used in computational fluid dynamic simulation to show the membrane flux distribution.

7. Computational fluid dynamic simulation

7.1 Flow behaviors under crossflow conditions

A two-dimensional computational fluid dynamic simulation (CFD) was conducted to analyze the fluid behavior near membrane surface under crossflow conditions, using Comsol Multiphysics (Comsol 5.4, COMSOL Inc, USA). Rectangular simulation domain with or without ridge and valley structure were used for simulation. The overall domain size is 26 μm (width) × 2000 μm (height) and the heights of ridge structures range from 100 nm to 500 nm. For ridge and valley structure, the ridges are randomly distributed on membrane surface; for patterned structure, rectangular patterns with height of 400 nm and width of 1 μm are used. The distance between two patterns are 800 nm. The number of elements for ‘ridge and valley’, smooth and surface-patterned membrane are 125026, 100874 and 109746, respectively.

Navier-Stokes equation (Eq. (S6)) was combined with fluid continuity equation (Eq. (S7)) to solve the flow near membrane surface by the finite element method,

\[
\rho (u \nabla)u = -\nabla p + \mu \nabla^2 u \tag{S6}
\]

\[
\nabla u = 0 \tag{S7}
\]

where \( u \) is the velocity vector of the fluid, \( p \) is pressure, \( \rho \) is the density of the fluid (1 g/ml) and \( \mu \) is the viscosity of the fluid (1 mPa·s).
Assuming incompressible and fully developed Newtonian fluid, the boundary condition is given by the equation below:

\[ u_x(y) = \frac{4u_{\text{max}}y(D-y)}{D^2} \]  

(S8)

where \( u \) is the inlet velocity, \( u_{\text{max}} \) is the maximum inlet velocity, \( y \) is the coordinate and \( D \) is the channel height. The maximum inlet velocity was set as 10 mm/s. The pressure of outlet flow was 0 and non-slip boundary condition was applied to the walls.

7.2 Water transport across composite membranes in reverse osmosis

Similarly, a 2-D rectangular domain with or without ridge and valley structure were used for simulation. The overall domain size is 6000 nm in width and the thicknesses for conventional and free-standing membrane are 200 nm and 35.81 nm respectively, based on the FESEM and AFM images (Figures 1, S3 and S13). The height of ridge structures on conventional membrane is 300 nm and the shape of void structures was assumed to be semi-circles. It was also assumed that the permeability in the void structure is 10000 times higher than the solid phase of the selective layer. The number of elements for free-standing and conventional membrane with void fraction of 0, 0.25, 0.49, 0.64, 0.81 are 4069, 40132, 56208, 49110, 46534 and 50716, respectively.

The water flux in reverse osmosis is given by the equation below:

\[ J_w = A(\Delta P - \Delta \pi) \]  

(S9)
where $J_w$ is the water flux, $A$ is the permeability, and $\Delta P$, $\Delta \pi$ denote the applied pressure and osmotic pressure, respectively. Therefore, a pseudo-Darcy law was assumed to describe the water transport across the composite membrane (Eq. (S10)):

$$u = -\frac{\kappa}{\mu} \nabla p$$  \hspace{1cm} (S10)

where $u$ is the flux ($= J_w$), $\kappa$ is the permeability ($A$, $2 \text{ L}\cdot\text{m}^2\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$), $\mu$ is the viscosity of the fluid ($1 \text{ mPa}\cdot\text{s}$) and $p$ is pressure. The boundary conditions are the pressures for inlet and outlet flow, which are 15 bar and 0, respectively. Eqs. S9 and S10 were employed in 2-D CFD simulations to give the water flux distribution on conventional and freestanding membranes.

8. Additional figures
**Figure S1.** Schematic illustration of the crossflow cell used in desalination and fouling tests.

**Figure S2.** Schematic illustration of the dead-end cell used in static and reverse osmosis fouling tests.
**Figure S3.** (a)–(b) FESEM image of the (a) cross section of and (b) top layer of “ridge and valley” structure on conventional membrane. c) AFM height image and profile of a conventional membrane at three random places.

**Figure S4.** Properties of conventional and free-standing polyamide TFC membranes. (a) XPS survey spectra. (b) contact angle and surface energy.
Figure S5. Surface chemistry of two membranes. (a) the element ratio of conventional membrane and free-standing membrane. (b)–(c) the N 1s narrow scan data of (b) conventional membrane and (c) free-standing membrane.

Figure S6. pH value of solutions used in fouling tests.
Figure S7. (a)–(d) FESEM image of bacteria on membrane surface under static condition. ((a), (b), (c), (d) refer to S. epi on conventional membrane, S. epi on free-standing membrane, E. coli on conventional membrane, E. coli on free-standing membrane, respectively). (e),(f)
FESEM image of bacteria on membrane surface under dead-end filtration condition; (g),(h) FESEM image of bacteria on membrane surface under cross-flow condition ((e), (g) refer to E. coli on conventional membrane, (f), (h) refer to E. coli on free-standing membrane)

Figure S8. Shear stress profile of (a) conventional, (b) free-standing membrane and (c) surface-patterned membrane obtained from CFD simulations.
Figure S9. FETEM images of gold nanoparticles on (a)–(d) conventional membrane and (e)–(h) free-standing membrane.
Figure S10. (a)-(d) Water flux profile with streamline of conventional membrane with void fraction (VF) of (a) 0, (b) 0.25, (c) 0.49, (d) 0.81. (e) Flux distribution on of conventional membrane with different void fraction (VF).

Figure S11. Schematic illustrations of the impacts of surface roughness on membrane fouling in (a) static, (b) crossflow, and (c) reverse osmosis processes.
Figure S12. Illustrations of (a) patterned membranes with uniform and uneven selective layer thickness; and (b) flux distributions by CFD studies.

Figure S13. (a) AFM image and (b) height profiles of the cross-section of free-standing membrane
Figure S14. FESEM images of fouled membranes. ((a)~(h) refer to conventional membrane fouled with BSA, free-standing membrane fouled with BSA, conventional membrane fouled with humic acid, free-standing membrane fouled with humic acid, conventional membrane fouled with alginate, free-standing membrane fouled with alginate, conventional membrane fouled with Ca/alginate, free-standing membrane fouled with Ca/alginate, conventional membrane fouled with Ca/alginate.)
fouled with Ca-alginate mixed solution and free-standing membrane fouled with Ca-alginate mixed solution, respectively).

References


