Supporting information

A Cleaning-Healing-Interfacial Polymerization Strategy for Upcycling Real End-of-Life PVDF Microfiltration Membranes

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Number of pages (including the cover page): 16

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Section S1. Chemicals

Sodium hypochlorite solution (4.0 % active chlorine) and oxalic acid dihydrate (AR) for membrane cleaning was purchased from Macklin (China). Dopamine hydrochloride (98%) and tris(hydroxymethyl)aminomethane (ACS, ≥99.8%) used for healing was obtained from Aladdin (China). Piperazine (PIP, 99%), trimesoyl chloride (TMC, 98%), and n-hexane (≥98%) from Aladdin were used for interfacial polymerization to form the PA selective layer. Inorganic salts (NaCl, MgCl₂, MgSO₄ and Na₂SO₄) and dextrose as the neutral probe were also supplied by Aladdin. Con A and SYPRO Orange used for labelling polysaccharides and proteins on membrane surface were purchased from Molecular Probes Inc., USA.
Section S2. Basic calculations

The rejection rate \( R \) was determined as follows:

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

(1)

where \( C_p \) (mg/L) and \( C_f \) (mg/L) represent the solute concentration in the permeate and feed water, respectively.

Water flux of a nanofiltration membrane is determined as follows:

\[
J_v = \frac{\Delta m}{\rho \times A_m \times \Delta t}
\]

(2)

in which \( J_v \) (L m\(^{-2}\) h\(^{-1}\)) is the water flux, \( \Delta m \) (g) is the mass of permeate water over a specific time interval \( \Delta t \) (h), \( A_m \) (m\(^2\)) is the effective membrane area, and \( \rho \) (g L\(^{-1}\)) is the density of permeate water. Water permeance \( A \) (L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) was calculated by:

\[
A = \frac{J_v}{\Delta P}
\]

(3)

where \( \Delta P \) (bar) is the applied trans-membrane pressure.

The solute permeability \( B \) (L m\(^{-2}\) h\(^{-1}\)) was calculated by:

\[
B = \left(\frac{1}{R} - 1\right) \times J_v
\]

(4)

In the literature, the \( A/B \) ratio is commonly used to represent the water/solute selectivity of reverse osmosis and NF membranes\(^{1-3}\). The selectivity \( A/B \) (bar\(^{-1}\)) could be obtained from Eq. (3) and Eq. (4):

\[
A / B = \frac{R}{(1 - R) \times \Delta P}
\]

(5)

The \( A/B \) is a direct indicator of membrane selectivity for a certain solute, and \( A/B \) is related to the rejection at a fixed \( \Delta P \).
Section S3. Calculation of cross-linking degree of membranes

The O/N ratio of membrane was directly obtained from XPS results. The following equation was used to calculate the cross-linking degree:\(^4\):

\[
\frac{O}{N} = \frac{3m + 4n}{3m + 2n}, \quad m + n = 1
\]  

(6)

where \(m\) and \(n\) are the cross-linking portion and linear portion, respectively. The cross-linking degree was then obtained by \(m \times 100\%\).
Section S4. Photos of full-scale membrane bioreactor and flat-sheet membranes

Figure S1. Photos of (a) engineered membrane bioreactor under maintenance, (b) end-of-life PVDF MF membrane, and (c) pristine PVDF MF membrane.
Section S5. Teflon module for membrane healing

Figure S2. Photo of Teflon module for PDA healing on cleaned end-of-life PVDF MF membranes.
Section S6. CLSM images visualizing organic foulants on various MF membrane surfaces

Figure S3. CLSM images visualizing polysaccharides and proteins on various membrane surfaces: (a) 3D images of polysaccharides on the membrane surfaces; (b) 3D images of proteins on the membrane surfaces; (c) images showing polysaccharides and proteins distribution from cross-sectional views.

The CLSM characterization visualizes that the cleaning removed most polysaccharides and proteins (Figure S3), which are typical organic species causing membrane fouling, as indicated by significantly decreased fluorescence intensity and reduced distribution.
Section S7. XRD characterizations of PVDF MF membranes

Figure S4. XRD characterizations of various PVDF MF membranes.

XRD characterizations show that the intensity of characteristic peaks on 22° and 25°, possibly representing crystalline inorganic foulants on membrane surface, weakens after membrane cleaning.
Figure S5. Pore size distributions of various PVDF MF membranes: (a) Pristine; (b) EOL; (c) Cleaned; (d) Healed membranes. The data on the top right corner represent the average pore size of corresponding membranes.
Section S9. XPS spectra of NF membranes upcycled from various PVDF MF membranes

Figure S6. XPS spectra of NF membranes upcycled from various PVDF MF membranes.
Section S10. Surface roughness of NF membranes upcycled from various PVDF MF membranes

\[ R_q = 81.2 \pm 12.3 \text{ nm} \]

NF-Pristine

\[ R_q = 138.9 \pm 49.6 \text{ nm} \]

NF-Cleaned

\[ R_q = 117.0 \pm 7.1 \text{ nm} \]

NF-EOL

\[ R_q = 105.0 \pm 23.7 \text{ nm} \]

NF-Healed

**Figure S7.** Surface roughness and AFM scanning images of NF membranes upcycled from various PVDF MF membranes.
Section S11. Comparison of pure water permeances and Na$_2$SO$_4$ rejections of various membranes

Figure S8. Comparison of the performance of the NF-Healed and NF-EOL membranes to those of commercial NF membranes and NF membranes prepared on the surface of PES membrane. The PES membrane had a pore size same to the pristine PVDF MF membrane and their conditions of IP were identical.
Section S12. Solute permeability of NF membranes upcycled from various PVDF MF membranes

Figure S9. Solute permeability for Na$_2$SO$_4$ of NF membranes upcycled from various PVDF MF membranes
Section S13. Stability of the NF-Healed membrane

Figure S10. Variation of water flux and rejection of the NF-Healed membrane as a function of time (Na\textsubscript{2}SO\textsubscript{4} concentration: 10 mM; applied pressure: 8 bar).
References:


