Supporting Information for

Iron-Containing Poly(ionic liquid)s Membrane: Heterogeneous Fenton Reaction and Enhanced Anti-fouling Ability

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1. Experimental

1.1 Chemicals

Polysulfone resins (PSF, P3500) were obtained from Solvay (China), drying overnight in a vacuum oven before use. PSF terminated with hydroxyl groups (PSF-OH) was synthesized according to literature report [1]. Polyvinylpyrrolidone K30 (PVP K30) was bought from Energy Chemical (China). 2-chloropropionyl chloride (CPC, 97%), 4-vinylpyridine (4-VP, 96%), *N*, *N*-dimethylacetamide (DMAC, 99%), 1-methyl-2-pyrrolidinone (NMP, 99%), *N*, *N*-dimethylformamide (DMF, 99%), dimethyl sulfoxide (DMSO, 99%), triethylamine (TEA, 99%), dichloromethane (DCM, 99.5%), copper chloride ($CuCl_2$, 99.99%), 3-bromo-1-propanol (97%), iron bromide ($FeBr_2$, 99.98%), ascorbic acid (AA, 99%), 30% H_2O_2, bovine serum albumin (BSA, >96%), and MB were bought from Aladdin Industrial Co., Ltd. (China). Tris(2-(dimethylamino)ethyl)amine (Me_6TREN) was prepared according to previous studies and stored sealed with nitrogen (N_2) at the 4 °C refrigerator [2-3].

1.2 Synthesis of Polysulfone (PSF) with terminal hydroxyl groups

The polymerization of polysulfone (PSF) with terminal hydroxyl groups was performed under nitrogen (N_2) protection, and the typical procedures were shown as follows. BPA (45 mmol) and DFBP (37 mmol) were dissolved in a mixed solvent of DMAC and toluene. Then, the mixture was stirred vigorously and added with dried K_2CO_3 (117 mmol). The whole reaction system was carried out at 155°C for 4 hours and then heated to 190°C for 6 hours. After the reaction, the mixture was setting overnight until K_2CO_3 settles to the bottom. The upper homogeneous solution was precipitated in methanol/DI water (v/v=1/1) and washed multiple times with the methanol/DI water mixture. Finally, the reaction product (marked as PSF-OH) was dried at a 40 ^{o}C vacuum oven for one day.

1.3 Synthesis of PSF-Cl macroinitiator

PSF-OH (5.0 g) and TEA (1.5 mL) were solubilized with 150 mL DCM in a three-neck flask. Then a mixture of CPC (1 mL) and DCM (10 mL) was added dropwise into the flask under an ice water bath (0 °C) for 1 hour and then reacted at 25 ^{o}C for 24 hours. After reaction, the polymer was precipitated in methanol and washed with excess methanol. The final product (marked as PSF-Cl) was dried at a 40 ^{o}C vacuum oven for one day.

1.4 Synthesis of block copolymer PSF-*b*-P4VP

The synthesis procedure of the PSF-*b*-P4VP block copolymer is shown as follows. PSF-Cl (0.2 g), 4-VP (4.0 mmol), $CuCl_2$ (0.016 mmol), DMSO (2 mL), and Me_6TREN (0.016 mmol) were mixed to a 20 mL-glass *via*l and purged with N_2 for 15 minutes. At the same time, 3 cm copper wire was surrounded with a magnetic stir bar, activated with hydrochloric acid for 15 minutes, rinsed with plenty of deionized (DI) water, and dried under N_2 atmosphere. Then, a dry magnetic stir bar was transferred to the above glass *via*l under N_2 atmosphere. Subsequently, the reaction system was sealed for polymerization for 24 hours at 25 ^{o}C. Finally, reaction product (marked as PSF-*b*-P4VP) was recovered *via* lyophilization.

1.5 Preparation of Fe-PILs membrane

PSF-*b*-P4VP/PSF membranes were prepared *via* the nonsolvent induced phase separation (NIPS) process. Different amounts of PSF, PSF-*b*-P4VP, and PVP K30 dissolved in NMP and mixed mechanically for 24 hours at 60 ^{o}C as casting solutions. Then, the above casting solutions were standing for 24 hours at room temperature until the bubbles vanished. Subsequently, the casting knife (a knife gap of 250 μm) was used to cast the solutions evenly on a clean glass plate with 10 s of setting. The glass plate with casting solutions was in DI water for 48 hours at room temperature to complete the phase inversion process. The prepared PSF-*b*-P4VP/PSF blend membranes with different ratios settled were marked as M1, M2, M3, and M4, respectively.

Subsequently, the PSF-*b*-P4VP/PSF blend membrane was immersed in a 10% 3-bromo-1-propanol solution for quaternization reaction for 24 hours at 60 ^{o}C. After repeated washing with DI water, the quaternized PSF-*b*-P4VP/PSF blend membrane (PSF-based PILs membrane, marked as M5) was immersed in a saturated ethanol solution of $FeBr_2$ for 24 hours under ambient temperature to prepare the Fe-PILs membrane (marked as M6).

1.6 Characterization of PSF-based polymers

Fourier transform infrared (FTIR) spectra of PSF-based polymers were recorded in the range of 4000 to 500 cm^{-1} on FTIR spectrometer (Nicolet iS5, Thermo Fisher). The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of PSF-based polymers were measured by gel permeation chromatography (GPC, Waters 1515 Pump, Waters 2489 refractive index detector) in DMF at 40 °C with a flow rate of 1.00 mL min^{-1}. The measurement of GPC was applying a 20 μm guard column, HR_1, HR_3, and HR_4 Styragel columns (4.6 × 300 mm, Waters). The GPC system calibration was used polystyrene standards in the range of 5.4×10^2 to 7.4×10^5 g mol^{-1}. A Bruker AV 500 M spectrometer recorded ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra of PSF-based polymers.

1.7 Membranes Characterization

Top surface and cross-section images of different membranes were measured with the scanning electron microscope (SEM, Hitachi S-4800, Japan). The surface element component of different membranes were analyzed by an X-ray photoelectron spectrometer (XPS, PHI Quantera II, Japan) and energy-dispersive X-ray spectroscopy (EDS). The membrane surface roughness was obtained by atomic force microscope (AFM, MFP-3D, UK). The surface hydrophilicity of different membranes was measured with a static contact angle meter (JC2000D1, POWEREACH, China) with five different positions.

The membrane porosity (ε) was calculated according to the following equation (1):

$$\varepsilon = \frac{W_{\mathrm{w}} - W_{\mathrm{D}}}{S \cdot L \cdot \rho} \times 100\% \tag{1}$$

Where W_{w} and W_{D} represent wet and dry membrane mass (g); S is effective membrane area (cm^2); ρ is water density (g cm^{-3}); L is average membrane thickness (cm) [4].

The average membrane pore size (r_{m}) was acquired by Guerout-Elford-Ferry equation (2):

$$r_{\mathrm{m}} = \sqrt{\frac{(2.9 - 1.75\varepsilon)8\eta LQ}{\varepsilon S \Delta P}} \tag{2}$$

Where Q is volume of pure water permeated per unit time (m^3 s^{-1}); ε is membrane porosity; η is viscosity of water (Pa s); S is membrane area (m^2); L is average membrane thickness (m); ΔP is operating pressure (bar) [5].

1.8 Membrane filtration and anti-fouling performance

A homemade across-flow filtration system with 3.14 cm^2 of effective filtration area (**Fig. S1**) was applied to evaluate membrane filtration and anti-fouling performance [6]. A stable permeate flux was measured *via* pre-press at 2 bar transmembrane pressure for 30 minutes, and then the pure water flux (J_{w1}) was obtained under 1 bar transmembrane pressure, which was calculated as following equation (3):

$$J_{\mathrm{w1}} = \frac{V}{A\Delta t} \tag{3}$$

Where J_{w1} is pure water flux (L m^{-2} h^{-1} bar^{-1}); V is water volume (L); A is effective membrane area (m^2); Δt is filtration time (h).

A 1 g L^{-1} BSA solution (pH 7.4) was chosen as model fouling for membrane rejection test. The BSA concentration was measured with ultraviolet-visible spectroscopy (Shimadzu, UV 2600, Japan) at 278 nm. After testing the pure water flux (J_{w1}) for 1 h, the deionized water was switched to the BSA solution, which continuously monitored the fouled flux (J_{P}) for 2 h under 1 bar transmembrane pressure.

The membrane was taken out and placed in deionized water for shaking and cleaning after the membrane rejection test to further evaluate the anti-fouling performance. The pure water flux (J_{w2}) of the cleaned membrane was measured for 1 h at 1 bar, and the flux recovery ratio (FRR), the total fouling resistance (R_{t}), reversible fouling resistance (R_r), and irreversible fouling resistance (R_{ir}) were acquired by calculation using these equations (4−7):

$$FRR = \frac{J_{\mathrm{w2}}}{J_{\mathrm{w1}}} \times 100\% \tag{4}$$

$$R_{\mathrm{t}} = \left(1 - \frac{J_{\mathrm{p}}}{J_{\mathrm{w1}}}\right) \times 100\% \tag{5}$$

$$R_{\mathrm{r}} = \left(\frac{J_{\mathrm{w2}} - J_{\mathrm{p}}}{J_{\mathrm{w1}}}\right) \times 100\% \tag{6}$$

$$R_{\mathrm{ir}} = \left(\frac{J_{\mathrm{w1}} - J_{\mathrm{w2}}}{J_{\mathrm{w1}}}\right) \times 100\% \tag{7}$$

1.9 Treatment of dye wastewater by heterogeneous Fenton membrane

MB was used to evaluate the performance of PSF-based Fe-PILs membranes (M6) as a heterogeneous Fenton membrane. The concentration of MB was analyzed using ultraviolet-visible spectroscopy (SHIMADZU, UV 2600, Japan) at a wavelength of 664 nm.

The static heterogeneous Fenton reaction was evaluated as follows: 20 mg PSF-based Fe-PILs membranes (M6) were added in an initial concentration of 20 mg L^{-1} MB solution (50 mL), which was started with H_2O_2 and AA. The pH effect (3.0−11.0), the dosage effect of H_2O_2, and the dosage effect of AA on the MB degradation were also investigated. Each test is performed in triplicate to reduce experimental error. The MB degradation efficiency of heterogeneous Fenton membrane was calculated by the following equation (8):

$$R = \frac{C_0 - C_1}{C_0} \times 100\% \tag{8}$$

Where $C_0\ and\ C_1$ is initial and real-time concentration of MB (mg L^{-1}).

Dynamical heterogeneous Fenton reactions were evaluated as follows: A homemade across-flow filtration system was also used to evaluate PSF-based dynamical heterogeneous Fenton reaction Fe-PILs membrane (M6). The detailed process is similar to evaluating different membranes' filtration and anti-fouling performance.

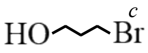
Membrane	PSF (g)	PSF-*b*-P4VP (g)	PVP (g)	NMP (g)	 [c] (mL)	$FeBr_2$ (g)
M1	1.80	-	0.4	7.8	-	-
M2	1.62	0.18	0.4	7.8	-	-
M3	1.53	0.27	0.4	7.8	-	-
M4	1.44	0.36	0.4	7.8	-	-
M5	1.44	0.36	0.4	7.8	10	-
M6	1.44	0.36	0.4	7.8	10	0.5

Table S1. Compositions[a] and casting conditions[b] of membrane casting solutions.

[a] Total polymer concentration 18 wt%, PVP as porogen at concentration of 4 wt%, NMP as solvent at concentration of 78 wt%.

[b] Coagulation bath temperature 25 °C, casting temperature 25 °C, relative humidity of atmosphere 70%.

[c]  expressed as 3-bromo-1-propanol.

Membrane	Porosity (%) [a]	Average pore size (nm) [a]	Ra (nm) [b]
M1	79.78±0.75	10.95±0.25	8.01
M2	83.45±1.70	35.26±2.69	8.20
M3	80.40±0.63	40.95±0.85	12.80
M4	80.74±1.24	45.45±2.35	17.01
M5	78.69±0.07	53.28±1.59	10.02
M6	78.40±0.21	51.91±2.79	11.14

Table S2. Porosity, average pore size, and Ra of membranes

[a] Porosity and average pore size were calculated by equations (1) and (2).

[b] The three-dimensional surface roughness of different membranes were obtained by atomic force microscope (AFM, MFP-3D Origin+, Oxford Instruments, UK).

Table S3. Surface elemental composition of the membrane as measured by XPS

Membrane	C1s	O1s	Fe2p
M1	79.3%	15.4%	-[a]
M4	78.5%	16.7%	-
M6	70.3%	23.5%	2.9%

[a] defined as no element detected in the corresponding membrane.

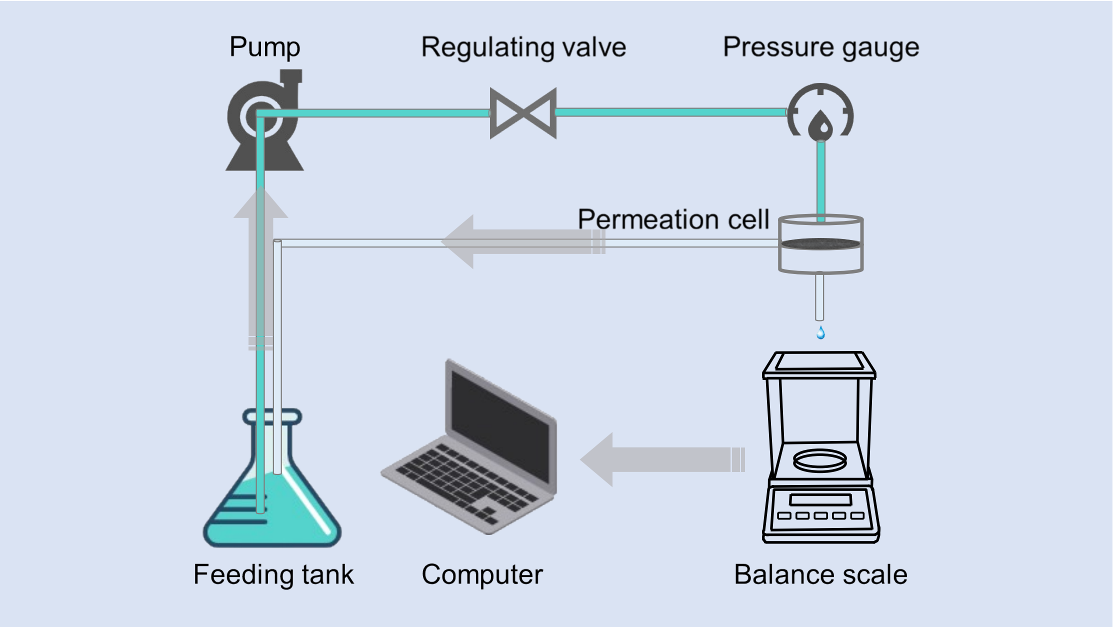


Fig. S1. Schematic diagram of the catalytic membrane.

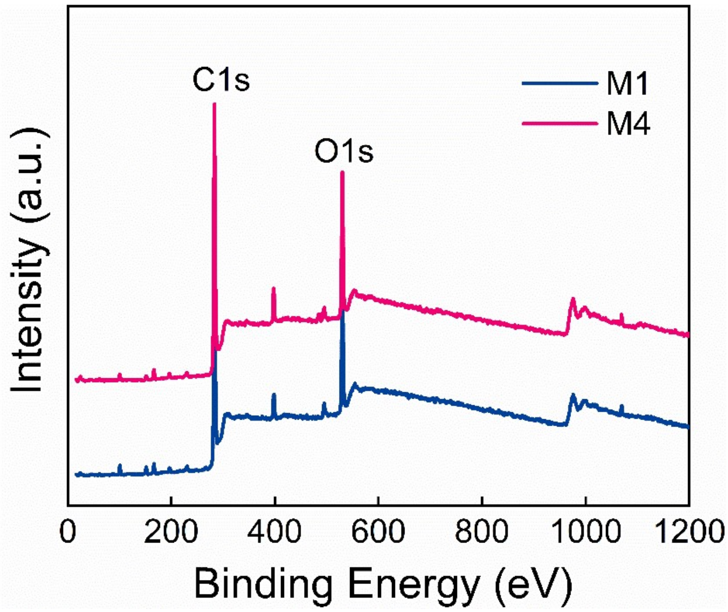


Fig. S2. The X-ray photoelectron spectroscopy (XPS) survey spectra of M1 and M4.

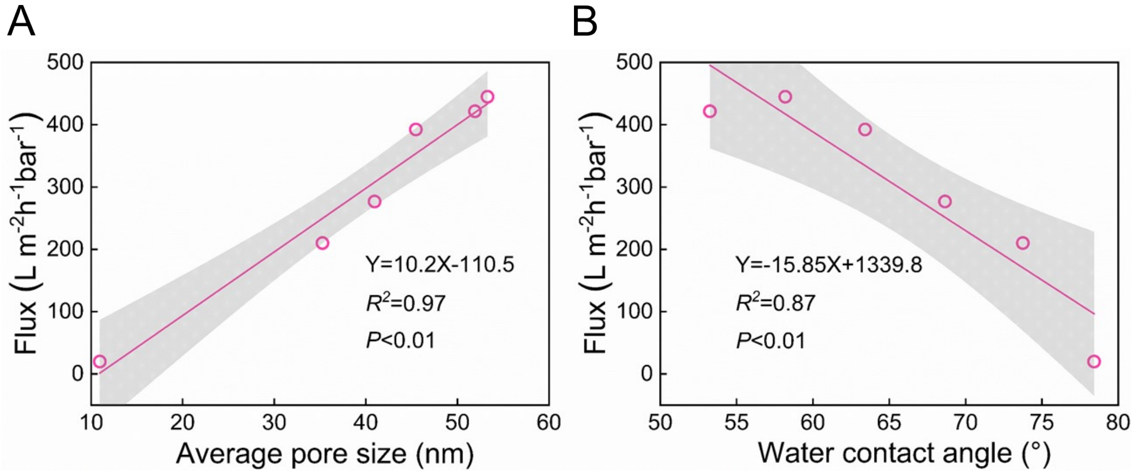


Fig. S3. The linear fitting relationship between the static contact angle or pore size of the M6 membrane and the pure water flux of the M6 membran

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