Supporting Information

Poly(homopiperazine-amide) thin-film composite membrane for nanofiltration of heavy metal ions

Syed Ibrahim[a], Mahdi Mohammadi Ghaleni[c], Arun M. Isloor[*a,b], Mona Bavarian[c], and Siamak Nejati[*c]

[a]Membrane Technology Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore 575 025, India

[b]Apahatech Solutions LLP, Science and Technology Entrepreneurs Park, National Institute of Technology Karnataka, Surathkal, Mangalore 575 025, India

[c]Department of Chemical and Biomolecular Engineering, University of Nebraska−Lincoln, Lincoln, Nebraska 68588-8286, United States

Corresponding authors: Arun M. Isloor (isloor@yahoo.com) and Siamak Nejati (snejati2@unl.edu)

S1. **Characterization of HTFC membranes.** Fourier-transform infrared spectra were collected in attenuated total reflectance (ATR) mode, using a Bruker Alpha spectrometer. A small area of the HTFC membrane was cut (1 cm × 1 cm) and placed on the diamond window of the ATR module. The spectra were collected with a resolution of 4 cm^{-1} and averaged over 24 scans.

The wettability of the membrane surfaces was evaluated by measuring the water contact angle on each sample using an automated contact angle measurement instrument (KRUSS DSA 100E). To do so, a 5 μL water droplet was dispensed on the dried membrane, and the water contact angle was measured after 10 seconds. The measurements were performed at three different locations on each sample. The reported values show the average of three measurements with one standard deviation.

The surface charge of NF membranes was measured using a streaming potential analyzer (SurPASS, Anton Paar). The membranes were attached to parallel planar surfaces (sample holders) of an adjustable gap cell (Anton Paar). Subsequently, the membranes (1 cm × 2 cm) were fixed on the sample holders. The gap between the samples was adjusted to be about 100 μm using two knobs. A solution of KCl (1mM) was used as the background electrolyte; the solution was pumped through the gap. Membrane Zeta potential was estimated from the generated streaming potential using the Helmholtz–Smoluchowski equation.[1] For each measurement, the pH of the electrolyte was adjusted by an auto titrator using 0.05M NaOH or 0.05M HCl solutions.

Scanning electron microscopy (SEM) images were collected using a FEI Helios NanoLab 660 instrument. The membranes were air-dried overnight, cut in size, and mounted on SEM stubs using conductive carbon tape. The samples were sputter-coated with ~60 nm of gold using a Ted Pella sputtering machine (108 Auto). For the cross-section images, the samples were dipped in liquid nitrogen and freeze-fractured before drying.

Atomic force microscopy (AFM) height images were acquired at ambient conditions using a Bruker Dimension Icon probe microscope. The experiments were conducted in peak force tapping mode (SCANASYST-Air) using a silicon tip with a nominal tip radius of 2 nm and resonance frequency (fo) of 70 kHz. The measurements were performed on a 3 μm × 3 μm area of the sample, and the average roughness values were determined over the entire region.

X-ray photoelectron spectroscopy (XPS) measurements were performed on the ThermoFisher Scientific instrument, operating with a monochromatic Al Kα X-ray source ($h\nu$ = 1486.6 eV). The survey spectra were obtained over the range of 0-1200 eV at 100 W with a 200 eV pass energy and 100 ms dwell time for the detector. The data were collected with 1 eV resolution. High-resolution XPS core electron spectra were obtained over a spot size of ~400 μm using 50 W beam power. The spectra were collected with 50 eV pass energy and 100 ms dwell time and averaged over five scans with 0.1 eV resolution.

C1s, N1s, and O1s XPS Core Electron Spectra

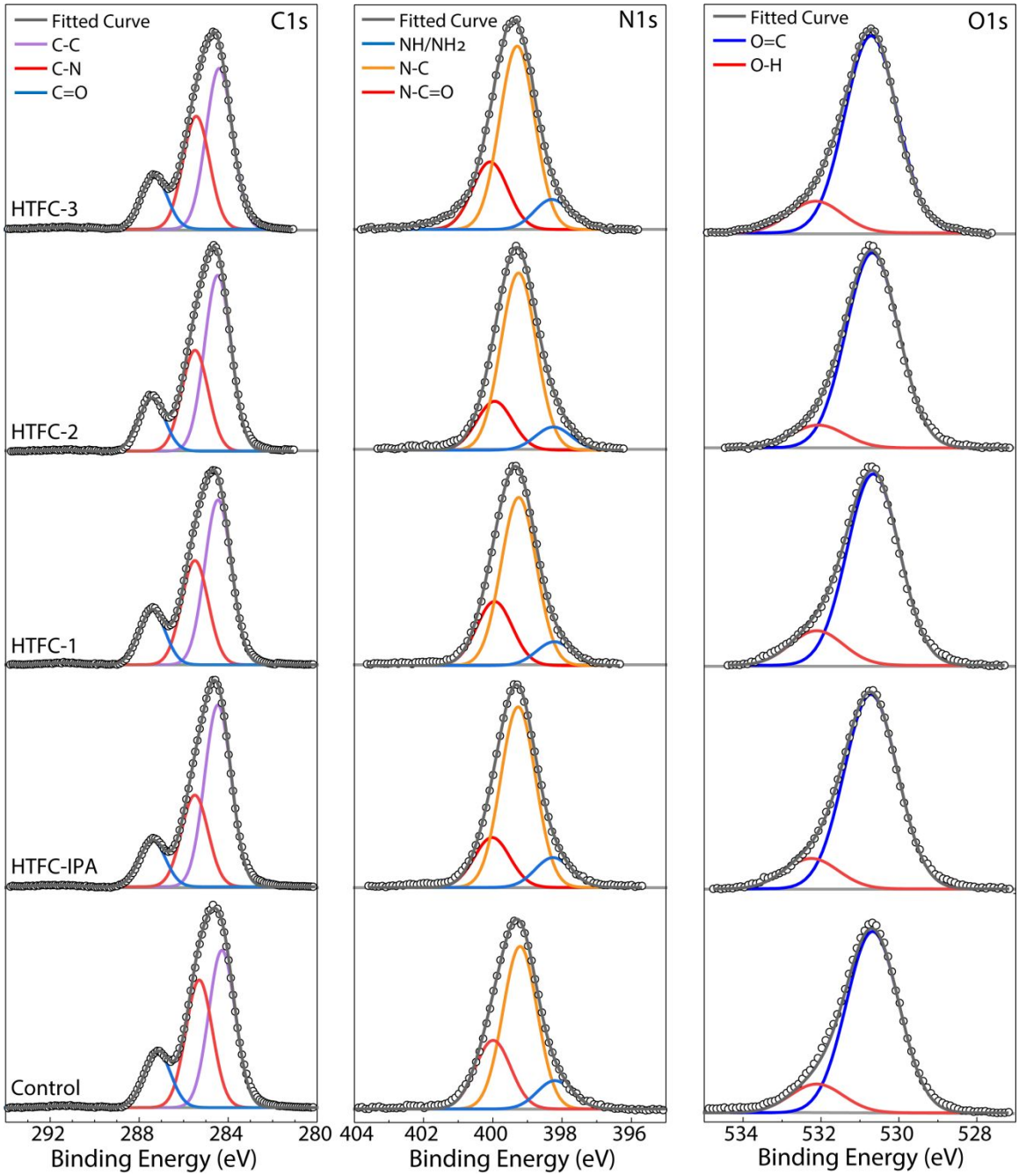
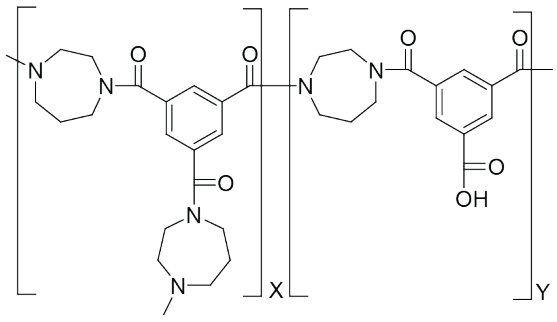


Figure S1. High-resolution C1s, N1s, and O1s XPS core electron spectra for HTFC nanofiltration membranes.

Calculating degree of cross-linking using XPS measurements

Degree of cross-linking of control and HTFC-IPA membranes

Figure S2 includes the complete set of calculations used to find the degree of cross-linking for control and HTFC-IPA membranes.



Calculation of X and Y value

X formula: $C_{19}O_3N_4$ Y formula: $C_{14}O_4N_2$

i) Control TFC membrane

$$\frac{O}{N} = \frac{3X+4Y}{4X+2Y} = 1.0, X + Y = 1 \rightarrow X = 50.0\%, Y = 50.0\%$$

$$\frac{O}{C} = \frac{3X+4Y}{19X+14Y} = 0.18, X + Y = 1 \rightarrow X = 78.0\%, Y = 22.0\%$$

$$\frac{N}{C} = \frac{4X+2Y}{19X+14Y} = 0.18, X + Y = 1 \rightarrow X = 47.0\%, Y = 53.0\%$$

$\therefore X = 58.3\%, Y = 41.7\%$

ii) HTFC-IPA membrane

$$\frac{O}{N} = \frac{3X+4Y}{4X+2Y} = 1.24, X + Y = 1 \rightarrow X = 44.0\%, Y = 56.0\%$$

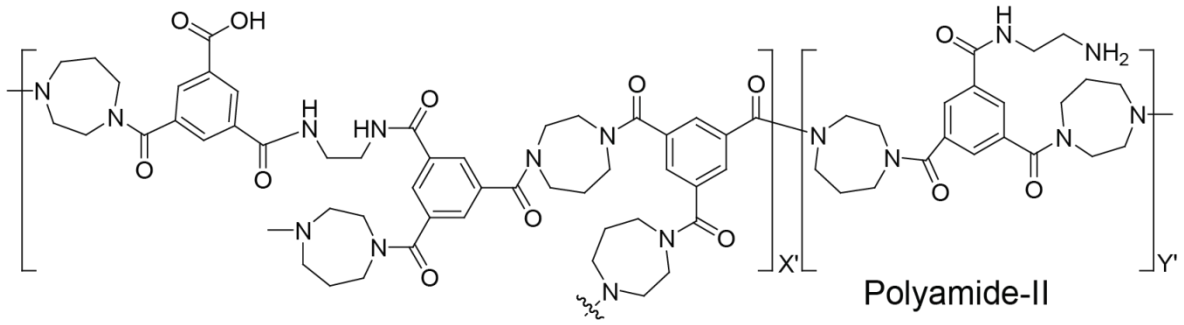
$$\frac{O}{C} = \frac{3X+4Y}{19X+14Y} = 0.19, X + Y = 1 \rightarrow X = 69.0\%, Y = 31.0\%$$

$$\frac{N}{C} = \frac{4X+2Y}{19X+14Y} = 0.15, X + Y = 1 \rightarrow X = 8.0\%, Y = 92.0\%$$

$\therefore X = 40.3\%, Y = 59.7\%$

Figure S2. Calculation of degree of cross-linking of control and HTFC-IPA NF membranes.

Crosslinking density for HTFC-1, HTFC-2, and HTFC-3 membranes (after EDA treatment)



Scheme S1. Proposed cross-linking scheme for the HTFC membrane after EDA treatment

Tables S1 to S3 include the XPS chemical states and elemental analysis for HTFC-1, HTFC-2, and HTFC-3 membranes, respectively. To calculate the degree of cross-linking (X_{EDA}) for the membranes, after EDA treatment, we calculated the concentration of the C-NH species. Then, we divided that number by the concentration of C-N species. For this purpose, the following Equation was defined and used:

$$X_{EDA}\% = \frac{[\mathrm{HN\text{-}C}]}{[\mathrm{O{=}CN}]} = \frac{[\mathrm{C\text{-}N}] - 2([\mathrm{C{=}O}] - [\mathrm{C\text{-}OH}])}{[\mathrm{C\text{-}N}]} \times 100 \quad \text{(S1)}$$

Table S1. XPS chemical states and elemental analysis for HTFC-1 membrane

Species	Center	Area (CPS . eV)	Area/SF	Chemical %	Atomic %
C-C	284.64	177126	177126	0.35	69.1
C-N	285.67	111989	111989	0.22	
C=O	287.6	58053	58053	0.12	
Shake-up	291.5	2749	2749	0.005	
N-C=O	400.2	23500	14687	0.029	11.3
N-C	399.5	60649	37906	0.075	
N-H/NH_2 (unreacted)	398.5	7359	4600	0.009	
O=C	530.7	140786	48867	0.096	11.4
O-H	532.2	25767	8944	0.018	
Na 1s	-	331662	31324	0.062	6.2
Cl 2p	-	27455	10016	0.02	2
SUM			506262	1	100

Table S2. XPS chemical states and elemental analysis for HTFC-2 membrane

Species	Center	Area (CPS . eV)	Area/SF	Chemical %	Atomic %
C-C	284.6	1876812	1876812	0.366	68.8
C-N	285.62	106916	106916	0.209	
C=O	287.57	56054	56054	0.109	
Shake-up	291.6	1789	1789	0.003	
N-C=O	400.25	18547	11592	0.022	11.4
N-C	399.48	63932	39957	0.078	
N-H/NH_2 (unreacted)	398.45	10807	6755	0.013	
O=C	530.8	144335	50099	0.098	11.6
O-H	532.2	26947	9353	0.018	
Na 1s	1071.12	308959	29180	0.057	5.7
Cl 2p	197.87	35125	12814	0.025	2.5
SUM			512191	1	100

Table S3. XPS chemical states and elemental analysis for HTFC-3 membrane

Species	Center	Area (CPS . eV)	Area/SF	Chemical %	Atomic %
C-C	284.6	171603	171603	0.374	76.3
C-N	285.63	120432	120432	0.261	
C=O	287.52	56306	56306	0.122	
Shake-up	291.74	2954	2954	0.006	
H-N-C=O	400.25	24024	15015	0.033	11.3
C-N-C=O	399.47	51053	31908	0.069	
N-H/NH_2 (unreacted)	398.47	8366	5228	0.011	
O=C	530.87	132628	46035	0.1	11.6
O-H	532.3	21460	7449	0.016	
Na 1s	1071.12	40480	3823	0.008	0.8
Cl 2p	197.87		0	0	0
			460755	1	100

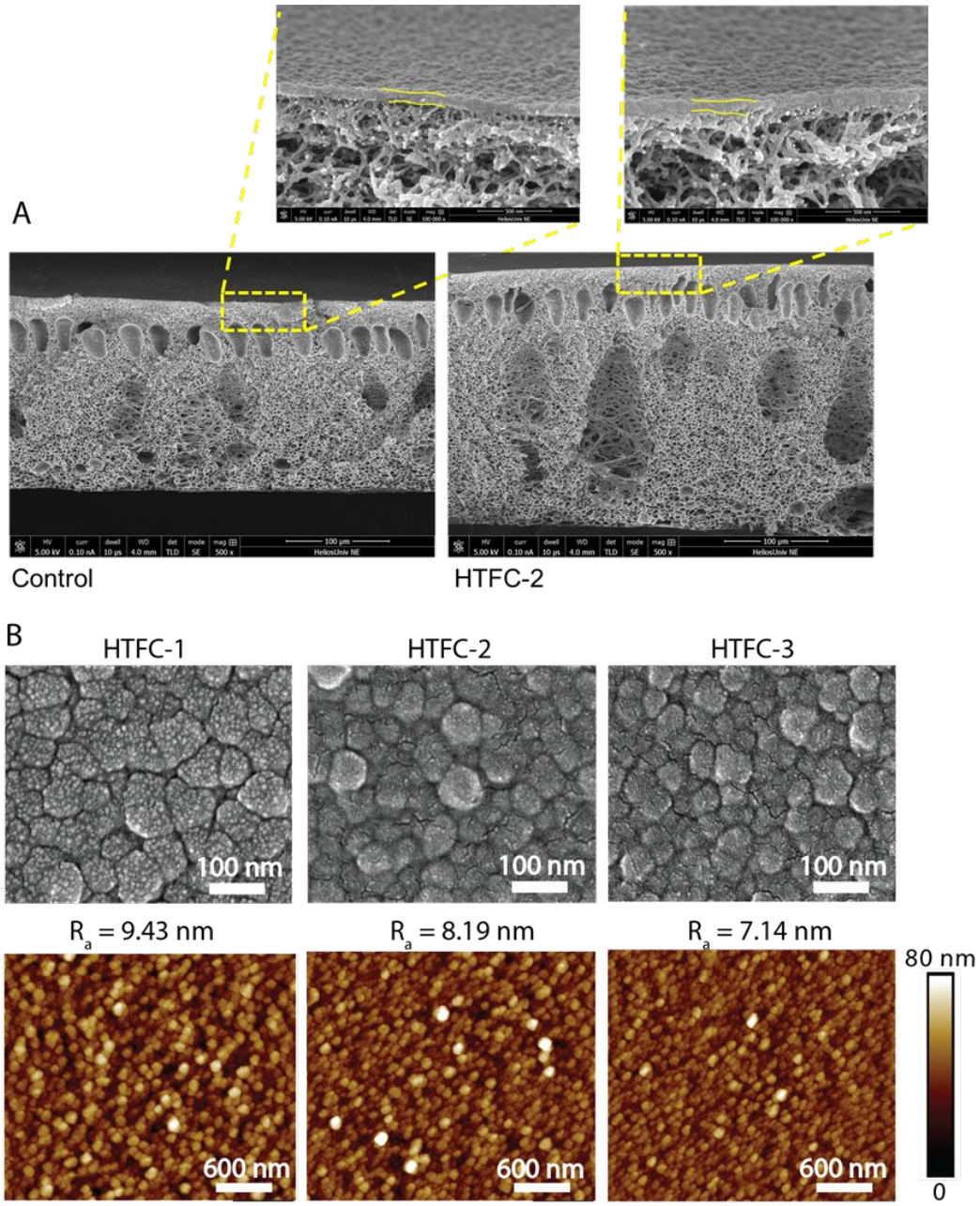


Figure S3. A) SEM cross-sectional images of HTFC-1 and HTFC-4 membranes and B) SEM and AFM surface images of HTFC-1, HTFC-2 and HTFC-3 membranes.

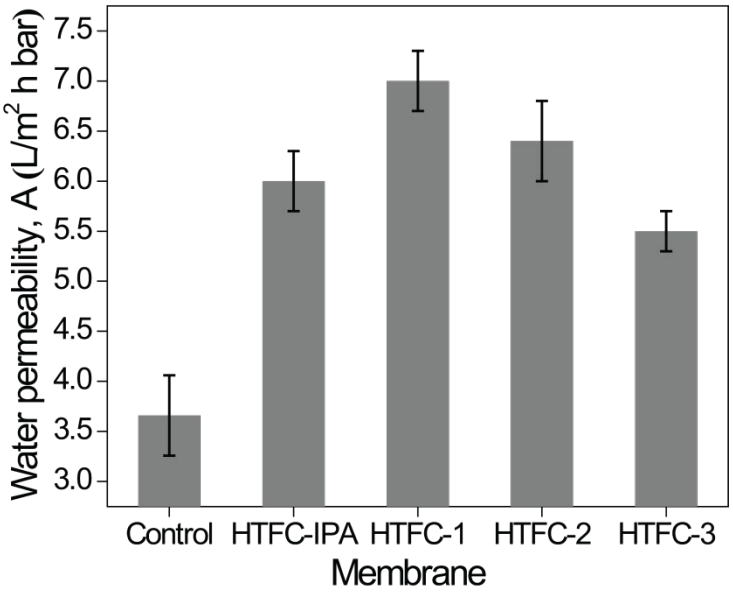


Figure S4. Water permeability (A) of control and HTFC nanofiltation membranes at 150 psi (10.3 bar) and 20 ^{o}C.

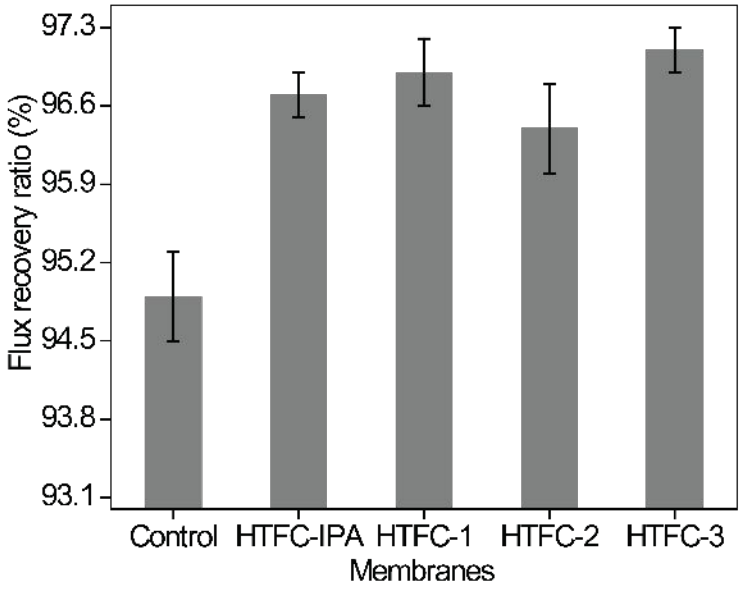


Figure S5. Flux recovery ratio of HTFC membranes.

References

1. Mohammadi Ghaleni, M.; Al Balushi, A.; Kaviani, S.; Tavakoli, E.; Bavarian, M.; Nejati, S., Fabrication of Janus Membranes for Desalination of Oil-Contaminated Saline Water. *ACS Appl. Mater. Interfaces* **2018,** 10, (51), 44871-44879.