

Supporting Information

Multifunctional amine enables formation of polyamide nanofilm composite ultrafiltration and nanofiltration membranes with modulated charge and performance

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Preparation of support membrane

The support membrane was prepared on a nonwoven fabric (TS-100, France) by the conventional phase inversion process using semi-automated casting machine. Typically, polyethersulfone (PES) powder was dried overnight at 60 °C. The PES was dissolved in DMF at concentration of 14% (w/w) under stirring at 60 °C. After complete dissolution of PES, the additive PVP (4% w/w) was added to the admixture. The solution was stirred for 2 h. The solution was allowed to settle for 12 hours at room temperature. After that, the solution was cast on the nonwoven fabric (0.3 m width and 20 m long) by semi-automatic blade casting machine at speed of 7 m/min. The gap of the blade from the platform surface was adjusted such that the thickness of the membranes was 30–40 mm excluding fabric thickness. The humidity and temperature inside the casting chamber were 30–40% and 25–27 °C respectively. The fabric was then passed through a gelation bath (rete 4 m/min) containing water. The membranes were kept in water bath for 5 h. This membrane was used as support for the preparation of TFC membranes.

Attenuated total reflection infrared (ATR-IR) Spectroscopy

The membranes formed by the SIP were directly subjected to the ATR-IR analysis. On the other, the PA films formed by the SFIP were placed on PES-based support membrane for the ATR-IR analysis. Furthermore, The PA films formed by the SFIP were directly placed on silicon wafer substrate facing upside down and were also subjected to ATR-IR analysis. Furthermore, PA films from the TFC membranes formed by SIP were isolated on mica surface. The isolated PA films faced backside up. The isolated films were used for the analysis to confirm the complete leaching of support substrate. Samples of area 3x6 cm² were employed for the analysis. All the samples were dried at air for 24 h and then placed inside a CaCl₂ filled desiccator. ATR-IR (Agilent Cary 600 series FTIR) spectra on the membrane surfaces were recorded at room temperature. A Germanium-Selenite crystal was used for recording ATR-IR spectra on 5 different positions. The degree of PA formation was obtained by the following equation:

$$DG_{PA} = \frac{I_{1637}}{I_{1585}} \quad (1)$$

where I_{1637} is the intensity of band at 1637 cm⁻¹ which is characteristic of -C=O stretching vibration of amide bond, and I_{1585} cm⁻¹ is the intensity of aromatic C=C vibration of PES support. The calculated I_{1637}/I_{1585} data are the average of at least five independent spots on each sample. The penetration depth of IR beam is about 1 μ which is much higher than the PA film thickness. Hence, it may be considered that the intensity of band at 1585 cm⁻¹ remained almost unchanged in different membranes and the variation of I_{1637}/I_{1585} value for different membrane is due to the variation of intensity of band at 1637 cm⁻¹.

Cross-sectional TEM analysis

The polyester fabric was detached from PES support. The PES supported PA film was then put in isopropanol for an hour and then embedded in epoxy resin (Epon-812 substitute, Sigma Aldrich). The embedded sample was cured at 45 °C for 12 h and then at 60 °C for 24 h. The cross-sections (70–90 nm thick) were prepared using Leica EM UC 6 ultramicrotome and mounted onto carbon coated copper grids. The cross-sectional TEM analysis was then performed on JEOL JEM 2100.

Determination of molecular weight cut-off (MWCO) of support membrane

The support membrane was prepared by the addition of PVP (4% w/w) additive to the solution of PES (14% w/w) in DMF through conventional non-solvent induced phase inversion process to make it porous. The PEO (400 kDa) solution (500 mg/L) was permeated through the different membrane swatches. The support membrane gave about 90% rejection of PEO of molecular weight (M_n) 400 kDa. The GPC traces (Fig. S1) of feed

PEO (400 kDa) and permeates confirmed that the MCWO of the membrane is 400 kDa. This membrane was used for the preparation of TFC membranes via the conventional supported interfacial polymerization (SIP).

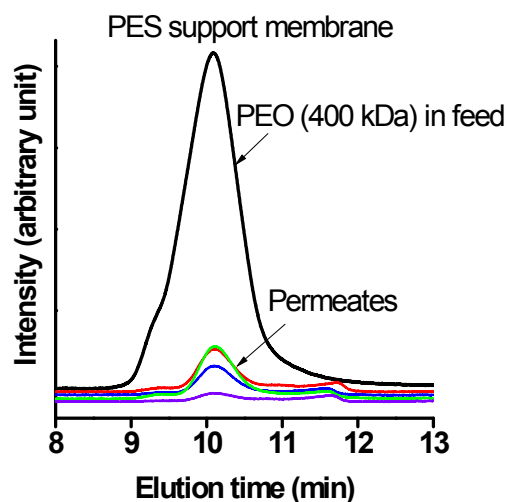


Fig. S1 GPC traces of PEO (400 kDa) in feed and permeates. The permeation experiments were undertaken with PES support membrane at applied pressure 3.5 bar. Permeates were collected after 10 min of permeation through different membrane swatches. Before the permeation of PEO solution, the membranes (four different membrane swatches) were pressurized with pure water at 4 bar for 4 h to obtain steady flux. The average rejection of PEO (400 kDa) was calculated to be about 90%.

ATR-IR analysis of the nanofilms

The TFC membranes formed by the SIP were placed on mica substrate facing backside up. The support membrane was leached out as described in the experimental part (main manuscript). The ATR-IR spectra of the isolated PA films were recorded (Fig. S2). The spectra shows band (1660 cm^{-1}) of amide stretching vibration and no band for PES support. This indicates the complete leaching of PES substrate. On the other hand, the blank substrate shows no band at 1660 cm^{-1} .

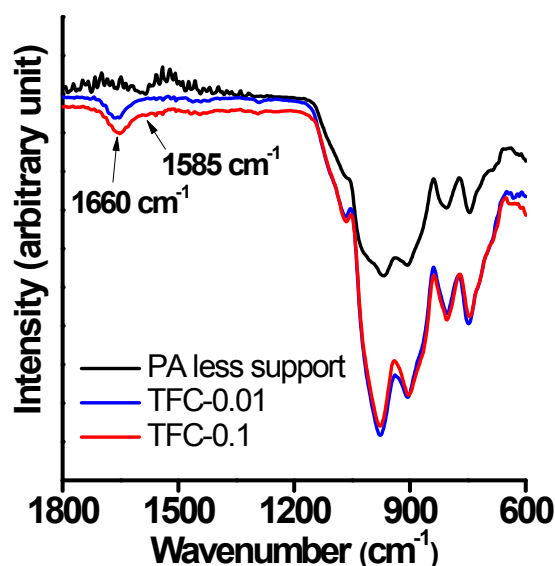


Fig. S2 ATR-IR spectra of the blank substrate surface, and isolated PA nanofilm on the substrate. The membrane after detaching from polyester fabric were placed on the surface with backside up and then the support membrane was leached out (experimental, main text) for the ATR-IR analyses.

Standardization experiments

The amount of TMC required to obtain best TFC membrane in terms of salt rejection efficiency was evaluated. This was performed by preparing supported and support free PA films using fixed concentration of PEI (0.05% w/v) and different concentration of TMC.

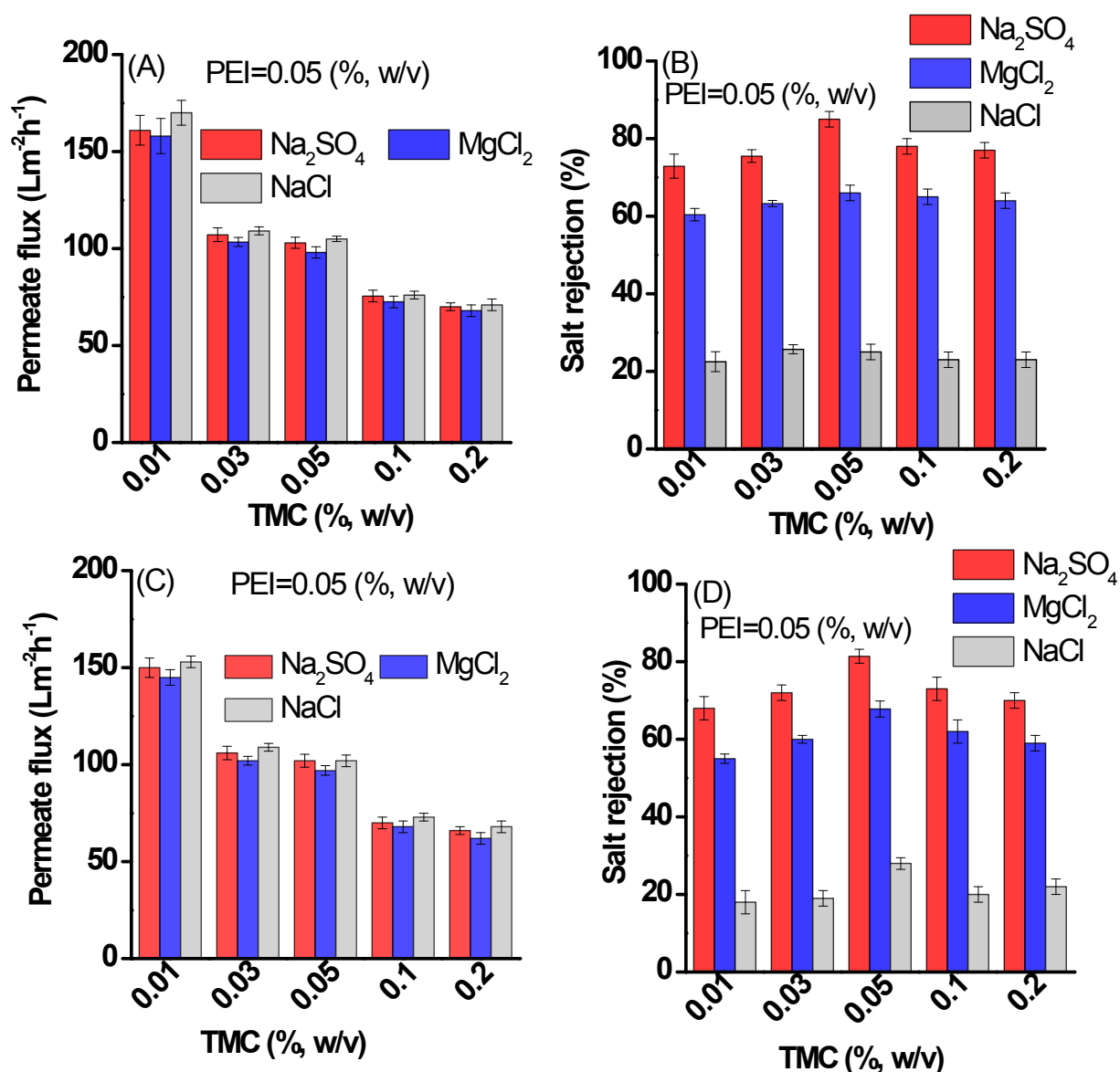


Fig. S3 Performance of TFC NF membranes prepared by varying the concentration TMC with fixed concentration of PEI (0.05%, w/v in water) via the (A and B) SIP, and (C and D) SFIP. The contact time of base membrane in PEI and TMC was 3 min and 2 min respectively. The NF operation was undertaken using 1500 mg/L of aqueous salt as feed solutions at 28 ± 4 °C and at applied pressure 5.2 bar. The membranes were first pressurized at 7 bar for 2 h to obtain steady flux and then the NF operations were performed at applies pressure of 5.2 bar.

The support free polyamide film was placed on the support membrane for the evaluation of performance. Fig. S3A and S3B shows the permeate flux and different salts rejection by the supported TFC membranes. The results of permeate flux and salt rejections of the TFC membranes (SF-TFC) obtained by SFIP are summarized in Fig. S3 C and D. The results show that TMC concentration of 0.05% w/v gave best salt rejection performance.

Hence, focused was oriented to prepare PA layer of TFC membranes using 0.05% w/v TMC and varying the concentration of PEI. The lowering of rejection of Na_2SO_4 with lowering of TMC concentration is attributed to the increase of pore size of the membranes, since the zeta potential of the membranes did not change significantly. It was found that a 0.05% w/v concentration of TMC gave best glucose rejection efficiency of the resultant membrane.

Variation of contact time in TMC solution

Fig. S4 shows the variation of performance in terms of salt (A), and glucose rejection (B) efficacy of the membranes with the variation of reaction time of PEI absorbed membrane with TMC. The concentration of PEI and TMC was kept to 0.05% w/v as obtained by the standardization experiments. The contact time of the base membrane in PEI was 3 min. The reaction time with TMC of about 2 min of PEI amine absorbed membrane gave best salt rejection efficacy. The membrane obtained after 2 min reaction time with TMC gave about 90% rejection of glucose (Fig. S10 B, vide infra) and was defect free as confirmed by TEM analysis (Fig. S8, vide infra). The rejection of glucose reduced to about 50% and 70% when the contact time was 0.5 min and 1 min respectively (Fig. S4B). Thus sufficient reaction time is required to obtain defect free films on support membrane at low concentration of the monomers. Previously, formation of defect in the film was reported at short contact time in TMC bath for piperazine-based (PIP) membrane.¹

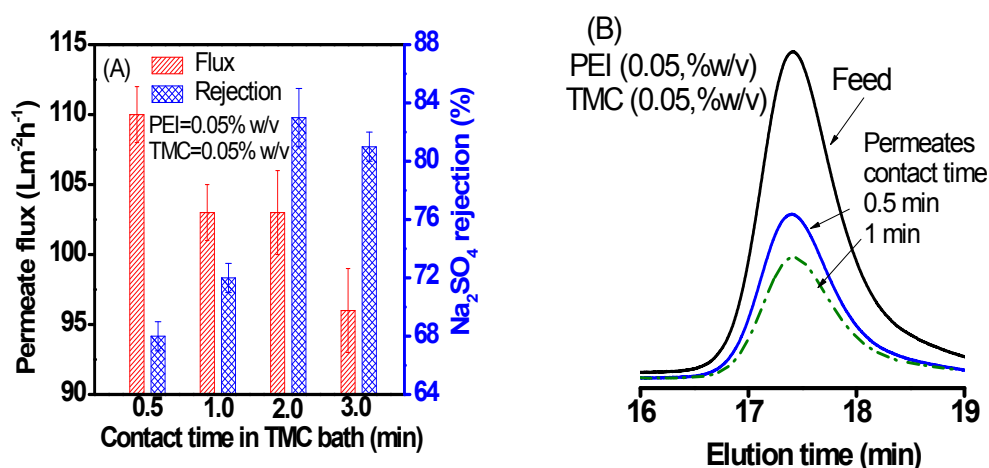


Fig. S4 (A) Variation of salt rejection and permeate flux, and (B) rejection of glucose (GPC traces of feed glucose and permeates) by the membrane with the variation of contact time of PEI (0.05% w/v) absorbed membrane with TMC (0.05% w/v). The membranes were first pressurized at 7 bar for 2 h to obtain steady flux and then the NF operations were performed at applies pressure of 5.2 bar. Salt concentration was 1500 mg/L and glucose concentration was 500 mg/L in the feeds.

Front surface SEM and AFM images of the PA films of SF-TFC membranes

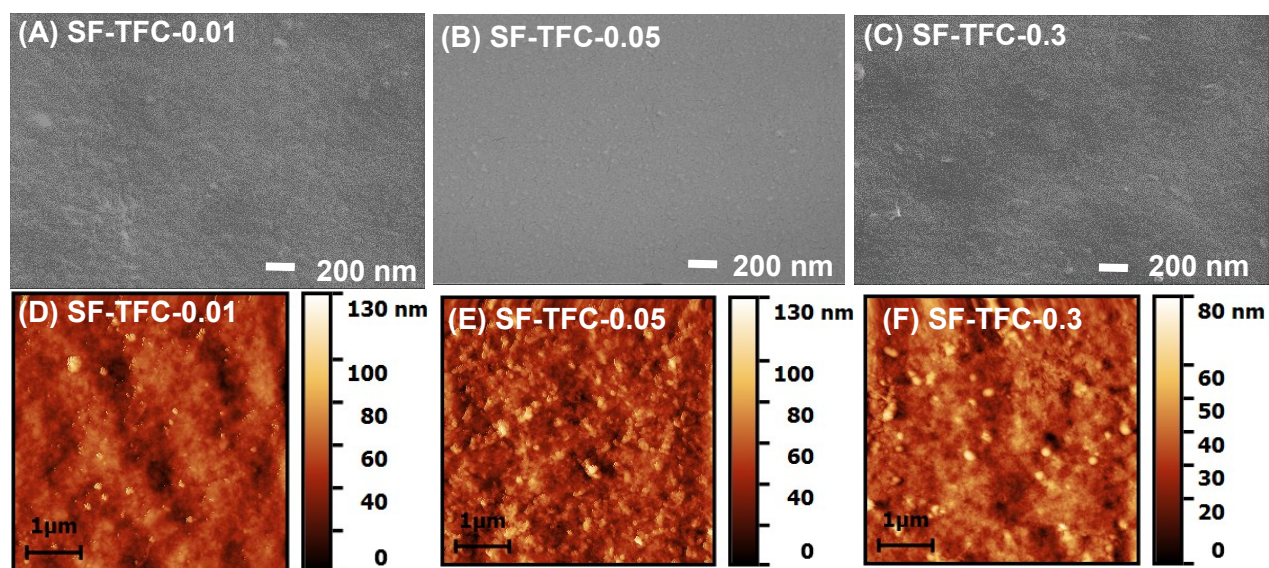


Fig. S5 (A-C) Front surface SEM (x50k), and (D-F) AFM images of representative SF-TFC-0.01, SF-TFC-0.05, and SF-TFC-0.3 membranes.

Determination of thickness of PA films of SF-TFC membranes by AFM and SEM analyses

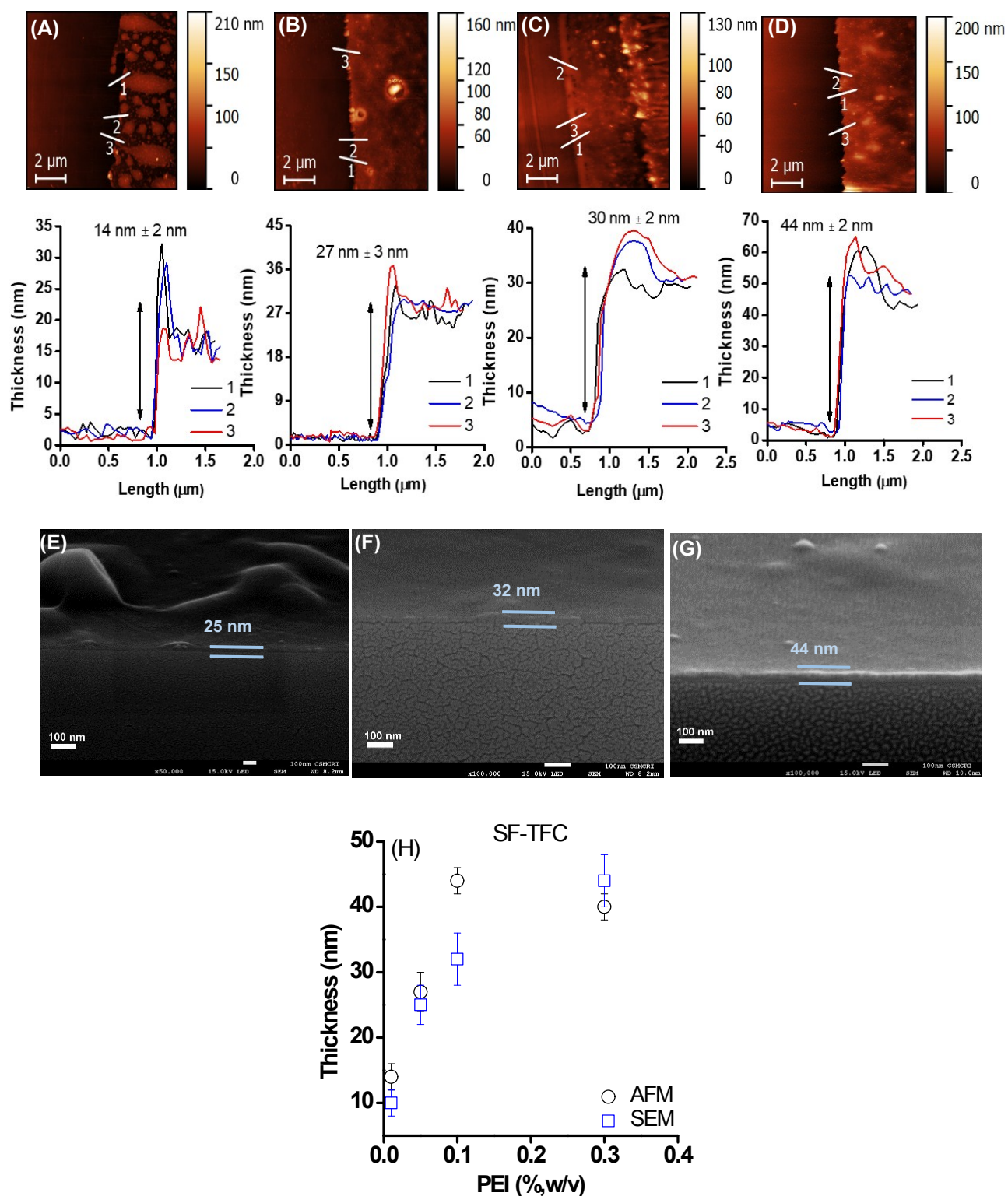


Fig. S6 (A-D) AFM images and cross-sectional height profiles of isolated PA films of SF-TFC-0.01, SF-TFC-0.05, SF-TFC-0.1, and SF-TFC-0.3 membranes. (E-G) Cross-sectional SEM images of PA films of SF-TFC-0.05, SF-TFC-0.1, and SF-TFC-0.3 membranes. (H) Variation of thickness of PA films with the variation of PEI concentration in the IP process. The PA films formed by SFIP were directly placed on silicon wafer.

ATR-IR spectra of TFC membranes

Fig. S7 A shows the ATR-IR spectra of as prepared (SIP) TFC membranes. Fig. S7B shows the ATR-IR spectra of the SF-TF membranes. In the later membranes, the PA films were placed on PES support and then characterized by ATR-IR spectroscopy. The membranes show a characteristic band at 1660 cm^{-1} due to amide-I vibration. The band at 1585 cm^{-1} is attributed to the aromatic C=C vibration of PES support. The band at 1585 cm^{-1} remained almost unchanged in the thickness range of PA films of 10-50 nm since the penetration depth of IR beam is about $1\text{ }\mu\text{m}$. The degree of polyamide formation was calculated by equation 1 as described above. The degree of PA formation is plotted against the concentration of PEI used for the preparation of PA films (Fig. 4K, main text).

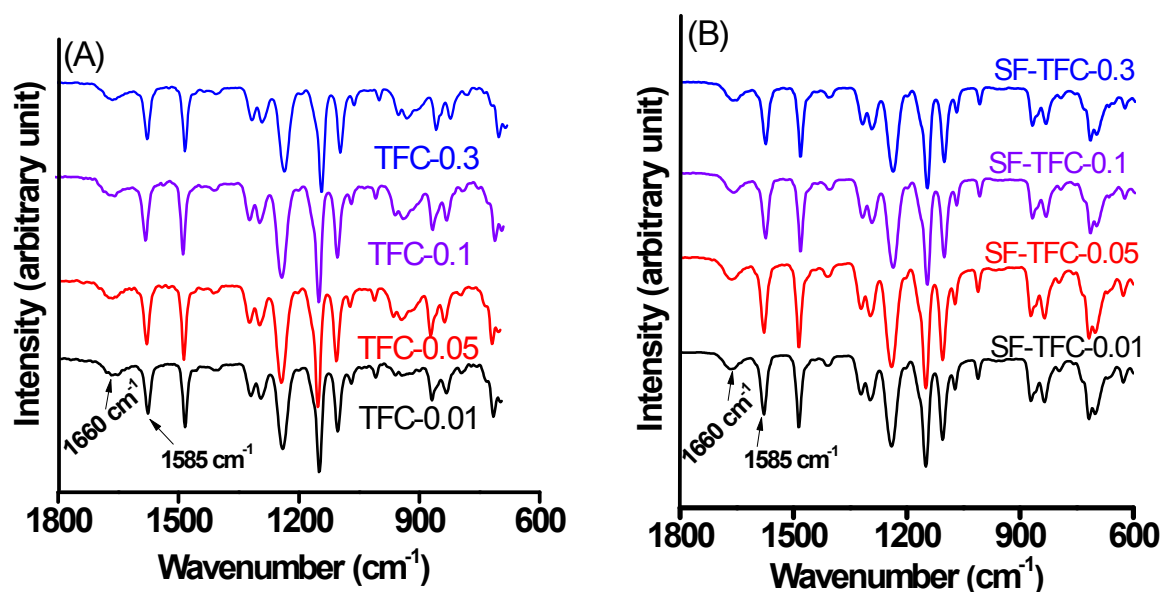


Fig. S7 ATR-IR spectra of TFC membranes formed by SIP and SFIP processes. (A) ATR-IR spectra of as prepared TFC-0.01, TFC-0.05, TFC-0.1, and TFC-0.3 membranes were recorded wherein the membranes were prepared by conventional way (SIP process). (B) The PA films formed by the SFIP process were placed on PES membrane substrate to obtain SF-TFC-0.01, SF-TFC-0.05, SF-TFC-0.1, and SF-TFC-0.3 membranes and then the ATR-IR spectra were recorded. The membranes were dried in air and then kept inside CaCl_2 filled desiccator for 48 h before the analysis.

Morphology of PA film through TEM

First the PA films formed in the liquid-liquid interface were floated in water. Next, the films were attached on carbon coated copper grid.¹ The PA films of SF-TFC-0.03 and TFC-0.03 membranes prepared by reacting TMC of concentration 0.05% w/v and PEI of concentration of 0.03% showed no defect at the micron scale (Fig. S8). High magnification TEM images (Fig. S8C and S8D) show the formation of defect free PA film on entire sub-micron length scale. Thus concentration of PEI as low as 0.03% w/v also gave defect free PA film.

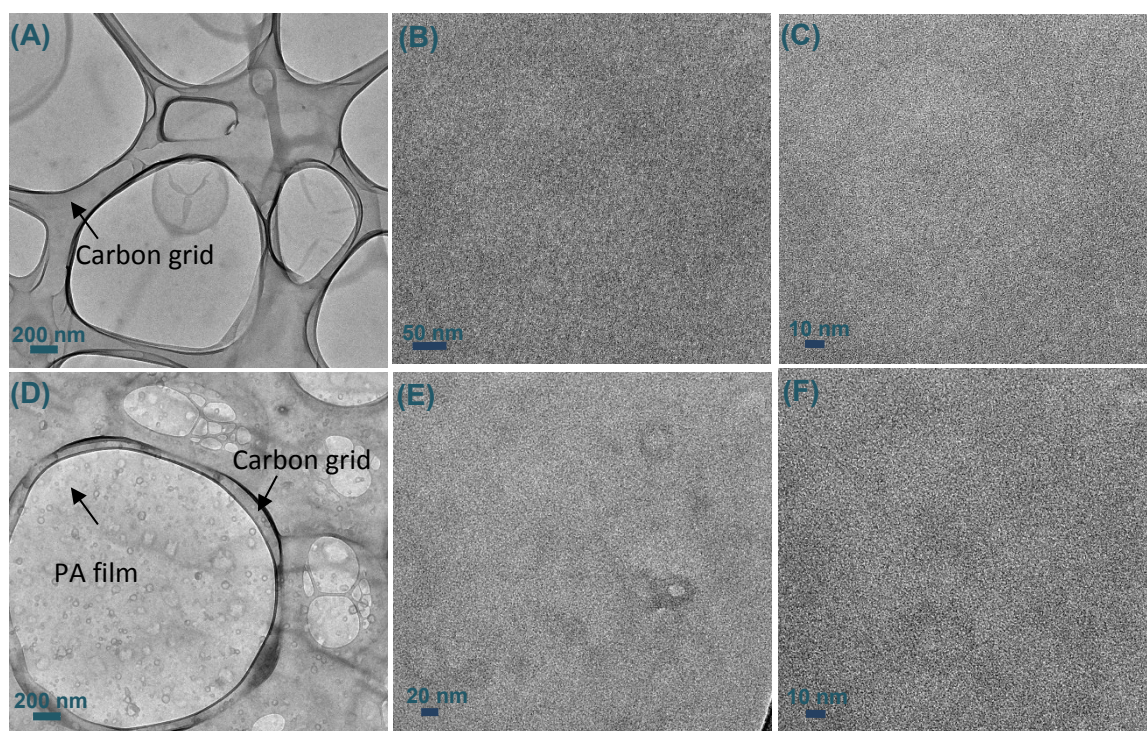


Fig. S8 Isolated PA films formed by SFIP process were observed under TEM on carbon coated grid where (A-C) SF-TFC-0.03, and (D-F) TFC-0.03 respectively.

Glucose rejection and salt rejection efficacy of PIP-based membrane

A PIP-based membrane was prepared by IP between PIP (0.1 % w/v) and TMC (0.05% w/v) on top of PES support. The salt rejection efficacy and glucose rejection was evaluated. This membrane gave poor Na_2SO_4 (77%) and glucose (50%) rejections. Fig. S9 shows the GPC traces of feed glucose and permeates water. In contrast to the above results, TFC NF membrane formed by PIP (2% w/v) and TMC (0.1% w/v) shows high Na_2SO_4 (>96%) and glucose (~90%) rejections. This is attributed to the formation of defect in PIP-based membrane at this low PIP concentration.

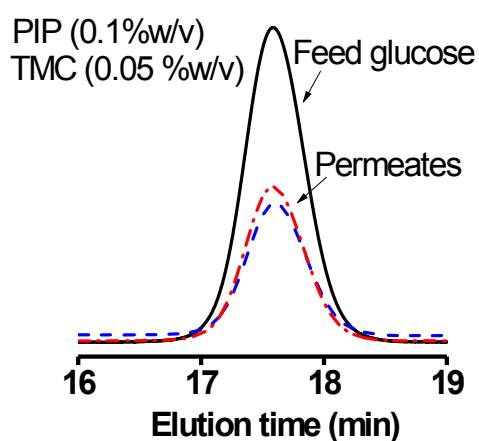


Fig. S9 Rejection of glucose by the PIP-based membrane as determined by GPC analysis.

Evaluation of MWCO of different TFC membranes by glucose and PEG permeation experiments

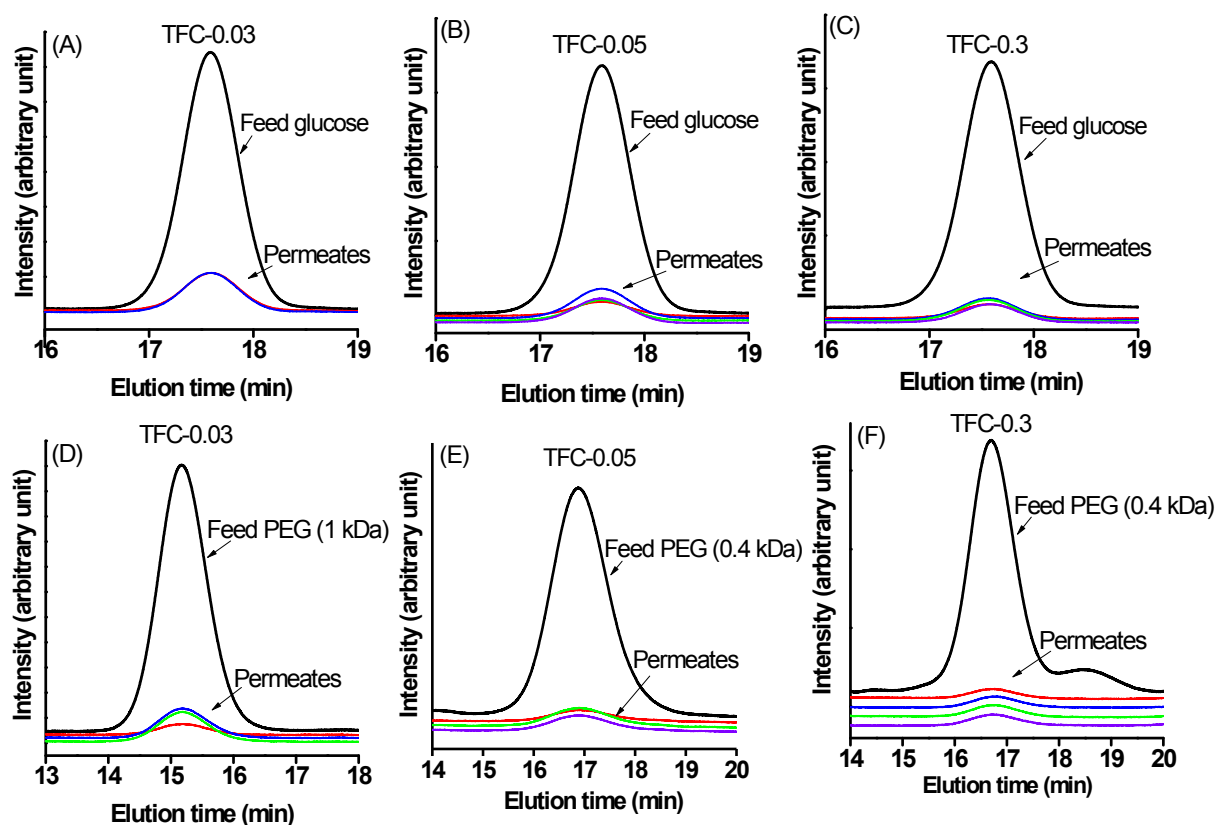


Fig. S10 (A-C) GPC traces of feed solutions of glucose (500 mg/L) and permeate solutions obtained after NF operation with TFC-0.03, TFC-0.05, and TFC-0.3 membranes. (D-F) GPC traces of PEG in feed solutions (500 mg/L) and permeates obtained after NF operation. The M_n of PEG was 1 kDa (D) for TFC-0.03 membrane and 0.4 kDa (E and F) for TFC-0.05 and TFC-0.3 membranes. Four different membrane swatches of each kind of membranes were employed for the permeation operation. Average rejection of different batches of the membranes was taken.

Performance of TFC ultrafiltration membrane (TFC-0.03) during concentration of PEG (2 kDa)

The rejection of PEG molecules of M_n s 1 kDa (Fig. 4D, main text) and 2 kDa (Fig. S11) slightly increases with filtration time while the permeate flux decreases. This is attributed to the initial fouling of the membranes by the PEG molecules. It may be noted that the initial flux during PEG (2 kDa) concentration is less than that of PEG (1 kDa). This indicates fouling is more prevalent with increasing M_n of PEG. About 20% decrease of initial flux occurred during concentration of PEG solutions.

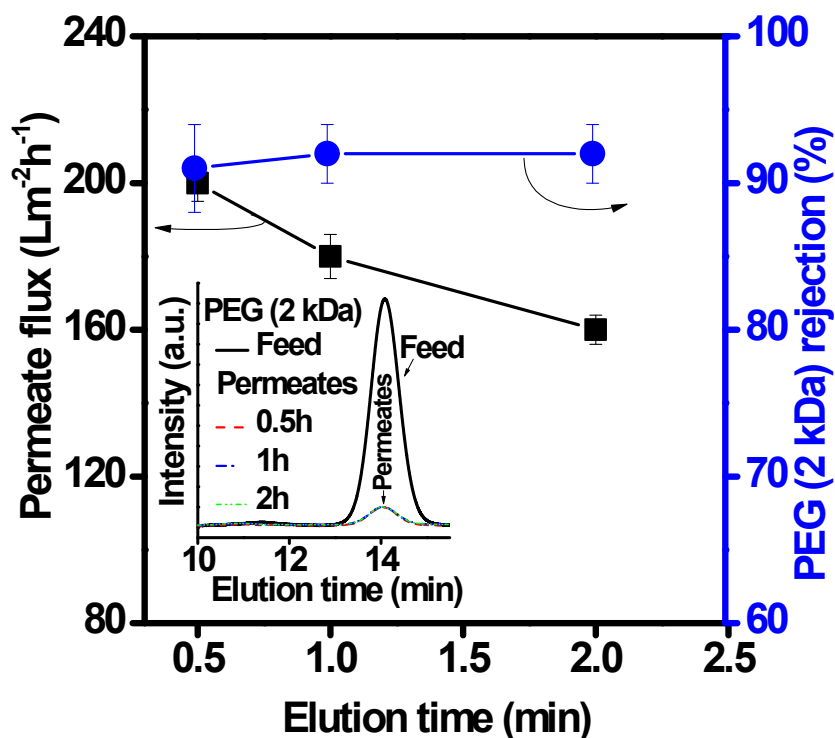


Fig. S11 Variation of permeate water flux and rejection of PEG (2 kDa) with time during concentration of feed containing PEG (2 kDa) using TFC-0.03 membrane. Inset: GPC traces of PEG in the feed and permeates. The PEG concentration in the feed was 500 mg/L and applied pressure was 5.2 bar. The membranes were pressurized with pure water at 7 bar for 4 h to reach steady flux and then the permeation experiments were undertaken.

Performance of SF-TFC set of membranes during removal of different salts from feed water

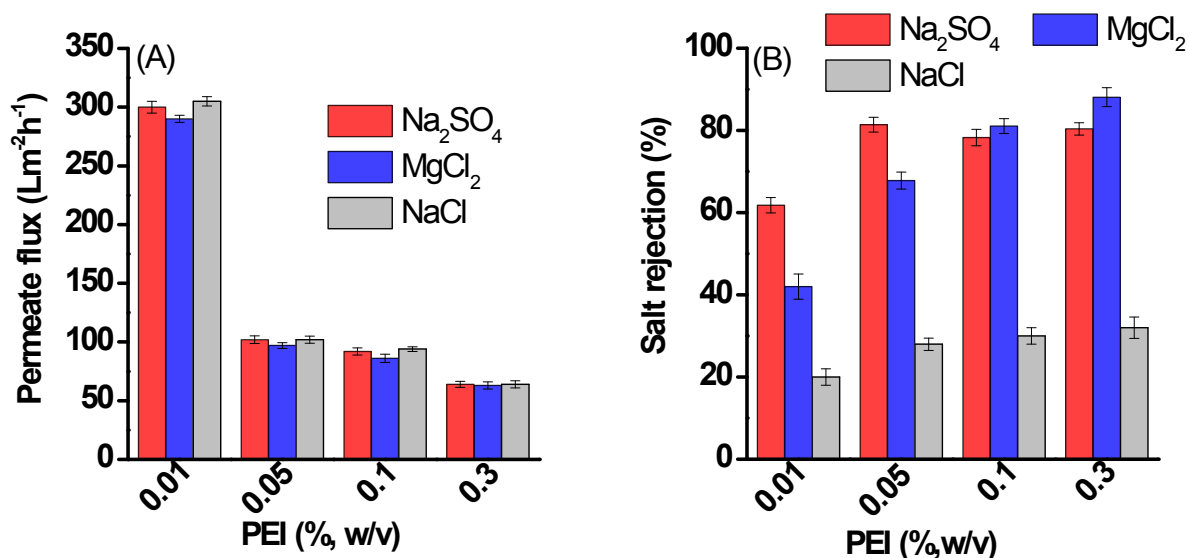


Fig. S12 (A) Permeate water flux, and (B) salts rejection efficiency of SF-TFC sets of membranes prepared with varying concentration of PEI. The concentration of feed solution was 1500 mg/L for the separate feeds, and the applied pressure was 5.2 bar. The membranes were pressurized with pure water at 7 bar for 4 h to reach steady flux and then the permeation experiments were undertaken.

Separation of NaCl and PEG (1 kDa) from feed by permeating through TFC-0.03 membrane

Separation of NaCl (1000 mg/L) from PEG (1 kDa, 500 mg/L) was undertaken using TFC-0.03 membrane at applied pressure 5.2 bar. After permeation of solution containing mixture of NaCl and PEG, GPC was performed. GPC traces of initial feed and permeates obtained after different time of permeation showed >90% rejection of PEG molecules (Fig. S13). The NaCl rejection was only about 12-15%. The GPC trace of concentrated feed is also shown in the Figure.

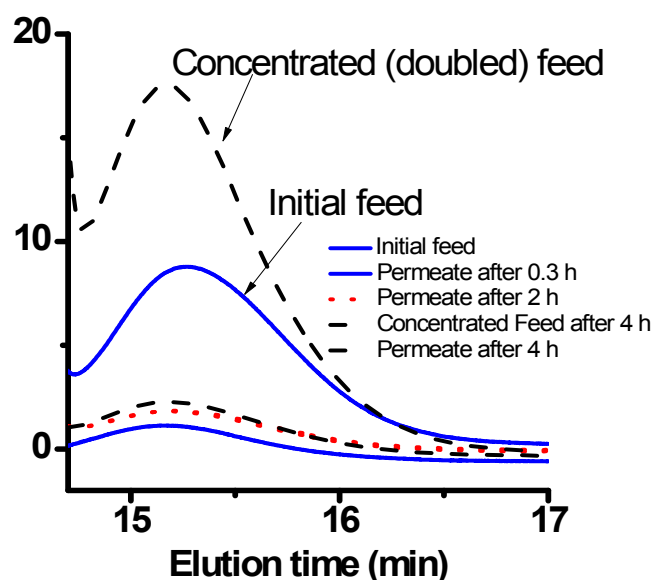


Fig. S13 GPC traces of initial feed containing NaCl (1000 mg/L) and PEG (1 kDa, 500 mg/L), feed obtained after 4 h of permeation through the membrane (doubly concentrated), and different permeates obtained after 0.3 h, 2 h and 4 h of continuous filtration.

Antifouling property of TFC NF membranes

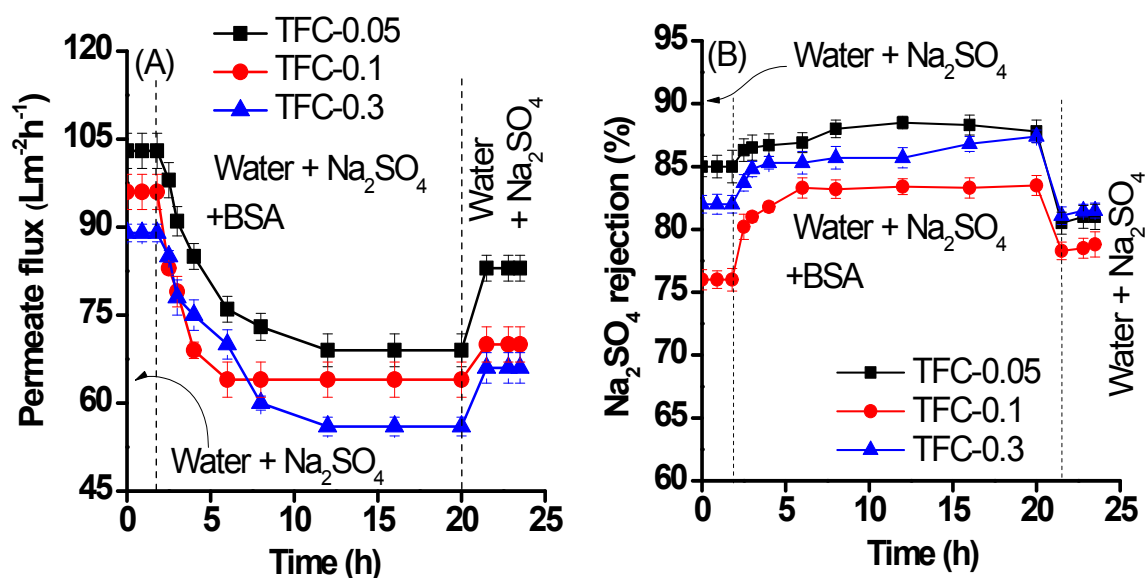


Fig. S14 (A) Permeate water flux, and (B) rejection of Na_2SO_4 with time during NF of water containing Na_2SO_4 (1500 mg/L) and additionally spike with BSA (300 mg/L). The feed pH=7, temperature~27 °C and applied pressure=5.2 bar. The membranes were pressurized with pure water at 7 bar for 4 h to reach steady flux and then the permeation experiments were undertaken.

Mechanical stability of the membranes

The performance of the membranes in terms of Na_2SO_4 rejection efficiency and permeate water flux was determined at different applied pressure. Up to 20 bar pressure was applied. The membranes performance was recorded with time at each applied pressure. The experiment was again repeated to evaluate the change of performance if any (Fig. S15).

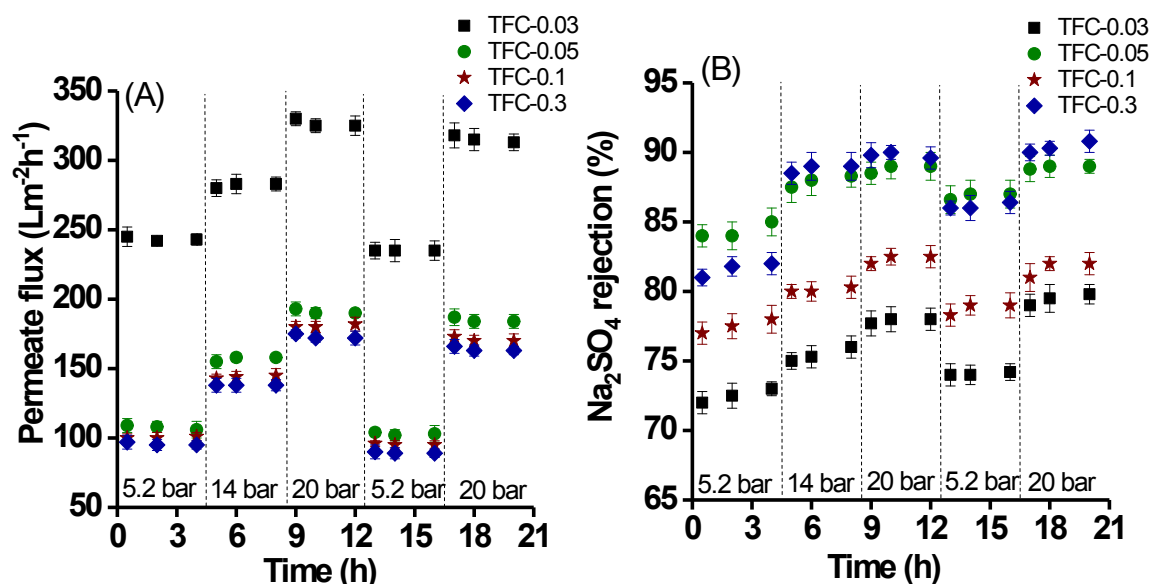


Fig. S15 (A) Permeate water flux, and (B) Na_2SO_4 rejection by the membranes with time at each applied pressure. The experiments were conducted with feed water containing 1500 mg/L Na_2SO_4 at pH 7 and at temperature about 28 °C. The membranes were initially pressurized at each pressure for 4h to obtain steady flux.

References

- 1 S. Karan, Z. Jiang, A. G. Livingston, *Science*, 2015, **348**, 1347.