Tailoring polyamide thin film composite nanofiltration membrane by polyethyleneimine and its conjugates for enhancement of selectivity and antifouling property

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Estimation of permeability coefficient, effective pore radius (r_p), effective thickness to porosity ratio (l_p/ε_p)

Separation performance of TFC membranes was evaluated using stainless steel dead end filtration system with a feed volume of 500 mL and an effective membrane area of 13.8 cm^2. The solute rejection (SR) experiments were performed using 500 ppm solutions of sucrose. The pore size was estimated from SR under limiting conditions where the SR reaches a limiting. The concentrations of solutes in the feed and permeate were analyzed by gel permeation chromatography. The rejection of sucrose was determined from eqn. 3 (manuscript). Although SR is influenced by concentration polarization, its effect was assumed negligible due to the high stirring rates employed in the permeation tests. The r_p derived from rejection data of sucrose was obtained as follows. The pore size was estimated from SR under limiting conditions where the SR reaches a limiting value, $SR_{(lim)}$ at a certain applied pressure. In the steric exclusion model, $SR_{(lim)}$ is expressed as

$$SR_{(lim)} = 1\text{-}\Phi K_{ic} \qquad (1)$$

wherein the steric term, $\Phi = (1-\lambda)^2$; hindrance factor, $K_{ic} = (2-\Phi)\, G\,(\lambda,0)$ when solute velocity is fully developed inside the pore where G=lag coefficient, and λ=ratio of solute radius, r_s to r_p. The r_s value of sucrose was taken from the literature. For $0<\lambda<0.8$, G is expressed as

$$G\,(\lambda,0) = 1.0 + 0.054\lambda\text{-}0.988\lambda^2 + 0.441\lambda^3 \quad (2)$$

Values of r_p of the membranes were obtained by fitting eqn. 4 to the observed rejection data. The volumetric permeate flow rate for pure water, Q_p, was converted into membrane permeability coefficient, L_p, using Eq. 6,

$$L_p = Q_p/PA \qquad (3)$$

where P and A are the applied hydraulic pressure and membrane area in the test cell, respectively. Data of L_p and r_p were used to determine the pore structure factor (l_p/ε_p) from the Hagen–Poiseuille pore flow model (eqn. 7).

$$Lp = \frac{r_p^2}{8\mu(l_p/\varepsilon_p)} \qquad (4)$$

Where μ is the viscosity of pure water (assumed to be 0.001 Pa s at room temperature), l_p is the active layer thickness and ε_p is the porosity.

Organic antifouling property during NF of water contaminated with BSA and sealants

The membranes swatches were initially pressurized at 1 MPa pressure for 1 h with Na_2SO_4 solution (1500 ppm) and then initial flux and Na_2SO_4 rejection were measured at pressure 0.7 Mpa. Then permeation of Na_2SO_4 (1500 ppm) solution spiked with BSA protein (250 ppm) was performed for 24 h with different membrane swatches. The pH of the feed solution was 7.1. The temperature during testing was ~24 ^{o}C. The rejection efficiency and flux during filtration experiments were evaluated. Antifouling property was determined in terms of flux reduction ratio (%FR) by the following equation:

$$\%FR = \frac{J_0 - J_t}{J_0} \times 100 \quad (5)$$

where J_0 is the initial flux during water desalination (containing Na_2SO_4) (after 1 h of pressurization) and J_t is the flux at a given time of desalination of water contaminated by BSA. After 25 h of filtration, membranes were washed with deionized water for 10 min and the flux (J_c) and rejection of the cleaned membranes were measured again by permeating water (containing 1500 ppm Na_2SO_4). In order to evaluate the fouling property of the membrane, the flux recovery ratio (FRR %) was also calculated by the following equation:

$$FRR\% = \frac{J_c}{J_0} \times 100 \quad (6)$$

Estimation of Mg^{2+}, Ca^{2+}, SO_4^{2-}, Na^+, K^+ and Cl^-

EDTA, standardized against $ZnSO_4$ by using Eriochrome Black T (EBT) indicator, was used to titrate for estimation of Mg^{2+} and Ca^{2+}. Firstly, total concentration of Mg^{2+} and Ca^{2+} in solutions of both feed and filtrate was determined. Then, 10 ml aliquot was taken in 100 ml Erlenmeyer conical flask followed by addition of 10 ml NH_4OH-NaCl buffer. Now, standardized EDTA was added dropwise from burette till color was changed from pink to dark blue at end point titrated against using EBT.

For estimation of only Ca^{2+} from feed water, 10 ml aliquot was taken in 100 ml Erlenmeyer conical flask followed by addition of 10 ml 1(N) NaOH. Then, standardized EDTA was added dropwise from burette till color was changed from violet to sky blue at end point titrated against using PNR indicator.

To estimate the Na^+ and K^+ concentration for evaluation of rejection of both salts Digital Flame Analyzer (Cole-Parmer Instrument, Model 2655-00) was used. The instrument was initially calibrated by NaCl and KCl of 0.05% for determination of concentrations of NaCl and KCl respectively.

Cl^- ion was estimated titration method. First, the stock solution was dilute 200 times. Then, 10 ml aliquot was titrated with silver nitrate solution using chromate indicator. At the end point of titration, pale yellow color of the solution was changed to reddish brown.
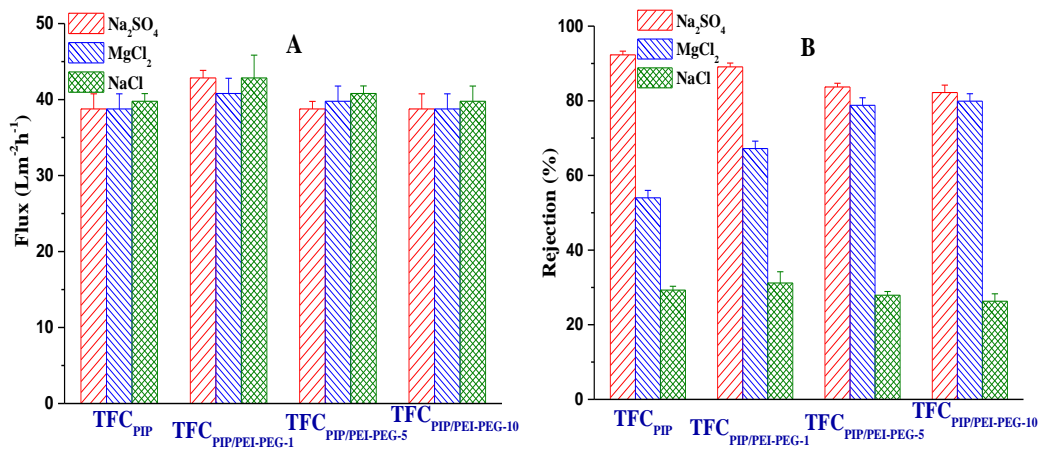
Sulphate ion (SO_4^{2-}) concentration was estimated gravimetrically. Aliquot was heated at 75 ^{o}C for 3 hr and acidified by hydrochloric acid. Then excess barium chloride solution (6%) was added to it until complete precipitation. This solution was then centrifuged at 8000 rpm for 10 minutes and washed thoroughly with hot water. Obtained mass was dried at 100 ^{o}C to get constant weight. From this weighted value, amount of SO_4^{2-} was calculated.

**Quantification of amine functional group**

The amine functional group was quantified by using Acid Orange II. The membrane surface (5 cmx5cm) in triplicate was exposed to aqueous solution (500 µmol/L) of Acid Orange II at pH 3 for 24 h at room temperature. Then the membrane surface was thoroughly washed with distilled water of pH 3 for 1 h at room temperature. Then the absorbed dye was allowed to release in distilled water of pH 12. Next, absorbance of the released dye solution was recorded at 464 nm by using UV-Visible spectrophotometer (Shimadzu 2700). The concentration of adsorbed dye was determined by using a standard calibration curve of concentration vs. absorbance.
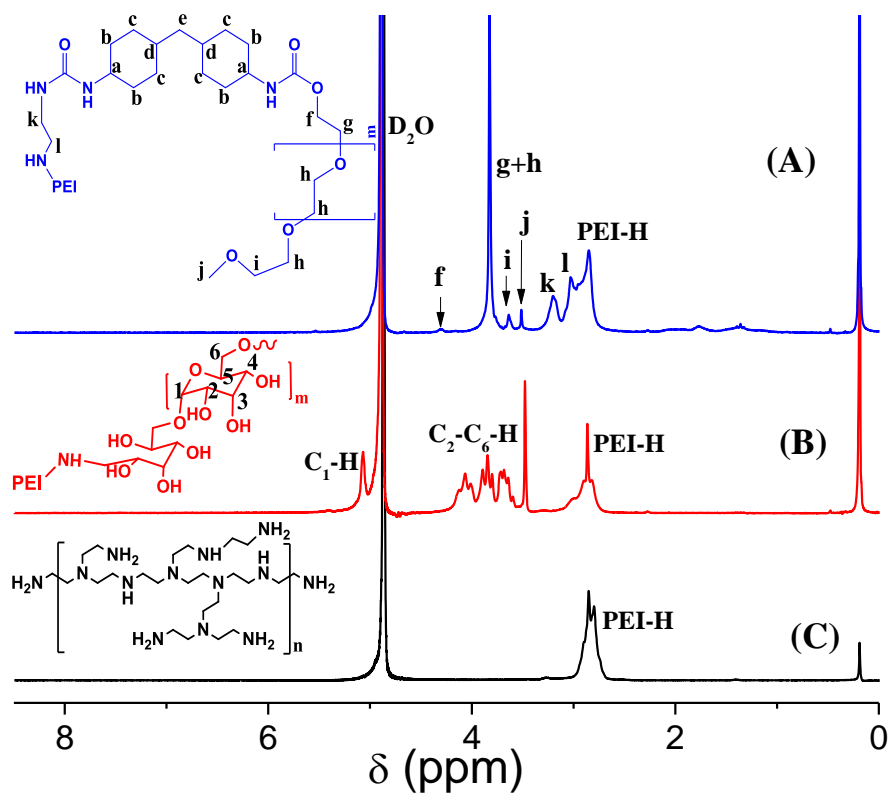
Figure S1. ^{1}H NMR spectra of (A) PEI-PEG conjugate, (B) PEI-Dex conjugate and (C) PEI were taken in D_2O. For PEI-PEG the δ 4.2 (f–H), δ 3.7 (g+h–H), δ 3.5 (i–H), δ 3.4 (j–H), δ 3.0 (k–H), δ 2.9 (l–H) and δ 2.7 (PEI–H); for PEI-Dex, the δ 4.99 (C1–H, dextrose), δ 4.0–3.4 (C2–C6–H, dextrose), and δ 2.7 (PEI–H); for PEI, the δ 2.69 (PEI–H).

Figure S2. Bar diagrams showing (A) permeate flux and (B) SR data of TFC$_{PIP}$ and membranes post modified by 1%, 5% and 10% (all in w/v) of PEI-PEG solutions respectively. Permeation experiments were carried out with separate Na$_2$SO$_4$, MgCl$_2$ and NaCl feed solutions. Feed concentration: 1500 mg/L; pH: ca.7 and operating pressure: 0.5 MPa. Averages of 4 membrane swatches with error bar are taken.
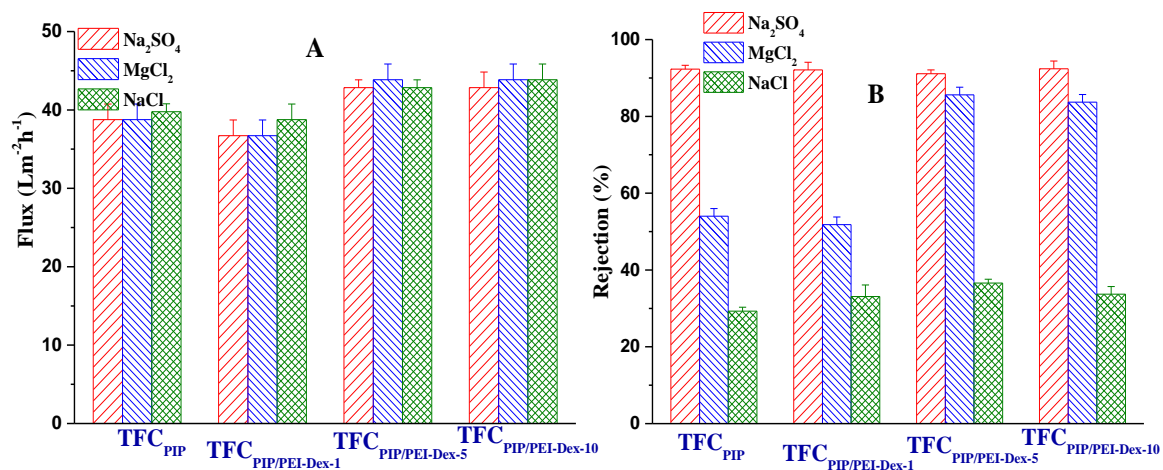
Figure S3. Bar diagrams showing (A) permeate flux and (B) SR data of TFC_{PIP} and membranes post treated with 1%, 5% and 10% PEI-Dex solutions respectively. Permeation experiments were carried out with separate Na_2SO_4, $MgCl_2$ and NaCl feed solutions. Feed concentration: 1500 mg/L; pH: ca.7; operating pressure: 0.5 MPa. Averages of 4 membrane swatches with error bar are taken.
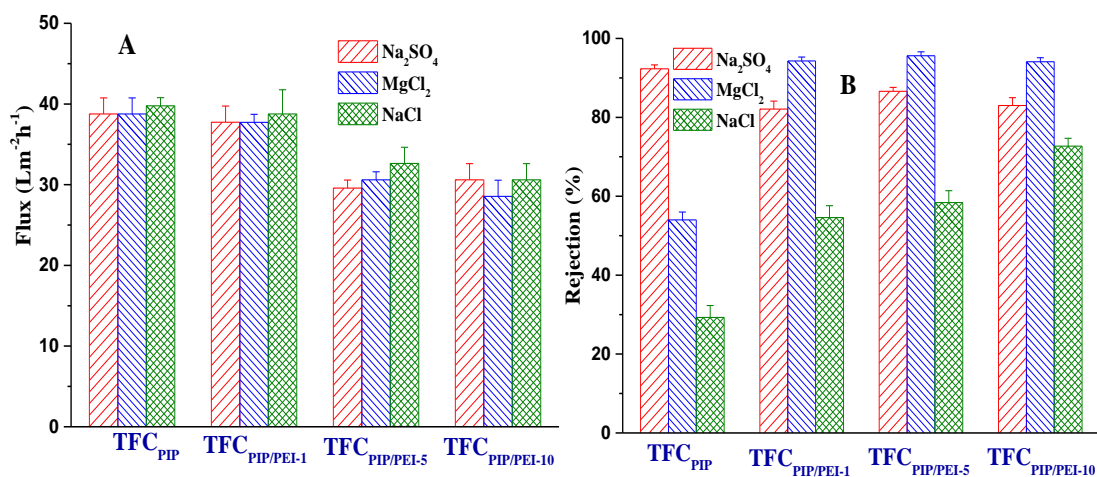
Figure S4. Bar diagrams showing (A) permeate flux and (B) SR data of TFC$_{PIP}$ and membranes post treated with 1%, 5% and 10% PEI solutions respectively. Permeation experiments were carried out with separate Na$_2$SO$_4$, MgCl$_2$ and NaCl feed solutions. Feed concentration: 1500 mg/L; pH: ca.7; operating pressure: 0.5 MPa. Averages of 4 membrane swatches with error bar are taken.
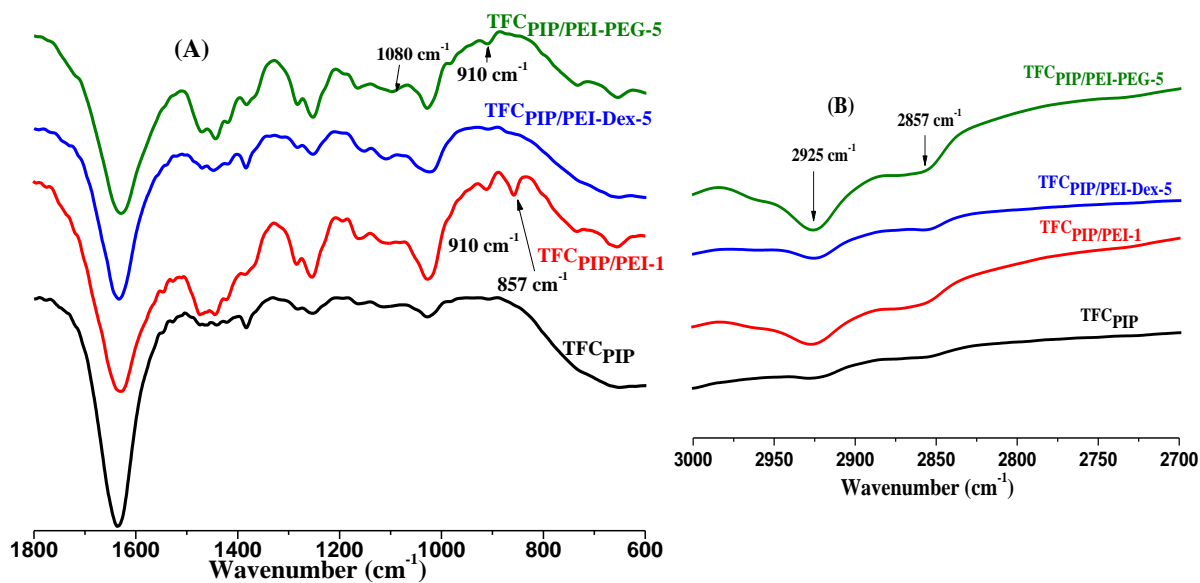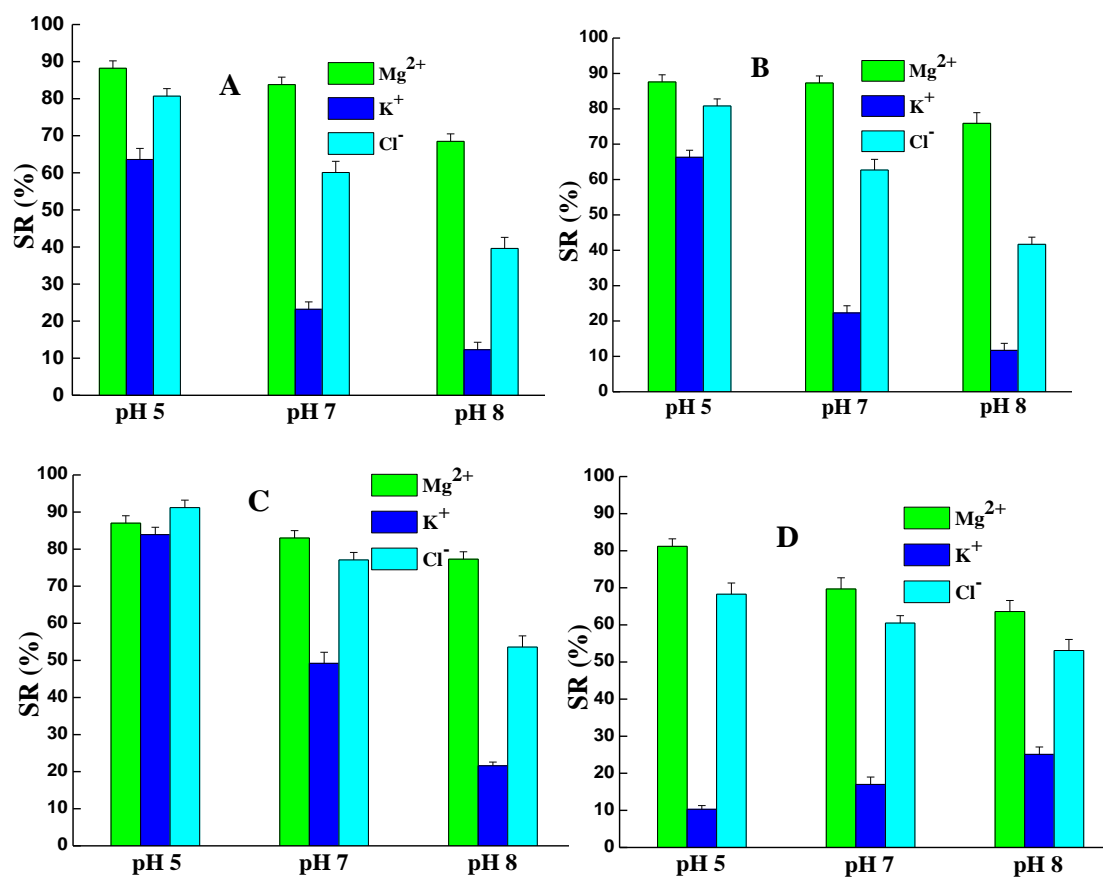
Figure S5. IR spectra of cross linked masses collected from TFC$_{PIP/PEI-PEG-5}$, TFC$_{PIP/PEI-Dex-5}$, TFC$_{PEI-1}$ and TFC$_{PIP}$. The membranes were detached from fabric and PSf support was completely leached out by DMF. The masses were then again extracted with DMSO and then water and THF followed by drying in vacuum oven for IR analysis.
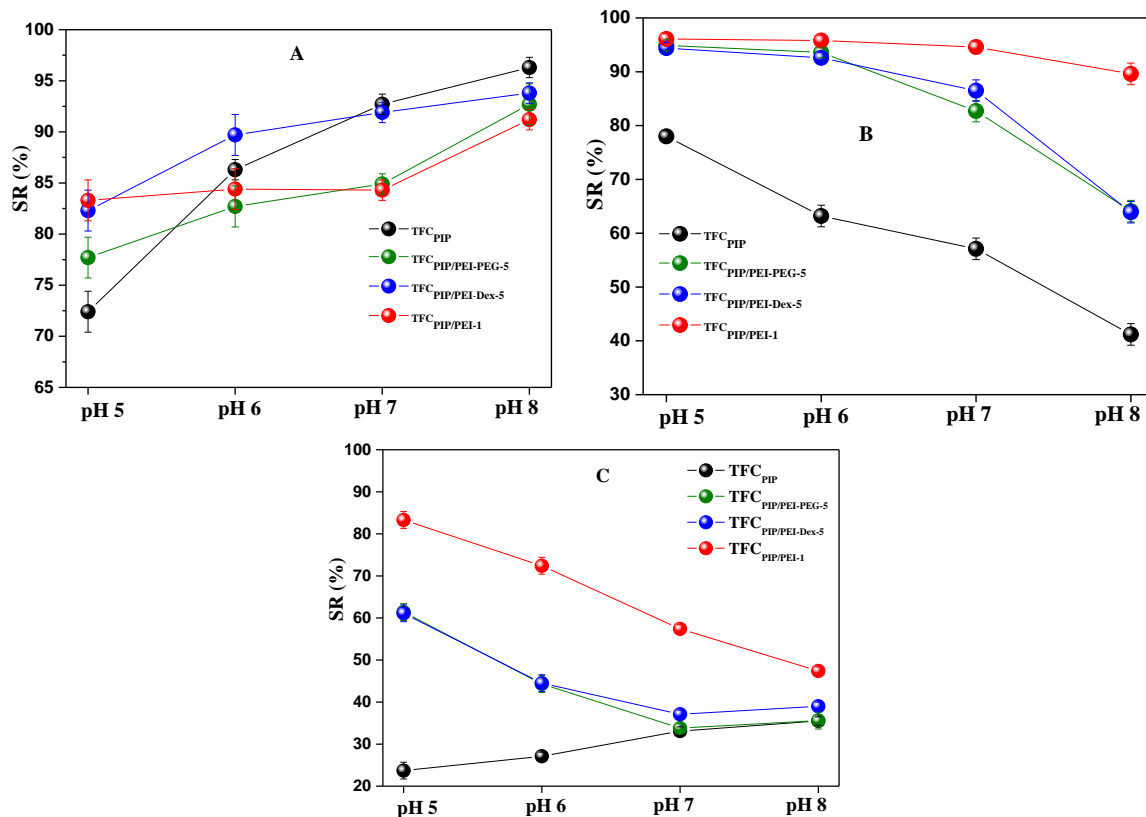
Figure S6. Variation of Na$_2$SO$_4$, MgCl$_2$ and NaCl SR with the variation of feed pH by the TFC$_{PIP/PEI-PEG-5}$, TFC$_{PIP/PEI-Dex-5}$, TFC$_{PIP/PEI-1}$, and TFC$_{PIP}$, during NF of separate feed solutions. Plots A-C are for NF experiments with feed solutions containing Na$_2$SO$_4$, MgCl$_2$ and NaCl respectively. Feed concentration: 1500 mg/L; feed temperature: 27 ^{o}C and operating pressure: 0.5 MPa. Averages of 4 membrane swatches with error bar are taken.

Figure S7. Mg^{2+}, K^+ and Cl^- SR by the (A) $TFC_{PIP/PEI-PEG-5}$, (B) $TFC_{PIP/PEI-Dex-5}$, (C) $TFC_{PIP/PEI-1}$ and (D) TFC_{PIP}, during NF of feed solutions containing mixture $MgCl_2$ (750 mg/L) and KCl (750 mg/L). Total feed concentration: 1500 mg/L feed temperature: 27 °C and operating pressure: 0.5 MPa. Feed pH varied from 5-8. Averages of 4 membrane swatches with bar error are taken.

Table S1. Selectivity of different membranes at three different pH.

Membrane	[a]Selectivity	pH 5	pH 7	pH 8
TFC$_{PIP}$	$S_{Na^+/Mg^{2+}}$	2.7	1.4	1.3
	$S_{Na^+/SO_4^{2-}}$	1.7	3.7	5.3
TFC$_{PIP/PEI-PEG-5}$	$S_{Na^+/Mg^{2+}}$	4.1	3.6	1.7
	$S_{Na^+/SO_4^{2-}}$	2.3	2.9	4.5
TFC$_{PIP/PEI-Dex-5}$	$S_{Na^+/Mg^{2+}}$	3.9	2.8	1.8
	$S_{Na^+/SO_4^{2-}}$	2.4	3.6	3.9
TFC$_{PIP/PEI-1}$	$S_{Na^+/Mg^{2+}}$	0.8	3.8	3.1
	$S_{Na^+/SO_4^{2-}}$	0.5	3.5	5.4

a-Selectivity= $(100-SR_{Na})/(100-SR_{ion})$