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

Anupam Bera and Suresh K. Jewrajka[*]

Reverse Osmosis Membrane Division, AcSIR, CSIR-Central Salt and Marine Chemicals Research Institute, Bhavnagar, Gujarat, India

We report here a suitable surface modification process for state-of-art poly(piperazineamide) thin film composite (TFC) nanofiltration (NF) membrane by polyethyleneimine (PEI) and its conjugates (PEI-polyethylene glycol and PEI-dextran) for enhancement of monovalent ion to divalent ion selectivity and antifouling property. The nascent TFC NF membrane was treated with PEI and its conjugates for the modification purpose. The modified membranes exhibited high rejection of divalent cations (88-91%), high rejection of divalent anions (85-92%) and low rejection of NaCl (30-50%). The membranes modified under optimized conditions exhibited much enhanced antifouling/anti-scaling property, similar permeate flux, similar Na^+ to SO_4^{-2} selectivity and much better Na^+ to Mg^{+2} selectivity compared to that of pristine membrane during desalination of water containing mixture of salts and real seawater. The adjustment in permeation property and improvement in antifouling behaviour is attributed to the adjustment of surface charge and pore size by the incorporation of multi-amine containing antifouling polyethylene glycol or dextran on the membrane surfaces by post modification process.

1. Introduction

Softening of groundwater and seawater is highly desirable for further use in domestic purpose and utilization of natural resources from the retentate and permeate streams. Nanofiltration (NF) provides great opportunity for this purpose. Specifically, NF of seawater was proposed as an advanced pretreatment step in seawater desalination by reverse osmosis (RO).[1–4] The permeate obtained from NF of seawater when used as feed for RO process significantly reduces the RO membrane fouling caused by scaling and biological and/or chemical foulants.[1-3] State-of-art poly(piperazineamide) [poly(PIP)] thin film composite (TFC) NF membranes are widely used for water purification.[5,6] Some examples of commercially available poly(PIP) TFC NF membranes are NF270 (Dow Film Tec), NF 90 (Dow Film Tec), TFC-SR2 (Koch Membrane Systems) and TFC-SR3 (Koch Membrane Systems).[7,8] Polyamide NF membranes generally show low NaCl rejection (25-50%), low $MgCl_2$ rejection (40-60%) and high rejection of SO_4^{-2} salts (92-98%) depending on the membrane preparation conditions and quality of the feed water.[9-13] This is attributed to the enhanced charge-charge repulsion between SO_4^{-2} and membrane surface whereas the Mg^{+2} ion experiences electrostatic attraction with the negatively charged membrane surface, facilitating its transport through the barrier layer.[13-15] In contrast, positively charged NF membranes exhibit higher rejection of divalent cationic salt e.g. $MgCl_2$ (90-96%) and relatively lower rejection (ca. 50-60%) of divalent anionic salts e.g. Na_2SO_4.[16,17] Chiang et al. prepared TFC NF membranes by the interfacial polymerization (IFP) of polyethyleneimine (PEI) with trimesoyl chloride (TMC) or terephthaloyl chloride (TPC).[18] The PEI/TMC and PEI/TPC membranes had the pure water permeabilities around 9.5 $Lm^{-2}h^{-1}bar^{-1}$ and 3.1 $Lm^{-2}h^{-1}bar^{-1}$ respectively. The $MgCl_2$, Na_2SO_4 and NaCl rejections by the PEI/TMC membrane were ca. 80%, 50% and 44% respectively whereas the rejections were ca.

93%, 73% and 60% respectively for PEI/TPC membrane. The positively charged NF membrane prepared with PEI and epichlorohydrin exhibited ca. 93%, 70% and 61% rejections of $MgCl_2$, $MgSO_4$ and NaCl respectively.[19] Apart from trade-off rejection between bivalent cationic salt (e.g. $MgCl_2$) and bivalent anionic salts (Na_2SO_4) by most of the NF membranes, one serious shortcoming with these membranes is the fouling during desalination and purification of water.[15,20-24] Indeed, TFC RO membranes also undergo severe fouling.[25-27]

Post or in situ modification of TFC NF membranes is simple strategy to cope with the fouling problem and tuning the performance of the membranes.[27] Poly(amidoamine) dendrimer was grafted on TFC NF membrane surface for improving the rejection of heavy metal ions and enhancing surface hydrophilic character.[28] Recently, Shaffer et al. reported post modification TFC forward osmosis membrane by amine terminated polyethylene glycol (PEG) based block copolymer for improvement of organic fouling resistant.[29] Sequential IFP between PEI and TMC on support membrane led to formation of TFC NF membrane with improved salt separation.[30] The salts (NaCl, Na_2SO_4, $MgCl_2$ and $MgSO_4$) rejections enhanced with numbers of IFP cycle. TFC NF membranes prepared by mixture of PEI and PIP exhibited higher $MgCl_2$ rejection (>90%) and low Na_2SO_4 rejection (50-60%) with improved permeate flux (30-40 $Lm^{-2}h^{-1}$) at applied pressure 0.8 MPa.[31] Interestingly, poly(PIP) membrane prepared with 3% PIP for IFP with TMC exhibited high rejection of both divalent cation and anion due to much higher cross-linking density which excessively reduced the permeate flux (5 $Lm^{-2}h^{-1}$ at 0.8 MPa applied pressure).[31] Moreover, the membrane usually is not antifouling.

In view of fouling tendency and trade-off rejection berween SO_4^{-2} and Mg^{+2} or Ca^{+2} ions by the NF membranes, the objective of this work is the simple treatment of nascent poly(PIP) NF membrane for (i) enhancing SO_4^{-2}, Mg^{+2} and Ca^{+2} rejections keeping Na^+ rejection almost unaltered and (ii) improving the antifouling property for softening of both contaminated water and natural seawater without compromising the permeate flux. It was hypothesized that the treatment of freshly prepared poly(PIP) NF membrane (containing unreacted –COCl moieties) by PEI (A) and its conjugates viz. PEI-PEG (B) or PEI-Dextran (PEI-Dex) (C) will be useful for lowering the extent of surface charge (negative or positive) and enhancing the antifouling character of the resulted membranes compared to pristine membrane (Fig. 1).
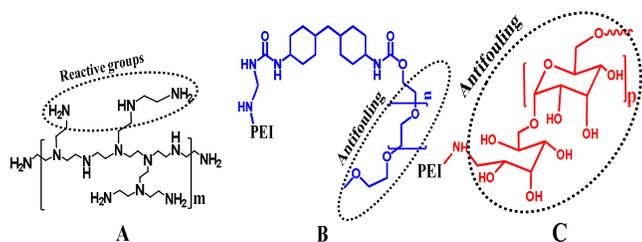

Fig. 1 (A) PEI, (B) PEI-PEG and (C) PEI-Dex used for post treatment of poly(PIP) TFC NF membrane.

With the above mentioned objective and hypothesis, herein, we report preparation of low charge poly(PIP) TFC NF membranes by IFP between PIP and TMC followed by treatment with PEI-PEG or PEI-Dex conjugates. Treatment of nascent membrane with neat PEI was also performed to compare the properties of the modified membranes. The modified membranes exhibited higher rejection of both the divalent salts from model ground water and real seawater from Gujarat coast. The membranes obtained by treatment with PEI-PEG, PEI-Dex and PEI conjugates under optimized conditions exhibited superior antifouling/anti-scaling property and similar permeate flux than that of pristine membrane during desalination of water containing protein or desalination of seawater. Best antifouling property was obtained with PEI-PEG and PEI-Dex modified membranes. In best of our knowledge there is no report for the improvement of both antifouling/anti-scaling property and rejection of bivalent cationic and anionic salts by PEI conjugates modified poly(PIP) NF membrane.

2. Experimental

2.1. Materials

Polysulfone (PSf, Udel P-3500) obtained from Solvay Polymers was dried at 80 ^{o}C for 2 h. TMC (98%), PEI (M_n=2000 g/mol), Dex (M_n=12000 g/mol), polyethyleneglylcol methylether (HO-PEG-OMe, M_n=750), sodium cyanoborohydride (NaBH$_3$CN, 98%), 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI), dibutyltin dilaurate and Acid Orange II, all Aldrich products were used as received. PIP, bovine serum albumin (BSA), dichloromethane (DCM) and dimethylformamide (DMF) all from SD Fine Chemicals, India and were used as received. Non-woven polyester fabric (Nordlys-TS100) was used as received. All salts namely NaCl, KCl, CaCl$_2$, MgCl$_2$ and Na$_2$SO$_4$ were procured from Spectrochem, India.

2.2. Preparation of PEI-Dex and PEI-PEG Conjugates

PEI-Dex conjugate was prepared by following the procedure as reported earlier.[32] Dex (10 g, M_n=12000 g/mol) was solubilized in DMSO-water mixture (100 mL, 9:1, v/v). PEI (3.75 g, M_n=2000

g/mol) was added to dextran solution under vigorous stirring. Next, NaBH$_3$CN (0.2 g) was added in the reaction mixture and the admixture was stirred for 48 h at room temperature. The NaBH$_3$CN was added into the reaction vessel in an amount of 0.05 g each after each 12 h interval. The reaction mixture was precipitated into methanol (300 mL). The precipitated mass was then again solubilized in DMSO and re-precipitated into methanol. This step was done to remove unreacted PEI from the PEI-Dex conjugate. ^{1}H NMR spectrum (200 MHz) of the product in D$_2$O indicated formation of PEI-Dex conjugate (Fig. S1, [†]ESI). The δ 5.0–4.9 (C1–H, dextrose), δ 4.1–3.4 (C2–C6–H, dextrose), and δ 2.8–2.5 (PEI–H).

Synthesis of PEI-PEG conjugate was accomplished by two-step process.[33] The steps include synthesis of isocyanate terminated PEG (PEG-NCO) followed by synthesis of PEI-PEG. Briefly, to synthesis PEG-NCO, azeotropically dried HO-PEG-OMe (4 g) was dissolved in dry DCM (5 mL). HMDI (10 mL) was also taken in dried DCM (5 mL). Then, HO-PEG-OMe was added drop wise to HMDI solution placed in round bottom flask (100 mL) containing 3 drops dibutyltin dilaurate with proper stirring. After complete addition, the reaction mixture was refluxed for 8 h. The product was concentrated and precipitated in hexane. The product was again re-dissolved in DCM and re-precipitated in hexane. After execution of this process several times, the viscous polymer (PEG-NCO) was obtained.

PEI-PEG was synthesized by reacting PEI and previously synthesized PEG-NCO. Briefly, azeotropically dried PEI (5 g) was dissolved in dry DCM (100 mL). PEG-NCO (5 g) was dissolved dry DCM (50 mL). Then, PEG-NCO solution was added slowly to PEI solution with continuous stirring. The reaction mixture was refluxed for 12 h. Then, the solution was concentrated and precipitated in diethyl ether. The precipitated mass was re-dissolved in DCM and re-precipitated in diethyl ether 3-4 times. Yellowish product was procured and characterized by ^{1}H NMR. ^{1}H NMR spectrum of the product in D$_2$O assured formation of PEI-PEG conjugate (Figure S1, [†]ESI). The δ 4.2 (h–H, dextrose), δ 3.7 (g+h–H, dextrose), δ 3.5 (i–H, dextrose), δ 3.4 (j–H, dextrose), δ 3.0 (k–H, dextrose), δ 2.9 (l–H, dextrose) and δ 2.7 (PEI–H).

2.3. Preparation of Poly(PIP) TFC NF Membrane

The PSf support membrane (molecular weight cutoff 100 KDa) was prepared on non-woven fabric following the previously reported procedure.[15,25] Water wet PSf support membrane (20 cm x 20 cm) was then attached on a glass slide using tape and immersed in 2% (w/v) aqueous solution of PIP for 20 s. It was then removed from the PIP solution. The surface of the membrane was gently rolled with a soft rubber roller to eliminate small bubbles, if any. The membrane was then dipped into a 0.125% (*w/v*) solution of TMC in hexane for 60 s. It was thereafter heat cured at 60 ^{o}C for 2 min, washed several times with water thoroughly and finally stored in 10% (*w/v*) glycerol in water.[15]

2.4. Treatment of nascent poly(PIP) Membrane

The poly(PIP) membranes were prepared same way as described earlier by the interfacial polymerization (IFP) between PIP and TMC on PSf support membrane. After that, TMC solution in hexane was completely drained off at room temperature (relative humidity 60% and temperature 27±2 ^{o}C) for 10s. Then the membranes were separately dipped into the aqueous solution of PEI, PEI-Dex and PEI-PEG respectively for 180 s. The concentrations of PEI-PEG, PEI-Dex and PEI were varied for post-modification. After post-modification, the membranes were washed with water to remove the excess amine from their surfaces. The membranes were then washed

several times with water prior to storage in water containing 10% (w/v) glycerol.

The membranes were characterized by Attenuation total reflectance infrared spectroscopy (ATR-IR), Zeta potential (ξ), atomic force microscopy (AFM) and scanning electron microscopy (SEM) as described earlier.[15,26] The permeability coefficient (L_p), effective pore radius (r_p) pore structure factor (l_p/ε_p) (where, l_p=thickness and ε_p=porosity) were calculated from the Hagen–Poiseuille pore flow model as described earlier.[15,34] The amine groups on the membrane surface were estimated by the modified procedure (supporting information).[35]

2.5. Permeation Property of Membranes

The performance of the membranes were evaluated in a RO test kit for water desalination using 1500 mg/L concentration of NaCl, KCl, MgCl$_2$, CaCl$_2$, Na$_2$SO$_4$ and combination of some of these salts separately as feed solutions at 0.5 MPa after obtaining steady flux through initial pressurization at 0.7 MPa for 1 h. The permeate flux was calculated by using the following equation.[15,19,20]

$$J = \frac{V}{At} \quad (1)$$

where J is the permeate flux (Lm^{-2}h^{-1}); V is the volume of water permeated (L), A is the membrane area (m^2) and t is the permeate time (h). The salt concentrations in the feed and permeate were determined by measuring the electrical conductivity of the solutions using digital conductivity meter (EuTech Instrument, Con 700). The salt rejection (SR) was determined using the following expression:[15]

$$SR\% = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

where C_f and C_p stands for the salt concentrations in the feed and permeate, respectively. Averages of 6-8 swatches were taken with standard deviation. The protein antifouling property was determined as reported earlier (supporting information).[15,25,26]

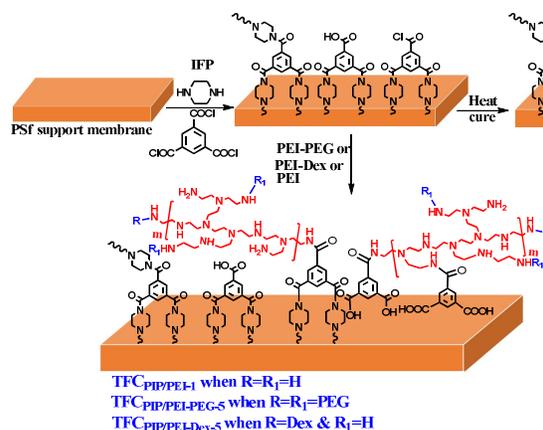### 2.6. Seawater desalination by NF and evaluation of anti-scaling property

For NF of seawater with total dissolved solid (TDS) 35000 mg/L and to evaluate the anti-scaling property of the membranes, initially the membrane swatches were pressurized at 1.7 MPa for 1 h and performance were recorded at 1.4 MPa. Then the NF process was allowed to continue for 25 h. After different time intervals, the performance (flux and SR) were recorded. Detailed of evaluation of rejection of salts have been discussed in supporting information. The pH and temperature were ca. 7.4 and 26 °C. Flux reduction during the desalination process and flux recovery ratio was calculated as per Eq. 5 and Eq. 6 described in supporting information.

3. Results and discussion

3.1. Treatment of nascent poly(PIP) TFC NF membranes by PEI, PEI-Dex and PEI-PEG

Typical NF membranes contain high surface charge and the r_p values of the membranes are higher than that of hydrated divalent ions.[34] Hence, both charge-charge repulsion and size effect play an important role for the separation of ions by NF membranes. The electrostatic repulsion and attraction between membrane surface and ions are the main reasons of trade-off rejection between divalent cation and divalent anion.[9-18] Any efforts of nullifying such rejection behaviour of NF membranes by way of lowering of r_p may lead to enhancement of rejection of monovalent ions. Therefore, the monovalent to divalent ion selectivity will be lowered.[30] Hence, our main efforts is to keep the membrane surface charge close to neutral and r_p value greater than monovalent ions but comparatively close to

divalent ions. Hence, we modify nascent (uncured) polyamide NF membrane to lower the surface charge and to introduce antifouling polymers on the surface. PEI-PEG and PEI-Dex were employed for the treatment of nascent poly(PIP) TFC NF membrane owing to antifouling behavior of PEG and Dex while PEI is essential for covalent bond formation through reaction with unreacted acyl chloride (-COCl) present in the polyamide network and membrane surface. The PEI to PEG or Dex ratio in the PEI-PEG or PEI-Dex was adjusted to obtain best performance in terms of salt selectivity and antifouling property. The best results were obtained when the PEI to PEG ratio was ca. 65:35 (w/w) and PEI to Dex ratio was 15:85 (w/w). The permeate fluxes of the membranes increased with increasing amount of PEG and Dex in the conjugates in expense of significant reduction of rejection of divalent cationic salt. The antifouling property of the membranes remained almost similar with increased amount of PEG or Dex in the conjugate. Hence, two conjugates with the above mentioned compositions were employed for modification of nascent poly(PIP) membranes. The compositions of the conjugates were confirmed by ^{1}H NMR (Fig. S1, †ESI). Treatment of TFC NF membrane was also performed with neat PEI for comparison purpose. Scheme 1 shows the post treatment of nascent poly(PIP) TFC membrane. The hexane solution of TMC was drained off after IFP with PIP and then the membranes were directly treated with PEI and its conjugates. The modification took place by the reaction of amine groups of PEI and its conjugates with unreacted acyl chloride (-COCl) present in the nascent polyamide network. There is also possibility of reaction of –COCl moieties of free TMC present on the membrane surface. The unreacted free TMC was difficult to remove from the membrane surface after IFP without affecting the polyamide attached –COCl groups. This is because the removal of TMC just after IFP leads to exposure of the membrane in air which may hydrolyse the reactive –COCl present in the polyamide network. The possibility of physical adsorption of PEI and its conjugates on membrane surface cannot be ruled out due to electrostatic interaction of negatively charged membrane surface and amine groups of the modifying agents. The above mentioned process is simple, only a continuous online system is required for the preparation and post treatment of the nascent membrane for large scale preparation.

Scheme 1. Post treatment of freshly prepared poly(PIP) NF membranes for inducing antifouling/anti-scaling property and enhancement of rejection of both divalent cation and anion.

Our treatment process provided enhancement of amine moieties and lowering of carboxylic acid content on the modified membrane surfaces compared to that of the pristine membrane. This process thus limits the complete reaction of –COCl due to non-accessibility of all the unreacted –COCl to the incoming PEI and its conjugates due to steric hindrance and partial hydrolysis of the

–COCl during post modification. On the other hand, if all the -COCl moieties convert to amide then the positive surface charge will be increased a lot. This is not desirable in our targeted work since, high degree of positive or negative charge is responsible for trade-off rejection between bivalent cation and divalent anion.[16-19,31]

Initial efforts were oriented towards the standardization of required concentration of PEI-PEG, PEI-Dex and PEI for treatment of nascent poly(PIP) membrane based on permeates flux and rejection of bivalent cationic and anionic salts (Fig. S2 to Fig. S4, [†]ESI). TFC NF membranes (TFC$_{PIP/PEI-PEG-5}$, TFC$_{PIP/PEI-Dex-5}$ and TFC$_{PIP/PEI-1}$) obtained after post treatment of nascent poly(PIP) with 5% (w/v) PEI-PEG, 5% (w/v) PEI-Dex and 1% (w/v) PEI respectively exhibited similar permeate flux (ca. 40 Lm^{-2}h^{-1}) to that of pristine membrane (TFC$_{PIP}$) during NF of separate Na$_2$SO$_4$, MgCl$_2$ and NaCl feed solutions of pH 7. The permeate flux of the membranes (TFC$_{PIP/PEI-PEG-10}$ or TFC$_{PIP/PEI-Dex-10}$ or TFC$_{PIP/PEI-5}$) prepared with 10% (w/v) PEI-PEG or PEI-Dex or 5% PEI decreased to ca. 32 Lm^{-2} h^{-1} during NF of all three feed solutions (Figure. S2 to S4, supporting information). There is a dramatic effect of concentration of PEI and its conjugates used for post treatment on SR of MgCl$_2$. The SR of MgCl$_2$ reached a maximum value of 85-91% when the concentration of PEI-PEG or PEI-Dex was 5% (w/v) and concentration of PEI was 1% (w/v). On the other hand, MgCl$_2$ rejection efficiency of TFC$_{PIP}$ was only ca. 53% (Fig. S2 to S4, [†]ESI). Hence, 1%(w/v) PEI and 5%(w/v) PEI-PEG or PEI-Dex were suitable for post treatment of nascent poly(PIP) membrane. Therefore, detail characteristic features, properties and performance of TFC$_{PIP/PEI-PEG-5}$, TFC$_{PIP/PEI-Dex-5}$ and TFC$_{PIP/PEI-1}$ had been evaluated and compared with TFC$_{PIP}$ and previously reported different NF membranes.

The IR spectrum of DMSO/DMF/water leached TFC$_{PIP/PEI-PEG-5}$ mass show intensity enhanced peaks at around 1080 cm^{-1}, 910 cm^{-1}, and 2875 cm^{-1} which are ascribed to the C-O and C-C stretch, CH$_2$ rock and C-C stretch and the CH$_2$ symmetric stretch of PEG respectively (Fig. S5, [†]ESI). An intensity enhanced band for all modified membranes appears at 2925 cm^{-1} due to N-H stretching vibration (Fig. S5, [†]ESI). This result suggests that the cross-linked polyamide mass contains modifying agents which were not leached out by solvent extraction.

3.2. Characteristic features of the membranes

The concentration of amine on the surfaces of TFC$_{PIP}$ and modified membranes was determined. Fig. 2A shows the results of Acid Orange II dye tests quantifying the densities of amine groups on membrane surfaces. The Acid Orange II electrostatically bound on the membrane surfaces at pH 3, when the amine groups were protonated.[35] Shaffer et al. also reported the determination of carboxylic acid density by Toluidine Blue O dye which was electrostatically bound to the surfaces at pH 11, when the surface carboxylic groups were deprotonated.[29] Our modified membranes showed two to four fold higher amine density than that of TFC$_{PIP}$. Specifically, estimated amine groups on the membrane surfaces follows the order, TFC$_{PIP/PEI-1}$>TFC$_{PIP/PEI-PEG-5}$>TFC$_{PIP/PEI-Dex-5}$>>TFC$_{PIP}$. The above order of amine on the membrane surfaces may be attributed to the attachment of number of PEI and its conjugates in the similar order. This may be due to the increasing steric congestion from PEI to PEI-PEG and to PEI-Dex owing to higher molecular weight of Dex chain (12000 g/mol) than that of each PEG chain (750 g/mol). The possibility of effect of surface roughness on the adsorption of dye has been ruled out, since the surface roughness followed the order for the membranes, TFC$_{PIP}$>TFC$_{PIP/PEI-Dex-5}$>TFC$_{PIP/PEI-PEG-5}$>TFC$_{PIP/PEI-1}$ (Table 1). This order of surface roughness is just opposite to that observed for dye

adsorption. The adsorption of dye should be higher in case of TFC$_{PIP}$, if there is an effect of surface roughness. Moreover, after thorough washing out of the unbound dye on the membrane surfaces at pH 3, the bound dye was completely removed only at pH 11, once again suggests binding of negatively charged dye on membrane surfaces by the protonated amine groups. Fig. 2B shows the amine contents by the obtained cross-linked polyamide masses which were obtained by sequential solvent extraction of TFC NF membranes with DMF, DMSO and THF. The amine content in the cross-linked extracted masses of the membranes followed similar order as described for membrane surfaces (compare Fig. 2A and 2B). This fact indicated possible cross-linking of PEI and its conjugates by the reaction with -COCl which were not washed out even after solvent extraction.
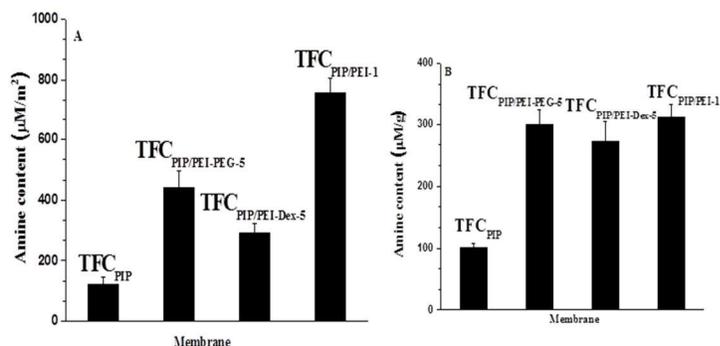

Fig. 2 Quantification of amine density on (A) surfaces and (B) in the extracted masses of TFC$_{PIP}$, TFC$_{PIP/PEI-PEG-5}$, TFC$_{PIP/PEI-Dex-5}$ and TFC$_{PIP/PEI-1}$ membranes. Each test was conducted on three square membrane pieces (5 cm x 5 cm) of each membrane type. The membranes were detached from fabric and the PSf support was completely leached out by DMF. The complete removal of PSf was confirmed by IR (Figure S5, absence of band at 1585 cm^{-1}). The masses were then again extracted with DMSO and then water and THF followed by drying in vacuum oven for dye test.

The above mentioned different concentration of amine on the membrane surfaces was also supported by surface ξ values of these membranes. TFC$_{PIP/PEI-1}$ and TFC$_{PIP/PEI-PEG-5}$ showed low positive ξ values (+3 and +1 mV respectively) while TFC$_{PIP/PEI-Dex-5}$ showed low negative ξ value (-4 mV) at neutral pH (Table 1). In contrast, TFC$_{PIP}$ showed high negative ξ value (-20 mV) at pH 7. This result supports the estimated values of amine groups on the membrane surfaces (Figure 2). The modified membranes showed moderate to high positive ξ values (+8 to +15 mV) at pH 5 due to protonation of free amine at lower pH (Table 1). On the other hand, TFC$_{PIP}$ membrane showed almost neutral ξ value (-1 mV) at pH 5 due to protonation of carboxylic acid groups. At pH 8, the ξ values of the modified membranes become negative (-8 to -12 mV) but the extent of negative charge was much lower (-25 mV) than that of TFC$_{PIP}$ (Table 1). This suggests that the modified membranes contain both amine and free carboxylic acid groups.

The lowering of r$_p$ values of the modified membranes as evident from glucose rejection experiment compared to that of TFC$_{PIP}$ may be attributed to the extra cross-linking due to treatment with PEI and its conjugates (Table 1). The lowest r$_p$ value of the TFC$_{PIP/PEI-1}$ among the membranes is ascribed to the greater number of PEI chain attachment than that of its conjugates. The estimated amine density on membrane surfaces also supports the obtained r$_p$ values of the membranes. The water permeability (L$_p$=9.44 to 11.11,

Table 1) was less affected by the post treatment under optimized conditions. This may be caused by the enhanced

Table 1 Summary of characteristic properties of TFC$_{PIP/PEI-PEG-5}$, TFC$_{PIP/PEI-Dex-5}$, TFC$_{PIP/PEI-1}$ and TFC$_{PIP}$

Membrane	Average ξ (mV) pH			L_p (μm/MPa s)	Average glucose rejection (%)/r_p (nm)	Roughness rms/ar(nm)
	5	7	8			
TFC$_{PIP/PEI-PEG-5}$	+9	+1	-12	11.11	88/0.50	99/78
TFC$_{PIP/PEI-Dex-5}$	+8	-4	-11	11.67	87/0.52	111/86
TFC$_{PIP/PEI-1}$	+15	+3	-8	8.33	94/0.44	15/13
TFC$_{PIP}$	-1	-20	-25	9.44	77/0.60	170/143

hydrogen bonding by the modified membrane surfaces with water molecules which offset the effect of r_p on membrane flux.

All the membrane surfaces show typical ridge-valley type of structure as confirmed by AFM height images of these membranes (Fig. 3). The height of ridges from the valley become more uniform for the post-modified membranes (middle images in rows B to D) compared to that of pristine membrane (middle image in row A). The root mean square (rms)/average surface roughness (ar) values of TFC$_{PIP}$, TFC$_{PIP/PEI-PEG-5}$ TFC$_{PIP/PEI-Dex-5}$ and TFC$_{PIP/PEI-1,}$ were 170/143, 99/78, 111/86 and 15/13 respectively. Lowering of surface roughness of modified membranes indicated grafting of PEI and its conjugates. The lowest surface roughness of TFC$_{PIP/PEI-1}$ is attributed to the higher degree of PEI chain attachment on this membrane which makes the surface more uniform. The surface SEM images (right, Fig. 3) clearly show the lowering of surface roughness of the modified membranes (right images, rows B to D) compared to pristine one (right image, row A). The pristine membrane show less surface penetrated globules than the modified membranes owing to presence of extra polymer on the surface of the modified membranes. The lowering of depth of globule (SEM image in Fig. 3) or the uniform and reduced height of ridges from the valley for the modified membranes may be explained by the taking into consideration of predominant presence of modifying agents in between ridges.

The water contact angle (Θ) of pristine ($\Theta=47\pm2$) and modified membrane ($\Theta=48\pm2$) surfaces show similar value, although the expected hydrophilic character of the modified membrane should be enhanced compared to that of pristine membrane. This result may be explained as follows. The surface water Θ mainly influenced by hydrophilic character and roughness of the membrane surface as depicted in Wenzel Model by the following equations.[36]

Cos Θ_w = r cos Θ (3)

where Θ_w is the apparent contact angle, r is the surface roughness factor (r=the real contact area/the nominal contact area). According to this equation when the Θ of a liquid on hydrophilic surface is <90°, the Θ_w on the smooth surface will be higher. On the other hand, for hydrophobic surface (Θ>90°), the Θ_w will be lower on smooth surface. Since, the surface roughness of modified membranes were much decreased this might have enhanced the apparent Θ values of the modified membranes. Hence, almost similar Θ values coupled with much lower surface roughness of the modified membranes to that of pristine one actually indicates greater hydrophilic character of the modified membranes to that of pristine membrane.
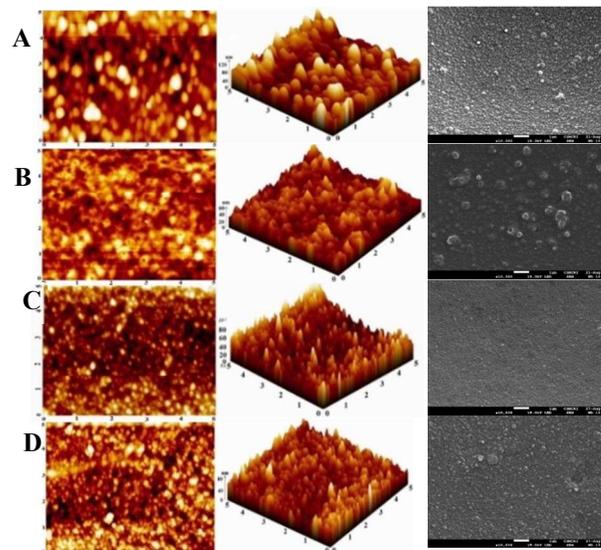

Fig. 3 AFM topological (left column), corresponding height (middle column) and surface SEM (right column) images of (row A) TFC$_{PIP}$, (row B) TFC$_{PIP/PEI-1}$, (row C) TFC$_{PIP/PEI-Dex-5}$ and (row D) TFC$_{PIP/PEI-PEG-5}$.

3.3. Transport property of TFC NF membranes during water desalination by NF process

Fig. 4 summarizes the Na$_2$SO$_4$, MgCl$_2$, CaCl$_2$ and NaCl SR efficiencies and permeate fluxes of TFC$_{PIP}$, TFC$_{PIP/PEI-PEG-5,}$ TFC$_{PIP/PEI-Dex-5}$ and TFC$_{PEI-1}$ during desalination of separate feed solutions. The SR of Na$_2$SO$_4$ remained ca. 85-92% by the modified membranes whereas the TFC$_{PIP}$ exhibited somewhat higher Na$_2$SO$_4$ SR (ca. 93%). The SR of MgCl$_2$ and CaCl$_2$ followed the order for the membrane, TFC$_{PIP/PEI-1}$>TFC$_{PIP/PEI-Dex-5}$~TFC$_{PIP/PEI-PEG-5}$>>TFC$_{PIP}$. This order of MgCl$_2$ and CaCl$_2$ SR is attributed to the lowering of both surface negative charge (ξ values, at ca. pH 7) and r_p of these membranes in similar order as discussed earlier (Table 1). The NaCl SR by the TFC$_{PIP}$, TFC$_{PIP/PEI-Dex-5}$ and TFC$_{PIP/PEI-PEG-5}$ remained almost similar (34-40%). On the other hand, NaCl SR of TFC$_{PIP/PEI-1}$ increased to that of TFC$_{PIP/PEI-PEG-5}$, TFC$_{PIP/PEI-Dex-5}$ and TFC$_{PIP}$ membranes due to lowering of r_p of the former membrane compared to other membranes to a greater extent (Table 1).
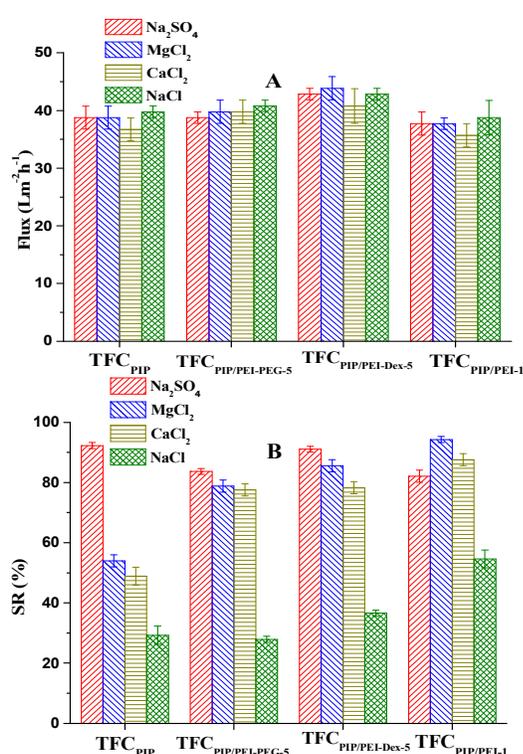
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Fig. 4 Bar diagrams showing (A) permeate flux and (B) SR data of TFC$_{PIP}$, TFC$_{PIP/PEI-PEG-5}$, TFC$_{PIP/PEI-Dex-5}$ and TFC$_{PIP/PEI-1}$ during NF of separate feed solutions. Pressure: 0.5 MPa. Feed concentration: 1500 mg/L; pH ca.7; operating pressure: 0.5 MPa.

Table 2 summarizes a comparative SR data of different reported membranes during NF of separate feed solutions. Clearly, our membranes (entries 2-4) exhibited superior divalent cation salt and divalent anion salt SR (average) by keeping the NaCl SR as low as observed for the typical NF membranes. Among the membranes listed in Table 2, PIP/TMC-multilayer (entry 7)

showed high MgCl$_2$ and Na$_2$SO$_4$ SR.[30] However, it is noted that the NaCl SR also excessively increased by this membrane. The membrane is thus not true NF membrane, since, the selectivity between Na$^+$ to Mg^{+2} or SO$_4^{-2}$ also decreased. The novel effect of our post treatment process on SR of both divalent cation and divalent anion was also observed when desalination was performed using mixture of salts as feed solution as discussed below.

3.4. Effect of feed pH on the permeation characteristics of TFC NF membranes during NF of water containing mixture of salts

Figures 5A to D show Mg^{+2}, SO$_4^{-2}$, Na$^+$ and Cl$^-$ SR by the membranes with the variation of feed pH during NF of feed solution containing mixture of Na$_2$SO$_4$ and MgCl$_2$. The SO$_4^{-2}$ SR increased with increasing feed pH from 5 to 8 by all the membranes and the effect was more pronounced with the pristine membrane. This fact clearly suggests similar trend of enhancement of negative charge on the membrane surfaces as the feed pH enhances from 5 to 8 (Table 1). The SO$_4^{-2}$ SR by the pristine membrane was in the range 84-88% at pH range 7-8. The modified membranes also showed similar rejection of SO$_4^{-2}$ viz. 80-88%.

Independent of pH, Mg^{+2} SR follows the order for the membranes, TFC$_{PIP/PEI-1}$>TFC$_{PIP/PEI-PEG-5}$~TFC$_{PIP/PEI-Dex-5}$>>TFC$_{PIP}$. The rejection of Mg^{+2} followed decreasing trend for TFC$_{PIP}$ with increasing feed pH whereas the modified membranes showed noticeable decrease of Mg^{+2} SR at pH 8 only. The modified membrane showed much higher (80-90%) of Mg^{+2} SR than that of pristine membrane (59%) at pH 7. The low charge at pH 7 on the modified membrane surfaces and in conjunction with relatively smaller r$_p$ compared to that of pristine membrane maintained the high degree of both Mg^{+2} and SO$_4^{-2}$ ions SR by the modified membranes.

Table 2 Comparative performance of different NF membranes

TFC Membrane[a]	Amine monomer	SR (%)			Applied pressure (MPa)/concentration of feed (mg/L)	Reference
		MgCl$_2$ or CaCl$_2$	NaCl	Na$_2$SO$_4$		
TFC$_{PIP}$	PIP	54/48.9	37	92	0.5/1500	In this work
TFC$_{PIP/PEI-PEG-5}$	PIP and PEI-PEG	79/78	34	84	0.5/1500	In this work
TFC$_{PIP/PEI-Dex-5}$	PIP and PEI-Dex	86/78	36	91	0.5/1500	In this work
TFC$_{PIP/PEI-1}$	PIP and PEI	93/87	54	82	0.5/1500	In this work
Hollow fiber	PIP	10/-	27	99	0.35/1000	13
mm-BTEC/PIP	PIP	30/-	65	95	0.5/500	12
PIP/TMC-multilayer	PIP and PEI	95/-	85	81	0.8/500	30
PEI/TMC	PEI	95	75	68	0.8/500	31
NF-CA30	-	-	30	60-70	1.5/-	34
NF5 (G1)	PAMAM	84/-	48	47	0.6/1000	17
NF5 (G3)	PAMAM	95/-	72	58	0.6/1000	17
PEI/TMC	PEI	80/-	44	50	0.4/1000	18 and cross reference

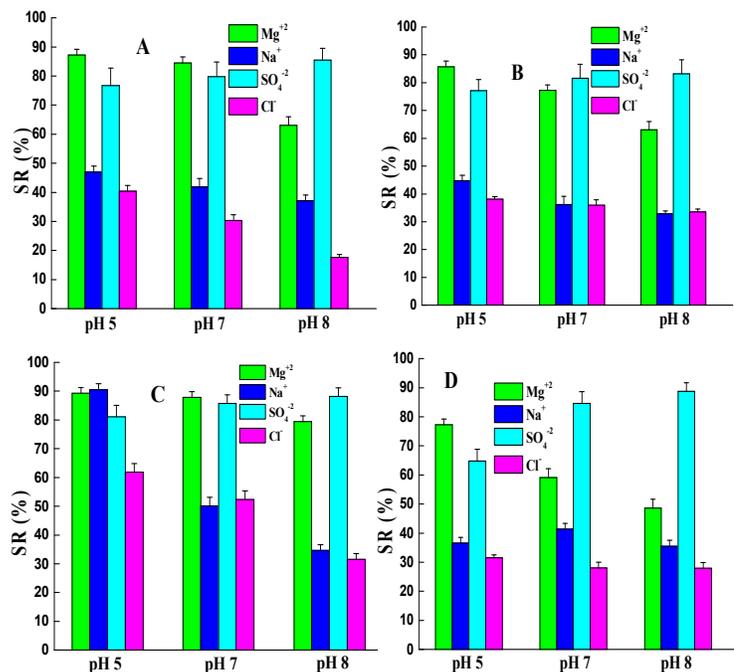a-abbreviations of the membranes have been taken from respective paper

Fig. 5 Mg^{+2}, Na^+, SO_4^{-2} 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 of Na_2SO_4 (750 mg/L), $MgCl_2$ (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 were taken.

The Na^+ SR by the TFC_{PIP} remained almost unaltered with increasing feed pH while the modified membranes showed decreasing trend. $TFC_{PIP/PEI-1}$ gave much higher (ca. 90%) Na^+ SR at feed pH 5. This phenomenon is explained by the somewhat enhancement of negative charge on TFC_{PIP} with increasing feed pH while the other three membranes showed lowering of positive charge with increasing feed pH and the charges become still low negative value for these membranes at pH 8. This effect is particularly more pronounced for $TFC_{PIP/PEI-1}$. Among the membranes, the extent of positive charge was highest for $TFC_{PIP/PEI-1}$ at pH 5. Both high degree of positive and negative charge on membrane surface is necessary for efficient rejection of NaCl by either Donnan exclusion of negatively charged membrane surface with Cl^- or positively charged membrane surface with Na^+.[37]

Clearly, the Na^+ to Mg^{+2} selectivity ($S_{Na^+/Mg^{+2}}$) of the modified membranes were noticeably higher (ca. 2.8-3.8) than that of pristine membrane (ca. 1.4) at pH 7 (Table S1, †ESI). The $S_{Na^+/Mg^{+2}}$ improved for the membranes at pH 5 except $TFC_{PIP/PEI-1}$. The high positive charge at pH 5 on $TFC_{PIP/PEI-1}$ enhanced the SR of Na^+ which lowers the $S_{Na^+/Mg^{+2}}$. The $S_{Na^+/SO4^{-2}}$ values of modified membranes are not much differ from $S_{Na^+/SO4^{-2}}$ value of pristine membrane. The selectivity data obtained at different pH (Table S1, †ESI) implicated that both anionic and cationic divalent ions can effectively be separated by the modified membranes at pH ca. 7. Similar trend in SR of $MgCl_2$, Na_2SO_4 and NaCl was obtained by the membranes with variation of feed pH during NF of separate feed solutions of $MgCl_2$, Na_2SO_4 and NaCl (Fig. S6, †ESI) as described above for mixture of salts.

Nutritious salts such as KCl and $MgCl_2$ may also be separated from their mixture at pH range 7-8 with higher selectivity

by the modified membranes than that of pristine membranes (Fig. S7, †ESI). The pH range 7-8 is more preferable to work as the groundwater and seawater pH is in this range.

3.5. Natural seawater desalination by NF process

NF of seawater was performed with the membranes (Fig. 6) at pressure ca. 1.4 MPa. The pH of the solution was ca. 7.4. The modified membranes exhibited ca. 12% Na^+ and K^+ SR, ca. 60-70% Mg^{+2} SR, ca. 50-55% Ca^{+2} SR and 72-75% SO_4^{-2} SR. The pristine membranes showed nearly similar Na^+ and K^+ SR and relatively Mg^{+2} (ca. 40%) and Ca^{+2} (ca. 35%) SR. The $S_{Na^+/Mg^{+2}}$ values were 1.5 for TFC_{PIP} and 2.3-2.6 for the modified membranes without adjusting any feed parameters. The $S_{Na^+/SO4^{-2}}$ values were ca. 3.9 for TFC_{PIP} and ca. 3 for the modified membranes. The $S_{Na^+/Ca^{+2}}$ values were also higher for the modified membranes compared to that of TFC_{PIP}. This offers good selectivity for the removal of monovalent ions from divalent ions from seawater by the modified membranes without adjusting the feed pH. The permeate fluxes were ca. 35-40 $Lm^{-2}h^{-1}$ for all membranes. Thus multistep low pressure NF treatment of seawater will provide monovalent ions (Na^+ and K^+) rich permeate for further treatment with RO process for the use in domestic purpose and utilization of residue salts from retentate and permeate streams.
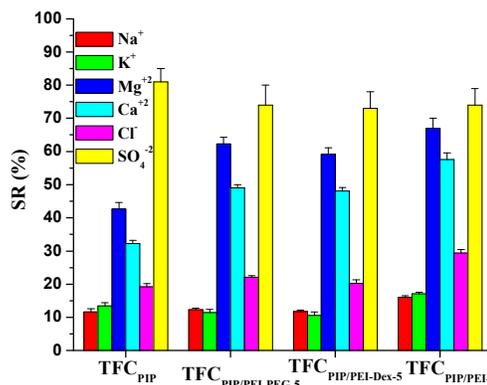

Fig. 6 Na^+, K^+, Mg^{+2}, Ca^{+2}, Cl^- and SO_4^{-2} SR by TFC_{PIP}, $TFC_{PIP/PEI-PEG-5}$, $TFC_{PIP/PEI-Dex-5}$, and $TFC_{PIP/PEI-1}$ during NF of seawater (TDS=35000 mg/L) at 1.4 MPa at pH ca. 7.4 and at temperature ca. 28 °C.

3.6. Anti-fouling and anti-scaling properties of the membranes

The modified membranes exhibited superior antifouling property than that of pristine membrane during NF of water containing Na_2SO_4 and BSA (Fig. 7A). The rejection of Na_2SO_4 by the membranes remained similar in presence and absence of BSA. Careful observation of flux reduction (FR) data obtained with different filtration time indicated that the $TFC_{PIP/PEG-PEI-5}$ and $TFC_{PIP/PEI-Dex-5}$ were better resistant to protein than that of $TFC_{PIP/PEI-1}$. The flux reduction (FR) of pristine membrane was much higher (37%) than that of modified membranes (12-15%) after 25 h of filtration operation. Among the modified membranes, the FR values of $TFC_{PIP/PEI-1}$ showed increasing trend even after 15 h of filtration test whereas the FR values remained almost constant for $TFC_{PIP/PEI-PEG-5}$ and $TFC_{PIP/PEI-Dex-5}$. This indicated superior resistance to protein by the latter two membranes. The flux recovery ratio (FRR) of TFC_{PIP}, $TFC_{PIP/PEI-PEG-5}$, $TFC_{PIP/PEI-Dex-5}$ and $TFC_{PIP/PEI-1}$ after 25 h of NF operation of BSA contaminated salt water were 72%, 90%, 88% and 81% respectively. The improved antifouling behavior of the modified membranes than that of pristine membrane is attributed to the (i) enhanced steric hindrance by the PEI, PEG and Dex

towards the incoming organic foulants, (ii) hydrogen bonding ability of PEI, PEG and Dex with water molecules, (iii) lowering of surface roughness and (iv) lowering of carboxylic acid concentration on the modified
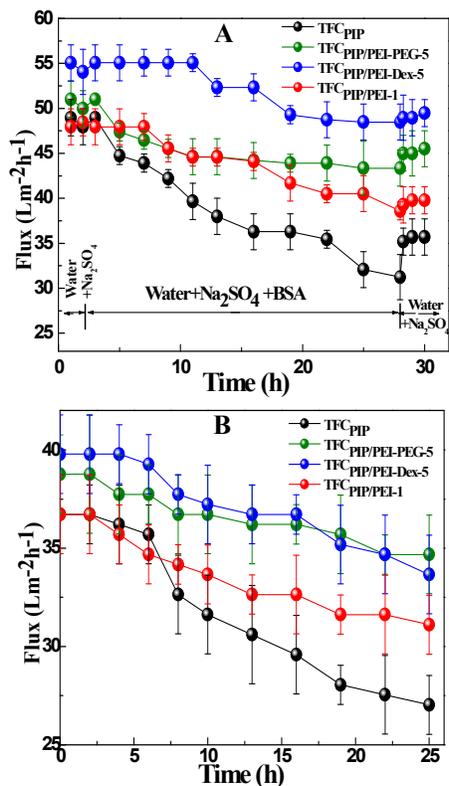

Fig. 7 Flux of membranes with time during (A) NF of water (containing 1500 mg/L Na_2SO_4 spiked with 250 mg/L BSA at pH 7.1±1) at operating pressure 0.7 MPa and (B) during seawater (TDS=35000 mg/L) softening at operating pressure 1.4 MPa.

membranes.[38] The effect of steric hindrance towards the foulants and hydrogen bonding with water especially by PEG and Dex on antifouling behavior have been well documented in the literatures.[15,25,32,39] These are the reasons of superior antifouling behavior of TFC $_{PIP/PEI-PEG-5}$ and TFC$_{PIP/PEI-Dex-5}$ among the membranes.

Seawater contains scale forming Ca^{+2}, SO_4^{-2}, Mg^{+2}, CO_3^{-2}. The anti-scaling test during seawater NF for 25 h also indicated much better anti-scaling property of the modified membranes (Fig. 7B). The FR values of the modified membranes were 10-14% whereas it was ca. 25% for TFC$_{PIP}$. The anti-scaling property of the modified membranes is ascribed to the low charge on the membrane surfaces which lowers the pre-adsorption of scale forming salts. The modified membranes exhibited ca. 100% FRR after simple water washing whereas pristine membrane show ca. 90% FRR. The TFC$_{PIP/PEI-PEG-5}$ and TFC$_{PIP/PEI-Dex-5}$ membranes exhibited better anti-scaling property than that of TFC$_{PIP/PEI-1}$ during seawater NF which may be due to additional effect of PEG and Dex on anti-scaling behaviour of these membranes. The low positive charge in conjunction with presence of fouling resistant Dex and PEG enhanced the overall anti-scaling behavior of the TFC$_{PIP/PEI-PEG-5}$ and TFC$_{PIP/PEI-Dex-5}$ to greater extent.

4. Conclusions

The problems of trade-off rejection between bivalent cation and divalent anion by the conventional nanofiltration (NF) membrane along with its fouling tendency can be overcome by adjusting the charge on the membrane surface, lowering the membrane pore size and introducing antifouling polyethylene glycol and dextran on the membrane surface. Therefore, antifouling/anti-scaling thin film composite NF membranes with relatively high rejection of both divalent cation and divalent anion have been successfully prepared by the post treatment of nascent poly(piperazineamide) membrane with polyethyleneimine or its conjugates of polyethylene glycol or dextran. In addition to low surface charge, modified membranes showed lower surface roughness, lower pore size and higher amine content compared to pristine membrane. Presence of both unreacted carboxylic acid and amine groups on the membrane surfaces necessarily balances the charge at neutral pH. Lower surface charge couple with lower pore size of the modified membranes help to remove the bivalent cationic salt without much affecting the rejection of bivalent anionic salt by the modified membranes. Judicious adjustment of concentration of modifying agents gave modified membranes having similar permeate flux, enhanced antifouling/anti-scaling property and enhanced monovalent to divalent ions selectivity than that of pristine membrane . This type of membranes are suitable candidates for mitigating environmental problems associated with water purification especially removal of hardness and softening of water for further utilization in domestic applications after RO treatment.

Conflicts of interest
The authors declare no competing financial interest.

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Graphical Abstract

Post modification of nascent polyamide thin film composite membranes with polyethyleneimine-conjugate-polyethylene glycol or polyethyleneimine-conjugate-dextran exhibited novel properties such as high monovalent to divalent cation or divinely anions selectivity and improved antifouling/anti-scaling properties and may be suitable for water nanofiltration