Performance of PS/PIMA/ PPEES nanofiltration membranes before and after alkali treatment for filtration of CaCl$_2$ and NaCl

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Abstract. Present article describes about the preparation of Nanofiltration (NF) composite membranes by a simple chemical treatment to the polymeric membrane composed of Poly (isobutylene-alt-maleic anhydride). After composition, anhydride functionality was converted to diacid functionality by hydrolysis using sodium hydroxide solution. Further, membrane was characterized by ATR-IR, DSC and SEM. Charge confirmation was done by IEC. Water uptake and contact angle analysis was carried out to study the hydrophilicity of the membrane. The performance study was carried out by using NaCl and CaCl$_2$ solutions. Membranes were having higher charge density, which has resulted in better performance in terms of rejection of CaCl$_2$ and NaCl solutions. The main focus of this research is to evaluate the effect of alkali treatment on Donnan and size exclusion mechanism during membrane filtration.

Introduction

Nanofiltration (NF) membrane is a type of pressure-driven membrane [1] with properties in between reverse osmosis (RO) and ultrafiltration (UF) membranes. NF membranes have several advantages such as low operating pressure, higher flux, higher retention of mono and multivalent salts. Due to these advantages, the applications of NF membranes have increased worldwide [2]. NF permeates have a very good quality, as the process is capable of removing most inorganic as well as organic foulants. This makes NF a good candidate for wastewater treatment and for water reusability. Membrane filtration process is being incorporated in variety of applications such as traditional water-softening processes like inorganic and organic ion exchange systems, as well as processes such as cold and hot lime softening and pellet softening [3, 4]. A sufficient but incomplete organics rejection is obtained with NF membranes with a relatively high molecular weight cut-off (MWCO) [5, 6]. Membrane technology is widely used for removal of different pesticides from water [7], treatment of effluents from the textile industry [8], treatment of leachates from landfills and composting plants [9], reclamation of municipal wastewater and ground water remediation [10], water reuse in the pulp and paper industry [11], waste water purification in leather industry [12], removal of fluoride, aluminum [13] and uranium from natural waters [14].

NF membranes also find vast applications in desalination. By definition, desalination refers to the process of removing salt from seawater or brackish water. In a broader sense of the definition, desalination can also be inferred as removal of various inorganic ions from solution with the final target so as to produce clean and potable water [15].

Due to low energy consumption and good selectivity, NF membranes are more economical than the RO membranes. However getting the symmetric pore size is difficult task. Performance of the membrane depends on the materials used and the preparation parameters. For commercially viable nanofiltration membranes however, new materials systems were needed that, (1) can be synthesized inexpensively in large quantities, (2) capable to fabricate into large area membranes, (3) exhibit permeability computable to or above current NF membranes (4) and exhibit low susceptibility to fouling [16].

Our research work aims at developing a composition of the polymers which increases the productivity as well as selectivity of membrane. Recently we have reported NF membranes of PSf and PIMA composite membranes and studied their performance after alkali treatment [17]. The membrane showed good rejection with comparable flux, this is because of the charge on the membrane surface by hydrolysis of anhydride group from the PIMA. However it showed less rejection at higher pressure because of an increase in the pore size. Keeping this drawback in view

and with the aim of increasing productivity, we have synthesized NF membrane by the integrated usage of polysulfone (PS), poly (1, 4-phenylene ether ether-sulfone) (PPEES) and poly (isobutylene-alt-maleic anhydride) (PIMA). Prepared membranes were then treated with alkali solution for hydrolysis of anhydride group into carboxylic acid group. Further they were verified by means of water flux study and filtration using mono- and divalent salt solutions.

Experimental

Materials and instruments. Polysulfone (PS) having molecular weight of 35,000 poly(1,4-phenylene ether ether-sulfone) (PPEES) and poly(isobutylene-alt-maleic anhydride) (PIMA) having molecular weight 6,000 were obtained from Sigma Aldrich. Reagent grade N-methyl pyrrolidone (NMP) was obtained from Merck-India and was used without any further purification. All analytical grade chemical reagents used in the experiment were purchased from Merck India Ltd. K- Control Coater 202 (UK) was used to cast the polymer solution into membranes. IR spectra were recorded using Nicolet Avatar 330 FTIR (Thermo Corporation) spectrometer. SEM images of the cross section of the newly prepared membranes were recorded on Jeol JSM-84. DSC study was carried out on a Shimadzu DSC 60 instrument, Japan. The permeation experiments were performed by a self fabricated salinity checking apparatus with membrane disk having an effective area of 6.5 cm^2. VCA-Optima (AST products Inc., MA, USA) were used to measure contact angle of the membranes.

Synthesis of PS / PIMA / PPEES NF Membrane. For the synthesis of membranes, we have followed diffusion induced phase separation (DIPS) technique as reported in recent article [18]. Solutions containing different wt. % of PS, PIMA and PPEES (Table-1) in 4.5 mL of 1-methyl-2-pyrrolidone (NMP) were prepared. The solution was stirred for 24 hours at 75 ºC for completion of dissolution. Obtained viscous solution was then cast using K-Control coater. Casted membrane was again annealed at 220ºC. The membranes were separated by dipping the glass plates in distilled water. Further separated membranes were dipped in distilled water for another 24 hours; these membranes were washed several times with distilled water before storage. Synthesized NF membranes were coded as PNM1, PNM2, PNM3 and PNM4. Synthetic route for the membranes has been presented in Fig.1. The composition concentration of polymers as tabulated in Table-1.

Table 1 Solutions containing different wt. % of PS / PIMA / PPEES.

Membrane Code	Wt % composition (PS)	Wt % composition (PPEES)	Wt % composition (PIMA)
PNM1	90	5	5
PNM2	80	5	15
PNM3	70	5	25
PNM4	60	5	35
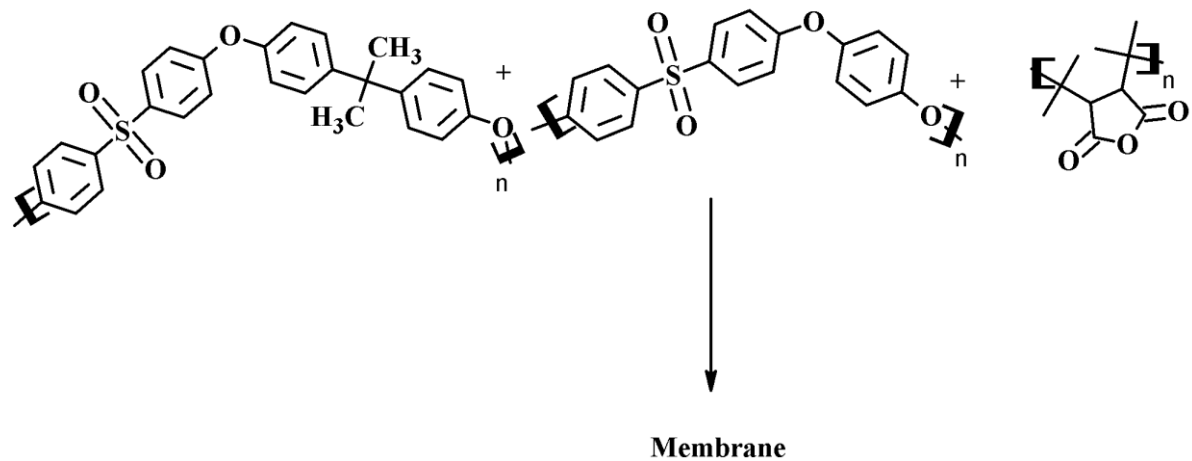
Fig. 1, Synthetic route for the membranes.

Further synthesized membranes were immersed in 1N NaOH solution for 20 h to hydrolyze anhydride group as shown in Fig.2. It was then washed and stored in distilled water. Using the above procedure, membranes with different composition of PS:PIMA:PPEES were prepared and subjected to further characterization.
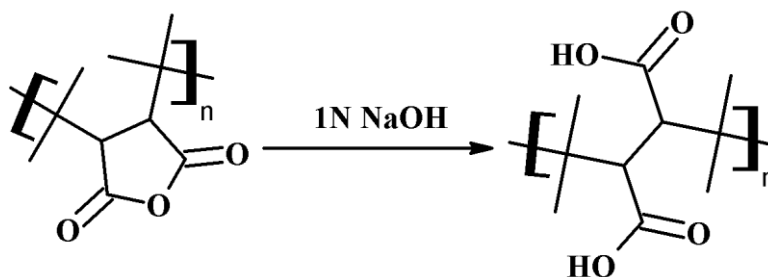
Fig. 2, Schematic representation of the PIMA polymer after alkali treatment.

Structural characterization. For the confirmation of the blend membranes, IR spectra were recorded using Nicolet Avatar 330 FTIR (Thermo Corporation) spectrometer. Scanning electron microscope (Jeol JSM-84) was used to observe the morphology of the dried membranes.

Water uptake. The water uptake of the membrane was determined by measuring the change in the weight after hydration. The membrane was first immersed in deionized water for 24 h. Then the membrane was weighed quickly after removing the surface adhering water to determine the weight of wet membrane (w_w). The weight of the dry membrane (w_d) was determined after drying. The percentage of water uptake was calculated by using the following equation [19]

$$\% Water uptake = \left(\frac{w_w - w_d}{w_d} \right) x100$$

Ion-exchange capacity (IEC). The ion exchange capacity of the membranes was determined through an acid–base titration. The dry composite membrane was immersed in 50 mL of 1M sodium chloride aqueous solution for 24 h in order to extract all protons from the membrane. After taking out the membrane, electrolyte solution was titrated with 5M sodium hydroxide solution using phenolphthalein as an indicator. The ion exchange capacity (IEC) was calculated using the following equation:

$$IEC(meqiv/g) = \left(\frac{V \times M}{w_d} \right)$$

where IEC is the ion exchange capacity (meq/g), V is the added titrant volume at the equivalent point (mL), M is the molar concentration of the titrant (mL) and w_d (g) is the dry mass of the membrane [20].

Measurement of contact angle (CA). The water contact angle of the membranes was measured to study the surface hydrophilicity. The CA measurements were performed using the VCA-Optima (AST products Inc., MA, USA). Samples of 4 cm^2 area (2 cm×2 cm) at random positions were prepared from each membrane. The samples were then placed on the glass plate holder and fixed with scotch tape. The equipment syringe filled with distilled water was installed to stand vertically. 2 µl of water was deposited on the membrane surface. The CA was measured at five different spots on each membrane sample, for both top and bottom surfaces [21].

DC Analysis. A DSC-60 Shimadzu calorimeter was used to analyze the thermal behavior of differently processed membranes, with the heating rate of 10 ℃ /min up to 300 ℃. DSC curve of the resultant membranes were studied with increase in temperature at the rate of 10℃/min. Each sample was subjected to several heating/cooling cycles to obtain reproducible Tg values. The initial onset of the change midpoint of slope in the DSC curve is taken to be the Tg [22].

Permeation experiment. Water flux and salt rejection study was done at different pressures varying from 2 to 14 bar with difference of 2 bar. Rejection (%) was studied by conductivity measurements [23]. Fig.3 represents the self made salinity checking instrument. Salts with different valence distribution are used for NF membrane experiments to investigate membrane properties. The permeability of pure water through this NF membrane was also measured. Flux, F (l / m^2 h), was calculated as Eq.1:

$$F = \frac{W}{At}$$

(1)

where, W (l) is the total volume of the water or solution permeated during the experiment, A (m^2) is the membrane area, and t (h) is the operation time. Rejection, R, is calculated as Eq. 2:

$$R = 1 - \frac{C_p}{C_f}$$

(2)

where, C_p and C_f represent the concentration of permeate and feed, respectively.

1. Nitrogen Cylinder
2. Feed
3. Storage container
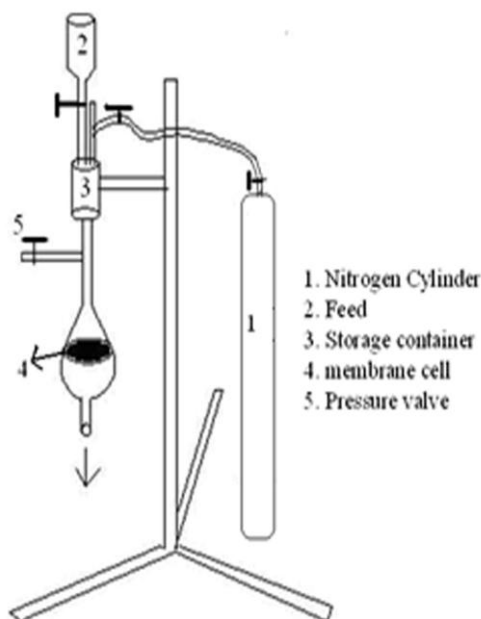4. membrane cell
5. Pressure valve

Fig.3. Schematic representation of the self made salinity checking instrument.

Results and discussion

Spectral characterization. Fig. 4 and 5 shows the FTIR spectra of PNM4 membrane before and after alkali treatment respectively. Generally speaking, both (Fig 4a and Fig 4b) FTIR curves were very similar, due to the presence of similar polymer composition. In both samples, common peaks such as 3600 -3200 cm^{-1} for -OH stretching vibrations, 2980 -2880 cm^{-1} for asymmetric and symmetric C-H stretching vibrations involving entire methyl group, 1325 -1298 cm^{-1} for doublet resulting from asymmetric O=S=O stretching of sulfone group, 1244 cm^{-1} for symmetric C-O-C stretching of aryl ether group, 1170 cm^{-1} for asymmetric O=S=O stretching of sulfonate , 1107-1092 cm^{-1} for aromatic ring vibration were observed. Interestingly moderate absorption peaks at around 3443 cm^{-1} were observed in Fig. 4a, which indicates the existence of O-H vibration. Whereas (Fig. 4b), strong absorption peak at around 3399 cm^{-1} and 1777 cm^{-1} can be interpreted as the existence of carboxylic OH bonds and for carbonyl group respectively after hydrolysis of PIMA.
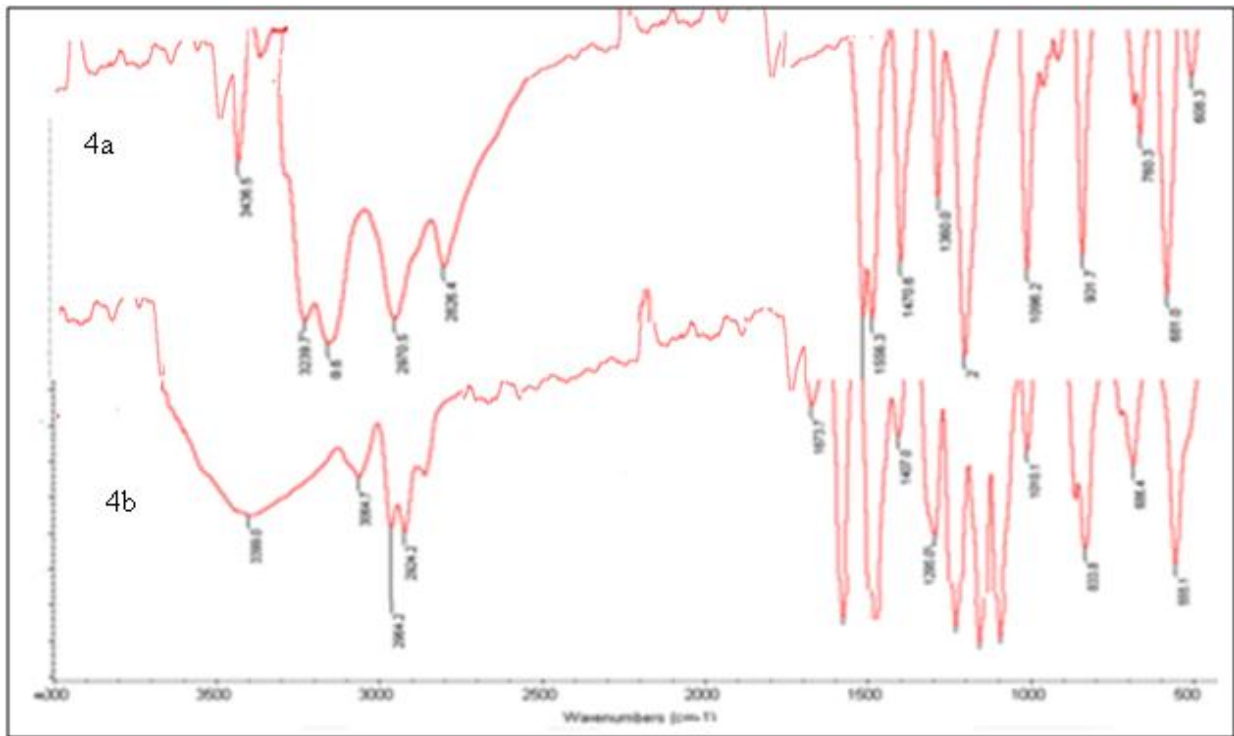
Fig. 4a, b. FTIR- Spectrum of PNM4 before (4a) and after (4b) alkali treatment.

Water uptake and ion exchange capacity (IEC). The water uptake plays important role in membrane filtration performance. From Fig.6, it was observed that, water uptake of the PS:PIMA:PPEES NF membranes increased with increase in PIMA concentration. This is due to the fact that the carboxylic groups are hydrophilic and hence the membranes with higher carboxylation can absorb more water. Carboxyl groups lead to increase in the hydrogen bonding on the membrane surface. Hence water uptake decreases with decrease in the concentration of the PIMA.

IEC of the membrane was calculated by titration method. It was observed that value of IEC increases with increase in the concentration of PIMA. These effects can be correlated to the increased hydrophilicity behavior of the treated membranes as more –COOH groups facilitate more hydrogen proton conduction through the membrane matrix. IEC values indicate the capacity of dissociated ions in the membrane. Comparison of IEC gives an idea of the capability of exchange of the proton feed solution. Fig-7 shows IEC of the membranes.
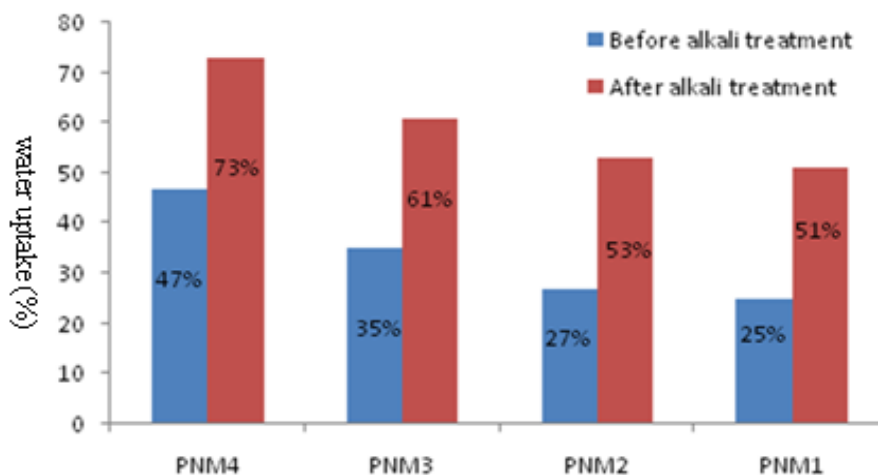
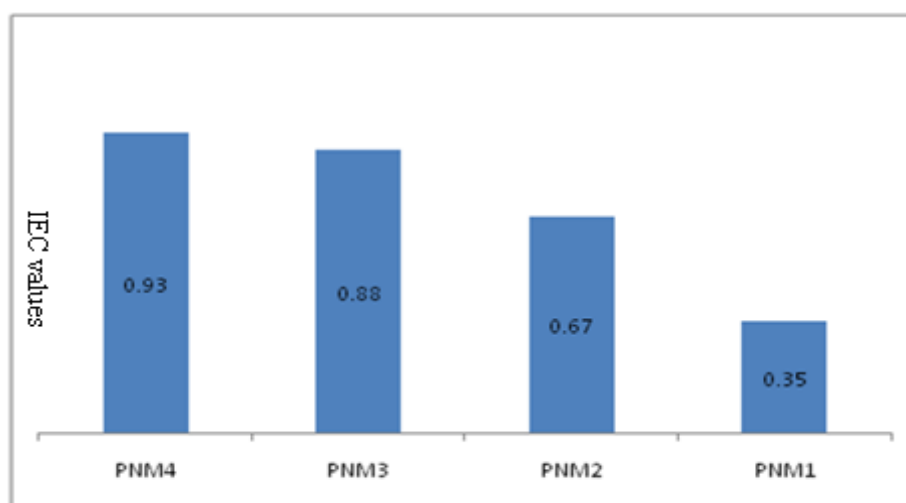**Fig. 6.** Water uptake of the PS:PIMA:PPEES NF membranes.

Fig.7. IEC values of the membranes after alkali treatment.

Contact angle measurements. The contact angle is an important parameter for measuring surface hydrophilicity. In general, a smaller contact angle corresponds to more hydrophilic materials. The contact angle (CA) was measured by sessile drop method. Table. 2 shows contact angles of the membranes. The contact angle decreases with increasing concentration of PIMA. Usually, lower the contact angle, higher is the hydrophilicity which in turn increases the flux [24]. As can be seen from Table.2, after alkali treatment with more PIMA concentration there is a decrease in the contact angle. This decreased value of contact angle further confirms introduction of carbonyl group to PIMA after the hydrolysis reaction so attached carbonyl group enhances hydrophilic nature of the membrane.

Table. 2. Contact angle measurements of different membranes.

Membrane Code	Before alkali treatment	After alkali treatment
	Contact angle in degree	Contact angle in degree
PNM4/ PRM4	64±4	33±5
PNM3/ PRM3	55±3	41±6
PNM2/ PRM2	63±2	52±3
PNM1/ PRM1	73±3	61±4

Morphology of the membranes. The surface and cross section morphology of the PS:PIMA:PPEES NF composite membrane was examined using SEM, as shown in Fig. 8 (a-c). In general there is no notable significant change in the membrane surface morphology before and after alkali treatment. The composite membrane has a uniform and smooth surface.

The NF membranes were dipped in liquid N_2 for SEM images of cross-section. Which shows, support layer with "finger-like" prijection and a denser skin layer with sponge pores with an average pore dimension of 10 μm as shown in Fig.8b and Fig.8c. From the surface SEM image (Fig. 8a), it is observed that smallest pores have the dimension in the range of 1-3 nm which corresponds to nanofiltration membranes pore size.
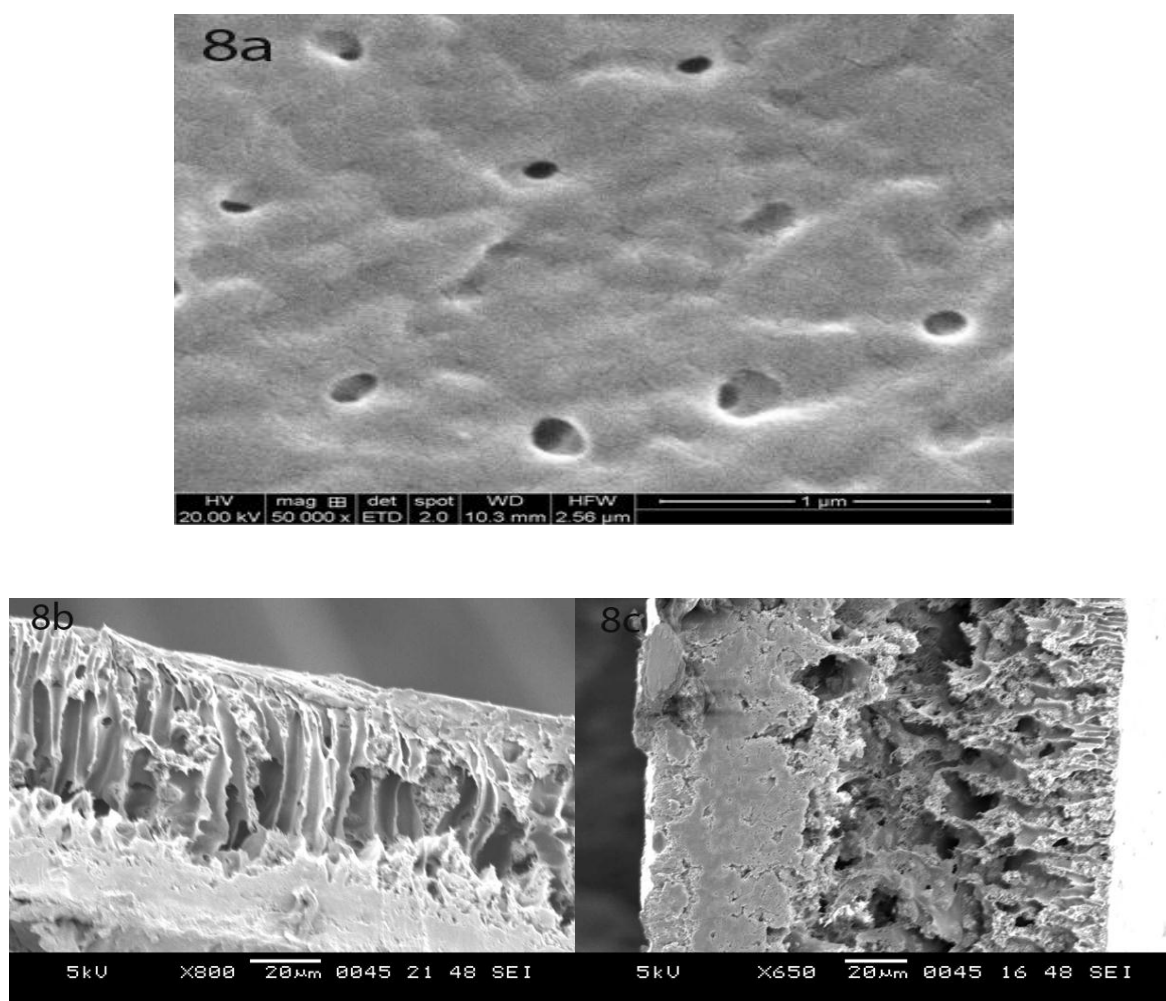
Fig. 8. (a) Surface image of the membrane, (b) and (c) Cross section image of the membranes.

DSC Study. DSC was used to evaluate the T_g of the prepared membranes and results were summarized in Fig. 9a. From the thermal study, it is clear that T_g of blend membrane was different from that of PS, PPEES and PIMA alone and also it showed single T_g value. This confirmed the formation of composite, as a result of many Van der Waals interactions between two polymers which lose their individual identity and show different T_g. T_g of PIMA is 141 ^{o}C, PS has 194 ^{o}C and PPEES has 191.1^{o}C. Thus our prepared membranes clearly indicated that, higher the polysulfone content, higher is the T_g. Fig 9b represents DSC thermogram of the different membrane
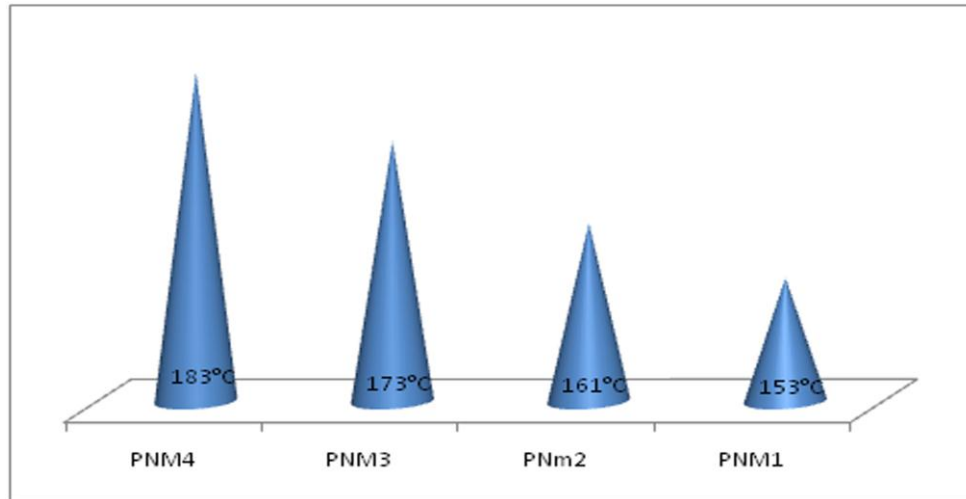
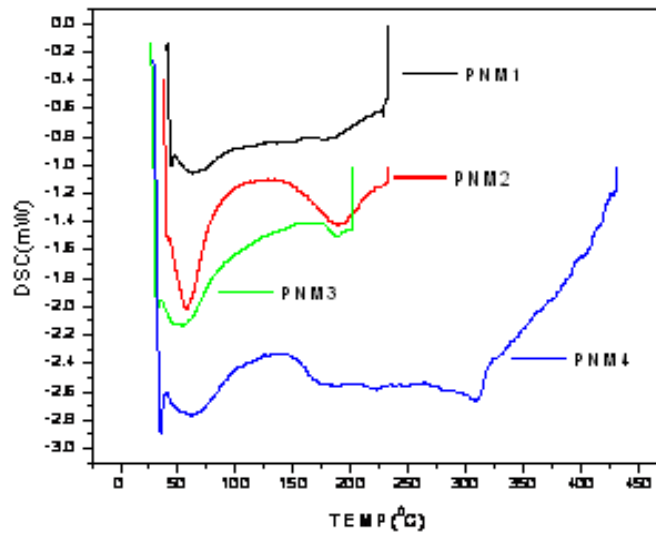**Fig. 9a.** T_g values of the different membranes.

Fig. 9b. DSC thermogram of the different membrane

Performance of the membrane

Pure water permeability. At different pressure (bar) flux for pure water is shown in Fig. 10. The plot depicts a linear relationship between pure water flux and applied pressure. It is seen that there is slow and steady increase of pure water flux with respect to increase in PIMA wt %. This is due to the fact that PIMA predominantly enhances hydrophilicity nature of the membranes and also increases permeability of the membrane.
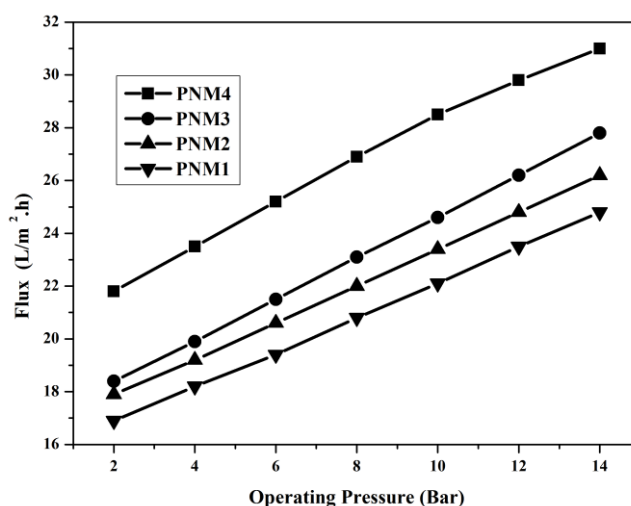
Fig.10. Pure water flux at different pressure (bar).

Performance of the membrane. Fig. 11a and 11b shows flux and rejection of the NF membranes before alkali treatment and Fig. 12a and 12b after the alkali treatment with 0.1% NaCl. Fig. 13a and 13b shows flux and rejection of the NF membranes before alkali treatment and Fig. 14a and 14b after the alkali treatment with 0.1% $CaCl_2$.

The membranes, before and after alkaline treatment shows higher calcium rejection than sodium. The Na^+ rejection by the NF membrane after alkaline treatment are presented in Fig 12b and in the same way Ca^{2+} rejection results of the NF membrane after alkaline treatment are presented in Fig 14b. Due to the special feature of the NF membrane surface (mostly having fixed negative surface charges), the capacity of separation is influenced by the steric effect (due to small pore diameter) and the charge on surface of the membrane (Donnan exclusion phenomena) [25]. This explains why these membranes exhibit ion-selectivity. At low ionic environment (i.e., low concentration of ionic solute), the multivalent negative ions are separated by the NF membrane to a higher degree than monovalent ions, the latter can pass more freely through the pore of the membrane [26].

Donnan exclusion of the electrolyte ions separation occurs at the interaction with fixed charges of the membrane. Due to the formation of carboxylic acid group on the surface of the membrane by the breakage of anhydride linkage, cations like Na^+ are attracted towards carboxylate group to create charge on membrane surface. Hence, due to the small size of Cl^- and Na^+ ions, they pass easily through the membrane to maintain the neutral charge across the membrane whereas larger

Ca^{2+} rejected to greater extent. From the above mentioned facts it is clear that, Donnan effect increases with increase in % of PIMA. PNM4 contains 35% of PIMA polymer whereas PNM1 contains only 5 % of PIMA polymer, so the formation of carboxylic acid groups is more in PNM4. Consequently these membranes showed more rejection than the others and rejection decreases with decrease in the concentration of PIMA polymer.
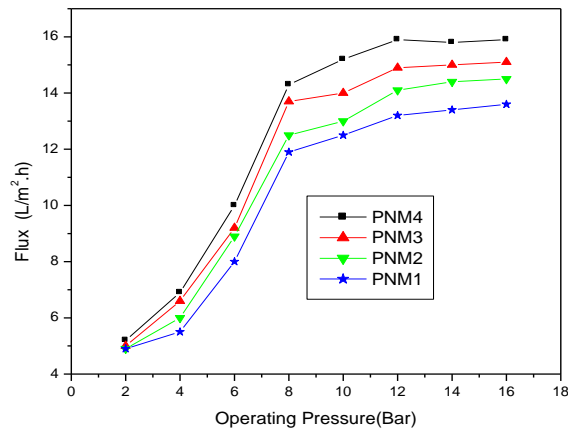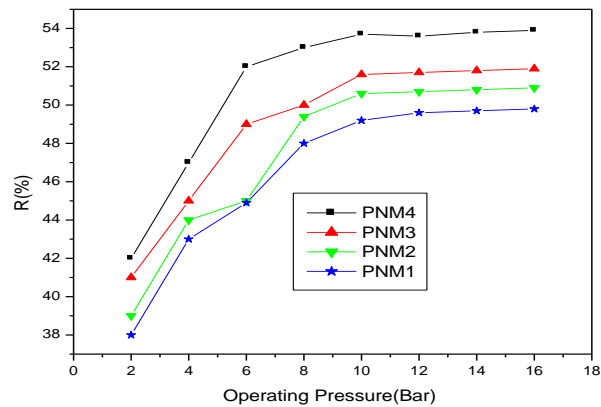

Fig. 11a. Flux of the NF membranes before alkali treatment with 0.1% NaCl.

Fig. 11b. Rejection of the NF membranes before alkali treatment with 0.1% NaCl.
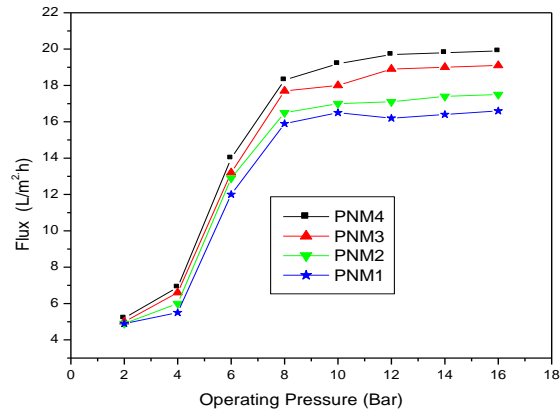
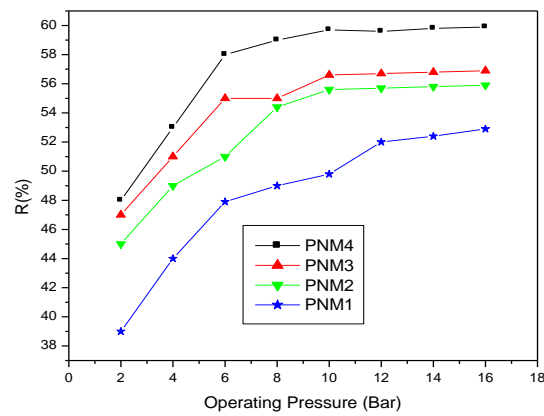**Fig. 12a**. Flux of the NF membranes after alkali treatment with 0.1% NaCl.

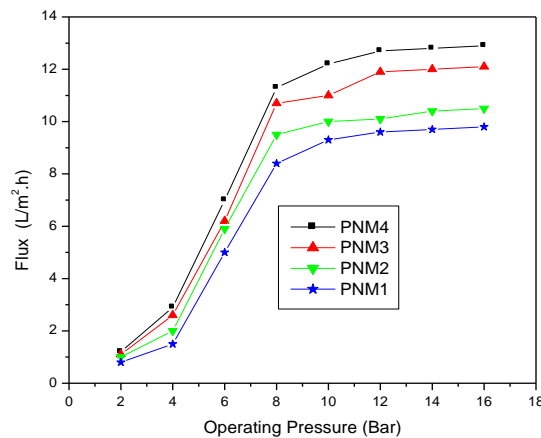**Fig. 12b.** Rejection of the NF membranes after alkali treatment with 0.1% NaCl.

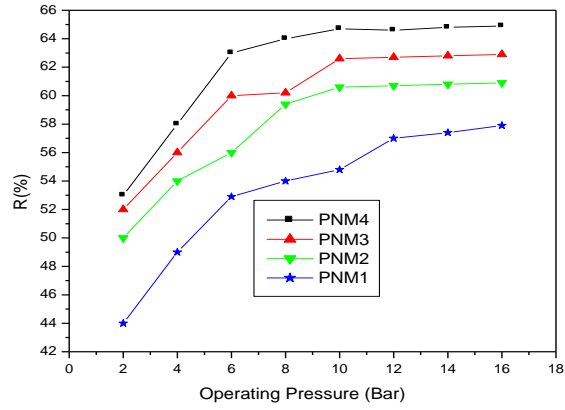**Fig. 13a.** Flux of the NF membranes before alkali treatment with 0.1% $CaCl_2$.

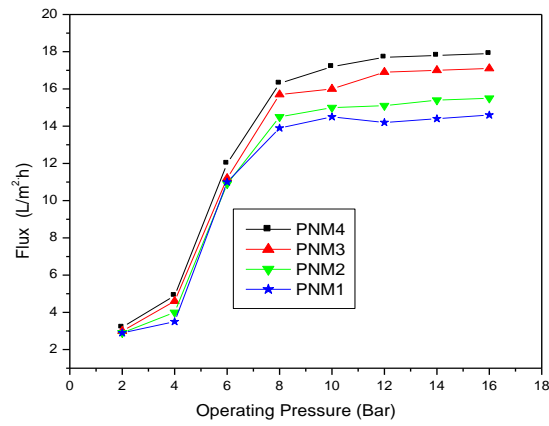**Fig. 13b.** Rejection of the NF membranes before alkali treatment with 0.1% $CaCl_2$.

Fig. 14a. Flux of the NF membranes after alkali treatment with 0.1% $CaCl_2$.
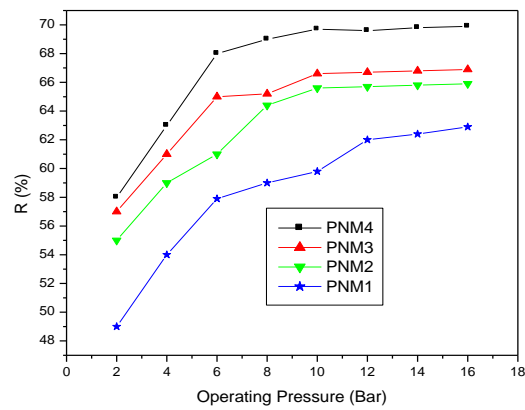

Fig. 14b. Rejection of the NF membranes after alkali treatment with 0.1% $CaCl_2$.

Conclusions

The following conclusions can be drawn from this research work; DIPS method proved to be effective for the synthesis of NF membranes. Synthesized NF membranes are confirmed by the IR studies. NF membranes showed improved water uptake, swelling with respect to increased concentration of PIMA. Prepared NF membranes exhibit higher contact angle value and the same decreased with increase in PIMA concentration after hydrolysis. Hence it is established that, introduction of carbonyl group after hydrolysis of PIMA enhances wettability of the membranes. Thermal study of the different synthesized membranes indicated that PS contents play major role in thermal stability of the membranes. SEM pictures of the membranes were used to identify pore size and presence of channel like microvoids on membranes. Membranes showed better $CaCl_2$ retention than NaCl after alkali treatment. Synthesized NF membranes exhibited better sodium chloride rejection, hence it is concluded that these membranes can be used effectively for desalination.

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