



Synthesis, characterization and desalination study of novel PSAB and mPSAB blend membranes with Polysulfone (PSf)

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ABSTRACT

The present paper describes the synthesis of poly sulphonyl amino benzamide (PSAB) and methylated poly sulphonyl amino benzamide (mPSAB) polymer, using terephthalic acid chloride and substituted 4-amino-1-benzensulphonamide in N-methyl-2-pyrrolidone. Polymers were characterized by FT-IR, NMR and GPC. Polysulfone composite membranes were prepared using these novel polymers by DIPS (Diffusion Induced Phase Separation) method. These composite membranes are useful for water purification with special emphasis on sea water desalination. Newly prepared membranes were studied for salt rejection, water flux, molecular weight cut off by PEG solution, effect of the pH on water swelling and salt rejection and flux decline was also studied. 30 to 70% of the salt rejection was observed in all membranes. Effect of the dilution on salt rejection was studied using different concentration of NaCl solution varying from 1000 ppm to 3500 ppm. All the membranes showed 80% rejection for PEG having 1000 Da molecular weight. Contact angle and water swelling was measured to determine hydrophilicity of the membrane. Water swelling and salt rejection in different pH was also studied.

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1. Introduction

Nanofiltration membrane is a kind of membrane used in pressure driven filtration processes whose pore size lies between reverse osmosis and ultrafiltration membranes. In recent years, NF membranes are gaining more importance amongst the polymer chemists for the filtration process owing to its advantages such as low operating pressure, high flux, and high retention of multivalent ions [1]. Nowadays NF membranes are commonly employed in water purification applications, such as ultra pure water production, water softening, desalination, waste water treatment [2–11]. One also finds its application in the separation of organics, heavy metal from water. Industrially they are important in pigment industries and pharmaceutical industries.

NF separation is achieved by charge and size exclusion [12]. Charge on the membrane is positive below the iso-electric point and negative above it. The charge exclusion of ions is dependent on the charge of the membrane, the ionic strength and the valency of the ions. The latter two influence the membrane charge density and the iso-electric point. The size exclusion is dependent on the membrane structure, more dense structure leading to lower permeation.

Presently, lot of research is going on for preparing efficient NF membranes. Bolong et al. in [13] 2010, reported that, charged membranes are more effective for removal of bisphenols from waste water. Abu Seman

et al. [14] in 2011 developed membranes with antifouling properties and studied the performance of nanofiltration membranes modified by interfacial polymerization. Miao et al. [15] in 2006 prepared and characterized N,O-carboxymethyl chitosan (NOCC)/polysulfone (PSf) composite nanofiltration membranes. In that, ultrafiltration membrane of polysulfone was used to convert nanofiltration membrane by coating NOCC. Zhang et al. [16] in 2006 reported investigations on the structure and performance of a polypiperazine amide/polysulfone composite membrane. Polypiperazine was cross linked to the polysulfone membrane. Many literatures have reported polysulfone or modified polysulfone as the material for the NF membrane [17,18] due to its advantages such as high chemical resistance; tolerance to wide range of pH and ease of making composites with other polymers. Hydrophobic property of polysulfone affects on the productivity of the membrane [19]. In NF membranes, main challenge is to increase the flux and salt rejection while minimizing the operating pressure. According to Nowak (1989), transport and separation properties of Polysulfone membranes depend on the substrate composite with polysulfone [20]. Hydrophilic polymer is required to blend with polysulfone to increase the performance of the membrane. Keeping these challenges in view, we have designed NF blend membranes of different weight proportion of novel polymers and polysulfone by DIPS (Diffusion Induced Phase Separation) method. The main aim of this research is to increase the efficiency of the NF by using charged membranes.

Poly(sulfonyl-amino-benzamide) and methylated poly(sulfonyl amino benzamide (PSAB and mPSAB) novel polymers were prepared. The novel polymer was characterized by FT-IR and NMR. Blend

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membranes of polysulfone with novel polymers were prepared. The performance of the membrane was studied by water flux, salt rejection and flux decline using 3500 ppm of NaCl solution. Molecular weight cut off was studied by using PEG solutions of different molecular weight. Contact angle and water uptake studies were carried out to show hydrophilicity of the membranes, also reported the effect of pH on water swelling and salt rejection of the membrane.

2. Experimental part

2.1. Synthesis of polymers

All the chemicals were obtained from Aldrich (India) and were used without any further purification. 2 g (0.00985 moles) of freshly prepared terephthalic acid chloride was dissolved in 30 mL of N-methyl-2-pyrrolidone, in this solution, 2 g (0.0116 moles) of substituted 4-amino-1-benzensulphonamide, 3.1 g (0.0232 moles) of LiCl and 2–3 drops of Di-methyl formamide (DMF) were added and then the reaction mixture was heated at 100 °C for 20 hours. After cooling the reaction mass to room temperature, it was poured into ice cold water. The solid mass was separated by filtration, washed with water and finally purified with ethyl acetate. The product was dried in vacuum oven at 50 °C for 15 h. The dried solid product was used further for characterization. Fig. 1 represents the synthesis of PSAB & mPSAB.

2.2. Preparation of membrane

The membrane was prepared by DIPS method. Udel Polysulfone (PSf) having molecular weight of 35,000 Da was procured from (Sigma-Aldrich Co). Poly sulphonyl amino benzamide (PSAB) and methylated Poly sulphonyl amino benzamide (mPSAB) were synthesized in the laboratory and reagent grade N-methyl pyrrolidone (NMP) was obtained from (Merck-India) and was used without any further purification. Both PSf and novel polymers in required amount were dried in vacuum oven for 10 h. Different compositions of polymers were taken into a beaker and specified amount of NMP was added. The mixture was stirred for 24 h at 60 °C to get viscous solution and then stirring was stopped for 60 m to avoid the formation of air bubbles. The solution was filtered using G4 sand filtration. Filtered polymer solution was casted on a glass plate using glass rod. Thickness was maintained as 0.20 mm. It was then allowed to stand at room temperature for 40 s. Then membrane was separated by dipping the glass plate in ice cold distilled water bath to allow phase separation. Further, separated membrane was washed with distilled water for several times and stored in distilled water for 24 h. The following compositions of membrane

were prepared. The thickness of the all prepared membranes was 180 μm.

2.3. Characterization of polymers and membranes

2.3.1. Characterization of polymer

ATR-IR spectra of the polymer as well as membranes were measured using JASCO FT/IR 4100 spectrophotometer. Before recording the spectrum, the membrane was dried in desiccator for 24 h. Spectra were recorded in the range of 4000–400 cm⁻¹.

¹H-NMR spectra of the polymer were recorded on Varian 400 MHz NMR spectrometer (Varian Co., USA) with DMSO-d₆ as solvent. ~5 mg of sample was dissolved in DMSO-d₆ and spectra was taken keeping relaxation delay time as 1 s and 32 number of scans using an exclusive ¹H probe.

Molecular weight of the polymer was measured by using GPC. Analysis was done in Sardar Patel center for science and technology, Gujarat, India, using Perkin Elmer series-200 GPC instrument.

2.3.2. Characterization of the membranes

2.3.2.1. Contact angle measurement and water swelling study of the membrane. The contact angle of water on prepared membranes was determined at room temperature using sessile droplet method on a FTA-200 Dynamic contact angle analyzer. At least five angles were measured for each sample and then the average value was calculated and reported.

Swelling behavior of membrane was determined by taking pieces of the membranes having 1 cm² area. These membrane samples were rinsed with deionized water and then dried in vacuum desiccator for 24 h. The dried membrane was then immersed in distilled water for 24 h. The swollen membranes were taken out and excess water on the surfaces was gently removed by a blotter. Then swollen weight of membrane was quickly measured. After that, membrane was again dried under vacuum desiccator for 24 h. Dried membrane was quickly weighed. Degree of swelling was calculated using following formula

$$\% \text{ swelling} = \left(\frac{w_w - w_d}{w_d} \right) \times 100 \quad (2.1)$$

where w_w and w_d are the weight of swollen and dried membranes respectively [21].

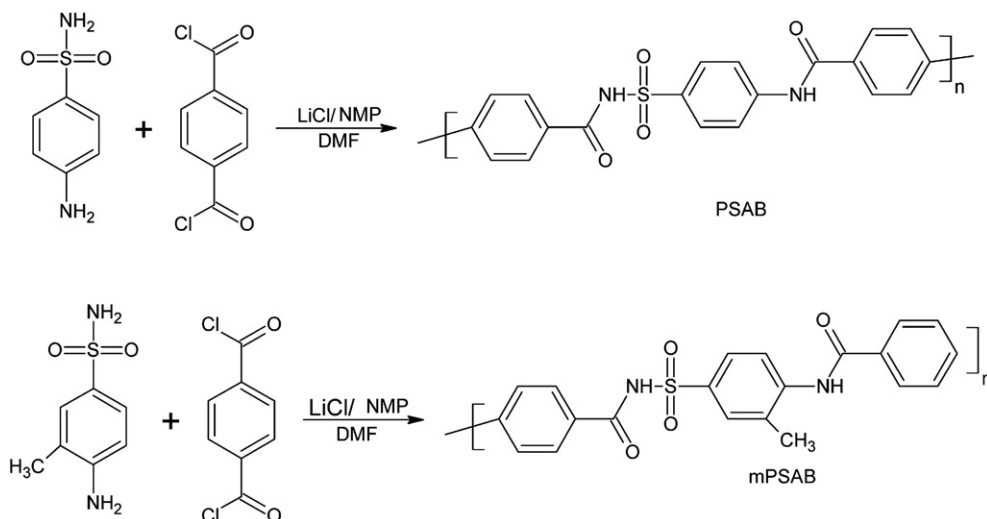


Fig. 1. Synthetic route for the polymers.

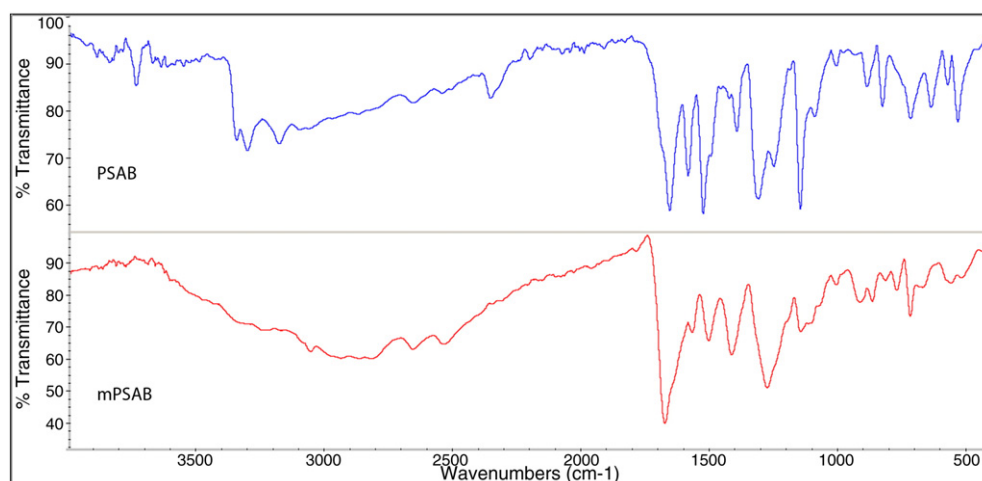


Fig. 2. ATR-IR spectra of PSAB and mPSAB polymer.

2.4. Performance setting and analytical methods

2.4.1. Pure water flux

All the permeation experiments were performed at room temperature using self constructed desalination cell, described in our recent publication [22].

A circular membrane sample with diameter of 60 mm was placed in the test cell with the top surface facing towards the incoming feed. Effective membrane diameter was 50 mm. The water flux was measured by direct measurement of the permeate flow in terms of liter per meter square per hour (L/m^2h). Hydraulic permeability coefficient of the membrane (L_p) was estimated from the slope between water flux and the applied pressure

$$L_p = \text{slope} \times 2.77 \times 10^{-10} \quad (2.2)$$

2.4.2. Molecular weight cut-off (MWCO)

Molecular weight cut-off is the characteristic of a membrane which gives an idea about the pore size of the membrane and it is related to the rejection of a spherical solute of given molecular weight. The molecular weight cut-off has linear relationship with the pore size of the membrane [23]. In general, the molecular weight cut-off of the membrane was determined by identifying an inert solute of lowest molecular weight that has a solute rejection of 80–100% in steady state filtration experiments [24]. Thus, the polymer such as polyethylene glycol (PEG) of different molecular weights varying from the 900 Da to 4000 Da was taken for rejection studies of the all membranes. The permeation cell was filled with PEG solution and pressurized at a constant pressure of 200 kPa. During filtration, the permeate solutions of corresponding membranes were collected over a period of time in a graduated tube and were analyzed for the concentration of PEG by UV-vis spectrophotometer (Shimadzu, Model UV-160A) [23]. From

the feed and permeate concentrations, the percentage rejection was calculated using the following equation.

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2.3)$$

where C_p and C_f are the concentrations of the permeate and feed respectively.

2.4.3. Salt rejection study

The rejection experiment was carried out as same as water flux study. The percent salt rejection was determined by conductivity method. These samples were analyzed for their salt concentration by conductivity measurement, and then the percent retention was calculated using the same equation which is used for molecular weight cutoff study.

The salt rejection study was done under different operating pressure varying from 200 kPa to 1000 kPa. Effect of pH and dilution on salt rejection was studied using same concentration of NaCl solution under 200 kPa applied pressure. The pH of the solution was varied from 3, 7, 9 and 11, and the dilution from 1000 ppm to 3500 ppm.

Above mentioned experiments were repeated three times with different membranes of same composition. The average results were reported.

3. Results and discussion

3.1. Characterization of polymer

ATR-IR spectra of the polymers were measured to confirm the structure. The spectra showed 3308 cm^{-1} for the NH stretching, 3220 cm^{-1} for the C=C stretching, 1661 cm^{-1} for the C=O, $1169\text{--}1170\text{ cm}^{-1}$ due to O=S=O stretching and additional peak in mPSAB at 2943 cm^{-1} of CH_3 stretching. Fig. 2 represents ATR-IR Spectra of the polymers.

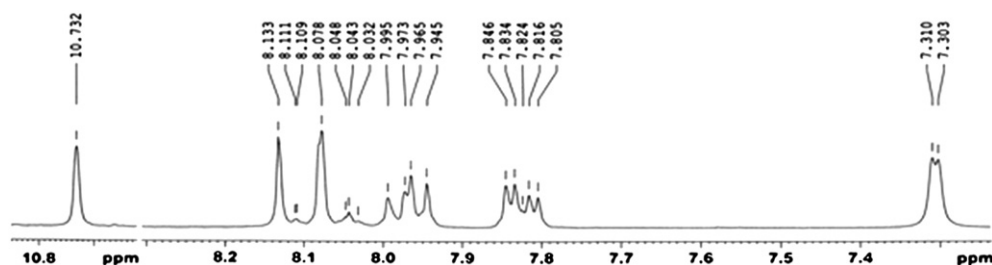


Fig. 3. ^1H NMR spectrum of PSAB polymer.

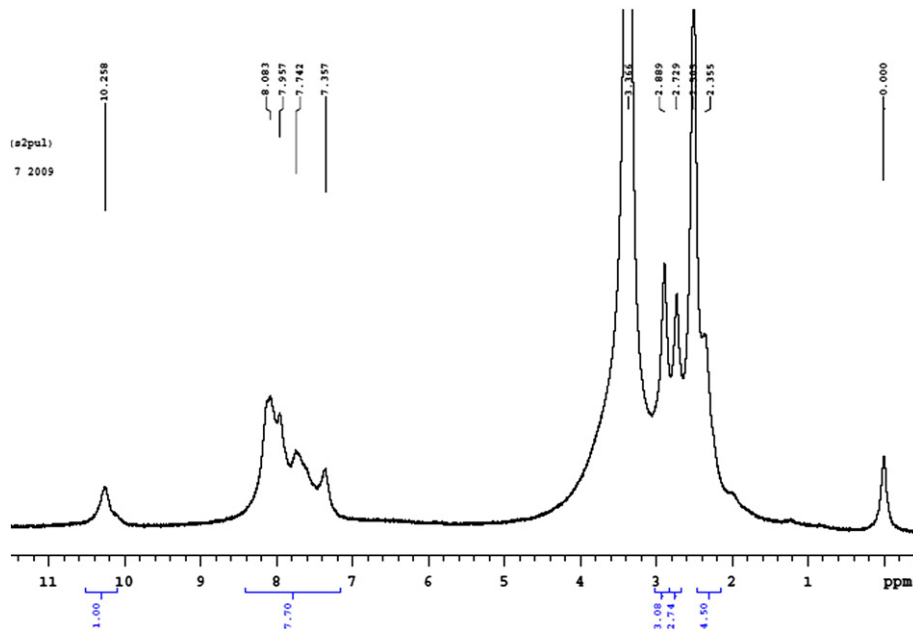


Fig. 4. ^1H NMR spectrum of mPSAB polymer.

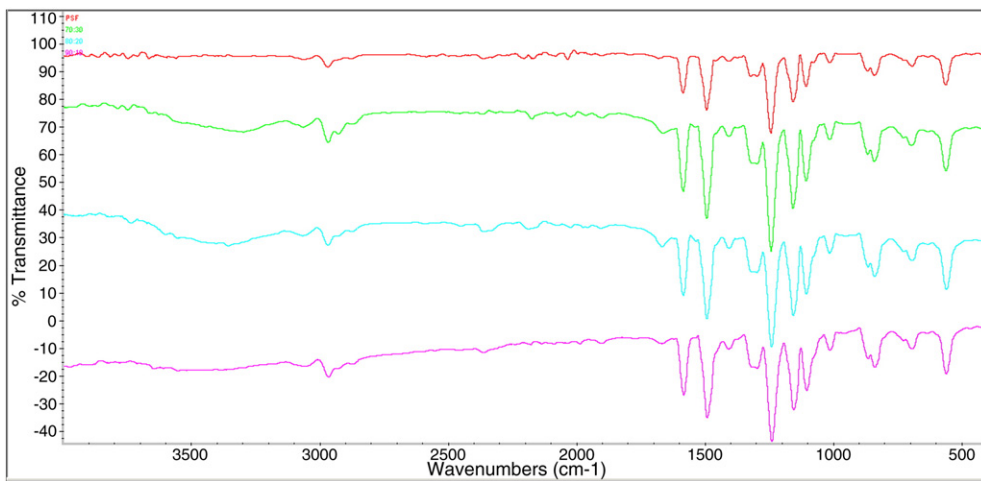


Fig. 5. ATR-IR spectra of PSf:PSAB membranes.

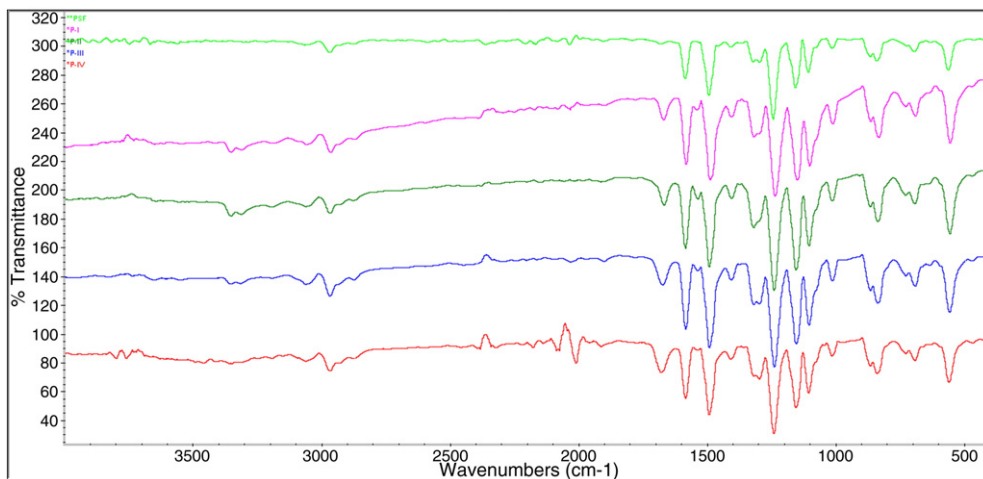


Fig. 6. ATR-IR spectra of PSf:mPSAB membranes.

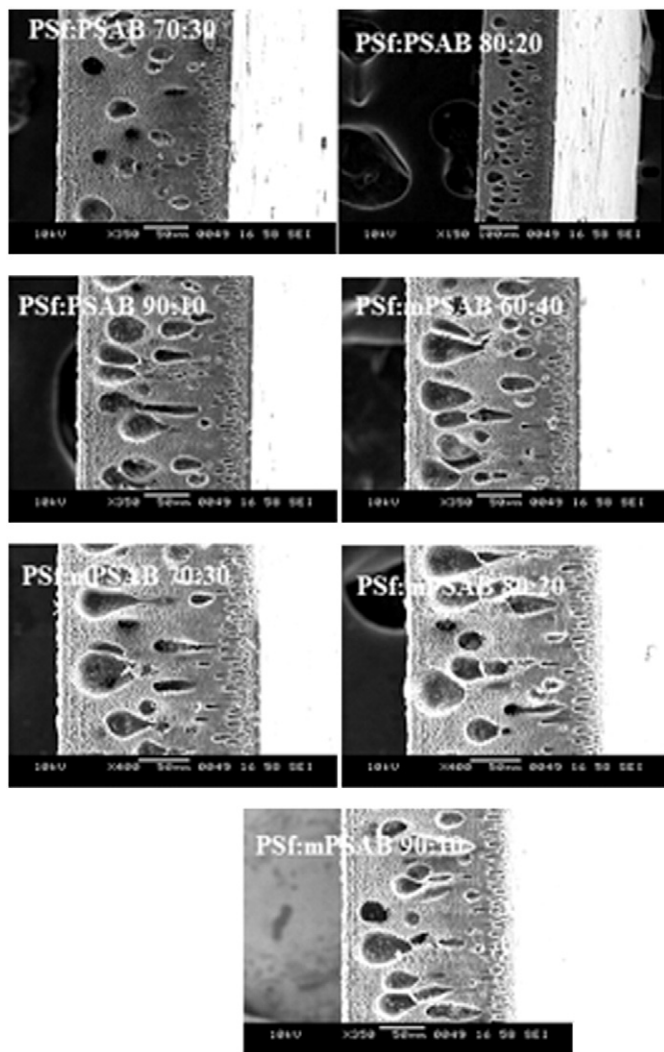


Fig. 7. SEM images of the membranes.

From ¹H-NMR spectrum of PSAB (Fig. 3) it was clear that, the peak at δ 10.73 corresponds to bridge amide NH, whereas the terminal NH peak merge and with the aromatic peak and peaks at δ, 7.3, 7.8, 7.9 and 8.1 (2 H each) correspond to 8 aromatic protons. Hence, confirmed the structure.

The ¹H NMR spectrum of mPSAB (Fig. 4) showed a multiplet at around δ 7.3 to 8.3 which includes all the aromatic protons as well as a terminal -NH proton in it. The bridged -NH resonates at δ 10.7. The methyl group attached to aromatic ring is seen resonating at δ 2.3. Hence confirmed the structure of the polymer.

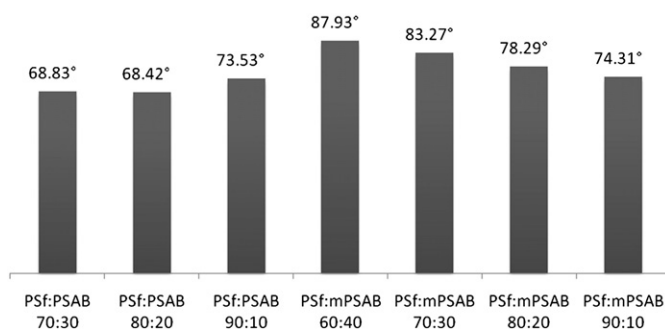


Fig. 8. Contact angle of the membranes.

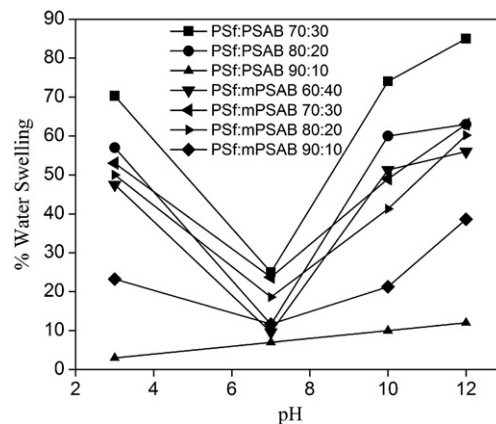


Fig. 9. Water uptakes of membranes in different pH.

Molecular weight of the polymer was determined by GPC (Gel Permeation Chromatography) using polystyrene as a standard. PSAB and mPSAB shows Mw 3733 Da and 2084 Da with polydispersivity 3.4 and 2.1 respectively.

3.2. ATR-IR of membranes

ATR-IR of the membranes was done for the confirmation of the composition of the polymers. The peaks which are present in the PSAB and mPSAB can also be seen in the IR Spectra of the membrane. Figs. 5 and 6 are ATR-IR spectra of PSf:PSAB and PSf:mPSAB blend membranes respectively.

3.3. Morphology study of the membrane

The surface morphology study of the membrane by SEM was bit difficult as it requires more magnification. At higher magnification the electron bombardment is more and it causes surface damage of the membrane. Hence, cross section of the membranes was prepared to study the morphology. The cross section of the membrane was differentiated into three different regions. Upper layer is called skin layer, which is responsible for selectivity, middle finger like projections are called middle layer which is responsible for productivity and bottom layer which gives mechanical support to the membrane. Fig. 7 shows the SEM images of cross section of the all membranes.

3.4. Contact angle measurement and water swelling study

The contact angle was measured by sessile drop method. Fig. 8 shows the contact angles of the membranes with water. It was observed that,

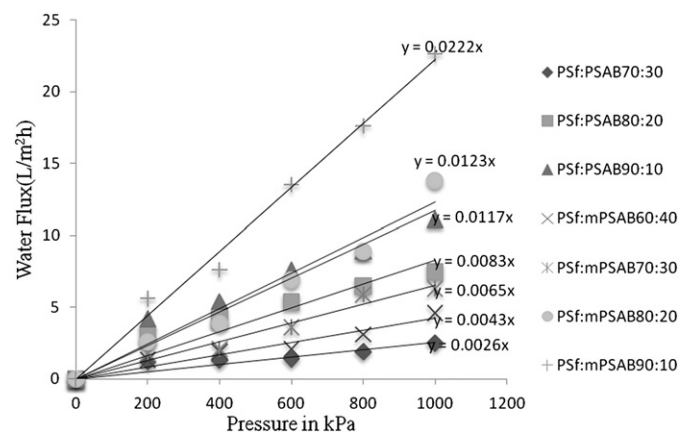


Fig. 10. Water Flux study of the membranes in different pressure.

Table 1
Hydraulic permeability coefficient of the membrane (L_p).

Membrane	L_p (m/sPa)
PSf:PSAB 70:30	7.2×10^{-12}
PSf:PSAB 80:20	3.3×10^{-12}
PSf:PSAB 90:10	3.2×10^{-12}
PSf:mPSAB 60:40	1.1×10^{-12}
PSf:mPSAB 70:30	1.8×10^{-12}
PSf:mPSAB 80:20	3.4×10^{-12}
PSf:mPSAB 90:10	6.1×10^{-12}

with increase in the percent composition of polysulfone, there is an increase in the contact angle in PSAB series of membranes and decrease in the mPSAB series of membrane. In mPSAB, one additional methyl group decreases the hydrophilicity of the membrane. Hence the mPSAB membranes showed higher contact angle as compared to PSAB membranes. The contact angle of pure polysulfone was found to be 73° from the literature [25].

Hydrophilicity of the membrane can be explained by water swelling test. Affinity for water is an important property of the filtration membranes designed for water filtration. However, hydrophilic materials may lead to large swelling and loss in mechanical resistance. The swelling ratio is a parameter which is frequently used to characterize the affinity of the membranes towards water. The PSf:PSAB 70:30 showed highest water uptake and lowest contact angle. Fig. 9 showed that an increase in the percentage composition of the polysulfone, increases the water swelling of the membrane in the PSAB series. Whereas, mPSAB series showed lesser water swelling. While comparing the water swelling study of PSAB and mPSAB series of membranes, mPSAB series showed lesser water swelling and higher contact angle. Hence, PSAB composite membranes are more hydrophilic than the mPSAB composite membranes.

Water swelling test was performed in different pH. The data presented in Fig. 9 indicate a slight increase in swelling ratio with the PSAB content in the initial blend. And also acidic and basic pH membrane showed more water swelling as compared to neutral pH. The overall swelling ratio consists of a part due to the absorption into the polymer matrix and a part due to water retained by capillary in the pores. There is a possibility of opening of the pores under different pH conditions. The membrane PSf:PSAB 70:30 showed more water swelling and PSf:PSAB 90:10 and PSf:mPSAB 90:10 showed lesser water swelling as compared to other membranes.

3.5. The performance characteristics of PSAB membranes

Pure water permeability was obtained by measuring the flux for pure water against operating pressure. As shown in Fig. 10, the flux increased linearly with the operating pressure. The hydraulic permeability coefficient has been calculated from the slope of the line obtained from the

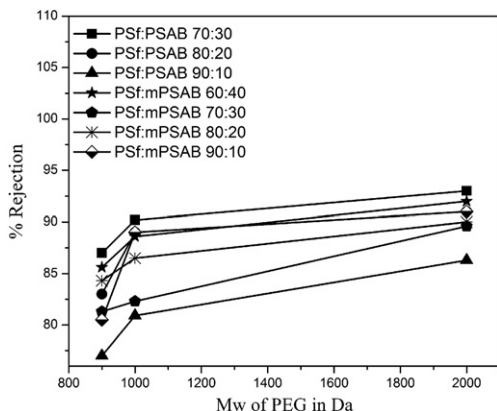


Fig. 11. MWC0 study of the membrane.

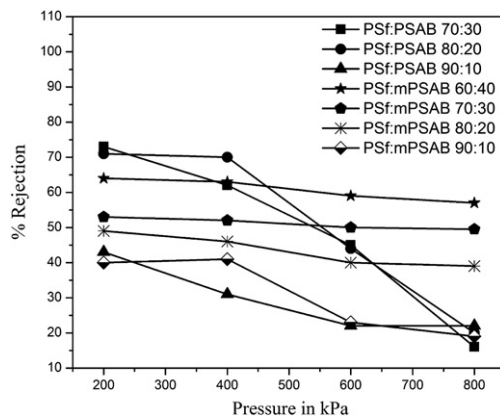


Fig. 12. Salt rejections in different pressure.

proportionality relationship between the water flux and the applied pressure as shown in Table 1.

The composition of the PSf:mPSAB 90:10 showed the highest water flux and PSf:PSAB 70:30 showed lowest flux. PSf:PSAB 90:10 membrane is more hydrophobic in the PSAB series of membranes which was confirmed by the contact angle and water swelling test. The increasing PSAB and mPSAB composition in the membranes increased the water flux and hence, hydraulic permeability coefficient. However the water swelling test and contact angle measurement showed different behavior. This anomalous behavior leads to study of MWCO. Fig. 11 shows the molecular weight cutoff of the all membranes. In which all the membranes showed nearly 80% rejection of 1000 Da PEG solution. Since all the membranes showed the same behavior, it means there is not much difference in their pore size. Hence, we can conclude that water flux and water swelling properties dependent on the nature of the polymer used in the membrane.

The salt rejection experiment was done using 3500 ppm of NaCl solution under different pressures and pH. Fig. 12 shows rejection of the membranes under varying pressure. All the membranes showed the same tendency of decrease in retention with increase in the pressure, whereas, in the case of water flux, it increased with the increase of pressure. The same tendency was observed in all the membranes. It indicates that, membrane pore size increased under higher pressure. It was confirmed by water flux study of the same membrane used for rejection test. It started percolating through membrane without applying pressure. The membrane showed higher water swelling at acidic and basic pH. It may be due to of the pore openings or chemical property of the polymers at different pH. This promotes us to study the rejection of the membrane in different pH.

The data for salt retention in Fig. 13 suggest that, all the membranes showed more retention in the basic and neutral pH. In acidic

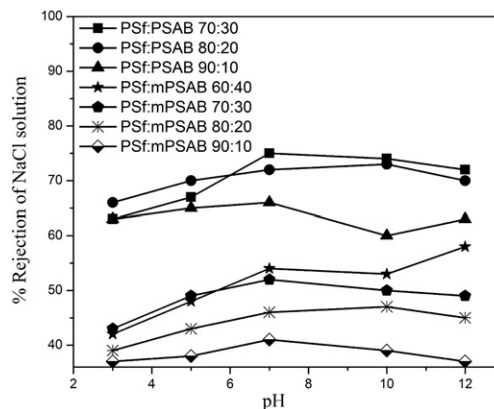


Fig. 13. Salt rejection study of NaCl solution in different pH.

pH, pore opening is more and hence less retention was observed. Several factors might have contributed in the membrane performance to different pH conditions. Literature has shown that, the presence of ions can affect the retention of uncharged molecules [26]. Studies have correlated such changes in the performance to the membrane charge density under different pH conditions [27,28].

From Fig. 12 it was clear that, in basic pH 11, membranes showed more retention because in pH-11 membrane surface gets charged and the ionic interaction is more with feed sample. And also in feed sample, ionic concentration is more leading to the more retention. Whereas in acidic pH, the amide and sulfonamide bonds in the membrane are detached and openings in the membranes lead to less retention. It was confirmed by water uptake study. In this, membranes showed more water uptake in acidic pH because they are possessing large pore size in acidic pH. Sometimes ionic concentration of the feed also plays a vital role in the salt rejection. Hence it is necessary to study rejection of different concentration of salt solution. Fig. 14 shows the effect of dilution on the membrane rejection. It was observed that, there is an increase in the rejection of the ions with increase in ionic concentration of the feed sample. All the membranes showed same tendency. The feed sample having concentration of 3500 ppm showed more rejection than the other concentration. These salt effects could be explained by different mechanisms. More pores on membrane surface were opened under different pH hence salt rejection was performed under different pH, which was also supported by previous researchers [28–32]. Similarly, membrane thickness also increases by swelling of membrane surface. However, to our knowledge, there has been no direct observation to prove that membrane pores or thickness increased when salt was added. Instead, [33] detected that, the membrane thickness in 15% (w/v) NaCl solution at pH=3 and pH=10 was thinner than that in pure water at pH=7, suggesting that membrane underwent swelling when the properties of solution changed. Moreover, for a membrane having an inter-connected porous structure, smaller solutes were expected to go through longer paths because they could permeate through the smaller pores of network [34,35], thus enlarging the effective membrane thickness as solutes effective size reduced. This could reasonably explain why the rejection values increased with increasing salt concentration. Also, when the number of salt ions in membrane pores grew, the probability of collision between ions increased, thus prolonging the moving path of ions when passing through membrane, therefore leading to greater rejection values.

3.6. Flux decline study

Increase in rejection with higher concentration forced us to study the flux decline of the membrane. Flux decline study was done using 2000 ppm of NaCl solution because 3500 ppm solution leads

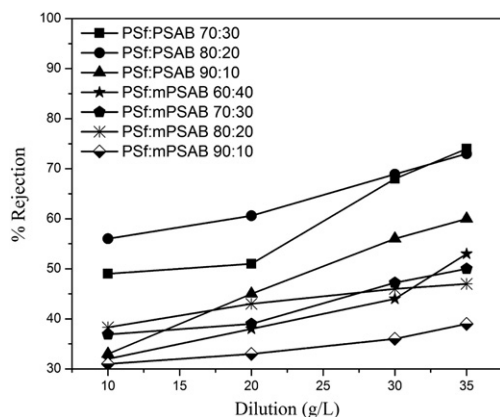


Fig. 14. Effect of dilution on rejection study.

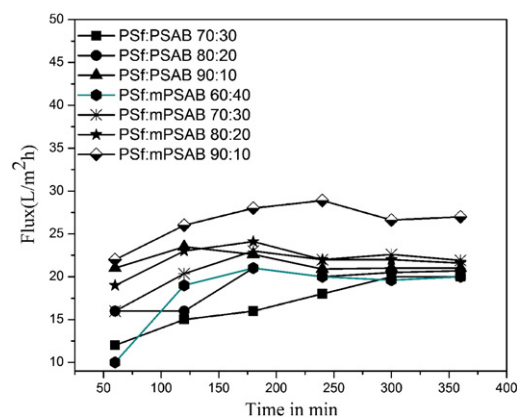


Fig. 15. Flux decline study of the membrane.

concentration polarization. The flux was determined at different intervals of time starting from 60 min to 360 min with a difference of 60 min. Fig. 15 shows the flux of the membrane in different intervals of the time. Initially, there was an increase in the flux and after 300 min it was constant and in few cases, it was in decrease trend. The flux decline occurred by a combination of two effects: the molecule should have the appropriate size to fill the membrane pores, and adsorption process is enhanced by the hydrophobicity of the component. The rejection of the salt solution was 100% after 240 min, hence it can be concluded that the rejection at higher concentration is because of membrane fouling.

4. Conclusions

Polymers were synthesized, characterized and the same were used to prepare composite NF membranes with polysulfone. Membrane performance, especially MWCO, hydrophilicity and desalination was studied. All the membranes showed 1000 Da of MWCO of the PEG solution, enhanced hydrophilicity confirmed by water uptake and contact angle measurement. Water uptake is more in acidic and basic pH as compared to distilled water because instability of amide and sulfonamide bond leads to more porosity or increase in the pore size. Membranes performance was excellent for the desalination of salty water (3500 ppm of NaCl solution). The salt rejection of the membrane was enhanced in an effective way. The salt rejection decreased in acidic and basic pH and there is decrease in the rejection rate with dilution of feed sample.

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