

## Abstract

*Poly(ethersulfone) (PES) / poly(vinylpyrrolidone) (PVP) blend membranes modified with calcium chloride ( $\text{CaCl}_2$ ) were prepared by phase inversion method. Effect of  $\text{CaCl}_2$  on the morphology, filtration and performance characteristics of the PES/PVP membranes was studied in detail. Results indicated that  $\text{CaCl}_2$  blend membranes possessed better porosity and flux than the pristine PES membrane. Dye separation efficiency of  $\text{CaCl}_2$  blend membranes was also increased considerably. Especially, the PES/PVP blend membrane with 1 wt%  $\text{CaCl}_2$  showed highest permeate flux and improved dye rejection. Fouling analysis carried out on  $\text{CaCl}_2$  blend membranes clearly showed that these membranes possessed better antifouling effect than pure PES membrane. Thus the  $\text{CaCl}_2$  blended PES/PVP membranes are more promising for the treatment of dye polluted wastewater.*

## Keywords

*Polyethersulfone, Polyvinylpyrrolidone, Calcium chloride, Membrane fouling, Dye rejection*

## 1 Introduction

Membrane separation is one of the largely used advanced separation technologies for the separation of macromolecules from solutions [1]. Membrane based operations has several advantages which includes compact nature, low energy consumption, room temperature operation, low investment and less pollution, as compared with other conventional separation methods [2, 3]. In general, organic polymers are more suitable starting materials for the preparation of industrial grade membranes, especially for effluent treatment [4]. Several polymers such as polyvinylidene fluoride [5-8], polysulfone [9-11], polyacrylonitrile [12, 13], polyethersulfone [14-17] and cellulose acetate [18-20] have been reported for the development of microfiltration (MF) and ultrafiltration (UF) membranes for various applications.

Polyethersulfone (PES) is one among the better polymeric materials for membrane synthesis, specifically for water and wastewater treatment applications [21]. PES has many merits like wide range of pH tolerance, excellent chemical resistance, good mechanical strength, high thermal stability and ease of fabrication. PES has been successfully employed in the preparation of MF/UF membranes with different pore sizes and varying surface geometry [22, 23]. PES has been reported as one of the most suitable membrane material for separation processes including biological, pharmaceutical, and sterilization [24]. However, PES membranes suffer from the limitations of low flux and membrane fouling owing to its hydrophobic surface. The hydrophobic nature of the PES membrane leads to the adsorption or deposition of the solute molecules on membrane pores and causes serious fouling issues [25]. Also, the water permeability through pure PES membrane is greatly reduced due to its hydrophobic nature, resulting in very low fluxes [26]. These limitations of PES membrane is overcome by enhancing the surface hydrophilicity of the PES using different methods [27-29]. A number of research studies have been reported on the hydrophilization of PES membranes [30-38]. In these studies, a hydrophilic additive (usually inorganic or polymeric) is often added to the casting dope to prepare hydrophilic composite PES membranes. Although, addition of hydrophilic polymers to the PES matrix increased the permeate flux, serious issues of

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polymer miscibility and uniform dispersion of additives were identified with these hydrophilic polymer blend PES membranes [39]. Polyvinylpyrrolidone (PVP) is one of the widely studied hydrophilic polymer additive for blending with PES membrane due to its good miscibility nature with PES [34, 35, 39]. PVP increases the cast solution viscosity and thus ensures better pore interconnectivity when added in the optimum amount [40]. PES membranes blended with inorganic additives, especially metal oxide nanoparticles, resulted in composite membranes of increased flux but decreased solute rejection [36-39]. This was mainly due to the enlargement of the surface pores caused by the agglomeration of the metal oxide particles and their subsequent leaching during phase inversion [39]. Thus, achieving a PES blend membrane with enhanced flux, improved rejection and better fouling resistance without affecting the other properties of PES is an important objective for the membrane industry.

In recent times, calcium salts are investigated as a potential inorganic additive for the polymeric membranes resulting in high flux and enhanced rejection [41-44]. Calcium chloride ( $\text{CaCl}_2$ ) blended with polyacrylonitrile resulted in membrane with high permeation and no loss on the protein rejection efficiency [41]. Polyacrylonitrile and polyvinylidene fluoride membranes mineralized with calcium carbonate ( $\text{CaCO}_3$ ) showed increased surface hydrophilicity and water flux as compared to the unmodified PES membranes. These membranes were identified to be suitable for dye and salt desalination [42, 43].  $\text{CaCO}_3$  nanoparticles incorporated polyvinylidene fluoride membrane was successfully applied for membrane distillation studies. The blend membrane resulted in a high permeate flux and produced a salt rejection of 99.99% [44]. In general, calcium salts, particularly  $\text{CaCl}_2$ , would improve the hydrophilicity and flux of the resulting blend membrane [41]. Also, the chloride resistance of the resulting membrane would be enhanced due to the control of cleavage of the polymer chain [45]. This would be highly beneficial for the membranes to handle feed solution containing free chlorine and also during chemical cleaning processes.

In the present study, modification of PES membrane using  $\text{CaCl}_2$  as the inorganic additive and PVP as non-solvent additive has been carried out by phase inversion method. The concentration of  $\text{CaCl}_2$  was varied in the casting dope to study its effect on the performance of the membranes. Morphology analysis of the pure and blend membranes was analyzed using SEM and AFM. Membrane properties like porosity, hydrophilicity, mechanical stability and pure water flux were evaluated for the virgin and blend PES membranes. Dye rejection capacity for all the prepared membranes was analyzed using various dye solutions. Fouling analysis for all the prepared membranes were done through flux recovery ratio calculation and by estimating the various mass transport resistances across the membrane. The obtained results for the characterization and performance analysis of the composite membranes were compared with that of pure PES membrane.

## 2 Materials and methods

### 2.1 Materials

Polyethersulfone (PES, Veradel 3200P) in powder form was supplied by Solvay Specialities India Pvt. Ltd (India) and it was dried at 120 °C for 8 h before being used. Anhydrous calcium chloride ( $\text{CaCl}_2$ , 96%) and Polyvinylpyrrolidone ( $M_w = 40,000$ ) were purchased from Sigma-Aldrich Ltd (India). *N, N*-dimethyl formamide (DMF, 99%) solvent was procured from SRL Chemicals Ltd (India). Dyes such as Congo red ( $M_w = 696.7$ ), Orange II ( $M_w = 350.3$ ) and Crystal violet ( $M_w = 407.9$ ) in powder form, were obtained from local dyeing industries at Tirupur, Tamilnadu (India) as gift samples. The molecular structures of all the dyes are presented in Appendix. Freshly prepared deionized water was employed for the preparation of gelation bath, dye solution preparation and membrane storage. All the reagents used in the membrane preparation process were of analytical grade and were used as such in the experimental work.

### 2.2 Membrane preparation

PES flat sheet membranes were prepared using a combined dry and wet phase inversion method. The casting dope for each membrane consisted of fixed amount of PES and PVP while the concentration of  $\text{CaCl}_2$  was varied in regard to the DMF solvent, as shown in Table 1. Based on previously reported works, it was understood that the optimum concentration of PES and PVP for good miscibility and polymer interaction was 18 wt% and 2.5 wt% respectively [39, 46]. Hence the PES and PVP concentration were fixed to 18 wt% and 2.5 wt% while the concentration of  $\text{CaCl}_2$  was varied from 0 wt% to 3 wt%. Cast solution was prepared by first dissolving the PES polymer in DMF and then by adding the additives (PVP and  $\text{CaCl}_2$ ) in a sequential manner into the polymer solution at 60 °C for 8 h using mechanical stirring at 400 rpm. Then the homogenous solution was allowed to stand for 4 h at room temperature for removal of air bubbles. Subsequently, the blend solution was cast on smooth glass substrate with the help of a doctor's blade for a fixed thickness of 200  $\mu\text{m}$ . The casted membrane was air dried on the glass plate for 30 sec and then it was immersed in the water bath (gelation medium) of 20 °C. After 12 h of gelation, the membrane was removed from the non-solvent bath and washed with deionized water to remove any residual solvent. The prepared membrane sheet was subsequently stored in deionized water till usage.

### 2.3 Membrane characterization

The visual information on the cross section morphology of the prepared membranes was provided by the scanning electron microscopy (SEM) (Quanta FEG 200, FEI Co., USA). The membrane sample was cut into small pieces, dried using a filter paper, snapped in liquid nitrogen (for 30 sec) and dried. The dried samples were sputtered with gold for producing electric conductivity and were subjected for SEM analysis.

**Table 1** Composition for the pure and composite PES membranes

Membrane ID	Membrane Composition (weight %)			
	PES	PVP	CaCl <sub>2</sub>	Solvent (DMF)
M0	18	0	0	82
M1	18	2.5	0	79.5
M2	18	2.5	0.5	79
M3	18	2.5	1	78.5
M4	18	2.5	2	77.5
M5	18	2.5	3	76.5

Surface roughness of the synthesized membranes was analyzed by atomic force microscopy (AFM) (SPM CP-II, Veeco Co., USA). Samples were cut into rectangular pieces of 10 mm by 30 mm and glued on glass substrate. AFM analysis was carried out on an effective area of 15  $\mu\text{m} \times 15 \mu\text{m}$  for each sample by tapping mode.

Hydrophilicity (or) surface wettability of the pristine and composite membranes surface was measured in terms of water contact angle. The static contact angle on the membrane surface was measured using a goniometer (DGX Digidrop, France). De-ionized water was used as the probe molecule in all measurements. The mean contact angle of each membrane was obtained by averaging the static contact angle measured at four different positions on the membrane sample's surface.

Mechanical stability of all the prepared membranes was analysed by measuring the tensile strength and elongation ratio of the membrane sample using a material test-machine (Zwick Z010, Germany) at a loading velocity of 100 mm/min. The reported values for tensile strength and elongation ratio were average values for three sample runs.

Equilibrium water content (EWC) of the synthesised membranes was calculated by observing the water uptake capacity of the respective membrane sample. Membrane sample (in rectangular form) was soaked in deionized water for 24 hours. The wet weight was weighed after wiping the excess water on the sample surface using filter paper. Subsequently the wet sample was placed in a vacuum oven at 80 °C for 24 h. The dry weight of the membrane sample was then weighed until the weight became constant. EWC of the membrane sample was calculated using Eq. (1), where  $W_w$  (kg) and  $W_d$  (kg) are the wet and dry membrane weights respectively.

$$EWC = \frac{W_w - W_d}{W_w} \times 100 \quad (1)$$

Porosity of the prepared membranes was calculated by dry-wet weight method in which the wet weight and dry weight of the respective sample was observed. Membrane porosity ( $\varepsilon$ ) was calculated using Eq. (2).

$$\varepsilon = \frac{W_w - W_d}{\rho_w V_m} \times 100 \quad (2)$$

where  $W_w$  (kg) and  $W_d$  (kg) are the wet and dry weight of the membrane sample,  $V_m$  (m<sup>3</sup>) is membrane volume on dry basis and  $\rho_w$  (kg m<sup>-3</sup>) is water density. The measurement process was repeated for three times and the average values were reported.

## 2.4 Pure water permeation and dye rejection

Pure water permeation and dye rejection studies were studied in a dead-end stirred cell filtration setup connected to a nitrogen gas cylinder. The stirred cell (Amicon, Model 8400, Millipore, USA) had an inner diameter of 76 mm and a volume capacity of 400 mL with teflon coated magnetic paddle. The effective area of membrane filtration was 45.6 cm<sup>2</sup>. Nitrogen gas was used as a pressure source on the feed side of the stirred cell. Distilled water was used as the probe liquid to measure the pure water flux (PWF) of the membranes. All the membranes were compacted at a transmembrane pressure of 414 kPa for 2 h and then the PWF measurements were evaluated at 30 °C. Pure water flux for each membrane was calculated using Eq. (3).

$$J_w = \frac{Q}{A\Delta T} \quad (3)$$

where,  $J_w$  (L m<sup>-2</sup> h<sup>-1</sup>) is the pure water flux,  $Q$  (L) is the volume of water collected;  $A$  (m<sup>2</sup>) is the effective membrane area and  $\Delta T$  (h) is the sampling time.

Estimation of average pore radius ( $r_m$ ) for the synthesised membranes was carried out on the basis of filtration velocity method using Guerout–Elford–Ferry equation as given by Eq. (4) [47].

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta_w l q}{\varepsilon \times A \times \Delta P}} \quad (4)$$

where,  $\eta_w$  is the dynamic viscosity of water (Pa s), ' $l$ ' is the membrane thickness (m),  $q$  is the volume of the water permeated per unit time (m<sup>3</sup>/s),  $A$  is the effective area of the membrane (m<sup>2</sup>), and  $\Delta P$  is the transmembrane pressure (Pa).

Separation performance of the prepared membranes was analysed through dye rejection studies. Congo red, Orange II and Crystal violet dyes were used as probe molecules for the rejection analysis. The feed concentration for all dye solutions was taken as 0.1 g L<sup>-1</sup> and the rejection studies were carried out at a transmembrane pressure of 414 kPa in the dead-end stirred cell filtration setup. The permeate samples were collected over defined time intervals and analysed for dye concentration. Solute rejection percentage (%SR) was calculated using Eq. (5).

$$\%SR = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (5)$$

where,  $C_p$  and  $C_f$  are the dye concentrations ( $\text{g L}^{-1}$ ) in the permeate and feed streams, respectively. The concentration was measured using a UV-Vis-NIR spectrophotometer (UV-3600, Shimadzu Corp., USA) at the respective maximum absorption band for each dye molecule, as mentioned in Appendix.

## 2.5 Fouling Analysis

Fouling resistance ability of the prepared membranes was evaluated in terms of flux recovery ratio. The necessary experiments for the fouling analysis were carried out in the same setup used for pure water flux and dye rejection studies. For all the fouling studies, distilled water and Congo red (CR) dye solutions were used as the probe liquids. For a given membrane sample, the pure water flux ( $J_w$ ) was evaluated initially. Subsequently, the sample was subjected to CR rejection and the CR permeate flux ( $J_{CR}$ ) was measured. The membrane was then cleaned with deionized water for 15 min to remove traces of dye adsorbed on its surface. Consequently, the membrane was again subjected for pure water flux measurement and the water flux obtained was recorded as pure water flux through fouled membrane ( $J_{w2}$ ). The flux recovery ratio (FRR) was calculated using Eq. (6). All the flux measurements were made at a transmembrane pressure of 414 kPa and the membrane samples were well compacted prior to flux calculation.

$$FRR = \frac{J_{ws2}}{J_{ws}} \times 100 \quad (6)$$

Fouling could also be quantified by estimating the various mass transport resistance terms for the solute transport across the membrane [25]. In general, the total resistance for the mass transport ( $R_t$ ) could be obtained from the basis of Darcy's law and is given by Eq. (7).

$$J = \frac{\Delta P}{\eta R_t} \quad (7)$$

where  $J$ ,  $\Delta P$ ,  $\eta$  and  $R_t$  are the permeate flux, transmembrane pressure (Pa), viscosity of the permeate (Pa s), and total resistance for mass transport ( $\text{m}^{-1}$ ) across the membrane, respectively. This total resistance for mass transport ( $R_t$ ) is composed of the inherent hydraulic resistance of the membrane ( $R_m$ ) and the resistance to mass transport due to fouling ( $R_f$ ). The fouling resistance ( $R_f$ ) is made of reversible fouling resistance to mass transport ( $R_r$ ) (concentration polarization effect) and irreversible fouling resistance to mass transport ( $R_{ir}$ ) (pore blocking) [47, 48]. Thus the components of total membrane resistance ( $R_t$ ) is given through Eq. (8).

$$R_t = R_m + R_r + R_{ir} \quad (8)$$

The intrinsic membrane resistance ( $R_m$ ) is commonly estimated from the initial pure water flux study and is given through Eq. (9).

$$R_m = \frac{\Delta P}{\eta_w J_w} \quad (9)$$

The reversible fouling resistance ( $R_r$ ) and the irreversible fouling resistance ( $R_{ir}$ ) are given through Eq. (10) – (12).

$$R_f = \frac{\Delta P}{\eta J_{CR}} - R_m \quad (10)$$

$$R_{ir} = \frac{\Delta P}{\eta J_{ws2}} - R_m \quad (11)$$

$$R_r = R_f - R_{ir} \quad (12)$$

Equation (9) – (12) were used to calculate various types of resistances for the mass transport across the prepared membranes and thereby to quantify their respective fouling resistant ability.

## 3 Results and Discussion

### 3.1 Effect of $\text{CaCl}_2$ on membrane morphology

SEM images of the cross sections of pure and blended PES membranes are shown in Fig. 1. The prepared membranes exhibited an asymmetric structure comprising of a very thin skin layer and a porous support layer. A comparison between the cross section SEM images of the membranes with and without  $\text{CaCl}_2$  indicated that the  $\text{CaCl}_2$  blend membranes possessed a more porous support layer than the membranes without  $\text{CaCl}_2$ . Analysis of the cross section SEM images of the  $\text{CaCl}_2$  blend membranes clearly revealed the dual opposing effects of PVP and  $\text{CaCl}_2$  addition to the dope solution. It has been reported that the addition of hydrophilic additives to the polymeric solution increases the viscosity of the cast dope [39]. At low additives concentration (up to 1%  $\text{CaCl}_2$ ), the hydrophilic effect of the additives was dominant which caused the formation of more regular fingerlike voided support layer. However, at high additives concentration, the cast dope was less stable due to high viscosity. This dominant viscous effect delayed the polymer demixing rate during membrane formation resulting in more spongy support layer (Fig. 1f).

The surface AFM images of the pure and blended PES membranes are presented in Fig. 2. In these images, the bright areas denote the 'nodules' while the dark region shows the 'valleys' or pores of the membrane surface. AFM analysis was confined to an effective area of  $15 \mu\text{m} \times 15 \mu\text{m}$  and the average surface roughness ( $R_a$ ) was calculated using the XEI image processing software. The obtained results, as presented in Table 2, clearly indicated that the surface roughness of the membranes was increased due to the PVP and  $\text{CaCl}_2$  addition. Similar results have been reported by other related works [22, 40]. Also, the concentration ratio of the hydrophilic additives had an effect on the surface roughness enhancement of the blend membranes.



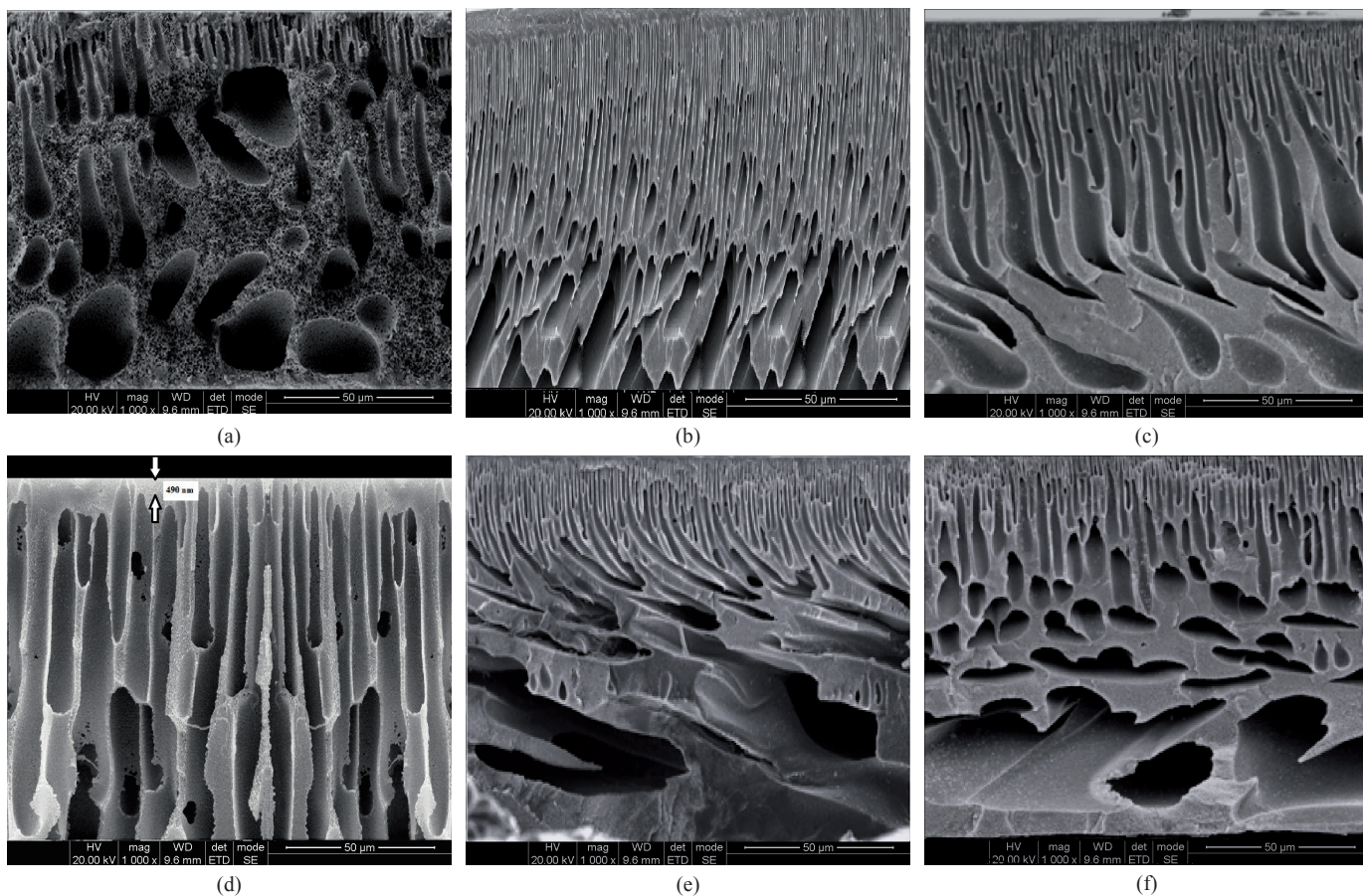


Fig. 1 Cross section SEM images of membranes – a) M0, b) M1, c) M2, d) M3, e) M4 and f) M5

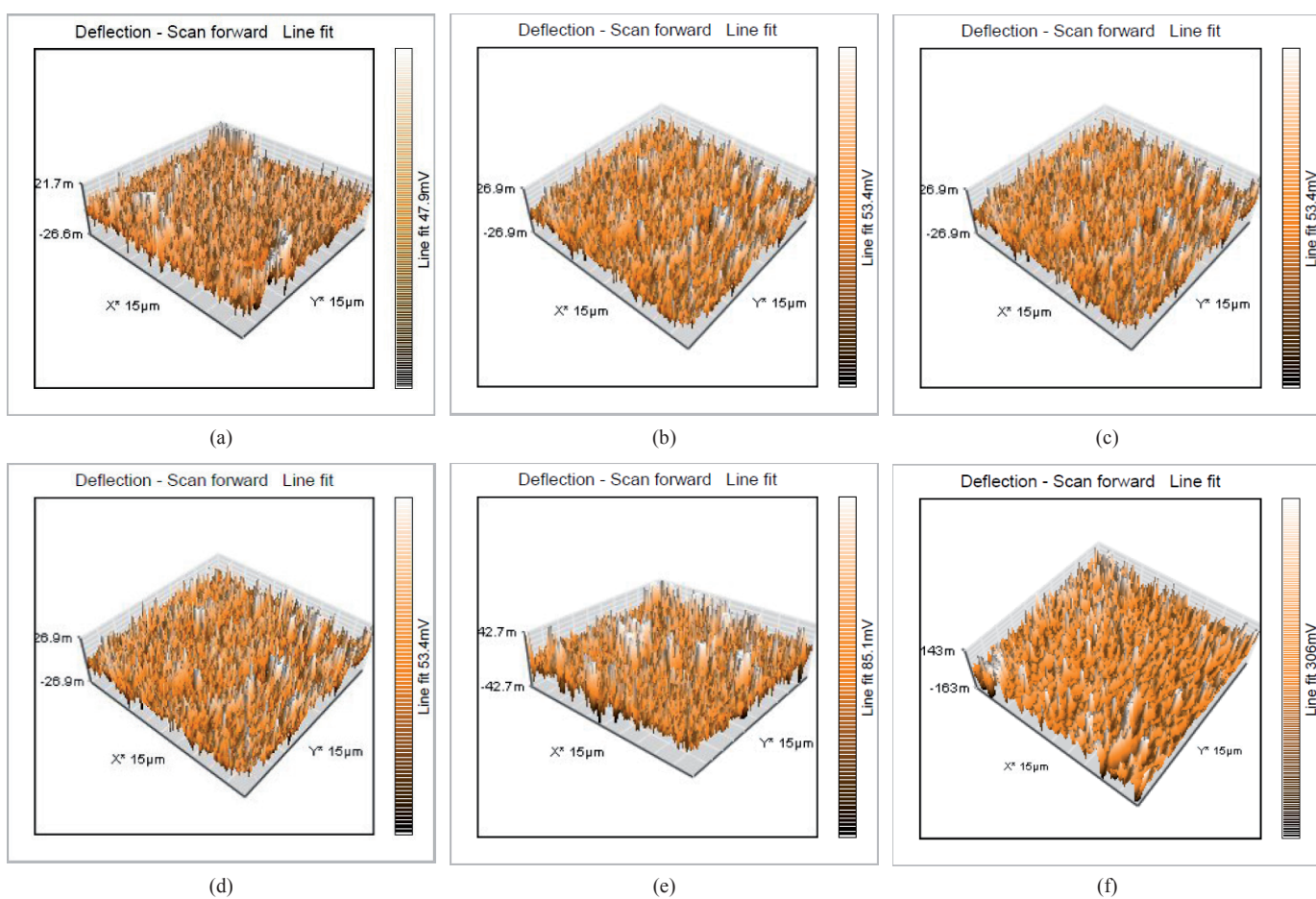


Fig. 2 AFM images of pure and blend PES membranes – a) M0, b) M1, c) M2, d) M3, e) M4 and f) M5

**Table 2** Characterization results for the pure and composite PES membranes

Membrane ID	Surface roughness, $R_a$ (nm)	Contact angle ( $^\circ$ )	Equilibrium water content (%)	Porosity, $\varepsilon$ (%)	Pure water flux ( $L \cdot m^{-2} \cdot h^{-1}$ )	Average pore radius, $r_m$ (nm)
M0	13.92	66.5	43.33	15.05	31.87 ( $\pm 0.8$ )	21.91
M1	20.23	65	45.65	24.81	62.53 ( $\pm 1.2$ )	23.07
M2	22.11	63.5	53.19	38.87	126.19 ( $\pm 1.7$ )	24.84
M3	26.36	61	64.58	58.76	240.25 ( $\pm 1.4$ )	25.6
M4	68.94	56	65.31	45.03	166.36 ( $\pm 1.0$ )	25.85
M5	120.62	49.5	64.71	44.33	157.42 ( $\pm 0.7$ )	25.42

At low values of  $CaCl_2$  to PVP ratio (up to 1%  $CaCl_2$ ), the increase in the surface roughness was small as compared against the high values of  $CaCl_2$  to PVP ratio. It has been reported that membranes with low surface roughness have stronger antifouling abilities [49]. Hence the blend membranes with low values of PVP to  $CaCl_2$  ratio were expected to have better fouling resistances. Results of SEM and AFM analysis clearly showed that the addition of PVP and  $CaCl_2$  to the PES polymer has influenced the morphology of the blend membranes. Also, the morphology of blend membranes showed a drastic change at a cut-off concentration of 1%  $CaCl_2$  indicating that this membrane was expected to have better permeability and comparatively fouling resistant.

### 3.2 Effect of $CaCl_2$ on hydrophilicity, water uptake and mechanical stability

Surface contact angle (CA) is one of the most suitable methods for the measurement of hydrophilicity or surface wettability of the membranes [50]. Low CA value of membrane surface indicates the pronounced hydrophilicity and low hydrophobicity in the membrane. As shown in Table 2, the CA of PES membrane was decreased due to the addition of PVP and  $CaCl_2$ . A significant decrease in the CA value was observed at higher concentration of  $CaCl_2$  which clearly demonstrated that a more hydrophilic surface was obtained due to  $CaCl_2$  addition. This increase in surface wettability could be ascribed to the attachment of the polar functional groups to  $CaCl_2$  molecules. It has been reported that the enhanced hydrophilicity of membrane surfaces would reduce membrane fouling to a larger extent [51]. Hence the  $CaCl_2$  blend membranes were expected to have better antifouling abilities than the pristine PES membrane.

Equilibrium water content (EWC) of an asymmetric membrane is directly related to its support layer's porosity [25]. As presented in Table 2, it could be seen that the EWC of the blend membranes was increased due to the addition of  $CaCl_2$ . This increasing trend confirmed the higher porosity in the membrane support layer due to the addition of  $CaCl_2$  to the dope solution. As confirmed from the cross section SEM images, the large size macrovoids present in the support layer of the  $CaCl_2$  blend membranes attributed for the increased water uptake. However

the EWC was decreased marginally when the  $CaCl_2$  concentration was increased from 2% to 3%  $CaCl_2$ . This could be due to the formation of highly spongy support layer for the 3%  $CaCl_2$  membrane caused by the delayed liquid-liquid demixing. In general, the EWC for all  $CaCl_2$  blend membranes was higher than the pristine PES membrane.

Table 3 shows the results obtained for the mechanical stability studies for all the prepared membranes. It was observed that the addition of  $CaCl_2$  to the PES matrix increased the breaking strength from 3.18 MPa to 4.12 MPa with a reduction in the elongation ratio from 9.9% to 8.3%. The increase in the breaking strength implied that there was a good interaction of the  $CaCl_2$  particles in the PES matrix and this boosted the rigidity of the polymer chain. The decrease in the elongation ratio clearly showed that the  $CaCl_2$  membranes were brittle due to the addition of  $CaCl_2$  as compared with the pure PES membrane.

**Table 3** Effect of  $CaCl_2$  content on the mechanical stability of the membranes

Membrane ID	Breaking strength (MPa)	Elongation ratio (%)
M0	3.18 ( $\pm 0.01$ )	9.9 ( $\pm 0.03$ )
M1	3.35 ( $\pm 0.01$ )	9.8 ( $\pm 0.02$ )
M2	3.54 ( $\pm 0.02$ )	9.6 ( $\pm 0.01$ )
M3	3.81 ( $\pm 0.01$ )	9.35 ( $\pm 0.02$ )
M4	3.97 ( $\pm 0.02$ )	8.95 ( $\pm 0.01$ )
M5	4.12 ( $\pm 0.01$ )	8.3 ( $\pm 0.02$ )

### 3.3 Effect of $CaCl_2$ on porosity and average pore size of the membrane

Estimation of membrane porosity and average pore radius for all the synthesized membranes are presented in Table 2. Results clearly indicated that all  $CaCl_2$  blend membranes have better porosity than the pure PES membrane. This was in direct corroboration with the results of the SEM analysis and EWC evaluation. It was certain that the addition of  $CaCl_2$  in low concentrations to the casting dope has resulted in the formation of big macrovoids on the membrane structure which enhanced the membrane porosity. Conversely, at high concentrations of



CaCl<sub>2</sub> in the casting dope, the dominant viscous effects delayed the phase separation resulting in lower membrane porosity. The average pore size obtained on the basis of velocity filtration method revealed that the pore size of all the prepared membranes were close to each other. This implied CaCl<sub>2</sub> addition had a dominant effect on the pore size of the support layer rather than the membrane surface.

### 3.4 Effect of CaCl<sub>2</sub> on pure water permeability and dye rejection

Pure water permeability of all the prepared membranes was measured using dead end stirred cell unit, as described above. As shown in Table 2, the PWF of CaCl<sub>2</sub> blend membranes were higher than that of pristine PES and PES/PVP (0% CaCl<sub>2</sub>) membrane. Also, the 1% CaCl<sub>2</sub> membrane recorded the highest PWF of 240.25 L m<sup>-2</sup> h<sup>-1</sup> which was nearly eight times greater than the pristine PES membrane. Addition of CaCl<sub>2</sub> has two major effects during membrane formation: (i) enhanced hydrophilicity and (ii) change in support layer morphology. It was seen that upto a CaCl<sub>2</sub> concentration of 1%, both these effects resulted in high PWF through the blend membrane. Increase of CaCl<sub>2</sub> concentration beyond 1% resulted in a drop of the PWF, indicating that the change in support layer morphology had a diminishing effect on PWF inspite of enhanced hydrophilicity. In other words, the change in the support layer morphology due to the CaCl<sub>2</sub> addition has greater influence on pure water flux compared to surface hydrophilicity.

Rejection characteristics of an asymmetric membrane are mainly regulated by the skin layer which is composed of surface pores [1-4, 39]. Figure 3 shows the rejection of dyes as a function of CaCl<sub>2</sub> concentration in the casting dope. It could be seen that the dye rejections were increased for the blend membranes due to the addition of CaCl<sub>2</sub> and were higher than that of pristine PES membrane. Increase in the rejection could be explained by the adsorption of the dye molecules on the membrane surface in addition to rejection by steric hindrance. CaCl<sub>2</sub> deposited on the membrane surface as well as along the pore wall of the blend membrane served as adsorption sites where calcium ions attracted these anionic dye molecules. This inference also explained the increase in the dye rejection along with the increase in the CaCl<sub>2</sub> concentration in the blend membranes. Among the various dyes used, Congo red (CR) recorded the highest dye rejection of around 85% while the other dyes had a rejection efficiency of less than 70%. This observation was used to conclude that the molecular weight cut-off (MWCO) ratio for the CaCl<sub>2</sub> membranes would be around 700. Rejection studies on the CaCl<sub>2</sub> blended PES membrane clearly indicated that the possible separation principles for these membranes were steric hindrance and adsorption.

Steady state permeates fluxes for the dye rejection studies are presented in Table 4. The dye fluxes followed the similar pattern like that of PWF. All CaCl<sub>2</sub> blend membranes had an increased dye flux than the membranes without CaCl<sub>2</sub> addition. The hydrophobic tail of the dye molecules interacted with the membrane while the hydrophilic head was still available which resulted in the high permeate fluxes for the calcium blend membranes. As explained for the PWF, the enhanced hydrophilicity and support layer morphology modifications favoured a high flux through the CaCl<sub>2</sub> blend membrane upto a cut-off concentration of 1% CaCl<sub>2</sub>. The decrease in the dye fluxes for CaCl<sub>2</sub> blend membrane with more than 1% CaCl<sub>2</sub> was due to the collapse of the fingerlike macrovoids which made the support layer more tortuous. From the results, it could be seen that the CR dye flux was lowest in comparison with other two dyes indicating that this dye has a strong adsorption on the membranes surface. Hence CR dye solution was selected as the probe liquid for fouling analysis.

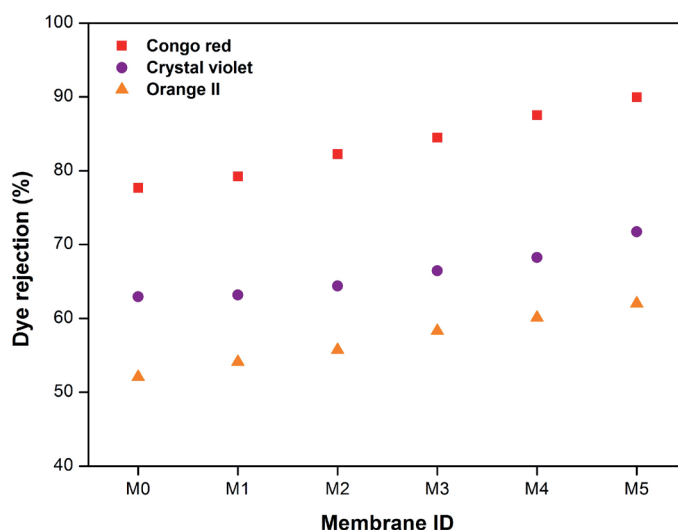


Fig. 3 Effect of CaCl<sub>2</sub> on dye rejection performance

Table 4 Dye permeate fluxes for the pure and composite PES membranes

Membrane ID	Steady state rejection flux (L m <sup>-2</sup> h <sup>-1</sup> )		
	Congo Red	Orange II	Crystal Violet
M0	12.55 (±0.7)	26.7 (±0.5)	21.59 (±0.7)
M1	32.19 (±0.4)	48.12 (±0.3)	41.06 (±0.4)
M2	67.62 (±0.4)	83.65 (±0.2)	75.92 (±0.3)
M3	101.38 (±0.3)	147.33 (±0.1)	118.29 (±0.2)
M4	72.45 (±0.4)	120.82 (±0.2)	83.47 (±0.2)
M5	63.29 (±0.3)	103.33 (±0.2)	78.89 (±0.3)

### 3.5 Fouling analysis of the pure and modified PES membranes

Fouling recovery ratio is one of the easiest ways to analyze fouling mitigation for a membrane surface. A high value of FRR denotes the better antifouling ability of the membrane [25]. The FRR, dye and water fluxes for all of the prepared membranes are presented in Table 5. FRR studies clearly showed that the 1% CaCl<sub>2</sub> membrane possessed the maximum resistance against fouling than the pure PES and other modified membranes. As the average surface pore size was almost constant for all the prepared membranes, it could be concluded that FRR values were regulated by the adsorption effect and hydrophilicity of the membrane. Addition of CaCl<sub>2</sub> favored antifouling nature by increasing the permeate flux through enhanced hydrophilicity. On other hand, it led to increased adsorption effect of the dye along the pore wall and eventually for pore blocking. For a concentration of 1% of CaCl<sub>2</sub> in the casting dope, a trade-off between these opposing features of CaCl<sub>2</sub> addition must have been achieved which has resulted in the high FRR value for the 1% CaCl<sub>2</sub> blend membrane among the synthesized membranes. In general, FRR analysis indicated the enhanced antifouling nature of the CaCl<sub>2</sub> blend membranes, especially for the 1% CaCl<sub>2</sub> membrane.

Table 5 FRR, dye and water fluxes for fouling analysis

Mem. ID	J <sub>w</sub> x10 <sup>-6</sup> (m <sup>3</sup> m <sup>-2</sup> s <sup>-1</sup> )	J <sub>CR</sub> x10 <sup>-6</sup> (m <sup>3</sup> m <sup>-2</sup> s <sup>-1</sup> )	J <sub>w2</sub> x10 <sup>-6</sup> (m <sup>3</sup> m <sup>-2</sup> s <sup>-1</sup> )	FRR (%)
M0	8.85	3.49	3.59	40.56
M1	17.37	8.94	9.61	55.33
M2	35.05	18.78	24.29	69.3
M3	66.74	28.16	48.8	73.12
M4	46.21	20.13	30.08	65.09
M5	43.73	17.58	25.72	58.82

To have a further insight towards the antifouling effect of the membranes, various resistances for mass transport across the membrane, namely, the intrinsic membrane resistance ( $R_m$ ), reversible fouling resistance ( $R_r$ ) and irreversible fouling resistance ( $R_{ir}$ ) were determined using Eq. (10) – (12) for all the prepared membranes. The obtained results are presented in Fig. 4. It could be seen that the enhanced hydrophilicity of the CaCl<sub>2</sub> blend membranes resulted in comparatively low  $R_m$  than the membranes without CaCl<sub>2</sub>. As expected from the PWF measurements, the  $R_m$  of the 1% CaCl<sub>2</sub> was the lowest among the synthesized membranes.

Analyzing the fouling tendency of the membranes, it was seen that the addition of CaCl<sub>2</sub> increased the mass transport resistance due to  $R_r$ . This could be explained by the increased surface roughness of the calcium blend membranes. Increase in surface roughness caused more accumulation of the dye particles in the

'valleys' of the membrane surface leading to high  $R_r$  values. As indicated in Table 2, the increased surface roughness of the CaCl<sub>2</sub> blend membranes led to more reversible fouling resistance in them. This reversible fouling effect could be easily removed by membrane washing and thus does not affect the membrane performance on a long run [39]. Further analysis on the fouling tendency indicated that the mass transport resistance due to irreversible fouling ( $R_{ir}$ ) was dramatically reduced with the addition of CaCl<sub>2</sub> and reached a lowest value for a CaCl<sub>2</sub> concentration of 1% in the casting dope. Further increase in concentration of CaCl<sub>2</sub> resulted in an increase of  $R_{ir}$  value for calcium blends. The reason for such a behavior has already been explained in FRR discussion. The minimum pore blocking due to adsorption and the enhanced hydrophilicity effects were optimally pronounced at the 1% CaCl<sub>2</sub> concentration, making it more resistant for irreversible fouling effects. Ultimately, this resulted in the lowest  $R_{ir}$  value of  $2.85 \times 10^{12} \text{ m}^{-1}$  for the 1% CaCl<sub>2</sub> membrane. The obtained results for the fouling analysis, as presented in Fig. 4, clearly indicated that the calcium blend membranes had a remarkable antifouling tendency, especially towards dye desalination, in comparison with the PES membranes without CaCl<sub>2</sub>.

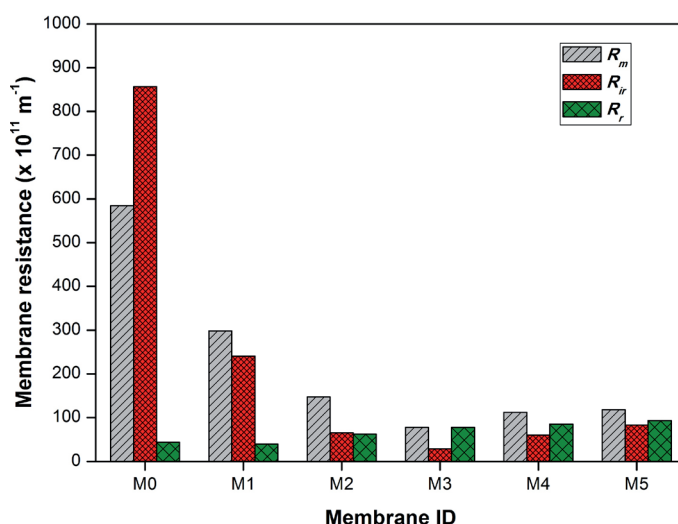


Fig. 4 Various types of membrane resistances for mass transport across the prepared membranes

Analyzing the results of the membrane characterizations, dye rejection performance and fouling studies, it was clear that the 1 wt% CaCl<sub>2</sub> blend membrane was possessing better separation characteristics and antifouling properties in comparison with the other CaCl<sub>2</sub> blend membranes.

### 4 Conclusions

Modified PES composite membranes were prepared by phase inversion method by blending PES with PVP and varying amounts of CaCl<sub>2</sub>. Synthesized membranes were characterized by studying the membrane morphology, surface hydrophilicity, equilibrium water content, mechanical strength, porosity



and pure water flux. All the prepared membranes possessed asymmetric morphology and the inclusion of CaCl<sub>2</sub> in PES matrix influenced the support layer morphology remarkably. Contact angle and water uptake measurements proved that the CaCl<sub>2</sub> addition enhanced the hydrophilicity of modified PES membranes. Mechanical stability studies clearly indicated the boosted strength of composite PES membranes due to CaCl<sub>2</sub> addition. Porosity analysis implied that the CaCl<sub>2</sub> addition has no significant effects on the average surface pore radius of the prepared membranes. Performance examination showed that the pure water flux of the calcium blend membranes was greatly enhanced to a maximum of eight times as compared with pristine PES membrane. Dye rejection studies using several dye solutions clearly confirmed the improved rejection capacity of the CaCl<sub>2</sub> blend membranes. Steric hindrance and adsorption were identified as the dominant separation mechanisms in the blend membranes. Fouling analysis indicated the excellent antifouling ability of the CaCl<sub>2</sub> blend membranes. High FRR values were achieved for the CaCl<sub>2</sub> blend membranes than the PES membranes without CaCl<sub>2</sub>. The irreversible fouling effect due to dye rejection was greatly reduced in the CaCl<sub>2</sub> modified PES membrane than the unmodified PES membrane. The reversible fouling effect was easily removed by water cleaning and the CaCl<sub>2</sub> blend membranes can be reused for several continuous runs with high flux recovery. A very close analysis on the obtained results revealed the better performance characteristics of 1% CaCl<sub>2</sub> membrane among the synthesized series. The performance of the prepared CaCl<sub>2</sub> blend membranes in terms of real time industrial effluent treatment is to be subsequently carried out as an extension of the current research work. Thus the CaCl<sub>2</sub> and PVP blended PES composite membrane seems to be a promising candidate for treatment of dye polluted waste water, ensuring high fluxes and elevated rejection rates.

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