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# Fabrication and characterization of new PSF/PPSU UF blend membrane for heavy metal rejection

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## ABSTRACT

Polysulfone and polyphenylsulfone-blend ultrafiltration membranes of different compositions were prepared by the phase inversion method, with and without hydrophilic additive poly (ethylene glycol) 1,000 (PEG). The membrane morphology was studied using scanning electron microscope, which displayed the asymmetric structure of the membrane. The hydrophilicity of the membranes was measured by contact angle, porosity, water uptake, and permeability studies. The blend membrane showed enhanced permeability, hydrophilicity, and antifouling property as compared to the pristine polymer membrane. The pure water flux of the membrane, which was blended with PEG additive was relatively higher than the blend membranes without the additive. The flux recovery ratio (FRR) was measured to study the antifouling property. The membranes with PEG additive exhibited better antifouling property with maximum FRR of 72.84%. The heavy metal rejection by the membrane was carried out by complexing the metal ions with polyethyleneimine, which exhibited highest rejection of 99.48 and 95.5% of $Pb^{2+}$ and $Cd^{2+}$, respectively.

*Keywords:* Polymers; Membranes; Flux recovery ratio; Metal complexes; Heavy metal rejection

## 1. Introduction

Currently, the membrane filtration has become one of the areas of interest, where it is used predominantly for water treatment. Ultrafiltration (UF) is an efficient process which eliminates the suspended or dissolved impurities from the water, as it requires low energy and mild operating conditions [1]. Increased water flux, high solute rejection, good antifouling property and long-term stability of membrane are the inherent characteristics of an ideal membrane. Phase inversion is one of the common methods by which asymmetric membranes are prepared [2]. The membrane

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performance can be improved by controlling the membrane structures influenced by factors like polymer, solvents, nonsolvents, and additives [3].

Inappropriate disposal of industrial waste has led to the contamination of the water with heavy metal in turn adversely affecting the public health. The heavy metals like lead, cadmium, mercury, chromium are toxic in nature, and it is very important to eliminate these from the water. Out of many approaches, membrane filtration is a method where the heavy metal removal can be done effectively and economically. Polymer-enhanced ultrafiltration (PEUF) technique is performed by complexing the heavy metal with polymeric ligand like polyacrilic acid (PAA) [4], polyethyleneimine (PEI) [5], sodium dodecyl sulfate (SDS) [6], to increase the size of the heavy metal ion for the selective removal of heavy metal ions by sieving mechanism.

Polymers like polysulfone (PSF) [7], polyphenylsulfone (PPSU) [8], polyethersulfone (PES) [9], poly (vinylidene fluoride) [10], and poly(ether ether ketone) [11] are normally used for the fabrication of UF membranes. The makers of PPSU reported that, it is more resistant to hydrolysis, plasticization or stress cracking by number of solvents and cost effective than polymers like PSF and PES [12]. PPSU also has an excellent thermal and chemical resistance. These characteristic of PPSU makes it a good membrane material over PSF and PES. However, like PSF, PPSU is also hydrophobic [13] in nature, which is the major drawback of this polymer as a membrane material as it can lead to severe fouling. Therefore, the membrane characteristics and morphology can be modified by the use of additives or by blending it with other hydrophilic polymer. Kumar et al. [14] studied the heavy metal rejection property of blended PSF-based membrane, which showed maximum rejection of 98% for $Cu^{2+}$ ions with flux of 112 $L/m^2/h$. Hwang et al. [13] reported the blending of PPSU and polyetherimide (PEI) to prepare UF membrane for the humic acid (HA) separation, where the membrane exhibited good HA resistance. Therefore, polymer blends results in formation of new type of materials for UF purpose whose property can be improved by the addition of additives like polyethylene glycol (PEG), hyperbranched polyglycerol (HPG), polyvinylpyrrolidone (PVP) [15]. Sinha and Purkait [16] reported that the polyethylene glycol methyl ether (PEGME) of different molecular weights when added to PSF membrane, improved the rejection as well as flux of BSA. Liu et al. [17] found that the presence of PEG-400 in PES hollow fiber membranes could enhance the pore interconnectivity and hydrophilicity of the membrane.

However, membrane preparation from blend of PSF and PPSU has not yet reported. Moreover, the blend membranes are expected to exhibit improved flux as well as antifouling property when compared to the pristine membranes. Hence, in this present study, the blend of two polymers PSF and PPSU were investigated as membrane materials for the heavy metal removal and antifouling property. The polymer blends were prepared by varying PSF and PPSU concentration by the phase inversion technique and studies were conducted to observe the effect of blend composition on the membrane morphology and water permeation. Pore forming agent PEG-1000 was used as hydrophilic additives to improve the hydrophilicity of the blend polymer (PSF/PPSU) and the membrane performance were analyzed by water permeation and heavy metal rejection behavior.

## 2. Experimental

### 2.1. Materials used

PSF (Mw ~ 35,000), PEG-1000, were purchased from Sigma–Aldrich Co., India. PPSU (Radel R-5000) (average Mw ~ 50,000 $g\ mol^{-1}$) was provided by Solvay Advanced Polymer (Belgium). N-methyl-2-pyrrolidone (NMP) was purchased from Merck India, Ltd. Bovine serum albumin (BSA) (MW ~ 69 kDa) was purchased from CDH Chemicals, India. PEI (Mn ~ 60,000) wt% aq. Solution (branched), was purchased from Acros Organics, USA. Cadmium nitrate tetrahydrate and lead nitrate were purchased from Sigma–Aldrich Co., India.

### 2.2. Preparation of PSF–PPSU-blend membranes

PSF–PPSU-blend membranes were prepared by wet phase inversion method [18] based on the literature. As mentioned in (Table 1) above, defined ratio of PSF–PPSU-blend membranes 20% (w/v) were prepared with different concentrations of PEG-1000 by dissolving it in NMP. The solutions were subjected to constant mechanical stirring at 60°C for 24 h to form a homogeneous mixture. The polymer solution was then filtered, degassed and casted onto a glass plate using casting blade [19,20]. Later, it was immersed into a bath containing distilled water and the membranes formed were rinsed and stored in deionized water for the further analysis.

### 2.3. Morphology study of the membrane

The membrane morphology were analyzed with a JEOL JSM-6380LA scanning electron microscope

Table 1
Compositions of PSF–PPSU-blend membranes

| Membrane code | Casting solution compositions (wt%) | | | |
|---|---|---|---|---|
| | PSF | PPSU | PEG | NMP |
| P0 | 100 | 0 | 0 | 80 |
| P25 | 75 | 25 | 0 | 80 |
| P50 | 50 | 50 | 0 | 80 |
| P75 | 25 | 75 | 0 | 80 |
| P100 | 0 | 100 | 0 | 80 |
| P0-P | 100 | 0 | 5 | 80 |
| P25-P | 75 | 25 | 5 | 80 |
| P50-P | 50 | 50 | 5 | 80 |
| P75-P | 25 | 75 | 5 | 80 |
| P100-P | 0 | 100 | 5 | 80 |

(SEM). The membranes prepared were initially frozen using liquid nitrogen, then fractured and finally sputtered with gold to obtain the cross-sectional image.

### 2.4. Contact angle measurement

The contact angle of the membranes was measured using FTA-200 dynamic contact angle analyzer by sessile droplet method [19]. The contact angle of a membrane sample was taken for at least three different sites and the average value was reported.

### 2.5. Water uptake measurements and porosity

The membrane samples were cut into pieces of 1 cm$^2$ size and dipped in distilled water for 24 h. These swollen membranes were then taken out of the water and weighed it after removing excess of water on its surface using blotting paper. The wet membranes were dried in a vacuum oven for 24 h, and then, the dry membrane samples were weighed [21]. The water uptake of the membranes was calculated using the following equation:

$$\%\,\text{uptake} = \left(\frac{W_\text{w} - W_\text{d}}{W_\text{d}}\right) \times 100 \tag{1}$$

where $W_\text{w}$ and $W_\text{d}$ are the wet and dry weight of membrane respectively.

### 2.6. Porosity and membrane mean pore radius ($r_m$)

The membrane porosity is a measure of the volume of void space to the total volume. To determine the porosity, the membrane samples of 1 cm$^2$ were initially immersed in distilled water for 24 h. Then, the membrane surface was dabbed with tissue paper and weighed. This wet membrane was dried in an oven for 24 h and it was weighed again in dry state. From the literature [21], membrane porosity was calculated using the following equation:

$$\varepsilon\,(\%) = \left(\frac{W_\text{w} - W_\text{d}}{Al\rho}\right) \times 100 \tag{2}$$

where $W_\text{w}$ and $W_\text{d}$ are the wet and dry weight of membrane respectively, $A$ is the area of the sample (cm$^2$), $l$ is the membrane thickness (cm) and $\rho$ is the density of water (0.998 g/cm$^3$).

Porosity of the membrane is then used to determine the mean pore radius of membrane by using the filtration velocity method as mentioned in the Guerout–Elford–Ferry equation [22,23]:

$$r_\text{m} = \sqrt{\frac{(2.9 - 1.75\epsilon) \times 8\eta lQ}{\epsilon \times A \times \Delta P}} \tag{3}$$

where $\eta$ is the water viscosity, $l$ is the membrane thickness, $Q$ is the volume of permeate water per unit time, $A$ is the membrane area and $\Delta P$ is the operational membrane pressure of 0.5 MPa.

### 2.7. Water flux study

The permeation of the membrane was analyzed by pure water flux (PWF) study of the membranes using dead end filtration cell with an effective membrane area of 5 cm$^2$ [18]. The membranes were immersed in water for 24 h before carrying out the permeation experiments. The membranes were subjected to compaction at 0.4 MPa transmembrane pressure (TMP) for 30 min in the beginning. Then pressure-dependent PWF of the different membranes was measured at 0.1–1.0 MPa TMP at room temperature. The PWF of the membranes was calculated using the following equation:

$$J_\text{w} = \frac{V}{\Delta t \times A} \tag{4}$$

where $J_\text{w}$ is water flux expressed in L/m$^2$/h, $V$ is amount of water passing through the membrane in Liter (L), $\Delta t$ is the time in hours (h) and $A$ is the effective membrane area responsible for the filtration, expressed in (m$^2$).

### 2.8. Antifouling studies

The BSA solution was used as a model protein to study the antifouling property of the membrane.

Initially, the PWF $J_{w1}$ (L/m$^2$/h) of the membranes was measured at 0.5 MPa TMP for 1 h. Later, the membrane was subjected to permeation of BSA solution of 1.0 g/L concentration for 1 h at 0.5 MPa pressure. The flux for BSA solution measured based on the quantity of water permeating the membranes is $J_p$ (L/m$^2$/h). After the BSA filtration, the membranes were washed with pure water for 20 min, and then, the water flux $J_{w2}$ (L/m$^2$/h) was measured again. The antifouling property was evaluated by calculating flux recovery ratio (FRR) by the equation:

$$\mathrm{FRR}\,(\%) = \frac{J_{w2}}{J_{w1}} \times 100 \tag{5}$$

The membrane fouling was further evaluated by calculating the reversible $R_{rev}$ and irreversible $R_{irr}$ fouling ratio by following equation [24]:

$$R_{rev}\,(\%) = \frac{(J_{w2} - J_p)}{J_{w1}} \times 100 \tag{6}$$

$$R_{irr}\,(\%) = \left(\frac{J_{w1} - J_{w2}}{J_{w1}}\right) \times 100 \tag{7}$$

### 2.9. Heavy metal rejection study

PEUF technique for the heavy metal rejection was done based on the literature [25]. Here, the heavy metal ions were complexed using PEI. Aqueous solutions of Pb(II) and Cd(II) were prepared at concentrations of 1,000 ppm in a 1 wt% solution of PEI in deionized water. The pH of these aqueous solutions was adjusted to 6 ± 0.25 by the addition of a small amount of either 0.1 M NaOH or 0.1 M HCl. Solutions containing PEI and individual metal ions were thoroughly mixed and left standing for five days to complete binding. The metal ion-complexed PEI solutions were filtered through the membranes at 0.5 MPa pressure and permeate was collected. The rejection of the metal ions by membrane was evaluated by measuring the concentration of the metal ions in the feed and permeates using atomic absorption spectrophotometer (AAS) (GBC 932 Plus) [26]. Metal ion rejection percentage by the membranes was calculated using the formula:

$$\text{Percent Rejection} = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{8}$$

where $C_p$ (mg/mL) is the concentration of the solute in permeate and $C_p$ (mg/mL) is the concentration of the solute in feed solution.

## 3. Results and discussion

### 3.1. Membrane morphology

The membrane morphology was studied using scanning electron microscopy. All the prepared membranes exhibited similar asymmetric nature, which is the typical structure of UF membranes, with a dense skin layer and a porous sublayer with finger-like projection followed by macrovoids [27]. The cross-sectional images of the prepared membrane showed that, blending of PPSU changed the PSF membrane structure and increase in PPSU concentration improved the finger-like projection (Fig. 1). The addition of PEG in the casting solution improved the membrane structure, which further gets entrapped during the phase inversion process. PEG being soluble in water leaches out of the solution resulting in the interconnected finger-like projection [28]. The larger macrovoids and thin top layer were therefore observed in the blend membranes. On addition of PEG-1000, these macrovoids in turn transforms in to extended finger-like projections [3]. Therefore, the obtained SEM images displayed appreciable correlation between the morphology and the permeation results of membrane.

### 3.2. Porosity and water uptake measurements

The porosity of the blend membrane increased with the increase in the concentration of PPSU in the blend, which may be due to the rise in number of finger-like projection (Fig. 1). However, the increase in porosity of blend membrane is not appreciable, and therefore the pore former PEG is added to the blends to increase the porosity. It is observed from the Fig. 2 that, there is agreeable rise in the porosity on addition of PEG-1000 and the porosity increased from 42.59 to 64.79%. The macrovoids and finger-like projection in the blend membrane led to rise in porosity, which further increased on the addition of PEG as the finger-like structure seep into the membranes enhancing pore interconnectivity [29]. The addition of PEG-1000 into blend membranes resulted in an appreciable improvement in the porosity, which may be due faster demixing of solvent present in the casting solution and nonsolvent in the coagulaton bath as the affinity of the PEG toward water is higher.

Water uptake (%) study is also performed to determine the hydrophilicity of the membrane. The water uptake of blend increased with the increase in PPSU concentration in the blend due to the higher porosity and increased finger-like projection of the blend membrane. The water uptake of the blend membrane increased with the addition of PEG-1000. The water-soluble additive when incorporated to polymer blend,

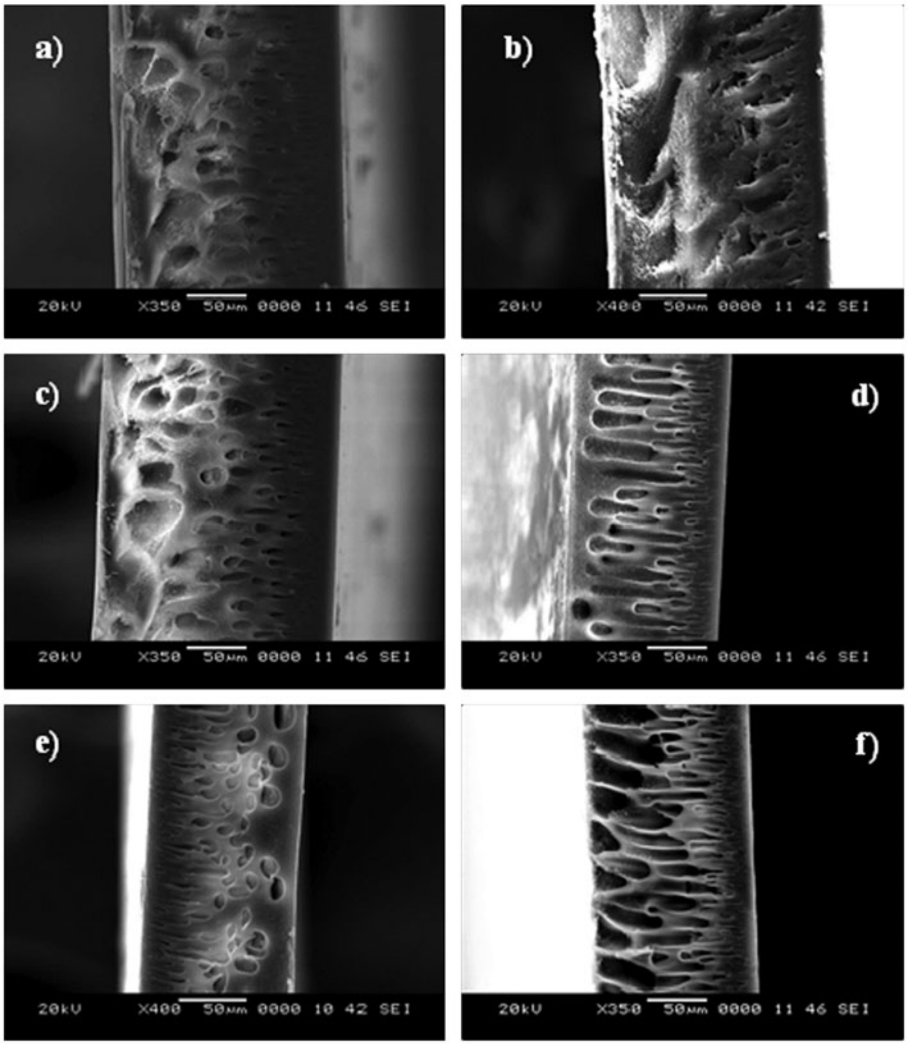

Fig. 1. Cross-sectional SEM images of: (a) P0, (b) P100, (c) P25, (d) P25-P, (e) P75, and (f) P75-P.

resulted in increased porosity of the blend membrane, which is due to increased affinity of PEG toward the water. From Fig. 3, the highest water uptake was observed for P75-P which is 57.98% whereas P75 (without PEG) showed water uptake of 38.11%.

### 3.3. Contact angle and membrane mean pore radius ($r_m$)

The contact angle measurement relates the surface hydrophilicity of the membrane i.e. lower the contact angle, higher is the surface hydrophilicity. The blend membranes showed lower contact angle than that of the pristine membrane since there is rise in porosity and water uptake of the blend membrane (Fig. 4). The hydrophilicity was further improved by the addition of PEG-1000 to the blend membranes due to the high affinity of PEG 1000 to water. The PEG present in the polymer solution diffused to the membrane surface during phase inversion in turn improving the surface wettability [30]. Moreover, the increased porous nature of the membrane on PEG addition also caused higher hydrophilicity [31]. Hence, order of decrease in contact angle is as follows: P0 > P100 > P0-P > P25 > P50 > P75 > P100-P > P25-P > P50-P > P75-P (Fig. 4).

The mean pore radii were calculated using the filtration velocity method as mentioned in the Guerout–Elford–Ferry equation [32]. The addition of PEG, which is a pore former caused the formation of finger-like structure and pores on the membrane by dissolution of entrapped PEG during the phase inversion process. Hence, there is increase in mean pore radius of the blend membrane. The mean pore radius of the prepared membrane ranges from 3.2 to 7.6 nm (Fig. 5).

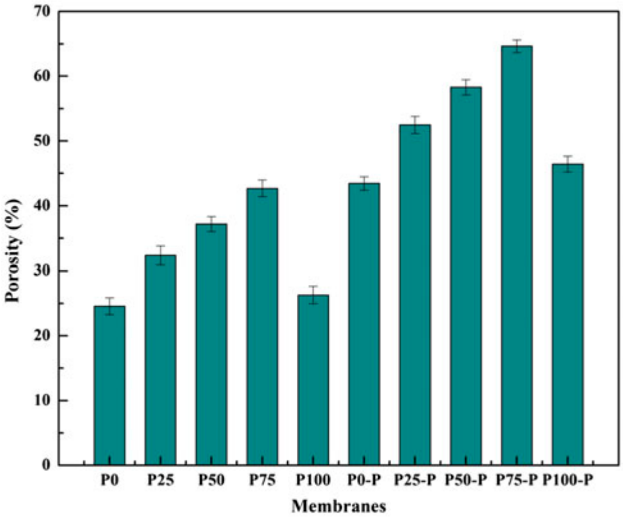

Fig. 2. Porosity of blend membranes.

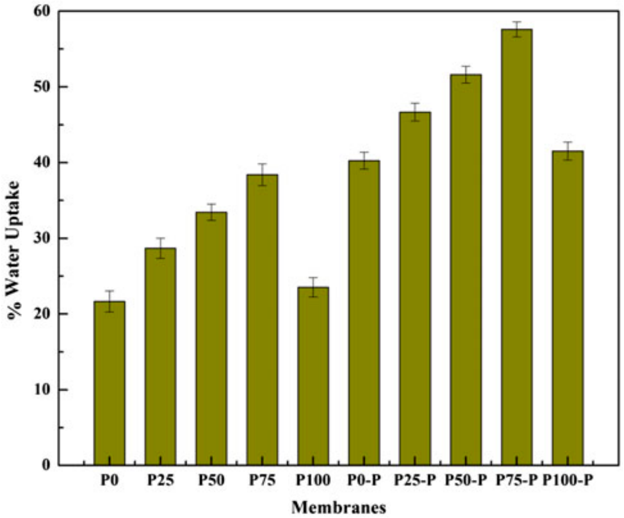

Fig. 3. Water Uptake values of blend membranes.

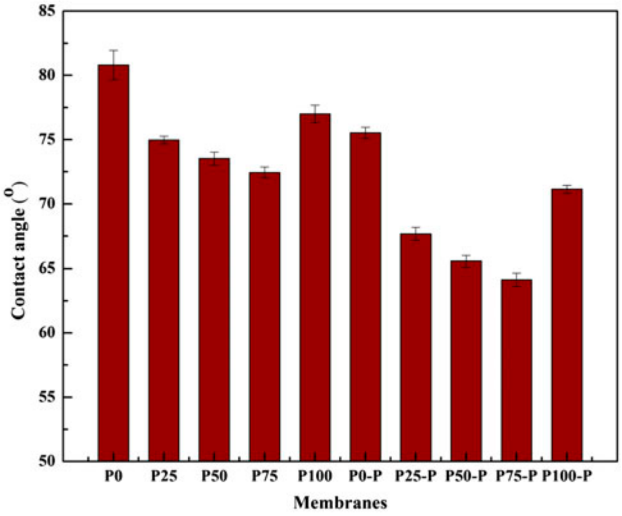

Fig. 4. Contact angle values of blend membranes.

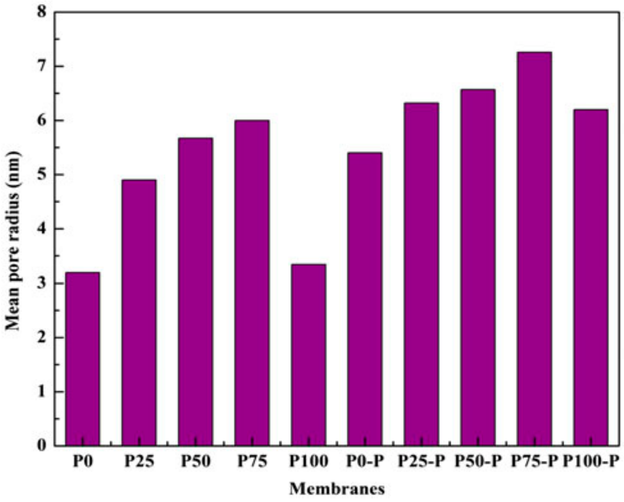

Fig. 5. Mean pore radius of blend membranes.

### 3.4. *Water flux study*

PWF of the membrane was evaluated by varying the pressure from 0.1 to 1.0 MPa TMP, where the PWF increased linearly with increase in pressure (Fig. 6). The reduced PWF for pristine PSF and PPSU membrane were observed due to lower hydrophilicity and tight UF nature of the membranes. However, the PWF of blend membranes is found to be higher than the pristine PSF and PPSU membrane which further increased with the addition of the PEG, which is in accordance with membrane hydrophilicity (Fig. 6). Moreover, the increase in the porosity and mean pore radius of blend membranes also resulted in enhanced permeability. The PWF of blend membranes, increased considerably with the addition of PEG-1000 due its pore forming property. It can be observed from the figure (Fig. 6) that, the membrane P75 and P75-P exhibited PWF of 29.06 and 65.88 L/m$^2$/h, respectively, at 0.5 MPa TMP. PEG-1000 being a pore former enhanced the mean pore radius of the membranes. Also, the hydrophilic nature of PEG gave rise to higher porosity and permeability. Therefore, the overall permeability of membranes had increased.

### 3.5. *Antifouling study*

Fouling is one of the major drawbacks confronted in the membranes due to the hydrophobic nature of

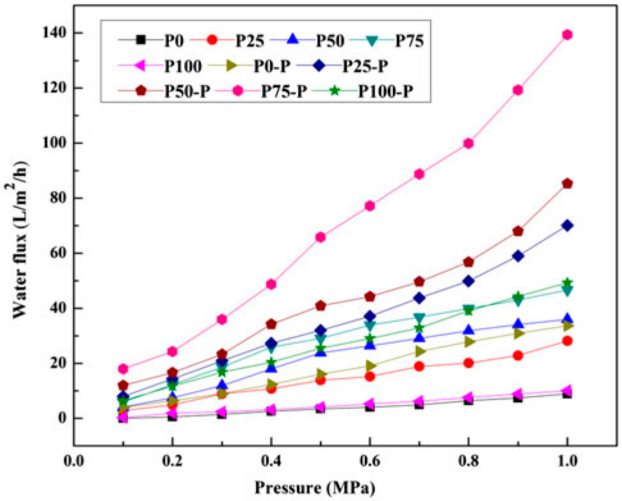

Fig. 6. Pressure dependent PWF values of blend membranes.

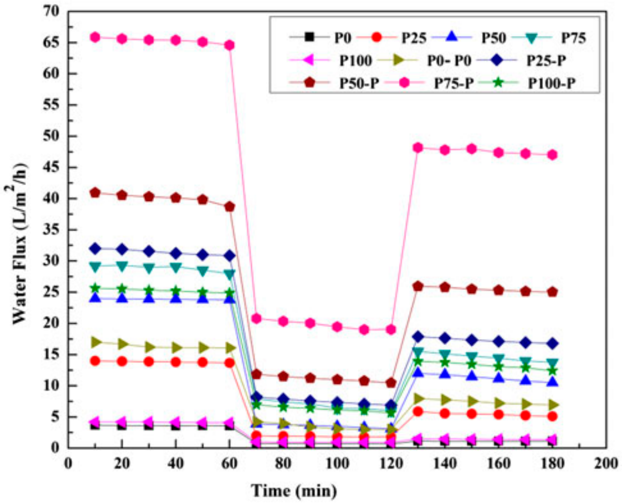

Fig. 7. Flux vs. time for the PSf/PPSU blend membranes at 0.5 MPa TMP during three steps: water flux for 60 min, BSA flux (pH 7 ± 0.1) for 60 min, and water flux for 60 min after 20 min washing with distilled water.

membranes, resulting in flux reduction and adversely affecting the membrane durability. Therefore, preparation of membranes with fouling resistance is the chief challenge in present scenario. From the Fig. 7, it is clear that the water flux declined on BSA filtration which may be due to the clogging of the membrane pores by the protein molecules. The adsorption of protein foulant on the membrane surface also caused the decline in water flux of the membrane. However, the presence of PEG in the membrane could lower the hydrophobic interaction between the foulant and the membrane surface. Hence, there is improved flux observed as the membrane hydrophilicity and mean pore radii increased with the addition of PEG-1000 to the blend membranes [33].

The FRR of the membrane is the measure of antifouling property of the membrane i.e. higher the FRR value higher is the antifouling property [34]. The pristine PSF and PPSU membranes showed lower FRR value due to their hydrophobic nature. The increase in membrane hydrophilicity is due to the formation of hydration sphere on the membrane surface. Therefore, the adsorbed protein foulant could be easily removed from the hydrophilic surface of membranes by simple hydraulic cleaning [35]. The blend membrane exhibited better FRR value which was further enhanced on addition of PEG-1000. The P75-P and P0 membrane shows maximum FRR value of 72.84% and the minimum FRR value of 31.14%, respectively (Fig. 8).

The reversible and irreversible fouling was calculated to understand the self-cleaning property of the membrane which in turn represents the membrane reusability. If the foulant adsorbed on membrane surface could be removed by simple water washing it is reversible fouling.

Conversely, the irreversible fouling is when the foulant is strongly adhered to the membrane and cannot be removed by hydraulic cleaning. From the Fig. 8, it can be observed that the irreversible fouling ($R_{\mathrm{irr}}$) for the pristine PSF and PPSU membrane is highest due to lower hydrophilicity and the $R_{\mathrm{irr}}$ value decreased with increase in membrane hydrophilicity. Therefore, rise in membrane hydrophilicity and pore interconnectivity led to the lower irreversible fouling.

### 3.6. Heavy metal rejection study

The heavy metal rejection is performed by complexing the metal ions with polyelectrolyte like PEI, consequently increasing the metal ion size [36]. Here, the heavy metals, like cadmium nitrate tetrahydrate and lead nitrate complexed with PEI, were filtered and the rejections were studied by AAS. PEI which is a water-soluble polymer forms complex with the metal ions by chelation i.e. the lone pair of electrons present on nitrogen atom binds selectively to the transition metal ions [37] (Fig. 9).

The complexing capacity of the metal ion with PEI depends on the atomic size of the metal ion and the number of functional group. Therefore, $Pb^{2+}$ ions being larger than $Cd^{2+}$ ions might undergo higher complexing with PEI, resulting in the enhanced rejection of $Pb^{2+}$ ions than $Cd^{2+}$ ions [38]. Moreover, the rejection results (Fig. 10) of these membranes depended on the pore size, where the membranes with larger pore size showed smaller rejection. The

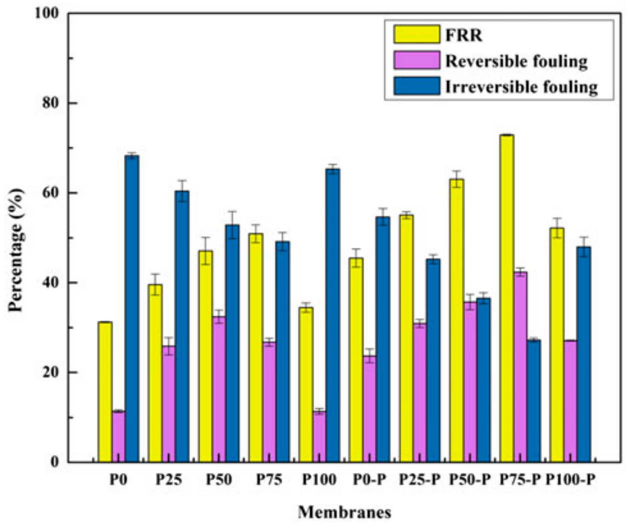

Fig. 8. FRR and fouling resistance of the prepared membranes.

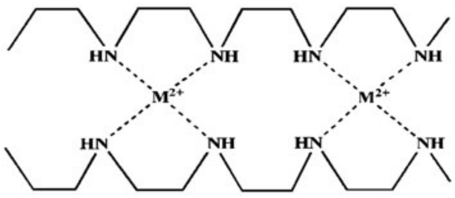

Fig. 9. Complexation of PEI with the heavy metal ion ($M^{2+} = Pb^{2+}, Cd^{2+}$).

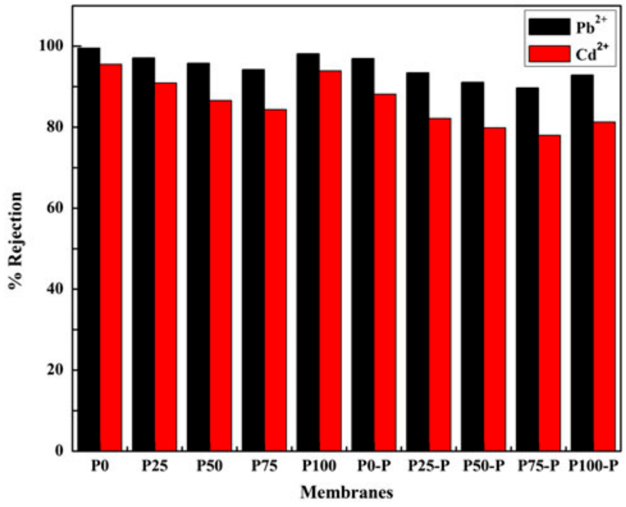

Fig. 10. Heavy metal rejection of blend membranes.

PEG-1000 is a pore former which lead to increased pore size and porosity of the membranes. Therefore, heavy metal could easily pass through the membrane due to larger pore radii and the higher porosity also favored easy movement of heavy metal ion through the membrane. Hence, the rejection reduced in the membranes with increase in mean pore radii as the rejection occurred based on size exclusion principle. The maximum rejection of $Pb^{2+}$ ions and $Cd^{2+}$ ions is 99.48 and 95.5%, respectively, is exhibited by P0 membranes with least mean pore radius.

## 4. Conclusion

PSF–PPSU-blend membranes of different compositions with or without additive were synthesized and their heavy metal rejection behavior was analyzed. The effect of polymer composition and the PEG-1000 addition on the morphological of membrane were indicated by SEM images. The membrane showed asymmetric structure with top dense layers and the bottom porous layer were the macrovoids and finger like projection increased with the addition of PEG. Thus, the prepared membranes showed higher porosity and water uptake. Addition of PEG 1000 as a hydrophilic additive into the casting solution increased the hydrophilicity of the membrane blend therefore increasing the flux and antifouling property. The P75-P membrane exhibited good antifouling property with FRR value of 72.84% and $R_{\mathrm{irr}}$ value of 27.26%. The blend membrane without additives showed lower heavy metal rejection than the one with additive since the mean pore radius and porosity of the membrane increased with the PEG addition. The pristine membrane showed highest rejection to $Pb^{2+}$ ions than $Cd^{2+}$ when complexed with PEI with maximum rejection of 99.48% and 95.5%, respectively. Therefore, the P75-P membranes exhibited the best performance with highest flux of 65.88 $L/m^2/h$ at 0.5 MPa, and good rejection of 89 and 79% for $Pb^{2+}$ ions than $Cd^{2+}$ ions, respectively.

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