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The effect of glycine betaine additive on the PPSU/PSF ultrafiltration membrane performance

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ABSTRACT

A series of new ultrafiltration (UF) membranes were prepared by blending polyphenylsulfone and polysulfone with glycine betaine (GB) and polyethylene glycol-1000 (PEG-1000) as additive. GB of varying concentrations (0–2 wt.%) were dissolved in N-Methyl-2-pyrrolidone to prepare the membranes by phase inversion method. The membranes were characterized by Scanning Electron Microscope and dispersive X-ray analysis to study the asymmetric nature of membranes and the retention of GB in membranes, respectively. The stability tests were conducted to study the stability of additives in the membranes. The membrane hydrophilicity was determined by contact angle, porosity, water uptake, and permeability studies. The addition of GB additives enhanced the membrane performance like permeability, antifouling property, and heavy metal rejection. Also, the antifouling property improved with the addition of GB. The antifouling nature was calculated by flux recovery ratio, reversible and irreversible fouling. Polymer-enhanced UF of heavy metals like Pb^{2+} and Cd^{2+} was performed and rejection of 80.23 and 71.45%, respectively, was exhibited by the GB 1 membrane with agreeable permeability and antifouling property.

Keywords: Polyphenylsulfone; Polysulfone; Zwitterion; Glycine Betaine; Heavy metal

1. Introduction

The ultrafiltration (UF) membranes are widely used for the water purification and heavy metal rejection. Nevertheless, the efficiency of UF membranes reduces due to membrane fouling. Development of an ideal membrane with high permeability, low fouling, and excellent rejection has been a major challenge till date. Sulfone-based polymers like polyphenylsulfone (PPSU) and polysulfone (PSF) are often used as membrane materials for UF membrane due to its excellent properties such as chemical resistance, good mechanical strength and hydrolytic stability [1–3]. However, the major drawback of these polymers is its lower hydrophilic nature. The cost-effectiveness of PPSU makes it preferred over PSF. The foulant molecules present in feed solution lead to fouling of these membranes either by adsorption of the macromolecules on the hydrophobic surface or by blocking the pore of the membranes [4]. Therefore, there is need for increasing the surface hydrophilicity of

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membranes which can be carried out by various methods like blending with additive [5,6], surface modification [7], polymer blending [8,9], membrane grafting [10], and crosslinking [11].

The hydrophilicity of the membranes is therefore improved using various organic molecules like polyethylene glycol (PEG) [12], polyvinylpyrrolidone [13], inorganic salts like LiCl, NH_4HCO_3 [14], zwitterion molecules [15], and nanoparticles [16]. Garcia-Ivars et al. [17] reported the synthesis of hydrophilic membrane by incorporation of nanosized PEG/Al_2O_3 as additive which exhibited improved antifouling property with polyethersulfone membranes. The effect of PEG on the morphology and transport property of membrane was studied by Chakrabarty et al. [18] and also reported that, the hydraulic permeability of membrane increased with the increase in molecular weight of the PEG, due to its good pore forming ability.

Zwitterions are considered to have protein adsorption resistance property [19] and ability to reject heavy metal ion by adsorption [20,21]. Phosphorylcholine, sulfobetaine, and carboxybetaine are zwitterionic groups that have been widely used to improve antifouling nature of membranes [22,23]. Meng et al. [24] developed a polyacrylonitrile (PAN)-based zwitterionic UF membrane to improve its anti-protein-fouling capacity and it exhibited higher flux recovery ratio (FRR) on comparison with hydrolyzed PAN membrane by the formation of zwitterion hydration layer over the surface of membranes. Sun et al. [25] reported that, the incorporation of zwitterionic N,N-dimethyl-N-methacryloxyethyl-N-(3-Sulfopropyl) (DMMSA) groups on PAN-based membranes that could remarkably improve the irreversible fouling as the protein adsorption sites are reduced due to minimized conformational change of protein as the DMMSA molecules bind to the water molecules bound to protein. The structural morphology and hydraulic permeability of the membranes can be altered by using zwitterions as additive. However, the modification of membranes by PEG could enhance membrane performance, but the oxidation of these molecules in organic solvents cause a major challenge [26]. It was also observed that, grafting of zwitterion on the membrane surface to improve fouling resistance lead to lower flux [27]. Hence, it is important to develop membranes with better antifouling nature as well as good permeability.

Glycine betaine (GB) is a zwitterionic molecule which is naturally as well as synthetically obtained. GB being an osmolyte can serve as an excellent additive to improve the hydrophilicity of the membrane due to its ability to retain water. Its nontoxic nature and abundant availability makes it an ideal additive. The cationic charge in GB due to a quaternary ammonium group and the anionic charge due to carboxylate group may be expected to assist in the removal of heavy metal. Nevertheless, studies on zwitterion as additive to improve the membrane performance was not performed so far.

In the current work, different composition of GB is incorporated in to the polymer blend of PPSU/PSF (75:25) and the membranes were prepared by phase inversion technique. The morphology of the membranes was analysed using scanning electron microscope (SEM). The hydraulic permeability and fouling resistance of the prepared membranes were examined. The membranes were also tested for its protein and heavy metal rejection property.

2. Experimental

2.1. Materials used

PSF (Mw ~ 35,000), Polyethylene glycol (PEG-1000), and GB (Mw ~ 117.15) 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) and Sodium hypochlorite solution (4% w/v available chlorine) were purchased from Merck India, Ltd. Bovine Serum Albumin (BSA) (Mw ~ 69 kDa) were purchased from CDH Chemicals, India. Polyethyleneimine (PEI) (Mn ~ 60,000) 50 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 PPSU/PSF blend membranes

PPSU/PSF blend membranes were prepared by wet phase inversion method [28] based on the literature. Initially, GB of varied concentrations (0.5, 1.0, and 2.0%) in NMP was stirred for complete dissolution. To this solution, polyethylene glycol-1000 (PEG-1000) and PPSU/PSF (75:25) were added so as to prepare a casting solution of 20% (w/v) (Table 1). 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, and sonicated to remove the trapped air. Finally the solution was casted onto a glass plate using casting blade [29], and it was immersed into coagulation bath containing distilled water. The membranes formed were rinsed and stored with deionized water for the further analysis.

2.3. Morphological study

The membrane morphology was analysed with a JEOL JSM-6380LA SEM. The membranes prepared

Table 1
Composition of prepared membranes

Membrane code	Casting solution compositions			
	Polymer composition (20 wt.%)			Solvent
	PPSU/PSF (%)	PEG (%)	GB (%)	NMP (wt.%)
GB 0	75:25	5.0	0.0	80
GB 0.5	75:25	5.0	0.5	80
GB 1	75:25	5.0	1.0	80
GB 2	75:25	5.0	2.0	80

were initially frozen using liquid nitrogen, then fractured and finally sputtered with gold to obtain the cross-sectional image. Moreover, the dispersive X-ray analysis (EDAX) detector present in SEM device was used to examine retention of GB particles in the surface of the formulated membranes [30].

2.4. Contact angle measurement

The contact angle of the membranes was measured using FTA-200 dynamic contact angle analyser by sessile droplet method [29]. 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

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 from the water and weighed after removing the 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 [31]. The water uptake of membranes were 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_w” and “W_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 [32], membrane porosity was calculated using the following equation:

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

where “W_w” and “W_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 “ρ” is the density of water (0.998 g/cm^3).

The mean pore radius of membrane was calculated using porosity of the membrane which is determined using the filtration velocity method as mentioned in the Guerout–Elford–Ferry equation [33,34].

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

where “η” 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 “ΔP” is the operational membrane pressure.

2.7. Water flux study

The permeation of the membrane was analysed by pure water flux (PWF) study of the membranes using dead end filtration cell with an effective membrane area of 5 cm^2 [28]. The membranes were immersed in water for 24 h before carrying out the permeation experiments. The membranes were subjected to compaction at 0.5 MPa transmembrane pressure (TMP) for 30 min in 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:

$$J_w = \frac{Q}{\Delta t \times A} \tag{4}$$

where "J_w" is water flux expressed in L/m^2/h, "Q" is amount of water passing through the membrane in Liter (L), "Δt" is the time in hours (h), and "A" is the effective membrane area responsible for the filtration, expressed in (m^2).

2.8. Antifouling and BSA rejection study

The BSA solution is used as 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 TMP. 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 FRR by the equation:

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

The extent of membrane fouling was further assessed by calculating the reversible R_{rev} and irreversible R_{irr} fouling ratio by following equation:

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

$$R_{\text{irr}}(\%) = \left(\frac{J_{w1} - J_{W2}}{J_{w1}}\right) \times 100 \tag{7}$$

The concentration of BSA in the feed and permeate was measured using a UV-spectrophotometer at a wavelength of 280 nm. The percentage of BSA rejection was calculated using the equation:

$$\text{Percent rejection} = \left(1 - \frac{c_p}{c_f}\right) \times 100 \tag{8}$$

2.9. Heavy metal rejection Study

Polymer-enhanced ultrafiltration technique for heavy metal rejection was conducted based on the literature [35,36]. 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 1.0 wt.% solutions 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 to stand for 5 d to complete the binding. The metal ion-complexed PEI solutions were filtered through the membranes at 0.5 MPa pressure and the permeate was collected. The rejections of the metal ions by membranes were evaluated by measuring the concentration of the metal ions in the feed and permeate, using atomic absorption spectrophotometer (GBC 932 Plus) [37]. 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_f" (mg/mL) is the concentration of the solute in feed solution.

2.10. Stability test

The stability of the additives in the blend membrane was analysed by soaking membrane sample in the water (room temperature (RT = 29˚C) and 50˚C) and sodium hypochlorite solution (active chlorine concentration 400 mg/L). The PWF at 0.5 MPa TMP and contact angle of membrane studies were conducted. Initially, samples with (GB 1) and without (GB 0) GB additive were tested before soaking and then soaked in water (50˚C) and sodium hypochlorite solution for 24 h. Subsequently, the contact angle and PWF studies were conducted to study the change in membrane performance [38].

3. Results and discussion

3.1. Morphological study

SEM was used to study the membrane morphology. The cross-sectional images of the prepared membranes displayed the asymmetric nature of membrane with dense top layer and thick porous sublayer. The SEM images (Fig. 1) showed that, the thickness of the skin layer decreased with increase in the GB additive concentration due to the migration of the GB molecules towards the surface during the phase inversion. Moreover, there is development of interconnected finger-like projection on the porous sublayer. This is because, during the membrane preparation, GB molecules dissolved in the casting solution and when the phase inversion occurs it percolates as it gets mixed

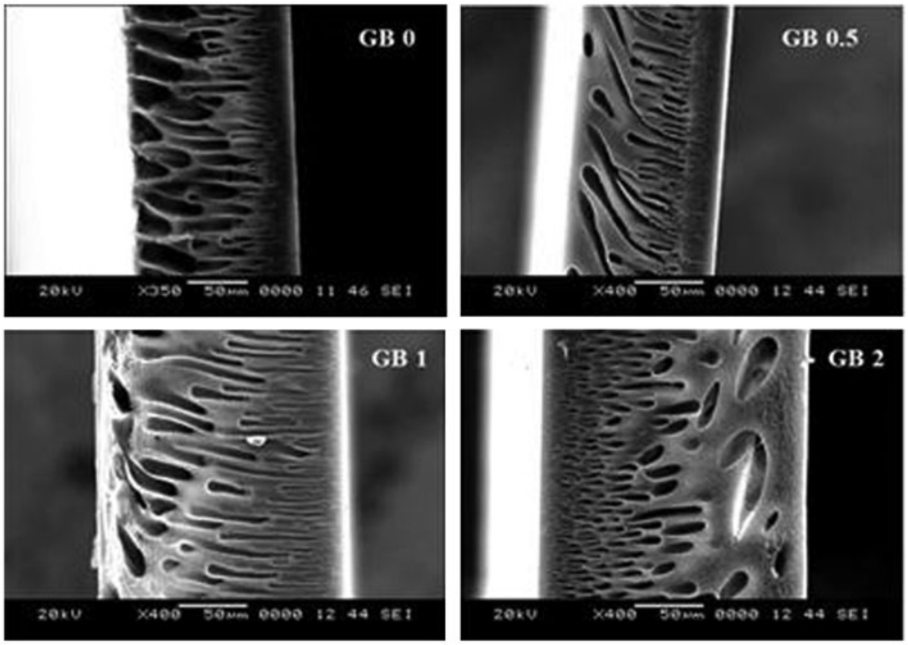

Fig. 1. Cross section image of prepared membranes.

into the water bath. The viscosity of the casting solution also increased with the increase in GB concentration which leads to delayed liquid–liquid demixing and low rate of membrane formation. Hence, reduced macrovoid formation [39] and thicker wall of finger-like projections [40] were observed. However, the solubility of GB was found to reduce with increase in concentration of GB in the casting solution, which leads to increased viscosity and larger pore size on the membrane surface of GB 2. Therefore, the concentration of GB additive in the casting solution was limited to 2.0%. Moreover, the retention of GB in the membrane was confirmed by EDAX analysis of membrane surface (Fig. 2). The presence of nitrogen in the membrane (with GB additive) is indicated by the elemental mapping as the GB contains nitrogen, whereas the neat membrane (without GB additive) doesn't contain nitrogen.

3.2. Contact angle

The surface hydrophilicity of the membrane was studied by measuring the contact angle. The hydrophilic surface would display wettability to a greater extent as its affinity to water is higher, hence resulting in a lower contact angle for hydrophilic surface. The contact angle of the prepared membranes decreased with addition of additive in the following order (Fig. 3): GB 0 > GB 0.5 > GB 2 > GB 1. The GB molecule being an osmolyte has an ability to take up water, therefore acts as hydrophilic additive, hence increasing the wettability of the membrane. However, GB 1 showed slightly lower contact angle than that of GB 2, as the GB molecule might leach out to larger amount when present in higher concentration. The addition of PEG-1000 to membranes is also responsible for better hydrophilicity as the PEG molecule could aid in the interaction of the water molecule with membrane surface [41].

3.3. Porosity, mean pore radius and water uptake

Fig. 4 shows the porosity and water uptake of the prepared membranes. The porosity and water uptake of the prepared membranes increased with the increase in addition of GB as additive in the following order: GB 0 < GB 0.5 < GB 1 < GB 2. The rise in porosity is evident from the SEM images as the thickness of dense top layer is reduced with increase in GB concentration. However, the hike in porosity of GB 2 is not remarkable when compared to the GB 1 membrane as the finger-like projection and pore interconnectivity is reduced due to leaching of GB molecule. The polymer blend which contains PEG as additive, also contributed to the increase in porosity of the membrane as it acts as a pore forming agent [42]. The addition of hydrophilic additive GB made the membranes more hydrophilic, in turn increasing the water uptake (%) of membranes. Moreover, there is increase in porosity of membranes observed which also contributed to higher water

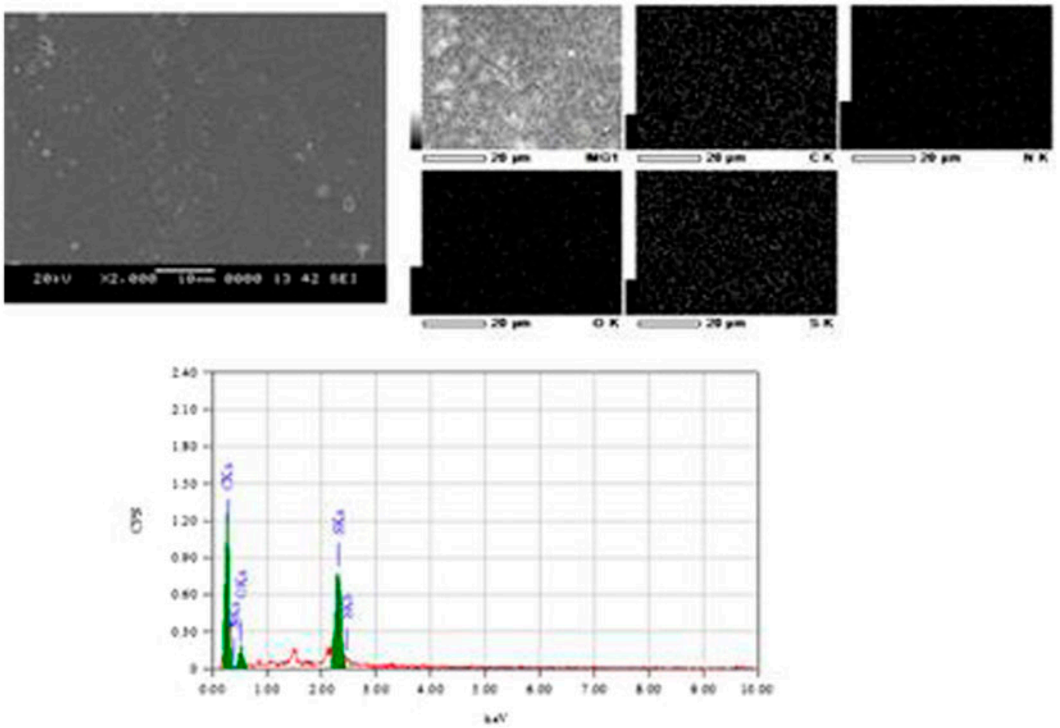

Fig. 2. EDAX and elemental mapping of the GB 1 membrane surface.

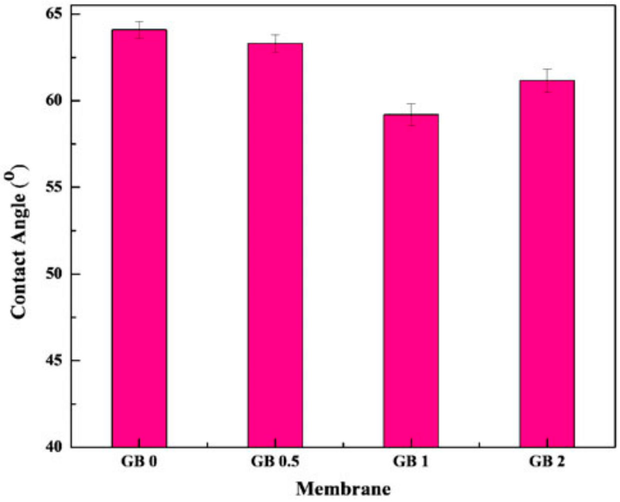

Fig. 3. Contact angle of the membranes.

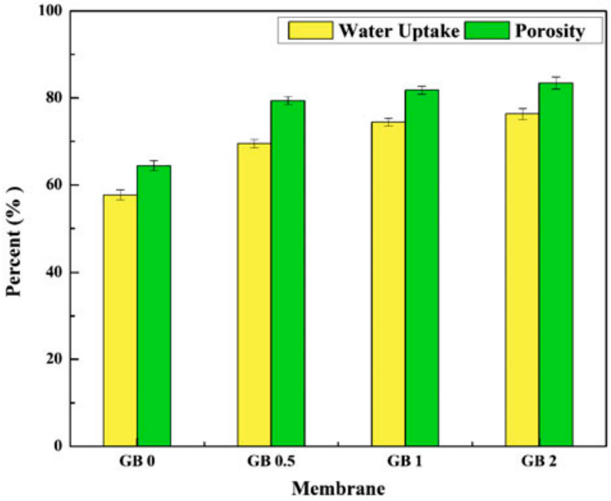

Fig. 4. Water uptake and porosity of the membranes.

uptake by membranes. The mean pore radius increased from 7 to 21 nm on incorporation of GB additive to the membranes. From Fig. 5, it can be noted that there is anomaly in the increase in the pore radius with GB concentration, which is due to the slow demixing of solvent and nonsolvent during phase inversion. But the pore radius further increased at higher concentrations of GB additive as a result of leaching of the suspended particles.

3.4. Water flux study

Pressure-dependent PWF study was conducted to study the permeability of the prepared membranes,

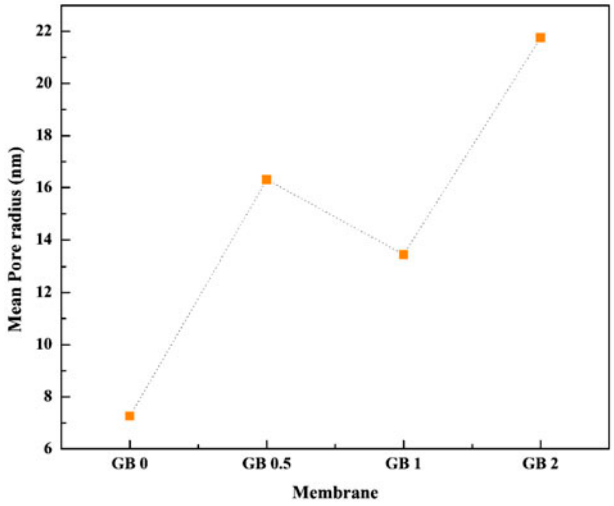

Fig. 5. Mean pore radius of the membranes.

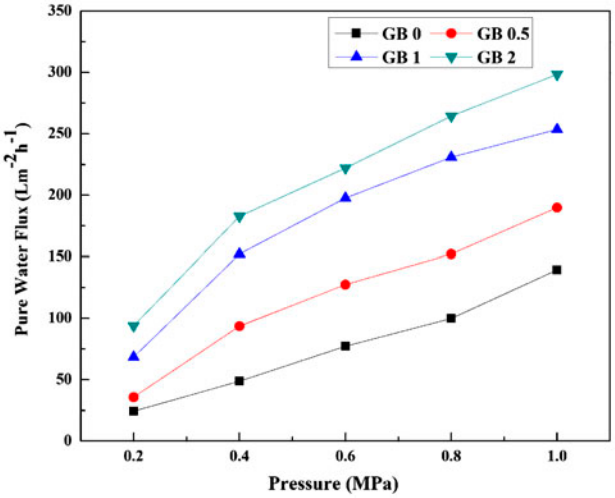

Fig. 6. Pressure-dependent PWF values of prepared membranes.

where the PWF increased with increase in GB concentration, in the following order: GB 0 < GB 0.5 < GB 1 < GB 2. The membranes were subjected to pressure range of 0.2–1.0 MPa TMP and the PWF of membranes increased linearly with rise in pressure (Fig. 6). The PWF of membranes with GB as additive showed higher flux when compared to pristine membrane. It is clear from SEM images that, the decrease in skin layer of membrane caused the higher flux. Addition of GB could bring about increased porosity, water retention property, and higher hydrophilicity of the membrane which paved to hike in PWF. In spite of lower hydrophilicity, GB 2 exhibited highest PWF because of higher porosity and larger pore size, as the flux is influenced by pore size than the hydrophilicity of membrane [43].

3.5. Antifouling study

Fig. 7 indicates the flux of membranes when pure water and BSA solution were passed to the membranes at 0.5 MPa TMP, alternately. This experiment was performed to study the fouling nature of the membranes. Decline in flux was observed when BSA solution was used as feed which is due to the clogging of pores by the BSA and the extent of decline varied with the membrane hydrophilicity [29]. The membranes exhibited reduced PWF after subjecting it to BSA, in turn depicting the flux recovery of the membranes. The FRR ratio was calculated to find the extent of fouling occurring on membranes. The membranes with GB additive showed good FRR value with highest FRR value of 78.1% by GB 1 membrane (Fig. 8). However, this exhibited the self-cleaning nature of the membranes. The irreversible fouling (R_{irr}) results were also determined to analyse the reusability. The lower value of irreversible fouling (R_{irr}) indicates that the addition of GB in membrane has caused good fouling resistance.

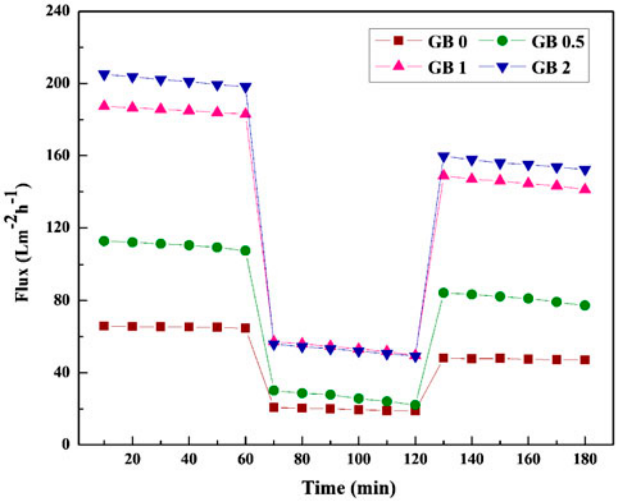

Fig. 7. Flux vs. time for the PSf/PPSU blend membranes at 0.5 MPa TMP during three steps: water flux for 60 min, BSA flux (pH 7 ± 0.1) for 60 min, and water flux for 60 min after 20 min washing with distilled water.

3.6. Rejection study

The prepared membranes were subjected to BSA and Heavy metal rejection study (Fig. 9). The BSA rejection study was conducted to study the UF

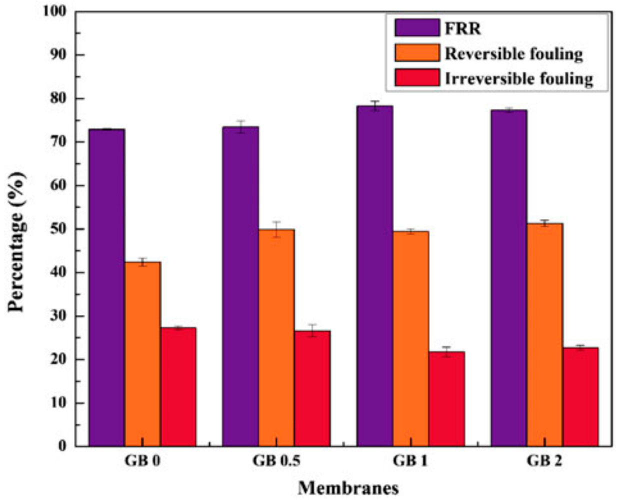

Fig. 8. FRR and fouling resistance of the prepared membranes.

property of the membranes. The membranes showed BSA rejection in the range 75–94%, which is significantly a desirable rejection value for an UF membrane. Conversely, the BSA rejection signifies the pore size of the membranes.

Heavy metals like cadmium nitrate tetrahydrate and lead nitrate were filtered and the filtrate was analysed by AAS for rejection. Polymer-enhanced heavy metal rejection was conducted by complexing heavy metals like lead and cadmium with PEI, where the lone pair of electrons present in the nitrogen atom binds to the transition metal [44]. Complexingof the heavy metal increased the size of the metal ion [45], where the degree of complexation is proportional to the size of metal ion. That is, the bigger the metal ion, the higher is the complexation. Pb^{2+} ions are comparatively large in size than Cd^{2+} ions, hence the rejection of former is higher (Fig. 9). Here, the rejection of heavy metal depends on the pore size as well as the charge on the membranes surface. The GB being a zwitterion also caused adsorption of the uncomplexed heavy metal ions. Nevertheless, the polymer-enhanced rejection works mainly on the basis of size exclusion principle that the higher rejection is observed with membranes with small pore size and larger metal ions. Hence, the rejection is observed is in the following order: GB 2 < GB 0.5 < GB 1 < GB 0.

3.7. Stability test study

The membrane stability study is essential as the cleaning of membrane is inevitable membrane process. Hence, the stability of additive in membranes was studied by soaking membrane samples in water and hypochlorite solution, which is a chemical cleaning agent to remove irreversible fouling. The stability test for GB 0 and GB 1 membranes was conducted to study the stability of membranes with and without the GB additive. From Fig. 10, it is observed that the contact angle increased slightly on soaking in NaOCl solution for both the membrane samples, which may be due to the extraction of additive. Therefore, the hydrophilicity of the membranes decreased with extraction of PEG and GB molecules. However,

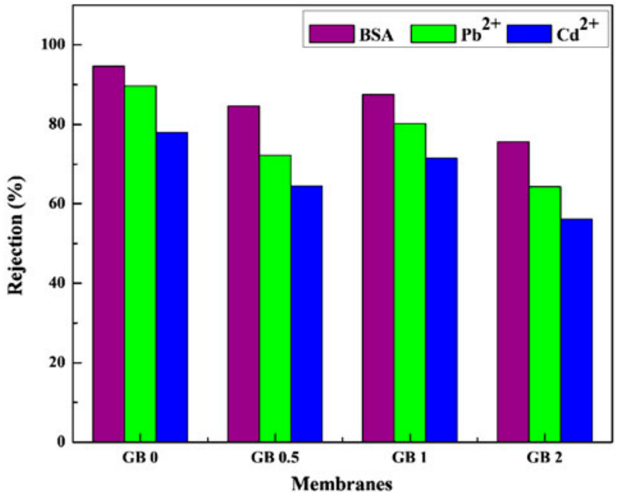

Fig. 9. BSA and heavy metal rejection by prepared membranes.

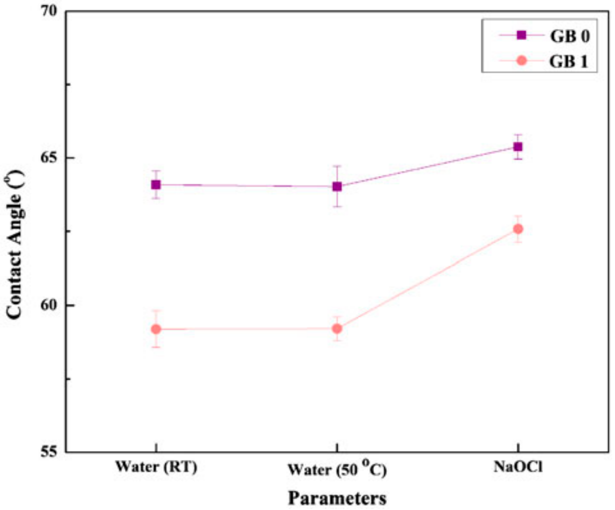

Fig. 10. Stability test investigated by measuring the contact angle.

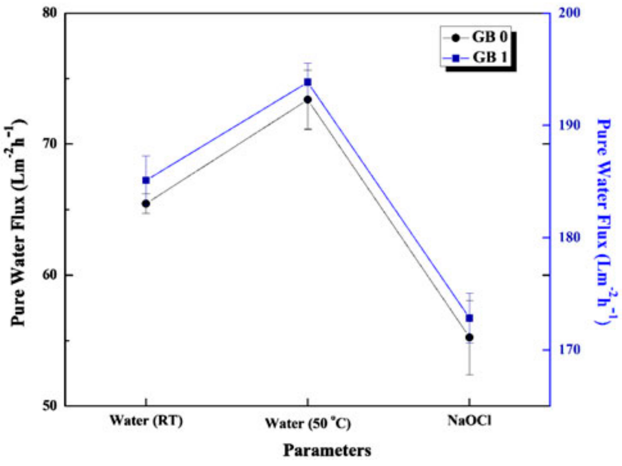

Fig. 11. Stability test investigated by measuring the PWF at 0.5 MPa TMP.

the contact angle value didn't change when dipped in water (50˚C). Moreover, from the contact angle values, it is clear that the decrease in hydrophilicity due to extraction of PEG from the membrane is more evident than the extraction of GB additive. Fig. 11 shows the PWF for membranes soaked in NaOCl solution and water (RT and 50˚C). There is a slight increase in PWF observed for membrane samples soaked in water (50˚C), which may be due to increase in porosity of membranes; while, the PWF for membrane sample decreased when soaked in NaOCl, which may be due to extraction of the additives. Therefore, the additives PEG 1000 and GB present in membranes showed lower stability in NaOCl solution. However, the membranes were found to be stable when incubated at 50˚C.

4. Conclusions

The PPSU/PSF blend membranes were effectively prepared by phase inversion method. The prepared asymmetric membranes showed improved permeability and antifouling property on addition of GB as additive. The thickness of skin layer reduced with increase in GB concentration. The GB molecule could successfully improve membrane hydrophilicity due to the water retention property. Moreover, the membrane containing GB additive showed better stability when soaked in water (50˚C) than in NaOCl solution. The GB 1 membrane with 1.0 wt.% of GB showed better performance among the prepared membranes as it showed higher hydrophilicity, good porosity and water uptake value which resulted in increased FRR and antifouling property. The GB 1 showed good rejection of 87.51, 80.23, and 71.45% for BSA, Pb^{2+} and Cd^{2+}, respectively. Conversely, addition of 2.0 wt.% could increase the permeability, but the membrane showed less rejection due to larger pores formed by seepage of suspended GB molecules during phase inversion.

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