Metal ion removal from the aqueous feed using PVDF/PS blend ultrafiltration membranes

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Abstract
Polyvinyledenefluoride-polystyrene (PVDF/PS) blend ultrafiltration membranes were prepared using phase inversion technique. Casting solutions were prepared with different compositions of poly (vinylidene fluoride) (PVDF) and polystyrene (PS) both in the presence and absence of the additive, poly (vinylpyrolidone) (PVP) using di-methylacetamide as solvent. The effects of compositions of PS and concentrations of PVP on shrinkage ratio, pure water flux and percentage of water content of the blend ultrafiltration membranes were studied. The application of the PVDF/PS blend membranes in separation of toxic heavy metal ions from aqueous streams was also attempted and the results are discussed.

Keywords: Ultrafiltration membrane, heavy metal separation.

Introduction
There has been an increasing demand for developing ultrafiltration (UF) membranes with high performance to price ratio. An investigation on an innovative, energy saving membrane separation technology in view of its low cost and eco-friendly nature is need of the hour. UF membranes could be obtained from blending two polymers. Blending of polymers in the membrane casting solution is a useful technique for modifying the properties of the prepared membrane. Polymer blending provides simpler, more feasible technology than any other method (Sajitha *et al.*, 2002). Polyvinylidene fluoride (PVDF) has increased popularity in membrane fabrication due to its excellent chemical resistance and thermal stability (Yeow et al 2005; Young & Lovell, 1991). In recent years, PVDF has been blended as auxiliary polymer with several membrane-forming polymers such as polyethersulfone (Lishun *et al.,* 1996), polyacrylonitrile (Yang & Liu, 2003), poly (methyl methacrylate) (Pereiranunes & Peinemann, 1992), sulfonated poly (ether ether ketone) (Xue & Yin, 2006) for improving the membrane properties.

In the present study, attempts were made to develop new UF membranes that combine the advantages of the both PVDF and PS by blending them together. Polystyrene (PS) is an amorphous polymer with an excellent resistance towards acid, alkali and bacterial attack (Fox & Flory, 1954). Hence, PS has great potential for making membranes with high performance to price ratio. However, it is difficult to obtain desirable UF membrane with PS because the membrane prepared are brittle and are not uniform. So it was blend with PVDF. The influences of PVDF/PS compositions in the casting solution on membrane performance and morphology were investigated. These membranes were prepared both in the presence and absence of the additive polyvinylpyrollidone (PVP) and their applications are discussed.

Experimental
Materials
Polyvinylidene fluoride (Kynar grade 760, Mw 444,000) was used in powder form and was obtained from ARKEMA, Singapore. Polystyrene was procured from Supreme Petrochemicals Pvt. Ltd., India. The solvent, Dimethylacetamide (DMAc) and the surfactant, Sodium lauryl sulphate (SLS) of AR grade were purchased from Sisco Research Laboratories Pvt. Ltd., India. Acetone and Poly (vinyl pyrollidone) (PVP) (Mw 40,000) were procured from Hi-Pure Pvt. Ltd., India.

Membrane preparation
The UF membranes were prepared by the phase inversion method using immersion precipitation technique. The blend solutions based on PVDF and PS polymers were prepared by dissolving two polymers at different compositions in DMAc as solvent by thoroughly mixing it for 4 h at room temperature in the presence and absence of PVP at various concentrations as pore former. The detailed description of the preparation of the membranes is explained elsewhere (Malaisamy & Mohan, 2002). The homogeneous solution was poured and cast on a glass plate, allowed to evaporate for definite time followed by immersion of glass plate with casting solution in a non-solvent water bath, which was kept at 10° C.

Shrinkage ratio
A piece of wet membrane immersed in the glycerin solution was cut into square shape. The length and width were measured with a square caliper; the average value was obtained after measuring the value three times. The

membrane was dried at 45°C for 3 h (Lishun *et al.,* 1996).The shrinkage ratio was calculated using the formula as follows:

Shrinkage ratio (%) = $1 - \left(\frac{ab}{a_0 b_0}\right) \times 100$

Where a_0 and b_0 and a, b are the length and breath of the wet and dry membranes, cm.

Water content

The membranes were soaked in distilled water for 24 h. The soaked membranes were mopped with the blotting paper and weighed with an electronic balance with 0.0001 g accuracy. The dry weights were measured after the wet membrane samples were placed in the dryer at 75°C for 48 h and cooled it to room temperature in the desiccators (Malaisamy *et al.,* 2002). The percentage water content was determined as follows:

% Water content = $\left(\frac{W_1 - W_2}{W_1}\right) * 100$

W_1 and W_2 are the wet and dry weight of the membrane, g.

Pure water flux (PWF)

Membranes after compaction were subjected to pure water flux at a trans-membrane pressure of 345 kPa. The permeate was measured under steady state flow. Pure water flux was calculated as follows:

$$J_w = \frac{Q}{At}$$

Where, Q-quantity of permeate collected; IJW- The pure water flux, $lm^{-2}h^{-1}$; t- sampling time, hA-membrane area, m.

Metal-ion rejection

Aqueous solutions of Zn^{2+} and Cu^{2+} with an approximate 1000 ppm concentration were prepared in 1 wt % solution of Polyvinylalcohol (PVA) in deionized water. The pH of these aqueous solutions was adjusted to 6.25 by adding small amount of either 0.1 M HCl or 0.1 M NaOH. Solutions containing PVA and individual metal ions or metal chelates were thoroughly mixed and left standing for 5 days for complete binding (Jarvis & Wagener, 1995; Kobayashi, 1997). The concentration of each metal ion in feed and permeate after passing through the membrane in the filtration kit was measured using atomic absorption spectrophotometer Perkin Elmer-2380). The % metal ion rejection (% SR) was evaluated from the concentration of the feed and permeate using equation.

% SR = $\left(1 - \frac{Cp}{Cf}\right) * 100$

Where, Cp and C_f are the concentration of permeate and feed.

Results and discussion

Effect of polymer blend composition and additive concentration on the shrinkage ratio of the membranes

Shrinkage ratio plays a vital role on the porosity of the membrane. Above 30% shrinkage will bring much negative effect on porosity and mean pore size of membranes. Fig. 1 shows the variation in shrinkage ratios of membranes prepared from the casting solution with different PS compositions. The casting solution was prepared from PVDF and PS polymers at a total polymer concentration of 17.5 wt% in the presence of 2.5 and 5 wt% PVP as additive. It is evident from the Fig. 1 that pure PVDF membrane has exhibited a higher shrinkage ratio, 20%. However, the addition of PS in the blend reduces the shrinkage ratio sharply. This may be due to the fact that the macro molecular chains of PS are less flexible and could not change their position freely at room temp in view of the fact that T_g of PS (80) is much higher at room temp. Hence, PS acts as reinforcement in the blend membrane, which prevents the membrane from shrinking further.

Effect of polymer blend composition and additive concentration on water content and pure water flux (PWF) of the membranes

Effect of water content and PWF of the membranes are shown in the Fig. 2 and 3. The pure water flux and water content of pure PVDF were found to be very low. The addition of PS in the blend have modified the above parameters of the membrane. Thus the addition of PS in the blend , PWF, water content of the membrane were increased to 8.87 $lm^{-2}h^{-1}$ and 60.6% respectively. It is postulated that the miscibility of blending polymers depends on the difference between the solubility parameter of each polymer. The difference between the solubility parameter of PVDF and PS is very high, which makes PVDF and PS thermodynamically incompatible system. This in turn makes PS to form the dispersed phase in the continuous matrix of PVDF at low concentration of PS. Further weak interactions between PVDF and PS chains lead to larger distance between these two polymeric chains and results in pores with larger pores (Malaisamy & Mohan, 2002). As the PS in the blend was further increased to 25wt% the water content, and PWF further increased to 64.70% and 14.79 $lm^{-2}h^{-1}$ respectively. There was a further increase in the water content and the WF with the addition of PVP additive to the blend. This increase is due to the addition of PVP, the pore former, in the casting solution of membrane which has changed the composition and the assembled state of the macromolecules which in turn has produced a great impact on the pore shape, size and its distribution.

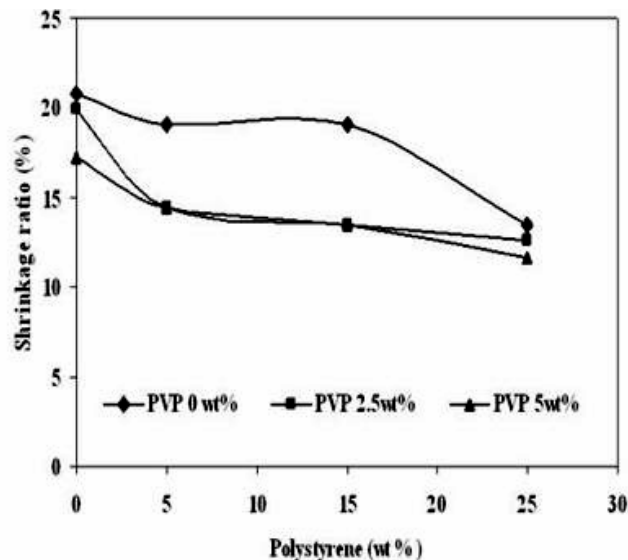Fig.1. Effect of PVP on the shrinkage ratio of
PVDF/PS blend membranes

Fig.2. Effect of PVP on the Pure Water Flux of
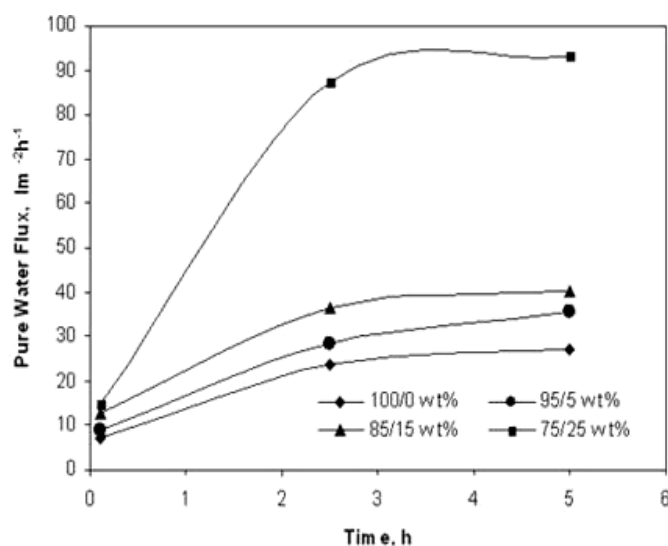PVDF/PS blend membranes

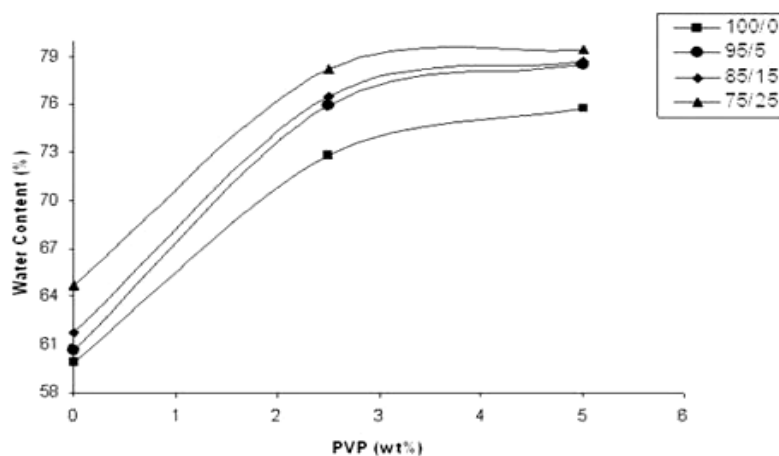Fig.3. Effect of PVP on the water content of PVDF/PS blend
membranes

Fig.4. Effect of PVP concentrate on the rejection Zn^{2+}
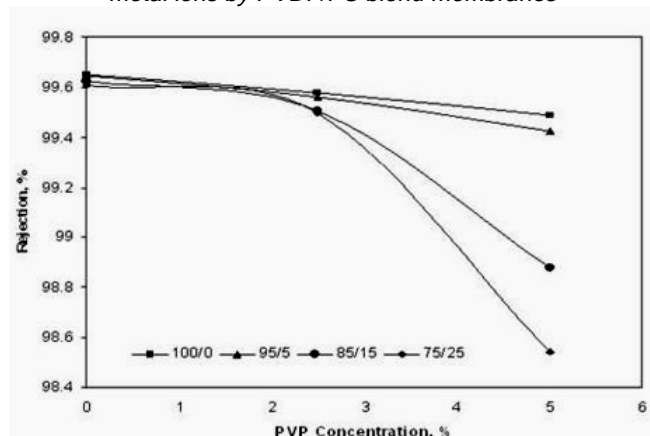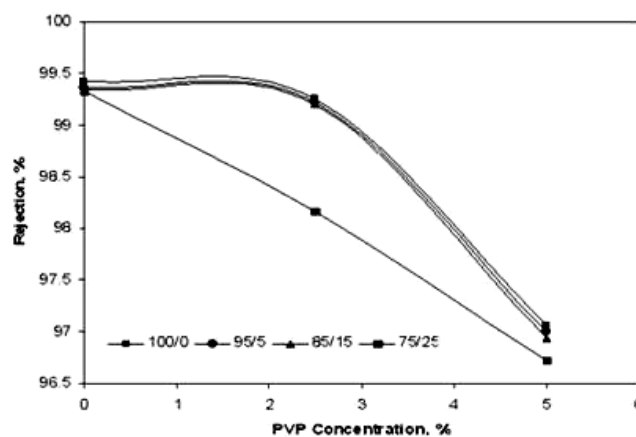metal ions by PVDF/PS blend membranes

Fig.5. Effect of PVP concentration on rejection of Cu^{2+}
metal ions by PVDF/PS blend membranes

Role of polymer blend composition and additive concentration on metal ion rejection studies

Ultrafiltration processes cannot be directly applied for ionic level rejection owing to the larger pore size of the membranes. Hence to apply this membrane in metal ion rejection, the size of the metal ions need to be enlarged there by enhancing the rejection of the metal ions. In this study, a water soluble chelating polymer, PVA, was used as the complexing agent for the metal ions Cu^{2+} and Zn^{2+} and were subsequently rejected individually from the aqueous stream by using PVDF/PS blend ultrafiltration membranes at 345 kPa.

The rejection of the metal ions using PVDF/PS blend membranes in the absence of the additive was carried out individually after the metal ions were complexed by PVA and the results are shown in the Fig. 4 and 5. Thus, the pure PVDF membrane in the absence of additive yielded a highest separation. It was observed that with the PVDF/PS blend membranes, the separation of Zn^{2+} remained constant at 99.6%. When, the PS content was increased from 5 to 25 wt% in the blend in the absence of additive. Similarly, the rejection for Cu^{2+} also remained constant at 99.4% with the increase of PS in the blend from 5 to 25 wt%. The rejection of metal ion remained closed to 99% with the addition of PVP, the pore former to the blend. Thus, the addition of PS and PVP in the blend has resulted in the increased pore size as evidenced water content and pure water flux. However, the size of the metal ion chelate may be greater than the pore size of the blend membrane with 25 wt% PS. Thus an increase in PS content in the blend up to 25 wt% has no effect on separation of Cu and Zn ions.

Conclusion

Ultrafiltration membranes are widely used in the chemical process industries for separation and removal of wide variety of chemicals due to its high efficiency, low energy requirements and its compact nature. The ultrafiltration membranes were prepared using PVDF and PS blend membranes in absence and presence of additive PVP in the solvent DMAc. By adding certain amount of PS into PVDF, the flux of membranes increased greatly while maintaining the retention ratio nearly unchanged. The shrinkage ratio decreases with the increase in the PVDF content in the membrane which establishes that by adding PS to the membrane. The size of the pores increased with the increase in the amount of PVP in the casting solution. It should be noted that a small amount of PVP was enough to initiate the formation of pores in the skin layer. Since, the skin layer dictates the perm selectivity of a membrane; it is probable to have a control of the membrane performance by the addition of PVP in the casting solution.

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