

# Cellulose Acetate–Poly(ether sulfone) Blend Ultrafiltration Membranes. II. Application Studies

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**ABSTRACT:** Ultrafiltration membranes are largely applied as macromolecular solutes and heavy-metal-ion separation from aqueous streams. Cellulose acetate and poly(ether sulfone) blend ultrafiltration membranes were prepared by the precipitation phase-inversion technique in 100/0, 95/5, 85/15, and 75/25% polymer blend compositions in the absence and presence of a polymeric additive, poly(ethylene glycol) 600, at different additive concentrations and were used for the rejection of proteins trypsin, pepsin, egg albumin, and bovine serum albumin; a maximum of 94% rejection was achieved. The toxic heavy metal ions copper, nickel, and cadmium from dilute aqueous solutions were subjected to rejection by the blend membranes

by complexation of the ions with the water-soluble polymeric ligand, polyethyleneimine (PEI). Permeate flux studies of proteins and metal ions were performed simultaneously with the rejection experiments. The atomic absorption spectra results reveal maximum rejection for copper complex and a minimum rejection of about 60% for the cadmium complex. The rejection and permeate flux of the blend membranes were compared with those of pure cellulose acetate membranes. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3659–3665, 2004

**Key words:** poly(ether sulfones); membranes; blends; phase separation

## INTRODUCTION

Efficient separation processes are needed in the food and pharmaceutical industries to obtain high-grade products,<sup>1–3</sup> to supply communities and industries with high-quality water,<sup>4</sup> and to remove and recover toxic or valuable components from industrial effluents.<sup>5–7</sup> With the advent of membrane technology, separation, concentration, and purification have become industrially viable unit operations because of a higher separation efficiency. Further, the low energy of operation, special requirements, and simplicity of operation with modern compact modules, along with the added advantages of the recycling and reuse of chemicals and water, promote the membrane process as a promising technique in the separation processes. As the heart of the process, the membrane plays a key role in dictating the applicability and efficiency of the process.

The performance of cellulose acetate (CA) membranes may be improved by blending with appropriate polymers because polymer blends provide an efficient way to fulfill new requirements for material properties.<sup>8</sup> CA–polyurethane blend ultrafiltration

membranes with polyvinylpyrrolidone (PVP) as an additive have been prepared and applied to the rejection of proteins, including bovine serum albumin (BSA), egg albumin (EA), pepsin, and trypsin, with the achievement of more than 90% rejection.<sup>9,10</sup> Because of the excellent film-forming properties of CA, polymer blends based on CA were chosen for this investigation.<sup>11</sup> Similarly, several chemical, electronic, electrocoating, metal-refining, and finishing industries face severe problems in terms of the disposal of their waste streams when highly toxic or valuable constituents such as heavy metal ions are present.

From these waste streams, heavy metals, such as Cu, Ni, Zn, and Co, could be separated and concentrated through the binding of the target metal ions in a polyelectrolyte with water-soluble macromolecular compounds and the subsequent ultrafiltration of the bound metals from the unbound components.<sup>12</sup> Thus, toxic heavy metals could be eliminated from aqueous streams, and the precious metals could be recovered and reused. A process for the recovery metal ions, such as Cu(II), Ni(II), Pb(II), and Cd(II), from industrial wastewater by their complexation with polyethyleneimine (PEI) was attempted.<sup>13</sup> Other researchers have studied the retention of metal ions from mixtures of divalent metal ions with water-soluble polymers at a constant ionic strength.<sup>14</sup> CA was also blended with polyurethane, and the blend membranes were applied for the rejection of Cu(II), Ni(II), Zn(II), and Cd(II).<sup>15</sup>

This study was one in a series of investigations on the preparation of CA/poly(ether sulfone) (PES) blend

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ultrafiltration membranes. The main objective of this study was to examine the effects of the CA/PES blend composition and the concentration of a water-soluble additive, poly(ethylene glycol 600 (PEG 600)), on the rejection and the product rate efficiencies of the proteins trypsin, pepsin, EA, and BSA, and the rejection of metal ions of copper, nickel, and cadmium from aqueous streams.

## EXPERIMENTAL

### Materials

A PEI [weight-average molecular weight ( $M_w$ ) = 600,000–1,000,000] 50% aqueous solution was procured from Fluka Chemie AG (Steinheim, Switzerland) and was used as a 1 wt % aqueous solution. Anhydrous sodium monobasic phosphate and sodium dibasic phosphate heptahydrate were procured from CDH Chemicals, Ltd. (Mumbai, India), and were used for the preparation of phosphate buffer solutions in the protein analysis.

Proteins, namely, BSA ( $M_w$  = 69 kDa), pepsin ( $M_w$  = 35 kDa), and trypsin ( $M_w$  = 20 kDa), were purchased from SRL Chemicals, Ltd. (Mumbai, India), and were used as received. EA ( $M_w$  = 45 kDa) was obtained from CSIR BioChemical Centre (New Delhi, India). Copper(II) sulfate (AR), nickel(II) sulfate (analytical reagent grade), and cadmium(II) chloride were procured from Merck (I), Ltd. (Mumbai, India) and were used as such for the preparation of aqueous metal ion solutions. Deionized and distilled water was used for the preparation of the metal, protein, and 1 wt % PEI aqueous solutions.

### Rejection studies

The ultrafiltration experiments for solute rejection were carried out with pure CA membranes and CA/PES blend membranes at compositions of 95/5, 85/15, and 75/25% at various additive concentrations. The rejection and flux experiments were carried out at room temperature with an ultrafiltration kit with a 450-mL capacity and a holdup volume of 10 mL that was supplied by M/s Spectrum, Inc. The effective membrane surface area was 38.5 cm<sup>2</sup>, and the applied pressure was 345 kPa. A constant agitation speed of 500 rpm was used throughout the study to reduce concentration polarization.

#### Rejection of protein solutions

The proteins, BSA, EA, pepsin, and trypsin, were dissolved in a 0.1 wt % phosphate buffer (0.5M, pH 7.2) solution and used as standard feed solutions for the analysis of the proteins. For all of the experiments, the concentration of the feed solution was kept constant at

0.1%, and the volume was 10 mL. After the membrane was mounted in the ultrafiltration test kit, the chamber was filled with the individual protein solution and pressurized under a nitrogen atmosphere at 345 kPa, which was maintained constant throughout the run. Permeate was collected over measured time intervals in graduated tubes, and the tube contents were analyzed for protein content by ultraviolet spectrophotometry (Hitachi, model U-2000) at  $\lambda_{\max}$  = 280 nm. The percentage solute rejection (% SR) was calculated from the concentration of the feed ( $C_f$ ) and the concentrate of the permeate ( $C_p$ ) with the following equation:

$$\text{SR} = 1 - \frac{C_p}{C_f} \times 100$$

#### Rejection of metal ion solutions

Aqueous solutions of Cu(II), Ni(II), and Cd(II) were prepared at concentrations of 1000 ppm in a 1 wt % solution of PEI in deionized water. The pH of these aqueous solutions were adjusted to  $6 \pm 0.25$  by the addition of a small amount of either 0.1M NaOH or 0.1M HCl. Solutions containing PEI and individual metal ions were thoroughly mixed and left standing for 5 days to complete binding.<sup>16,17</sup>

For the presetting of the membranes and the maintenance of a constant flux, each metal ion–PEI complex solution was run in the ultrafiltration test kit at 345 kPa with compressed air. The percentage rejection of the metal ions were determined by analysis of the concentrations of the feed and permeate with an atomic absorption spectrophotometer (PerkinElmer 2380, California). In the absence of metal ions, the concentration of PEI was measured by ultraviolet–visible spectrophotometry (Hitachi, model U-2000) at  $\lambda_{\max}$  = 269 nm, and % SR was determined with the same formula as that for protein rejection.

## RESULTS AND DISCUSSION

The rejection of the proteins BSA, EA, pepsin, and trypsin were attempted individually with the blend membranes with 95/5, 85/15, and 75/25% compositions with 0–10 wt % additive concentrations. The lowest molecular weight protein, trypsin, was taken first for the study to prevent fouling and possible cake formation by the higher molecular weight proteins. The ultrafiltration processes could not be directly applied for ionic level rejections because of the larger pore sizes of the membranes, which were not suitable for rejecting ions. Hence, to enhance the size and, consequently, the rejection of metal ions, a water-soluble chelating polymer, PEI, was used for the complexation of the metal ions Cu(II), Ni(II), and Cd(II) and were subsequently rejected individually from

TABLE I  
% SR by CA/PES Blend Membranes

Polymer blend composition		Additive concentration of PEG 600 (wt %)	% SR			
CA (%)	PES (%)		BSA	EA	Pepsin	Trypsin
100	0	0	94	93	82	80
95	5	0	93	91	74	68
85	15	0	86	76	70	64
75	25	0	84	74	63	61
100	0	2.5	89	86	76	70
95	5	2.5	87	84	71	62
85	15	2.5	86	74	60	58
75	25	2.5	86	72	59	56
100	0	5.0	86	80	74	69
95	5	5.0	84	75	65	60
85	15	5.0	84	72	60	55
75	25	5.0	81	69	59	53
100	0	7.5	82	77	72	70
95	5	7.5	80	76	61	57
85	15	7.5	80	73	58	53
75	25	7.5	79	70	52	51
100	0	10.0	76	74	65	62
95	5	10.0	74	70	58	54
85	15	10.0	74	68	54	53
75	25	10.0	70	60	50	46

aqueous streams by the CA/PES blend ultrafiltration membranes.

### Protein rejection studies

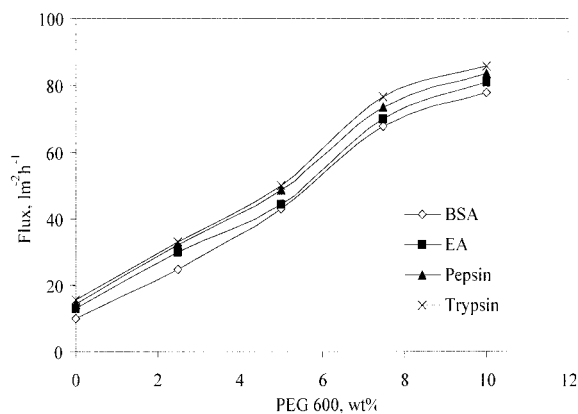
The fractionation of proteins with ultrafiltration has not been successfully scaled up to an industrial level because selectivity poses a threat to the industry. The interaction of the solutes with the membrane results in adsorptive fouling and interferes with the performance of the membranes. The CA/PES blend membranes with compositions of 95/5, 85/15, and 75/25% in the presence and absence of different additive concentrations of PEG 600 were used for the rejection of proteins under a nitrogen atmosphere, and the results were compared with the rejection by the pure CA membranes. Initially, a protein of low molecular weight, trypsin, was used for the ultrafiltration experiments because we expected the use of a high-molecular-weight protein at the beginning would spoil the originality of the pores for the separation and comparison of low-molecular-weight proteins. Thus, the rejection of proteins were performed in the order trypsin, pepsin, EA, and BSA.

### Role of the polymer blend composition and additive concentration on the rejection of proteins

The composition of the polymer blend membrane had the effect of altering the protein rejection efficiency. The pure CA membrane exhibited rejections of 94% for BSA and 80% for trypsin. The higher

rejection of BSA may have been due to the larger size of the BSA compared with trypsin. As the PES composition was increased from 5 to 25% in the CA/PES blend in the absence of any additive, the percentage rejection decreased, as shown in Table I. This may have been because the higher PES content created inhomogeneity between the polymer matrices, resulting in the formation of aggregate pores in the membranes. Similar results were also observed for CA/sulfonated polysulfone (SPS) blend membranes by Malaisamy and Mohan.<sup>18</sup> For the 95/5% blend composition, the percentage rejection values were 87, 84, 71, and 62 % for BSA, EA, pepsin, and trypsin, respectively. The decrease in rejection may have been the decrease in the solute size of the proteins in the aforementioned order.

The effects of the additive (PEG 600) concentration on the rejection of the blend membranes is shown in Table I. The additive concentration was increased, from 2.5 to 10 wt %, in each blend composition, and the percentage rejection decreased. For the 100% CA membrane with 2.5 wt % additive, the BSA rejection was 89%, and it decreased to 76% with the increase of the additive concentration to 10 wt %. A similar trend was also observed for other proteins, with varying magnitudes. This may have been due to the leaching out of the additive (PEG 600) from the membranes during gelation, which created pores proportionately on the membrane. Comparable results were also obtained by Mukai et al.<sup>19</sup> In the CA/PES blend membranes also, for a given polymer composition, when



**Figure 1** Effect of the PEG 600 concentration on the flux of proteins for the 100% CA membranes.

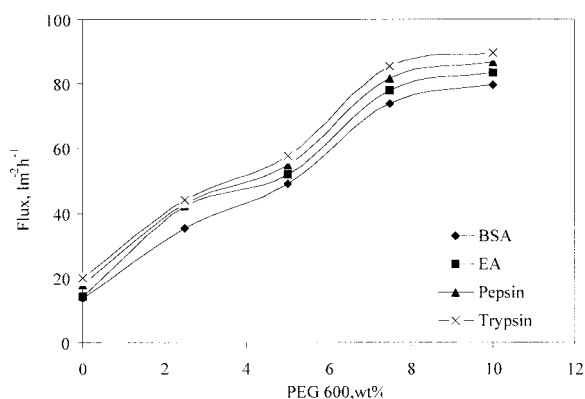
the additive concentration was increased, from 2.5 to 10 wt %, the separation efficiency decreased. All of the blend membranes with various additive concentrations showed similar trends for all of the protein molecules. The higher percentage rejection of BSA and the lower percentage rejection of trypsin was obviously due to their molecular sizes.

### Protein flux studies

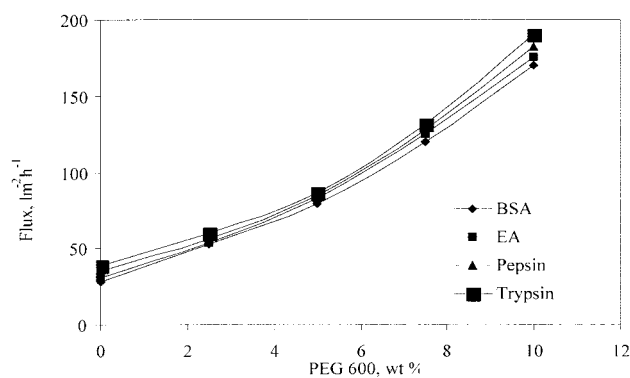
The permeate protein flux is the measure of the product rate of the membrane for the given protein solutions.

Role of the polymer blend composition and additive concentration on the product rate efficiency of the proteins

The permeate flux of the proteins BSA, EA, pepsin, and trypsin by the 100/0, 95/5, 85/15, and 75/25% CA/PES blend membranes in the absence of the additive is shown in Figures 1–4. The pure 100% CA membrane, in the absence of additive, showed the



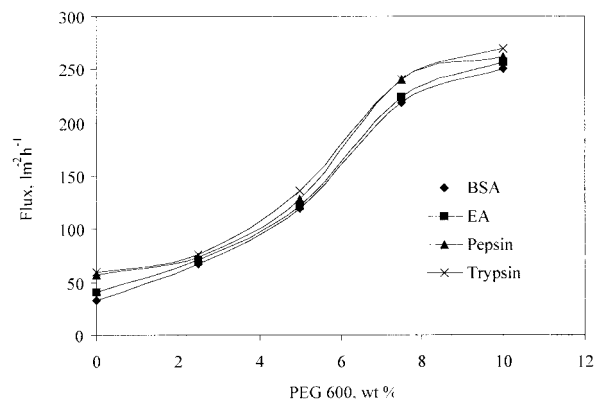
**Figure 2** Effect of the PEG 600 concentration on the flux of proteins for the 95/5% CA/PES blend membranes.



**Figure 3** Effect of the PEG 600 concentration on the flux of proteins for the 85/15% CA/PES blend membranes.

lowest permeate flux of  $10.01 \text{ lm}^{-2} \text{ h}^{-1}$  for BSA. The other proteins, EA, pepsin, and trypsin, showed comparatively higher fluxes with the pure CA membranes. For the CA/PES blend membranes, without additive, for a given protein molecule (e.g., BSA), when the PES content in the blend was increased, from 5 to 25%, the flux also increased from  $13.88$  to  $32.51 \text{ lm}^{-2} \text{ h}^{-1}$ . A similar trend was observed for all of the proteins. This trend may have been due to the hydrophilic PES, which could have reduced the fouling of protein, thereby enhancing the product rate efficiency.

The presence of additive in the casting solution had a significant role in the morphology and, in turn, on the flux of the resulting membranes. Thus, the pure CA membrane for a given protein molecule had an enhanced flux when the additive was increased from 2.5 to 10 wt %, as shown in Figure 1. In the 100% CA membrane, BSA had a flux of  $24.86 \text{ lm}^{-2} \text{ h}^{-1}$  for 2.5 wt % PEG 600 and  $77.89 \text{ lm}^{-2} \text{ h}^{-1}$  for 10 wt % PEG 600. The other proteins also exhibited a similar trend. For the 95/5% CA/PES blend membrane, the increase of additive from 2.5 to 10 wt % increased the protein permeate flux from  $35.38$



**Figure 4** Effect of the PEG 600 concentration on the flux of proteins for the 75/25% CA/PES blend membranes.



TABLE II  
Percentage Separation of Metal Chelates by CA/PES Blend Membranes

Blend composition		PEG 600 (wt %)	Percentage rejection		
CA (%)	PES (%)		Cu(II)	Ni(II)	Cd(II)
100	0	0	98.42	95.67	88.76
85	15	0	94.33	91.09	83.78
75	25	0	90.17	87.45	85.63
100	0	2.5	95.46	93.74	84.45
85	15	2.5	86.70	85.01	79.65
75	25	2.5	83.21	81.67	75.34
100	0	5.0	93.21	91.24	81.68
85	15	5.0	83.25	81.67	74.56
75	25	5.0	80.05	77.67	70.34
100	0	7.5	90.34	86.67	79.05
85	15	7.5	79.98	79.45	71.23
75	25	7.5	76.45	74.68	65.87
100	0	10.0	87.04	83.37	77.45
85	15	10.0	76.26	76.34	66.23
75	25	10.0	73.45	69.97	61.67

to  $79.69 \text{ lm}^{-2} \text{ h}^{-1}$  for BSA, as shown in Figure 2. All of the other blend compositions also exhibited similar behavior when the additive was increased from 2.5 to 10 wt %, as shown in Figures 3 and 4. A similar trend was also observed for the other proteins. This may have been due to the formation of macrovoids in the membrane, due to the faster rate of leaching out of the additive during gelation. In all of the membranes, regardless of the additive concentration and polymer blend composition, the order of protein flux was trypsin > pepsin > EA > BSA. The reason for this trend may be explained by the fact that the flux of the proteins was inversely proportional to their size.

### Metal ion rejection studies

A definite volume of 10 mL of feed and permeate was taken for the sake of comparison and reliability of the results throughout the study.

#### Role of the polymer blend composition and additive concentration on the rejection of metal ions

The rejection of metal ions, with CA/PES membranes in the absence of additive, was carried out individually after the complexation of the metal ions with the polymeric water-soluble ligand PEI, and the results of the rejection studies are given in Table II. The pure CA membrane exhibited 98.42% rejection for Cu(II) ions, which was higher than that of the CA/PES blend membranes. This may have been due to the smaller pore size of the pure CA membranes. The other metal ions, Ni(II) and Cd(II), had rejections of 95.67 and 88.76%, and the decrease in the rejection of these metal ions may have been due to the size of the metal ion-PEI complex. When

the PES composition in the blend was increased from 15 to 25%, the rejection decreased for all of the metal ions. This lower rejection efficiency of the 75/25% blend membranes compared to the 85/15% blend membranes may have been due to the presence of a higher amount of PES in the blend, which caused changes in the macroscopic structure. A similar trend was also observed for CA/SPS blend membranes by Malaisamy and Mohan.<sup>18</sup>

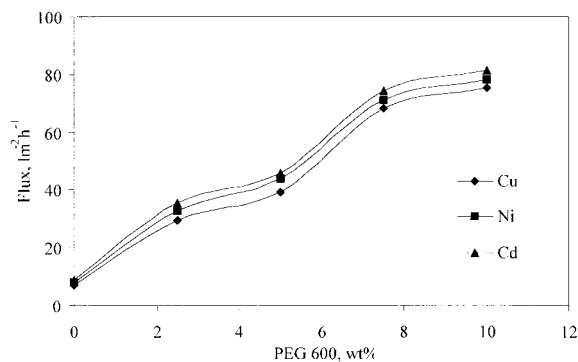
It was obvious in these experiments that in all of the membranes, Cu(II) exhibited a higher rejection than Ni(II), which in turn was higher than Cd(II). In the 85/15% CA/PES blend membrane, the percentage of rejection of metal ions decreased as the additive concentration increased. This may have been due to the formation larger pores by the leaching out of additive from the membrane during gelation. A similar trend was also observed for the 75/25% CA/PES membranes.

All of the previous experiments showed that the binding capacity of Cu with PEI was stronger than that of other metal ions in the order Cu(II) > Ni(II) > Cd(II). Further, the binding capacity depended on the number of functional groups present in the macromolecular complex and the atomic size of the metal ions.

In all cases, the metal ions complexed with PEI exhibited higher rejections than the pure metal ion solutions because of the complex formation with PEI, on the basis of John-Teller distortion effect.<sup>20</sup>

### Metal ion permeate flux studies

The permeate flux studies of the membranes showed the product rate efficiency and predict the economics of the membrane process. The metal ion permeate



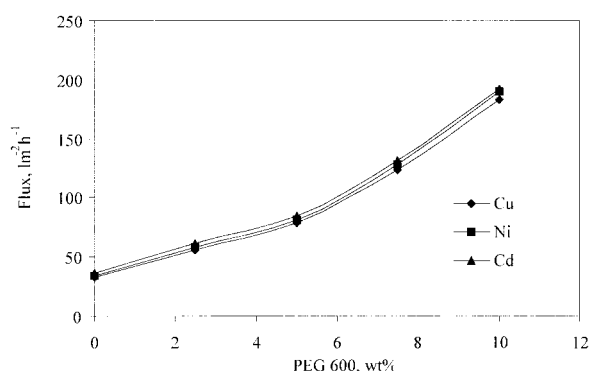
**Figure 5** Effect of the PEG 600 concentration on the flux of metal chelates for the 100% CA membranes.

fluxes, measured simultaneously during rejection with 100/0, 85/15, and 75/25% CA/PES blend membranes in the absence and presence of the additive, are shown in Figures 5–7.

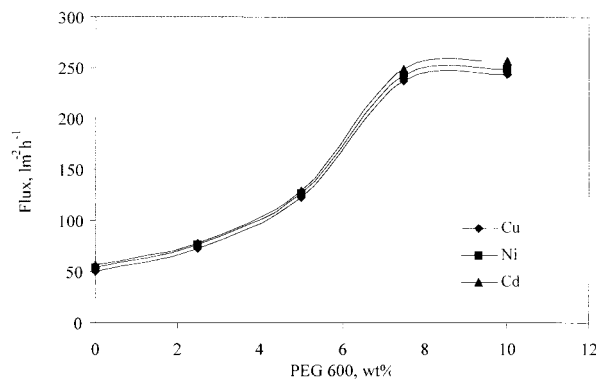
#### Role of the polymer blend composition and additive concentration on metal ion permeate flux studies

The metal permeate fluxes were measured simultaneously during the rejection experiments by the 100/0, 85/15, and 75/25% CA/PES membranes in the presence and absence of the additive. The pure 100% CA membrane offered a lower flux value of  $6.98 \text{ lm}^{-2} \text{ h}^{-1}$  for Cu(II) and a higher value of  $9.02 \text{ lm}^{-2} \text{ h}^{-1}$  for Cd(II), as shown in Figure 5. When the PES content was increased to 25%, the flux of Cu(II) increased to  $50.12 \text{ lm}^{-2} \text{ h}^{-1}$ . The increase in flux on the increase in PES composition may have been due to the higher hydrophilicity of PES in the blend system.

The additive played a major role in the membrane performance and the results of metal ion rejection by the membranes with various additive concentrations, as shown in Figure 4. The increase in flux with an increase in the additive concentration may have been due to the formation of bigger pores by the mem-



**Figure 6** Effect of the PEG 600 concentration on the flux of metal chelates for the 85/15% CA/PES blend membranes.



**Figure 7** Effect of the PEG 600 concentration on the flux of metal chelates for the 75/25% CA/PES blend membranes.

branes. However, in the 85/15% CA/PES membranes, as the additive concentration was increased from 2.5 to 10 wt %, the flux was also increased significantly from  $55.43$  to  $182.13 \text{ lm}^{-2} \text{ h}^{-1}$  for Cu(II) ions, as shown in Figure 6. A similar trend was exhibited for the 75/25% blend composition and other metal ion fluxes, as shown in Figure 7, unlike for the 100% and 95/5% membranes. The increase in flux due to the increase in the additive was obviously due to the pore former, PEG 600, which got leached out during gelation, creating pores.

The order of flux for the metal chelates,

$$\text{Cd(II)} > \text{Ni(II)} > \text{Cu(II)},$$

was primarily due to the larger metal chelate size of Cu(II)–PEI and the smaller size of the Cd(II)–PEI complex.

## CONCLUSIONS

CA/PES blend ultrafiltration membranes with different polymer blend compositions in the presence and absence of various additive concentrations were used for the rejection of the proteins BSA, EA, pepsin, and trypsin. The maximum percentages of rejection achieved for the proteins in the blend system were 93, 91, 74, and 68%, respectively. The toxic heavy metal ions Cu(II), Ni(II), and Cd(II) were also rejected by complexation with PEI, and the maximum percentages of rejection were 94, 91, and 83% in the CA/PES blend systems. The polymer composition and additive concentration had a considerable impact on the rejection and permeate flux of the proteins and metal ion complexes. The rejection of proteins and metal ions were lower and the flux higher for blend membranes compared to pure CA membranes.

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