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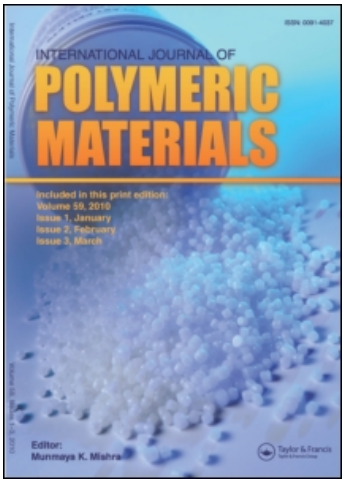

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Effect of Poly(ethylene glycol) on Separations by Cellulose Acetate/poly(ether imide) Blend Membranes

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Ultrafiltration membranes are largely being applied for macromolecular and heavy metal ion separations from aqueous streams. In this study, cellulose acetate (CA) and polyetherimide (PEI) based ultrafiltration blend membranes prepared in the absence and presence of poly(ethylene glycol) 600 (PEG 600) in various compositions were subjected to the separation of macromolecular proteins such as bovine serum albumin (BSA), egg albumin (EA), pepsin and trypsin. Toxic heavy metal ions such as Cu(II), Ni(II), Zn(II) and Cd(II) were subjected to separation by the blend membranes by complexing them with the polymeric ligand polyethyleneimine. The effects of polymer blend compositions and additive concentrations on the rejection and permeate flux of both proteins and metal ions are discussed. In general, it was found that CA/PEI blend membranes displayed higher permeate flux and lower rejection compared to pure cellulose acetate membranes at all additive concentrations. The extent of separation of proteins was found to be directly proportional to the molecular weight of the protein, while the extent of removal of metal ions depends on the affinity of metal ions to polyethyleneimine and the stability of the formed complexes.

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Keywords: metal ion separation, poly(ethylene glycol) 600, polyethyleneimine, protein separation, ultrafiltration

INTRODUCTION

Macromolecular protein removal from food and bio-related industrial waste streams and toxic heavy metal ion separation from industrial

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effluents are gaining increased visibility due to environmental concerns and interest in saving precious materials. In recent years, ultrafiltration (UF) and reverse osmosis (RO) have become standard procedures for the separation of macromolecular solutions. Separation of colloidal suspensions by ultrafiltration can be achieved by permselective membranes, which allow the passage of solvent and small solute molecules but retain macromolecules [1]. Separation of proteins by membranes was found to be advantageous because it is nondestructive and the process limits denaturation of proteins [2]. Intensive research has been carried out by several researchers on the transmission and rejection of proteins using cellulose acetate and polysulfone membranes, and it has been concluded that the membrane ultrafiltration is a reliable process for macromolecular separations [3–6].

Arthanareeswaran et al. studied the performance of cellulose acetate and polyethylene glycol blend ultrafiltration membranes using the design of experiments concept [7]. Cellulose acetate and polyurethane blend ultrafiltration membranes using poly vinyl pyrrolidone (PVP) as a pore-forming additive have been applied to the separation of proteins such as BSA, EA, pepsin and trypsin, achieving more than 90% separation [8]. PEG 200 has been used as a pore-forming additive in the preparation of polyetherimide asymmetric membranes. The results reveal that increasing the amount of PEG 200 in the polymer solution used to prepare the membrane drastically improved the solute rejection rate [9]. In a recent investigation, separation of proteins and metal ions by modified cellulose acetate membranes with PEG 600 and PVP has been attempted [10].

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Several chemical, electronic, electro-coating, food, pharmaceutical and biotechnological industries face severe problems over 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(II), Zn(II) and others could be separated and concentrated through binding of the target metal ions to water-soluble polyelectrolyte and subsequent ultrafiltration of the bound metals from the unbound components [11,12].

Muslehiddinoglu et al. have studied the effect of operating parameters on the selective separation of mercury and cadmium from binary mixtures through polymer-enhanced ultrafiltration using polyethyleneimine as a water-soluble polymer to bind the metals [13]. Polysulfone–cellulose acetate blend membranes have also been prepared and used to separate copper from feed with 1000–3000 ppm concentration [14].

Cellulose acetate was also blended with polyurethane, and the blend membranes were applied for rejection of Cu(II), Ni(II), Zn(II)

and Cd(II) using polyethyleneimine as a ligand [15]. Cellulose acetate has also been blended with polysulfone and applied for the separation of chromium using polyvinylalcohol (PVA) as the macromolecular chelating agent [16].

The present study is one in a series of investigations into the preparation of cellulose acetate/polyetherimide (CA/PEI) blend ultrafiltration membranes and their characterization and applications. The objective of the present work is to examine the effect of polymer blend composition of cellulose acetate and polyetherimide and the concentration of polymeric additive, PEG 600, on the rejection and permeate flux of proteins, such as bovine serum albumin, egg albumin, pepsin and trypsin and toxic heavy metal ions such as Cu(II), Ni(II), Zn(II) and Cd(II) from aqueous streams.

EXPERIMENTAL

Materials

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Commercial grade cellulose acetate was procured from Mysore Acetate and Chemical Co. Ltd. (Mysore, India). CA was recrystallized from acetone and then dried in a vacuum oven at 70°C for 24 h prior to use. Polyetherimide (Ultem® 1000) was supplied by GE Plastics, India as a gift sample. It was dried at 150°C for 4 h before use. Polyethyleneimine (weight-average molecular weight (Mw) = 600,000–1,000,000) 50% aqueous solution was procured from Fluka Chemie AG (France) and was used as a 1 wt.% aqueous solution. N-methyl-2-pyrrolidone (NMP), acetone and sodium lauryl sulphate (SLS) of analar grades from SD Fine Chemicals (India) were used as such without further purification. Anhydrous sodium monobasic phosphate and sodium dibasic phosphate heptahydrate were procured from CDH Chemicals, Ltd. (Mumbai, India), and used for the preparation of phosphate buffer solutions in the protein analysis. Proteins, namely bovine serum albumin (BSA) (69 kDa), from Himedia Laboratories, India; egg albumin (EA) (45 kDa), from CSIR Biochemical Centre India; pepsin (35 kDa) and trypsin (20 kDa) from SRL Chemicals Limited, India were used as received. Copper (II) sulfate (AR), nickel (II) sulfate (analytical reagent grade), zinc (II) sulphate (AR) and polyethylene glycol 600 were procured from Merck (I), Ltd. (Mumbai, India) and used as such for the preparation of aqueous metal ion solutions. Cadmium (II) chloride (AR) was procured from Qualigens Fine Chemicals Ltd., India and used as such. Deionized and distilled water was employed for the ultrafiltration experiments and for the preparation of the gelation bath.

TABLE 1 Compositions and Casting Conditions of Cellulose Acetate-Polyetherimide Blend Membranes

Blend Composition (wt.%)			
Cellulose acetate (%)	Polyetherimide (%)	PEG 600 (wt.%)	Solvent, NMP (wt.%)
100	0	0	82.5
95	5	0	82.5
85	15	0	82.5
75	25	0	82.5
100	0	2.5	80.0
95	5	2.5	80.0
85	15	2.5	80.0
75	25	2.5	80.0
100	0	5.0	77.5
95	5	5.0	77.5
85	15	5.0	77.5
75	25	5.0	77.5
100	0	7.5	75.0
95	5	7.5	75.0
85	15	7.5	75.0
75	25	7.5	75.0
100	0	10.0	72.5
95	5	10.0	72.5
85	15	10.0	72.5
75	25	10.0	72.5

Note: total polymer concentration at 17.5 wt.%
Casting solution temperature = 42 ± 2°C; Casting temperature = 25 ± 1°C;
Casting relative humidity = 50 ± 2%; Solvent evaporation time = 30 sec.

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Preparation of Solution Blending of Polymers

The blend solutions based on cellulose acetate and polyetherimide polymers (total polymer concentration = 17.5 wt.%) were prepared by dissolving the two polymers with different compositions (Table I) in the presence on absence of additive PEG 600, in a solvent (NMP) under constant mechanical stirring at a moderate speed of rotation in a round-bottomed flask for 4 h at 40°C. The homogeneous solution that was obtained was allowed to stand at room temperature for at least 1 day in an airtight condition to get rid of air bubbles.

Membrane Preparation

The method of preparation involved is the same as that of the "phase inversion" method employed in earlier works as reported by other researchers [17]. The casting environment (relative humidity and

temperature) was standardized for the preparation of membranes with better physical properties such as the homogeneity, thickness, and smoothness. The membrane-casting chamber was maintained at a temperature of 24 ± 1°C and a relative humidity of 50 ± 2%. The total polymer concentration was maintained at 17.5 wt.% in order to have a balanced casting solution viscosity to yield membranes between a spongy type and a high macrovoidal type. The casting and gelation conditions were maintained constant throughout, because the thermodynamic conditions would largely affect the morphology and performance of the resulting membranes [18].

Prior to casting, a 2L gelation bath, consisting of 2.5% (v/v) NMP solvent (to reduce the rate of liquid–liquid demixing and macrovoids) and 0.2 wt.% surfactant, SLS (to reduce surface tension at the polymer–nonsolvent interface) in distilled water (nonsolvent), was prepared and kept at 20 ± 1°C. The membranes were cast over a glass plate using a doctor blade. After casting, the solvent present in the cast film was allowed to evaporate for 30 sec, and the cast film along with the glass plate was gently immersed in the gelation bath. After 1–2 h of gelation, the membranes were removed from the gelation bath and washed thoroughly with distilled water to remove all NMP and surfactant from the membranes. The membrane sheets were subsequently stored in distilled water, containing 0.1% formalin solution to prevent microbial growth. The thickness of the cast membrane was measured using a micrometer (Mityutoyo, Japan). The thickness of the membrane used in this study was 0.22 ± 0.02 mm.

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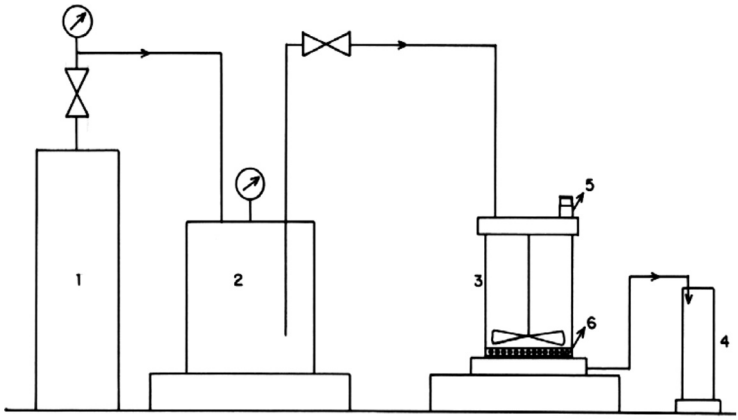
Rejection Studies

The ultrafiltration experiments were carried out using pure CA membranes and cellulose acetate/polyetherimide (CA/PEI) blend membranes at compositions of 95/5, 85/15 and 75/25% at various additive concentrations. The rejection and flux experiments were carried out in a 400 ml batch type stirred cell (Ultrafiltration cell-S76-400-Model, Spectrum, USA) fitted with a Teflon-coated magnetic paddle (as shown in Figure 1). The effective membrane area available for ultrafiltration was 38.5 cm^2. The solution filled in the cell was stirred at 300 rpm using a magnetic stirrer. All the experiments were carried out at 30 ± 2°C and 345 kPa transmembrane pressure.

Protein Rejection

Proteins such as BSA, EA, pepsin, and trypsin, were dissolved in a 0.1 wt.% phosphate buffer (0.5 M, pH 7.2) solution and used as standard feed solutions for the analysis of the proteins. For all the



(1) compressor; (2) feed tank; (3) UF cell; (4) permeate collector;

(5) pressure relief valve; (6) membrane.

FIGURE 1 Schematic diagram of ultrafiltration test kit.

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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:

$$\% \; SR = \left[1 - \frac{C_p}{C_f}\right] \times 100$$

where C_p and C_f are the concentrations of permeate and feed solutions, respectively.

Metal Ion Rejection

To find the influence of polyethyleneimine on metal ion rejection, preliminary experiments were carried out to separate metal salt solutions in the absence of polyethyleneimine using the pure CA membrane. Hence, in this study, polyethyleneimine was used to create complex metal ions. Aqueous solutions of Cu(II), Ni(II), Zn(II) and Cd(II) were

prepared at concentrations of 1000 ppm in a 1 wt.% solution of polyethyleneimine in deionized water. The pH of these aqueous solutions was adjusted to 6.25. Solutions containing polyethyleneimine and individual metal ions were thoroughly mixed and left standing for 5 days to complete binding [19,20]. These solutions were then used for the rejection studies using CA, CA/PEI and CA/PEI/PEG 600 blend membranes. The metal ion solutions were filled in the UF kit at a transmembrane pressure of 345 kPa. The permeate solutions of corresponding membranes were collected in graduated tubes and analyzed for the concentration of the metal ions using an atomic absorption spectrophotometer (Perkin-Elmer 3110). The percentage rejections of metal ions were calculated from the concentration of metal ions in feed and permeate using the same formula as that for protein rejection.

RESULTS AND DISCUSSION

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The rejection of macromolecular solutes such as BSA (69 kDa), EA (45 kDa), pepsin (35 kDa), and trypsin (20 kDa) were attempted individually using pure CA membranes and 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 applied directly for ionic level rejections because of the larger pore sizes of the membranes, which were not suitable for rejecting ions. Hence, to enhance the rejection of metal ions, a water-soluble chelating polymer, polyethyleneimine, was used for the complexation of the metal ions Cu(II), Ni(II), Zn(II) and Cd(II) and were subsequently rejected individually from aqueous streams by pure CA, CA/PEI and CA/PEI/PEG 600 blend ultrafiltration membranes.

Protein Rejection Studies

The CA/PEI 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, 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 rejections of proteins were performed in the order trypsin, pepsin, EA, and BSA.

Role of Polymer Blend Composition

The composition of the polymer-blend membrane had the effect of altering the protein rejection efficiency. The pure CA membrane exhibited rejections of 95% for BSA and 81% for trypsin. The higher rejection of BSA may have been due to the larger size of the BSA compared with trypsin. As the PEI composition was increased from 5 to 25% in the CA/PEI blend in the absence of any additive, the percentage rejection decreased, as shown in Table 2. This may have been because the higher PEI contents created inhomogeneity between the polymer matrices, resulting in the formation of aggregate pores in the membranes. Similar results were also observed for CA/sulfonated onated polysulfone (SPS) blend membranes by Malaisamy and Mohan [21]. For the 95/5% blend composition, the percentage rejection values were, 94, 86, 75 and 70% for BSA, EA, pepsin, and trypsin, respectively. The decrease in rejection may be related to the decrease in the solute size of the proteins in the aforementioned order.

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Role of Additive Concentration

The effects of the additive (PEG 600) concentration on the rejection of the blend membranes are shown in Table 2. The additive

TABLE 2 Percentage Rejection of Proteins by CA/PEI Blend Membranes

Polymer blend composition		Additive concentration of PEG 600 (wt.%)	Percentage rejection			
CA (%)	PEI (%)		BSA	EA	Pepsin	Trypsin
100	0	0	95	90	84	81
95	5	0	94	86	75	70
85	15	0	90	82	72	67
75	25	0	86	76	70	63
100	0	2.5	90	85	78	72
95	5	2.5	88	79	73	68
85	15	2.5	87	76	68	64
75	25	2.5	83	72	65	61
100	0	5.0	86	80	72	68
95	5	5.0	84	74	67	65
85	15	5.0	80	72	65	60
75	25	5.0	79	70	62	57
100	0	7.5	81	74	68	65
95	5	7.5	80	71	63	61
85	15	7.5	76	69	59	54
75	25	7.5	74	66	55	52
100	0	10.0	75	69	62	60
95	5	10.0	73	68	57	52
85	15	10.0	72	65	52	48
75	25	10.0	69	59	49	44

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 90%, and it decreased to 75% 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. [22]. In the CA/PEI blend membranes also, for a given polymer composition, when 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.

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Protein Permeate Flux Studies

The protein permeate flux values for the CA and CA/PEI blend membranes both in the absence and in the presence of additive were measured, and the results are discussed.

Role of Polymer Blend Composition

The permeate flux of the proteins BSA, EA, pepsin, and trypsin by the 100/0, 95/5, 85/15, and 75/25% CA/PEI blend membranes in the absence and presence of additive is shown in Figures 2–5. The pure

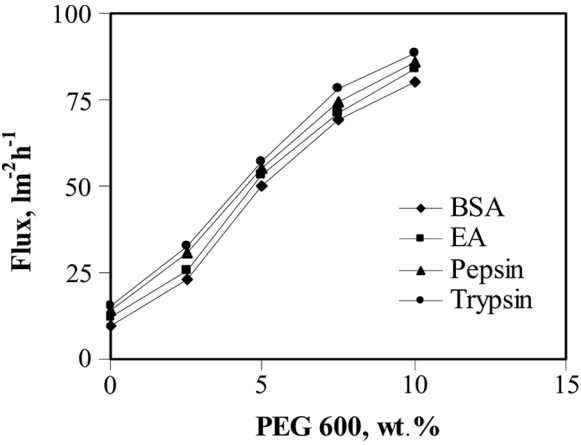

FIGURE 2 Effect of the PEG 600 concentration on the flux of proteins for the 100% CA membranes.

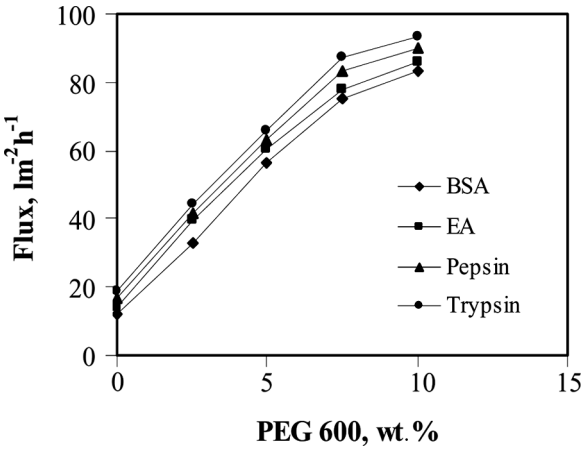

FIGURE 3 Effect of the PEG 600 concentration on the flux of proteins for the 95/5% CA/PEI blend membranes.

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100% CA membrane, in the absence of additive, showed the lowest permeate flux of 9.5 $lm^{-2}h^{-1}$ for BSA. The other proteins, EA, pepsin, and trypsin, showed comparatively higher fluxes with the pure CA membranes. For the CA/PEI blend membranes, without additive, for a given protein molecule (e.g., BSA), when the PEI content in the blend was increased, from 5 to 25%, the flux also increased from

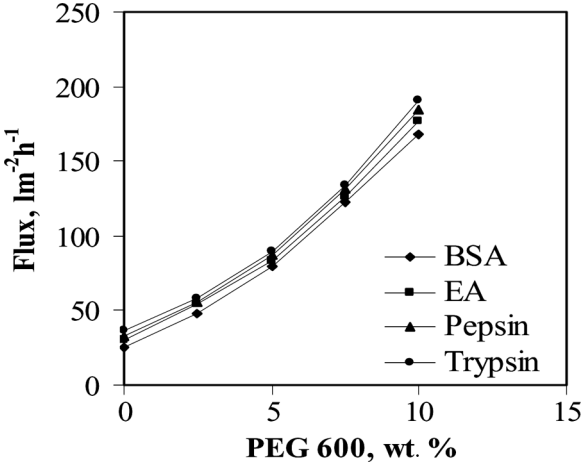

FIGURE 4 Effect of the PEG 600 concentration on the flux of proteins for the 85/15% CA/PEI blend membranes.

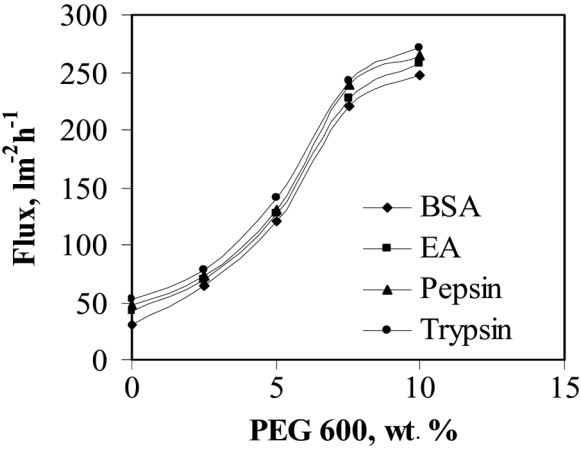

FIGURE 5 Effect of the PEG 600 concentration on the flux of proteins for the 75/25% CA/PEI blend membranes.

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12.3 to 30.6 $lm^{-2}h^{-1}$. A similar trend was observed for all of the proteins. This trend may have been due to the immiscible phase behavior of blend which predominates due to low molecular attractive forces between the blend components [23]. This in turn increases the void volume of membranes, which consequently increases the flux of membranes with higher PEI content.

Role of Additive Concentration

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 2. In the 100% CA membrane, BSA had a flux of 22.9 $lm^{-2}h^{-1}$ for 2.5 wt.% PEG 600 and 80.0 $lm^{-2}h^{-1}$ for 10 wt.% PEG 600. The other proteins also exhibited a similar trend. For the 95/5% CA/PEI blend membrane, the increase of additive from 2.5 to 10 wt.% increased the protein permeate flux from 33.1 to 83.2 $lm^{-2}h^{-1}$ for BSA, as shown in Figure 3. 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 4 and 5. 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 consistency of the results throughout the study.

Role of Polymer Blend Composition

The rejection of metal ions, with CA/PEI blend membranes in the absence of additive, was carried out individually after the complexation of the metal ions with the polymeric water-soluble ligand polyethyleneimine, and the results of the rejection studies are given in Table 3. The pure CA membrane exhibited 98.5% rejection for Cu(II) ions, which was higher than that of the CA/PEI blend membranes. This may have been due to the smaller pore size of the pure CA membranes. The other metal ions, Ni(II), Zn(II) and Cd(II), had rejections of 95.8, 93.4 and 90.6%, and the decrease in the rejection

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TABLE 3 Percentage Separation of Metal Chelates by CA/PEI Blend Membranes

Polymer blend composition		Additive concentration of PEG 600 (wt.%)	Percentage rejection			
CA (%)	PEI (%)		Cu(II)	Ni(II)	Zn(II)	Cd(II)
100	0	0	98.5	95.8	93.4	90.6
85	15	0	95.6	93.1	90.5	87.4
75	25	0	81.7	78.1	75.4	71.9
100	0	2.5	96.1	92.5	88.1	85.9
85	15	2.5	88.8	86.7	84.7	80.7
75	25	2.5	77.0	73.8	70.0	68.0
100	0	5.0	94.1	90.0	86.1	83.2
85	15	5.0	85.1	82.8	79.0	75.2
75	25	5.0	72.7	69.5	66.5	62.3
100	0	7.5	91.8	87.7	83.9	80.2
85	15	7.5	80.1	78.8	74.7	72.5
75	25	7.5	68.1	65.0	59.2	57.6
100	0	10.0	88.6	84.4	80.3	78.3
85	15	10.0	76.9	75.2	70.0	66.4
75	25	10.0	64.5	60.2	55.8	53.1

of these metal ions may have been due to the size of the metal ion–polyethyleneimine complex. When the PEI 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 PEI 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 [21].

Role of Additive Concentration

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/PEI blend membrane, the percentage of rejection of metal ions decreased as the additive concentration increased. This may have been due to the formation of larger pores by the leaching out of additive from the membrane during gelation. A similar trend was also observed for the 75/25% CA/PEI membranes. All of the previous experiments showed that the binding capacity of Cu with polyethyleneimine was stronger than that of other metal ions in the order Cu(II) > Ni(II) > Zn(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 polyethyleneimine exhibited higher rejections than the pure metal ion solutions because of the complex formation with polyethyleneimine, on the basis of the John–Teller distortion effect [24].

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Metal Ion Permeate Flux Studies

The permeate flux studies of metal ions is essential to predicting the economics of the membrane separation process. The metal ion permeate fluxes, measured simultaneously during rejection with 100/0, 85/15, and 75/25% CA/PEI blend membranes in the absence and presence of the additive, are shown in Figures 6–8.

Role of Polymer Blend Composition

The metal permeate fluxes were measured simultaneously during the rejection experiments by the 100/0, 85/15, and 75/25% CA/PEI membranes in the presence and absence of the additive. The pure 100% CA membrane offered a lower flux value of $5.3\,lm^{-2}h^{-1}$ for Cu(II) and a higher value of $8.6\,lm^{-2}h^{-1}$ for Cd(II), as shown in Figure 6. When the PEI content was increased to 25%, the flux of Cu(II) increased to $47.6\,lm^{-2}h^{-1}$. The increase in flux with increasing PEI

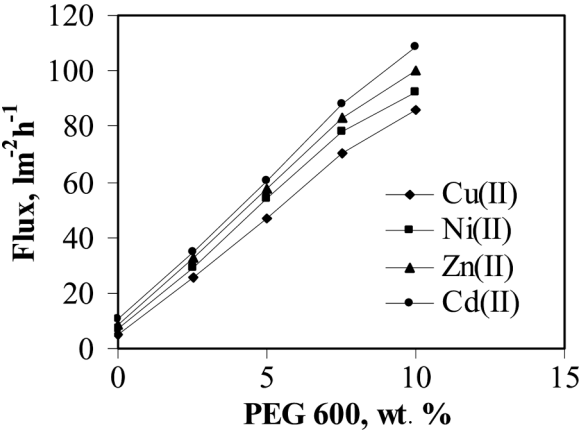

FIGURE 6 Effect of the PEG 600 concentration on the flux of metal chelates for the 100% CA membranes.

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content may be due to the larger pore size/segmental gap between the two polymers, i.e. CA/PEI.

Role of Additive Concentration

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 Table 3. The increase in flux with an

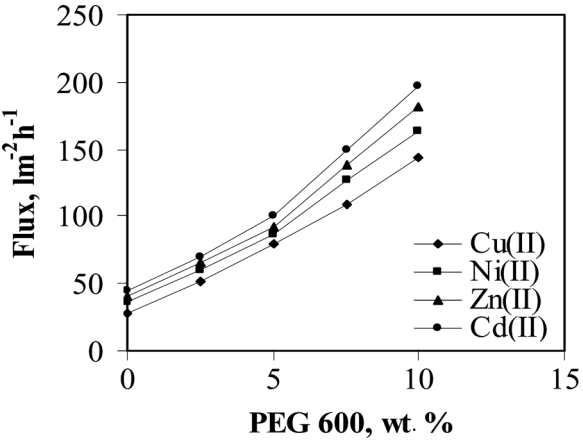

FIGURE 7 Effect of the PEG 600 concentration on the flux of metal chelates for the 85/15% CA/PEI blend membranes.

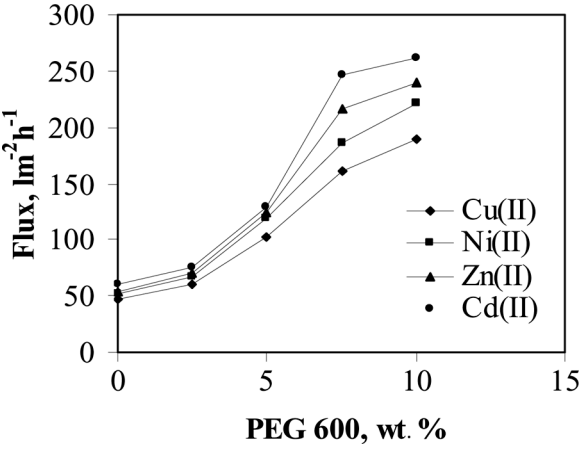

FIGURE 8 Effect of the PEG 600 concentration on the flux of metal chelates for the 75/25% CA/PEI blend membranes.

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increase in the additive concentration may have been due to the formation of bigger pores by the membranes. However, in the 85/15% CA/PEI membranes, as the additive concentration was increased from 2.5 to 10 wt.%, the flux was also increased significantly from 51.5 to 143.6 $lm^{-2}h^{-1}$ for Cu(II) ions, as shown in Figure 7. A similar trend was exhibited for the 75/25% blend composition and other metal ion fluxes, as shown in Figure 8, 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 was leached out during gelation, creating pores.

The order of flux for the metal chelates,

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

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

CONCLUSIONS

Cellulose acetate and polyetherimide-based novel ultrafiltration blend membranes with different compositions, in the absence and in the presence of the additive polyethylene glycol 600 were subjected to the rejection of macromolecular proteins such as BSA, EA, pepsin and trypsin. The polymer composition and additive concentration were found to have considerable impact on the rejection and permeate flux

values of the proteins. The toxic heavy metal ions such as Cu(II), Ni(II), Zn(II) and Cd(II) were also separated by complexing them with polymeric ligand polyethyleneimine. The extent of rejection of metal ions follows the order Cu(II) > Ni(II) > Zn(II) > Cd(II), which depends on the complexation ability to form macromolecules and ligand-field stability of individual metal ions. The rejection of both proteins and metal ions in the presence of the additive PEG 600 were lower and the flux higher for CA/PEI blend membranes compared to pure CA membranes. In general, the additive PEG 600 played a major role in the separation of macromolecular proteins and toxic heavy metal ions.

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