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Application Studies of Cellulose Acetate and Polymethylmethacrylate Blend Ultrafiltration Membranes

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The preparation of novel membranes based on cellulose acetate and polymethylmethacrylate blends in the absence and presence of the pore former by solution blending and ultrafiltration set up was carried out. The effect of compaction time on pure water flux at higher transmembrane pressure for various polymer compositions of the above blends both in the presence and absence of the pore former PEG 600 at different concentrations were reported for individual polymer blends. The pure water flux at 345 kPa, Molecular weight cut-off (MWCO). The application of the characterized CA/PMMA blend membranes for the separation of proteins such as Bovine Serum albumin, Egg Albumin, Pepsin, and Trypsin, and toxic heavy metals such as Cu(II), Ni(II), and Zn(II) using polyethyleneimine as complexing agent have been attempted and the results indicate the efficiency of the ultrafiltration blend membranes.

Keywords cellulose acetate; metal ion separation; polymethylmethacrylate; protein rejection; ultrafiltration polymeric blend membranes

INTRODUCTION

The development of membranes for separation processes is increasing linearly during the last decade. In recent years, a lot of modifications were carried out on various polymers like cellulose acetate, polysulfone, polymethylmethacrylate, polystyrene, polycarbonate, polyethersulfone etc., either by altering the physical and chemical structures of polymeric membranes or by blending of polymeric materials. The chemical nature, molecular structure, physical and mechanical properties, and the morphology of polymers affect the performance and selectivity of the resulting membrane. Materials for industrial separations have become an important research objective (1).

Cellulose acetate is universally recognized as the most important membrane polymer due to its availability in a wide variety of viscosity grades, low cost, good fouling resistance, etc. A lot of modification was carried out on cellulose acetate in recent years, which enabled its use in various industries. Due to excellent film-forming properties of cellulose acetate, polymer blends based on cellulose acetate were selected for the present investigation.

In the present investigation commercially available polymethylmethacrylate (PMMA) was blended with cellulose acetate. PMMA was chosen due to its good mechanical, thermal, and optical properties. PMMA is a glassy polymer and has a wide variety of industrial and biomedical applications as a membrane material. The influence of morphology on the transport properties of PMMA blend membranes was studied earlier (2,3). The water flux of PMMA membrane is too low for commercial purposes owing to its hydrophobic property.

Since cellulose acetate has some disadvantages like low oxidation and chemical resistance, poor mechanical strength and not suitable for aggressive cleaning, modification of cellulose acetate gains more importance (4). Polymer blends are used in increasing areas of application because they are cost effective and have the potential for the design of materials with properties tailored to specific use (5). Blending of polymer not only modifies the properties of the membrane made from a single polymer but also increases the flux of the membranes (6).

Synthesis of a polymer blend membrane is motivated by the necessity to superimpose requisite properties upon the basic transport properties of the base polymer. Thus, the hydrophilic-hydrophobic balance as well as properties of a membrane system can be easily altered if the membrane is prepared from multi-component polymer blends (7). The dense and asymmetric alloy membrane with the dense skin may be produced from a homogenous blend of different polymer. Hence, cellulose acetate was blended with polymethylmethacrylate using N,N-dimethyl formamide as the solvent.

The blend membranes prepared using cellulose acetate – polymethylmethacrylate was characterized by compaction,

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Pure water flux (PWF), membrane hydraulic resistance (R_m), water content, and molecular weight cut-off (MWCO) studies. The characterized ultrafiltration blend membranes were subjected to the rejection of macromolecular and scientifically and technologically important proteins viz., Bovine Serum Albumin (BSA), Egg albumin (EA), Pepsin, and Trpsin.

Further, the study was also engaged in the application of these membranes for the removal of toxic and environmentally harmful metal ions such as Cu^{2+}, Ni^{2+}, and Zn^{2+} by complexing them with macromolecular complexing agent, polyethyleneimine (PEI), as it forms a complex with divalent ions due to a stronger tendency of branched structure (8,9) and amino groups, PEI was preferred to other complexing agents such as polyacrylic acid, polyvinyl alcohol, etc.

The objective of the investigation centered on the preparation of membranes with high rejection and high flux. Further, to improve the performance of blend membranes, a compatible and water–soluble additive was chosen. After preparing membranes by optimizing compatible blend ratio and additive concentration in casting solution, emphasis was made on the application along with characterization and determination of morphology and structure of membranes. Since the product rate and rejection of the solute molecule depend not only on the dimension of the solute but also on the shape and its flexibility, it became indispensable to determine the pore size by SEM. Molecular weight cut off measurements can be carried out using different types of solutes of different molecular weight such as polyethylene glycol (a linear polymer), dextran (a branched polymer), and proteins (globular molecules). Proteins such as trypsin (20 kDa), pepsin (35 kDa), egg albumin (45 kDa), and bovine serum albumin (69 kDa) were chosen for the present study at dilute concentration.

EXPERIMENTAL METHODOLOGY

Materials

Commercial grade MYCEL Cellulose diacetate CDA 5770 (Acetyl content 39.99%) from Mysore Acetate and Chemicals Co. Ltd., India was used after recrystallization from acetone. Commercial grade polymethylmethacrylate as a gift sample by Amoco Polymers Inc., USA, and N,N dimethylformamide (DMF) (analar grade), Sodium lauryl sulfate (SLS) were procured from SISCO Research laboratories Pvt. Ltd., India and used as solvent, surfactants respectively. DMF was sieved through molecular sieves (Type-4A°) to remove moisture and stored in dried conditions prior to use. Proteins viz, Bovine Serum Albumin (BSA); $\overline{M_W} = 69$ kDa, Pepsin; $\overline{M_W} = 35$ kDa, Trypsin; $\overline{M_W} = 20$ kDa were purchased from SRL chemicals. Egg Albumin $\overline{M_W} = 45$ kDa was obtained from CSIR Bio-Chemical Centre, New Delhi, India.

PREPARATION OF BLEND MEMBRANES

The casting solutions (17.5 wt%) were prepared by blending of CA/PMMA polymers in presence of the pore former, PEG 600 at different concentrations in DMF (Table 1). The polymers were blended 40 ± 5°C under constant stirring for about 4–5 h. The blend solutions were kept for 2 h to remove the air bubbles and then used for membrane casting.

Membrane Preparation

The preparation method involved is the same as that of the "Phase inversion" method employed in earlier works reported by other researchers (10). Membranes were cast on a glass plate using "Doctors" blade to which oil sheets

TABLE 1
Composition and casting conditions of Table 3. Pure water flux of cellulose acetate/polymethylmethacrylate

Blend composition (wt%)		Additive wt%	Solvent wt%
CA	PMMA	PEG 600	DMF
100	0	0	82.5
95	5	0	82.5
90	10	0	82.5
85	15	0	82.5
80	20	0	82.5
75	25	0	82.5
100	0	2.5	80.0
95	5	2.5	80.0
90	10	2.5	80.0
85	15	2.5	80.0
80	20	2.5	80.0
75	25	2.5	80.0
100	0	5.0	77.5
95	5	5.0	77.5
90	10	5.0	77.5
85	15	5.0	77.5
80	20	5.0	77.5
75	25	5.0	77.5
100	0	7.5	75.0
95	5	7.5	75.0
90	10	7.5	75.0
85	15	7.5	75.0
80	20	7.5	75.0
75	25	7.5	75.0
100	0	10.0	72.5
95	5	10.0	72.5
90	10	10.0	72.5
85	15	10.0	72.5
80	20	10.0	72.5
75	25	10.0	72.5

Note. Total polymer concentration at 17.5 wt%.

were attached to obtain the desired thickness. After 30 seconds of evaporation the glass plate with the blend solution film was immersed into the gelation bath containing non-solvent, surfactant and solvent whose temperature was maintained at $22 \pm 2^{\circ}C$. After 30 minutes of gelation, the membranes were taken out, washed with distilled water, and stored in 0.1% formalin solution in distilled water to prevent microbial attack.

Experimental Set up

The UF experiments were carried out in a batch type, dead end cell (UF AMICON kit, capacity 350 ml, USA) filled with a Teflon coated magnetic paddle. The cell was connected to a compressor with pressure valve and gauge through a feed reservoir.

CHARACTERIZATION OF BLEND MEMBRANES

The thickness of the membranes maintained in the present studies was 0.26 ± 0.02-mm. The prepared membranes cut into the desired size needed for fixing it up in the UF cell. The feed is employed with agitation under pressure to minimize concentration polarization effect. The membranes were initially pressurized with distilled water at 414 kPa as trans membrane pressure (TMP) for 4–5 h using UF kit. The initial water flux was taken about 10 min after the pressurization in the test cell at 414 kPa. The water flux was measured every 1 h and the flux in later hours decrease and then leveled off after 4−5 h. These pre-pressurized membranes were subsequently characterized and utilized for further studies.

Compaction

The compaction of fresh membranes was carried out by loading the thoroughly washed membrane in the UF test cell connected to the pressure reservoir with distilled water. The water flux was measured at every 1 h and it was found that there was a sharp decline in flux, which attains steady state after 5 h. These membranes were then used in subsequent UF experiments at 345 kPa (11) (Table 3).

Pure Water Flux (PWF)

Membranes after compaction were subjected to pure water flux at various trans membrane pressure of 69, 138, 207, 276, 345 kPa. The permeability was measured under steady state flow. The pure water flux is determined as follows: (12)

$$J_W = \frac{Q}{A(\Delta T)}$$

where Q is the quantity of permeate collected (in liters)

J_W is the water flux (in $lm^{-2}h^{-1}$)
ΔT is the sampling time (in h)
A is the membrane area (in m^2)

PROTEIN REJECTION

All the protein solutions were prepared separately at 0.1 wt% concentration in phosphate buffer medium of 7.2 pH and trans membrane pressure (TMP) was maintained at 345 kPa in nitrogen atm. Proteins such as Trypsin (20 kDa), Pepsin (35 kDa), Egg Albumin (45 kDa), and Bovine serum Albumin (69 kDa) were dissolved in 0.1 wt% in phosphate buffer (0.5 M, pH 7.2) and used as standard solutions. For all experiments, concentration of the feed solutions was kept constant. The permeate was collected over measured time intervals and the concentration of the proteins in the permeate were estimated by UV–Vis spectrophotometer at $\lambda_{max} = 280$ nm. The percentage solute rejection (% SR) was calculated as follows:

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

where, % SR is the percent solute rejection, C_p and C_f are the concentration of the permeate and feed solutions respectively.

Application Studies

The characterized CA membranes were used for cadmium ion rejection studies at 345 kPa. Aqueous solution

TABLE 2
Molecular weight cut-off of cellulose acetate/ polymethylmethacrylate blend membranes

Blend composition (%)			
CA	PMMA	Solvent wt%	MWCO
100	0	82.5	20
95	5	82.5	35
85	15	82.5	45
75	25	82.5	69
100	0	80.0	45
95	5	80.0	45
85	15	80.0	69
75	25	80.0	>69
100	0	77.5	45
95	5	77.5	69
85	15	77.5	>69
75	25	77.5	>69
100	0	75.0	69
95	5	75.0	69
85	15	75.0	>69
75	25	75.0	>69
100	0	72.5	69
95	5	72.5	>69
85	15	72.5	>69
75	25	72.5	>69

Note: Total polymer concentration at 17.5 wt%.

TABLE 3
Effect of compaction on pure water flux of CA/PMMA blend membranes

Blend composition (%) (17.5 wt%)		PEG	Pure water flux ($lm^{-2}h^{-1}$)					
			Time, h					
CA	PMMA	600 wt%	0	1	2	3	4	5
100	0	0	26.3	22.3	19.5	17.2	16.0	16.0
95	5	0	43.6	38.9	31.1	28.0	23.3	23.3
90	10	0	62.3	49.8	43.6	38.9	31.1	31.1
85	15	0	85.7	71.6	59.2	46.7	40.5	40.5
80	20	0	112.2	102.8	90.3	70.1	59.2	59.2
75	25	0	124.7	118.4	105.9	93.1	81.0	81.0
100	0	2.5	65.2	52.3	48.3	36.4	30.7	30.7
95	5	2.5	78.5	66.7	54.4	48.2	36.0	36.0
90	10	2.5	89.4	74.5	63.2	55.1	45.7	45.7
85	15	2.5	102.2	92.8	65.4	59.2	52.6	52.6
80	20	2.5	128.3	111.3	101.0	90.1	70.2	70.2
75	25	2.5	168.4	128.4	116.6	102.6	82.3	82.3
100	0	5.0	72.2	68.2	57.3	45.6	40.2	40.2
95	5	5.0	83.2	72.1	63.6	54.2	49.7	49.7
90	10	5.0	92.3	85.2	74.5	69.8	60.2	60.2
85	15	5.0	123.2	111.1	90.1	82.3	75.2	75.2
80	20	5.0	147.7	136.9	127.2	115.8	104.6	104.6
75	25	5.0	188.0	169.2	148.2	130.6	122.9	122.9
100	0	7.5	98.1	80.1	72.1	68.4	60.4	60.4
95	5	7.5	122.3	101.4	92.3	80.3	72.3	72.3
90	10	7.5	163.5	142.2	123.2	103.4	90.1	90.1
85	15	7.5	184.4	163.2	146.5	125.4	105.3	105.3
80	20	7.5	210.3	188.0	169.2	139.3	112.6	112.6
75	25	7.5	246.1	220.1	201.0	189.4	153.2	153.2
100	0	10.0	132.3	122.4	114.2	96.3	82.1	82.1
95	5	10.0	182.4	153.7	140.8	122.1	108.6	108.6
90	10	10.0	221.6	184.4	161.5	140.8	120.7	120.7
85	15	10.0	264.1	242.0	200.2	172.8	143.1	143.1
80	20	10.0	320.1	300.1	260.5	232.6	184.1	184.1
75	25	10.0	421.4	380.1	330.1	293.7	254.0	254.0

TABLE 4
Pure water flux of CA/PMMA blend membranes

Blend composition (%) (17.5 wt%)		Pure water flux at 345 kPa ($lm^{-2}h^{-1}$)				
		PEG 600 concentration, wt%				
CA	PMMA	0	2.5	5.0	7.5	10.0
100	0	13.7	23.5	28.2	42.3	64.5
95	5	19.2	26.2	37.1	56.3	85.7
90	10	26.4	35.3	46.1	67.6	96.1
85	15	37.4	47.2	62.3	86.1	121.4
80	20	43.6	53.8	88.1	95.6	143.1
75	25	60.6	72.6	94.6	126.5	174.3

of cadmium ion has been prepared with 1000 ppm of PEI complex in distilled water. For all the experiments, the concentration of the feed solution was maintained as constant. The pH of these aqueous solutions was adjusted to 6 ± 0.25 by adding a small amount of either 0.1 M HCl or 0.1 M NaOH. Solutions containing PEI and individual cadmium ions were thoroughly mixed and left standing for 5 days to complete binding (13). After mounting the membrane in the UF cell, the chamber was filled with a known volume of copper solution and immediately pressurized to the desired level (345 kPa) and maintained constant throughout the run. The permeate was collected under stirred (200 rpm) UF cell over measured time intervals in graduated tubes and the test contents were analyzed for copper content by UV-Visible Spectroscopy (Hitachi, model U-2000) at $\lambda_{max} = 620$ nm (14). The percentage Copper/Polyethyleneimine (Cu/PEI) complex rejection (% R) was calculated from the concentration of feed and permeates using the following relation. The same procedure was repeated for nickel and zinc solutions and the percent rejection was calculated.

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

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

RESULTS AND DISCUSSION

The use of PMMA for aqueous phase is restricted due to its hydrophobic nature. Hence, in order to apply PMMA membranes for aqueous based rejection, hydrophilicity of PMMA was improved by blending PMMA with cellulose acetate (15). The prepared membranes were characterized in terms of pure water flux (PWF) (Table 4), hydraulic resistance (R_m), water content, molecular weight cut off (MWCO) (Table 2) were studied. The characterized membranes were then subjected to rejection of proteins and heavy metal ions as discussed below.

Protein Rejection Studies

The blend membranes prepared in the present investigation were subjected to the rejection of macromolecular and industrially important solute proteins. In order to determine the efficiencies of blend membranes based on CA and PMMA for protein rejections an attempt on rejection of various proteins by ultrafiltration was made. The UF experiments with individual solutions of different proteins viz., Bovine Serum Albumin (BSA), Egg Albumin (EA), Pepsin, and Trypsin were carried out using blend membranes of CA and CA/PMMA of 100/0 wt%, 85/15 wt% and 75/25 wt% composition in the absence and presence of various additive concentrations were subjected to protein separation.

TABLE 5
Percent rejection of proteins by CA/PMMA blend membranes

Blend composition (%) (17.5 wt%)			Percent rejection of proteins			
CA	PMMA	PEG 600 wt%	BSA 69 kDa	EA 45 kDa	Pepsin 35 kDa	Trypsin 20 kDa
100	0	0	95.5	93.1	89.4	85.2
95	5	0	93.1	91.2	82.5	77.4
85	15	0	88.4	85.3	76.3	72.8
75	25	0	82.2	75.2	69.5	65.8
100	0	2.5	92.3	85.6	74.3	65.4
95	5	2.5	88.7	80.2	70.2	62.8
85	15	2.5	82.0	72.3	62.3	57.3
75	25	2.5	75.0	66.2	56.3	54.6
100	0	5.0	86.3	80.2	70.7	62.4
95	5	5.0	83.4	76.2	68.5	60.1
85	15	5.0	75.3	69.3	60.1	55.3
75	25	5.0	70.1	62.3	57.3	50.1
100	0	7.5	84.2	76.1	68.4	60.5
95	5	7.5	80.1	70.2	62.3	57.4
85	15	7.5	70.2	65.4	58.3	50.2
75	25	7.5	60.2	55.2	52.4	45.1
100	0	10.0	80.1	74.2	65.4	57.3
95	5	10.0	76.4	68.3	57.3	52.3
85	15	10.0	68.4	60.2	53.6	48.7
75	25	10.0	58.6	50.1	47.2	44.1

All protein solutions (0.1 wt%) were prepared in phosphate buffer medium of 7.2 pH, since the permeation and rejection of proteins depend on the feed pH (16) and the transmembrane pressure was maintained at 345 kPa in nitrogen atmosphere. In order to determine the reference permeation fluxes, water and buffer fluxes were determined at the start of all UF experiments at 345 kPa transmembrane pressure.

Since the experiments with higher molecular weight solutes may cause fouling of membranes which would spoil the pores for the separation and comparison of low molecular weight proteins, the separation was performed in the order trypsin, pepsin, egg albumin, and bovine serum albumin and the permeate flux were also simultaneously measured.

Effect of Polymer Blend Composition and Additive Concentration

Cellulose acetate in the absence of additive when subjected to separation of BSA, EA, pepsin and trypsin offered a higher separation of 95.5%, 93.1%, 89.4%, and 85.2% respectively as shown in Table 5 and Fig. 1a.

For the CA/PMMA blend membranes in the absence of additive as the PMMA content was increased the separation decreased for all proteins. Thus for 85/15 wt% CA/PMMA blend membrane BSA exhibited a rejection of 88.4% and reduced to 82.2% for 75/25 wt% blend membrane. The other proteins also showed a similar trend.

The addition of the pore former PEG-600 in the casting solution of CA and CA/PMMA membranes showed considerable effect in the separation efficiency as shown in Figs. 1a–1c. In the pure CA membrane with 5.0 wt % additive BSA rejection was found to be 86.3% and it decreased to 80.1% on increasing the additive to 10 wt%. A similar trend was observed for other proteins. This may be due to the leaching out of additive PEG too, from the membrane during gelation creating pores proportionately on the membrane surface. The same trend was observed for all the blend membranes with various additive concentrations. Similarly, for a given additive concentration and for a given protein molecule when the PMMA content was increased to 25 wt% the rejection decreased as shown in Figs. 1a–c. However, the rejection of BSA for all the above membranes was higher than EA pepsin and typsin (17). These trends may be due to influence of formation of larger pore size and void spaces among the neighboring polymer aggregates resulting from the use of higher PMMA content (25 wt%) in the film casting process. This may be explained by the fact that lower molecular attractive forces between the blend components are responsible for the formation of larger void spaces.

Protein Solution Permeate Flux Studies

The protein solution permeate flux values of CA and CA/PMMA membranes both in the absence and presence of additive are shown in Table 6.

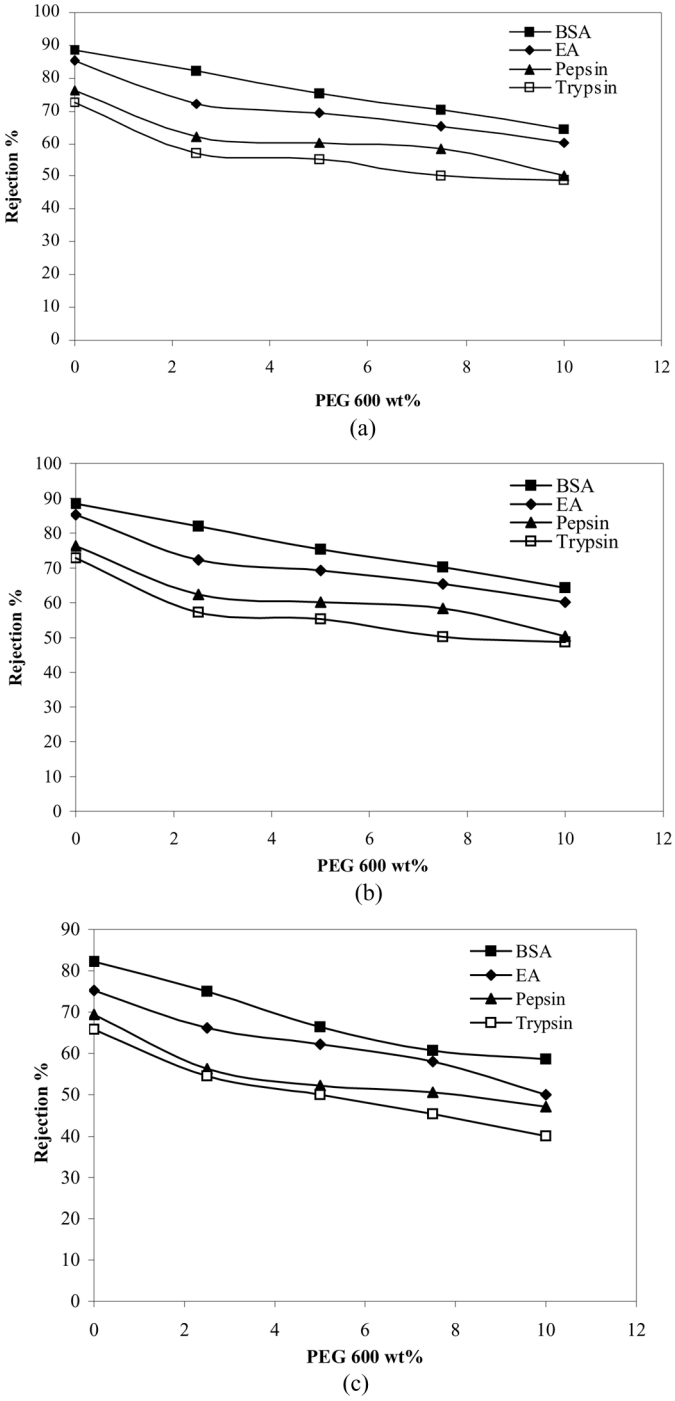


FIG. 1. Effect of PEG concentration on percent rejection of protein (a) 100/0 wt%; (b) 85/15 wt%; and (c) 75/25 wt%.

Role of Polymer Blend Composition and Additive Concentration

The permeate flux in the case of 100% CA membrane without the additive is shown in Fig. 2. BSA showed a low value of flux of 3.8 $lm^{-2}h^{-1}$ compared to other

TABLE 6
Protein permeate flux of CA/PMMA blend membranes

Blend composition (%) (17.5 wt%)			Permeate flux ($lm^{-2}h^{-1}$)			
CA	PMMA	PEG 600 wt%	BSA 69 kDa	EA 45 kDa	Pepsin 35 kDa	Trypsin 20 kDa
100	0	0	3.8	4.2	6.1	8.2
95	5	0	5.4	8.2	11.6	15.3
85	15	0	12.1	15.2	20.1	28.2
75	25	0	32.6	38.2	44.8	52.0
100	0	2.5	11.6	14.0	23.6	26.8
95	5	2.5	14.0	20.3	30.4	39.8
85	15	2.5	23.5	32.4	37.8	45.7
75	25	2.5	46.2	56.6	61.4	65.8
100	0	5.0	31.8	41.2	53.6	62.2
95	5	5.0	40.3	56.5	63.2	76.5
85	15	5.0	55.8	64.5	72.9	82.8
75	25	5.0	65.6	73.2	76.5	87.2
100	0	7.5	51.1	53.8	58.2	65.3
95	5	7.5	58.4	64.1	71.6	79.2
85	15	7.5	62.8	71.4	80.3	86.3
75	25	7.5	75.2	80.4	88.7	89.3
100	0	10.0	70.1	81.3	92.4	101.4
95	5	10.0	75.4	86.3	94.5	106.2
85	15	10.0	82.8	90.5	98.7	110.0
75	25	10.0	95.3	108.2	116.4	125.4

proteins. The value of the permeate flux for EA, Pepsin, and Trypsin are 4.2, 6.1, and 8.2 $lm^{-2}h^{-1}$ respectively. The flux in the case of trypsin is higher than pepsin, which in turn is higher than that of EA which is shown in the Fig. 2a. When the PMMA content was increased to 25 wt% without the additive in the CA/PMMA blend the flux value with respect to BSA increased to 32.6 $lm^{-2}h^{-1}$. Similar increases were observed for other proteins for all other blend compositions (Figs. 2a–2c). In all of the above studies, the value of the flux of trypsin was higher than pepsin which in turn was higher than ESA. The lowest flux in BSA may be due to both larger solute size (Einstein-stroke radius 37.1 mm) and higher molecular weight (69 kDa) (18).

The role of additive PEG 600 composition on the permeate flux is shown in Figs. 2a, 2b, and 2c. In 100% CA when the additive concentration was increased from 5 to 10 wt% the flux of a given protein molecular also increased. Thus BSA showed an increase of flux from 31.2 $lm^{-2}h^{-1}$ for 2.5 wt% to 70.1 $lm^{-2}h^{-1}$ for 10 wt % PEG 600. A similar trend was shown for other protein molecules.

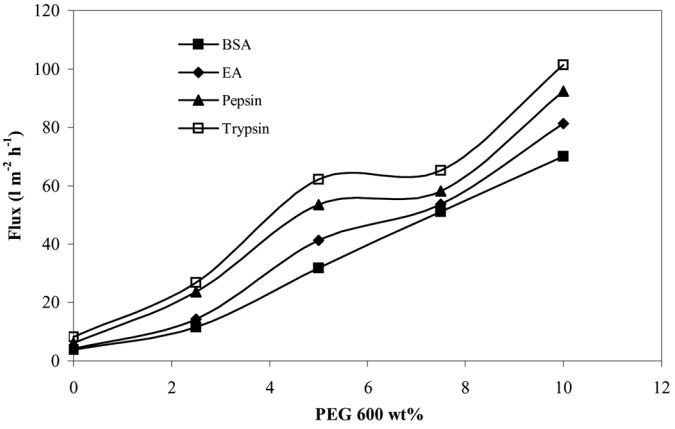
Metal Ion Rejection Studies

During recent years, water soluble polymeric ligands such as polyethyleneimine, polyvinylalcohol, polyacrylic acid, etc., are being employed successfully to remove traces of metal ions from industrial effluents by ultrafiltration technique.

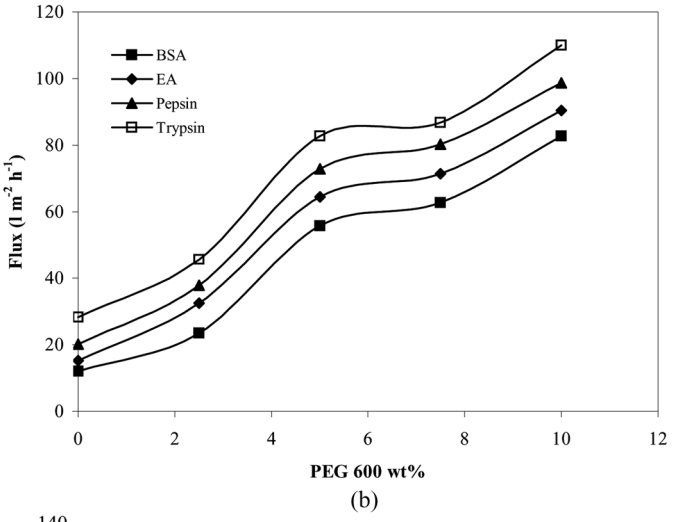
Effect of Polymer Blend Composition and Additive Concentration

In the present investigation the removal of Cu(II), Ni(II), and Zn(II) from aqueous streams containing one metal ion at a time, by complexing them with a particular concentration of polyethyleneimine through ultrafiltration using CA and CA/PMMA blend membranes were attempted. The aqueous feed solutions containing heavy metal ions such as Cu^{2+}, Ni^{2+}, and Zn^{2+} were prepared at a metal ion concentration of 1000 ppm and were complexed with 1 wt% polyethyleleimine solution. The amino group present in the PEI cannot be easily hydrolysed owing to the competitive reactions between OH ions and amino groupwith such metal ions (19). The decrease in rejection may be due to higher PMMA content, creating voids on the blend membranes. Copper exhibited higher separation due to stronger complex formation with the polymeric ligand, PEI.

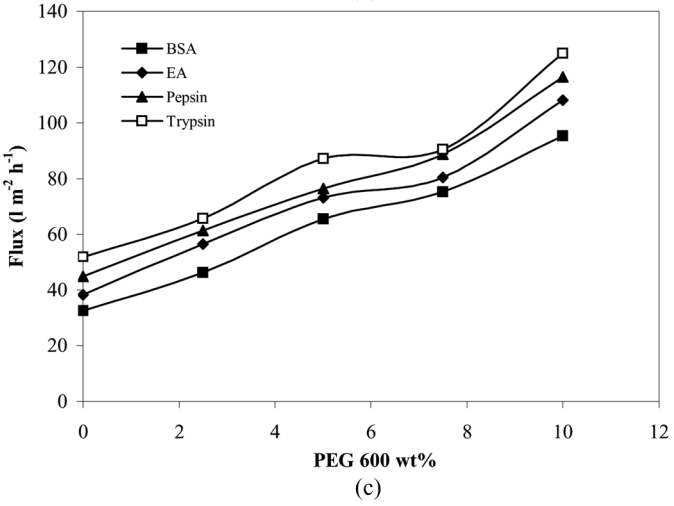
The addition of PEG 600 to pure CA and CA/PMMA blend membrane casting solution, the metal ion rejection behavior was altered as shown in Table 7. From Fig. 3a



(a)



(b)



(c)

FIG. 2. Effect of PEG concentration on protein permeate flux (a) 100/0 wt%; (b) 85/15 wt%; and (c) 75/25 wt%.

it is clear that pure CA membranes, exhibited a decrease in rejection behavior from 97.52% to 86.45% when the additive concentration was increased from 0 wt% 10 wt% for copper ions. The same trend was observed for the other ions Ni^{2+} and Zn^{2+}.

In the CA/PMMA blend membranes of 85/15 wt% for Cu^{2+} ions as the additive was increased, from 5 to 10 wt% the rejection decreased linearly from 80.17% to 75.48% as shown in Fig. 3b. All the blend membranes and all the metal ions studied in this investigation showed the same trend. The decrease in the rejection value on increase of additive concentration may be due to leaching out of the additive during gelation creating pores (20). It is evident from the Figs. 3a–c, that of the metal ions Cu^{2+}, Ni^{2+} and Zn^{2+}, Zn^{2+} showed the lowest rejection, while Cu^{2+} exhibited higher rejection. This is due to the formation of a stronger complex through stable and short bonds of Cu^{2+} with PEI due to the Jahn–Teller effect.

TABLE 7
Percent rejection of proteins by CA/PMMA blend membranes

Blend composition (%) (17.5 wt%)		PEG	Percent rejection		
CA	PMMA	600 wt%	Cu^{2+}	Ni^{2+}	Zn^{2+}
100	0	0	97.52	95.4	89.3
95	5	0	95.64	92.3	85.4
85	15	0	93.33	90.5	82.1
75	25	0	91.27	88. 6	80.4
100	0	2.5	96.24	93.25	86.62
95	5	2.5	90.16	88.17	83.07
85	15	2.5	86.34	82.38	80.61
75	25	2.5	84.72	80.47	78.2
100	0	5.0	94.18	90.15	80.2
95	5	5.0	82.36	80.24	75.16
85	15	5.0	80.17	78.03	73.24
75	25	5.0	78.25	76.82	70.15
100	0	7.5	90.28	86.4	80.7
95	5	7.5	81.46	79.18	76.43
85	15	7.5	78.64	76.24	72.7
75	25	7.5	75.46	73.14	68.14
100	0	10.0	86.45	80.19	75.4
95	5	10.0	79.26	75.26	70.21
85	15	10.0	75.48	73.18	65.16
75	25	10.0	72.16	66.15	61.28

Metal Ion Permeate Flux Studies

To specify the product rate and predict the economics of the membrane processes, it is essential to know the permeate flux of metal ions. The effect of PMMA composition and PEG 600 concentration on the permeate flux for all CA and CA/PMMA membranes are shown in Table 8 and Figs. 4a–c and the trends are discussed.

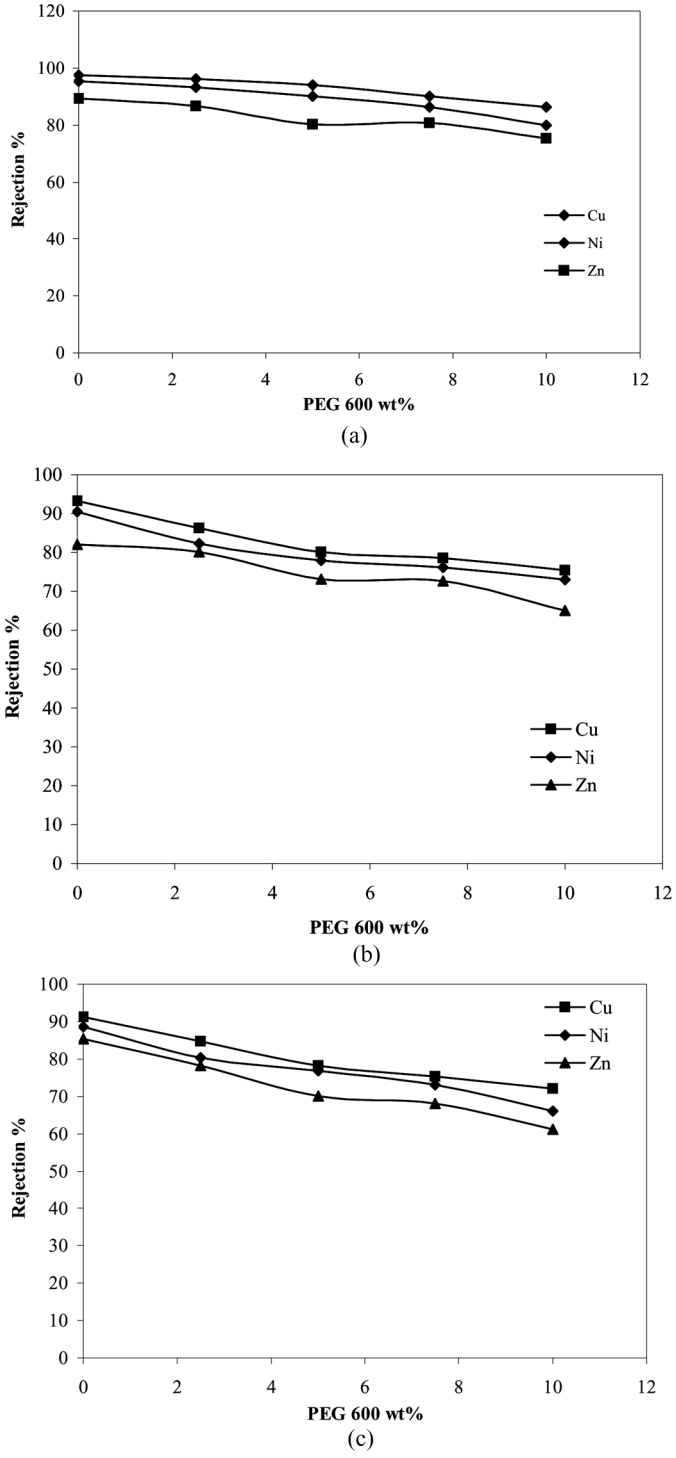


FIG. 3. Effect of PEG concentration on percent rejection of metal ion (a) 100/0 wt%; (b) 85/15 wt%; and (c) 75/25 wt%.

Effect of Polymer Blend Composition and Additive Concentration

The pure CA membrane in the absence of additive showed a permeate flux of 3.2 $lm^{-2}h^{-1}$ for Cu^{2+} ion. The other metal ions also showed a lower flux value than that exhibited by CA/PMMA blends as shown in Figs. 4a–c.

In CA/PMMA blend membranes as the PMMA content was increased from 0 to 25 wt% for Cu^{2+} ions the flux also increased from 3.2 lm^2h^{-1} to 8.2 lm^2h^{-1} in the absence of the additive. The similar trend for other metal ions was observed. This is due to the proper hydrophilic-hydrophobic balance of CA/PMMA blend membranes. The lowest flux of Cu^{2+} is due to the highest Cu–PEI complex stability and larger size compared to $Ni^{2+}$and Zn^{2+}. Zn^{2+} exhibited the highest flux for the above membranes due to its smaller size.

On addition of PEG 600 the permeate flux of pure CA membranes increased from 23.2 to 36.5 $lm^{-2}h^{-1}$ with an increase in PEG 600 concentration from 5 wt% to 10 wt% for Cu^{2+} ions. The same trend was shown by Ni^{2+} and Zn^{2+} ions. Similarly for 85/15 wt% and 75/25 wt% membranes the flux value increased linearly on increasing the concentration PEG 600 from 5 to 10 wt% as shown in Figs. 4b and 4c. A similar trend was observed for other blend compositions and other metal ions for various additive concentrations. It is seen from Figs. 4a–c, that Cu^{2+} showed a lower flux compared to other metal ions, which is due to strong and stable complex formation of Cu^{2+} with PEI due to the Jahn–Teller theorem (21).

TABLE 8
Metal permeate flux of CA/PMMA blend membranes

Blend composition (%) (17.5 wt%)		PEG	Permeate flux ($lm^{-2}h^{-1}$)		
CA	PMMA	600 wt%	Cu^{2+}	Ni^{2+}	Zn^{2+}
100	0	0	3.2	4.8	5.9
95	5	0	4.6	5.1	6.2
85	15	0	5.1	6.2	8.2
75	25	0	8.2	11.2	16.1
100	0	2.5	8.2	15.6	17.5
95	5	2.5	10.1	16.1	20.5
85	15	2.5	12.4	18.6	23.2
75	25	2.5	20.5	26.2	32.6
100	0	5.0	23.2	29.2	32.6
95	5	5.0	27.6	38.4	43.1
85	15	5.0	30.5	41.6	52.3
75	25	5.0	40.4	51.9	58.3
100	0	7.5	26.2	40.4	45.6
95	5	7.5	30.5	45.6	51.6
85	15	7.5	36.8	49.2	56.5
75	25	7.5	45.6	58.3	62.7
100	0	10.0	36.8	46.4	52.3
95	5	10.0	41.6	52.7	60.4
85	15	10.0	51.9	58.3	64.9
75	25	10.0	62.8	70.4	76.2

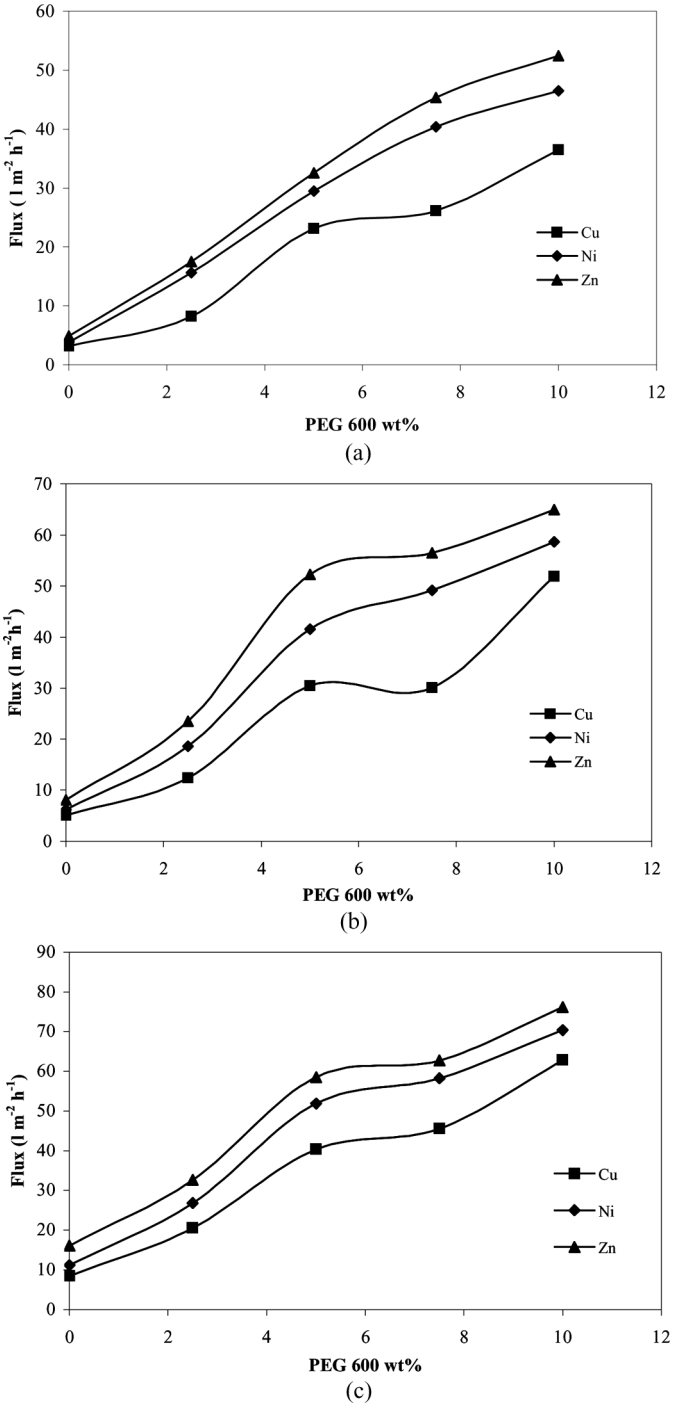


FIG. 4. Effect of PEG concentration on metal-chelate permeate flux (a) 100/0 wt%; (b) 85/15 wt%; and (c) 75/25 wt%.

CONCLUSION

Ultrafiltration membranes were prepared by the phase inversion technique from blend solutions of CA/PMMA with different polymer compositions i.e., 100/0, 95/5, 90/10, 85/15, 80/20, and 75/25 wt% using DMF as solvent. Increase in polymer compositions beyond 75/25 of CA/PMMA resulted in phase separation of the polymers and hence formation of membranes at these compositions was not possible. Compared to other additives, Polyethylene glycol (PEG 600) was found to be the suitable pore former at various concentration of 0, 2.5, 5.0 7.5, and 10.0 wt% in UF membranes and is effective in controlling the morphology of the membranes. Further, it also enhances the compatibility of blends in the casting solution.

The above blend membranes were compacted and characterized in terms of PWF, water content, MWCO and pore size. Further the hydraulic resistance of these membranes was studied at different transmembrane pressures.

MWCO of all the membranes were determined using dilute concentrations of proteins such as trypsin. Pepsin, egg albumin, and bovine serum albumin of molecular weights 20, 35, 45, and 69 kDa respectively. In CA/PMMA system MWCO was the lowest for 95/5 wt% and the maximum was found to be for 75/25 wt% in the absence of the pore former. The morphology of the membranes was investigated using SEM and the top surface of the membranes was studied in the presence and absence of the additive PEG 600.

The separation of proteins viz., BSA, EA, pepsin, and trypsin were carried out to investigate the applicability of these blend membranes for separation of proteins in aqueous solutions. The separation of BSA was found to be comparatively higher with reduced flux, in view of its higher molecular weight.

Further, the separations of metal ions such as Cu(II), Ni(II), and Zn(II) were carried out using PEI as complexing agent to enhance the ultrafiltration of ionic solutes. The percent rejection of Cu(II) ions were found to be higher compared to other metal ions, with comparatively lower flux due to the formation of stable complex formation with PEI and its bigger size. This paved the way to the emerging problem of pollution abatement by recycling chemicals.

In all the membranes, the composition of PMMA and the hydrophilic additive PEG 600 dictated the membrane characteristics, and the separation and product rate efficiencies.

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