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Preparation and Characterization of Cellulose Acetate/Aminated Polysulfone Blend Ultrafiltration Membranes and their Application Studies

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Preparation and Characterization of Cellulose Acetate/Aminated Polysulfone Blend Ultrafiltration Membranes and their Application Studies

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Abstract: Ultrafiltration membranes are largely being applied for heavy metal ion separations from aqueous streams. Cellulose acetate (CA) and aminated polysulfone (APSf) based membranes are prepared in the absence and presence of the polymeric additive, polyethylene glycol, PEG 600, in various compositions. The effects of polymer blend composition and additive concentration on compaction, pure water flux, membrane hydraulic resistance, water uptake, and contact angle has been investigated to evaluate the performance of the membranes and the results are discussed. Surface and cross-sectional morphologies of membranes were also analyzed using scanning electron microscopy. Toxic heavy metal ions such as Cu^{2+}, Ni^{2+}, Cd^{2+}, and Zn^{2+} were separated by the blend membranes using polyethyleneimine (PEI) as polymeric ligand. The rejection and permeate flux efficiencies of the blend membranes are compared with pure cellulose acetate membranes.

Keywords: Blend membranes, cellulose acetate, metal ion separation, PEG 600, polyethyleneimine, polysulfone, ultrafiltration

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INTRODUCTION

The preservation of water resources to prevent their pollution by toxic elements has become one of the most important challenges for the human race due to the exuberant growth of textile, leather, surface treatment, mining, motorcar, and chemical industries which generate toxic heavy metals are released into the environment. Heavy metals constitute a major portion of the contaminants in chemical effluents and they cannot be degraded or destroyed. Heavy metals are dangerous due to bioaccumulation. In water bodies, they get accumulated in sediment and organisms from where they may be transferred into the food chain. Heavy metals such as cadmium, copper, nickel, and zinc are considered to be most hazardous, and they are included on the Environmental Protection Agency (EPA) list of priority pollutants (1). The increased concerns in the environment, health and the strengthened regulations demand more strict treatment of water and wastewater.

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Traditional methods for elimination, concentration and/or recovery of heavy metals such as precipitation, ion exchange, electrodeposition, crystallization, evaporation, liquid–liquid extraction, etc., have great disadvantages by operating in a succession of steps of heterogeneous reactions, or distribution of substances between different phases which usually require a lengthy operating period. Moreover, the final metal recovery requires additional treatments, which complicates the process (2). These techniques have been used for the removal of metal ions from aqueous effluents (3–5). However, these techniques are either incapable of reducing the concentration to the required level or prohibitively expensive. Membrane processes gains much interest and significance as they reduce the number of unit operations and are now used to obtain effluents without contaminants, for recycling process water, and to recover valuable products, which can be reused in the process itself or in other applications (6). For the last two decades most of the scientific workers have focused their attention on the application of the ultrafiltration (UF) membrane in pollution prevention (7–9) and the success of membrane technology lies on the membrane material. Cellulose acetate (CA) is one of the first membrane polymers that are being used for aqueous based separations for both reverse osmosis (RO) and ultrafiltration membranes (10). These membranes yield low water flux; has narrow pH range, restricted compaction, and biodegradation properties, which restricts its application. The performance of CA may be improved by blending it with an appropriate polymer in view of the fact that polymer blends have provided an efficient way to fulfill new requirements for material properties. Cellulose acetate has been blended with polyurethane and the blend membranes have been used for the rejection of Cu^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} using polyethyleneimine as a chelating ligand (11). Cellulose acetate has been

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blended with polysulfone and applied for the separation of chromium using polyvinyl alcohol (PVA) as the macromolecular chelating agent (12). Polysulfone-cellulose acetate blend membranes have also been prepared and used to separate copper ions from feed with 1000–3000 ppm concentration (13). 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 (14).

Bisphenol-A-polysulfone (PSf) is being widely used as a membrane material for the fabrication of ultrafiltration membranes in view of its excellent chemical and mechanical properties. Since, polysulfone is hydrophobic in nature; it is desirable to make the PSf membrane hydrophilic for ultrafiltration applications. Hydrophilicity of polysulfone has already been improved in several investigations through the application of chemical modification methods. In this investigation polysulfone was aminated in order to increase the hydrophilicity. Adding additives, such as polyethylene glycol (PEG) was widely employed to alter the structure of the membrane and also enhance the diffusive transport properties of the solute through the ultrafiltration membrane (15–17). The presence of hydrophilic additive, PEG 600 and its concentration are important factors in changing porosity, pore volume, pore size, and subsequently the pure water flux, water content, membrane hydraulic resistance of the resulting membranes.

The latest researches have shown the influence of PEG additives in cellulose acetate ultrafiltration membrane characteristic in terms of pore sizes, the permeate flux, and the protein rejection rates (18). Moreover, poly ethylene glycol (PEG) is chosen as an additive because of their water-solubility nature and its easy availability. In view of this, the main objective of this study is to investigate the effect of incorporations PEG 600 on the CA/APSf membranes performance in terms of compaction, pure water flux, hydraulic resistance, percentage water content, contact angle measurement, surface and cross section morphologies by scanning electron microscopy. The rejection behavior of Cu^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} from aqueous streams containing one metal ion at a time, by complexing with a particular concentration of polyethyleneimine through ultrafiltration using blend membranes of CA/APSf has also been studied.

EXPERIMENTAL

Materials

Commercial grade MYCELL cellulose diacetate CDA5770 (acetyl content 39.99 wt%) was procured from Mysore Acetate and Chemicals

Company Limited, India and it was used after reprecipitation from acetone. Udel P–3500 Polysulfone was supplied by Amoco Polymers and aminated polysulfone was prepared by two-stage process as reported earlier (19). Polysulfone was first chloromethylated by using a mixture of trioxane, hydrochloric acid, aceticanhydride in the presence of Lewis acid catalyst Zinc chloride ($ZnCl_2$) and then aminated by triethyl amine. Trioxane was procured from Sigma Aldrich. Analytical grade N, N-Dimetylformamide (DMF), Qualigens Fine Chemicals, Glaxo India Ltd., India) was seived through 4Å molecular seives to remove moisture and stored in dry conditions prior to use. Poly (ethylene glycol) 600 [PEG 600, Merk (I) Ltd.] was used as supplied as a solvent additive for the entire study. Acetone and sodium lauryl sulphate (SLS), zinc chloride, hydrochloric acid, aceticanhydride were purchased from SD Fine Chemicals, India. Polyethyleneimine (M.Wt. 60,000–1,00,000) was procured from FLUKA, Germany, chemicals and used as a macromolecular chelating ligand. Deionized water was used throughout this study.

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Methods

The fourier transform infrared (FT-IR) measurements were performed on a Perkin Elmer FT-IR spectrometer. The ^{1}H-NMR spectra were obtained from BRUKER 300 MHz spectrometer at 298 K with deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as the standard. The temperature of degradation was obtained by a thermo gravimetric analyzer with heating rate of 10°C min^{-1} (Mettler, Model TA 3000) with a TG 50 thermo balance. Contact angle measurement was performed by using a DST Dynamic Surface Tensiometer. The surface and cross sections of the membranes were viewed using JEOL JSM-840A scanning electron microscope. The ultrafiltration experiments were carried out in a batch type, dead end cell (UF cell–S76–400–Model, Spectrum U.S.A) with a diameter of 76 mm, fitted with a Teflon coated magnetic paddle. This cell was connected to a compressor with a pressure control valve and gauge through a feed reservoir. The schematic representation of the ultrafiltration kit is shown in Fig. 1.

Membrane Preparation

The phase inversion technique was employed for the preparation of CA/APSf blend asymmetric membranes. Blend membranes of cellulose acetate and aminated polysulfone were prepared from casting solutions

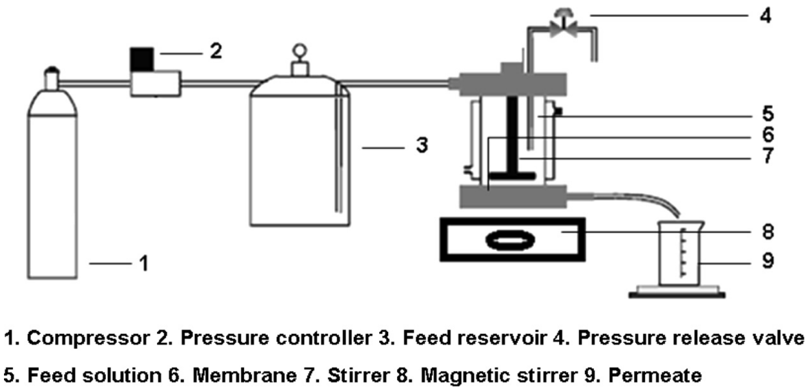

Figure 1. Representation Ultrafiltration experimental setup.

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containing 17.5 wt% polymer with blend compositions of 100/0, 95/5, 90/10, 85/15, 80/20, 75/25, 70/30 wt% of CA/APSf. The maximum blend composition was found to be 70/30 wt%, beyond which phase separation takes place. The blend solutions were prepared under constant mechanical stirring for 4 h at 40°C. The homogeneous solution thus obtained was allowed to stand still at room temperature for six hours in an airtight condition to get rid off air bubbles. 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 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 25 ± 2°C with a relative humidity of 50 ± 2%. The casting and gelation conditions were maintained constant throughout, because the thermodynamic conditions would largely affect the morphology and performance of the resulting membranes (20). The membranes were cast over a glass plate using a doctor's blade. After casting, the solvent present in the cast film was allowed to evaporate for 30 s, and the cast film along with the glass plate was gently immersed in the gelation medium (water 2 L, DMF 2 wt%, sodium lauryl sulfate (SLS) 0.2 wt%). After one hour of gelation, the membranes were removed from the gelation bath and washed thoroughly with distilled water to remove all DMF and surfactant from the membranes. The membrane sheets were subsequently stored in distilled water, containing 0.1% formalin solution to prevent microbial growth.

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Compaction

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. The prepared membranes were cut in to effective membrane area 38.5 cm^2 and kept in the ultrafiltration cell. The membranes were initially pressurized with distilled water at 414 kPa for 5 h. These pre-pressurized membranes were used in subsequent ultrafiltration experiments at 345 kPa.

Pure Water Flux

Membranes after compaction were subjected to pure water flux studies at a trans-membrane pressure of 345 kPa. The flux was measured under steady-state flow (21). The pure water flux is determined by

$$J_w = \frac{Q}{A\Delta t} \tag{1}$$

Where, Q is the quantity of permeate collected (l), J_w is the water flux ($1\,m^{-2}\,h^{-1}$), Δt is the sampling time (h), and A is the membrane area (m^2). The run was carried out in triplicate, and the average values were taken for all flux experiments.

Water Uptake

Percent water content of the membranes was obtained after soaking membranes in water for 24 h and the membranes were weighed followed by mopping it with blotting paper. The wet membranes were placed in vacuum drier at 100°C for 5 h and the dry weights of the membranes were determined. From the wet and dry weights, percentage water content was determined by

$$\%\text{Water content} = \frac{\text{Wet sample weight} - \text{ Dry sample weight}}{\text{Wet sample weight}} \times 100 \tag{2}$$

Contact Angle Measurement

DST-Dynamic Surface Tensiometer was employed to determine the static contact angle of 100 wt% CA and CA/APSf of various compositions of blend ultrafiltration membranes.

Membrane Hydraulic Resistance

To determine the membrane hydraulic resistance of the membrane (R_m), the pure water flux of the membranes were measured at transmembrane pressures (ΔP) of 69, 138, 207, 276, and 345 kPa after compaction at 414 kPa for 5 h. The resistance of the membrane, R_m was evaluated from the slope of pure water flux (PWF) *vs* transmembrane pressure (ΔP) using the following equation (22)

$$J_w = \frac{\Delta P}{R_m} \tag{3}$$

Where, R_m is the hydraulic membrane resistance (kPa/l m^{-2} h^{-1}).

Morphological Studies

The top and cross-section view of the CA and CA/APSf blend membranes was studied with a scanning electron microscopy (SEM). The membranes were cut into pieces of various sizes and mopped with filter paper. These pieces were immersed in liquid nitrogen for 20–30s and were frozen. Frozen bits of the membranes were broken and kept in a desicator. These dry membrane samples were used for morphological studies. The samples were gold sputtered for producing electrical conductivity, and photomicrographs of the samples were taken under very high vacuum conditions operating between 15 and 25 kV, depending on the physical nature of the sample. Various SEM images were taken for CA, 100 wt% and CA/APSf (80/20 wt%) blend membranes.

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Metal Ion Separation

Aqueous solutions containing Cu^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} of 1000 ppm in 1 wt% solution of polyethyleneimine (PEI) in deionized water were prepared. The pH of these solutions was adjusted to 6.5 using 0.1 N HCl and 0.1 N NaOH. Solutions containing PEI and metal ions (metal chelates) were thoroughly mixed and left for 5 days at 25°C for complete binding to occur before being subjected to an ultrafiltration study at 345 kPa. For each run, the few mL of permeate were discarded. The percent separations of metal ions in the feed and the permeate streams by an atomic absorption spectrophotometer (Perkin–Elmer 2380) and also using the following equation.

$$\%R = 1 - \frac{C_p}{C_f} \times 100 \tag{4}$$

Where, C_p is the concentration of the permeate, C_f is the concentration of the feed, and % R is the percentage rejection.

RESULTS AND DISCUSSION

Chloromethylation allows the attachment of various functional groups onto polysulfone, often quantitatively. In this investigation, aminated polysulfone (APSf) were prepared via chloromethylation followed by reaction with triethylamine (Et_3N). Chloromethylated polysulfone were prepared with a mixture of HCl, acetic anhydride, and trioxane as a formaldehyde precursor with $ZnCl_2$ as a catalyst. The structure of the aminated polysulfone is shown in Fig. 2. The structure of chloromethylated and aminated polysulfone was confirmed by ^{1}H-NMR, and FT-IR spectrum. From the FT-IR spectrum, the substitution of chloromethyl and trimethyl amine group in polysulfone was identified by C-Cl and C-N stretching at 1248, 1019 cm^{-1} respectively. The degree of substitution was obtained by ^{1}H-NMR. On comparison with the integration of the quaternary amine ethyl groups with the isopropylidene signal (6 H), the degree of substitution was obtained. The degree of substitution was found to be 0.40 (19). The thermal behavior of chloromethylated and aminated polysulfones was examined over a temperature range of 40–700°C in air at a heating rate of 10°C min^{-1}. The weight loss as a function of temperature of the chloromethylated and aminated polysulfones is presented in Fig. 3. The curves show the degradation with onset of weight loss at about 350°C and 250°C for chloromethyl and tertiary amine groups in polysulfone respectively. The initial degradation may be attributed to loss of chloromethylated amine content in polysulfone, while the decomposition above 400°C may be assigned to the loss of sulfone group.

The casting solution based on CA and APSf polymers at a total polymer concentration of 17.5 wt% contains 0, 2.5, 5.0, 7.5 wt% PEG 600 by

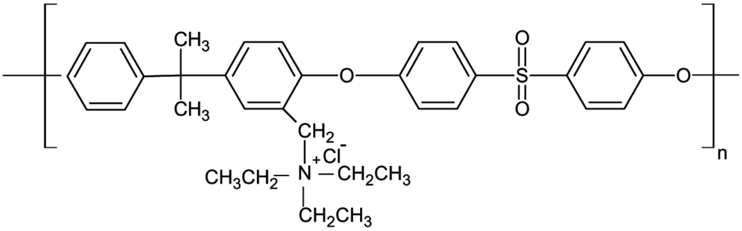

Figure 2. Structure of aminated polysulfone (APSf).

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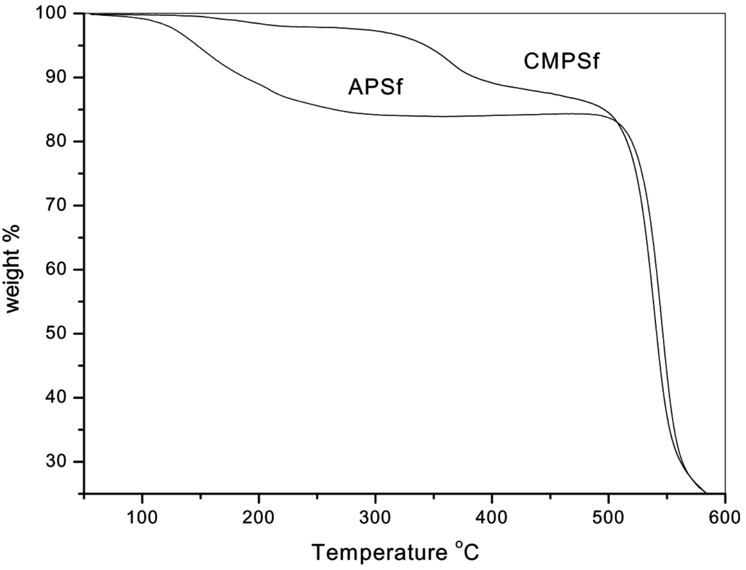

Figure 3. TGA curve of Chloromethylated Polysulfone (CMPSf) and aminated Polysulfone (APSf).

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using DMF as a solvent were used for the preparation of membranes. The blend membranes were found to be compatible up to a composition of 70/30 wt% of CA/APSf in DMF, further increase in APSf concentration led to phase separation. Beyond 7.5 wt% of PEG600 resulted in macrovoid structure underneath the skin layer which reduced the strength of the membrane. Hence, in the present investigation the maximum additive concentration was restricted to 7.5 wt% and the blend composition was restricted to 70/30 wt%. With these preliminary optimizations, studies of the effects of various blend compositions on the compaction, pure water flux, membrane hydraulic resistance, water content, contact angle, and separation of Cu^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} using PEI as a chelating ligand were performed and the findings are discussed below.

Compaction

The compaction study was carried out to form rigid pores and to obtain a steady state flux. Pre-compression of the membranes at a pressure higher than the operating pressure, permits stress relaxation during operation. During compaction, the reorganization of polymeric chains occurs, leading to change in the membrane structure with reduced the volume porosity. This in turn increases the hydraulic resistance offered by the membranes as a result of a dense membrane structure resulting in the decline of the permeate flux. At a constant operating pressure (414 kPa), the pure water flux of CA and CA/APSf blend membranes upon compaction was measured for every one hour. During the compaction, the water flux was found to be high initially and declined gradually and reached a steady state after 5 h of compaction for all the membranes. The effect of compaction on CA and all blend compositions were shown in Fig. 4a. From the Fig. 4a it was observed that, membranes prepared from pure cellulose acetate with 17.5 wt% casting solution showed a steady state pure water flux of 20.31 $\mathrm{l\,m^{-2}\,h^{-1}}$. When aminated polysulfone was incorporated into cellulose acetate, an increase in flux behavior was observed. As the percent content of APSf in the casting solution was increased from 5 to 30%, the initial flux had shown an increase from 23.5

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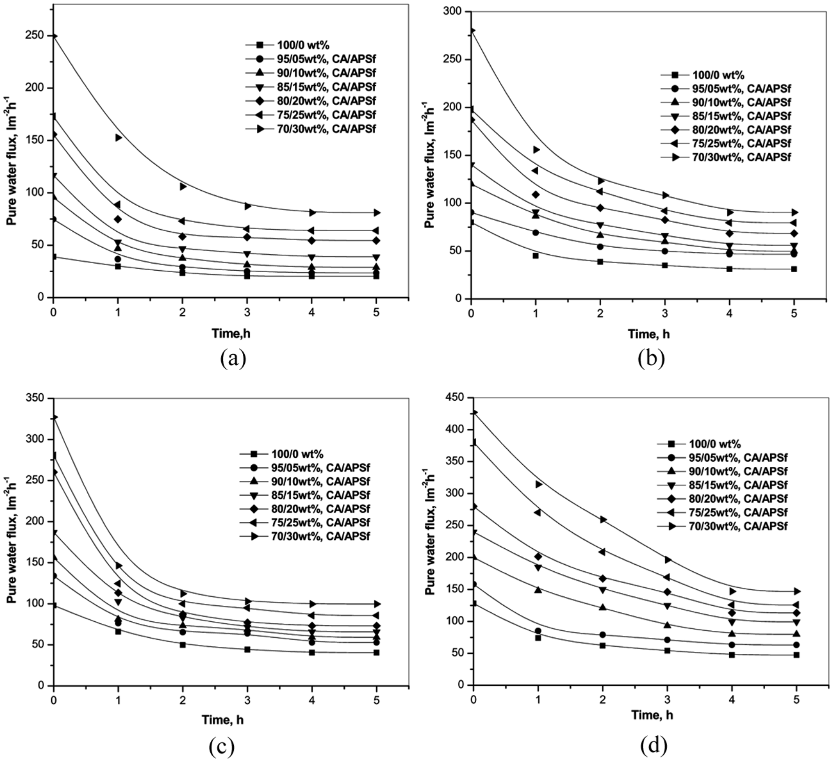

Figure 4. Effect of compaction time on pure water flux-CA/APSf blend membranes with different additive concentrations; (a) without additive; (b) with 2.5 wt% PEG 600; (c) with 5 wt% PEG 600; and (d) with 7.5 wt% PEG 600.

to 98.0 l m^{-2} h^{-1} as evidenced from Fig. 4a. Thus, with the increase in the composition of APSf in the blend enhances the hydrophilicity of the membrane and hence the higher steady state flux has been observed. Comparatively higher steady state flux in membranes with higher APSf content may also be due to the partial compatibility of blends, which leads to a larger segmental gap between CA and APSf.

The effect of PEG 600 was carried out for all the blend compositions in order to architect the membrane structure (Figs. 4b–d). It was observed that, for PEG concentration of 2.5, 5.0, and 7.5 wt% the flux which was high at the initial hour, reduced on compaction and attained a steady state after 5 h and also a steady state flux increased steadily with the increasing PEG concentration. This might be due to a faster leaching rate of PEG 600 in the blend solution. A similar trend has also been reported for the CA/Carboxylated blend ultrafiltration membranes (23).

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Pure Water Flux

After initial compaction of the membranes for 5 h at 414 kPa, the trans-membrane pressure was maintained at 345 kPa for further characterization. All the membranes were washed thoroughly with deionized water and loaded on to the ultrafiltration kit. The pure water fluxes were measured by subjecting them to a pressure of 345 kPa using deionized water as the feed. For pure cellulose acetate membranes, the pure water flux of 15.48 lm^{-2} h^{-1} was observed. When the APSf composition was increased from 5 to 30 wt% in the blend, there was an increase in the flux of the blend membranes, from 23.3 to 52.9 lm^{-2} h^{-1}, as shown in Table 1. It is seen that the permeate flux of all blend (CA/APSf) membranes exhibited

Table 1. Pure water flux values for CA and CA/APSf blend membranes

	Pure water flux (lm^{-2}h^{-1})			
Blend compositions (CA/APSf wt%)	Zero additive	2.5 wt% PEG 600	5.0 wt% PEG 600	7.5 wt% PEG 600
100/0	15.6	26.0	34.2	41.2
95/5	23.0	31.2	40.5	48.2
90/10	28.0	38.0	46.7	58.3
85/15	34.0	44.6	53.0	70.0
80/20	40.0	53.4	59.2	84.1
75/25	46.7	60.4	67.0	97.7
70/30	52.9	69.0	77.0	112.3

higher flux values compared to pure CA (100%) membranes. This linear trend with an increase in APSf composition may be due to the higher hydrophilic nature of APSf. In addition, the enhancement in flux may be attributable to that of the presence of a higher amount of the two polymeric components resulting in phase separation and inhomogeneity, leading to the formation of cavities in the sub layer, which gives way to the mobility of the water molecules (24).

The effect of additive concentration on pure water flux of CA and CA/APSf membranes was investigated and shown in Table 1, in order to find the possible improvement in the efficacy of the membranes. It is seen that the pure water flux is increased upon increase in the PEG 600 concentration in the casting solution. The influence of PEG 600 as additive to all blend composition of CA/APSf membranes was also studied. It was observed that with the addition of 2.5 wt% of PEG 600 to CA/APSf blend membranes, the pure water flux increased from 31.12 to 69.0 $\mathrm{lm^{-2}h^{-1}}$. It was also observed that pure water flux increased linearly for 5 wt% and 7.5 wt% of PEG 600 for all the blend membranes. This trend indicates the leach ability of the water-soluble additive leading to the formation of a larger and a higher number of pores (25).

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Membrane Hydraulic Resistance

Membrane hydraulic resistance (Rm) is the intrinsic resistance of the membrane determined using pure water flux as the feed. It is an indication of the tolerance of the membrane towards hydraulic pressure and is determined by subjecting the membranes to different transmembrane pressures (69–414 kPa) and measuring the pure water flux of the membranes. Thus, the Rm values for the membranes were obtained as the inverse of the slope of plot of transmembrane pressure *vs* pure water fluxes and the plots are shown in Figs. 5a d and R_m values are given in Table 2.

The pure water flux was observed to increase with increase in the operating pressure which increases the driving force for permeation of water. The membranes prepared from pure cellulose acetate showed highest Rm values. On incorporation of aminated polysulfone in the blend resulted in a decline of Rm value which is evident, from Table 2. This decline in Rm value in membranes with varied polymer compositions is most likely due to the fact that the membranes prepared with aminated polysulfone as the blend component have enhanced hydrophlicity of the membranes, resulting in declined Rm value with an enhanced permeability.

The presence of an additive in the casting solution has considerable effect in the membrane hydraulic resistance. When the PEG 600

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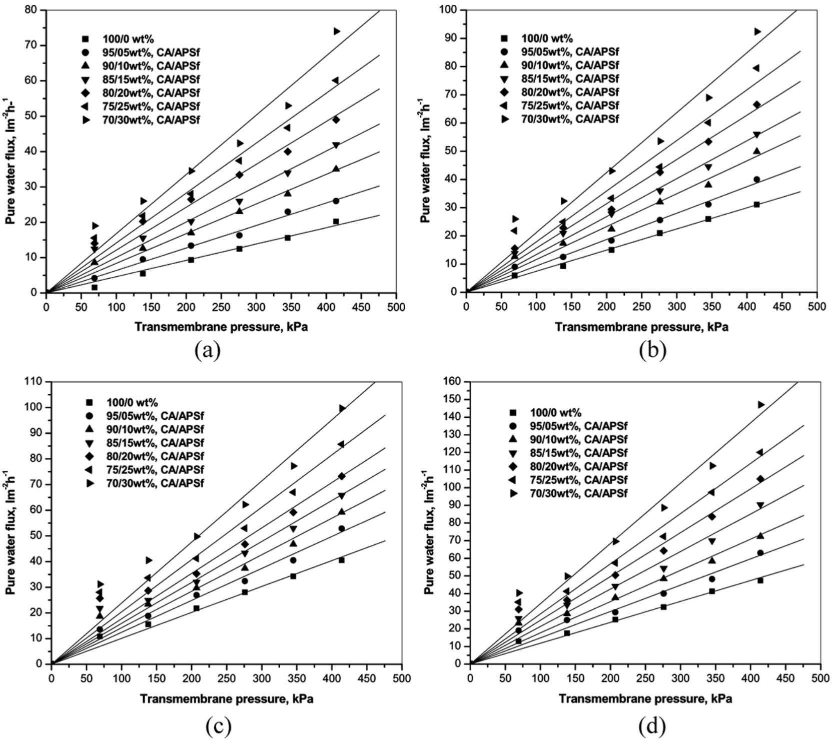

(a) (b)

(c) (d)

Figure 5. Effect of compaction time on transmembrane pressure on pure water flux-CA/APSf blend membranes with different additive concentrations; (a) without additive; (b) with 2.5 wt% PEG 600; (c) with 5 wt% PEG 600; and (d) with 7.5 wt% PEG 600.

concentration was increased from 2.5 to 7.5 wt%, in the casting solution of pure cellulose acetate, there was a corresponding decrease in resistance of membrane, from 21.65 to 8.44 kPa/lm^{-2}h^{-1} and the values are depicted in Table 2. Similarly, for a given blend composition, when the additive concentration was increased, the Rm decreased linearly. Membranes with all blend compositions also exhibited the same trend. This may be due to the fact that the addition of a pore former in the casting solution resulted in the formation of macropores on the membrane surface due to thermodynamical instability, which enhanced the precipitation and the porous nature (26). This can also be supported by the observation that with an increase of the PEG 600 content, it increased the flux due to higher and larger pore formation, and thereby reduced the membrane hydraulic resistance.

Table 2. Membrane hydraulic resistance (Rm) values for CA and CA/APSf blend membranes

	Membrane hydraulic resistance (Rm) values ($kPa/lm^{-2}h^{-1}$)			
Blend compositions (CA/APSf wt%)	No additive	2.5 wt% PEG 600	5.0 wt% PEG 600	7.5 wt% PEG 600
100/0	21.65	13.35	9.9	8.44
95/5	15.72	10.67	8.04	6.71
90/10	11.92	8.58	7.03	5.85
85/15	9.96	7.45	6.27	4.70
80/20	8.24	6.37	5.65	4.06
75/25	7.08	5.57	4.90	3.52
70/30	5.96	4.71	4.18	2.92

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Water Uptake

The water uptake of membranes was determined by the measurement of the change in mass before and after hydration. When the hydrophilicity of the membranes increases the flux of the membranes also increases due to excessively larger water uptake but higher swelling leads to lowering the mechanical strength, which is incompatible for ultrafiltration applications. Thus, this parameter is essential for the characterization of ultrafiltration membranes. Water content studies were carried out for various compositions of CA/APSf in presence and absence of water-soluble additive PEG 600 as shown in Fig. 6. The water uptake of the blend membranes with 5wt% APSf in the absence of an additive was found to be 76.5%. When the APSf composition was further increased to 10, 15, 20, 25, 30 wt%, the water content values are 79.5, 80.2, 80.6, 80.8, 81, and 81.4 respectively. This increase in the water content with the increase in the APSf composition confirmed that the hydrophilicity is directly proportional to the water content. In the presence of the additive concentrations in the blend component, the percentage water content was increased due to the leachability of the water-soluble polymeric additive which in turn increased the hydrophilicity of the membrane.

Contact Angle Measurement

Contact angle measurement was performed on CA/APSf films using a DST Dynamic Surface Tensiometer. The change in the contact angle of

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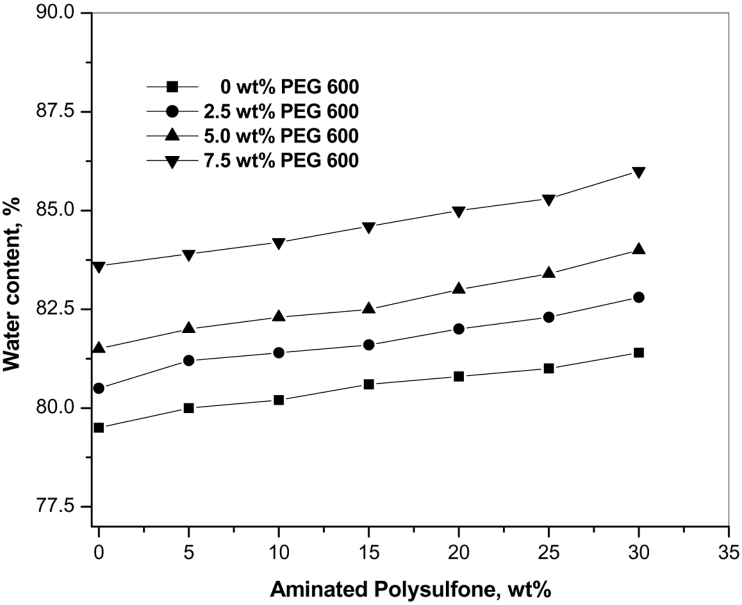

Figure 6. Effect of PEG 600 concentration on water content-CA/APSf blend membranes.

the films was measured by dipping the membrane in distilled water for a 10 mm depth. The contact angle experiment was carried out ten times and the average values are presented in this article. The contact angle of CA (100 wt%) membrane had the highest contact angle (58°), corresponding to the lowest hydrophlicity. The contact angle decreased with the enhancement of APSf concentration in a blend component 5 to 30 wt%, corresponding values are 54°, 51°, 49°, 46°, 44°, and 39° respectively. The decrease in the water contact angle of the modified membranes implies that the polar surface was obtained by increasing the amine group and the hydrophlicity of CA/APSf membranes was improved by increasing the polar group in the blend polymeric unit. As expected, the introduction of the trimethyl amine (TMA) group in the polymer unit increased the hydrophlicity of the CA/APSf membranes. Therefore, it was proposed that the aminated membranes would sorb more permeate into the membrane and thus enhance the flux rate. A similar trend was observed for PES/DMMSA-BMA (polyethersulfone/N,N-dimethyl-N-(3-sulfopropyl)-butyl methacrylate) blend membranes by T. Wang et al. (27). The effect of the contact angle on polyether sulfone by increasing sulfonated polycarbonate was also reported by Y. Wang et al. (28). Zhu et al., have reported improved hydrophilic blend membranes by blending PES with SMA (poly (styrene-alt-maleic anhydride), decreasing the contact angle with increasing SMA concentration (29).

Morphological Studies

The SEM images were taken after testing the compaction studies of pure CA and CA/APSf blend membranes in the absence and presence of pore former, PEG 600. SEM images of top surfaces and cross-section of membranes, prepared from 100 wt% CA without and with 5 wt% additive concentration for PEG 600 are shown in Figs. 7a–d depicts a less porous layer with on the top surface of CA (100%) membrane without additive (Fig. 7a). Upon increase of 5 wt% PEG 600, the pore size increases which is shown in Fig. 7b. The presence of 5 wt% PEG 600 in the blend polymer incorporates the bigger pore size on the CA membrane compared to that prepared in the absence of an additive. This confirms the concept of

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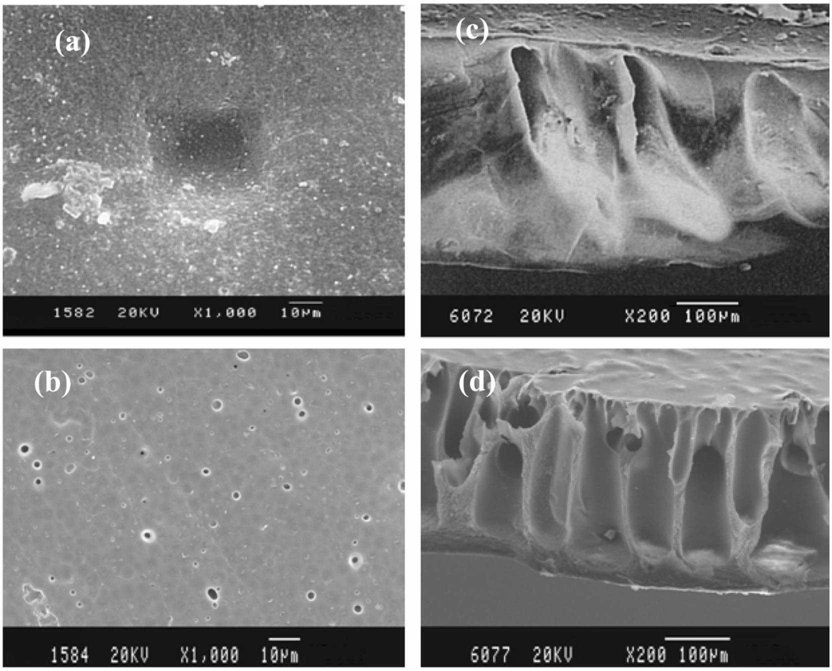

Figure 7. SEM Micrographs of top and cross section of CA membranes Surface (1000X); (a) 100 wt% CA without additive; (b) 100 wt% CA with 5 wt% EG 600 Cross (200X); (c) 100 wt% CA without additive; (d) 100 wt% CA with wt% PEG 600.

leaching out of the additive during the gelation (30). The finger-like structures shown in Figs. 7c and d are the cross section of the above-mentioned respective membranes. Similar finger like structures are reported in the case of CA-inorganic salt membranes (31). A comparison of Figs. 7a–d clearly shows that the addition of PEG 600 in the blend increased the pore size and finger like voids formed an asymmetric structure of membrane.

Figs. 8a–d shows the SEM photographs of the top surface and cross section of the membrane prepared from CA/APSf blend with 80/20 wt% composition in the absence and presence of PEG 600. Figures. 8a and 8b depicts a porous layer with on the top surface of CA/APSf (80/20 wt%) membrane without and with 5 wt% PEG 600. The presence of 5 wt% PEG 600 in the blend polymer incorporates the bigger pore size, uniform pore size distribution, and number of pores also increased on the top surface of the CA/APSf (80/20 wt%) blend membrane. This may be attributed

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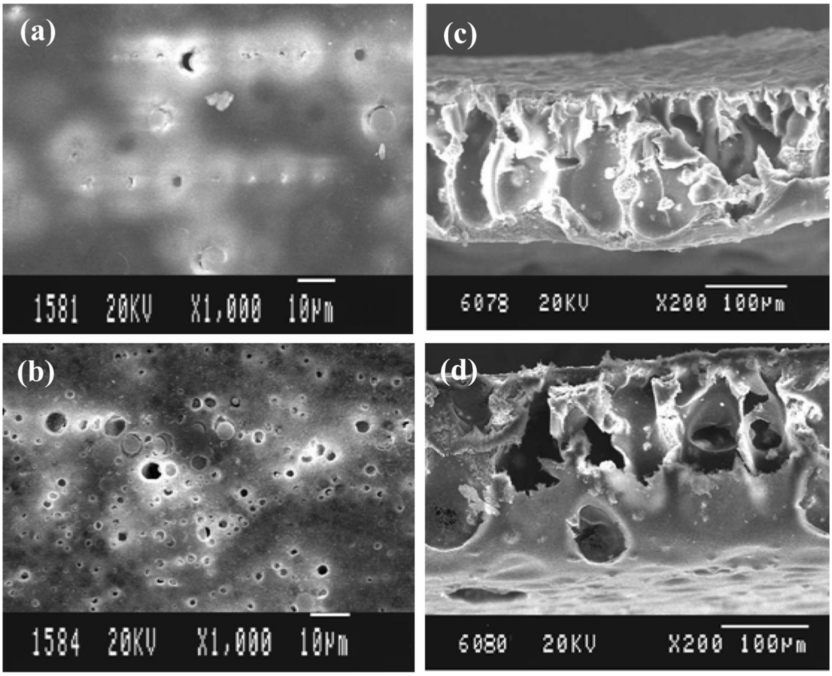

Figure 8. SEM Micrographs of top and cross section of (CA/APSf 80/20 wt%) blend membranes. Surface (1000X); (a) CA/APSf (80/20 wt%) without additive; (b) CA/APSf (80/20 wt%) with 5wt% PEG 600; Cross (200X); (c) CA/APSf (80/20 wt%) without additive; and (d) CA/APSf (80/20 wt%) with 5wt% PEG 600.

to the distribution of individual domains of CA and APSf with their respective morphologies as well as the leaching out of the water soluble pore forming agent PEG 600 during the gelation.

The cross section views of CA/APSf of above blend membrane are displayed in Fig. 8c and 8d, where the fingers-like structures are commonly found beneath the skin layer of the ultrafiltration membranes are seen. The large microvoids extend through most of the substructure, the medium sized microvoids extend through one-third of the membrane, and the small microvoids are situated near the nodular layer. The skin becomes porous and a spongy structure is observed along the penetrating cavity. While with the presence of PEG 5 wt%, the tear size of the pores has also increased. The SEM results confirm the effect of the additive on pure water flux, water content, hydraulic resistance, and contact angles of CA/APSf blend membranes.

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Metal Ion Rejection Studies

In recent years, water-soluble polymeric ligands such as polyethyleneimine, polyvinyl alcohol, and polyacrylic acid, etc. are being employed successfully to remove traces of metal ion from industrial effluents by the ultrafiltration technique. In this investigation the removal of Cu^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+}, from aqueous streams, containing one metal ion at a time, by complexing them with 1 wt% concentration of polyethyleneimine through ultrafiltration using CA and CA/APSf blend membranes was attempted. Further, due to the fact that the amino groups present in polyethyleneimine cannot be easily bound to hydrolyzed metal ions owing to the competitive reactions between OH ions and amino groups with such metal ions, metallic salts viz., sulphates were taken for preparation of feed solution. The feed consists of each metal ion of 1000 ppm. Accordingly, different aqueous feeds of Cu^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} were prepared individually. In order to study the effect of PEI on rejection, an experiment was carried out in the absence of PEI and it was observed that all metal ions of sulfate solutions were completely passing through membranes over the entire range of acidic pH.

Further, at pH beyond 7.0, all metal ions precipitate as insoluble hydroxides. Hence, the pH of feed was kept exactly at 6.00 ± 0.25 and rejections were carried out in the presence of PEI due to the fact that at this pH, strong protonation of metal chelates along with relatively larger extent of stretching of complex takes place.

Figure 9a shows the effect of additive concentration (0–7.5 wt% PEG 600), in the casting solution of the pure cellulose acetate membrane, on the rejection of Cu^{2+}, $Ni^{2+,}$ Zn^{2+}, and Cd^{2+} ions. The percent rejection

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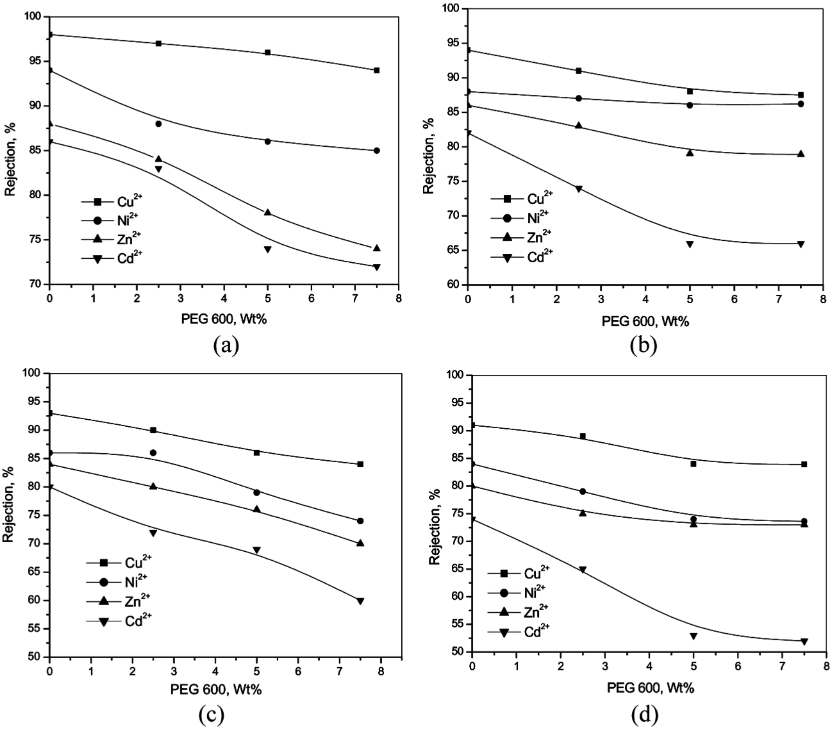

(a) (b)

(c) (d)

Figure 9. Effect of PEG 600 concentration on rejection of metal chelates; (a) 100 wt% CA; (b) 90/10 wt% CA/APSf; (b) 80/20 wt% CA/APSf; and (d) 70/30 wt% CA/APSf.

of metal ions decreased linearly from 98 to 94% in the case of Cu^{2+} for pure cellulose acetate membrane when PEG 600 concentration was increased from 0 to 7.5 wt%. A similar trend was found for the rejection of other metal ions such as Ni^{2+}, Zn^{2+}, and Cd^{2+}. The effect of concentration of PEG 600 on the percentage rejection of metal ions for the CA/APSf (90/10 wt%) is depicted in Fig. 9b. For 90/10 wt% CA/APSf blend membrane the percentage rejection decreased linearly from 94 to 86% when the PEG 600 concentration was increased from 0 to 7.5 wt%. A similar trend was observed for blend composition 80/20 and 70/30 wt% which are shown in Fig. 9c and 9d. This decreased trend may be due to the fact that the pore size of the membranes increased as the concentration of PEG 600 in the membrane casting solution increased as shown in Figs. 9a–d. The same trend was observed for other metal ions for the blend composition of 80/20 and 70/30 wt% of CA/APSf. Further Cu^{2+} has higher separation than other metal ions due to a stronger ligand

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formation with the polymer chelating agent, polyethyleneimine (32) due to the Jahn-Teller effect. The order of the degree of rejection is $Cu^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+}$. The higher rejection in Cu^{2+} may be related to the strong complexing nature of Cu-PEI chelates compared to that of Ni^{2+}, Zn^{2+}, and Cd^{2+}. The complexing capacity depends on the number of functional groups (ligand site) in the macromolecular complex and the atomic weight of the metal. A similar observation was also observed by Mandel and Lyte, for the polymethacrylate system (33). According to Jahn–Teller distortion effect, the Cu-PEI complex is more stable. This theorem states that any non-linear molecule with the degenerate electronic ground state will undergo a geometrical distortion that removes the degeneracy. This also has the effect of lowering the overall energy and enhances the stability of the complex. The Jahn Teller effect is most often encountered in octahedral complexes of the transition metals, and is very common in six coordinate Cu(II) complexes.

Further, at a higher concentration of PEG 600, a larger amount of the pore former is being leached out at a higher rate, which leaves a larger pore size on the membranes which led to a lower rejection at high additive concentration. The larger pores at higher PEG 600 concentration is also established by observing bigger pores in SEM.

Metal Ion Solution Permeate Flux

It is proposed that metal chelates in the feed will deposit or adsorb on the membrane surface (cake formation), causing a flux drop in the few minutes of operation. Under constant pressure, the effects of membrane fouling and concentration polarization are usually observed by considerable decline in permeate flux with time. In the present work, the concentration polarization (reversible fouling) was minimized because of high molecular weight PEI and rigorous stirring near the membrane surface. Irreversible fouling, absorption of small metal chelate inside the pores, ie., blockage of the pores of the membrane may be reduced due to the formation of microvoids underneath the skin layer or substructure of the membrane. Generally the phase inversion method results in asymmetric membranes. The permeate flux of metal ion is essential to specify the product rate and predict the economics of the membrane process. Thus, the metal ion permeate fluxes, measured simultaneously during rejection with 100/0, 90/10, 80/20, 70/30 wt% of CA/APSf blend membranes in the absence and the presence of the additive, are shown in Fig. 10 a–d. The pure CA membrane in the absence of an additive offered a less permeates flux value of $8.2 lm^{-2}h^{-1}$ for the Cu^{2+} ion. The other metal ions also had lower flux values as shown in Fig. 10a, due to smaller

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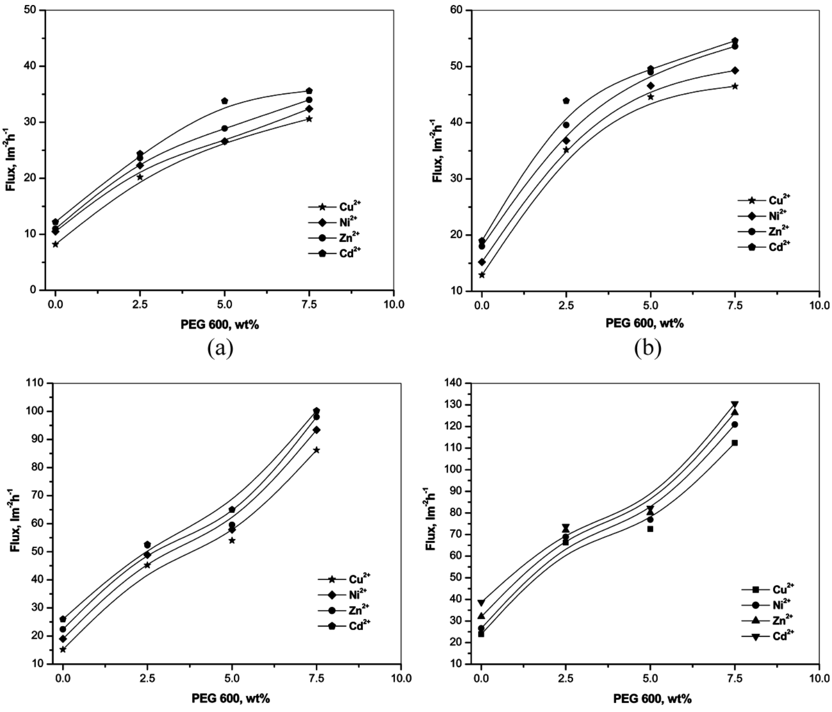

(a) (b)

(c) (d)

Figure 10. Effect of PEG 600 concentration on flux of metal chelates; (a) 100 wt% CA; (b) 90/10 wt% CA/APSf; (c) 80/20 wt% CA/APSf, (d) 70/30 wt% CA/APSf.

pore size and less number of pores of the pure CA membrane. It is seen that from Fig. 10a, the permeate flux values increased with increasing APSf content in all blend compositions. Comparatively higher permeate flux in membranes with higher APSf content may also be due to the partial compatibility of blends, which leads to a larger segmental gap between CA and APSf. However, in the 90/10 wt% CA/APSf membranes, as the additive concentration was increased from 2.5 to 7.5 wt% the flux was also increased significantly from 12.9 to 54.6 lm^{-2}h^{-1} for Cu^{2+} ions, as shown in Fig. 10b. 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 the gelation, creating the pores. The permeate flux of Cu^{2+} is lower than the other metal ion solutions and the order of permeate flux is Cd^{2+} > Zn^{2+} > Ni^{2+} > Cu^{2+} which inverse the trend observed in the metal ion rejection studies (34). This is because of the fact that Cu^{2+} has higher affinity for N-donors ligands compared to Cd^{2+} other metal ions chosen in this study. So it is suggested that Cu^{2+} can easily form more stable macromolecules than other metal chosen in this work. This led to the reduced permeate flux for Cu^{2+}, while enhancing the rejection. Hence it can be concluded that the extent of removal of metal ion depends on the formation of macromolecules using PEI complexing agent as well as the pore size of the membrane.

CONCLUSIONS

The preparation and characterization of CA/APSf blend membranes in terms of their pure water flux, hydraulic resistance, water content, contact angle, and morphological properties had been studied in the presence of the pore former, PEG 600 at different concentrations. Membranes with high permeation were prepared from CA/APSf with PEG 600 as additive, DMF as solvent, and water as the coagulation bath. Separation studies of metal ions were carried out at transmembrane pressure of 345 kPa. Furthermore, a higher rejection in Cu^{2+} may be related to the strong complexing nature of Cu-PEI chelates compared to other metal ions. The polymer composition and additive concentration were found to have considerable impact on the rejection and permeate flux values of the metals. The results presented here may be extended to the commercial purpose.

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NOTE

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