

Toxic metal ion separation by cellulose acetate/sulfonated poly(ether imide) blend membranes: Effect of polymer composition and additive

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Abstract

Toxic heavy metal ion removal from industrial effluents are gaining increased visibility owing to environmental concern and saving precious materials. In this work, an attempt has been made to remove the valuable metal ions using modified ultrafiltration (UF) blend membranes based on cellulose acetate (CA) and sulfonated poly(ether imide) (SPEI) were prepared in the presence and absence of additive, poly(ethylene glycol) 600 (PEG600) in various compositions. Prepared membranes were characterized in terms of pure water flux (PWF), water content and membrane hydraulic resistance. High flux UF membranes were obtained in the range of 15–25 wt% SPEI and 2.5–10 wt% PEG600 in the polymer blend. The molecular weight cut-off (MWCO) of the blend membranes were determined using protein separation studies found to vary from 20 to greater than 69 kDa. Surface morphology of the blend membranes were analysed with scanning electron microscopy. Studies were carried out to find the rejection and permeate flux of metal ions such as Cu(II), Ni(II), Zn(II) and Cd(II) using polyethyleneimine as the chelating ligand. On increasing the composition of SPEI and PEG600, the rejection of metal ions is decreasing while the permeate flux has an increasing trend. These effects are due to the increased pore formation in the CA/SPEI blend membranes because of the hydrophilic SPEI and polymeric additive PEG600. In general, it was found that CA/SPEI blend membranes displayed higher permeate flux and lower rejection compared to pure CA membranes. The extent of separation of metal ions depends on the affinity of metal ions to polyethyleneimine to form macromolecular complexes and the stability of the formed complexes.

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1. Introduction

Efficient separation and recovery of metal ions from industrial waste streams is gaining more and more importance because of the increasing demand for high purity products and also for environmental concerns [1]. Currently, ultrafiltration (UF) becomes standard procedure for the separation of macromolecular solutions [2]. The term UF is usually applied to a membrane separation process where the solute dimensions are significantly larger than the solvent dimensions. UF has been widely used for product recovery and pollution control in the chemical, electrocoating, electronic, metal refining as well as in the food,

pharmaceutical, and biotechnological industries [3,4]. Indeed, UF is a membrane technique commonly used to separate and concentrate high molecular weight species present in solution [5].

Conventional techniques such as sorption and chemical precipitation have been used for the removal of metal ions from aqueous effluents [6–8], however, these techniques are either incapable of reducing the concentration to the required levels or prohibitively expensive. The use of membrane separation process in the treatment of wastewater and groundwater containing toxic metal ions is an attractive and suitable technique, since it offers concentration and separation of metals or valuable chemicals without a change of state and without the use of chemicals or thermal energy [9,10].

Cadmium, copper, lead, mercury, nickel and zinc are considered the most hazardous heavy metals and are included on the EPAs list of priority pollutants [11]. Many industries including chemical, electronic, metal plating industries face severe

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problems in terms of disposal of their waste streams when highly toxic or valuable constituents such as heavy metal ions are present. From these waste streams, heavy metals such as Cu, Ni, Zn, and Co could be separated and concentrated through binding of the target metal ions with water-soluble macromolecular compounds and subsequent ultrafiltration of the bound metals from the unbound components [12]. Thus, toxic heavy metals could be eliminated from waste streams, and the precious metals could be recovered and reused. The separation of Cu(II) and Ni(II) from Fe(III) ions by complexation with alginic acid has been attempted [13]. Muslehiddinoglu et al. have studied the effect of operating parameters on the selective separation of heavy metals from binary mixtures via polymer-enhanced ultrafiltration [14]. In the present work, polyethyleneimine was used as the poly-electrolyte for binding with the metal ions thereby enhancing the separation.

Conventionally cellulose acetate membranes are used in ultrafiltration and reverse osmosis membrane processes. The performance of cellulose acetate (CA) membranes can be improved by blending it with appropriate polymers in view of the fact that polymer blends have provided an efficient way to fulfill new requirements for material property [15]. Cellulose acetate/sulfonated poly(ether ether ketone) (CA/SPEEK) blend UF membranes have been used for separating chromium (III) ions [16]. Recently, cellulose acetate/poly(ether imide) (CA/PEI) blend UF membranes have been prepared and applied for the rejection of proteins and metal ions [17].

In the present investigation, modified cellulose acetate-based membranes were prepared by blending CA with sulfonated poly(ether imide) (SPEI) and poly(ethylene glycol) 600 (PEG600) in various compositions and the effects of polymer blend composition and additive concentration in the casting solution on pure water flux, water content, hydraulic resistance, molecular weight cut-off (MWCO) and surface morphology of the blend membranes are discussed and compared with membranes made from pure cellulose acetate. Further, the effect of CA/SPEI blend composition and concentration of the polymeric water soluble additive PEG600 in the casting solution on the rejection and permeate flux of toxic heavy metal ions such as Cu(II), Ni(II), Zn(II), and Cd(II) were investigated and the results are discussed.

2. Experimental

2.1. Materials

Commercial grade MYCELL cellulose diacetate CDA5770 (acetyl content 39.99 wt%) was procured from Mysore Acetate and Chemicals Company Limited, India and was used after reprecipitation from acetone and vacuum dried at 25 °C for 12 h. Polyetherimide (Ultem®1000) supplied by GE Plastics, India as a gift sample. It was dried at 150 °C for 4 h before used. *N*-Methyl-2-pyrrolidone (NMP), 1,2-dichloroethane (DCE), isopropanol, *N,N*-dimethyl acetamide (DMAc), 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 were used for the preparation of phosphate buffer solutions in the protein analysis. Proteins, viz., 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. Chlorosulfonic acid, copper (II) sulphate (AR), nickel (II) sulphate (analytical reagent grade), zinc (II) sulphate (AR) and poly(ethylene 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 for the preparation of aqueous metal ion solutions. Polyethyleneimine [weight-average molecular weight (M_w) = 600,000–1,000,000] 50% aqueous solution was procured from Fluka Chemie AG (France) and was used as a 1 wt% aqueous solution. Deionized and distilled water was employed for the ultrafiltration experiments and for the preparation of gelation bath.

2.2. Sulfonation of PEI

Polyetherimide (Ultem®1000) was sulfonated by chlorosulfonic acid as the sulfonating agent as reported earlier [18]. Twenty grams of PEI dissolved in 100 ml of DCE at 60 °C and subsequently the PEI solution was kept at 30 °C was placed in a three-necked, round bottom flask. The solution was stirred using a mechanical stirrer in a nitrogen atmosphere. Then 10 ml of chlorosulfonic acid, diluted with 200 ml of DCE, was slowly added dropwise to the PEI solution by using a dropping funnel within 1 h with vigorous stirring. After being reacted for a definite period, the reaction product, which precipitated in the reaction medium, was dissolved in DMAc at 50 °C, coagulated with excess isopropanol, filtered, washed with isopropanol, and dried at 40 °C in a vacuum oven. The sodium salt form of the product was obtained by soaking it in excess 0.1 mol/l NaOH aqueous solution for 2 days.

2.3. Fabrication of membranes

The blend solutions based on CA and SPEI (total polymer concentration = 17.5 wt%) were prepared by dissolving the two polymers with different compositions of 100/0, 85/15, 75/25 wt% in presence and absence of additive PEG600 (0–10 wt%) in a solvent, NMP (72.5–82.5 wt%) 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.

The method of preparation involved is the same as that of the “phase inversion” method employed in earlier works as reported by other researchers [19]. 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 $24 \pm 1^\circ\text{C}$ and a relative humidity of $50 \pm 2\%$. 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]. Prior to casting, a 21 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–non-solvent interface) in distilled water (non-solvent), was prepared and kept at $20 \pm 1^\circ\text{C}$. 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 s, 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.

2.4. Experimental setup

The ultrafiltration experiments were carried out in a batch type, dead end cell (UF cell–S76–400–Model, Spectrum, USA) with an internal diameter of 76 mm, fitted with Teflon-coated magnetic paddle (as shown in Fig. 1). This cell was connected to a compressor with a pressure control valve and gauge through a feed reservoir.

2.5. Characterization of membranes

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 to the required size for use in the UF 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. 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. The pure water flux is determined as follows [21]:

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

where J_w is the pure water flux ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$), Q the quantity of pure water permeated (m^3) A the membrane area (m^2) and Δt is the sampling time (s).

The water content of the membranes was determined by soaking the membranes in water for 24 h and weighing after mopping with blotting paper. The wet membranes were placed in a vacuum oven at 75°C for 48 h and the dry weights were determined. From these values, the percent water content was derived as follows [22]:

$$\text{water content (\%)} = \frac{\text{wet sample weight} - \text{dry sample weight}}{\text{wet sample}} \times 100$$

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, 345 and 414 kPa after compaction. The resistance of the membrane, R_m was evaluated from the slope of pure water flux (PWF) versus transmembrane pressure difference (ΔP) using the following equation [23]:

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

2.6. Molecular weight cut-off

MWCO is a pore characteristic of membranes and is related to rejection for a given molecular weight of a solute. The molecular weight has a linear relationship with the pore radius or pore size of a membrane [24]. In general, the MWCO of a membrane is determined by the identification of an inert solute, which has the lowest molecular weight and has a solute rejection of 80–100% in steady state UF experiments [25].

Therefore proteins of different molecular weights such as trypsin (20 kDa), pepsin (35 kDa), egg albumin (45 kDa) and bovine serum albumin (69 kDa) were chosen for the estimation of MWCO. All the protein solutions were prepared individually at a concentration of 0.1 wt% in phosphate buffer (0.5 M, pH 7.2) using deionized and distilled water and used as standard solutions and filtered through each membrane individually. The permeate protein concentration was estimated using UV–vis spectrophotometer at a wavelength of 280 nm. The percentage rejection was calculated using the formula:

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

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

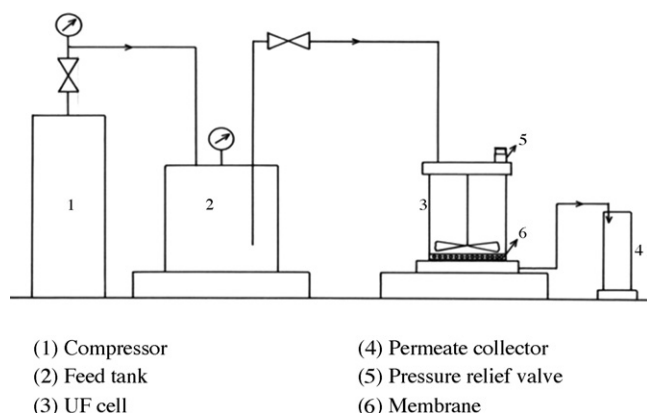


Fig. 1. Schematic diagram of ultrafiltration test kit.

2.7. Morphological studies

The top surfaces of the CA/SPEI blend membranes in the presence and absence of additive, PEG600 were studied with a scanning electron microscopy (SEM) (LEICA Stereoscan, Cambridge, UK). The membranes were cut into pieces of various sizes and mopped with filter paper. These pieces were immersed in liquid nitrogen for 20–30 s and were frozen. Frozen bits of the membranes were broken and kept in a desiccator. These dry membrane samples were used for SEM 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 top surface views of the polymeric membranes.

2.8. 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 complex the 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 [26,27]. These solutions were then used for the rejection studies using pure CA and CA/SPEI 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 were analysed for the concentration of the metal ions using an atomic absorption spectrophotometer (Perkin-Elmer 3110). The percentage metal ion rejection (%SR) was calculated with the same formula as that for protein rejection.

3. Results and discussion

Ultrafiltration membranes based on CA and SPEI with various compositions were prepared. The composition of SPEI in blend solution was varied from 0 to 25 wt% of the 17.5 wt% polymer concentration in the casting solution. Furthermore, an increase in SPEI composition in the casting solution beyond 25 wt% of the 17.5 wt% polymer concentration resulted in phase separation. Hence, the composition of SPEI in the blend casting solution was restricted up to 25 wt% of the 17.5 wt% of polymer concentration in the casting solution. Thus, compositions of 0–25 wt% SPEI in CA were selected for further studies. Further the hydrophilic polymeric additive PEG600 concentrations in the polymer casting solution were varied from 2.5 wt% in an increment of 2.5 wt% for all the polymer blend solutions, and the maximum compatible additive concentration was found to be 10 wt%. Beyond this concentration, all the polymer blend solutions exhibited incompatibility with the additive, as soon as solution blending was mechanically arrested. Hence,

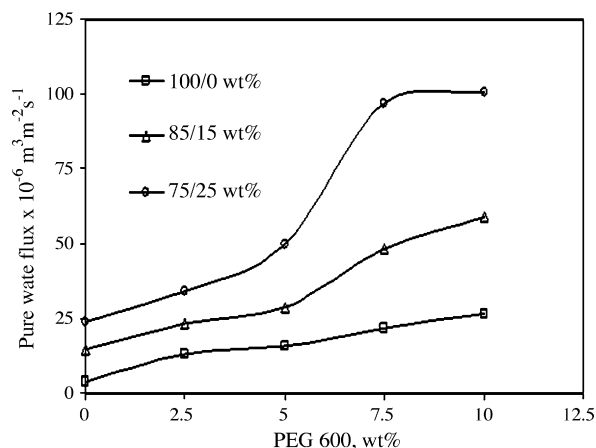


Fig. 2. Effect of concentration of PEG600 on pure water flux for CA/SPEI blend membranes.

the maximum additive concentration in the present system was restricted to 10 wt%. The effects of polymer blend composition and additive concentration on PWF, water content, and hydraulic resistance (R_m) on the cast membrane were studied. The MWCO of these membranes and the separation of toxic metal ions in aqueous solutions are also discussed.

3.1. Pure water flux and water content

The influence of SPEI content and PEG600 concentration in the casting solution of CA/SPEI blend membranes on the PWF and water content are depicted in Figs. 2 and 3, respectively. The pure water flux of cellulose acetate is $3.8 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ and water content is 79.64% in absence of both SPEI and PEG600. Further, the PWF increases from 3.8 to $26.5 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ and the water content increases from 79.64 to 81.12% with increase in the concentration of pore former, PEG600 from 0 to 10 wt% in 100% pure cellulose acetate membrane. Similar observation had also been reported by Schchori and Grodzinski [28] for polyether–polyamide membranes. Further the incorporation of SPEI in to the cellulose acetate up to 25 wt%, as expected, increases the flux to $24 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$

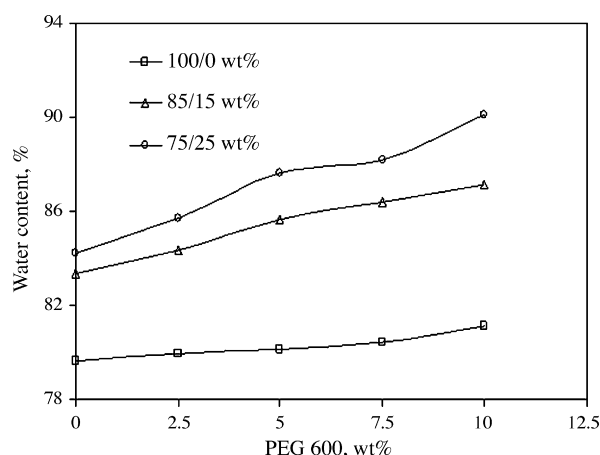


Fig. 3. Effect of concentration of PEG600 on water content for CA/SPEI blend membranes.

in absence of PEG600 which is due to the macro phase separation of blend membrane which in turn enhances the pore size of membranes [29]. When increasing PEG600 concentration from 0 to 10 wt% an upward trend in PWF from 24 to $100.6 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ for CA/SPEI blend composition of 75/25 (wt%), have been observed. Similarly, the percent water content increases from 84.21 to 90.10% for the blend composition of 75/25 (wt%), when increasing the PEG600 concentration from 0 to 10 wt%, the increase in PEG600 concentration in blend may favor the formation of larger pore size of the membrane. When the concentrations of both SPEI and PEG600 increased simultaneously, the repulsive forces between polymer segments along with leachability of PEG600 are enhanced and this favors the formation of macrovoids due to occurrence of more number of large size pores [30] resulting in higher pure water flux and percent water content at higher SPEI and PEG600 content in cellulose acetate membrane. Similar trends were also reported by Malaisamy et al. [31].

3.2. Membrane hydraulic resistance

In order to determine the membrane hydraulic resistance (R_m), membranes prepared from cellulose acetate and blends of CA/SPEI in the presence and absence of PEG600 after compaction, under steady state flux conditions, were subjected to different transmembrane pressures. The pure water flux at different transmembrane pressures of 69–414 kPa was determined by the time required for permeation of a known volume of water. As the operating pressure (transmembrane pressure difference) increases, the driving force for the water permeation also increases and hence an increase in pure water flux is observed. From Fig. 4, it is evident that the R_m decreases from 92.59 to $13.26 \times 10^6 \text{ kPa}/(\text{m}^3 \text{ m}^{-2} \text{ s}^{-1})$ for pure cellulose acetate (100%) when PEG600 concentration increases from 0 to 10 wt%. It is due to the instability of pores, which are formed by leaching out the PEG600 during the coagulation process in membrane casting technique. Similar trend had also been observed for blend membranes prepared from 15 and 25 wt% SPEI with CA in the presence of additive, PEG600. Thus, blend membrane resistance of CA/SPEI (85/15, wt%) and CA/SPEI (75/25,

wt%) have reduced from 21.1 to $5.93 \times 10^6 \text{ kPa}/(\text{m}^3 \text{ m}^{-2} \text{ s}^{-1})$ and $14.29\text{--}3.51 \times 10^6 \text{ kPa}/(\text{m}^3 \text{ m}^{-2} \text{ s}^{-1})$, respectively, when PEG600 concentration in blend polymer casting solution increased from 0 to 10 wt%.

This decrease in membrane hydraulic resistance may be explained by the fact that an increase in the proportion of SPEI in the blend not only increases the amorphous nature of the membranes, but also enhances the pore size to a greater extent owing to an extended segmental gap between polymer chains which leads to the decrease in the value of R_m [32]. Furthermore, the presence of PEG600 increases this gap further leading to the formation of macrovoids on the membrane surface resulting from faster rate of leaching of PEG600 at higher concentration gradient from casting solution during gelation. This in turn results in lowering the membrane resistance at higher PEG600 concentration [33].

3.3. Molecular weight cut-off

Pure cellulose acetate membrane without additive, PEG600, had the MWCO of 20 kDa. MWCO values are dependent on the polymer composition. Thus, in the CA/SPEI blend membranes, in absence of additive, as the SPEI content was increased to 25 wt%, the MWCO value also increased to 69 kDa. This result has good correlation with the permeability results of the membrane. It was believed that the incorporation of additive in casting solution would alter the MWCO of all the CA and CA/SPEI membranes. Thus, for pure CA (100%) membranes, when the additive concentration was increased, from 2.5 to 10 wt%, the MWCO values enhanced from 45 to greater than 69 kDa. Various additive concentrations have significant effect on MWCO of the CA/SPEI blend membranes. For a given blend composition, an increase in the additive concentration increased the MWCO linearly. Similar observations were also observed for the other blend composition. Further, for a given additive concentration of 2.5 wt%, as the SPEI content in the blend was increased to 25 wt%, the MWCO value also increased to greater than 69 kDa. Corresponding increasing values were also observed for the other additive concentrations. Similar results were reported for cellulose acetate/sulfonated polysulfone blend membranes by Malaisamy et al. [25].

3.4. Morphological studies

The surface structure of a flat sheet, ultrafiltration membrane, is the most critical part, helping to identify the role of the membrane in the mechanism of permeation and rejection. SEM is important for the determination of morphology of the membranes. To attain high performance membranes for specific applications, it is essential to manipulate the morphological structures of the membranes [34]. Hence, the morphological studies of the blend membranes were made using SEM. The SEM micrographs of top surface of CA/SPEI (75/25, wt%) blend membranes in the presence and absence of additive, PEG600 are shown in Fig. 5(a–c). It shows that the membrane pore size become larger with the increase of SPEI and PEG600 in the

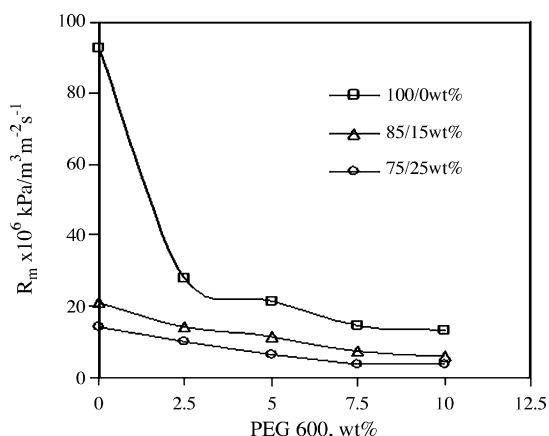


Fig. 4. Effect of concentration of PEG600 on hydraulic resistance (R_m) for CA/SPEI blend membranes.

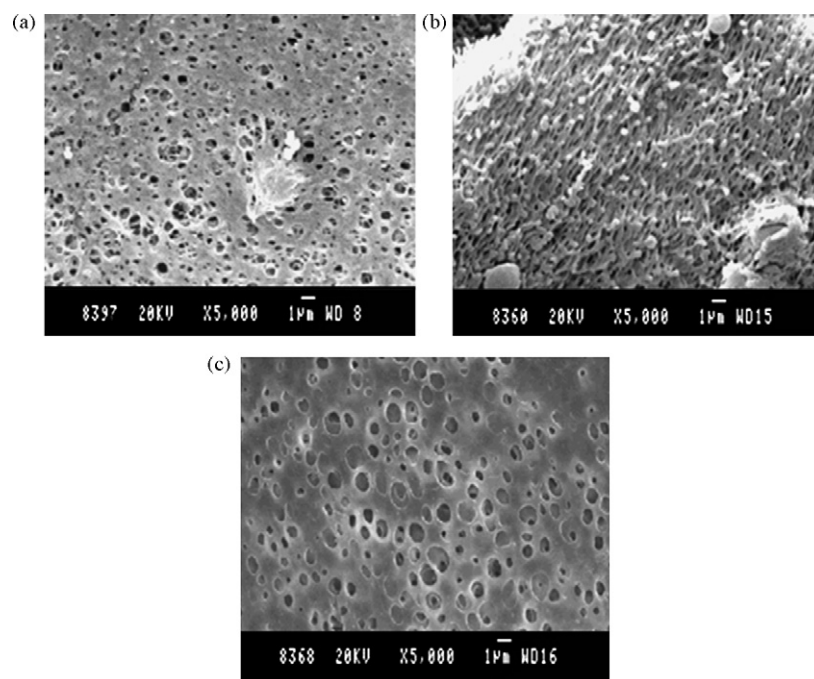


Fig. 5. SEM micrographs of top surface of CA/SPEI (75/25, wt%) blend membranes with different concentrations of additive, PEG600. (a) 0 wt% (5000 \times), (b) 5 wt% (5000 \times) and (c) 10 wt% (5000 \times).

blend composition. A similar trend was observed in the blend membranes of cellulose acetate and sulfonated polysulfone [25].

3.5. Metal ion rejection

Ultrafiltration processes cannot be directly applied for ionic level rejections owing to the larger pore sizes of the membranes, which are not suitable to reject ions. Hence, to enhance the size and consequently the rejection of heavy metal ions, a water-soluble chelating polymer polyethyleneimine, was used for the complexation of metal ions such as Cu(II), Ni(II), Zn(II) and Cd(II) and were subsequently rejected individually from aqueous streams by the CA/SPEI blend ultrafiltration membranes. The CA/SPEI blend membranes of 100/0, 85/15 and 75/25 (wt%) composition in the absence and in the presence of various concentrations of additive, PEG600, from 0 to 10 wt%, were subjected to the rejection of metal chelates and the results are discussed.

3.5.1. Effect of concentration of SPEI

The separation of metal ions was found to be influenced by the polymer composition. The separation of metal chelates of Cu(II), Ni(II), Zn(II) and Cd(II) by the 100/0, 85/15, and 75/25 (wt%) CA/SPEI blend membranes in the absence and presence of additive is shown in Figs. 6 and 7(a–c). The pure cellulose acetate membranes in the absence of additive yielded the highest separation of 98.5% for Cu(II) ion. The other metal ions Ni(II), Zn(II) and Cd(II) also exhibited their highest separations of 95.8, 93.4, and 90.6%, respectively. The CA/SPEI blend membranes, on the other hand, showed decreasing separations from 92.2 to 80.1% for Cu(II) metal ion when the SPEI content was increased from 15 to 25 wt% in the blend in the absence of

additive as shown in Fig. 6. Similar trends were observed for all other metal ions. This decreasing order of separation with increasing SPEI content in blend might be due to the inhomogeneity arising as a result of the higher SPEI content creating voids in the blend membranes. Similar results were reported for polyurethane/sulfonated polysulfone blend membranes by Malaisamy et al. [35].

In all of the CA and CA/SPEI membranes, Cd(II) exhibited a lower percent separation than Zn(II), which, in turn, was lower than that of Ni(II). Copper exhibited higher separation because of its stronger complex formation with the polymeric ligand polyethyleneimine [12]. Also the trend coincides with the dependence of molecular or complex size on the rejection behavior of the metals ions.

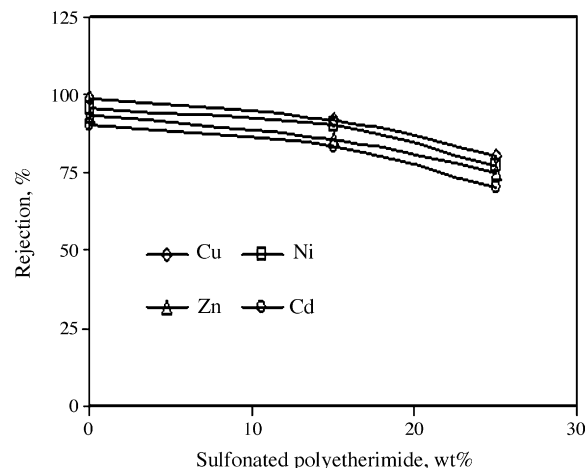


Fig. 6. Effect of concentration of SPEI on rejection of metal ions for CA membranes.

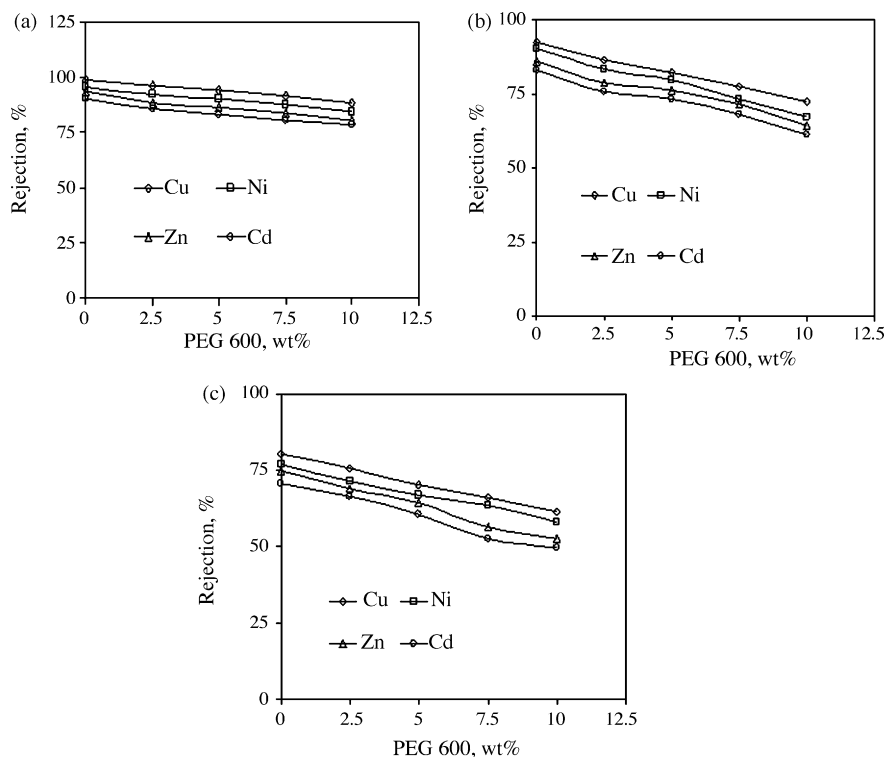


Fig. 7. Effect of concentration of PEG600 on rejection of metal ions. (a) Pure (100 wt%) CA, (b) 85/15 (wt%) CA/SPEI and (c) 75/25 (wt%) CA/SPEI.

3.5.2. Effect of concentration of PEG600

The effect of concentration of PEG600 on the metal ion rejection behavior of pure CA and CA/SPEI membranes were determined, and it was observed that pure CA membranes exhibited a decrease in rejection behavior from 96.1 to 88.6% when the additive concentration was increased from 2.5 to 10 wt% for copper ions as shown in Fig. 7(a). In CA/SPEI blend membranes of 85/15 (wt%) composition, for Cu(II) metal ion, as the additive concentration was increased from 2.5 to 10 wt%, the rejection decreased linearly from 86.2 to 72.4% as shown in Fig. 7(b). Blend membranes with 75/25 (wt%) CA/SPEI composition exhibited a similar trend as shown in Fig. 7(c). The decrease in rejection upon the increase of PEG600 concentration in the casting solution may be due to the fact that the higher amount of non-solvent additive leads to rapid formation of larger pores during gelation because of thermodynamical instability and to lower the free energy of the system [36].

Similarly at 2.5 wt% additive concentration, when the SPEI composition was increased from 15 to 25 wt% in the blend, the rejection decreased from 86.2 to 75.8% for Cu(II). This trend was observed for all the additive concentrations and may be due to the fact that the SPEI matrix has a larger segmental gap due to its swelling behavior and that the solvent non-solvent replacement during gelation takes place rapidly leading to the formation of macro pores. The decrease in rejection in the presence of additive may be attributed to the rapid leaching out of pore former creating larger pores [37].

For all of the membranes, irrespective of their polymer composition and additive concentration, Cd(II) showed the lowest

rejection, whereas Cu(II) exhibited higher separations than the other metal ions. This highest separation of Cu(II) might be due to the formation of stronger complexes with polyethyleneimine through stable short bonds, in accord with the John–Teller effect [38].

3.6. Metal ion solution permeate flux

The permeate flux of metal ion solution is essential to specify the product rate and predict the economics of the membrane process. The metal ion solution permeate fluxes were measured simultaneously during rejection experiments for 100/0, 85/15

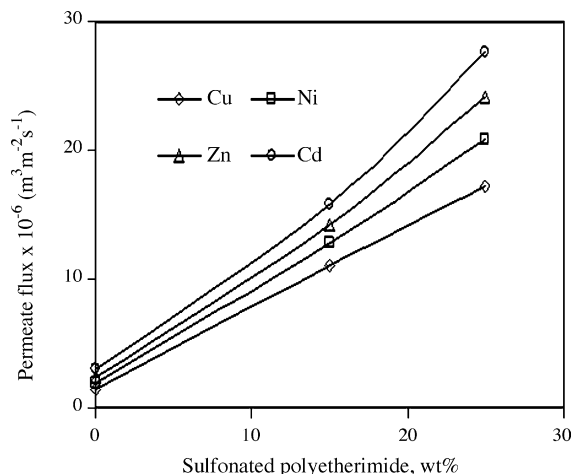


Fig. 8. Effect of concentration of SPEI on permeate flux of metal ions for CA membranes.

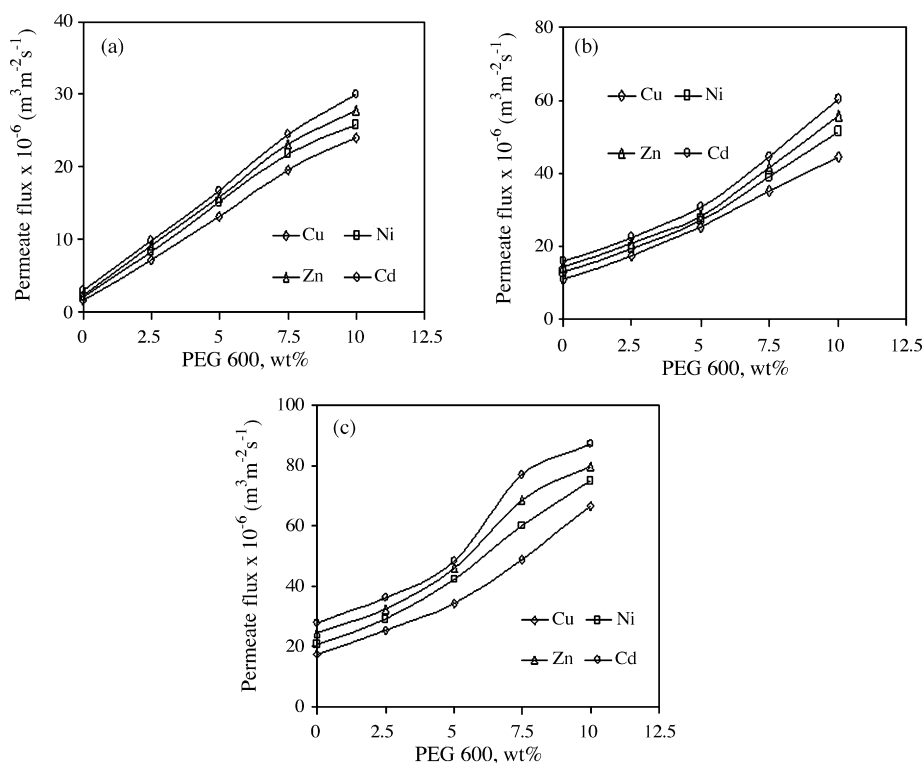


Fig. 9. Effect of concentration of PEG600 on permeate flux of metal ions. (a) Pure (100 wt%) CA, (b) 85/15 (wt%) CA/SPEI and (c) 75/25 (wt%) CA/SPEI.

and 75/25 (wt%) CA/SPEI membranes in the absence and presence of additive, PEG600.

3.6.1. Effect of concentration of SPEI

The pure (100%) CA membrane offered a lower flux value of $1.50 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ for Cu(II) and a higher value of $2.94 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ for Cd(II). When the SPEI content was increased from 15 to 25 wt%, the flux of Cu(II) increased from 11.08 to $17.25 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ as shown in Fig. 8. All the metal ions showed similar trends for the system. The increase in flux upon increase of SPEI composition may be due to the formation of higher hydrophilicity incorporated by sulfonated polyetherimide [39].

3.6.2. Effect of concentration of PEG600

As evidenced from Fig. 9(a–c), the water soluble additive played a major role in enhancing the permeate flux values of CA/SPEI blend membranes. An increase in permeate flux was expected for all the metal ion solutions upon increase in additive concentration.

In the pure (100%) CA membrane, as the additive concentration increased from 2.5 to 10 wt%, the flux also increased significantly from 7.19 to $23.92 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ for Cu(II) ions, as shown in Fig. 9(a). Further, for a given blend composition of 85/15 (wt%) CA/SPEI, at 2.5 wt% additive, Cu(II) yielded a flux of $17.08 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ which is higher than for the membrane of same composition without additive. The flux further increased to 25.03, 35.31 and $44.64 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$, respectively, when the additive concentration was increased to 5, 7.5 and 10 wt% as shown in

Fig. 9(b). Blend membranes with 75/25 (wt%) CA/SPEI blend composition also exhibited a similar trend as shown in Fig. 9(c). This increase in flux due to increase in additive is, obviously, because of the pore former which got leached out during gelation, creating pores. The order of flux for the metal chelates is

$$\text{Cd} > \text{Zn} > \text{Ni} > \text{Cu}$$

which is primarily due to the larger metal chelate size for Cu and lowest size for Cd.

4. Conclusions

In this work, toxic heavy metal ion removal has been studied using modified cellulose acetate membranes prepared by blending CA with SPEI and PEG600 in different compositions. Blending of cellulose acetate with SPEI in the presence and absence of PEG600 resulted in blend membranes with enhanced ultrafiltration membrane characteristics such as higher water content and lower hydraulic resistance coupled with higher pure water flux. The MWCO results obtained from protein rejection studies demonstrate that the MWCO of blend membranes increases with increasing concentration of SPEI and PEG600 in the casting solution. In general, all the modified membranes prepared from CA/SPEI polymer blends in the presence of PEG600 exhibited improved permeate flux for metal ion separation compared to the pure CA membranes. Permeate flux increases as a function of concentration of SPEI and PEG600. Due to the higher porosity, CA/SPEI blend membranes in the presence of PEG600 had higher permeate flux compared to pure CA blend

membranes. However, increasing concentrations of SPEI and PEG600 in the membrane casting solution resulted in decreased rejection of metal ions. This is due to the formation of pores by the addition of hydrophilic SPEI and pore former PEG600. The rejection of metal ions through CA/SPEI blend membranes in the presence of PEG600 was lower than that of pure CA membranes. The extent of rejection of metal ions follows the order $\text{Cu(II)} > \text{Ni(II)} > \text{Zn(II)} > \text{Cd(II)}$, which depends on the complexation ability to form macromolecules and ligand-field stability of individual metal ions.

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