



Preparation and Performance of PU/Cpsf Blend Ultrafiltration Membranes for Removal of Heavy Metal Ion Rejection Studies

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HIGHLIGHTS

- Polymer blend membranes composed of polyurethane and carboxylated polysulfone fabricated
- An additive polyethylene glycol 600 is used for morphology-controlled membranes
- PU/CPSf (80/20 and 75/25 %) concentration was found to be optimum
- Toxic heavy metal ions were separated by complexing them with polyethyleneimine.

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ABSTRACT

The performance of membranes for a specific application can be determined with the help of structural properties such as molecular weight cut-off (MWCO), morphology, and pore statistics. Heavy metal ions from aqueous streams can be separated with the help of ultrafiltration membranes. In the presence and absence of the various components of the additive poly (ethylene glycol) 600, MWCOs and pore statistics of polyurethane (PU) and carboxylated polysulfone (CPSf) blend ultrafiltration (Total Polymer Concentration = 17.5 wt %) were studied with the help of dextran of various molecular weights ranging from 19 to 150 kDa. The derived pore size, pores number, and porosity have a remarkable relationship with the MWCO, morphology, and the flux of the membranes. The blend membranes rejected certain toxic divalent heavy metal ions such as copper, cadmium, nickel, and zinc by complexing them into a polymeric ligand, poly(ethyleneimine) (PEI). The influence of the compositions of the polymer blend and concentrations of the additive on metal ions' removal and permeate flux are discussed.

1. Introduction

Important membrane properties that decide the mechanism, permeation, and application, are pore statistics, morphology, and MWCO [1,2]. Membrane efficiency is evaluated by analyzing its critical properties (i.e., morphology, MWCO, phase-inversion kinetics, etc.) for various separation processes, such as ultrafiltration, microfiltration, and reverse osmosis membrane systems [Velu et al., [3]Arthanareeswaran et al., [4]Chin-San and Liao[5], Monika et al.,[6] and Sivakumar et al. [7] In addition, the average pore size, MWCO, and morphology were performed for polyacrylonitrile/polyurethane blend membranes and applied for water purification (Swapna Rekha Panda and Sirshendu De, 2015[8]). The parameters mentioned above are major factors that decide the membrane applications, viz., pharmaceutical, food, and biotechnological applications.

In general, the surface of the membrane is composed of cylindrical pores and is defined by pore size distribution value. The size of the solute molecules should be smaller than the actual membrane pore diameter and can be penetrated and travel through the membrane Benjamin J. McCoy [9]. Most commercially available membranes are specified by their MWCO or pore size value Burgal et al. [10]. They are important parameters affecting the separation characteristics of the ultrafiltration membranes Klimonda and Kowalska. Pore statistics are evaluated and summarized using major existing methods, bubble pressure mercury porosimetry, breakthrough, electron microscopy, solute retention challenge, thermometry, adsorption base methods, NMR measurements, and permporometry, Khulbe et al. [11] Most descriptions involve a combination of these methods. The incorporation of additives alters membrane hydrophilicity and porosity Rahimpour et al. [12]

In the current investigation, the solute retention method is used to determine the pore statistics due to its simplicity and advantage in estimating MWCOs. Further, the filtration characteristics of dextran with various molecular weights can also be utilized to correlate pore statistics and MWCO, Mkhedize et al. [13]

Chemical, electro coating, food, pharmaceutical, biotechnological, and finishing industries pose a severe threat to the environment and human health because of waste stream disposal, especially hazardous or valuable components (heavy metal ions). Toxic heavy metals such as copper, nickel, zinc, and cobalt are separated by a polyelectrolyte binding the target metal ions with macromolecular compounds (water-soluble). The subsequent UF membrane separation of the bound metals from the unbound components was carried out [Volchek K., 1993]. MF-UF adsorptive polyamide-6 membranes were fabricated and used for copper ions removal Ayman et al. [13] Huang and Feng carried out the influence of operating parameters on the separation of heavy metals from binary mixtures via polymer-enhanced UF. The effective polymer blend composition for heavy metal ion rejection, reported by the cellulose acetate and polyurethane blend UF membranes, was proved to have better results than individual cellulose acetate, Sivakumar et al. [7]

Similarly, modified polyethersulfone with gelatin ultrafiltration membranes performed better for tannery and distillery wastewater treatment [Velu et al.][3] PU/CA blend membranes were prepared and used in treatment of the wastewater of the textile industry Zavastin et al. [14] Hybrid ultrafiltration polymeric membranes with or without carrier were utilized for oil/water separation and recovery of heavy metals (Melita, Larisa, et al.[15] Similarly, PVDF/PU blend membranes were developed and showed improved pervaporation performance concerning pure PU membranes in phenol wastewater treatment Yanhui et al. [16] Exploration of membrane-based technology in blood purification therapy was presented by Nie et al. [17]

Membranes are based on polyurethane (PU), carboxylated polysulfone (CPSf), and their characterizations and performances Latha C.S. et al. [18]. The first part of this investigation mainly dealt with preparing polyurethane and carboxylated polysulfone (PU/CPSf) blend UF membranes and their specifications. PU/CPSf blend membranes were fabricated using different N, N, dimethyl formamide as a solvent, and poly (ethylene glycol) 600 of different concentrations (as additive- pore former) by a phase inversion technique [Latha C.S. et al., 18]. Compositions of 80/20 and 75/25 % at 0, 2.5, 5, and 7.5 weight percentage PEG 600 concentration were compatible and subjected to compaction, water content, pure water flux, membrane hydraulic resistance, and morphological studies. The results were discussed regarding the effect of polymer blend composition and additive concentrations. The morphological studies were carried out by scanning electron microscope. Based on the literature survey, the key objective of this investigation is to evaluate the influence of the composition of polymer blend (polyurethane and carboxylated polysulfone) and PEG 600 concentration of polymeric additive on MWCO, pore statistics, and the toxic heavy metal ion such as Cu^{2+} , Ni^{2+} , Cd^{2+} , and Zn^{2+} rejection and permeation process. The morphological characterization discussed in the first part is compared with pore statistics results.

2. Experimental Studies

2.1 Materials

Dextran with molecular weights 19, 42, 77, and 150 kDa were purchased from Sigma-Aldrich Company (USA) and kept at a suitable temperature before use. In addition, phenol and sulfuric acid were purchased from SRL Chemicals Ltd. and used for the analysis of dextran.

Poly (ethyleneimine) with ($M_w = 6\ 00\ 000 - 10\ 00\ 000$) 50 % aqueous solutions were purchased from Fluka Chemicals, AR grade (Steinheim), and used as aqueous solutions with 1 weight % for the metal complexation studies.

Copper (II) sulfate (AR), Zinc (II) sulfate (AR) and Nickel (II) sulfate (AR), were purchased from Merck Ltd. and used as such for the preparation of aqueous metal ion solutions. Cadmium (II) chloride (AR) was purchased from Qualigens Fine Chemicals Ltd., India.

A deionized and distilled water was used to prepare dextran, metal ion solution, and 1 weight % PEI aqueous solution.

2.2 Preparation of membranes

The blend PU and CPSf polymers solutions (total polymer content 17.5 wt. %) were prepared by dissolving them with various contents as shown in Table 1 with and without PEG 600 additive in a dimethyl formamide (DMF) under mechanical stirring in a round-bottomed flask at 40°C for 3– 4 h. The homogeneous polymeric solution obtained was kept to stand for three hours in an air-tight condition for air bubbles elimination. The total concentration of the polymers was fixed at 17.5 wt % to have a balanced polymeric solution viscosity to prepare membranes between a spongy like and a high microvoids like structure. The membrane thickness was fixed at 0.22 ± 0.02 mm, measured with a micrometer. The casting and gelation conditions were kept constant throughout because the thermodynamic conditions would largely affect the morphological structure and then on the resulting membranes performance. Before the membrane casting, a 2-L freezing bath with 2.5 (v/v) of solvent DMF (to reduce the rate of solvent-nonsolvent demixing process and microvoids) and 0.2 wt % SLS surfactant (to reduce surface tension at the interface of polymer-nonsolvent) in distilled water as nonsolvent, was prepared and maintained at $20 \pm 1^\circ\text{C}$. The membranes were cast over a glass plate using a doctor's blade. After membrane casting, the solvent in the cast film was kept to evaporate for 30 s, and the cast film and the glass plate were gently moved in the freezing bath. After 30 min of casting solidification, the membranes were transfer from the freezing bath and washed thoroughly with pure water to make sure that all DMF and surfactant removed from the membranes. The membrane sheets were subsequently kept in pure water containing 0.1% formalin solution to prevent microbial growth.

2.3 Characterization

2.3.1 Pure water flux

The pure water flux was studied at a transmembrane pressure of 345 kPa. The flux was measured under steady-state flow

$$J_w = \frac{Q}{A(\Delta t)} \quad (1)$$

where Q is the quantity of permeate collected (L), J_w is the water flux ($L\ m^{-2}\ h^{-1}$), T is the sampling time (h), and A is the membrane area (m^2).1277

2.3.2 Pore statistics

Ultrafiltration technology is used with a different molecular weight of dextran to calculate PU/CPSf membranes pore size, porosity, and the number of pores. Throughout the investigation, dextran solutions concentration of 1 wt % was maintained as feed because permeate flux declines with increasing feed concentration, affecting rejection performance (Hong S., 1997). In addition, the molecular weight of solute, which has a solute rejection value above 80 %, was used to evaluate the average pore size, R of the membranes using the following equations.

$$\% SR = [1 - (C_p/C_f)] \times 100 \quad (2)$$

Where: %SR- percentage Solute Rejection of PEG; C_p and C_f are concentration (ppm) of permeate and feed, SR- Solute Rejection respectively. The analysis of dextran was performed by UV-Visible spectrophotometer at $\lambda_{max} = 485\ nm$.

$$\% SR = 100(\alpha/R), \quad (3)$$

%SR- percentage Solute Rejection of Dextran;

R - average pore radius of the membrane (\AA)

α - average pore radius of solute and constant for each molecular weight.

The surface porosity or percentage porosity (ϵ) of the membrane can be calculated by following the slit model and assuming membranes as symmetric skin types using Javaid Zaidi S.M 19].

$$\epsilon = (3\pi\eta J/R\Delta P) \times 100 \quad (4)$$

η - viscosity of permeate (centipoise)

J - flux of the solvent in the presence of solute ($Lm^{-2}h^{-1}$)

R - average pore radius (\AA)

ΔP - applied pressure.

Using the values of ϵ and R, the number of pores per unit area, n, can be calculated using this Equation (5).

$$n = \epsilon/\pi R^2 \quad (5)$$

2.3.3 Molecular weight cutoff (MWCO)

MWCO of PU/CPSf membrane is investigated using an inert solute (with the lowest molecular weight) and a solute rejection of 80 – 100 % in a steady-state ultrafiltration module Da Silva Burgal et al. [10] Low molecular weights were chosen in the range of 19, 42, 77, and 150 kDa compounds (carbohydrate, dextran). The rejection percentage of blend and pristine membranes was determined by UV-Visible spectrophotometer (Robert E.J., 1983) at $\lambda_{max} = 485\ nm$. The concentration of dextran was maintained at 1.0 wt %.

2.3.4 Ion Exchange Capacity (IEC)

The dried sample of the membrane is immersed in saturated sodium chloride solution for a day to liberate the H^+ ions (Javaid Zaidi S.M.,)[19]. The mixture was then titrated with 0.1 M sodium hydroxide (NaOH) solution to determine the H^+ content, and the IEC was calculated as follows

$$IEC = (\text{NaOH consumed} \times \text{Molarity of NaOH}) / \text{Weight of dried membrane (meq/g)} \quad (6)$$

2.3.5 Metal ion rejection

Metal ion rejection and flux analysis were carried out using an ultrafiltration kit (Amicon model 8400, Millipore Ltd., Bangalore, India) of 450 ml capacity and holdup volume of 10 ml at room temperature. The active membrane area of $38.5\ cm^2$ with the applied pressure was 345 kPa, and the agitation/stirring was kept uniform.

Aqueous metal ion solutions (Cu^{2+} , Ni^{2+} , Cd^{2+} , and Zn^{2+}) were prepared at approximate concentrations of 1000 ppm in 1 wt % solution of polyethylene imine (PEI) in deionized water. The aqueous solution's pH was adjusted to 6 ± 0.25 by adding a

small amount of either 0.1 M HCl or 0.1 M NaOH. PEI and individual metal ion solutions were thoroughly mixed and left standing for 5 days to complete the binding process Huang, Yifeng and Feng, Xianshe [20], Sivakumar et al. [6]

During the Ultrafiltration process, the first few ml of permeate were discarded for each experimental run. Then, the pre-setting (compacting) routine of membranes (maintain constant flux), each metal ion-PEI chelate solutes were run using an ultrafiltration kit at 345 kPa (with compressed air). Permeate flux and rejection % were determined by analyzing concentrations of the feed and permeate streams.

The metal ion concentrations in permeate and feed were measured using an Atomic Absorption Spectrophotometer (Perkin-Elmer 2380), and the pH of the feed and permeate solutions using an Elico pH meter. In the absence of metal ions, PEI concentration was confirmed by UV-Visible Spectrophotometer (Hitachi model U- 2000) at $\lambda_{\max} = 269$ nm.

3. Results and Discussion

Uniform continuous agitation is maintained to avoid concentration polarization and cake formation during dextran rejection analysis and calculate pore statistics and MWCOS. Without proper stirring/agitation, the membrane surface would influence flux values and ultimately affect the partition coefficient and aggregate size of pores K. C. Khulbe et al. [11]

Due to the larger pore size, it is impossible for an ionic level rejection of metal ions. To enhance the size and rejection of metal ions, a water-soluble chelating polymer polyethyleneimine (PEI) acts as a complexing agent for metal ions (Cu^{2+} , Ni^{2+} , Zn^{2+} , and Cd^{2+}). Every metal ion solution was subjected individually to aqueous streams through PU/CPSf blend membranes. As a result, PU/CPSf membranes of 80/20, 75/25 % composition in the presence and absence of various additive (PEG 600) concentrations (0 to 7.5 wt %) undergo rejection of metal chelates and the results displayed in Figures 1 and 2. All the experiments were conducted in triplicate to get reproducibility with a small negligible deviation.

Table 1: Pore statistics and Molecular weight cut-off of PU/CPSf blend Membranes

Blend composition		PEG 600, Wt %	Pore radius, R(Å)	Porosity, ϵ (%)	No. of pores/cm ² , n(X 10 ⁻¹⁰ m)	MWCO, (kDa)
PU	CPSf					
80	20	0	32.68	0.0112	2.941	42
75	25	0	61.86	0.0184	1.648	42
80	20	2.5	47.14	0.019	1.728	42
75	25	2.5	66.1	0.0206	1.187	77
80	20	5.0	49.4	0.021	1.632	42
75	25	5.0	69.34	0.0241	1.056	>77
80	20	7.5	50.12	0.0383	1.56	>42
75	25	7.5	73.02	0.0434	0.943	>77

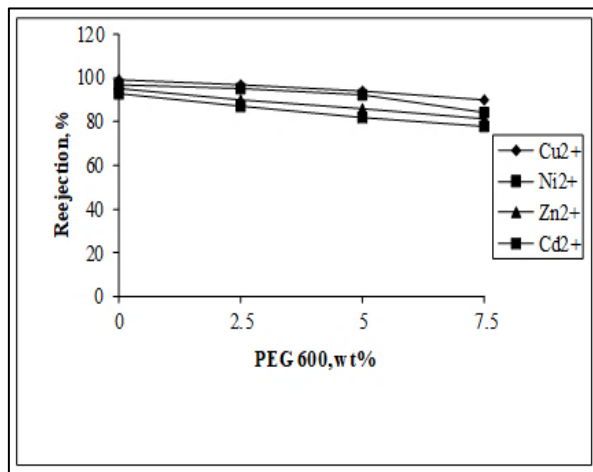


Figure 1: Effect of PEG 600 concentrations on the rejection of metal chelates of PU/CPSf (80/20%) blend membranes

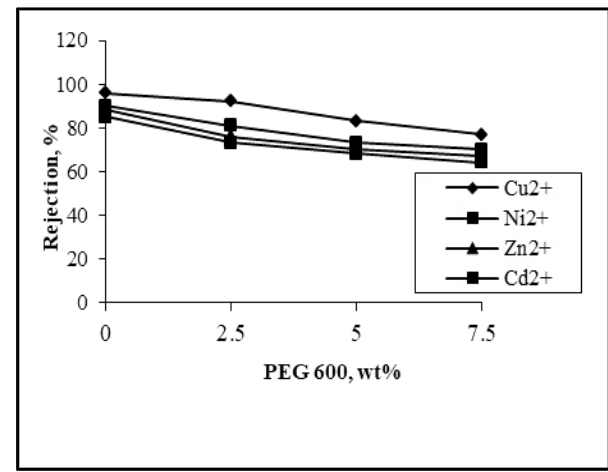


Figure 2: Effect of PEG 600 concentrations on the rejection of metal chelates of PU/CPSf (75/25%) blend membranes

3.1 Pore Statistics

3.1.1 Effect of Polymer blend composition

In polymer composite blend, the concentration of CPSf increases from 20 to 25 %, marked changes observed in pore statistics data. In addition to the above, CPSf composition increment (from 20 to 25 %) also impact the pore radius increase

(from 32.68 Å to 61.86 Å) shown in Table.1 . The percentage porosity has increased. In contrast, the number of pores per unit area decreased (from 2.941×10^{-10} to 1.648×10^{-10}) with CPSf concentration increase (from 20 to 25 %), as shown in Table 1. The total number of pores is lesser at 75/25 % composition without additives. An increase in pore radius, porosity, and decrease in several pores per unit area result from CPSf addition in the system. Another reason may be the phase separation between polymeric components and the formation of inhomogeneity that leads to cavities/voids in the membrane sub-layer (Brousse C. L., 1976). A similar trend was observed in flux values, which matches our previous studies (Latha C.S. et al., 2006).[18]

3.1.2 Effect of Additive concentration

The addition of PEG 600 in the polymer membrane blend affects the pore statistics. An increase of CPSf from 20 to 25 % at 2.5 wt % PEG 600 concentration enhances porosity and pore radius. In contrast, the number of pores per unit area decreases. This may result from large size pore formation in smaller numbers due to CPSf and PU inhomogeneity in the presence of PEG 600 (Young T.H., 1998). The same trend is obtained for 5 and 7.5 wt %, and similar performance was observed for flux measurements, too Latha C.S. et al. [16]

3.1.3 Molecular Weight Cutoff

MWCO of a membrane is a parameter that specifies the membrane's rejection behavior and is determined by using an inert solute of stable molecules with various molecular weights. Therefore, the MWCO of a membrane was evaluated by identifying an inert solute with the lowest molecular weight and a solute rejection of 80 – 100 % in steady-state conditions (Balakrishnan M., 1993) UF experiments. Thus, dextrans of different molecular weights such as 19, 42, 77, and 150 kDa were chosen to calculate the MWCO of all PU/CPSf membranes.

3.1.4 Effect of Polymer blend composition

The membrane of 80/20 % with 0 wt % additive PU/CPSf composition showed the highest separation for 42 kDa, and the rejection was very low for 19 kDa dextran, i.e., less than 80 %. Hence MWCO of 80/20 % blend membrane was considered as 42 kDa. Similarly, 75/25 % PU/CPSf composition membrane in the absence of additive shows a higher percentage separation of 92 % for 42-kDa dextran, whereas it exhibits a lower separation percentage for dextran of 19 kDa.

3.1.5 Effect of Additive concentration

Molecular weight cut-off values changed when the additive was included in the PU/CPSf blend casting solution. In the case of additive concentration, increase from 0 to 7.5 wt % at 2.5 %, there were no appreciable changes in MWCO, and percentage separation of 42 kDa falls in the least needed 80 % separation to fix MWCO Table 1. For PU/CPSf (75/25 %) membranes, when additive concentration is enhanced to 2.5 wt %, MWCO also shows an increase of 77 kDa. On further increase in additive showed no appreciable change in MWCO. This phenomenon concludes that the increase of additive increases the pore size. Therefore, an increase in MWCO with an additive concentration increases pore size. The probable reason may be the initiation of surface tension gradient in gelation medium for the convective mass transfer phenomena (non-solvent to solvent or vice versa). This convective flow is influenced by a higher density of the nascent membrane, which leads to the formation of macro voids and lowers MWCO, similar results reported for PU membranes in literature Brousse C. L., 1976 and Malaisamy R. et al., [21]

3.2 Ion Exchange Capacity (IEC)

IEC for all membranes was calculated by a simple titration method.

3.2.1 Effect of polymer blend composition

IEC for 80/20 PU/CPSf blend membrane was found to be 1.84 meqg^{-1} , and for 75/25 PU/CPSf blend membrane is 2.59 meqg^{-1} at 0 % additive. This increase may be due to a higher concentration of CPSf in the blend, which may liberate more H^+ ions.

3.2.2 Effect of additive concentration

When the PEG 600 at 2.5 wt % showed the IEC of 80/20 PU/CPSf slightly increased to 2.3 meqg^{-1} , 75/25 PU/CPSf was found to be increased to 3.2 meqg^{-1} . An increase in IEC with an increase of PEG 600 concentration may be due to the development of microvoids and leaching out PEG 600 from the membrane structure during the gelation process, which becomes the domain of H^+ ions Sivakumar M. et al. [6] A similar trend was observed for other membranes too. It has been concluded that the number of H^+ ions released increased as more pores were opened.

3.3 Metal Ion Rejection Studies

All the metal salts were prepared at the concentration of 1000 ppm. They were complexed with a water-soluble chelating polymer PEI as the ionic level separation through the UF process is impossible due to the larger pore size of membranes that are unsuitable for rejecting ions. Hence, the salts were complexed with PEI and subsequently rejected individually from aqueous streams by the PU/CPSf blend UF membranes. Separating hazardous metal ions from aqueous solution is a major serious industrial activity in recent times. Generally, the UF's pore size is not suitable for separating hazardous materials from aqueous solutions. Therefore, polymer Enhanced Ultrafiltration (PEUF) methods are effectively used to remove metal ions

from solutions. This method consists of two steps: (i) metal ions binding to the water-soluble polymer to form a macromolecular complex, and (ii) separating the polymer-metal complex utilizing ultrafiltration.

In the present study, PEI has been chosen as the macromolecular chelating agent, instead of other binding/complexing agents, such as polyacrylic acid, polyvinyl alcohol, polydiallyldimethylammoniumchloride, EDTA, etc., due to the presence of a nitrogen donor atom. This has gained increased attention in the separation of heavy metal ions due to the following reasons. (i) PEI increases the metal ion uptake; (ii) the metal ion removal efficiency is unaffected at pH 1 ;(iii) both the metal cations and other anions can be removed simultaneously from the aqueous phase and (iv) there is no release of counter ions in the treated water concerning polymers that work with an ion-exchange mechanism (Kawano et al. 2002).

Ultrafiltration membranes of PU/CPSf blend (80/20 and 75/25 % composition) in the absence and presence of PEG 600 concentrations difference (from 0 to 7.5 wt %) subjected to metal chelates rejection Figures 1 and 2. Metal ion rejection studies and permeates flux measurements were repeated twice for reproducibility. The results are reproducible with small negligible deviations.

3.4 The Role of Polymer Blend Composition

The rejection of metal ions was carried out with PU/CPSf membranes without additive after complexation of metal ions with the polymeric water-soluble ligand PEI. The results of rejection studies are given in Figures 1 and 2.

When the concentration of CPSf (20%) in the blend solution, 99 % rejection (Cu^{2+}), while Ni^{2+} , Zn^{2+} and Cd^{2+} shows 97, 95 and 93% respectively. Further increase in CPSf concentration (25 %) displayed a decrease in rejection percentage for all metal ions, for Cu^{2+} , Ni^{2+} , Zn^{2+} and Cd^{2+} are 96, 90, 88 and 85 %. Much lower rejection efficiency was observed for 75/25 % PU/CPSf blend membranes than 80/20 % membranes with a higher amount of CPSf. These membranes tend to act less efficiently in the divalent cations rejection process. The terminology better explains the Donnan effect and has been confirmed with PU/SPSf blend membranes (Malaisamy R. et al., 2002)[21]. These results also have a good correlation with the pore statistics data.

From this experiment, it is obvious that in all the membranes, Cu^{2+} exhibited higher rejection than Ni^{2+} , which in turn was higher than Zn^{2+} . On the other hand, Cd^{2+} exhibited the lowest rejection, and the size of the ion and its complex suggest the reason for the observation.

3.5 The Role of Additive Concentration

Metal ion rejections by PU/CPSf membranes of various additive concentrations are shown in Figures 1 and 2.

When additive concentration increased from 2.5 to 7.5 wt% for PU/CPSf (80/20 %) blend membranes, Cu^{2+} rejection decreased linearly from 97 to 90 %. A steady decrease in rejection percentage with increased PEG 600 concentration in the casting solution or blend membranes. The key reason behind this is the presence of a higher amount of non-solvent additive, which leads to the formation of bigger pores during the gelation process. In addition, thermos-dynamical instability also lowers the system's free energy (Chen M.H. et al., 1996).

Similarly, when CPSf concentration was increased (from 20 to 25 %) in the blend at 2.5 wt %, additive concentration rejection percentage decreased (from 97 to 92 %) for copper metal ions. A similar trend was observed for all additive concentrations; the reason behind the phenomena is the CPSf matrix's larger segmental gap. The gap developed due to swelling, and solvent - non-solvent replacement during gelation rapidly leads to the formation of macro pores (Broens L., 1980). However, additive and decrease in rejection correlated to the rapid leaching out of pore former, creating larger pores Sivakumar M. et al. [6]

The results mentioned above reveal that the binding capacity of copper with PEI is stronger than following other metals ions $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. Similarly, complexing capacity depends on functional groups' presence (number) in macromolecular complex and metal ions' atomic weight. Mandel M. and Leyte J.C., 1964 reported similar results with poly(methacrylate). In all the cases mentioned above, metal ion complexed with PEI exhibits better rejections when compared to pure metal ion solutions as feed due to complex formation with PEI based on the Jahn-Teller distortion effect (Huheey J. E., 1983).

4. Metal Ion Permeate Flux Studies

The permeate flux of metal ions is essential for predicting the economics of the membrane processes and specifying the product rate. Therefore, the permeate flux studies were carried out simultaneously during metal rejection studies for 80/20 and 75/25 %. The permeate flux values of PU/CPSf membranes in the absence and the presence of additive are shown in Figures 3 and 4.

4.1 The Role of Polymer Blend Composition

In the absence of additive, the 80/20 % PU/CPSf blend membrane showed a lower flux of $2.94 \text{ Lm}^{-2}\text{h}^{-1}$ for copper ions, where the values were higher for Ni^{2+} (3.12), Zn^{2+} (3.64), and Cd^{2+} . The flux value was highest for Cd^{2+} with a value of $3.99 \text{ Lm}^{-2}\text{h}^{-1}$ as depicted in Figure 3.

When CPSf content was increased to 25 wt %, the flux value of Cu^{2+} also increased to $13.24 \text{ Lm}^{-2}\text{h}^{-1}$, as shown in Figure 4. All other metal ions also exhibited a similar trend for the system. The increase in flux upon increasing CPSf composition may be due to the formation of higher hydrophilicity incorporated by carboxylated polysulfone Malaisamy R. et al. [21] The blend membranes give the highest permeate flux value for Cd^{2+} than other metal ions. They can be corroborated by a decrease in metal ion size and chelating behavior with the polymeric ligand, PEI.

4.2 The Role of Additive Concentration

As shown in Figure 3, the additive played a major role in enhancing the permeate flux values of PU/CPSf membranes. Thus for 80/20 % PU/CPSf at 2.5 wt %, additive copper yielded a flux of $5.21 \text{ Lm}^{-2}\text{h}^{-1}$, much higher than for the membrane of the same composition without additive ($2.94 \text{ Lm}^{-2}\text{h}^{-1}$). Further, the flux increased to 6.36 and $8.31 \text{ Lm}^{-2}\text{h}^{-1}$, respectively, when the additive concentration was increased to 5, and 7.5 wt % and a similar trend was also observed for other metal ions.

Similarly, PU/CPSf blend membrane (75/25 %) at 2.5 wt % of additive concentrations, flux value was $15.12 \text{ Lm}^{-2}\text{h}^{-1}$, whereas, at 7.5 wt%, the value was $34.65 \text{ Lm}^{-2}\text{h}^{-1}$. Increment in additive concentration enhances flux values, which can be related to the pore former leaching out during gelation, thereby creating pores. The order of flux for the metal chelate is $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+}$, primarily due to the larger metal chelate size for Cu and smallest Cd size.

In the present investigation, a given additive concentration (2.5 wt %) when CPSf composition in blend increased to 25% from 20% simultaneously, flux values also reached $15.12 \text{ Lm}^{-2}\text{h}^{-1}$ from $5.21 \text{ Lm}^{-2}\text{h}^{-1}$ for copper ion. Similar observations were also seen for other additive concentrations. The other metal ions such as Ni, Zn & Cd showed a similar trend with flux values of 5.63, 5.96, and 6.26 and of 15.86, 16.27, and $16.93 \text{ Lm}^{-2}\text{h}^{-1}$, respectively, at 20 and 25 % CPSf content in the blend. Thus, the increase in flux with increasing CPSf composition in blend favors phase separation, facilitating the generation of macro voids.

5. Conclusion

Ultrafiltration blend membranes based on polyurethane and carboxylated polysulfone were prepared in the presence and absence of additive polyethylene glycol 600. The 80/20 and 75/25 % PU/CPSf blend membranes were found suitable compositions, and the maximum compatible additive concentration was 7.5 wt %. The molecular weight cut-off and pore statistical studies of blend membranes were calculated with the help of dextran of different molecular weights ranging from 19 to 150 kDa, depending on the composition of polymers and concentration of the additive PEG 600. Also, the blend membranes were subjected to the rejection of toxic heavy metal ions such as Cu^{2+} , Ni^{2+} , Zn^{2+} , and Cd^{2+} . Toxic heavy metal ions were separated by complexing them with polyethyleneimine. The permeate flux studies have also been carried out. The polymer composition and additive concentration considerably impact metal ions' rejection and permeate flux.

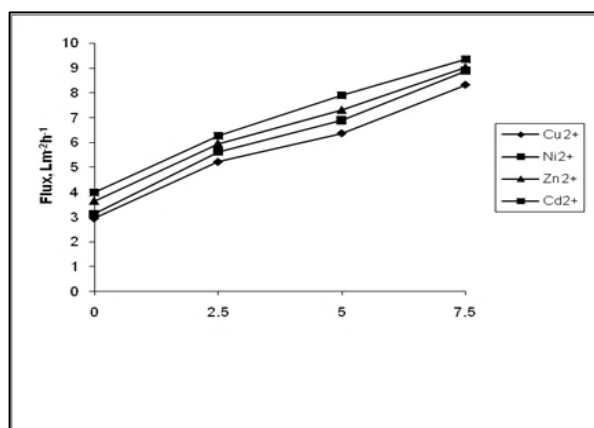


Figure 3: Effect of PEG 600 concentration on the flux of metal chelates PU/CPSf(80/20 %) blend membranes

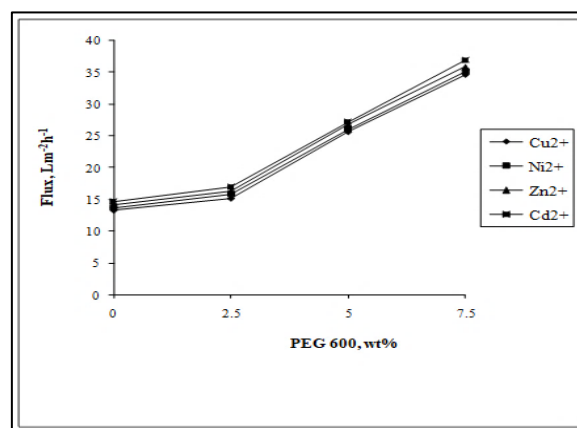


Figure 4: Effect of PEG 600 concentration on the flux of metal chelates PU/CPSf (75/25 %) blend membranes

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Author contribution

All authors contributed equally to this work.

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Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

Conflicts of interest

The authors declare that there is no conflict of interest.

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