# DEVELOPMENT OF PES MEMBRANES FOR SEPARATION OF METAL IONS: EFFECT OF POLYMER COMPOSITION

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## ABSTRACT

Asymmetric ultrafiltration (UF) membranes were prepared from poly (ether sulfone) (PES) using N,N′-dimethylformamide (DMF) solvent by phase inversion method. Solution cast PES membranes were homogeneous for all studied compositions, 12.5 to 20% polymer and 87.5 to 80% of solvent. The fabricated membranes were characterized for their UF performance such as pure water flux, water content and membrane hydraulic resistance and found to be moderate changes. It is estimated that the pure water flux of 20% PES membrane increases from 12 to 76 $L/m^2.h$, when the polymer concentration was decreased to 12.5% in the casting solution. The membranes were also characterized for their separation performance through metal ions in aqueous solution. The percentage rejection of metal ions was increased while the permeate flux has decreasing trend.

**Key words**: Ultrafiltration, PES compositions, Phase inversion, Toxic metal ion separation, Rejection of metal ions.

## INTRODUCTION

In last two decades, membrane separation by ultrafiltration (UF) has been employed for wide range of applications such as concentration or purification of solutes, wastewater treatment, solute separation etc. However, the main drawback in the extensive use of membranes includes membrane life, fouling, which results in reduced performance of the membranes. Polymeric membrane materials with functional groups have gained more attention because their excellent film forming property, easy to fabricate any shape and hydrophilicity[1]. Many studies have been conducted concerning the effect of hydrophilic polymers such as poly(ethylene glycol) or poly(vinyl pyrrolidone) (PVP) in the membrane casting solution to improve the membrane performance[2,3]. Poly(ether sulfone) (PES) has

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been widely used as membrane material due to its excellent chemical resistance, good thermal stability and mechanical properties[4]. In membrane development, formation of symmetric membrane depends on kinetic parameters and thermodynamic parameters, such as exchange rate between solvent and non-solvent, kinetics of phase inversions, polymer-solvent interactions, solvent-nonsolvent interactions and interfacial stability. Therefore, the membrane materials selection, such as polymer, solvents, non-solvents and its concentration are very important for the fabrication of asymmetric membranes, according to its applications[5]. PES has crystalline structure to some degree because of harder benzene ring and softer ether bond existed in the structure. The main factors affecting membrane performance are polymer composition, solvent concentration and nature of gelation medium. DMF is one of the good polar solvent widely used in the preparation of phase inversion membrane. DMF has a wide range of solubility with all polymers such as PES, poly(vinylidene fluoride) (PVDF), poly(acrylonitrile), poly(vinyl chloride), cellulose triacetate, etc[6]. In recent years, development of polymer membranes with varying polymer and solvent ratio has been studied for different membrane applications[7-9]. Liu and Bai[10] have been prepared chitosan membrane by varying the composition of polymer and solvent. They reported chitosan polymer range between 12 to 18 wt% and depending on the coagulant compositions and polymer compositions, the surface pore sizes, the specific surface areas and the porosities of membranes were changed. During the formation of membrane, solvent and polymer composition is influenced the performance of membrane.

Membrane separation processes can be successfully used for the separation of inorganic species and for their enrichment from dilute solutions with the aid of polymer ligand. This technique is called the liquid-phase polymer-based retention technique (LPR)[11,12]. Ultrafiltration is a fast emerging, new, and versatile technique in concentration, purification, and separation processes. Heavy metals such as Cu, Ni, Zn, Co, etc., from the waste streams of several chemical, electronic, metal plating and refining industries, have been separated and concentrated through membranes separation processes[13]. However, effects on polymer composition on membrane formation for UF applications like metal ions separation are very limited.

In this investigation, an effort has been made to prepare membranes in four compositions of PES/DMF ratio for UF application. The formulated membranes have been characterized for pure water flux, membrane hydraulic resistance and water content. Furthermore, the effect of polymer composition in the casting solution on the rejection and permeate flux of toxic heavy metal ions such as Cu (II), Co (II), Zn (II), and Cd (II) has also been investigated.

# EXPERIMENTAL

## Materials and methods

Commercial grade poly (ether sulfone) (Gafone 3300) was obtained as a gift sample from Gharda Chemicals Pvt. Ltd., India and was used as supplied. DMF and sodium lauryl sulfate (SLS) were obtained from Qualigens Fine Chemicals, Glaxo India Ltd., India, which were of analytical grade. DMF was sieved through molecular sieves (Type - 4Å) to remove moisture and stored in dry condition prior to use. Poly (ethylene imine) (PEI) was procured from Fluka, Germany. Analytical grade copper sulfate, cobalt sulfate, zinc sulfate and cadmium sulfate were procured from Merck (India) Ltd., and used as received. Deionized and distilled water was employed for preparation of protein and metal ion solutions.

## Preparation and formation of PES membranes

PES polymer was dissolved in DMF at 12.5, 15, 17.5 and 20 wt% concentration under constant mechanical stirring in a two necked round bottom flask for 3 h at $50^{\circ}C$. A series of such PES solutions were prepared by varying the composition of PES and DMF as shown in Table 1. The preparation method of membranes is shown in Fig. 1.

**Table 1: Effect of polymer composition on UF characteristic of membranes**

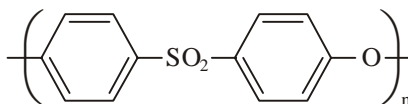| Polymer/solvent composition | | Pure water flux $(m^3/m^2.s)$ | Water content (%) | $R_m$ $(kPa/ L.m^{-2}.h^{-1})$ |
|---|---|---|---|---|
| PES (%) | DMF (%) | | | |
| 12.5 | 87.5 | 54 | 89 | 3.8 |
| 15 | 85 | 43 | 80 | 8.3 |
| 17.5 | 82.5 | 21 | 69 | 17 |
| 20 | 80 | 10 | 55 | 26.4 |



**Fig. 1: Molecular structure of polyethersulfone**

The homogeneous polymer solutions were allowed to stand for 1 h before casting to eliminate air bubbles. The dope solution was poured onto a glass plate and makes it as thin

film using a film applicator. Thickness of the membranes was adjusted to 0.20 mm. After casting a thin film, the film was allowed to evaporate solvent for 30 s in humidity control chamber. The casting and gelation conditions of prepared membranes are shown in Table 2.

**Table 2: Film casting and gelation conditions for PES membranes**

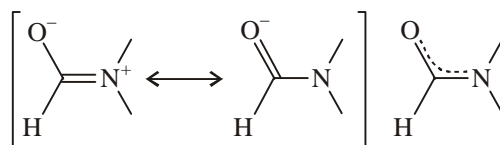| Conditions | Values |
|---|---|
| Temperature of casting solution ($^{o}$C) | 24-26 |
| Temperature of casting atmosphere ($^{o}$C) | 20-23 |
| Humidity of casting atmosphere (%) | 60-65 |
| Solvent evaporation (min) | 30 |
| Temperature of gelation bath ($^{o}$C) | 10-14 |
| Period of gelation (h) | >12 |
| Thickness of membrane (mm) | 0.18-0.22 |



**Fig. 2: Two resonance forms of DMF**

Next, partially evaporated film immersed in gelation bath which containing 2 liters of gelation medium (2.5% (v/v) DMF and 0.2 wt % SLS in distilled water (non solvent). The membranes were kept in gelation bath for overnight, and then washed with deionized water before UF experiments. Similar casting and gelation conditions were maintained for all the membranes.

**Characterization of membranes**

**Water content**

PES Membranes were cut into needed size and soaked in water for one day and weighed immediately after blotting the free surface water. These wet membranes were dried for 12 h at 100°C and weighed wet weight. The percent water contents were calculated using the equation given elsewhere[14].
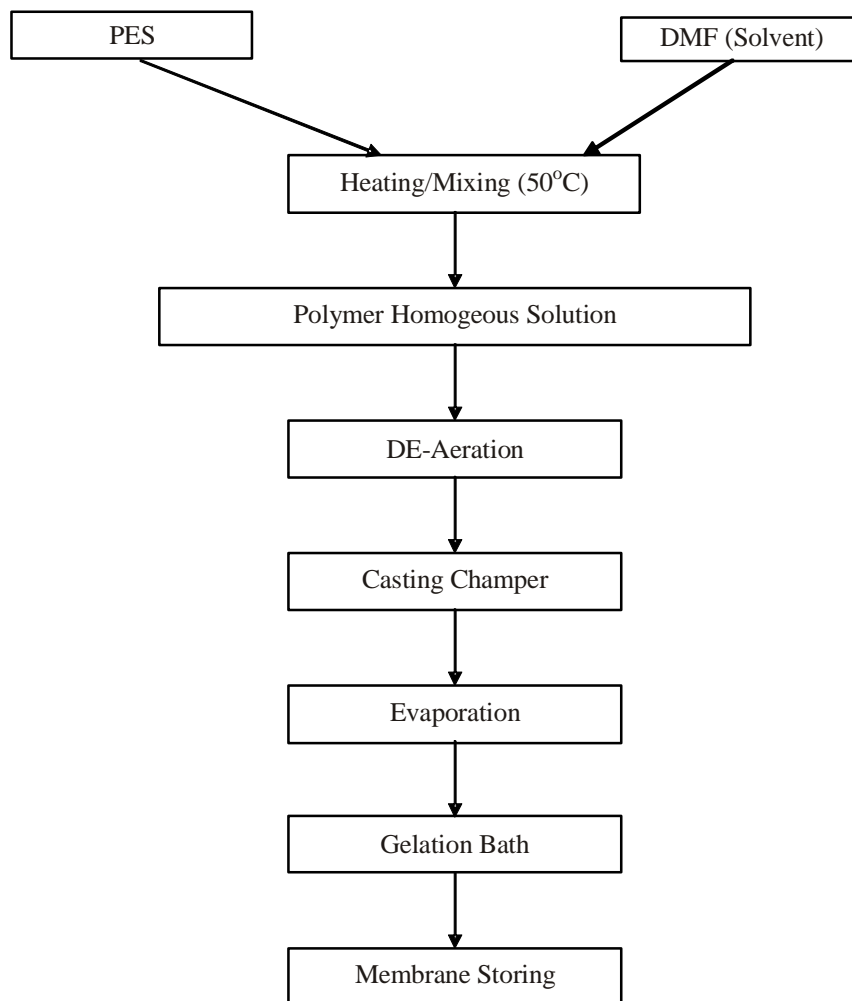
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┌──────────────┐                    ┌──────────────────┐
│     PES      │                    │  DMF (Solvent)   │
└──────────────┘                    └──────────────────┘
          ╲                        ╱
           ╲                      ╱
            ┌──────────────────────────┐
            │  Heating/Mixing (50°C)   │
            └──────────────────────────┘
                        │
                        ▼
     ┌──────────────────────────────────────┐
     │      Polymer Homogeous Solution       │
     └──────────────────────────────────────┘
                        │
                        ▼
            ┌──────────────────────────┐
            │        DE-Aeration        │
            └──────────────────────────┘
                        │
                        ▼
            ┌──────────────────────────┐
            │      Casting Champer      │
            └──────────────────────────┘
                        │
                        ▼
            ┌──────────────────────────┐
            │        Evaporation        │
            └──────────────────────────┘
                        │
                        ▼
            ┌──────────────────────────┐
            │       Gelation Bath       │
            └──────────────────────────┘
                        │
                        ▼
            ┌──────────────────────────┐
            │      Membrane Storing     │
            └──────────────────────────┘
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**Fig. 3: Preparation method of polymeric membranes**

## Membrane resistance

To determine the membrane resistance ($R_m$), the pure water flux of the membranes was measured at different transmembrane pressures ($\Delta P$) viz., 69, 138, 207, 276 and 345 kPa. The hydraulic resistances of the membranes were determined from the inverse of slopes using the following equation.

$$R_m = \frac{\Delta P}{J_w} \qquad \qquad \text{...(1)}$$

## Morphological studies

The membranes were cut into small pieces and mopped with filter paper. These pieces were immersed in liquid nitrogen for 20-30 s and frozen. The frozen bits of membranes were broken and kept in a desiccator. These membrane samples were used for SEM studies. The membrane samples were mounted on studs and gold-sputtered[15]. The top surface and cross sections of the membranes were viewed using Jeol JSM-840A scanning electron microscope.

## UF Experiments

The UF experiments were carried out in a stirred type, dead end cell fitted with Teflon coated magnetic paddle. This experimental setup was purchased from Millipore Ltd, USA (Millipore-XFUF 07601-Model, USA). The effective membrane area available for ultrafiltration was 38.5 cm$^2$. This stirring speed was chosen (600 rpm) because it could lead to an effective agitation but prevent the formation of a serious vortex in the dead end cell. All the experiments were carried out at 30°C and 345 kPa transmembrane pressures.

## Pure water flux

PES membranes were placed in UF cell and compressed with pure water at a constant stirring speed (600 rpm) for 10 min at 345 kPa. The pure water flux was calculated by measuring the volume of permeates that penetrated the membrane per unit time.

## Metal ion removal

Ultrafiltration is based on the membrane separation of small molecules from high molecular-weight molecules. When metal ions are separated by ultrafiltration, the ions passed through the membranes. Hence, metal ions are put in contact with a water-soluble polymer inside the ultrafiltration cell, those with high interaction rates with the polymer are retained by the polymer, which is not able to pass through the ultrafiltration membrane, while other ions are eluted through the membrane during the ultrafiltration run. PEI was used as water soluble polymer to complex the metal ions for their separation through the developed UF membranes[16]. To find the influence of PEI on metal ion rejection, preliminary experiments were carried out to separate metal salt solutions in the absence of PEI using 12.55 PES membrane after adjusting the pH to 6 ± 0.25. It was observed that virtually all the metal ions permeated through the membrane. Hence, PEI was used to complex the metal ions. Solutions of Cu (II), Co (II), Zn (II) and Cd (II) were prepared at a concentration of 1000 ppm in 1 wt% aqueous solution of PEI. The pH of these solutions was adjusted to 6 ± 0.25 by adding small amount of either 0.1 M HCl or 0.1 M NaOH. Metal ion removal was carried out as mentioned above through UF cell and the permeate solutions of corresponding

membranes were collected in graduated tubes. They were analyzed for the concentration of the metal ions using an atomic absorption spectrometer (Perkin-Elmer 3110). The percentage rejections of metal ions were calculated from the concentration of metal ions in feed and permeate using flowing equation (2).

$$\% \ SR = \left[ 1 - \left( C_p \Big/ C_f \right) \right] \times 100 \qquad \text{...(2)}$$

where, $C_p$ is the concentration of permeate, and $C_f$ is the concentration of feed.

## RESULTS AND DISCUSSION

### Membrane preparation

UF membranes based on PES with various compositions were prepared. The maximum polymer composition was found to be 20% of PES, beyond which miscibility occurred and membrane did not form. When a 12.5% of PES used to form UF membrane, phase separation obtained due to polymer lean phase. The inter phase regions between PES and DMF are probably the reason for phase separation. In addition, as DMF is a highly solvent phase, the presence of DMF will favor water ingression, which will increase phase separation. Hence with higher ratio (90%) of DMF, when the membrane was cast and immersed in a gelation bath, two separate layers were formed due to complete phase separation. Thus, membranes with the compositions of 12.5/87.5, 15/85, 17.5/82.5 and 20/80% of PES/DMF were prepared for further study.

### Characterization of the blend membranes

### Water content

The water content of the prepared membranes were measured and shown in Table 1. It was evidently seen that the water contents of the membranes with lowest weight of PES are higher than that of the highest weight of PES membrane, the water contents are decreased with an increase of PES compositions in the membrane matrix. Similar results have also been observed for poly (vinylidene fluoride) microfiltration membranes[17]. It was deduced that the higher amount of DMF enhanced the wettability of the PES membranes, more pores in the PES membranes with highest amount of DMF (87.5%) would be wetted and filled with water. These water content results clearly confirm that permeability of PES membranes. The water content actually represents the fraction of water molecules occupied in the pores of the membrane. An increase in the water content indicates that the membrane has become more porous.

### Membrane resistance

Membrane resistance, $R_m$, indicates the tolerance of the membrane toward hydraulic pressure. The variation of pressure or the intermediate pressure ranges are important conditions to be studied for ultrafiltration operations. Membrane resistances of the membranes were calculated from the inverse of slopes of the corresponding flux versus pressure lines and are shown in Table 1. It is evident from Table 1 that the membranes with lowest composition of PES showed smallest membrane resistance of 3.8 kPa/L.m$^{-2}$.h$^{-1}$ The membranes with 20% composition of PES showed their highest membrane resistance of 26.4 kPa/L.m$^{-2}$.h$^{-1}$. Their pore density and surface porosity is also higher than other membranes. Thus, they exhibited lower water flux. In other words, the backing PES polymer produced tighter membranes. This is also supported by the water content given in Table 1. The decrease in membrane resistance may be due to the presence of higher amount of DMF in polymer casting solution, which forms a segmental gap between PES and solvent, which can be directly related to the reduction in resistance toward hydraulic pressure[18].

### Pure water flux

Pure water permeability is the key specification for classification membranes and must be determined essentially. Pure water permeability of all membranes was measured, in order to evaluate their water permeability and reproducibility. All the membranes were subjected to pure water flux at a pressure of 345 kPa pressure, under steady-state conditions and at a constant sampling period. Pure water flux has a direct relationship with the number of pores and their size on the membrane surface (top layer porosity)[19]. DMF is a polar solvent and its presence in the casted film facilitates formation of pores on the membrane surface because it evaporate in room temperature and diffuse in non-solvent facilitates formation of more nucleuses after immersion of the casted film into the coagulation bath. Thus, it is evident that, according to Table 1, increasing DMF concentration from 80 to 87.5%, when PES concentration decreased from 20 to 12.5%.

### Separation of metal ions

### Effect of PES composition on permeate flux

The permeate flux of the metal ion solutions on increasing concentrations of PES is shown in Fig. 4. It is seen that the permeate flux of all the metal ions decreses as the composition of PES increases in the casting solution. The permeate flux of Cu (II) for the 12.5% of PES membrane is $14 \times 10^{-6}$ m$^3$.m$^{-2}$.s$^{-1}$, while for the membrane prepared from casting solution having 20 % PES, the permeate flux is decreased to $2 \times 10^{-6}$ m$^3$.m$^{-2}$.s$^{-1}$. The permeate flux of Cu (II) is lower than other metal ion solutions and the order of the permeate

flux is Cd (II) > Co (II) > Zn (II) > Cu (II). This is because of the fact that Cu (II) has higher affinity for N-donor ligands compared to Cd (II) and Zn (II)[20]. Hence, it is possible that Cu (II) can easily form more macromolecules than other metal ions chosen in this study.
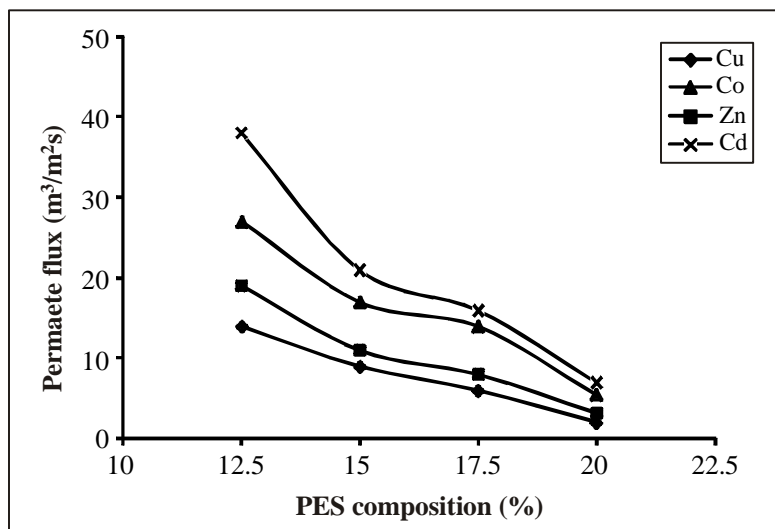


**Fig. 4: The effect of concentration of PES on permeate flux of metal ions**

This lead to the reduced permeate flux for Cu (II), 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 morphological structure of the membranes.

**Effect of PES composition on rejection**

The effect of PES composition on the percentage rejection of metal ions is shown in Fig. 5. In general, permeate flux and rejection possesses inverse relationship. The rejection of Cu (II) for 12.5% PES membrane is 78% and for the membrane prepared from casting solution having 20% PES, the rejection is increased to 98%. The rejection of Cd (II) for 12.5% PES membrane is 60% and this value is lower than that of Cu (II). Similar observations were also found for the rejection of other metal ions such as Zn (II), and Co (II).

The rejection of Cu (II) is found to be higher than other metal ions for all the membranes and the order of rejection is Cu (II) > Zn (II) > Co (II) > Cd (II). This may be due to the higher binding ability of Cu (II) with PEI. It has been shown that Cu (II) has higher complexation constant compared to Zn (II) and Cd (II)[21]. Further, it is known that

Zn (II) and Cd (II) complexes have low ligand-field stability due to the complete filling of d-orbitals.
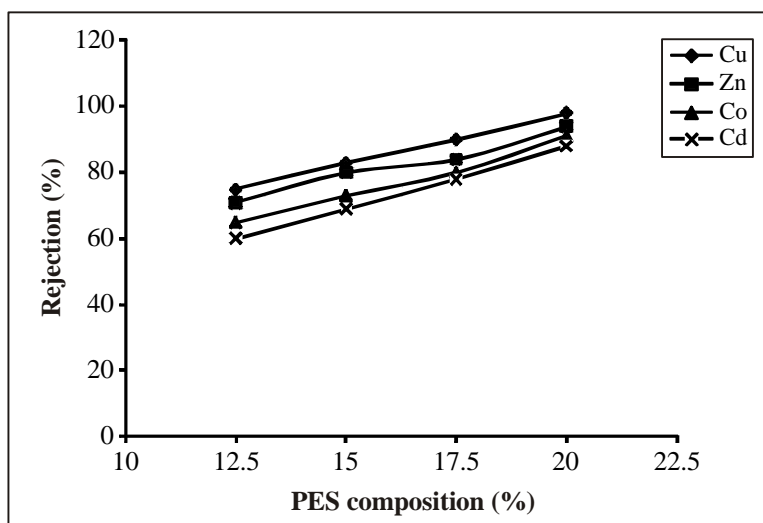


**Fig. 5: The effect of concentration of PES on rejection of metal ions**

## CONCLUSION

In this work, PES as a polymer material was mixed with DMF as polar solvent varying from 12.5 to 20% to prepare UF PES membrane. It was found that PES composition more than 20 did not form membrane. The characterization of prepared membranes demonstrates that the pure water flux and water content were decreased while the membrane hydraulic resistance was increased, as the composition of PES in the casting solution is increased. The extent of rejection of metal ions follows the order Cu (II) > Zn (II) > Co (II) > Cd (II), which depends on the complexation ability to form macromolecules and ligand-field stability of the individual metal ions. Results suggest that metal ion removal involve sieving mechanism influenced by the water content and membrane resistance of the membranes.

## ACKNOWLEDGEMENT

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