THE SEPARATION OF COPPER, NICKEL AND CHROMIUM METAL IONS USING WITH ULTRAFILTRATION MEMBRANE: EFFECT OF POLYMER MEMBRANE COMPOSITIONS

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ABSTRACT

New ultrafiltration membranes have been prepared with polyethersulfone as polymer and with different solvent by phase inversion tech que. The solvent used for the membrane preparation are N,N-dimethylformamide, N-methyl-2-pyrrolidone and Dimethyl sulphoxide. The membranes were prepared by two different methods i, dry/wet immersion method and ii, wet immersion method. Prepared membranes have been subjected to ultrafiltration characterizations such as pure water flux and membrane hydraulic resistance. The pore statistics and molecular weight Cut-off (MWCO) of the membranes have been estimated using proteins such as trypsin, pepsin and egg albumin. Surface and Cross-sectional morphologies of membranes were analyzed using scanning electron microscopy. The mechanical properties were analyzed. The effects of solvent and their compositions on the above parameters were analyzed and the results are compared and discussed. These membranes were used in the study of the metal ion separation performance. Cu(II), Ni (II) and Cr (III) metal ions were used in the separation studies.

Keywords: Ultrafiltration, Polyethersulfone, N, N-dimethylformamide, N-methyl-2-pyrrolidone, Dimethyl Sulphoxide, Molecular Weight Cutoff (MWCO)

1. INTRODUCTION

Polyethersulfone (PES) is selected as membrane material because of its commercial availability, processing ease and favorable selectivity-permeability characteristics, and possesses good mechanical and thermal properties. Moreover, it is generally easy to prepare asymmetric membranes from PES by the immersion phase inversion method using water as a coagulant. Polyethersulfone is an amorphous glassy and hydrophilic polymer, and containing sulfone group. Compared to polysulfone polymer, polyethersulfone is more hydrophilic polymer, and this gives
polyethersulfone better advantage over polysulfone. The main reason for the selection is because hydrophilic polymer like polyethersulfone can eradicate deposition of many solutes, such as protein, enzyme’s solutes, which cause fouling and concentration polarization phenomenon. A wide range of evidence shows that membranes with a greater degree of hydrophilicity had increased resistance to fouling.

PES is used in both the preparation of flat sheet membrane and the hollow fibre membrane. Hwang et al. [1] prepared PES asymmetric membranes with a cosolvent system of dichloromethane and NMP as volatile and nonvolatile solvent, respectively. And the effect of PVP additive was examined in terms of pure water flux and solute rejection of the membrane. Kim and Lee [2] investigated the effect of PEG additive as a pore-former on the structure formation of PES membranes and their performance of thermodynamic and kinetic properties in phase inversion process. Torrestiana-Sanchez et al. [3] studied the relationship among the presence of non-solvent additive, the rheological behavior of spinning solutions and properties of PES hollow fiber membranes. The additives were water, PVP and PEG. The effects of the water/PVP or water/PEG mixed additives were also studied. Chaturvedi et al. [4] focused on the effects of nature of additive, solvent, ambient humidity on membrane performance behavior of PES UF membranes. Xu et al. [5] studied the effect of ethanol concentration on characterization and performance of PES hollow fiber UF membranes fabricated using wet and dry/wet spinning process. And the effects of methanol, n-propanol and water as non-solvent additives were also investigated. In their paper [6], PVP and PEG were used as additives and NMP as solvent. Many solvents have been used for the preparation of membranes. The selection of solvent plays a vital role in the characteristics of the membranes. Chakrabarty et al. [7] prepared Psf asymmetric membrane with NMP and DMAc as solvents separately. Chaturvedi et al. studied the effects of nature of solvents, additives and the humidity during casting of membrane on membrane performance [8]. In his investigation he employed two different solvents, NMP and DMF. Khan et al. [9] described the synthesis and characterization of low molecular weight CU (II) (II)-off ultrafiltration (UF) membranes from cellulose propionate polymer using dimethyl acetamide solvent (DMAc). Hong-Yong et al. [10] described the preparation of membranes with N,N-dimethylaminoethyl methacrylate (DMEMA) and polyethylene glycol methyl ether methyl acrylate (PEGMEMA) and THF as solvent.

Phase inversion is one of the most important processes for preparing both symmetric and asymmetric polymeric membranes. The structure of phase inversion membranes results from a phase change of initially stable polymer solutions. These membranes are widely used today in various applications such as microfiltration, ultrafiltration, reverse osmosis and as supports for composite structures [11]. It is actually a diffusion-induced phase separation process, which involves conversion of a liquid polymer solution of two or more components into a two-phase system, like; solid polymer rich phase and the liquid polymer poor phase. The solid phase forms the membrane structure while the liquid phase forms the membrane pores. The conversion is generally carried out by addition of a precipitating fluid which is usually miscible with the solvent but immiscible with the polymer. Many industries including chemical, electro, metal plating and refining industries face severe problems in the disposal of their waste streams when highly toxic or valuable constituents such as metal ions are present. From these waste streams heavy metals such as Cr (VI), Cr (III), Cu (II), Zn(II), etc., could be separated and concentrated through binding of the target metal ions to water soluble polyelectrolyte and subsequent ultrafiltration of the bound metals from the unbound components [12,13]. In a previous investigation, 99.8% rejection of chromate from water has been achieved by polyelectrolyte enhanced ultrafiltration [14]. The separation of Cu (II) and Fe(III) ions by complexation with algic acid using EC-PEG 4000 alloy membrane has been attempted [15]. 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 [16]. Bernabe et al studied the
effect of various water soluble polymer ligand such as PDDA, PVA for the removal of metal ions [17]. Arthanareeswaran et al used PVA as water soluble polymer for the chromium ion separation [18]. In this present investigation PDDA and PVA were used as water soluble polymer for the enhancement of the metal ion removal.

2. MATERIALS AND METHODS

2.1. Materials
The polymer used for the membrane preparation in the present investigation is Poly (ether sulfone) (PES). The polymer procured from Solvay process, India, was used without any further treatment. Solvents used for the membrane fabrication in the present investigation were N, N-Dimethyl formamide (DMF), Dimethyl sulphoxide (DMSO) and N-methyl-2-pyrrolidone (NMP). All these solvents were purchased from Sisco research laboratories (SRL), India. These solvents were used without any further treatment. Distilled water was used for the preparation of the gelation bath. Sodium lauryl sulphate (SLS) was purchased from Sisco research laboratories (SRL), India and used as a surfactant in the gelation bath. Formalin purchased from Sisco research laboratories (SRL), India was used to store the membranes to avoid fouling. Proteins such as trypsin M.W= 20 kDa and pepsin M.W= 35 kDa were purchased from Sisco research laboratories (SRL), India. Egg albumin (EA) M.W= 45 kDa is purchased from central drug house, India. These proteins were used for the protein rejection studies, determination of MWCO and pore statistics. Sodium dihydrogen ortho phosphate and disodium hydrogen ortho phosphate were obtained from CDH Chemicals Ltd., India and used for the preparation of phosphate buffer solutions in protein analysis. Copper(II) sulfate (AR) was purchased from SRL, India. Nickel(II) sulfate (AR) was purchased from Fischer, India. Chromium (III) chloride (AR) procured from CDH, India Ltd. These metal ions were used as received and dissolved in 1wt% aqueous PVA or PDDA solution at an approximate concentration of 1000 ppm. Deionized and distilled water was preparation of protein and metal solutions. Polyvinylalcohol (PVA) was purchased from CDH, India. Poly (diallyl dimethylammonium chloride) (PDDA) was purchased from Aldrich chemical company. PVA and PDDA were used as a chelating agents to form complex with metal ions. Ammonia, chloroform, acetone, bromine and hydrogen peroxide were procured from Fischer, India. Diphenyl carbazide and sodium diethyl dithio carbamate were purchased from Loba chemie, India. Dimethyl glyoxime was purchased from Qualigens, India. Diphenyl carbazide, sodium diethyl dithio carbamate and Dimethyl glyoxime were used as a reagent for the UV spectrophotometric determination of chromium, copper and nickel metal ions respectively [19].

2.2. Membrane preparation
Membranes were fabricated by phase inversion technique. PES was weighed according to the composition of the polymer solution which is required. Two different compositions of polymer solution were prepared, one containing 17.5% PES and 82.5% solvent and the other containing 15% PES and 85% solvent. The polymer was dissolved in the solvent N, N-dimethyl formamide (DMF), N-methyl-2-pyrrolidone (NMP) and dimethyl sulphoxide (DMSO) separately by constant stirring in a low speed stirrer for 3-4 h until it forms a homogenous clear solution. The polymer solution prepared was deaerated to remove the air bubbles inside. The homogenous polymeric solution prepared after allowing for de-aeration was casted on a support (i.e. Glass plate). The casting was done by a Doctor k fe. The thickness of the membrane was maintained at 0.25 ± 0.02 mm with the help of an oil sheet rolled at both the ends of the blade [20, 21]. The polymer solution casted on the glass plate was allowed for 30 second. Before carrying out immersion precipitation a gelation bath was prepared. The gelation bath was made with 8 liters consisting of 1% (v/v) solvent used for preparing polymeric solution and 0.2 wt% SLS in distilled water (non solvent) and the bath was
cooled to 21 ± 2 °C [22, 23]. The casted membrane was allowed in the gelation bath for 1 hr. the prepared membranes were stored in a 1% (v/v) formalin solution to avoid fouling.

2.3. Experimental setup

The ultrafiltration (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. The flow sheet of the experimental apparatus is illustrated in Fig. 1. The effective membrane area available for ultrafiltration was 38.5 cm$^2$. The solution filled in the cell was stirred at 300 rpm using a magnetic stirrer. All the experiments were carried out at 30°C and 345 kPa transmembrane pressure.

![Fig. 1: UF experimental setup](image)

2.4. Membrane characterization

2.4.1. Pure water flux

The membranes prepared by the phase inversion method were compacted at a transmembrane pressure of 414 kPa. In order to conduct the experiments at steady state conditions, the prepared membranes have to be compacted at an elevated pressure than the pressure that is to be maintained in the ultrafiltration study, until a constant flux is reached. The pure water flux is a measure of hydrophilicity of a membrane. Thus, the compacted membranes were subjected to pure water permeation studies under steady state flow at a transmembrane pressure of 345 kPa [19, 20]. The volume of permeate collected in 10 min was measured. The flux can be calculated from the equation (1)

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

where, $J_w$ the water flux (l.m$^{-2}$.h$^{-1}$); $Q$ is the quantity of water permeated (l); $\Delta t$ is the sampling time (h); and $A$ is the membrane area (m$^2$).

2.4.2. Membrane hydraulic resistance

The pure water flux of the membranes was measured at different transmembrane pressures ($\Delta P$) viz., 69, 138, 207, 276 and 345 kPa [19, 20]. The flux values were calculated by using equation (1). The hydraulic resistances of the membranes ($R_m$) were determined from the inverse of slopes according to the equation (2).
\[ R_m = \frac{\Delta P}{J_w} \]  

Where, \( J_w \) is the water flux (l.m\(^{-2}\).h\(^{-1}\)); \( \Delta P \) is the transmembrane pressure (kPa); \( R_m \) is the membrane resistance (kPa/l m\(^{-2}\).h\(^{-1}\)) obtained from the pure water run.

2.4.3. 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 were frozen. The frozen bits of membranes were broken and kept in a desiccator. These membrane samples were used for SEM studies. The membrane sample was mounted on studs and gold-sputtered to provide electrical conductivity to very thin layer of the polymeric membrane. The top surface and the Cross section of the membranes were analyzed by Scanning Electron Microscopy (SEM) (LEICA Stereoscan, Cambridge, UK).

2.4.4. Mechanical properties

Tensile stress and elongation at break of the membrane were measured by using tensile test machine (Instron 4500 model) at a speed of 10 mm/min. Cross-sectional area of the sample of known width and thickness was calculated. The membranes were then placed between the grips of the testing machine. The tensile stress values and elongation at break values of the individual membranes are noted. Stress is defined as the force per unit area, normal to the direction of the applied force, and break elongation as the extension per gauge length at break.

2.4.6. Protein rejection studies

Proteins of different molecular weights such as trypsin (20 kDa), pepsin (35 kDa) and EA (45 kDa) were chosen for the protein rejection studies [22, 23]. Aqueous solutions of egg albumin (EA), pepsin and trypsin were prepared at a concentration of 1000 ppm by dissolving the proteins (0.1 wt %) individually in phosphate buffer (0.5 M, pH 7.2). The UF cell was filled with protein solution and pressurized at a constant pressure of 345 kPa. The permeate protein concentration was estimated using UV-Visible spectrophotometer (Jasco, model V-570) at a maximum wavelength \( \lambda_{\text{max}} \) of 280 nm. The percentage rejection were calculated using the equation (3)

\[ \%SR = 1 - \frac{C_p}{C_f} \times 100 \]  

Where, \( \%SR \) is the rejection percentage; \( C_p \) and \( C_f \) are the concentrations of permeate and feed solutions, respectively.

2.4.7. Molecular weight cutoff

Molecular weight cutoff is an attribute of pore size of the membranes and is related to the rejection of a spherical solute of given molecular weight cutoff. The molecular weight has a linear relationship with the pore size of the membrane [23]. In general, the molecular weight cutoff of the membrane is determined by identifying an inert solute of lowest molecular weight that has a solute rejection of 80-100 % in steady state UF experiments [24]. Thus, the proteins of different molecular weights such as, egg albumin (45 kDa), pepsin (35 kDa) and trypsin kDa) were taken for rejection studies of the membranes. Aqueous solutions of egg albumin (EA), pepsin and trypsin were prepared at a concentration of 1000 ppm by dissolving the proteins (0.1 wt%) individually in phosphate buffer (0.5 M, pH 7.2). The UF cell was filled with protein solution and pressurized at a constant pressure of 345 kPa. During ultrafiltration, the permeate solutions of corresponding membranes were collected over a period of time in a graduated tube and were analyzed for the concentration of protein by UV-visible spectrophotometer (Jasco, model V-570) at a maximum wavelength \( \lambda_{\text{max}} \) of 280 nm.
From the feed and permeate concentrations, the percentage rejection was calculated using the equation (3).

### 2.4.8. Pore statistics

The average pore radius ($R$), surface porosity or porosity percentage ($\varepsilon$), and number of pores ($n$) of PES membranes were determined by using the proteins trypsin (20 kDa), pepsin (35 kDa) and EA (45 kDa). The average pore size, surface porosity and number of pores per unit membrane surface area were determined by the ultrafiltration of protein solutions of different molecular weights. The molecular weight of the solute that has a solute rejection (SR) above 80% was used to evaluate the average pore size, $R$ of the membranes by using equation (4) [25, 26].

\[
R = 100 \left( \frac{\alpha}{\% \text{SR}} \right) \tag{4}
\]

where $R$ is the average pore radius of the membrane (Å), and $\alpha$ is the average solute radius (Å). The average solute radii also known as the Stoke radii was obtained from the plot of solute molecular weight versus solute radius in aqueous solution, which was developed by Sarbolouki [24].

The surface porosity, $\varepsilon$, of the membrane was calculated by the orifice model given below assuming that only the skin layer of the membrane is effective in separation [25, 26].

\[
\varepsilon = \frac{3\pi \mu J}{\Delta P R} \tag{5}
\]

Where, $\mu$ is the viscosity of the permeate water in (Pa.s); $J$ is the pure water flux of the membrane in (m$^3$/m$^2$.s); $R$ is the average pore radius in (m) and $\Delta P$ is the transmembrane pressure in (Pa).

From the values of $\varepsilon$ and $R$ the number of pores per unit area, $n$ can be calculated from the equation (6) [25].

\[
n = \frac{\varepsilon}{\pi R^2} \tag{6}
\]

### 2.4.9. Mass transfer coefficient

The concentration of the solute at the membrane surface is greater than that of the bulk resulting from concentration polarization. This can be studied using the film layer model that assumes a zone where the concentration decreases from the membrane to the surface at a distance inside the retentate phase. For partial retentions, the flux equation is

\[
Jv = k \ln \left( \frac{c_m - c_p}{c_f - c_p} \right) \tag{7}
\]

The observed retention, $R_{obs}$ and true retention, $R$ are expressed as in equation (8) and (9) respectively.

\[
R_{obs} = \frac{c_f - c_p}{c_f} \tag{8}
\]

\[
R = \frac{c_m - c_p}{c_m} \tag{9}
\]
Where, $J_v$ is volume flow per unit area and time through the membrane, m/s; $k$ is mass transfer coefficient, m/s; $C_m$ is membrane concentration in contact with the high pressure interface, mol/m$^3$; $C_p$ is permeate concentration, mol/m$^3$ and $C_f$ is feed concentration, mol/m$^3$.

Using the equation (8) and (9) the equation (7) can be rewritten as following form.

$$\ln \left( \frac{1-R_0}{R_0} \right) = \frac{1}{k} J_v + \ln \left( \frac{1-R}{R} \right) \quad \text{(10)}$$

Where, $R_o$ is the observed retention coefficient and $R$ is the true retention coefficient. $\ln \left( \frac{(1-R_0)/R_0} \right)$ was plotted against $J_v$ for experiments with various membranes. The plots showed a linear fit. From the corresponding line equation, the slope ($1/k$) and intercept $\ln \left( \frac{(1-R)/R} \right)$ were obtained. From which, the mass transfer coefficient, $k$, and true retention coefficient, $R$, were determined. The effects of concentration polarization, the observed retention can be compared to the true retention of a membrane system by the equation (10).

2.5. Metal ion separation

Experiments were carried out to separate metal ions from aqueous solutions in the absence of chelating agent using the membrane. It was observed that virtually all the metal ions permeated through the membrane. Hence, poly vinyl alcohol and poly (diallyl diammonium chloride) were used to complex with the metal ions. Solutions of Cu (II), Ni(II) and Cr(III) metal ions were prepared at a concentration of 1000 ppm in 1 wt% aqueous solution of the chelating agent. The solutions were then thoroughly mixed and allowed to stand for a day for the completion of binding. These solutions were then used for the rejection studies using prepared membranes [18, 27-29]. The metal ion solutions were filled in the UF kit and ultrafiltration was carried out at a transmembrane pressure of 345 kPa. The permeate solutions of corresponding membranes were collected in graduated tubes for a specified time period. Thus the product rate or permeate flux was calculated using equation (1).

The permeate solutions were analyzed for the concentration of the metal ions using UV-visible spectrophotometer (Jasco V-570). The percentage rejections of metal ions were calculated from the concentration of metal ions in feed and permeate using equation (3). Sodium diethyl dithiocarbamate, dimethyl glyoxime and diphenyl carbazide were used as the reagents for Cu (II), and Cr (III) metal ions respectively in UV spectroscopic determination [19].

3. RESULTS AND DISCUSSIONS

3.1. Pure water flux

The pure water flux is a measure of hydrophilicity of a membrane and from the knowledge of pure water flux we can predict the hydrophilicity of the membrane. Thus, the compacted membranes were subjected to pure water permeation studies under steady state flow at a transmembrane pressure of 345 kPa. The volume of permeate collected in 10 minutes was measured. From these readings the flux can be calculated using equation (1). The pure water flux of all the membranes is shown in Table 1. The pure water flux of the membrane M11 is higher than all the other membranes.

The membranes prepared with NMP as solvent had high pure water flux than the membranes prepared with other solvents. The pure water flux of the membrane M11 is 46.1 l.m$^{-2}$.h$^{-1}$ whereas the pure water flux of the membranes M10 and M12 were 32.1 l.m$^{-2}$.h$^{-1}$ and 38.6 l.m$^{-2}$.h$^{-1}$ respectively. The pure water flux of the membrane prepared with NMP as solvent was higher than the membranes prepared with other solvents in both the immersion method. The selection of solvents plays a vital role in the flux of the membrane. The membrane prepared with less polymer composition had more water flux. This is less polymer rich phase in the membranes. The polymer rich phase forms the solid layer of the membrane whereas the solvent rich phase forms the pores of the membrane. If the solvent rich phase is more in the membrane the water flux will be high. The membrane prepared with
15% PES and 85% NMP (M5) had a pure water flux of 33.9 l.m\(^{-2}\).h\(^{-1}\) whereas the membrane prepared with 17.5% and 82.5% NMP (M2) had a pure water flux of 19.6 l.m\(^{-2}\).h\(^{-1}\). Similar trends can be seen for all the solvents. The membrane prepared by the wet phase immersion method had more pure water flux compared to the dry/wet phase immersion method. The leaching of solvent from the polymer solution can be controlled by maintaining the gelation bath. The thermal effect plays a vital role in the membrane formation. The leaching of solvent from casted polymer solution is immediate compared to the evaporation of the solvent. Thus the pore formation in the membrane is faster in the wet immersion method. The membranes prepared by wet phase immersion method (M6 - M12) had high pure water flux compared to the membranes prepared by dry/wet immersion method (M1 - M6). The pure water flux value of the membrane prepared with 17.5% PES and 82.5% DMSO by wet phase immersion method was 31.7 l.m\(^{-2}\).h\(^{-1}\) whereas the membrane prepared with same composition but by dry/wet immersion method is 12.4 l.m\(^{-2}\).h\(^{-1}\).

### 3.2. Membrane hydraulic resistance

The effect of selection of solvent, the effect of concentration of solvent in the casting solution and effect of preparation method on pure water flux at different transmembrane pressures, viz., 69, 138, 207, 276, and 345 kPa is plotted. The plot depicts a linear relationship between the pure water flux and the transmembrane pressure for all the membranes. Membrane hydraulic resistances of the membranes were calculated from the inverse of slopes of the corresponding flux versus pressure lines and are shown in Table 1. The membrane hydraulic resistance is the resistance offered by the membrane for the permeation of water through the membrane. It is inversely proportional to the pure water flux of the membrane.

It is evident from these values that as the concentration of the solvent increases, the membrane hydraulic resistance decreases. The hydraulic resistance values of the membrane M1 is 34.1 kPa.l\(^{-1}\).m\(^{2}\).h\(^{-1}\) and the membrane M4 is 16.6 kPa.l\(^{-1}\).m\(^{2}\).h\(^{-1}\). The hydraulic resistance of the membrane prepared with 17.5% PES and 82.5% DMSO (M9) is 11.2 kPa.l\(^{-1}\).m\(^{2}\).h\(^{-1}\) which is high compared to the membrane prepared with 15% PES and 85% DMSO (M12) i.e 8.5 kPa.l\(^{-1}\).m\(^{2}\).h\(^{-1}\). The membrane prepared with NMP as solvent had less membrane hydraulic resistance compared to the membrane prepared with other solvent. The hydraulic resistance offered by the membrane M11 is 7.4 kPa.l\(^{-1}\).m\(^{2}\).h\(^{-1}\) whereas the hydraulic resistance offered by the membranes M10 and M12 are 10.3 kPa.l\(^{-1}\).m\(^{2}\).h\(^{-1}\) and 8.5 kPa.l\(^{-1}\).m\(^{2}\).h\(^{-1}\) respectively. The membrane prepared by wet phase immersion method had low hydraulic resistance compared to the membrane prepared by dry/wet phase immersion method.

<table>
<thead>
<tr>
<th>Membrane No.</th>
<th>Pure Water Flux (l.m(^{-2}).h(^{-1}))</th>
<th>Hydraulic Resistance (kPa. l(^{-1}).m(^{2}).h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>9.0</td>
<td>34.1</td>
</tr>
<tr>
<td>M2</td>
<td>19.6</td>
<td>18.5</td>
</tr>
<tr>
<td>M3</td>
<td>12.4</td>
<td>24.4</td>
</tr>
<tr>
<td>M4</td>
<td>19.3</td>
<td>16.6</td>
</tr>
<tr>
<td>M5</td>
<td>33.9</td>
<td>10.0</td>
</tr>
<tr>
<td>M6</td>
<td>26.4</td>
<td>12.3</td>
</tr>
<tr>
<td>M7</td>
<td>16.5</td>
<td>21.2</td>
</tr>
<tr>
<td>M8</td>
<td>33.9</td>
<td>9.7</td>
</tr>
<tr>
<td>M9</td>
<td>31.7</td>
<td>11.2</td>
</tr>
<tr>
<td>M10</td>
<td>32.1</td>
<td>10.3</td>
</tr>
<tr>
<td>M11</td>
<td>46.1</td>
<td>7.4</td>
</tr>
<tr>
<td>M12</td>
<td>38.6</td>
<td>8.5</td>
</tr>
</tbody>
</table>
3.3. Morphological studies

Fig. 2 represents the top layer micrographical view of the membrane prepared with 17.5% PES and 82.5% DMF by dry/wet immersion method respectively. These micrographs showed the pores present in the membrane. The magnification of the analysis should be increased so that the pores present in the top layer can be clearly seen. The presence of the pores in the top layer was confirmed from the morphological analysis of the cross section of these membranes. The porosity of the membranes can be compared to the morphological analysis of the membranes. The porosity of the membrane prepared by dry/wet immersion method with 17.5% PES and 82.5% DMF was 55.5% whereas the same membrane prepared by wet immersion method was 69.4%. The porosity of the 15% PES and 85% membrane was 61.9%. The formation of the macrovoids in the 17.5% PES and 82.5% DMF membrane prepared by dry/wet immersion method was less compared to the membrane prepared by wet immersion method. This may be due to the evaporation of the solvent in dry/wet immersion method allowing to form a top dense layer. In the wet immersion method the presence of nonsolvent, solvent and surfactant in the gelation bath controls the diffusion of the solvents in gelation bath. The top dense layer of the 17.5% PES and 82.5% DMF membrane prepared by dry/wet immersion method is longer than the 17.5% PES and 82.5% DMF membrane prepared by wet immersion method. The formation of dense layer in the top membrane surface may decrease the flux of the membrane. The pure water flux of the 17.5% PES and 82.5% DMF membrane prepared by wet immersion method was 16.5 l.m⁻².h⁻¹ which is higher than the membrane prepared by dry/wet immersion method. These pure water flux values clearly show that the presence of the macrovoids increase the flux.

![Fig. 2: Top surface view of PES membranes](image-url)
3.4. Mechanical properties

The mechanical properties of the membrane are given by the elongation at the break and tensile stress. The elongation at break and the tensile stress of the membranes were given in the Table 2. The membrane prepared with 17.5% PES and 82.5% DMF (M1) as solvent had tensile stress of 2.4260 MPa at the max load. The membrane prepared with 17.5% PES and 82.5% DMSO (M3) as solvent and the membrane prepared with 17.5% PES and 82.5% NMP (M2) as solvent had tensile stress of 2.0470 and 1.4080 respectively at the max load. The elongation at the break of these membranes was 2.2910 mm, 1.0950 mm and 1.8730 mm. The percentage strain at max load of these membranes was 11.460%, 5.475% and 9.365%. The membrane prepared with 17.5% PES and 82.5% DMF by dry/wet immersion method (M1) had a tensile stress of 2.4260 MPa whereas the membrane prepared with 15% PES and 85% DMF by wet immersion method (M4) had a tensile stress of 0.5617 MPa. The elongation at break of the membranes was 2.2910 mm and 1.5050 mm respectively. The percentage strain of these membranes was 11.460% and 7.525% respectively. Similar kind of trend is observed in other membranes. The mechanical properties of the membranes shows that the membrane prepared with DMF as solvent had more tensile strength compared to the membranes prepared with DMSO and NMP as solvents. The membrane preparation method does not affect the mechanical properties of the membranes.

<table>
<thead>
<tr>
<th>Membrane No</th>
<th>Elongation at break (mm)</th>
<th>Tensile stress (MPa)</th>
<th>% Strain at max load (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>2.29</td>
<td>2.42</td>
<td>11.4</td>
</tr>
<tr>
<td>M2</td>
<td>1.87</td>
<td>1.40</td>
<td>9.36</td>
</tr>
<tr>
<td>M3</td>
<td>1.09</td>
<td>2.04</td>
<td>5.47</td>
</tr>
<tr>
<td>M4</td>
<td>1.50</td>
<td>0.56</td>
<td>7.52</td>
</tr>
<tr>
<td>M5</td>
<td>0.89</td>
<td>0.49</td>
<td>4.49</td>
</tr>
<tr>
<td>M6</td>
<td>0.87</td>
<td>0.72</td>
<td>4.36</td>
</tr>
</tbody>
</table>

3.5. Protein rejection studies

The protein solutions were fed into the ultrafiltration test cell having a membrane. The permeate collected from the test cell were analysed with UV spectrometer at a λ<sub>max</sub> of 280 nm. From the concentration of the permeate the rejection percentage of the membrane can be determined by the equation (3).

3.5.1. Molecular weight cutoff (MWCO)

The molecular weight cutoff of the prepared membranes were determined individually based on the percentage rejection of proteins are shown in Table 3. Proteins like trypsin, pepsin and egg albumin having molecular weight of 20 kDa, 35 kDa and 45 kDa respectively were employed for the determination of the molecular weight cutoff. In general, the molecular weight cutoff of the membrane is determined by identifying an inert solute of lowest molecular weight cutoff that has a solute rejection of 80-100% in steady state UF experiments.

From the Table 3 the protein solute rejection and molecular weight cutoff of the membrane prepared with 17.5% PES and 82.5% Solvent by both dry/wet immersion method and wet immersion method. The membrane prepared with 17.5% PES and 82.5% DMF as a solvent by dry/wet immersion method (M1) had 86.24%, 88.74% and 91.32% of trypsin, pepsin and egg albumin rejection. The protein solute having lowest molecular weight of the three proteins is trypsin and it has the rejection percentage of 86.24%. Therefore the molecular weight cut off of the membrane is 20 kDa. The membrane prepared with DMF having 17.5% polymer composition had a good rejection.
The membrane prepared with 15% PES and 85% DMF as a solvent by dry/wet immersion method (M4) had 74.57%, 80.83% and 83.24% of trypsin, pepsin and egg albumin rejection. Trypsin having less than 80% of rejection so the protein having 80% of rejection was chosen as the molecular weight cut off. Therefore the molecular weight cut off of this membrane was 35 kDa. The membrane prepared with 15% PES and 85% DMSO by wet immersion method (M12) had 71.26%, 74.34% and 77.91%. In this case both trypsin and pepsin having a rejection percentage less than 80% so the molecular weight cut off of this membrane is 45 kDa.

The rejection percentage of the membrane prepared with 17.5% and 82.5% solvent such as DMF, DMSO and NMP was 84.23%, 79.62% and 78.77% respectively whereas the membranes prepared with 15% PES and 85% solvent had rejection percentage of 74.57%, 72.59% and 71.26% respectively. The membrane prepared with 17.5% PES and 82.5% DMF by dry/wet immersion method (M1) had a MWCO of 20 kDa. The membrane prepared with 15% PES and 85% DMF by dry/wet immersion method (M4) had a MWCO of 35 kDa. The molecular weight of the membrane prepared with 17.5% PES and 82.5% NMP by wet immersion method (M8) and the membrane prepared with 15% PES and 85% NMP by wet immersion method (M11) was 35 kDa and 45 kDa respectively. The results shows that the permeate flux and the rejection percentage are inversely proportional.

The membrane prepared with DMF as solvent had low molecular weight cut off compared to the membranes prepared with DMSO and NMP as solvent. The MWCo of membrane prepared with 15% PES and 85% DMF (M4) was 20 kDa whereas the membranes prepared with 15% PES and 85% solvent such as NMP (M5) and DMSO (M6) were 35 kDa. The MWCO of the membrane prepared with low polymer composition was less compared to the membrane prepared with high polymer composition. The MWCO of the membrane prepared with 17.5% PES and 82.5% NMP by dry/wet immersion method (M2) was 20 kDa whereas the membrane prepared with 15% PES and 85% NMP by dry/wet immersion method (M5) was 45 kDa. The membrane prepared with dry/wet immersion had low MWCO. The MWCO of the membrane prepared with 17.5% PES and 82.5% DMSO by dry/wet immersion method (M3) was 20 kDa whereas the membrane prepared with 17.5% PES and 82.5% DMSO by wet immersion method (M9) was 35 kDa.

### Table 3: Protein solute rejection and molecular weight cut off of the membranes

<table>
<thead>
<tr>
<th>Membrane No.</th>
<th>Protein rejection (%)</th>
<th>MWCO (kDa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trypsin (20 kDa)</td>
<td>Pepsin (35 kDa)</td>
</tr>
<tr>
<td>M1</td>
<td>86.2</td>
<td>88.7</td>
</tr>
<tr>
<td>M2</td>
<td>84.6</td>
<td>86.1</td>
</tr>
<tr>
<td>M3</td>
<td>85.4</td>
<td>87.6</td>
</tr>
<tr>
<td>M4</td>
<td>74.6</td>
<td>80.8</td>
</tr>
<tr>
<td>M5</td>
<td>71.3</td>
<td>76.1</td>
</tr>
<tr>
<td>M6</td>
<td>72.6</td>
<td>76.8</td>
</tr>
<tr>
<td>M7</td>
<td>84.2</td>
<td>86.5</td>
</tr>
<tr>
<td>M8</td>
<td>78.8</td>
<td>80.2</td>
</tr>
<tr>
<td>M9</td>
<td>79.6</td>
<td>82.1</td>
</tr>
<tr>
<td>M10</td>
<td>77.7</td>
<td>78.7</td>
</tr>
<tr>
<td>M11</td>
<td>63.9</td>
<td>67.6</td>
</tr>
<tr>
<td>M12</td>
<td>71.3</td>
<td>74.3</td>
</tr>
</tbody>
</table>

### 3.6. Pore statistics

The pore size, porosity and number of pores of the membranes determined from the protein rejection studies are shown in Table 4. The average pore radius is in the order of $10^{-10}$. The average
pore radius, porosity of the membrane and the pore density (i.e. the number of pores in the effective filtration area) were determined the equation (4), (5) and (6) respectively.

The average pore radius of the membrane prepared with 17.5% PES and 82.5% DMF by dry/wet immersion method (M1) was 29.56 Å whereas the same for the membrane prepared with 15% PES and 85% DMF by dry/wet immersion method (M4) was 39.26 Å. The porosity of these membranes was 2.31 and 3.73 respectively. The pore density of these membranes was 8.42 and 7.70.

The membranes prepared with 15% PES and 85% DMF by wet immersion method (M10), 15% PES and 85% DMSO by wet immersion method (M11) and 15% PES and 85% NMP by wet immersion method (M12) had the average pore radius as 39.26 Å, 43.52 Å and 44.09 Å respectively. These same membranes had porosity of 3.73, 4.60 and 5.84 respectively. The pore densities of these same membranes are 7.70, 7.74 and 9.56 respectively.

The average pore radius of the membrane prepared with 17.5% PES and 82.5% NMP by dry/wet immersion method (M2) was 30.13 Å. The membrane prepared with same composition but by the wet immersion method (M7) has a mass transfer coefficient of 4.484 X10\(^6\) m/s. The true retention percentage of these membranes was 91.69% and 92.34%

The mass transfer coefficient of the membranes prepared with 17.5% PES and 82.5% DMF by dry/wet immersion method (M1) has a mass transfer coefficient of 3.922 X10\(^6\) m/s. The membrane with the same composition but by the wet immersion method (M7) has a mass transfer coefficient of 4.484 X10\(^6\) m/s. The true retention percentage of these membranes was 91.69% and 92.34%

### Table 4: Molecular weight cut off and pore statistics of the membranes

<table>
<thead>
<tr>
<th>Membrane No.</th>
<th>MWCO (kDa)</th>
<th>Average pore radius (Å)</th>
<th>Porosity (\times 10^{-5})</th>
<th>Pore Density (\times 10^{12})</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>20</td>
<td>19.6</td>
<td>1.8</td>
<td>0.84</td>
</tr>
<tr>
<td>M2</td>
<td>20</td>
<td>30.1</td>
<td>4.9</td>
<td>1.73</td>
</tr>
<tr>
<td>M3</td>
<td>20</td>
<td>29.8</td>
<td>3.2</td>
<td>1.13</td>
</tr>
<tr>
<td>M4</td>
<td>35</td>
<td>30.3</td>
<td>4.1</td>
<td>1.44</td>
</tr>
<tr>
<td>M5</td>
<td>45</td>
<td>39.6</td>
<td>6.5</td>
<td>1.32</td>
</tr>
<tr>
<td>M6</td>
<td>45</td>
<td>38.7</td>
<td>6.2</td>
<td>1.32</td>
</tr>
<tr>
<td>M7</td>
<td>20</td>
<td>30.3</td>
<td>4.1</td>
<td>1.44</td>
</tr>
<tr>
<td>M8</td>
<td>35</td>
<td>39.6</td>
<td>6.5</td>
<td>1.32</td>
</tr>
<tr>
<td>M9</td>
<td>35</td>
<td>36.7</td>
<td>6.2</td>
<td>1.32</td>
</tr>
<tr>
<td>M10</td>
<td>45</td>
<td>41.1</td>
<td>5.5</td>
<td>0.91</td>
</tr>
<tr>
<td>M11</td>
<td>45</td>
<td>49.0</td>
<td>7.1</td>
<td>0.95</td>
</tr>
<tr>
<td>M12</td>
<td>45</td>
<td>44.9</td>
<td>6.5</td>
<td>1.03</td>
</tr>
</tbody>
</table>

### 3.7. Mass transfer coefficient

A plot of \(\ln[(1-R)/R]\) versus \(J_v\) was made for the protein which is determined as MWCO. The data were fit for linear models with a slope of \(1/k_m\) and an intercept of \(\ln[(1-R)/R]\) as per the Eq. (4.5). The calculated values of mass transfer coefficient (km) and true retention coefficient (R) are given in Table 5. The mass transfer coefficient for the membrane prepared with 17.5% PES and 82.5% DMF by dry/wet immersion (M1) method has a mass transfer coefficient of 3.922 X10\(^6\) m/s. The membrane with the same composition but by the wet immersion method (M7) has a mass transfer coefficient of 4.484 X10\(^6\) m/s. The true retention percentage of these membranes was 91.69% and 92.34%.
preparing with NMP as solvent is higher than the membranes prepared with DMF and DMSO as solvents. The true retention percentage of the membranes prepared with DMF is higher compared to the membranes prepared with DMSO and NMP as solvent. The membrane prepared with 17.5% PES and 82.5% DMSO (M3) as solvent had a mass transfer coefficient of 6.173 X10\(^6\) m/s. The membrane prepared with 15% PES and 85% DMSO (M9) as solvent had a mass transfer coefficient of 9.901 X10\(^6\) m/s. The true retention of these membranes was 91.01% and 86.83%. The mass transfer coefficient of the membrane prepared with 17.5% polymer composition is less than the membranes prepared with 15% polymer composition. Whereas the true retention percentage of the membrane prepared with 17.5% polymer is more than the membrane prepared with 15% polymer composition. The membrane prepared with 15% PES and 85% NMP as solvent by dry/wet immersion method (M5) had a mass transfer coefficient of 13.889 X10\(^6\) m/s. The membrane with same composition but prepared by wet immersion method (M11) had a mass transfer coefficient of 20.833 X10\(^6\) m/s. The true retention percentage of these membranes were 87.04% and 77.07%. The mass transfer coefficient of the membrane prepared by dry/wet immersion method is less than the membrane prepared by wet immersion method.

<table>
<thead>
<tr>
<th>Membrane No</th>
<th>Mass transfer Coefficient X10(^6) m/s</th>
<th>True retention %</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>3.9</td>
<td>91.7</td>
</tr>
<tr>
<td>M2</td>
<td>12.7</td>
<td>89.0</td>
</tr>
<tr>
<td>M3</td>
<td>6.2</td>
<td>91.1</td>
</tr>
<tr>
<td>M4</td>
<td>8.1</td>
<td>86.9</td>
</tr>
<tr>
<td>M5</td>
<td>13.9</td>
<td>87.0</td>
</tr>
<tr>
<td>M6</td>
<td>9.9</td>
<td>86.8</td>
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<tr>
<td>M7</td>
<td>4.5</td>
<td>92.3</td>
</tr>
<tr>
<td>M8</td>
<td>11.8</td>
<td>87.9</td>
</tr>
<tr>
<td>M9</td>
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<td>M10</td>
<td>11.4</td>
<td>85.9</td>
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<tr>
<td>M11</td>
<td>20.8</td>
<td>77.1</td>
</tr>
<tr>
<td>M12</td>
<td>11.1</td>
<td>82.9</td>
</tr>
</tbody>
</table>

### 3.8. Metal ions separation

The membrane characterized by the above mentioned characterization is used for the application studies. The metal ion solution prepared without chelating agent using only distilled water is first used. The permeate of the metal ion solution is collected and analyzed by UV spectrometer to find the concentration of the metal ion. The concentration of the metal ion in the permeate is almost equal to the concentration of metal ions in the feed solution. This states that the rejection of metal ion by the membrane without the chelating agent is impossible. So the chelating agent like PVA and PDDA were used in metal ion separation. The rejection percentage of the metal ion with two different chelating agents is given in the Fig.3 to 6. The percentage removal of metal ion with PDDA is higher than the PVA chelating agent. The percentage removal of metal ion in 17.5% PES and 82.5% DMF membrane prepared by dry/wet immersion method (M1) is high compared to the other membranes. The percentage removal of Cu (II) and Cr (III) for this membrane is 94.52%, 95.46% and 98.13% respectively. The same metal ion separation with PVA as chelating agent is 77.58%, 80.03% and 86.14% respectively. The percentage removal of Cr (III) was higher than the other two metals. The percentage removal of nickel, copper and chromium by the membrane prepared by 17.5% PES and 82.5% DMF by dry/wet immersion method (M1) was 77.58%, 80.03%
and 86.14%. The same membrane when metal ion solution is prepared with PDDA as chelating agents, the removal percentages are 94.52%, 95.46% and 98.13%. The metal ion rejection values for the membrane prepared with 17.5% PES and 82.5% NMP (M2) was 73.61%, 77.29% and 81.13% respectively. The same for the membrane prepared with 17.5% PES and 82.5% DMSO (M3) was 75.43%, 78.57% and 81.13% respectively. The metal ion separation for nickel, copper and chromium are 94.52%, 95.46% and 98.13% respectively for the membrane prepared with 17.5% PES and 82.5% DMF by dry/wet immersion method (M1). The same for the membrane prepared with 17.5% PES and 82.5% NMP by dry/wet immersion method (M2) is 87.61%, 89.19% and 93.58% respectively. The metal ion separation for the membrane prepared with 17.5% PES and 82.5% DMSO by dry/wet immersion method (M3) is 91.21%, 93.61 and 96.82% respectively. The metal ion separation for nickel, copper and chromium are 94.52%, 95.46% and 98.13% respectively for the membrane prepared with 15% PES and 85% DMF as solvent by dry/wet immersion method (M4). The metal ion separation for the membrane prepared with 15% PES and 85% DMS as solvent by wet immersion method (M10) are 79.16%, 80.27% and 83.89% respectively.

**Fig. 3:** Metal ions/PVA complex rejection of membranes from M1 to M6

**Fig. 4:** Metal ions/PVA complex rejection of membranes from M7 to M12
3.9. Metal ions permeate flux

The permeate rate was inversely proportional to the percentage rejection. The permeate rate or product rate of the membranes are given in the Fig. 7 to 10. The permeate rate followed a similar trend like the pure water flux. The permeate rate of the nickel ion is high compared to the copper and chromium metal ions. In 17.5% PES and 82.5% DMSO membrane prepared by dry/wet immersion method the product rate of the nickel, copper and chromium metal ions was 9.98 l.m⁻².h⁻¹, 7.45 l.m⁻².h⁻¹ and 6.19 l.m⁻².h⁻¹. The chelating plays a major role in the metal ion separation. The binding capacity of the chelating agent affects the separation performance. In this present investigation two chelating agents were employed (i.e PVA and PDDA). The metal ion permeate rate is high in the PVA chelating agent. The metal ion product rate of the membranes prepared with NMP as solvent was high compared to the metal ion product rate of the membranes prepared with DMF and DMSO as solvents. This is similar to the pure water flux of the membrane. The metal ion permeate rate of
the membrane prepared with low polymer composition was higher than the membranes prepared with high polymer composition. The membranes prepared by wet immersion method had high permeate rate compared to the membranes prepared by dry/wet immersion method. The metal ion permeate rate of Ni, Cu (II) and Cr (III) in the membrane prepared 17.5% PES and 82.5% DMSO by dry/wet immersion method was 9.98 l.m\(^{-2}\).h\(^{-1}\), 7.45 l.m\(^{-2}\).h\(^{-1}\) and 6.19 l.m\(^{-2}\).h\(^{-1}\) whereas, the same in the membrane prepared by wet immersion method was 23.27 l.m\(^{-2}\).h\(^{-1}\), 21.95 l.m\(^{-2}\).h\(^{-1}\) and 20.79 l.m\(^{-2}\).h\(^{-1}\).

**Fig. 7:** Metal ions/PVA complex flux of membranes from M1 to M6

**Fig. 8:** Metal ions/PVA complex flux of membranes from M7 to M12
CONCLUSION

In this investigation PES is chosen as a polymer to prepare membrane. It has been used with three solvents DMF, DMSO and NMP. Dry/wet immersion method and wet immersion method were employed to prepare membranes. The effects of selection of solvents, composition of solvent and the effects of preparation method on membrane performance are studied. Membrane characterization like pure water flux and membrane hydraulic resistance had been done. The characterization of prepared membranes illustrates that the pure water flux was increased while the membrane hydraulic resistance was decreased, as the concentration of solvent in the casting solution is increased. The MWCO and pore statistics results obtained from protein rejection studies demonstrate that the MWCO, pore radius and porosity show significant increase as the concentration of solvent in the polymer solution increased. The membranes were used in the application of toxic heavy metal ion removal. Heavy metal ions like, Cu (II) and Cr (III) were separated by using the prepared membranes. The results of the above mentioned methods were given and discussed.
REFERENCE


