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## Synthesis and Characterization of Polyethersulfone/Carbon Molecular Sieve Based Mixed Matrix Membranes for Water Treatment Applications

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### Abstract

Novel mixed matrix membrane was prepared by incorporating the carbon molecular sieves (CMS) into polyethersulfone (PES) matrix. Flat sheet membranes of different filler concentrations were synthesized through phase inversion technique. Scanning electron microscope and Thermogravimetric analyzer were used to investigate the morphology and thermal stability of synthesized membranes respectively. Finally membranes were tested for their pure water flux and sodium chloride (NaCl) rejection (100ppm aqueous solution). Investigation has shown that all synthesized membranes had asymmetric structure with thin dense top and well-defined macropores in sublayer. It is noticed that inclusion of inorganic filler has improved the thermal stability as well as pure water flux of mixed matrix membranes (upto 33.8LMH at 3 bar). Moreover, synthesized mixed matrix membranes also showed better NaCl rejection (upto 26.13% at 3 bar) than pure polymeric membranes.

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*Keywords:* Mixed matrix membranes, carbon molecular sieves, polymeric membranes, performance of mixed matrix membrane

### 1. Introduction

For the past several decades, synthetic polymeric membranes are being used for a wide variety of liquid separations such as microfiltration, ultrafiltration, reverse osmosis, nanofiltration. A common method for the preparation of polymeric membranes is the phase separation process [1]. Different techniques have been employed over the years to improve the different properties membranes to make it viable for range of applications [2]. Inclusion of inorganic material to enhance the properties such as flux, antifouling property, thermal and mechanical properties etc. Inclusion of any filler in form of disperse form in continuous matrix is defined as mixed matrix membrane [2, 3]. Polyethersulfone (PES) is widely used as a membrane material because of its commercial availability, processing ease, favorable selectivity, permeability characteristics and good mechanical and thermal properties. PES is an amorphous glassy and hydrophilic polymer containing sulfone groups [4]. Carbon molecular sieve (CMS) is added to this matrix as an inorganic filler to achieve the higher flux and higher retention since carbon based sieves are reported to be good adsorbent for heavy metal ions and also provide excessive filtration area for permeation [5, 6]. In this study, polyethersulfone is used as continuous matrix whereas carbon molecular sieve is added to polymer matrix as an inorganic filler to achieve a better overall performance in terms of flux and salt retention at low pressures.

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## 2. Methodology

### 2.1. Materials

Polyethersulfone (PES) was used as polymer to synthesize the membrane and it was purchased from BASF Co. (Ultrason® E6020P). Since, PES is hydrophilic in nature and absorbs moisture rapidly; it was dried for 5 hrs in a dry oven at 100 °C before its use in casting solution preparation. N-methyl-2-pyrrolidone (NMP) from Merck Co. was used as solvent. Deionized water at room temperature was used as a non-solvent in coagulation bath. Sodium chloride (NaCl-pure) was purchased from R & M chemicals Ltd. to study the membranes rejection for sodium salt. Carbon molecular sieve was purchased in granular form from Japan Enviro Chemicals, Ltd. and then it was grinded to achieve the desired size for mixed matrix membrane preparation.

### 2.2. Flat Sheet Membrane Preparation

Casting solution for flat sheet membrane was prepared by dissolving 15wt% PES into 85wt% of NMP. This solution was then stirred overnight at 200 rpm for complete dissolution of polymer into solvent. Then prepared solution was kept for 45 mins to remove any bubbles from solution. Flat sheet membranes were prepared by pouring the casting solution on immaculate glass plates and membranes were cast using casting knife at thickness of 200 microns. Glass plates were then immersed in water bath till membranes came off naturally after solvent exchange. Afterwards, synthesized membranes were put into separate water (deionized) bath for complete removal of solvent.

### 2.3. Carbon Molecular Sieve (CMS) Powder Preparation

Carbon molecular sieve was grinded by “Mortar Grinder” (RockLab) for 90 mins. Particle size analysis and distribution was determined by using “Mastersizer” particle size analyzer. After achieving the distribution of CMS particles, mechanical sieving was done using (63 microns) sieve.

### 2.4. Mixed Matrix Membrane Synthesis

For synthesis of mixed matrix membrane, known amount (1 wt%) of inorganic filler was dissolved into solvent (NMP) for 45 mins. at 200 rpm. 10% of polymer was then added to the casting solution and solution was stirred at 200 rpm for 1 hr. Later, remaining polymer was added to the solution and it was left for overnight stirring. Casting solution was then kept at room temperature for air bubbles removal for 45 mins. Finally, solution was sonicated for 45 min before membrane casting. Membrane casting was done on glass plates at 200 microns thickness with Elcometer casting knife. Table 1 presents the casting solution composition of synthesized membranes.

Table 1. Composition of Casting Solution Used for Membrane Synthesis

Membrane Code	PES (wt%)	CMS (wt%)	Casting Method	Casting Thickness ( $\mu\text{m}$ )
E5	15%	0%	wet phase inversion	200
E5C1	15%	1%	wet phase inversion	200
E5C5	15%	5%	wet phase inversion	200

### 2.5. Characterization

#### 2.5.1. Scanning Electron Microscope (SEM)

Surface morphology and cross section of prepared membranes was carried out using Variable Pressure Scanning Electron Microscope (VPFESEM, Zeiss Supra55 VP). All membrane samples were dipped in liquid nitrogen before imaging to achieve clean samples. Samples were attached to plates with two sided adhesive tapes in a lateral position. Membrane thickness and structural information was evaluated through SEM analysis.

#### 2.5.2. Thermogravimetric Analyzer (TGA)

Thermogravimetric analysis was accomplished to determine the thermal stability of the modified and unmodified membranes with PERKEN ELMER simultaneous Analyzer STA6000 under nitrogen atmosphere 100ml/min at a heating rate of 10°C/min.

#### 2.5.3. Filtration Experiment

Performance of flat sheet polymeric and mixed matrix membrane was tested using a stirred dead end filtration cell (UHP-90) from ADVANTEC. A 90 mm diameter circular membrane cut was used for testing while active surface area of membrane was

54.5 cm<sup>2</sup>. Nitrogen gas cylinder was used to create the desired pressure in filtration cell. All membranes were compacted at 3 bar for 3 hours before pure water flux (L/m<sup>2</sup>.hr) investigation. For rejection studies, sodium chloride (NaCl) model solution of 100ppm concentration was tested at different pressures. HANNA conductivity meter was employed to measure the concentration of ions in collected permeate.

### 3. Results and Discussion

#### 3.1. Scanning Electron Microscopy Analysis

Morphological studies of pure polymeric and mixed matrix membranes were accomplished by scanning electron microscope to attain the qualitative information about their thickness and microstructure. As shown in Fig. 1(a,b) all studied membranes have shown asymmetric structure with thin dense top layer and finger like structure underneath. Sponge like structure also fills in the area between the macropores present in membrane structure as shown in Fig. 1. To understand the formation of these pores and thin active layer on top of the membranes, mechanism of membrane formation is widely reported in literature [7-9]. Since immersion of glass plate containing spread of casting solution into coagulation bath, suddenly escalates the solvent exchange with non-solvent (water in this case). Solvent due to its affinity to non-solvent leaves the polymer rich phase behind due to its increased concentration (i.e. polymer rich phase) in solution, polymeric chains start to precipitate hence making the top active thin layer. Meanwhile, solvent keep diffusing into non-solvent leaving the finger like pores behind as can be seen in Fig. 1. Further analysis revealed that for mixed matrix membranes, CMS particles stayed below the thin dense top layer in macropores and no particle appeared on top surface hence resulting in pure polymeric selective layer.

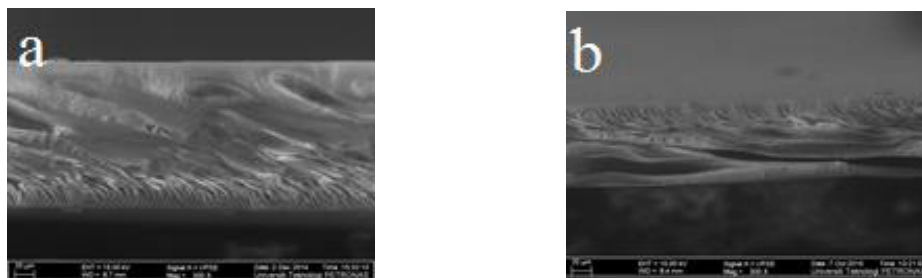


Fig. 1: Cross Section SEM Images Of (a) PES15%, (b) PES15% CMS5%

#### 3.2. TGA Analysis

TGA analysis was completed to evaluate the thermal stability of pure polymeric and mixed matrix membranes. Analysis has shown that for pure polymeric membranes thermal degradation started at 485°C. It is noted that addition of 1% and 5% CMS in polymeric membrane added significant stability to the mixed matrix membrane. Further analysis revealed that after heating to 800°C, addition of CMS reduced the percent weight loss in mixed matrix membranes as shown in Fig. 2. It is determined that weight percent loss in case of 5% CMS inclusion was slightly greater than 1%, yet both had better thermal stability than nascent polymeric membrane. Same results have been reported in [10, 11] where addition of 10% CMS increased the residual weight in comparison to pure polymeric membrane. So, it could be deduced that inclusion of CMS has raised the thermal stability of mixed matrix membrane while its weight percent could adversely affect the thermal stability if exceeds the certain limit.

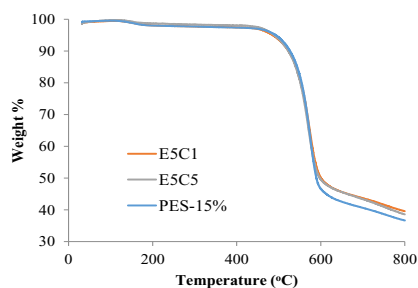


Fig.2: TGA graphs for PES, PES-CMS1%, PES-CMS5%

### 3.3. Performance of PES and PES/CMS based MMM

#### 3.3.1. Pure Water Flux

Pure water flux was investigated at different pressure from 1-3 bar with interval of 0.5 bar and permeates volume was collected from bottom of filtration cell after 30 mins. Pure water flux was calculated by Eq. 1, here  $J$ ,  $V$ ,  $A$  and  $\Delta t$  are notations for flux, and volume collected, membrane effective area and time respectively [12].

$$J = V/A.\Delta t \quad (1)$$

It can be noticed from the Fig. 3 that inclusion of CMS has significantly improved the pure water flux for mixed matrix membranes. For instance, in this study PWF for pure PES is determined 8.691 L.m<sup>-2</sup>.h<sup>-1</sup> and it soared to 33.8 L.m<sup>-2</sup>.h<sup>-1</sup> for mixed matrix membrane i.e. PES-CMS1%. The reason behind the increased flux could be rendered to increased pore sizes due to presence of filler particles. The same result has been reported by [13]. It is observed that inclusion of CMS upto 5 wt% resulted in decreased pure water flux i.e. 27.17 L.m<sup>-2</sup>.h<sup>-1</sup> in comparison to MMM with CMS1 wt% i.e. (E<sub>5</sub>C<sub>1</sub>). Likely reason for such behavior of membrane could be due to aggregation of filler particles in macropores which hindered the path for water permeation. Same results have been reported by [14, 15] where inclusion of TiO<sub>2</sub> particles (more than 2 wt%) decreased the pure water flux. It can also be noted from Fig. 3 that PWF is in a linear relationship with Trans membrane pressure since higher values of flux were noted at higher pressures. Results have shown that addition of filler particles has improved the pure water flux here and their appropriate weight percent is a vital parameter to achieve better membrane performance.

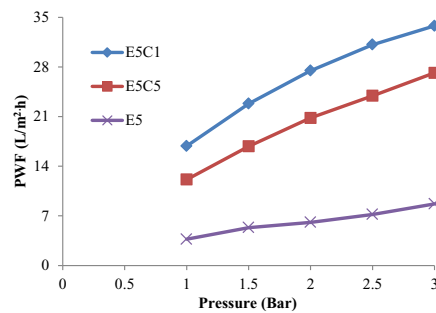


Fig.3: Comparison of Pure water flux (L/m<sup>2</sup>.hr<sup>-1</sup>) for synthesized membranes

#### 3.3.2. Observed Rejection ( $R_{obs}$ )

Rejection of pure and mixed matrix membranes was evaluated by filtering the model solution of sodium chloride of 100 ppm concentration. Observed rejection was calculated by Eq. 2, where  $C_p$  and  $C_f$  denotes permeate concentration and feed concentrations respectively [12].

$$R_{obs} (\%) = (1 - C_p/C_f) * 100 \quad (2)$$

It is noted that polymeric membrane with 1 wt% filler concentration has shown the maximum rejection (26.13 % at 3 bar) among the three membranes. It can be seen from Figure 4 that for all three membranes a sudden dip in rejection of sodium chloride is observed at 2 bar transmembrane pressure probably due to concentration polarization. Similar trend for rejection of sodium chloride have been reported in [16, 17] also where a sudden loss in rejection is noticed (at 2 bar) due to concentration polarization at membrane surface. Rejection for all three membranes were noted to be in order presented here; PES-CMS 1% > PES-CMS 5% > PES 15%. Increase in observed rejection in case of PES-CMS1% shows that presence of carbon molecular sieve has introduced charge to membrane hence improving the retention of solute through Donnan exclusion mechanism [18, 19]. Whereas in case of polymeric membrane with 5% CMS, increased pore size adversely affected the rejection and salt ions passed through rather easily hence reducing the overall rejection [16, 20].

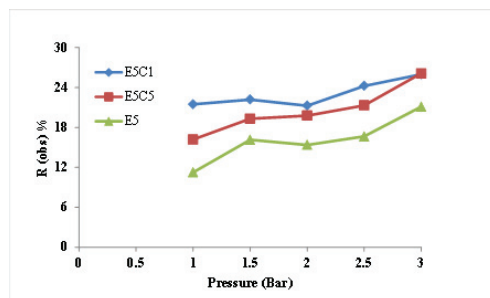


Fig.4: Rejection of synthesized membranes for 100ppm NaCl aqueous solution

#### 4. Conclusion

In this study, carbon molecular sieve was added to polymer matrix to increase its permeability and retention ability. SEM images have shown asymmetric structure with thin dense top layer with macropores in sublayer along with spongy structure near bottom. It is noted 1 wt% and 5 wt% carbon molecular sieves improved the pure water flux and rejection of sodium chloride in comparison to nascent membrane. It is deduced that amount of inorganic filler played an important role for membrane overall performance. Since MMM with 5 wt% CMS i.e.  $E_5C_5$  performed poor in comparison to MMM with CMS-1 wt% ( $E_5C_1$ ). It is suggested that further investigation is required to investigate the role of inorganic filler's weight percent in mixed matrix membrane for performance enhancement. Also, it can be safely assumed that this novel membrane has a large potential to be used as loose nanofiltration membrane because of its relatively better performance at lower pressures hence providing a less costly treatment option. Nevertheless, further investigation is required to fully understand its potential and performance capability under simulated conditions.

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