



Research Article

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Polyethersulfone / poly(acrylic acid) / calcium chloride composite membranes for improved dye removal

K. Rambabu* and S. Velu

Chemical Engineering Division, School of Mechanical and Building Sciences, Vellore Institute of Technology University, Vellore, India

ABSTRACT

A series of poly(ethersulfone) (PES) ultrafiltration membrane blended with poly(acrylic acid) (PAA) and calcium chloride (CaCl_2) was prepared by phase inversion technique. CaCl_2 was varied from 0 – 3 wt% in the casting solution composition to study its effect on the blend membranes. Prepared membranes were analyzed for their morphology, ultrafiltration (UF) features and dye rejection performance. Surface roughness was increased drastically for high concentration CaCl_2 composite membranes. Surface hydrophilicity was improved due to the addition of CaCl_2 in the composite membranes. Porosity measurements confirmed the enhanced porous nature of PES/PAA/ CaCl_2 blend membranes than the pristine PES membrane. Pure water flux of the CaCl_2 composite membranes was improved to a maximum of four times as compared with pure PES membrane. Dye rejection studies revealed that the blend membranes had almost the same rejection as that of the pristine membrane with a largely enhanced flux rate. Results obtained clearly indicated the better performance of 1 wt% CaCl_2 blend membrane among the synthesized UF membranes.

Keywords: Polyethersulfone, Calcium chloride, Polyacrylic acid, Membrane characterization, Dye rejection.

INTRODUCTION

In recent years, membrane separation is a promising technology for separation operations due to its potential advantages over other conventional separation methods like absorption, distillation etc., [1,2]. Ultrafiltration (UF) is a type of membrane separation operations for separating dissolved macromolecules from liquid streams using pressure difference as the driving force [2,3]. Industrially, UF is mainly applied for water and wastewater treatment processes [4]. UF membranes are usually prepared from a wide range of materials which includes polymers, ceramics, metal oxides, etc. Polymeric membranes are largely preferred for UF membrane synthesis owing to their ease of fabrication and preparation [5]. These polymers include polysulfone [6,7], polyethersulfone [8-10], polyvinylidene fluoride [11,12] and cellulose acetate [13,14]. Polyethersulfone (PES) is an excellent polymeric material for UF membrane synthesis due to its desirable thermal, mechanical and chemical properties [15]. Membranes prepared using PES are used in many broader applications including both industrial and domestic purposes. However, PES membranes suffer from the problem of low fluxes and membrane fouling affecting their potential applications [15]. To overcome these limitations, PES membranes are often improved by adding various modifiers to PES matrix to enhance the flux and fouling resistance of the resulting composite membranes [15]. These modifiers are usually of polymeric or inorganic type which modify the properties of the PES polymer to increase the permeate flux and antifouling ability of resulting membranes [16-20]. Most of the polymeric additives have uniform distribution throughout the base membrane matrix in comparison with inorganic additives [21].

However, the miscibility of the polymeric constituents (base and additive) is a serious limitation on the PES – polymeric additives blend system [22]. Rate of demixing of the polymeric constituents seriously affects the membrane structure during membrane synthesis via phase inversion technique [22]. Addition of inorganic modifiers to the PES membrane results in enlarged pore size (both surface and sublayer) causing high porosity of the blend membrane. This cause an increase in permeate flux, however, with considerable loss in the solute rejection percentage for the inorganic blend membranes [15]. Recent studies involve a systematic combination of both polymeric and inorganic additives to the PES matrix to have an enhanced flux without any decrease in the rejection efficiency [15].

Poly(acrylic acid) (PAA) is one of the most studied polymeric additive for UF membranes and it has been successfully employed as a modifier with various polymer systems such as polysulfone [7], polyvinylidene fluoride [11] and polyethersulfone [23]. PAA being an easily miscible additive, modifies the membrane morphology and thereby the permeate flux for the resulting blend membrane. Similarly, calcium salts are explored to larger extent as a potential inorganic additive for the various polymeric membranes resulting in high flux and enhanced rejection [24, 25]. In general, calcium salts, particularly CaCl_2 , would improve the hydrophilicity and flux of the resulting blend membrane [24]. Also, addition of CaCl_2 as an additive would boost the chloride resistance of the membrane, so that the resulting membrane could be subjected for chlorine containing feed stream and chlorine based chemical cleaning methods [26].

In this current study, modification of the PES membrane using polymeric additive PAA and inorganic salt CaCl_2 as modifiers has been carried out using phase inversion technique. Prepared membranes were characterized for surface roughness, hydrophilicity, porosity and pure water flux. Dye rejection capacity for the pristine and composite PES membranes were analyzed using various dyes solutions. Results for the characterization and performance analysis of the blend membranes were compared against the pure PES membrane.

EXPERIMENTAL SECTION

2.1. Materials

Polyethersulfone (PES, Veradel 3200P) in powder form was supplied by Solvay specialities India Pvt. Ltd (India) and it was dried at 120 °C for 8 h before being used. Low molecular weight Polyacrylic acid (PAA, average $M_w = 40,000$) was purchased from Sigma Aldrich (India). *N, N*-dimethyl formamide (DMF) solvent was obtained from SRL Chemicals (India). Congo red and Orange II dye powders were purchased from Avra Synthesis Pvt. Ltd (India). Freshly prepared deionized water was employed for the preparation of gelation bath, dye solution preparation and membrane storage. All the reagents used in the experimental work were of analytic grade and used as such without any further treatment.

2.2. Membrane Preparation

Phase Inversion technique is the most versatile and widely used membrane preparation method for asymmetric UF membrane synthesis [4]. The cast solution for a given membrane was prepared by dissolving required amounts of the PES, PAA and CaCl_2 in DMF solvent, as shown in Table 1. Based on previous studies, the polymeric additive PAA was fixed to a concentration of 2.5 wt% in the composite membrane for which the miscibility of PAA with PES was optimum [15]. The concentration of CaCl_2 was varied from 0 to 3 wt%. The cast solution was magnetically stirred (along with mild heating) for 10 h to ensure complete dissolution of the PES polymer and modifiers in the DMF solvent. Subsequently, the cast dope was debubbled for 4 h to remove the trapped air. The solution was then cast on smooth glass plate with the help of a doctor blade for a fixed thickness of 200 μm . The membrane film was allowed for dry phase inversion for 30 sec. Then the glass plate along with the resulting film was immersed in a water bath for wet phase inversion. After 30 min of gelation, the membrane was removed from the water bath and washed with distilled water to remove the residual solvent. The resulting membrane was then stored in a water bath until further usage.

2.3. Membrane Characterization

Atomic Force Microscopy (AFM) (NTEGRA PRIMA-NTMDT, Ireland) was used to analyze surface roughness (R_a) of all the synthesized membranes. Results obtained were for an effective sampling area of 25 $\mu\text{m} \times 25 \mu\text{m}$.

Hydrophilicity of all the prepared membrane was measured in terms of surface water contact angle. The contact angle on the membrane surface was measured using a goniometer (DGX Digidrop, France). The mean water contact

angle of each membrane was obtained by averaging the static contact angle measured at four different positions on the membrane sample's surface.

Membrane porosity for all the membranes was calculated by measuring the water uptake capacity of the membrane sample. A given membrane sample was soaked in deionized water for 24 hours. The wet sample weight was then weighed after mopping the excess water on the sample surface using filter paper. Then the wet sample was placed in a vacuum oven at 80 °C for 24 h. The dry weight of the membrane sample was then weighed until the sample weight became constant. The membrane porosity of the sample was then calculated using Eq. (1).

$$\varepsilon = \frac{W_w - W_d}{\rho_w A l} \quad (1)$$

where ε is the membrane porosity, W_w and W_d (kg) are the wet and dry weight of the membrane sample, A (m^2) is the membrane surface area, l (m) is the membrane thickness and ρ_w ($kg m^{-3}$) is water density.

Pure water flux and rejection analysis for the prepared membranes were carried out in a dead-end UF stirred cell filtration system connected to a nitrogen gas cylinder. The UF stirred cell (Amicon, Model 8400) had an inner diameter of 76 mm and a volume capacity of 400 mL with teflon coated magnetic paddle. The effective filtration area was 38.5 cm^2 . The nitrogen gas cylinder served as a pressure source for the feed stream. All membranes were compacted at a pressure for 414 kPa for about 1 h before water flux measurement. Pure water flux of every membrane sample was then measured at an operation pressure of 276 kPa using Eq. (2).

$$J_w = \frac{Q}{A \Delta T} \quad (2)$$

where, J_w – permeate flux ($L m^{-2} h^{-1}$), Q – quantity of permeate (L); A – membrane area (m^2), ΔT – filtration time (h)

Rejection performance of the pure and blended PES membranes was analyzed through dye separation studies. Congo red and Orange II dye solutions at a feed concentration of 0.1 g L^{-1} were used for the dye rejection studies. The ultrafiltration of the dye solutions was carried out at 276 kPa in the UF stirred cell. Permeate was collected over defined time intervals in graduated tubes and the tube contents were analyzed for dye concentration. Solute rejection percentage (%SR) was calculated using Eq. (3).

$$\% SR = \left(1 - \frac{C_p}{C_f} \right) \times 100 \quad (3)$$

where, C_p and C_f are dye concentrations in the permeate and feed streams, respectively. The dye concentration of the dyes in the permeate and feed streams was measured using a UV-Vis-NIR spectrophotometer (UV-3600, Shimadzu Corp., USA).

Table 1. Composition and characterization results for the pure and blended PES membranes

Membrane ID	Membrane Composition (by weight %)				Surface roughness, R_a (in nm)	Contact angle	Porosity, ε
	PES	PAA	CaCl ₂	Solvent (DMF)			
M1	18	0	0	82	39.55	65.5	0.53
M2	18	2.5	0	79.5	42.21	61	0.57
M3	18	2.5	1	78.5	54.03	54.5	0.72
M4	18	2.5	2	77.5	97.42	46	0.67
M5	18	2.5	3	76.5	153.86	37.5	0.6

RESULTS AND DISCUSSION

The various characterization and performance results for PES/PAA/CaCl₂ blend membranes were compared against the pure PES membrane. The advantages and limitations of the blend membrane system over the unmodified PES membrane is discussed in the below section.

3.1. Atomic Force Microscopy

In the AFM analysis, as shown in Fig. 1, the lighter or the brighter regions shows the nodular structures and the darker regions shows the depressions or pores of the membrane. In general, increase in surface roughness is one of the probable cause for more membrane fouling which will in turn results in flux decline [27]. As shown in Table 1, it was observed that the addition of CaCl₂ to PES matrix increased the surface roughness. However, the rate of increase in surface roughness had a rapid growth after a cut-off concentration of 1 wt% for CaCl₂ in the casting dope. This lead to a possible conclusion that CaCl₂ composite membrane with more than 1 wt% CaCl₂ would be prone to more fouling due to increased surface roughness. However, there are several factors which determine the fouling nature of a membrane [1,2].

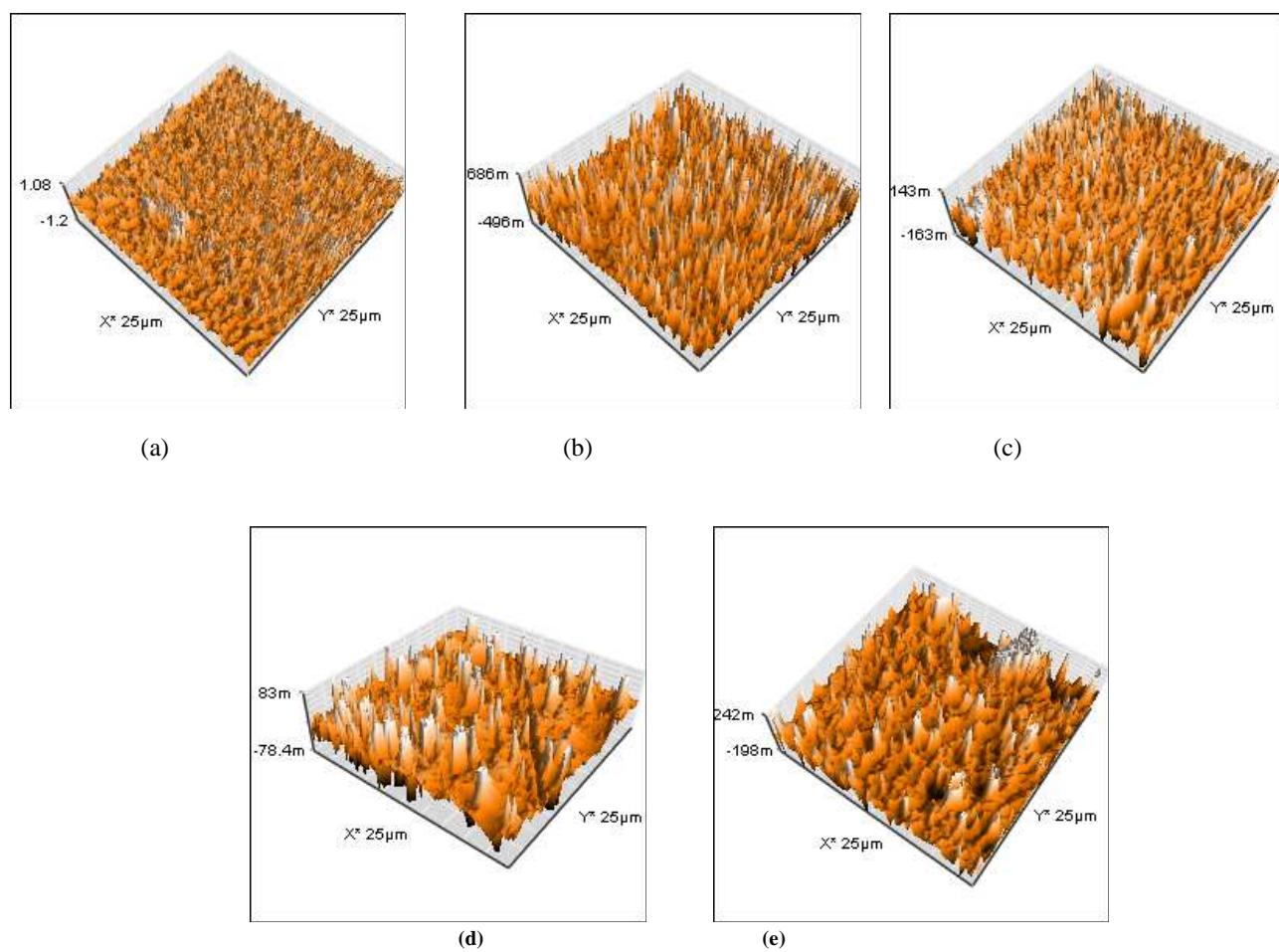


Fig. 1. AFM images of pure and blended PES membranes –
a) M1 b) M2 c) M3 d) M4 e) M5

3.2. Surface hydrophilicity, Porosity and Pure Water Flux

Water contact angle measurement is one of the most suitable methods for evaluating the surface hydrophilicity of UF membranes [15]. By theory, contact angle of hydrophilic surface should be less than that of hydrophobic surface [28]. As shown in Table 1, it could be seen that the contact angle of the PES/PAA/CaCl₂ blend membranes was decreased due to the addition of PAA and CaCl₂ to PES matrix. Especially, CaCl₂ composite membranes were more hydrophilic than the pure PES and PES/PAA (0% CaCl₂) membranes. Contact angle studies confirmed the enhanced

hydrophilicity of the CaCl_2 blend membranes. Increase in surface hydrophilicity could make the membrane more fouling resistant due to easy diffusion of solvent (water) through the membrane thickness [4]. Hence the CaCl_2 composite membranes have better chances of antifouling ability than the pristine PES membrane.

Results of the membrane porosity studies, as shown in Table 1, clearly indicated that the porosity of the blend membranes was altered due to the addition of CaCl_2 . It was evident that, for low concentration of CaCl_2 (1% CaCl_2) in the casting dope, the membrane structure was enhanced with better porosity. This could be due to enlargement of the support layer of the asymmetric composite membranes. However, at high concentrations of CaCl_2 in the casting dope, the dominant viscous effects, as confirmed visually, delayed the phase separation resulting in low membrane porosity. In general, all the CaCl_2 composite membranes possessed better porosity than the pristine PES and PES/PAA (0% CaCl_2) membranes.

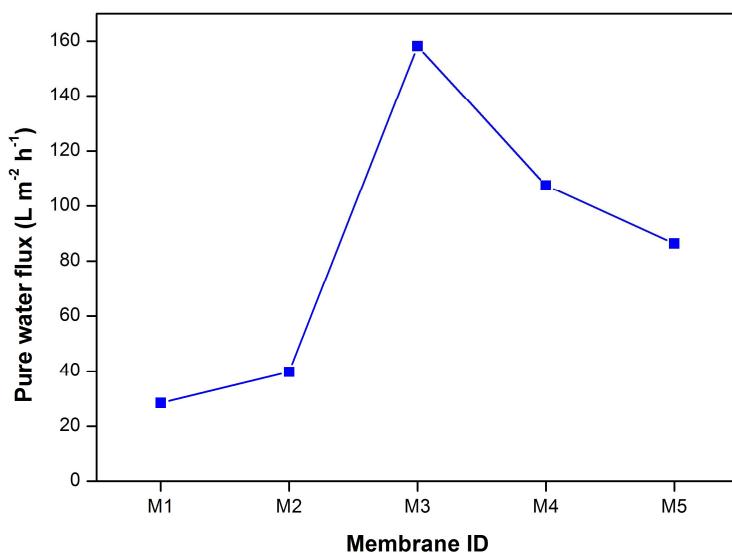


Fig. 2. Pure water flux measurement for the pure and blended membranes

Pure water flux results for all the prepared membranes are presented in Fig. 2. From the figure, it could be seen that the addition of CaCl_2 to the PES matrix had boosted the pure water flux upto a maximum of four times as compared with the pure PES membrane. Increase in the water flux was due to the enhanced hydrophilicity and the possibly enlarged sublayer (as confirmed from the porosity studies) of the blend membranes which was caused due to the addition of CaCl_2 . Further, it could be seen that the pure water flux was highest for the 1 wt% CaCl_2 membrane and there was a decrease in water flux for composite membranes with more than 1 wt% CaCl_2 . This observation was used to conclude that upto 1 wt% CaCl_2 concentration, the hydrophilic effects were dominant for the blend membrane and for high concentration CaCl_2 composite membrane (more than 1 wt%), the morphology (porosity) effects were dominant.

3.3. Dye rejection

Performance of all the prepared membranes was analyzed through dye rejection studies. Congo red and Orange II were used as probe agents for the rejection study. Results of the dye rejection study are presented in Fig. 4 and Fig. 5. From Fig. 4, it could be seen that the dye rejection percentage of the CaCl_2 composite membranes was almost same as that of the pure PES and PES/PAA (0% CaCl_2) blend membranes. There was a slight decrease in the rejection percentage for high concentration CaCl_2 composite membranes owing to their increased porosity. As shown in Fig. 5, the dye permeate flux was increased to a maximum of three times for the CaCl_2 composite membranes. The CaCl_2 blend membrane with 1 wt% concentration recorded the highest permeate flux among the synthesized membrane series. Also this membrane was expected to have low fouling due to its less surface roughness and enhanced hydrophilicity as compared with other CaCl_2 composite membranes.

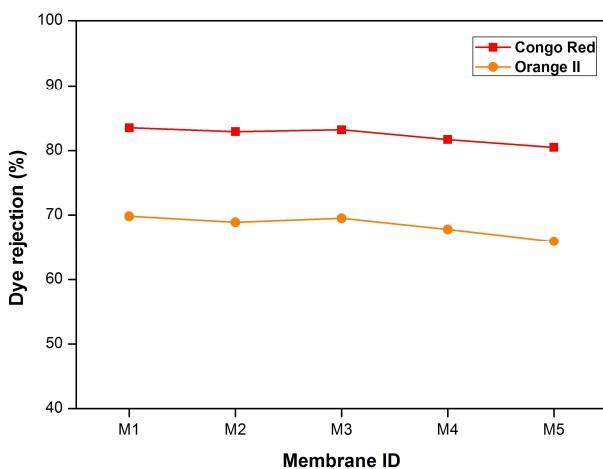


Fig. 4. Dye rejection percentage of the pure and blended PES membranes

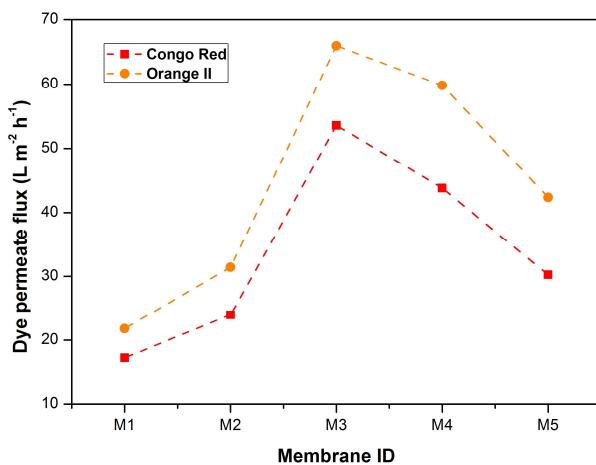


Fig. 5. Dye permeate flux of the pure and blended PES membranes

Analyzing the characterization and performance results, it was clear that the 1 wt% CaCl_2 composite UF membrane was possessing better separation characteristics as compared with all other synthesized membranes. Thus the 1 wt% CaCl_2 composite membrane seems to be a suitable and promising membrane for the application of dye polluted waste water treatment than the pure PES membrane.

CONCLUSION

A series of ultrafiltration membranes was prepared by blending fixed amount of polyacrylic acid (PAA) and varying amount of CaCl_2 as modifiers with polyethersulfone (PES). Effect of CaCl_2 on the membrane morphology, hydrophilicity, porosity and pure water flux of the blend membranes was studied. The addition of CaCl_2 to the base PES membrane influenced the membrane properties and morphology remarkably. Characterization studies showed that the PES/PAA/ CaCl_2 blend membranes had increased surface roughness, enhanced surface hydrophilicity and improved porosity. Pure water flux of the composite membranes was increased to a maximum of four times as compared to pure PES membrane. Dye rejection studies using Congo red and Orange II dye solutions clearly indicated that the rejection efficiency of the CaCl_2 blend membranes were almost constant but with an elevated flux than the pure PES membrane. A very close analysis on the obtained results revealed the better separation characteristics of 1 wt% CaCl_2 blend membrane among the synthesized series. Thus the 1 wt% CaCl_2 composite membrane seems to be a promising candidate for treatment of dye polluted waste water, ensuring high fluxes and effective rejection.

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