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Polyethersulfone – barium chloride blend ultrafiltration membranes for dye removal studies

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Abstract. A series of Polyethersulfone (PES) – barium chloride ($BaCl_2$) blend ultra filtration membrane was developed by varying the $BaCl_2$ concentration in the dope solution. Prepared membranes were subjected to membrane characterization and their performance was studied through dye rejection tests. Morphological studies through SEM and AFM showed that the composite membranes exhibited differences in morphologies, porosities and properties due to the $BaCl_2$ addition as compared with pristine PES membrane. Addition of the inorganic modifier enhanced the hydrophilicity and water permeability of the blend membrane system. Polymer enhanced ultrafiltration of dye solutions showed that the proposed blend system had better performance in terms of flux and rejection efficiency than the pure polymer membrane. The performance of the 2 wt% $BaCl_2$ blend membrane was more promising for application to real time dye wastewater studies.

1. Introduction
In recent decades, membrane based separation processes have been adopted in variety of process and allied industries for several purposes [1,2]. Membrane technology is cheap, clean, effective and advantageous as compared to other conventional separation process such as distillation, absorption etc. [3]. The usage of polymeric materials for industrial membrane synthesis has elevated the technology to new range of applications including ion exchange, wastewater treatment and desalination [3,4]. Recent studies clearly indicate that organic polymers are more suitable starting materials for the industrial grade membrane synthesis due to their ease of fabrication and remarkable properties [5]. These organic polymers include polysulfone [6,7], polyethersulfone [8-10], polyvinylidene fluoride [11,12] and cellulose acetate [13,14].

Polyethersulfone (PES) is one of the most preferred polymeric bases for membrane preparation due to its excellent mechanical, chemical, electrical, thermal properties and a high degree of flexibility [8]. However, the hydrophobic nature of the PES makes its membrane susceptible for fouling which is a serious limitation for its commercial and industrial application [9]. To overcome this restraint, bulk and surface modification methodologies such as blending, grafting, surface coating have been carried with PES membranes [9,15]. Ultrafiltration membrane prepared from PES polymer, blended with organic and inorganic materials have been reported to have desirable properties. These blend systems had improved solvent resistance, enhanced process ability, boosted hydrophilicity, better separation selectivity and high productivity[9,16]. The property enhancements were mainly due to the incorporation of the hydrophilic inorganic molecule into the polymeric matrix causing a thermodynamic instability and delayed demixing to aid solvent permeability [9]. A slight polarity shift

owing to the inorganic molecule addition leads to sharper selectivity and better rejection characteristics [16].

In this study, Barium chloride (BaCl$_2$) modified flat sheet PES membranes were prepared by varying the BaCl$_2$ from 0 to 4 wt% in the membrane cast solution. The membranes were prepared by combined dry and wet phase inversion method to improve the performance of resulting blend membrane. Effect of BaCl$_2$ concentration on the morphology, porosity and filtration characteristics were examined and compared with that of unmodified PES system. Separation performance of all of the prepared membranes was carried out dye removal studies. The obtained results are presented and discussed.

2. Experimental Methodology

2.1. Materials
Poly(ether sulfone) (Solef® 6010, Mw ≈ 3.1×10^5 g mol^{-1}, density = 1.76×10^3 kg m^{-3}) was purchased from Solvay Solexis Limited, India. Barium chloride was procured from Sigma-Aldrich Limited, India. N,N-dimethylformamide (DMF) and formalin solutions were purchased from SD Fine Chemicals Limited, India. Orange II and Congo red dye powders were purchased from Avra Synthesis Pvt. Ltd (India). Lab scale double distilled water was used for the membrane synthesis and membrane storage. All the reagents were of analytic grade and used as such in the experimental work without any further treatment.

2.2. Membrane Preparation
Phase inversion technique is the most widely used membrane preparation method especially for PES based membranes [9,17].BaCl$_2$ additive concentration was varied from 0 wt% to 4 wt% as shown in Table 1. The cast solution for a given membrane preparation was prepared by dissolving required amounts of the PES, BaCl$_2$ in DMF solvent in a round bottom flask. The solution was magnetically stirred (along with mild heating) for 8 h to ensure complete dissolution. Then the solution was the debubbled for 2 h at room temperature. The blend solution was then cast on smooth glass plate with the help of a doctor blade for a fixed thickness of 200 μm. Prior to casting, a gelation bath of deionized water was kept ready at 20 °C. After 30 sec of solvent evaporation (dry phase inversion), just after casting, the glass plate along with the resulting film was immersed in the gelation bath (wet phase inversion). After 30 min of gelation, the membrane was removed from the gelation bath and washed with distilled water to remove any residual solvent. The composite UF membrane sheet was subsequently stored in 1% formalin solution to prevent microbial attack on the membrane surface.

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

Membrane ID	Membrane Composition (by weight %)			Surface roughness, Ra (in nm)	Contact angle	Porosity, ε
	PES	BaCl$_2$	Solvent (DMF)			
M1	18	0	82	39.55	65.5	0.53
M2	18	1	81	41.45	62	0.56
M3	18	2	80	53.27	55.5	0.71
M4	18	3	79	87.16	49.5	0.73
M5	18	4	78	135.11	41.5	0.74

2.3. Membrane Characterization

Scanning electron microscopy (SEM) (Supra 55-Carl Zeiss, Germany) was used to analyze the morphology of the blend membranes. The membranes were cut into pieces of various sizes and mopped with filter paper. These pieces were immersed in liquid nitrogen for 20–30 s and were frozen. Frozen bits of the membranes were broken and kept in a desiccator. These membrane samples were used for SEM studies. SEM images were taken for top surface and cross-sectional surface of the blend membrane. Atomic Force Microscopy (AFM) (NTEGRA PRIMA-NTMDT, Ireland) was used to analyze surface roughness (R_a) of all the synthesized membranes. AFM analysis was carried out through tapping mode and the results obtained were for an effective sampling area of 25 μm × 25 μm for each membrane sample.

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 oC 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).

$$\varepsilon = \frac{W_w - W_d}{\rho_w A l} \tag{1}$$

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.

2.4. Performance analysis

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. A 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 414 kPa using Eq. (2).

$$J_w = \frac{Q}{A \Delta T} \tag{2}$$

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

Dye rejection studies were carried out to analyse the separation performance of the prepared membranes. Congo red and Orange II dyes were used as probe molecules for the rejection analysis. The dye solution with a feed concentration 0.1 g L^{-1} was given to the UF stirred cell at a transmembrane pressure of 414 kPa. The permeate samples were collected over defined time intervals and analyzed for output dye concentration. Solute rejection percentage (%SR) was calculated using Eq. (3).

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

where, C_p and C_f are the dye concentrations (g L^{-1}) in the permeate and feed streams, respectively. Dye concentration was measured using a UV-Vis-NIR

spectrophotometer (UV-3600, Shimazdu Corp., USA) at the absorption wavelength of 498 nm and 485 nm for Congo red and Orange II dye solutions.

3. Results & Discussions

3.1. Morphological characterization

In order to understand the asymmetric membrane formation mechanism, it is convenient to analyze the membrane as a two-layer structure: the dense top layer and the porous sub layer. Clearly, the top layer and the sub layer have different formation mechanism, leading to different morphologies. With the casting solution immersed into the water bath, the top layer was formed first at the casting solution-coagulant interface. Further, from the Figure 1, it is evident that the addition of $BaCl_2$ to CA had two effects – (i) Increase in the number of pores, (ii) Increase in the size of the pores. While the former effect was more predominant till 2 wt% of $BaCl_2$ in the blend membrane, the later effect was more predominant in blend membranes with more than 2 wt% $BaCl_2$.
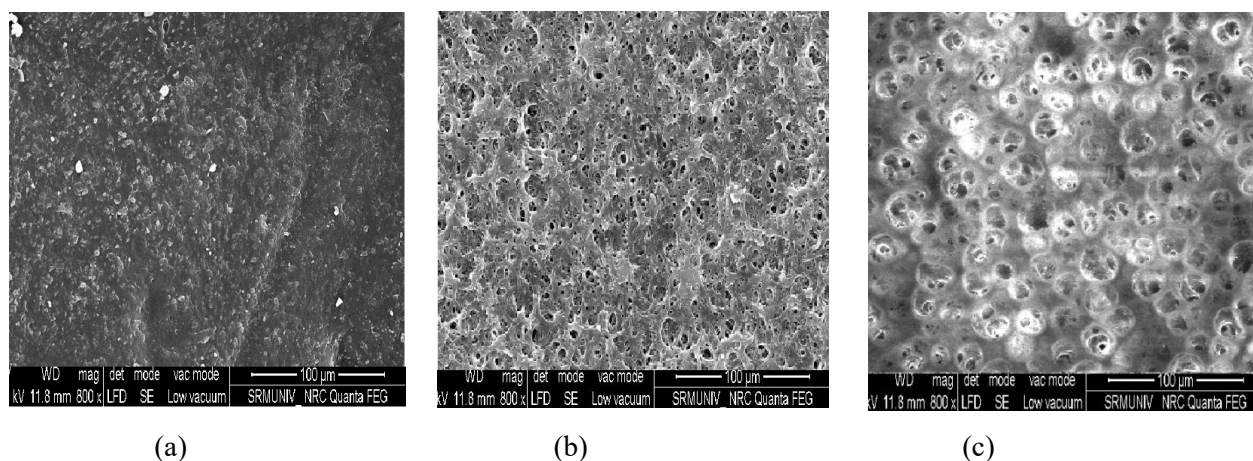

(a)   (b)   (c)

Figure 1. SEM images of top surface of pure and blended PES membranes –
(a) Pure PES   (b) 2 wt% $BaCl_2$ (c) 4 wt% $BaCl_2$

(a)   (b)   (c)
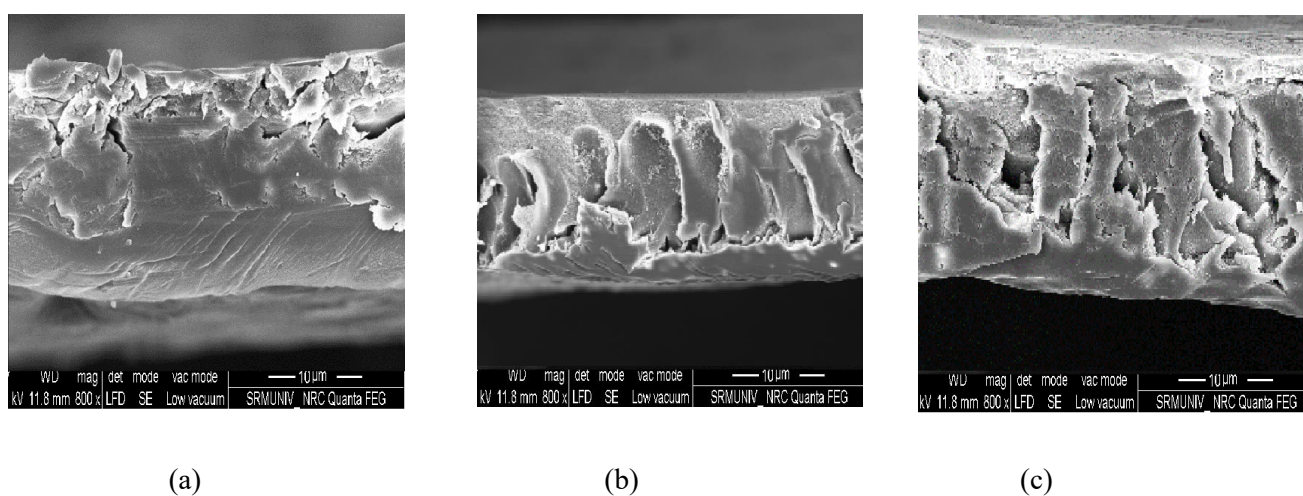
Figure 2. SEM images of the cross section of pure and blended PES membranes –
(a) Pure PES   (b) 2 wt% $BaCl_2$ (c) 4 wt% $BaCl_2$

The cross-section morphology helps to visualize the porous sublayer which could be clearly related with to the membrane permeability characteristics. As shown in Figure 2, the blend membranes exhibited clear demarcation of top and sublayer as compared to pristine PES. Also the sublayer resulted in more fingers like structure with increase in the $BaCl_2$ concentration in the membrane.

In the AFM analysis, as shown in Figure 3, 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 [18]. As shown in Table 1, it was observed that the addition of $BaCl_2$ 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 2 wt% for $BaCl_2$ in the casting dope. This lead to a possible conclusion that $BaCl_2$ composite membrane with more than 2 wt% $BaCl_2$ would be prone to more fouling due to increased surface roughness. However, there are several factors which determine the fouling nature of a membrane[19].
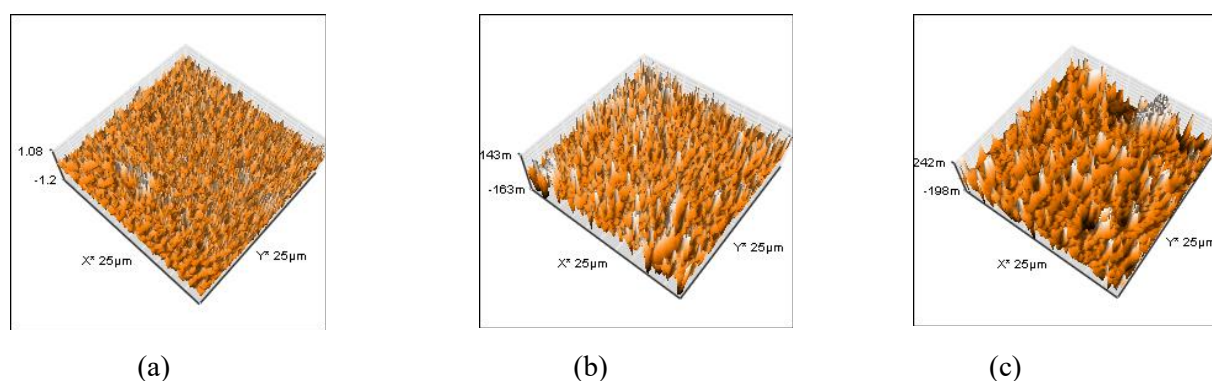

| (a) | (b) | (c) |

Figure 3. AFM images of the pure and blended PES membranes –
(a) Pure PES   (b) 2 wt% $BaCl_2$ (c) 4 wt% $BaCl_2$

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 [9,20]. By theory, contact angle of hydrophilic surface should be less than that of hydrophobic surface [20]. As shown in Table 1, it could be seen that the contact angle of the PES/$BaCl_2$ blend membranes was decreased with the continuous addition of $BaCl_2$ to PES matrix. Especially, $BaCl_2$ composite membranes were more hydrophilic than the pure PES membrane. Contact angle studies confirmed the enhanced hydrophilicity of the $BaCl_2$ blend membranes. Increase in surface hydrophilicity could make the membrane more fouling resistant due to easy diffusion of solvent (water) through the membrane thickness [9]. Hence the $BaCl_2$ 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 modified due to the addition of $BaCl_2$. It was evident that, for low concentration of $BaCl_2$ (2wt% $BaCl_2$) 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 $BaCl_2$ in the casting dope, the dominant viscous effects, as confirmed visually, delayed the phase separation resulting in low membrane porosity. In general, all the $BaCl_2$ composite membranes possessed better porosity than the pristine PES membrane.

Pure water flux results for all the prepared membranes are presented in Figure 4. From the figure, it could be seen that the addition of $BaCl_2$ to the PES matrix had boosted the pure water flux upto a maximum of seven times as compared with the pure PES membrane. Increase in the water flux was due to the enhanced hydrophilicity and the possibly enlarged sublayer of the blend membranes which

was caused due to the addition of $BaCl_2$. Further, it could be seen that the pure water flux increased with the increase in the modifier concentration and was highest for the 4 wt% $BaCl_2$ membrane. Also, the increase in the pure water permeability was rapid till 2 wt% of $BaCl_2$ addition and after which, the increase in the pure water permeability was comparatively low, This observation was used to conclude that upto 2 wt% $BaCl_2$ concentration, the hydrophilic effects were dominant for the blend membrane and for high concentration $BaCl_2$ composite membrane (more than 2 wt%), the morphology and the associated viscous effects were dominant.
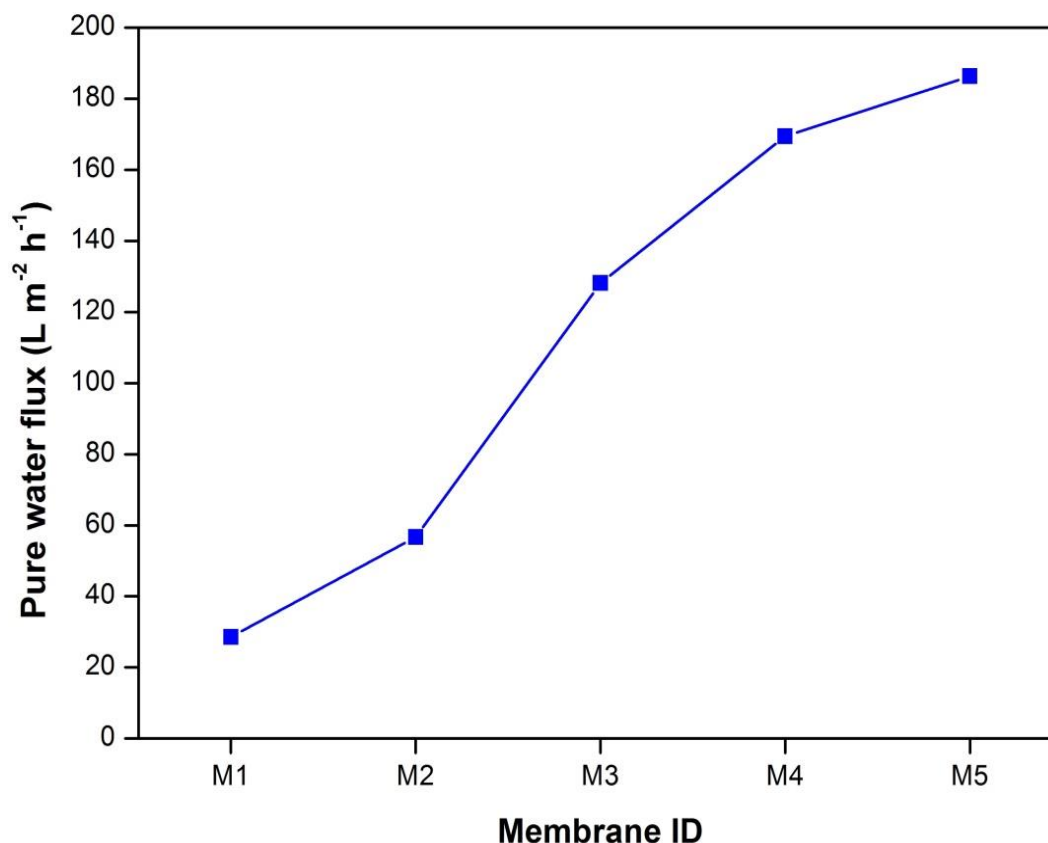

Figure 4. Pure water flux for the unmodified and modified PES membranes

3.3. Separation performance:

Performance of all the prepared membranes was analyzed through dye rejection studies using Congo red and Orange II as test agents for the rejection study. Results of the dye rejection study are presented in Figure 5 and Figure 6. From Figure 5, it could be seen that the congo red dye rejection percentage for all the prepared membranes was almost same constant with a peak performance for 2wt% $BaCl_2$ membrane. Orange II dye rejection studied clearly indicated the better separation efficiency of 2 wt% $BaCl_2$ membrane as compared with all other prepared membranes. As shown in Figure 6, the dye permeate flux was increased to a maximum of five times for the $BaCl_2$ composite membranes with a low increase in flux after a cutoff concentration of 2 wt% $BaCl_2$. The smaller surface pore size (as comparable to that of unmodified PES membrane) and considerably enlarged sublayer resulted in high rejection and better flux for the 2 wt% $BaCl_2$ among the synthesized membrane series. The combined effect of high separation efficiency and better flux makes the 2 wt% $BaCl_2$ blend membrane as a promising candidate for potential application in dye polluted wastewater treatment studies.
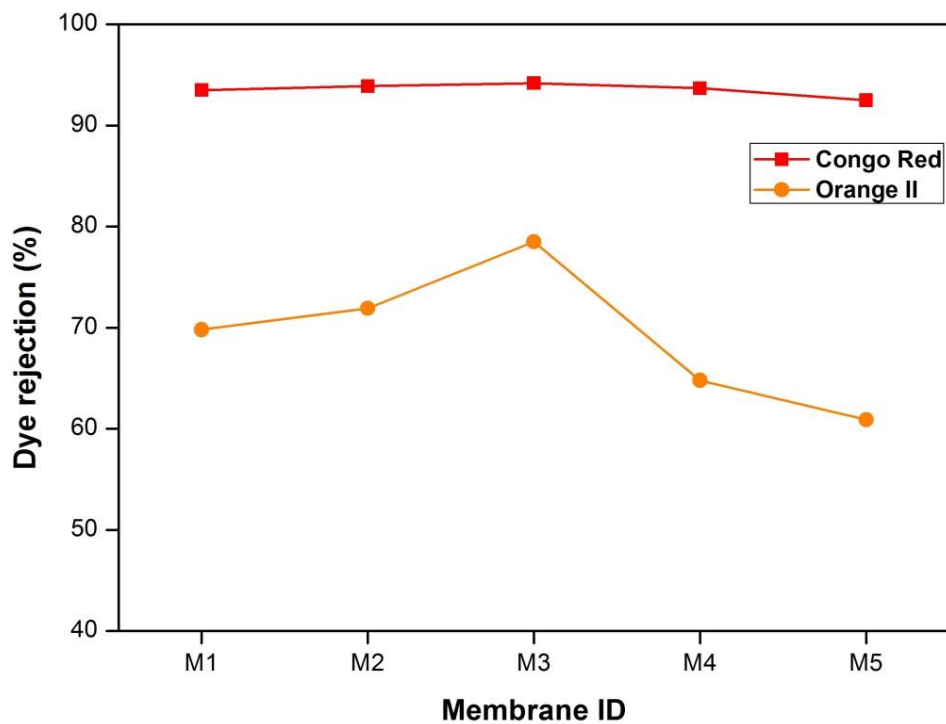
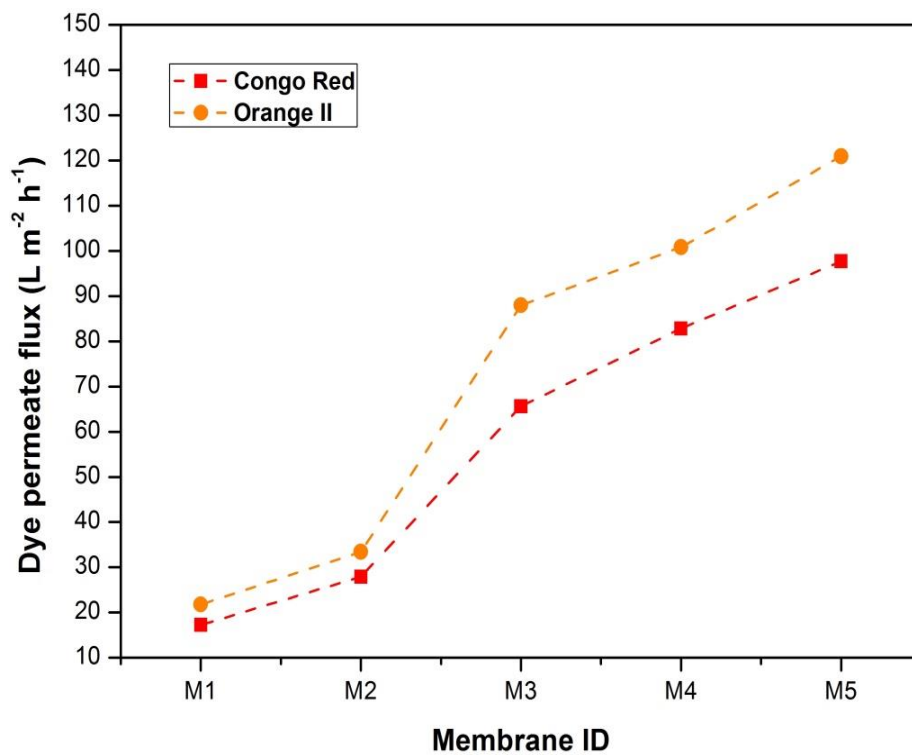Figure 5. Dye rejection efficiency of the pure and blended PES membranes

Figure 6. Dye permeate flux for the pure and blended PES membranes

4. Conclusion

Novel ultrafiltration membranes were prepared by blending varying amount of $BaCl_2$ modifier with the base polymer, polyethersulfone (PES). Effect of $BaCl_2$ on the membrane morphology, hydrophilicity, porosity and pure water flux of the blend membranes was studied. The addition of $BaCl_2$ to the base PES membrane influenced the membrane properties and morphology remarkably. Characterization studies showed that the PES/$BaCl_2$ 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 nine 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 $BaCl_2$ blend membranes were better with an elevated permeate flux than the pure PES membrane. A very close analysis on the obtained results revealed the better ultrafiltration characteristics of 2 wt% $BaCl_2$ blend membrane among the synthesized series. Thus the 2 wt% $BaCl_2$ composite membrane seems to be a promising candidate for treatment of dye polluted waste water, ensuring high fluxes and effective rejection. A detailed study on fouling parameters and applying the blend membranes to real time effluent treatment could be a further scope for the proposed work.

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