ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Cellulose acetate / Poly (ethylene glycol) / Iron oxide composite membranes for improved dye removal

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ABSTRACT

A series of cellulose acetate (CA) ultrafiltration membrane blended with poly(ethylene glycol) (PEG) and Iron oxide (Fe_2O_3) was prepared by phase inversion technique. Fe_2O_3 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 pore studies revealed the increase in the number of pores as well as pore size due to the addition of Fe_2O_3 to CA. Surface roughness was increased drastically for high concentration Fe_2O_3 composite membranes. Surface hydrophilicity was improved due to the addition of Fe_2O_3 in the composite membranes. Porosity measurements confirmed the enhanced porous nature of CA/PEG/Fe_2O_3 blend membranes than the pristine PES membrane. Pure water flux of the Fe_2O_3 composite membranes was improved to a maximum of three 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% Fe_2O_3 blend membrane among the synthesized UF membranes.

Keywords: Ultra filtration, Cellulose acetate, Polyethylene glycol, Iron oxide, Dye rejection.

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INTRODUCTION

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 common mode 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].

Cellulose acetate (CA) is an excellent polymeric material for UF membrane synthesis due to its desirable thermal, mechanical and chemical properties [15]. Advantages of CA membranes over other membranes such as high rejection efficiency, low cost, easy synthesis and antifouling ability have made CA quite popular in ultrafiltration applications [16]. However, pure CA membranes suffer from the limitation of lower fluxes [15,16]. It has been reported that by blending CA polymer base with other materials, the resulting membrane possessed improved physical properties [15-21]. CA membranes blended with polyether ether ketone [PEEK] showed increased pore size, higher flux and greater hydraulic resistance [17]. CA blended with polyurethane and polyvinylpyrrolidone (PVP) exhibited improved protein rejection efficiency [18].The excellent film-forming nature of CA has made it as an ideal base polymer for UF membrane development especially for commercial applications [19]. CA and low cyclic dimmer polysulfone blended with poly ethylene glycol (PEG) as additive resulted in increased water flux, porosity and water content [20]. CA and polyethylene glycol blended membranes have also been successfully investigated [21].

In recent years, Iron oxide particles are widely used as additives for polymeric and ceramic membranes [22-25]. Iron nanoparticles are excellent absorbent and their presence in the membrane could enhance the membrane's thermo-mechanical stability. Iron oxide blended ceramic / polymeric membranes have been studied for the treatment of phenol /organic matter polluted water [22] and for arsenic removal in water [23,24]. Incorporation of polyaniline and iron oxide to PES membrane resulted in better rejection of copper ions [25].

In this current study, modification of the CA membrane using polymeric additive PEG and inorganic additive Fe_2O_3 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 METHODS

Materials

Cellulose acetate (approximately 45% acetyl content) was procured from Mysore Acetate & Chemical Co. Ltd., India and it was dried at 120 ^{o}C for 8 h before being used. Iron nanoparticles were procured from Reinste Nanoventures Pvt. Ltd., India. Low molecular weight polyethylene glycol (PEG, average M_w= 600) 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.

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 CA, PEG and Fe_2O_3 in DMF solvent, as shown in Table 1. Based on previous studies, the polymeric additive PEG was fixed to a concentration of 2.5 wt% in the composite membrane for which the miscibility of PEG with CA was optimum [15]. The concentration of Fe_2O_3 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 CA 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.

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 (^{o})	Porosity, ε
	CA	PEG	Fe_2O_3	Solvent (DMF)			
M1	18	0	0	82	29.55	56.5	0.27
M2	18	2.5	0	79.5	33.18	53	0.29
M3	18	2.5	1	78.5	39.24	51.5	0.37
M4	18	2.5	2	77.5	57.68	47	0.35
M5	18	2.5	3	76.5	85.19	42	0.32

Membrane Characterization

Scanning electron microscopy (SEM) (Supra 55-Carl Zeiss, Germany) was used to analyze the top morphology of the prepared 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 membrane samples were used for SEM studies. Surface roughness (R_a) of all the synthesized membranes was measured through atomic Force Microscopy (AFM) (NTEGRA PRIMA-NTMDT, Ireland). Roughness results obtained were for an effective sampling area of 25 µm × 25 µm. 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).

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

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. 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 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).

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

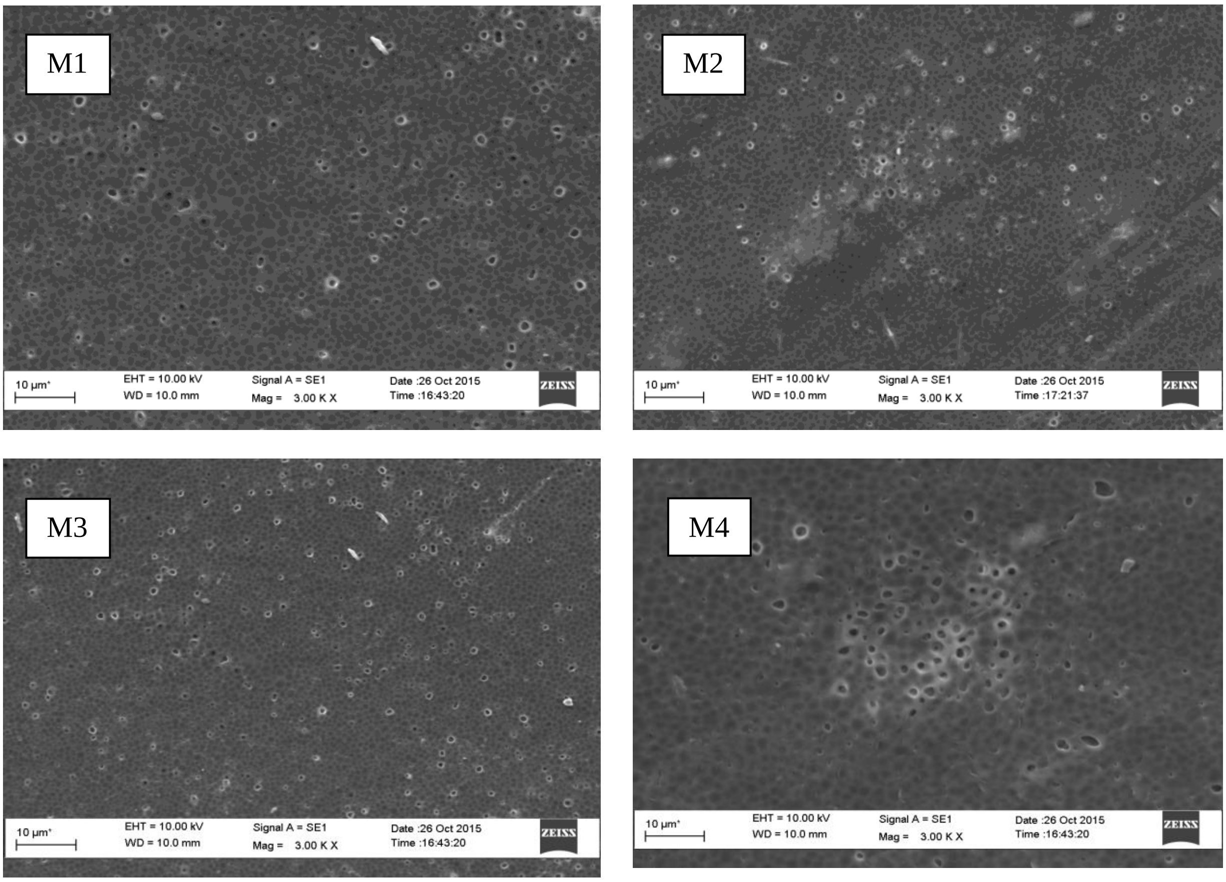
Where, C_p and C_f are dye concentrations in the permeate and feed streams, respectively. The dye concentration of the dyes in the permeate and feed streams was measured using a UV-Vis-NIR spectrophotometer (UV-3600, Shimazdu Corp., USA).

RESULTS AND DISCUSSION

The various characterization and performance results for CA/PEG/Fe_2O_3 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.

Scanning Electron Microscopy

SEM analysis of the top surface morphology revealed that the Fe_2O_3 blended CA membranes showed better porosity when compared to pristine CA membrane. As shown in Fig. 1, it could be seen that the porosity of the Fe_2O_3 blended CA membranes increased due to 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 1% Fe_2O_3 in the blend membrane the later effect was more predominant in blend membranes with more than 1% Fe_2O_3.



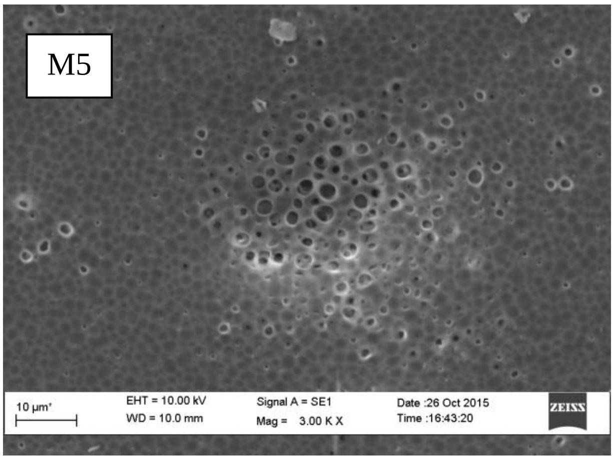
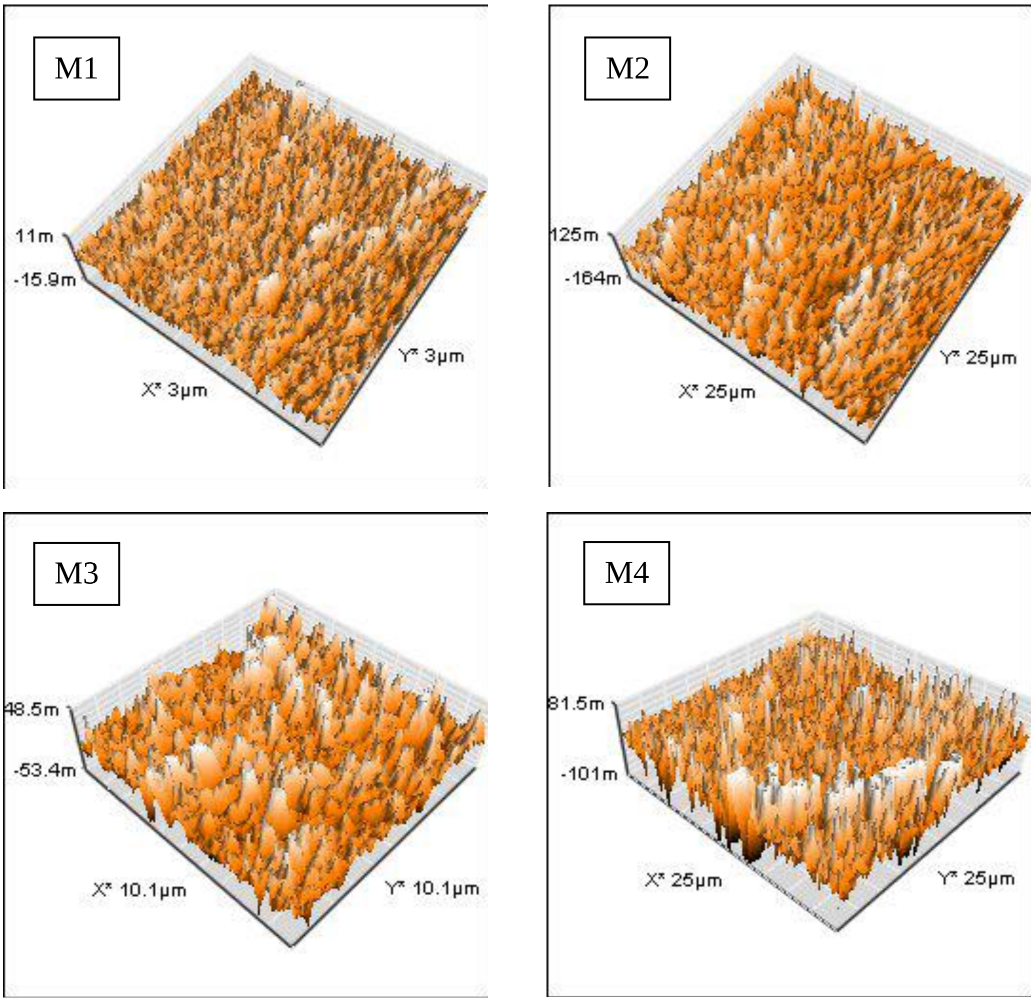


Fig. 1. SEM images of the top surface of the membranes

In the AFM analysis, as shown in Fig. 2, the lighter or the brighter regions shows the nodular structures and the darker regions shows the depressions or pores of the membrane. As shown in Table 1, it was observed that the addition of Fe_2O_3 to CA matrix increased the surface roughness. However, the rate of increase in surface roughness had a rapid growth after a cut-off concentration of 1% for Fe_2O_3 in the casting dope. Increase in surface roughness is an indication for the enhancement in flux through membranes.



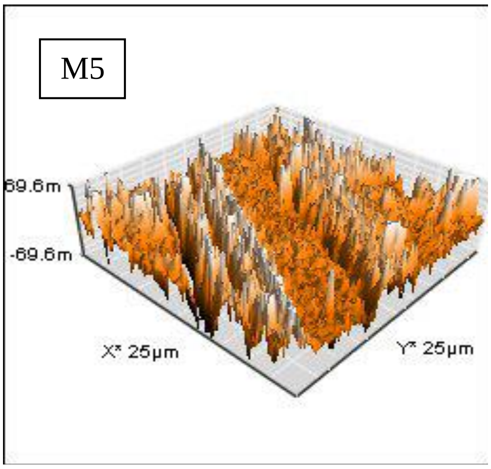


Fig. 2. AFM images of the top surface of the membranes

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 [26]. As shown in Table 1, it could be seen that the contact angle of the CA/PEG/ Fe_2O_3 blend membranes was decreased due to the addition of PEG and Fe_2O_3 to CA matrix. Especially, Fe_2O_3 composite membranes were more hydrophilic than the pure CA and CA/PEG (0% Fe_2O_3) membranes. Contact angle studies confirmed the enhanced hydrophilicity of the Fe_2O_3 blend membranes due to the pronounced hydrophilic effect of the Fe_2O_3 particles. 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 Fe_2O_3 composite membranes have better chances of antifouling ability than the pristine CA 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 Fe_2O_3. It was evident that, for low concentration of Fe_2O_3 (1% Fe_2O_3) in the casting dope, the membrane structure was enhanced with better porosity. However, at high concentrations of Fe_2O_3 in the casting dope, the dominant viscous effects, as confirmed visually, delayed the phase separation resulting in low membrane porosity. In general, all the Fe_2O_3 composite membranes possessed better porosity than the pristine CA and CA/PEG (0% Fe_2O_3) membranes.

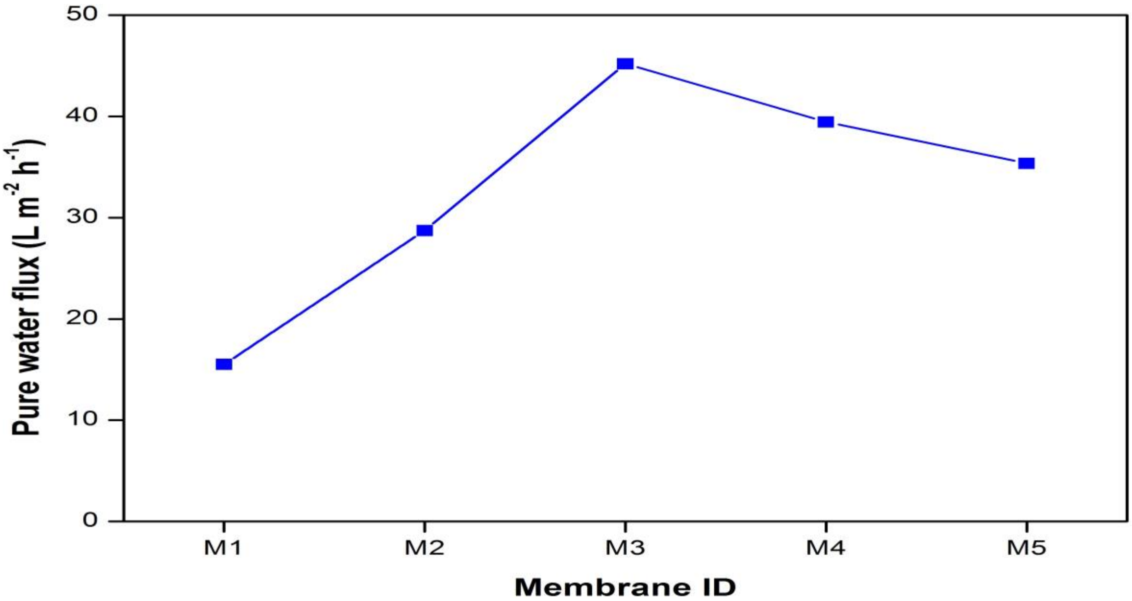


Fig. 3. Pure water flux measurement for the pure and composite CA membranes

Pure water flux results for all the prepared membranes are presented in Fig. 3. From the figure, it could be seen that the addition of Fe_2O_3 to the CA matrix had boosted the pure water flux upto a maximum of three times as compared with the unmodified CA 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 Fe_2O_3. Further, it could be seen that the pure water flux was highest for the 1 wt% Fe_2O_3 membrane and there was a decrease in water flux for composite membranes with more than 1% Fe_2O_3. This observation was used to conclude that upto 1% Fe_2O_3 concentration, the hydrophilic effects were dominant for the blend membrane and for high concentration Fe_2O_3 composite membrane (more than 1 wt%), the morphology (porosity) effects were dominant.

Dye rejection studies

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 Fe_2O_3 composite membranes was almost same till 1% Fe_2O_3 blend membrane. There was an appreciable decrease in the rejection percentage for high concentration Fe_2O_3 composite membranes owing to their increased porosity. As shown in Fig. 5, the dye permeate flux was greatly increased for the Fe_2O_3 composite membranes. The Fe_2O_3 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 Fe_2O_3 composite membranes.

Analyzing the characterization and performance results, it was clear that the 1 wt% Fe_2O_3 composite UF membrane was possessing better separation characteristics as compared with all other synthesized membranes. Thus the 1 wt% Fe_2O_3 composite membrane seems to be a suitable and promising membrane for the application of dye polluted waste water treatment than the pure PES membrane.

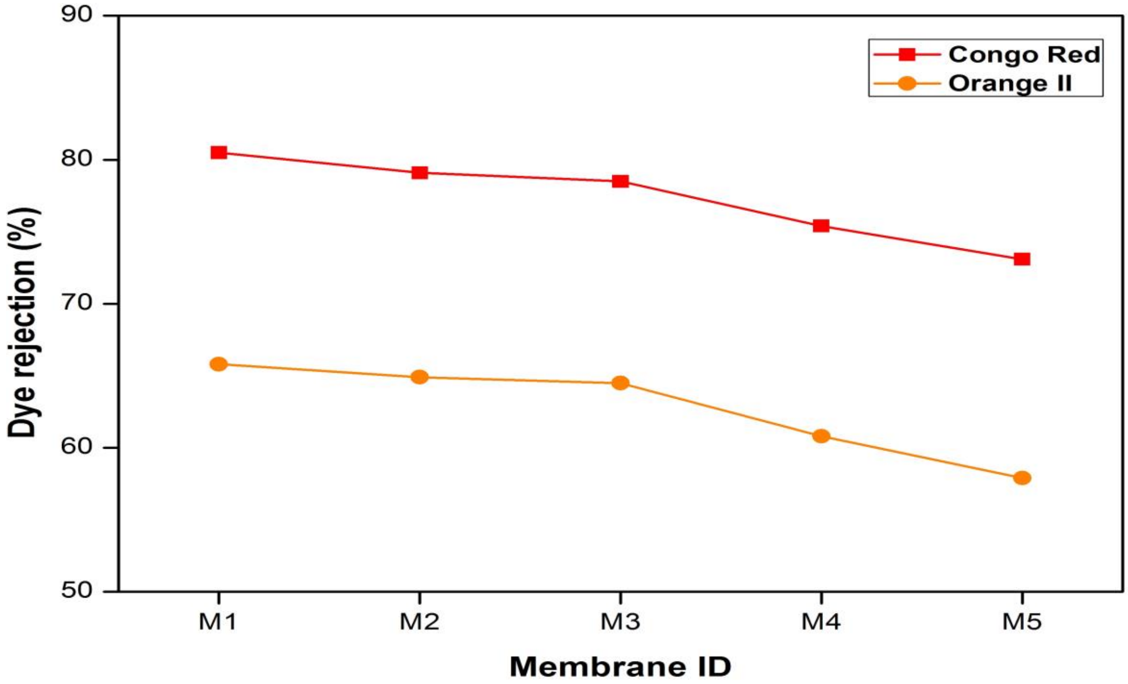


Fig. 4. Dye rejection percentage of the pure and composite CA membranes

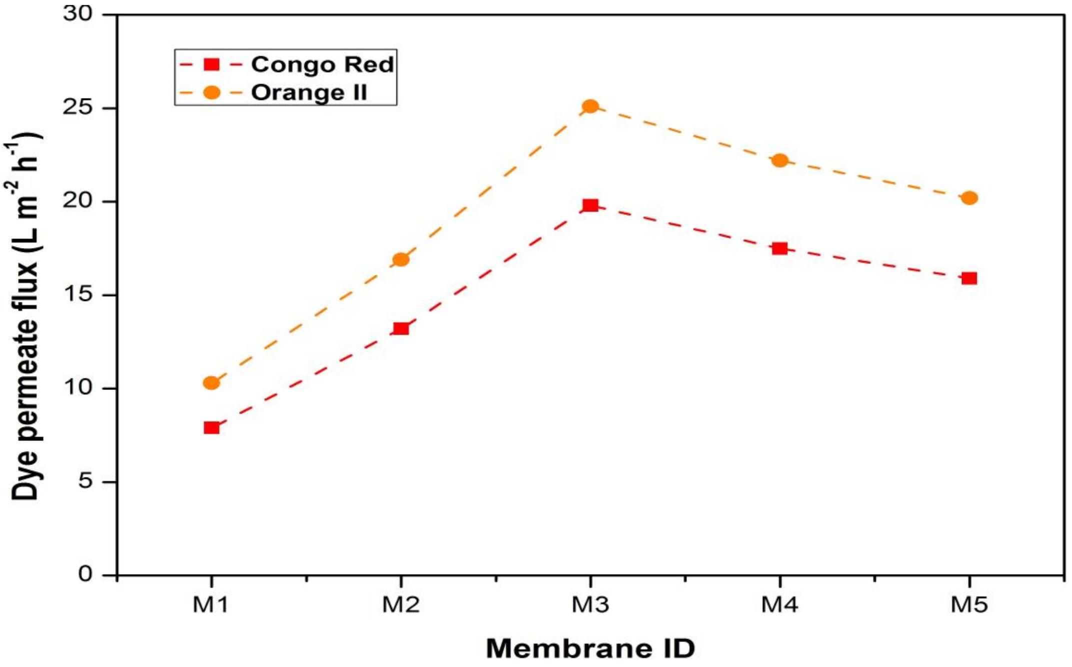


Fig. 5. Dye permeate flux of the pure and blended CA membranes

CONCLUSIONS

A series of ultrafiltration membranes was prepared by blending fixed amount of polyethylene glycol (PEG) and varying amount of Fe_2O_3 as modifiers with cellulose acetate (CA). Effect of Fe_2O_3 on the membrane morphology, hydrophilicity, porosity and pure water flux of the blend membranes was studied. The addition of Fe_2O_3 to the base PES membrane influenced the membrane properties and morphology remarkably. Characterization studies showed that the PES/PEG/ Fe_2O_3 blend membranes had increased porosity, surface roughness, enhanced surface hydrophilicity and improved porosity. Pure water flux of the composite membranes was increased to a maximum of three 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 Fe_2O_3 blend membranes got reduced slightly but with an elevated flux than the pure CA membrane. A very close analysis on the obtained results revealed the better separation characteristics of 1 wt% Fe_2O_3 blend membrane among the synthesized series. Thus the 1 wt% Fe_2O_3 composite membrane seems to be a promising candidate for treatment of dye polluted waste water, ensuring high fluxes and effective rejection.

REFERENCES

[1] Crull A. Membranes for the Nineties: Highlighting Surface Modification Technology. Business Communications Co., Nonvalk, CT, 1990.
[2] Escobar IC, Bruggen Vd. In Modern applications in membrane science and technology. American Chemical Society Books. 2011.
[3] Escobar IC, Schäfer A. Sustainable water for the future: Water recycling versus desalination. Elsevier, Netherlands, 2010.
[4] Cheryan M. Ultrafiltration and microfiltration handbook. CRC press, Florida, 1998.
[5] Escobar IC. Environ Prog 2005. 24: 355-357.
[6] Fan Z, Wang Z, Sun N, Wang J, Wang S. J Membrane Sci 2008; 320: 363-371.
[7] Mbareck C, Nguyen QT, Alaoui OT, Barillier. J Hazard Mater 2009; 171: 93-101.
[8] Wu G, Gan S, Cui L, Xu Y. Appl Surf Sci 2008; 254:7080-7086.
[9] Basri H, Ismail AF, Aziz M. Desalination 2011; 273: 72-80.
[10] Liu Y, Koops GH, Strathmann H. J Membrane Sci 2003; 223: 187-199.
[11] Zhi SH, Wan LS, Xu ZK. J Membrane Sci 2014; 454: 144-154.

[12] Yuliwati E, Ismail AF. Desalination 2011; 273: 226-234.
[13] Sivakumar M, Mohanasundaram AK, Mohan D, Balu K, Rangarajan R. J Appl Polym Sci 1998; 67: 1939-1946.
[14] Velu S, Rambabu K, Muruganandam L. Journal of Chemical and Pharmaceutical Research 2013; 5: 1418-1428.
[15] Arthanareeswaran G, Thanikaivelan P, Srinivasan K, Mohan D, Rajendran M. Eur Polym J 2004; 40: 2153-2159.
[16] Lv C, Su Y, Wang Y, Ma X, Sun Q, Jiang Z. J. Membrane Sci. 2007: 294: 68-74.
[17] Arthanareeswaran G., Srinivasan K, Mahendran R, Mohan D, Rajendran M, Mohan V. Eur Polym J 2004; 40: 751-762.
[18] Sivakumar M, Malaisamy R, Sajitha CJ, Mohan D, Mohan V, Rangarajan R. Eur Polym J 1999; 35: 1647-1651.
[19] Loeb S, Sourirajan S. Adv Chem Ser , ACS publications, 1962; 117–132.
[20] Arthanareeswaran G, Latha CS, Mohan D, Raajenthiren M, Srinivasan K, Separ Sci Technol 2006; 41: 2895-2912.
[21] Saljoughi E, Sadrzadeh M, Mohammadi T. J Membrane Sci 2009; 326: 627-634.
[22] Harman BI, Koseoglu H, Yigit NO, Beyhan M, Kitis M. Desalination 2010; 261: 27–33.
[23] Sabbatini P, Yrazu F, Rossi F, Thern G, Marajofsky A, de Cortalezzi MF. Water Res 2010; 44: 5702 – 5712.
[24] Park H, Choi H. Water Res 2010; 45: 1933–1940.
[25] Daraei P, Madaeni SS, Ghaemi N, Salehi E, Khadivi MA, Moradian R, Astinchap B. J Membrane Sci 2012; 415: 250-259
[26] Nath K. Membrane separation processes. PHI Learning Pvt. Ltd., New Delhi, 2008.