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CELLULOSE ACETATE – MANGANESE CHLORIDE BLEND ULTRAFILTRATION MEMBRANES FOR TANNERY EFFLUENT TREATMENT

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Received on: 10-02-2017

Accepted on: 27-03-2017

Abstract

In this work, a series of cellulose acetate (CA) – manganese chloride (MnCl₂) blend ultra filtration membrane was developed by phase inversion method. Prepared membranes were subjected to membrane characterization and their performance was studied using partially treated tannery effluent. The influence of MnCl₂ on the morphologies and the properties of the membrane were investigated through scanning electron microscopy (SEM) and ultra filtration experiments. The CA/MnCl₂ composite membranes exhibited differences in morphologies, porosities and properties due to the MnCl₂ addition in comparison with pure CA membrane. With the addition of MnCl₂ in the blend membrane, the composite membranes exhibited excellent water permeability and hydrophilicity. Based on the improved ultrafiltration properties, performance test on the blend membranes was carried out by subjecting the representative membranes for a partially treated tannery effluent to study the reduction of total suspended solids, total dissolved solids, sulfides, chlorides, sulphates and COD/BOD regulation. The obtained results are discussed.

Keywords: Ultrafiltration, Cellulose acetate, Manganese chloride, Membrane characterization, Tannery effluent.

1. Introduction

Membrane based separation operations are finding importance in the recent days due to their superior advantages and benefits as compared to other conventional separation methods, especially in the field of effluent treatment [1,2]. Among the various types of membrane processes, ultrafiltration (UF) is the most common industrial operation for the separation of suspended and dissolved macromolecules from aqueous streams [2,3]. Industrially, UF is mainly applied for water and wastewater treatment processes [4]. An extensive range of materials including polymers, ceramics and metal oxides are used as starting materials for the synthesis of ultrafiltration membranes. Recent studies clearly indicate that organic

polymers are more ideal materials for the synthesis of industrial grade ultrafiltration membranes 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]. Cellulose acetate (CA) is one of the most studied polymeric materials for UF membrane synthesis due to its desirable properties and applications [15]. Advantages of CA membranes over other polymeric membrane materials such as high rejection efficiency, low cost, easy synthesis and pH tolerance have made CA quite popular for ultrafiltration applications [16]. The major drawbacks of using CA for UF membrane synthesis is the resulting low permeate flux and ease to foul tendency [15,16]. Studies indicate that these limitations of CA could be overcome by blending CA with range of hydrophilic materials (mostly metal oxides and salts) which improve the ultrafiltration properties of the resulting blend membrane [15-21]. CA blended with polyether ether ketone [PEEK] revealed increased pore size, higher flux and greater hydraulic resistance [17]. CA combined with polyurethane and polyvinylpyrrolidone (PVP) showed 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 mixed with poly ethylene glycol (PEG) as additive gave increased water flux, porosity and water absorption [20]. CA and polyacrylic acid blended membranes have also been successfully investigated [21]. Based on the above considerations, a series of modified flat sheet CA membrane using manganese chloride ($MnCl_2$) as the modifier was prepared. Effect of $MnCl_2$ composition on the blend system for their UF characteristics such as pure water permeability, hydrophilicity, porosity and morphology was examined. BOD & COD reduction studies for a typical tannery effluent were examined using the synthesized membranes.

2. Experimental methods

2.1. Materials

Cellulose acetate (approximately 50 wt% acetyl content) was procured from Mysore Acetate & Chemical Co. Ltd., India and it was dried at 120 °C for 8 h before being used. Manganese chloride ($MnCl_2$) was procured from Sigma-Aldrich Limited. *N, N*-dimethyl formamide (DMF) solvent was obtained from SRL Chemicals (India). The partially treated tannery effluent was obtained from a nearby tannery industry at Ranipet SEZ (Special Economic Zone), Tamilnadu (India). Freshly prepared deionized water was employed for the preparation of gelation bath 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 commonly used membrane preparation method for polymeric blend UF membrane synthesis [4]. The cast solutions for a given membrane composition was prepared by dissolving required amounts of the CA and MnCl₂ in DMF solvent, as shown in Table 1.

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

Membrane ID	Membrane Composition (by weight %)			Contact angle (°)	Porosity, ϵ
	CA	MnCl ₂	Solvent (DMF)		
M1	18	0	82	56.5	0.27
M2	18	1	81	51.5	0.45
M3	18	2	80	48.8	0.49
M4	18	3	79	43.1	0.4
M5	18	4	78	38.8	0.37

The cast solution was magnetically stirred (along with mild heating) for 6 h to ensure complete dissolution of the CA polymer and MnCl₂ modifier in the DMF solvent. Subsequently, the cast dope was debubbled for 1 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 μ m. The membrane film was allowed for dry phase inversion for 10 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 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

Morphology analysis for the prepared blend membranes was done using scanning electron microscopy. 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

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).

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

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 414 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)

The tannery effluent was collected from nearby tannery plant located at Ranipet, Tamil Nadu. The effluent was passed through prepared CA-MnCl₂ blend membranes system in the dead-end ultrafiltration stirred cell. Fluxes were calculated using equation (2) at every half an hour. The rejection rate can be evaluated by using equation (3).

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

where, C_p and C_f are concentrations in the permeate and feed streams, respectively. The BOD, COD and other properties of the treated tannery effluent were analyzed and given in Table 2.

3. Results and Discussion

The various characterization and performance results for CA/MnCl₂ blend membranes were compared against the pure CA membrane. The advantages and limitations of the blend membrane system over the unmodified CA membrane is discussed in the below section.

3.1. Scanning Electron Microscopy

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 Fig. 1, it is evident that the addition of MnCl₂ 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 MnCl₂ in the blend membrane, the later effect was more predominant in blend membranes with more than 2 wt% MnCl₂.

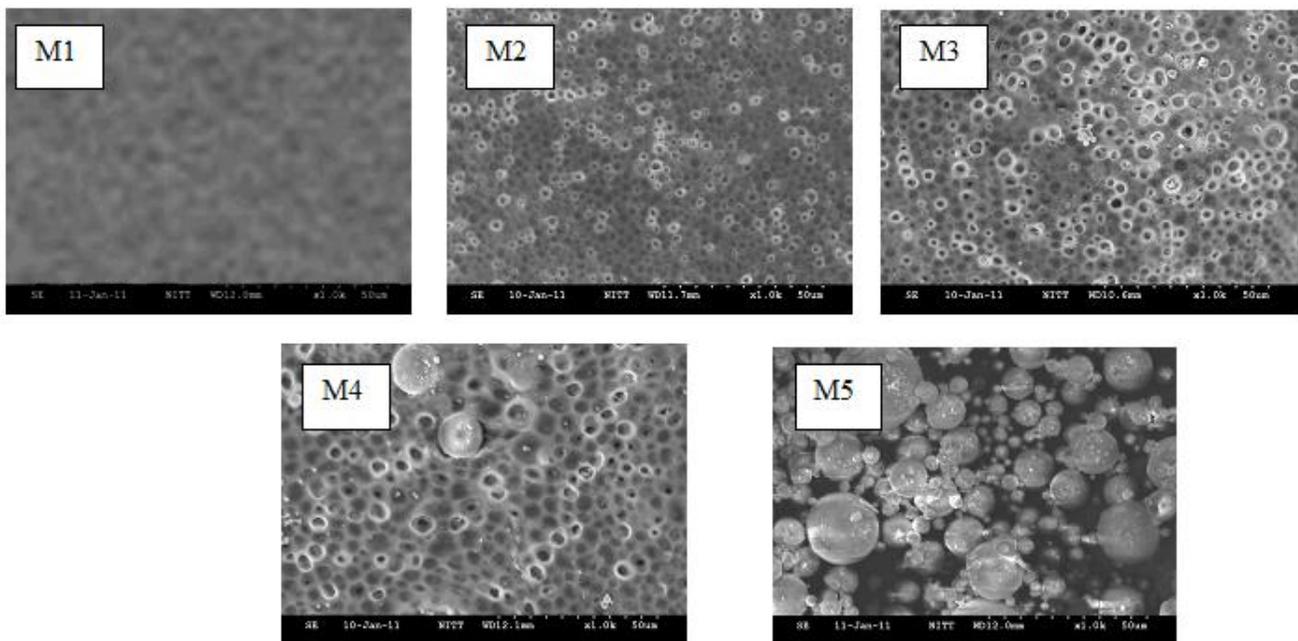


Fig. 1. SEM images of the top surface of the membranes.

The cross section morphology analysis as shown in Fig. 2 clearly indicated that the increase in MnCl_2 concentration increased the void in the sub layer which is extending to the central or even toward the bottom region of the membrane. A dense top layer is also formed since the additive and solvent in the casting solution desolates into the coagulation bath before the coagulant medium diffuses into the casting solution. The dense top layer stops growing when enough coagulant medium diffuses into the casting solution. The dense top layer stops growing when enough coagulant medium diffuses into the sub layer solution to create pores. Thus, these inferences made from morphological studies confirmed that the addition of MnCl_2 increased the porous nature of the membrane.

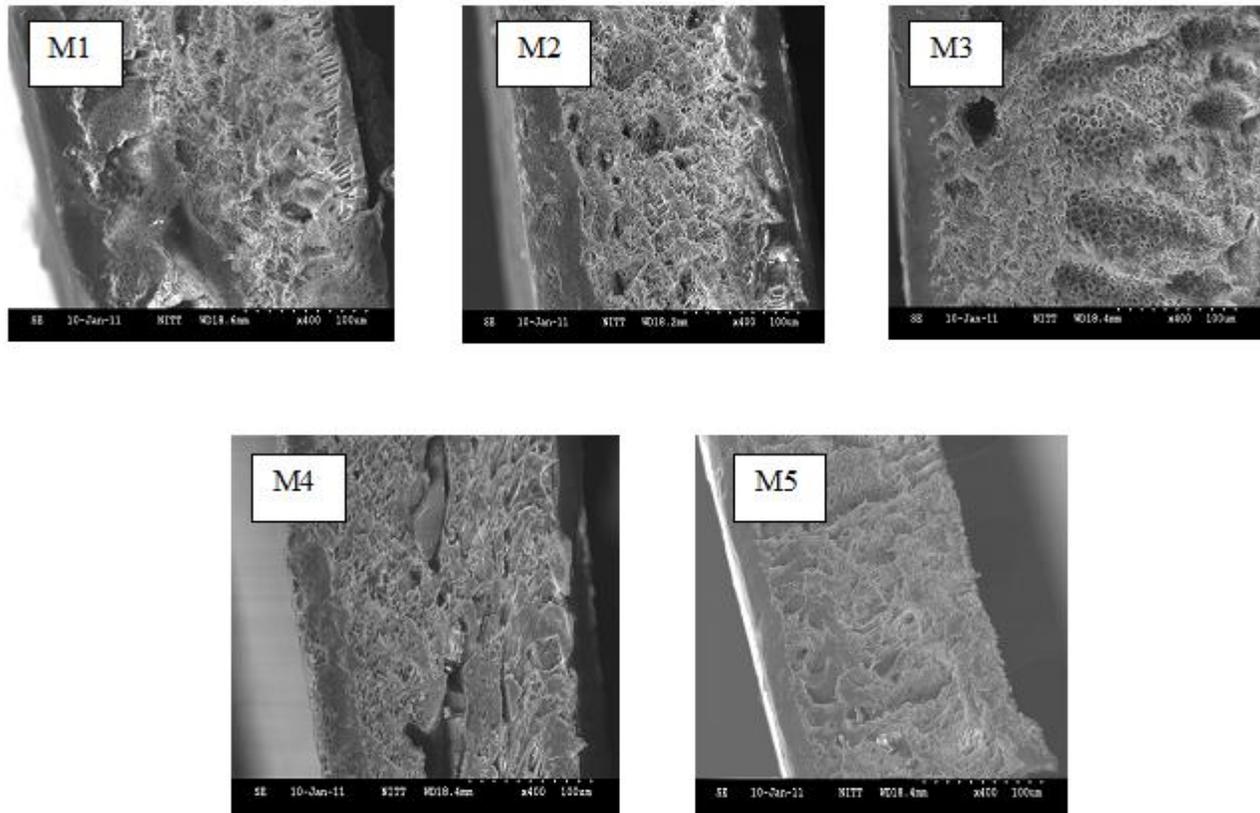


Fig. 2. SEM images of the cross section surface of the membranes.

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 [22]. As shown in Table 1, it could be seen that the contact angle of the CA/ MnCl_2 blend membranes was decreased due to the addition of MnCl_2 to CA matrix. Contact angle studies confirmed the enhanced hydrophilicity of the MnCl_2 blend membranes due to the pronounced hydrophilic effect of the MnCl_2 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 MnCl_2 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 MnCl_2 . It was evident that, for low concentration of MnCl_2 (1 wt% & 2 wt%) in the casting dope, the membrane structure was enhanced with better porosity. However, at high concentrations of MnCl_2 in the casting dope, the dominant viscous effects, as confirmed visually during membrane formation, delayed the phase separation resulting in low membrane porosity. In general, all the MnCl_2 composite membranes possessed better porosity than the pristine CA membrane.

As shown in Fig. 3, pure water flux of the blended CA membranes were better than the pure CA membrane and recorded an increasing pattern with the increase in concentration of MnCl_2 modifier. This was due to the increased void structures in the support layer as shown by the morphological studies. 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 MnCl_2 . Further, it could be seen that the pure water flux was highest for the 2 wt% MnCl_2 membrane and there was a decrease in water flux for composite membranes with more than 2 wt% MnCl_2 . This observation was used to conclude that upto 2 wt% MnCl_2 concentration, the hydrophilic effects were dominant for the blend membrane and for high concentration MnCl_2 composite membrane (more than 2 wt%), the morphology (viscous) effects were dominant.

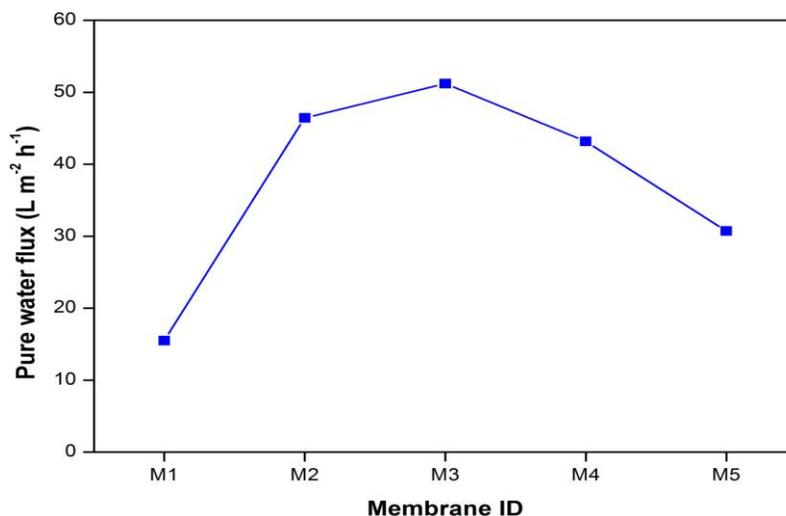


Fig. 3. Pure water flux measurement for the pure and composite CA membranes.

3.4. Performance studies for tannery effluent treatment

The synthesized pure CA membrane and CA/ MnCl_2 blend membrane was used in UF stirred cell to carry out treatment of a typical pretreated tannery effluent collected from a tannery industrial unit of industrial region of Ranipet, Tamilnadu.

The effluent was treated with addition of chlorine so that build up of organic materials on the surface of membrane will not lead to immediate fouling. The chlorinated effluent was further filtered in a conventional filter to remove the macro impurities (if any) in the range of mm. The resulting effluent was cooled to room temperature and then it was subjected UF treatment with the synthesized membranes in the ultra-filtration unit at an applied pressure difference of 414 kPa. The technical assay of the feed and permeate obtained through the various membranes are presented in Table 2.

The membrane developed with 2 wt% of MnCl₂ overall showed better performance compared to other membranes. Particularly, the value of sulfides removal for 2 wt% MnCl₂ recorded the very lowest value. The concentration of the permeate was very low, such that the treated effluent can be reused in the pre-tanning step adjusting the tannin concentration to the desired value. The treated product pertaining to 2 wt% CA – MnCl₂ blend had the properties closer to that of potable water to be used more readily for agriculture. The feed solution with large quantities of insoluble substances when subjected to ultrafiltration resulted in stream that can be recycled and reused. Pure CA membranes without MnCl₂ showed more than 28% reduction of the COD whereas the 2 wt% of MnCl₂ – CA membrane resulted in 78% reduction of COD. BOD calculation was done for 3 days basis as the resulting product was available at a lower temperature of around 27°C. Also, as shown in Fig.4, a high permeate flux of 28.5 lit/m² h was obtained through the 2 wt% of MnCl₂ – CA membrane for an effective filtration area of 0.02 m².

The obtained results indicate that a CA – MnCl₂ blend membrane is comparatively superior in performance than a pure CA membrane in terms of all aspects of UF. Having a closer analysis on the results, it could be concluded that even within the CA–MnCl₂ blend system, the 2 wt% MnCl₂ membrane has a better performance. A comparative study on the permeate flux at 414 kPa also proves that the better permeate flux rate was observed for the 2 wt% MnCl₂ membrane. Further this combination provides desirable results in terms of rejection and flux in handling higher quantity of tannery effluent.

Table 2. Analytical determinations of treated tannery effluent using prepared membranes.

Sl. No	Parameters	Feed	Permeate				
			M1	M2	M3	M4	M5
1	pH	6.3	6.8	7	7.1	6.7	6.5
2	Total suspended solids	36	22	20	16	27	31

	(mg/l)						
3	Total dissolved solids (mg/l)	4000	2250	1402	1328	1680	2152
4	Chlorides (mg/l)	950	826	564	320	698	1142
5	Sulphates (mg/l)	2470	405	218	178	266	817
6	B.O.D 3 days at 27 ⁰ C (mg/l)	189	72	46	28	68	122
7	C.O.D (mg/l)	1010	728	314	218	364	984
8	Oil & Grease (mg/l)	4	3.4	3.2	1.5	3.6	3.8
9	Sulphides (mg/l)	42	12	8.7	2.2	10.3	21
10	Ammonical Nitrogen (mg/l)	35	28	23	14	26	29
11	Potassium (mg/l)	48	26	14	8	22	34
12	Sodium)	77	56	48.3	26	52	63

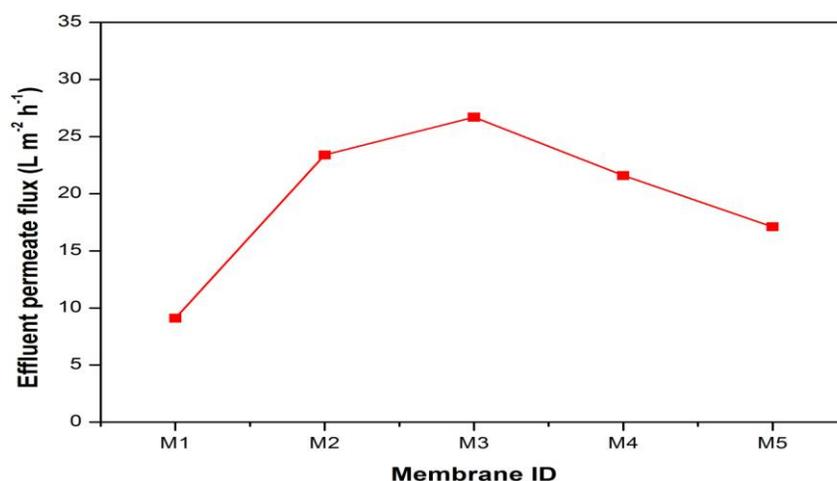


Fig. 4. Tannery permeate flux measurement for the pure and composite CA membranes.

4. Conclusions

The performance of the modified CA membrane for tannery effluent treatment through ultrafiltration was investigated. Various combinations of CA/MnCl₂ polymer membranes with increased porosity and water uptake was successfully prepared by immersion precipitation method. The prepared membrane displayed asymmetric membrane morphology with the variation in MnCl₂ content. Contact angle results confirmed the enhancement of MnCl₂ on the membrane surfaces indicating that the hydrophilicity of CA/MnCl₂ membranes are higher than that of neat CA membranes. The membrane surfaces incorporated with MnCl₂ possessed enhanced porosity and water permeability. The applicability of the membranes for industrial waste water treatment in terms of tannery effluent was also investigated. Ultra filtration performance of tannery effluent for all the CA/MnCl₂ membranes produced acceptable results as per standards. A very

close analysis on the obtained results revealed the better performance characteristics of 2 wt% MnCl₂ membrane among the synthesized series. The better performance of the 2 wt% MnCl₂ membrane could be ascribed to the balanced hydrophilic and viscous effects due to MnCl₂ addition. Blending of CA membranes with MnCl₂ produced uniform pore sizes and uniformly distributed pores which results in comparatively high permeate fluxes (as compared with pristine CA). Thus, a new type of polymeric blend membrane material based on Cellulose acetate / Manganese chloride has been identified for treatment of tannery industrial effluents..

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