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# Effect of Additive Concentration on Cellulose Acetate Blend Membranes-Preparation, Characterization and Application Studies

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**Abstract:** Ultrafiltration techniques have particular advantages for simultaneous purification, concentration, and fractionation of macromolecules. A comparative study is presented on novel ultrafiltration polymeric blend membranes based on cellulose acetate (CA) prepared in the absence and presence of polymeric additives such as polyethylene Glycol 200 (PEG) and polyvinylpyrrolidone (PVP) by phase inversion technique using N,N′-dimethylformamide (DMF) as solvent. Polymer blend composition, additive concentration and casting, and gelation conditions were standardized for the preparation of asymmetric membranes by pore statistics and morphology. These blend membranes were characterized for compaction in ultrafiltration experiments at 414 kPa pressure in order to attain steady state flux and is reached within 4–5 h. The pure water flux was measured at 345 kPa pressure. Membrane hydraulic resistance derived by measuring water flux at various transmembrane pressures and found to be inversely proportional to pure water flux. Water content is estimated by simple drying and weighing procedures and found proportional to pure water flux for all the membranes. The molecular weight cut-offs (MWCOs) of different membranes were determined with proteins of different molecular weights and found to vary from 20 to 69 kDa depending on the PEG 200 and PVP content in the blend in the casting solution. Skin surface porosity of the membranes was analyzed by scanning the samples at various magnifications. The characterized CA, CA/PEG200 and CA/PVP membranes were used for cadmium ion rejection studies at 345 kPa.

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**Keywords:** Blends; Phase behavior; Polyethylene glycol 200; Polyvinylpyrrolidone; Ultrafiltration

## INTRODUCTION

As water resources become more limited and waste discharge becomes increasingly expensive, the concept of water reclamation or water "reuse" is gaining acceptance in industry. Effective wastewater treatment is essential for protecting human health and the Environment. Membrane technology is a cost-effective means of complying with increasingly stringent federal, state, and local environmental regulations concerning industrial wastewater treatment and discharge. With tougher regulations, increases in land fill costs and rises in environmental related insurance a more environmentally friendly process can also be a sound economic investment. With membrane technology, waste treatment processes do not have to be restricted for conversion of waste from one form to another. Because of increased media attention on issues of food, beverages, and drug purity that can affect consumer health, the variety of purification processes supported by membrane technologies can be a cost-effective way to satisfy that increased demand of quality. Companies that elevate their quality can often achieve a corresponding elevation of brand image that results in increased sales. In terms of energy, membrane separations have an important advantage, that is, no change of phase is involved in dewatering or solvent removal, thus avoiding latent heat requirement.

The method is simple in operation and compatible with existing equipment and technology. Sample collection and concentration efficiency up to 100% can be achieved. Membrane technology has the potential for not only producing a superior product, but for considerable savings in capital and operating costs, by eliminating filter processes, cartridge filters, and centrifuge.

At present membrane separation processes in general and ultrafiltration (UF) in particular have become effective in the separation of molecular solutions. The main reason for the emergence of UF as an industrial process is the breakthrough in polymer manipulation through blending of polymers.

Cellulose Acetate (CA) was one of the first membrane polymers that has been used for aqueous based separations and used as both reverse osmosis and UF membrane material (1) CA membranes have been prepared by many of the membrane researchers and characterized for their compaction, hydraulic permeability, and osmotic permeability (2) Asymmetric UF membranes based on CA were prepared and studied extensively on variation of casting solution, Composition and membrane formation mechanism (3) CA and its derivatives made them suitable as membrane materials because of the advantages such as moderate flux, high salt rejection properties, cost effectiveness, relatively easy manufacture, renewable source of raw material, and non-toxicity. Homopolymers, due to their variety of drawbacks, suffer from a wide range UF membrane applications. Thus CA also suffer from drawbacks such as fairly narrow temperature range of usage (max. 30°C), a narrow pH range restricted to pH 2–8, poor chlorine resistance, and greater compaction phenomena which reduces membrane life time and high biodegradability which decreases its usage. Further, for the preparation of efficient membranes with better performance, the membrane material should be tolerant to a wide range of pore sizes. Hence to circumvent, the above drawbacks of the homopolymeric membranes, blend membranes based on polymers of desirable qualities would satisfy the necessity. The blend membranes based on CA-Polysulphone and CA-Polyethersulphone have already been prepared in our laboratory (4,5).

Further, the presence of a suitable hydrophilic additive was expected in resulting a membrane with desired flux behavior and hence attempts have also been made to prepare these membranes in the presence of additives and hence the pore former plays a key role for the formation of pore sizes in the asymmetric membranes. On leaching the pore former and casting solvent during gelation, the gel is stabilized to form the membrane. The factors influencing the porosity and pore size of the membrane are complex. The choice of pore former will depend upon polymers (6,7). The pore former may be a solvent or a solid particle and must have high boiling point and should be polar when compared with the solvent. The concentration of pore former and its polarity, will strongly influence the membrane Characterization (8).

Therefore an attempt has been made to incorporate the above properties by blending CA with macromolecular additive PEG 200 and PVP separately using N,N′-dimethyl Formamide (DMF) as solvent and the results are discussed in detail in the present paper.

## EXPERIMENTAL

### Materials and Methods

Commercial grade MYCELL cellulose diacetate CDA5770 (acetyl content 39.99 wt%) was procured from Mysore Acetate and Chemicals Limited, India and was used after precipitation from Acetone. Poly (ethylene Glycol) (PEG) s obtained from Fluka AG were used as organic additive. Polyvinylpyrrolidone (PVP) K30 was procured from CDH

Ltd., India and used as a pore former. Dimethyl formamide (DMF) of analar grade were purchased from SD fine chemicals, India, were used as such without further purification. Proteins, viz., bovine serum albumin (BSA) (69 kDa), from Himedia Laboratories, India; Egg Albumin (EA) (45 kDa) from CSIR Biochemical Centre, India; pepsin (35 kDa) and trypsin (20 kDa), from SRL, India. Polyethylenimine (PEI) MW: 30–40 Kg Mol$^{-1}$, 50% aqueous solution from Fluka AG (France) was used. Deionized and distilled water was employed for the ultra filtration experiments and for the preparation of the gelation bath.

## Preparation of Solution Blending

The blend solution based on cellulose acetate with different molecular weight of PEG at various compositions as shown in Table 1 using DMF as a solvent under constant mechanical stirring at a moderate speed of rotation in a round bottomed flask for 4 hr at 40°C. The homogeneous solution that was obtained was allowed to stand at room temperature for at least 1 day in an air right condition to get rid off air bubbles.

## Membrane Preparation

The casting environment (relative humidity and temperature) was standardized for the preparation of membranes with better physical properties such as the homogeneity, thickness, and smoothness. The relative

**Table 1.** Membrane hydraulic resistance ($R_m$) and molecular weight cut-off of cellulose acetate blend membranes

| Blend Composition (%) | | | | | |
|---|---|---|---|---|---|
| CA (wt%) | DMF (wt%) | PEG200 (wt%) | Additive, PVP (wt%) | Membrane Hydraulic Resistance | MWCO |
| 100 | 82.5 | 0 | 0 | 33.33 | 20 |
| 97.5 | 82.5 | 0 | 2.5 | 20.12 | 45 |
| 95 | 82.5 | 0 | 5 | 8.01 | 45 |
| 92.5 | 82.5 | 0 | 7.5 | 6.21 | 69 |
| 90 | 82.5 | 0 | 10 | 3.51 | >69 |
| 97.5 | 80.5 | 2.5 | 0 | 9.43 | 45 |
| 95 | 77.5 | 5 | 0 | 5.75 | 45 |
| 92.5 | 75 | 7.5 | 0 | 3.75 | 69 |
| 90 | 72.5 | 10 | 0 | 2.82 | >69 |

humidity was maintained between 50 ± 2% and the temperature was kept at 35 ± 2°C for all casting experiments. The total polymer concentration was maintained at 17.5 wt% in order to have a balanced casting solution viscosity to yield membranes between a spongy type and a high macrovoidal type. The membrane film thickness was maintained at 0.22 ± 0.02 mm, which was measured with a micrometer having a precision of 0.01 mm. The casting and gelation conditions were maintained constant throughout, because the thermodynamic conditions would largely affect the morphology and performance of the resulting membranes. Prior to casting a 2 L gelation bath, consisting of 2.5 (v/v) DMF solvent (to reduce the rate of liquid-liquid demixing and macro voids) and 0.2 wt% SLS surfactant (to reduce surface tension at the polymer-non solvent interface) in distilled water (non solvent), was prepared and kept at 20 ± 1°C. The membranes were cast over a glass plate using a doctor blade. After casting, the solvent present in the cast film was gently immersed in the gelation bath. After 1–2 hr of gelation, the membrane was removed from the gelation bath and washed thoroughly with distilled water to remove all DMF and surfactant from the membranes. The membrane sheets were subsequently stored in distilled water, containing 0.1% formalin solution to prevent microbial growth.

## Characterization of Membranes

### UF Set Up

The UF experiments were carried out in a batch type, dead end cell (UF cell-S76–400-Model, Spectrum, USA) with a diameter of 76 mm, fitted with Teflon coated magnetic peddle. This cell was connected to a compressor with pressure control valve and gauge through it feed reservoir. The prepared membranes were cut into the necessary size for use in the ultrafiltration cell for the following various studies.

### Compaction

The membranes prepared were cut into necessary size, to use in the ultra filtration kit of 38.5-cm$^2$ effective membrane area and initially pressurized with distilled water at 414 kPa for 4 hours. The water flux was measured at every one-hour interval. The compaction factor was calculated as follows (9)

$$\text{Compaction factor} = \frac{\textit{initial pure water flux}}{\textit{Steady state pure water flux}}$$

The pre-pressurized membranes were used in subsequent UF experiments at 345 kPa applied pressure.

### Pure Water Flux

Membranes after compaction were subjected to pure water flux estimation at a transmembrane pressure of 345 kPa. The permeability was measured under steady state flow. The pure water flux is determined as follow (10).

$$J_w = \frac{Q}{A.\Delta T}$$

Where $J_{\mathrm{w}}$ = Water flux, $1\,\mathrm{m}^{-2}\,\mathrm{h}^{-1}$, $Q$ = Quantity of permeate, $A$ = Membrane area, $\mathrm{m}^2$ $\Delta T$ = Sampling time, h.

### Water Content

Water content of the membranes was obtained as follows. The membranes were soaked in water for 24 hr and weighed after mopping with blotting paper. These wet membranes were placed in a vacuum oven at 75°C for 48 hr and the dry weights were determined. From these two values, the percent water content was derived as follows (11).

$$\%\ Water\ Content = \frac{W_{\mathrm{w}} - W_{\mathrm{d}}}{W_{\mathrm{w}}} \times 100$$

$W_{\mathrm{w}}$ = Wet sample weight, $W_{\mathrm{d}}$ = Dry sample weight

## Membrane Hydraulic Resistance ($R_{\mathrm{m}}$)

Membrane hydraulic resistance is an important parameter, which reflects the tolerance of membranes towards hydraulic pressure. It would be more useful to apply the membrane for a particular environment and to identify the suitability of the membranes for a particular membrane process. Membrane hydraulic resistance ($R_{\mathrm{m}}$) was evaluated by measuring pure water flux at different transmembrane pressures such as 69, 138, 207, 276, and 345 kPa after compaction. The resistance of the membrane was evaluated from the slope of the transmembrane pressure difference ($\Delta$P) vs water flux ($J_{\mathrm{w}}$) using the following equation.

$$J_{\mathrm{w}} = \frac{\Delta P}{R_{\mathrm{m}}}$$

## Morphological Studies

The top surfaces and cross section of the membranes were examined using scanning electron microscopy (SEM). The membranes were freeze, dried then frozen in liquid nitrogen and fractured to expose the cross-sectional areas. The dried sample was gold-coated and viewed with SEM (LEICA Stereos can, Cambridge, UK).

## Protein Rejection

All the protein solutions were prepared separately at 0.1 wt% concentration in phosphate buffer medium of 7.2 pH and trans membrane pressure (TMP) was maintained at 345 kPa in nitrogen atm. Proteins such as Trypsin (20 kDa), Pepsin (35 kDa), Egg Albumin (45 kDa), and Bovine serum Albumin (69 kDa) were dissolved in 0.1 wt% in phosphate buffer (0.5 M, $P^H$ 7.2) and used as standard solutions. For all experiments, concentration of the feed solutions was kept constant. Permeate was collected over measured time intervals and the concentration of the proteins in the permeate were estimated by UV–visible spectrophotometer at $\lambda_{\max} = 280\,\text{nm}$. The percentage solute rejection (% SR) was calculated as follows:

$$\%\,SR = \left(1 - \frac{C_\text{p}}{C_\text{f}}\right) \times 100$$

where, % SR is the percent solute rejection, $C_\text{p}$ and $C_\text{f}$ are the concentration of the permeate and feed solutions respectively.

## Application Studies

The characterized CA membranes were used for cadmium ion rejection studies at 345 kPa. (12) Aqueous solution of cadmium ion has been prepared with 1000 ppm of PEI complex in distilled water. For all experiments, the concentration of the feed solution was maintained as constant. The pH of these aqueous solutions was adjusted to 6 ± 0.25 by adding a small amount of either 0.1 M HCl or 0.1 M NaOH. Solutions containing PEI and individual cadmium ions were thoroughly mixed and left standing for 5 days to complete binding (13,14). After mounting the membrane in the UF cell, the chamber was filled with a known volume of cadmium solution and immediately pressurized to the desired level (345 kPa) and maintained constant throughout the run. The permeate was collected under stirred (200 rpm) UF cell over measured time intervals in graduated tubes and the test contents were analyzed for cadmium content by UV-Visible Spectroscopy (Hitachi, model U-2000) at $\lambda$max = 620 nm (15,16). The percentage Cadmium/Polyethyleneimine (Cd/PEI) complex rejection (%R) was calculated (17) from the concentration of feed and permeates using the following relation.

$$\%\ \mathit{Solute\ rejection} = \left[\frac{1 - C_\mathrm{p}}{C_\mathrm{f}}\right] \times 100$$

where $C_\mathrm{p}$ and $C_\mathrm{f}$ are the concentration of permeate and feed solutions, respectively.

## RESULTS AND DISCUSSIONS

In order to study the blending of CA with the additives PEG 200 and PVP, the total concentration of total polymer in the casting polymer in the casting solution was first selected. Thus, taking CA as base polymer, the effect of CA concentration in the casting solution on the pure water flux of membrane was measured and the results are shown in Fig. 1. It can be seen from Fig. 1 that an increase in concentration of CA in the casting solution from 10 to 20 wt% decreases the pure water flux from 23.1 to 15.5 $\mathrm{l\,m^{-2}\,h^{-1}}$. Furthermore, the membranes made with less than 17.5 wt% CA in the casting solution were taken as the total polymer concentration for further studies.

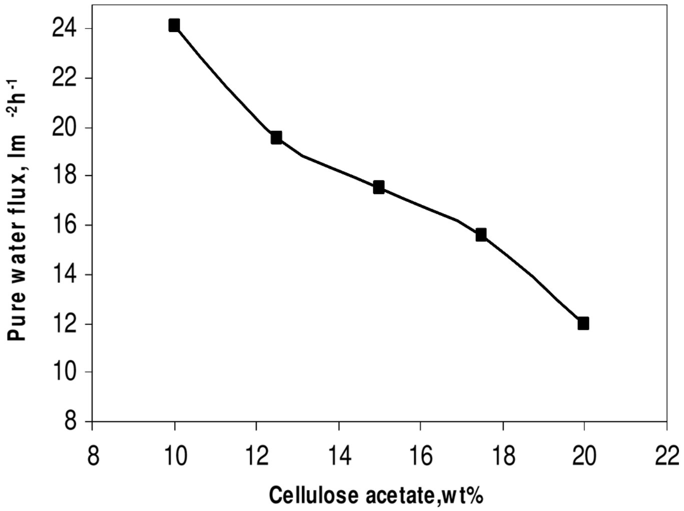


*Figure 1.* Effect of CA concentration in casting solution on PWF of CA.

The composition of additive in the blend solution was varied from 0 to 10 wt% of the 17.5 wt% polymer concentration in the casting solution (Table 1). The composition of hydrophilic polymeric additive, pore former PEG 200, and Polyvinylpyrrolidine concentrations in the polymer casting solution was varied, from 2.5% in an increment of 2.5% of the 17.5 wt% polymer concentration in the casting solution (Table 1) for all the polymer blend solutions and the maximum compatible additive concentration was found to be 10 wt%. Beyond this concentration, all the polymer blend solutions exhibited incompatibility with the additive, as soon as solution blending is mechanically arrested. The role of polymeric additives on compaction time, PWF, water content and the hydraulic resistance ($R_m$) on the cast membrane was studied. The MWCO of these membranes and the separation of metal ions in aqueous solution are also discussed.

## Hydraulic Compaction

Precompression of the membranes at a pressure higher than operating pressure, permits stress relaxation during operation. During compaction, the re-organization of the polymeric chain occurs, leading to change in the membrane structure with reduced volume porosity. This in turn increases the hydraulic resistance offered by the membrane as a result of a dense membrane structure resulting in a decline in the permeate flux. The membranes prepared from various blend composition were washed thoroughly with deionized water and were compacted at 414 kPa for 4–5 h. The pure water flux of the membranes prepared from polymer blends of CA/PEG and CA/PVP with compositions ranging from 100/0 to 90/10 wt% at different compaction time is shown in Fig. 2.

## Effect of Concentration PEG

The effect of concentration of PEG 200 on the hydraulic compaction of CA/PEG 200 blend membranes is shown in Fig. 2a. It is seen from Fig. 2a that pure water flux of membrane decreases with increasing compaction time in the initial 3 h for all polymer blend composition. Further increase in the compaction time does not change the pure water flux. This indicates that complete compaction of the blend membrane occurred in the first 3 h. The decline in pure water pure water flux in the early stages of the compaction can be attributed to the reduction in the porosity volume due to closer rearrangement of polymer segments and chains. From the graph it was evident that the membrane prepared from pure CA with

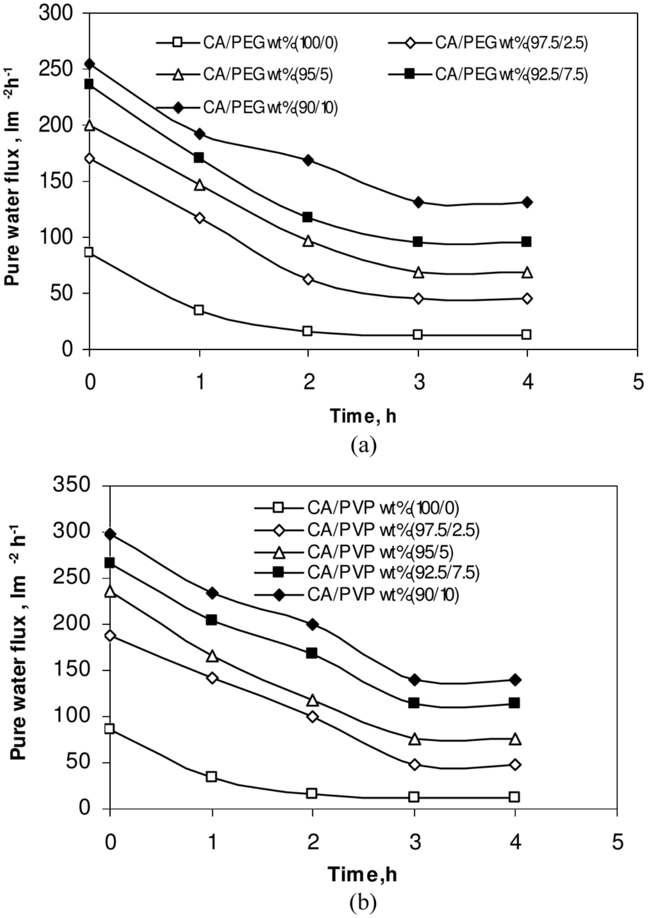


***Figure 2.*** (a) Effect of compaction time on PWF for CA/PEG 200 blend membranes and (b) Effect of compaction time on PWF for CA/PVP blend membranes.

17.5 wt% casting solution showed a steady state pure water flux of 12.5 lm$^{-2}$ h$^{-1}$ after 3 hrs. Membranes made using CA/PEG 200 wt% (97.5/2.5) blend membranes have a flux of 170.3 lm$^{-2}$ h$^{-1}$initially which decreased to a constant value of 44.74 lm$^{-2}$ h$^{-1}$ afer 4 hr of compaction where it remained constant. These membranes have a higher flux compared to membranes made in the absence of PEG 200. Further increase in pore former (PEG 200) concentration to 5 wt% increased the flux from 44.74 to 68.21 lm$^{-2}$ h$^{-1}$. This trend was also observed when the concentration of PEG 200 was increased to 10 wt%. The higher PEG 200 content in the blend may stem from partial compatibility due to higher free energy of mixing of the blends, which leads to a larger polymer chain segmental gap between CA and PEG (18).

## Effect of Concentration PVP

The effect of concentration of PVP on the hydraulic compaction of membranes for CA/PVP blend membranes is shown in Fig. 2b. Membranes made using CA/PVP wt% (97.5/2.5) blend membranes have a flux of 188.56 l $m^{-2} h^{-1}$ initially which decreased to a constant value of 47.18 l $m^{-2} h^{-1}$ afer 4 hr of compaction where it remained constant. Further increase in pore former (PVP) concentration to 5%wt increased the flux from 235.7 to 75.26 $m^{-2} h^{-1}$. This trend was also observed when the concentration of PVP was increased to 10 wt%. In line with the trend observed for PVP, it can be observed that the increase in the concentration of PVP results in the increase in the pure water flux as seen in the case of CA/PEG 200. This increasing trend can be explained in a similar way as explained for CA/PEG 200 blend membranes. It should be noted that the pure water flux using CA/PEG 200 blend membranes is slightly lower than the membranes made using CA/PVP in all concentrations. This is because of the fact that PVP is more hydrophilic compared to PEG. (19,20).

The increased flux of membrane in the presence of PVP may be due to the fact that PVP contribute to formation of larger aggregative pores of resultant blend membrane segments (21). The relatively higher flux in presence of PVP may be due to increase in network pore size (22) of membranes with increasing PVP content in the blend, in addition to enhancement of the aggregate pore size due to segmental gap between polymers chains (22).

Compaction factors for reported membranes were shown in Table 1 which indicated that a large pore size membrane i.e. 10% has a high tendency of compacting under pressure. Because of the large void space created by PVP, the internal structural reorganization is more in 10%, which leads to a high compaction factor.

## Effect on Pure Water Flux

After initial compaction of the membranes for 4–5 hr at 414 kpa, the transmembrane pressure was maintained at 345 kpa for further characterization. The pure water flux of all the compacted membranes were measured after an initial stabilization period of 30–60 min and the results are shown in the graph. The pure cellulose acetate (100%) membrane, prepared in the absence of additive PEG 200 and PVP exhibited a low pure water flux value 29.13 l $m^{-2} h^{-1}$.

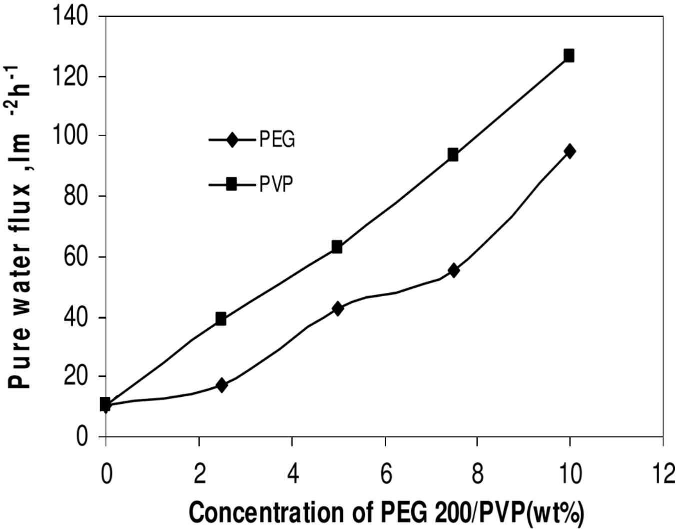


*Figure 3.* Effect of PWF on CA/PEG 200 and CA/PVP blend membranes.

In this study, it was assumed that the presence of the additive in the membrane casting solution would have a considerable effect on the pure water flux. The effect of the concentration of PEG 200 on pure water flux is shown in Fig. 3. In general it is seen that there was a linear increase of pure water flux from 10.43 $\mathrm{l\,m^{-2}\,h^{-1}}$ to 95.56 $\mathrm{l\,m^{-2}\,h^{-1}}$ when the concentration of PEG 200 was increased from 2.5 to 10 wt%.

The comparatively higher flux was observed when PVP was used as an additive. When PVP concentration was increased from 2.5% to 10%, there was a linear increase of pure water flux from 10.43 $\mathrm{l\,m^{-2}\,h^{-1}}$ to 126.64 $\mathrm{l\,m^{-2}\,h^{-1}}$. The increase in the additive content in blend may favour the formation of larger pores in membranes. The increase in additive concentration increases simultaneously the repulsive force between polymer segments along with leachability of the additive are enhanced and this favors the formation of macro voids due to occurrence of more number of large size pores (23,24), when compared with the values of PEG 200 and PVP it is seen that PVP is more water soluble than PEG 200 and it gets leached out easily leading to the formation of larger number of pores.

## Effect on Water Content

Water content of the membranes is an indirect indication of the hydrophilicity and flux behavior of membranes. Membranes were thoroughly washed with distilled water before the estimation of the water content.

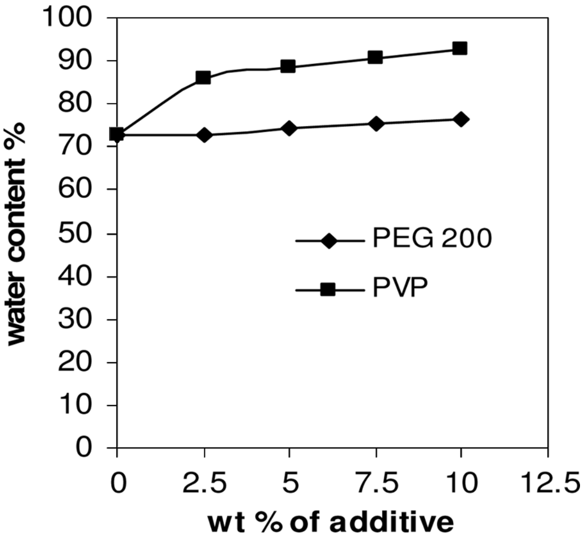


*Figure 4.* Effect of Water Content on CA/PEG 200 and CA/PVP blend membranes.

Pure cellulose acetate membrane in the absence of both PEG 200 and PVP was found to have a water content of 72. 67% as shown in the Fig. 4. From Fig. 4 it is evident when PEG content in the blend was increased from 2.5 wt% to 10wt%, the water content also increased to 73.01% to 76.27%. The addition of PEG 200 in the blend not only increases the hydrophilicity of the blend but may also increase the macro phase separation of the blend membrane which in turn enhance the pore size of membranes. Furthermore, coagulation of PEG 200 content increases during gelation, and may result in enlargement of the pore size of the membrane (9) and becomes the domain of water molecules.

When PVP concentration is increased from 2.5 wt% to 10 wt% increases the water content from 85.67% to 92.45%. The increases in the PVP content in blend may favor the formation of larger pores in membranes which in turn holds more water content. (25). This is found to be greater than CA/PEG 200 blend membranes. (26) Then the concentration of PVP is increased, the repulsive forces between polymer segments along with leachability of PVP are enhanced and this favors the formation of macro voids. One could expect that as the PVP is hydrophilic, that could attract the water molecule inside the membrane matrix. This higher water had reflected the higher pure water flux in the previous experiment.

## Membrane Hydraulic Resistance

Membrane hydraulic resistance $R_m$, is an indication of tolerance of membrane towards hydraulic pressure. The resistance in UF membranes is offered by or due to dense top "skin" layer and the porosity. Generally for the pure water feed, the flux is proportional to the TMP. In our case, the $R_m$ value measured by subjecting the membranes to various pressures from 69 to 414 kPa and measuring the pure water flux. The linear proportionality of pure water flux to applied pressure can be directly associated to the transport resistance. The hydraulic resistance of the membrane was evaluated using eon (3). The $R_m$ value was calculated from the inverse of the slope of the corresponding transmembrane pressure versus pure water flux plots are shown in Table 1. It is found from Table 1 that the pure Cellulose acetate membranes in the absence of PEG 200 and PVP, exhibited a higher membrane resistance of 33.33 kappa $m^2h\,L^{-1}$ due to its low porosity.

The hydraulic resistance offered by CA/PEG 200 blend membranes is shown in Table 1. In the blend membranes when PEG was increased from 2.5 to 10% the hydraulic resistance decreased gradually from 9.43 to 2.82 kappa $m^2h\,L^{-1}$. This decrease in membrane hydraulic resistance may be explained by the fact that an increase in the proportion of PEG in the blend not only increases the amorphous nature of the membranes but also enhances the pore size to a greater extent owing to an extended segmental gap between polymer chains which leads to the decrease in the value of $R_m$.

From Table 1 it is evident that the hydraulic resistance decreases from 20.12 to 3.51 kappa $m^2h\,L^{-1}$ in CA/PVP blends membranes when the concentration of PVP is increased from 2.5 wt% to 10 wt%. The addition of PVP to CA enhances segmental gap between polymer chains which reduces the membrane resistance. The presence of PVP increases the gap further leading to the formation of macro voids on the membrane surface resulting from faster rate of leaching of PVP at higher concentration gradient from casting solution during gelation. This in turn results in lowering the membrane resistance at higher PVP concentration (27), which is slightly higher than the CA/PEG 200 blend membranes, as PVP is more hydrophilic than PEG.

## Molecular Weight Cutoff

Molecules having a molecular weight larger than the molecular weight cutoff (MWCO) of a membrane will not pass through the membrane. The MWCO of the membranes were determined using different reference solutions. The solutes generally used are proteins, which are considered to be spherical. Since MWCO of a particular membrane corresponds to the molecular weight of the proteins having solute rejection beyond 80% the MWCO of different membranes were determined from the knowledge of percent rejection of BSA, EA, trypsin, and pepsin by CA/PEG 200 and CA/PVP blend membranes were prepared in phosphate buffer medium of 7.2 PH and the transmembrane pressure was maintained at 345 kPa in nitrogen atmosphere. In order to determine the reference permeation fluxes, the flux of water and buffer were determined at the start of all UF experiments at 345-kPa transmembrane pressure. As it was feared that experiments with high molecular weight solutes might result in the clogging of the pores, and vitiate interpretation of data, separation of lower molecular weight solutes were carried out first. From Table 1 it was evident pure CA membrane without PEG 200/PVP content had the MWCO of 20 kDa because of smaller pore size.

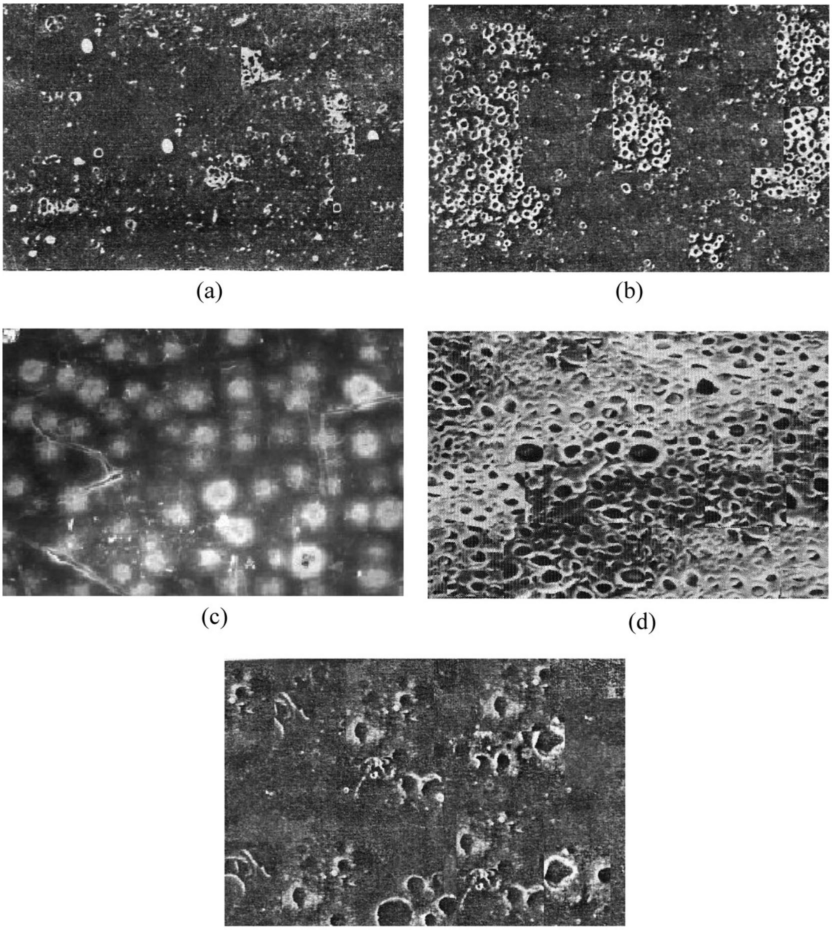
In the CA/PEG 200 blend membranes when PEG 200 content was increased from 2.5 to 10% the MWCO value also increased from 45 to 69 kDa and it is shown in Table 1. This has good correlation with the permeability results of the membrane. An increase in PEG/PVP content in the blend enhanced the MWCO, because of the large pore size of these blend a membrane which was due to the partial miscibility of CA and additive.

It is depicted from Table 1 that an increase in PVP content in CA/PVP blends membranes from 2.5 to 10%. MWCO of pure CA increases from 20 to $>69$ kDa. The increase in MWCO with the increasing PVP may be due to fast rate of leachability of PVP during gelation process, which leaves a large pore on membrane surface.

## Scanning Electron Microscopy

Membrane morphology is a powerful tool to investigate the structure of polymeric integrally skinned membrane. To develop high performance polymeric membranes, it is essential to design the morphological structures of the membranes for their specific applications. The micrographs of the top surfaces of pure CA, CA/PEG 200 (97.5/2.5 wt%), CA/PEG PEG 200 (95/5 wt%), CA/PVP (97.5/2.5 wt%) and CA/PVP (95: 5 wt%) are shown in Fig. 5a, b, c, d, and e respectively.

From Fig. 5b and Fig. 5c it can be seen that the pore sizes of CA/PEG 200 are bigger than those of pure CA membrane. The increase in pore size of blend membranes with increasing PEG content in the blend was also confirmed by scanning electron microscopy.



(a) (b)

(c) (d)

(e)

***Figure 5.*** SEM Micrographs of top surface of CA/PEG 200 and CA/PVP blend membranes. (a) Pure CA Membrane (b) CA/PEG 200 wt% (97.5/2.5) (c) CA/PEG 200 wt% (95/5) (d) CA/PVP wt% (97.5/2.5) (e) CA/PVP wt% (95/5).

It can be seen that the pore sizes of CA/PVP (97.5/2.5 wt% and 95: 5 wt%) blend membranes (Fig. 5d and Fig. 5e respectively) are bigger than those of pure CA and CA/PEG 200 (97.5/2.5 wt% and 95: 5 wt%) blend membranes. Thus a higher PVP concentration in blend polymer incorporates more number of pores as well as the bigger pore size on CA membranes compared with CA/PEG 200 blend membranes. A comparison of Fig. 5a–e clearly shows that the increasing pore size and increase in the number of voids is due to the increase in the concentration of PVP. This may be attributed to the distribution of individual domains of PVP and CA with their respective morphology and established the observed trends on PWF, water content, and hydraulic resistance of blend membranes prepared in presence of various concentrations of PVP.

## Application Studies

The rejection of Cd/PEI complex is one of the criteria for the evaluation of the performance of membranes. The effect of additive on membrane performances was shown in Figs. 6 and 7 and it indicated that these permeate flux values are low compared to PWF values presented in Fig. 3. The reason is due to the high resistance to flow that was offered by Cd/PEI complex ion deposited at the surface of the membrane and the viscosity of the solution.

## Effect of Applied Pressure

The effect of applied pressure from 69 to 345 kPa on Cd/PEI complex ion rejection and permeate flux for different were reported in Figs. 6 and 7. Figure 6 clearly shows that the pure CA membrane exhibits a higher rejection value of Cd/PEI at 345 kPa and this rejection increases significantly with increasing pressure.

The effect of Concentration of PEG 200 on the percentage rejection of metal ions for the CA/PEG blend membranes is shown in Fig. 6a. The increase in concentration of PEG 200 results in the decrease of rejection of Cd/PEI complexes. For 2.5 wt% of PEG 200 in the blend membranes the percent rejection was found to be 80.3% and this is decreased to 67.4% when PEG 200 concentration was increased to 10 wt% at 345 kPa. This decreasing trend in rejection is due to the fact that the pore size of the membranes increases as the concentration of PEG 200 in the membrane casting solution increased (Jean 2002, chuang). Fig. 7a indicates the significant flux variation with respect to applied pressure. At 345 kPa, when PEG 200 concentration was increased from 2.5 to 10 wt% in the blend flux also increases from 14.71 to 32.14 $\mathrm{l\,m^{-2}\,h^{-1}}$. This is due to the fact that at higher concentration of the additive PEG 200, larger amount of pore former leaches out at higher rate, which leaves larger pore size on the membrane and hence led to higher fluxes with lower rejection.

The effect of concentration of PVP on the percentage rejection of metal ions for the CA/PVP blend membranes is shown in Fig. 6b. The increase in concentration of PVP results in the decrease of rejection of

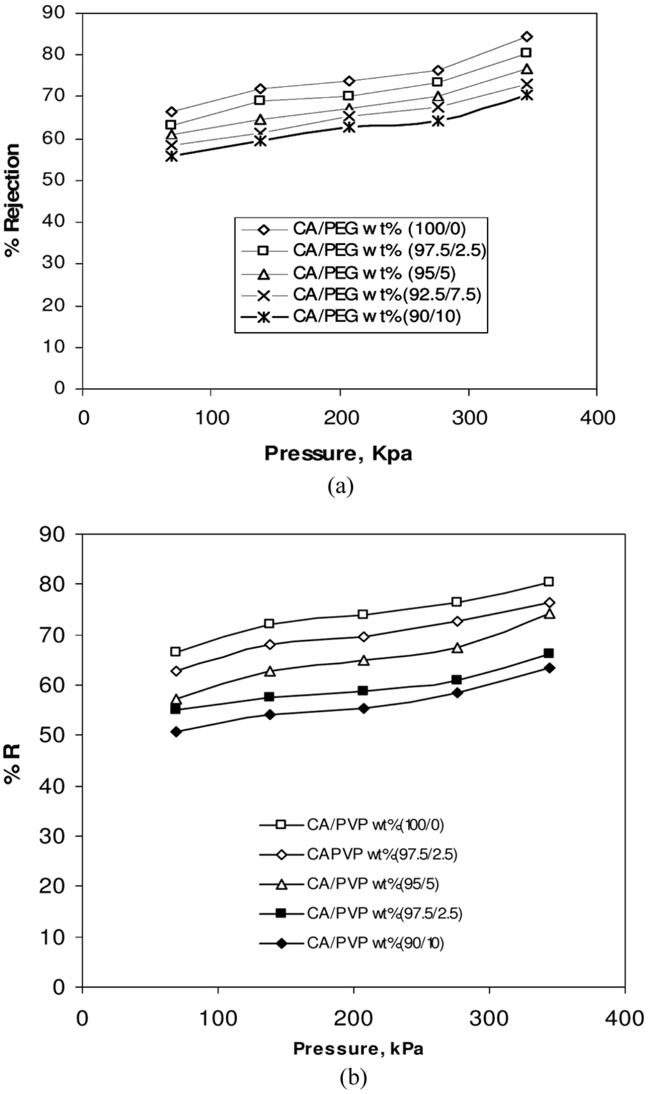


***Figure 6.*** (a) Effect of pressure on Cd/PEI complex ion rejection for CA/PEG 200 blend membranes and (b) Effect of pressure on Cd/PEI complex ion rejection for CA/PVP blend membranes.

Cd/PEI complexes. For 2.5 wt% of PVP in the blend membranes the percent rejection was found to be 76.42% and this is decreased to 63.43% when PVP concentration was increased to 10 wt% at 345 kPa.

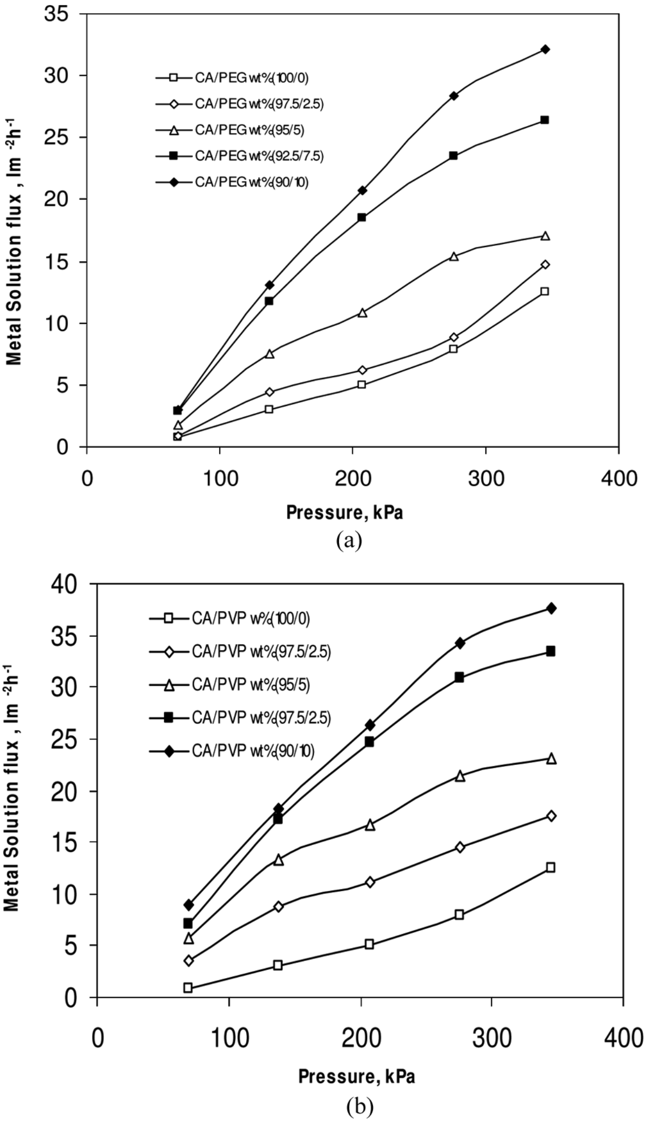


***Figure 7.*** (a) Effect of pressure on Cd/PEI complex ion flux for CA/PEG 200 blend membranes and (b) Effect of pressure on Cd/PEI complex ion flux for CA/PVP blend membranes.

This decreasing trend in rejection is due to the fact that the pore size of the membranes increases as the concentration of PVP in the membrane casting solution increased (20).

Figure 7b indicates the significant flux variation with respect to applied pressure. At 345 kPa, the Cd/PEI product rate for the pure CA without any additive (PEG/PVP) is 12.51 $m^{-2} h^{-1}$. It has been observed that pure CA membrane has the lowest flux compared to the other membranes. When PVP concentration was increased from 2.5 to 10 wt% in the blend flux also increases from 17.62 to 37.61 $m^{-2} h^{-1}$. This is due to an increase in the number of pores in the membranes.

It is seen from Figs. 6a and 6b that the rejection of Cd/PEI complexes follow similar pattern for increasing concentrations of both PEG 200 and PVP in the membrane casting solution. However, there seems to be slight variation in the extent of rejection of Cd/PEI complex. In general, the PEG added membranes provide slightly higher rejection for the Cd/PEI complex when compared to PVP added membranes. When the concentration of the additive is 2.5 wt% the rejection of Cd/PEI complex is 76.42% for PVP, while it is 80.3% for PEG. This is because of the higher hydrophilic nature of PVP than PEG 200 which results in increased porosity in PVP. Similarly the Fig 7a and 7b shows that the flux values are greater for PVP than PEG 200 content in the blend, due to higher hydrophilic nature of PVP than PEG 200.

## CONCLUSIONS

In this work, ultrafiltration membrane based on cellulose acetate was modified by blending with PVP and PEG 200 in different compositions. In general, all the modified membranes prepared from both CA/PVP and CA/PEG 200 polymer blends exhibited improved membrane properties and morphology compared to pure CA membranes. Experiments show that the increase in the concentration of PVP/PEG 200 in casting solution resulted in the increase of the pure water flux, the water content and the porosity. Scanning electron micrographs illustrate that the morphology of CA/PEG 200 and CA/PVP blend membranes changed with increase in the increase in concentration of PEG 200 and PVP respectively. The blend membranes were subjected to $Cd^{2+}$ ions separation. CA/PEG 200 and CA/PVP blends exhibited improved permeate flux of cadmium ions. The permeate flux increases as a function of concentration of PVP and PEG 200. CA/PVP blend membranes had higher permeate flux compared to CA/PEG 200 blend due to the higher porosity of CA/PVP membranes. However, increasing concentration of PVP and PEG in the membrane casting solution resulted in decreased rejection of $Cd^{2+}$ ions. This is due to the formation of pores by the addition of PVP or PEG 200 as demonstrated through porosity. The rejection of $Cd^{2+}$ through CA/PVP membranes was slightly lower than that of CA/PEG 200 membranes. In general, all the modified membranes prepared from both CA/PVP and CA/PEG 200 polymer blends exhibited improved membrane properties. However, comparatively CA/PVP showed slightly higher performance than CA/PEG membranes due to higher hydrophilic nature of PVP.

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