



## Synthesis and characterization of CMC/PVA/PVP composite microfiltration membrane

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### ABSTRACT

The aim of this study was to develop a composite membrane by phase inversion using carboxymethyl cellulose (CMC) as a basic material followed by characterization and performance testing. CMC was prepared from cellulose by alkalization and etherification of cellulose. CMC along with polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) were used to prepare composite membranes. Polyethylene glycol (PEG) was used as a pore forming agent. Characterization was done using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), thermo-gravimetric analysis (TGA), and universal testing machine. SEM results indicated that the addition of PVP resulted in a smoother surface with a pore size ranged 0.1–10 micron as compared to the membrane fabricated without PVP. FTIR spectroscopy gave the bands that are attributed to the dispersion of PVA and PVP in substrate matrix. Weight loss started at 270°C with PVP treatment as compared to 210°C in the absence of PVP indicating the improved thermal stability of the membrane. Salt rejection efficiency was in the following order: NaCl < KCl < CaCl<sub>2</sub> with solutions passed through having 0.1%, 0.3%, 1.0%, and 3.0% salinity. Overall salt removal or salt rejection efficiency ranged from 27% to 37%. It was concluded that PVP had a positive effect on thermal stability, surface morphology, and mechanical properties of the membrane. The properties highlight the potential usage of the synthesized membrane in pretreatment for removal of larger particles such as macromolecules, proteins, colloids, and microbes.

*Keywords:* Carboxymethyl cellulose; Composite membranes; Polyvinyl alcohol; Polyvinylpyrrolidone

### 1. Introduction

Water is vital for existence and survival of life on earth. This entity is significant for all features of human life, including food production, community health, ecosystem

biodiversity, and economic vitality. World population clock concluded that population has surpassed 7 billion currently and by 2050, it will reach up to 10 billion. For developing countries around the world, pure, and clean drinking water is an issue along with its scarcity for crop production [1].

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Desalination and reuse of the ocean and groundwater have been evaluated and worked by researchers effectively to deliver additional production of freshwater reservoirs for societal consumption than traditional freshwater resources [2]. Reuse of water provides options such as supplying water for industrial processes, groundwater recharge, power plant cooling, and irrigation. It is also accepted as an approach for indirect production of safe drinking water resource. Thermal desalination methods evolved since last 50 y and membrane technology that emerged in the last four decades provide freshwater for drinking [3]. Multiple approaches for developing various kinds of membranes with additional characteristics like bio-fouling resistant [4] and antibacterial [5] properties are currently being considered. However, reducing the cost and improving the efficiency of water treatment is an important challenge to eliminate portable water scarcity.

Middle East countries founded the strategy and implementation for thermal desalination of seawater, primarily through a process known as multi-effect distillation (MED) and secondly by means of a multi-stage flash distillation process [6]. Currently, Middle East cooperatively possesses 49% of desalination capacity in total [7] by principally using multi-stage flash (MSF) distillation technology.

Although thermal desalination is a primary choice of water treatment technology for Middle East, other membrane practices have promptly established since the 1960s and at present exceed thermal procedures in novel plant installations. Other than Middle East, innovative reverse osmosis (RO) installations for desalination have been progressively developed and have become one of the most important technologies [8]. By the year, 2002, 50% of established desalination capacity utilized RO desalination technology and by 2003, RO desalination facilities resulted in 75% of new production capabilities [9].

Hydrogels and membranes characterized with significant properties and structures regarding contaminant removal can simply be prepared with cellulose containing abundant OH and carboxylic groups. Composite membranes with chitosan/polyvinyl alcohol/polyacrylonitrile [10] and cellulose acetate (CA)/polyethylene glycol (PEG) doped with 10%–30% by weight fumed silica particles [11] were prepared and are reported helpful in pretreatment or treatment of wastewater. Processed products of cellulose, comprising carboxymethyl cellulose (CMC) and methyl cellulose (MC) have been utilized for fabrication of hydrogels centered on cellulose by chemical as well as physical cross-linking [12]. Blending and unification of diverse polymers are an exceptionally inexpensive, attractive, and beneficial method for achieving new and innovative structural materials [13] that can be utilized for pretreatment and desalination.

Previously, CMC was prepared from cellulose extracted from cotton gin waste that is basically an agricultural residue. Detailed procedure of extraction is reported in Haleem et al. [14]. The present work was focused on the development of a novel membrane and its efficiency testing for water pretreatment purpose. The modification approaches of membrane materials were employed through the incorporation of PVP which increased its mechanical strength, thermal stability as well as surface properties.

## 2. Experimental

### 2.1. Materials and reagents

Chemicals used in this research study were of analytical grade. Isopropyl alcohol ( $C_3H_8O$ ), acetone ( $C_3H_6O$ ), glacial acetic acid ( $CH_3COOH$ ), and sodium hydroxide (NaOH) were purchased from Scharlau, Spain. Methyl alcohol ( $CH_3OH$ ), ethyl alcohol ( $C_2H_6O$ ), monochloroacetic acid ( $C_2H_3ClO_2$ ), polyvinyl alcohol ( $C_2H_4O$ )<sub>n</sub>, ammonium persulfate ( $(NH_4)_2S_2O_8$ ), and polyvinylpyrrolidone ( $C_6H_9NO$ )<sub>n</sub>, PEG were obtained from Sigma Aldrich, Germany. Distilled water was used throughout the experimental work for preparation of solutions.

### 2.2. Synthesis of CMC

Cellulose isolated from cotton gin waste was converted into CMC with two step process under heterogeneous conditions. In the first step, 5 g of cellulose was added to 300 mL of water with an appropriate ratio (1:4) of isopropyl alcohol solvent. Then, 40 mL of sodium hydroxide with changing concentrations like 4%, 8%, 12%, 16%, 20%, and 24% w/v were added drop-wise to the beaker. Assembly was assisted with continuous magnetic stirring for 2 h on a hot plate. Etherification underwent by adding varying concentrations of sodium monochloroacetic acid (MCA) (1–5 g) to the reaction mixture in 250 mL beaker on magnetically stirred hot plate. The blend mixture was then heated at different temperatures (40°C–60°C) with continuous stirring for 3 h. The reaction mixture was then filtered and the filtrate was suspended in 100 mL of methyl alcohol for 45 min. Diluted glacial acetic acid was used to neutralize suspended slurry. It was followed by filtration and then it was washed with absolute methyl alcohol. The residue from the filtration was then oven dried at 60°C overnight and the powder obtained was CMC [14].

### 2.3. Synthesis of composite membrane

For membrane fabrication, 1 g of CMC was dissolved in 70 mL distilled water in a 500 mL three neck flask, equipped with a reflux condenser. The flask was placed on magnetic hot plate for constant stirring. Assembly was attached to nitrogen cylinder (99.99% pure) for inert environment. After being purged with nitrogen for 30 min, excess dissolved oxygen was removed from the system. To CMC solution, 3 mL of 0.1% of ammonium persulfate, as an initiator was added and the mixture was immediately stirred at 60°C for 40 min under nitrogen [15]. Meanwhile, 4 g of PVA was left to get dissolved in 70 mL distilled water at 60°C. The solution prepared was then added drop wise to the reaction mixture at 150°C for 2 h to complete polymerization. Different volumes (2, 4, 6, and 8 mL) of PEG were introduced as pore former in order to achieve optimization. The addition of additive (PVP) in the casting solution is one of the significant step that affects the membrane performance and structure. To enhance the hydrophilic properties of the membrane, the addition of PEG as a polymeric additive has been proposed to achieve new requirements of the present era [16].

For comparative studies for two types of membranes were fabricated; one with PVP as a filler on CMC/PVA

substrate in comparison with simple PVA/CMC membrane. Varying concentrations (4%, 6%, 8%, 10%, and 12%) of PVP were added at 150°C to achieve optimization. Membranes were prepared by using phase inversion method [17]. The resultant homogenous polymer mixture was transferred into Petri dishes, cooled at room temperature and washed with distilled water numerous times till it got neutralized. Membranes were achieved by drying in ambient air for 48 h at room temperature. Water bath was used to remove membranes from Petri dishes at 60°C. The acquired membranes were then heat treated in an oven at 60°C for 8 h.

## 2.4. Characterization of membranes

### 2.4.1. Scanning electron microscopy

The topography and morphology of the membranes were examined by SEM (JEOL JSM-6490A, Japan Analytical SEM) at different magnifications. The SEM was used for the direct estimation of pore size. The membranes were subjected to freezing under liquid nitrogen at extreme low temperatures for 1 min and then frozen membrane fragments were split and coated with a thin layer of conducting material (gold) by sputtering to generate electrical conductivity. The SEM images of the membrane surface were captured in a low vacuum environment, working at 10–25 KeV.

### 2.4.2. Fourier transform infrared spectroscopy

FTIR spectroscopy is used for the identification of certain functional groups in a sample. In this study, FTIR spectra were collected using a spectrophotometer (Model-spectrum 100, Perkin Elmer FTIR, USA). The mixture of sample and potassium bromide KBr (2:98 mg w/w) was used to prepare the sample disc by applying high pressure through hydraulic press. The spectra were measured in both absorbance and transmittance modes on resolution over 4,000–500  $\text{cm}^{-1}$ . However, the results presented here are in absorbance mode.

### 2.4.3. Thermogravimetric analysis

TGA is used to determine the degradation temperatures, absorbed moisture content of materials, thermal stability, and moisture residues. The TGA analyses were performed on Pyris-1, diamond TG/DTA Perkin Elmer. In a typical experiment, samples with a weight of around 15–20 mg were placed in a clean platinum pan and the data was recorded by heating the samples at 10°C/min and ambient temperature (around 25°C) to 450°C in an inert nitrogen atmospheric condition. A principal TGA curve representing the mass percentage (wt.%) of a sample as a function of temperature was constructed and used to compare the thermal decomposition behavior of different membrane samples.

### 2.4.4. Material testing machine

Tensile and compressive strengths of the samples were tested on AG-XPlus UTM, Shimadzu, Japan. Ultimate tensile strength (UTS) was determined by carrying out a tensile test and by plotting a stress vs. strain graphs. The highest

point shown in the stress, strain curve is UTS. Its value does not depend on the size of the testing material because it is an intensive characteristic. It is dependent on different factors like the presence of apparent defects, preparation of the sample, and the temperature of the testing environment and the prepared sample [10]. Tensile strength is usually taken in terms of a stress, which is basically measured as force per unit area. It could be reported as a force per unit width for non-homogenous samples.

### 2.4.5. Physicochemical analysis

To evaluate physicochemical properties of the acquired membranes, water solubility, sorption, and salt rejection analysis with varying concentrations of three different salts and flux rates were determined. For water sorption and dissolution analysis, the cast membranes were weighed and weight, that is,  $W_1$  was obtained. Then the membranes were immersed in deionized water at room temperature for 2 h. After that the extra water was poured out and the surface was gently wiped off with tissue paper to obtain the weight ( $W_2$ ). Then the membranes were dried in oven at 40°C and  $W_3$  was obtained. The experiment was repeated thrice for an average weight. For each soaking cycle, the percent water sorption and percent solubility were calculated as under [18,19].

$$\% \text{ Water sorption} = \frac{W_2 - W_3}{W_3} \times 100 \quad (1)$$

$$\% \text{ Solubility} = \frac{W_2 - W_3}{W_3} \times 100 \quad (2)$$

For salt rejection analysis, four different concentrations, that is, 0.1%, 0.3%, 1.0%, and 3.0% (w/v) of salts including NaCl, KCl, and  $\text{CaCl}_2$  were prepared. Solutions were passed through obtained membranes via filtration assembly with vacuum pump with constant pressure of 40 KPa. The difference between the electrical conductivity (EC) readings of inlet and outlet gave salt rejection results. Water flux of all the samples was measured at steady state conditions and at constant pressure of 40 KPa. Flux rate was calculated using the following formula:

$$\text{Flux rate } (J) = \frac{Q_p}{A_m} \quad (3)$$

In case of 3% salt solution:

- Flow rate,  $Q_p = 0.05 \text{ L/h}$
- Area,  $A_m = 19.6 \text{ cm}^2$  or  $0.00196 \text{ m}^2$
- Flux,  $J = 25.5 \text{ L/m}^2/\text{h}$ .

The data collected at different concentrations was then plotted on the graph and direct relationship was observed. The flow rate was determined by simple experiment performed on filtration assembly with a vacuum pump for about 24 h. In order to check the flow rate and fouling trend of membrane with the passage of time ( $t$ ), 3% (w/v) salt solution was prepared and poured on top of the filtration assembly.

### 3. Results and discussion

#### 3.1. Characterization of membranes

Solutions were prepared in reflux condenser assembly in heterogeneous conditions at an optimized temperature of about 150°C for continuous 24 h. The PEG optimized amount was 6 mL, where it gave good hydrophilicity but increasing the concentration of PEG resulted into more flexibility and lesser tensile strength [20]. With the addition of PVP on CMC/PVA substrate, tensile strength was enhanced and optimized 10% PVP concentration gave a membrane with excellent tensile strength in addition to hydrophilic properties. By adding 12% PVP, similar results were achieved, so 10% PVP casting solution was selected for characterization and further experimental work.

##### 3.1.1. Surface morphology by SEM

Scanning electron microscopy (SEM) was used to analyze surface morphology of the membranes, particularly with reference to surface smoothness between two comparative membranes, that is, with and without addition of PVP. The SEM micrographs are presented in Fig. 1. In Fig. 1a, homogenous surface can easily be observed at just 50× magnifications for PVA/CMC/PVP membrane. However, in Fig. 1b simple PVA/CMC membrane showed a rough surface. The SEM results indicated that the surface morphology of the acquired membranes was dependent on the type of the filler added. Morphology of membranes may also be affected by the rate of demixing process. Formation of macro-voids in membrane structure could be the result of instantaneous de-mixing, whereas slow mixing is responsible for denser structure with no macro-voids.

With the addition of PVP in the membrane matrix, it can be noticed that the smooth membrane surface was formed and smaller pores were found. Smaller pores lead to increase in surface area, thereby the retention of cations on

the sorbent may enhance [16]. On the other hand, absence of filler in the casting solution resulted in a rough membrane surface. It can be perceived that the decrease in PVP concentration, possibly cause the thermodynamic membrane-forming system to get unstable. These results showed increased rates of precipitation and the formation of porous membranes [21]. In Fig. 2, the SEM images indicated the pore size at 15,000× magnification. It shows acquired pore sizes in the membrane with PVP ranged between 0.1 and 10 microns. The resulted membrane can be used in micro-filtration. The changes in the morphologies and sizes can be attributed to the changes in the blend composition by the addition of PVP and different concentrations of PEG. The membrane surface hydrophilicity was increased by blending with PEG. It could be due to the preferential orientation of carboxymethyl groups toward water during the formation of membrane process [22].

The composite of CMC/PVA/PVP as a hydrophilic composition may have intensified the thermodynamic instability of the cast film. Increasing the PEG concentration resulted in an accelerated rate of precipitation in the coagulation bath that ultimately started instantaneous demixing which might result in the development of macro-voids at the surface of membrane [23]. Composite with PEG increases viscosity of the cast film due to higher molecular weight of PEG and intra-molecular aggregations or entanglements of the polymer chains in the presence of PEG [21]. The diffusional exchange rate gets slowed down with the increase in viscosity that results in the suppression of macro-voids and consequently the development of relatively denser structures. It can be perceived that the addition of hydrophilic additives in the casting solution, such as PEG, has numerous positive or negative effects on surface morphology of the membrane. It is believed that the characteristics of CMC membranes can be improved by adding PEG which would enhance the membrane performance in terms of selectivity and permeability [24].

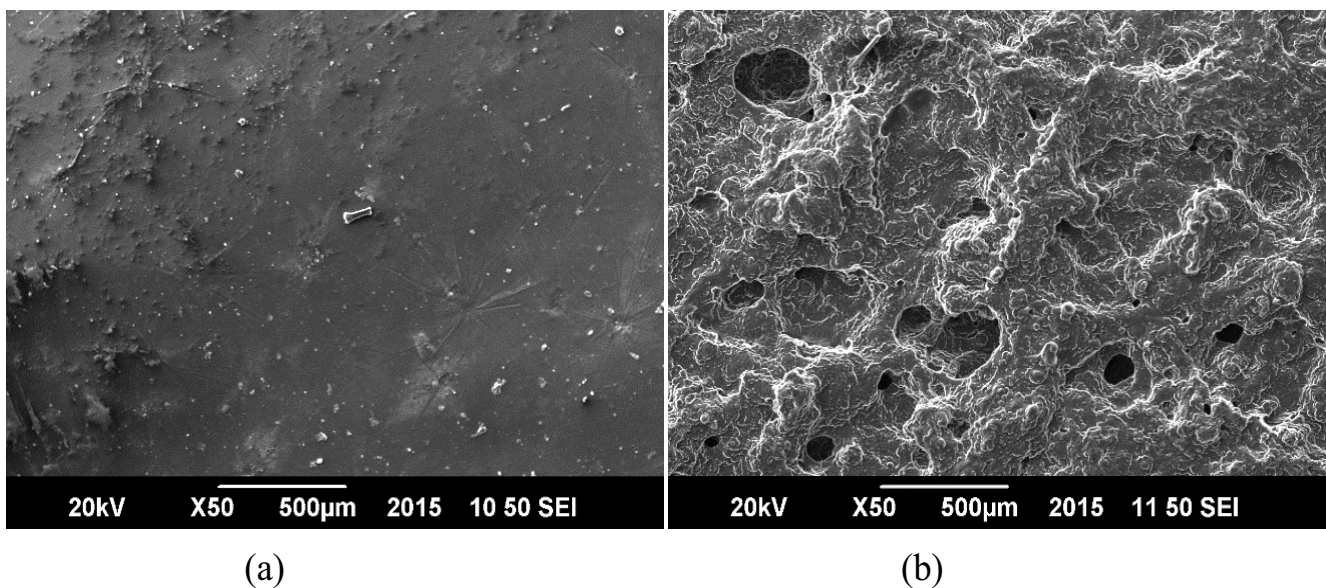


Fig. 1. Surface morphology of membranes through scanning electron microscopy. (a) PVA/CMC/PVP and (b) PVA/PVP.

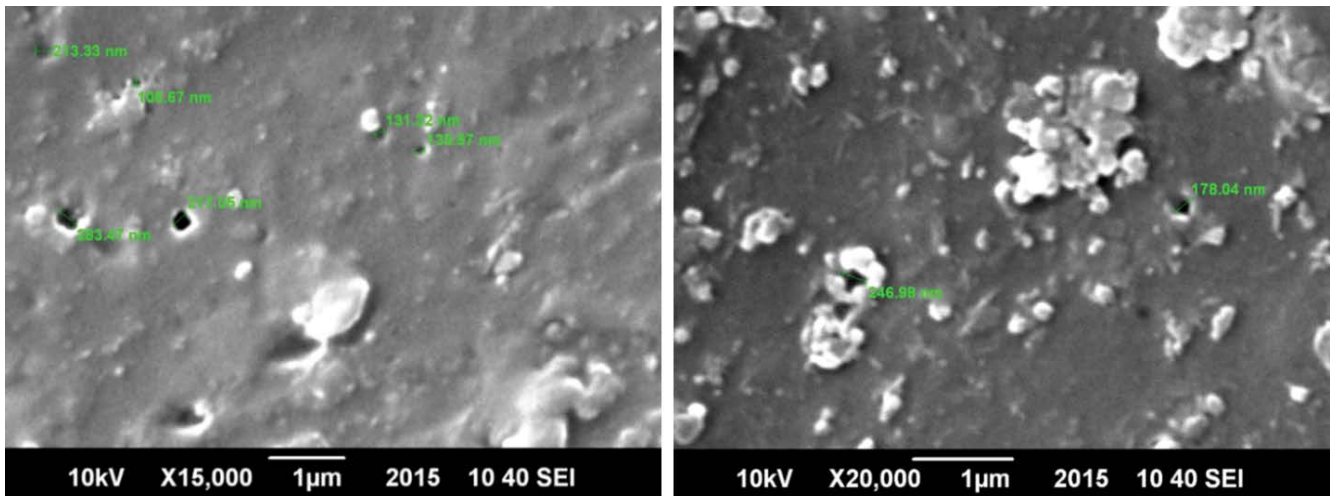


Fig. 2. Pore size of PVA/CMC/PVP membrane at different magnifications.

### 3.1.2. Functional group analysis

The FTIR gave the spectra of acquired membrane that showed the presence of functional groups and confirmed that the substitution occurred between PVA, CMC, and PVP. The FTIR spectra of PVA/CMC/PVP membrane are illustrated in Fig. 3. The peaks in the region of 1,600–1,750  $\text{cm}^{-1}$  show C=O double bond stretching, vibration which is attributed to the functional group CMC and PVP. At 2,920  $\text{cm}^{-1}$ , peak is due to C–H stretching vibration. This peak can be assigned to C–H stretching vibration of CMC in the supporting data. Peak at 952  $\text{cm}^{-1}$  is due to O–H bending vibration which is a characteristic of CMC. Peak at 1,052  $\text{cm}^{-1}$  represents C–O–C bonding which is a characteristic of CMC as can be seen in supporting data. The peak in the region of 3,460  $\text{cm}^{-1}$  is also due to hydrogen bonded O–H stretching vibration

which is a characteristic of CMC and PVA. The band in the area 1,052  $\text{cm}^{-1}$  involve C=O that is stretching vibration of aliphatic primary and secondary alcohols present mainly in cellulose, hemicellulose and lignin [25,26]. The peak at 858  $\text{cm}^{-1}$  is due to N–H wagging. At 1,365  $\text{cm}^{-1}$  peak shows C–H rocking vibration which is associated with the deformation of the plane in CH groups. The presence of these bands is ascribed to the partial dispersion of PVP in PVA/CMC matrix.

### 3.1.3. Thermal stability analysis

In TGA, variations in physical and chemical properties of given samples are measured as a function of increasing temperature (with constant heating rate), or as a function of

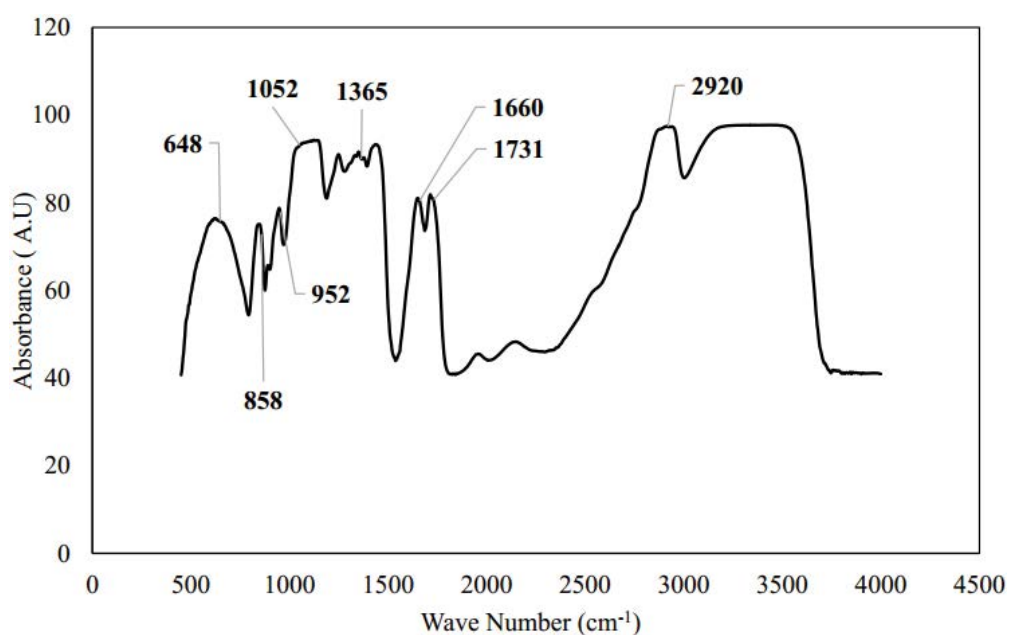


Fig. 3. FTIR spectrum of PVA/CMC/PVP membrane.

time (with constant temperature and/or constant mass loss) [27]. Fig. 4 shows thermo-gravimetric curves of two comparative membranes, that is, PVA/CMC and PVA/CMC/PVP membrane. It is noticed that the onset of weight loss ( $T_s$ ) for the membrane with PVP started at about 270°C, and in membrane without PVP, the weight loss started at 210°C. These  $T_s$  values indicated that PVP addition, as an additive, resulted in membranes with higher thermal stability which could be supportive in industrial application. Also, most weight loss, that is, burn off in treatment without PVP leads to decreased carbon content and thereby reduced affinity for contaminants/salt removal. Another group also prepared PVA, cellulose/PVA, and PVA/CMC membranes and weight loss ( $T_s$ ) started at 275°C, 175°C, and 75°C, respectively. The weight loss ( $T_s$ ) started at a lower temperature in case of PVA/CMC membranes. This can probably be associated with the fractional oxidation of the OH groups in the polymer chains of substrate matrix [15].

#### 3.1.4. Mechanical strength

The mechanical property of the microfiltration membrane is another major concern for the practical application. This property was analyzed using Universal Material Testing Machine. The graph between stress and strain in Fig. 5 shows the maximum value where the membrane started to fracture. Only the optimized PVA/CMC/PVP membrane was run under this test to find out the maximum stress that can be applied to it during practical applications. The PVA/CMC membrane was so fragile that it was unable to go through test procedures. Maximum stress that membrane can bear was found to be 17 N/m<sup>2</sup> or MPa. After this point, it started to fracture. The MAX-D shows the point at which fracture is completed and it ends up with total breakage.

This result may be associated with the addition of PVP into the membranes that increased the degree of substitution in CMC/PVA. This incorporation ultimately enhanced the mechanical strength of the resultant composite membrane. Nevertheless, it could be assumed that the acquired membrane could definitely meet the mechanical requirements for practical application of microfiltration at pilot scale. Thermo-gravimetric analysis (TGA) of acetate blended membranes was prepared and results for tensile strength were about 4 N/m<sup>2</sup> under similar conditions [24]. So, the prepared membrane in present study had relatively high strength as compared to the reported earlier in literature.

### 3.2. Physicochemical analysis

#### 3.2.1. Water solubility

Soluble parts of the membranes with and without PVP were calculated and found 0.5% and 9%, respectively. Results showed that the addition of PVP reduced the amount of soluble parts present in the membranes that probably was due to the decrease in the unreacted PVA molecules which could otherwise leach down into the water. It has been reported in literature that solubility of PVA/CMC membrane was 7%, while for pure PVA membrane, solubility was 68% [15]. It can be justified that it was due to the absence of crosslinking matrix and substitution. On the other hand, membrane with PVP as filler, high crosslink matrix is formed that reduced the solubility up to 0.5%.

#### 3.2.2. Salt rejection analysis

Salt rejection analysis was performed with three different salts at different concentrations. Graphical representation has been made in Fig. 6. In case of NaCl, average efficiency

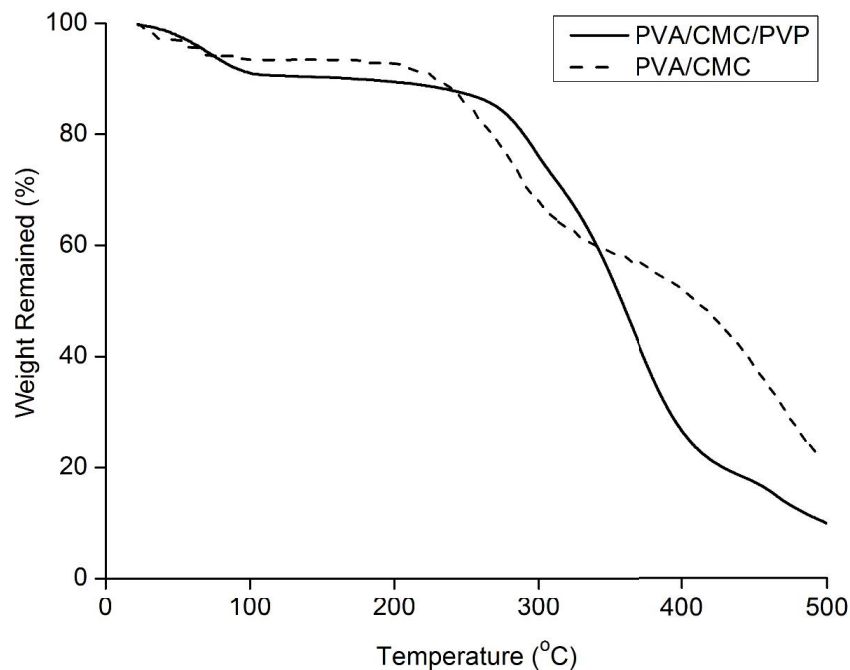


Fig. 4. Thermo-gravimetric analysis (TGA) of membranes.

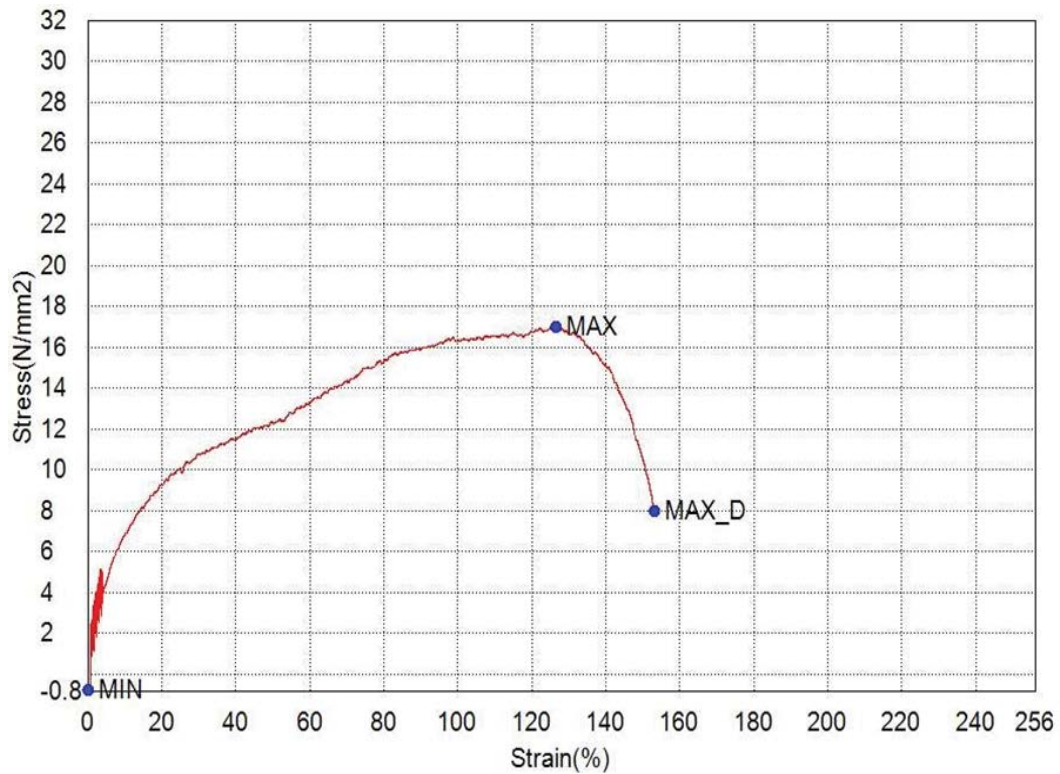


Fig. 5. Mechanical strength of PVA/CMC/PVP membrane.

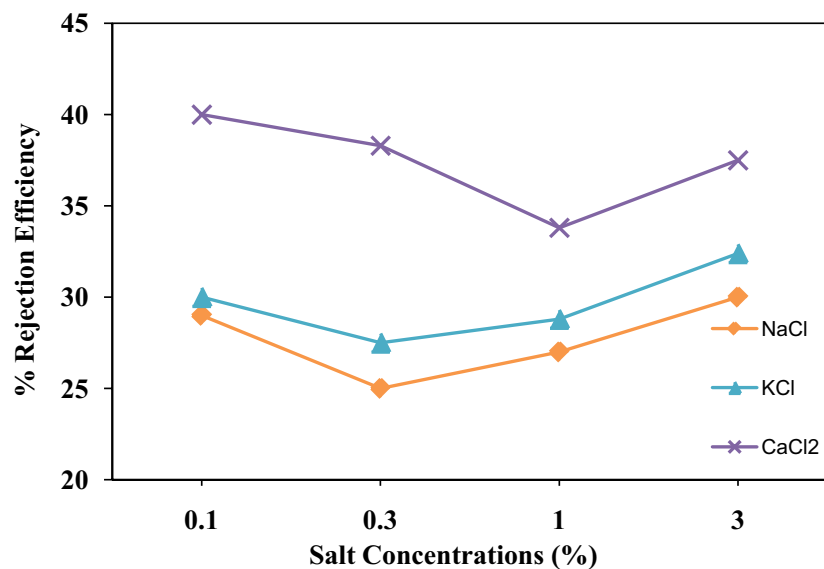


Fig. 6. Salt rejection rates at different salt concentrations.

for all the concentrations was 27.75%. The presence of NaCl contributes to the destabilization of hydrogen bond network in cellulose [24] thereby can affect the efficiency of membrane in the current study with NaCl treatment. For KCl, average efficiency for all the concentrations was 29.67%, which was comparatively higher than that for NaCl. Salt rejection efficiency for CaCl<sub>2</sub> was the maximum, that is, 37.42%.

The partially permeable membrane allowed selective particles to pass through it and as the size of molecule increased, it became more difficult to pass through the porous membrane structure. The trend of increase in salt rejection rate with selected salts was NaCl < KCl < CaCl<sub>2</sub> and it can be attributed to their molecular mass 58.4 < 74.55 < 110.98 g/mol, or ionic hydration radii, that is, the matrix affinity for

the ions decreases with an increase in cations hydration radii from Ca to Na, respectively [23]. The overall average efficiency for all the three salts came out to be 30.84%, which is considerably helpful in pretreatment of water prior to reverse osmosis (RO). The salt rejection efficiency of the acquired membrane ranged from 27% to 37% that mainly attributed to adsorption or sorption. Since the pore size falls in the category of microfiltration; hence the membrane can be used as a pre-treatment to reverse osmosis. The combined effect of higher recovery and higher flux rate ensures significantly reduced costs of the RO plant [28].

### 3.2.3. Flow rate and change in flux

The long-term steady state flux was calculated by extrapolating flow rate to the time axis to attain time lag. It was observed that there was a long lead time before a steady state which attributes that, first the permeate might have started to dissolve which delayed the time required for stable state to be achieved. It is worth mentioning that the addition of either PEG or PVP as an additive, plays an important role in the overall membrane properties [15]. Graphical illustrations (Fig. 7) showed that after 24 h fouling occurred to about 17% (Fig. 7a). Membrane fouling

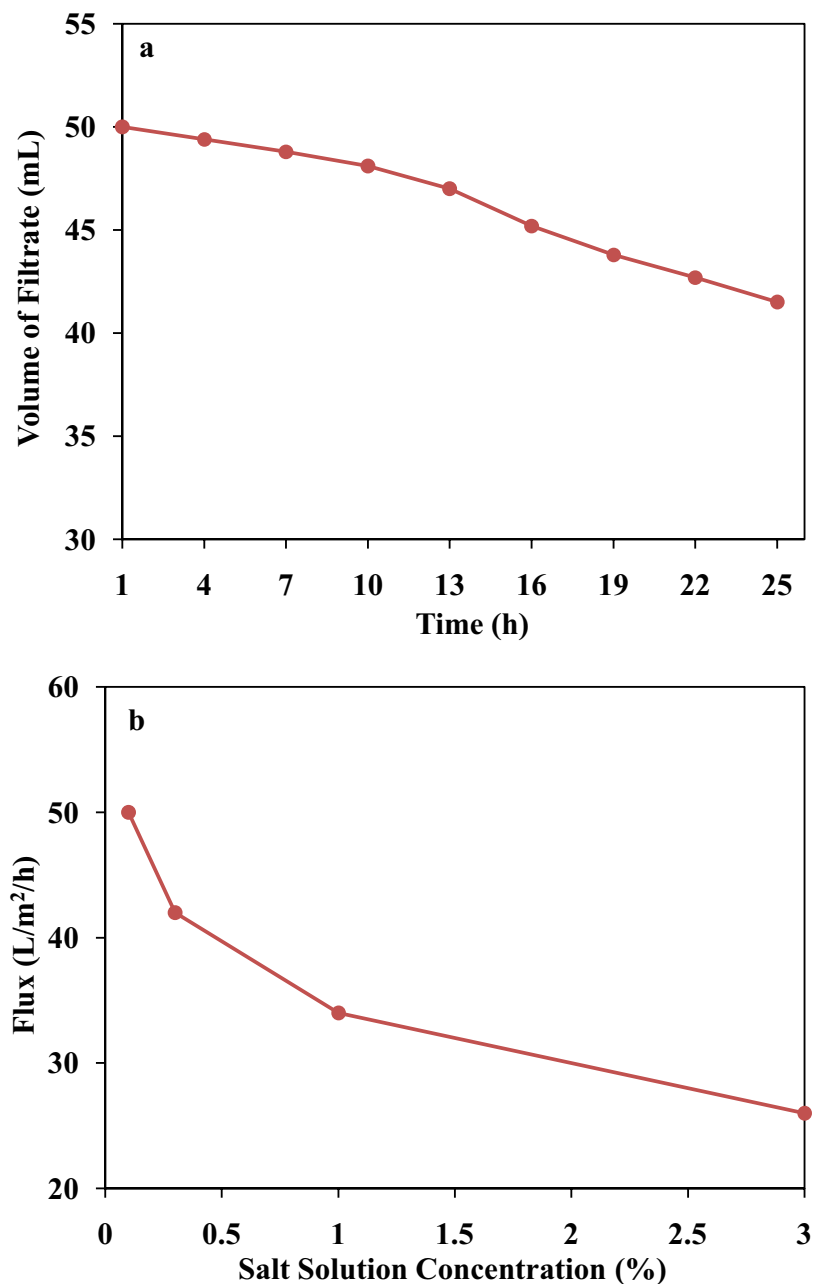


Fig. 7. Membrane testing for desalination potential. (a) Change in flow rate as a function of time and (b) change in flux as a function of feed concentration ranging from 0% to 3% salinity.



could reduce the permeation efficiency and restrict the wide application of microfiltration membrane. Permeation efficiency is reduced due to membrane fouling that restricts its wide application in microfiltration technology. Hydraulic cleaning is offered to improve membrane flux [29]. Other antifouling agents are also in use to enhance the membrane's function and to increase its life.

The flux decline behavior of the CMC/PVA/PVP blended membranes during filtration at 40 KPa are presented in Fig. 7b. This result demonstrated that there was an inverse relationship between flux and the concentration of feed solution. Minimum flux was 26 L/m<sup>2</sup>/h at 3% salt concentration that was the highest feed concentration while the maximum was 50 L/m<sup>2</sup>/h. It is reported several times in the literature that flux rate decreases with the increase in feed concentration in filtration membranes due to fouling. It is also reported in the literature that cellulose acetate and carboxymethyl acetate blended membranes gave pure water flux of 56 L/m<sup>2</sup>/h while sea water clarification, pre-treatment tests used membranes of instant fluxes lower than 100 L/m<sup>2</sup>/h [28]. With the addition of PVP modifier in the blend component, the flux recovery ratio increased which might be due to the increased hydrophilicity [24]. It was also reported that long-term seawater pilot testing used 0.1 μm filtration membrane for RO pretreatment and desalination systems [27] that confirms the possible application of the prepared membranes in present study.

#### 4. Conclusions

Fabricated CMC/PVA/PVP composite membrane was micro porous. The PVP had a positive effect on surface morphology, thermal stability, and mechanical strength of the acquired membrane. Pore size falls in the category of microfiltration; hence the membrane can be used as a pre-treatment to reverse osmosis. The salt rejection efficiency of the acquired membrane ranged from 27% to 37% that mainly attributed to adsorption or sorption. Since the starting material for the present work was agricultural residue, it can help to recover useful resources from the waste and reduce emissions from burning of the bio-waste. Moreover, it is cost effective and economical to develop this sorbent due to easy and cheaper availability of raw material (cotton gin) under local conditions. This cheap source of cellulose can also be exploited for further applications [30,31].

#### Geolocation information

This work is done primarily at National University of Sciences and Technology (NUST), Islamabad, Pakistan with active collaboration among the institutes mentioned in the affiliation list.

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