

Separation performance of poly(vinyl alcohol) based nanofiltration membranes crosslinked by malic acid for salt solutions

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ABSTRACT

In this study, poly(vinyl alcohol) (PVA) based nanofiltration (NF) membranes were prepared by coating a thin PVA film on polysulfone ultrafiltration support substrates. The PVA film was cross-linked using malic acid in the presence of HCl as a catalyst. The impacts of crosslinker content and PVA molecular weight on physicochemical properties and separation performance of the prepared membranes were investigated. The obtained membranes were characterized using FTIR spectra, swelling degree, and sessile drop contact angles, respectively. Then, the separation performance of the NF membrane was systematically evaluated for pure water; magnesium sulfate

(MgSO₄) as well as sodium chloride (NaCl) solutions using a custom fabricated 4-cell crossflow desalination system. On increasing the malic acid content, the extent of crosslinking degree increased and disrupted the crystallinity of the PVA film. The salt rejection of the prepared membranes was found to increase and then decrease through the maximum point of malic acid content for 20 wt%, while the water permeability showed the opposite trend. Moreover, the results revealed that the prepared membrane with higher molecular weight exhibited lower water permeability but better salt rejection.

Key words: nanofiltration, membrane, poly (vinyl alcohol), brackish water, desalination.

1. INTRODUCTION

Nanofiltration (NF) membranes, a particular category of driven-pressure membranes, provide the separation properties of reverse osmosis (RO) membranes and ultrafiltration (UF) membranes.

Accordingly, they are favorable to the separation of hardness metal ions, toxic and dissolved organic molecules (>500 Da) [1-6]. NF membranes have been widely applied for

desalination as well as water treatment due to its low operation pressure, high flux, good rejection of multivalent metal ions, excellent elimination of organic molecules and moderate retention of monovalent metal ions. Moreover, NF process availably offers several advantages such as low capital, operation and maintenance cost as compared with RO process [2].

Polyamide (PA) based NF membranes have been successful commercialized for brackish water desalination. PA membranes are fabricated through the interfacial polymerization using multifunctional amine and acyl chloride monomers. They show high water flux, good rejection multivalent ions, but low anti-fouling property, low chemical stability, and weak chlorine tolerance [1-6]. In developing countries, the high fabrication cost also is one of the obstacles restricting the application of PA based NF membranes [2]. Recently, poly(vinyl alcohol) (PVA) has been intensively used for preparing NF membranes owing to its good physical and chemical stability, low cost, commercial availability and excellent film-forming property [2-6]. The PVA-based NF membranes were mostly prepared by the chemical crosslinking reaction using multifunctional compounds, such as dialdehydes, dicarboxylic acids, and dianhydrides, which are capable of reacting with hydroxyl groups of PVA. The water permeability and salt rejection of the PVA-based NF membrane were found to depend on the variations of PVA concentration, PVA molecular weight, crosslinking agents, crosslinker concentration, porous substrate's characteristics and preparing conditions [1,3,5,6]. It notes that the PVA concentration in the range of 0.1-0.5 wt% was capable of making NF membranes with good separation performance for brackish water

desalination [1,4-6]. The multivalent salt rejection (MgSO_4) and monovalent salt retention (NaCl) were approximately 70-85% and 15-35%, respectively, while the water permeability was from 2 to 10 $\text{mPa}^{-1}\text{s}^{-1} \times 10^{-12}$ (8-43 $\text{L/m}^2\text{h}$) [1]. Additionally, the PVA molecular weight (M_w) in the range of 27-100 kDa was used for making NF membranes. Although the higher M_w showed, the more stability of the PVA membranes in aqueous solution during NF process, the PVA membranes made by M_w from 27 kDa to 61 kDa exhibited high water permeability [1,3-6]. Previous studies demonstrated that malic acid, a dicarboxylic acid with an additional hydroxyl group in its molecule, was a good crosslinking agent for making PVA membranes [1,4-6]. The PVA membranes crosslinked by malic acid exhibited not only good chemical stability and separation performance but also high anti-fouling property [1,6].

This work focuses on the preparation of PVA based NF membranes by coating a crosslinked PVA thin film on the surface of polysulfone ultrafiltration (UF) substrates. The PVA thin film was crosslinked by malic acid in the presence of HCl as a catalyst. The effects of malic acid content and PVA molecular weight on the physicochemical properties water permeability and salt rejection of the prepared membranes were systematically investigated and thoroughly discussed.

2. EXPERIMENTAL

2.1 Chemicals and materials

PVA powders (M_w 31kDa and M_w 61kDa) were purchased from Sigma-Aldrich. Malic acid ($\text{C}_4\text{H}_6\text{O}_5$) with the purity of 99% received from Merck was used as crosslinking agent. The commercial UF membrane (PS20-Dow-filmtec)

was utilized as the supporting substrate where the crosslinked PVA film was coated. HCl (35%) was received from Merck.

2.2 Membrane preparation

PVA solutions with a concentration of 0.1 wt/v% were prepared by dissolving PVA in deionized (DI) water at 90°C under constant stirring for 2h. Next, PVA solutions were cooled to room temperature and then, crosslinking agent malic acid was added along with 2M HCl as catalyst under continuous stirring to produce the coating solution. The content of malic acid was varied according to the crosslinker per PVA weight ratio of 5 wt% to 60 wt%. The supporting substrate was taped onto the glass plate, and only the membrane surface side was contacted with PVA solution in dip coating process. PVA solution was coated onto supporting membrane for 10 min. The PVA coated membrane was dried at the ambient temperature for 24h. The obtained membrane was immersed into the same PVA solution again for 10s and dried in air for 24h. Finally, the obtained membrane was cured at 100°C for 1h to accelerate the crosslinking reaction in PVA film [3].

2.3 Membrane characterization and separation performance

The derived membranes were characterized by using a Bruker FTIR spectrometer. Three replicate FTIR spectra were obtained for each membrane type, with each spectrum averaged from 100 scans collected from 400 to 4000 cm^{-1} at 4 cm^{-1} increments. Pure water contact angles were determined from measured sessile drop contact angles on membranes using the contact angle goniometer. Six equilibrium contact angles were measured for each sample.

For swelling experiments, the pieces of dried membranes with the dimension of 3×3 cm were immersed in pure water at 30°C for 48h to reach equilibrium swelling. The swollen membranes were wiped carefully using tissue paper for removing residual solution on the membrane surfaces. Then, the swollen membranes were weighted by a mass balance (accuracy ± 0.0001 g). The degree of swelling was defined as

$$\text{Swelling degree (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

Wherein, W_s (g) and W_d (g) were the mass of the swollen membrane and the mass of the dried membrane, respectively. The data of swelling degree were collected from three replicate experiments.

Brackish water desalination experiments were carried out by using a custom fabricated bench-scale crossflow RO desalination simulator. Four plate-and-frame membrane modules were designed with an individual membrane area of 21 cm^2 . Water was maintained well mixed in the feed tank by magnetic stirring. The feedwater was pressurized by a high-pressure pump (Catpump, USA) with a steady feed flow of 0.12 gpm. The temperature of feedwater was maintained at 25 ± 0.5 °C by a custom fabricated chiller. All permeate and concentrate were returned to the feed tank to avoid concentrating the electrolyte in the system. First, DI water was filtered through the membranes at 350 psi for at least 12 h. After achieving stable flux, the permeability of membrane was determined by measuring the water flux at an applied pressure of 300 psi. Second, the MgSO_4 solutions at a fixed concentration were filtered through the membranes at 300 psi. The permeate flow rate

and conductivity of feed and permeate samples were collected after the system performance was stable for at least 2h. Next, the separation of NaCl solutions was carried out as filtering MgSO_4 solutions. The permeate flow rate and conductivity were indicated using a mass balance (AWS-602, USA) and a conductivity meter (Hach-Sension 378). The data of flux and salt rejection reported in this paper were based on the average of four experimental runs. Water flux was determined from permeate water flow rate as

$$J_w = \frac{Q_p}{A_m} \text{ (L/m}^2\text{h)} \quad (2)$$

Where Q_p was the permeate water flow rate and A_m was the effective membrane area. The water permeability of the prepared membranes was determined as

$$J_w = A(\Delta P - \Delta \pi) \quad (3)$$

Wherein, A was the water permeability, ΔP was the operational pressure and $\Delta \pi$ was the osmotic pressure of the salt solution. Feed and permeate conductivities were used to calculate the observed salt rejection using the following equation

$$X_s = 1 - \left(\frac{k_p}{k_f} \right) \quad (4)$$

Where k_f and k_p were the feed and permeate conductivity

3. RESULTS AND DISCUSSION

3.1 Effect of malic acid content on separation performance of prepared NF membrane

The FTIR spectra of the prepared membrane was presented in Fig. 1. The peaks 3200 - 3600 cm^{-1} assigned to hydroxyl band (-OH) in the PVA thin film. The peaks at 1725 cm^{-1} and 1094 cm^{-1} represented the -C=O- and -C-O- stretches in -C=O-O-C-, which reflected the crosslinking

bonds. The FTIR spectra were evidence of crosslinking reactions between the hydroxyl groups of PVA and the carboxylic groups of malic acid in the PVA film. [3-5].

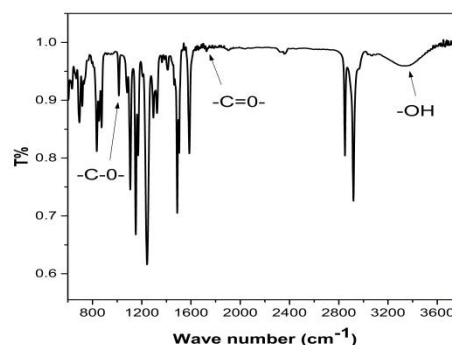


Figure 1. FTIR spectra of PVA membranes crosslinked with different malic acid content

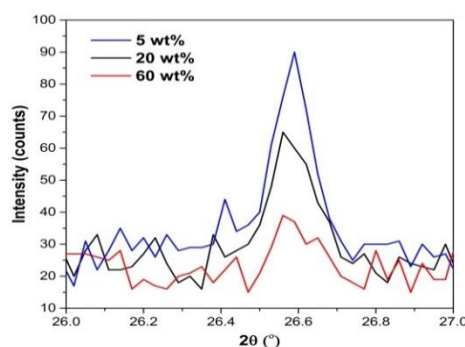


Figure 2. XRD spectra of PVA membranes crosslinked with different malic acid content

The extent of crosslinking was demonstrated to change the crystallinity of the PVA films, which affected the water permeability and salt rejection of the PVA membranes [5,6]. It was obviously acknowledged that semi-crystalline PVA had the impermeable crystalline region and the permeable amorphous matrix [1,3-6]. The crystal structure, forming from hydrogen linkage, depleted both the sorption sites and the mobility of the polymer chains, which allowed the high transport of solvent and solute molecules through the membrane [1,3-6]. Meanwhile, the polymer

chains in the amorphous structure were much more mobile and thus, the mass transfer of water and solute molecules throughout the membrane was promoted. The XRD spectra described the crystallinity of the prepared membranes were shown in Fig. 2. It revealed that the crystalline peak (at $2\theta = 26.6^\circ$) was reduced with the increase in malic acid content. Moreover, at higher malic acid content (>20 wt%) the crystalline peak was observed to destroy mostly and separate into two small peaks. The decrease in the crystalline peak implied that crosslinking reaction disrupted the crystallinity and induced the increase in the amorphous fraction of the PVA film. The decrease in the crystalline peak implied that crosslinking reaction disrupted the crystallinity and induced the increase in the amorphous fraction of the PVA film. The decrease in the crystallinity of the PVA film might be due to the incomplete crosslinking reaction, resulting in the addition of large carboxylic acid moieties in the PVA film. Moreover, the large molecular network with high degree of crosslinking was also contributed to inhibited the chain segment motion for crystallization in the PVA film.

Fig. 3 showed the effects of the malic acid content on the water contact angle and swelling degree of the prepared membranes. The swelling degree was observed to reduce significantly when raising the malic acid content from 5 wt% to 20 wt%, and go up as increasing the malic acid content above 20 wt%. The water contact angle indicated the hydrophilic property of the membrane surface. The higher water contact angle signified the lower hydrophilicity of the membrane surface. The water contact angle was found to rise as increasing malic acid content. On increasing the crosslinker content, much more hydroxyl groups in the PVA matrix reacted with carboxylic groups on the malic acid to produce the ester crosslinking linkages [1,3-7]. Thus, the increase of the crosslinking density resulted in

the decrease of hydrophilicity of the membrane surface.

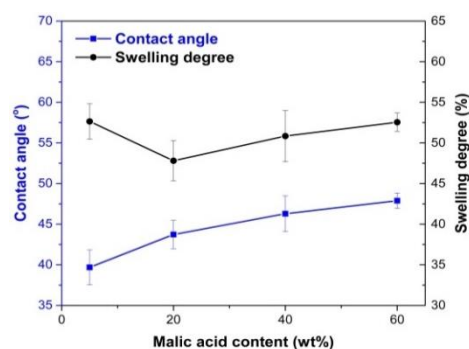


Figure 3. Contact angle and swelling degree of PVA membranes crosslinked with different malic acid content

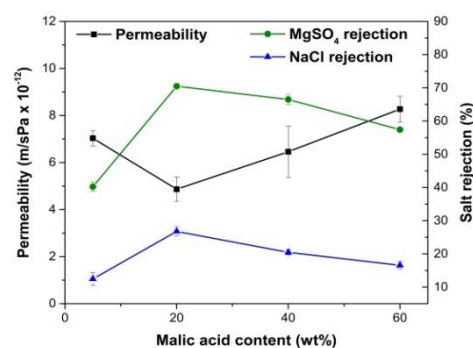


Figure 4. Effects of malic acid content on the separation performance of prepared PVA-based NF membranes

The water permeability and solute rejection of the PVA-based membranes were evaluated using pure water and salt solution of MgSO₄ and NaCl for 2 g/L (Fig. 4). The water permeability of the prepared membranes decreased with malic acid content increasing from 5 wt% to 20 wt%, and then increased when increasing malic acid content above 20 wt%. Meanwhile, solute rejection presented the opposite trend. Salt rejection of the prepared membranes increased and then decreased with the malic acid content of 20 wt%. From the results, it was suggested that both the hydrophilic and crystallinity affected the

separation performance of the prepared membranes. At lower crosslinker content (<20 wt%), the crystallinity of the resulting membrane was not completely demolished, while the hydrophilic property was declined. The reduction in hydrophilicity dominantly diminished the affinity between the water molecules and membrane surface. Therefore, the permeability was reduced, but the salt rejection of the prepared membranes was improved. However, at higher crosslinking agent content (>20 wt%), the disruption of the crystalline regions in the PVA membrane was superior. The more amorphous fractions were formed in the PVA membrane, promoting the higher permeability and transport of the water and salt molecules through the resulting membranes. Accordingly, the crosslinked PVA membranes had higher water permeability but lower salt rejection as increasing the malic acid content above 20 wt%.

3.2 Effect of PVA molecular weight on the separation performance of NF membranes

For investigating the effect of PVA molecular weight on the separation performance of the prepared NF membranes, two PVA with the different molecular weight of 61 kDa and 31 kDa were used. The PVA concentration and the malic acid content in the coating solution were fixed at 0.1 wt% and 20 wt%, respectively. The XRD spectra presented the crystallinity of the prepared membranes were shown in Fig. 5. It was observed that the NF membrane made from PVA molecular of 31 kDa had the intensity of crystalline peak (at $2\theta = 26.6^\circ$) lower than that made from PVA molecular of 61 kDa. It indicated that the 31 kDa PVA membrane had much more amorphous regions than the 61 kDa PVA membrane.

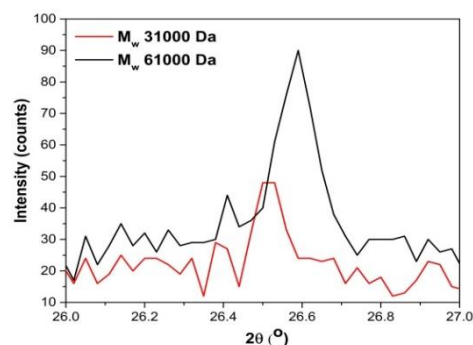


Figure 5. XRD spectra of cross-linked PVA-based NF membranes prepared by different PVA M_w

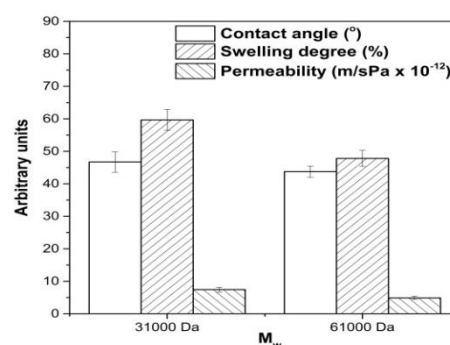


Figure 6. Contact angle, swelling degree and permeability of membranes developed by various PVA M_w

The pure water contact angle, swelling degree and water permeability of the cross-linked PVA-based NF membranes were presented in Fig. 6. It was found that the NF membrane prepared by PVA molecular weight of 61 kDa had lower hydrophilic property, swelling degree and water permeability as compared with that made by PVA molecular weight of 31 kDa. Meanwhile, the $MgSO_4$ and $NaCl$ rejection of 61 kDa PVA membrane was double as compared to 31 kDa PVA membrane (Fig. 7). It could be explained by XRD results that the NF membrane formed by PVA molecular of 31 kDa possessed higher amorphous fractions than that formed by 61 kDa. In the amorphous regions, the PVA chain

network was more flexible resulting in the easy penetration and diffusion of the species, like water and solute molecules in the PVA membrane. As a result, the membrane made from PVA molecular of 31 kDa exhibited higher permeability but lower salt rejection than that made from PVA molecular of 61 kDa.

The crosslinked PVA-based NF membrane synthesized with 61 kDa PVA concentration of 0.1 wt%, the malic acid content of 20 wt% was utilized to evaluate the separation performance for salt solutions with different concentration from 0.5 to 15 g/L. The results of water permeability, MgSO_4 rejection and NaCl rejection of the prepared membrane were shown in Fig. 8. It described that the water permeability was slightly reduced from 5.0 to $4.2 \times 10^{-12} \text{ mPa}^{-1} \text{ s}^{-1}$ and the salt rejection was also decreased with the increase of salt concentration in the range of 0.5 – 15 g/L . In particular, the retention of MgSO_4 was decreased approximately from 73% to 62% and the rejection of NaCl was reduced from 39% to 16% , respectively.

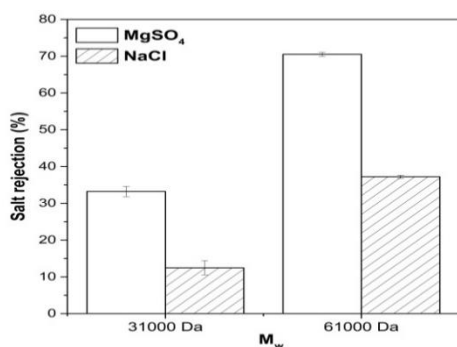


Fig 7. Effects of PVA Mw on the separation performance of prepared NF membranes

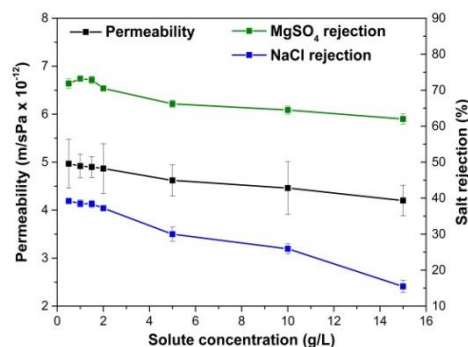


Fig 8. Water permeability and salt rejection of 61 kDa PVA-based NF membrane

4. CONCLUSIONS

Poly(vinyl alcohol) (PVA) based composite nanofiltration (NF) membranes were prepared by coating a thin PVA film on polysulfone ultrafiltration support substrates. The PVA film was crosslinked using malic acid in the presence of HCl as a catalyst. The results indicated that the malic acid content and PVA molecular weight affected the hydrophilicity and crystallinity of the resulting membranes. In little malic acid content ($<20 \text{ wt\%}$), the reduction of hydrophilicity was favorable but at higher malic acid content the decline of crystallinity was more dominant in the changes of water permeability of the prepared membranes. Moreover, the higher PVA molecular weight gave better salt rejection for the PVA-based NF membrane, although the permeability was observed to decreased. The PVA molecular weight of 61 kDa and malic acid content of 20 wt% were suitable for making the crosslinked PVA-based NF membranes with good retention of MgSO_4 and NaCl solutions in the range of 0.5 – 2 g/L .

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Khả năng phân tách muối của màng lọc nano trên nền poly(vinyl alcohol) được nối mạng bởi axit malic

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TÓM TẮT

Trong nghiên cứu này, màng lọc nano (NF) trên cơ sở vật liệu poly (vinyl alcohol) (PVA) được chế tạo bằng cách phủ một lớp màng PVA lên lớp đỡ màng siêu lọc polysulfone. Lớp màng PVA được nối mạng bởi axit malic với xúc tác HCl. Ảnh hưởng của nồng độ chất nối mạng axit malic và khối lượng phân tử PVA lên các đặc tính lý hóa và hoạt động phân tách của màng tạo thành đã được khảo sát. Màng đã chế tạo được đánh giá bởi phổ FTIR, tính trương nở và phương pháp đo góc tiếp xúc với nước cất. Hoạt động phân tách của màng NF được đánh giá bởi quá

trình lọc nước tinh khiết, dung dịch muối $MgSO_4$ và muối NaCl bằng hệ thống lọc muối dạng dòng chảy bang ngang qua màng. Khi tăng nồng độ axit malic, mật độ nối mạng của màng tăng và phá vỡ độ tinh thể hóa của màng PVA. Độ lọc muối của màng tăng và giảm qua nồng độ axit malic 20 %kl, nhưng độ thấm thấu nước của màng thể hiện xu hướng nước lại. Ngoài ra, kết quả cho thấy, màng tạo thành với khối lượng phân tử PVA cao hơn thể hiện độ thấm thấu nước thấp, nhưng lại cho độ lọc muối tốt hơn so với màng tạo thành từ khối lượng phân tử PVA thấp.

Từ khóa: lọc nano, màng lọc, polyvinyl alcohol, nước lợ, lọc muối.

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