



## Research Paper

# Fabrication and Characterization of Chitosan/Alginate Multilayer Composite Membrane Supported by a Porous Poly (Acrylonitrile) Substrate for Pervaporation Dehydration of Alcohol

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## Highlights

- Chitosan/sodium alginate composite membrane was fabricated by a press-driven process.
- The prepared polyelectrolyte composite membrane was employed for alcohol dehydration.
- Microporous poly (acrylonitrile) substrate was hydrolyzed for the subsequent deposition.
- The separation mechanism was dependent on the number of deposition layer.
- The prepared composite membrane exhibited desirable pervaporation performance.

## Abstract

Chitosan (CS) and alginate (Alg) are complementary in their membrane performance, but the combination of them is normally difficult to use due to their different solubilities. Layer-by-Layer deposition appears to be an effective method for improving the separation efficiency of a composite membrane. In this work, the polyelectrolyte multilayer composite membranes (PEMCMs) were fabricated by depositing CS and Alg solutions alternatively onto a hydrolyzed porous poly(acrylonitrile) (PAN) substrate under a reduced pressure, as evidenced by Attenuated total reflectance Fourier transform infrared spectroscopy, contact angle and zeta potential measurement. Pervaporation results showed that the water selectivity increased while the flux decreased with the growth of CS/Alg-based polyelectrolyte layer. It was interesting that the sorption process dominated the pervaporation process when the numbers of polyelectrolyte layers were less than 7. However, the diffusion effect was more profound than the sorption effect as more than 8 polyelectrolyte layers were deposited on the PAN substrate. In particular, the prepared CS/Alg PEMCMs exhibited highly improved water selectivities towards alcohol/water mixtures, and a good compromise between flux and separation factor was observed when compared to other polyelectrolyte-based membranes. For separating 90% IPA/water mixtures at 60 °C, the (CS/Alg)<sub>4</sub> composite membrane displayed a separation factor of 4491 and a flux of 596 g/m<sup>2</sup>.h, respectively. These results indicate that the fabricated CS/Alg composite membranes are excellent water-permselective ones for alcohol dehydration.

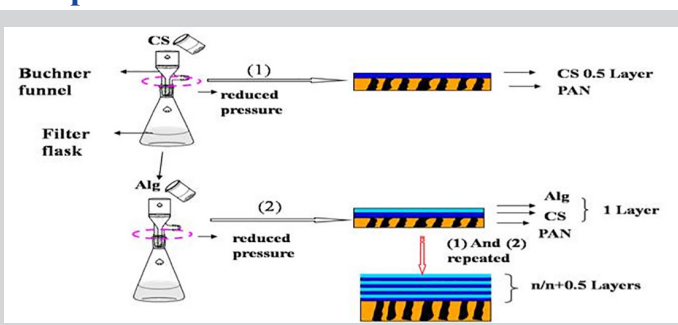
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## 1. Introduction

Pervaporation is considered as a promising energy-efficient alternative to conventional separation technique. It has been widely used for the dehydration of organic solvents, removal of organics from water, and separation of organic/organic solvent mixtures [1, 2]. Especially,

pervaporations is more attractive for the separation of heat-sensitive, close-boiling, and azeotropic liquid mixtures. In general, a pervaporation process involves in sorption of component in the feed mixtures at the upstream side of the membrane, diffusion of the absorbed components across the membrane,

## Graphical abstract



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and desorption of those components at the downstream side. Therefore, the structure optimization of a membrane plays a vital role in its separation efficiency and practical application.

Polyelectrolyte multilayer membranes are rapidly emerged as desirable pervaporation membrane materials because their structures are readily adjusted via changing deposition circles, charge density, or the kinds of polycation or polyanion [3]. In addition, polyelectrolyte multilayer membranes can combine a desirable property of a polyanion with that of a polycation, and they even display improved separation efficiency when compared to the pristine polyanion or polycation membranes [4, 5]. Generally, solution blending and interfacial complexation have been used for the preparation of polyelectrolyte multilayer membranes. In the case of solution blending, a cationic polyelectrolyte solution mixes directly with an anionic polyelectrolyte solution to form a homogeneous casting solution. However, precipitate or phase separation would occur in the direct blending of oppositely charged polyelectrolyte solution unless the ionization degree is controlled. On the other hand, the interfacial complexation method involves alternative layer-by-layer (LBL) deposition of polycation and polyanion solutions onto a charged substrate. In fact, more deposition circles are normally required for the fabrication of a complex membrane with an acceptable separation property [5, 6]. In order to speed up the multilayer growth, dynamic LBL technique [7, 8] and electric field driving [9-12] have been introduced.

Alginate (Alg), obtained from the cell walls of brown algae, is a prospective membrane material because of its excellent water selectivity. However, the mechanical strength of Alg membrane is required to be further improved [13]. Kalyani et al. [14] blended Alg with poly(vinyl pyrrolidone) (PVP) for pervaporation separation. Due to the brittleness, the obtained membranes were not suitable for use except for a 3:1 Alg to PVP blend. In addition, cross-linking with multivalent ions [15, 16] was also favorable to enhance the mechanical strength of an Alg membrane. On the other hand, chitosan (CS) membrane has been paid much attention due to its excellent chemical and mechanical stability, but its water selectivity is not high enough, esp. for practical application. For the sake of separation efficiency, CS is generally blended with other polymers such as poly(vinyl alcohol) [17, 18], hydroxyethylcellulose [19, 20] and poly(acrylic acid) [21, 22]. The combination of Alg with CS seems to be a promising candidate for improving membrane properties [23]. However, Alg is soluble in water, in which CS is insoluble [24], and thus the preparation of CS/Alg-based membrane becomes difficult. Lee et al. [25] proposed that the combination of Alg and CS could be achieved by immersing a dried Alg membrane in a chitosan solution instead of directly blending their solution. In another work, Kariduraganavar et al. [26] found that a gel would be formed when the CS acid solution was added to SA solution. This gel was required to be re-dissolved by the addition of NaOH solution in order to obtain a homogeneous solution, and thus the succeeding CS/Alg membrane preparation could proceed.

In fact, CS and Alg are considered as ideal polycations and polyanions in LBL deposition procedure, respectively [27, 28], which makes their combination possible. Huang et al. [29, 30] prepared novel two ply CS/Alg composite membrane by casting CS and Alg solutions in succession, and found these composite membrane displayed desirable mechanical strength and pervaporation performance. This interfacial complexation appears to be a facile method for the combination of CS and Alg. In the present work, CS/Alg polyelectrolyte multilayer composite membranes (PEMCMs) were fabricated by alternatively depositing CS and Alg onto a hydrolyzed porous poly(acrylonitrile) (PAN) substrate under a reduced pressure. The effect of hydrolysis time, numbers of polyelectrolyte layer, operating temperature and feed composition on pervaporation performance of these PEMCMs was investigated in detail.

## 2. Experimental

### 2.1. Materials and reagents

Chitosan (CS) was supplied by Yuhuan Ocean Biology Company (Zhejiang, China), and was purified as reported in our previous work [31]. The resulting CS has a degree of deacetylation of 90% and a viscosity average molecular weight of  $6 \times 10^5$  Da. Alg (sodium alginate) was provided by Sinopham Chemical Reagent Co., China. PAN flat-sheet ultrafiltration membrane with an average surface pore diameter of 25.4 nm was purchased from Development Center of Water Treatment Technology, Hangzhou, China. Other reagents such as sulfuric acid, methanol, ethanol and isopropanol (IPA) were purchased from Hangzhou Gaojing Fine Chemical Company, China and were of analytical grade. They were used without further purification. The feed mixtures used for the pervaporation experiments were prepared by blending methanol, ethanol, IPA and de-ionized water with

a pre-determined composition.

### 2.2. Membrane preparation

#### 2.2.1. Hydrolysis of PAN supporting substrate

For the sake of subsequent adsorption experiment, the  $-\text{CN}$  groups on PAN substrate surface should be converted into carboxyl groups, which can normally be achieved by a hydrolysis process. The hydrolysis of PAN supporting substrate was conducted as follows [32]: PAN ultrafiltration membrane with an area of  $10 \times 10 \text{ cm}^2$  was hydrolyzed by immersing in 1 mol/L NaOH aqueous solution at  $50^\circ\text{C}$  for a given time and then washed thoroughly with deionized water until neutral. The hydrolyzed PAN substrate was immersed in 1 mol/L HCl aqueous solution for 20 min, washed with water until the pH values of the rinsed water reached about 7.0. The carboxyl groups on the resulting PAN substrate are favorable to react with  $-\text{NH}_2$  from CS in the preparation of multilayer composite membrane [32, 33].

#### 2.2.2 Preparation of multilayer composite membrane

The preparation of PEMCMs was conducted by a press-driven interfacial complexation method. CS solution was prepared by dissolving CS in aqueous acetic acid, while Alg solution was formed by dissolving sodium alginate in de-ionized water at room temperature. Prior to the preparation of PEMCMs, the hydrolyzed porous PAN membrane (the supporting substrate) with a surface area of  $50 \text{ cm}^2$  was placed in a Buchner channel, as shown in Figure 1. The CS/Alg PEMCMs were fabricated by depositing polycation and polyanion alternatively onto the hydrolyzed PAN substrate. The following steps were successively carried out: (1) A 1-wt% CS solution was poured onto the hydrolyzed PAN substrate which had been located in a Buchser channel under a reduced pressure, excessive CS solution was removed from the Buchser channel after 5 min, and then dried completely. (2) After the drying of CS layer, a 1-wt% Alg solution was introduced into the Buchser channel under the same condition as the deposition of CS solution above. When the Alg layer was dried, it was rinsed using de-ionized water, and then dried completely before next deposition. (3) Steps (1) and (2) were repeated till the pre-determined deposition cycles were attained. The layer number of  $n$  and  $n+0.5$  suggested the CS and Alg layer were on the top surface of the composite membrane, respectively. The resulting PEMCMs are denoted as  $(\text{CS}/\text{Alg})_n$  or  $(\text{CS}/\text{Alg})_{n+0.5}$ , and the subscript  $n$  or  $n+0.5$  means the number of polyelectrolyte layer. It should be noted that only membranes of  $(\text{CS}/\text{Alg})_{n+0.5}$  (namely Alg layer is on the top surface of PEMCM) need to be further treated with sulfuric acid solutions containing 50 vol% IPA for 10 min at room temperature in an effort to further insolubilize the top Alg layer [30].

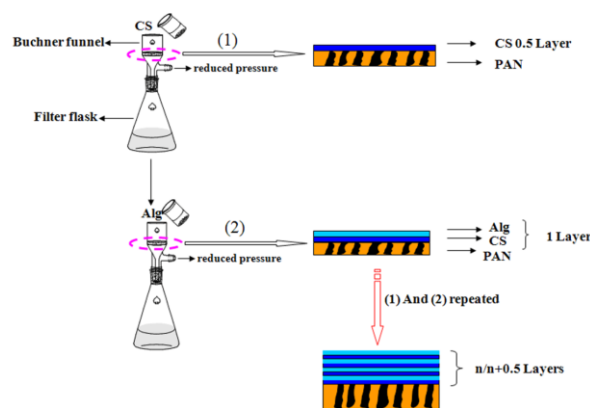


Fig.1. Schematic diagram of the fabrication of CS/Alg PEMCMs.

### 2.3. Membrane characterization

#### 2.3.1. ATR-FTIR characterization

The attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was obtained using a Nicolet Avatar 370 FTIR spectrometer with ZnSe crystal at a  $45^\circ$  incidence angle. The reported spectra were the accumulated averages of 64 scans at  $4 \text{ cm}^{-1}$  resolution.

#### 2.3.2. Contact angle measurement

The contact angles of water were measured by the Sessile water drop method using a Krüss DCA-10 (Germany) instrument in a temperature and humidity controlled room ( $25^\circ\text{C}$ , 60% relative humidity). Water droplets (about  $3 \mu\text{l}$  volume) were dropped carefully onto the sample surface. The

average contact angle was obtained by measuring the same sample at 10 different sites. The error of measurement was  $\pm 1^\circ$ .

### 2.3.3. Zeta potentials determination

Zeta potential was determined on a Beckman Coulter instrument (Delsa™ Nano C) at room temperature. The ionic strength of aqueous KCl solution was maintained at 0.01 mol/L, and the de-ionized water containing standard particles was used as the conductive medium.

### 2.3.4. Scanning electron microscope (SEM)

SEM images of the cross-section layer of the composite membranes were taken by a Hitachi S-4800 scanning electron microscope (Japan). The membrane samples were fractured in liquid nitrogen, and then coated with a thin layer of gold prior to SEM measurement.

### 2.3.5. Mechanical strength measurement

Mechanical strength measurements were carried out using an INSTRON 5543 machine (USA) at room temperature. The extension speed of the instrument was 10 mm/min.

## 2.4. Pervaporation experiment

The pervaporation experimental set-up is shown in Figure 2. The feed mixtures were circulated through the upper side of the permeation cell, and then sent back to the feed tank. The amount of the permeate was much less than that of the feed in each run, so the concentration in the feed stream could be considered constant throughout the experiment. The operating temperature varied in the range of 30–60 °C. The effective membrane area in contact with feed was about 25 cm<sup>2</sup>. The pressure at the downstream side was kept at 100–200 Pa by a vacuum pump. The tested composite membrane was supported on a porous steel disk in the pervaporation cell. The permeated vapor was collected in a cold trap immersed in liquid nitrogen, and then weighed accurately by electronic balance with 0.0001 g of balance sensitivity. The compositions of the collected permeate were determined with a Varian GC-3800 gas chromatography. The separation factor/separation selectivity ( $\alpha_{sep}$ ), and permeate flux ( $J$ ) are defined as follows:

$$\alpha_{sep} = \frac{Y_{water} / Y_{organic}}{X_{water} / X_{organic}} \quad (1)$$

$$J = \frac{Q}{At} \quad (2)$$

where  $Y$  and  $X$  are the concentrations of a certain component in the permeate and in the feed, and the subscripts (water and organic component) indicate the species.  $Q$ ,  $A$  and  $t$  represent the weight of permeate (g), the effective membrane area (m<sup>2</sup>) and the permeate collection time (h), respectively. Each measurement was carried out at least three times in order to ensure the reproducibility of the measurements. The errors inherent in these permeation measurements were of the order of a few percent.

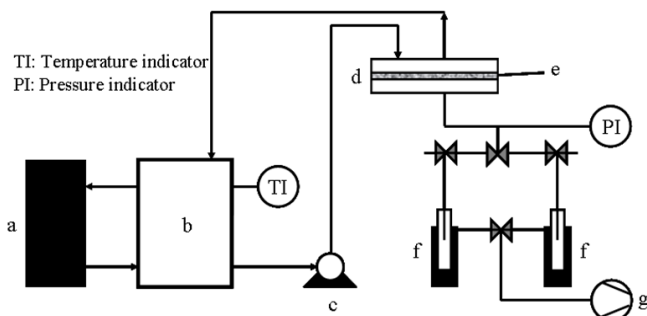


Fig. 2. Schematic diagram of pervaporation experimental set-up: (a) water bath, (b) feed tank, (c) pump, (d) permeation cell, (e) membrane, (f) cold trap, (g) vacuum pump.

## 2.5. Sorption experiment

Generally, the sorption experiment was carried out by immersing membrane sample in the feed solution. In fact, the upstream side of a membrane was always in contact with the feed solution during pervaporation.

In this paper, therefore, the sorption experiment on the one-side surface was employed in an effort to describe the *in-situ* sorption behavior of PEMCMs. The feed solution was pumped into the pervaporation cell where the PEMCMs had been fixed. The upstream side of the membrane was in contact with the feed solution for at least 24 h to allow the membrane to reach equilibrium sorption. After the swollen membrane was removed from the pervaporation cell and carefully wiped the adherent liquid, it was put into a sealed vessel. Under reduced pressure, the solution absorbed into the swollen membranes was completely desorbed and collected in a cold trap. The composition of the solution in the swollen membrane was analyzed by Varian GC-3800 gas chromatography. The sorption selectivity was obtained using Eq. 3:

$$\alpha_{sorp} = \frac{M_{water} / M_{organic}}{F_{water} / F_{organic}} \quad (3)$$

where  $M_{water}$  and  $M_{organic}$ ,  $F_{water}$  and  $F_{organic}$  are weight fractions of water and organic component in the swollen membrane and the feed solution, respectively. The diffusion selectivity can be calculated by Eq. 4.

$$\alpha_{diff} = \frac{\alpha_{sep}}{\alpha_{sorp}} \quad (4)$$

## 3. Results and discussion

### 3.1. Characterization of the hydrolyzed PAN supporting substrate

A charged substrate was necessary for the subsequent assembly of polyelectrolyte pairs. In this work, the carboxyl groups were introduced onto the surface of PAN substrate by a hydrolysis process. ATR-FTIR spectra of PAN substrate with different hydrolysis times were shown in Figure 3. For pristine PAN substrate, the peaks at 2243 cm<sup>-1</sup> and 1452 cm<sup>-1</sup> were due to –CN stretching vibration and –CH<sub>2</sub> bending vibration in the PAN polymer [34]. As it could be expected, the intensities of these two peaks decreased with hydrolysis time. On the other hand, the intensities of the peaks at 3310 cm<sup>-1</sup> and 1568 cm<sup>-1</sup>, which are resulted from carboxyl groups, increased with hydrolysis time. These results suggested that more –CN groups on the PAN surface are converted into carboxyl groups [35], and a negatively charged PAN substrate is formed.

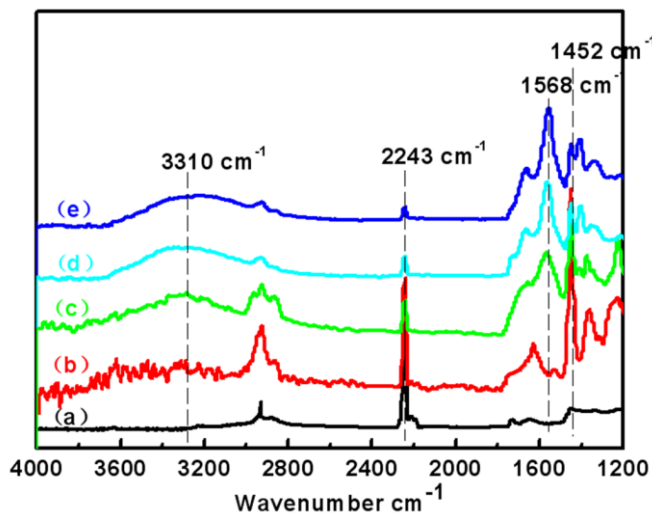


Fig. 3. ATR-FTIR spectra of PAN supporting substrate with different hydrolysis times. The hydrolysis time: (a) 0 min; (b) 10 min; (c) 20 min; (d) 30 min; (e) 50 min.

### 3.2. Fabrication of the CS/Alg charged polyelectrolyte multilayer composite membrane

The CS/Alg PEMCMs were fabricated by casting CS solution and Alg solution alternatively onto a porous PAN substrate till a desirable deposition cycle was achieved. This process was readily demonstrated by the change in surface composition and property of the resultant composite membrane.

Figure 4 shows the ATR-FTIR spectra of the CS/Alg PEMCMs with different numbers of polyelectrolyte layer. The weak peaks at  $1650\text{ cm}^{-1}$  were owing to the C=O stretching of the secondary amide, which may be attributed to the fact that the CS was not completely deacetylated [36]. It should be pointed out that the peaks at  $1590\text{ cm}^{-1}$  were resulted from the overlap of -NH bending vibration of CS and carboxyl anions asymmetric stretching vibration of Alg [37]. When the layer number was  $n+0.5$ , the peaks at  $1650\text{ cm}^{-1}$  were observed, indicating the CS dominated the surface of the polyelectrolyte composite membrane. Similarly, when the number of polyelectrolyte layer was  $n$ , the intensity of peak at  $1590\text{ cm}^{-1}$  increased, suggesting the Alg layer was located on the surface of composite membrane.

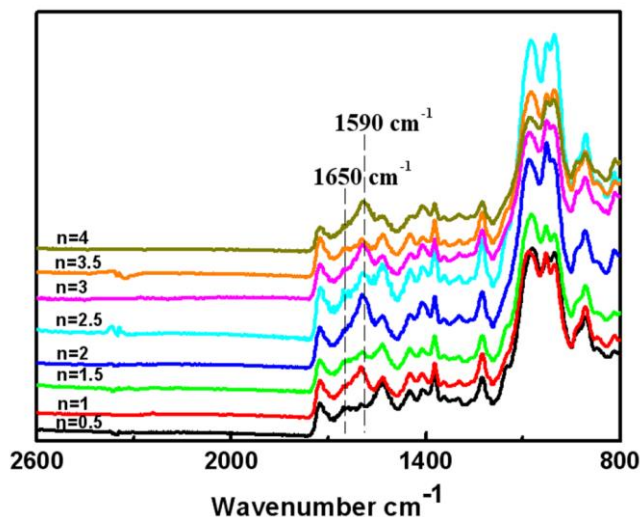


Fig. 4. ATR-FTIR spectra of the CS/Alg PEMCMs with different numbers of polyelectrolyte layer ( $n$ ).

Furthermore, the change in surface wettability of the PEMCMs indicated this alternative absorption of CS and Alg. As shown in Figure 5, the water contact angle changed alternatively with the number of deposition cycle. When the layer number was  $n+0.5$ , the hydrophilicity of the prepared composite membrane was similar to that of CS [36, 38]. As the number of polyelectrolyte layer was  $n$ , however, the composite membrane displayed the same water contact angle ( $45^\circ$ ) as Alg [39]. Further characterization on the stepwise growth of the CS/Alg composite membrane was conducted by zeta potential measurement. As could be observed in Figure 6, the zeta potential alternated between about  $+5\text{ mV}$  and  $-6\text{ mV}$  when the number of polyelectrolyte layer was  $n+0.5$  and  $n$ , respectively. This reversal change in surface zeta potential confirmed the alternative deposition of CS and Alg during the fabrication of the PEMCMs.

### 3.3. Cross-sectional structures of the CS/Alg composite membranes

The cross-sectional structures of the CS/Alg composite membranes with different layer numbers are presented in Figure 7. Both  $(\text{CS}/\text{Alg})_2$  and  $(\text{CS}/\text{Alg})_6$  composite membrane displayed a dense separation layer and a porous supporting substrate. In addition, the structure of the separation layer seemed consistent, and was composed of irregular lamellae in a direction approximately parallel to the surface plane [40]. It can also be seen from Figure 6 that the thickness of  $(\text{CS}/\text{Alg})_2$  and  $(\text{CS}/\text{Alg})_6$  composite membrane was  $0.56$  and  $1.95\text{ }\mu\text{m}$ , respectively, namely, the thickness of a single deposition layer was about  $0.3\text{ }\mu\text{m}$ . This indicates that a defect-free polyelectrolyte pervaporation membrane can be achieved with fewer deposition cycles.

### 3.4. Mechanical strength of the CS/Alg polyelectrolyte multilayer membrane

The mechanical properties of CS, Alg membrane and free-standing  $(\text{CS}/\text{Alg})_n$  membranes are given in Table 1. The tensile stress and strain at break of PEMCMs changed in the range of  $40\text{--}45\text{ MPa}$ , and  $6.4\text{--}6.8\%$ , respectively. It was more approaching the values of the pristine CS membrane, implying that the mechanical properties of Alg membranes were much improved upon the complexation of CS. This enhancement may be attributed to the interaction between polycations and polyanions.

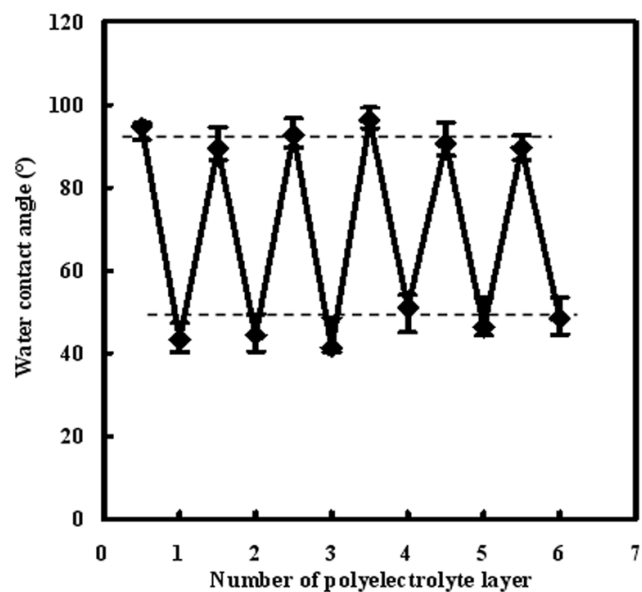


Fig. 5. Water contact angle of the CS/Alg composite membrane as a function of the number of polyelectrolyte layer.

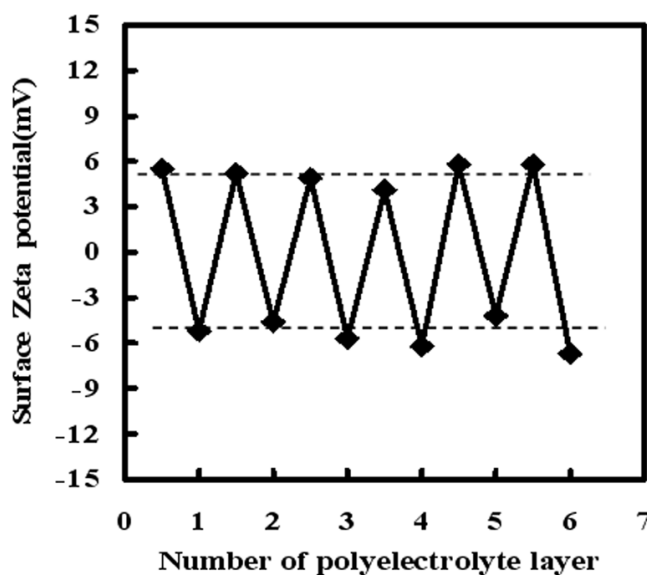


Fig. 6. Surface zeta potential of the CS/Alg composite membrane as a function of the number of polyelectrolyte layer.

### 3.5. Pervaporation performance

#### 3.5.1. Effect of hydrolysis time

It's well known that the -CN groups of PAN supporting substrate can be converted into carboxyl groups by a hydrolysis process, which is normally influenced by the alkaline concentration, hydrolysis temperature and hydrolysis time. In the present work, the hydrolysis of PAN porous membrane was performed under the condition of  $1\text{ mol/L NaOH}$  at  $50\text{ }^\circ\text{C}$ , and the hydrolysis time was varied. Figure 8 shows the effect of hydrolysis time on pervaporation performance of  $(\text{CS}/\text{Alg})_4$  composite membrane. The hydrolysis time had profound influence on the pervaporation performance of the  $(\text{CS}/\text{Alg})_4$  composite membrane. The flux decreased significantly while the water content in permeate increased with hydrolysis time. As the hydrolysis proceeded, more -CN groups on the PAN substrate were converted into carboxyl groups as shown in Figure 3. In the fabrication of the PEMCMs, CS (polycation) was firstly deposited on the hydrolyzed PAN substrate. The enhancement in carboxyl groups meant the increase in the negative charge density of the substrate, and accordingly a more compact interfacial layer between CS and PAN was formed. This compact interfacial layer resulted in a decrease in flux, but its hydrophilicity was in favor of the absorption of water. However, by the consideration of the fact that the mechanical strength of



PAN substrate would be reduced as the hydrolysis proceeded, 30 min was selected as the hydrolysis time for the following experiments.

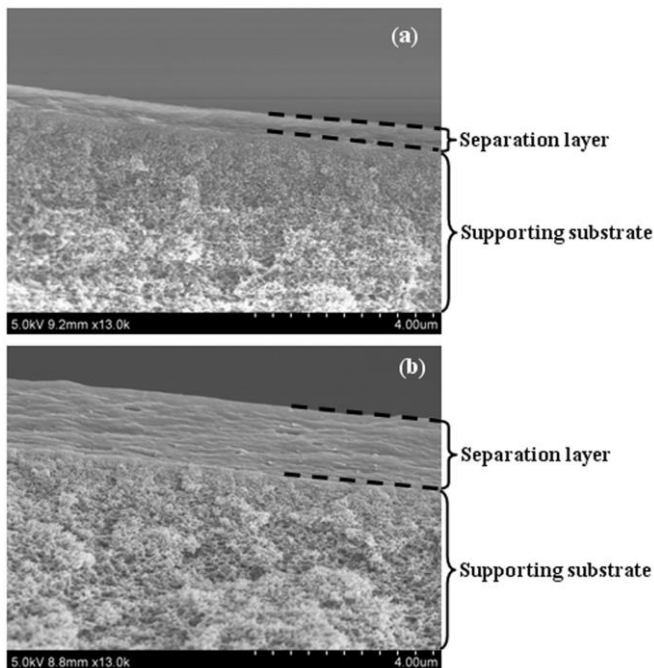


Fig.7. SEM cross-sectional views of (a) (CS/Alg)<sub>2</sub> and (b) (CS/Alg)<sub>6</sub> composite membrane.

Table 1  
Mechanical properties of CS, Alg membrane and free-standing (CS/Alg)<sub>n</sub> membranes.

Membrane	Tensile stress (MPa)	Strain at break (%)
CS	58.7±1.9	7.4±1.2
Alg	20.1±1.5	4.6±1.5
(CS/Alg) <sub>2</sub>	40.1±2.1	6.8±0.8
(CS/Alg) <sub>6</sub>	45.2±2.6	6.4±1.1

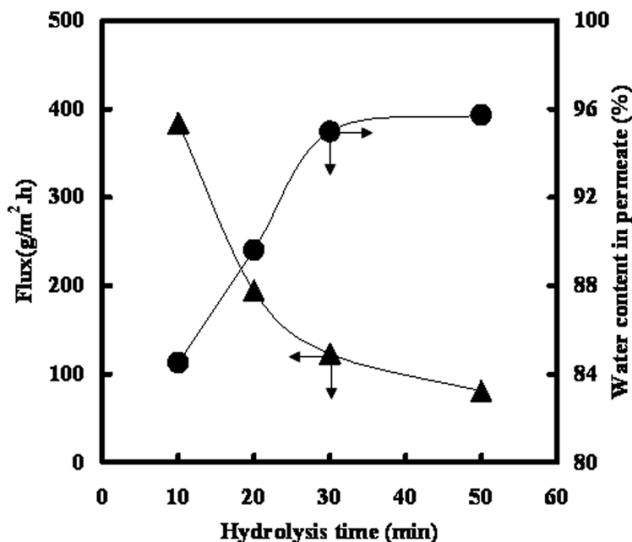


Fig.8. Effect of hydrolysis time on pervaporation performance of (CS/Alg)<sub>4</sub> composite membrane. Feed: 90 wt.% methanol/water mixtures, operating temperature: 50 °C.

3.5.2. Effect of the number of polyelectrolyte layer

The number of polyelectrolyte layer normally plays an import role in the pervaporation performance of the resulting composite membrane. Pervaporation experiments were carried out for the separation of 90 % methanol/water mixtures at 60 °C. The permeation flux and water content in permeate versus the layer number are displayed in Figure 9. The flux decreased from 625 to 36 g/m<sup>2</sup>.h while the water content in permeate increased from 66.1% to 99.9%, when the number of polyelectrolyte layer increased from 2.5 to 10. This changing trend in permeability and selectivity was also observed upon varying feed methanol concentration and operating temperature.

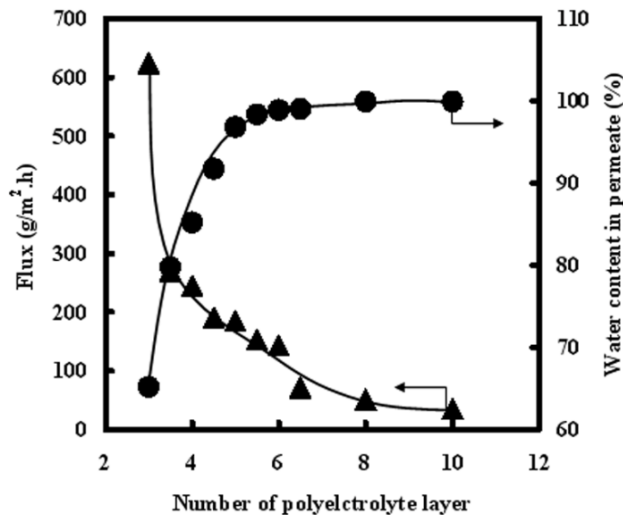


Fig.9. Effect of number of polyelectrolyte layer on pervaporation performance of the CS/Alg composite membrane. Feed: 90 % methanol/water mixtures, operating temperature: 60 °C.

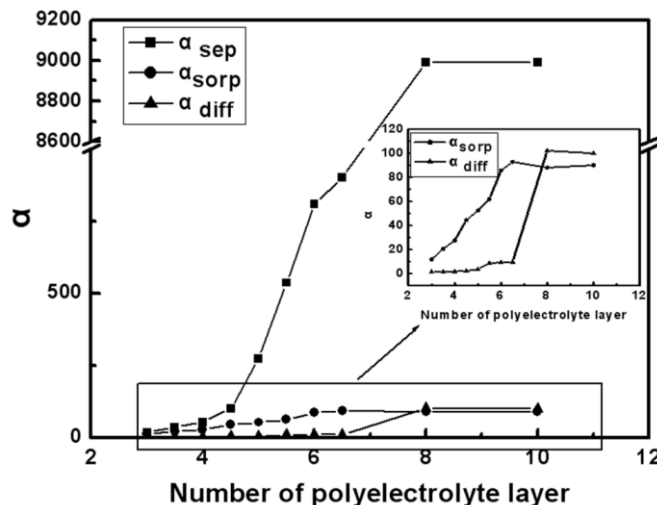


Fig.10. Sorption selectivity, diffusion selectivity and separation selectivity of polyelectrolyte membrane with different layer numbers. Insert: sorption selectivity and diffusion selectivity as a function of the number of polyelectrolyte layer.

It's widely accepted that both sorption selectivity and diffusion selectivity contribute to the separation selectivity in a pervaporation process. In order to better understand the pervaporation process of polyelectrolyte multilayer membrane, selectivities (including sorption selectivity, diffusion selectivity and separation selectivity) versus number of polyelectrolyte layer are given in Figure 10. It is apparent that the separation selectivity increased significantly when the layer number varied from 4 to 8, and remained almost unchangeable as the layer number exceeded 8. However, it is interesting that the sorption selectivity and diffusion selectivity exhibited different dependence towards the numbers of polyelectrolyte layers when compared to separation selectivity. The sorption selectivity was always higher than

diffusion selectivity when the numbers of polyelectrolyte layers were less than 7, implying that the separation selectivity was mainly resulted from the sorption selectivity. On the other hand, the diffusion process had more profound influence on the separation efficiency than the sorption process when 8 polyelectrolyte layers were deposited on a PAN substrate.

The effect of polyelectrolyte layers on the pervaporation process was related to the structure of CS/Alg polyelectrolyte layers. As shown in Figure 11, the CS/Alg polyelectrolyte interfacial complex was formed by electrostatic adsorption. Driven by pressure, the thickness of a single deposition layer was about 0.3  $\mu\text{m}$ , as shown in Figure 7. This suggests that

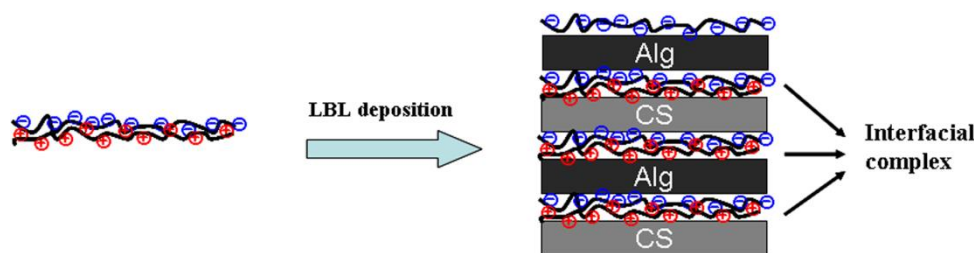


Fig.11. Schematic diagram of the structure of CS/Alg polyelectrolyte layers.

### 3.5.3. Effect of operating temperature and feed methanol concentration

Pervaporation performance of the composite membrane prepared by depositing 4 polyelectrolyte layers on a hydrolyzed PAN substrate was evaluated over the experimental temperature range of 30–60  $^{\circ}\text{C}$ . As shown in Figure 12, the pervaporation performance of the  $(\text{CS}/\text{Alg})_4$  composite membrane exhibited typical temperature dependence, namely, the flux increased while the water selectivity decreased. Similar behavior was also observed for other polyelectrolyte-based membranes [41, 42]. This temperature dependence of pervaporation performance was normally explained by the fact that the free volume of the membranes increased with operating temperature, and accordingly the transport of both water and methanol across the membrane became easy.

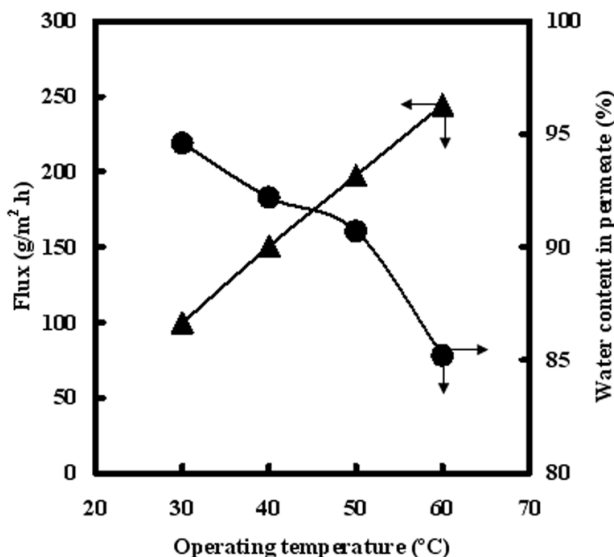


Fig.12. Effect of operating temperature on pervaporation performance of  $(\text{CS}/\text{Alg})_4$  composite membrane. Feed: 90 % methanol/water mixtures.

The relationship between the permeate flux ( $J$ ) and the operating temperature ( $T$ ) is described well by the Arrhenius equation ( $J=J_0 \exp(-E_p/RT)$ ) (see Figure 13). The activation energy of pervaporation process ( $E_p$ ) for the  $(\text{CS}/\text{Alg})_4$  composite membrane was estimated as 24.9 kJ/mol according to the slope of the plots in Figure 12. The  $E_p$  was normally considered as the energy required for the permeate molecules to transport through the membrane barrier [43]. For many polymeric membranes,  $E_p$  was found to be varied from 20 to 56 kJ/mol [44–46]. The comparatively lower  $E_p$

each polyelectrolyte deposition layer was composed of not only a thin interfacial complex, but also the CS or SA layer. For the first 6 SA/CS layers, the hydrophilicity of the resulting composite membrane was enhanced, which was favorable for the adsorption of water and hindered the adsorption of methanol [24]. In this case, therefore, the sorption selectivity dominated the separation selectivity. However, the thickness of polyelectrolyte deposition layer increased greatly when more than 8 CS/Alg layers were deposited, and thus diffusion effect became more significant than sorption effect during pervaporation separation.

in the present study suggests that the transport of methanol and water across the PEMCMs may be more facilitated.

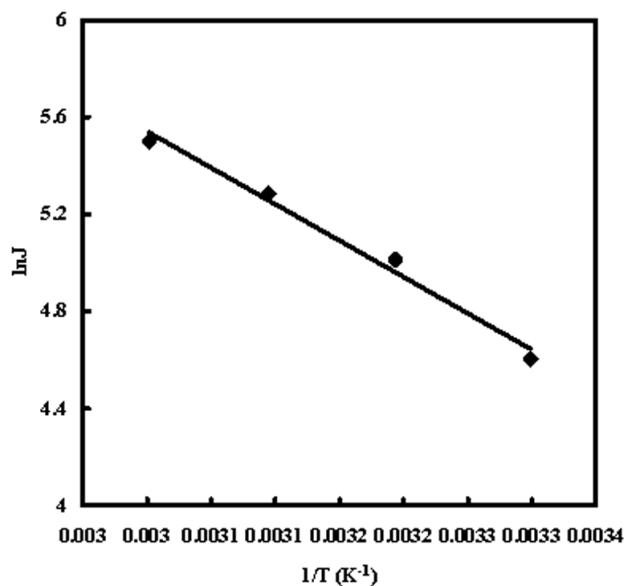


Fig.13. Arrhenius plots of pervaporation separation of the  $(\text{CS}/\text{Alg})_4$  composite membrane. Feed: 90 % methanol/water mixtures.

The effect of feed composition on the pervaporation performance of the  $(\text{CS}/\text{Alg})_4$  polyelectrolyte composite membrane is shown in Figure 14. The water selectivity increased while the flux decreased with increasing feed methanol concentration. This behavior was generally explained by the fact that the polyelectrolyte membrane was inherently hydrophilic and swelled in the feed solution, making the polymer chains more flexible for both water and methanol to transport in the membrane. In particular, the water content in permeate increased significantly from 85.6% to 91.7%, correspondingly the separation factor enhanced from 54 to 210 when methanol concentration in the feed varied from 90% to 95%. In fact, the separation of methanol/water mixtures is difficult due to the strong interaction between the two components, and thus the separation factor is normally low [36]. It was recently reported that the pervaporation performance for dehydrating methanol could be enhanced by a  $(\text{PAA}-\text{Co}-\text{AN})/\text{SiO}_2$  membrane, which displayed a separation of about 250 and a flux of about 120  $\text{g}/\text{m}^2 \cdot \text{h}$  [47]. By contrast, the  $(\text{CS}/\text{Alg})_5$  composite membrane exhibited a separation factor of 272 and a flux of 185  $\text{g}/\text{m}^2 \cdot \text{h}$  when used for the separation of 90% methanol/water mixtures. Obviously, more polyelectrolyte layers seemed to

be a good candidate for increasing the water selectivity for methanol dehydration.

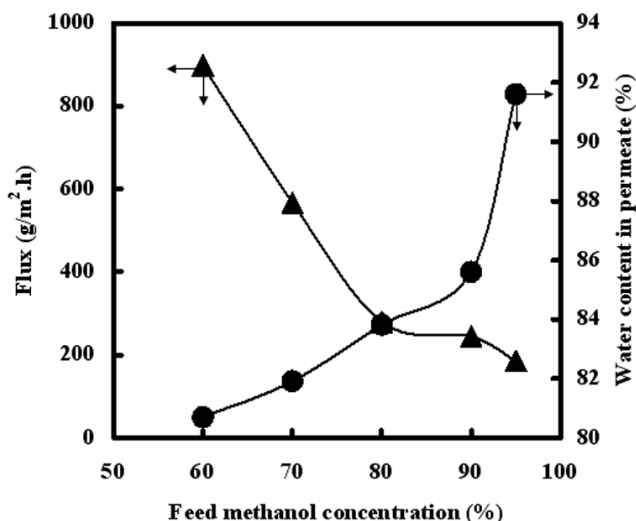


Fig.14. Effect of feed methanol concentration on pervaporation performance of the (CS/Alg)<sub>4</sub> composite membrane at 60 °C.

### 3.5.4. Pervaporation performance of polyelectrolyte composite membrane for dehydrating ethanol and IPA

The pervaporation performance of the PEMCMs for the separation of ethanol/water and IPA/water mixtures is presented in Figure 15. Under the operating temperature of 60 °C, the permeate flux for dehydrating ethanol and IPA was 210 and 596 g/m<sup>2</sup>.h, and the water content in permeate was 99.3% and 99.8%, respectively, implying that the (CS/Alg)<sub>4</sub> composite membrane displayed excellent water selectivity.

Furthermore, for dehydrating both ethanol and IPA, the permeate flux increased remarkably while water selectivity seemed almost unchangeable with increasing operating temperature. This behavior was very different from that for the separation of methanol/water mixtures (see Figure 12). The transport of ethanol and IPA across the compact polyelectrolyte separation layer was severely restricted due to the fact that ethanol and IPA molecules

are larger than methanol molecules. Therefore, the water selectivity for dehydrating ethanol and IPA was less affected by operating temperature, and was much higher than that towards methanol/water mixtures.

Table 2 lists the pervaporation performance of polyelectrolyte-based membrane for the separation of alcohol/water mixtures. The prepared CS/Alg composite membranes presented improved separation properties, esp. water selectivities when compared to other polyelectrolyte-based membranes, and compromised well between flux and selectivity. The much higher water selectivity may be due to the higher hydrophilicity and more compact structures of polyelectrolyte separation layer. In general, the resulting CS/Alg polyelectrolyte composite seems to be an excellent water-permselective membrane for the separation of alcohol/water mixtures even though its permeation flux should be further optimized.

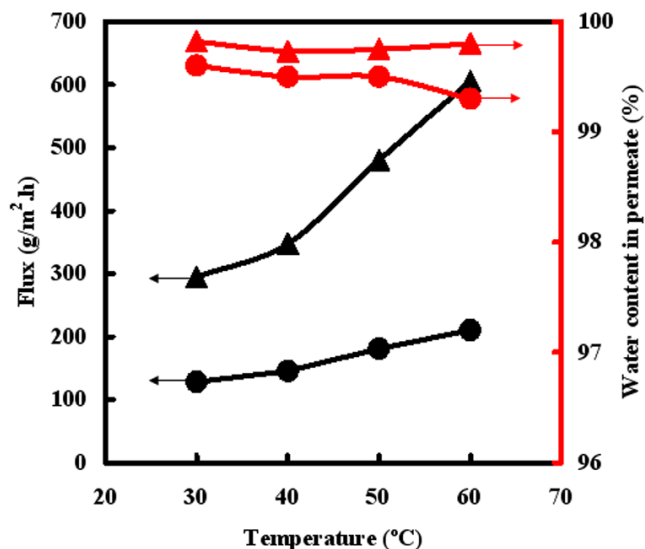


Fig.15. Pervaporation performance for the separation of 90 wt% (●) ethanol/water and (▲) IPA/water mixtures through the (CS/Alg)<sub>4</sub> polyelectrolyte composite membrane.

Table 2

Comparison of pervaporation performance for the membranes from the present work with that of polyelectrolyte-based membranes.

Membranes	Supports	Temperature (°C)	J(g/m <sup>2</sup> .h)	$\alpha$	References
<b>Feed: 90% ethanol/water mixtures</b>					
(PEI/PAA) <sub>6</sub>	Polyamide-6	50	20	1400	[24]
(PEI/PAA) <sub>2.5</sub>	PAN	70	400	231	[35]
(PAH/PSS) <sub>60</sub>	PAN/PET <sup>a</sup>	58.5	700	36	[48]
(PVA <sup>c</sup> /PVS) <sub>60</sub>	PAN/PET <sup>a</sup>	58.5	250	700	[48]
(CS/Alg) <sub>4</sub>	PAN	60	210	1277	This work
<b>Feed: 90% IPA/water mixtures</b>					
PVA <sup>b</sup> /PEC7030	Polysulfone	60	800	441	[42]
(PVA <sup>c</sup> /PVS) <sub>60</sub>	PAN/PET <sup>a</sup>	58.5	650	900	[48]
SA/CS two-ply polyelectrolyte	None	60	554	2010	[29]
(CS/Alg) <sub>4</sub>	PAN	60	596	4491	This work

<sup>a</sup> PAN/PET, a thin PAN layer was deposited onto a poly (ethylene terephthalate) (PET) fleece

<sup>b</sup> PVA, poly (vinyl alcohol)

<sup>c</sup> PVA, poly (vinylamine)

## 4. Conclusions

CS/Alg polyelectrolyte multilayer composite membranes (PEMCMs) were successfully fabricated by a press-driven layer-by-layer deposition process, which was confirmed by ATR-FTIR spectra, contact angle and surface zeta potential measurement. The pervaporation results showed that the sorption behavior of the resulting CS/Alg PEMCMs was dependent on

the number of deposition layer. The sorption process dominated the transport of the permeate across the membrane when the numbers of deposition layer were less than 7. However, the diffusion effect would surpass the sorption effect as more than 8 polyelectrolyte layers were deposited on the PAN substrate. Such different dependence towards deposition circles was resulted from the higher hydrophilicity and more compact structure of PEMCMs. For the separation 90% ethanol/water and IPA/water mixtures at 60 °C, the

separation factor of the (CS/Alg)<sub>4</sub> composite membrane was as high as 1277 and 4491, and the corresponding flux was 210 and 596 g/m<sup>2</sup>·h, respectively, which was higher than that of most polyelectrolyte-based membranes reported in the literatures. In addition, these PEMCMs compromised well between flux and selectivity. These results indicate that the prepared CS/Alg composite membranes have promising potential for the separation of alcohol/water mixtures even though a further improvement in their permeation fluxes is needed.

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### Nomenclatures

A	effective membrane area (m <sup>2</sup> )
E <sub>p</sub>	activation energy of pervaporation process (kJ/mol)
F <sub>water/organic</sub>	weight fraction of water/organic component in the feed solution (%)
J	flux (g/m <sup>2</sup> ·h)
M <sub>water/organic</sub>	weight fraction of water/organic component in the swollen membrane (%)
PEMCMs	polyelectrolyte multilayer composite membranes
Q	weight of permeate (g)
t	permeate collection time (h)
X <sub>water/organic</sub>	concentration of water/organic in the feed (wt.%)
Y <sub>water/organic</sub>	concentration of water/organic in the permeate (wt.%)
α <sub>diff</sub>	diffusion selectivity
α <sub>sep</sub>	separation factor/separation selectivity
α <sub>sorp</sub>	sorption selectivity

### References

- [1] X. Feng, R. Y. M. Huang, Liquid separation by membrane pervaporation: a review, *Ind. Eng. Chem. Res.* 36 (1997) 1048-1066.
- [2] P. Shao, R. Y. M. Huang, Polymeric membrane pervaporation, *J. Membr. Sci.* 287 (2007) 162-179.
- [3] Q. Zhao, Q. F. An, Y. Ji, J. Qian, C. Gao, Polyelectrolyte complex membranes for pervaporation, nanofiltration and fuel cell applications, *J. Membr. Sci.* 379 (2011) 19-45.
- [4] P. S. Rachipudi, A. A. Kittur, S. K. Choudhari, J. G. Varghese, M. Y. Kariduraganavar, Development of polyelectrolyte complexes of chitosan and phosphotungstic acid as pervaporation membranes for dehydration of isopropanol, *Eur. Polym. J.* 45 (2009) 3116-3126.
- [5] Y. Li, H. Jia, Q. Cheng, F. Pan, Z. Jiang, Sodium alginate-gelatin polyelectrolyte complex membranes with both high water vapor permeance and high permselectivity, *J. Membr. Sci.* 375 (2011) 304-312.
- [6] L. Krasemann, A. Toutianoush, B. Tieke, Self-assembled polyelectrolyte multilayer membranes with highly improved pervaporation separation of ethanol/water mixtures, *J. Membr. Sci.* 181 (2001) 221-228.
- [7] D. M. Sullivan, M. L. Bruening, Ultrathin, cross-linked polyimide pervaporation membranes prepared from polyelectrolyte multilayers, *J. Membr. Sci.* 248 (2005) 161-170.
- [8] G. Zhang, W. Gu, S. Ji, Z. Liu, Y. Peng, Z. Wang, Preparation of polyelectrolyte multilayer membranes by dynamic layer-by-layer process for pervaporation separation of alcohol/water mixtures, *J. Membr. Sci.* 280 (2006) 727-733.
- [9] S. Ji, G. Zhang, Z. Liu, Y. Peng, Z. Wang, Evaluations of polyelectrolyte multilayer membranes assembled by a dynamic layer-by-layer technique, *Desalination* 234 (2008) 300-306.
- [10] G. Zhang, X. Gao, S. Ji, Z. Liu, Electric field-enhanced assembly of polyelectrolyte composite membranes, *J. Membr. Sci.* 307 (2008) 151-155.
- [11] P. Zhang, J. Qian, Y. Yang, Q. F. An, X. Liu, Z. Gui, Polyelectrolyte layer-by-layer self-assembly enhanced by electric field and their multilayer membranes for separating isopropanol-water mixtures, *J. Membr. Sci.* 320 (2008) 73-77.
- [12] M. Yin, J. Qian, Q. F. An, Q. Zhao, Z. Gui, J. Li, Polyelectrolyte layer-by-layer self-assembly at vibration condition and the pervaporation performance of assembly multilayer films in dehydration of isopropanol, *J. Membr. Sci.* 358 (2010) 43-50.
- [13] P. D. Chapman, T. Oliveira, A. G. Livingston, K. Li, Membranes for the dehydration of solvents by pervaporation, *J. Membr. Sci.* 318 (2008) 5-37.
- [14] S. Kalyani, B. Smitha, S. Sridhar, A. Krishnaiah, Separation of ethanol-water mixtures by pervaporation using sodium alginate/poly (vinyl pyrrolidone) blend membrane crosslinked with phosphoric acid, *Ind. Eng. Chem. Res.* 45 (2006) 9088-9095.
- [15] R.Y.M. Huang, R. Pal, G. Y. Moon, Characteristics of sodium alginate membranes for the pervaporation dehydration of ethanol-water and isopropanol-water mixtures, *J. Membr. Sci.* 160 (1999) 101-103.
- [16] T. Uragami, M. Nanno, T. Miyata, Dehydration of an ethanol/water azeotrope through alginate-DNA membranes cross-linked with metal ions by pervaporation, *Carbohydr. Polym.* 134 (2015) 38-45.
- [17] K. Rao, M. C.S. Subba, M. Sairam, N. N. Mallikarjuna, T. M. Aminabhavi, Blend membranes of chitosan and poly (vinyl alcohol) in pervaporation dehydration of isopropanol and tetrahydrofuran, *J. Appl. Polym. Sci.* 103 (2007) 1918-1926.
- [18] M. N. Hyder, P. Chen, Pervaporation dehydration of ethylene glycol with chitosan-poly (vinyl alcohol) blend membranes: Effect of CS-PVA blending ratios, *J. Membr. Sci.* 340 (2009) 171-180.
- [19] R. Jiratananon, A. Chanachai, R. Y. M. Huang, D. Uttapap, Pervaporation dehydration of ethanol-water mixtures with chitosan/hydroxyethylcellulose (CS/HEC) composite membranes. I. Effect of operation conditions, *J. Membr. Sci.* 195 (2002) 143-151.
- [20] R. Jiratananon, A. Chanachai, R. Y. M. Huang, Pervaporation dehydration of ethanol-water mixtures with chitosan/hydroxyethylcellulose (CS/HEC) composite membranes. II. Analysis of mass transport, *J. Membr. Sci.* 199 (2002) 211-222.
- [21] J.-J. Shieh, R. Y. M. Huang, Pervaporation with chitosan membranes. II. Blend membranes of chitosan and polyacrylic acid and comparison of homogeneous and composite membrane based on oleylectrolyte complexes of chitosan and polyacrylic acid for the separation of ethanol-water mixtures, *J. Membr. Sci.* 127 (1997) 185-202.
- [22] S. Y. Nam, Y. M. Lee, Pervaporation and properties of chitosan-poly (acrylic acid) complex membranes, *J. Membr. Sci.* 135 (1997) 161-171.
- [23] P. Kanti, K. Srigowri, J. Madhuri, B. Smitha, S. Sridhar, Dehydration of ethanol through blend membranes of chitosan and sodium alginate by pervaporation, *Sep. Purif. Technol.* 40 (2004) 259-266.
- [24] J. Meier-Haack, W. Lenk, D. Lehmann, K. Lunzwitz, Pervaporation separation of water/alcohol mixtures using composite membranes based on polyelectrolyte multilayer assemblies, *J. Membr. Sci.* 184 (2001) 233-243.
- [25] S.-G. Kim, G.-T. Lim, J. Jegal, K.-H. Lee, Pervaporation separation of MTBE (methyl tert-butyl ether) and methanol mixtures through polyion complex composite membranes consisting of sodium alginate/chitosan, *J. Membr. Sci.* 174 (2000) 1-15.
- [26] A. M. Sajjan, B. K. Jeevan Kumar, A. A. Kittur, M. Y. Kariduraganavar, Novel approach for the development of pervaporation membranes using sodium alginate and chitosan-wrapped multiwalled carbon nanotubes for the dehydration of isopropanol, *J. Membr. Sci.* 425-426 (2013) 77-88.
- [27] H. Lv, Z. Chen, X. Yang, L. Cen, X. Zhang, P. Gao, Layer-by-layer self-assembly of minocycline-loaded chitosan/alginate multilayer on titanium substrates to inhibit biofilm formation, *J. Dent.* 42 (2014) 1464-1472.
- [28] M. G. Sankalia, R. C. Mashru, J. M. Sankalia, V. B. Sutariya, Reversed chitosan-alginate polyelectrolyte complex for stability improvement of alpha-amylase: Optimization and physicochemical characterization, *Eur. J. Pharm. Biopharm.* 65 (2007) 215-232.
- [29] G. Y. Moon, R. Pal, R. Y. M. Huang, Novel two-ply composite membranes of chitosan and sodium alginate for the pervaporation dehydration of isopropanol and ethanol, *J. Membr. Sci.* 156 (1999) 17-27.
- [30] R. Y. M. Huang, R. Pal, G. Y. Moon, Pervaporation dehydration of aqueous ethanol and isopropanol mixtures through alginate/chitosan two ply composite membranes supported by poly (vinylidene fluoride) porous membrane, *J. Membr. Sci.* 167 (2000) 275-289.
- [31] W. Zhang, Z. Yu, Q. Qian, Z. Zhang, X. Wang, Improving the pervaporation performance of the glutaraldehyde crosslinked chitosan membrane by simultaneously changing its surface and bulk structure, *J. Membr. Sci.* 348 (2010) 213-223.
- [32] X. Wang, N. Li, W. Wang, Pervaporation properties of novel alginate composite membranes for dehydration of organic solvents, *J. Membr. Sci.* 193 (2001) 85-95.
- [33] T. Zhou, Y. Luo, Y. Lin, Q. Li, P. Yu, M. Zeng, Study of pervaporation for dehydration of caprolactam through blend NaAlg-poly (vinyl pyrrolidone) membranes on PAN supports, *Sep. Purif. Technol.* 74 (2010) 242-252.
- [34] C. Qiu, S. Qi, C. Y. Tang, Synthesis of high flux forward osmosis membranes by chemically crosslinked layer-by-layer polyelectrolytes, *J. Membr. Sci.* 381 (2011) 74-80.
- [35] G. Zhang, H. Yan, S. Ji, Z. Liu, Self-assembly of polyelectrolyte multilayer pervaporation membranes by a dynamic layer-by-layer technique on a hydrolyzed polyacrylonitrile ultrafiltration membrane, *J. Membr. Sci.* 292 (2007) 1-8.
- [36] W. Zhang, G. Li, Y. Fang, X. Wang, Maleic anhydride surface-modification of crosslinked chitosan membrane and its pervaporation performance, *J. Membr. Sci.* 295 (2007) 130-138.
- [37] M. Muller, M. Brissova, T. Rieser, A. C. Powers, K. Lunzwitz, Deposition and properties of polyelectrolyte multilayers studied by ATR-FTIR spectroscopy, *Mater. Sci. Eng. C* 8-9 (1999) 163-169.
- [38] V. Tangpasuthadol, N. Pongchaisirikul, V. P. Hoven, Surface modification of chitosan films. Effects of hydrophobicity on protein adsorption, *Carbohydr. Res.* 338 (2003) 937-942.
- [39] C. Gao, M. Zhang, J. Ding, F. Pan, Z. Jiang, Y. Li, J. Zhao, Pervaporation dehydration of ethanol by hyaluronic acid/sodium alginate two-active-layer composite membranes, *Carbohydr. Polym.* 99 (2014) 158-165.
- [40] E.J. Flynn, D. Keane, J. D. Holmes, M. A. Morris, Unusual trend of increasing selectivity and decreasing flux with decreasing thickness in pervaporation separation of ethanol/water mixtures using sodium alginate blend membranes, *J. Colloid Interface Sci.* 370 (2012) 176-182.
- [41] X. Liu, Y. Sun, X. Deng, Studies on the pervaporation membrane of permeation water from methanol/water mixture, *J. Membr. Sci.* 325 (2008) 192-198.



- [42] Q. Zhao, J. Qian, Q. F. An, M. Zhu, M. Yin, Z. Sun, Poly (vinyl alcohol)/polyelectrolyte complex blend membrane for pervaporation dehydration of isopropanol, *J. Membr. Sci.* 343 (2009) 53-61.
- [43] S. G. Adoor, M. Sairam, L. S. Manjeshwar, K. V. S. N. Raju, T. M. Aminabhavi, Sodium montmorillonite clay loaded novel mixed matrix membranes of poly (vinyl alcohol) for pervaporation dehydration of aqueous mixtures of isopropanol and 1,4-dioxane, *J. Membr. Sci.* 285 (2006) 182-195.
- [44] W. Zhang, Y. Xu, Z. Yu, S. Lu, X. Wang, Separation of acetic acid/water mixtures by pervaporation with composite membranes of sodium alginate active layer and microporous polypropylene substrate, *J. Membr. Sci.* 451 (2014) 135-147.
- [45] C.-Y. Tu, Y.-L. Liu, K.-R. Lee, J.-Y. Lai, Hydrophilic surface-grafted poly (tetrafluoroethylene) membranes using in pervaporation dehydration process, *J. Membr. Sci.* 274 (2006) 47-55.
- [46] M. C. Burshe, S. B. Sawant, J. B. Joshi, V. G. Pangarkar, Sorption and permeation of binary water-alcohol systems through PVA membranes crosslinked with multifunctional crosslinking agents, *Sep. Purif. Technol.* 12 (1997) 145-156.
- [47] X. Liu, Y. Sun, X. Deng, Studies on the pervaporation membrane of permeation water from methanol/water mixture, *J. Membr. Sci.* 325 (2008) 192-198.
- [48] A. Toutianoush, L. Krasemann, B. Tiede, Polyelectrolyte multilayer membranes for pervaporation separation of alcohol/water mixtures, *Colloid Surf. A: Physicochem. Eng. Asp.* 198-200 (2002) 881-889.