



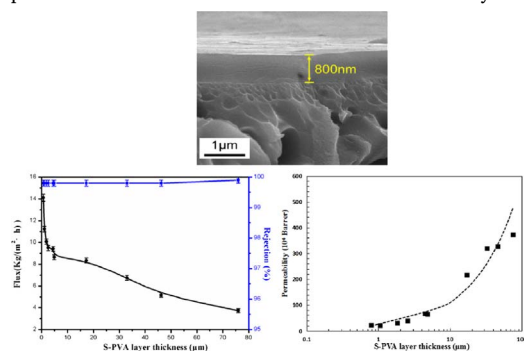
Water permeance, permeability and desalination properties of the sulfonic acid functionalized composite pervaporation membranes

Bin Liang¹, Qian Li¹, Bing Cao*, Pei Li*

College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

GRAPHICAL ABSTRACT

The thickness of S-PVA layer affects pervaporation performance, but the high water flux could not be obtained by reducing the selective layer thickness simply. Water permeance increases with the decrease in the S-PVA layer thickness, but water permeability greatly decreases.



ARTICLE INFO

Keywords:

Pervaporation desalination
4-sulfophthalic acid crosslinker
Water permeability
Water permeance

ABSTRACT

In spite of the great promise of pervaporation (PV) in production of fresh water from salty water, major challenge still lies in the developments of PV membranes with high water flux to compete reverse osmosis membranes. Here, we fabricated composite PV membranes consisting of a porous polyacrylonitrile (PAN) substrate and a dense selective layer of polyvinyl alcohol (PVA) crosslinked by 4-sulfophthalic acid (SPTA) of which sulfonic acid groups acted as facilitate transport agents to water molecules. Effects of the SPTA concentration and thickness of the PVA layer to the desalination performance were studied at temperatures from 30 to 70 °C and NaCl concentrations up to 100,000 ppm. A high water flux of 46.3 kg/(m²·h) with a salt rejection of 99.8% was achieved when separating a 35,000 ppm NaCl solutions at 70 °C. However, water permeance only increased 5.3 times as the PVA layer thickness decreased 95 times (from 76 μm to 800 nm). Our study showed that water permeability of the PVA layer significantly decreased with thickness of the PVA layer. This phenomenon indicated that a thin and dried region close to the downstream side of the PVA layer governed the water transport property.

1. Introduction

Shortage of fresh water is ranked the third world crisis after food and oil shortages that threaten human livings and social development

[1,2]. Desalination from seawater and brackish water becomes a major method to provide fresh water in many water limited areas [3–6]. Nowadays, reverse osmosis (RO) is the dominant technology for desalination due to its advantages including low operation cost, small foot

* Corresponding authors.

E-mail addresses: bcao@mail.buct.edu.cn (B. Cao), lipei@mail.buct.edu.cn (P. Li).

¹ These authors contributed equally to this work and should be considered co-first authors.

print, and easy to cope with other water filtration methods [7–10]. However, every technology has its pros and cons. RO requires a feed pressure up to 70 bars depending on the feed salinity and recovery [11]. Moreover, RO concentrated water causes secondary pollution to environment. Hence, new technology is required to treat the high-concentration-salt water.

Pervaporation(PV) as one of the developing membrane technologies is mainly applied in removal of trace amount of water from organics such as ethanol dehydration or concentration of alcohols from their dilute solutions such as bio-fuel enrichments [12–16]. Mass transport in PV processes is well described by the solution-diffusion model [17,18]. In a typical PV process, a liquid mixture contacts with the feed side of a PV membrane, diffuses to the permeate side, and leaves the membrane in a gaseous state which is then condensed by a cold medium. The driving force of a PV process is supplied by applying vacuum or air blow in the membrane permeate side. Because of resistant differences of a PV membrane to different components, liquid mixtures can be separated. Since chemical potential is more sensitive to changes in concentration than in pressure [19], it is easier to achieve a high membrane driving force in a PV process than in a RO system. Although membrane distillation (MD) also shows promise in brine water treatment, it encounters serious fouling problem [20]. Rather, PV membranes having a defect-free hydrophilic selective layer possess an essentially better fouling resistance than MD membranes. Energy efficiency is another crucial factor that determines the applicability of any desalination technology. Table 1 lists energy requirements of different desalination processes including PV, RO, MD, multi-stage flash distillation (MSF), and multi-e distillation (MED) [21–28]. The energy consumption of PV is comparable to RO, but much less than MD, MSF, and MED. Moreover, high pressure is not required for pervaporation. This makes PV desalination more applicable for treating high concentrated brine water.

Nevertheless, water fluxes of pervaporation membrane are still not high enough to compete RO membranes [29–31]. To increase the water flux of a PV desalination membrane, a thin dense layer with high water permeability and salt rejection with a porous substrate having negligible transport resistance is preferred. In this study, polyvinyl alcohol (PVA) was selected as the base material because of its good chemical stability and hydrophilicity for achieving high water permeability and fouling resistance. Since PVA is soluble in water, it has to be crosslinked using bifunctional or multifunctional acid, aldehyde, acid chloride, and so forth [32–34]. In this paper, we used 4-sulfophthalic acid (SPTA) to crosslink PVA in the purpose of maintaining hydrophilicity and introducing water transport agent by incorporating the sulfonic acid group into the crosslinked PVA networks. We used PAN UF membrane as supporting layer to provide mechanical strength to the PV membrane. To optimize surface structure of the PAN membrane, a hydrolysis method was adopted [35]. Impact of the hydrolysis time to surface morphology of the PAN membrane was studied. In addition, effects of the SPTA concentrations and SPTA crosslinked PVA (S-PVA) layer thickness to desalination performance of the S-PVA/PAN composite membranes were systematically studied. At last, water permeance and water permeability of the S-PVA layers as well as geometric restriction and resistance of the PAN substrate were estimated by modeling analysis. The modeling results were used to explain the dependence of water flux to the S-PVA layer thickness of the composite membranes.

Table 1
Different energy requirements for industrial desalination techniques.

Technique	Combined energy demand [(kwh)/m ³]	Ref
PV	1.5–5.9	[21]
RO	4–6	[22–24]
MD	22–90	[25]
MSF	21–58	[22,23,26]
MED	5–58	[22,27,28]

2. Experimental

2.1. Materials

Hydrophilic PAN flat-sheet ultrafiltration (UF) membrane with a molecular weight cut-off of 400,000 Da was purchased from AMFOR Inc. (Beijing, China). PVA, with Mw of 124,000 g/mol and a degree of hydrolysis at 99.4%, sodium hydroxide (NaOH) and sodium chloride (NaCl) with purities > 99.9% were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). 50 wt% 4-sulfo-phthalic acid (SPTA) aqueous solution was obtained from Tokyo Chemical Industry Co., Ltd. All chemicals were used as received. Deionized (DI) water was produced from a lab equipped Millipore ultrapure water system and used to prepare the PVA solutions and the aqueous salt solutions.

2.2. Preparation of the S-PVA films

To study the physiochemical properties of the S-PVA polymer, a series of PVA dense films were crosslinked by different amounts of SPTA. Specifically, PVA polymer powder (4 g) was dissolved in 100 mL of DI water at 95 °C. After the PVA solution was cooled down to room temperature, its pH value was adjusted to 1.7 ± 0.1 by adding 1 M HCl solution drop-wisely. Then, a predetermined amount of SPTA was added to the solution which was mega-stirred till a homogeneous solution was obtained. The solution was filtered and casted into a PTFE dish followed by air-dried for 3 days till a S-PVA dense film formed. After that, the S-PVA film was heated at 120 °C for 2 h in a fan forced oven for crosslink. The S-PVA dense films were labeled as S-PVA a-b where a-b referred to a molar ratio of the carboxyl groups in SPTA to the hydroxyl groups in PVA. For instance, the name ‘S-PVA 1–25’ indicated that the ratio of the carboxyl to hydroxyl groups was 1: 25. Using this method, dense S-PVA films crosslinked by different amounts of SPTA were prepared and labeled as S-PVA 1–25, 1–20, 1–15, and 1–10, respectively. Note that, a S-PVA 1–5 film was also prepared. However, this film was broken in pieces in water at 30 °C. Therefore, it was not used for further tests.

2.3. Preparation of the S-PVA/PAN composite PV membranes

2.3.1. Hydrolysis treatments of the PAN UF membranes

PAN UF membrane is a widely applied substrate for preparing PV composite membranes. Moreover, nitrile groups ($-\text{C}\equiv\text{N}$) on the PAN membrane surface can be hydrolyzed in an alkali solution and form carboxyl acid groups ($-\text{COOH}$) as shown in Fig. 1. This treatment improves the adhesion between the PAN surface and PVA coating layer by increasing the hydrophilicity and surface energy of PAN [35]. In this study, PAN UF membranes were soaked in a 1 M NaOH aqueous solution for 1 h, or 2 h at 60 °C, respectively. After that, the PAN UF membranes were soaked in DI water for 2 days to remove the residual

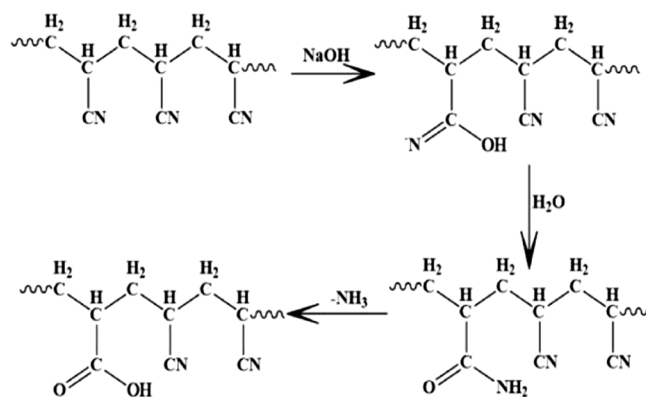


Fig. 1. The hydrolysis mechanism of PAN in NaOH.

Download English Version:

<https://daneshyari.com/en/article/7007983>

Download Persian Version:

<https://daneshyari.com/article/7007983>

[Daneshyari.com](https://daneshyari.com)