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Tubular hydrophobic ceramic membrane with asymmetric structure for water desalination via vacuum membrane distillation process

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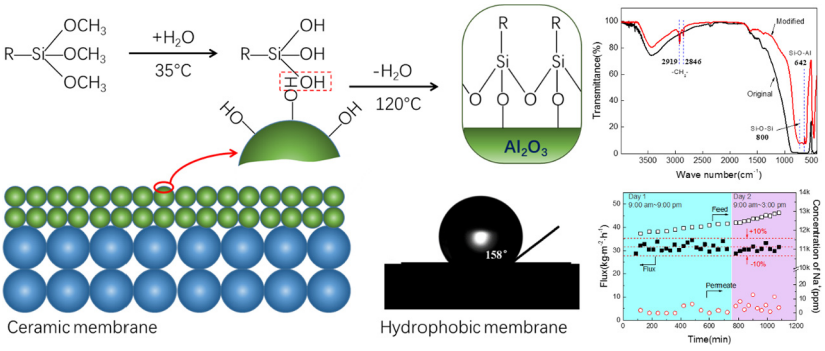
GRAPHICAL ABSTRACT



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ABSTRACT

A porous ceramic membrane without water wetting is essential for the application of water desalination in membrane distillation. In this study, we report a hydrophobic tubular asymmetric alumina membrane that was modified by grafting hexadecyltrimethoxysilane (C16) molecules. The grafting efficiency and hydrophobicity of the grafted membrane were characterized by its morphology, contact angle and FTIR spectrum, as well as the changes in terms of nitrogen permeance and pure water flux over various pressures. Four kinds of tubular asymmetric alumina membranes were employed in the vacuum membrane distillation (VMD) process. The effects of membrane thickness and pore size on the water flux or salt retention were investigated. The mass transport resistance in substrate was non-negligible and sometimes could be the main contributor to the total mass transport resistance. The membrane with a top layer thickness of 20 μm, pore size of 150 nm and support pore size of 3.2 μm was appropriate in the VMD process. After > 1000 min desalination, the permeate flux and salt rejection were maintained as high as at the beginning, i.e., approximately 30 $kg \cdot m^{-2} \cdot h^{-1}$ and 99.9%, respectively.

1. Introduction

Membrane distillation (MD), which combines the advantages of the novel membrane separation with the conventional distillation, is attracting more and more attention of society and academer [1, 2]. It has been applied in many separation fields, including water recovery and

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brine disposal [3–5]. The MD process can be considered as a thermally driven transport of vapors through a porous membrane, which serves as a physical barrier and a thermal insulator [6]. The distillate at the hot side of the membrane is heated to a certain temperature, then passes through membrane pores and finally condenses into liquid at the cold side [7]. Several MD modes, e.g., direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweep gas membrane distillation (SGMD) and vacuum membrane distillation (VMD), are commonly used for separation based on their corresponding advantages and the properties of the mixture to be separated. Among these processes, VMD could provide higher flux and rejection performance [8–10] than other modes. However, due to the high energy consumption, the VMD system becomes expensive especially when the feed temperature is higher than 75 °C [11]. There are three main strategies to bring MD technology closer to practical application. The first is the utilization of the cheap and renewable energy such as solar energy, geothermal energy as well as the waste heat from industrial systems [11–15]. The second is to optimize the VMD process [8, 16]. The third is to fabricate membranes with high performance [17–19]. Sometimes, the VMD system could perform high energy efficiency (permeate flow rate/energy consumption) at certain conditions [8].

In the term of membrane materials, the most commonly used membranes for wastewater treatment are made of polymeric material, such as polyvinylidenefluoride (PVDF) [20–22], polypropylene (PP) [23] and polytetrafluoroethylene (PTFE) [10, 24]. However, for the uses in MD, these membranes need good mechanical strength and chemical/thermal stability, and their surface should be highly hydrophobic. Ceramic membranes represent another class of separators and are famous for their high mechanical strength, chemical and thermal stabilities as well as their high flux. Ceramic membranes exhibit significant potential in wastewater treatment [25, 26]. Therefore, ceramic membranes attracted a lot of interests in MD processes in recent years [27–32]. Ko et al. [33] achieved a very high permeate flux of about 60 $kg{\cdot}m^{-2}{\cdot}h^{-1}$ by using hydrophobic Al_2O_3 hollow fibers in a VMD process.

However, conventional ceramic membranes exhibit hydrophilic character because of the presence of hydroxyl groups (−OH) on the membrane surface, and thus require hydrophobic modification for application in MD [34]. To address this issue, grafting is frequently practiced due to its high performance, convenient operation and easy adjustability [35, 36]. Fluorinated silanes are the most common but not the only modifying agents to obtain hydrophobic ceramic membranes [25, 37–39]. Hydrophobic ceramic membranes could also be obtained by using fluoride-free modifying agent [36]. In our previous work, Gao et al. [34] reported a modification method for the fabrication of hydrophobic ZrO_2 membrane by grafting hexadecyltrimethoxysilane (C16, CAS number: 16415-12-6) ethanol solution. This grafted ZrO_2 membrane possessed high hydrophobicity and performed effectively in the treatment of water-in-oil (W/O) emulsions. C16 is cheap and easy to store (superior to FAS in these two aspects). Moreover, ethanol, unlike certain traditional grafting solvents, such as acetone, is physiologically harmless and non-toxic and can be considered as an environment-friendly alternative to hazardous solvents in the grafting process.

Considering the wetting problem caused by liquid entry pressure (LEP) [33], the pore size should be as small as possible to provide high LEP. However, the membranes with smaller pores are typically subject to the tradeoff effect of higher LEP but lower permeability [40]. Fabrication of ceramic membrane with asymmetric structure has been considered as a common way to balance the tradeoff effect [41]. The thin membrane layer with small pore size could provide high LEP. While the substrate with large pore size could reduce the mass transfer resistance. In the last decade, most of the MD studies focused on heat and mass transfer [6, 8], operation conditions [26], and industrial applications [5, 42]. However, these studies did not address the dependence of the mass transfer and performance on the asymmetric membrane structural property with which the membrane can achieve increased flux and avoid fouling and hence can perform well and operate stably for a long time [43]. The mass transfer resistance in membrane layer was generally considered as the main resistance in membrane process. However, due to the large mean free path of permeate in the vacuum environment, the mass transfer resistance in the substrate cannot be ignored in the VMD process.

Here, we report a highly hydrophobic tubular asymmetric Al_2O_3 membrane grafted by hexadecyltrimethoxysilane in ethanol solution. The potential of the resultant Al_2O_3 membranes in water desalination via VMD were evaluated by inspecting their structures and properties. The relationship between the performance of the asymmetric membrane structures, such as pore size of the membrane layer and substrate as well as the membrane thickness, was systematically studied.

2. Experimental

2.1. Materials

Hexadecyltrimethoxysilane (≥85 vol%, Aladdin) and ethanol (≥99.7 vol%, Wuxi City Yasheng Chemical Co., Ltd., China) were used for the surface modification. The salt solution was prepared by mixing sodium chloride (NaCl) (≥99.5 wt%, Sinopharm Chemical Reagent Co., Ltd., China) with deionized water to a NaCl concentration of 30 $g{\cdot}L^{-1}$ for desalination in VMD.

Four specifications (differing in pore size and thickness of the top layer and substrate) of tubular asymmetric Al_2O_3 membranes with internal/external diameter of 8/12 mm and length of 110 mm were supplied by Jiuwu Hi-Tech Co., Ltd. for hydrophobic modification. The details of these membranes were listed in Table 1, where the parameters of microstructure were measured before the hydrophobic modification.

M1 and M4 have the same substrate structure and membrane pore size, while the membrane thickness of them was different. M1 and M2 have the same membrane layer structure and the thickness of substrate, while the pore sizes of substrates were different. M2 and M3 have the same substrate structure and membrane thickness, while the membrane pore sizes of them were different. The cross-sectional FESEM images of these four membranes were shown in Fig. 1.

2.2. Preparation of the hydrophobic membrane

The surface modifier was prepared by mixing concentrated hexadecyltrimethoxysilane (indicated hereafter as C16) with ethanol to a C16 concentration of 0.1 $mol{\cdot}L^{-1}$ at room temperature for 24 h. The dried raw membranes were immersed into the modifier solution at 35 °C for 2 h. The membranes were then removed and rinsed with deionized water, followed by dried at 120 °C for 4 h. The membranes were stored at room temperature before characterization and water desalination.

As shown in Fig. 2, the hydrophobic modification process of the ceramic membrane can be described as: the organosilane undergoes hydrolysis reaction to become a new compound containing multiple hydroxyl groups (−OH), then the compound reacts with the −OH on the membrane surface to form a hydrophobic grafted product by means of dehydration.

Table 1
Characteristics of the four ceramic membranes.

Name	Membrane layer			Substrate		
	d_p(nm)	ε	δ(μm)	d_p(μm)	ε	δ(mm)
M1	150	0.36	20	1.1	0.38	2
M2	150	0.36	20	3.2	0.33	2
M3	480	0.36	20	3.2	0.33	2
M4	150	0.36	60	1.1	0.38	2