



Enhanced dehydration performance of hybrid membranes by incorporating fillers with hydrophilic-hydrophobic regions

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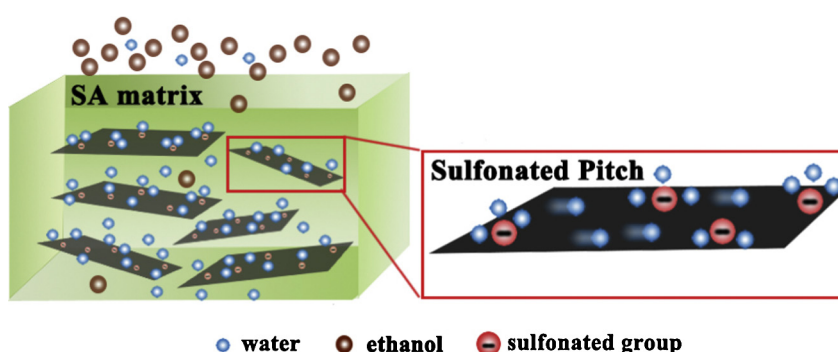
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HIGHLIGHTS

- Hybrid membrane with sulfonated pitch was prepared for pervaporation dehydration.
- Sulfonated pitch consisted of hydrophilic groups and hydrophobic backbone.
- Hydrophilic groups ensured high water occupancy in the membranes.
- Hydrophobic backbone provided transport “highways” for water molecules.
- Hybrid membranes showed enhanced permeability and selectivity.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, sulfonated pitch (SP), composed of hydrophilic sulfonate groups and hydrophobic polycyclic aromatic hydrocarbons, was incorporated into sodium alginate (SA) membranes for ethanol dehydration via pervaporation. The morphologies and structures of the SP and hybrid membranes were confirmed by transmission electron microscopy (TEM), Fourier transform infrared spectra (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscopy (SEM), positron annihilation lifetime spectroscopy (PALS) and water contact angle measurement. Hydrophilic sulfonate groups in SP formed hydrophilic regions which can bind water molecules, ensuring sufficient water occupancy in the membranes, while the hydrophobic polycyclic aromatic hydrocarbons provided continuous transport “highways” for the water molecules. Meanwhile, the introduction of SP created more polymer-filler interface cavities, rendering the membrane with suitable free volume property for separation. Consequently, the membrane demonstrated a maximum permeation flux of $1879 \pm 80 \text{ g/m}^2 \text{ h}$ coupled with an optimal separation factor of 1913 ± 69 in separating 90 wt% ethanol aqueous solution. These resulted in an increase over the SA control membrane of 1.5-fold and 4-fold respectively. Moreover, the hybrid membranes exhibited good operation stability. The results suggested that incorporating fillers with hydrophilic-hydrophobic regions in the membranes can be an effective strategy to improve the performance of water-permeable membranes.

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1. Introduction

Separation process of chemicals in industry can be rather energy-intensive. More than 80% of energy consumption related to chemical separations is used in conventional distillation and similar processes such as evaporation (Lively and Sholl, 2017; Shannon et al., 2008). Pervaporation (PV) has the potential to reduce energy consumption relative to conventional distillation because it only requires the latent heat of evaporation for the target permeate while conventional distillation requires the heat supplied to the whole feed solution (Hua et al., 2017; Ong et al., 2016). In the past decades, pervaporation has been widely utilized in organic solvent dehydration, especially for the production of biofuels such as ethanol and isopropanol (Magalad et al., 2011). Effective PV membranes typically have good characteristics such as high selectivity, permeability and stability (Bachman et al., 2016; Gao et al., 2015; Hua et al., 2017). Inorganic membranes possess favorable selectivity and permeability but are brittle and fragile. Pure polymeric membranes have good stability but usually can't achieve both high selectivity and permeability simultaneously. Incorporating dispersed fillers into the polymer matrix to fabricate hybrid membranes have been considered as a new alternative to achieve a high separation performance due to the superiorities unique to each phase (Su et al., 2016). Controlling the physical structure or chemistry of the fillers in hybrid membranes is an efficient approach to improve the separation performance owing to the adjustable preferential adsorption and/or diffusion of the target permeate (Liu et al., 2015; Xu et al., 2017).

Researchers have mainly focused on the hydrophilic fillers in previous studies, such as calcium carbonate (CaCO_3) (Shan et al., 2017), titanium dioxide (TiO_2) (Gong et al., 2014) and silica (Wang et al., 2011) due to their preferential adsorption of water molecules in the membranes. Many experiments and simulations in recent years have proved the water molecules move faster on a hydrophobic substrate than a hydrophilic substrate (Cai et al., 2006; Mondal et al., 2011; Willard and Chandler, 2014), since the weaker adhesion of water molecules to hydrophobic surface/channels decreases the flow friction (Cai et al., 2006; Moskowitz et al., 2014; Ruiz et al., 2015; Strong and Eaves, 2016; Willard and Chandler, 2014). However, the water permeability cannot be easily achieved by incorporating hydrophobic fillers because of the insufficient water occupancy on the surfaces/channels. Mittal et al. found that both desired water occupancy and high water flow would be achieved if the surfaces/channels comprised hydrophobic and hydrophilic domains and kept a rational fraction of hydrophilic domains (Moskowitz et al., 2014). Hydrophilic domains ensured the water occupancy on the surfaces/channels while hydrophobic domains benefited water transfer. Inspired by these studies, hybrid membranes consisting of fillers with hydrophilic-hydrophobic regions are expected to improve the selective water permeation across the membrane.

Sulfonated pitch (SP), a very cheap commercial product, has been extensively used in the well drilling industry to strengthen the mud cake quality (Zhang et al., 2017). It is prepared by the sulfonation of coal tar pitch or petroleum pitch that consists of large polycyclic aromatic hydrocarbons (Zhang et al., 2015). The polycyclic aromatic hydrocarbons are rather hydrophobic while the introduced sulfonate groups display high hydrophilicity. Shao et al. (2010) reported that sulfonate groups could bind water molecules tightly via strong electrostatic interaction. Compared with other hydrophilic groups, e.g., poly(ethylene glycol) and carboxyl groups, the sulfonate group could adsorb a larger quantity of water molecules while preserving a higher transfer freedom and lower residence time of water molecules which was beneficial for diffusion (Shao et al., 2010; Wu et al., 2012). The above-mentioned charac-

teristics endow SP with a combination of hydrophilic and hydrophobic regions. Therefore, the separation performance of the SP-containing hybrid membranes is expected to be highly improved relative to the unfilled membrane. Sodium alginate (SA) has been proven as a low-cost and easily available natural polymer that presents outstanding performance for the dehydration of alcohol–water mixtures. The large amounts of hydroxyl groups and carboxyl groups in the carbohydrate backbone endow SA with extraordinary hydrophilicity and permselectivity to water in the sorption step. In this study, SP was incorporated into SA matrix to fabricate hybrid membranes. The morphology, structure, hydrophilicity, swelling degree of the resultant hybrid membranes were characterized. The separation performance and the operation stability of the membranes were evaluated using water/ethanol mixture as a model system.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN) ultrafiltration membranes as the supporting membranes with a molecular weight cutoff 100 kDa were purchased from MegaVision Membrane Engineering & Technology Co. Ltd. (China). SA was supplied by Qingdao Bright Moon seaweed Group Co. Ltd. (China). Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and absolute ethanol (99.7 wt%) were obtained from Tianjin Chemart Technology Development Co. Ltd. (China). SP was a gift from Originchem Co. Ltd. (China). SP was a commercial product and should be purified by filtration and centrifugation before use. Other reagents and chemicals were of analytical grade and utilized as received. Deionized water was used in the whole experiment.

2.2. Preparation of hybrid membranes

SP powder was added into deionized water and then filtered with a 200 mesh filter cloth and centrifuged at 6000 rpm for 10 min to get the SP dispersion. The hybrid membranes in this study were prepared via spin-coating method. For the SA control membrane, 0.38g SA was dissolved in 25 ml deionized water to form a 1.5 wt% SA casting solution and was mechanically stirred at 303 K for 5 h. The obtained casting solution was then spin-coated on the pre-dried PAN substrate (0.1 m × 0.1 m). In a spin-coating procedure, the PAN support typically spun at 500 rpm for 20 s and then 800 rpm for 40 s using MYCRO WS-650Mz-23NPPB spin coater. After drying at room temperature for 24 h, the as-prepared membrane was then immersed in 0.5 M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ aqueous solution for 10 min at room temperature to get cross-linked. At last, the membrane was obtained after drying at room temperature for another 24 h and was marked as SA/PAN. With regard to the preparation of hybrid membranes, a certain amount of SP aqueous dispersion was diluted to 25 ml with deionized water and sonicated for 1 h. Subsequently, 0.38g SA was added into the dispersion and formed a 1.5 wt% casting solution with SP fillers. The spin-coating and cross-linking procedure were the same as the SA control membrane. The hybrid membranes were designated as SA-SP (X)/PAN, where X (=1, 2, 3, 4, 6) represented the SP content (wt%) in the SA matrix. Homogeneous membranes named as SA-SP (X) were fabricated on the homemade glass mold for characterization.

2.3. Pervaporation and sorption experiment

The pervaporation experiment apparatus was a lab-scale cross-flow cell with an effective area (A) of 36.0 cm^2 and had been

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