Journal of Membrane Science 546 (2018) 31–40

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Enhanced dehydration performance of hybrid membranes by incorporating lanthanide-based MOFs

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ARTICLE INFO

Keywords:
Hybrid membrane
Lanthanide-based two-dimensional MOFs
Ethanol dehydration
Pervaporation

ABSTRACT

Metal-organic frameworks (MOFs) with high hydrolytic stability are highly needed to prepare polymer-MOFs hybrid membranes working in aqueous solution media. In this study, $[Eu(BTB)(H_2O)_2{\cdot}solvent]_n$ (abbreviated as EuBTB), a kind of lanthanide-based two-dimensional MOFs, was utilized to prepare hybrid membranes for organic solvent dehydration owing to their hydrolytic stability arising from the relatively strong coordination bond between lanthanide ions and oxygen-containing groups. The detailed structure and properties of the hybrid membranes were well characterized. The hybrid membranes exhibited high mechanical strength and swelling resistance due to the strong interfacial interaction benefiting from the well complexation of EuBTB and sodium alginate (SA) through carboxylic groups. The horizontally aligned lamellar EuBTB could render ordered channels with the diameter of 0.5–0.8 nm. Each Eu^{3+} in EuBTB could coordinate two water molecules and serves as carriers to facilitate the transportation of water molecules. Moreover, the incorporated EuBTB could render decreased crystallinity. Accordingly, the hybrid membranes exhibited superior permeability and selectivity for ethanol dehydration. Especially, the membrane containing 5 wt% EuBTB exhibited an optimum performance with permeation flux of 1996 g/m^2 h and separation factor of 1160 for 90 wt% ethanol aqueous solution at 350 K. Meanwhile, the hybrid membranes showed good long-term stability. This study may offer a generic and efficient approach to prepare MOFs-based hybrid membranes with high performance and stability for water-selective separation.

1. Introduction

Polymer-metal organic frameworks (MOFs) hybrid membranes, prepared by incorporating MOFs materials into polymer matrix, have received extensive attention, due to its favorable separation performance and the potential ability to overcome the "trade-off" limitation between permeability and selectivity [1,2]. MOFs fillers with ordered pores and tunable structure could enhance the affinity of the membranes towards preferable penetrants and decrease the mass transfer resistance of the hybrid membranes [3]. Therefore, polymer-MOFs hybrid membranes containing various MOFs, such as CuBTC, ZIF-8 and MOF-5, have been widely investigated for their gas separation and organic solvent separation applications [4,5]. However, only a limited number of these membranes are used in aqueous solution media suffering from the poor hydrolytic stability of MOFs due to the weak coordinate interaction [6,7].

Based on the considerations mentioned above, selecting MOFs with high hydrolytic stability is the key to prepare polymer-MOFs hybrid membranes for aqueous solution separation. To enhance the hydrolytic stability of MOFs, a straightforward strategy is the application of high oxidation state metal ions (such as Fe^{3+}, Al^{3+}, Cr^{3+} and Zr^{4+}) to form stronger coordination bond with ligands rather than low-valence metal ions [8]. Accordingly, many highly stable MOFs have been designed and synthesized, such as UiO-66 [9] and MIL-101(Cr) [10]. Among the various metal centers available for the construction of MOFs, lanthanide (Ln) ions usually possess relatively high coordination affinity toward oxygen atoms, thus Ln-based MOFs are vested with high stability [11]. Meanwhile, the high coordination number of Ln ions could benefit the formation of node with multiple connections and solvent occupied potential open metal sites, which can favor the mass transfer properties.

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http://dx.doi.org/10.1016/j.memsci.2017.10.005
Received 10 August 2017; Received in revised form 19 September 2017; Accepted 3 October 2017
Available online 05 October 2017
0376-7388/

Nomenclature

Variables

A	membrane area (m^2)
l	membrane thickness (m)
Q	mass of permeate (g)
t	time interval (h)
SD	Swelling degree (%)
F_E	mass fraction of ethanol in feed solution (wt%)
F_W	mass fraction of water in feed solution (wt%)
P_E	mass fraction of ethanol in permeate solution (wt%)
P_W	mass fraction of water in permeate solution (wt%)
J	permeation flux (g/m^2 h)
J_i	permeation flux of component i (g/m^2 h)
$(P/l)_E$	ethanol permeance (GPU)
$(P/l)_W$	water permeance (GPU)
$(P/l)_i$	the permeance of component i (GPU)
p_{i0}	partial pressures of component i in the feed side (Pa)
p_{il}	partial pressures of component i in the permeate side (Pa)
p_{i0}^{sat}	saturated vapor pressure of pure component i at operation temperature (Pa)
W_D	the mass of dry membrane (g)
W_S	the mass of membrane immersed in the feed mixture (g)
x_{i0}	mole fraction of component i

Greek letters

α	separation factor
β	selectivity
γ_{i0}	activity coefficient of component i
θ	diffraction angle (°)

$[Eu(BTB)(H_2O)_2 \cdot solvent]_n$ (abbreviated as EuBTB) is a kind of Ln-based two-dimensional MOFs materials (Fig. 1). The strong interaction between Eu^{3+} and carboxyl groups endowed EuBTB relatively high stability [12]. The Eu^{3+} ions with nine coordinated sites could coordinate with carboxylate groups from BTB ligands and oxygen atoms from water molecules [12]. Meanwhile, the two-dimensional morphology of EuBTB also provided anisotropy, high specific surface area and high aspect ratio, which are more effective in optimizing the properties and performance of the hybrid membranes [13]. Therefore, EuBTB may become the potential candidates to prepare polymer-MOFs hybrid membranes for aqueous solution separation.

In this study, EuBTB was blended with sodium alginate (SA) and deposited onto polyacrylonitrile (PAN) support layer to prepare hybrid membranes aiming at application in aqueous solution separation. The abundant carboxylic groups in SA could provide high hydrophilic property and superiority dehydration performance [14]. Meanwhile, those carboxylic groups can serve as bonding sites to increase the interfacial affinity between SA and EuBTB to boost the stability and performance of the resulted membranes. Beyond the rational construction of the hybrid membranes, the physical morphology, chemical structure and thermal stability of the hybrid membranes were characterized. The dehydration performance of the hybrid membranes were evaluated using ethanol-water mixtures. The effect of EuBTB content, operation temperature and feed concentration on the separation performance were investigated, and the long-term operation stability of the membranes were also evaluated.

2. Experiment

2.1. Materials

$Eu(NO_3)_3 \cdot 9H_2O$ (99.9 wt%), LiCl (99.9 wt%) and benzene-1,3,5-tribenzoate (99 wt%) were supplied by Shanghai Aladdin Bio-Chem Technology Co. Ltd. CH_3CN and DMF were supplied by Tianjin Kemiou Chemical Reaqent Co. Ltd. Sodium alginate (SA) was supplied by Qingdao Bright Moon seaweed Group Co. Ltd. (Shandong, China). Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$), absolute ethanol was bought from Tianjin Guangfu Technology Development Co. Ltd. (Tianjin, China). Polyacrylonitrile (PAN) ultrafiltration membranes used as membrane substrates with a molecular weight cut-off of 100 kDa were obtained from Shanghai Mega Vision Membrane Engineering & Technology Co. Ltd. (Shanghai, China).

All the reagents were of analytical grade and used without further purification. Deionized water through a Millipore system (MillisQ) was used in all experiments.

2.2. Membrane preparation

2.2.1. Preparation of EuBTB

EuBTB was prepared through the solvothermal reaction according to the reported procedure [12]. $Eu(NO_3)_3 \cdot 9H_2O$ (30 mg), H_3BTB (27 mg) and LiCl (20 mg) were solved in a mixture of CH_3CN (2 ml), DMF (1 ml) and H_2O (0.3 ml), then reacted at 100 °C for 24 h. The product was solvent exchanged in CH_3CN for three days and then degassed under vacuum at 220 °C overnight to remove the residue solvent and coordinated water molecules.

2.2.2. Fabrication of SA-EuBTB hybrid membranes

The hybrid membranes were fabricated by spin-coating method. PAN support layer after soaking in deionized water for two days were cut into pieces with the size of 0.1 m × 0.1 m, then hung up and dried at room temperature for 3 h. SA suspension was obtained by dissolving an appropriate amount of SA in deionized water stirring at 30 °C for 1 h. EuBTB solution was acquired by dispersing certain amounts of EuBTB in aqueous solution and sonicating by ultrasonic vibration (achieved by Noise Isolating Tamber SCIENTZ-IID) for 5 min. The EuBTB suspension

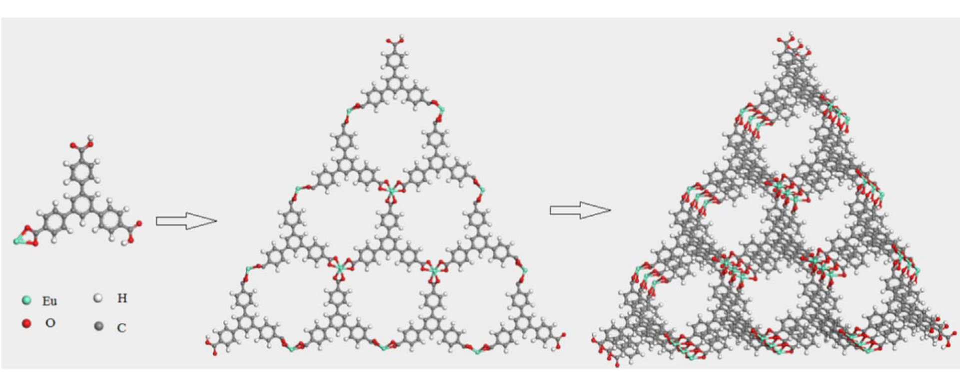

Fig. 1. Molecular structure of EuBTB.