Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–9

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Thin film nanocomposite membrane containing zeolitic imidazolate framework-8 via interfacial polymerization for highly permeable nanofiltration

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ARTICLE INFO

Article history:
Received 8 June 2017
Revised 12 September 2017
Accepted 28 November 2017
Available online xxx

Keywords:
Nanofiltraion
ZIF-8
Interfacial polymerization
Thermal stability

ABSTRACT

Performance of thin film nanocomposite (TFN) membranes can be enhanced by intercalation of nanofillers with special wettability and surface charge in the thin film layer. Properties of the nanofillers have great influence on the interfacial polymerization of polyamide. In this study, nano-porous zeolitic imidazolate framework-8 (ZIF-8) crystals were dispersed in amine monomer (piperazine) solution and intercalated in the polymeric thin film layer. Structure and surface property of the polyamide layer were changed by adding this hydrophobic and negative charged ZIF-8, which was identified by attenuated total reflectance infrared, scanning electron microscope, X-ray photoelectron spectroscopy, atomic force microscopy and water contact angle measurement. The TFN membranes containing ZIF-8 showed a water flux high to 55 L/m^2 h with Na_2SO_4 rejection higher than 95% at 0.6 MPa. Moreover, this high performance remained stable for long-term testing during 36 h and even temperature reaching to 70 °C.

1. Introduction

Nanofiltration (NF) membrane, with a pore size around 1 nm (molecular weight cut-off of 300–500 Da), is a pressure-driven membrane with separation performance between reverse osmosis (RO) and ultrafiltration (UF) [1,2]. NF membranes have higher flux and lower manipulating pressures than RO membranes because of its very thin outer layer, while retaining organic compounds and di/multi-valent ions [3].

Generally, an NF membrane consists of a separation layer and a support layer with the least mass transfer resistance. The two layers can be fabricated together via phase separation of a dope solution of polymer with suitable concentration and additives [4,5]. However, the integrated NF membrane possesses higher transfer resistance than that of thin film composite (TFC) membrane since the thin film with 50–100 nm in thickness can be made by interfacial polymerization. Piperazine (PIP) and *m*-phenylene diamine (MPD) are the most usual monomers in the aqueous solution for interfacial polymerization. Nevertheless, running of NF membrane fabricated by MPD (due to its denser thin film) needs higher driving force than the one by PIP, so we choose PIP for the aqueous solution to prepare NF membranes. Although the permeance of TFC membrane has been greatly enhanced, it still cannot meet the requirement of sustainable development and energy-saving process. Therefore, several methods have been developed to prepare TFC membranes to enhance their performance, such as chemical grafting [6], surface coating [7] and addition of different nano-materials [8–10].

The addition of nanomaterials will provide a more serviceable, cleaner, securer, and smarter product, which is significant in the field of molecular-scale functional systems [11–13]. Many hydrophilic nanofillers such as SiO_2 [14], TiO_2 [15], zeolite 4A [16], and Ag nanoparticles [17], were encapsulated in TFC membrane during interfacial polymerization to enhance its performance. It was thought that the hydrophilic nanofillers increased membrane affinity to water and made a faster water transport through the membrane [18]. However, experimental results [19] and simulation [20] both proved water permeability has not reached as high as it expected. It was deemed that the strong interaction between water molecules and the hydrophilic nanofillers reduced water diffusion rate through the membrane. Interestingly, researchers found that thin film nanocomposite (TFN) membranes integrated with hydrophobic nanofillers, such as POSS [21], silicalite-1 [22], carbon nanotubes [23], and ZIF-8 [24,25] possessed flux higher than the hydrophilic counterparts. This phenomenon can be attributed to

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https://doi.org/10.1016/j.jtice.2017.11.033
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two facts, (1) the hydrophobic nanofillers located beneath the surface of the TFC membrane, where the water molecules adsorbed, and (2) water passing through the hydrophobic pores without directly contacting the pore, and therefore, there is no effect of friction on water penetration [25].

Size and adding manners of the nanofillers have important influence on the structure of the TFN membrane. Considering the hundred nanometers scale in thickness of TFC, larger particles tend to trans-pierce the TFN membrane to the surface or result in thicker film because of continuous growth of the film until it can cover the particles [25]. These two scenarios generally lead to reduction of the salt rejection or water flux of the membrane. The nanofillers can be introduced into the TFN membrane through adding them in the aqueous phase or organic phase. Huang et al. [26] found that TFN membrane prepared by adding zeolite A in organic phase has better performance than that in aqueous phase. However, there is no evidence for relationship between membrane performance and the addition manners of the nanofillers [27,28]. Where the nanofillers can better disperse is one reason for the choice. Usually, the hydrophilic nanofillers were added in the organic phase, and vise versa. Exceptionally, some hydrophilic nanofillers were also added in aqueous phase comprehensively considering their particles size, surface charge and other properties.

In recent years, zeolitic imidazolate framework (ZIF) nanoparticles have attracted great interest in terms of the modified composite membranes. Zhang et al. prepared ZIF-8/PDMS mixed matrix membrane to enhance selectivity of propylene/propane [29]. Duan et al. fabricated TFN membrane containing ZIF-8 for high performance reverse osmosis membrane [25]. Sorribas et al. also added MOFs, including ZIF-8, in TFN membrane for organic solvent nanofiltration [24]. ZIFs, especially ZIF-8, with high stability in water and other solvents [30], have attracted increasing attention due to its high thermal ($>$673 K) and chemical stability compared to other MOFs structures [31,32]. Compared with other nanoparticles, ZIF-8 performs better compatibility with polymer matrix since the organic linkers in ZIF-8 can provide stronger interaction with polymer chains [24,33]. There is a reaction between the N−H groups which come from 2-methylimidazole in ZIF-8 and the acylchloride groups of TMC, generating amide structure [34].

The main goals of this study are to fabricate TFN membranes containing ZIF-8 crystals in the skin layer, and to investigate the effect of ZIF-8 addition on improving the permeability and maintaining a high rejection in nanofiltration applications. It was hypothesized that the TFN membrane in conjunction with appropriate concentrations of ZIF-8 would equip the nanofiltration membrane a highest water flux. In this study, PSF UF membranes were used as a support membrane. Trimesoyl chloride (TMC) and piperazine (PIP) were used as monomers for interfacial polymerization. The polypiperazine-amide TFN membranes were prepared by interfacial polymerization with adding ZIF-8 in aqueous phase. Performances of the TFN membrane in terms of water permeability and salt rejection were evaluated by using stainless steel membrane evaluation system with salt aqueous. Furthermore, the membrane structures and chemical alterations were characterized by attenuated total reflectance infrared (ATR-IR), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Different polymerization conditions on membrane performance were investigated.

2. Experimental section

2.1. Materials

2-methylimidazole (99%), zinc nitrate hexahydrate (98%), methanol (99.99%), trimesoyl chloride (TMC, 99%), piperazine (PIP, 99.5%), n-hexane and sodium hypochlorite solution (12%) were obtained from Sinopharm Chemical Reagent. NaCl, $MgSO_4$ and Na_2SO_4 were purchased from Kermel Chemical Reagent Co., Ltd. (Tianjin, China). All chemicals were used as received without further treatment. Polysulfone ultrafiltration (PSF-UF) sheet membrane (MWCO = 20,000) with nonwoven fabric supporting was supplied by GE company. Deionized water was used throughout the study.

2.2. Fabrication of ZIF-8 nanoparticle

ZIF-8 was synthesized based on a typical method [35]. 2.231 g (7.5 mmol) zinc nitrate hexahydrate ($Zn(NO_3)_2 \bullet 6H_2O$) and 2.464 g (30 mmol) 2-methylimidazole was dissolved in 75 mL methanol individually. The former solution was rapidly poured into the latter solution, and the mixture was then kept for 1 h under vigorous stirring. The synthesized product was separated from the resultant solution through centrifugation, washed twice with fresh methanol and dried under 75 °C for 24 h.

2.3. Fabrication of TFN membranes

The TFC membrane was synthesized by interfacial polymerization between PIP and TMC [36]. The UF support membrane was washed with de-ionized water firstly, then fixed it between two Teflon frames. The aqueous phase containing 2 (w/v %) PIP was poured on the top of the support membrane and it was kept for 20 min at room temperature. Excess aqueous phase on the surface was removed by an air knife. Then this membrane was immersed in the organic phase (0.15 w/v % TMC in hexane) and kept in the organic solution to proceed interfacial polymerization. After a predetermined time (10, 15, 20, 30, 60 s), the excess organic solution was discarded, then the frame with membrane was maintained at 60 °C for 5 min to carry out post polymerization. Finally, the resulting membrane was stored de-ionized for later use. For synthesis of TFN membranes with ZIF-8, varied amount of ZIF-8 (0.01 and 0.5 w/v %) was dispersed in 2 w/v% PIP aqueous phase by ultrasonication for 30 min at 25 °C, and then polymerized with TMC for 30 s. Although not all ZIF-8 particles were transferred to the polyamide layer of the membrane, we called the corresponding membranes as ZIF-0% for bare polypiperazine-amide membrane and ZIF-0. XX% for ZIF-8 incorporated ones, where XX is the amount of added ZIF-8.

2.4. Characterization

X-ray diffraction (XRD) patterns were acquired using a Rigaku Ultima III diffractometer with Cu Kα X-ray radiation. Each XRD pattern was acquired from 3° to 40° at a rate of 4°/min. Morphology and crystal size were determined using field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan), and transmission electron microscopy (TEM, H7650, Hitachi, Japan). The specific surface area and micropore volume of the nanoparticles were tested using a fully automatic surface and porosity analyzer (BET, ASAP2020, Quantachrome, United States). Nitrogen adsorption measurements were performed at 77.35 K. Before the adsorption/desorption measurements, the ZIF-8 nanoparticles were degassed for 5 h under vacuum at 150 °C. The specific surface area was worked out on the basis of Brunauer–Emmett–Teller (BET) method.

Chemical structure of membranes was characterized with a Vector-22 FTIR spectrometer (Bruker Company, Germany). All samples were dried thoroughly in vacuum at 60 °C for 24 h. The XPS data were obtained on an AXIS-Ultra instrument Kratos Analytical (SHIMADZU, Japan). FE-SEM was used to analyze the surface and

Please cite this article as: F. Xiao et al., Thin film nanocomposite membrane containing zeolitic imidazolate framework-8 via interfacial polymerization for highly permeable nanofiltration, Journal of the Taiwan Institute of Chemical Engineers (2017), https://doi.org/10.1016/j.jtice.2017.11.033