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Effect of non-solvent additives on the morphology and separation performance of poly(*m*-phenylene isophthalamide) (PMIA) hollow fiber nanofiltration membrane

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HIGHLIGHTS

- PMIA hollow fiber NF membranes were fabricated.
- Effects of non-solvent additives on the morphology and separation performance were studied.
- High content of non-solvent additives resulted in narrow pore size, pore size distribution and high rejection.

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ABSTRACT

Newly designed poly(*m*-phenylene isophthalamide) (PMIA) hollow fiber nanofiltration membranes were fabricated containing non-solvent additives, i.e., lithium chloride (LiCl), acetone and PVP by dry-jet wet spinning technology. The effects of non-solvent additives on the morphology and separation performance were investigated. The addition of non-solvent additives in the dopes enhanced the viscosity significantly. The membrane cross-sections were monitored by scanning electron microscopy (SEM). The results indicated that by increasing the concentration of non-solvent additives, the morphologies changed from finger-like to sponge-like, and the outer skin-layer thickness was slightly increased. The rejections to various salts and pure water permeability (PWP) of these membranes were determined. The mean pore size and molecular weight cut-off (MWCO) were estimated using the solute rejection method. The results showed that the salt rejection of the membranes decreased in the order of $R(Na_2SO_4) > R(MgSO_4) > R(NaCl) > R(MgCl_2)$, and as the concentrations of non-solvent additives increased, the PWPs, mean pore sizes and MWCOs of the PMIA membranes all decreased. The atomic force microscope (AFM) experiments demonstrated that a smooth membrane surface was formed by adding non-solvent additives. Furthermore, the stress values at break, the elongation at break and the elastic modulus of the fibers increased as non-solvent additive contents increased.

1. Introduction

Nanofiltration (NF) membrane was firstly introduced in the late 1980s with separation characteristic between ultrafiltration (UF) and reverse osmosis (RO) membrane. The pore size in NF membrane is nominally 1.0 nm and its MWCO (molecular weight of solute that is 90% rejected by the membrane) ranges from 200 to 1000 Da [1–6]. The separation mechanism of NF membrane involves a combination of steric (size exclusion) effect and electric (Donnan exclusion) effect. In the last few decades NF membrane technique has gained significant attention and be applied successfully in many fields such as drinking water [7–13], dye wastewater [14–19], food industry [20,21] and other industrial applications [22–29].

At present, most of commercial NF membranes are thin-film composite (TFC) membranes which are made by spreading a thin selective layer on the top of porous asymmetric substrate [30]. The thin layer is typically fabricated using interfacial polymerization (IP), in-situ polymerization, chemical modification or surface coating et al. Although these techniques are proved to be effective, their fabrication processes are complicated. On the contrary, fabrication of a wholly integrally asymmetric hollow fiber membrane with an ultra-thin selective layer and highly porous substrate by the Loeb–Sourirajan phase-inversion technology can avoid the sophisticated and time consuming procedure to form the thin layer of the composite membrane. Today, most commercialized NF membranes are still limited to flat-sheet, spiral wound

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or tubular configurations [31,32]. Compared with them, hollow fiber configuration has some intrinsic advantages such as higher packing density, smaller foot print, relatively larger membrane surface area per unit volume, and lower operation cost [33,34]. Therefore, many researchers from both industry and academia focus on developing hollow fiber NF membranes.

For instance, Wang and Chung used polybenzimidazole (PBI) to fabricate hollow fiber NF membranes through the phase-inversion method [35]. These PBI membranes exhibited outstanding mechanical strength and good chemical stability with a mean pore size of 0.348 nm and a pure water permeability (PWP) of 1.861 L/(m^2·h·bar). Yang et al. developed the poly(phthalazinone ether sulfone ketone) (PPESK) hollow fiber NF membranes with a MWCO of approximately 600 Da [36]. They also fabricated a polypiperazine amide/PPESK hollow fiber composite NF membrane via interfacial polymerization of piperazine (PIP) in water with trimesoyl chloride (TMC) in hexane [37]. The resultant composite membrane showed a high rejection to Na_2SO_4 and a high water flux of 45 L/(m^2·h) under 0.35 MPa. Bolong et al. developed a hollow fiber NF membrane using polymer blends which consisted of polyethersulfone and a charged surface modifying macromolecule [38]. The modified membrane possessed a mean pore size of 1.2 nm. Sun et al. fabricated a dual-layer composite hollow fiber NF membrane by the simultaneous co-extrusion of polyamide-imide and cellulose acetate dopes [39]. The dual-layer NF hollow fiber membrane had a relatively high PWP of 11.93 L/(m^2·h·bar), and a mean effective pore radius of 0.63 nm. Yu et al. fabricated NF hollow fiber membranes from polypropylene (PP) hollow fiber microfiltration membranes through dip-coating sodium carboxymethyl cellulose (CMCNa) on the outer surface of the membrane followed by cross-linking with $AlCl_3$ and $FeCl_3$ [40,41]. The modified membrane had a MWCO of 760 Da and a high PWP of 10.8 L/(m^2·h·bar). Moreover, the rejection of Congo red and Methyl blue was higher than 99.8% and 99.6%, respectively. He and coworkers developed a novel composite NF membrane by coating sulfonated poly (ether ether ketone) (SPEEK) on the polyethersulfone hollow fiber substrate [42]. The membrane exhibited a good retention of 97–100% to organic dyes.

Above all, many hollow fiber NF membranes with good separation performances have been developed. However, membrane materials, which are crucial for achieving better separation performance, excellent mechanical properties and good stabilities at harsh operation conditions, are still limited to CA, PPESK, PES, etc. PMIA whose chemical structure is shown in Fig. 1 has been widely used as a promising structural material because of its outstanding thermal resistivity (T_g = 270 °C) and chemical stabilities that are attributed to its 3-D jungle-gym-type hydrogen bond network [43,44]. The good physiochemical properties make PMIA a promising membrane material. Huang and Zhang have successfully fabricated the PMIA flat-sheet nanofiltration membranes which showed good separation performance in the dye purification and desalination processes [45]. Compared to their work, our PMIA nanofiltration membranes were in a hollow fiber form. Unlike flat sheet membrane which typically required a supporting layer such as a non-woven substrate used in Huang and Zhang's work, hollow fiber membrane has a self-supporting character. Hence, developing hollow fiber NF membranes gives an alternative (maybe more suitable) solution for future application of PMIA membranes. Moreover, formation of PMIA nanofiltration membrane is controlled by a number of variables including the dope composition and fabrication conditions. So it is important to understand the effects of the variables on the membrane structure and performance in order to have a proper control on the properties of the resultant membrane. In a previous relevant work, Huang and Zhang investigated the effects of additives on the separation performance of the PMIA flat sheet membrane for dye treatment. However, the effects of additives on membrane morphology were not addressed. To the best of our knowledge, no reports have discussed the effect of non-solvent additives on the morphology and performance of the PMIA hollow fiber nanofiltration membrane. Therefore, the purpose of this work is to explore suitable spinning parameters for developing PMIA hollow fiber NF membranes. In this study, the dope solutions, which consist of N,N-dimethylacetamide (DMAc) as a less volatile solvent, acetone as volatile non-solvent, lithium chloride (LiCl) as inorganic additive, and PVP as organic additive, were mixed to form homogeneous dope solutions, and the effects of these non-solvent additives on the membrane morphologies and separation performances were studied.

Table 1
Diffusivities and Stokes radii of neutral solutes in aqueous solutions (at 25 °C).

Solute	M_W (g mol^{-1})	D_s ($\times 10^{-9} m^2 s^{-1}$)	r_s (nm)
Glucose	180	0.67	0.365
Saccharose	342	0.52	0.471
Raffinose	504	0.42	0.584
α-Cyclodextrin	972	0.35	0.701

2. Experimental

2.1. Materials

PMIA was purchased from DuPont (USA) and was dried at 120 °C in vacuum for 24 h before use. N,N-dimethylacetamide (DMAc, >99%) was

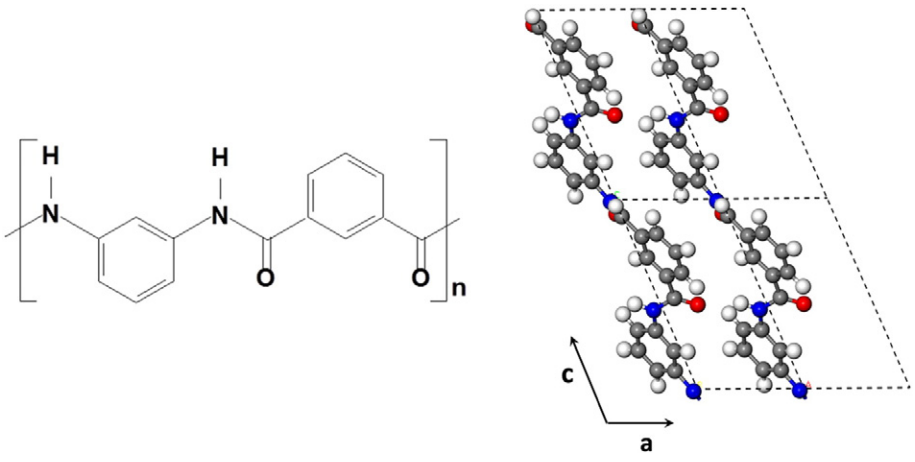

Fig. 1. Chemical structure and three-dimensional crystal structure of PMIA.