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Acid stable thin-film composite membrane for nanofiltration prepared from naphthalene-1,3,6-trisulfonylchloride (NTSC) and piperazine (PIP)

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ABSTRACT

Acid stable thin-film composite membrane for nanofiltration was fabricated by interfacial polymerization of naphthalene-1,3,6-trisulfonylchloride (NTSC) and piperazine (PIP) on porous polysulfone support membrane. The performance of the membrane was optimized by studying the preparation parameters including monomer content, reaction temperature and additive in organic phase. The separation performance of the resultant membrane was evaluated through permeation experiments, the membrane property was characterized by ATR-FTIR, XPS AFM, SEM and streaming potential measurements, and the acid stability was investigated through both static acid soaking tests and long-term permeation tests under acidic condition. After exposure to 20%(w/v) H_2SO_4 for 2 months or running with 4.9%(w/v) H_2SO_4 for 60 day, the PIP-NTSC composite membrane showed minor change in separation performance and no evident chemical change in the active skin layer, indicating that the developed membrane possessed good acid stability. The desired membrane exhibited a pure water permeability of about 5.8 l/m^2 h bar, a MWCO of as high as 5000 Da, and an attractive solute rejection of higher than 86.5% for a feed containing 500 mg/l Na_2SO_4 at 0.5 MPa. Furthermore, the PIP-NTSC composite membrane could be used to treat acidic effluents from metal industries with good perm-selectivity and long-term stability.

1. Introduction

Nanofiltration (NF) is a pressure-driven separation process employing a semi-permeable membrane with the separation characteristics in the intermediate range between reverse osmosis (RO) membrane and ultrafiltration (UF) membrane [1–3]. Compared with UF membrane, NF membrane has a smaller pore size, so organic molecules with molecular weight larger than 200 g/mol can be retained. Compared with RO membrane, NF membrane exhibits lower retention rates and higher permeability to monovalent ions and solvent, respectively, so a relatively higher solvent flux can be obtained at lower operating pressure. Therefore, NF process is now extremely attractive for water softening, drinking water purification, wastewater reclamation, as well as industrial process fluids treatment [4–9].

Effluents from ferment industry, rinse process, extraction process, textile dyeing process, pulp and paper industry, as well as metal industry, usually contain abundant acids like HCl, H_2SO_4, HNO_3, H_3BO_3, HBF_4 and other valuable substances [10]. These acidic industrial effluents can be potentially separated and recycled through nanofiltration. Unfortunately, the most commonly used commercial nanofiltration membranes made from cellulose acetate (CA) and polyamide (PA) fail to achieve the separation validity due to their sensitivity to strong acids in long-term applications [11–13]. To date, only membranes such as SelRO series made by Koch Membrane Systems, D-series by Desal/Osmonics and BPT series by Bio Pure Technology have been reported to be suitable for extreme pH conditions [14,15]. However, these membranes are costly and their compositions are not completely open. Therefore, it is in our best interest as membrane researchers to exploit novel NF membranes with outstanding acid resistance associated with good separation property and reasonably low cost.

Polysulfonamide (PSA) is a sort of polymer having similar chemical structure with polyamide. It has been reported that PSA exhibited superior chemical and thermal stabilities due to the stable sulfonyl and phenyl units and the conjugation effect [16]. The oxygen of S=O bond of polysulfonamide is less likely to be attacked by acid than that of C=O bond of polyamide. However, it is difficult to prepare polysulfonamide through the reaction of

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sulfonyl chloride and diamine due to the weak reactivity [17]. Few papers on the preparation of polysulfonamide composite semi-permeable membranes through interfacial polymerization of polysulfonyl chloride with diamine have been reported and thus this still remains an important objective. Trushinski et al. [18] prepared ploysulfonamide composite membranes with good separation performance through the interfacial polymerization of diamine with naphthalene-1,6-disulfonylchloride and naphthalene-1,3,6-trisufonylchloride, respectively, in carbon tetrachloride/chloroform/acetone–water system. However, no details of the acid stability of this type of membrane were demonstrated. Kurth et al. [19] developed the acid stable ploysulfonamide thin-film composite NF membrane by in situ interfacial polymerization of naphthalene-1,3,6-trisulfonylchloride in Isopar G with triethylenetetramine in water. It was reported that the obtained composite membrane possessed excellent acid resistance to 20% (w/v) H_2SO_4 aqueous solution.

Accordingly, this study focused on the development of polysulfonamide (PSA) thin-film composite membrane with improved acid stability for nanofiltration from naphthalene-1,3,6-trisufonylchloride (NTSC) and piperazine (PIP) by in situ interfacial polymerization on porous polysulfone support membrane. Parametric studies including monomer content, reaction temperature, and additive in organic phase were conducted, which resulted in the optimal preparation conditions for the fabrication of the PIP-NTSC composite nanofiltration membrane. The chemical structure of the skin layer of the resultant membrane was characterized by using attenuated reflectance infrared (ATR-IR) and X-ray photoelectronic spectroscopy (XPS), while scanning electron microscopy (SEM) and atomic force microscopy (AFM) were employed to study the membrane morphology including top surface and cross-section. Surface streaming potential measurements were also carried out to explore the membrane surface charge. The separation performance of the obtained NF membrane in terms of pure water permeability, molecular weight cut-off, rejection rates to different salts and removal rates to different anionic dyes were characterized via cross-flow permeation tests. Furthermore, the acid stability of the prepared PIP-NTSC thin-film composite membrane was studied through both static acid soaking tests and long-term permeation tests under acidic condition. Finally, the application of the developed membrane to the treatment of acidic waste water was also studied through long-term permeation test using copper/acid mixture.

2. Experimental

2.1. Materials and reagents

Such monomers as naphthalene-1,3,6-trisufonylchloride (NTSC) and piperazine (PIP) were used to prepare the thin-film composite polysulfonamide nanofiltration membrane on porous polysulfone support membrane. Monomer PIP (powder, 99.5%) was purchased from Shanghai Amino-Chem. Co. Ltd. China. Monomer NTSC was synthesized in our laboratory according to the literature procedure [20] through the reaction of trisodium-1,3,6-naphthalenetrisulfonate (NTSNa) (TCI, Japan) with thionyl chloride ($SOCl_2$) (Tianjin Bodi Chemical Company, China) in N,N-dimethylformamide (DMF) as outlined in Scheme 1. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.530∼8.579 (1H, d), δ 8.989 (1H, s), δ 9.048 (1H, s), δ 9.139 (1H, s), δ 9.177∼9.200 (1H, d). IR (cm^{-1}, KBr): 1370, 1180 ($-SO_2$).

Isopar G (Isoparaffin type hydrocarbon oil purchased from Guangdong Jesan Chemical Ltd. China) was used to prepare the organic phase solution. Acid acceptor triethylamine (TEA) (liquid, 99.5%; Sigma-Aldrich) and sodium dodecylsulfate (SDS, purchased from Shantou Xilong Chemical Factory, China) were used as the additives to the aqueous phase solution, while ethylene glycol monomethyl ether (EGME, got from Sinopharm Chemical Reagent Shanghai Co., Ltd, China) was the additive to the organic phase solution. Polyethylene glycol (PEG) with molecular weights of 600, 1000, 4000, 6000, 10,000, 20,000, 35,000 and 100,000 Da (purchased from Sigma-Aldrich) were used as the model solutes to determine the molecular weight cut-off (MWCO) of the resultant membrane. Organic anionic dyes including Congo red (M_W=696.7 g/mol; Fisher Scientific, Hong Kong), Sunset yellow (M_W=452.4 g/mol; Aladdin) and Alizarine yellow R (M_W=287.2 g/mol; Aladdin), as shown schematically in Fig. 1, were used as model solutes for investigating the dye removal performance of the resulting composite membrane.

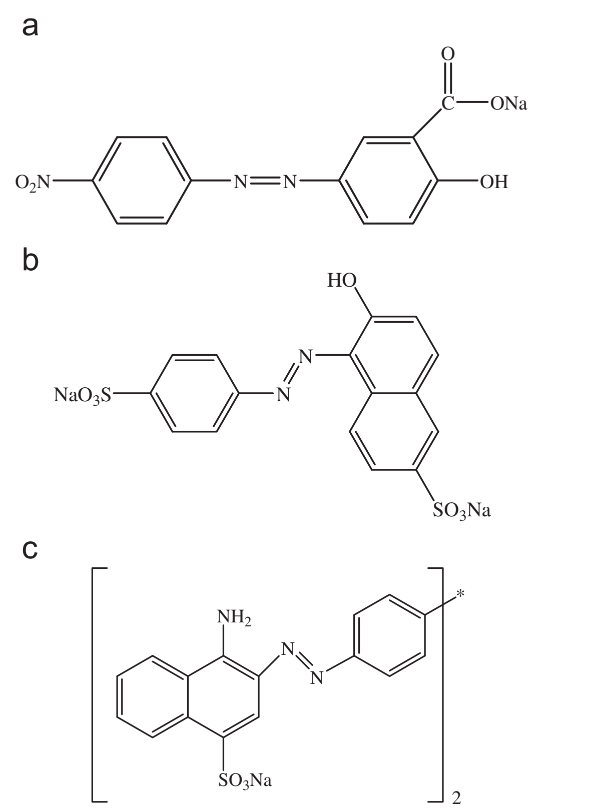
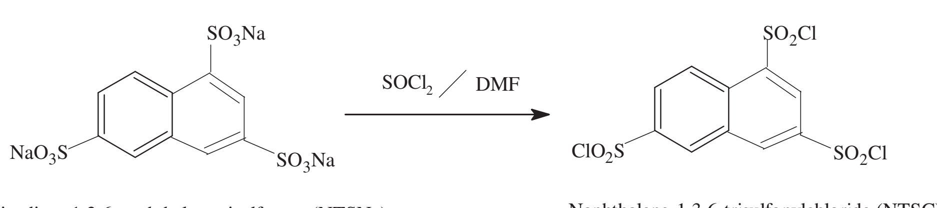


Fig. 1. Molecular structures of the organic anionic dyes used in the experiments. (a) Alizarine yellow R, (b) Sunset yellow and (c) Congo red.



Scheme 1. Synthetic routine of monomer NTSC.