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A novel crosslinking technique towards the fabrication of high-flux polybenzimidazole (PBI) membranes for organic solvent nanofiltration (OSN)

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ABSTRACT

A green crosslinking method has been proposed to design high-flux polybenzimidazole (PBI) membranes for organic solvent nanofiltration (OSN). Integrally skinned asymmetric PBI membranes were crosslinked using a solution containing trimesoyl chloride (TMC) and environmentally benign 2-methyl tetrahydrofuran (2-MeTHF) for the first time. The separation performance of the crosslinked PBI (X-PBI) membranes towards various solutes and solvents, including polar and nonpolar solvents, have been carefully studied. The X-PBI membrane shows a rejection of 99.6% to remazol brilliant blue R (MW of 627 g/mol) while it has pure acetonitrile, acetone, ethanol, and isopropanol permeances of 40.7, 29.0, 13.8, and 5.8 LMH/bar at 10 bar, respectively. Moreover, the X-PBI membrane exhibits superlative performance during the 2-step filtration of tetracycline, an antibiotic compound with a MW of 444 g/mol. It has rejections of 90.4% and 97.8% in the first and second steps of filtration, respectively. The X-PBI membrane is also able to concentrate solutions containing L-α-lecithin, a food additive with a MW of 758 g/mol, from hexane. It has a L-α-lecithin rejection of 92% and a pure hexane permeance of 80.8 LMH/bar at 10 bar. Besides, it shows great potential to separate mixed dyes and stable OSN performance during 96-h continuous tests.

1. Introduction

Liquid separation plays a crucial role in chemical, food, pharmaceutical and petrochemical industries. The most conventional processes employed for fractional separation are adsorption, flash chromatography, and distillation but they are usually energy intensive or/and use a large amount of solvents. These lead to higher production costs and more environmental concerns. To minimize energy consumption, waste generation, and plant footprint, organic solvent nanofiltration (OSN) is a cost-effective alternative separation technique with high energy efficiency and environmental benign. OSN, equally known as solvent resistant nanofiltration (SRNF), is an emerging membrane-based separation technology which can be directly employed in the current manufacturing systems [1–5].

Regardless of advantages, OSN still experiences some shortcomings which have to be solved for broader applications [1,6]. Out of them, the chemical stability of OSN membranes in harsh organic solvents is of great concern to membrane scientists and industrial users. Therefore, most studies on this topic have been aimed at novel materials [7–10] and improvements of the existing ones [11–21], with the aid of knowledge from other membrane processes, e.g. gas separation, pervaporation, aqueous nanofiltration (NF), and reverse osmosis (RO). For example, polymer crosslinking, which has been investigated tremendously for polyimide-based pervaporation membranes, is the most effective and facile approach to substantially improve the chemical stability and separation performance of OSN membranes [1–4,22–27]. Similarly, polybenzimidazole (PBI), which have been used for RO, NF and pervaporation membranes in harsh environments due to their outstanding chemical, thermal, and mechanical stability [28–31], is a popular material for OSN [13,14,32–34]. Xing et al. [13] reported PBI-based membranes fabricated from ionic liquid/PBI dope solutions were stable in dimethyl sulfoxide (DMSO) after being crosslinked with 1,2,7,8-diepoxyoctane (DEO). Valtcheva et al. [14] crosslinked PBI membranes with α,α′-dibromo-p-xylene (DBX). The resultant membranes showed superior chemical stability in high concentrations of acids and bases as well as N,N-dimethylformamide (DMF). Sun et al. [33] introduced a facile method to fabricate dual-layer OSN hollow fiber membranes where non-crosslinked PBI acted as the selective layer and crosslinked P84 used as the support layer. The membrane showed a high rejection of ∼100% to methylene blue (MW = 319.85 Da) in

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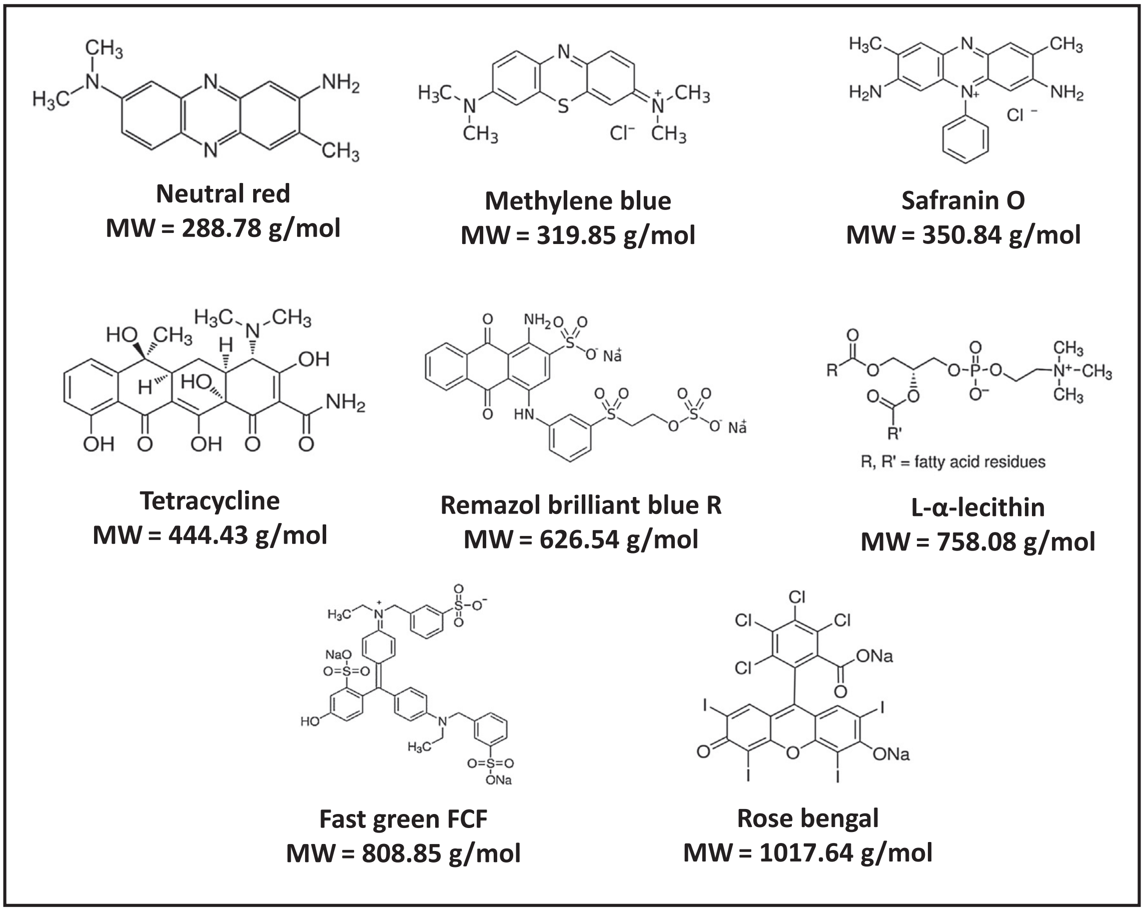

Fig. 1. The molecular structures of model solutes used in OSN tests.

water, methanol, and acetonitrile. Generally, the dual-layer membranes consist of two layers co-fabricated using different materials. The selective layer is usually made up of a polymer with an outstanding performance while the support layer is made up of a relatively cheap and commercially-available polymer [35,36]. This cost-effective and convenient fabrication process could be apt for OSN. Chen et al. [34] studied the modification of PBI asymmetric membranes with p-xylylene dichloride (PXDC). The modified PBI membranes had much higher rejections than the unmodified ones due to the formation of crosslinking networks. Moreover, the former had significantly improved solvent stability compared to the latter. PBI membranes crosslinked with α,α′-dichloro-p-xylene had also been reported for the separation and concentration of cephalexin from aqueous solutions over a pH range from 2 to 10 [37].

Recently, Zhu et al. [38] reported a technique to crosslink PBI dense membranes using a solution containing terephthaloyl chloride (TCL) and tetrahydrofuran (THF). They showed that the reaction rate between TCL and PBI was extremely fast; however, the rate-controlling step for the crosslinking of PBI dense membranes was the diffusion of TCL molecules into the membranes, which depended upon the degree of PBI swelling in the TCL/THF solution. Therefore, an extended crosslinking time resulted in a higher degree of crosslinking and better solvent resistance. Despite the fact that PBI membranes can be crosslinked by the TCL/THF solution at room temperature, both THF and TCL are relatively hazardous and toxic. These may limit their broad applications in the industry.

Trimesoyl chloride (TMC) is known as a common monomer with a less toxicity (compared to TCL) for the interfacial polymerization of the polyamide layer in RO membranes for decades [39]. However, there is no report on the utilization of TMC for the chemical modification of PBI membranes. The reaction between the three acyl chloride groups of TMC and the secondary amines on imidazole rings of PBI can result in tertiary amide groups and thus crosslink the PBI chains. To facilitate the diffusion of TMC molecules into the PBI membrane, a solution containing TMC and green 2-Methyl tetrahydrofuran (2-MeTHF) would be used. 2-MeTHF was initially proposed as a biofuel; but, it is currently used as a renewable and green alternative to THF [40,41]. Early studies have shown its low toxicity. Thus, it has been approved to be used in pharmaceutical processes [42]. Moreover, 2-MeTHF can be abiotically degraded by air and sunlight, probably via oxidation and ring-opening [40]. In this study, we have used both THF and its green alternative, e.g. 2-MeTHF, to prepare TMC containing crosslinking solutions. Although a TCL/THF solution was previously used by Prof. Lin and his coworkers to crosslink PBI for gas separation [38], our preliminary study disclosed that the TMC/2-MeTHF crosslinking solution is more effective than the TMC/THF solution to crosslink PBI for OSN applications. Accordingly, most of the experiments, characterizations, and discussions are allocated to the membranes crosslinked with the TMC/2-MeTHF solution.

Since the reported PBI crosslinking methods need either multiple steps, elevated temperatures, or utilizing of hazardous chemicals [13,14,38], a single-step, room temperature, and environmentally-friendly crosslinking technique is desired for the development and scale-up of PBI-based OSN membranes. Accordingly, the objectives of this work are to (1) propose a novel, effective, and rather green crosslinking method using TMC/2-MeTHF solution for the fabrication of PBI-based OSN membranes, (2) study the separation performance of crosslinked PBI membranes for various solutes and solvents as well as their potential applications in pharmaceutical and food industries, and (3) explore the performance of the crosslinked PBI membranes for