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A new technique to fabricate high-performance biologically inspired membranes for water treatment

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ABSTRACT

Aquaporin, a highly selective water channel protein, has received worldwide attention because of its potential to form biomimetic membranes with high flux and rejection for water reuse and desalination. In this study, purified aquaporins were incorporated into the active layer of the polybenzimidazole (PBI) nanofiltration membrane. Aquaporins were dispersed in gum arabic and embedded in amphiphilic polyvinyl alcohol with alkyl side chains (PVA-alkyl). PVA-alkyl embedded with treated aquaporins was then attached to flat sheet PBI membranes using carbodiimide chemistry. PVA-alkyl acted as support for aquaporins to prevent their chemical alteration and also gave the membranes mechanical strength. It was found that membranes modified with PVA-alkyl-AqpZ displayed lower flux declines and higher flux recoveries as compared to unmodified PBI membranes. Higher protein and salt rejections were also observed using PVA-alkyl-AqpZ modified membranes as compared to unmodified PBI membranes.

1. Introduction

Water is an essential component in all separation processes involved in any application. Water is required in varying degrees of purity depending on the application for which it is used. Membrane separations play an important role in different industrial applications related to water, energy, pharmaceutical and life sciences. These membranes provide an alternative to conventional separation processes to obtain cost effective and high quality water [1–3]. However, there are some drawbacks involved with membrane separation processes; in particular, desalination membranes provide very low water flux values. In addition, limited lifetime of membranes, insufficient pollutant rejection, further treatment of concentrates, and chemical resistance of membranes are some of the problems faced while dealing with membrane separations [4–8] Nanofiltration membranes can be used for brackish water desalination but membrane fouling, pretreatment, membrane cleaning, limited recoveries, feed water loss, and short lifetimes of membranes are some of the problems involved in it [1]. Therefore, even though membrane separations are now established processes for water treatment, there is still need to develop improved membranes that would avoid these limiting issues.

Aquaporin is a bidirectional water channel protein present in cell membranes, and it regulates the flow of water in and out of cells. Aquaporin has, therefore, a potential to improve the water flux through incorporation into synthetic polymeric membranes. Water passes through porous structures as a single unbroken column of molecules with hydrogen bonds between adjacent water molecules. These water molecules can carry protons as well through these structures in the form of H_3O^+ ions. However, this flow of protons along with water is prevented while passing through aquaporins. Aquaporins have pores which are constricted in the middle and wider at the openings. This constriction leads to a high dielectric barrier for charged entities like protons or other ions, while allowing the passage of small, neutral solutes. The backbone amide and carbonyl groups in the Asparagine-Proline-Alanine motif that lines the pore walls in aquaporin make

Abbreviations: PBI, Polybenzimidazole; PVA-alkyl, Polyvinyl alcohol with alkyl side chains; AqpZ, AquaporinZ; GA, Gum arabic; PVA, Polyvinyl alcohol; DMAc, N,N-Dimethylacetamide; LiCl, Lithium chloride; DI water, Deionized water; CMBA, 4-chloromethyl benzoic acid; PVA–COOH, carboxy methyl polyvinyl alcohol; NaOH, Sodium hydroxide; $ClCH_2COONa$, Sodium monochloroacetate; DMSO, Dimethyl sulfoxide; $CH_3(CH_2)_{14}CHO$, Hexadecanal; HCl, Hydrochloric acid; LB, Luria broth; SDS–PAGE, Sodium dodecyl sulfate–Polyacrylamide gel electrophoresis; OG, *n*-octyl-D-glucopyronoside; EDCH, N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride; NHS, N-hydroxysuccinimide; MES, 2-(N-morpholino) ethanesulfonic acid; NaCl, Sodium chloride; FTIR, Fourier Transform Infrared spectroscopy; ATR, Attenuated Total Reflectance; BSA, Bovine Serum Albumin; UV–VIS, Ultraviolet–visible; ESEM, Environmental Scanning Electron Microscopy; $CaCl_2$, Calcium chloride.

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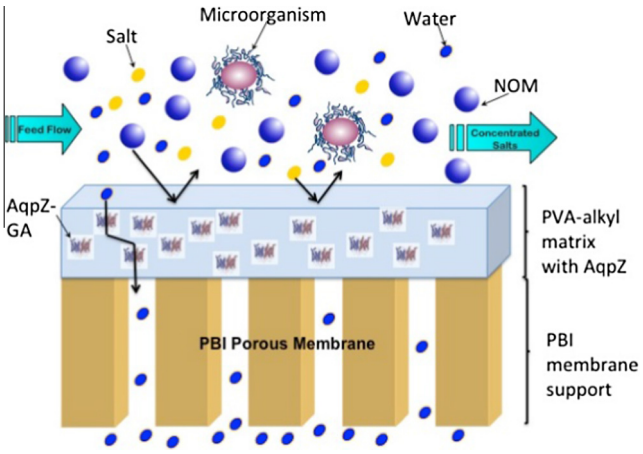

Fig. 1. Schematic of biomimetic membranes.

hydrogen bonds with the water oxygen atoms, causing reorientation of water molecules to become perpendicular to the pore axis. In this orientation the water hydrogen atoms can't make H-bonds with adjacent water molecules. All of the other groups present on the pore-walls are hydrophobic, leaving the water hydrogen atoms without hydrogen bonding partners. This raises the energy by nearly equal 3 kcal/mol [9–12] thus allowing water passage with a minimal energy barrier. The activation energy for the transport of water through Aqp is about 3 kcal which is close to hydrogen-bonding energy, suggesting breakage of hydrogen bonds in the water flow [13].

For this research project, AqpZ, a water channel protein found in *Escherichia coli* was used, since it is inexpensive and can be expressed in large quantities. AqpZ has been shown to be robust under different reducing conditions and at low temperatures. It can retain 100% activity for up to 6 months of storage at 4 °C. [11,14]. The overarching purpose is to improve water permeability while enhancing ion rejection, by incorporating AqpZ into the membrane. Successful formulation could then lead to the formation of biomimetic membranes with high selectivity and high water flux. In this study, aquaporins were treated with gum arabic (GA), a polysaccharide used previously to disperse carbon nanotubes to PVA successfully with the key purpose of preventing excessive functionalities that lead to disruption of the original structures.[15]. Gum arabic is a water soluble polysaccharide produced by Acacia Senegal trees. . In modern times, the most important applications of gum arabic have been as an emulsifier in the food and pharmaceutical industries and as an adhesive [16–18]. Gum arabic has been used in the food industry as a stabilizer, thickener, emulsifier, anti-caking agent as well as color preservative [19]. It has also been used to slow down the deterioration of inks [20,21], and it has been observed to be significantly enhance the stability of iron-gall inks [22]. Gum arabic has been used to increase the durability of the functional textiles and add value to them [23]. Gum arabic conjugated polysaccharides showed an unusually high tolerance to salts, thermal instability and lower stability in alkaline conditions [24]. This ability of GA to prevent functionality of materials is exploited here with the purpose to have it protect the aquaporins from being functionalized in the presence of PVA. GA acted as an intermediate layer to enhance the interfacial interaction between the selective layer and the substrate, thus making the assembly stronger. Aqp-GA was then dispersed in a polyvinyl alcohol matrix carrying alkyl side chains (PVA-alkyl). PVA-alkyl is amphiphilic in nature with high hydrophilicity of PVA and hydrophobicity of the long alkyl side chains. This polymer has good film forming properties and outstanding physical and chemical stability [25], and is proposed to be an excellent material to support aquaporins. Thus, by attaching PVA-alkyl matrix with Aqp-GA dispersed in it to the hydrophilized PBI membranes, the assembly was made mechanically stronger and was designed to withstand higher hydraulic water pressure gradients.

2. Research objective

The objective of the project is to make a new class of biomimetic nanofiltration membranes made of aquaporin dispersed in a membrane selective layer and capable of operation under high hydraulic pressure. The PVA-alkyl with embedded aquaporins will be used as the nanofiltration membrane active layer (Fig. 1). Aquaporins are dispersed into PVA-alkyl layer, but not necessarily aligned into the layer. Aquaporins are bidirectional in nature; hence, even if their orientation is different than aligned, it does not affect the transmembrane water transport.

3. Methodology

3.1. PBI membranes casting

The dope polymer used to cast the backbone of the membranes was polybenzimidazole (PBI). PBI is stable polymer, which has robust mechanical strength with thermal stability for a wide range of high temperature applications and it also provides chemical stability over a wide pH range. PBI membranes are hydrophobic [26,27], and are strong but brittle [28–30]. The structure of PBI molecule is shown in Fig. 2. The imidazole ring of PBI contains two nitrogen atoms, one protonated to serve as a potential hydrogen bond donor and the other nitrogen has a lone pair, which can act as a proton acceptor.

The solvent used to make the dope solution was N,N-Dimethylacetamide. Commercially-available 26% w/w dope solution, containing 26% PBI polymer, 72% N,N-Dimethylacetamide (DMAc) and 2% Lithium chloride (LiCl), was used and obtained from PBI Performance Products, Inc. (Charlotte, NC). LiCl served the function of a pore former, preventing PBI polymer from phasing out of the solution [29,31] and imparting long shelf life to the solution. The dope solution was diluted to 21% PBI by adding solvent, and the solution was sealed with parafilm to prevent air bubbles from being trapped inside the solution and affecting its homogeneity. Because of very high viscosity of the solution, the solution was kept in the sonicator and degassed for 2 days in order to ensure homogeneous mixing of the solvent and the solute. After sonication, the solution was allowed to come to room temperature and then the solution was ready for membrane casting using the phase inversion process. Phase inversion is the phenomenon whereby the phases of a liquid–liquid dispersions interchange such that the dispersed phase spontaneously inverts to become the continuous phase [30,32]. The non-solvent phase that was used in this process was water. The PBI chemistry used here was identical to that of previous studies which made nanofiltration membranes with a pore size of 0.61 nm, so the unmodified PBI membranes of this study should also be suitable for nanofiltration [28].

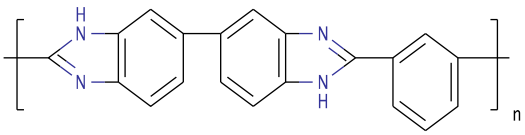

Fig. 2. PBI molecule structure.