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Flux performance and macrosolute sieving behavior of environment responsive formed-in-place ultrafiltration membranes

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ABSTRACT

The structure of the macro-porous gel-filled (MPG) ultrafiltration membranes used in this study consist of a porous support matrix filled with an 'active polymer network' which allows for dynamic control of the effective pore size of the membrane through appropriate adjustment of the solution pH and/or ionic strength. The performance of MPG membranes was shown to be significantly different from commercially available thin-film composite (TFC) ultrafiltration membranes. With MPG membranes, only charge based rejection was observed to affect the sieving behavior of dextran solutes. In this study MPG membranes made from three different porous supports were extensively characterized. Flux measurements at various solution pH and salt concentrations were used to quantify the 'valve effect' of the MPG membranes and indicated that the porosity of the support matrix had a significant effect on the membrane performance. The transmissions of neutral and charged dextrans were also found to be dependent on the support matrix.

1. Introduction

Environment responsive (ER) membranes are potentially attractive separation media due to their ability to dynamically change their pore size and charge properties in response to applied stimuli. The use of 'active polymer networks' in these membranes enable responsiveness to various environmental stimuli including pH/ionic strength [1–10], specific ions [4], electrical field [11], and temperature [12,13]. Membranes that are responsive to environmental stimuli are generally prepared by two distinct methods. The first method combines the responsive polymer component with standard membrane polymers to form a copolymer blend which is then processed through a typical membrane fabrication technique. The product is a membrane with directly embedded functionality within the polymer matrix [6,9,14]. The second method is a two-step process where the responsive polymer component is attached to a previously prepared porous matrix (e.g. an ultrafiltration (UF) or micro-filtration membrane). Two different types of membranes can be prepared by this attachment technique. The first type is designated as pore filled-wall grafted (PF-WG) and involves covalent bonding of an active polymer to the walls of the porous matrix to create a pseudo-brush structure that extends away from the membrane surface towards the center of the pore [2–4,8]. The second type, designated as pore filled-cross-linked (PF-CL), is prepared by completely filling the porous support with a polymer solution followed by a cross-linking step which locks the active polymer network within the porous matrix [7,10,12,13,15]. The matrix constrains the swelling properties of the gel and gives mechanical strength to the membrane.

Recently, Childs et al. [16] developed a class of PF-CL membranes known as macro-porous gel-filled (MPG) membranes. These composite materials are composed of a polymeric support matrix whose pores are uniformly filled with a macro-porous cross-linked gel. The macro-porous gel is non-self supporting and as such is formed-in-place within the matrix through a cross-linking step. The pore size of the support matrix is much greater than the mesh size of the gel. Therefore, the effective pore size of the MPG membrane, and hence the transport properties, is determined by the average distance between the polymer chains. The membranes are made to be pH-sensitive by the incorporation of weak acid or weak base functional groups within the gel network. A change in solution pH shifts the degree of ionization of the charged groups. This increase or decrease in charge repulsion effects controls the effective pore size of the membrane by balancing the natural coiling tendency of the polymer chain.

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Table 1
Properties of porous supports used to prepare MPG membranes.

Membrane ID	Support supplier	Support material	Support thickness (μm)	Support max pore diameter (μm)	Support mean pore diameter (μm)	Membrane porosity (%)
MPG-3M	3M	PP[a]	125	N/A	0.45	85
MPG-HV6	HV[b]	PP[a]	270	32.9	6.5	79
MPG-HV15	HV[b]	PP[a]	159	48	15	67

[a] Polypropylene.
[b] Hollingsworth & Vose (HV).

The objective of this study was to characterize the flux performance and macrosolute sieving behavior of MPG membranes. Three different micro-porous supports with a range of pore size (0.45–15 μm) were filled with the same polyelectrolyte gel network. Carboxylic acid functionality within the gel network allowed for dynamic control of the effective pore size of the membrane by varying the solution pH and/or ionic strength. The results from the study are used for two distinct comparisons: the first is to compare the effect of the properties of the support matrix on the MPG membrane performance, the second is to compare the transport properties of MPG membranes to a thin-film composite (TFC) membrane which is the standard membrane morphology for existing commercial processes. The functionality and structure of TFC membranes are substantially different than MPG membranes since their effective pore size is not responsive to environmental stimuli and is determined exclusively by a thin active layer supported on a porous substrate which provides mechanical strength. The Omega^{TM} membrane (Pall Corporation) has been well studied in the literature and was used for comparison.

Previous studies have investigated the effect of the support material on gel-filled membranes. Mika et al. [7] reported that for poly(4-vinylpyridine) gels, the ratio of volumetric throughput for the open and closed structure significantly increased as the average pore diameter of the support increased (0.19–0.82 μm). In contrast, Buehler and Anderson [17] reported minimal change in the water permeability for polyacrylamide gel-filled membranes prepared from five different support materials with a pore diameter range of 0.09–0.48 μm. Comparison of flux measurements for various feed solution conditions is the classical technique used to characterize the stimuli responsive performance (i.e. 'valve effect') of ER membranes. Also, the rejection behavior of macromolecular solutes has been used to characterize the performance of ER membranes [2,6,8,12–14] with the typical protocol employing an apparatus to achieve pseudo-steady state conditions and collection of samples followed by off-line sample analysis. Ghosh and Cui [18] developed the pulsed sample injection technique (PSIT) for rapid characterization of UF membranes. This is an advanced characterization technique that analyzes the solute sieving behavior in constant flux experiments along with an integrated analysis of the solute transport kinetics and membrane fouling tendency. It was previously demonstrated to be a valid technique for the analysis of protein [18] and dextran [19] UF with TFC membranes and therefore is employed for the characterization of MPG membranes. The information presented herein is unique in that there have been no previous reports of the use of charged dextran solutes to characterize the combined steric and electrostatic repulsion effects of ER membranes.

In this study, a detailed investigation of the microstructure, function, and performance of MPG membranes is presented. Charge information is obtained from potentiometric titration experiments, membrane functionality is determined from flux measurements, and macromolecular solute sieving behavior is determined from stirred cell UF experiments. These results are used in combination to determine the effect of the properties of the support material on the MPG membrane performance.

2. Experimental

2.1. Materials

All chemicals were used as received unless otherwise specified. The following salts were purchased from Sigma–Aldrich: sodium chloride (S-7653), sodium phosphate monobasic (NaH_2PO_4) (S-0751), and sodium phosphate dibasic (Na_2HPO_4) (S-0876). All solutions were prepared using ultra-pure water from a NANOpure DIamond Life Science (Barnstead International) purification system. The solutions were micro-filtered and degassed using a membrane filtration unit fitted with a 0.45 μm cellulose acetate membrane (Nalgene Nunc International). Two different buffer solutions were used for the experiments: 10 mM NaCl–34.8 mM NaH_2PO4 and 10 mM NaCl–20 mM Na_2HPO_4 with corresponding solution pH of 4.8 and 8.7 verified with an Oakton pH 1100 meter.

Neutral dextrans of various weight-average molecular weight (Mw) were purchased from Sigma–Aldrich: dextran 71 kDa (D-1537, Lot 51K1607), dextran 464 kDa (D-1037, Lot 062K1415), and dextran 2000 kDa (D-5376, Lot 023K0952). Two different charged dextran solutes were also purchased from Sigma–Aldrich: a polycationic dextran derivative, diethylaminoethyl dextran chloride form (DEAE-dextran) (D-9885, Lot 013K0753), and a polyanion dextran derivative, dextran sulfate sodium salt (DSSS) (D-8906, Lot 113K1483). According to the supplier, both charged solutes were synthesized by appropriate substitution onto a 500 kDa neutral dextran. Dextran solutions were prepared by mixing 2 g of solute in 50 ml of solution to create a 40 mg/ml test solution. Omega^{TM} membranes with a nominal molecular weight cut-off of 300 kDa were purchased from Pall Corporation.

2.2. Membrane preparation and conditioning

Three MPG membranes were fabricated using porous supports of different properties (see Table 1). MPG-3M was prepared using a polypropylene (PP) support supplied by 3M with a mean pore diameter of 0.45 μm. MPG-HV6 and MPG-HV15 were prepared using a non-woven PP support supplied by Hollingsworth and Vose (HV) Company with mean pore diameters of 6.5 and 15 μm respectively. The same polymer solution was used within each support material to produce a polyelectrolyte gel network that contained weak carboxylic acid groups. The gel network was formed as per the technique described by Childs et al. [16] using photoinitiated free radical polymerization of acrylic acid (ionic monomer), acrylamide, and trimethylolpropane triacrylate as a cross-linker. The molar ratio of acrylic acid to acrylamide was 1:1 and 1,4-dioxane was used as a solvent in all experiments. The total concentration of monomer in all mixtures was 24%, the degree of cross-linking was approximately 10% and UV was irradiated for 10 min. After polymerization, the responsive composite material was washed with de-ionized water for about 16 h. The sample was thoroughly washed and stored in a 0.1 wt% sodium azide solution to prevent bacterial growth. Circular membrane discs were cut from each membrane sheet and placed in a custom stirred cell module (description is given below). Before any experiments, each membrane disc was first 'conditioned' by alter-