Journal of Membrane Science 365 (2010) 302–310

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

# Inverse colloidal crystal microfiltration membranes

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ARTICLE INFO

*Article history:*
Received 19 May 2010
Received in revised form
12 September 2010
Accepted 14 September 2010
Available online 18 September 2010

*Keywords:*
Dead-end filtration
Lateral permeability
Microfiltration
Particle fractionation
Porosity

ABSTRACT

Uniform pore size, high porosity membranes are important for applications such as microfiltration and ultrafiltration, as well as for use as membrane adsorbers. In this work, uniform pore size, high porosity microfiltration membranes were developed using three-dimensionally ordered macroporous templates. A membrane casting cell was designed for self-assembly of silica spheres into a colloidal crystal template. The resulting close-packed colloidal crystal was infiltrated with a reactive monomer solution. After polymerization, the silica spheres were etched away, resulting in an inverse colloidal crystal (ICC) membrane with high porosity and uniform pores that are highly interconnected.

ICC membranes have been fabricated with a range of pore sizes and thicknesses. The membrane casting cell facilitates easy variation of membrane thickness. The membrane pore size is varied by changing the diameter of the silica spheres used to prepare the colloidal crystal template. By changing the composition of the reactive monomer solution, membranes have been fabricated with different hydrophilicities. Following synthesis, the ICC membranes were tested in a commercially available stirred cell. Particle fractionation was studied in normal flow filtration experiments. For bi-disperse particle suspensions, significant passage of particles smaller than the membrane pore size was observed if the ratio of large to small particles was around 14.

## 1. Introduction

Microfiltration is used frequently for solid–liquid separations involving aqueous streams [1]. It is used in the biotechnology, electronics, chemical and food industries to separate particulate matter from the suspending liquid [2]. Microfiltration may be run in either tangential flow or dead-end mode. Typical applications include rejection of bacteria and colloids in the production of drinking water, rejection of microparticles in the production of ultrapure water and other liquid streams in the semiconductor industry, rejection of pyrogens in sterile filtration applications, and validation of virus clearance in the manufacture of biopharmaceutical products. In all of these applications, the desired product is the permeate stream that passes through the membrane pores.

In addition to particle clearance, particle fractionation by microfiltration has been studied by several groups. For example, Leiviskä et al. [3] investigated the use of 8, 3, 0.45 and 0.22 μm nominal pore size membranes for fractionation of wood extractives, lignin and trace elements in pulp and paper mill wastewater. Gan et al. [4] investigated beer clarification by microfiltration. Here the process requirements involve rejection of colloidal particles such as yeast cells, flocs, etc, and passage of large macromolecules such as carbohydrates, proteins, flavor and color compounds. Wakeman and Akay [5] have investigated concentration and fractionation of latex particles, while Kromkamp et al. [6] studied concentration and fractionation of model fluorescent particles. Brans et al. [7] have developed micro-machined membranes or microsieves with carefully controlled pore size, geometry and porosity. They indicate that by carefully controlling pore geometry, size and porosity, one can optimize processes aimed at either complete rejection of particles or fractionation of particles, while maximizing permeate flux. In a more recent study, Brans et al. [8] investigated transmission and fractionation of micron-sized particles in both tangential flow and normal flow filtration.

Optimization of microfiltration processes involves maximizing membrane capacity, productivity and selectivity [9]. Membrane capacity refers to the maximum volume of feed that can be treated before the permeate flux drops to unacceptably low values. In the case of tangential flow filtration, filtration is stopped and the membrane cleaned; while, for normal flow filtration, the membrane usually is replaced. Membrane productivity refers to the rate at which the feed can be processed (i.e., maximum sustainable per-

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doi:10.1016/j.memsci.2010.09.020

meate flux). Selectivity refers to the ability to yield high product recovery and removal of unwanted particulate matter.

This work focuses on normal flow microfiltration, as used in the biopharmaceutical industry for sterile filtration and virus clearance applications [2]. Ho and Zydney have investigated the effects of membrane morphology on membrane capacity during normal flow microfiltration [10–14]. They indicate that membrane morphology can have a significant effect on flux decline due to membrane lateral permeability. For membranes with non-connected straight through pores, the rate of flux decline tends to vary inversely with membrane porosity but becomes independent of porosity at higher porosities due to the possibility of a single particle blocking more than one pore. The rate of flux decline for isotropic membranes with highly interconnected pores is much slower than for membranes with non-connected pores, even for membranes with similar porosity. Pore interconnections allow fluid to flow around a deposited particle as it passes through the membrane. Thus, blockage of a pore mouth does not result in blockage of the entire pore. This result highlights the importance of lateral permeability within the membrane.

Ho and Zydney note that for asymmetric membranes with a tight skin layer, the flux decline is often similar to a membrane with non-interconnected pores. For a thin, tight skin layer, the flow has insufficient time to pass around blocked pores resulting in a behavior similar to a membrane consisting of non-interconnected pores. They discuss the effect of a membrane support structure in a composite membrane on flux decline due to the different lateral permeabilities of the different layers [13].

These previous studies highlight the benefits of fabricating microfiltration membranes with a high porosity, regular pore structure and high lateral permeability (highly interconnected pore network). This contribution describes the use of colloidal crystal templates for the development of such a membrane. Colloidal crystals or photonic crystals are three-dimensionally periodic structures formed from monodisperse colloids [15]. Self-assembly of the colloidal spheres into a close-packed arrangement results in a colloidal crystal that displays a periodically modulated dielectric constant with a period similar to that of visible light (380–790 nm), resulting in a partial photonic band gap [16,17]. Natural opals are an example of a colloidal crystal composed of face-centered arrays of amorphous silica spheres.

Conceptually, colloidal crystals may easily be converted into inverse colloidal crystals or inverse opals, which are three-dimensionally ordered macroporous (3DOM) materials. The close-packed colloidal crystal is infiltrated with a reactive monomer solution. After polymerization, the colloidal particles are removed by thermal processing, solvent extraction or chemical etching. The resulting 3DOM structure will have a very regular pore size, high porosity and high level of pore interconnectivity. Numerous potential applications for inverse colloidal crystals have been described [18] including photonic crystals and optical devices [16,19,20], sensors [21–24], catalysts [25,26], magnetic materials [27,28], electrodes and batteries [29] and bioactive materials [30].

Here, inverse colloidal crystal (ICC) microfiltration membranes have been developed. Previous studies report the use of colloidal crystal templates as sieves for separation applications [31–33]. A few investigators also have described fabrication of ICC membranes. Though numerous methods have been described for the preparation of very small surface area colloidal crystal templates, fabrication of ICC membranes requires self-assembly of a large defect-free template that can be fabricated into a defect-free membrane. Park and Xia [34,35] and Gates et al. [36] describe the fabrication of ICC membranes using polystyrene and silica particles. They measured permeabilities of various solvents and found Darcy's law to be applicable. However, given the very small membrane surface areas (around 0.2 $\text{cm}^2$) they were able to fabricate, they needed to custom design an apparatus to measure membrane permeability. Yan and Goedel [37] and Jiang and McFarland [38] describe the formation of wafer-sized ICC membranes. However, their fabrication method leads to very thin membranes that lack the mechanical stability for testing in commercially available stirred cells, which limits their practical applicability.

A method for fabrication of ICC microfiltration membranes has been developed. These defect-free membranes are mechanically stable and large enough to be tested in a commercial stirred cell. A method is described for self-assembly of the colloidal crystal template and fabrication of the membrane. Permeate fluxes have been determined for a number of membranes with different pore sizes and thicknesses. In addition, particle fractionation using ICC membranes has been investigated.

## 2. Experimental

### 2.1. Materials

The following chemicals were obtained from Sigma Aldrich (St Louis, MO): ethylene glycol dimethacrylate (EGDMA, 98%); hydroxybutyl methacrylate, mixture of isomers (HBMA, 94%); 2-hydroxyethyl methacrylate (HEMA, 97%); benzoin isobutyl ether (BIE, 90%); hydrofluoric acid (HF, 40%); tetraethylorthosilicate (TEOS, 99%); hydrogen peroxide (30%); sulfuric acid (95–98%) and ammonium hydroxide (28–30%). EGDMA, HBMA and HEMA were passed through a neutral $Al_2O_3$ column to remove polymerization inhibitors prior to use. TEOS was vacuum distilled prior to use. BIE and HF were used as received.

Ethanol (200 proof) was obtained from Pharmaco Products (Brookfield, CT) and used as received. Microscope cover glasses (24 mm × 50 mm × 0.1 mm) were obtained from VWR International (West Chester, PA) and cleaned using a mixture of 1:3 hydrogen peroxide-sulfuric acid before use. Mylar films with thicknesses of 25, 50 and 100 μm (to produce membranes with thicknesses of 25, 50 and 100 μm) were obtained from Grafix (Cleveland, OH) and cut into strips (25 mm × 10 mm). In some experiments, polyethersulfone microfiltration membranes (pore size 0.22 μm, thickness 100 μm, Pall Corp., NY) were used instead of Mylar. Silica particles (60 nm, 20% in water) were obtained from Allied High Tech (Rancho Dominguez, CA). All other silica particles were made as described below. A Millipore 8010 stirred cell (Millipore Corp., MA) was used for normal flow microfiltration experiments.

### 2.2. Preparation of monodisperse silica particles

Monodisperse silica particles were prepared based on the method by Stöber–Fink–Bohn [39]. Ethanol (210 mL) was added to a 500 mL flask. HPLC water (17 mL), ammonium hydroxide solution (11 mL), and TEOS (11 mL) were added sequentially. The reaction was conducted at room temperature for 4 h with agitation. The contents of the flask were centrifuged at 5000 rpm for 10 min. The solvent was then decanted, and a 50:50 (v/v) mixture of ethanol–water was added to resuspend the particles. The suspension was centrifuged at 5000 rpm for 10 min. The solvent was decanted and the particles again resuspended in a 50:50 (v/v) mixture of ethanol–water and centrifuged as before. This procedure was repeated three times to wash the particles.

Laser diffraction light scattering (Beckman Coulter LS 230, Fullerton, CA) was used to determine the particle size distribution. The resulting mean particle diameters were found to be 300–500 nm. Though there is batch-to-batch variation in the mean