Electronic Supplementary Information

Electrospun Nanofiber Membranes Surface Functionalized with 3-Dimensional Nanolayers as an Innovative Adsorption Medium with Ultra-High Capacity and Throughput

Todd J. Menkhaus*[a], Hemanthram Varadaraju,[a] Lifeng Zhang,[b] Steven Schneiderman,[a] Stephany Bjustrom,[a,b], Li Liu,[b,c] and Hao Fong*[b]

[a] *Department of Chemical and Biological Engineering, South Dakota School of Mines and Technology, Rapid City, South Dakota 57701, USA*
[b] *Department of Chemistry, South Dakota School of Mines and Technology, Rapid City, SD 57701, USA*
[c] *College of Materials Science and Engineering, Beijing University of Chemical Technology, Chao-Yang District, Beijing 100029, China*

Experimental

Materials: Regenerated cellulose microfiber filter paper was purchased from Fisher Scientific. Cellulose acetate (CA, M_n ~ 30,000 g/mol), acrylic acid (anhydrous), 2-bromoisobutyryl bromide, triethylamine, 1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam), methanol, H_3PO_4, KBr, tetrahydrofuran (anhydrous), Na_3PO_4 (anhydrous), NaCl, dimethyl sulfoxide (DMSO), and lysozyme from chicken egg white, were purchased from Sigma Aldrich. Copper (I) chloride and NaOH were purchased from Fisher Chemicals. Fast flow packed bed resin with carboxy-methyl functionality was purchased from GE Healthcare. Commercial membrane adsorbers (Mustang S) were purchased from Pall Corporation.

Electrospinning and hydrolysis/deacetylation: 20 wt.-% CA in 1:1 (wt/wt) THF/DMSO with 0.1 wt.-% diethylamino ethyl chloride was first prepared at room temperature. Subsequently, the solution was electrospun into CA nanofibers using the previously reported method[13]; the electrospun CA nanofiber membranes were then hydrolyzed/deacetylated by immersion in a 0.05 M NaOH aqueous solution for 24 hrs. The products (regenerated cellulose nanofibers) were rinsed with distilled water for 3 times and dried in a vacuum oven at 60° C. The nanofiber membrane had a thickness of ~200 μm and a mass per unit area of ~50 g/m^2.

Functionalization of membranes with surface-initiated ATRP of poly (acrylic acid) (PAA): Detailed ATRP methods have been published elsewhere,[S1] and were used here without modification. Briefly, membranes were contacted for 2 hrs with a solution comprising 2-bromoisobutyryl bromide (2-BIB, 10 mM) and triethylamine (10 mM) in anhydrous THF. The polymerization solution was comprised of the monomer of acrylic acid (AA, 5.43 wt.-%); catalyst, CuCl (0.005 wt.-%)/Me_4Cyclam (0.016 wt.-%), and HPLC-graded water as the solvent. AA was deprotonated by the addition of NaOH (12.92 wt.-%) to reach a pH end point of 10.2 followed by the addition of NaCl (18.57 wt.-%). Initiator-functionalized membranes were placed in the PAA polymerization solution for up to 2 hrs.

Sample characterizations: A Zeiss Supra 40VP field-emission SEM was employed to examine morphologies of the prepared samples. FT-IR spectra were obtained using a Bruker Tensor-27 FT-IR spectrometer equipped with a liquid nitrogen-cooled mercury-cadmium-telluride detector.

Protein Batch Adsorption: Batch adsorption experiments were completed with all varieties of the cation-exchange adsorption media. For membranes, a single layer was weighed, and placed into tubes. Lysozyme, in 20 mM sodium phosphate pH 7.0 buffer, was added to the tubes with an initial protein concentration between 0.0 and 2.0 mg/mL. After mixing for 24 hrs, liquid protein concentration determined by UV-280-nm absorbance with a Genesys 10 UV spectrophotometer (Thermo Electron Corporation, Madison, WI). By difference, protein adsorbed could be calculated. Langmuir adsorption isotherms were then prepared and modeling constants (Q_{max} and K_d) determined by least-squares regression fit to the equation:

$$Q = \frac{Q_{\max} C}{K_d + C} \qquad (1)$$

For kinetic uptake rate experiments, the same procedure was followed, but liquid samples were removed every 30 seconds for evaluation of protein concentration. Packed bed resin was evaluated in the same fashion described above, except resin was vacuum filtered to remove solution prior to weighing the adsorbent. For each

trial ~20 mg of adsorbent were used. Following the adsorption analysis, liquid was decanted away and the adsorption media was washed. 20 mM sodium phosphate plus 1.0 M NaCl, pH 7.0, was added to the tubes, mixed for 1 hr, and liquid sampled for lysozyme concentration. Elution percentage was calculated based on binding amounts found during the adsorption phase of the study. All experiments were completed in duplicate.

Permeability and Flow Distribution Analysis: Permeability of 20 mM sodium phosphate, pH 7.0, was measured with an AKTA purfier (GE Healthcare) with online measurement of pressure. The pressure drop was evaluated for one, three, and five layers of PAA functionalized nanofiber felts and a 15 cm packed bed of resin. The system pressure drop was subtracted from the measured pressure drop with the media in place to calculate permeability. A minimum of five flow rates and corresponding pressure readings were made. Flow distribution was monitored similarly by tracing the breakthrough of a non-binding solute (acetone) and monitored by UV absorbance at 280 nm. The response curve was fit the following equation to determine the Peclet number (Pe), where where C_{out} is the effluent 280-nm absorbance, C_{in} is the inlet 280-nm absorbance, V is the volume of acetone solution added, and V_{50} is the volume when $C_{out}/C_{in} = 0.50$. Larger values of Pe were used to indicate the desirable property of being a closer approximation to plug flow (less axial dispersion).

$$\frac{C_{out}}{C_{in}} = \frac{1}{2}\left\{1 + erf\left[\frac{(Pe)^{1/2}(V - V_{50})}{2(V \cdot V_{50})^{1/2}}\right]\right\} \qquad (2)$$

References

[S1] N. Singh, J. Wang, M. Ulbricht, S. R. Wickramasinghe and S. M. Husson, *J. Memb. Sci.*, 2008, **309**, 64.