

**Tailoring Filtration Membranes Using Photo-Induced Graft
Polymerization to Reduce Fouling by Natural Organic Matter and
Proteins, and to Manage Risk of EPA Candidate Contaminants**

by

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ABSTRACT

The overall objectives of this research were to better understand and develop ways to mitigate membrane fouling by organic substances and to increase rejection of water contaminants during filtration via UV-assisted graft polymerization of vinyl monomers on membrane surfaces. Approaches to membrane comparison and the effect of membrane surface properties on fouling were relevant to this research; therefore, they were also investigated.

Membrane research often presents the need to compare the performance of different membranes. In this thesis, we developed criteria and approaches to assess the performance of membranes having different properties by performing a sensitivity analysis using the combined pore blockage and cake filtration model for constant pressure dead-end filtration. When comparing membranes with different resistance, flux (or normalized flux) plotted versus either operating time or volume throughput tends to underestimate the fouling potential of membranes having higher intrinsic resistance. A better approach for comparing the fouling of different membranes is to plot the fouling resistance versus volume throughput, or versus accumulated mass on membrane surface when the solute rejection is different. This is strictly valid only when pore blockage is absent, but is an excellent approximation as long as the transition from pore blockage to a cake filtration has commenced. When pore blockage dominates fouling, we do not know how to separate the effects of fouling and membrane resistance; therefore, total resistance is the best criterion to compare membranes.

In this research, effect of membrane pore size and surface roughness on fouling and cleaning was investigated using a series of membranes having same material but a wide range of molecular weight cut-off (MWCO). These membranes were fouled by humic acid and nano-silica colloids, and subsequently cleaned with water and sodium hydroxide solution. We discovered that under our experimental conditions, when membrane roughness was lower than 30 nm, in general, fouling decreased with increasing membrane MWCO; therefore, the effect of pore size and rejection on flux was more important than roughness. However, when roughness was higher than 45 nm, it started to have effect on fouling. Results also demonstrate that larger foulants caused greater fouling for both organic (HA in presence of calcium, size of aggregates over 150

nm) and inorganic (40-50 nm colloidal silica) colloids. Membranes exhibiting lower roughness were easier to clean when affinity of foulant for the membrane surface was high (*e.g.* HA in presence of calcium), and/or when the foulant was similar in size to the membrane surface roughness value (as in the case for 10-20 nm silica colloids).

A novel high throughput method for synthesis and screening of customized foulant-resistant surfaces was developed by combining a high throughput platform (HTP) approach together with our patented photo-induced graft polymerization (PGP) method, to allow facile modification of commercial poly(aryl sulfone) membranes. The reproducibility of the HTP approach was verified, and the method was validated by comparing measures of membrane performance obtained using the HTP-PGP approach with literature data. The HTP-PGP approach is fast and efficient at selecting the best polymeric surface for filtration applications. It was employed in a discovery mode to identify surfaces that perform better than the as-received membrane. Using this approach, a library of 66 monomers was evaluated for their potential to reduce fouling by 6 feed solutions, including natural organic matter (NOM), bovine serum albumin (BSA), lysozyme, supernatant from a suspension of Chinese Hamster Ovary (CHO) cells, and a model precipitation process, immunoglobulin G (IgG) salt precipitation in the absence and presence of BSA. Feed-specific fouling resistant surfaces were identified, and the results are generally consistent with the rules governing general features of surfaces having low affinity for proteins. Bench-scale verification was conducted with the feed solutions of BSA, NOM and IgG precipitate in the presence of BSA. A good correlation between the two scales was obtained for BSA, while no correlation for NOM and IgG precipitate was observed.

In this research, we investigated the effect of membrane modification on improving the removal of water contaminants during filtration. Four chemicals including 2,4-dinitrophenol (2,4-DNP), perchlorate, arsenic and metolachlor were chosen as model compounds to evaluate modified membranes. They represent ionizable aromatic, inorganic salt, metallic oxyanion, and a fairly large, neutral chloroacetanilide herbicide, respectively. Results showed that grafting of negative 3-sulfopropyl methacrylate (SPMA) to 1 kDa poly(ether sulfone) (PES) membrane could significantly increase the density of negative charge on membrane surface, and improve rejection of charged

solutes, including arsenate, perchlorate and ionized 2,4-DNP in single and binary solute solutions. Charge repulsion was the possible dominant rejection mechanism for charged solutes. The rejection of neutral chemicals, including metolachlor and 2,4-DNP at low pHs (3 and 4.3 in this research) was dominated by adsorption, therefore, rejection was not enhanced by modification.

During membrane filtration of small synthesis organic chemicals, sorption by membranes lead to a breakthrough phenomenon of solute in the permeate solution. Breakthrough behavior was modeled using a one-dimensional solute transport model, treating the membrane as a porous medium, coupled with hindered diffusive and convective transport theory to account for the pore wall effect on solute transport. The model parameters were estimated by using separate measurements, by using empirical correlations, and by fitting the parameter to experimentally determined curves. This new modeling approach accurately fitted experimental data, and is a promising approach for predicting membrane performance.