

**Crossflow Filtration of Natural Organic Matter (NOM),
polysaccharides and Silica Colloids: Transport, Fouling and
Mixture Effects**

by

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Abstract

The overall objective of this research was to provide a better understanding of the fouling processes of nanofiltration (NF) and tight ultrafiltration (UF) membranes caused by aquatic organic matter (NOM), polysaccharides (PS) and inorganic colloids (nanoparticles, $< 1 \mu\text{m}$) in natural waters. Emphasis was on how the interactions between them affected their transport characteristics, cake structure, flux decline and solute selectivity. Experiments were designed to evaluate: 1) the fouling by individual NOM; 2) the fouling by individual polysaccharides; 3) the fouling by individual inorganic colloids; 4) the fouling by inorganic colloid-NOM mixtures; and 5) the fouling by inorganic colloid-polysaccharide mixtures. Natural water samples, model polysaccharides and silica colloids were selected and tested in a bench scale crossflow membrane test system for this purpose.

The transport behavior of three NOM from natural waters and the fouling of two polyethersulfone (PES) UF membranes were investigated using hydrodynamic transport models. The whole NOM was fractionated by an anion exchange resin (IRA 958) into charged and neutral fractions to investigate the impact of charge density. It was found that diffusion governed the overall mass transport, and increasing permeate flux would reduce the observed sieving coefficient when the nominal molecular weight cutoff (MWCO) was smaller than 5 kDa. When the nominal MWCO was greater than 10 kDa, convection became dominant and increasing flux would increase the NOM passage. Increasing ionic strength could significantly increase the observed sieving coefficient of charged fractions by reducing the effective size of molecules while no significant change was seen for neutral fractions. Neutral NOM fractions were found to cause serious flux decline by forming a gel/cake layer on the membrane surface. ATR-FTIR results showed that polysaccharides and amino sugars were two important components in the neutral fraction of the Tomhannock (TMK) reservoir NOM.

Physico-chemical properties of the polysaccharides appeared to be very important factors in controlling their fouling behaviors on the membranes. Xanthan has a rigid conformation due to its double helical structure, making it relatively stable to salts, acids and alkalis. By contrast, flexible linear alginate was found to be very sensitive to Ca^{2+} ions, and the membrane fouling increased with increasing Ca^{2+} concentration due to more

alginate deposition, likely due to the conformation change of alginate when bound with Ca^{2+} ions. The combined pore blockage and cake formation model developed for crossflow fit the permeate flux data very well. To better describe colloid deposition on the membrane, a new transport model was developed incorporating hydrodynamic-induced back transport in terms of J^* and first order particle desorption/reentrainment induced by surface interaction.

A remarkable difference in the silica particle (MP 1040, 125 nm) deposition between a PES UF membrane and a polyamide NF membrane was observed under the same experimental conditions, which was attributed to the influence of ionic strength on the back transport of particles. This revealed that particle surface interaction played an important role in determining the overall particle transport/deposition. The cake porosity formed on the UF membrane was estimated using the Carman-Kozeny equation and found to be closed packing (porosity 0.266). The deposited cake enhanced the salt concentration polarization above the NF membrane, however, the resulting increase in salt osmotic pressure was not a major fouling mechanism in part because concentration polarization dramatically reduced the salt selectivity. This phenomenon was predicted well with a two-layer hydrodynamic transport model.

Marked effects of the deposited silica particle cake on the selectivity of NOM and salt was observed with the NF membrane. A significant reduction in NOM selectivity was observed in the presence of silica colloids, especially when the deposited colloidal cake was thick. This is likely due to enhanced NOM concentration polarization caused by hindered back transport caused by the deposited colloidal cake, or effective size reduction due to the presence of a large amount of silica colloids in the mixture. On the other hand, the presence of NOM in the cake layer matrix substantially attenuated the enhancement of salt concentration polarization and thus increased the salt retention.

No synergistic interactions between polysaccharides and silica colloids were observed. The combined fouling of any polysaccharide- silica colloid mixture was more than that of either individual colloids or polysaccharides, but less than the sum of these two, which was attributed to less colloidal and polysaccharide deposition. A marked reduction in the colloidal deposition caused by the neutral dextran was observed, in contrast with the charged alginate.