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Revisiting membrane rejection: On the relationship between solute size and pore size in the nanofiltration regime

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EFFECTS OF HINDRANCE TRANSPORT AND SIEVING MODEL ON MEMBRANE REJECTION IN THE NANOFILTRATION REGIME

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Abstracts:

The molecular resolution of nanofiltration depends on resistance to solute transport along the permeation channel, manifesting steric hindrance and hydrodynamic friction. To date there is little direct experimental evidence of reporting on rejection in nanofiltration for ideal membranes with uniform pores, and defined size solutes. However the recent availability of defined nanoparticles in the range of 1-20 nm makes new investigations feasible. Phenomenological models for predicting solute permeation through defined cylindrical channels started with the Hagen-Poiseuille equation, which includes viscosity as the key parameter for solvent permeation. The Bowen-Welfoot model was developed to incorporate several correction terms to account for solute-pore interaction. However, the Bowen-Welfoot model generates ideal rejection curves only under the conditions of low pressure-driven flow. Under high-pressure conditions, the rejection curve as predicted by Bowen-Welfoot model assumes a broad spread, similar to the rejection profile predicted by Ferry's sieving model, demonstrating steric hindrance based on solute-pore interaction at the pore entrance as the key parameter in rejection. We set out to obtain new fundamental experimental evidence to interrogate these nanofiltration models.

In this work, transport of spherical nanoparticle (NP) imaging probes through model polycarbonate track etch (PCTE) and alumina (Al) membranes were studied empirically using citrate-coated gold nanoparticles of defined sizes (1, 5, 15 nm) and straight channel PCTE (nominal pore diameters 10 and 30 nm) and Al (nominal pore diameters 40 nm) membranes with uniform pore sizes. *A priori* calculations of theoretical rejections of the membranes with respect to different solute sizes were computed using Bowen-Welfoot pore-flow model. Two simulation approaches were used to describe both discrete and continuous (Gaussian distribution) pore size distributions using probability density functions and taking into account the solvent viscosity as a function of pore radii. Empirically measured rejections of nanoparticle imaging probes were compared with simulation results to confirm the phenomena of hindered transport of NPs inside defined cylindrical nanochannels. Given the experimentally observed evidence of hindered transport of solute moving through pores of commensurate dimensions, we revisited the measurement of rejection in nanofiltration regime in different operational modes: dead-end filtration, diafiltration and cross-flow using a same combination of nanoparticle solute size and membrane pore size. Our results show that dead-end and cross-flow measurements of rejection values do not always agree well with each other; while our diafiltration experiments provide evidence of solutes getting trapped inside membrane pores of commensurate sizes (permanent loss) or solutes in retarded movement through the pores due to much faster solvent flow (transient accumulation). In summary, this fundamental study will illustrate the relationship between solute sizes and pore sizes, the implications of it on measurements of rejection values, and the applications of the use of nanoparticle imaging agents for quantifying pathway dimensions in commercial membranes such as reverse osmosis thin film composites and integrally skinned asymmetric nanofiltration membranes with tortuous pore channels that are otherwise difficult to imaging the sizes directly using electron micrographic techniques.

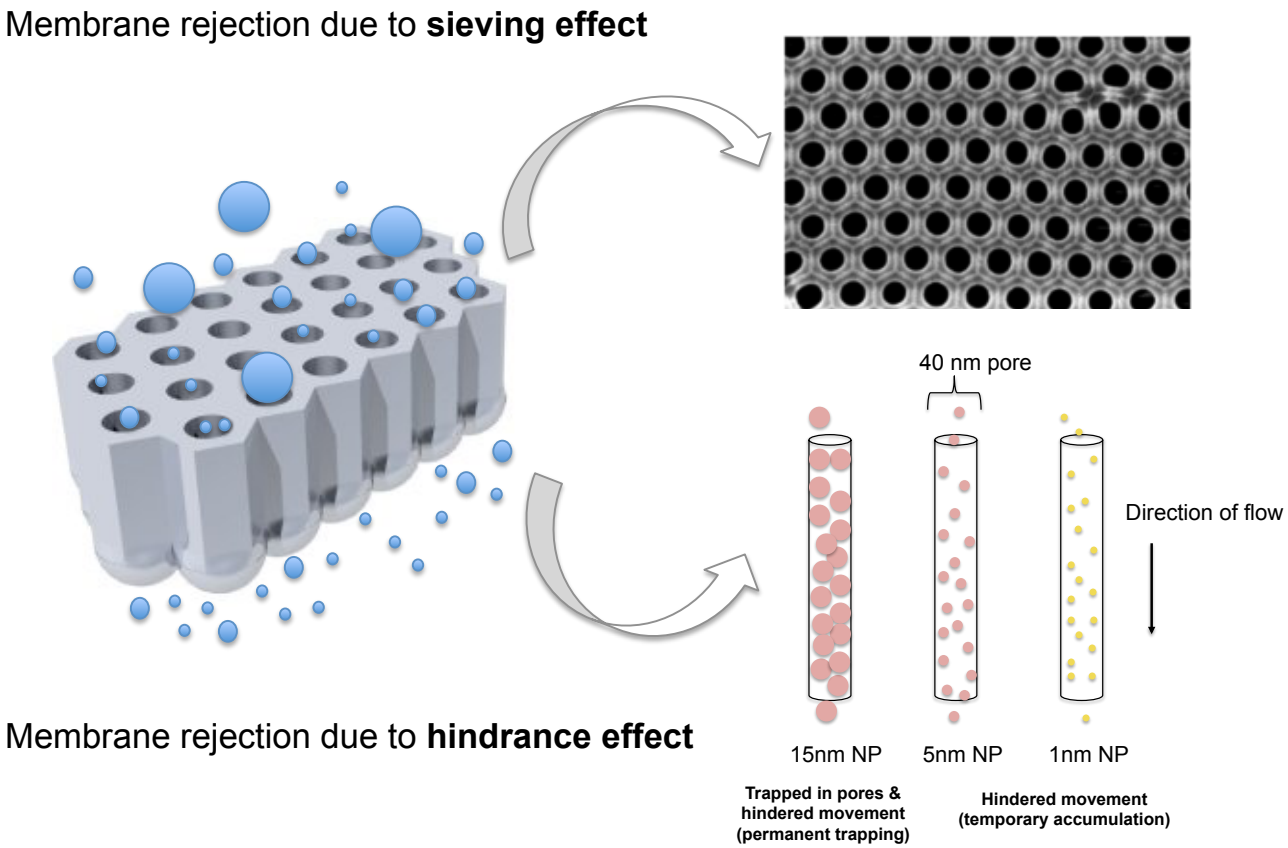

Figure 1: The combined effects of hindrance transport and sieving model on the measurement of rejection value, which is a dynamic process parameter.