

Diffusive Tortuosity of Reactive Porous Media: Application to Colloidal Fouling and Biofouling During Membrane Filtration

Problems and Research Objectives

Fouling in microfiltration (MF) and ultrafiltration (UF) processes has been extensively studied for the crossflow filtration technique in which the flow direction is parallel to the membrane surface but perpendicular to the permeate flux. When rigid colloidal particles are removed by MF/UF membranes, the particles quickly form a concentration polarization (CP) layer above the membrane surface and contribute to the initial stage of permeate flux decline. During filtration, the concentration (i.e., volume fraction) of the colloidal particles above the membrane surface is mainly governed by particle size, solution ionic strength, Hamaker constant of the particles, membrane resistance, and applied pressure. Unless the inter-particle interactions are highly repulsive (e.g., small particles with high zeta potential in a feed solution of low ionic strength), the retained particles between the CP layer and the membrane surface form a cake layer whose volume fraction reaches a maximum packing ratio. In a (quasi-)steady state, the thickness of the cake layer increases with applied pressure, due to the increase in permeate velocity that accelerates particle transport from the bulk phase toward the membrane surface. The cake layer, therefore, provides much higher hydraulic resistance than the CP layer and causes significant permeate flux decline during MF/UF membrane processes.

The colloidal fouling mechanism in nanofiltration (NF) and reverse osmosis (RO) processes has quite different features from that in MF/UF processes. In the absence of particulate matter, the main cause of flux decline in NF/RO processes is the CP of solute ions. This is because the wall concentration, i.e., solute concentration on the membrane surface, determines the effective driving force, i.e., the applied pressure minus the osmotic pressure difference between the surface and permeate sides of the membrane. In the presence of colloidal particles within the feed solution of NF/RO processes, the particles also form CP and cake layers on the membrane surfaces, where the hydraulic resistances from the layers are almost negligible compared to the inherent resistances of NF/RO membranes. Nevertheless, the cake layer containing retained particles produces significant permeate flux decline by obstructing back diffusion of the solutes. To diffuse from the vicinity of the membrane surface toward the bulk phase, the solutes need to avoid the retained particles by taking tortuous paths within the colloidal cake layer. Therefore, back diffusion is hindered, CP is enhanced, osmotic pressure is elevated, and permeate flux is suppressed to a certain extent. This phenomenon is called cake-enhanced osmotic pressure or cake-enhanced concentration polarization.

When biological matters are rejected by pressure-driven membrane processes, the filtered material forms a biological cake layer, called a biofilm, which causes deleterious biofouling. This is operationally defined as an unacceptable degree of system performance loss. The initial formation of the biofilm involves the accumulation of microorganisms (e.g., bacteria, fungi, microalgae) at a phase transition interface between the microorganism CP layer and the membrane surfaces. The bacterial accumulation occurs in two consecutive steps: initial attachment followed by ensuing growth. In this light, biofouling of the membrane surfaces is more problematic than abiotic colloidal fouling or solute precipitation because attached cells degrade the surface of polymeric membranes and multiply in a geometric fashion using nutrients continuously supplied from the feed water. Therefore, a single bacterium entering a membrane module may cause extensive biofouling if the growth rate of the sessile population is high.

The adhesion capability of bacteria to the membrane surface increases with respect to time, due to the biosynthesis of adhesive extracellular biopolymers that are abundantly produced and envelop the attached cells in viscous hydrated gels. The biopolymers are referred to as *extracellular polymeric substances* (EPS). They enhance the survival and robustness of the biofilm microorganisms by serving as a transport barrier to reactive chemicals such as antimicrobial agents trying to penetrate the biofilm by convective and diffusive transport mechanisms. Turbulent mixing above the membrane surface is also diminished by the presence of EPS that causes enhanced concentration polarization of solutes accumulating in the viscous sublayer. The biofouling is greatly affected by the micro-structure and composition of the membrane biofilms. In contrast to the axial shear flow experienced by biofilms, a noticeable proportion (10% to 15%) of the fluid containing water, nutrients, and other solutes can continuously pass through the biofilms due to the transmembrane pressure, thereby feeding the microorganisms and accelerating biofilm growth kinetics. High transmembrane pressure either condenses or compresses the biofilms and generates highly dense structures with minute porosity. The thickness of the biofilm varies from mono- to multi-layers of cells that are typically distributed throughout the EPS matrix. The voids and heterogeneity of the biofilms are still not well understood, but the impact can be extraordinary because the solutes, including nutrients present in the feed solution and biocides added for cleaning of biofouled membranes, will be trapped within the small void pores of the biofilm. Their back diffusion will be commonly hindered, causing a similar phenomenon to the cake-enhanced osmotic pressure in colloidal fouling, but to a more severe extent.

In this light, a fundamental understanding of solute diffusion within colloidal cakes and biofilms is of great importance, especially when the solutes are reactive to the sphere surfaces due to electric/chemical/physical interactions. In membrane filtration, the porous media consisting of rejected matter on the membrane surfaces can be classified into two categories: solid and soft cakes. The solid cake refers to the colloidal cake layer composed of rigid and (typically) spherical particles, whereas the soft cake characterizes the biofilm composed of deformable or compressible microorganisms usually surrounded by EPS. In both cases, the finite sizes of the cake reduce the free spaces in which the solute can perform Brownian random motion, and so the solute back diffusion from the membrane surface to the bulk phase is greatly hindered by their presence. In addition to the role of the cakes as geometrical obstacles to the diffusing solutes, interaction between the sphere surface and the solutes remarkably affects overall effective solute diffusion. Only solutes present in void spaces of the cake layers can contribute to the osmotic pressure.

Methodology

Two fundamental approaches were used to investigate the effects of solid and soft cakes on pressure-driven membrane filtration: Pearsonian random walk simulation and mean-field transport theory.

Pearsonian Random Walk Simulation

Solid cake (i.e., deposition layer of colloidal particles) and non-reactive soft cake (i.e., deformable biofilm surrounded by EPS in an equilibrium state) were investigated using the random walk simulation method. In the simulation, inert solutes were arbitrarily located within void spaces of the cake layers (described above) and allowed to move in a random manner. Their movements, being partially rejected by solid and deformed cake structures, were traced and statistically analyzed.

Theoretical Approach for EPS Biofouling Using Mean Field Approximation

Mass transport through a biofilm in the presence of EPS layers was modeled using a spherical cell model with a mean-field approximation. A cell is composed of a bacterium surrounded by excreted EPS. Transport of solutes through the EPS layer is represented by a solute diffusivity which is assumed to be smaller than bulk diffusivity. Solute uptake flux by bacteria was neglected because the flux is assumed to be small enough not to change solute concentration on the membrane surface.

Principal Findings and Significance

Random walk simulation analyzes the significance of deformed cake structure on solute diffusion. Cake deformation changes the pore structure from partially restricted free space to network-like, connected void channels. Therefore, the non-reactive, deformed soft cake provides a remarkable increase in diffusive tortuosity and causes the permeate flux decline. Results appear in a *Journal of Membrane Science* article that is currently in press (see list of publications for this project). In addition, results were presented at the International Congress on Membranes and Membrane Processes, Seoul, Korea, August 21-26, 2005. The conference presentation was entitled "Diffusive Tortuosity Factor of Colloidal Cake and Biofilm."

The theory of EPS effects on permeate flux provides a clear understanding that hindered diffusion within an EPS layer inhibits solute back diffusion from the membrane surface to the bulk phase. This is mainly because of the presence of bacteria causing geometrical obstruction as well as partition of solutes between the EPS layer and bulk phase. Results are reported in a paper submitted to the *Journal of Colloid and Interface Science* (see list of publications). In addition, research outcomes will be presented at the annual symposium of the American Chemical Society, to be held in San Francisco, September 2006, pending acceptance of the abstract, entitled "EPS Biofouling in Membrane Filtration: An Analytic Modeling Study."