MODELING CONCENTRATION POLARIZATION AND FOULING LAYERS IN CROSSFLOW ULTRAFILTRATION

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Summary
We present a boundary layer approximation (BLA) method for calculating the concentration-polarization (CP) layer and dispersion flow in crossflow ultrafiltration with a cylindrical membrane [1]. Results are discussed for various feed dispersions of colloidal particles, namely hard spheres, charge-stabilized particles [2], solvent-permeable non-ionic microgels [3, 4], and deswelling ionic microgels [5]. State-of-the-art methods are used for the gradient diffusion coefficient and viscosity entering the calculation of filtration profiles [3, 5]. We show that the BLA profiles are in quantitative agreement with predictions by a finite-element method [1]. The BLA results are compared with predictions by a similarity solution [4]. The BLA method is extended to conditions where a filter cake is formed at the membrane, with permeate flux results presented for a hard-sphere system [6].

INTRODUCTION
Crossflow ultrafiltration (UF) is a pressure-driven separation and enrichment process for colloidal dispersions where the feed dispersion is continuously pumped through a membrane pipe (Fig. 1, left). The applied transmembrane pressure (TMP) causes the solvent to flow out of the membrane, while the colloidal particles are retained inside the tube. Consequently, a particle-enriched diffuse layer is formed near the membrane, which reduces the filtration efficiency. This concentration-polarization (CP) layer is due to the balance of flow advection of particles towards, and gradient diffusion away from the membrane. The CP layer reduces the permeate flux, which can be attributed to the particles-created osmotic pressure counteracting the TMP. With increasing TMP, the particles near the membrane become immobilized, forming a crystalline so-called cake layer (Fig. 1, right). The cake layer is commonly believed to be at the origin of the limiting flux behavior, i.e., the experimentally observed horizontal flattening of the mean permeate flux at large TMP.

We have developed an efficient boundary layer approximation (BLA) method for accurately calculating the flow and concentration profiles in the UF of colloidal dispersions, on accounting for the concentration dependence of transport properties and osmotic pressure inside the inhomogeneous CP layer [1]. The BLA method is easily applied to feed dispersions including hard spheres (HS), solvent-permeable non-ionic microgels (MG), and ionic microgels (ion-MG) which deswell with increasing concentration [5]. To illustrate the importance of the concentration dependence of gradient diffusion and dispersion viscosity, we also report concentration profiles for constant transport (CT) coefficients. Fig. 2 shows BLA results for the particle volume fraction profile \( \phi_w(z) \) at the membrane wall for different dispersions, in comparison with finite-element method (FEM) results (symbols), demonstrating the excellent agreement between both methods. We further compare with CP layer predictions for hard spheres by an earlier boundary layer similarity solution (sBLA) [4], which differs significantly from the FEM/BLA results. Gradient diffusion away from the membrane is the largest (smallest) for hard spheres (ionic microgels). Hence, hard spheres have the most strongly developed CP layer and osmotic pressure for equal operation conditions, and hence the lowest permeation efficiency. For hard spheres, there is only a moderate increase of gradient diffusion with increasing concentration, differently from charge-stabilized particles. Regarding the filtration efficiency, this is over-compensated by an accordingly increasing viscosity, resulting in a \( \phi_w(z) \) curve only mildly larger than that for constant transport (CT) coefficients of values taken at the feed concentration.

We have extended the BLA to conditions where a crystalline filter cake is formed (Fig. 1, right). The cake layer contributes to the hydraulic resistance entering the employed Darcy-Starling law relating permeate flux to TMP and osmotic pressure. For hard spheres, Fig. 3 illustrates the effect of the cake layer on the pipe-length averaged permeate flux \( \langle v_w \rangle \), as a function of the length-averaged TMP. According to the figure, the cake is responsible indeed for an (apparent) limiting flux behavior at large TMP where a large fraction of the membrane is covered by the cake (inset).

Figure 1: Left: Sketch of inside-out crossflow in a cylindrical membrane pipe. Right: CP and cake layers of particles near a perfectly retentive membrane, with an axially declining solvent permeate flux. In our model, a cake is formed for particle volume fractions \( \phi \) exceeding the freezing transition value \( \phi_f \), which for hard spheres is equal to 0.494.

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THEORY AND MODEL

We consider crossflow of a monodisperse feed dispersion inside a cylindrical membrane (see Fig. 1), for a small feed volume fraction and constant pressure values \( p_{\text{in}} > p_{\text{out}} > p_{\text{perm}} \) at the inlet, outlet and inside the permeate, respectively. The particles are small enough that diffusion is dominated by Brownian motion, and sedimentation is negligible (ultrafiltration regime). The suspension-averaged incompressible flow and the particles flux are described macroscopically by coupled effective Stokes and diffusion-advection equations, respectively, incorporating a concentration-dependent gradient diffusion coefficient and effective viscosity, which we calculate with the salient hydrodynamic interactions included. The permeate flux through the fully particle-reactive membrane is described by the Darcy-Starling law, using an accurate input for the osmotic pressure derived microscopically from the particle interactions [1], and using the width-dependent hydraulic resistance due to the cake layer determined by the Carman-Kozeny relation for hard spheres [6]. The FEM results were generated using the COMSOL Multiphysics software for meshing and numerical solution [1].

CONCLUSIONS

The CP layer predictions by the simplifying BLA method based on a leading-order matched asymptotic expansion were shown to be in quantitative agreement with elaborate FEM results, for all considered feed dispersions and operating conditions. This justifies the approximations in the BLA method. The differences in the wall concentration curves of the similarity solution (sBLA) can be attributed to the less accurate pressure profiles obtained by the latter method.

The CP layer influence on ultrafiltration is small for ionic microgels since the gradient diffusion coefficient is distinctly larger than the one for neutral particles (e.g., HS and MG), with the accordingly small viscosity contribution by the charged particles. We have shown that the additional hydraulic resistance due to the cake layer leads to an apparent limiting flux behavior. The qualification apparent is used since the permeate flux is still weakly increasing with increasing at large TMP values where most (>80%) of the membrane wall is covered by the filter cake. If only the permeate flux reduction due to the osmotic pressure is considered, the permeate flux profile in Fig. 3 with an inflection point is obtained, showing linear growth at large TMP of slope inversely proportional to the hydraulic resistance of the bare membrane.

Figure 2: CP layer particle volume fraction \( \phi_w(z) \) at membrane wall, as function of distance \( z \) to the inlet of the tube of length \( L \). Results are shown by the finite-element method (FEM: symbols), boundary layer method (BLA: solid curves), and similarity solution (sBLA: dashed curves), respectively. The considered aqueous dispersions are hard spheres with concentration-dependent (HS; green color) and constant transport properties (CT; blue color), solvent-permeable non-ionic microgels (MG: brown color), and ionic microgels (ion-MG: red color). See [1].

Figure 3: CP and cake layer effects on the tube-length averaged permeate flux \( \langle v_w \rangle \) as a function of length-averaged TMP, quantified using the BLA method. The permeate flux is normalized by its value \( v_w^\ast \) at 5 kPa (open circles). The pure solvent line is the permeate flux for vanishing CP and fouling layers. The colored areas hallmark the flux reduction due to the CP (blue) and cake (sepia) layers. Filled squares: permeate flux including CP layer effect (see text). Dashed and dotted lines are guides to the eyes.

References