Electronic Supplementary Information

Ultrafiltration modeling of non-ionic microgels

Rafael Roa,[1,*] Emiliy K. Zholkovskiy,[2] and Gerhard Nägele[1]
[1] *Forschungszentrum Jülich, Institute of Complex Systems (ICS-3), 52425, Jülich, Germany*
[2] *Ukrainian Academy of Sciences, Institute of Bio-Colloid Chemistry, 03142, Kiev, Ukraine*

PROCESS INDICATORS

We discuss here in more detail the process indicators introduced in Subsec. IV C. These are functions of the adjustable operation parameters and here in particular of the volume fraction, ϕ_0, of colloidal particles in the homogeneous feed dispersion. For inside-out cross-flow UF in a hollow cylindrical fiber membrane (see Fig. S1) the indicators are obtained from the calculated spatial distributions of the local particle volume fraction, $\phi(r,z)$, and the dispersion velocity,

$$\mathbf{v}(r,z) = u_r(r,z)\,\mathbf{e}_r + u_z(r,z)\,\mathbf{e}_z\,, \tag{S.1}$$

expressed in cylindrical coordinates, (r,z), with the radial velocity component u_r along the unit vector $\mathbf{e}_r$ and the axial velocity component u_z along the unit vector $\mathbf{e}_z$. In this global coordinate frame, the velocity components at the inner membrane surface, $r = R$, are $u_r(R,z) = u(x, y = 0)$ and $u_z(R,z) = v(x, y = 0) = -v_w(x)$ for $x = z$, where $u(x,y)$ and $v(x,y)$ are the longitudinal and axial velocity components measured, respectively, in the membrane surface anchored local coordinate frame used in our CP layer analysis (see Eq. (7) and Fig. 2).

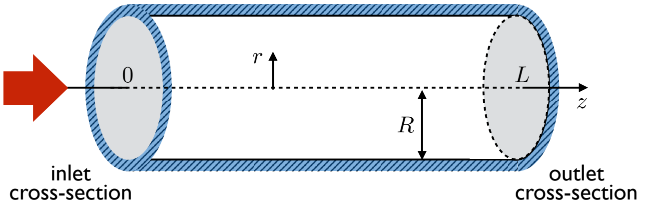

FIG. S1. Global cylindrical coordinate system (r,z). The z-coordinate line extends along the axis of the hollow cylindrical fiber membrane of length L and inner radius R.

A. Final product efficiency

The final product is identified in the present work with the retentate dispersion of mean volume concentration ϕ_f, flowing through the outlet cross-section at $z = L$ into a final reservoir. The particle advective flux through the outlet cross-section is $\int_S dS\ \phi(r,z)u_z(r,L)$ where $\int_S dS = 2\pi\int_0^R rdr$. Hence, ϕ_f is given by the ratio of the longitudinal particle advective to the longitudinal dispersion volume flux,

$$\phi_f = \frac{\int_S dS\,\phi(r,L)u_z(r,L)}{\int_S dS\,u_z(r,L)}\,, \tag{S.2}$$

where we have neglected the very small longitudinal diffusion flux contribution.

For a steady-state UF process where $\nabla\cdot\mathbf{J} = 0$ is valid according to Eq. (2) and for a fully particle retentive membrane where Eq. (18) applies to, the longitudinal particle fluxes through different fiber cross-sections should be equal. In particular,

$$\int_S dS\,\phi(r,L)u_z(r,L) = \phi_0\int_S dS\,u_z(r,0) \tag{S.3}$$

where we have ignored once again the small longitudinal diffusion flux contribution. The right-hand-side of Eq. (S.3) is the inlet particle flux of the feed dispersion of uniform volume fraction $\phi(r,0) = \phi_0$. By combining Eqs. (S.2) and (S.3), the expression

$$\alpha = \frac{\phi_f}{\phi_0} = \frac{\int_S dS\,u_z(r,0)}{\int_S dS\,u_z(r,L)} \tag{S.4}$$

for the Degree of Concentration factor α is obtained, equal to the ratio of inlet to outlet dispersion volume flux.

Another expression for α, particularly suitable for the presented boundary layer analysis, is obtained from dispersion volume conservation ($\nabla\cdot\mathbf{v} = 0$),

$$\int_S dS\,u_z(r,0) = \int_S dS\,u_z(r,L) + 2\pi R\int_0^L dz\,u_r(R,z)\,, \tag{S.5}$$

stating that the volume inflow through the inlet cross-section is equal to the sum of the volume outflows through the outlet cross-section and the cylindrical membrane of area $2\pi RL$. The combination of Eqs. (S.4) and (S.5) yields

$$\alpha = \frac{1}{1-\beta}\,, \tag{S.6}$$

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[*] r.roa@fz-juelich.de

with the Solvent Recovery indicator,

$$\beta = \frac{2\pi R \int_0^L dz\, u_r(R,z)}{\int_S dS\, u_z(r,0)}\,, \tag{S.7}$$

equal to the fraction of initial dispersion volume recovered in the permeate compartment. Using $u_r(R,z) = -v_w(x)$ together with Eq. (54) for $\langle v_w \rangle$ and the cylindrical Pouiseuille flow profile for $u_z(r,0)$, the Eq. (57) for β in the main text is obtained.

The logical way of calculating the final product efficiency indicators is to determine first β using Eq. (S.7), with α and ϕ_f determined subsequently using Eq. (S.6).

B. Productivity per unit membrane area

The indicator of Productivity per Unit Membrane Area, θ, is defined here as the retentate flux divided by the membrane area,

$$\theta = \frac{\int_S dS\, u_z(r,L)}{2\pi R L}\,, \tag{S.8}$$

giving this indicator the dimension of a velocity. Using Eqs. (S.4)-(S.6), θ can be related to β by

$$\theta = \frac{\int_S dS\, u_z(r,0)}{(1-\beta)2\pi R L} = \frac{\int_0^L dz\, u_r(R,z)}{\beta(1-\beta)L}\,. \tag{S.9}$$

The integral in the second equality is proportional to the fiber-length-averaged permeate velocity. Using Eqs. (54) and (56) in the previous expression, Eq. (58) in the main text is obtained.

C. Energy cost

We discuss first the indicator of Specific Energy Consumption, ω, defined as the energy consumed to produce a unit volume of final product which, in our case, is the retentate dispersion of volume fraction ϕ_f. Thus, for a steady-state process, ω is equal to the ratio of consumed power to the outlet volume per unit time. Assuming that basically the whole external power is spent in pressing the solvent through the membrane, this implies

$$\omega = \frac{2\pi R \int_0^L dz\, \Delta P(z) u_r(R,z)}{\int_S dS\, u_z(r,L)}\,, \tag{S.10}$$

where $\Delta P(z)$ is the local transmembrane pressure difference which in general depends on the axial distance z from the inlet. In our calculations, the TMP has been taken as constant. Note that the physical dimension of ω is energy per volume.

In general, one can expect that variations of $\Delta P(z)$ along the hollow fiber membrane are much smaller than the mean pressure value, denoted here as ΔP, so that $\Delta P(z)$ approximated by ΔP can be shifted out of the integral in Eq. (S.10). Consequently, by using in addition Eqs. (S.4) and (S.6), Eq. (59) in the main text is obtained wherein ω is expressed by the product of the fiber-length-averaged TMP ΔP and $(\alpha - 1)$.

As discussed in Subsec. IV C, the Specific Energy Efficiency indicator, ϵ, is defined as the ratio of the thermodynamically necessary minimal reverse-osmosis compression work, $\omega_{\min}$, required to produce a unity of retentate dispersion to the Specific Energy Consumption ω. According to Eq. (60), ϵ can be expressed in terms of ϕ_0, ΔP, and osmotic pressure $\Pi(z)$ along the membrane surface as

$$\epsilon = \frac{\alpha\,\phi_0}{(\alpha-1)\,\Delta P} \int_{\phi_0}^{\phi_f} d\phi \left(\frac{\Pi(\phi)}{\phi^2}\right). \tag{S.11}$$

Substituting $\Pi(\phi)$ as described by the CS Eq. (37) for colloidal hard spheres into Eq. (S.11), we obtain the analytic expression

$$\epsilon = \frac{3\,k_B T}{4\pi a^3} \frac{\alpha\,\phi_0}{(\alpha-1)\,\Delta P} \left[\ln(\alpha) + \frac{3-2\phi_f}{(1-\phi_f)^2} - \frac{3-2\phi_0}{(1-\phi_0)^2}\right] \tag{S.12}$$

for ϵ in terms of the input parameters ϕ_0, ΔP, and hard-core radius a, and also in terms of $\alpha = \phi_f/\phi_0$ which must be determined prior to ϵ. The factor to the left of the bracket in Eq. (S.12) can be recast into the suggestive form $(k_B T n_b/\Delta P)\,(\alpha/(\alpha-1))$ invoking the ratio of the van't Hoff pressure $k_B T n_b$ and the TMP, where n_b is the number density of the injected feed dispersion. Note further the explicit $1/a^3$ dependence of ϵ which renders this indicator very small for larger colloidal particles where the osmotic pressure buildup along the membrane is small.