CHAPTER 3
Microfiltration, Ultrafiltration

Models for Predicting Flux for MF, UF

1) Capillary Model
2) Film Theory Model
3) Flux Paradox (back-transport)
4) Resistance in series Model
- **Model flux** is predicted as a function of system operation parameters (pressure, flow rate, etc.) and physicochemical properties (viscosity, density, charge, diffusivity, etc.).

- Although the operating techniques of MF, UF, NF, and RO are similar, the separation mechanisms should be different:
  
  i) MF and UF have most frequently been visualized as sieve filtration.

  ii) NF and RO are almost certainly not merely separation by size, but by other parameters (charge, solubility, diffusivity, size, etc.)
A number of mathematical models are available that attempt to describe the mechanism of transport through membrane.

None are wholly satisfactory:

i) The major problem appears to be an inability to precisely model the phenomenon occurring near the membrane surface.

ii) The contribution and importance of the chemical nature of the membrane to membrane processes is still not clearly identified.
- The best description of fluid flow through microporous membrane in an ideal situation: i) uniformly distributed evenly sized pores in the membrane, ii) no fouling, iii) negligible concentration polarization, etc.

- Predicting Flux from pore statistics **using Hagen-Poiseuille Equation**.

\[ J = f(d_p, \varepsilon, \Delta P_T, \eta, \Delta x) \]
1) Capillary Model

Hagen-Poiseuille Model for Laminar flow through channels:

\[ J = \frac{\varepsilon \cdot d_P^2 \cdot \Delta P_T}{32 \Delta x \cdot \eta} \quad (l / h \cdot m^2) \]

- \( d_P \): Pore diameter
- \( \varepsilon \): Surface porosity (total open area of pores per unit membrane surface)
- \( \Delta P_T \): Transmembrane pressure (\( \Delta P_T = P_F - P_P \))
- \( \eta \): Viscosity of solvent (usually water)
- \( \Delta x \): Thickness of membrane skin
1) Capillary Model

\[ J = f(d_p, \varepsilon, \Delta P_T, \eta, \Delta x) \]

\[ J = \frac{\varepsilon \cdot d_p^2 \cdot \Delta P_T}{32 \Delta x \cdot \eta} \quad (l / h \cdot m^2) \]
Example of capillary model

Example)

Membrane ; XM 100A UF (Amicon)
    dp ; Mean pore diameter = 175 A˚
    N ; Number of pores/cm² = 3 x 10⁹
    Δ x ; Skin thickness = 0.2 μm

[Δ PT = 100kPa = 106g /cm·sec²]
[η = 1 centipoise = 10⁻² g/cm·sec]

What is the water flux, \( J( l/m²·h ) \) through this membrane?
Direct microscopic observation of membrane surface

Figure 3.4. SEM micrograph of the surface structure of Amicon XM100A ultrafiltration membrane (From Fane, et al., 1981).
Example of capillary model

Answer

\[
\text{porosity}(\varepsilon) = N \cdot (\pi/4) \cdot dp^2 \\
= 3 \times 10^9 \times (\pi/4) \times (175 \times 10^{-8})^2 \\
= 7.216 \times 10^{-3} \text{ cm}^2/\text{cm}^2 \\
\therefore 0.72\% \text{ of the membrane surface is occupied by pores.}
\]

\[
J = \frac{7.216 \times 10^{-3} \times (175 \times 10^{-8})^2 \text{ cm}^2 \times 10^6 \text{ g/cm} \cdot \text{sec}^2}{32 \times 0.2 \times 10^{-4} \text{ cm} \times 10^{-2} \text{ g/cm} \cdot \text{sec}} \\
= 3.45 \times 10^{-3} \text{ cm/sec} \\
= 3.45 \times 10^{-3} \text{ cm/sec} \times (\text{m}/100\text{cm}) \times (1000\text{L}/\text{m}^3) \times (3600\text{sec/hr}) \\
= 124.3 \text{ L/m}^2 \cdot \text{h (LMH)}
\]
Comparison of experimental flux with calculated flux

Table 3.5. Membrane pore statistics and water flux calculations.

<table>
<thead>
<tr>
<th></th>
<th>XM300\textsuperscript{a}</th>
<th>XM100A\textsuperscript{a}</th>
<th>PM30\textsuperscript{a}</th>
<th>PTGC\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mean Pore Dia (Å)</strong></td>
<td>245</td>
<td>175</td>
<td>75</td>
<td>59</td>
</tr>
<tr>
<td><strong>Material</strong></td>
<td>Acrylic copolymer</td>
<td>Acrylic copolymer</td>
<td>Polysulfone</td>
<td>Polysulfone</td>
</tr>
<tr>
<td><strong>M.W. Cut-off</strong></td>
<td>300,000</td>
<td>100,000</td>
<td>30,000</td>
<td>10,000</td>
</tr>
<tr>
<td><strong>Pores/cm\textsuperscript{2}</strong></td>
<td>$6.7 \times 10^8$</td>
<td>$3.0 \times 10^9$</td>
<td>$4.5 \times 10^{10}$</td>
<td>$4.0 \times 10^{11}$</td>
</tr>
<tr>
<td><strong>Surface Porosity</strong></td>
<td>0.3%</td>
<td>0.75%</td>
<td>2.0%</td>
<td>7–12%</td>
</tr>
<tr>
<td><strong>Water flux (L/m\textsuperscript{2}/hr)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated\textsuperscript{*}</td>
<td>104</td>
<td>124</td>
<td>–</td>
<td>214</td>
</tr>
<tr>
<td>Experiment</td>
<td>98</td>
<td>80</td>
<td>63</td>
<td>(18)</td>
</tr>
</tbody>
</table>

\textsuperscript{*}Calculated from Hagen-Poiseuille equation with $\Delta P_T = 100$ kPa, 20\textdegree C, $\Delta x = 0.2 \mu m$.

\textsuperscript{a}Data of Fane, et al., 1981.

\textsuperscript{b}Data of Merin and Cheryan, 1980. Experimental flux (18) converted from original data at 275 kPa, 50\textdegree C.
Several factors causing the discrepancy between calculated and experimental flux:

1) Hagen – Poiseuille Equation assumes all pores are right circular cylinders, which is highly unlikely with those membranes. A “tortuosity” \((\text{actual pore length/cylinder length})\) factor should have been included in the equation.

\[
J(l/h \cdot m^2) = \frac{\varepsilon \cdot d \cdot p^2 \cdot \Delta P \cdot T}{32 \Delta x \cdot \eta \cdot \tau}
\]

\(\tau:\text{ pore tortuosity}\)

2) As the pores get smaller in diameter, the number of pores in various sizes increases, which makes estimation of pore size distribution and pore density more difficult.

3) Smaller pores could be more tortuous.

4) The number of “dead end” pore can not be accounted for.

5) The contribution of the chemical nature of the membrane material is not taken into account.
- According to this model, flux is proportional to $\Delta P_T$, but inversely proportional to $\eta$.

$$J(l/h \cdot m^2) = \frac{\varepsilon \cdot d_P^2 \cdot \Delta P_T}{32\Delta x \cdot \eta \cdot \tau}$$

As $\eta$ is controlled by Temp. and feed concentration, increasing $\Delta P_T$ or Temp. increases flux.

- This equation is applicable under restricted conditions, where concentration polarization effects are negligible. The following conditions are required:

  i) $\Delta P_T$ should be low,
  ii) Feed concentration should be low,
  iii) Flow velocity should be high.

If not, concentration polarization develops and Hagen-Poiseuille equation no longer adequately describes the MF/UF process and mass-transfer limited model should be used.
Remark:

- Pore size and Flow distribution

• For a single capillary of diameter $d_{pi}$, the flow rate,

\[ q_i(L/h) = J \times \frac{\pi}{4} \cdot d_{pi}^2 \]

\[ = \frac{d_{pi}^2 \cdot \Delta PT}{32 \Delta x \cdot \eta} \times \frac{\pi}{4} \cdot d_{pi}^2 \]

\[ = \pi \cdot d_{pi}^4 \cdot \Delta pt / 128 \cdot \eta \cdot \Delta x \]

• If $f_i$ is the number fraction of pores with diameter $d_{pi}$, the fraction of solvent passing through the pores, $F_i$, is

\[ F_i = \frac{f_i \cdot d_{pi}^4}{d_{p\text{max}}} \sum_{d_{p\text{min}}} f_i \cdot d_{pi}^4 \]
Remark:

From Fig. 3.5 & Fig. 3.7

- The flow is strongly biased to the larger pores, with 50% of the solvent flow passing through 20-50% of the pores.

- Membrane permeability will be very sensitive to the population of large pores, and their loss by plugging or obstruction.

- Preferred flow through a minority of larger pores will produce heterogeneous flow patterns normal to the membrane.
Direct microscopic observation of membrane surface

Figure 3.4. SEM micrograph of the surface structure of Amicon XM100A ultrafiltration membrane (From Fane, et al., 1981).
Distribution of pore size and volume throughput

Figure 3.5. Distribution of pore size and volume throughput for Amicon XM100A membrane shown in Figure 3.4 (From Fane, et al., 1981).
2) Film-Theory (Mass transfer) Model

As solution is filtered, solute is brought to the membrane surface by convective transport which results in concentration gradient (or concentration polarization).

The resulting concentration gradient causes the solute to be transported back into the bulk of solution due to diffusional effects.
2) Film-Theory (Mass transfer) Model

i) Longitudinal mass transport within the boundary layer is assumed negligible
   (mass transfer within the film is one dimensional)

ii) At steady state, the solute flux is constant throughout the film \[ CJ_v - D(dC / dx) \]
    and equal to the solute flux through the membrane \[ C_p \cdot J_v \].

- A material balance for the solute in a different element gives the equation.

\[
J_S = C_p \cdot J_v = CJ_v - D(dC / dx)
\]

Boundary Condition: \( C = \begin{cases} C_b & \text{at } x=0 \\ C_w & \text{at } x= \delta \end{cases} \)

- \( C_b \): bulk solute concentration
- \( \delta \): thickness of the boundary layer
- \( C_p \): permeate solute concentration
- \( C_w \): solute concentration at the membrane surface
- \( D \): diffusion coefficient of solute
Derivation of the equation

\[ D \cdot \frac{dC}{dx} = J_V (C - C_P) \]

\[ \int_{C_b}^{C_w} D \cdot \frac{dC}{C - C_P} = \int_0^\delta J_V \cdot dx \to D \cdot \ln(C - C_P) \bigg|_{C_b}^{C_w} = J_V \cdot \delta \]

\[ \therefore J_V = \frac{D}{\delta} \ln\left(\frac{C_w - C_P}{C_b - C_P}\right) = k_s \cdot \ln\left(\frac{C_w - C_P}{C_b - C_P}\right) \]

\[ J_V = k_s \cdot \ln\frac{C_w}{C_b} \text{ (if } C_P = 0) \]

\[ \frac{D}{\delta} = k_s \]

\[ k_s : \text{mass-transfer coefficient} \]

- If \( C_w \to C_g \) \( J_{\text{lim}} = k_s \cdot \ln\frac{C_g}{C_b} \) \text{ (Gel polarization Model)}

\[ C_g : \text{Gel Concentration} \]

\[ J_{\text{lim}} : \text{limiting flux} \]
Figure 4.14. Schematic of concentration polarization during UF of colloidal and macromolecular solutes, showing the buildup of the polarized (gel) layer and associated boundary layer. The same phenomenon occurs with MF membranes, depending on the rejection of the solutes.
Retention and Concentration Polarization

- **Observed retention**; \( S = 1 - \frac{C_p}{C_b} \),

- **True retention**; \( R = 1 - \frac{C_p}{C_w} \)

- **Concentration polarization**; \( M = \frac{C_w}{C_b} = 1 - S + S \exp\left(\frac{J_v}{k_s}\right) \)

So, \( M \) can be calculated from the measurement of the retention and the permeate flux, when \( k_s \) is known.
Correlation between operating parameters and flux

Figure 4.12. Generalized correlation between operating parameters and flux, indicating the areas of pressure control and mass transfer control.

\[ J_V = \frac{D}{\delta} \ln \left( \frac{C_w - C_P}{C_b - C_P} \right) = k_s \cdot \ln \frac{C_w}{C_b} \quad (\text{for } C_P \to 0) \]
Effect of feed velocity, temperature and bulk concentration on flux

Figure 4.19. Effect of feed velocity (m/s), temperature and solids concentration of skim milk on flux in a hollow fiber HF15-43-PM50 module. Solids levels correspond to 1-, 3-, and 5-fold concentrations (From Chiang, 1982).
Figure 4.17. Relationship between flux and protein concentration during concentration of human albumin (open circles) and whole bovine serum (closed circles). The module was a thin-channel laminar flow unit (LTC-15) with 15-mil channel and Amicon PM-10 membrane. Theoretical lines were drawn using the Leveque solution and the film theory, with the diffusion coefficients as shown (From Porter, 1979).
-For colloidal suspensions:

Experimental flux values are often **one to two orders of magnitude higher** than those indicated by the Lévêque and Dittus-Boelter relationships. But the reason is not clear.
Film theory model for colloidal suspensions

Figure 4.21. Ultrafiltration of styrene-butadiene polymer latex in LTC-1, 15-mil channel, XM-50 membrane, 60 psig pressure (From Porter, 1979).
In colloidal suspensions, the diffusion coefficient calculated from the ultrafiltrate flux using the Lévéque or Dittus-Boelter equations generally from one to three orders of magnitude higher than the theoretical Stokes-Einstein diffusivity.

Minor adjustments in molecular parameters such as diffusivity (\(D\)), kinematic viscosity (\(\nu\)), or gel concentration (\(C_g\)) are incapable of resolving order of magnitude discrepancies.
- Back-diffusive transport of colloidal particles away from the membrane surface into the bulk stream \( (D \cdot \frac{\partial C}{\partial x}) \) is substantially augmented over that predicted by the Lévêque and Dittus-Boelter relationships.

- For colloidal suspensions, mass transfer from the membrane into the bulk stream is driven by some force other than the “concentration gradient”.

- M.C. Porter’s opinion (1972):
  “Tubular Pinch Effect is responsible for this augmented mass transfer.”
How to solve the flux paradox?

Fig. IV-1. Forces and torques acting on a charged, spherical particle suspended in a viscous fluid undergoing laminar flow in the proximity of a flat porous surface. [modified from Wiesner (1992)]
Forces acting on particles in a viscous flow undergoing laminar flow

<table>
<thead>
<tr>
<th>Factor</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Toward the membrane</strong></td>
<td></td>
</tr>
<tr>
<td>Gravity</td>
<td>( v_k = \frac{\pi}{18\eta} d_p^2 \rho_p g )</td>
</tr>
<tr>
<td>Van der Waals attraction</td>
<td>( v_A = \frac{A}{36\pi \eta s^2} )</td>
</tr>
<tr>
<td>Permeation drag (flux)</td>
<td>( J )</td>
</tr>
<tr>
<td><strong>Away from the membrane</strong></td>
<td></td>
</tr>
<tr>
<td>Buoyancy</td>
<td>( v_b = \frac{\pi}{18\eta} d_p^2 \rho_l g )</td>
</tr>
<tr>
<td>Electrical double layer repulsion</td>
<td>( v_m = \frac{2\kappa\varepsilon\zeta^2 \exp(-\kappa s)}{3\eta} )</td>
</tr>
<tr>
<td>Browian diffusion</td>
<td>( v_n = \frac{kT}{3\pi\eta d_p \delta} )</td>
</tr>
<tr>
<td>Shear-induced diffusion</td>
<td>( v_s = 0.0225 \frac{u_o d_p^2}{h \delta} )</td>
</tr>
<tr>
<td>Lateral migration</td>
<td>( v_l = \frac{13.8 \rho_p u_o^2 d_p^3}{128 \eta h^2} )</td>
</tr>
</tbody>
</table>

* Membrane module: plate and frame.
+ \( d_p \), particle diameter; \( \rho_p \), particle density; \( \eta \), dynamic viscosity; \( A \), Hamaker constant; \( s \), separation distance; \( \rho_l \), liquid viscosity; \( \kappa \), Debye-Hückel parameter; \( \varepsilon \), fluid permittivity; \( \delta \), boundary layer thickness calculated by the Lévêque equation; \( \zeta \), zeta potential; \( u_o \), average fluid velocity; \( h \), half-channel height.
Back transport velocity of particles under laminar flow

**Back transport velocity**
= diffusion + shear induced diffusion + lateral migration

![Graph showing back transport velocity vs particle size](image)
Back transport velocity of particles under laminar flow

Back transport velocity = Diffusion + shear induced diffusion + lateral migration + interaction induced

Fig. Comparison of different models explaining a critical flux over a range of particle size.
Back transport velocity as a function of particle size and fluid velocity

Fig. 6. Profiles of the net back-transport velocity based on Brownian diffusion, shear-induced diffusion, and lateral migration as a function of particle size and fluid velocity: temperature, 55°C; particle density, 0.99 g/cm³; channel height, 1.0 mm.
Particle size distributions deposited on the membrane surface = f (size, flux).

Fig. IV-5. Depositing particle size distribution for each flux condition. Size distribution when flux is infinite means the initial particle size distribution measured experimentally ($T = 298$ K, $\phi_0 = 50$ mV, $A = 3.4 \times 10^{-20}$ J).
1) Crossflow MF/UF are occasionally operated in the turbulent regime, whereas **all of the models described are restricted to laminar flow**.

2) Brownian and shear-induced diffusion may be considered simultaneously by adding the diffusion coefficients, although recent simulations have shown that **the diffusion coefficients are not strictly additive**.

3) The models described are based on idealized suspensions of equisized spheres, which do not irreversibly stick to the membrane or cake surfaces but rather are free to diffuse or lift away. Further experiments and models are needed to study Brownian, shear induced diffusion, and inertial lift **in real suspensions of non-spherical, deformable particles having both narrow and broad size distributions**.
4) Considerable experimental and theoretical research remains to complete our understanding of crossflow microfiltration.

For example, issues of direct membrane fouling by the attachment of particles and precipitates to the membrane pores and surface have not been adequately addressed.
Definitions of various Fluxes

Flux (J)

i ) Critical Flux (J_c)

ii ) Limiting Flux (J_{lim})

iii ) Steady-state Flux (J_{ss})

\[ J_c \]

\[ J_{lim} \]

\[ J_{ss} \]

\[ J \]

\[ J \]

\[ J \]

\[ \Delta P_c \]: critical transmembrane pressure

\[ \Delta P_t \]
4) Resistance in series Model

\[ J = \frac{\Delta P_T}{\mu (R_m + R_s)} \]  \hspace{1cm} -(1) \]

if \( R_s \gg R_m \),

\[ J = \frac{\Delta P_T}{\mu R_s} \]  \hspace{1cm} -(2)
If the solute is thought of as a ‘cake’ of deposited particles, the gel (cake, deposit, etc) resistance can be obtained from conventional filtration theory.

\[
J = \frac{\Delta P_r}{(R_m + R_S) \cdot \eta} \quad - - - - - (1)
\]

\[
R_S = \alpha \cdot V \cdot C_b / A_m = \alpha \cdot m_s / A_m \quad - - - - - (2)
\]

- \( R_s \): solute resistance (1/m)
- \( R_m \): membrane resistance (1/m)
- \( V \): cumulative solvent volume (m^3)
- \( C_b \): Bulk solute concentration (kg/m^3)
- \( A_m \): membrane area (m^2)
- \( m_s \): mass of solute (kg)
- \( \alpha \): specific resistance (m/kg)
4) Resistance in series Model

For unstirred conditions $R_s$ grows and combining equation (1) with (2) gives,

\[ J(t) = \frac{1}{A_m} \frac{dv}{dt} = \frac{\Delta P_T}{(R_m + \alpha \cdot V \cdot C_b / A_m) \cdot \eta} \]  

\[ \text{---(3)} \]

From eqn.(3)

\[ \int_0^t dt = \int_0^V \frac{R_m \cdot \eta}{\Delta P_T \cdot A_m} dV + \int_0^V \frac{\alpha \cdot V \cdot C_b \cdot \eta}{\Delta P_T \cdot A_m^2} dV \]  

\[ \text{---(4)} \]

At constant pressure, integration of eqn. (4) gives,

\[ t = \frac{R_m \cdot \eta}{\Delta P_T \cdot A_m} V + \frac{\alpha \cdot V^2 \cdot C_b \cdot \eta}{2 \Delta P_T \cdot A_m^2} \]

\[ \therefore \frac{t}{V} = \frac{R_m \cdot \eta}{\Delta P_T \cdot A_m} + \frac{\alpha \cdot V \cdot C_b \cdot \eta}{2 \Delta P_T \cdot A_m^2} \]  

(well-known filtration equation)
From a plot of $\frac{t}{V}$ vs. $V$, $\alpha$ is obtained experimentally.

If $R_m$ is negligible,

$$V^2 = \left( 2 \cdot \Delta p_T \cdot A_m^2 / C_b \cdot \alpha \cdot \eta \right) \cdot t$$

Which predicts that filtrate (permeate) accumulates according to $t^{1/2}$
Carman-Kozeny eqn. for $\alpha$

- $\alpha$, the specific resistance of the deposit can be related to “Particle” properties by the Carman-Kozeny relationship.

$$\alpha = \frac{180(1 - \varepsilon)}{\rho_s \cdot d_s^2 \cdot \varepsilon^3} \quad -(6)$$

$\varepsilon$ : voidage (or porosity)

$\rho_s$ : solute density

$D_s$ : solute particle diameter

- The effect of pressure on $\alpha$ is frequently expressed by the relationship,

$$\alpha = \alpha_o \cdot \Delta P^s$$

$\alpha_o$ : constant

$s$ : compressibility factor

For compressible solids, typical values of $s = 0.2 \sim 0.7$
- Comparison the values of $\alpha$ obtained from the Carman-Kozeny eqn. (eq.6) with those measured experimentally.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bovine Serum Albumine</td>
<td>$\alpha = 3.0\sim7.0 \times 10^{15}$ (m/kg) (depending on $\varepsilon$)</td>
<td>$\alpha = 1.0\sim7.0 \times 10^{15}$ (m/kg) (depending on $\Delta P$)</td>
</tr>
<tr>
<td>colloidal silica</td>
<td>$\alpha = 3.0\sim6.0 \times 10^{14}$</td>
<td>$\alpha = 5.0\sim15.0 \times 10^{14}$</td>
</tr>
</tbody>
</table>

- The similarity between calculated and experimental $\alpha$ values for these ‘particulate’ solutes supports the use of a conventional filtration model for MF/UF.