Lecture 9.
Continuous Adsorption Systems

- McCabe–Thiele Method for Purification
- Kremser Method
- McCabe–Thiele Method for Bulk Separation
- Simulated–Moving–Bed Systems
- Models for SMB Systems
  - TMB equilibrium–stage model using a McCabe–Thiele–type analysis
  - Steady–state local–adsorption–equilibrium TMB model
  - Steady–state TMB model
  - Dynamic SMB model
Continuous, Countercurrent Operation

- Advantage of continuous, countercurrent operation:
  countercurrent flow maximizes the average driving force for transport → increases adsorbent use efficiency

- McCabe–Thiele and Kremser methods for purification

  - If the system is dilute in solute, and solute adsorption isotherms for feed solvent and purge fluid are identical
  - The operating and equilibrium lines are straight because of the dilute condition
McCabe–Thiele Method for Purification

• Position of operating lines based on direction for mass transfer
  – Adsorption operating line lies below the equilibrium line
  – Desorption operating line lies above the equilibrium line

• Adsorption operating line
  \[ q = \frac{F}{S} (c - c_F) + q_F \]

• Desorption operating line
  \[ q = \frac{D}{S} (c - c_D) + q_R \]

• Equilibrium line
  \[ q = Kc \]

• When \( c_D \) and \( c_R \) approach zero, in order to avoid a large number of stages:
  \[ \frac{F}{S} < K < \frac{D}{S} \]
McCabe–Thiele Method for Desorption at Elevated Temperature

- If the temperature or pressure for the two sections can be altered to place the equilibrium line for desorption below that for adsorption → it becomes possible to use a portion of the raffinate for desorption
  - F/S can be greater than D/S
  - With a portion of raffinate used in Bed 2 (DES), the net raffinate product is F–D
  - The two operating lines must intersect at the point \((q_R, c_R)\)
  - By adjusting D/F, intersect point can be moved closer to the origin to increase raffinate purity, \(c_R\), but at the expense of more stages and deeper beds
Kremser Method

• When the equilibrium and operating lines are straight

\[ N_t = \frac{\ln \left[ \frac{c_1 - q_1/K}{c_2 - q_2/K} \right]}{\ln \left[ \frac{c_1 - c_2}{q_1/K - q_2/K} \right]} \]

1 and 2 refer to opposite ends which are chosen so \( q_1 > q_2 \)

• For a number of theoretical stages, \( N_t \), in the adsorption or desorption sections

\[ L = N_t (\text{HETP}) \]

Bed height

- Values of HETP, which depend on mass-transfer resistances and axial dispersion, must be established from experimental measurements
- For large-diameter beds, values of HETP are in the range of 0.5–1.5 ft
McCabe–Thiele Method for Bulk Separation

- Continuous, countercurrent bulk separation for binary mixture

- To provide flexibility, a thermal swing is used, with Sections II and III operating at low or ambient temperature, while Sections I and IV operate at elevated temperature.

- The top two sections (III and IV) provide a stripping action to produce a product rich in the less strongly adsorbed component B.

- The two bottom sections (I and II) provide an enriching action to produce a product rich in component A.
Simulated-Moving-Bed Systems (1)

- True-moving bed

- Concept of a SMB system

- Steady state after the start-up
- Time independent model
Simulated-Moving-Bed Systems (2)

- Difficulties in operating continuous, countercurrent moving-bed (true-moving-bed, TMB) systems: adsorbent abrasion, failure to achieve particle plug flow, fluid channeling
- Continuous, countercurrent operation can be simulated by using a column containing a series of fixed beds and periodically moving the locations at which streams enter and leave the column: simulated moving-bed (SMB) systems
  - Widespread commercial application for liquid separations in the petrochemical, food, biochemical, pharmaceutical, and fine chemical industries
  - An SMB can be treated as a countercurrent cascade of sections (or zones) rather than stages, where stream entry or withdrawal points bound the sections
  - As each section is divided into more subsections, the SMB system more closely approaches the separation achieved in a corresponding TMB
Simulated-Moving-Bed Systems (3)

• Operation of SMB

- By periodically shifting feed and product positions by one port position in the direction of fluid flow, movement of solid adsorbent in the opposite direction is simulated.
- Flow rates in the four sections are different.

• Cyclic steady state
• Time dependent model

- Feed
- Raffinate
- Extract
- Desorbent

Step N

Direction of port switching

Switching time or port-switching interval, \( t^* \)

Step N+1
Models for SMB Systems

- Models for designing and analyzing SMBs
  - Models assuming steady-state conditions with continuous, countercurrent flows of fluid and solid adsorbent, approximating SMB operation with a TMB
    - TMB equilibrium-stage models using a McCabe–Thiele–type analysis
      - simplest, but difficult to apply to systems with nonlinear adsorption–equilibrium isotherms
    - TMB local–adsorption–equilibrium models
      - ignoring effects of axial dispersion and fluid–particle mass transfer; useful for establishing reasonable operating flow rates in multiple sections of an SMB (∵ for many applications, behavior of an SMB is determined largely by adsorption equilibria)
    - TMB rate–based models
      - account for axial dispersion in the bed, particle–fluid mass–transfer resistances, and nonlinear adsorption isotherms; preferred for a final design
  - SMB rate–based models: apply to transient operation for startup, approach to cyclic steady state, and shutdown
Steady-State Local–Adsorption–Equilibrium TMB Model (1)

- TMB local–adsorption–equilibrium model for a single section

• Assumptions
  - One-dimensional plug flow of both phases with no channeling
  - Constant volumetric flow rates (Q for liquid and Q_s for solid)
  - Constant external void fraction, \( \varepsilon_b \), of solids bed
  - Negligible axial dispersion and particle–fluid mass–transfer resistances
  - Local adsorption equilibrium between solute concentrations, \( c_i \), in the bulk liquid and adsorption loading, \( q_i \), on the solid
  - Isothermal and isochoric conditions

• Mass balance
  \[
  Q \frac{dc_i}{dz} - S \frac{dq_i}{dz} = 0
  \]

• Boundary conditions
  \( z = 0, c_i = c_{i,\text{in}} \) and \( z = Z, q_i = q_{i,\text{in}} \)
Steady-State Local-Adsorption-Equilibrium TMB Model (2)

• Usefulness of local-equilibrium theory
  : approximate determinations of the amount of solid adsorbent and fluid flow rates, in each TMB section, to achieve a perfect separation of two solutes
• Assuming adsorption equilibrium is linear for a dilute feed, with $K_A > K_B$
• Flow rate ratios for each section $j$
  \[ m_j = \frac{Q_j}{Q_s} = \frac{\text{volumetric fluid phase flow rate}}{\text{volumetric solid particle phase flow rate}} \]

• For local adsorption equilibrium, the necessary and sufficient conditions at each section for complete separation
  \[ K_A < m_I < \infty \quad \text{Ensures that net flow rates of components A and B will be positive (upward) in Section I} \]
  \[ 0 < m_{IV} < K_B \quad \text{Ensures that net flow rates of components A and B will be negative (downward) in Section IV} \]
Ensure sharpness of the separation by causing net flow rates of A and B to be negative (downward) and positive (upward), respectively, in the two central Sections II and III.

Inequality constraints can be converted to equality constraints using the safety margin, $\beta$

\[
\begin{align*}
\frac{Q_1}{Q_S} &= K_A \beta \\
\frac{(Q_1 - Q_E)}{Q_S} &= K_B \beta \\
\frac{(Q_1 - Q_E + Q_F)}{Q_S} &= K_A / \beta \\
\frac{(Q_1 - Q_E + Q_F - Q_R)}{Q_S} &= K_B / \beta
\end{align*}
\]

\[Q_S = \frac{Q_F}{K_A / \beta - K_B \beta}\]

\[Q_E = Q_S (K_A - K_B) \beta\]

\[Q_R = Q_S (K_A - K_B) / \beta\]

\[Q_I = Q_C + Q_D = Q_S K_A \beta\]

\[Q_C = Q_S K_A \beta - Q_D\]

\[Q_C : \text{fluid recirculation rate before adding makeup desorbent}\]

By an overall material balance, \[Q_D = Q_E + Q_R - Q_F\]
Steady-State Local-Adsorption–Equilibrium TMB Model (4)

• Triangle method

- If values $m_{\|}$ and $m_{\|\|}$ within the triangular region are selected, a perfect separation is possible
  - If $m_{\|} < K_B$, some B appears in extract
  - If $m_{\|\|} > K_A$, some A appears in raffinate
  - If $m_{\|} < K_B$ and $m_{\|\|} > K_A$, extract contains some B and raffinate contains some A

• Safety margin, $1 \leq \beta \leq \sqrt{\frac{K_A}{K_B}}$

  - Above a maximum $\beta$, some sections will encounter negative fluid flow rates, and when $\beta < 1$, perfect separation will not be achieved
  - As the value of $\beta$ increases from minimum to maximum, fluid flow rates in the sections increase, often exponentially
  - As separation factor $K_A/K_B \to 1$, permission range of $\beta$ becomes smaller
Steady-State TMB Model (1)

- Unlike the local-adsorption-equilibrium model, axial dispersion and fluid-particle mass transfer are considered.
- Mass-balance equation for the bulk fluid phase, $f$

$$-D_{L_j} \frac{d^2 c_{i,j}}{dz^2} + u_{f_j} \frac{dc_{i,j}}{dz} + \frac{(1 - \varepsilon_b)}{\varepsilon_b} J_{i,j} = 0$$

$J_f$: mass-transfer flux between the bulk fluid phase and the sorbate in the pores
$u_f$: interstitial fluid velocity \( u_f = \frac{Q_j}{\varepsilon_b A_b} \)

- Mass-balance for sorbate, $s$, on the solid phase

$$u_s \frac{d\bar{q}_{i,j}}{dz} - J_{i,j} = 0$$

$u_s$: true moving-solid velocity \( u_s = \frac{Q_s}{(1 - \varepsilon_b) A_b} \)

- Fluid-to-solid mass transfer

$$J_{i,j} = k_{i,j} \left(q^*_{i,j} - \bar{q}_{i,j}\right)$$

- Adsorption isotherm

$$q^*_{i,j} = f\{\text{all } c_{i,j}\}$$
Steady-State TMB Model (2)

• Boundary conditions
  
  - At the section entrance, z=0 (accounting for axial dispersion)
    
    \[ u_{f_j} (c_{i,j,0} - c_{i,j}) = -\varepsilon_b D_{L_j} \frac{dc_{i,j}}{dz} \]
  
  - At Sections I and II where extract is withdrawn
    
    \[ c_{i,1,z=L_j} = c_{i,II,z=0} \quad q_{i,1,z=L_j} = q_{i,II,z=0} \]
  
  - At Sections III and IV where raffinate is withdrawn
    
    \[ c_{i,III,z=L_j} = c_{i,IV,z=0} \quad q_{i,III,z=L_j} = q_{i,IV,z=0} \]
  
  - At Sections II and III where feed enters
    
    \[ c_{i,III,z=0} = \left( \frac{Q_{II}}{Q_{III}} \right) c_{i,II,z=L_j} + \left( \frac{Q_F}{Q_{III}} \right) c_{i,F} \quad q_{i,II,z=L_j} = q_{i,III,z=0} \]
  
  - At Sections IV and I where make-up desorbent enters
    
    \[ c_{i,1,z=0} = \left( \frac{Q_{IV}}{Q_{I}} \right) c_{i,IV,z=L_j} + \left( \frac{Q_D}{Q_{I}} \right) c_{i,D} \quad q_{i,IV,z=L_j} = q_{i,1,z=0} \]
Steady-State TMB Model (3)

• Volumetric fluid flow rates

\[ \dot{Q}_1 = \dot{Q}_{IV} + \dot{Q}_D \]
\[ \dot{Q}_{II} = \dot{Q}_1 - \dot{Q}_E \]
\[ \dot{Q}_{III} = \dot{Q}_{II} + \dot{Q}_F \]
\[ \dot{Q}_{IV} = \dot{Q}_{III} - \dot{Q}_R \]

• To obtain the same true velocity difference between fluid and solid particles, upward fluid velocity in the SMB must be the sum of the absolute true velocities in the upward-moving fluid and the downward-moving solid particles in the TMB

\[
(\dot{Q}_j)_{\text{SMB}} = (\dot{Q}_j)_{\text{TMB}} + \left( \frac{\varepsilon_b}{1 - \varepsilon_b} \right) (\dot{Q}_S)_{\text{TMB}}
\]
Dynamic SMB Model

- Equations take into account time of operation, t, use a fluid velocity relative to the stationary solid particles, and must be written for each bed subsection, k, between adjacent ports.

- Mass–balance equation for the bulk fluid phase, \( f \)

\[
\frac{\partial c_{i,k}}{\partial t} - D_{Lj} \frac{\partial^2 c_{i,k}}{\partial z^2} + u_{f_k} \frac{\partial c_{i,k}}{\partial z} + \frac{(1 - \varepsilon_b)}{\varepsilon_b} J_{i,k} = 0
\]

- Mass–balance for sorbate on the solid phase

\[
\frac{\partial q_{i,k}}{\partial t} - J_{i,k} = 0
\]

Interstitial fluid velocity \((u_f)_{\text{SMB}} = (u_f)_{\text{TMB}} + |(u_s)|_{\text{TMB}}\)

\[
u_s = \frac{L_k}{t^*}
\]

- Boundary conditions for TMB models apply to SMB models.
In addition, initial conditions are needed for \( c_{i,j} \) and \( \bar{q}_{i,j} \).