Adsorption Process Development

Basics & Methodology

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Outline

- Objectives;
- Adsorbents;
- Terminology;
- Modeling;
- Equilibrium theory;
- Intraparticle kinetics - LDF model;
- Old models;
- Methodology;
- PSA and SMB technologies.
Objectives

1) Purification

2) Recovery of solutes

3) Separations (bulk)

Examples

a. Phenolic waste waters
b. Recovery of antibiotics from fermentation broths
c. Parex/Sarex
d. Separation of enantiomers
e. $\text{O}_2$ from air
f. $\text{N}_2$ from air
g. $\text{H}_2$ purification
h. Propane/propene
i. Landfill gas
Adsorbents

Types

▪ Activated carbons
▪ Carbon molecular sieves
▪ Zeolites
▪ Polymers
▪ Metal organic frameworks (MOFs)

Structures

▪ Homogeneous
▪ Porous
▪ Bidisperse
Adsorbents: properties

- Adsorption capacity;
- Adsorption kinetics;
- Selectivity;
- Mechanical stability;
- Thermal stability;
- Chemical stability.
Adsorption capacity: Amount of each species that is retained by the adsorbent

Adsorption kinetics: rate at which each species is retained by the adsorbent

**Equilibrium selectivity** – ratio between the adsorption capacities of the more adsorbed species and the less adsorbed species;

**Kinetic selectivity** – ratio between the kinetic parameter of the more adsorbed species and the less adsorbed species;
Mechanical stability:

Resistance of the adsorbent – the formation of dust may damage the valves and contaminate the product.

It also limits the height of the columns.

Thermal stability:

It is important to know how the adsorbent reacts to temperature increase.

Some adsorbent can be damaged when increasing the temperature.

Chemical stability:

Some adsorbents can be damaged in presence of some species such as water vapour or ammonia.

It is important to know if these species are in the feed streams and if so, take measures to avoid the degradation of the adsorbent.
Equilibrium-controlled separation

Adsorption capacity of H₂ and CO₂ in activated carbon

There is a significant difference between the H₂ and CO₂ adsorption capacities. This difference in the adsorption capacity allows the separation of these two gases. This is an equilibrium-controlled separation.

Kinetic-controlled separation

Adsorption capacity of $N_2$ and $O_2$ in a carbon molecular sieve

Carbon molecular sieves are commonly used for nitrogen production from air by PSA.

How can the separation be possible if both gases adsorb almost the same?

Adsorption kinetics of $\text{N}_2$ and $\text{O}_2$ in a carbon molecular sieve

Oxygen diffuses faster than nitrogen.

This difference in the adsorption kinetics allows the separation of these two gases.

This is a kinetic-controlled separation.

An accurate process simulator is an important tool for learning, designing and optimization purposes.
Terminology

Concentration profiles - $C_i(z)$ at a given $t$

Concentration histories - $C_i(t)$ at a given $z$

At $z=L$ Breakthrough Curve

$t_{bp}$ – breakthrough time
$t_{st}$ – stoichiometric time
Terminology

Overall balance

\[ Q C_{i0} t_{st} = \varepsilon C_{i0} V + (1 - \varepsilon) q_{i0} V \]

Moles introduced in the column

\[ t_{st} = \tau (1 + \xi) \]

Space time

\[ \tau = \frac{\varepsilon V}{Q} \]

Capacity factor

\[ \xi = \frac{(1 - \varepsilon)}{\varepsilon} \frac{q_{i0}}{C_{i0}} \]

Total capacity

\[ \int_{0}^{t_f} (C_{i0} - C_i) dt \]

Useful capacity

\[ \int_{0}^{t_{bp}} (C_{i0} - C_i) dt \]
Terminology

Concentration profile at $t = t_{bt}$

$C_{in}$

$C_{out}$

LES

Length of Equilibrium Section

LUB

Length of Unused Bed

$z_{st}$

$MTZ$

$L = LES + LUB$

$L = \frac{u_{i}}{1 + \xi} t_{st}$

$z_{st} = LES = \frac{u_{i}}{1 + \xi} t_{bp}$

$LUB = L - LES = L - \frac{L}{t_{st}} t_{bp}$

$LUB = L \left(1 - \frac{t_{bp}}{t_{st}}\right)$

$MTZ = 2 LUB$
“Le Génie Chimique c’est pas de la plomberie”

Modelling

Pierre Le Goff

a) conservation equations (mass, energy, momentum, electric charge)
b) equilibrium laws at the interface(s)
c) constitutive laws
d) kinetic laws of heat/mass transfer and reaction
e) initial and boundary conditions
f) optimization criterion
Factors influencing the behavior of adsorptive processes

- Equilibrium
- Hydrodynamics
- Film mass transfer
- Intraparticle diffusion
- Intraparticle convection
- Heat transfer
Batch adsorption (isothermal)

Mass balance in a batch adsorber

\[ -V \frac{dC_i}{dt} = W \frac{dq_i}{dt} \]

At equilibrium:

\[ q_{ie} = \frac{V}{W} C_{i0} - \frac{V}{W} C_i \]

\[ q_{ie} = f(C_{ie}) \]
\[
\frac{V_{sol}}{W_{ads}} C_{io} \quad \frac{q_{if}}{W_{ads}}
\]

ads. equl. isotherm

\[ q_{if} = f (c_{if}) \]

operating line

\[
\text{Solve}
\begin{align*}
q_{if} &= f (c_{if}) \\
q_{if} &= \frac{V_{sol}}{W_{ads}} C_{io} - \frac{V_{sol}}{W_{ads}} c_{if}
\end{align*}
\]
Linear isotherm

$$c_if = \frac{c_{i0}}{1+\xi_m}$$

Rectangular

$$q_if = q \quad \text{for } c_if > 0 \quad \xi f = c_{i0} (1-\xi_m)$$

Langmuir

$$q_if = \frac{q K c_if}{1+K c_if} \quad \xi_f = \frac{-[1+K'(\xi_m-1)]+\sqrt{[1+K'(\xi_m-1)]^2+4K'}}{2K'}$$

$$K' = k' c_{i0}$$

$$\xi_f = c_{if}/c_{i0}$$
Kinetics of batch adsorption

Mass balance

\[ V \frac{dC_i}{dt} = W \frac{dq_i}{dt} \]

\[ q_i = \frac{V(C_{i0} - C_i)}{W} \]

Kinetic law

\[ \frac{dq_i}{dt} = k_h(q_i^* - q_i) \]

LDF model

Equilibrium law

\[ q_i^* = KC_i \]

Linear isotherm

Initial condition

\[ t = 0; C_i = C_{i0}; q_i = q_{i0} \]
Linear Driving Force model

Glueckauf

\[
\frac{\partial \langle q \rangle}{\partial t} = k_h [q_s - \langle q \rangle]
\]

\[
k_h = \frac{15 D_h}{R_p^2}
\]
$C_i(t) = \frac{C_{i0}}{1 + e^{kh(1+x)t}}$
Mass balance for species i

Isothermal operation
Axial dispersed flow

\[ \text{Flux in} \quad \frac{(\varepsilon \ A)}{m^2} \ \varphi_z \]\n
\[ \text{Flux out} \quad \frac{(\varepsilon \ A)}{m^2} \ \varphi_{z+dz} \]

\[ \text{Acumulation} \]

\[ \begin{align*}
\text{Interparticle} & \quad \varepsilon \ A \ dz \ \frac{\partial C_i}{\partial t} \\
\text{Intraparticle} & \quad (1 - \varepsilon) \ A \ dz \ \frac{\partial q_i}{\partial t}
\end{align*} \]

\[ (\varepsilon \ A) \ \varphi_z = (\varepsilon \ A) \varphi_{z+dz} + \varepsilon \ A \ dz \ \frac{\partial C_i}{\partial t} + (1 - \varepsilon) \ A \ dz \ \frac{\partial q_i}{\partial t} \]

\[ 0 = \frac{\partial \varphi_i}{\partial z} + \frac{\partial C_i}{\partial t} + \frac{(1 - \varepsilon)}{\varepsilon} \frac{\partial q_i}{\partial t} \]

Average adsorbed concentration in the particle (mol/m$^3$$_{ads}$)
Mass balance for species $i$

- Isothermal operation
- Axial dispersed flow

\[ 0 = \frac{\partial \varphi_i}{\partial z} + \frac{\partial C_i}{\partial t} + \left(1 - \varepsilon\right) \frac{\partial q_i}{\partial t} \]

\[ \varphi = u_i C_i - D_{ax} \frac{\partial C_i}{\partial z} \]

\[ u_i = \frac{u_0}{\varepsilon} \]

\[ \varepsilon D_{ax} \frac{\partial^2 C_i}{\partial z^2} = u_0 \frac{\partial C_i}{\partial z} + \varepsilon \frac{\partial C_i}{\partial t} + \left(1 - \varepsilon\right) \frac{\partial q_i}{\partial t} \]
Mass balance for species $i$

**Dimensionless variables**

\[ x = \frac{z}{L} \quad \theta = \frac{t}{\lambda} \quad \tilde{C}_i = \frac{C_i}{C_{i0}} \quad \tilde{q}_i = \frac{q_i}{q_{i0}} \]

\[
\frac{1}{Pe} \frac{\partial^2 \tilde{C}_i}{\partial x^2} = \frac{\partial \tilde{C}_i}{\partial x} + \frac{\partial \tilde{C}_i}{\partial \theta} + \xi \frac{\partial \tilde{q}_i}{\partial \theta}
\]

**Peclet number**

\[ Pe = \frac{u_0 L}{\varepsilon D_{ax}} \]

\[ Pe \rightarrow \infty \quad \text{Plug flow of fluid phase} \]

**Capacity factor**

\[ \xi = \frac{(1 - \varepsilon)}{\varepsilon} \frac{q_{i0}}{C_{i0}} \]

\[ \xi \rightarrow 0 \quad \text{No adsorption, inert packing} \]
Equilibrium law at interfaces

Adsorption equilibrium isotherm

$q_i^* = f(C_i)$

Favorable isotherms

$\frac{d^2 q_i^*}{d C_i^2} < 0$

Unfavorable isotherms

$\frac{d^2 q_i^*}{d C_i^2} > 0$

Linear isotherms

$\frac{d^2 q_i^*}{d C_i^2} = 0$

Rectangular or irreversible

$\frac{d^2 q_i^*}{d C_i^2} = 0$

With an inflection point (BET)
Equilibrium theory

The simplest model

✓ Isothermal operation
✓ Instantaneous equilibrium in each point of the bed

✓ Plug flow
✓ No pressure drop (negligible)

\[ q_i = q_i^* \]

- Mass balance for i
  \[ u_0 \frac{\partial C_i}{\partial z} + \varepsilon \frac{\partial C_i}{\partial t} + (1 - \varepsilon) \frac{\partial q_i^*}{\partial t} = 0 \]

b) Equilibrium law
  \[ q_i^* = f(C_i) \]

Combining a) and b)
  \[ u_i \frac{\partial C_i}{\partial z} + \frac{\partial C_i}{\partial t} + \frac{(1 - \varepsilon)}{\varepsilon} f'(C_i) \frac{\partial C_i}{\partial t} = 0 \]

\[ u_i \frac{\partial C_i}{\partial z} + \left[ 1 + \frac{(1 - \varepsilon)}{\varepsilon} f'(C_i) \right] \frac{\partial C_i}{\partial t} = 0 \]
Equilibrium theory

$$u_i \frac{\partial C_i}{\partial z} + \left[ 1 + \frac{(1-\varepsilon)}{\varepsilon} f'(C_i) \right] \frac{\partial C_i}{\partial t} = 0$$

Since

$$\left( \frac{\partial z}{\partial t} \right)_C = - \left( \frac{\partial C}{\partial t} \right)_z$$

It results in:

$$u_C = \left( \frac{\partial z}{\partial t} \right)_C = \frac{u_i}{1 + \frac{1-\varepsilon}{\varepsilon} f'(C_i)}$$

De Vault’s equation (1943)

Adsorption as a wave phenomenon

The velocity of propagation of a concentration C, i.e. $u_C$, is inversely proportional to the local slope of the isotherm $f'(C_i)$.
Equilibrium theory

Unfavorable isotherms

As $C_i$ increases, the slope $f'(C_i)$ increases and $u_c$ decreases.

Higher concentrations travel at lower velocities

Concentration profiles - $C_i(z)$ at a given $t$
Equilibrium theory

Favorable isotherms

As $C_i \rightarrow$ the slope $f'(C_i)$ $\downarrow$ and $u_c \uparrow$

Higher concentrations travel at higher velocities

Step $C_{i0}$

Physically not possible $\rightarrow$ Compressive front $\rightarrow$ shock
Equilibrium theory

Favorable isotherms

Shock velocity

\[ u_{sh} = \frac{u_i}{1 + \frac{1 - \varepsilon}{\varepsilon} \frac{\Delta q_i}{\Delta c_i}} \]

Slope of the chord
Equilibrium theory

Linear isotherms

The input is just delayed without change

BET

Breakthrough curve – feed at $C_{i0}$

Composite front: shock up to $C_t$ then dispersive
The nature of the breakthrough curve is governed in first place by the adsorption equilibrium isotherm.

Favorable isotherms

Unfavorable isotherms

Compressive fronts (shock)

\[ u_{sh} = \frac{u_i}{1 + \frac{1 - \varepsilon}{\varepsilon} \frac{\Delta q_i}{\Delta c_i}} \]

Dispersive fronts

\[ u_{ci} = \frac{u_i}{1 + \frac{1 - \varepsilon}{\varepsilon} f'(c)} \]
Intraparticle kinetics

Homogeneous particle

\[
\frac{\partial q}{\partial t} = D_h \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q}{\partial r} \right)
\]

Parabolic profile

\[
q = a_0 + a_2 r^2 \\
q_s = a_0 + a_2 R_p^2 \\
\frac{\partial q}{\partial r} = 2a_2 r \\
\left. \frac{\partial q}{\partial r} \right|_{R_p} = 2a_2 R_p
\]

\[
\langle q \rangle = a_0 + a_2 \frac{3}{5} R_p^2
\]

Averaging

\[
\frac{R_p^3}{3} \frac{\partial \langle q \rangle}{\partial t} = D_h \left[ r^2 \frac{\partial q}{\partial r} \right]_{R_p}^{R_p} = D_h R_p \left. 2 \frac{\partial q}{\partial r} \right|_{R_p}
\]

\[
\frac{\partial \langle q \rangle}{\partial t} = D_h \frac{3}{R_p^2} 2a_2 R_p = 6a_2 D_h
\]

Linear driving force – LDF (Glueckauf)

\[
\frac{\partial \langle q \rangle}{\partial t} = k_h \left[ q_s - \langle q \rangle \right]
\]

\[
k_h = \frac{15 D_h}{R_p^2}
\]

\[
6a_2 D_h = k_h \left[ a_0 + a_2 R_p^2 - a_0 + a_2 \frac{3}{5} R_p^2 \right]
\]
Intraparticle kinetics

Porous particle

\[\varepsilon_p \frac{\partial C_p}{\partial t} + \frac{\partial q}{\partial t} = D_{pe} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_p}{\partial r} \right)\]

Averaging

\[\varepsilon_p \frac{\partial \langle C_p \rangle}{\partial t} + \frac{\partial \langle q \rangle}{\partial t} = k_p \left( C_{ps} - \langle C_p \rangle \right)\]

Linear isotherms

\[q = K C_p \quad \frac{\partial \langle C_p \rangle}{\partial t} = \frac{k_p}{\varepsilon + K} \left( C_{ps} - \langle C_p \rangle \right)\]

Equivalence with homogeneous particles

\[\frac{\partial \langle q \rangle}{\partial t} = k_h \left[ q_s - \langle q \rangle \right] \]

\[k_h = \frac{k_p}{K_h} = \frac{k_p}{\varepsilon_p + K}\]
Constant pattern

Stationary front

\[ C_i(z + dz, t + dt) = C_i(z, t) \]

Velocity of the stationary front

\[ \lambda = \frac{\partial z}{\partial t} \bigg|_{C_i} = \frac{L}{t_{st}} = \frac{u_i}{1 + \xi} \]

Velocity of the stationary front
Old models

I) Chemical kinetic type

II) Physical kinetic type
Old models

Chemical kinetic type – Thomas model

Mass balance

\[ u_0 \frac{\partial C_i}{\partial z} + \varepsilon \frac{\partial C_i}{\partial t} + (1 - \varepsilon) \frac{\partial q_i}{\partial t} = 0 \]

Kinetic law

\[ \frac{\partial q_i}{\partial t} = k_1 \left[ C \left( Q - q_i \right) - \frac{1}{K} q_i (C_0 - C_i) \right] \]

Boundary and initial conditions

\[ z = 0 \quad C = C_0 \quad \forall t \]
\[ t = \frac{z}{u_i} \quad q_i = 0 \quad \forall z \]

\[ \frac{C_i}{C_0} = \frac{J(rN, NT)}{J(rN, NT) + [1 - J(N, rNT)]} \times e^{(r-1)N(T-1)} \]

\[ r = \frac{1}{K}, \quad N = k_1 \frac{Q}{u_0} \left( 1 - \varepsilon \right), \quad NT = k_1 \frac{C_0}{C_0} \left( t - \frac{z}{u_i} \right) \]
Old models

Chemical kinetic type – Simplifications

\[ r = 0 \quad K \to \infty \quad \text{Bohart} \]

\[ \frac{C_i}{C_0} = \frac{e^{NT}}{e^{NT} + e^N - 1} \]

\[ r = 1 \quad \text{Walter} \]

\[ \frac{C_i}{C_0} = J(N, NT) \]

\[ \text{high } r \quad \text{(Unfavorable isotherm } K<1) \]

\[ \frac{C_i}{C_0} = \frac{\sqrt{r}}{1 - r} \]

\[ r = 1, N \text{ and } NT \text{ high} \quad \text{Klinkenberg} \]

\[ \frac{C_i}{C_0} = \frac{1}{2} \left[ 1 + \text{erf} \left( \sqrt{NT} - \sqrt{N} \right) \right] \]
Old models

Physical kinetic type – Rosen model

Mass balance

\[ u_0 \frac{\partial C_i}{\partial z} + \varepsilon \frac{\partial C_i}{\partial t} + (1 - \varepsilon) \frac{\partial q_i}{\partial t} = 0 \]

Kinetic law for film mass transfer

\[ \frac{\partial q_i}{\partial t} = k_f a \left( C_i - C_i^* \right) \]

Intraparticle diffusion

\[ \frac{\partial q_i(r, z, t)}{\partial r} = D_h \left[ \frac{\partial^2 q_i}{\partial r^2} + \frac{2}{r} \frac{\partial q_i}{\partial r} \right] \]

Average

\[ q_i(z, t) = \frac{3}{R_p} \int_0^{R_p} q_i(r, z, t) r^2 \, dr \]

Isotherm

\[ q_i = \frac{Q}{C_0} C_i = m C_i \]

A and B depend on the model parameters

\[ Bi = \frac{k_f R_p}{D_h}, \quad N_f = k_f a \tau, \quad m \]
Methodology

Prior to any simulation, necessary data must be gathered independently:

I. measurement of single adsorption isotherms;

II. measurement of intraparticle diffusivities (ZLC);

III. measurement of film mass transfer (shallow bed);

IV. measurement of axial dispersion (tracer);

V. measurement of breakthrough curves for single and feed mixtures;

VI. modeling breakthrough curves and model validation;

VII. modeling/simulation of process (PSA; SMB);

VIII. lab-scale operation of process and model validation;

IX. sizing and scale-up of industrial process.
Methodology

Single adsorption isotherms - Liquid phase in batch systems
Methodology

Single adsorption isotherms - Gas phase in Rubotherm magnetic balance
Intraparticle diffusivities - Zero-length column (ZLC) method

FID – flame ionization detector
TCD – thermal conductivity detector
MV – multiport valve
**Methodology**

Film mass transfer - shallow-bed technique

![Diagram of film mass transfer - shallow-bed technique]

- Ci/Cit vs Time
- Adsorbent

Graph showing Ci/Cit vs Time with two curves and labels Nf 1 and 2.
Methodology

Axial dispersion / model validation - tracer experiments and breakthrough curves for single and feed mixtures
Methodology

Experiments → Process Modelling

Process Simulation

Experimental Runs → Results agree?

Yes → Process Optimization

No → Refine the model

Yes → Process Optimization
How can we obtain B from a mixture of A+B?

Let’s choose an operating pressure considering:

- Acceptable capacity and selectivity;
- Maximum pressure allowed by the adsorbent and unit/equipment;
- Energy consumption;
- Product requirements.
Pressure Swing Adsorption

How can we obtain B from a mixture of A+B?

If we pass a stream containing A+B at the operating pressures, through a bed packed with this adsorbent:

- A will be preferentially adsorbed (retained by the adsorbent);
- B will move through the bed and leave it at the top.

This will happen until the adsorbent is saturated with A.

What should we do next?
How can we obtain B from a mixture of A+B?

If we decrease the pressure the adsorption capacity also decreases.

For example, if we open the bed to the atmosphere and let the gas out, the final pressure will be 1 bar.
Pressure Swing Adsorption

PSA units are usually composed by two or more columns packed with one or more adsorbents
Pressure Swing Adsorption

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PSA units are usually composed by two or more columns packed with one or more adsorbents.
Adsorbent regeneration - PSA, TSA, CSA

Pressure Swing Adsorption

The adsorbent is regenerated by lowering the pressure.

Temperature Swing Adsorption

The adsorbent is regenerated by increasing the temperature.

Concentration Swing Adsorption

The adsorbent is regenerated by lowering the concentration.
SMB principle (Sorbex Processes-UOP)