Adsorption modelling as a tool to estimate transport properties

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✓ Introduction – Concepts
  ✓ Aims and basics
  ✓ Adsorption
  ✓ Adsorbents
  ✓ Column dynamics

✓ Modelling – Theoretical Background
  ✓ Definitions and terminology
  ✓ Momentum, Material and Energy Balances
  ✓ Equilibrium theory
  ✓ Adsorption kinetics

✓ Assessing mass transfer
  ✓ Simple fit to breakthrough curves
  ✓ From uptake curves
  ✓ From calorimetry

✓ Final remarks
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Designing a process

Column dynamics

Diagram showing the process flow and the graph representing the relative concentration over time.
What is your aim?

- Synthesize better sorbents?
  - Material
  - Shape
  - Properties

- Design process units?
  - Size
  - Material
  - Control

- Optimize operations?
  - Costs
  - Maintenance
  - Facilities

- Understand the phenomena?
  - Effects
  - Simplifications
  - Improvements
Necessary knowledge

- Which column size?
- Which flowrate?
- Is it reversible?
- How long do cycles last?
- Should columns be thermostated?
- Which operating conditions maximize purity, recovery from the feed, and minimize energy/solvent consumption?

etc
Basics

**Conservation equations**
(mass, energy, momentum, electric charge)

**Equilibrium laws** at the interface(s)

**Constitutive laws**

**Kinetic laws** of heat/mass transfer and reaction

**Initial and boundary conditions**

**Optimization criterion**
Classification of systems

- Nature of equilibrium relationship
  - Linear isotherm
  - Favorable isotherm
  - Unfavorable isotherm

- Thermal effects
  - Isothermal
  - Near isothermal

- Concentration level
  - Trace systems
  - Nontrace systems

- Flow model
  - Plug flow
  - Dispersed flow

- Complexity of kinetic model
  - Negligible transfer resistance
  - Single transfer resistance
  - Multiple transfer resistance
Adsorbents

- Types
- Structures
  - Homogeneous
  - Porous
  - Bidisperse
- Properties
  - Adsorption capacity
  - Selectivity
  - Kinetics
  - Stability
    - Mechanical
    - Thermal
    - Chemical
Outline

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

• Concentration profiles – $C_i(z)$ at a given $t$

• Concentration histories – $C_i(t)$ at a given $z$
Definitions and terminology

• Overall balance

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

Moles introduced in the column

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

\[ \tau = \frac{\varepsilon V}{Q} \quad \text{Space time} \]

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

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

Useful capacity = \[ Q \int_{0}^{t_{bp}} (C_{i0} - C_i) dt \]

Alírio E. Rodrigues (2014)
Definitions and terminology

• Concentration profile at \( t = t_{bt} \)

\[
L = \text{LES} + \text{LUB}
\]

\[
L = \frac{u_i}{1 + \xi} t_{st}
\]

\[
z_{st} = \text{LES} = \frac{u_i}{1 + \xi} t_{bp}
\]

\[
\text{LUB} = L - \text{LES} = L - \frac{L}{t_{st}} t_{bp}
\]

\[
\text{MTZ} = 2 \text{LUB}
\]
In general, one is interested in re-using the adsorbent for a relatively large numbers of cycles. Industrial sep processes alternate two steps:

- **Adsorption**: fluid phase is enriched with the weakly adsorbed species (raffinate)

- **Desorption**: fluid phase is enriched with the strongly adsorbed components (extract) and the adsorbent is regenerated to be used in another cycle (by temperature, pressure, pH or concentration swings)
Breakthrough of mixtures

Shape depends on capacity, selectivity and mass transfer

Graph showing:
- Component A with concentration $C / C_0$ over time (peaks at 1.50 and then drops to 1.00)
- Component B with concentration $C / C_0$ over time (peaks at 1.50 and then drops to 1.00)
Modelling adsorption processes

- Equilibrium
- Kinetics
- Feed
- Co-adsorption
- Heat data
- Hydrodynamics
- Cycle time
- Purity
- Adsorber dimensions
Modelling adsorption processes
Modelling a fixed bed

Transport Phenomena

Outlet

Final Concentration

Bed Porosity

Adsorptive

Pressure

Fluid Heat Capacity

Column

Axial Dispersion

Feed

Flow Speed

Initial Concentration

Mass Transfer into the Particle

Heat Transfer (Gas - Solid)

Heat Transfer (Solid - Solid)

Convection, Heat, Fluid Film, and Mass (Flow)

Solid Heat Capacity

Adsorption through the Wall

Environment

Adsorbent Particle
To model the dynamic behavior of an adsorption column is a problem far from trivial.
Pressure drop in packed beds:

\[-\frac{\partial p}{\partial z} = \frac{150 \mu_g (1 - \varepsilon)^2}{\varepsilon^3 d_p^2} \nu + \frac{1.75(1 - \varepsilon) \rho_g}{\varepsilon^3 d_p} \nu^2\]

**Blake-Kozeny equation**

**Burke-Plummer equation**

**Laminar Flow**

**Turbulent Flow**
Material balance

**Continuity** – General Form: \( \frac{\partial}{\partial t} C_T(z, t) + \nabla \cdot \mathbf{F}(z, t) - s(z, t) = 0 \)

Considering the interparticle volume: \( C_T = \frac{m}{V_T} = \varepsilon \frac{m}{V} = \varepsilon C_g \)

Flux – Accounting convective and dispersive effects: \( \mathbf{F} = \nu C_T - D_{ax} \frac{\partial C_T}{\partial Z} \) or \( \mathbf{F} = \varepsilon \nu C_g - \varepsilon D_{ax} \frac{\partial C_g}{\partial Z} \)

Material “removal” rate: \( s = -\frac{\partial Q}{\partial t} \) where \( Q \) is the amount of the species leaving the bulk phase in the control volume

Concentration inside the particle: \( Q = \frac{m_p + m_A}{V_T} \)

Defining the adsorbent (particle) volume: \( V_A = V_T (1 - \varepsilon) \) and the pore volume: \( V_p = V_A \varepsilon_p \)

Then: \( Q = (1 - \varepsilon) \cdot \left[ \frac{m_p}{V_A} + \frac{m_A}{V_A} \right] = (1 - \varepsilon) \cdot \left[ \varepsilon_p \frac{m_p}{V_p} + \frac{m_A}{V_A} \right] \)
Material balance

Defining the particle density: \( \rho_s = \frac{m_s}{V_A} \)

Thus: \( Q = (1 - \varepsilon) \left[ \varepsilon_p C_g + \rho_s \frac{m_A}{m_S} \right] = (1 - \varepsilon) \left[ \varepsilon_p C_g + \rho_s \bar{q} \right] \)

Deriving to obtain \( s = -\frac{\partial Q}{\partial t} \)

We get: \( s = -\frac{\partial}{\partial t} \left( (1 - \varepsilon) \left( \varepsilon_p C_g + \rho_s \bar{q} \right) \right) \)

Where \( \bar{q} \) is defined as the average specific amount adsorbed: \( \bar{q}(t) = \frac{1}{V_A} \int_0^V q(r, t) \cdot dV \)

Substituting equations: \( \frac{\partial}{\partial t} (\varepsilon C_g) + \nabla \cdot \left( \varepsilon v C_g - \varepsilon D_{ax} \frac{\partial C_g}{\partial z} \right) + \frac{\partial}{\partial t} \left( (1 - \varepsilon) \left( \varepsilon_p C_g + \rho_s \bar{q} \right) \right) = 0 \)

Three reasonable assumptions are very often made:

(i) bed porosity is homogeneous and constant along the bed
(ii) particle porosity is the same for every adsorbent particle and
(iii) the gas flows in only one dimension – axially

\[
\varepsilon \frac{\partial C_g}{\partial t} + \varepsilon \frac{\partial (\varepsilon C_g)}{\partial z} - \varepsilon D_{ax} \frac{\partial^2 C_g}{\partial z^2} + \left( 1 - \varepsilon \right) \left( \varepsilon_p \frac{\partial C_g}{\partial t} + \rho_s \frac{\partial \bar{q}}{\partial t} \right) = 0
\]
Energy Balance

Analogously to the Continuity:

$$\frac{\partial}{\partial t} E(z, t) + \nabla \cdot \mathbf{F}(z, t) - s(z, t) = 0$$

Volumetric sensible heat in the control volume:

$$E = \frac{m}{V_T} c T = C c T$$

Temperature changes in the given control volume is represented by the temperature changes in the gas and in the solid phases

For the gas phase:

$$E_g = \frac{m_g}{V_T} \tilde{c}_g T_g = \varepsilon C_g \tilde{c}_g T_g$$

For the solid:

$$E_s = \frac{m_s}{V_T} \hat{c}_s T_s = (1 - \varepsilon) \rho_s \hat{c}_s T_s$$

infinitesimal cross sectional cut of the adsorbent column
Energy Balance

Summing up and differentiating:

\[
\frac{dE}{dt} = E_g + E_s = \varepsilon C_g \tilde{c}_g \frac{dT_g}{dt} + (1 - \varepsilon) \rho_s \hat{c}_s \frac{dT_s}{dt}
\]

Considering identical temperature profiles for the fluid and solid phase in the adsorbent column operating at cyclic steady state: \( T_g = T_s \)

Then:

\[
\frac{dE}{dt} = [\varepsilon C_g \tilde{c}_g + (1 - \varepsilon) \rho_s \hat{c}_s] \frac{dT_g}{dt}
\]

Heat is transported through the adsorbent bed along with the fluid flow and dispersed analogously to the mass. The dispersion term can be simplified and evaluated by applying Fourier's method of separation of variables. Thus, the energy flux can be written as:

\[
F = E_{conv} + E_{disp} = \varepsilon \nu C_g \tilde{c}_g T_g - \varepsilon \lambda \frac{\partial T_g}{\partial z}
\]

Applying the same assumptions as before:
(i) bed porosity is homogeneous and constant along the bed
(ii) particle porosity is the same for every adsorbent particle and
(iii) the gas flows in only one dimension – axially

\[
\nabla \cdot \mathbf{F}(z, t) = \varepsilon \tilde{c}_g \left[ C_g T_g \frac{\partial \nu}{\partial z} + \nu T_g \frac{\partial C_g}{\partial z} + \nu C_g \frac{\partial T_g}{\partial z} \right] - \lambda \frac{\partial^2 T_g}{\partial z^2}
\]
Energy Balance

Heat is generated in the system through adsorption and removed by conduction through the walls and later by convection with the environment.

\[ s = (1 - \varepsilon) \rho_s \left( -\Delta H \frac{\partial \tilde{q}}{\partial t} \right) - \frac{4 h_w}{d_i} (T_g - T_w) \]

Substituting and arranging:

\[
\begin{align*}
\left[ \varepsilon C_g \tilde{c}_g + (1 - \varepsilon) \rho_s \tilde{c}_s \right] \frac{\partial T_g}{\partial t} + \varepsilon \tilde{c}_g \left[ C_g T_g \frac{\partial v}{\partial z} + \nu C_g \frac{\partial T_g}{\partial z} \right] \\
- \lambda \frac{\partial^2 T_g}{\partial z^2} - \left( 1 - \varepsilon \right) \rho_s \left( -\Delta H \frac{\partial \tilde{q}}{\partial t} \right) - \frac{4 h_w}{d_i} (T_g - T_w) = 0
\end{align*}
\]

or

\[
\begin{align*}
\lambda \frac{\partial^2 T_g}{\partial z^2} - \varepsilon \tilde{c}_g \left[ C_g T_g \frac{\partial v}{\partial z} + \nu C_g \frac{\partial T_g}{\partial z} \right] - \frac{4 h_w}{d_i} (T_g - T_w) \\
- \left[ \varepsilon C_g \tilde{c}_g + (1 - \varepsilon) \rho_s \tilde{c}_s \right] \frac{\partial T_g}{\partial t} + (1 - \varepsilon) \rho_s (\Delta H) \frac{\partial \tilde{q}}{\partial t} = 0
\end{align*}
\]

Additional equation - heat transfer from the wall to the environment:

\[
\rho_w \hat{c}_w \frac{\partial T_w}{\partial t} = \alpha_w h_w (T_g - T_w) - \alpha_{wl} U_g (T_w - T_\infty)
\]
Summarizing

**Material Balance**

\[
\frac{\partial C_{g,i}}{\partial t} + \frac{(1 - \varepsilon)}{\varepsilon} \rho_b \frac{\partial \bar{q}_i}{\partial t} - D_{ax} \frac{\partial^2 C_{g,i}}{\partial z^2} + u \frac{\partial C_{g,i}}{\partial z} = 0
\]

accumulation  dispersion  convection

**Energy Balances**

\[
\frac{(1 - \varepsilon)}{\varepsilon} \rho_b \Delta H \frac{\partial \bar{q}}{\partial t} + \lambda \left( \frac{1 - \varepsilon}{\varepsilon} \rho_b c_{PS} + \rho_g c_{PG} \right) \frac{\partial T_g}{\partial t} + u \rho_g c_{PG} \frac{\partial T_g}{\partial z} + 4h_w \left( T_g - T_w \right) = 0
\]

generation  dispersion  accumulation  convection  transfer to wall

\[
\alpha_w h_w (T_g - T_w) - \rho_w C_{pw} \frac{\partial T_w}{\partial t} - \alpha_w L g (T_w - T_\infty) = 0
\]

gas to wall  wall to environment  accumulation

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D. Bathen and M. Breitbach, Adsorptionstechnik (2001)
Assumptions and Simplifications

- No gradients in the radial direction?
- Plug flow with axial mass dispersion?
- Mass transfer into the particle in accordance to the linear driving force (LDF) model?
- Thermal equilibrium between the gas and the adsorbent?
- Adiabatic operation?
- Constant heat transfer coefficients?
- Homogeneous porosity along the bed?
- No pressure drop?

D. Bathen and M. Breitbach, Adsorptionstechnik (2001)
Equilibrium law

At interfaces: \( q_i^* = f(C_{g,i}) \)

**favorable**

\[
\frac{d^2 q_i^*}{dC_{g,i}^2} < 0
\]

**unfavorable**

\[
\frac{d^2 q_i^*}{dC_{g,i}^2} > 0
\]

**linear**

\[
\frac{d^2 q_i^*}{dC_{g,i}^2} = 0
\]

**rectangular**

\[
q_i^*\bigg|_{C_i}
\]

**with an inflection**

\[
q_i^*\bigg|_{C_i}
\]

Primary influence

The shape and nature of the breakthrough curve are strongly influenced by the equilibrium.

\[ q^* = q_{\text{max}} \frac{K \cdot p}{1 + K \cdot p} \]
Increasing the partial pressure

<table>
<thead>
<tr>
<th>Flow [Norm]</th>
<th>P</th>
<th>y</th>
<th>P_i</th>
<th>Partial Flow</th>
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<td>bar</td>
<td>%</td>
<td>bar</td>
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<td>10</td>
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<td>300</td>
<td>30</td>
<td>10</td>
<td>3.0</td>
<td>10</td>
</tr>
</tbody>
</table>

Bastos-Neto et al., Chem. Ing. Tech., 83 (2011)
Equilibrium theory

“Simple is beautiful (and useful)”

- Isothermal operation
- Equilibrium reached instantaneously in each point of the bed: \( q_i^* = \bar{q}_i \)
- Plug flow
- Negligible pressure drop
- Negligible dispersion and mass transfer effects

the material balance

\[
\varepsilon \frac{\partial C_{g,i}}{\partial t} + \varepsilon \left( u_i \frac{\partial C_{g,i}}{\partial z} \right) - \varepsilon \ D_{ax} \frac{\partial^2 C_{g,i}}{\partial z^2} + (1 - \varepsilon) \left( \varepsilon_p \frac{\partial C_{g,i}}{\partial t} + \rho_s \frac{\partial \bar{q}_i}{\partial t} \right) = 0
\]

becomes

\[
u_i \frac{\partial C_{g,i}}{\partial z} + \frac{\partial C_{g,i}}{\partial t} + \left( 1 - \frac{\varepsilon}{\varepsilon} \right) \frac{\partial q_i^*}{\partial t} = 0
\]
Equilibrium theory

considering \( q^* = f(C_{g,i}) \)

then \[ u_i \frac{\partial C_{g,i}}{\partial z} + \left(1 + \frac{1-\varepsilon}{\varepsilon} f'(C_{g,i}) \right) \frac{\partial C_{g,i}}{\partial t} = 0 \]

since \[ \frac{\partial z}{\partial t} \bigg|_c = - \frac{\frac{\partial C_{g,i}}{\partial t}}{\frac{\partial C_{g,i}}{\partial z}} \bigg|_t \]

it results in \[ u_c = \frac{\partial z}{\partial t} \bigg|_c = \frac{u_i}{1 + \frac{1-\varepsilon}{\varepsilon} f'(C_{g,i})} \]

De Vault's Equation

Adsorption as a wave phenomenon

The velocity of propagation of a concentration \( C \), \textit{i.e.} \( u_c \), is inversely proportional to the local slope of the isotherm \( f(C) \)

D. DeVault, \textit{J. Am. Chem. Soc.} 65, 532 (1943)
Equilibrium theory

unfavorable isotherms

As $C_i$, the local slope of the isotherm $f(C_i)$ and $u_c$

Higher concentrations travel at lower velocities
favorable isotherms: “shock wave”

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

Higher concentrations travel at higher velocities.
**Equilibrium theory**

favorable isotherms: "shock wave"

\[ \Delta u_c = \frac{\partial z}{\partial t} \bigg|_c = \frac{u_i}{1 + \frac{1 - \varepsilon}{\varepsilon} \frac{\Delta q_i}{\Delta C_{g,i}}} \]

\[ u_{sh} = \frac{L_c}{t_{st}} \]

\[ t_{st} = \frac{\varepsilon V_c}{Q} \left[ 1 + \frac{1 - \varepsilon}{\varepsilon} \frac{\Delta q_i}{\Delta C_{g,i}} \right] \]
Influence of the equilibrium

**favorable**

\[
\frac{d^2 q_i^*}{dC_{g,i}^2} < 0
\]

**unfavorable**

\[
\frac{d^2 q_i^*}{dC_{g,i}^2} > 0
\]

**linear**

\[
\frac{d^2 q_i^*}{dC_{g,i}^2} = 0
\]
Axial dispersion

If non-idealities are present

Axial Dispersion Coefficient

$D_{ax,1} < D_{ax,2} < D_{ax,3}$
If non-idealities are present

**Mass transfer resistances**

![Graph showing mass transfer resistances with relative concentration on the y-axis and time (min) on the x-axis. The graph includes lines for different mass transfer coefficients: \(k_{LDF}\), \(k_{LDF} \times 0.2\), and \(k_{LDF} \times 5.0\).]
If non-idealities are present

**Axial dispersion** and **mass transfer resistances** are to be considered

For **favorable isotherms**, the concentration front disperses up to a certain extent and assumes a **CONSTANT PATTERN BEHAVIOR**

For **unfavorable and linear isotherms**, the concentration front disperses continuously as it moves along the bed and hence follows a **PROPORTIONATE PATTERN BEHAVIOR**
What about kinetics?
How to assess the phenomenon?
How relevant can it be to the process?
Intraparticle kinetics

Remembering the material balance

\[
\varepsilon \frac{\partial C_g}{\partial t} + \varepsilon \frac{\partial \left( \nu C_g \right)}{\partial z} - \varepsilon D_{ax} \frac{\partial^2 C_g}{\partial z^2} + (1 - \varepsilon) \cdot \left( \varepsilon_p \frac{\partial C_g}{\partial t} + \rho_s \frac{\partial q'}{\partial t} \right) = 0
\]

\[
\rho_s \frac{\partial q'}{\partial t} = \frac{\partial q}{\partial t}
\]

\( [q'] = \frac{\text{adsorbed amount}}{\text{adsorbent mass}} \)

\( [q] = \frac{\text{adsorbed amount}}{\text{adsorbent volume}} \)

**Homogeneous particle**

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

**Porous particle**

\[
\varepsilon \frac{\partial C_p}{\partial r} + \frac{\partial q}{\partial t} = D_{p,e} \cdot \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q}{\partial r} \right)
\]
Intraparticle kinetics

Adsorbed amount as a function of radius and time

\[ q = f(r, t) \]

Averaging:

\[ \bar{q}(t) = \frac{1}{V_A} \int_0^{V_A} q(r, t) \cdot dV \]

Linear Driving Force (LDF) approach:

\[ \frac{\partial \bar{q}}{\partial t} = k_{LDF} \cdot (q^* - \bar{q}) \]

E. Glueckauf, Trans. Far. Soc., 51(11), (1955)
The LDF model works in practice!

Adsorptive separation process models require several sets of averaging of local kinetic properties, which are often lost during a series of integration processes.

The overall adsorption kinetics for a heterogeneous adsorbent can be described by a heterogeneous-LDF model, even though the kinetics in each adsorption site is Fickian.

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Estimating $k_{LDF}$

“Simple Fit” - Experiment vs Simulation

$$\varepsilon \frac{\partial C_g}{\partial t} + \varepsilon \frac{\partial (v C_g)}{\partial z} - \varepsilon D_{ax} \frac{\partial^2 C_g}{\partial z^2} + (1 - \varepsilon) \left( \varepsilon_p \frac{\partial C_g}{\partial t} + \rho_s \frac{\partial q'}{\partial t} \right) = 0$$

$$\frac{\partial \bar{q}}{\partial t} = k_{LDF} \cdot (q^* - \bar{q})$$
Estimating $k_{LDF}$

From uptake curves

**Convenience:** during the measurement of equilibrium isotherms

- Continuous measurement of mass variation for each pressure step
- Mass and energy balances are used to estimate the mass transfer coefficient
- Relatively simple, but reliable
- Restricted to “non-instantaneous” adsorption
- LDF approach
From uptake curves

Equilibrium model

\[ q_i = \frac{q_{m,i} (b_i P)^{1/n_i}}{1 + (b_i P)^{1/n_i}} \]

Adsorption kinetics

\[ \frac{\partial \bar{q}}{\partial t} = k_{\text{LDF}} \cdot (q^* - \bar{q}) \]

Energy Balance

\[ m_s \hat{c}_{p,s} \frac{\partial T}{\partial t} = m_s \frac{\partial q}{\partial t} (-\Delta H) - h_{\text{ave}} A (T - T_\infty) \]

Clausius-Clapeyron

\[ \Delta H = 28 \text{ kJ mol}^{-1} \]

Natural convection coefficient

\[ h = 70 \text{ W m}^2 \text{ K} \]
From uptake curves

film and macropore resistances are negligible

\[ \frac{\partial q}{\partial t} \propto k_{LDF} \]
From uptake curves

CO$_2$ and N$_2$ uptake curves

Estimated coefficients correspond to the minimum value fitting to experiments

From uptake curves

Breakthrough curves experiments were measured to validate the simulation model using the \( k_{LDF} \) values estimated from gravimetric experiments.

Model parameters used for fixed bed simulations

- Adsorbent mass [kg] 0.155
- Bed density \( \rho_L \) [kg m\(^{-3}\)] \( m_{ads}/V_{col} \)
- Bed porosity \( \varepsilon_L \) [-] \( 1-(\hat{V}_p+\hat{V}_s)\times \rho_L \)
- Particle density \( \rho_p \) [kg m\(^{-3}\)] \( \rho_L/(1-\varepsilon_L) \)
- Particle porosity \( \varepsilon_p \) [-] \( 1-[\hat{V}_s/(\hat{V}_s+\hat{V}_{po})] \)
- Heat transfer coefficient [W m\(^2\) K] 100
- Solid specific heat \( c_{p,s} \) [J kg\(^{-1}\) K\(^{-1}\)] 820
- Wall specific heat \( c_{p,w} \) [J kg\(^{-1}\) K\(^{-1}\)] 477
- Wall density \( \rho_w \) [kg m\(^{-3}\)] 786
- Axial mass dispersion \( D_{ax} \) [m\(^2\) s\(^{-1}\)] \( a) \) \( D_{ax} = \frac{2ur_p}{Pe} \); \( \frac{1}{Pe} = 0.7 \varepsilon + 0.5 \)
- Axial heat dispersion \( \lambda_{ax} \) [W m\(^{-1}\) K\(^{-1}\)] \( \frac{\lambda_{ax}}{k_g} = (7 + 0.5 Pr Re) \)
Simulated results using the estimated coefficients showed good agreement with the experimental breakthrough data.
From uptake curves

Different coefficient values were used to evaluate the influence of the $k_{LDF}$ on the relative concentration curve shape and the temperature history.

From uptake curves

Temperature histories are important to cross-check the method to estimate $k_{LDF}$.
Using adsorption-related heat effects and heat transport to estimate mass transfer
Estimating $k_{\text{LDF}}$

Tian-Calvet microcalorimeter

\[ \Delta h_{\text{ads},T,n} = \left( \frac{dQ_{\text{rev}}}{dn^\sigma} \right)_{T,A} + V_d \left( \frac{dp}{dn^\sigma} \right)_{T,A} \]
Discontinuous procedure:

\[
\left( \frac{dQ_{\text{rev}}}{dn_\sigma} \right)_{T,A} + V_c \left( \frac{dp}{dn_\sigma} \right)_{T,A} = \Delta h_{ad}^{T,n}
\]
Heat peaks

\[ Q_{ads} = \sum_{i=1}^{8} \int \dot{Q} \, dt \]

\[ Q_{desor} = \int \dot{Q} \, dt \]

\[ E_{regT} = |Q_{ads} - Q_{desor}| \]
Modelling – Defining the system

3 defined parts (volumes):
• Dosing cell
• Dead volume
• Calorimetric cell

Mass and Energy balances for each part
Modelling – Assumptions

- Ideal gas behavior
- The dosing cell and the dead volume are under **isothermal** and **non-adiabatic** operation
- The pressure in the dead volume is the same of the calorimetric cell
- Two approaches for mass transfer: **Linear Driving Force** and **Diffusion** in a spherical particle
Estimating $k_{LDF}$

Dosing cell

\[
\frac{dC_v}{dt} = -\frac{\dot{n}_s}{V_v}
\]

\[
C_v c_p \frac{dT_v}{dt} = \frac{h_v A_v}{V_v} (T_{01} - T_v)
\]

\[P_v = C_v R T_v\] (EOS)
Dead volume

\[
\frac{dC_d}{dt} V_d = \dot{n}_s - \dot{n}_e
\]

\[
V_a c_p C_d \frac{dT_d}{dt} - V_d \frac{dP}{dt} = \dot{n}_s c_p (T_v - T_d) - h_c A_d (T_d - T_{01})
\]

\[
P_d = C_d R T_d \quad \text{(EOS)}
\]

\[
P_d = P
\]
**Calorimetric cell**

**Calorimetric cell with temperature control**

\[
\frac{dC_c}{dt} V_c = \dot{n}_e - m_s \frac{d\bar{q}}{dt}
\]

\[
V_c c_p C \frac{dT}{dt} - V_c \frac{dP}{dt} + m_s c_{ps} \frac{dT}{dt} + m_c \frac{d\bar{q}}{dt} (-\Delta H) + m_s c_p \bar{q} \frac{dT}{dt}
\]

\[
= \dot{n}_e c_p (T_d - T) - h_c A_c (T - T_c (R1))
\]

\[
P = CRT \quad \text{(EOS)}
\]

\[
P = f(t) \quad \text{Measured – Needed for the solution}
\]
Estimating $k_{LDF}$

**Calorimetric cell wall – Energy Balance**

**R1 < R < R2:**

$$\rho c_1 c_2 \frac{dT_c}{dt} = \frac{1}{R} K_{c1} \left( \frac{\partial}{\partial R} \left( R \frac{\partial T_c}{\partial R} \right) \right)$$

**R2 < R < R3:**

$$\rho c_2 c_2 \frac{dT_c}{dt} = \frac{1}{R} K_{c2} \left( \frac{\partial}{\partial R} \left( R \frac{\partial T_c}{\partial R} \right) \right)$$

**Boundary conditions:**

$$h_c (T - T_c(t, R1)) = -K_{c1} \frac{dT_c}{dt} (t, R1) \quad T_c(t, R3) = T_{02}$$

**Initial condition:**

$$T_c(0, R) = T_{02}$$
Two approaches

1. **Linear Driving Force**

\[
\frac{d\bar{q}}{dt} = k_{LDF}(q^* - \bar{q})
\]

2. **Diffusion**

\[
\frac{dq_p}{dt} = D_c \left[ \frac{\partial q_p}{\partial r} + \frac{2}{r} \frac{\partial q_r}{\partial r} \right]
\]

Boundary conditions:

\[
\frac{\partial q_p}{\partial r}(t, 0) = 0 \quad q_p(t, r_p) = q_E(P)\rho_p
\]

Initial condition:

\[
q_p(0, r) = q_E(P_i)\rho_p
\]
Heat flux and total heat

The heat flux out of the cell is given by

\[ Q_1 = -K_{c1}A_c0 \frac{\partial T_c}{\partial R} (t, R2) \]

The total heat is calculated as follows

\[ Q_{total} = \int_0^{\infty} Q_1 dt \]
Experimental procedure

• Heat of adsorption is determined prior to each run according to the equation for the total heat
• The kinetic parameters are then fitted $k_{LDF}$ or $\frac{D_c}{R_c^2}$

Resistance transitions

Relationship between and the mass transfer resistances (film, macro and micropores)

$$\frac{1}{k_{LDF,i}} = \frac{R_p q_0}{3k_f,i C_0} + \frac{q_0 R_p^2}{15 \varepsilon_p D_{p,i} C_0} + \frac{R_c^2}{15 D_{c,i}}$$
Estimating $k_{LDF}$

**AC Norit RB4 – CO$_2$ adsorption**

- **Left Panel:**
  - Graph showing adsorbed amount (mmol/g) vs. pressure (bar).
  - Experimental data points with a blue line indicating the Langmuir fit.
  - Peak 3 highlighted.

- **Right Panel:**
  - Graph showing heat rate (mWatt) vs. time (s).
  - Experimental data points in black, simulation in red.
  - $k_{LDF} = 0.13$ s$^{-1}$
  - $D_c/R^2 = 0.0084$ s$^{-1}$
Estimating $k_{\text{LDF}}$

**AC Norit RB4 – CO$_2$ adsorption**

**Figure 1:**
- **Graph 1:**
  - Adsorbed amount (mmol/g) vs. Pressure (bar)
  - Experimental data points and Langmuir Fit line
- **Graph 2:**
  - Enthalpy of adsorption (kJ/mol) vs. Adsorbed amount (mmol/g)
  - Peak 5
- **Graph 3:**
  - Heat rate (mWatt) vs. Time (s)
  - Experimental and Simulation curves
  - $k_{\text{LDF}} = 0.13 \text{ s}^{-1}$
  - $D_c/R^2 = 0.009 \text{ s}^{-1}$

**Notes:**
- The graphs illustrate the adsorption behavior of AC Norit RB4 for CO$_2$ under different pressures.
- The enthalpy of adsorption increases with the adsorbed amount.
- The heat rate analysis shows the comparison between experimental and simulation results, indicating the rate of adsorption and its accuracy.
Estimating $k_{LDF}$

AC Norit RB4 – Comparing with the uptake measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method</th>
<th>$k_{LDF}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC Norit RB4</td>
<td>Uptake</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Calorimetry</td>
<td>0.13</td>
</tr>
</tbody>
</table>

AC Norit RB4 – Sensibility of the method

- $DcR2 = 0.0041 \text{ 1/s}$
- $DcR2 = 0.0041/5 \text{ 1/s}$
- $DcR2 = 0.0041/10 \text{ 1/s}$
Estimating $k_{\text{LDF}}$

ACPX series – $k_{\text{LDF}}$ x PSD

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k_{\text{LDF}}$ (1/s)</th>
<th>$D_c/R^2$ (1/s)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACPX 22</td>
<td>0.075</td>
<td>0.004</td>
<td>19.7</td>
</tr>
<tr>
<td>ACPX 41</td>
<td>0.120</td>
<td>0.009</td>
<td>13.3</td>
</tr>
<tr>
<td>ACPX 76</td>
<td>0.136</td>
<td>0.009</td>
<td>14.9</td>
</tr>
</tbody>
</table>

Estimating $k_{\text{LDF}}$

Zeolite 13X

$K_{\text{LDF}} = 0.022 \text{ s}^{-1}$

$D_c/R^2 = 0.0013 \text{ s}^{-1}$

Sample | Method | $D_c/R^2$
---|---|---
Binderless 13X zeolite | ZLC at 313 K | 0.0009-0.0012
Calorimetry at 298 K | 0.0013

https://www.explainthatstuff.com/zeolites.html
✓ Introduction – Concepts
  ✓ Aims and basics
  ✓ Adsorption
  ✓ Adsorbents
  ✓ Column dynamics

✓ Modelling – Theoretical Background
  ✓ Definitions and terminology
  ✓ Momentum, Material and Energy Balances
  ✓ Equilibrium theory
  ✓ Adsorption kinetics

✓ Assessing mass transfer
  ✓ Simple fit to breakthrough curves
  ✓ From uptake curves
  ✓ From calorimetry

✓ Final remarks
Final remarks

What about breakthrough curves of systems with non-conventional adsorption isotherms?

IUPAC classification for condensable vapors (e.g. N₂ at 77 K)

PX isotherm
MIL-53 (Al)
Remy et al., 2011

CO₂ isotherms
YO-MOF
Mulfort et al., 2010
Final remarks

A zoo of breakthrough curves

Hamon et al, JACS, 47, 17490, 2009
**Final remarks**

Xylenes adsorption in MOFs

**Langmuir**

Modeling the Effect of Structural Changes during Dynamic Separation Processes on MOFs

Tom Remy, Gino V. Baron, and Joeri F. M. Denayer*

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbates</th>
<th>Isotherms</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-53(Al)</td>
<td>EB/oX 383 K</td>
<td><img src="image1" alt="Isotherm" /></td>
<td><img src="image2" alt="Mechanism" /></td>
</tr>
<tr>
<td>MIL-47</td>
<td>pX/mX 343 K</td>
<td><img src="image3" alt="Isotherm" /></td>
<td><img src="image4" alt="Mechanism" /></td>
</tr>
</tbody>
</table>
Final remarks

MIL-47 (V) – Materiaux de l’Institute Lavoisier

Octahedral metallic clusters $\text{VO}_4(\text{OH})_2$ connected by terephthalic acid linkers

Final remarks


Breathing effect of (Al)MIL-53: narrowing of pores

Octahedral metallic cluster $\text{AlO}_4(\text{OH})_2$ connected by terephthalic acid linkers

Unit cell 1500 Å$^3$

up to 40%wt CO$_2$, organics

Serre et al, JACS 2002, 124, 13519-13526
Final remarks

CS 1: OX/EB breakthrough curves in MIL-53

From Rietveld refinement of in-situ DRX of OX adsorption in MIL-53 (Al), it was found that...
Final remarks

Fixed bed model equations (LDF)

\[
D_{ax} \frac{\partial^2 C_i}{\partial x^2} - \frac{u}{\varepsilon} \frac{\partial}{\partial t} \left(1 - \varepsilon\right) \frac{\partial C_i}{\partial t} + \frac{\partial q_i}{\partial t} \rho_s = 0
\]

\[
\frac{\partial q_i}{\partial t} = K_{LDF} \cdot (q_i^* - q_i)
\]

\[
t = 0: \quad C_i = 0 \quad (\forall z)
\]

\[
x = 0: \quad \frac{u}{\varepsilon} (C_i - C_{i,in}) - D_{ax} \frac{\partial C_i}{\partial x} = 0
\]

\[
x = L: \quad \frac{\partial C_i}{\partial x} = 0
\]

**ISOTHERM EQUATIONS**

\[
q_{oi} = q_{satoi} \cdot \frac{K_{oi} \cdot C_{oi}}{1 + K_{oi} \cdot C_{oi} + K_{EB} \cdot C_{EB}}
\]

\[
+ q_{logoi} \cdot \frac{K_{oi} \cdot C_{oi}}{1 + K_{oi} \cdot C_{oi}}
\]

\[
q_{logoi} = \left\{ \begin{array}{l}
K_{log} \cdot P_{log} \cdot \exp \left[ n_{log} \cdot \left( \frac{P_{tot}}{P_{go}} - 1 \right) \right] \\
K_{log} + P_{log} \cdot \exp \left[ n_{log} \cdot \left( \frac{P_{tot}}{P_{go}} - 1 \right) \right] - 1
\end{array} \right\}
\]

\[
q_{EB} = q_{satEB} \cdot \frac{K_{EB} \cdot C_{EB}}{1 + K_{EB} \cdot C_{EB} + K_{oi} \cdot C_{oi}}
\]
Final remarks

PoX = 0.0004 bar
Zone I

PoX = 0.002 bar
Zone II

PoX = 0.03 bar
Zone III
Final remarks

CS2: MIL-47 (V) – a rigid MOF

V + Terephthalic acid linker

Final remarks

PX and MX isotherms in MIL-47 at 343 K

- No breathing
- Similar isotherms, although PX shows an inflexion point at $10^{-3}$ and $10^{-2}$ bar
Final remarks

Same trick applied to provide a mathematical description of PX isotherm

\[
q_{pX}^* = q_{satpX} \cdot \frac{K_{\log pX} \cdot C_{pX}}{1 + K_{\log pX} \cdot C_{pX} + K_{mX} \cdot C_{mX}}
\]

\[
K_{\log pX} = K_{0,pX} \cdot \left[ 1 + \left( K_{\log} + P_{\log} \cdot \exp \left[ r_{\log} \cdot \left( \frac{q_{pX}}{q_{satpX}} - \left( \frac{q_{pX}}{q_{satpX}} \right)_{crit} \right) \right] - 1 \right) \right]
\]
Final remarks

Finsy et al., *JACS (2008)* 130, 7110

Remy et al., *Langmuir* (2011) 27, 13064
Final remarks

Finsy et al., *JACS* (2008) 130, 7110
Remy et al., *Langmuir* (2011) 27, 13064

**Experimental**

- $P_{px} = 0.03$ bar

**Simulation**

- $P_{px} = 0.03$ bar

- $P_{px} = 0.05$ bar
Final remarks

Coming back to the equilibrium theory...
Final remarks

• Classical concepts such as phase equilibrium and transport phenomena have been revisited and applied to the description of adsorption dynamics in a fixed bed

• The correct analysis of batch adsorption data should provide scalable (design) parameters that will be useful not only for process design and optimization, but also to plan experiments in fixed bed in lab scale
We hope this is a small brick in bridging the gap between different approaches of adsorption scientists from more fundamental and more applied backgrounds.
Our team

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D Sc

M Sc

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Thank you for your attention!