

Universidade Federal do Ceará





Laboratório de Pesquisa em Adsorção e Captura de CO<sub>2</sub>

## Adsorption modelling as a tool to estimate transport properties

## **Moises Bastos-Neto**

Universidade Federal do Ceará

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#### LEIPZIGER SYMPOSIUM on dynamic sorption

## 2019

Advanced Sorbent Materials on the Way to Application





#### ✓Introduction – Concepts

- $\checkmark$  Aims and basics
- ✓ Adsorption
- ✓ Adsorbents
- ✓ Column dynamics

## ✓ Modelling – Theoretical Background

- $\checkmark$  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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## **Column dynamics**







## 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?







## **Conservation equations**

(mass, energy, momentum, electric charge)



pressure (N m<sup>-2</sup>)

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





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





**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















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



Alírio E. Rodrigues





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



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





#### Overall balance

$$QC_{i0}t_{st} = \varepsilon C_{i0}V + (1-\varepsilon)q_{i0}V$$

Moles introduced in the column

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

Total capacity = 
$$Q \int_{0}^{t_f} (C_{i0} - C_i) dt$$
  
Useful capacity =  $Q \int_{0}^{t_{bp}} (C_{i0} - C_i) dt$ 

$$\tau = \frac{\varepsilon V}{Q}$$
 Space time  
$$\xi = \frac{(1-\varepsilon)}{\varepsilon} \frac{q_{i0}}{C_{i0}}$$
 Capacity factor









Concentration profile at t = t<sub>bt</sub>







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**







## Modelling adsorption processes











## **Modelling a fixed bed**



#### **Transport Phenomena**







# To model the dynamic behavior of an adsorption column is a problem far from trivial.



## Momentum balance



#### **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:  $\frac{\partial}{\partial t}C_{T}(z,t) + \nabla \cdot \mathbf{F}(z,t) - \mathbf{s}(z,t) = 0$ 

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

adsorbent mass: ∂m adsorbed amount:  $\partial q_i$ bed porosity:  $\varepsilon$ 

Flux – Accounting convective and dispersive effects:  $\mathbf{F} = v C_T - D_{ax} \frac{\partial C_T}{\partial z}$  or  $\mathbf{F} = \varepsilon v C_g - \varepsilon D_{ax} \frac{\partial C_g}{\partial z}$ 

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:  $Q = \frac{m_P + m_A}{V}$ 

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:  $\rho_s = \frac{m_s}{V_s}$ 

**Thus:** 
$$Q = (1 - \varepsilon) \cdot \left[ \varepsilon_P C_g + \rho_s \frac{m_A}{m_s} \right] = (1 - \varepsilon) \cdot \left[ \varepsilon_P C_g + \rho_s \overline{q} \right]$$

Deriving to obtain  $S = -\frac{\partial Q}{\partial t}$ 

We get: 
$$s = -\frac{\partial}{\partial t} \left( (1 - \varepsilon) \cdot \left( \varepsilon_P C_g + \rho_s \overline{q} \right) \right)$$

Where  $\overline{q}$  is defined as the average specific amount adsorbed:

$$\overline{q}(t) = \frac{1}{V_A} \int_0^{V_A} q(r, t) \cdot dV$$

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

#### 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

$$\varepsilon \frac{\partial C_g}{\partial t} + \varepsilon \frac{\partial (v C_g)}{\partial z} - \varepsilon D_{ax} \frac{\partial^2 C_g}{\partial z^2} + (1 - \varepsilon) \cdot \left( \varepsilon_P \frac{\partial C_g}{\partial t} + \rho_s \frac{\partial \overline{q}}{\partial t} \right) = 0$$



adsorbent mass:  $\partial m$ adsorbed amount:  $\partial q_i$ bed porosity:  $\varepsilon$ 



## **Energy Balance**



heat convection  $\partial T_{q}$ heat transfer дz *dT*<sub>s</sub> heat generation adsorbent mass: ∂m

adsorbed amount:  $\partial q_i$ bed porosity:  $\varepsilon$ 

infinitesimal cross sectional cut of the adsorbent column

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:

$$E = \frac{m}{V_{\tau}} c T = C c T$$

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:  $E_g = \frac{m_g}{V_\tau} \tilde{c}_g T_g = \varepsilon C_g \tilde{c}_g T_g$ 

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



## **Energy Balance**



Summing up and differentiating:

$$\frac{\partial E}{\partial t} = E_g + E_s = \varepsilon C_g \tilde{c}_g \frac{\partial T_g}{\partial t} + (1 - \varepsilon) \rho_s \hat{c}_s \frac{\partial T_s}{\partial t}$$

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

Then: 
$$\frac{\partial E}{\partial t} = \left[ \varepsilon C_g \tilde{c}_g + (1 - \varepsilon) \rho_s \hat{c}_s \right] \frac{\partial T_g}{\partial t}$$



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:

$$\mathbf{F} = \boldsymbol{E}_{conv} + \boldsymbol{E}_{disp} = \varepsilon \, v \, \boldsymbol{C}_{g} \, \tilde{\boldsymbol{c}}_{g} \, \boldsymbol{T}_{g} - \varepsilon \, \lambda \, \frac{\partial \boldsymbol{T}_{g}}{\partial z}$$

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

bed  
icle and 
$$\nabla \cdot \mathbf{F}(z,t) = \varepsilon \ \widetilde{c}_g \left[ C_g \ T_g \ \frac{\partial v}{\partial z} + v \ T_g \ \frac{\partial C_g}{\partial z} + v \ C_g \ \frac{\partial T_g}{\partial z} \right] - \lambda \ \frac{\partial^2 T_g}{\partial z^2}$$





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

$$\mathbf{s} = (1 - \varepsilon) \rho_{s} \left( (-\Delta H) \frac{\partial \overline{q}}{\partial t} \right) - \frac{4 h_{w}}{d_{i}} \left( T_{g} - T_{w} \right)$$

Substituting and arranging:

$$\begin{bmatrix} \varepsilon C_{g} \tilde{c}_{g} + (1-\varepsilon)\rho_{s} \hat{c}_{s} \end{bmatrix} \frac{\partial T_{g}}{\partial t} + \varepsilon \tilde{c}_{g} \begin{bmatrix} C_{g} T_{g} \frac{\partial v}{\partial z} + v C_{g} \frac{\partial T_{g}}{\partial z} \end{bmatrix} \quad \text{or} \\ -\lambda \frac{\partial^{2} T_{g}}{\partial z^{2}} - \left( (1-\varepsilon)\rho_{s} \left( (-\Delta H) \frac{\partial \overline{q}}{\partial t} \right) - \frac{4 h_{w}}{d_{i}} (T_{g} - T_{w}) \right) = 0 \quad \text{or} \\ -\lambda \frac{\partial^{2} T_{g}}{\partial z^{2}} - \left( (1-\varepsilon)\rho_{s} \hat{c}_{s} \end{bmatrix} \frac{\partial T_{g}}{\partial t} + (1-\varepsilon)\rho_{s} (-\Delta H) \frac{\partial \overline{q}}{\partial t} = 0 \end{bmatrix}$$

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

$$\rho_{w} \hat{c}_{w} \frac{\partial T_{w}}{\partial t} = \alpha_{w} h_{w} (T_{g} - T_{w}) - \alpha_{wL} U_{g} (T_{w} - T_{\infty})$$











- 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?



## Equilibrium law



## At interfaces: q

$$q_i^* = f(C_{g,i})$$

favorable







rectangular



#### with an inflection



D.M. Ruthven, Principles of Adsorption (1984) W. Kast, Adsorption aus der Gasphase (1987)



#### **Primary influence**

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



$$q^* = q_{\max} \frac{K \cdot p}{1 + K \cdot p}$$





#### Increasing the partial pressure

Flow [Norm]	Р	У	P <sub>i</sub>	Partial Flow
mL/min	bar	%	bar	mL/min
100	10	10	1.0	10
150	15	10	1.5	10
200	20	10	2.0	10
300	30	10	3.0	10







## "Simple is beautiful (and useful)"

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

#### the material balance

$$\varepsilon \frac{\partial C_{g,i}}{\partial t} + \varepsilon \frac{\partial (u_i C_{g,i})}{\partial z} - \varepsilon D_{ax} \frac{\partial^2 C_{g,i}}{\partial z^2} + (1 - \varepsilon) \cdot \left( \varepsilon_P \frac{\partial C_{g,i}}{\partial t} + \rho_s \frac{\partial \overline{q}}{\partial t} \right) = 0$$

#### becomes

$$u_{i} \frac{\partial C_{g,i}}{\partial z} + \frac{\partial C_{g,i}}{\partial t} + \left(\frac{1-\varepsilon}{\varepsilon}\right) \frac{\partial q_{i}^{*}}{\partial t} = 0$$





**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  $\left. \frac{\partial z}{\partial t} \right|_c = -\frac{\frac{\partial C_{g,i}}{\partial t}}{\frac{\partial C_{g,i}}{\partial z}}_t$   
it results in  $\left. u_c = \frac{\partial z}{\partial t} \right|_c = \frac{u_i}{1 + \frac{1 - \varepsilon}{\varepsilon}} f'(C_{g,i}) \right.$  De

**De Vault's Equation** 

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)





#### unfavorable isotherms





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

#### **Dispersive Front**

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"





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

#### Compressive (shock) Front

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

#### Higher concentrations travel at higher velocities


# **Equilibrium theory**



#### favorable isotherms: "shock wave"





# Influence of the equilibrium







#### **Axial dispersion**

LPA CO<sub>2</sub>





#### Mass transfer resistances







#### 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

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

$$\rho_s \frac{\partial q'}{\partial t} = \frac{\partial q}{\partial t}$$

 $[q'] = \frac{adsorbed \ amount}{adsorbent \ mass}$ 

 $[q] = \frac{adsorbed \ amount}{adsorbent \ volume}$ 

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* 



 $\mathsf{R}_{\mathsf{p}} \qquad \varepsilon \, \frac{\partial C_p}{\partial r} + \frac{\partial q}{\partial t} = D_{p,e} \cdot \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q}{\partial r} \right)$ 



## **Intraparticle kinetics**



### Adsorbed amount as a function of radius and time

q = f(r,t)

Averaging:

$$\overline{q}(t) = \frac{1}{V_A} \int_0^{V_A} q(r,t) \cdot dV$$

Linear Driving Force (LDF) approach:

$$\frac{\partial \overline{q}}{\partial t} = k_{LDF} \cdot \left(q^* - \overline{q}\right)$$







actual sorption kinetics



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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### **"Simple Fit" - Experiment vs Simulation**







### 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**

$$\frac{\partial \overline{q}}{\partial t} = k_{LDF} \cdot \left( q^* - \overline{q} \right) \qquad \qquad k_{LDF} = \frac{\Omega D_{\mu}}{r_{\mu}^2}$$

#### **Energy Balance**

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

Clausis-Clapeyron Natural convection coefficient

 $\Delta H = 28 \, kJ \, mol^{-1}$ 

 $h = 70 W m^2 K$ 





### From uptake curves







### From uptake curves



#### CO<sub>2</sub> and N<sub>2</sub> 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 <sup>-3</sup> ]	$m_{ m ads}/V_{ m col}$
Bed porosity $\varepsilon_L$ [-]	$1 - \left(\hat{V_p} + \hat{V_s}\right) \times \rho_L$
Particle density $\rho_p  [\text{kg m}^{-3}]$	$ ho_{\scriptscriptstyle L}/\!ig(1\!-\!arepsilon_{\scriptscriptstyle L}ig)$
Particle porosity $\varepsilon_p$ [-]	$1 - \left[\hat{V_s} / \left(\hat{V_s} + \hat{V_{\mathrm{po}}}\right)\right]$
Heat transfer coefficient [W m <sup>2</sup> K]	100
Solid specific heat $\hat{c}_{p,s}$ [J kg <sup>-1</sup> K <sup>-1</sup> ]	820
Wall specific heat $\hat{c}_{p,w}$ [J kg <sup>-1</sup> K <sup>-1</sup> ]	477
Wall density $\rho_w$ [kg m <sup>-3</sup> ]	786
Axial mass dispersion $D_{ax}$ [m <sup>2</sup> s <sup>-1</sup> ] <sup>a)</sup> $I$	$D_{ax} = \frac{2u_i r_p}{Pe}; \frac{1}{Pe} = \frac{0.7 \varepsilon}{Re Sc} + 0.5$
Axial heat dispersion $\lambda_{ax}$ [W m <sup>-1</sup> K <sup>-1</sup> ]	$\frac{\lambda_{ax}}{k_g} = (7 + 0.5  Pr  Re)$





#### From uptake curves

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  $k_{\text{LDF}}$  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





### **Tian-Calvet microcalorimeter**









### **Discontinuous procedure:**



$$\begin{pmatrix} \frac{dQ_{rev}}{dn^{\sigma}} \end{pmatrix}_{T,A} + Vc \left( \frac{dp}{dn^{\sigma}} \right)_{T,A} = \Delta h_{ads}T, n$$

$$V_{calorimetric cell}$$

$$n_{adsorbed}$$





### **Heat peaks**







### Modelling – Defining the system



- Dosing cell
- Dead volume
- Calorimetric cell

Mass and Energy balances for each part

*calorimetric cell with temperature control* 





### 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 e Diffusion in a spherical particle





### Dosing cell

$$\frac{dC_{v}}{dt} = -\frac{\dot{n}_{s}}{V_{v}}$$

$$C_{\nu}c_p\frac{dT_{\nu}}{dt} = \frac{h_{\nu}A_{\nu}}{V_{\nu}}(T_{01} - T_{\nu})$$



 $P_{v} = C_{v}RT_{v} \quad (EOS)$ 





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



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

 $P_d = C_d R T_d \qquad (EOS)$ 

 $P_d = P$ 







### Calorimetric cell

calorimetric cell with temperature control

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

$$V_c c_p C \frac{dT}{dt} - V_c \frac{dP}{dt} + m_s c_{ps} \frac{dT}{dt} + m_s \frac{d\bar{q}}{dt} (-\Delta H) + m_s c_p \bar{q} \frac{dT}{dt}$$
$$= \dot{n}_e c_p (T_d - T) - h_c A_c (T - T_c (R1))$$



P = CRT (EOS)

#### P = f(t) Measured – Needed for the solution





### Calorimetric cell wall – Energy Balance

R1 < R < R2:  

$$\rho_{c1}c_{c2}\frac{dT_c}{dt} = \frac{1}{R}K_{c1}\left(\frac{\partial}{\partial R}\left(R\frac{\partial T_c}{\partial R}\right)\right)$$

R2 <R < R3:

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

#### **Boundary conditions:**

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

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:** 

$$\frac{\partial q_p}{\partial r}(t,0) = 0 \qquad q_p(t,rp) = q_E(P)\rho_p$$

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  $\frac{D_c}{R^2}$

### **Resistance transitions**

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

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

















### AC Norit RB4 – Comparing with the uptake measurements



Sample	Method	k <sub>LDF</sub> (s⁻¹)
AC Norit RB4	Uptake	0.1
	Calorimetry	0.13





### AC Norit RB4 - Sensibility of the method



← KLDF.Q1 ← KLDF.Q1 ← KLDF.Q1


# Estimating k<sub>LDF</sub>



### ACPX series – $k_{LDF} \times PSD$





Sample	k <sub>LDF</sub> (1/s)	Dc/R <sup>2</sup> (1/s)	Ratio
ACPX 22	0.075	0.004	19.7
ACPX 41	0.120	0.009	13.3
<b>ACPX 76</b>	0.136	0.009	14.9





### Zeolite 13X



https://www.explainthatstuff.com/zeolites.html

	Sample	Method	Dc/R <sup>2</sup>
	binderless	ZLC at 313 K	0.0009-0.0012
	13X zeolite	Calorimetry at 298 K	0.0013







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- ✓ Momentum, Material and Energy Balances
- ✓ Equilibrium theory
- $\checkmark$  Adsorption kinetics

### ✓Assessing mass transfer

- Simple fit to breakthrough curves
- ✓ From uptake curves
- ✓ From calorimetry

### ✓ Final remarks





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







#### A zoo of breakthrough curves



Wang et al, Nature, 453, 207, 2008

Hamon et al, JACS, 47, 17490, 2009







#### Xylenes adsorption in MOFs





pubs.acs.org/Langmuir

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

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







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

Octahedral metallic clusters  $VO_4(OH)_2$  connected by terephthalic acid linkers







#### MIL-53 (Al) - Flexible MOF: "Breathing effect"

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

Octahedral metalic cluster  $AlO_4(OH)_2$  connected by terephthalic acid linkers



Unit cell 1500 Å<sup>3</sup>

1000 ų

up to 40%wt CO<sub>2</sub>, organics

Serre et al, JACS 2002, 124, 13519-13526 Llewellyn et al, JACS. 2008, 130, 12808-12814.





#### 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...







### Fixed bed model equations (LDF)

$$D_{ax} \cdot \frac{\partial^2 C_i}{\partial x^2} - \frac{u}{\varepsilon} \cdot \frac{\partial C_i}{\partial t} - \frac{(1-\varepsilon)}{\varepsilon} \cdot \frac{\partial q_i}{\partial t} \cdot \rho_s = 0$$
  
$$\frac{\partial q_i}{\partial t} = K_{LDF} \cdot (q_i^* - q_i)$$
  
$$t = 0: \ C_i = 0 \quad (\forall z)$$

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

$$x = L: \ \frac{\partial C_i}{\partial x} = 0$$

### **ISOTHERM EQUATIONS**

$$q_{\text{oX}}^{*} = q_{\text{satloX}} \cdot \frac{K_{\text{oX}} \cdot C_{\text{oX}}}{1 + K_{\text{oX}} \cdot C_{\text{oX}} + K_{\text{EB}} \cdot C_{\text{EB}}}$$
$$+ q_{\text{logoX}} \cdot \frac{K_{\text{oX}} \cdot C_{\text{oX}}}{1 + K_{\text{oX}} \cdot C_{\text{oX}}}$$
$$q_{\text{logoX}} = \left\{ \frac{K_{\text{log}} \cdot P_{\text{log}} \cdot \exp\left[r_{\text{log}} \cdot \left(\frac{P_{\text{tot}}}{P_{\text{go}}} - 1\right)\right]}{K_{\text{log}} + P_{\text{log}} \cdot \left[\exp\left[r_{\text{log}} \cdot \left(\frac{P_{\text{tot}}}{P_{\text{go}}} - 1\right)\right] - 1\right]} \right\}$$
$$q_{\text{EB}}^{*} = q_{\text{satEB}} \cdot \frac{K_{\text{EB}} \cdot C_{\text{EB}}}{1 + K_{\text{EB}} \cdot C_{\text{EB}} + K_{\text{oX}} \cdot C_{\text{oX}}}$$











### CS2: MIL-47 (V) – a rigid MOF



Barthelet et al, Angew. Chem. 2002, 41(2), 281-284.





### 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







### Same trick applied to provide a mathematical description of PX isotherm

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

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









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











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











- 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**















Diana Azevedo

Célio Cavalcante Jr.

**Eurico Torres** 

Moises Bastos-Neto Enrique Vilarrasa-Garcia

Post-Doc Fellows









































Laboratório de Pesquisa em Adsorção e Captura de CO2 *(Laboratory of Adsorption Research and CO2 Capture)* Universidade Federal do Ceara Campus do Pici – bloco 731 Fortaleza - Brazil





email: <u>mbn@ufc.br</u>

# Thank you for your attention!