Investigation of Industrial Adsorbents by Gas Flow Methods

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The presentation will begin shortly. Please be patient while other attendees log in.
Outline

1. Characterization of Industrial Adsorbents
2. Gas Flow Methods
3. Examples
   I. Breakthrough Curves
   CO₂ / N₂ on Activated Carbons
   II. Mixture Isotherms
   CO₂ / N₂ on Activated Carbons
   III. Natural Gas, Biogas Purification
   Separation of CO₂ / CH₄ on Activated Carbons and Zeolites
   IV. Air Separation
   Separation of O₂ / N₂ on Carbon Molecular Sieves
4. Simulation
5. Conclusions
1. Characterization of Industrial Adsorbents

- **Synthesis and First Characterization**
  - Chemists
  - Nova Touch
  - BET
  - Pore Volume
  - Pore Size Distribution

- **Determination of Thermodynamic Data**
  - Chemists, Physicists
  - iSorb HP
  - Isotherms
  - Heat of Adsorption

- **Basic Process Design, Granulation of Adsorbents**
  - Chemical Engineers
  - dynaSorb BT
  - Techn. Useable Sorption Capacity
  - Gas Mixtures
  - Selectivities
  - Kinetics for Process Conditions
  - Cycle Stability

- **Detailed Process Design, Application**
  - Engineers
  - Bench scale, Pilot plants, Industrial Plant
  - Process Optimization
  - Production

Number of Samples

Application Progress
1. Characterization of Industrial Adsorbents

Importance of Gas Flow Methods for Characterization:

• Most **industrial** adsorptive separation processes = **dynamic** processes *(Gas Flow)*

• Different **Kinetics** of guest molecules can play a key-role during separation

• In technical separation always **gas mixtures** are present

  ➔ Therefore the **selectivity of adsorbents** is very important

• Better transfer of results into technical processes.

• **Downscaling** of technical processes possible

  ➔ Characterization under **application-related conditions**
2. Gas Flow Methods

Examples of different Gas Flow Methods

• **Rapid Dynamic Flow**
  Gas Flow over sample, measuring during desorption, recording gas **composition**

• **Dynamic Vapor Sorption**
  Gas Flow over sample, recording **weight**

• **Inverse Gas Chromatography**
  Forced-Flow through sample bed, inlet **pulse** functions, recording gas **composition** downstream the sample

• **Breakthrough Experiments**
  Forced-Flow through sample bed, inlet **step** functions, recording gas **composition** downstream the sample
2. Gas Flow Methods

Static Volumetric Measurements

- Sorption takes place in enclosed chamber
- Pressure is recorded over time
- Pure Gases only

\[ n_{ads,i} = n_{dosed,i} - n_{free,i} \]
\[ n_{dosed,i} = \frac{p_{Dose,i} V_{Dose}}{RT} \]
\[ n_{free,i} = \frac{p_{Cell,i} (V_{Dose} + V_{Cell})}{RT} \]
\[ n_{ads} = \sum_{i=0}^{i} n_{ads,i} \]

Breakthrough Experiment

- Sorption takes place in open system
- Pressure is constant
- Outlet composition is recorded over time
- Gas Mixtures only

\[ n_{adsorbed} = \int \dot{n}_{in}(t) \, dt - \int \dot{n}_{out}(t) \, dt \]
\[ n_{adsorbed} = \int \dot{V}_{in}(t) \frac{y_{in}(t)}{V_m} \, dt - \int \dot{V}_{out}(t) \frac{y_{out}(t)}{V_m} \, dt \]
2. Gas Flow Methods

Breakthrough Curves

• Not all Gas Flow Experiments are Breakthrough Experiments!

• Requirement: **Fixed Adsorber Bed**
  → gas must not pass the sample without **interaction**!

• What is the result of a breakthrough experiment?
  
  ✓ **Time** until 5 %, 50 %,... of breakthrough is the **cycle or production time**
  ✓ **Integration** of the full curve gives **saturation capacity** of a gas on the adsorbent (equilibrium)
  ✓ **Integration** until cycle time gives **technically usable sorption capacity**
  ✓ **Shape of the curve** contains information about **kinetics/mass transfer**
Breakthrough Curves

2. Gas Flow Methods

Macroscopic
- Size of Adsorber
- Shape of Adsorber

Mesoscopic
- Nature of the Fixed Bed
- Bed Porosity
- Shape of Particles

Microscopic
- Textural Properties
- Surface Characteristics
- Accessibility
2. Gas Flow Methods

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- Fully automated
- Gas Mixing
- Up to 40 L/min Gas Flow, up to **10 bar**
- Up to **4 mass flow controllers (MFCs)**
- Up to **2 Vapors**
- Monitoring of gas composition by **TCD** at the outlet
### 2. Gas Flow Methods

dynaSorb BT Evaporators

**Saturator, “Bubbler”**

- Easy, cheap, but: Performance highly dependent on temperature and pressure
- No liquid mixtures
- Unstable long-time performance
- Vapor concentration indetermined

**Controlled Evaporation**

- More complex, but: Performance independent on temperature and pressure
- Liquid mixtures possible
- Vapor concentration defined by liquid flow rate and gas flow rate
- Gas-Liquid mixing up- or downstream of evaporation process
## 2. Gas Flow Methods
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Quantachrome INSTRUMENTS
3. Examples – I Breakthrough Curve

Procedure

1. Determining **100 %** and **0 %** Breakthrough Signal in **Bypass**
2. Introducing **Carrier Gas** to the Sample Cell (Adsorber)
3. Pressurizing the Adsorber
4. Waiting for **stable** Pressure and Temperatures
5. Introducing additionally **CO₂** to create the **Gas Mixture**
6. Monitoring Adsorber **Temperatures** along the Sample Bed and **Gas Composition** at the Adsorber Outlet
7. Finishing Experiment when Temperatures and TCD Signal are **stable**
3. Examples – I Breakthrough Curve

Watch a Measurement
3. Examples – I Breakthrough Curve

Resulting Curves

- 40 °C, 2 L min⁻¹
- 5 bar (pressurization with N₂)
- Inlet compositions: 5 % CO₂ in N₂

- Temperature Maxima Decrease in Flow Direction → Increasing Dispersion
- Area under Temperature Curves increases in Flow Direction → Transfer of heat through gas flow
3. Examples – I Breakthrough Curve

Calculating Loadings

\[ n_{\text{adsorbed}} = \int \dot{n}_{\text{in}}(t) \, dt - \int \dot{n}_{\text{out}}(t) \, dt \]

\[ n_{\text{adsorbed}} = \int \dot{V}_{\text{in}}(t) \frac{y_{\text{in}}(t)}{V_m} \, dt - \int \dot{V}_{\text{out}}(t) \frac{y_{\text{out}}(t)}{V_m} \, dt \]

Integrating over the full Curve

Integrating over the Curve to e.g. 1 % Breakthrough

Saturation Capacity
\[ dq = 0.611 \text{ mmol g}^{-1} \]

Technically Usable Sorption Capacity
\[ dq = 0.445 \text{ mmol g}^{-1} \]
3. Examples – II Mixture Isotherms

**General**

1. Gas Mixture (Green), consisting of Gas 1 (Blue) and Gas 2 (Yellow)
2. Dosing the Gas Mixture (Green) into the Manifold
3. Dosing the Gas Mixture (Green) from the Manifold into the Sample Cell → Which Gas is being adsorbed? You have to analyze the **Gas Composition**!
4. Assuming that Gas 1 (Blue) is preferentially adsorbed → Formation of a **Concentration Gradient** throughout the Sample Cell+Manifold

To measure **Mixture Isotherms**

- **In Closed System:** Analyze **Gas Composition** and **Pressure** and continuously **mix** the Gas Phase in the Sample Cell+Manifold!
- **In Open System:** Use **Gas Flow Methods** by analyzing **Gas Composition** and continuously supplying fresh gas
3. Examples – II Mixture Isotherms

Sequences of Breakthrough Curves

- 20 °C, 2 L min\(^{-1}\)
- 10 bar (pressurization with N\(_2\))
- Inlet compositions: From 5 % CO\(_2\) to 80 % CO\(_2\) in N\(_2\)

**Procedure:**
- Starting the next experiment with a higher concentration after breakthrough is steady-state
- **Integration** and **summation** gives the partial loadings of the analyzed component
- Volume Fraction and Total Pressure give the Partial Pressure of CO\(_2\)

→ Mixture Isotherm of CO\(_2\) in N\(_2\)
3. Examples – II Mixture Isotherms

Mixture Isotherm of CO$_2$ in N$_2$ @ 10 bar, 20 °C

- Measured data (red) compared to IAST model (Ideal Adsorbed Solution Theory)
- The model predicts mixture isotherms by using pure component isotherms (CO$_2$ and N$_2$)
- Mixture of CO$_2$ and N$_2$ shows ideal behavior

→ We determined the partial loading of CO$_2$ on an adsorbent in a CO$_2$/N$_2$ gas mixture
3. Examples – II Mixture Isotherms

x/y-Plot @ 10 bar, 20 °C

- **IAST** model allows to calculate the adsorbate composition at a certain gas composition
- x/y-plot
- Visualizes the enrichment of CO₂ on the surface
- Important information for separation processes
3. Examples – II Mixture Isotherms

Isotherms

- Using **Helium** as one component and assuming that it is not adsorbed allows measurement of pure component isotherms
- Using **other gases** than Helium yields in mixture isotherms
3. Examples – III Natural Gas, Biogas Purification

General

• Removal of CO$_2$ from Biogas or Natural Gas to increase **Heating Value**
• Raw Biogas contains up to 50% CO$_2$
• Biogas: Pressure during Adsorption = 2-16 bar.
• Natural Gas: Pressure during Adsorption = 20-80 bar.
• Adsorbents: Zeolites, Carbon Molecular Sieves

How about Activated Carbons?

Let’s compare an Activated Carbon with a Zeolite!

3. Examples – III Natural Gas, Biogas Purification

Activated Carbons: Isotherms

Methane

Carbon Dioxide

Specific loadings higher for CO₂ than for CH₄ \(\rightarrow\) separation should be possible


3. Examples – III Natural Gas, Biogas Purification

Breakthrough Experiment on Activated Carbon

- 25 °C, 2.5 L min⁻¹
- 5 bar (pressurization with He)
- Inlet composition: 15 % CH₄, 5 % CO₂, Balance: He

- Breakthrough of CH₄ and CO₂ according to their sorption capacities
  → system is under thermodynamic control

Zeolite 13X: Isotherms

Specific loadings higher for CO$_2$ than for CH$_4$ $\rightarrow$ separation should be possible

3. Examples – III Natural Gas, Biogas Purification

Breakthrough Experiment on Zeolite 13X

• Breakthrough of CH₄ and CO₂ according to their **sorption capacities** → system is under thermodynamic control

• Zeolite 13X show a very high separation performance

• Material should be used only with dry gas flows due to high affinity to water

![Graph showing the breakthrough of CH₄ and CO₂](image-url)

3. Examples – III Natural Gas, Biogas Purification

Activated Carbon – Zeolite 13X: Comparison

Classical Activated Carbons
Selectivity not high enough for economic separation of CH$_4$ and CO$_2$!

Zeolite 13X:
Very high selectivity enables applications for the separation of CH$_4$/CO$_2$ gas mixtures.
3. Examples – IV Air Separation

General

- Air separation for $\text{O}_2$ and $\text{N}_2$ production [production of inert gases, medical applications, steel industry,...]
- Usually done with Pressure Swing Adsorption (PSA)
- Carbon Molecular Sieves (CMS), Zeolites
- Ambient temperatures
- Pressure during Adsorption: 1.1 – 11 bar, typically 8 bar.
- Pressure during Desorption: 0.07 – 1 bar.
Video

Source: https://www.youtube.com/watch?v=j5mopdfEjq8
3. Examples – IV Air Separation

Isotherms: Carbon Molecular Sieve (CMS)

Nitrogen

Oxygen

Industrial relevant range

A. Möller, J. Guderian, J. Möllmer, M. Lange, J. Hofmann, R. Gläser, Chemie Ingenieur Technik 2013, 85, 11, 1680
3. Examples – IV Air Separation

Carbon Molecular Sieve (CMS) - Isotherms:

- Assuming 8 bar Air = N\textsubscript{2} : O\textsubscript{2} = 4 : 1
  \[\text{partial pressure } p(\text{O}_2) = 1.6 \text{ bar}\]
  \[\text{partial pressure } p(\text{N}_2) = 6.4 \text{ bar}\]

- According to isotherms, we would **more N}_2 than O}_2 in adsorbed phase
  \[1.2 \text{ mmol g}^{-1} \text{ N}_2\]
  \[0.5 \text{ mmol g}^{-1} \text{ O}_2\]

But this CMS material is used for the exact opposite case!

- More O\textsubscript{2} in the adsorbed phase

Adsorption of N\textsubscript{2} is much slower than adsorption of O\textsubscript{2} \[\Rightarrow\text{ Kinetic Separation under Flow Conditions.}\]
3. Examples – IV Air Separation

Carbon Molecular Sieve (CMS) - Breakthrough Curve:

- 25 °C, 5 L min⁻¹
- 8 bar (pressurization with He)
- Inlet composition: 80 % N₂, 20 % O₂
- Spontaneous Breakthrough of N₂
- Adsorption of O₂ is faster → O₂ is held back by the adsorber bed
- Production time of pure N₂
- Stopping cycle at a certain breakthrough of O₂
3. Examples – IV Air Separation

Carbon Molecular Sieve (CMS) - Breakthrough Curves:

Temperature Variation at 5 L min\(^{-1}\)

Flow Rate Variation @ 25 °C

With increasing temperatures ➔ Decreasing cycle times

With increasing flow rates ➔ No spontaneous breakthrough of O\(_2\)
4. Simulation

Parametric Studies & Kinetics

- **Understanding** of Sorption Characteristics on Fixed Bed Adsorbers
- **Experimental time** can be drastically **reduced** and parametric studies can be easily performed
- Calculation of **Equilibrium Data of Mixtures** from Pure Component Isotherms
- Evaluation of Breakthrough Curves based on **Mass- and Energy Balances**

![Graph showing volume fraction over time](image-url)
4. Simulation

Different Segments

- Determination of \textbf{technical usable sorption capacity}
- Can be used as \textbf{benchmark} for separation performance of adsorbents

\begin{itemize}
  \item \textbf{Mass Transfer} coefficient, axial dispersion, shape of isotherm
  \item \textbf{Heat effects}, heat dissipation
  \item The time interval of mass transfer zone has to be \textbf{minimized}
\end{itemize}

- Determination of \textbf{saturation capacity}
- By assuming of thermodynamic controlled system $\rightarrow$ Measurement of \textbf{isotherms} possible
4. Simulation

Mass Transfer coefficient $k_{LDF}$
4. Simulation

Mass Transfer coefficient $k_{LDF}$

- Fitting of simulated Breakthrough Curves to Experimental Data
- Requirement: Isotherms

Comparison for different materials under same testing conditions allows statements about the kinetic performance
4. Simulation

Fitting of Breakthrough Curves + Temperatures

- After fitting the $k_{LDF}$ Mass Transfer Coefficient $\Rightarrow$ Good Agreement of Experiment and Simulation in a Standard Breakthrough Example (5% CO$_2$ in N$_2$)
- Course of Volume Fraction and Temperatures is depicted correctly
4. Simulation

Fitting of Breakthrough Curves + Temperatures

- After fitting the $k_{LDF}$ Mass Transfer Coefficient $\rightarrow$ Good Agreement of Experiment and Simulation in a Standard Breakthrough Experiment (5% CO$_2$ in N$_2$)
- Course of Volume Fraction and Temperatures is depicted correctly

Overlay of Experiment (Points) and Simulation (Line)
Fitting of Example III: Activated Carbon – Zeolite 13X Comparison

- Co-Adsorption and Displacement Phenomena can also be simulated
5. Conclusions

- Gas-Flow Methods allow Characterization under **application-related conditions**
- Information that are only accessible by Gas-Flow Methods (*i.g.* Breakthrough Curves):
  - **Technically usable Sorption Capacity**
  - Separation performance under application-related conditions
  - Kinetic Data about Mass Transfer and Energy Transfer
- Measuring **Mixture Data** easily **possible**
- Better transfer of results into **technical processes**
- Simulation and fitting to measured data makes **mass transfer parameters** accessible
- Simulation then **reduces experimental effort** and improves the **understanding** of separation processes
Thank you for your attention!