

Modelling the adsorption process

1. Diffusion

- ▶ diffusion of the adsorbate in the bulk fluid (usually very fast)
- ▶ diffusion of the adsorbate to the adsorbent surface through the boundary layer
- ▶ diffusion of the adsorbate into the pore to an open site
 - ▶ steric (shape) effects may be an issue

2. Equilibrium considerations

- ▶ adsorbate will attach to a vacant site
- ▶ adsorbate will detach from an occupied site

Equilibrium modelling

Why?

We ultimately would like to determine **how much adsorbent is required** to remove a given amount of adsorbate (e.g. impurity); particularly in batch processes.

For now, assume we are only limited by equilibrium [we'll get there, we don't mind *how long* (due to kinetics of diffusion and mass transfer resistance) it takes to get there]

- ▶ Derive/Postulate a model relating bulk concentration to surface concentration of adsorbate
- ▶ We call these equilibrium equations: “isotherms”
- ▶ **Isotherm**: relates amount of adsorbate on adsorbent ($C_{A,S}$) at different concentrations of adsorbate in the bulk (C_A), but at a fixed temperature.

Equilibrium modelling: linear model

Linear isotherm (Henry's law)

$$C_{A,S} = KC_A$$

$$C_{A,S} = \frac{KP_A}{RT} = K'P_A$$

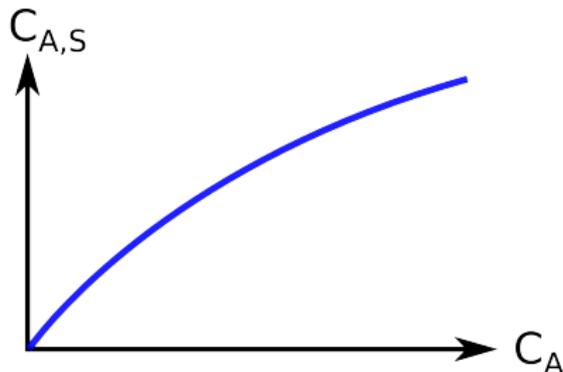
- ▶ $C_{A,S}$ = concentration of adsorbate A on adsorbent surface $\left[\frac{\text{kg adsorbate}}{\text{kg adsorbent}} \right]$
- ▶ C_A = concentration of adsorbate A in the bulk fluid phase $\left[\frac{\text{kg adsorbate}}{\text{m}^3 \text{ fluid}} \right]$
- ▶ P_A = partial pressure of adsorbate A in the bulk fluid phase [atm]
- ▶ K and K' are temperature dependent equilibrium constants (should be clear why)
- ▶ R is the ideal gas constant
- ▶ T is the system temperature
- ▶ Few systems are this simple!

Equilibrium modelling: Freundlich model

Freundlich isotherm

$$C_{A,S} = K (C_A)^{1/m} \quad \text{for } 1 < m < 5$$

- ▶ It is an empirical model, but it works well



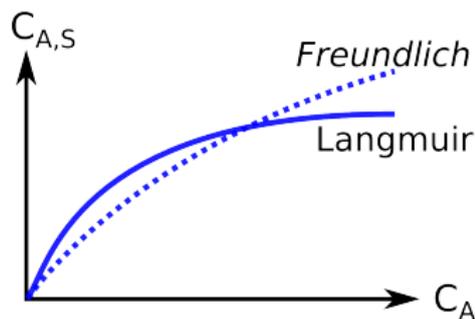
- ▶ Constants determined from a log-log plot
- ▶ How would you go about setting up a lab experiment to collect data to calculate K ?
- ▶ Which way will the isotherm shift if temperature is increased?

Equilibrium modelling: Langmuir isotherm

- ▶ we have a uniform adsorbent surface available (all sites equally attractive)
- ▶ there are a total number of sites available for adsorbate A to adsorb to
- ▶ $C_T =$ total sites available $\left[\frac{\text{mol sites}}{\text{kg adsorbate}} \right]$
- ▶ $C_V =$ vacant sites available $\left[\frac{\text{mol sites}}{\text{kg adsorbate}} \right]$
- ▶ rate of adsorption $= k_A P_A C_V =$ proportional to number of collisions of A with site S
- ▶ $C_{A,S} =$ sites occupied by A $\left[\frac{\text{mol sites}}{\text{kg adsorbate}} \right]$
- ▶ assuming 1 site per molecule of A, and only a monolayer forms
- ▶ rate of desorption $= k_{-A} C_{A,S} =$ proportional to number of occupied sites
- ▶ net rate $= k_A P_A C_V - k_{-A} C_{A,S}$

Equilibrium modelling: Langmuir isotherm

- ▶ Net rate = $k_A P_A C_V - k_{-A} C_{A,S}$
- ▶ define $K_A = \frac{k_A}{k_{-A}}$
- ▶ essentially an equilibrium constant: $A + S \rightleftharpoons A \cdot S$
- ▶ at equilibrium, the net rate is zero
- ▶ implying $\frac{k_A C_{A,S}}{K_A} = k_A P_A C_V$
- ▶ but total sites = $C_T = C_V + C_{A,S}$
- ▶ so $\frac{k_A C_{A,S}}{K_A} = k_A P_A (C_T - C_{A,S})$
- ▶ simplifying: $C_{A,S} = K_A P_A (C_T - C_{A,S})$



- ▶ then
$$C_{A,S} = \frac{K_A C_T P_A}{1 + K_A P_A} = \frac{K_1 P_A}{1 + K_2 P_A} = \frac{K_3 C_A}{1 + K_4 C_A}$$
- ▶ Fit data using **Eadie-Hofstee diagram** or nonlinear regression
- ▶ Same structure as Michaelis-Menten model (bio people)

Summary of isotherms

We aren't always sure which isotherm fits a given adsorbate-adsorbent pair:

1. Perform a laboratory experiment to collect the data
2. Postulate a model (e.g. linear, or Langmuir)
3. Fit the model to the data
4. Good fit?

Other isotherms have been proposed:

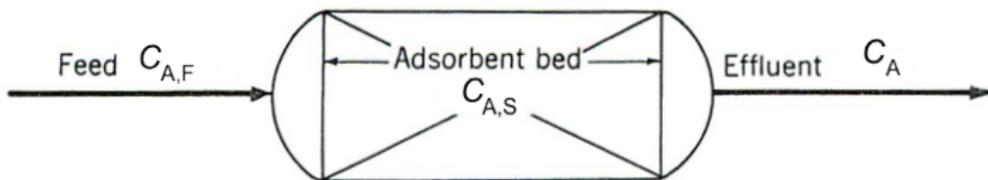
- ▶ BET (Brunauer, Emmett and Teller) isotherm
- ▶ Gibb's isotherm: allows for a multilayer of adsorbate forming

These are far more flexible models (more parameters); e.g. Langmuir isotherm is a special case of the BET isotherm.

Isotherms change at different temperatures

Temperature swing example

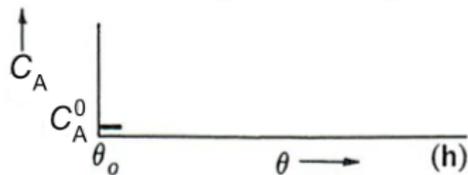
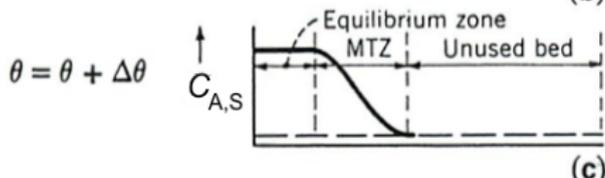
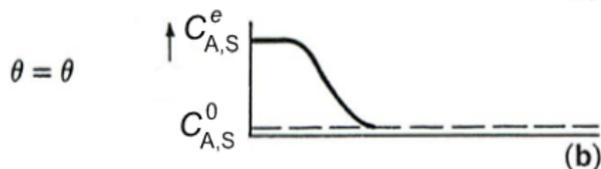
Understanding adsorption in packed beds (1 of 2)



Time

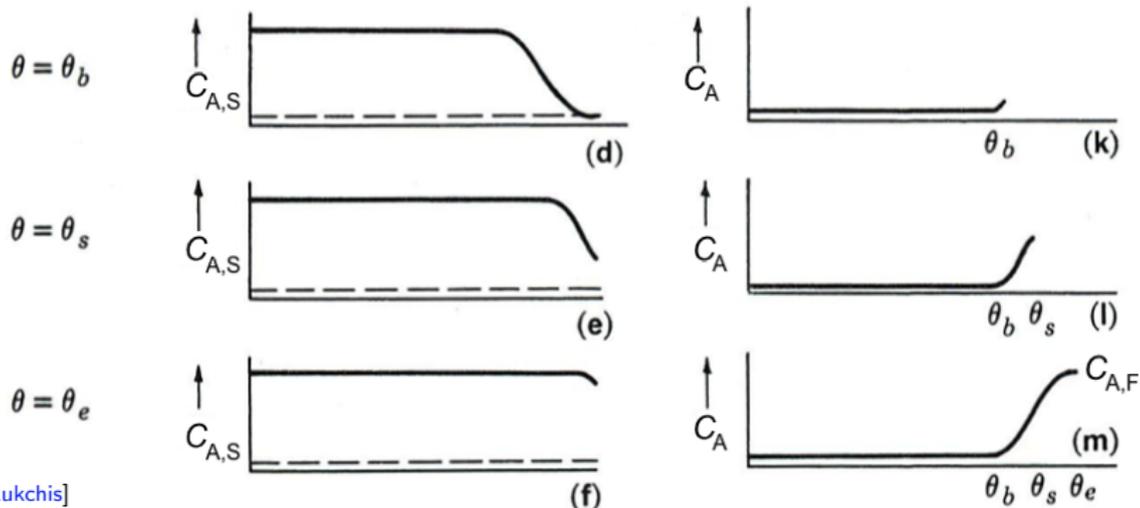
Analysis of Adsorbent
(Adsorbent loading vs. bed length)

Analysis of Effluent
(Concentration of sorbable
component vs. time)



L = length; θ = time; θ_0 = start-up time on a regenerated bed

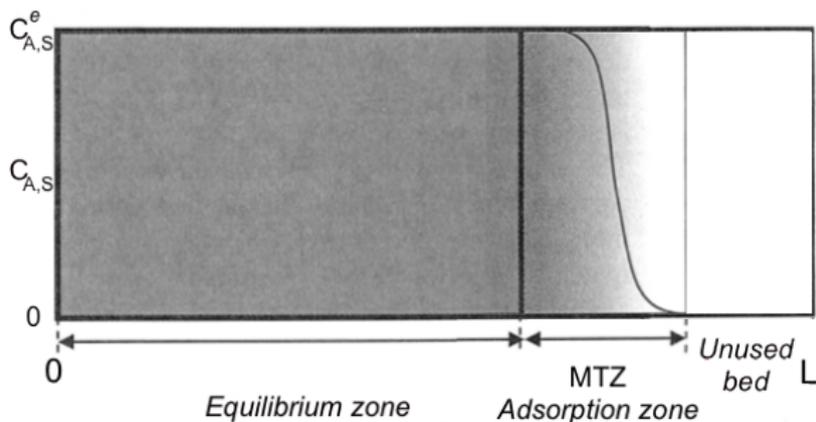
Understanding adsorption in packed beds (2 of 2)



[Lukchis]

- ▶ $C_{A,S}$ = concentration of adsorbate on adsorbent
- ▶ $C_{A,S}^e$ = concentration at equilibrium on the adsorbent (max loading)
- ▶ $C_{A,S}^0$ = concentration on the regenerated adsorbent at time 0
- ▶ θ_b = breakthrough time: *"time to stop using the packed bed!"*; usually when $C_A = 0.05C_{A,F}$
- ▶ θ_e = the bed at equilibrium time; packed bed is completely used
- ▶ $C_{A,S}$ values are not easy measured; outlet concentration C_A is easy

Bed concentration just prior to breakthrough

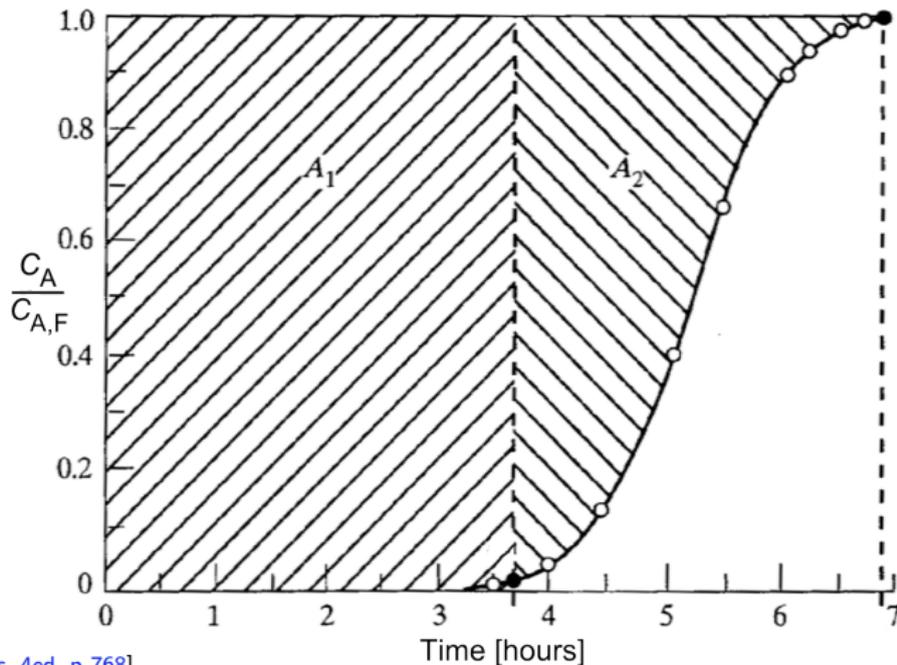


[Ghosh (adapted), p144]

- ▶ **MTZ**: mass transfer zone is where adsorption takes place.
- ▶ It is S-shaped: indicates there is mass-transfer resistance and axial dispersion and mixing. Contrast to the ideal shape: is a perfectly vertical line moving through the bed
- ▶ **Equilibrium zone**: this is where the isotherm applies!
- ▶ **Breakthrough**: arbitrarily **defined as time** when either (a) the lower limit of adsorbate detection, or (b) the maximum allowable adsorbate in effluent leaves the bed. Usually around 1 to 5% of $C_{A,F}$.

Example (and some new theory applied)

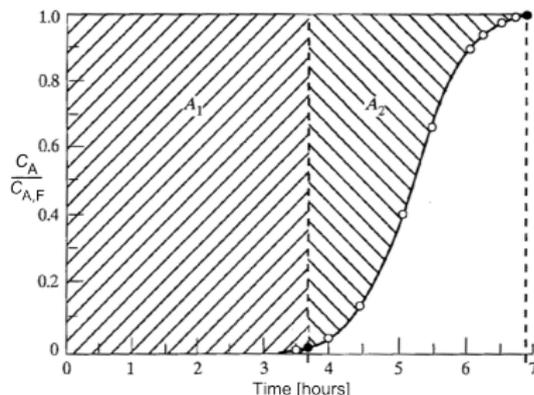
An adsorbate in vapour is adsorbed in an experimental packed bed. The inlet contains $C_{A,F} = 600$ ppm of adsorbate. Data measuring the outlet concentration over time from the bed are plotted below:



[Geankoplis, 4ed, p 768]

Example

1. Determine the **breakthrough time**, θ_b . [Ans: 3.65 hours]
2. What would be the **usable capacity** of the bed **at time** θ_b if we had an **ideal wavefront** (no mass transfer resistance)? [Ans: the fractional area of $A_1 = 3.65 / 6.9 = 53\%$]
 - ▶ Note plot area units = “total time”, since “height” of y-axis = 1.0
 - ▶ Note: (area up to θ_b) $\approx \theta_b$ when using a normalized y-axis



3. How long does it take to reach this ideal capacity? ≈ 3.65 hours
Ignore the tiny part missing from the integrated area.