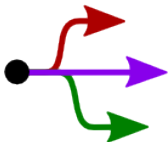


Separation Processes

ChE 4M3



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<http://learnche.mcmaster.ca/4M3>

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- ▶ if you let us know about **any errors** in the slides
- ▶ **any suggestions to improve the notes**

All of the above can be done by writing to

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Introduction to sorption processes

Sorption

Components in a fluid phase, **solutes**, are selectively transferred to insoluble, (rigid) particles that are suspended in a vessel or packed in a column.

- ▶ **(ad)sorbate**: the (ad)sorbed solute that's usually of interest
- ▶ **(ad)sorbent**: the (ad)sorbing agent, i.e. the MSA
- ▶ Is there an ESA?

Some sorption processes:

- ▶ **absorption**: gas into liquid phase [it is strictly speaking a sorption process, but not considered here (3M4)]
- ▶ **adsorption**: molecules bond with a solid surface
- ▶ **ion-exchange**: ions displace dissimilar ions from solid phase
 - ▶ Water softening: $\text{Ca}_{(\text{aq})}^{2+} + 2\text{NaR}_{(\text{s})} \longleftrightarrow \text{CaR}_{2(\text{s})} + 2\text{Na}_{(\text{aq})}^{+}$
- ▶ **chromatography**: solutes move through column with an eluting fluid. Column is continuously regenerated.

Sorption examples

We will focus on (ad)sorption for the next few classes.

Some well-known examples:

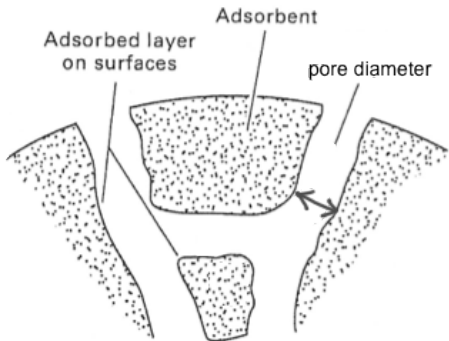
- ▶ adsorption: charred wood products to improve water taste
- ▶ adsorption: decolourize liquid with bone char
- ▶ adsorption: those little white packets in boxes of electronics
- ▶ ion-exchange: passing water through certain sand deposits removes salt
- ▶ ion-exchange: synthetic polymer resins widely used to soften water

Industrial use of adsorption picked up with molecular zeolites in the 1960s

Adsorbents

General principle (more details coming up soon)

Molecules attach to the particle's surfaces: outside and on the pore walls



Main characterization: **pore diameter** of adsorbent

Mechanisms during adsorption

- ▶ **equilibrium interaction**: solid-fluid interactions
- ▶ **kinetic**: differences in diffusion rates
- ▶ **steric**: pore structure hinders/retains molecules of a certain shape

Quick recap of some familiar concepts

- ▶ $1\text{m} = 100\text{cm} = 1000\text{mm} = 10^6\mu\text{m} = 10^9\text{nm} = 10^{10}\text{\AA}$
- ▶ Hydrogen and helium atoms: $\sim 1\text{\AA}$
- ▶ For a pore:

$$\frac{\text{Internal surface area}}{\text{Pore volume}} = \frac{\pi d_p L}{\pi d_p^2 L / 4} = \frac{4}{d_p}$$

- ▶ d_p = pore diameter: typically around 10 to 200 \AA

Adsorbents

Helpful to see what they look like to understand the principles:

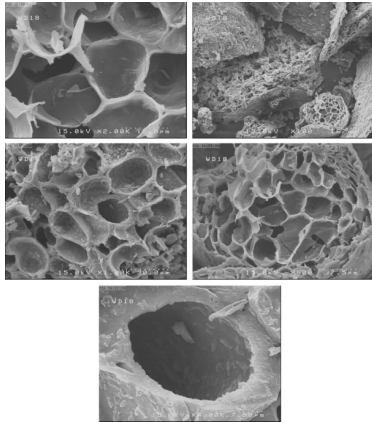


[Wikipedia]

Activated alumina

- ▶ made from from aluminum hydroxide
- ▶ $\sim 300 \text{ m}^2$ per gram
- ▶ most widely used adsorbent
- ▶ hydrophilic
- ▶ pore diameter: 10 to 75 \AA

Adsorbents



[DOI:10.1016/j.saa.2011.10.012]

Activated carbon

- ▶ partially oxidized coconut shells, nuts, wood, peat, bones, sewage sludge
- ▶ difference hardnesses of adsorbent
- ▶ 400 to 1200 m² per gram
- ▶ hydrophobic
- ▶ pore diameter: 10 to over 50Å

e.g. bone char: decolourizing syrups

Adsorbents



Molecular Sieve Type A
(a)



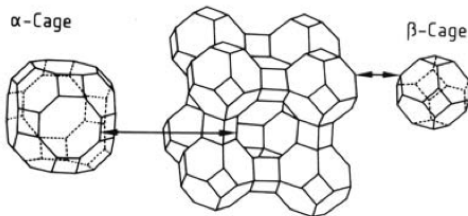
Molecular Sieve Type X
(b)

[Seader, 3ed, p575]

[Uhlmanns, p565]

Ⓐ

α -Cage



β -Cage

Zeolite lattices

Some examples

$K_{12}[(AlO_2)_{12}(SiO_2)_{12}]$:
drying gases [2.9Å]

$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$:
CO₂ removal [3.8Å]

$Ca_{43}[(AlO_2)_{86}(SiO_2)_{106}]$:
air separation [8Å]

Very specific pore diameters.

- ▶ 40 naturally occurring
- ▶ ~ 150 synthesized

Adsorbents

Molecular sieves (zeolites):

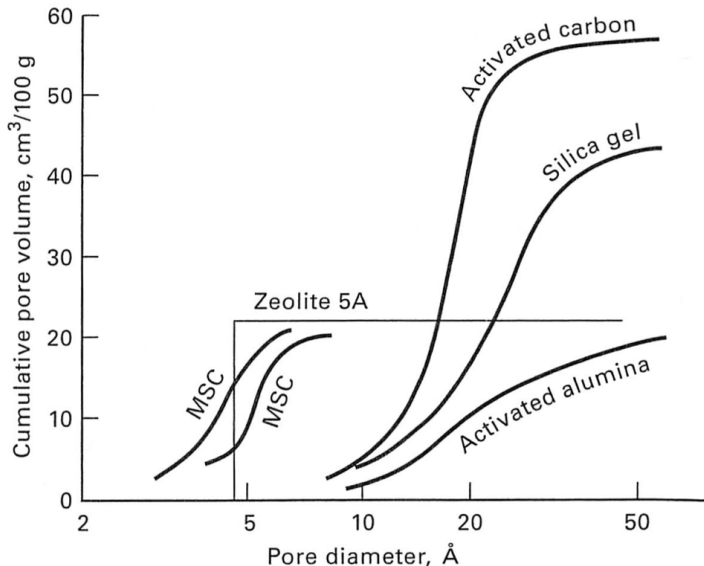
Size	Adsorbs ...	Dehydrates ...
3Å	H ₂ O, NH ₃	unsaturated hydrocarbons
4Å	H ₂ S, CO ₂ , C ₃ H ₆	saturated hydrocarbons
5Å	<i>n</i> -paraffins from iso-paraffins	
8Å	iso-paraffins and olefins	

[Johnston]

Rousseau, "Handbook of Separation Technology": market sizes in 1983

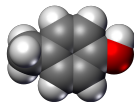
Adsorbent	Market size
Activated carbon	\$ 380 million ← 25% for water treatment
Molecular-sieve zeolites	\$ 100 million
Silica gel	\$ 27 million
Activated alumina	\$ 26 million

Pore diameter characterization



Adsorption examples

- ▶ Gas **purification**:
 - ▶ Volatile organics from a vent stream
 - ▶ Sulphur compounds from gas stream
 - ▶ Water vapour (we'll look at pressure swing adsorption)
 - ▶ Removal of CO₂ from natural gas [alternatives ?]
- ▶ Bulk **separation** in the gas phase:
 - ▶ O₂ from N₂ (adsorbed more strongly onto zeolites)
 - ▶ H₂O from ethanol
 - ▶ High acetone quantities from air vent streams
- ▶ Liquid-liquid separation and purification:
 - ▶ Organics and toxic compounds from water
 - ▶ Sulphur compounds from water
 - ▶ Normal vs iso-paraffin separation
 - ▶ Separation of isomers: *p*- vs *m*-cresol
 - ▶ Fructose from dextrose separation
 - ▶ Gold in cyanide solutions



p-cresol

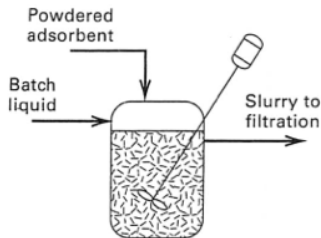


m-cresol

[Cresol figures from Wikipedia]

Gold leaching and adsorption

- ▶ Crushed rock has gold particles exposed
- ▶ Leaching: $4\text{Au} + 8\text{NaCN} + \text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{Na}[\text{Au}(\text{CN})_2] + 4\text{NaOH}$
- ▶ Adsorption: aurocyanide complex, $\text{Au}(\text{CN})_2^-$, is adsorbed onto activated carbon
 - ▶ drives the equilibrium in the leaching step forward
 - ▶ separates the gold from the pulp (slurry)
 - ▶ obtain $C_{A,s} = 8000$ grams of Au per tonne of carbon
- ▶ Desorption:
 - ▶ separate the highly concentrated gold-carbon pulp (screens/filter)
 - ▶ desorb the gold off the carbon with caustic contact
 - ▶ recycle the regenerated carbon



When to consider adsorption

Distillation, membranes, absorption, liquid-liquid extraction are sometimes viable alternatives.

But adsorption is considered when:

- ▶ relative volatility between components is < 1.5 (e.g. isomers)
- ▶ large reflux ratios would be required
- ▶ excessive temperatures or high pressure drops are to be avoided
- ▶ too large area for a membrane
- ▶ high selectivity is required
- ▶ feed is a very dilute stream of solute (adsorbate)

But, some disadvantages:

- ▶ only the surface of the adsorbent used
- ▶ regeneration of MSA adsorbent required
- ▶ MSA will break down mechanically over time
 - ▶ we can pump it, filter it, and/or put it through cyclones

Quantifying the adsorbent

Perry's, Ch 22: A fixed bed of porous adsorbent material. Bulk density is 500 kg.m^{-3} , and the **interparticle** [between] void fraction is 0.40. The **intraparticle** [within] porosity is 0.50, with two-thirds of this in cylindrical pores of diameter 1.4 nm and the rest in much larger pores. **Find:**

- ▶ surface area of the adsorbent
- ▶ if solute has formed a complete **monomolecular layer** 0.3 nm thick inside the pores, determine the percent of the particle volume and the percent of the total bed volume filled with adsorbate.

Solution: Assume from surface area to volume ratio that the internal area is practically all in the small pores [ignore large pores]. One gram of the adsorbent occupies 2 cm^3 as packed and has 0.4 cm^3 in small pores, which gives a surface area of $1150 \text{ m}^2/\text{gram}$ (university stadium field area ~ 5000 to 8000 m^2). Based on the area of the annular region filled with adsorbate, the solute occupies 22.5% of internal pore volume and 13.5% of the total packed-bed volume.

Physical principles

Adsorption releases heat. Why?

Thermodynamics: ...

Two types of adsorption:

1. Physical adsorption (**physisorption**):
 - ▶ Low heat of adsorption released: $\Delta H_{\text{ads}} \sim 30$ to 60 kJ/mol
 - ▶ Theory: **van der Waals attractions**
 - ▶ easily reversible
2. Chemical adsorption (**chemisorption**):
 - ▶ High heat of adsorption released: $\Delta H_{\text{ads}} > 100$ kJ/mol
 - ▶ chemical bond formation, in the order of chemical bond strengths
 - ▶ leads to reaction products
 - ▶ more energy intensive to reverse
 - ▶ e.g.: catalysis, corrosion

As adsorbate concentration increases:

- ▶ single layers form, then multiple layers, then condensation

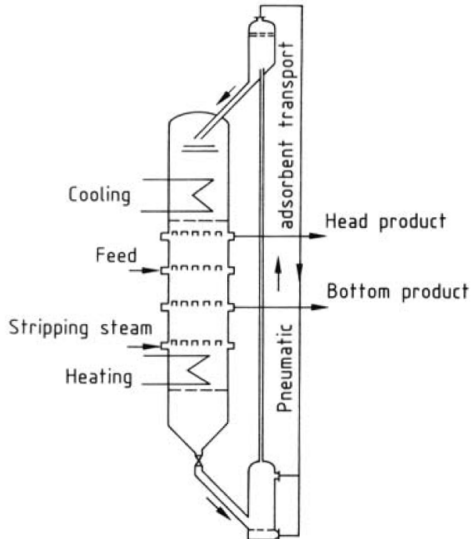
Adsorption equipment

Adsorption, Desorption and Recovery (ADR) plant in Burkina Faso



[Flickr #5043854546]

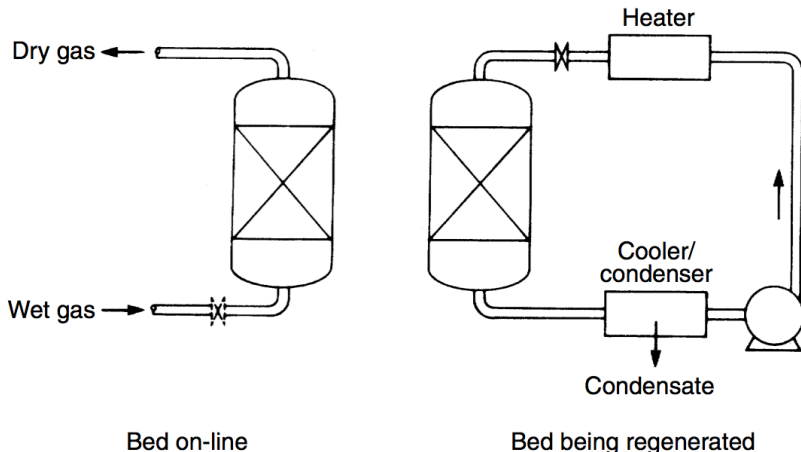
Fluidized beds



Materials of construction are important

Cyclones used to recover adsorbent

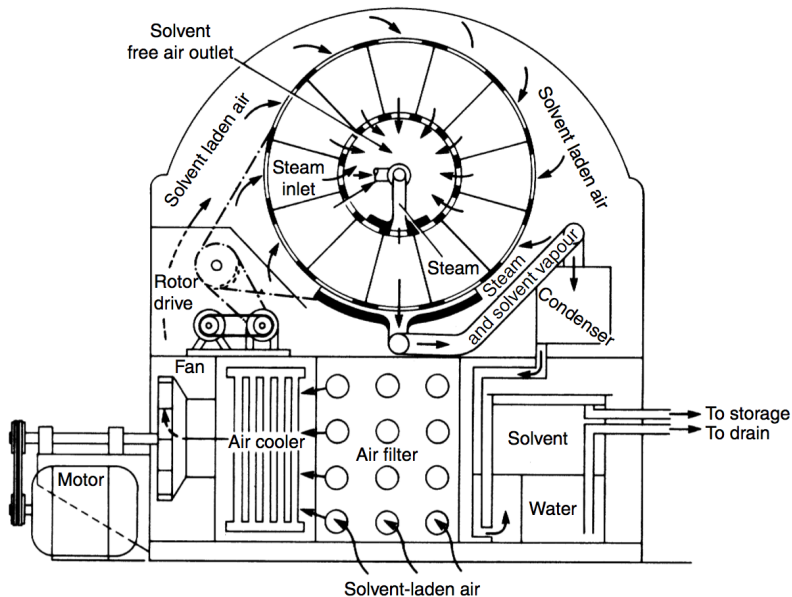
Packed beds: adsorption and desorption steps



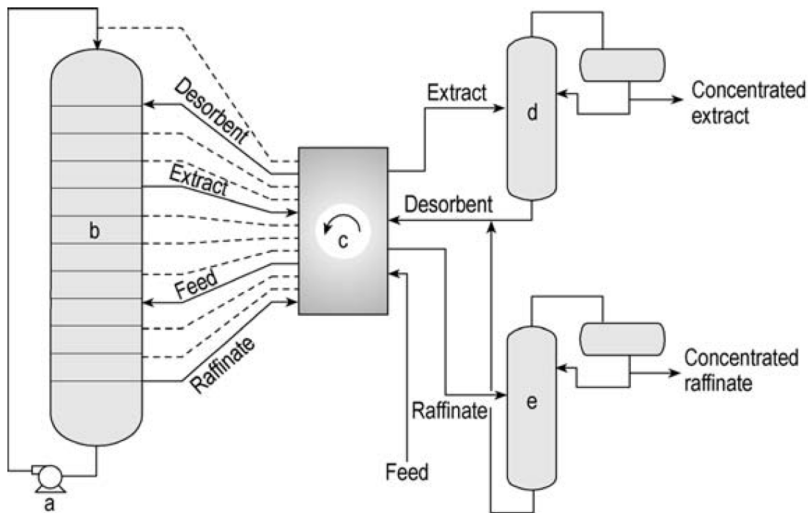
[Richardson and Harker, p 1028]

Regeneration: puts the adsorbate in a new solvent or medium, usually at a higher concentration than it was at originally, or at least in a medium that is much easier to separate from.

Rotary devices



Adsorption equipment: Sorbex column



[Uhlmanns, p 560]

a) Pump; b) Adsorbent chamber; c) Rotary valve; d) Extract column; e) Raffinate

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 (i.e diffusion resistance is negligible)

- ▶ Derive/Postulate a model relating bulk concentration to surface concentration of adsorbate
- ▶ We call these equations/models: “isotherms”
- ▶ **Isotherm**: relates amount of adsorbate on adsorbent at different concentrations, but at a fixed temperature.

Equilibrium modelling: linear model

Linear isotherm (Henry's law)

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

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

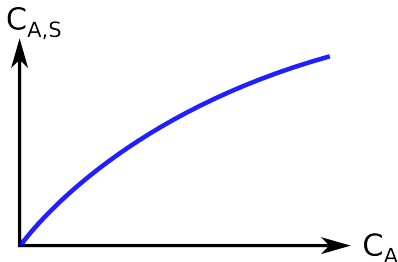
- ▶ $C_{A,s}$ = concentration of adsorbate A on adsorbent surface $\left[\frac{\text{kg adsorbate}}{\text{kg adsorbent}} \right]$
- ▶ C_A = concentration of adsorbate A in the bulk fluid phase $\left[\frac{\text{kg adsorbate}}{\text{m}^3 \text{ fluid}} \right]$
- ▶ P_A = partial pressure of adsorbate 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

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

- ▶ 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:

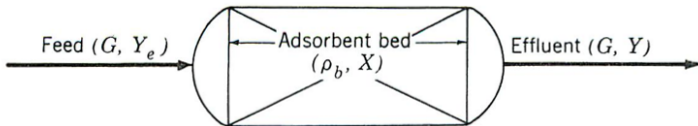
1. Postulate a model (e.g. linear, or Langmuir)
2. Perform a laboratory experiment to collect the data
3. Fit the model to the data
4. Good fit?

Other isotherms have been proposed:

- ▶ BET (Brunauer, Emmett and Teller) isotherm
- ▶ Gibb's isotherm

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

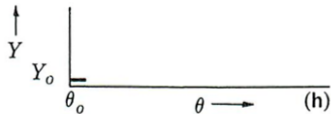
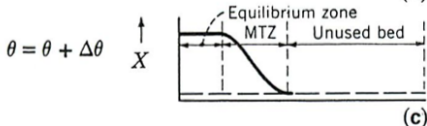
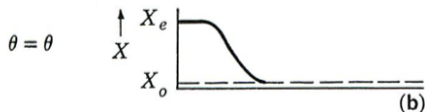
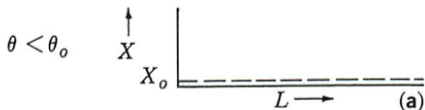
Understanding adsorption in packed beds



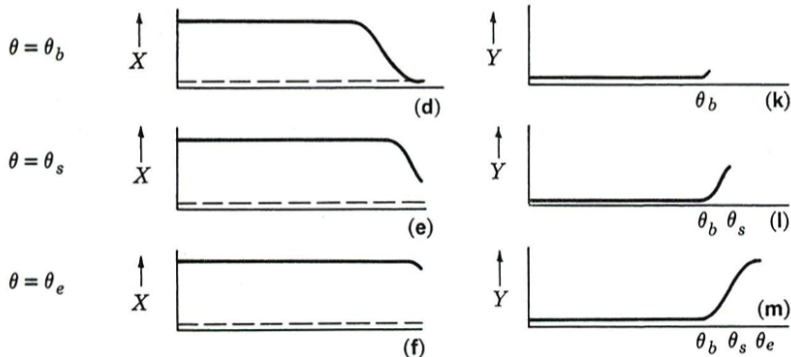
Time

Analysis of Adsorbent
(Adsorbent loading vs. bed length)

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



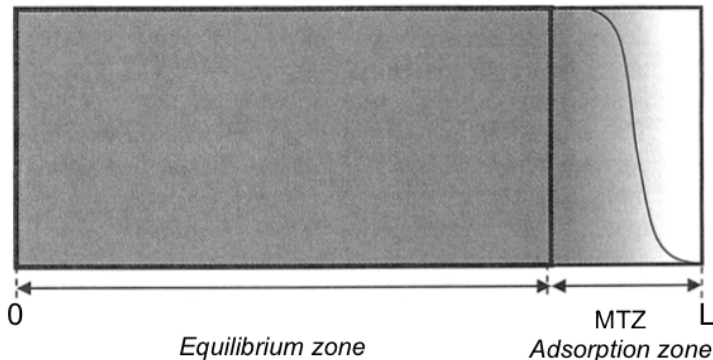
Understanding adsorption in packed beds



[Lukchis]

- ▶ X = concentration in the bulk of the bed = C_A in previous notation
- ▶ X_e = concentration of adsorbate at equilibrium in the bulk = feed conc
- ▶ X_0 = concentration of adsorbate in the regenerated adsorbent at time 0
- ▶ θ_b = breakthrough time
- ▶ θ_e = the bed at equilibrium time; adsorbent is completely used

Bed concentration just prior to breakthrough



[Ghosh (adapted), p144]

- ▶ **MTZ**: mass transfer zone is where adsorption takes place
- ▶ **Equilibrium zone**: this is where the isotherm applies!
- ▶ **Breakthrough**: arbitrarily defined as either (a) the lower limit of adsorbate detection, or (b) the maximum allowable adsorbate in effluent. Around 1 to 5% of $C_{A,feed}$.

References used (in alphabetical order)

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- ▶ Ghosh, "Principles of Bioseparation Engineering", chapter 8
- ▶ Johnston, "Designing Fixed-Bed Adsorption Columns", *Chemical Engineering*, p 87-92, 1972
- ▶ Lukchis, "Adsorption Systems: Design by Mass-Transfer-Zone Concept", *Chemical Engineering*, 1973.
- ▶ Perry's Chemical Engineers' Handbook, Chapter 22
- ▶ Richardson and Harker, "Chemical Engineering, Volume 2", 5th edition, chapter 17
- ▶ Schweitzer, "Handbook of Separation Techniques for Chemical Engineers", Chapter 3.1
- ▶ Seader, Henly and Roper, "Separation Process Principles", 3rd edition, chapter 15
- ▶ Uhlmann's Encyclopedia, "Adsorption", [DOI:10.1002/14356007.b03.09.pub2](https://doi.org/10.1002/14356007.b03.09.pub2)
- ▶ Wankat, "Separation Process Engineering", Chapter 16