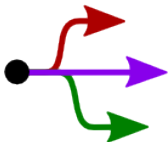


Separation Processes

ChE 4M3



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

Overall revision number: 123 (November 2012)

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

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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:

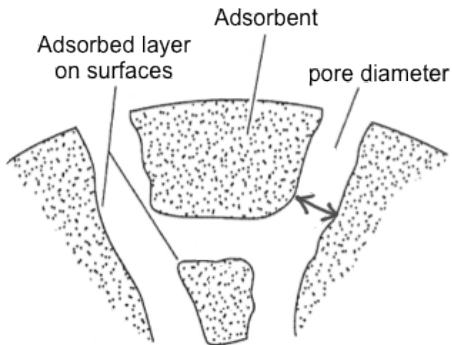
- ▶ adsorption: charred wood products to improve water taste
- ▶ adsorption: decolourize liquid with bone char
- ▶ adsorption: those little white packets in boxes of electronics
- ▶ ion-exchange: passing water through certain sand deposits removes salt
- ▶ ion-exchange: synthetic polymer resins widely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

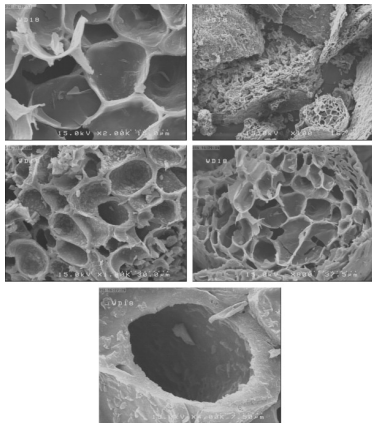


[Wikipedia]

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)



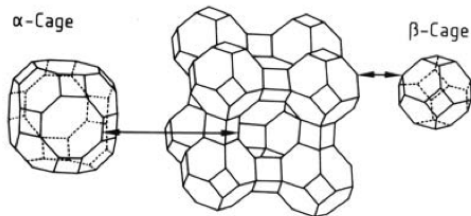
Molecular Sieve Type X
(b)

[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
- ▶ ~ 650 m² per gram

Adsorbents

Molecular sieves (zeolites):

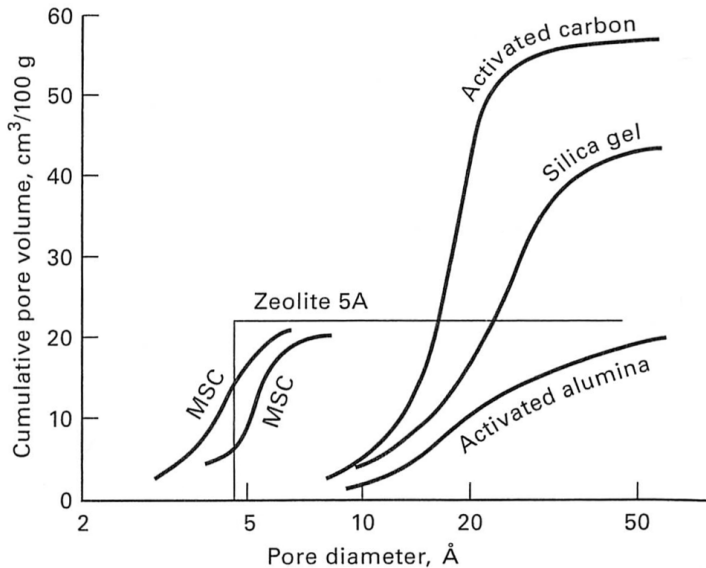
Size	Adsorbs ...	Dehydrates ...
3Å	H ₂ O, NH ₃	unsaturated hydrocarbons
4Å	H ₂ S, CO ₂ , C ₃ H ₆	saturated hydrocarbons
5Å	<i>n</i> -paraffins from iso-paraffins	
8Å	iso-paraffins and olefins	

[Johnston]

Rousseau, "Handbook of Separation Technology"

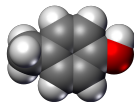
Adsorbent	Market size (1983)
Activated carbon	\$ 380 million ← 25% for water treatment
Molecular-sieve zeolites	\$ 100 million
Silica gel	\$ 27 million
Activated alumina	\$ 26 million

Pore diameter characterization

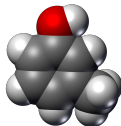


Adsorption examples

- ▶ Gas **purification**:
 - ▶ Volatile organics from a vent stream
 - ▶ Sulphur compounds from gas stream
 - ▶ Water vapour
 - ▶ 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

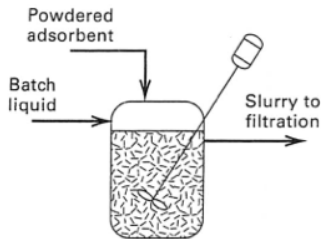


m-cresol

[Cresol figures from Wikipedia]

Example: 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 2cm^3 as packed and has 0.4cm^3 in small pores, which gives a surface area of $1150 \text{ m}^2/\text{gram}$ (university stadium field area ~ 5000 to 8000m^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: ...

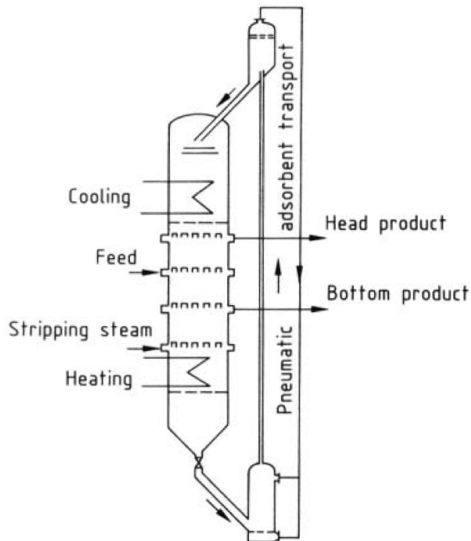
Two types of adsorption:

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

Fluidized beds



Materials of construction are important: carbon on carbon steel has a galvanic effect: leads to corrosion. Use stainless steel, or a lined vessel.

Cyclones used to recover adsorbent.

- ▶ Adsorbent life: ~ 100 cycles
- ▶ Bleed off old adsorbent and continuously replenish

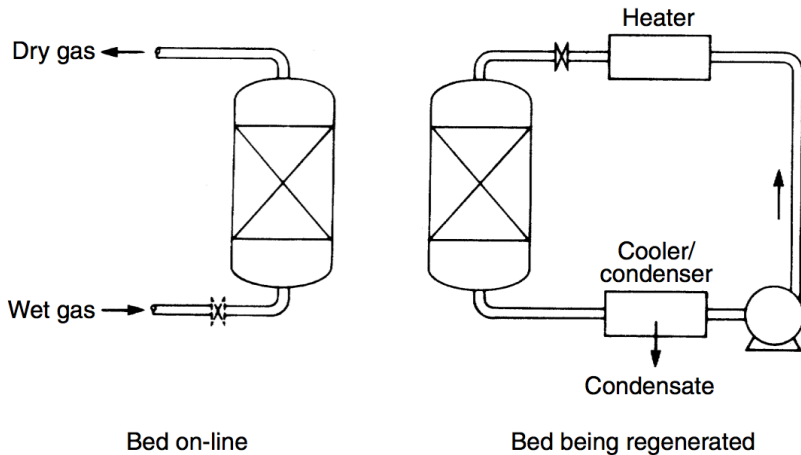
(Fluidized bed?) example

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



[[Flickr #5043854546](#)] *Zoom in on the high resolution photo to see details.*

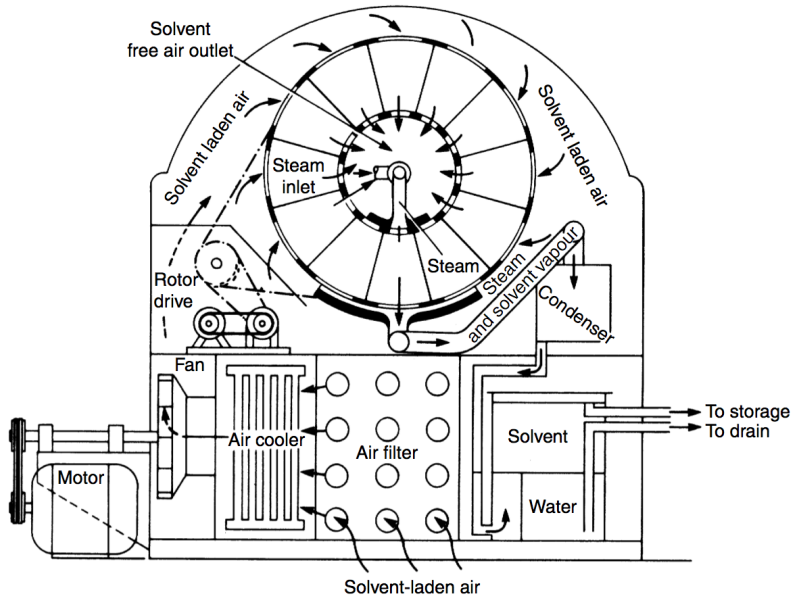
Packed beds: adsorption and desorption steps



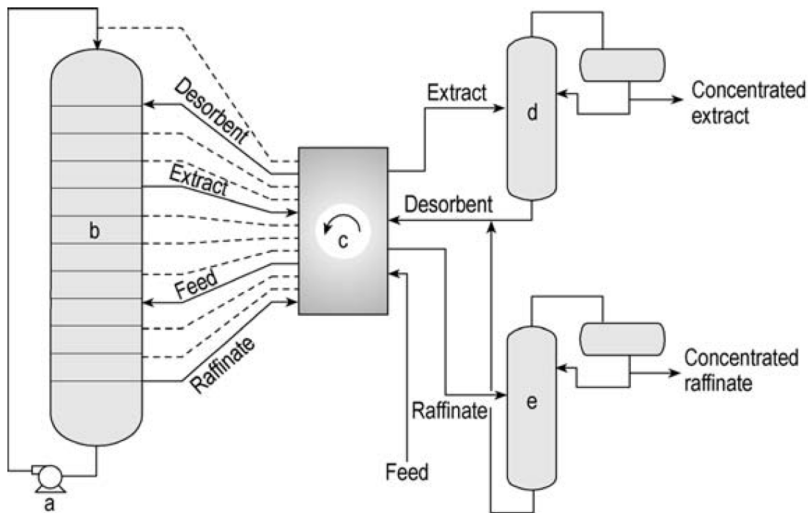
[Richardson and Harker, p 1028]

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 ($C_{A,S}$) at different concentrations of adsorbate in the bulk (C_A), but at a fixed temperature.

Equilibrium modelling: linear model

Linear isotherm (Henry's law)

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

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

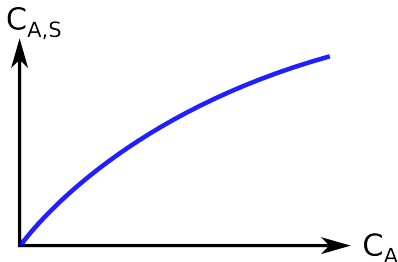
- ▶ $C_{A,S}$ = concentration of adsorbate A on adsorbent surface $\left[\frac{\text{kg adsorbate}}{\text{kg adsorbent}} \right]$
- ▶ C_A = concentration of adsorbate A in the bulk fluid phase $\left[\frac{\text{kg adsorbate}}{\text{m}^3 \text{ fluid}} \right]$
- ▶ P_A = partial pressure of adsorbate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



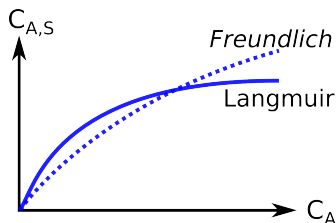
- ▶ Constants determined from a log-log plot
- ▶ How would you go about setting up a lab experiment to collect data to calculate K ?
- ▶ Which way will the isotherm shift if temperature is increased?

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:

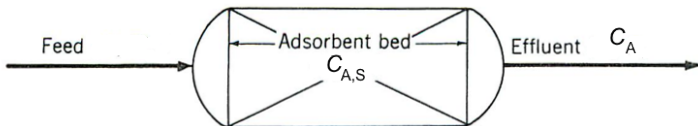
1. Perform a laboratory experiment to collect the data
2. Postulate a model (e.g. linear, or Langmuir)
3. Fit the model to the data
4. Good fit?

Other isotherms have been proposed:

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

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

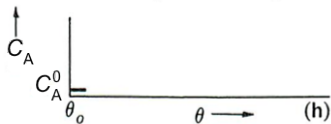
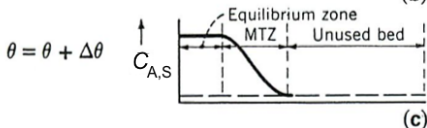
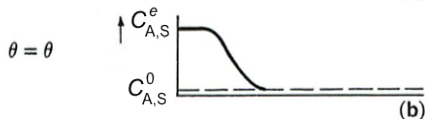
Understanding adsorption in packed beds



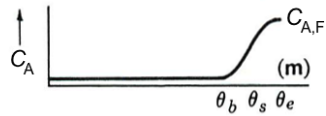
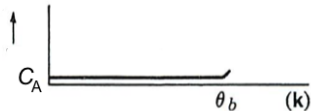
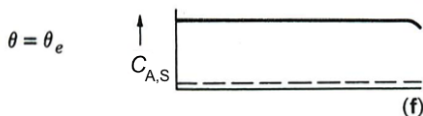
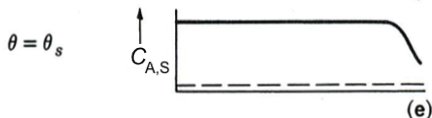
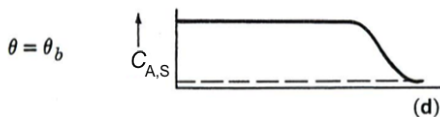
Time

Analysis of Adsorbent
(Adsorbent loading vs. bed length)

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



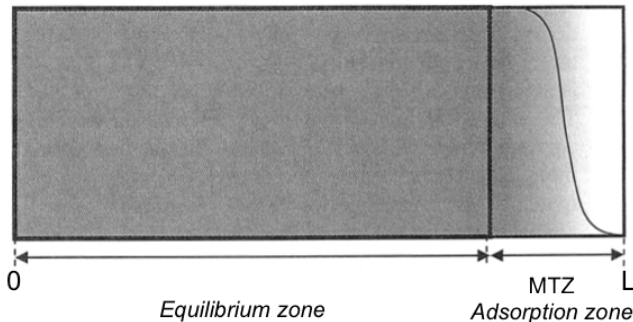
Understanding adsorption in packed beds



[Lukchis]

- ▶ $C_{A,S}$ = concentration of adsorbate on adsorbent
- ▶ $C_{A,S}^e$ = concentration at equilibrium on the adsorbent
- ▶ $C_{A,S}^0$ = concentration on the regenerated adsorbent at time 0
- ▶ θ_b = breakthrough time
- ▶ θ_e = the bed at equilibrium time; packed bed is completely used
- ▶ $C_{A,S}$ values are not measurable; outlet concentration C_A is easy

Bed concentration just prior to breakthrough



[Ghosh (adapted), p144]

- ▶ **MTZ**: mass transfer zone is where adsorption takes place. Assumed to be from 5 to 95% of the concentration range.
- ▶ It is S-shaped: indicates there is mass-transfer resistance.
- ▶ **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 $C_{A,F}$

Regenerating the bed

Aim

To remove adsorbate from the packed bed.

1: Temperature swing adsorption (TSA)

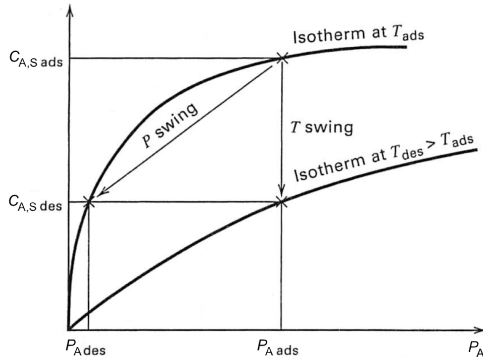
- ▶ heat the bed: usually steam is used (due to high latent heat)
- ▶ creates a thermal wave through the packed bed
- ▶ isotherm at higher temperature is shifted down
- ▶ causes the adsorbate to be diluted in the stripping fluid
- ▶ often leave residual solvent, since time to completely strip adsorbent would be excessive
- ▶ care must be taken with flammable adsorbates:
 - ▶ stripping temperature are high
 - ▶ often near flammable limits
 - ▶ carbon beds have been known to catch fire

See illustration on next page

Regenerating the bed

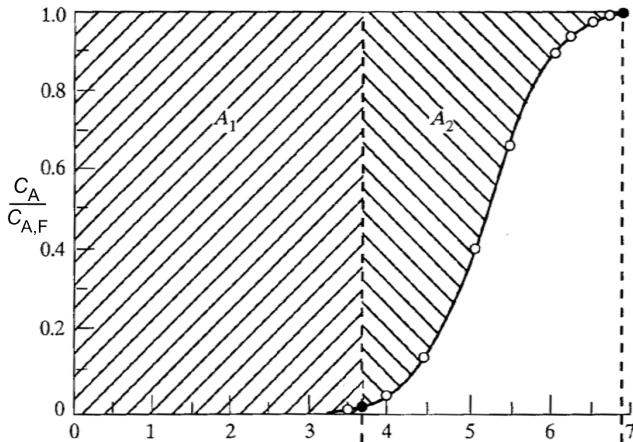
2. Pressure swing adsorption (PSA)

- ▶ used when the “product” is the cleaned (stripped) fluid
- ▶ add feed with adsorbate at high pressure (loads the adsorbate)
- ▶ drop the pressure and the adsorbate starts to desorb
- ▶ run two beds in parallel (one desorbing, the other adsorbing)
- ▶ widely used for portable oxygen generation, H_2S capture in refineries



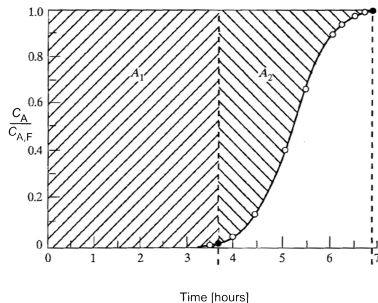
Example (and some theory)

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:



Example

1. Determine the **breakpoint time**, θ_b
2. What is the **usable capacity** of the bed?
 - ▶ Note total plot area = “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 capacity? 3.65 hours, but if we want to be exact, it is $t_{\text{used}} = \int_0^{\theta_B} \left(1 - \frac{C_A}{C_{A,F}}\right) dt \approx 3.65$

Example

4. But what actual fraction of the bed's capacity is used at θ_b ?



- ▶ The actual capacity used is the total shaded area = $A_1 + A_2$
- ▶ This is called the **stoichiometric capacity** of the bed
- ▶ Ideally, if there were no mass transfer resistance (i.e. spread in the breakthrough curve), then the
- ▶ **stoichiometric time**, θ_S , is defined as **time taken** for this actual capacity to be used
- ▶ θ_S is the point that breaks the MTZ into equal areas: in this case, A_2 vs the unshaded area
- ▶ $\theta_S = \int_0^{\infty} \left(1 - \frac{C_A}{C_{A,F}}\right) dt = \text{shaded area} = A_1 + A_2 = 3.65 + 1.5 = 5.15 \text{ hrs}$
- ▶ So actual bed capacity used at $\theta_b = \frac{t_{\text{used}}}{\theta_S} = 3.65/5.15 \text{ hours} \sim 71\%$

Example

5. If the lab-scale bed were originally 14cm long, what length is unused at time θ_b ?

- ▶ intuitively: $14 - 0.71 \times 14 = 4.1$ cm
- ▶ $L_{\text{UNB}} = \left(1 - \frac{t_{\text{used}}}{\theta_S}\right) L_{\text{total}} = \left(1 - \frac{3.65}{5.15}\right) 14 = 4.1$ cm
- ▶ where L_{UNB} is the **length of the unused bed**
- ▶ and L_{total} is the total bed length

6. If we wanted a break-point time of 7.5 hours instead, how much longer should the bed be (keeping the diameter fixed)?

- ▶ Ratio the bed lengths: $\frac{7.5}{3.65} \times 0.71(14) = 20.4$ cm
- ▶ But that's the length to get breakthrough in 7.5 hours
- ▶ We have to add on the length of the unused bed = 4.1 cm from before (same diameter!)
- ▶ So new bed length = $20.4 + 4.1 = 24.5$ cm
- ▶ And fraction actually used = $20.4 / 24.5 = 0.83$

References used (in alphabetical order)

- ▶ Geankoplis, "Transport Processes and Separation Process Principles", 4th edition, chapter 12
- ▶ 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
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- ▶ Schweitzer, "Handbook of Separation Techniques for Chemical Engineers", Chapter 3.1
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