Separation Processes

ChE 4M3

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Overall revision number: 112 (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:

- a**b**sorption: 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: $Ca^{2+}_{(aq)} + 2NaR_{(s)} \longleftrightarrow CaR_{2(s)} + 2Na^{+}_{(aq)}$
- 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.

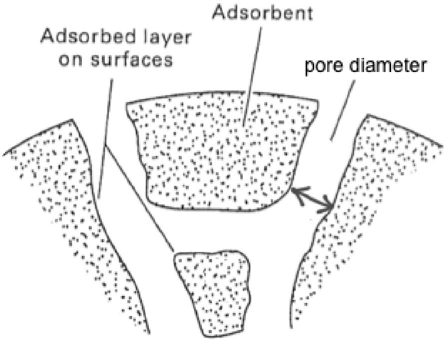
Some well-known examples:

- 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 removed 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)



[Modified from: Seader, 3ed, p 569]

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

Main characterization: pore diameter

Quick recap of some familiar concepts

- 1m = 100cm = 1000mm = $10^6 \mu$m= 10^9nm = 10^{10}Å
- Hydrogen and helium atoms: $\sim$ 1Å
- For a pore:
$$\frac{\text{Surface area}}{\text{Volume}} = \frac{\pi d_p L}{\pi d_p^2 L/4} = \frac{4}{d_p}$$
- d_p = pore diameter: typically around 10 to 200 Å

Adsorbents

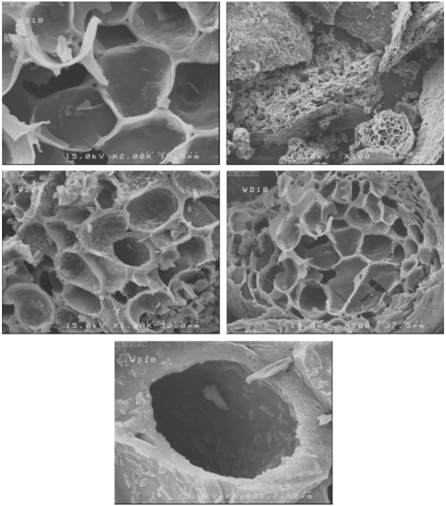
Helpful to see what they look like to understand the principles:

[Wikipedia]

Activated alumina

- made from from aluminum hydroxide
- ~ 300 m^2 per gram
- most widely used adsorbent
- hydrophilic
- pore diameter: 10 to 75 Å

Adsorbents

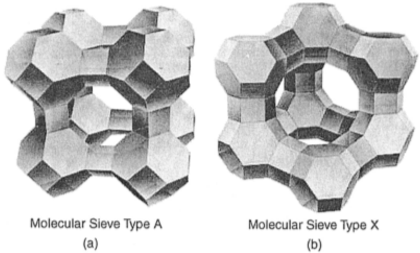


[DOI:10.1016/j.saa.2011.10.012]

Activated carbon

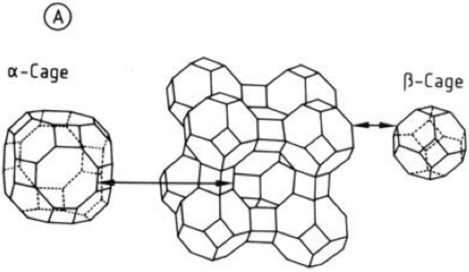
- partially oxidized coconut shells, nuts, wood, peat, bones
- 400 to 1200 m^2 per gram
- hydrophobic
- pore diameter: 10 to over 50 Å

Adsorbents



[Seader, 3ed, p575]

[Uhlmanns, p565]



Zeolite lattices

Some examples

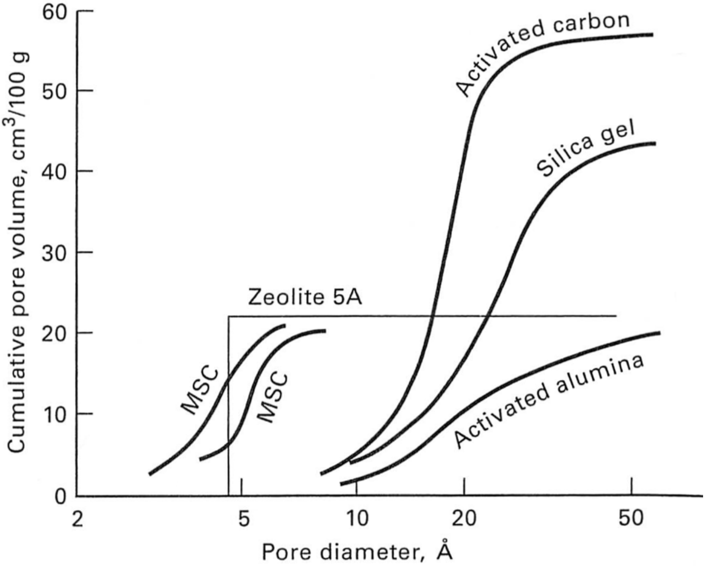
$K_{12}[(AlO_2)_{12}(SiO_2)_{12}]$:
drying gases [2.9Å]

$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$:
CO_2 removal [3.8Å]

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

Very specific pore diameters

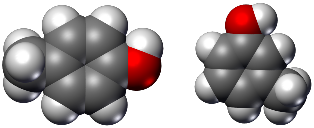
Pore diameter characterization



[Seader, 3ed, p574] Determined using He and Hg porosimetry (see reference for details)

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 CO_2 from natural gas [alternatives ?]
- Bulk separation in the gas phase:
  - N_2 (adsorbed more strongly onto zeolites) from O_2
  - H_2O from ethanol
  - High acetone quantities from air vent streams
- Liquid-liquid separation and purification:
  - Organics 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]

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
- too large area for a membrane
- high selectivity is required
- feed is a very dilute streams of solute (adsorbate)

But, some disadvantages:

- only surface of the adsorbent used
- regeneration of MSA adsorbent required
- MSA will break down mechanically over time

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 m^2/gram (university stadium field area $\sim$ 5000 to 8000m^2). Based on the area of the annular region filled with adsorbate, the solute occupies 22.5% of the internal pore volume and 13.5% of the total packed-bed

Physical principles

Adsorption releases heat. Why?

Thermodynamics ...

Two types of adsorption:

1. Physical adsorption:
   - Low heat of adsorption: 30 to 60 kJ/mol
   - van der Waals attractions
   - easily reversible
2. Chemical adsorption:
   - High heat of adsorption: > 100 kJ/mol
   - Chemical bond formation
   - more energy intensive to reverse

Conceptual steps as adsorbate concentration increases:

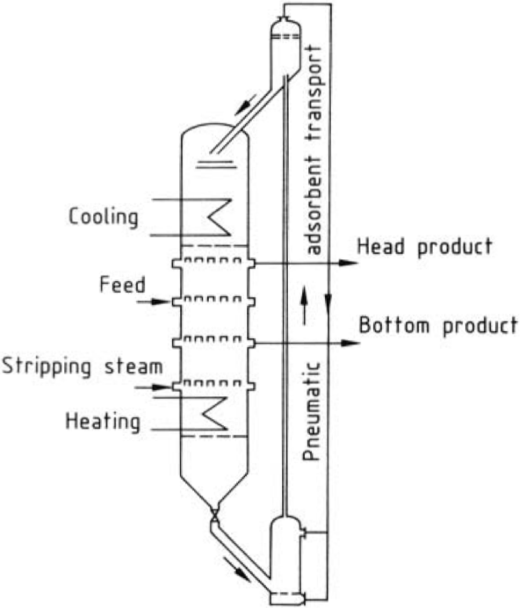
1. single layer of molecules first form on surface
2. then multiple layers form
3. condensation, once pore size limitations exceeded

Adsorption equipment

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

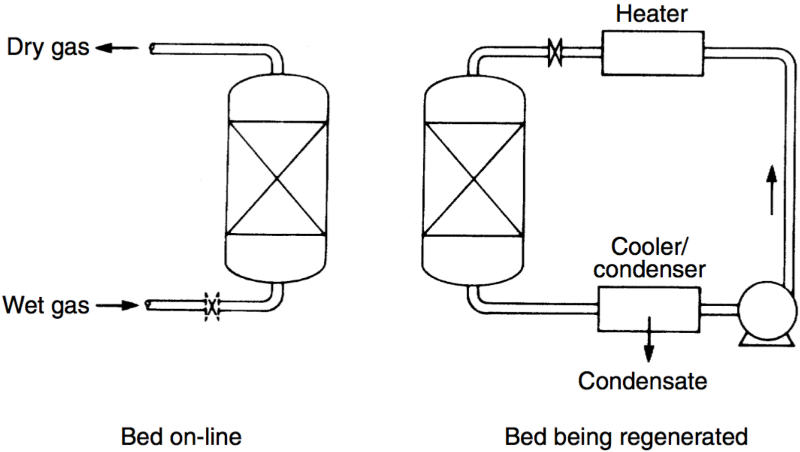
[Flickr #5043854546]

Fluidized beds



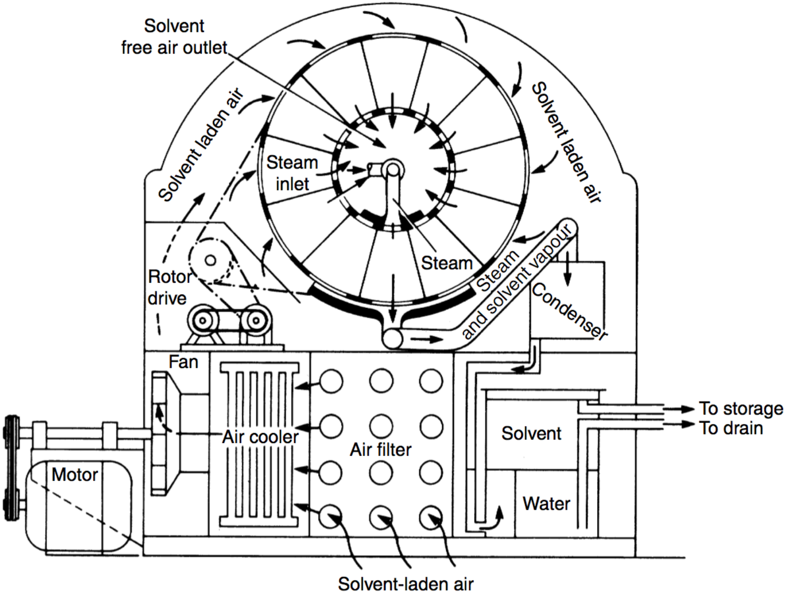
[Uhlmanns, p556]

Packed beds: adsorption and desorption steps



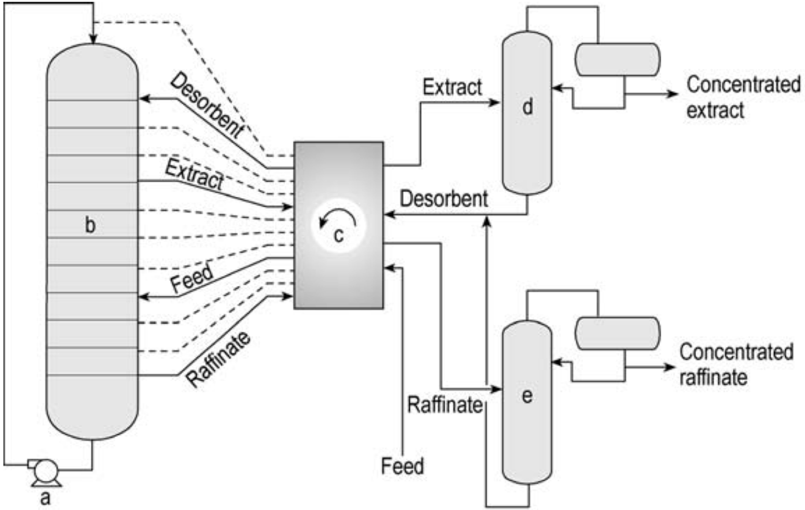
[Richardson and Harker, p 1028]

Rotary devices



[Richardson and Harker, p 1034]

Adsorption equipment: Sorbex column



[Uhlmanns, p 560]

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

Mechanisms during adsorption

- equilibrium interaction: solid-fluid interactions (later)
- kinetic: differences in diffusion
- steric: pore structure hinders/retains molecules of a certain shape

References

- Schweitzer, "Handbook of Separation Techniques for Chemical Engineers", Chapter 3.1
- Seader, Henly and Roper, "Separation Process Principles", 3rd edition, chapter 15
- Richardson and Harker, "Chemical Engineering, Volume 2", 5th edition, chapter 17
- Geankoplis, "Transport Processes and Separation Process Principles", 4th edition, chapter 12
- Ghosh, "Principles of Bioseparation Engineering", chapter 8
- Perry's Chemical Engineers' Handbook, Chapter 22
- Uhlmann's Encyclopedia, "Adsorption", DOI:10.1002/14356007.b03_09.pub2
- Wankat, "Separation Process Engineering", Chapter 16