Adsorption

Lecture 6

Learning outcomes

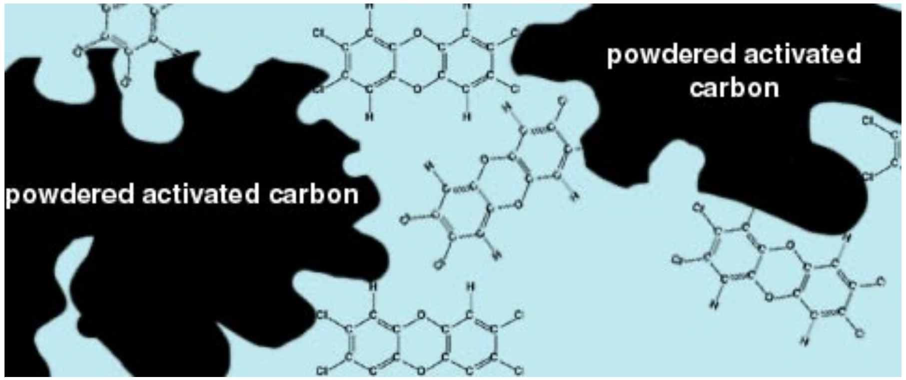
- Adsorption
- Chemical soil washing
- Activated carbon adsorption

Adsorption

Adsorption

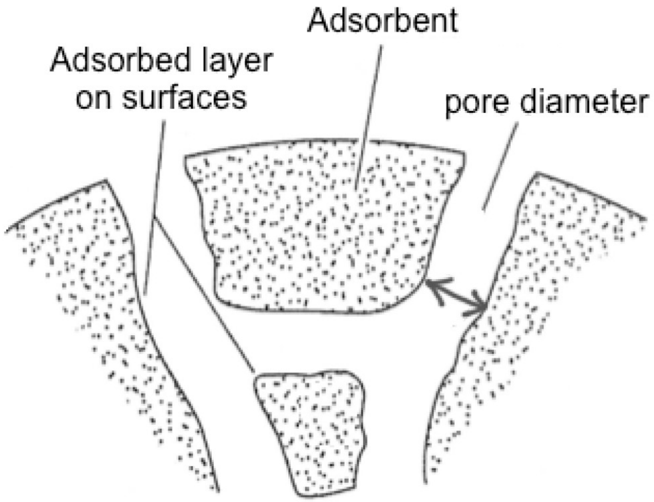
- **Ad**sorption is a process by which a component (the sorbate) moves from the aqueous or gaseous phase to the solid phase by association with a solid phase **surface**.

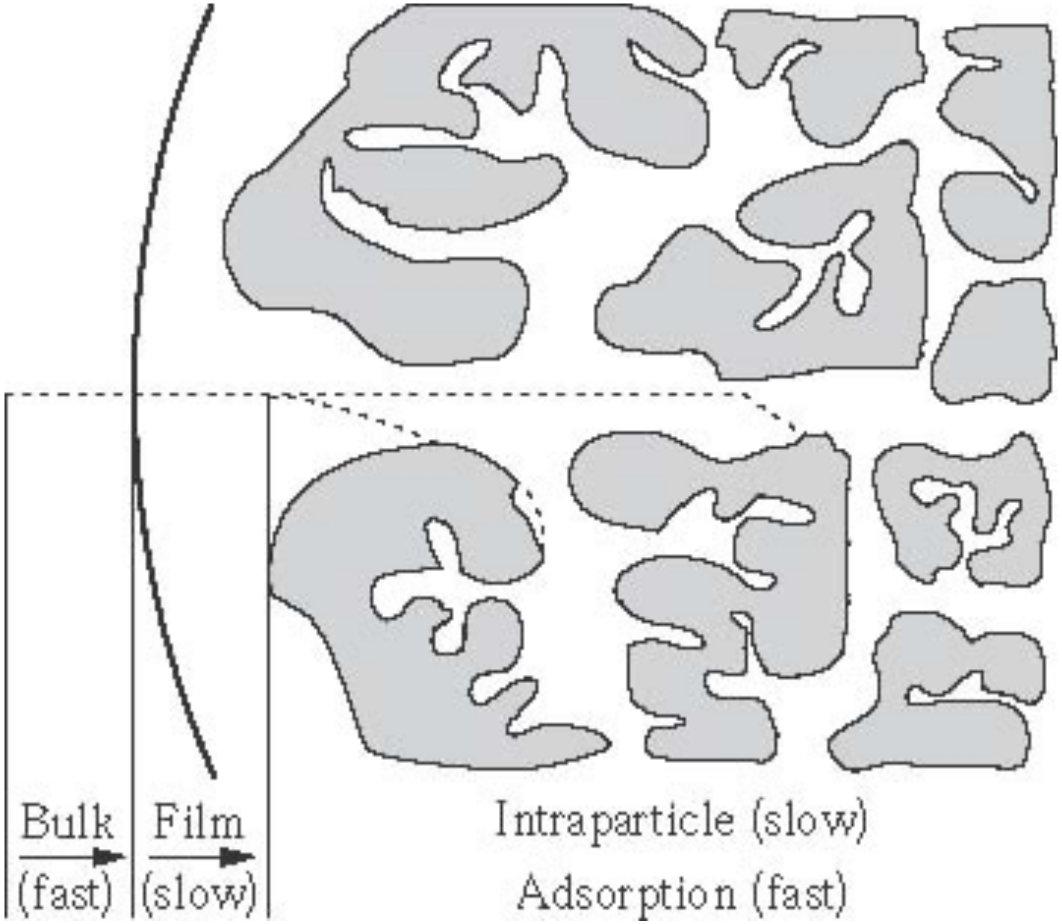
- In this lecture, we will cover:
  - Adsorption of metals to mineral surfaces (association of contaminants with soils/sediments)
  - Adsorption of contaminants to activated carbon (as a means of removal from water)



Adsorption theory

- Four separate phenomena (with varying kinetics):
  - Bulk fluid transport (fast)
  - Film transport (slow)
  - Intraparticle transport (slow)
  - Physical attachment (fast)





Types of mechanisms:
- Equilibrium interaction
- Kinetic effects (differences in diffusion rates)
- Steric hinderance: some molecules excluded or trapped

Equilibrium isotherms

- Several models have been proposed to describe the relationship between the adsorbed concentration and the bulk fluid concentration at constant temp:
  - Langmuir isotherm
  - Freundlich isotherm

Langmuir isotherm: based on kinetic theory and ideal conditions- often fails to match experimental data

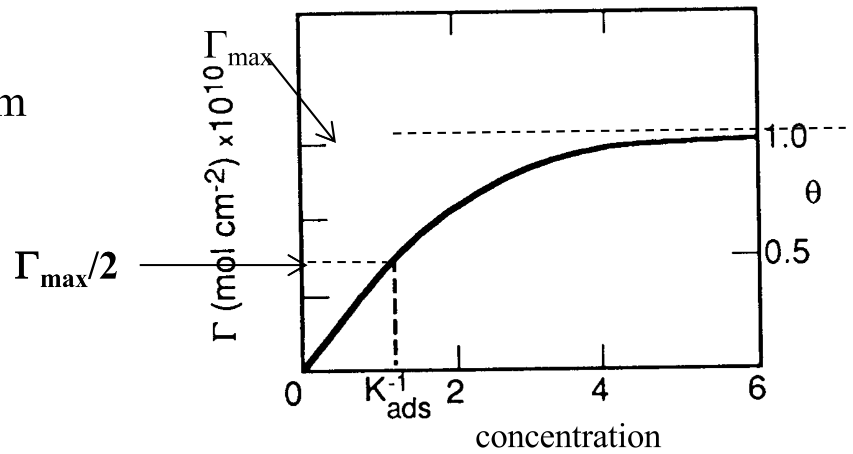
Assumptions:

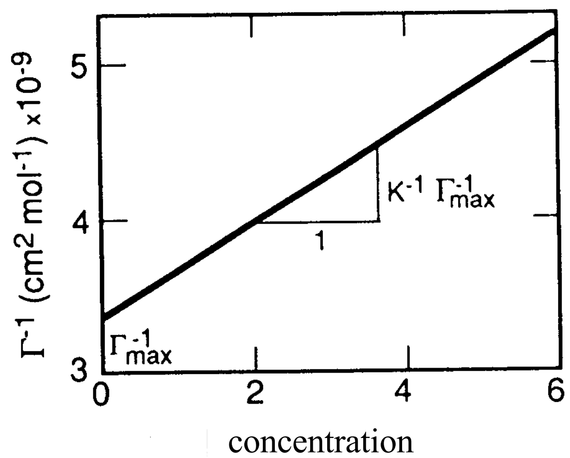
- constant energy of adsorption
- Homogeneous surface
- Monolayer distribution
- Adsorbed molecules immobile

$$C_{i,s} = C_{i,s,max}\,\frac{KC_{i,aq}}{1+KC_{i,aq}}$$

Where $C_{i,aq}$= aqueous solute concentration at **equilibrium** ($g.m^{-3}$)
$C_{i,s}$ = adsorbed concentration at equilibrium (g solute/g adsorbent)
$C_{i,s\ max}$=adsorbed concentration corresponding to a complete monolayer (g solute/g adsorbent)
K= half-coverage constant

Langmuir isotherm





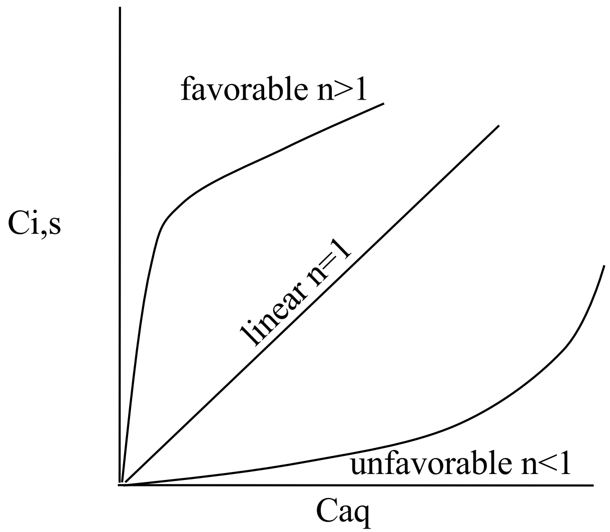
Equilibrium isotherms

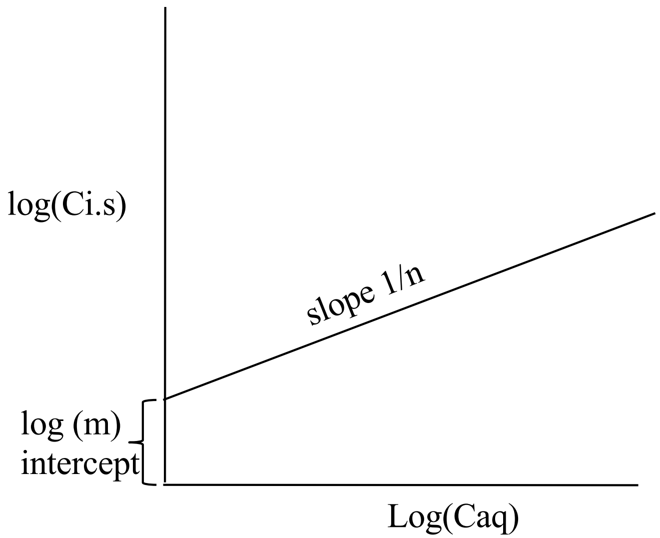
<u>Freundlich isotherm</u>: empirical equation with two adjustable constants. Usually fits well within 2 orders of magnitude of concentration

$$C_{i,s} = K C_{i,aq}^{1/n}$$

Where C= solute concentration at equilibrium (g.m^{-3})
K= Freundlich coefficient {proportional to RT exp (ΔH/RT)}
n= empirical constant

Forms of the Freundlich equation

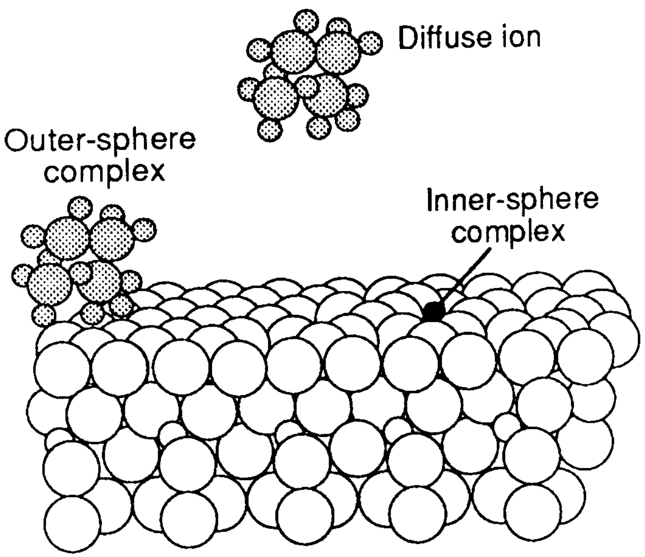


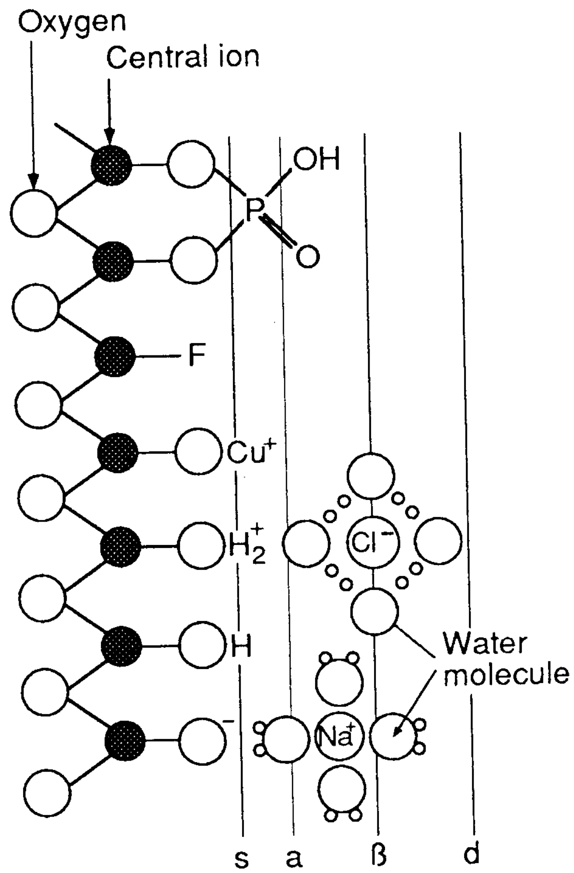


A favorable isotherm generally assures that the equilibrium adsorption capacity will be relatively high at low solution concentrations

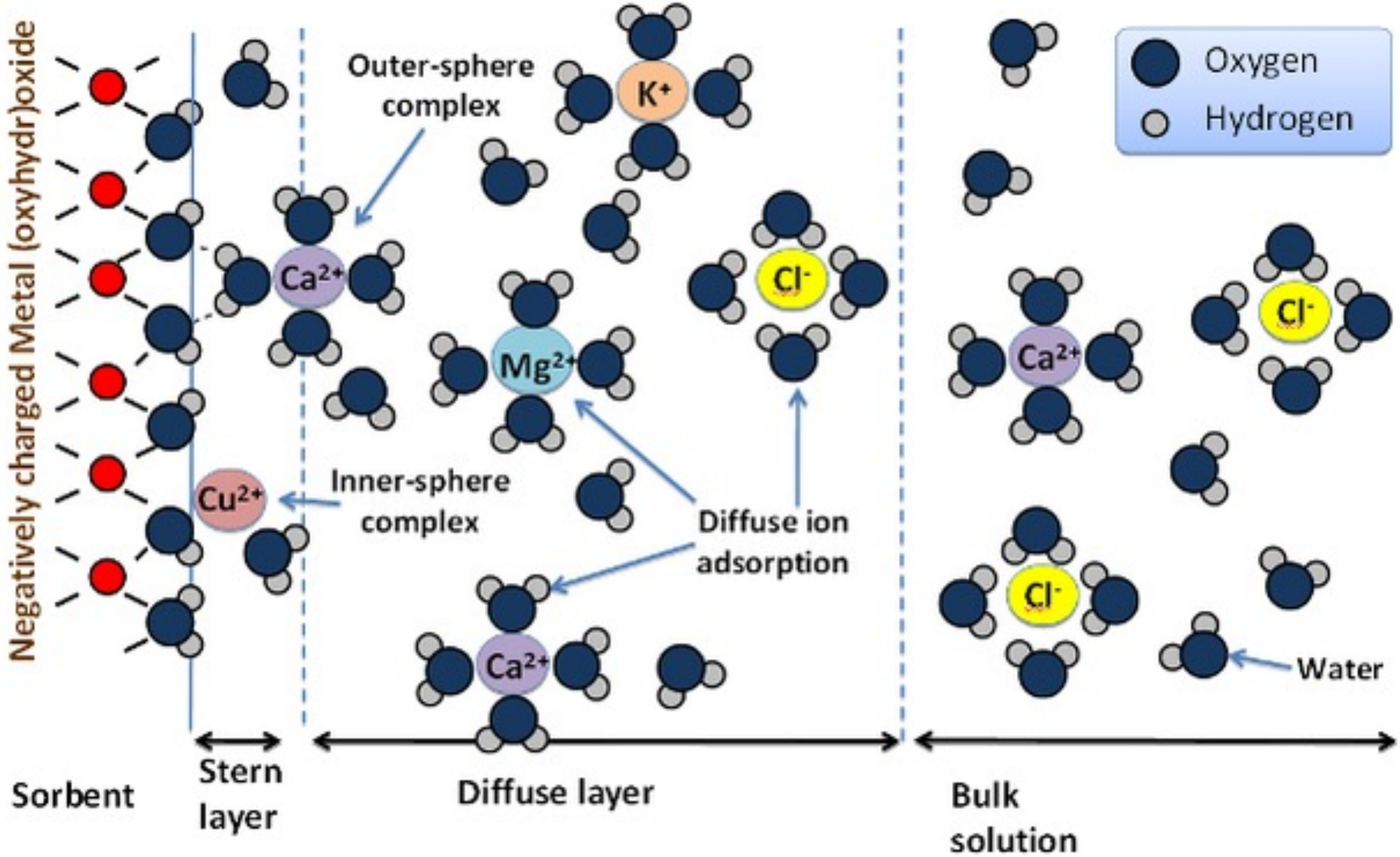
Adsorption of metals to mineral surfaces

Adsorption is described in terms of inner sphere and outer sphere surface complexes:
Inner sphere: the surface hydroxyl groups are directly covalently bound to the metal
Outer sphere: the metal retains its hydration layer



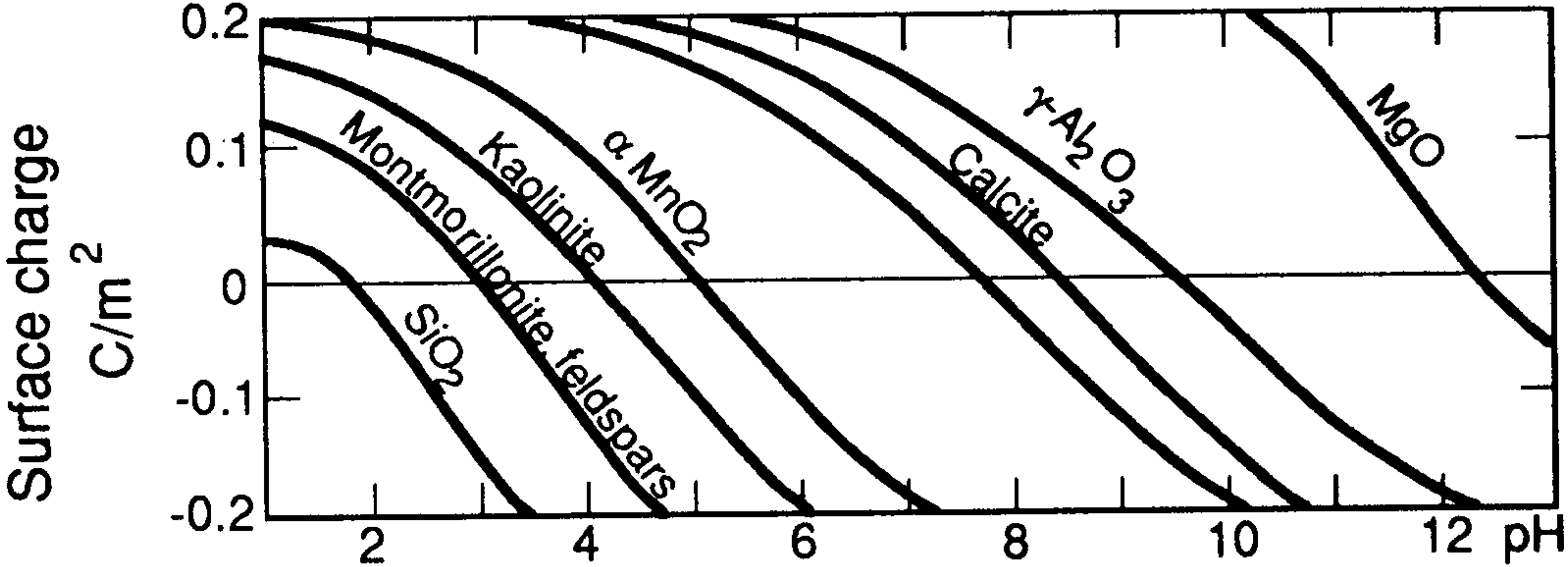


Adsorption of metals to mineral surfaces



Adsorption of metals to mineral surfaces

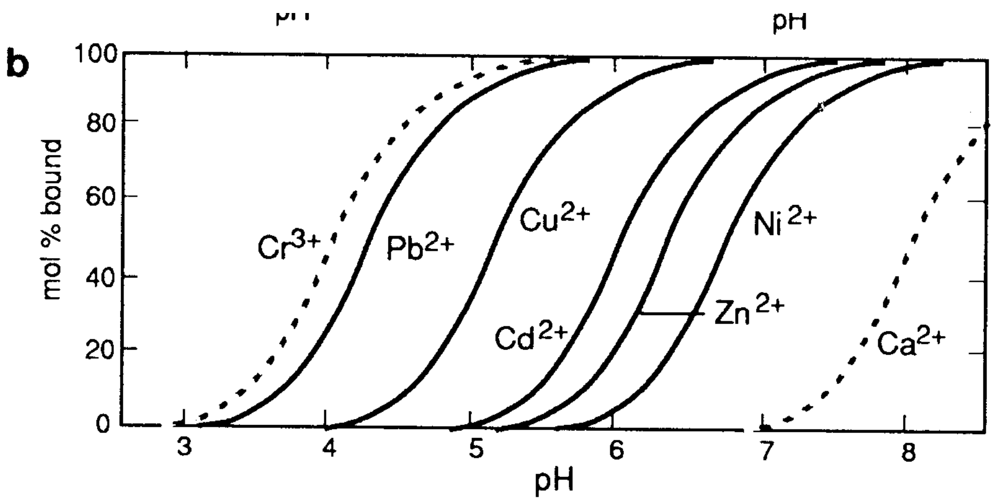
The surface charge of most minerals varies as a function of pH due to inherent characteristics of the minerals

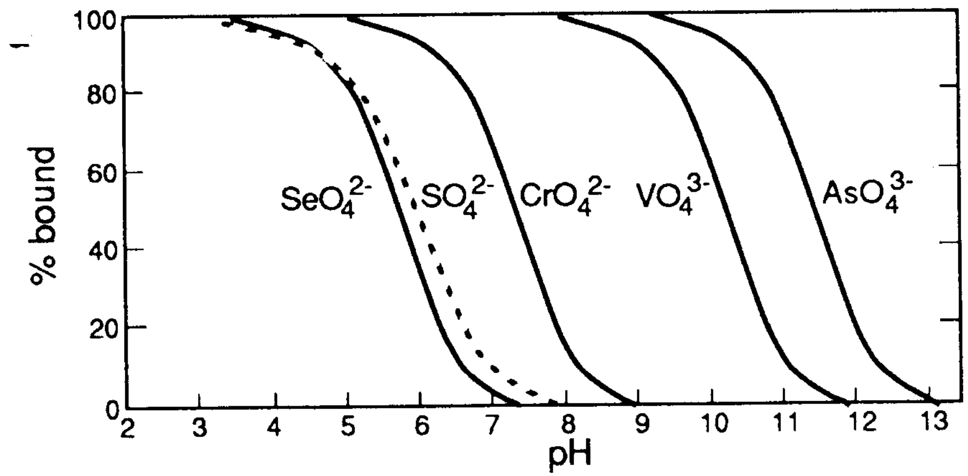


Adsorption of metals to mineral surfaces

The mineral surface charge is dependent on pH. Hence, the sorption of ions is also strongly linked to pH

Typical sorption edges (percent of metal adsorbed as a function of pH) have are S-shape with a strong pH dependence with sorption increasing with pH for cations and decreasing with pH for anions.





Soil-washing (chemical)

Contaminants are associated with fines

- Finer particles have higher area to volume ratio and adsorb most of the contaminants

COD=Chemical Oxygen Demand => equivalent of organic content

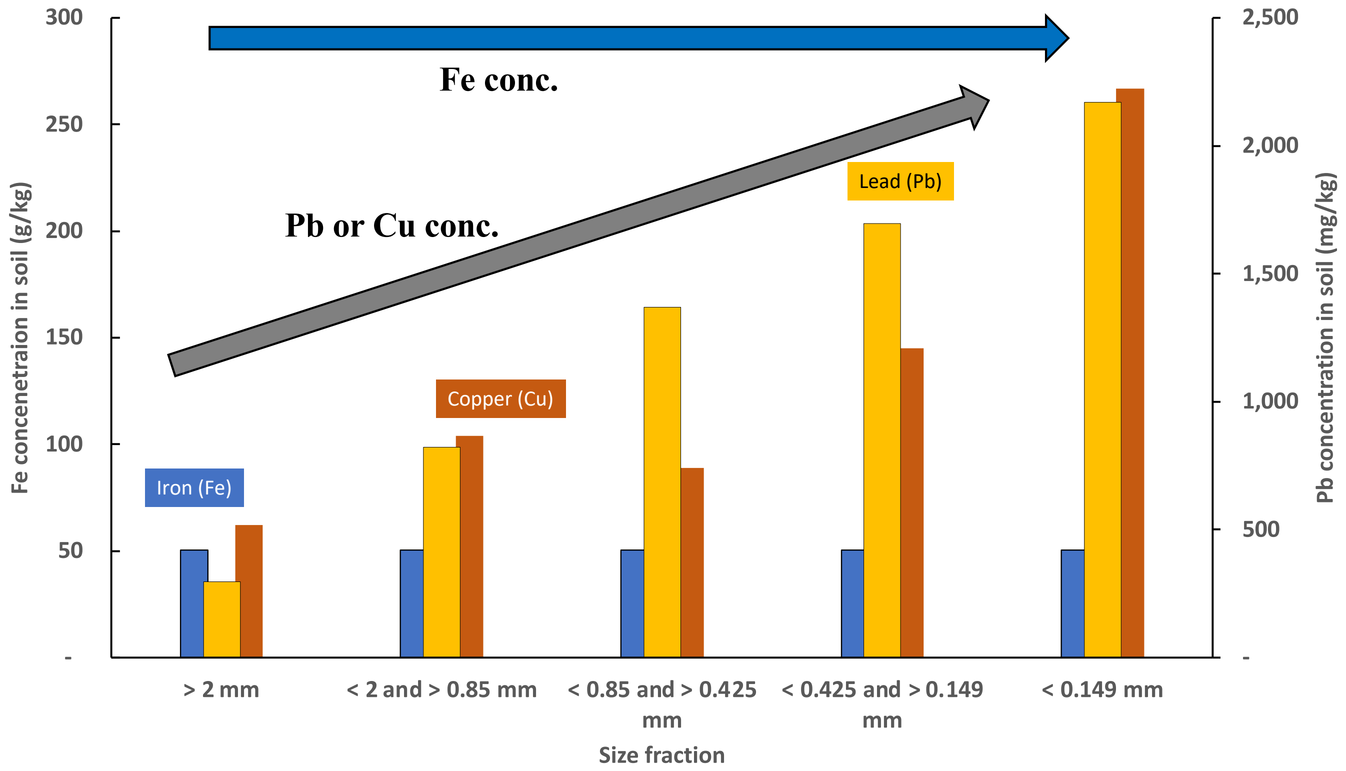
Example 1:

Distribution of COD by soil component

Component	% mass	% COD
Coarse	29	2.9
Fines	55	88.8
Tars	0.3	8.8
Water	15.7	0

Source: Black et al., 1991

Example 2:



Source: McCabe et al., 1997

Soil-washing

- Soil washing is a volume reduction/waste minimization treatment process
- The soil fine fraction carrying the largest amount of contaminant is separated from the bulk soil
- The rest of the soil (depending on its contaminant content) can be used as backfill, or disposed of as non-hazardous material
- Physical soil-washing: separation based on particle grain size, settling velocity, specific gravity, surface chemical behavior. Some removal of contaminant is possible through particle attrition
- **Chemical soil-washing: transferring the contaminants from the soil surface into solution (often using chemical compounds). The resulting suspension is separated from the aqueous solution (the latter is treated).**

Chemical soil-washing

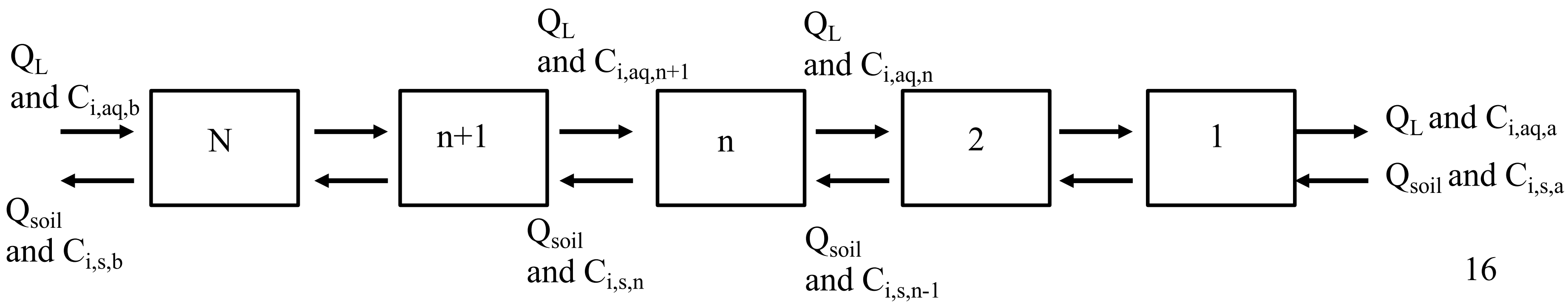
- Contaminants adsorbed onto fine soil particles are separated from bulk soil in an aqueous-based system based on particle size (remove sand and gravel).
- The wash water may be amended to enhance the removal of the compound into water
- For heavy metals, pH adjustment of a chelating agent may be used:
  - Removal of metals from soil through soil washing
  - Decrease the pH to a value below the edge (e.g., Pb^{2+}, pH <3)
  - Amendment of chelator that outcompetes the soil for the binding of the metal
- For organic contaminants, a surfactant may be used
- Equilibrium calculation of the aqueous concentration for batch systems

Soil washing

$$N = \frac{ln\left[\left(C_{i,s,a} - C^{*}_{i,s,a}\right)/\left(C_{i,s,b} - C^{*}_{i,s,b}\right)\right]}{ln\left[1/K * Q_L/Q_{soil}\right]}$$

$$C_{i,aq,n+1} = \frac{Q_{soil}}{Q_L} * C_{i,s,n} + \frac{Q_L * C_{i,aq,a} - Q_{soil} * C_{i,s,a}}{Q_L}$$

Where N= number of stages needed
$C_{i,s,n}$= solid phase inlet contaminant mass fraction (kg contaminant/kg soil)
$C_{i,s,n}{}^{*}$= solid phase equilibrium contaminant mass fraction (kg contaminant/kg soil) with respect to $C_{i,aq,n}$
K=equilibrium line slope (assuming linear relationship)
Q_L=extractant mass flow rate (kg/h)- constant at all stages
Q_{soil}= soil mass flow rate (kg/h)- constant at all stages
n= stage number
$C_{i,aq,n}$=effluent extracting fluid mass fraction (kg contaminant /kg extractant)



Countercurrent leaching cascade

Soil washing example

A soil contaminated with lead (Pb^{2+}) is being treated by soil washing under acidic conditions using a countercurrent leaching procedure. The <75 μm fraction contains the majority of Pb^{2+} (354 mg/kg) and will be treated. The ideal ratio of solid to liquid flow rate was found to be 0.025 kg soil/L water.

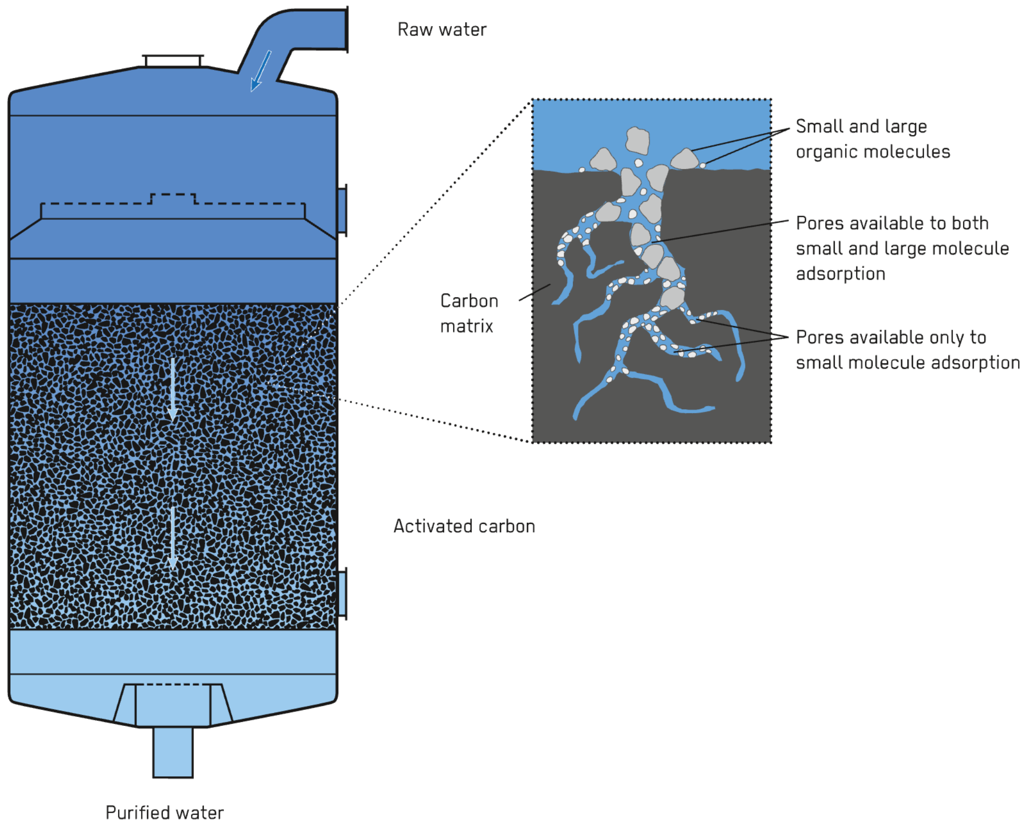
Due to the pH dependency of the sorption, the equilibrium isotherm is pH dependent with K=0.02 (L/kg) at pH 2. $C_{i,s} = KC_{i,aq}$

How many stages are needed for the treatment to the soil fraction at pH 2 to reach a concentration of 0.12 mg/kg given that the aqueous concentration of lead is 10 mg/L and 0.05 mg/L at the effluent and influent, respectively ?

Adsorption to activated carbon

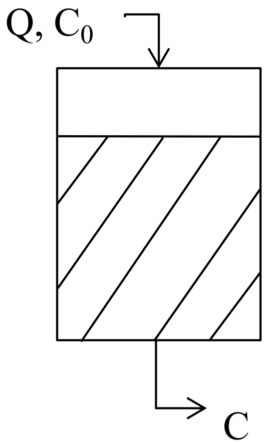
Carbon adsorption

- A treatment option to remove contaminant from water is sorption
- Most widely used adsorbent is granulated activated carbon (treated to increase internal surface area)- Many types of carbon available.
- Reactors where water enters at top and exits at bottom and backwashing capability to remove solid particles clogging bed
- Often set-up in series



Carbon adsorption

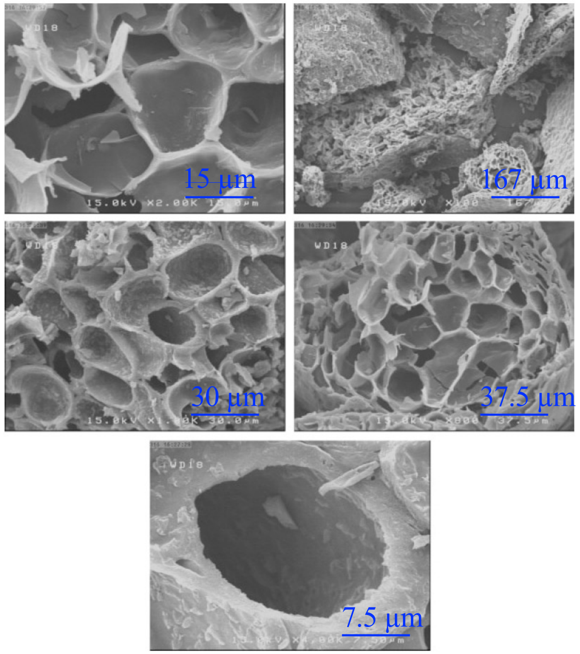
- Column reactors similar to plug flow reactors: Granular activated carbon (GAC)



A_b= x-section of bed (m^2)
Q=volumetric flow rate (m^3/h)
L=bed depth (m)
v_0= surficial velocity (m/h)= Q/A_b
EBCT (empty bed contact time)=V_T/Q

Activated carbon:
- precursor is coal, peat, wood, coconut
- manufacture: drying, pyrolysis and activation

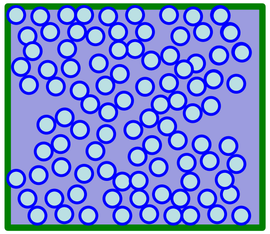
Grain size	PAC	$d_g = 0.01 - 0.1[mm]$
	GAC	$d_g = 0.5 - 3[mm]$
Pore volume		$V_p = 0.5 - 1.2[cm^3/g]$
Specific surface area		$A_s = 500 - 1200[m^2/g]$
Pore diameter:		10 Å to >50 Å



Pore structure: most of the surface area is situated in very small pores (r<1mm) called micropores.

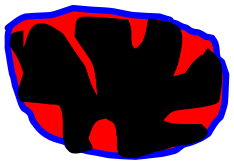
[DOI:10.1016/j.saa.2011.10.012]

Important properties



In green= total volume = V_T

In purple= bed void volume = V_V



In blue= volume of the grains = V_g
In red= volume of the internal voids = V_{ivoid}

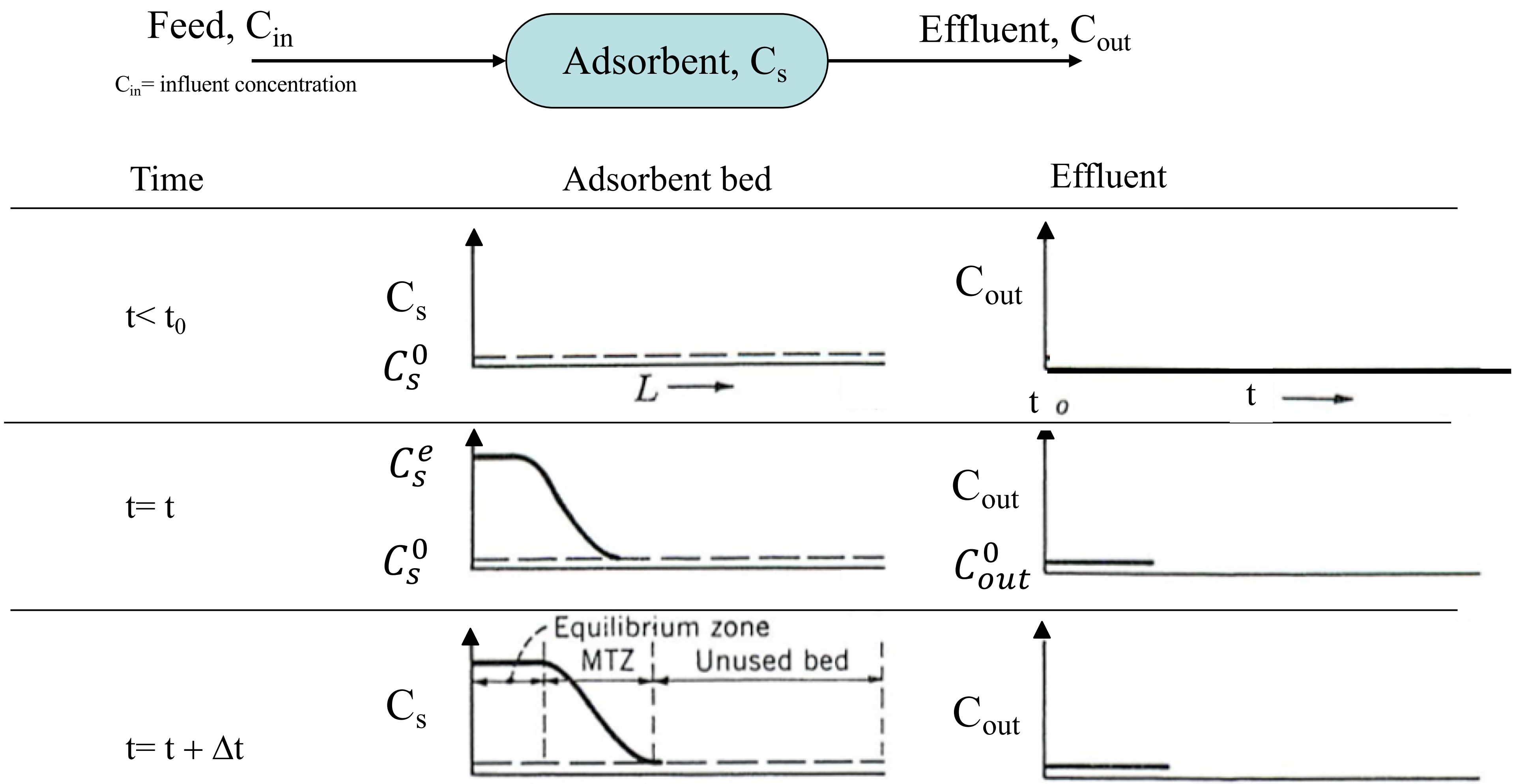
- Grain porosity $\varepsilon_i = \dfrac{vol\_internal\_voids}{vol\_particles} = \dfrac{V_{ivoid}}{V_g} = 0.5 - 0.8[-]$
- Bed porosity $\varepsilon_b = \dfrac{bed\_void\_volume}{total\_volume} = \dfrac{V_V}{V_T} = 0.5 - 0.8[-]$
- Solids density $\rho_s = \dfrac{mass\_solid}{vol\_solid} = \dfrac{M_s}{V_s} = 2{,}100[kg/m^3]$
- Grain density $\rho_g = \dfrac{mass\_particle}{vol\_particle} = \dfrac{M_g}{V_g} = 700[kg/m^3]$
- Bulk density $\rho_b = \dfrac{mass\_solid}{vol\_bed} = \dfrac{M_s}{V_T} = 300 - 500[kg/m^3]$

Uses for activated carbon adsorption

- Gas purification:
  - Volatile organics from industry
  - Sulfur compounds from industry

- Liquid separation:
  - Organic or toxic compounds from water
  - Gold in cyanide solutions

Adsorption in packed beds

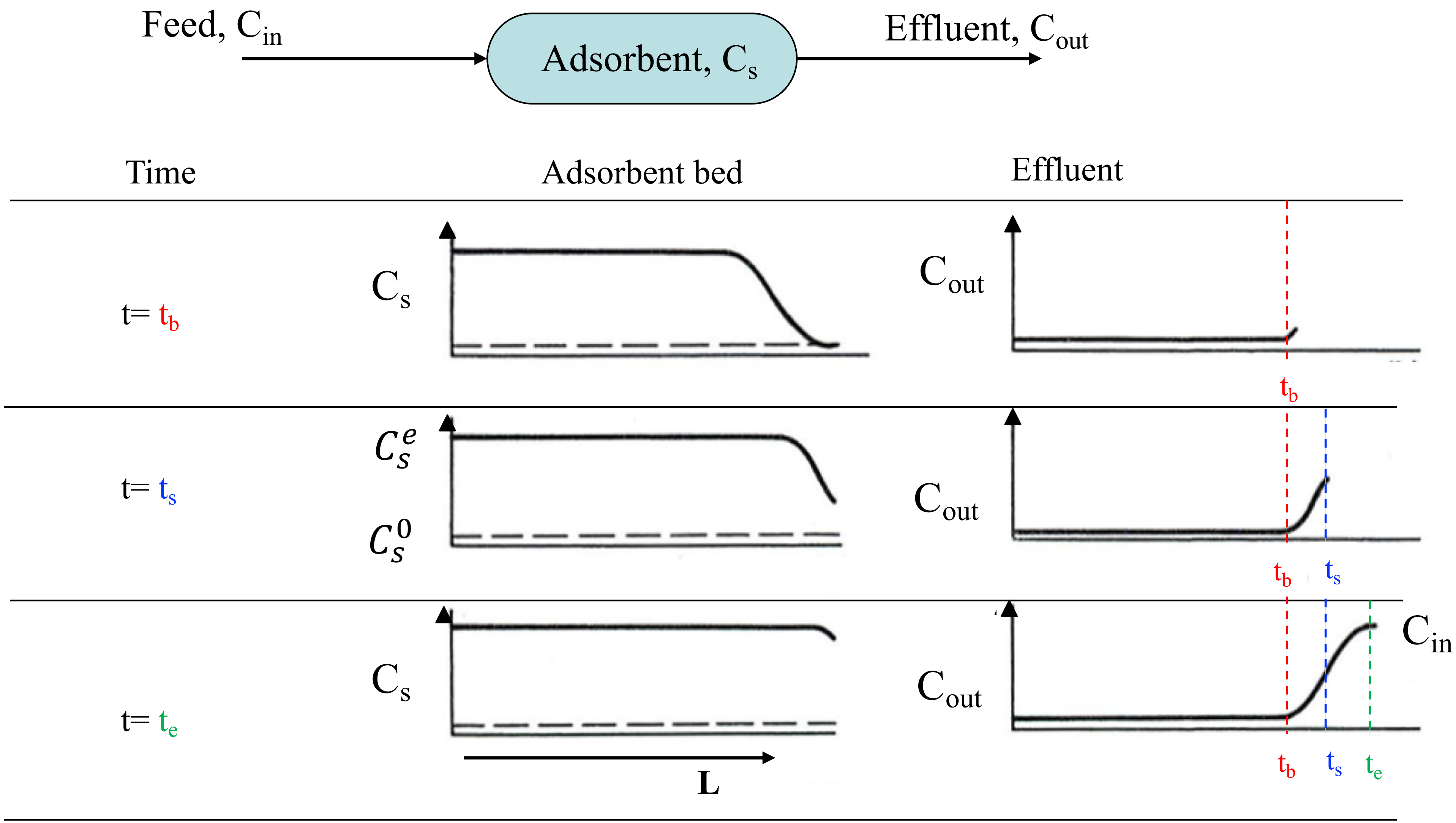


C_s= concentration on adsorbent
C_s^0= initial concentration on adsorbent
C_s^e= concentration on adsorbent at equil.

C_{out}= effluent concentration
C_{out}^0 = initial effluent concentration

L= length of the adsorbent bed
t= time
t_0= start-up time

Adsorption in packed beds



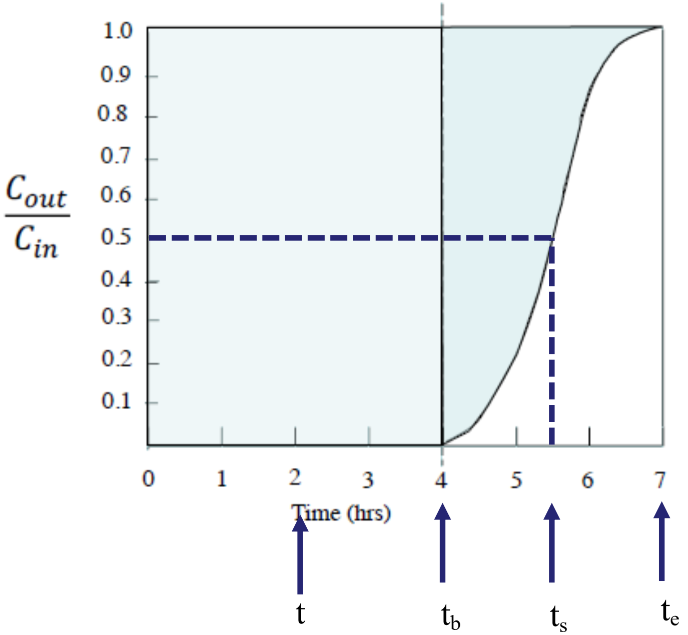
t= time
t_b= breakthrough time (when C_{out}=0.05 C_{in})
t_s= stoichiometric time; time for capacity to be used
t_e= exhaustion time; the adsorbent is fully used up

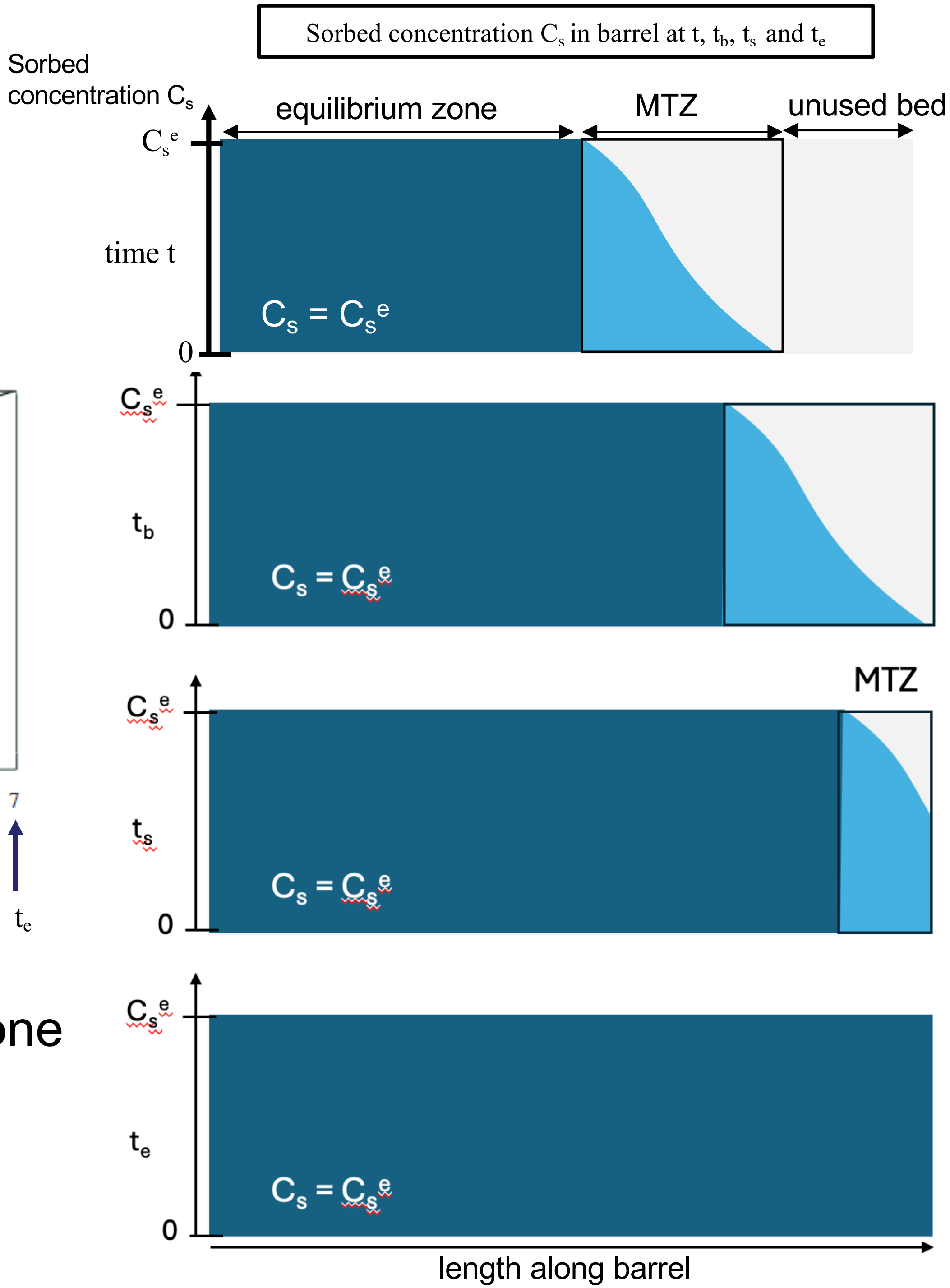
C_s^e: equilibrium with inlet

Adsorption in packed beds

Effluent concentration

Ideal S wave form:
symmetrical S-shape





Before reaching breakthrough, there is unused bed that no compound has yet reached

In the mass transfer zone, on average $C_s = 0.5C_s^e$ → half of the capacity is used in MTZ

In the mass transfer zone, on average $C_s = 0.75C_s^e$ → 3/4 of the capacity is used in MTZ

At exhaustion all the capacity of the bed is used → no MTZ

MTZ= mass transfer zone

Fixed bed activated carbon - equilibrium model

- Questions of interest:
  - How much of the compound of interest can be adsorbed?
  - How long until must change the activated carbon?

Consider a simple system:

$$C_{i,s} = KC_{i,aq}$$

- How much of the compound of interest can be adsorbed?
- How long until must change the activated carbon?
- What is the concentration in the solution?

Fixed bed activated carbon – example 1

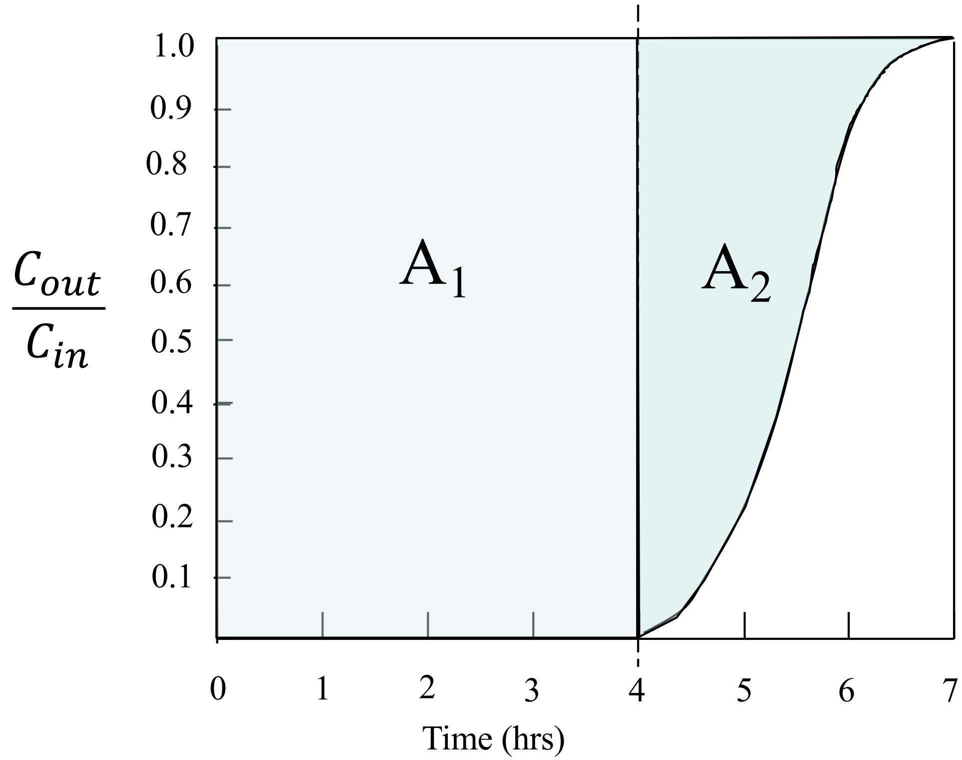
Consider a simple system: $$C_{i,s} = K C_{i,aq}$$

Batch adsorption

The goal is to remove 99% of compound A from 400 L of water containing 0.05 g/L of A. You do a lab experiment with 1 L and 3 g of AC and find that 96% of the contaminant is removed.

- How much of the compound of interest can be adsorbed?
- What is the concentration in the solution?
- For the full scale, how much adsorbent do you need?

Fixed bed activated carbon – example 2



1. Determine breakthrough time t_b, exhaustion time t_e, and stoichiometric time t_s
2. What would be fraction of unused capacity of the bed at time t_b with the ideal S-shape wave front?
3. What fraction of the bed is used at t_s?

Fixed bed activated carbon – mass balance

$Q_{in} * C_{in} * t_b = C_s^e * \rho_b * V_{bed,\ used}$

Where:

Q_{in}= flow rate into the bed (m^3 fluid/s)

C_{in}= concentration coming into the bed (kg A/m^3 fluid)

t_b = breakthrough time (s)

C_s^e = adsorbed concentration at equilibrium with inlet (kg A/kg adsorbent)

ρ_b= adsorbent's bulk density (kg adsorbent/m^3 occupied space)

$V_{bed,used}$= bed volume at equilibrium (m^3 of occupied space)

Can also consider volume of adsorbent required

$V_{ads,\ req}$= area* (LES +LUB)

Fixed bed activated carbon – mass balance- example 3

Trimethylethylene (TME) is being removed on a continuous basis in a GAC bed. A bench scale system indicates that the adsorbent follows a Langmuir isotherm:

$$C_s = \frac{0.05 * \ C_{aq}}{32.1 \ + C_{aq}} \qquad C_{aq} \ in \ \left(\frac{g \ TME}{m^3 \ water}\right) \quad C_s \ in \ \left(\frac{g \ TME}{g \ adsorbent}\right)$$

The inlet flow rate is Q_{in}= 1 L/min and ρ_b=300 kg/m^3

C_{in}=100 g/m^3

C_{out}=1 g/m^3

Mass of adsorbent= 15 kg

1. How much TME is adsorbed when the effluent concentration reaches of 1 g/m^3 at the breakthrough time?
2. How long will it take to reach this concentration in the effluent?

Application: Example 4

Groundwater with 5 mg/L of toluene

Reduce to <100 ppb (μg/L)

Large activated carbon units are to be used to remove toluene

Langmuir isotherm: $C_{i,s} = \frac{0.04 * C_{i,aq}}{1+0.002 C_{i,aq}}$

($C_{i,s}$ in kg toluene/kg activated carbon and with $C_{i,aq}$ in mg/L)

1 m high and 0.5 m diameter of carbon in drum

Bulk density= 485 kg/m^3

Flow rate= 140 L/min

(a) How much toluene can each unit remove before the activated carbon is fully spent (exhaustion)?

(b) How long until breakthrough?