Adsorption

Lecture 6

Learning outcomes

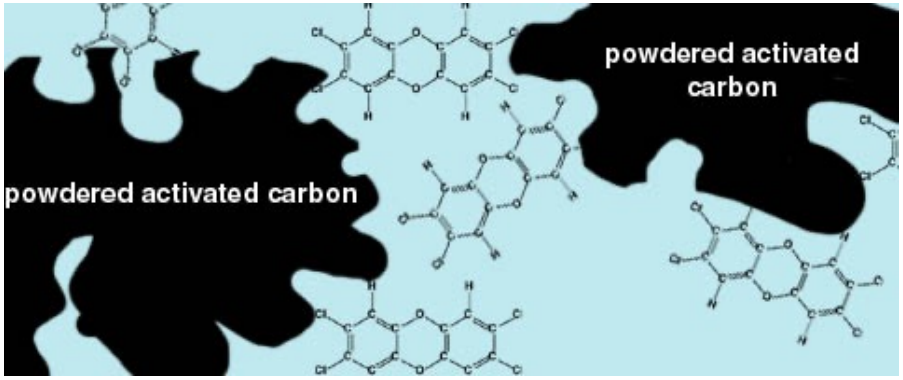
- Adsorption
- Activated carbon adsorption

Adsorption

Adsorption

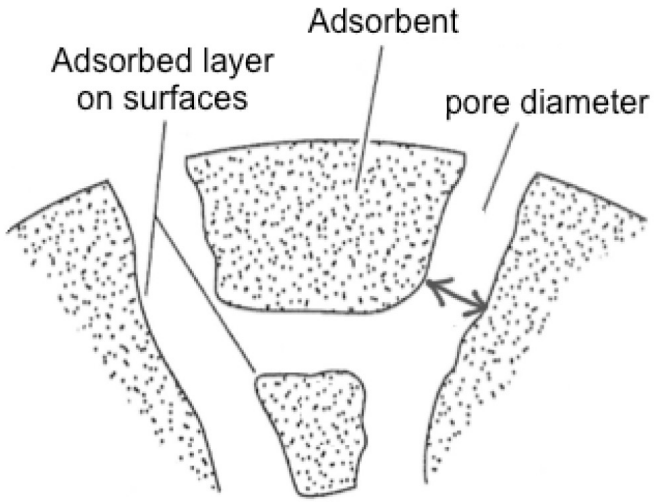
- **Ad**sorption is a process by which a component (the sorbate) moves from the aqueous or gaseous phase to the solid phase by association with a solid phase **surface**.

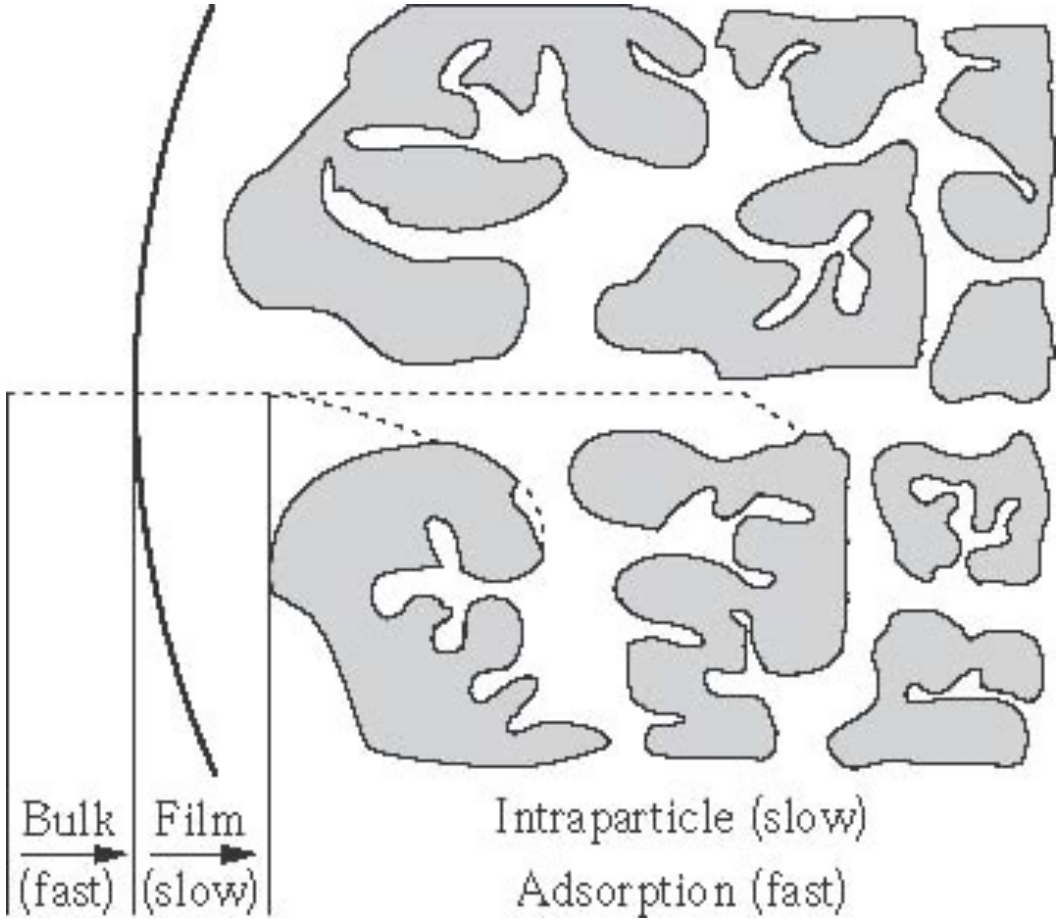
- In this lecture, we will cover:
  - Adsorption of metals to mineral surfaces (association of contaminants with soils/sediments)
  - Adsorption of contaminants to activated carbon (as a means of removal from water)



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

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
- No interactions between adsorbing molecules

$$q_e = q_m \frac{K_L C_e}{1+K_L C_e}$$ Original form (aqueous)

$$C_{i,s} = C_{i,s,max} \frac{K_L C_{i,aq}}{1+K C_{i,aq}}$$ Rewritten to fit our nomenclature

$$\frac{1}{C_{i,s}} = \frac{1}{C_{i,s,max} * K_L} * \frac{1}{C_{i.aq}} + \frac{1}{C_{i,max}}$$ Linear form

Where

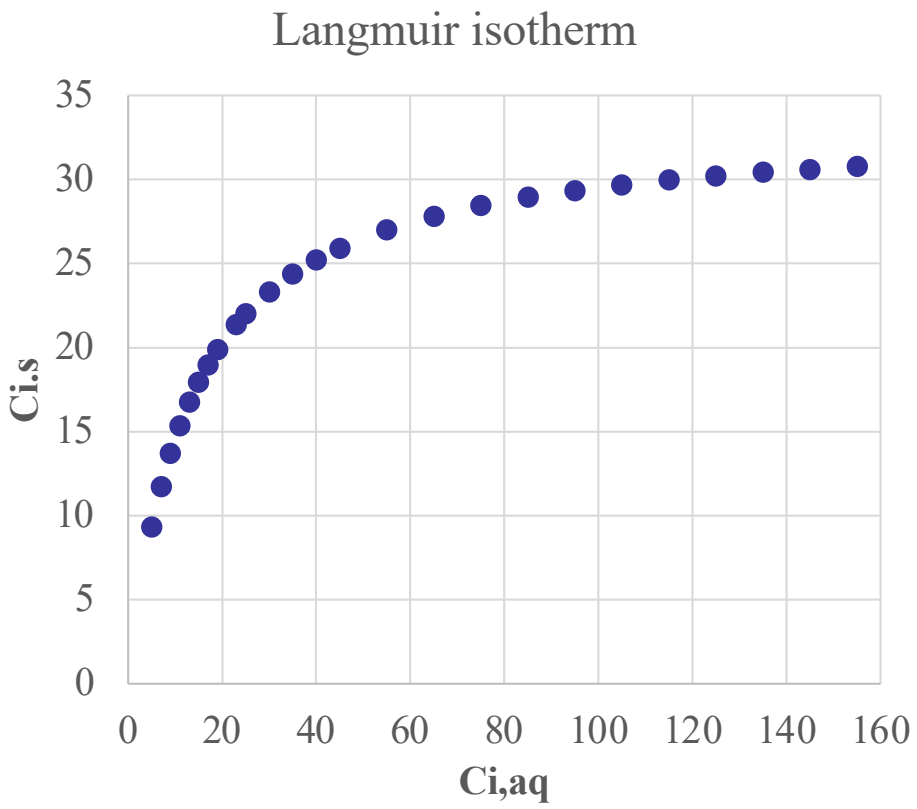
$C_{i,aq}$= aqueous solute concentration at **equilibrium** (g.m^{-3})

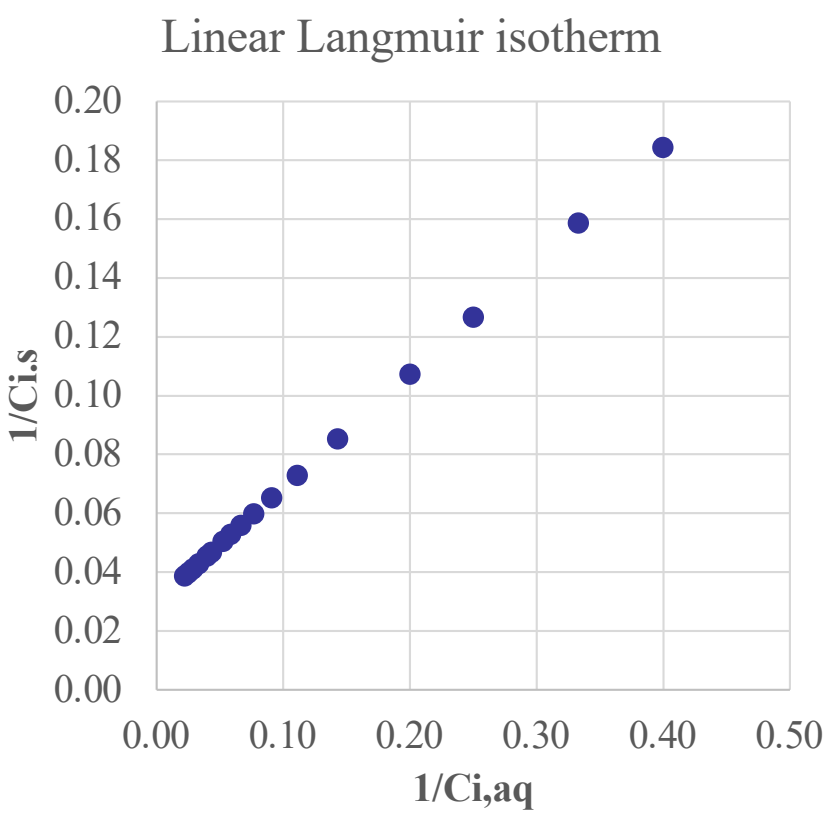
$C_{i,s}$ = adsorbed concentration **at equilibrium** (g solute/g adsorbent)

K_L= Langmuir constant

$C_{i,s\ max}$=adsorbed concentration corresponding to a complete monolayer (g solute/g adsorbent)

Langmuir isotherm





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

$$\frac{1}{C_{i,s}} = \frac{1}{C_{i,s,max}*K_L} * \frac{1}{C_{i.aq}} + \frac{1}{C_{i,max}}$$

Freundlich isotherm

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:

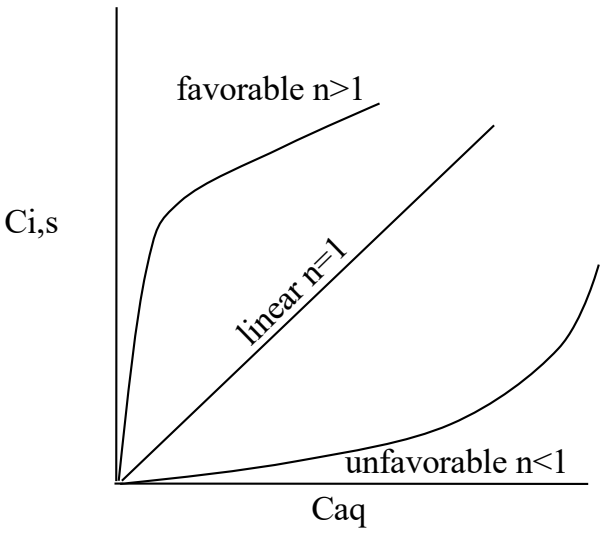
$C_{i,aq}$= aqueous solute concentration at **equilibrium** ($g.m^{-3}$)

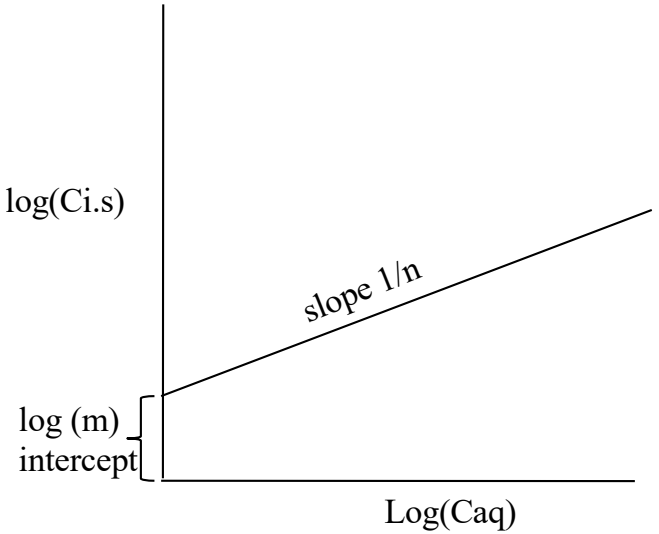
$C_{i,s}$ = adsorbed concentration **at equilibrium** (g solute/g adsorbent)

K= Freundlich coefficient {proportional to RT exp (ΔH/RT)}

n= empirical constant

Forms of the Freundlich equation

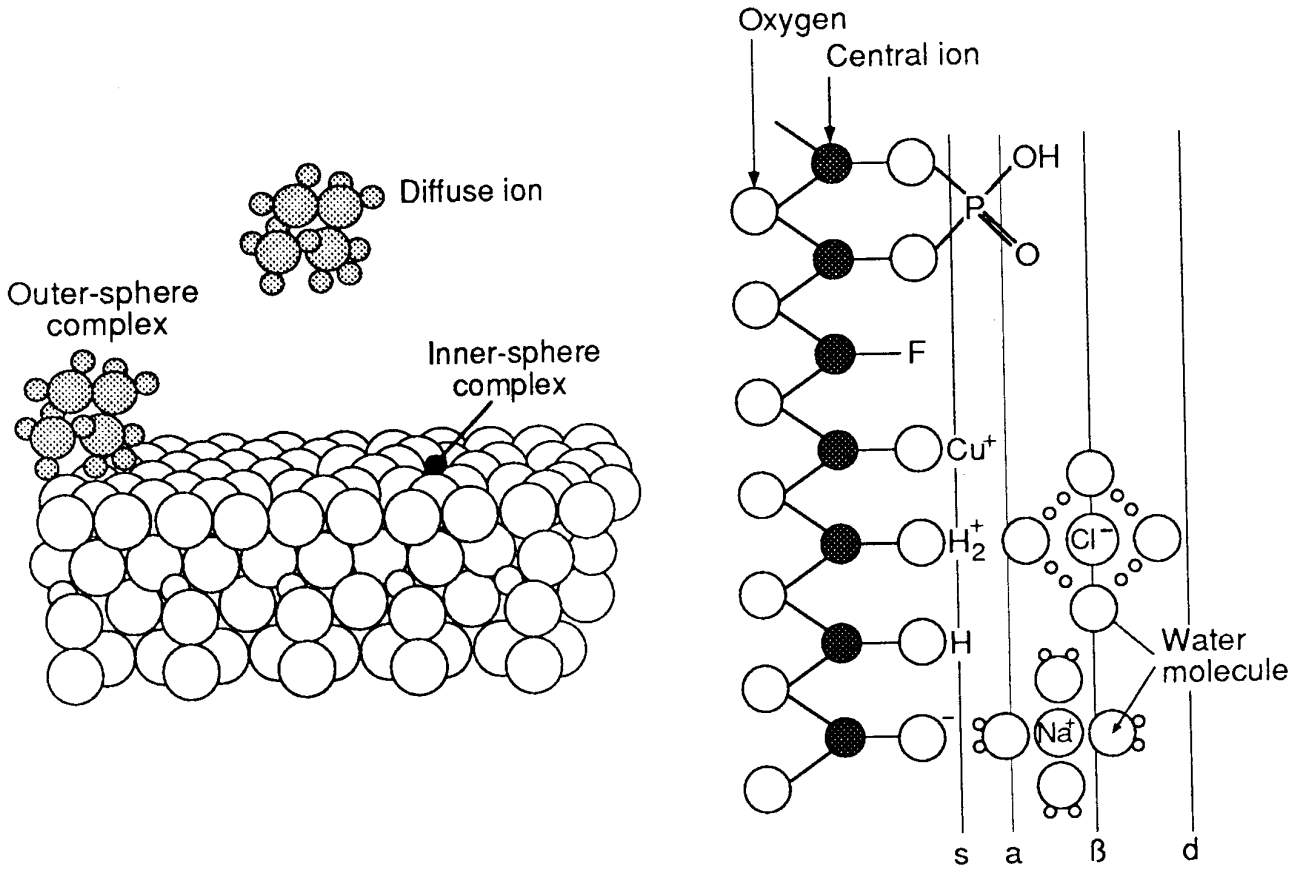




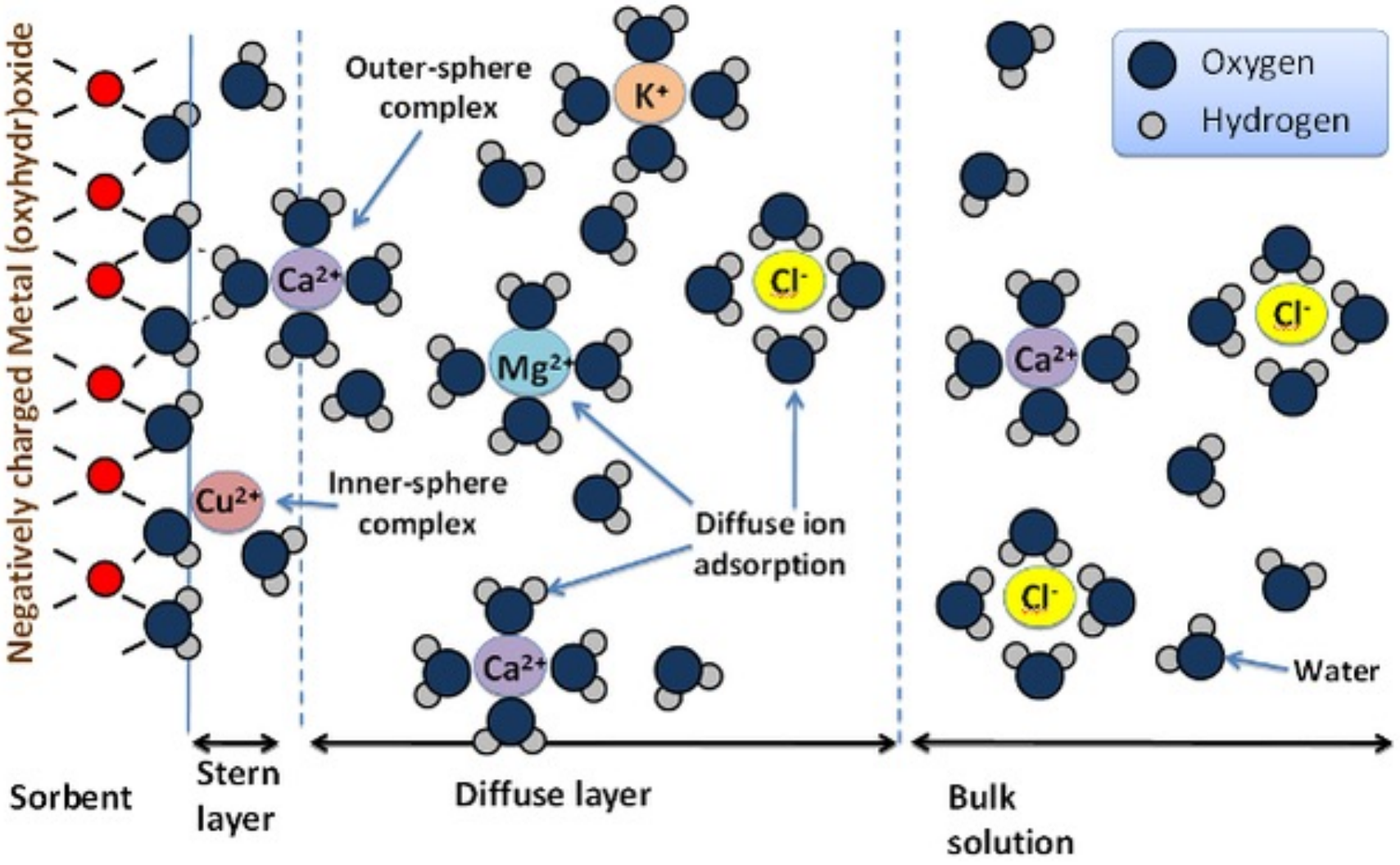
A favorable isotherm generally assures that the equilibrium adsorption capacity will be relatively high at low solution concentrations

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 sorbent retains its hydration layer

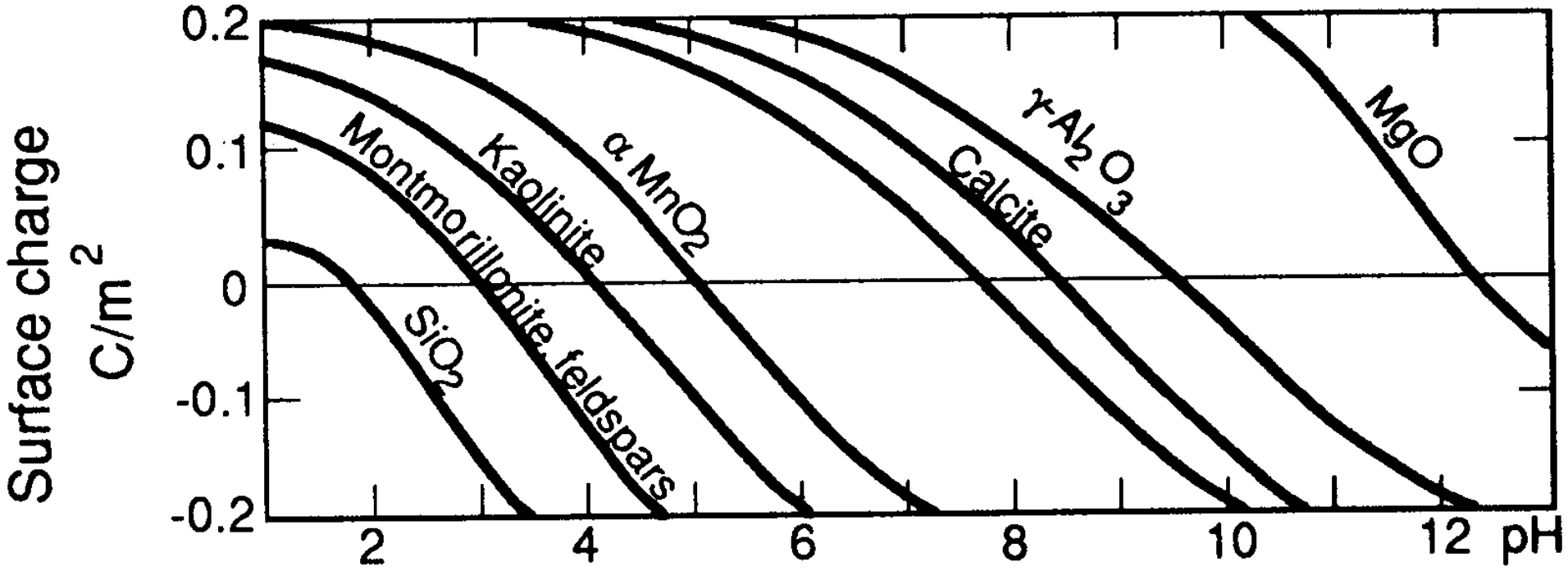


Adsorption of metals to mineral surfaces



Adsorption of metals to mineral surfaces

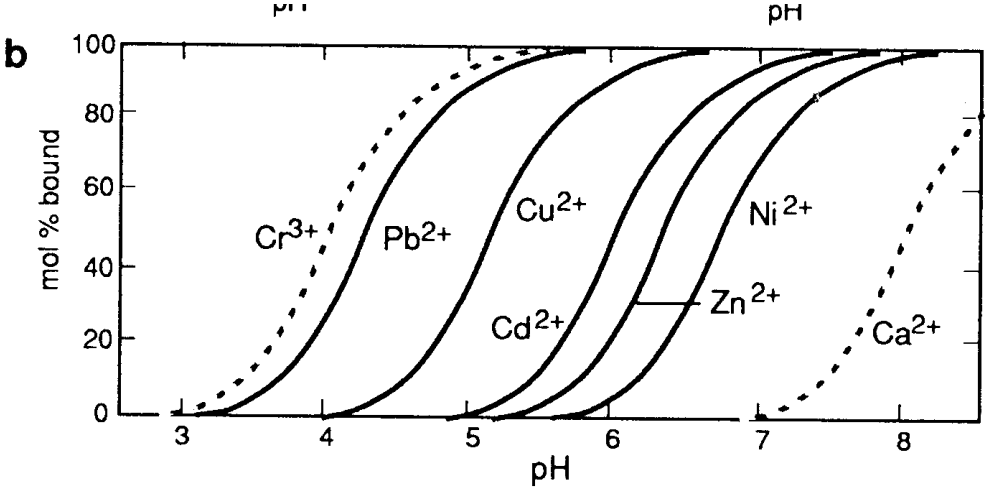
The surface charge of most minerals varies as a function of pH due to inherent characteristics of the minerals

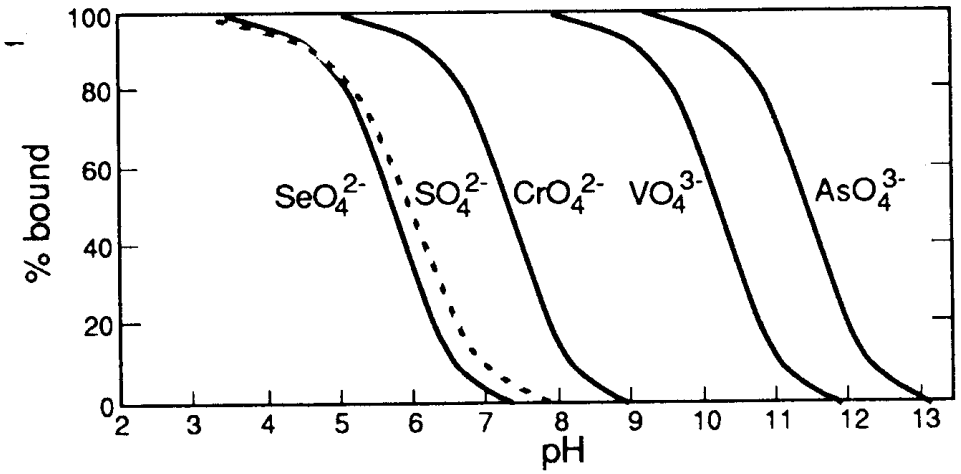


Adsorption of metals to mineral surfaces

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.

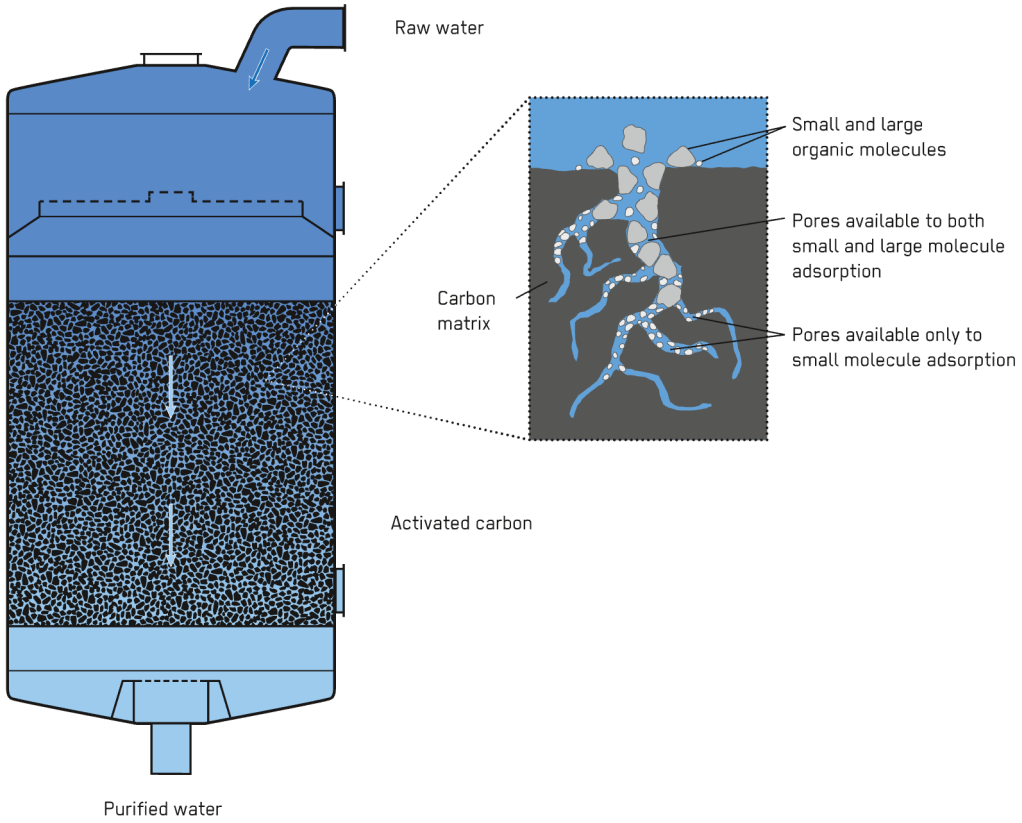




Adsorption to activated carbon

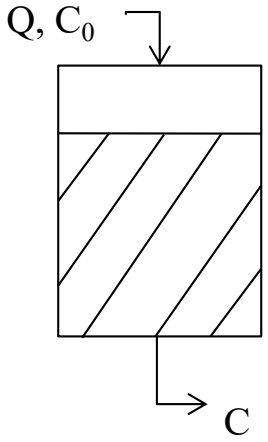
Carbon adsorption

- 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

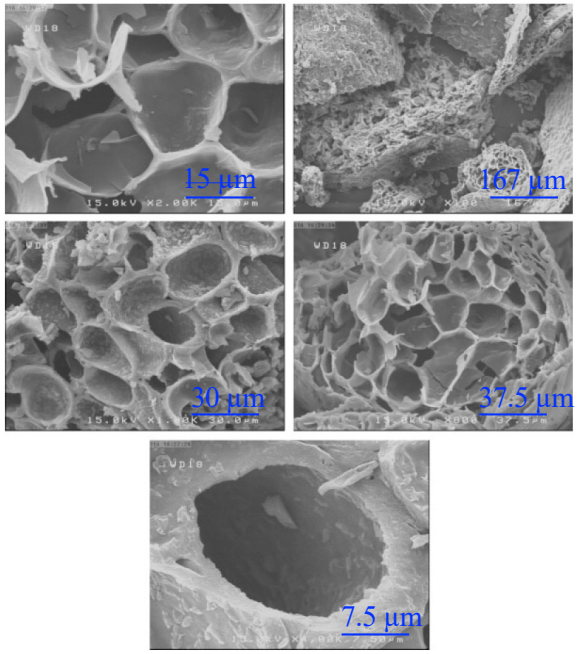
- Column reactors similar to plug flow reactors: Granular activated carbon (GAC)



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

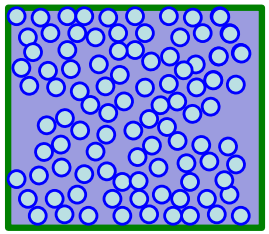
Grain size PAC $d_g = 0.01 - 0.1[mm]$
GAC $d_g = 0.5 - 3[mm]$
Pore volume $V_p = 0.5 - 1.2[cm^3/g]$
Specific surface area $A_s = 500 - 1200[m^2/g]$
Pore diameter: 10 Å to >50 Å



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

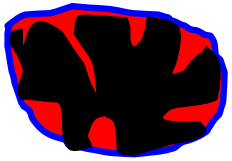
[DOI:10.1016/j.saa.2011.10.012]

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}

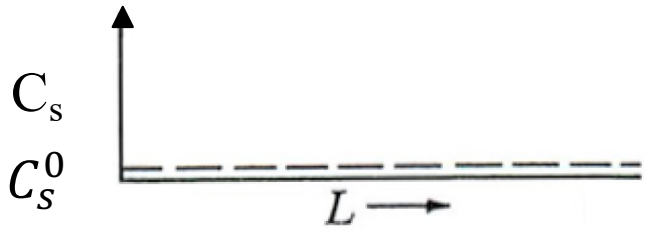
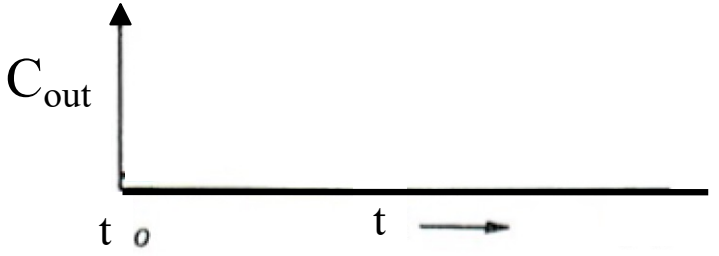
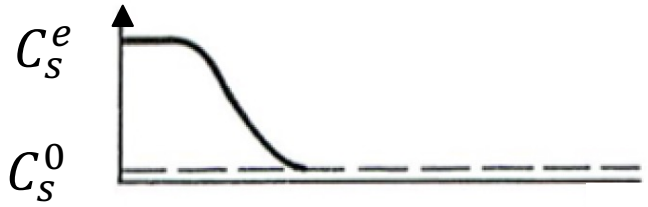
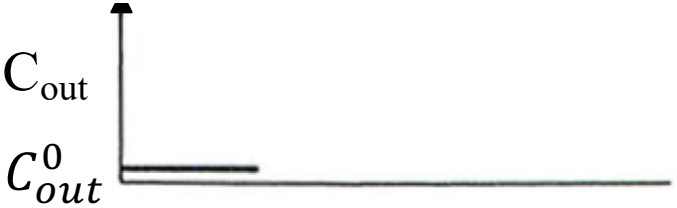
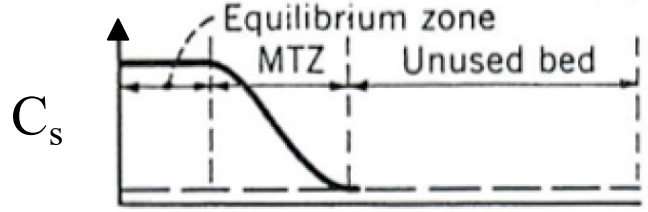
- Grain porosity $\varepsilon_i = \frac{vol\_internal\_voids}{vol\_particles} = \frac{V_{ivoid}}{V_g} = 0.5 - 0.8[-]$
- Bed porosity $\varepsilon_b = \frac{bed\_void\_volume}{total\_volume} = \frac{V_V}{V_T} = 0.5 - 0.8[-]$
- Solids density $\rho_s = \frac{mass\_solid}{vol\_solid} = \frac{M_s}{V_s} =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

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

Time	Adsorbent bed (soild phase)	Effluent (aqueous)
$t < t_0$		
$t = t$		
$t = t + \Delta t$		

C_s= concentration on adsorbent

C_s^0= initial concentration on adsorbent

C_s^e= concentration on adsorbent at equil.

C_{out}= effluent concentration (aqueous)

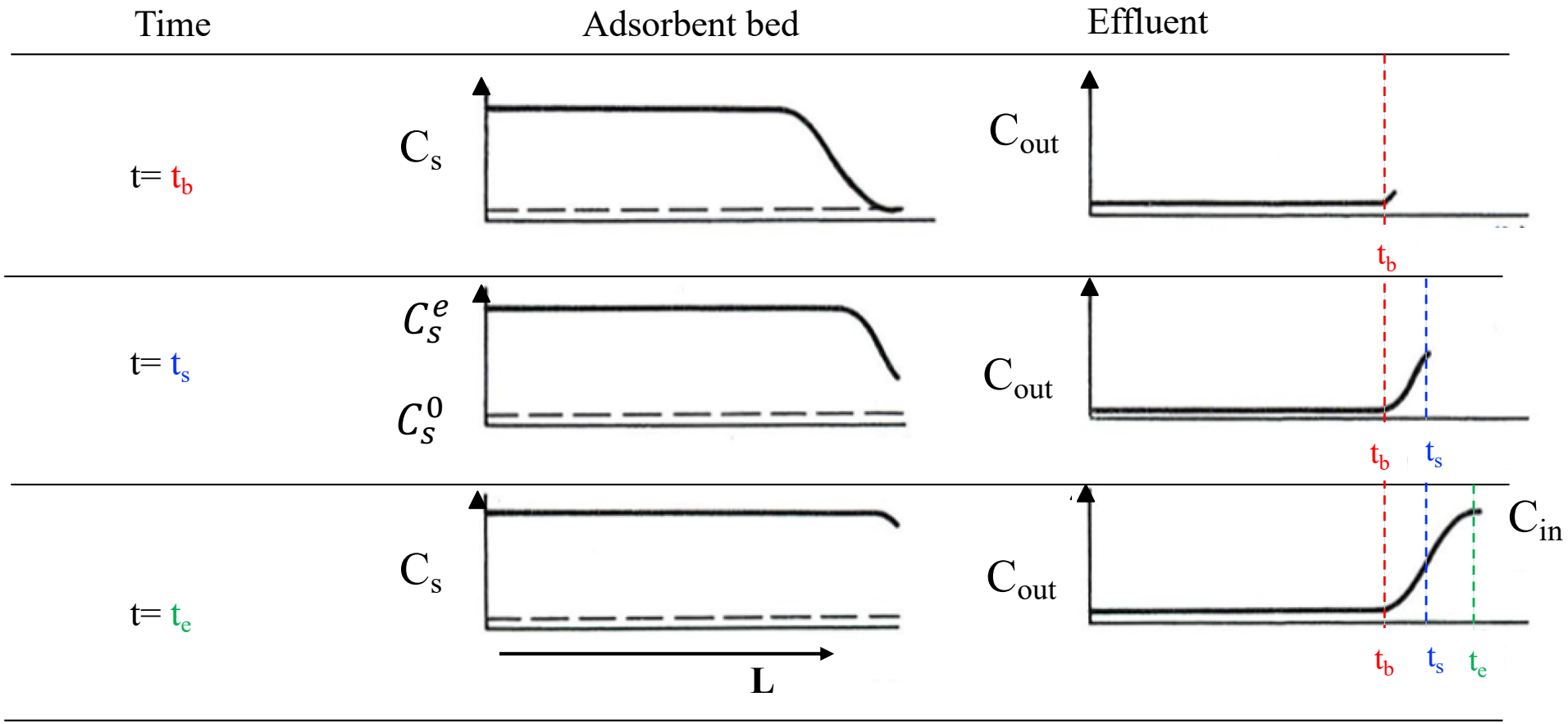
C_{out}^0 = initial effluent concentration (aqueous)

L= length of the adsorbent bed

t= time

t_0= start time

Adsorption in packed beds



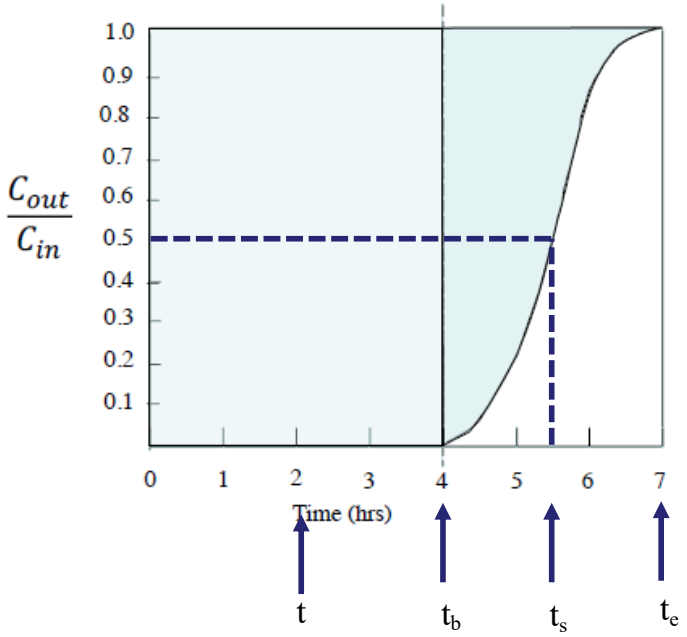
t= time
t_b= breakthrough time (when C_{out}=0.05 C_{in})
t_s= stoichiometric time; time for capacity to be used
t_e= exhaustion time; the adsorbent is fully used up

C_s^e: equilibrium with influent concentration

Adsorption in packed beds

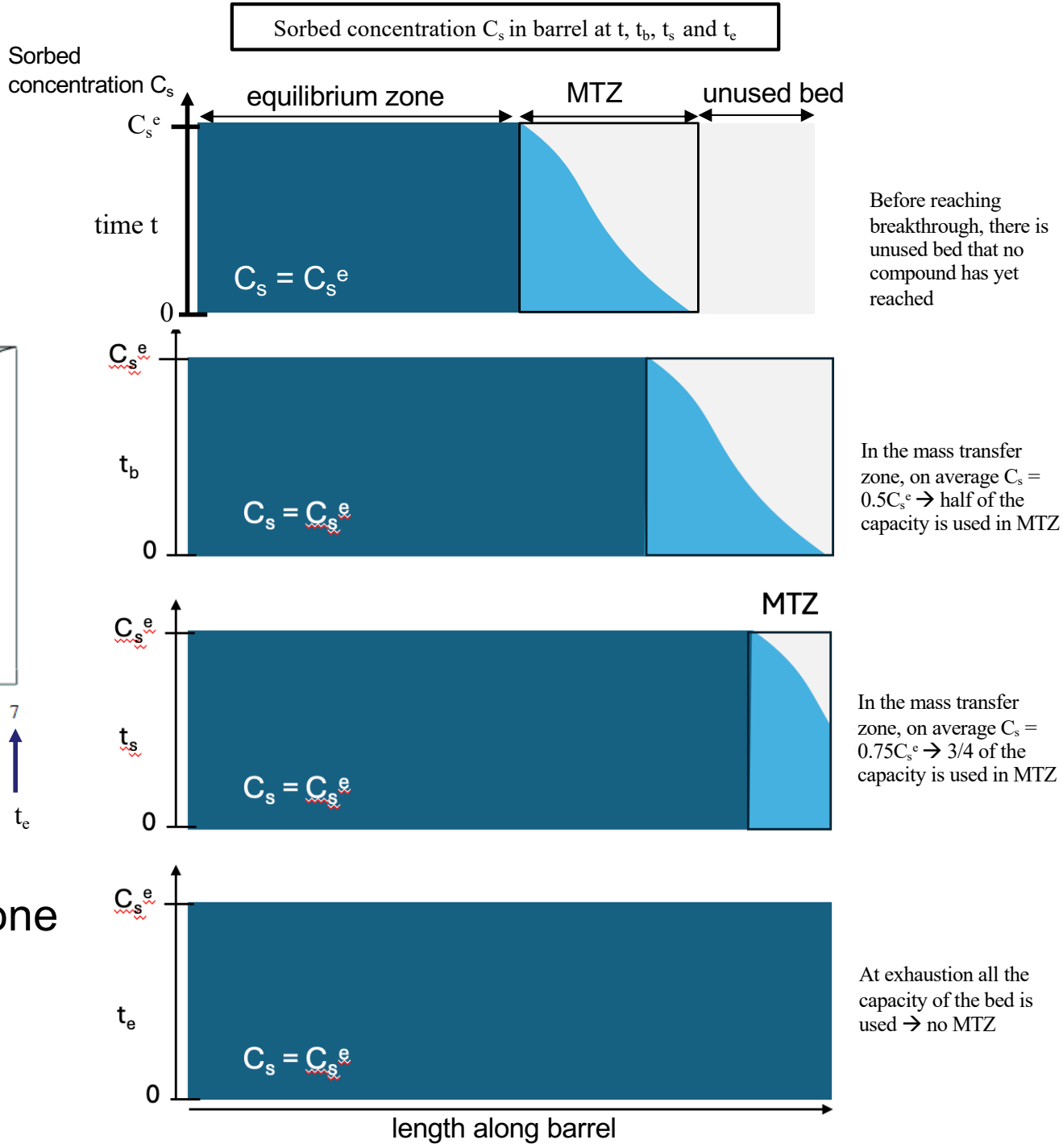
Effluent concentration

Ideal S wave form:
symmetrical S-shape



MTZ= mass transfer zone

Sorbed concentration C_s in barrel at t, t_b, t_s and t_e



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

Empty bed contact time

- EBCT= V_b/Q
- Q= flow rate into the GAC bed (m^3/min)
- V_b= bed volume (m^3)
- Empty bed contact time is the time it takes the liquid to pass through a GAC bed (min)
- It is important to differentiate EBCT and breakthrough time

- EBCT= L/v_f
- Where v_f= linear fluid velocity (e.g., m/h)
- L= length of GAC bed (m)

- Number of bed volumes over time θ_b
- $\theta_b = t_b/EBCT$

Rate of reactivation

- $rate_{AC}$ = how much AC is used per volume of fluid treated for example: grams of AC used per m^3 of water treated)

$$rate_{AC} = \frac{M_{AC}}{Q * t_b}$$

- M_{AC} = total mass of AC in bed= V_b * ρ_b

Mass balance

$$M_{AC} * C_s^e = Q * C_{in} * t_b$$

Mass of contaminant sorbed on AC

Mass of contaminant coming in in the water

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 effluent solution?

Example 1: Batch activated carbon

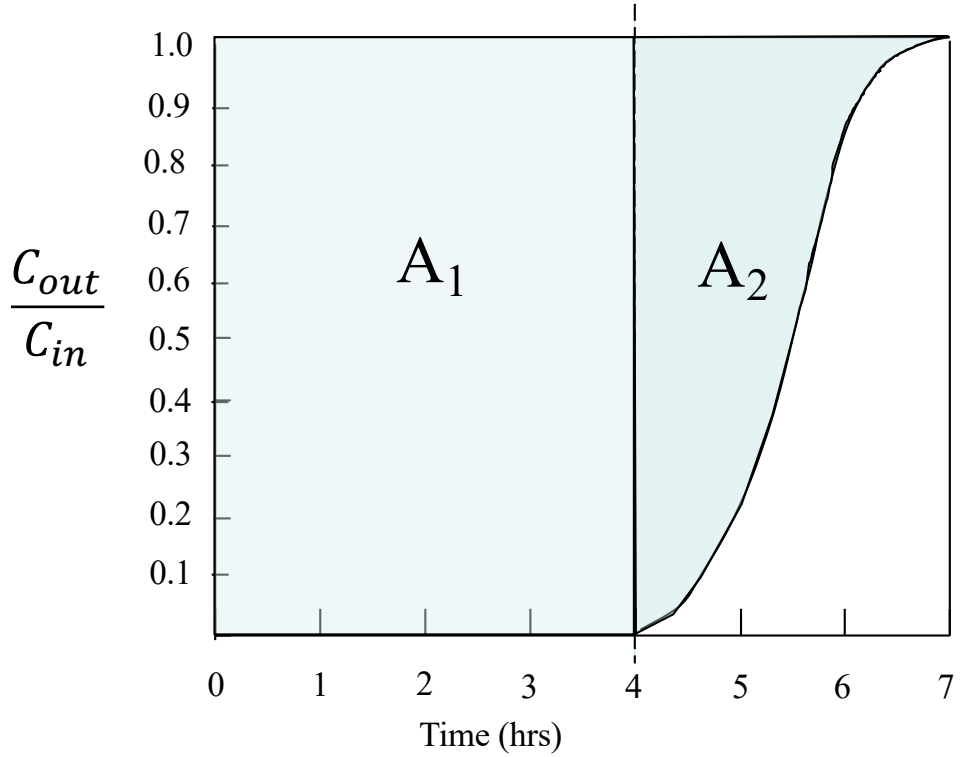
Consider a simple system: $C_{i,s} = KC_{i,aq}$

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?

Example 2: Fixed bed activated carbon



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

$$Q * (C_{in} - C_{out}) * t_b = C_s^e * \rho_b * V_{b,used}$$

Where:

Q= 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)

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

C_{out}= effluent conc. (sometimes neglected)

Example 3: Fixed bed activated carbon – mass balance

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:

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

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?

Example 4: Application

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?