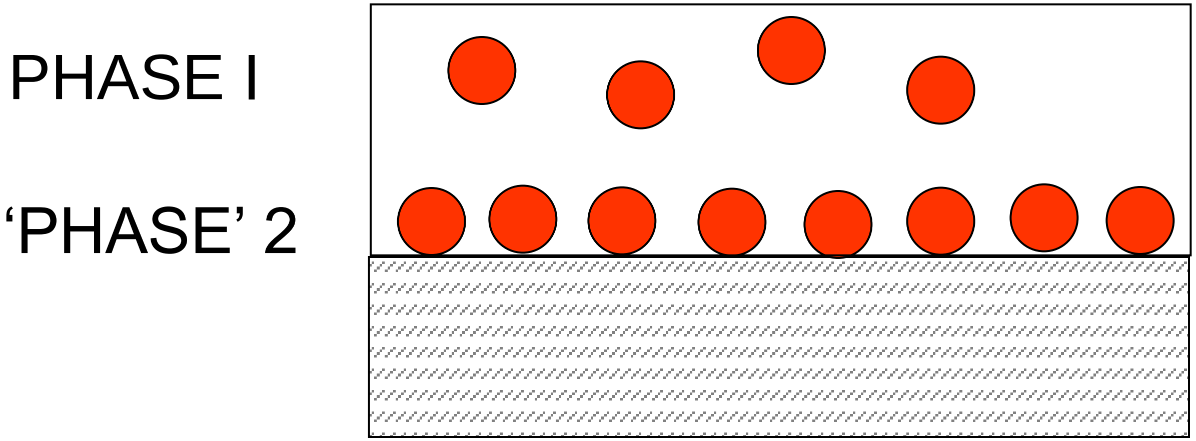
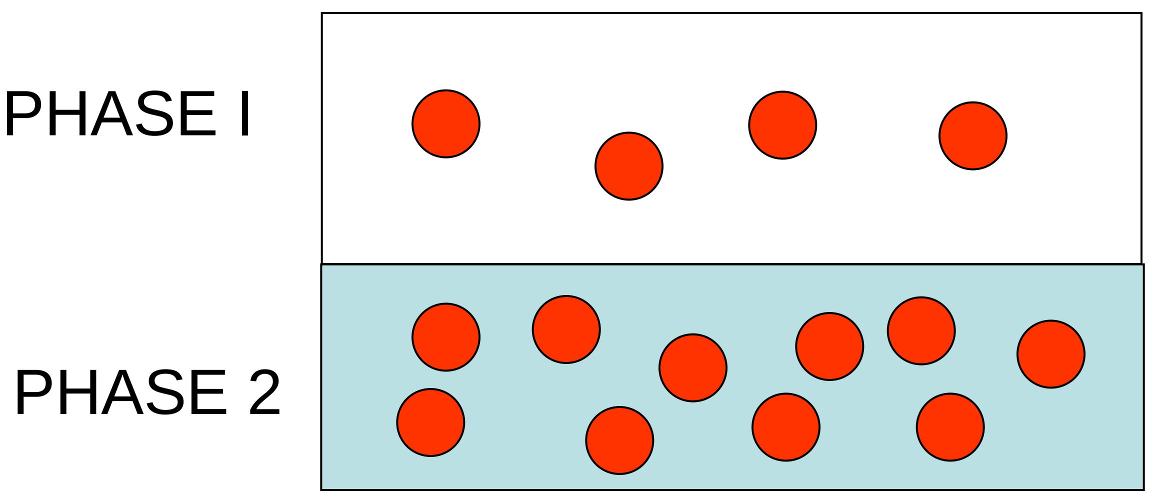
Adsorption Equilibrium

- Adsorption vs. Absorption
  - Adsorption is accumulation of molecules on a surface (a surface layer of molecules) in contact with an air or water phase
  - Absorption is dissolution of molecules within a phase, e.g., within an organic phase in contact with an air or water phase

Adsorption



Absorption (“partitioning”)



$$P_{gas} = K_H c_{aq}$$

Henry’s Law

Causes of Adsorption

- Dislike of Water Phase – 'Hydrophobicity'
- Attraction to the Sorbent Surface
  - van der Waals forces: physical attraction
  - electrostatic forces (surface charge interaction)
  - chemical forces (e.g., π- and hydrogen bonding)

Adsorbents in Natural & Engineered Systems

- Natural Systems
  - Sediments
  - Soils
- Engineered Systems
  - Activated carbon
  - Metal oxides (iron and aluminum as coagulants)
  - Ion exchange resins
  - Biosolids

Steps in Preparation of Activated Carbon

- Pyrolysis – heat in absence of oxygen to form graphitic char
- Activation – expose to air or steam; partial oxidation forms oxygen-containing surface groups and lots of tiny pores

Factors Affecting Activated Carbon Properties

- Starting materials (e.g., coal vs. wood based) and activation
- Pores and pore size distributions
- Internal surface area
- Surface chemistry (esp. polarity)
- Apparent density
- Particle Size: Granular vs. Powdered (GAC vs. PAC)

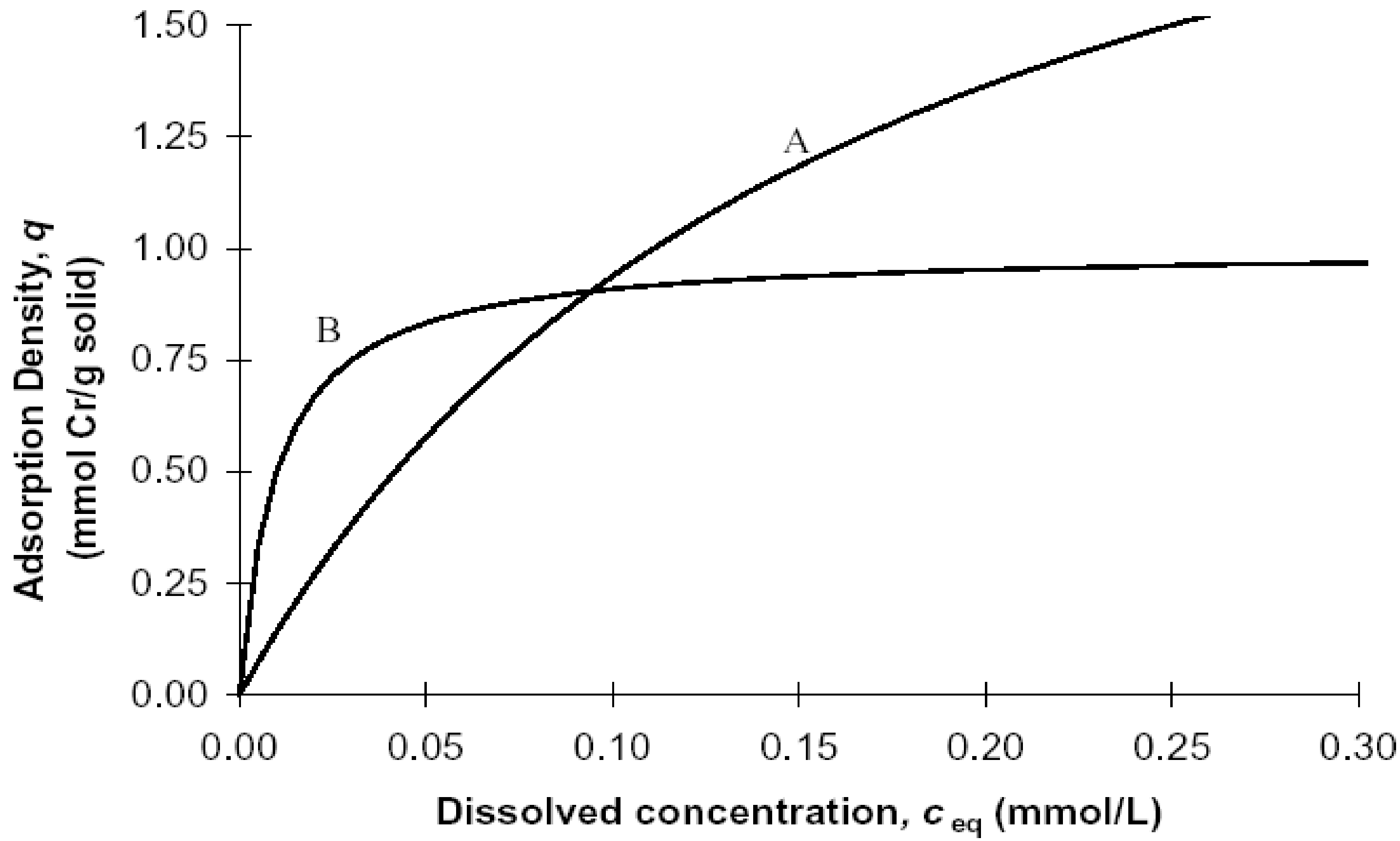
Characteristics of Some Granular Activated Carbons

Characteristics of Activated Carbons (Zimmer, 1988)			
Activated Carbon	**F 300**	**H 71**	**C25**
Raw Material	**Bituminous Coal**	**Lignite**	**Coconut Shell**
Bed Density, ρ_F (kg/m^3)	**500**	**380**	**500**
Particle Density, ρ_P (kg/m^3)	**868**	**685**	**778**
Particle Radius (mm)	**0.81**	**0.90**	**0.79**
Surface Area BET (m^2/g)	**875**	**670**	**930**
Pore Volume (cm^3/g)			
Micro- (radius < 1nm)	**0.33**	**0.21**	**0.35**
Meso- (1nm < r < 25nm)	**----**	**0.38**	**0.14**
Macro- (radius > 25nm)	**----**	**0.58**	**0.16**
Total	**----**	**1.17**	**0.65**

Example 7-1. Adsorption of CrO_4^{2-} onto two different minerals is studied, yielding the isotherms shown graphically below. You wish to reduce the concentration of CrO_4^{2-} in a wastewater from 0.2 to 0.02 mmol/L (roughly 10 to 1 mg Cr/L) by sorption in a batch treatmen process, using the minimum dose (g/L) of solid.

(a) Which adsorbent would you use, and why?

(b) What adsorbent dose is required?



Assuming mineral surface started with q = 0:

$$c_{\text{solid}} = \frac{c_{\text{init}} - c_{\text{fin}}}{q_{\text{fin}}}$$

$$= \frac{(0.20 - 0.02)\ \text{mmol CrO}_4{}^{2-}/\text{L}}{0.65\ \text{mmol CrO}_4{}^{2-}/\text{g solid}} = 0.277\ \text{g solid/L}$$

If mineral surface started with q >0:

$$c_{\text{init}}V_{\text{L}} + q_{\text{init}}c_{\text{solid}}V_{\text{L}} = c_{\text{fin}}V_{\text{L}} + q_{\text{fin}}c_{\text{solid}}V_{\text{L}}$$

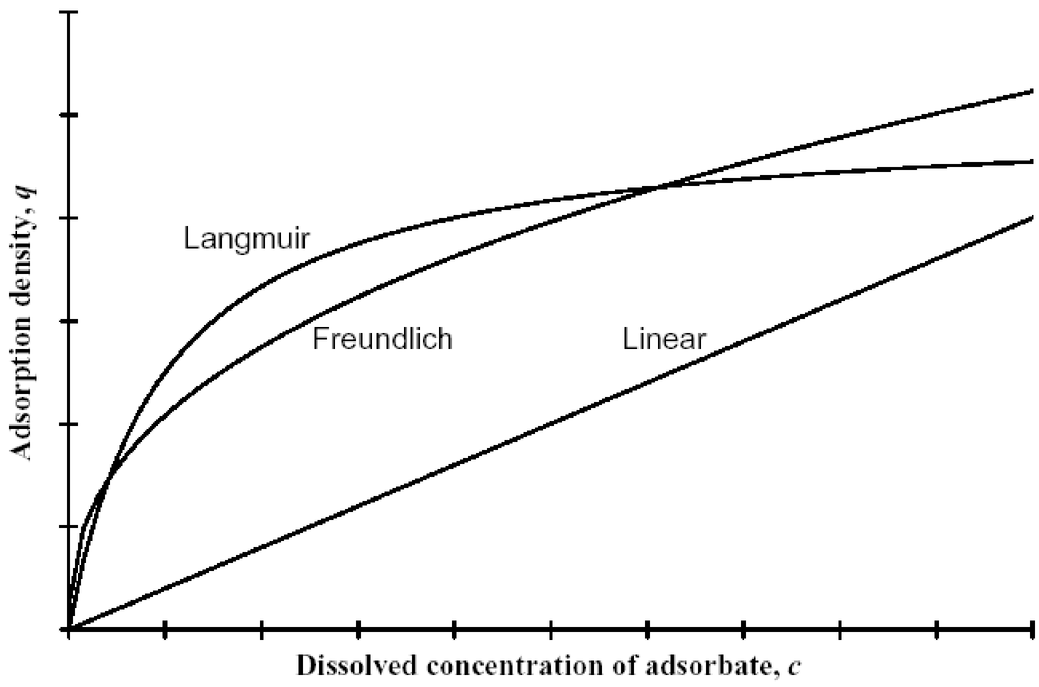
$$c_{\text{solid}} = \frac{c_{\text{init}} - c_{\text{fin}}}{q_{\text{fin}} - q_{\text{init}}}$$

Commonly Reported Adsorption Isotherms

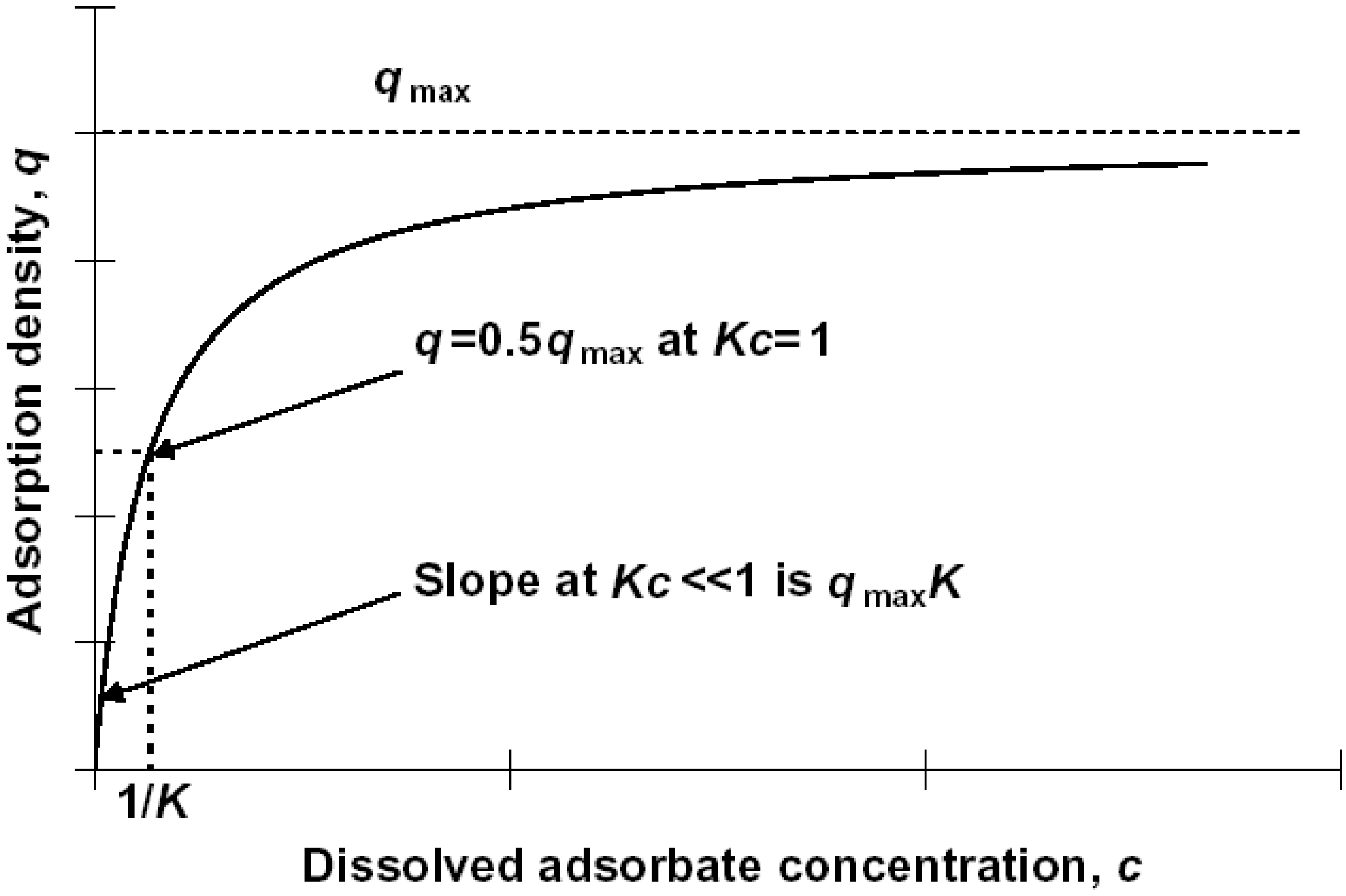
Linear: $q = k_{\text{lin}} c$

Langmuir: $q = q_{\max} \dfrac{K_L c}{1 + K_L c}$

Freundlich: $q = k_f c^n$

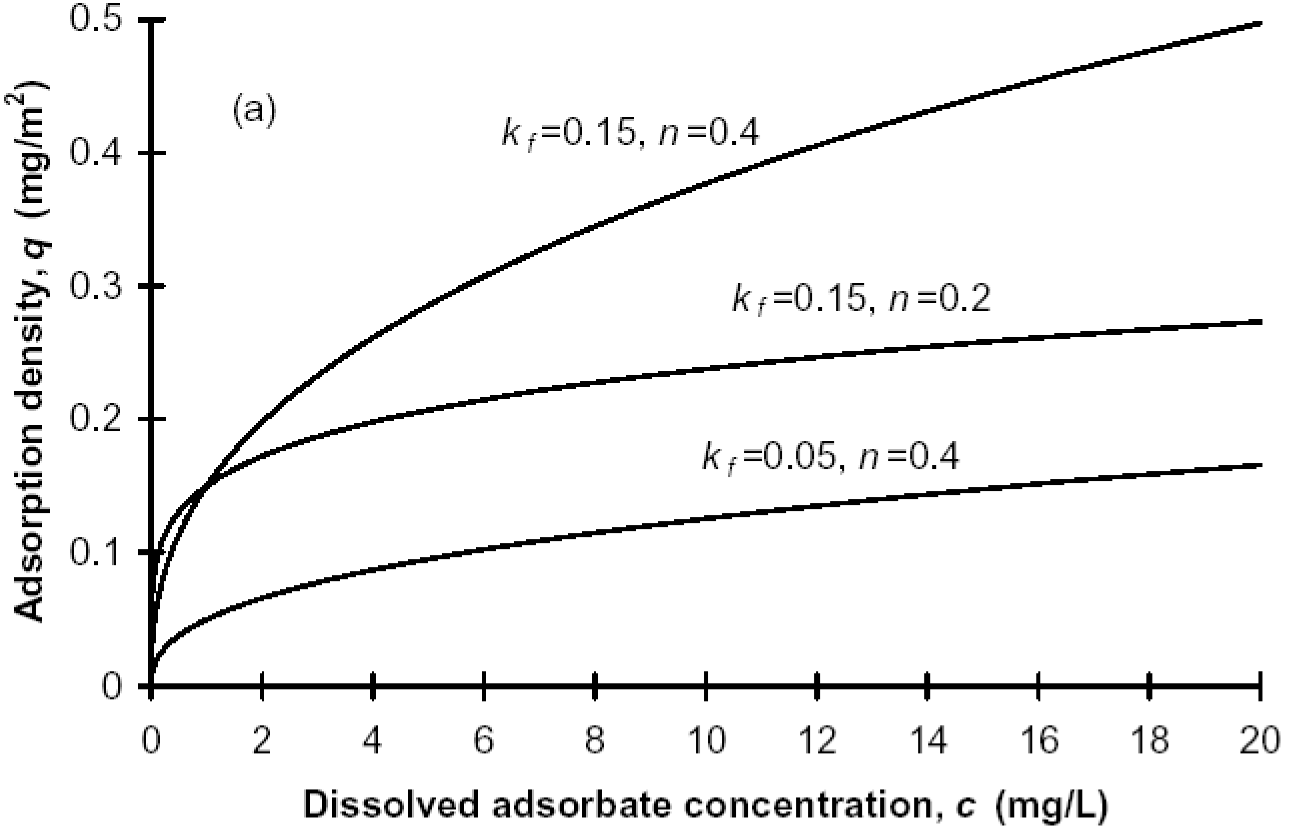


Shape of Langmuir Isotherm



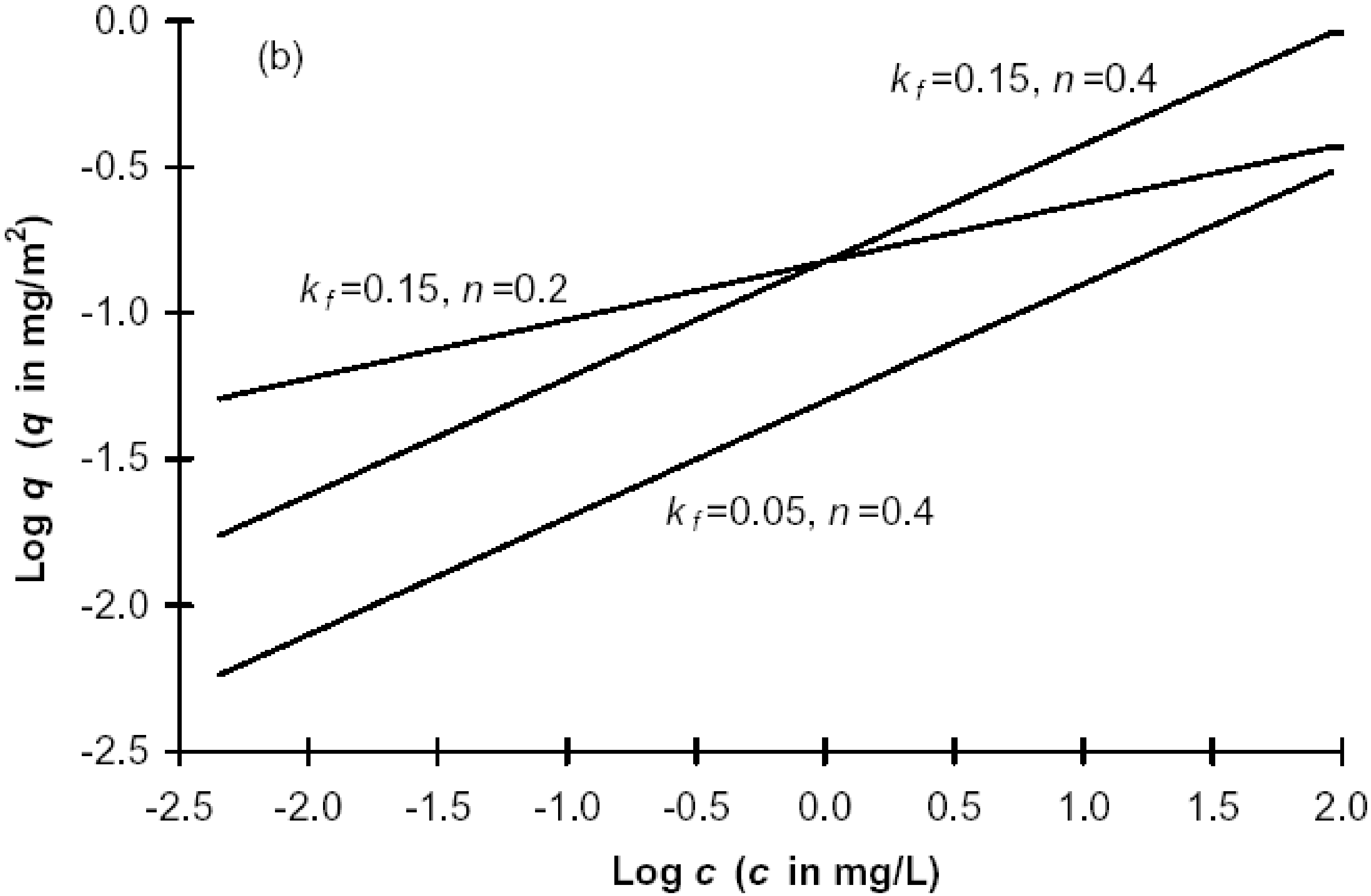
Shape of Freundlich Isotherm

$$q = k_f c^n$$



Shape of Freundlich Isotherm (log scale)

$$\log q = \log k_f + n \log c$$



Example. Adsorption of benzene onto activated carbon has been reported to obey the following Freundlich isotherm equation, where *c* is in mg/L and *q* is in mg/g:

$$q_{benz} = 50.1\, c_{benz}^{0.533}$$

A solution at 25°C containing 0.50 mg/L benzene is to be treated in a batch process to reduce the concentration to less than 0.01 mg/L. The adsorbent is activated carbon with a specific surface area of 650 m^2/g. Compute the required activated carbon dose.

Solution. The adsorption density of benzene in equilibrium with c_{eq} of 0.010 mg/L can be determined from the isotherm expression:

$$q_{benz} = 50.1\, c_{benz}^{0.533} = 4.30 \text{ mg/g}$$

A mass balance on the contaminant can then be written and solved for the activated carbon dose:

$$c_{tot,benz} = c_{benz} + q_{benz} c_{AC}$$

$$0.50 = 0.010 + \; 4.30 \text{ mg/g} \;\; c_{AC}$$

$$c_{AC} = 0.114 \text{ g/L} = 114 \text{ mg/L}$$

Example If the same adsorbent dose is used to treat a solution containing 0.500 mg/L toluene, what will the equilibrium concentration and adsorption density be? The adsorption isotherm for toluene is:

$$q_{tol} = 76.6\ c_{tol}^{0.365}$$

Solution. The mass balance on toluene is:

$$c_{tot,tol} = c_{tol} + q_{tol} c_{AC}$$

$$0.50 = c_{tol} + \ 76.6\ c_{tol}{}^{0.365} \quad 0.114\ \text{g/L}$$

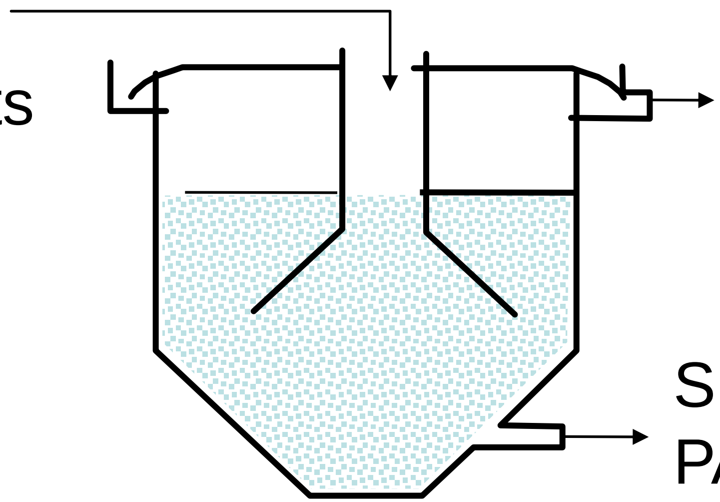
$$c_{tol} = 3.93\text{x}10^{-4}\ \text{mg/L}$$

General Process Design Features

- Contactors provide large surface area
- Types of contactors
  - Continuous flow, slurry reactors
  - Batch slurry reactors (infrequently)
  - Continuous flow, packed bed reactors
- Product water concentration may be
  - Steady state or
  - Unsteady state

Powdered Activated Carbon (PAC)

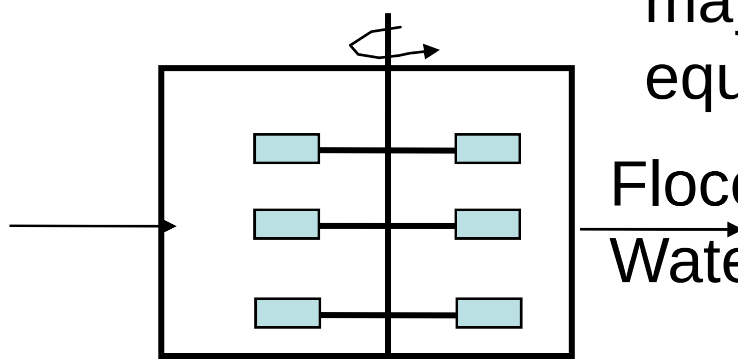
PAC + Coagulants



Settled Water

Sludge Withdrawal PAC particles may or may not be equilibrated

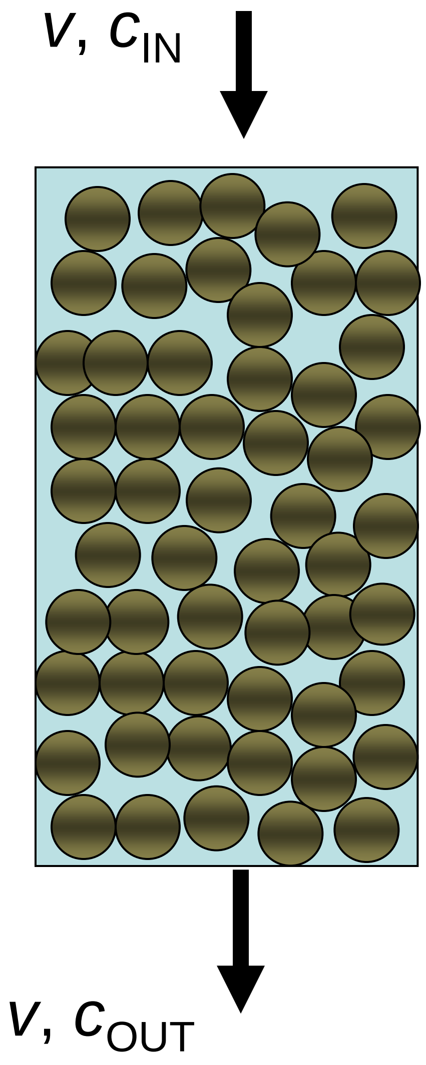
PAC + Coagulants



Flocculated Water

Process Operates at Steady-State, c_{out} = constant in time

Packed Bed Adsorption



Natural Packed Bed – subsurface with groundwater flow

Engineered Packed Bed- granular activated carbon

EBCT = empty-bed contact time (V_{bed}/Q)

Adsorptive capacity is finite (fixed amount of adsorbent in bed)

Process operates at unsteady state, c_{OUT} must increase over time