

ENVE 420

Industrial Pollution Control

ADSORPTION

Applications for Industrial Wastes

Dr. Aslihan Kerç

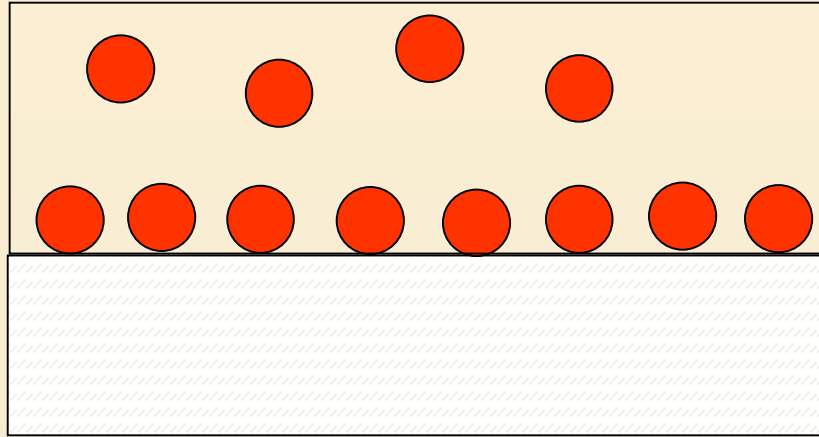
Adsorption Equilibrium

- Adsorption vs. Absorption
 - Adsorption is accumulation / adhesion of molecules at the surface of a solid material (usually activated carbon) 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

PHASE I

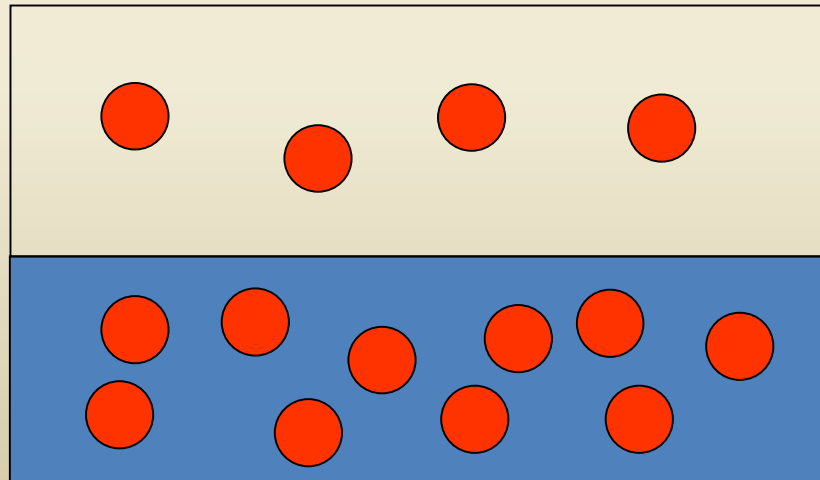
'PHASE' 2



Absorption ("partitioning")

PHASE I

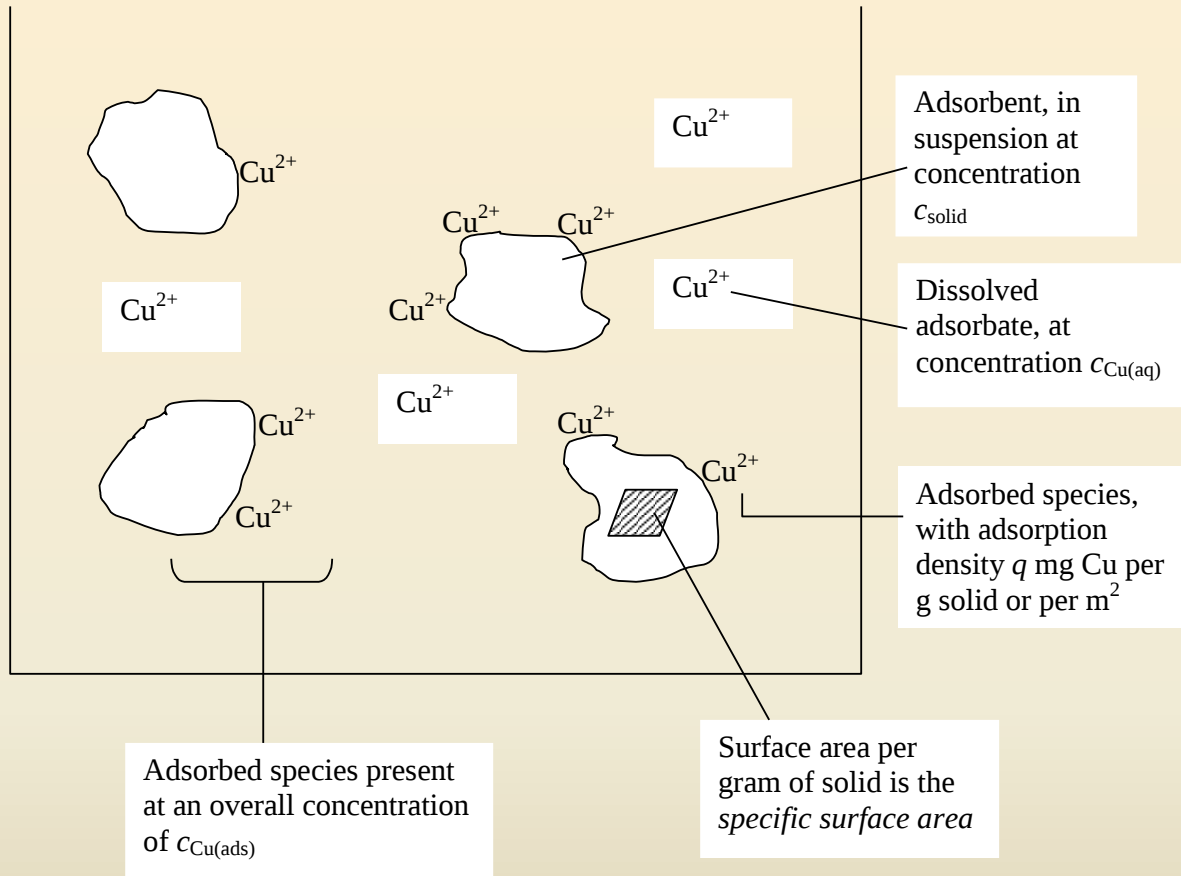
PHASE 2



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

Henry's Law

The Jargon of Adsorption



$$C_{i,ads} \left(\frac{\text{mg adsorbed}}{\text{per L of solution}} \right) = q_i \left(\frac{\text{mg adsorbed}}{\text{per g adsorbent}} \right) C_{solid} \left(\frac{\text{g solid per}}{\text{L of solution}} \right)$$

Causes of Adsorption

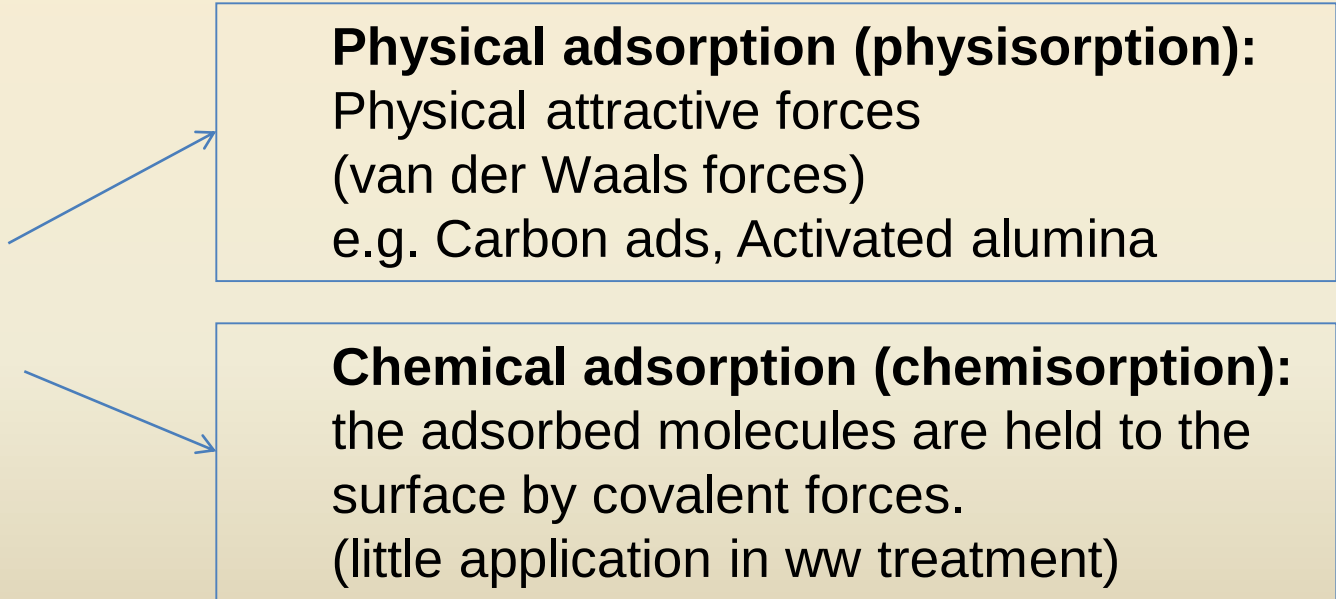
- Dislike of Water Phase – ‘Hydrophobicity’
- Attraction to the Sorbent Surface
 - van der Waals forces: physical attraction
 - electrostatic forces (surface charge interaction)
 - chemical forces (e.g., π - and hydrogen bonding)

Adsorption Phenomenon

The surface of a solid shows a strong affinity for molecules that come into contact with it.

Certain solid materials concentrate specific substances from a solution onto their surfaces.

Adsorption Phenomenon



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graph LR; A[Adsorption Phenomenon] --> B[Physical adsorption (physisorption)]; A --> C[Chemical adsorption (chemisorption)];
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Physical adsorption (physisorption):

Physical attractive forces
(van der Waals forces)

e.g. Carbon ads, Activated alumina

Chemical adsorption (chemisorption):

the adsorbed molecules are held to the
surface by covalent forces.

(little application in ww treatment)

Adsorbents in Natural & Engineered Systems

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

Engineered Systems - Removal Objectives

- Activated carbon (chemical functional groups)
 - Adsorption of organics (esp. hydrophobic)
 - Chemical reduction of oxidants
- Metal oxides (surface charge depends on pH)
 - Adsorption of natural organic matter (NOM)
 - Adsorption of inorganics (both cations & anions)
- Ion exchange resins
 - Cations and anions
 - Hardness removal (Ca^{2+} , Mg^{2+})
 - Arsenic (various negatively charged species), NO_3^- , Ba^{2+} removal

Activated Carbon Systems

Carbon systems generally consist of vessels in which granular carbon is placed, forming a filter bed through which ww passes.



Activated Carbon Systems

Area requirement: less

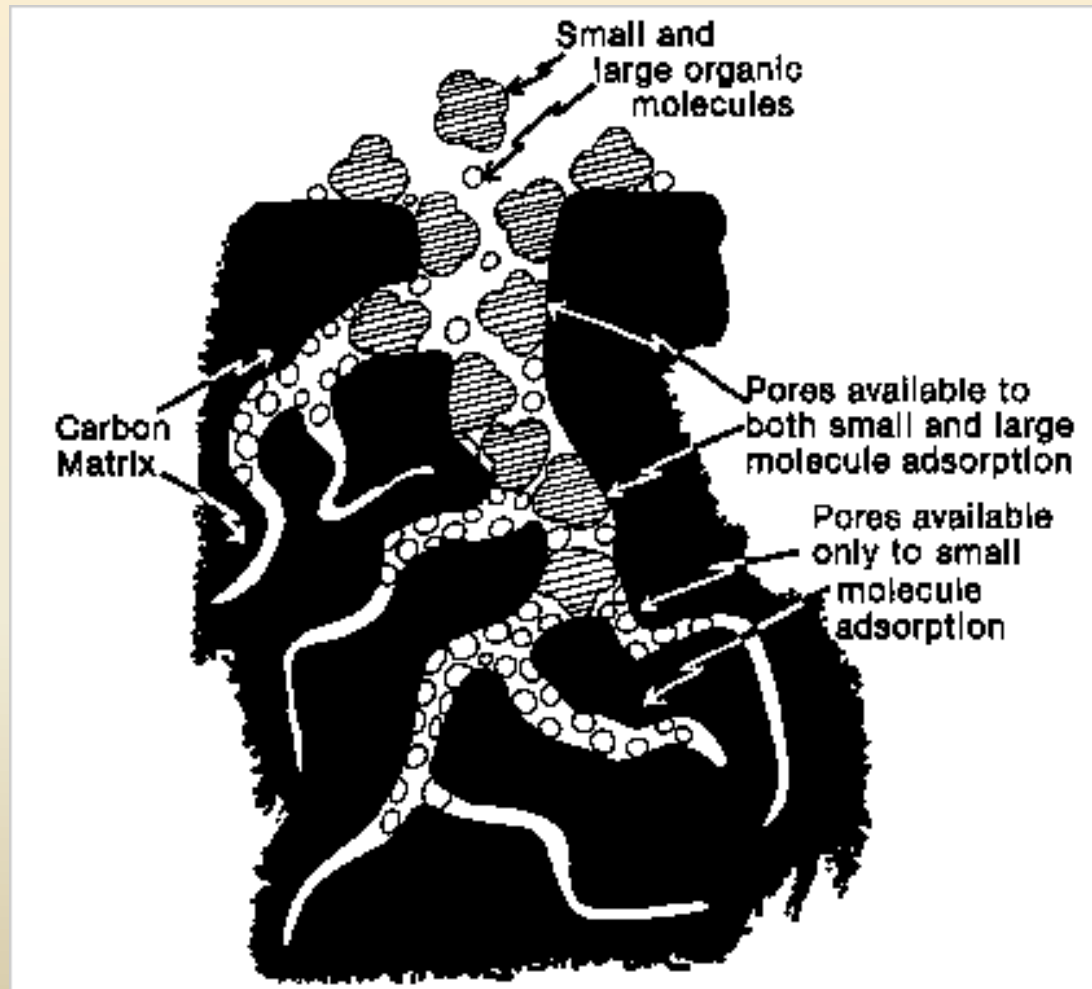
If anaerobic conditions occur

→ Biological activity in carbon beds →
 H_2S formation

Spent Carbon → land disposal problem,
unless regenerated

Regeneration systems → Expensive +
Air pollution problems

Activated Carbon



Activated Carbon Systems

Pretreatment is important to reduce solids loading to granular C systems.

Powdered Activated Carbon (PAC) can be fed to ww using chemical feed equipment.

Activated Carbon Systems

Mostly used for organic matter removal. AC remove variety of organics from water (not selective)

Metal removal:

Recent applications in metal removal

Few in full scale

Pretreatment by sedimentation / filtration to remove precipitated metals

Remaining dissolved metals adhere to the carbon until all available sites are exhausted.

Spent carbon → Replaced with new or regenerated C

Factors effecting Carbon Adsorption

- Physical and chemical characteristics of carbon (surface area, pore size)
- Physical and chemical characteristics of adsorbate ? (molecular size, molecular polarity, chemical composition)

Higher molecular weight $\rightarrow$ more easily adsorbed

Molecular weight $\leftrightarrow$ Size

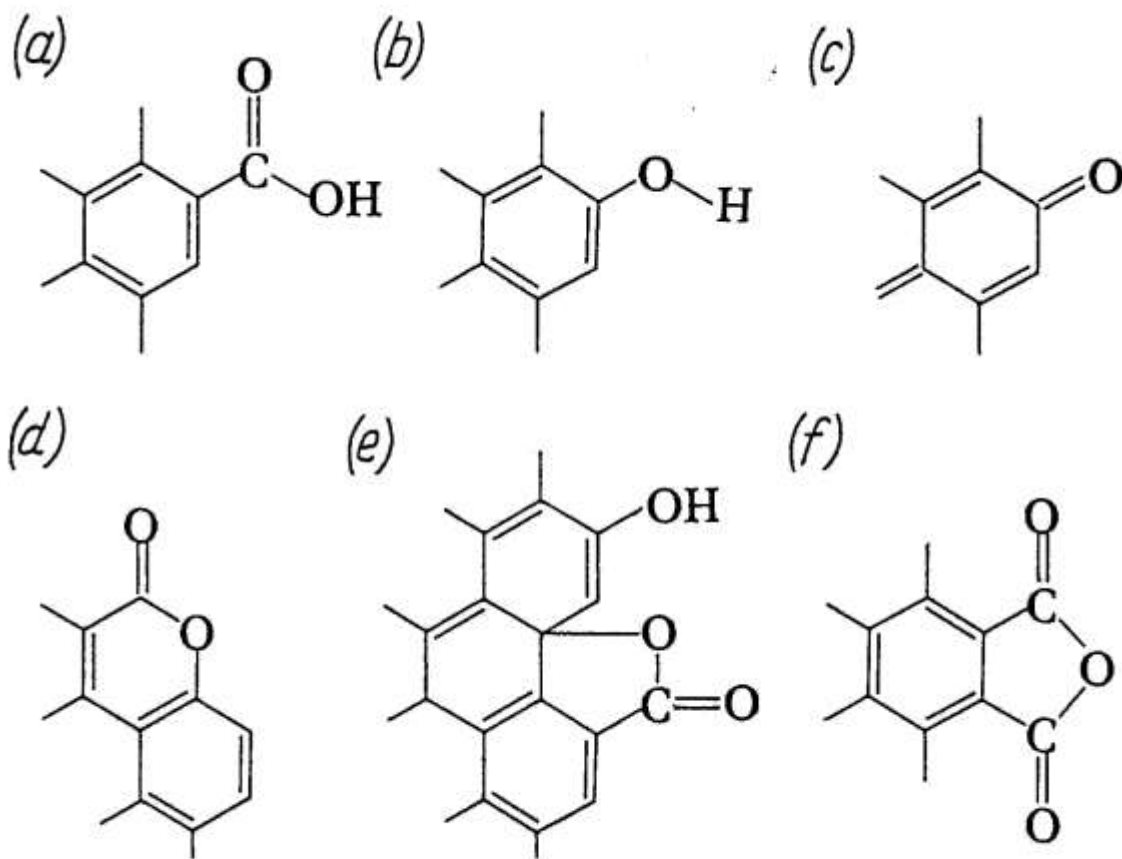
Factors effecting Carbon Adsorption

- Concentration of adsorbate in the liquid phase (solution)
- Characteristics of the liquid phase ? (pH, temperature)
- Contact time
- Increasing solubility of the solute in the liquid carrier decreases adsorbability
- Branched chains are usually more adsorbable than straight chains

Factors effecting Carbon Adsorption

- Substituent groups (hydroxyl, amino, carbonyl groups, double bonds)
- Molecules with low polarity are more sorbable than highly polar ones.

Oxygen-Containing Surface Groups on Activated Carbon



Mattson and Mark, Activated Carbon, Dekker, 1971

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

Properties of of Ativated Carbon

Made from: (?)

- Wood
- Lignin
- Bituminous coal
- Lignite
- Petroleum residues

Standards for specific applications:

- Pore size
- Surface area
- Bulk density

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

Other parameters used for AC characterization

- *Phenol Number*: Index of carbon's ability to remove taste and odor compounds
- *Iodine Number*: Adsorption of low-molecular weight substances

Micropores, radius $< 2 \mu\text{m}$

- *Molasses Number*: Carbon's ability to adsorb high molecular weight substances

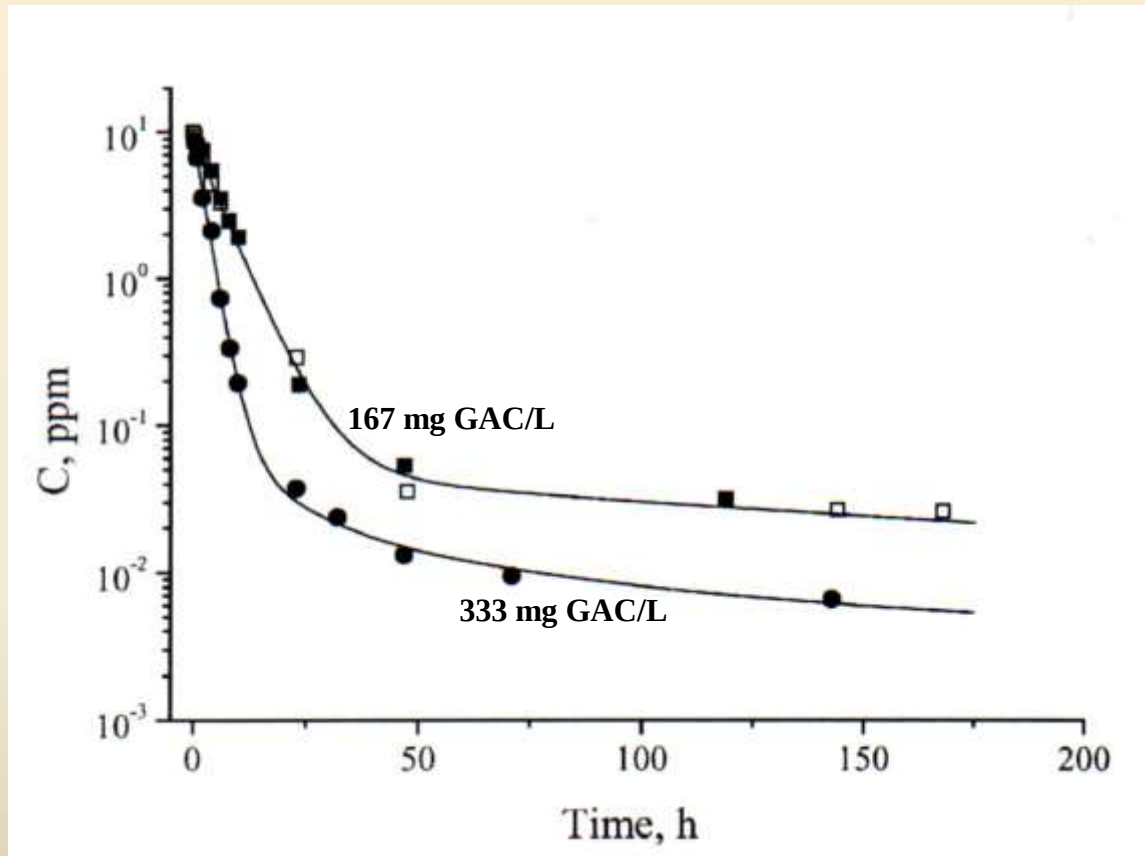
Pores $1 - 50 \mu\text{m}$

Other parameters used for AC characterization

High iodine number → Effective for ww with
low molecular weight organics

High molasses number → Effective for ww
with **high** molecular weight organics

Kinetics of Atrazine Sorption onto GAC



Carbon Regeneration

Objective: Remove the previously adsorbed materials from the carbon pore structure

Methods:

- Thermal
- Steam
- Solvent extraction
- Acid / base treatment
- Chemical Oxidation

Thermal Regeneration

Drying

Desorption

High temperature heat treatment (650 – 980°C) in the presence of water vapor, flue gas, oxygen

- Multiple heat furnaces
- Fluidized bed furnaces are used.

Adsorption Isotherms

- Technical feasibility of Activated Carbon



Adsorption tests



Generate adsorption isotherms

Adsorption Isotherms

- Technical feasibility of Activated Carbon

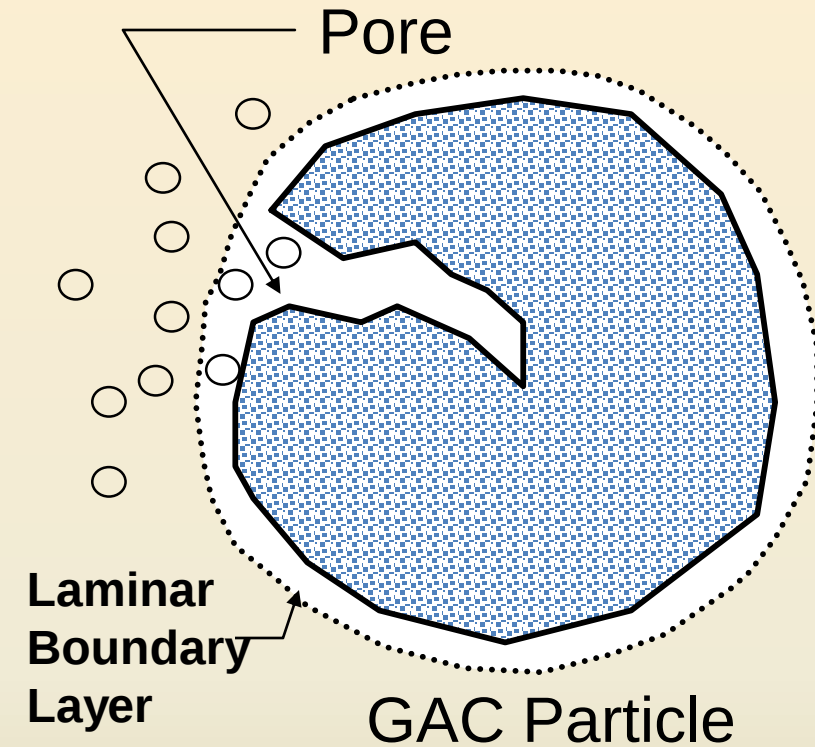


Adsorption tests



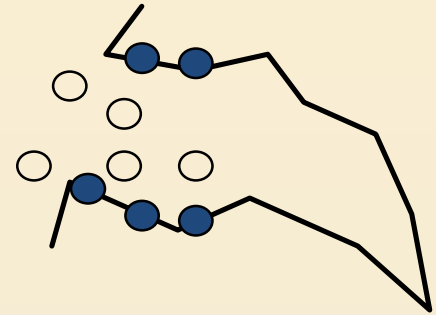
Generate adsorption isotherms

Adsorptive Equilibration in a Porous Adsorbent

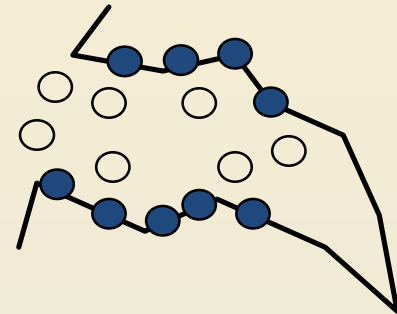


- Adsorbed Molecule
- Diffusing Molecule

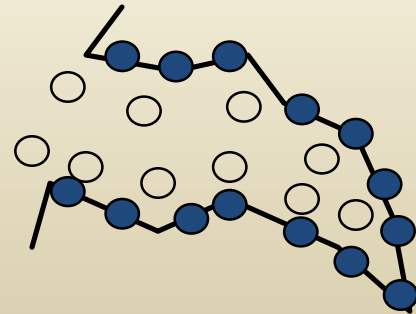
Early



Later

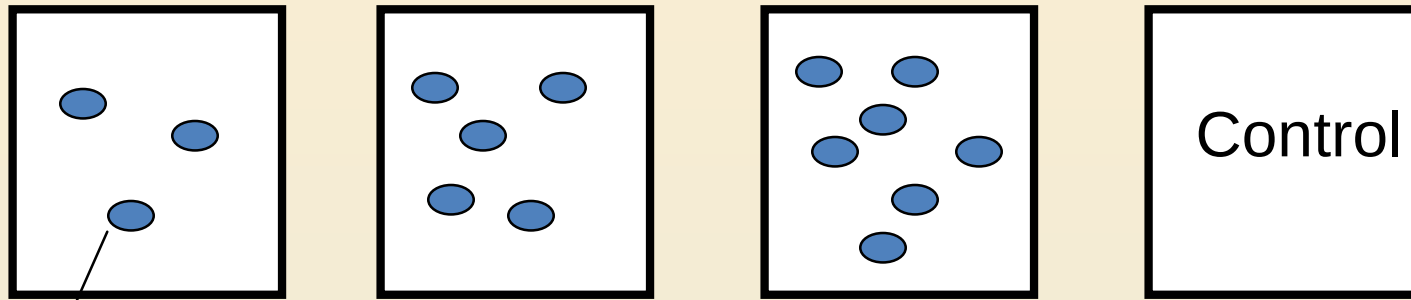


Equilibrium



Adsorption Isotherms

Add Same Initial Target Chemical Concentration, C_{init} , in each



— Different activated carbon dosage, C_{solid} , in each

$$q_{fin} \left(\frac{\text{mg}}{\text{g}} \right) = \frac{C_{init} - C_{fin} \text{ (mg/L)}}{C_{solid} \text{ (g/L)}}$$

An adsorption 'isotherm' is a q vs. c relationship at equilibrium

Metal Oxide Surfaces

Coagulants form precipitates of $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ which have $-\text{OH}$ surface groups that can adsorb humics and many metals

Humic substances where R is organic



Sorption of NOM on Metal Oxide

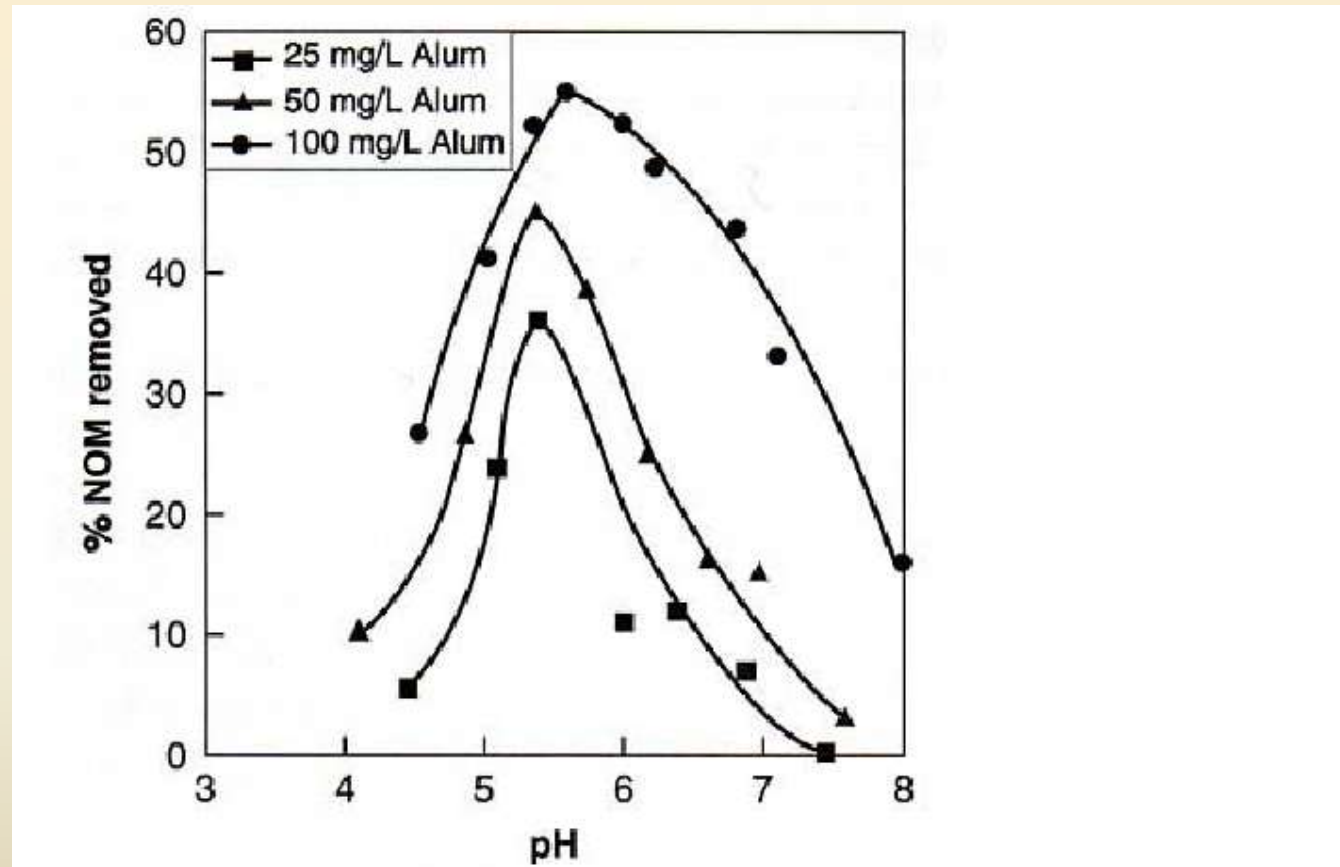


Figure 7-4. Removal of natural organic matter (quantified as TOC) by addition of aluminum sulfate (alum) as a function of pH (from Semmens and Field (1980)).

Sorption of Metals on Metal Oxide

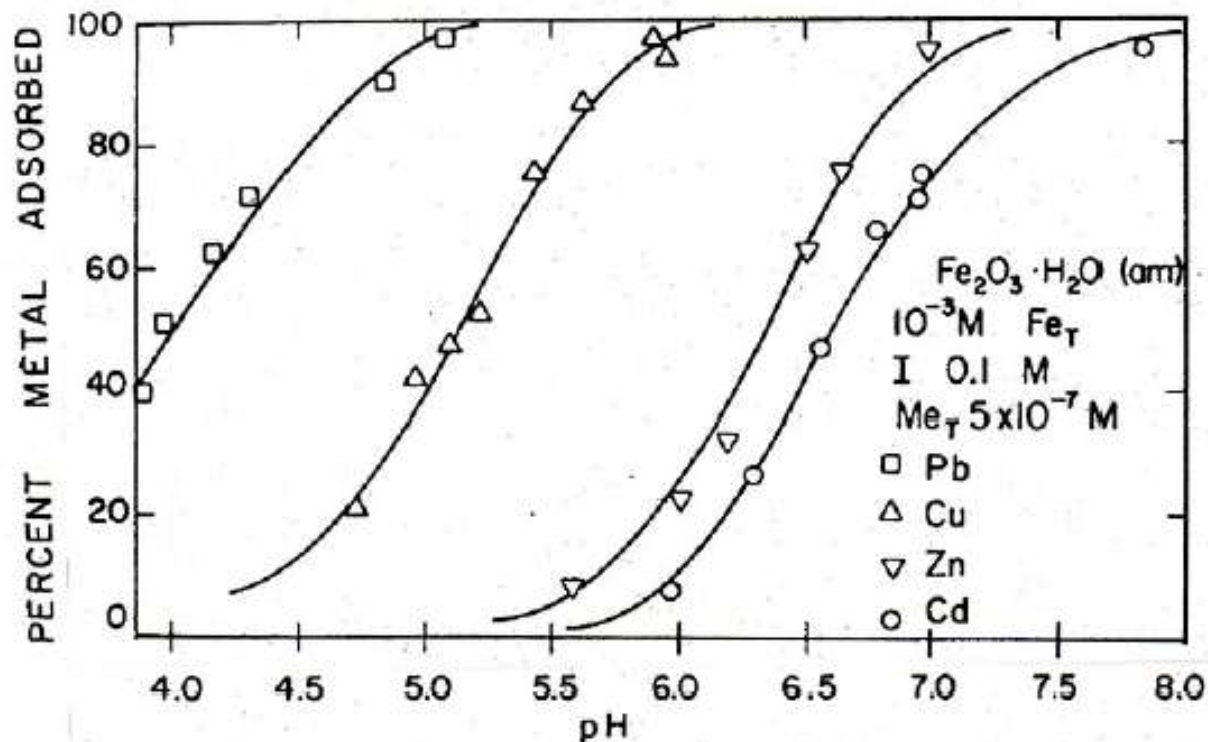
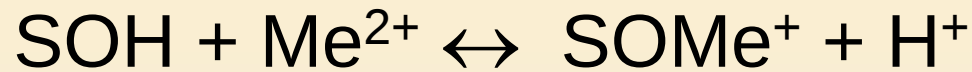
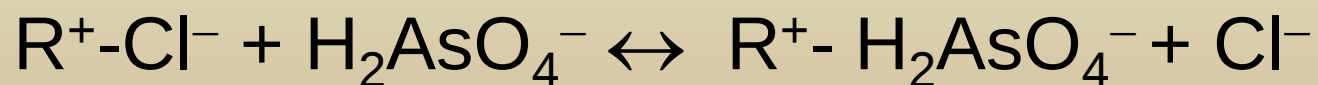
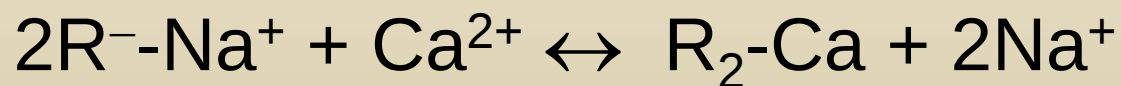
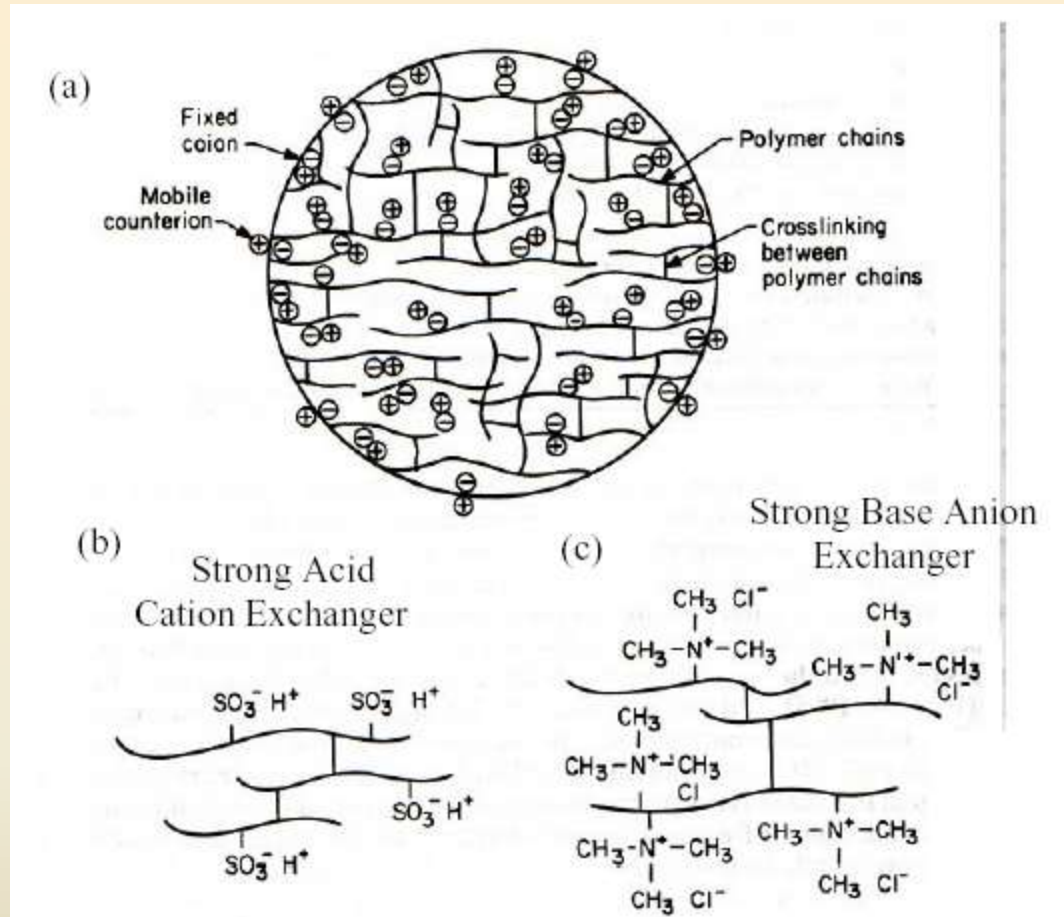


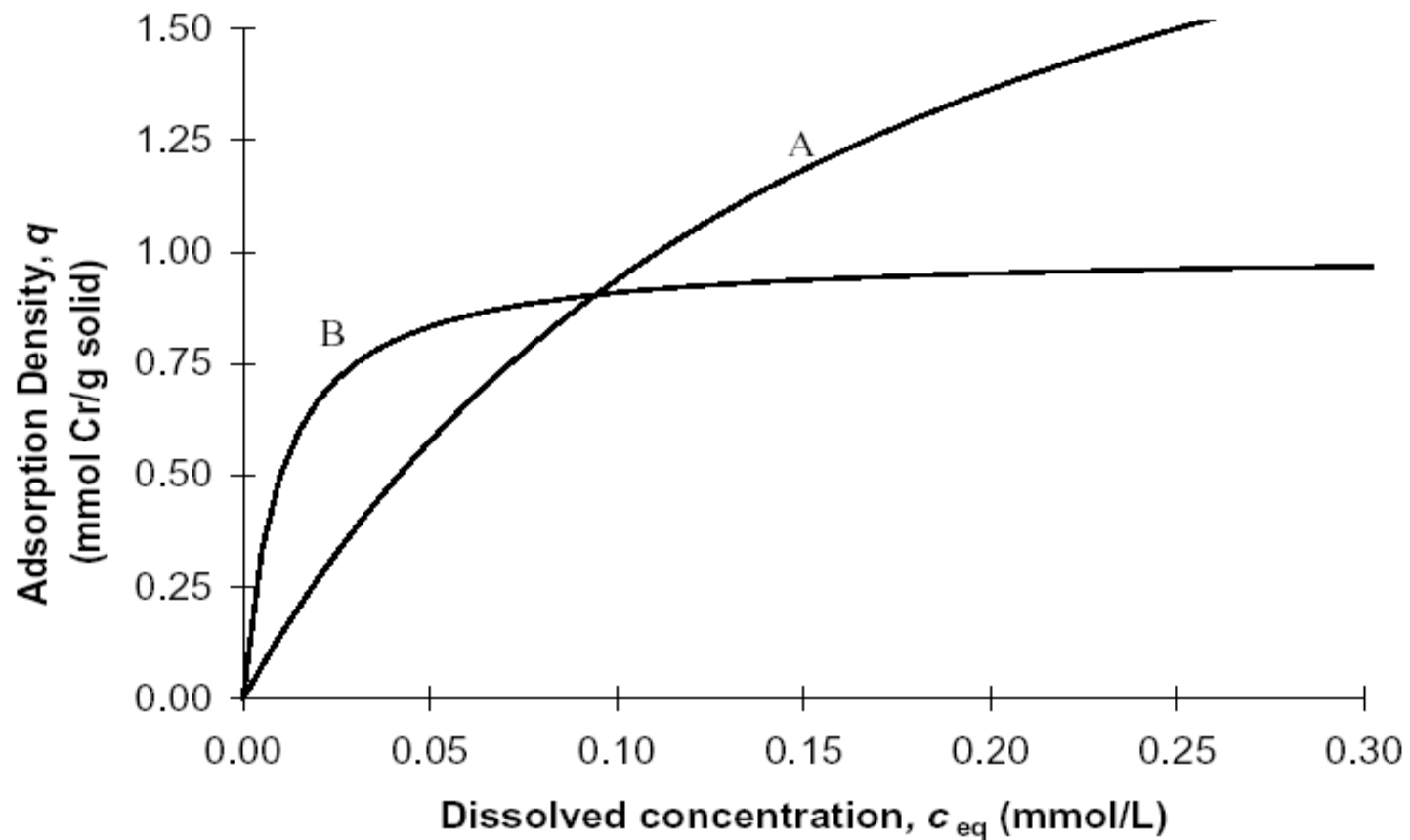
Figure 7-5. pH-adsorption edges for sorption of Pb^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+} onto $10^{-3} \text{ M Fe(OH)}_3(\text{s})$. After Benjamin and Leckie (1981).

Ion Exchange Resins



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 treatment 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 $q > 0$:

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

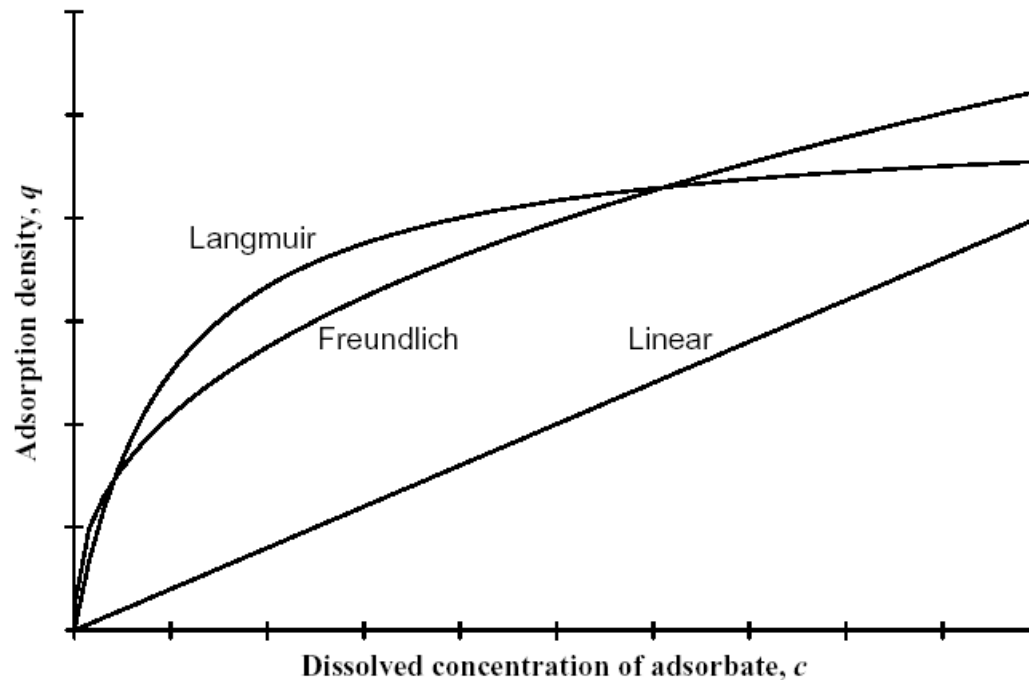
$$c_{\text{solid}} = \frac{c_{\text{init}} - c_{\text{fin}}}{q_{\text{fin}} - q_{\text{init}}}$$

Commonly Reported Adsorption Isotherms

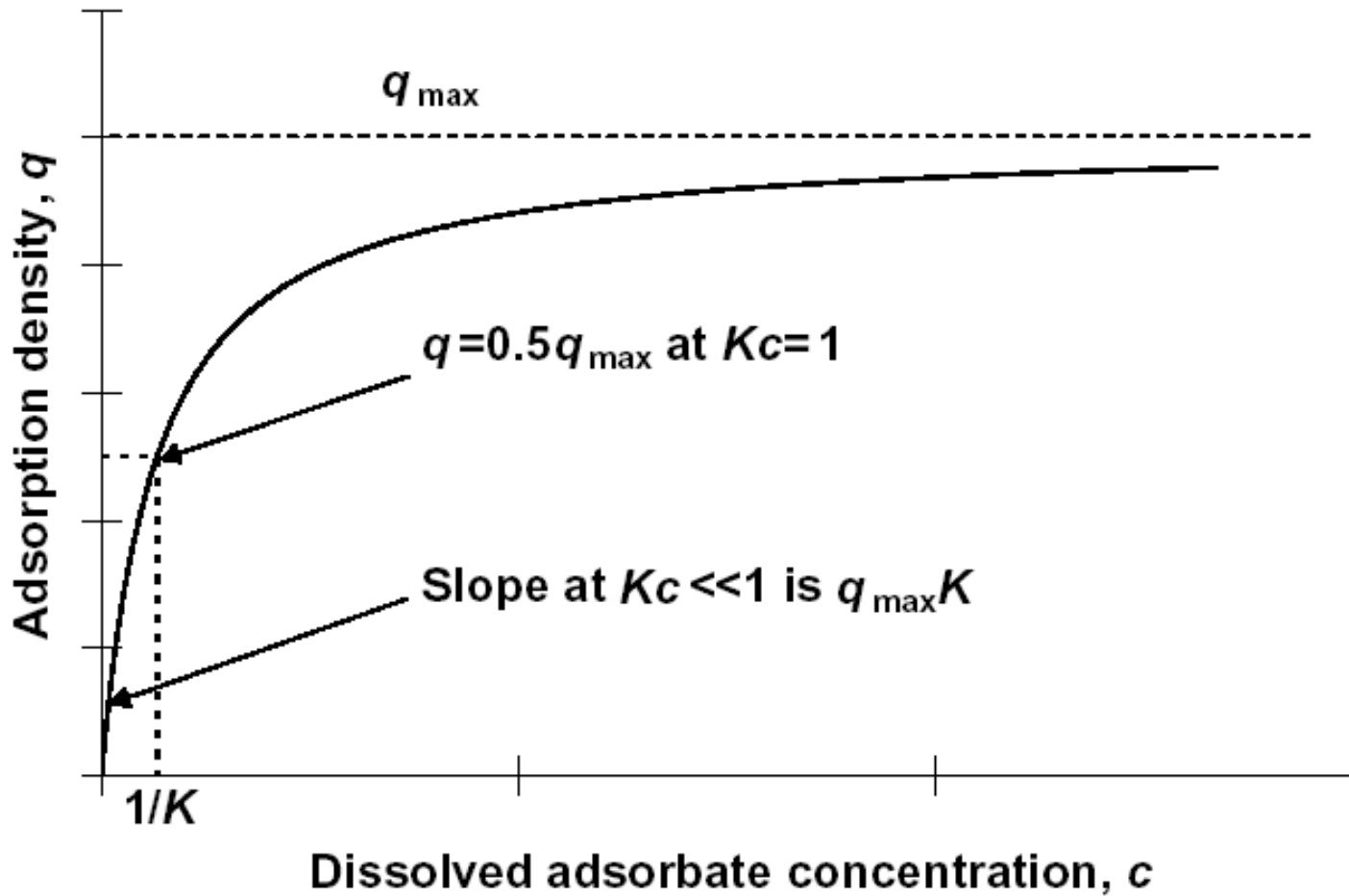
Linear: $q = k_{\text{lin}} c$

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

Freundlich: $q = k_f c^n$

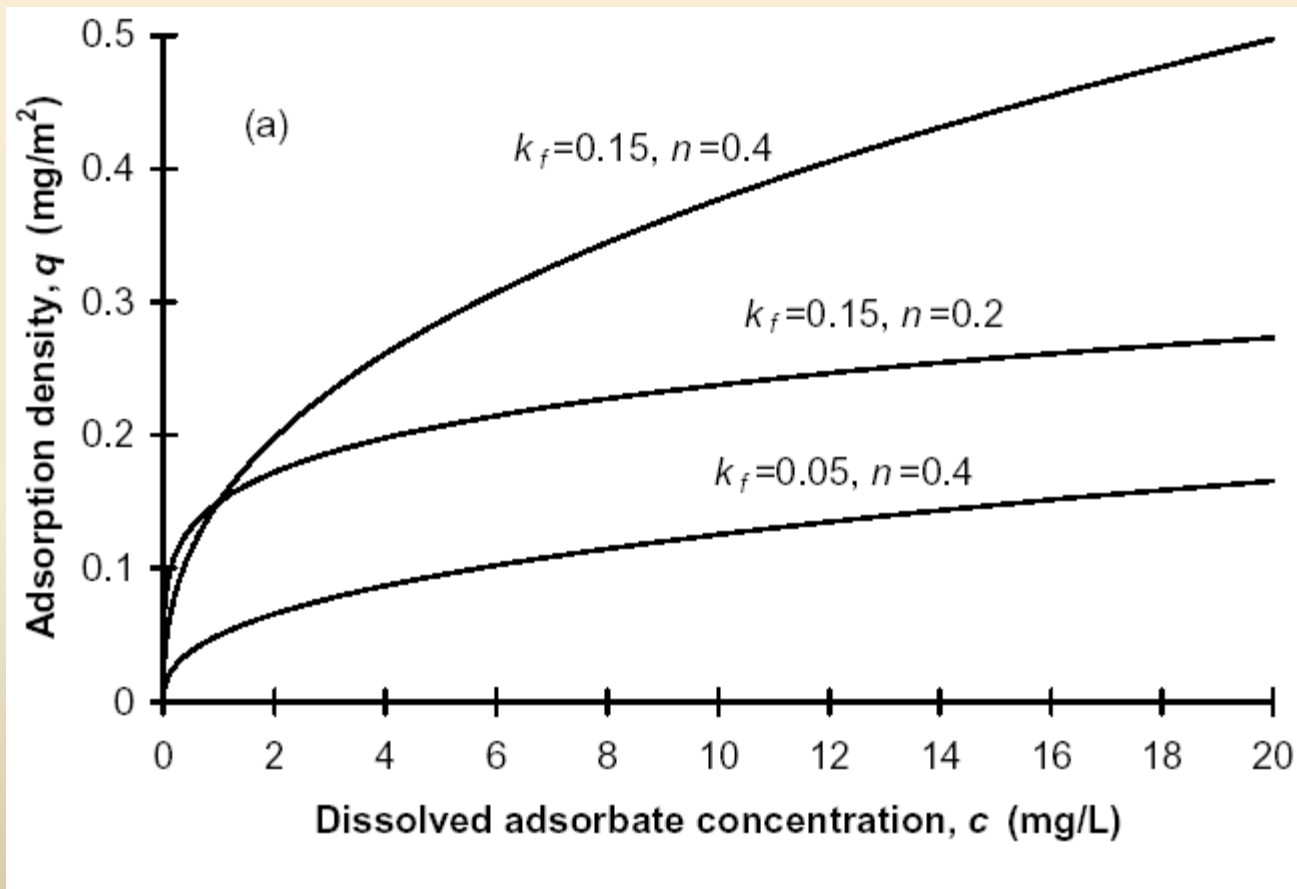


Shape of Langmuir Isotherm



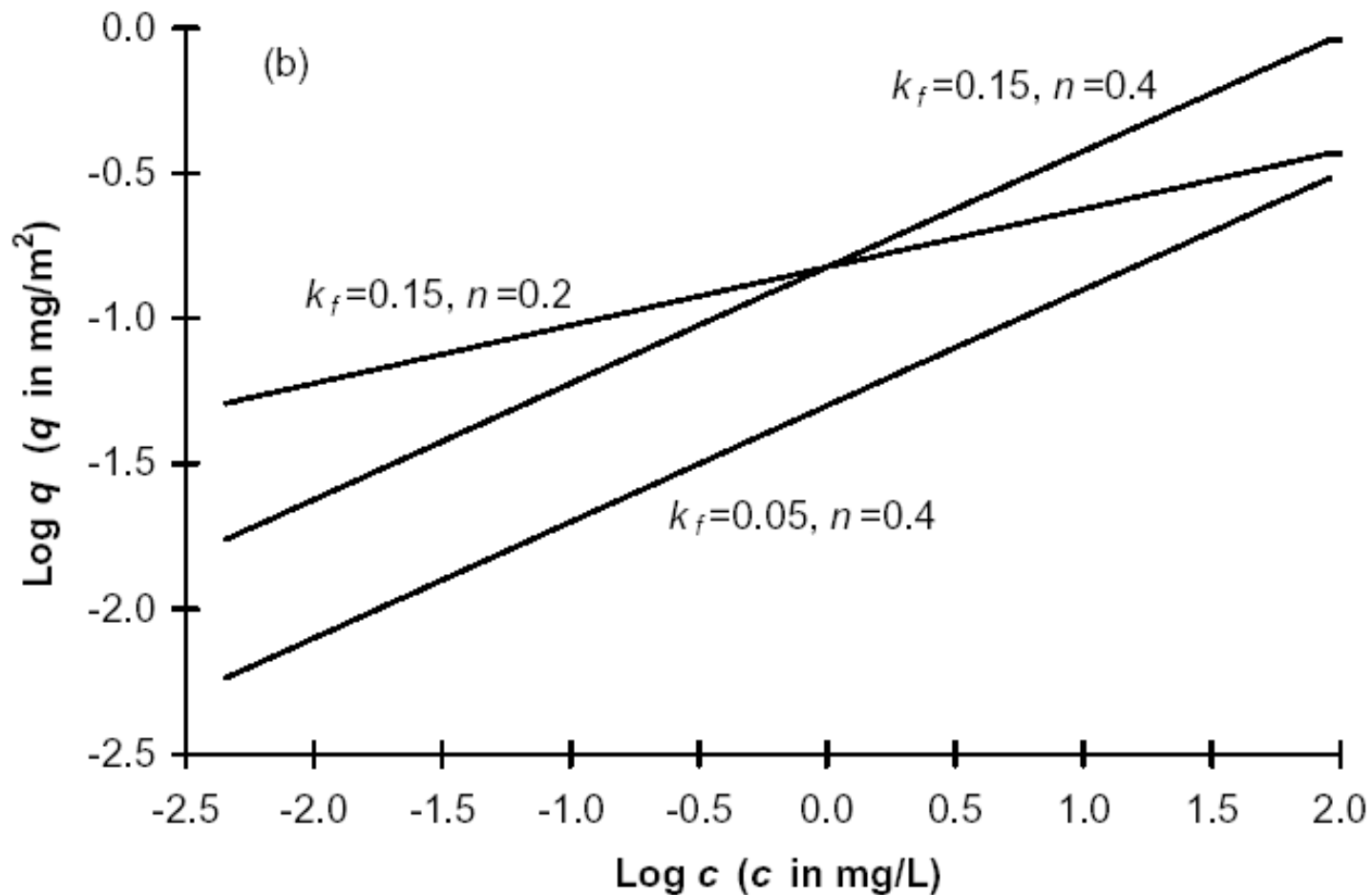
Shape of Freundlich Isotherm

$$q = k_f c^n$$



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:

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

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 m²/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:

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

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

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

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

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

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:

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

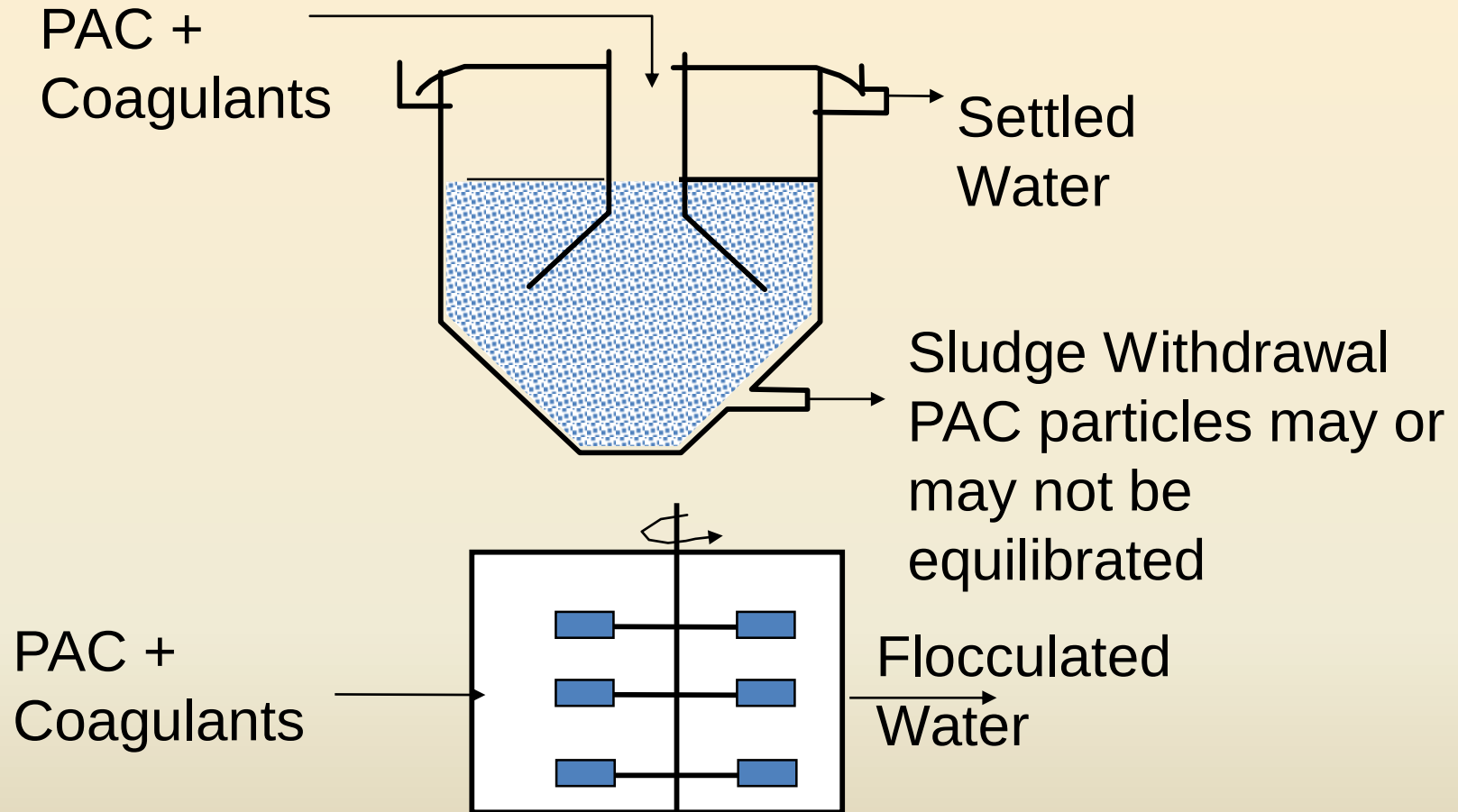
$$0.50 = c_{tol} + \left(76.6 c_{tol}^{0.365} \right) (0.114 \text{ g/L})$$

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

General Process Design Features

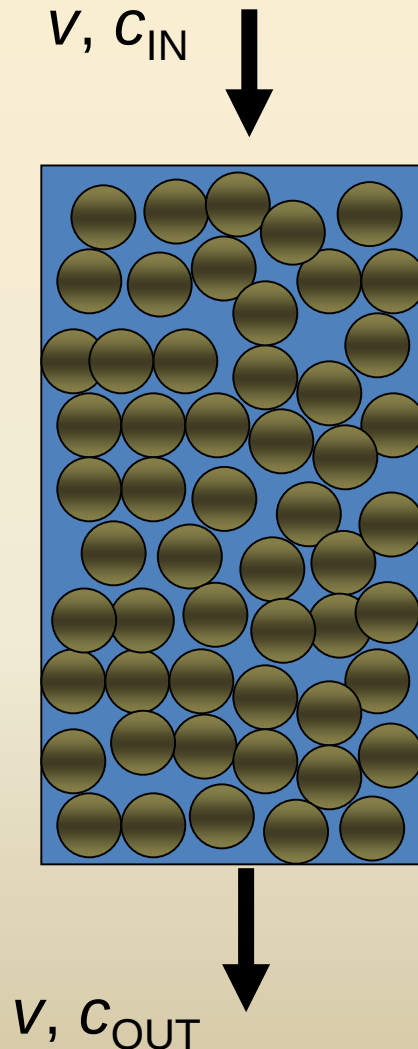
- Contactors provide large surface area
- Types of contactors
 - Continuous flow, slurry reactors
 - Batch slurry reactors (infrequently)
 - Continuous flow, packed bed reactors
- Product water concentration may be
 - Steady state or
 - Unsteady state

Powdered Activated Carbon (PAC)



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

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

ENVE 420

Industrial Pollution Control

FLOTATION

(Ref: 1- WPCF – Wastewater
Treatment Plant Design
2- Eckenfelder)

Dr. Aslihan Kerç

Objective of Using Flotation

- Used for
the removal of:
 - Suspended Solids
 - Oil and Greasefrom wastewater
the separation and concentration of
sludges

Mechanism of Flotation

- If density of particle $<$ density of water
→ can be separated by flotation

e.g. ?

Petroleum industry

Edible oil industry

Fiber recycling in paper industry

Flotation Types

1. Simple flotation
2. Flotation with aeration
3. Dissolved air flotation
4. Electroflotation
5. Vacuum flotation

Mechanism of Dissolved Air Flotation (DAF)

- Solid particles in liquid suspension become attached to microscopic air bubbles.
- Waste flow or a portion of clarified effluent is pressurized to 3.4 – 4.8 atm in the presence of sufficient air to approach saturation.
- When pressurized air-liquid mixture is released to atmospheric pressure, minute air bubbles are released from the solution.

Mechanism of Dissolved Air Flotation (DAF)

- Agglomerate rise to the surface to join other particles and form a blanket that can be removed mechanically.
- Flotation is used primarily to remove light SS.
- Sludge flocs, suspended solids, oil globules are floated by the air bubbles which:
 - Attach to floc particles
 - Become enmeshed in floc particles

Mechanism of Dissolved Air Flotation (DAF)

- Air-solids mixture → skimmed off from the surface
- Clarified liquid → removed from the bottom
- A portion of the effluent → recycled back to the pressure chamber

Primary variables for flotation design

- Pressure
- Recycle ratio
- Feed solids concentration
- Retention period

For clarification, retention time: 20 – 30 min

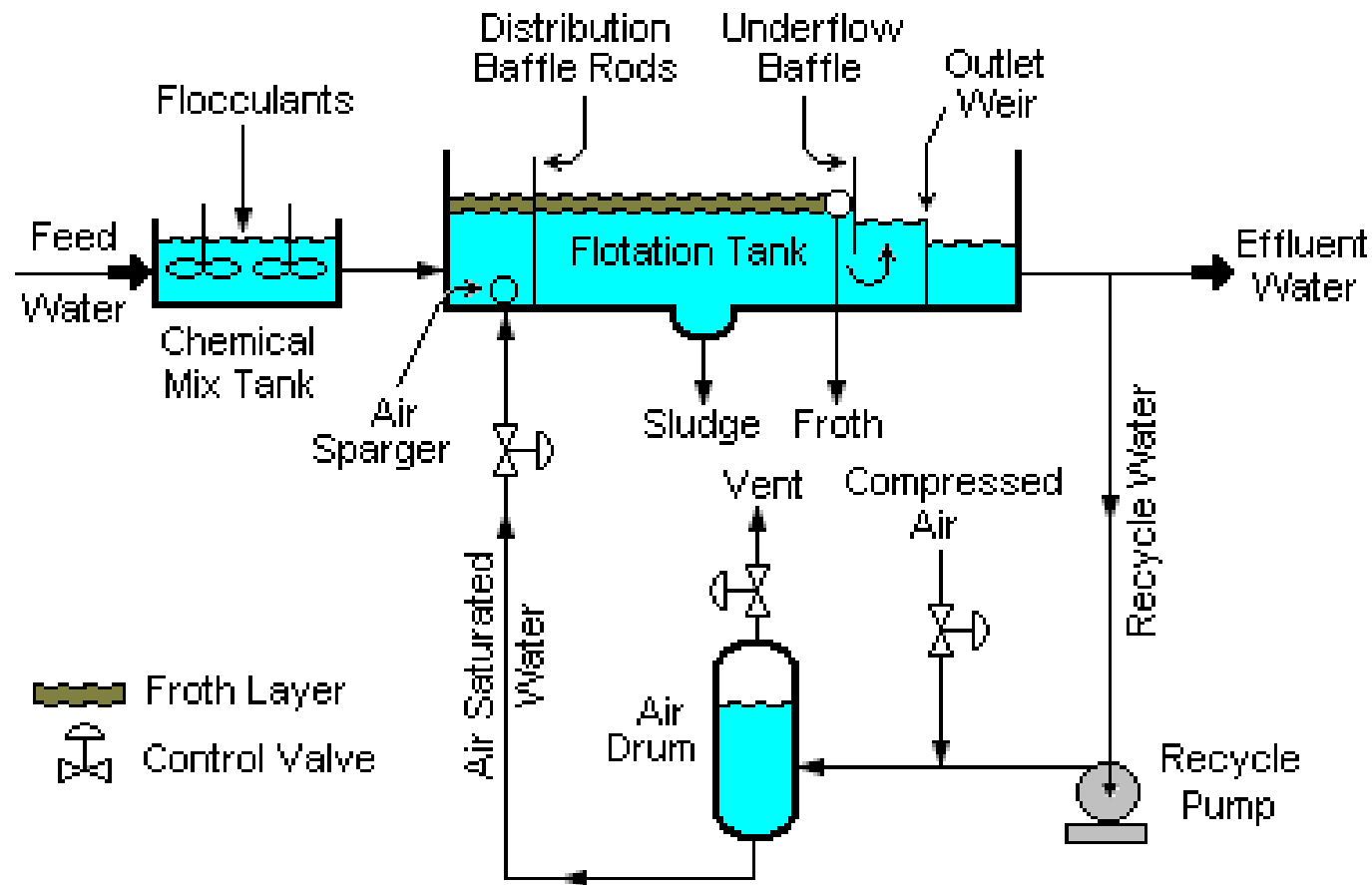
loading rate: 0.06 – 0.16 m³/min-m²

For thickening: longer t_R

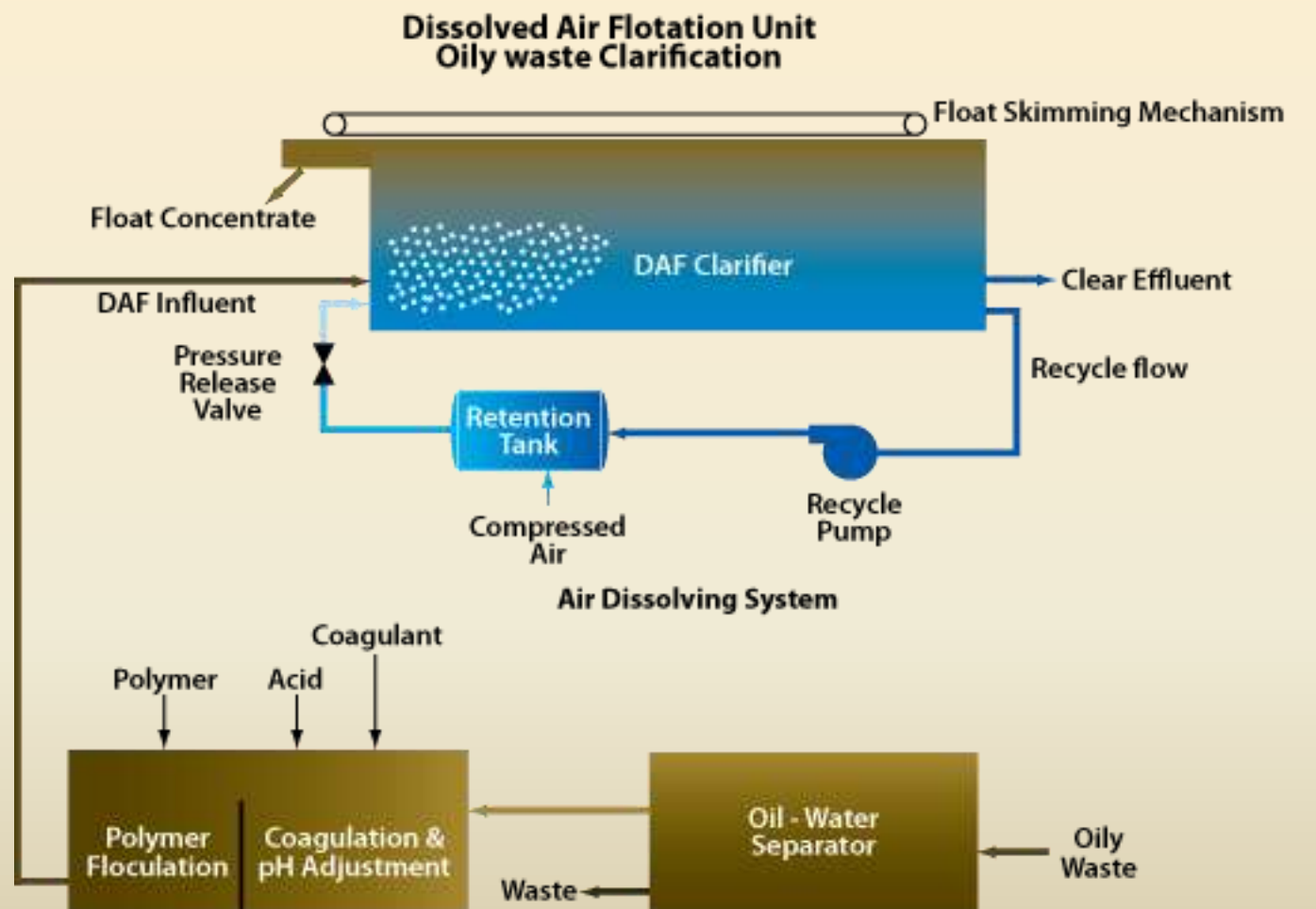
Principal components of flotation system

- Pressurized pump → elevated pressure to increase solubility
- Air-injection facilities
- Retention tank (saturation tank) → 1-3 min
- Back pressure regulation device → constant head on pressurizing pump
- Flotation unit → circular / rectangular with a skimming device

DAF Flow Diagram



DAF Flow Diagram



DAF



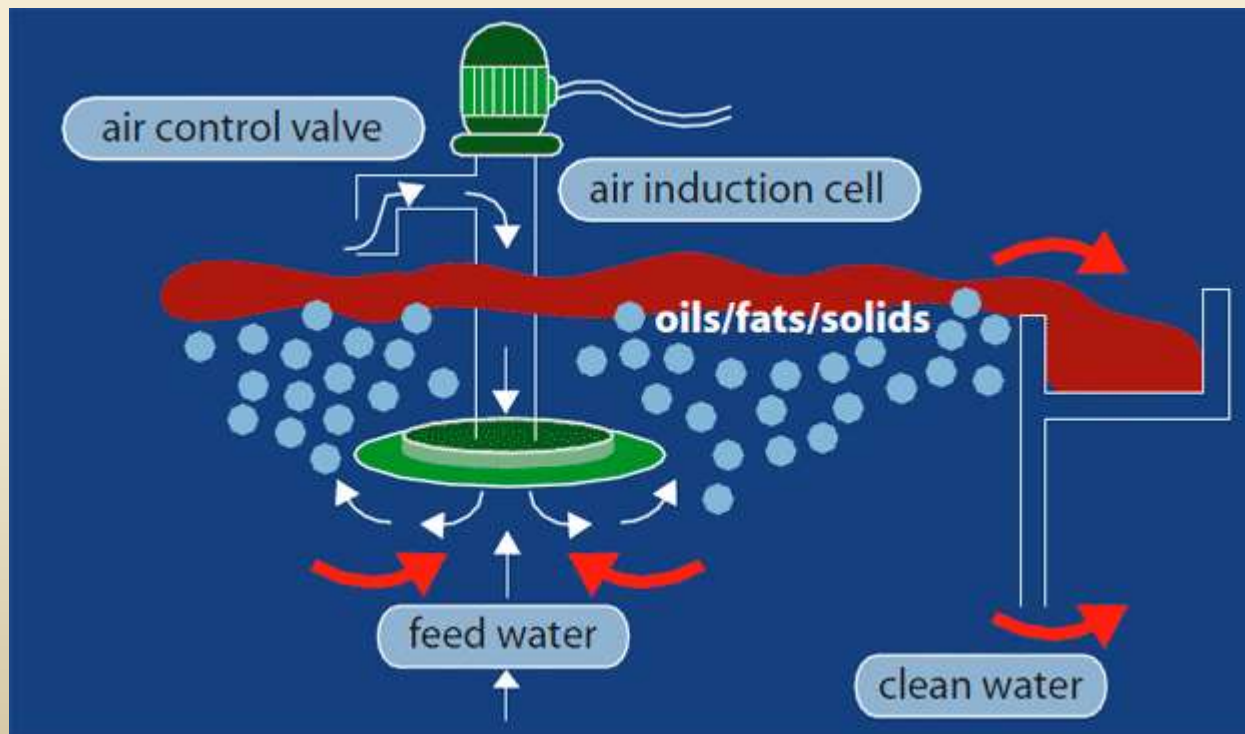
Application of flotation

- Flotation is applicable for wastewater containing high concentration of finely divided solids:
 - Wastes from canneries
 - Packing houses
 - Oil refineries
 - Laundries

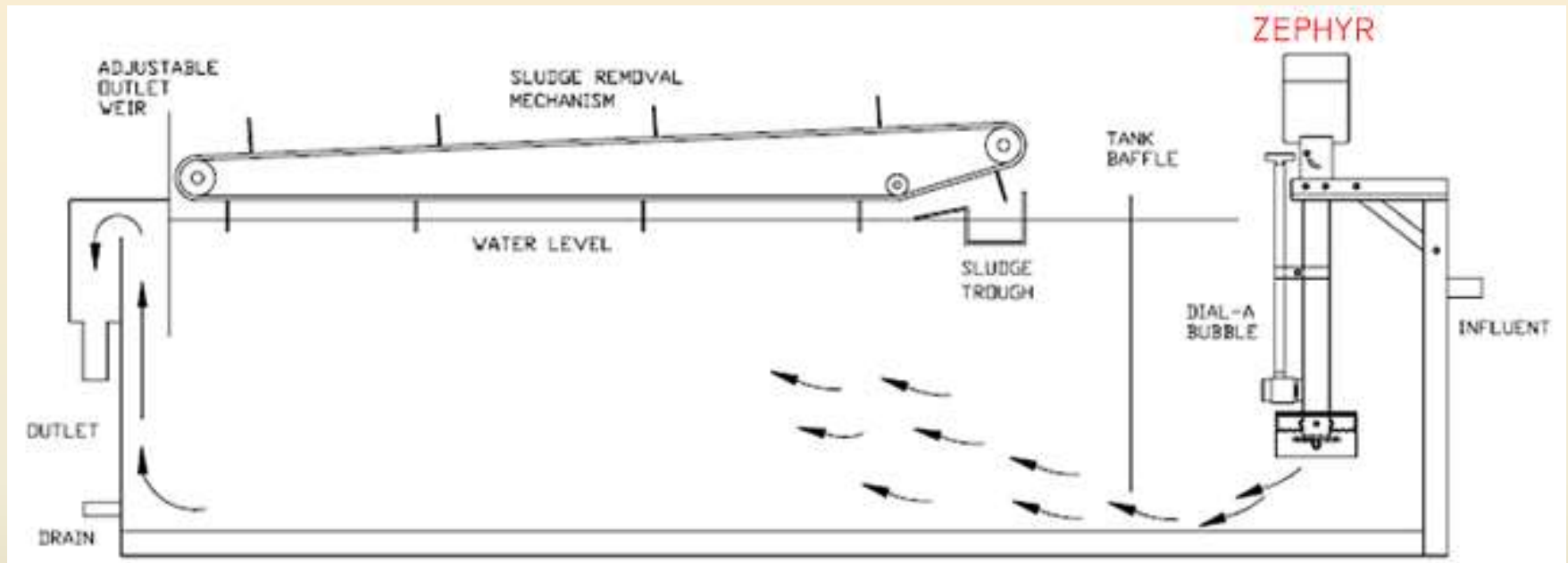
Recovered solids may be reusable → source of fuel

Induced Air Flotation System

- A submerged rotor forces the liquid through disperser opening, creating a negative pressure.



Induced Air Flotation System



OIL SEPARATION

- Free oil is floated to the surface of a tank and then skimmed.
- Design of gravity separators → American Petroleum Institute (API Separators)
- Removal of oil particles > 0.015 cm
- Effluent oil concentration : 50 mg/L
- Plate separators separate oil droplets > 0.006 cm
- Corrugated plates