

Physical unit processes III

Today's class

Physical processes utilizing interphase mass transfer

- Gas-liquid mass transfer
- Adsorption
- Ion exchange

Mass transfer processes

- **Phase partitioning:** in multi-phase systems, materials are distributed with some ratio between the phases at equilibrium

– Recall Henry's law (gas-liquid partitioning): $C_g/C_s = H_u$

ex) At 1 atm, 20°C, the saturation concentration of dissolved oxygen in pure water is 9.08 mg/L (0.208 atm partial pressure of O₂ in gas phase ↔ 9.08 mg/L O₂ in aqueous solution)

Mass transfer processes

- Transfer of material from one homogeneous phase to another
- Interphase mass transfer occurs **towards equilibrium**
- **Time as a factor**: it takes some time for the mass transfer processes to occur such that equilibrium is established

ex) Drying clothes

phase partitioning: moisture wetting the clothes vs. moisture in the ambient air

equilibrium: almost no moisture in the clothes because the amount of ambient air is almost infinite

time as a factor: it takes some time (~1 day) for the clothes to dry

Application of mass transfer in WW treatment

Type of reactor	Phase equilibria	Application
Absorption	Gas → liquid	Addition of gases to water (e.g., O ₂), NH ₃ scrubbing in acid
Adsorption	Gas → solid	Removal of organics with activated carbon
	Liquid → solid	Removal of organics with activated carbon, dechlorination
Desorption	Solid → liquid	Sediment scrubbing
	Solid → gas	Reactivation of spent activated carbon
Drying (evaporation)	Liquid → gas	Drying of sludge
Gas stripping	Liquid → gas	Removal of gases (e.g., CO ₂ , H ₂ S, NH ₃ , VOCs)
Ion exchange	Liquid → solid	Selective removal of chemical constituents, demineralization

Gas-liquid mass transfer

- **Modeling concentration change by mass transfer**
 - Mass transfer occurs at the interface (surface) -- **A**
 - Should depend on compound (rate of diffusion) & surface characteristics (calm or turbulent?) -- **K_L**
 - Should also depend on how far the current state is from equilibrium -- **$(C_s - C)$**
 - Flux = (mass transferred) / (area) / (time)

$$F = K_L(C_s - C)$$

F = flux of mass transfer [ML⁻²T⁻¹]

K_L = mass transfer coefficient with liquid as a reference phase [LT⁻¹]

A = area through which mass is transferred [L²]

C_s = liquid concentration in equilibrium with bulk gas concentration [ML⁻³]

C = current liquid concentration

Gas-liquid mass transfer

- **Modeling concentration change by mass transfer**
 - When gas concentration is constant, change in liquid concentration is represented as:

$$r_v = \left. \frac{dC}{dt} \right|_{\text{mass transfer}} = K_L \frac{A}{V} (C_S - C) = K_L a (C_S - C)$$

r_v = rate of mass transfer $[ML^{-3}T^{-1}]$

V = bulk liquid volume $[L^3]$

$K_L a$ = volumetric mass transfer coefficient $[T^{-1}]$ – 1st order rate constant

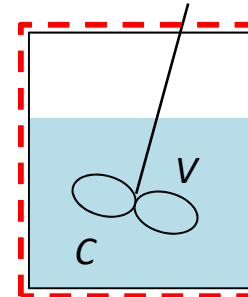
Gas-liquid mass transfer

- **Absorption of gas in a batch reactor**

(rate of accumulation)

= (rate of inflow) – (rate of outflow) + (rate of generation)

$$\frac{dC}{dt} = K_L a (C_s - C_t) \quad \Rightarrow \quad \frac{C_s - C_t}{C_s - C_0} = e^{-(K_L a)t}$$



- **Desorption of gas in a batch reactor**

$$\frac{dC}{dt} = -K_L a (C_s - C) \quad \Rightarrow \quad \frac{C_t - C_s}{C_0 - C_s} = e^{-(K_L a)t}$$

Gas-liquid mass transfer

Q: Secondary effluent is placed in a storage basin for reuse. If the initial DO concentration is 1.5 mg/L, estimate the time required for the DO concentration to increase to 8.5 mg/L due to surface reaeration. The surface area of the storage basin is 400 m² and the depth is 3 m. Assume the K_L value for oxygen is 0.03 m/hr. Use the saturation DO concentration of 9.09 mg/L at 20°C.

Gas-liquid mass transfer

This is the case of absorption of gas in a batch reactor, so use:

$$\frac{C_s - C_t}{C_s - C_o} = e^{-(K_L a)t}$$

$$t = -\frac{1}{K_L a} \cdot \ln \frac{C_s - C_t}{C_s - C_o}$$

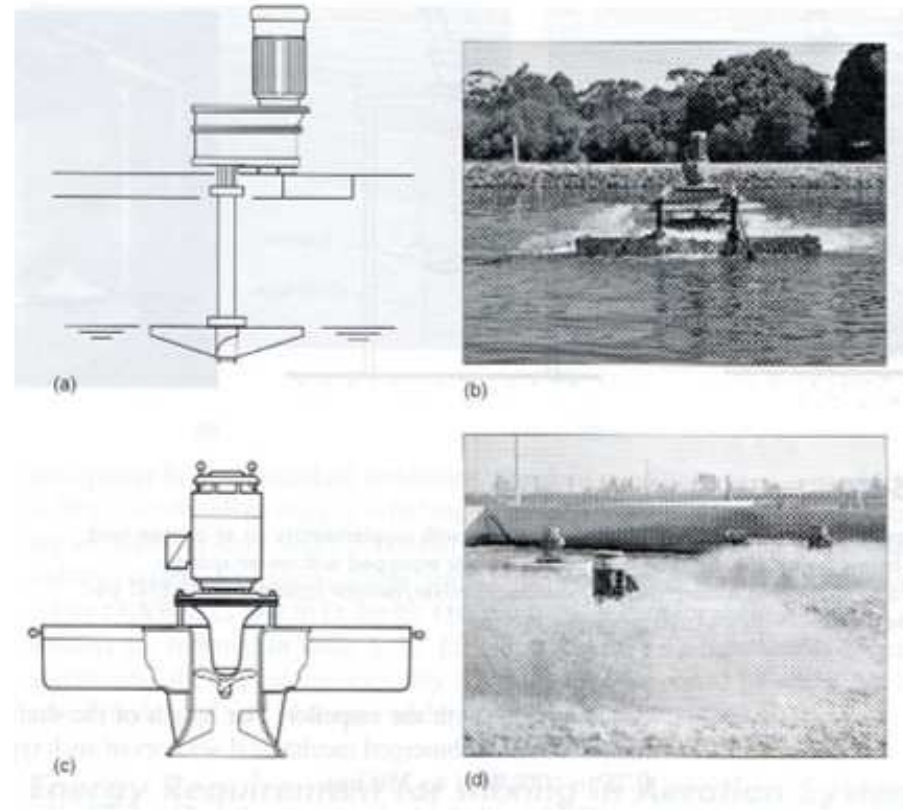
$$a = \frac{A}{V} = \frac{1}{H} = 0.33 \text{ m}^{-1}$$

$$t = -\frac{1}{(0.03 \text{ mhr}) \cdot (0.33 \text{ m}^{-1})} \cdot \ln \frac{9.09 - 8.5}{9.09 - 1.5} = 258 \text{ hr} = 10.8 \text{ d}$$

You see it takes a long time for surface reaeration from the atmosphere in the absence of mechanical agitation!

G-L mass transfer ex 1: Aeration

- Diffused air aeration vs Mechanical aeration



G-L mass transfer ex 2: Gas stripping

- **Mass transfer of a gas from the liquid phase to the gas phase**

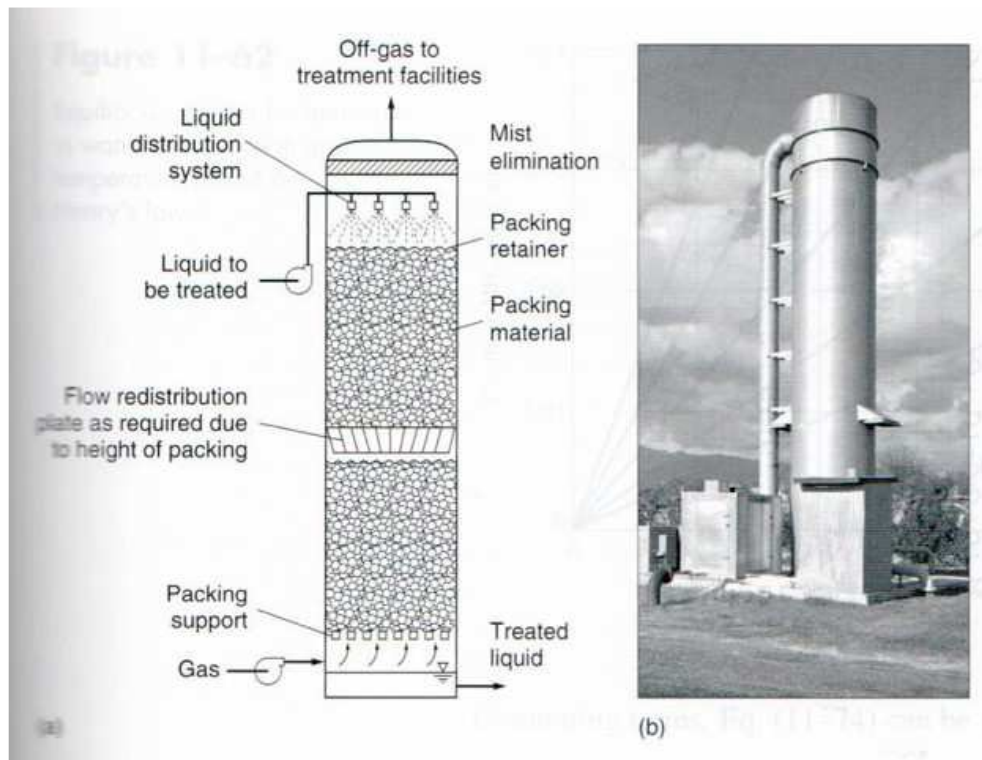
Recall:
$$\frac{dC}{dt} = K_L \frac{A}{V} (C - C_s) = K_L a (C - C_s)$$

(for desorption of gas)

- **Stripping (blowing) a contaminant-free gas into the water**
 - Creates large gas-liquid interfacial area for mass transfer
 - Most significant concern in the process design
 - Concentration gradient generated: $C_s \rightarrow 0$
- **Removal of NH_3 , odorous gases and VOCs**
 - For ammonia stripping, pH should be raised by addition of lime (why?)

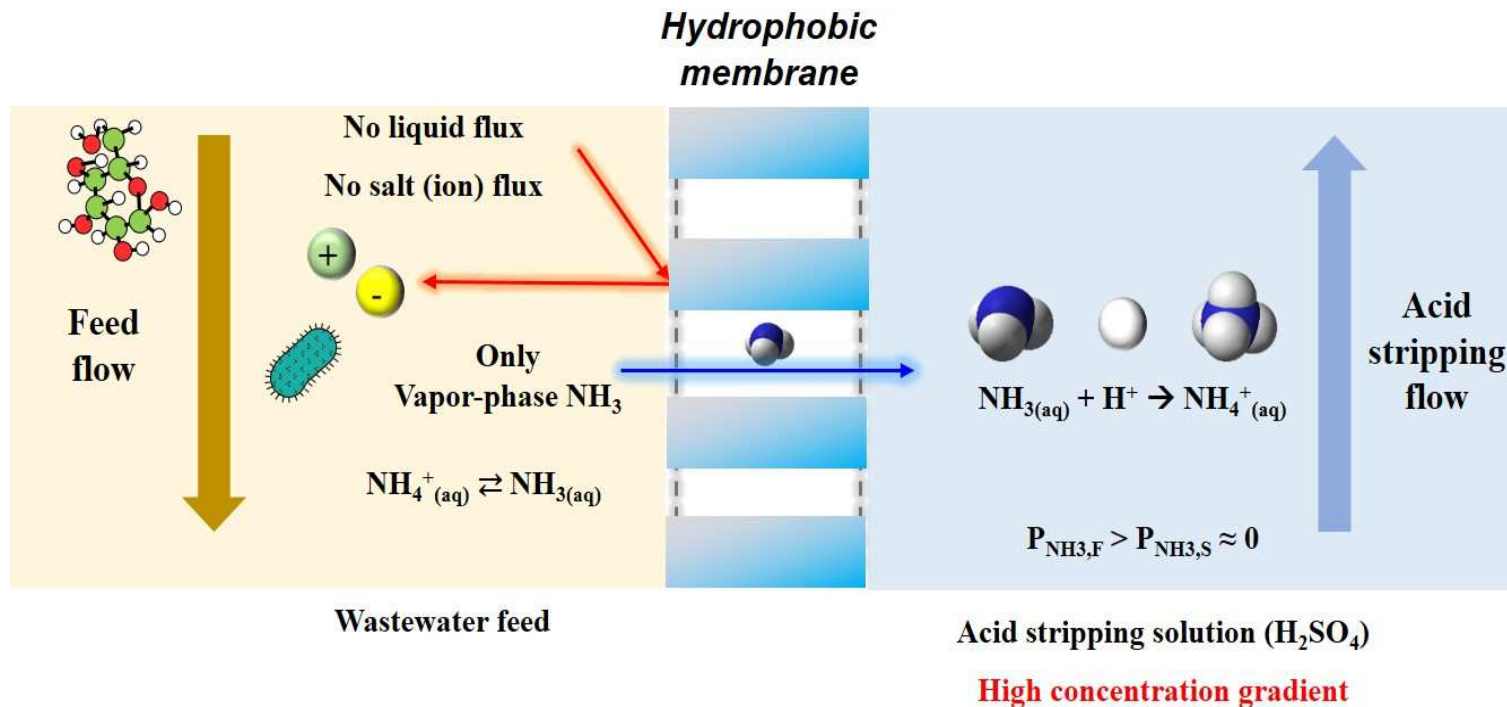
Gas stripping - methods

- **Methods to contact phases**
 - Cocurrent, countercurrent, cross-flow
 - Countercurrent most common



G-L mass transfer ex 3: Gas-permeable membrane

- An emerging technology
 - Gas-permeable membranes have been used for water production from water with high impurities (e.g., RO retentate from seawater desalination)
 - Opportunities to be used for recovery $\text{NH}_3/\text{NH}_4^+$ and CH_4 from wastewater



Adsorption

- **Removal of substances in solution by accumulation of those substances on a solid phase**
 - Adsorbate: the substance that is being removed from the solution
 - Adsorbent: the material onto which the adsorbate accumulates
- **Applications**

Removal of:

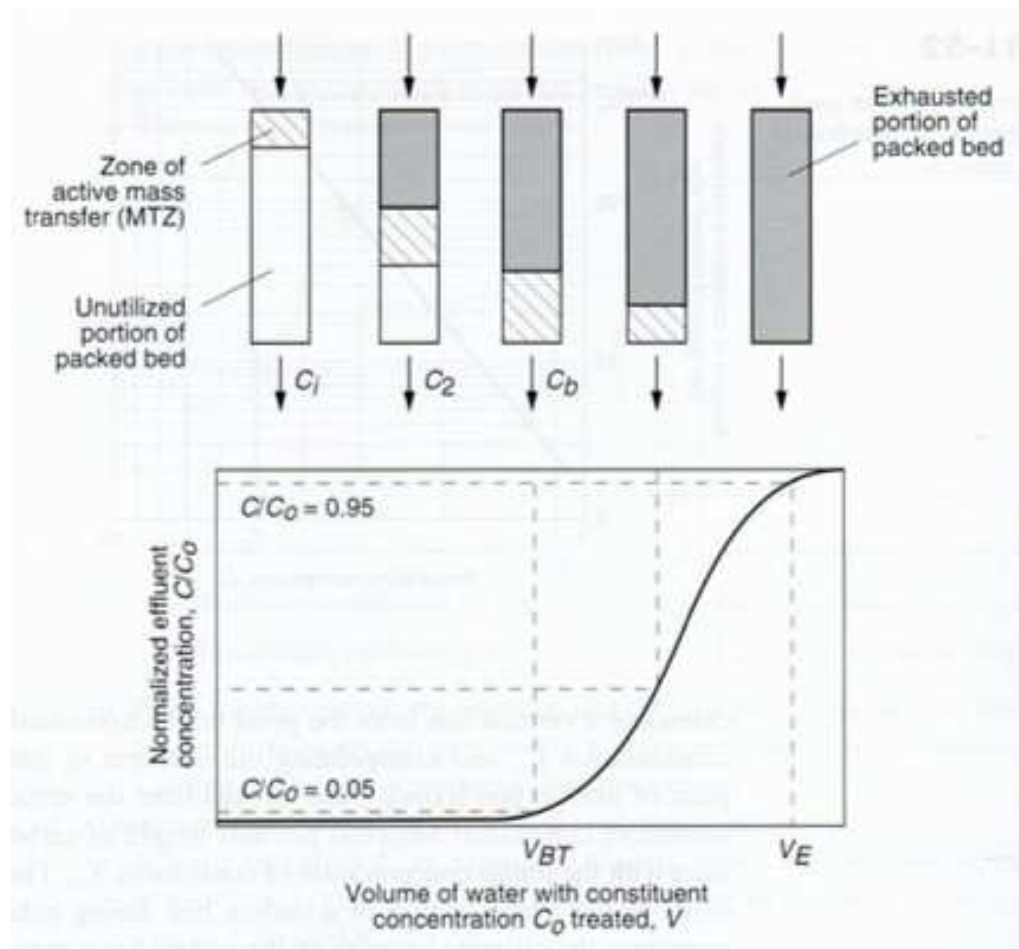
 - refractory organics
 - residual inorganic constituents (nitrogen, sulfides, heavy metals, etc.)
 - odor compounds

Types of adsorbents



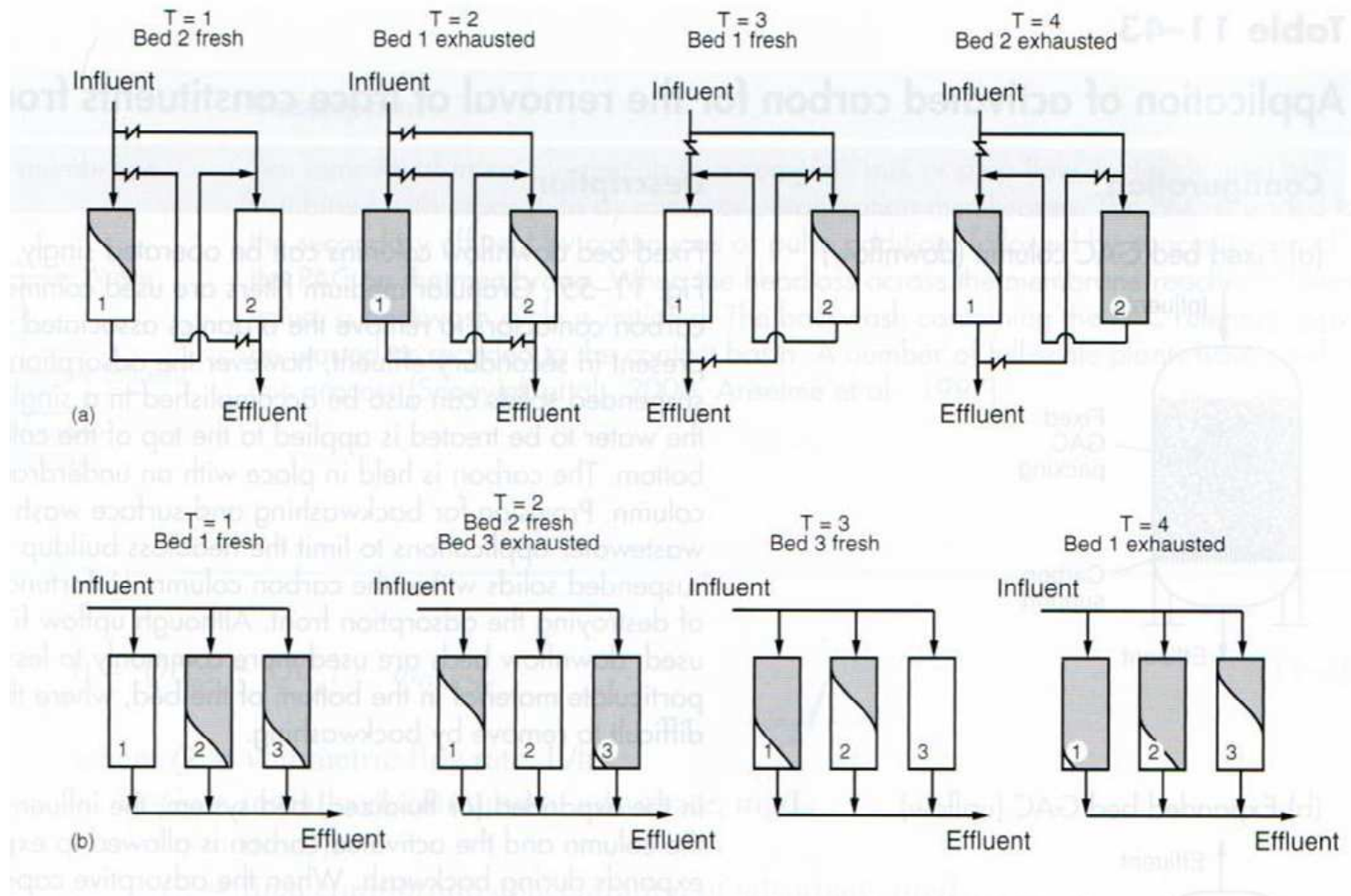
- **Activated carbon**
 - Most common – removal of refractory organics & residual COD
 - Derived by i) pyrolysis of organic materials (wood, coal, coconut, etc.) and ii) activation by steam or CO₂ at high temperatures
 - Two types based on particle size
 - GAC (granular activated carbon): > 0.1 mm, apply in columns
 - PAC (powdered activated carbon): < 0.074 mm, apply in well-mixed contact tanks
- **Granular ferric hydroxide**
 - Ferric hydroxides/oxides have high affinity to many metals and metalloids
 - Applicable for removal of arsenic, chromium, selenium, copper, etc.
- **Activated alumina**
 - May be considered in case of water reuse
 - Removal of arsenic and fluoride

GAC columns: breakthrough curve



- **Mass transfer zone** (MTZ; dashed zone): adsorption is occurring, some adsorbate conc. in pore-water
- Grey zone: GAC exhausted (adsorption equilibrium with influent), no further adsorption
- **Breakthrough** occurs after adding V_{BT} of influent, but **want full usage of the column!**

GAC columns: configurations



Ion exchange

- **A unit process in which ions of a given species are displaced from an insoluble exchange material by ions of a different species in solution**
- **So ions in the solution is exchanged by other ions originating from the insoluble exchange material**
- **Applications**
 - Most common: water softening (Na^+ from exchange material to solution; Ca^{2+} and Mg^{2+} from solution to exchange material)
 - Removal of nitrogen, heavy metals, and TDS
- **Commonly used exchange materials**
 - Natural mineral: zeolite
 - Synthetic material: ion exchange resin

Ion exchange – N & heavy metal removal

- **Nitrogen removal**
 - Remove NH_4^+ or NO_3^-
 - NH_4^+ : zeolite or synthetic cation exchange resins
 - NO_3^- : synthetic anion exchange resins
- **Heavy metal removal**
 - Zeolites, synthetic anion and cation resins, chelating resins
 - Some chelating resins are made to have a high selectivity for specific metals (cations – Cu, Ni, Cd, Zn, ...)

Key references

- Textbook sec 5-10, 5-11, 11-9~11-11

Next class

- Physical unit processes: recent development by WQ&EL, SNU