Physical unit processes III

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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 O_2 in gas phase ↔ 9.08 mg/L O_2 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 or 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_2S, 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 -- $(C_s\text{-}C)$
  - Flux = (mass transferred) / (area) / (time)

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

F = flux of mass transfer $[ML^{-2}T^{-1}]$

K_L *= mass transfer coefficient with liquid as a reference phase* $[LT^{-1}]$

A= area through which mass is transferred $[L^2]$

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:

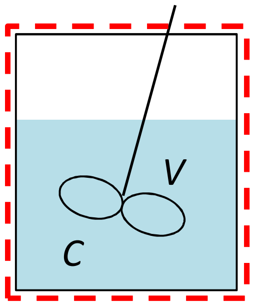
$$r_v = \left.\frac{dC}{dt}\right|_{mass\ transfer} = K_L \frac{A}{V}(C_s - C) = K_L a(C_s - C)$$

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)

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

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

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

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 m^2 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:

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

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

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

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

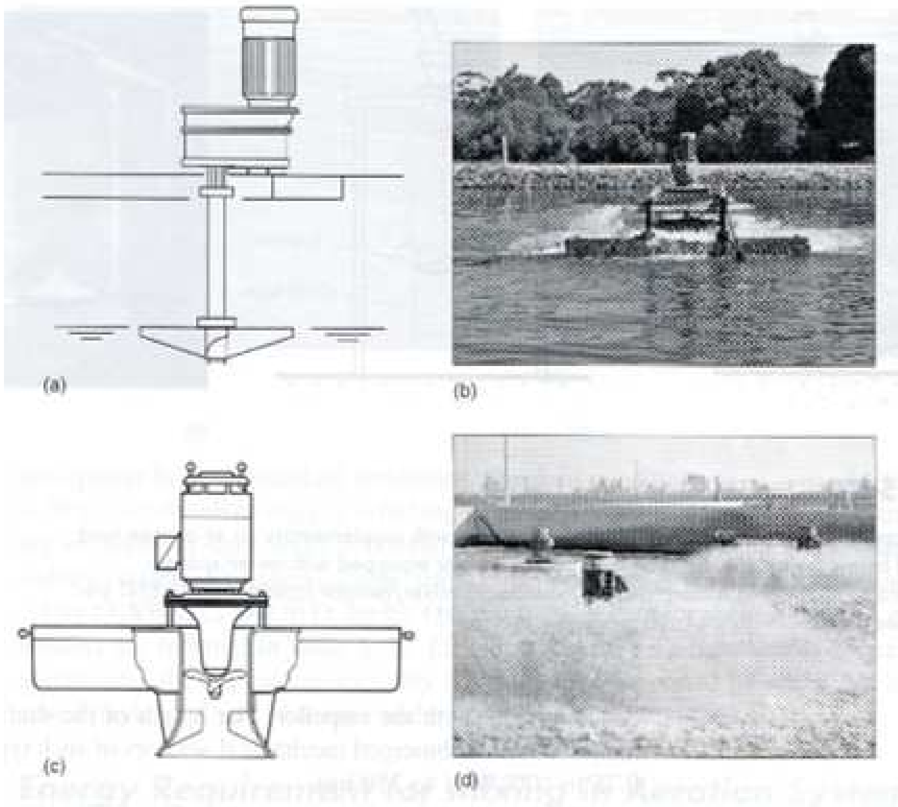
You see it takes a long time for surface reaeration from the atmosphere in the absence of mechanical agitation!

G-L mass transfer ex 1: Aeration

- **Diffused air aeration vs Mechanical aeration**

#1

#2



G-L mass transfer ex 2: Gas stripping

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

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

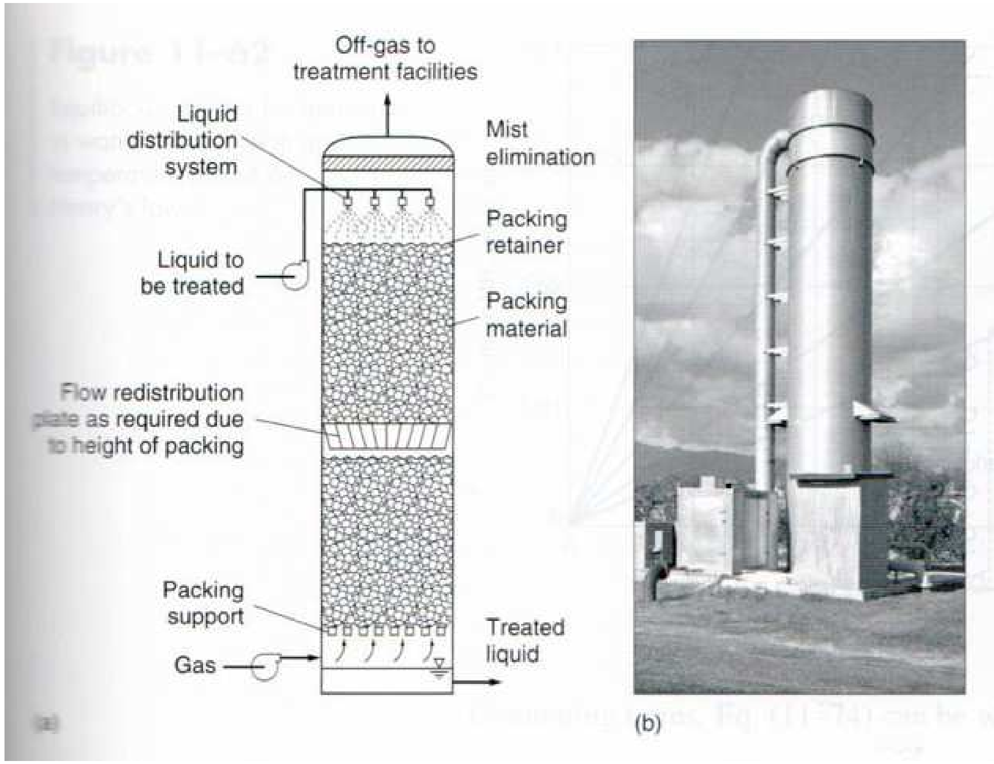
  (for desorption of gas)

- **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



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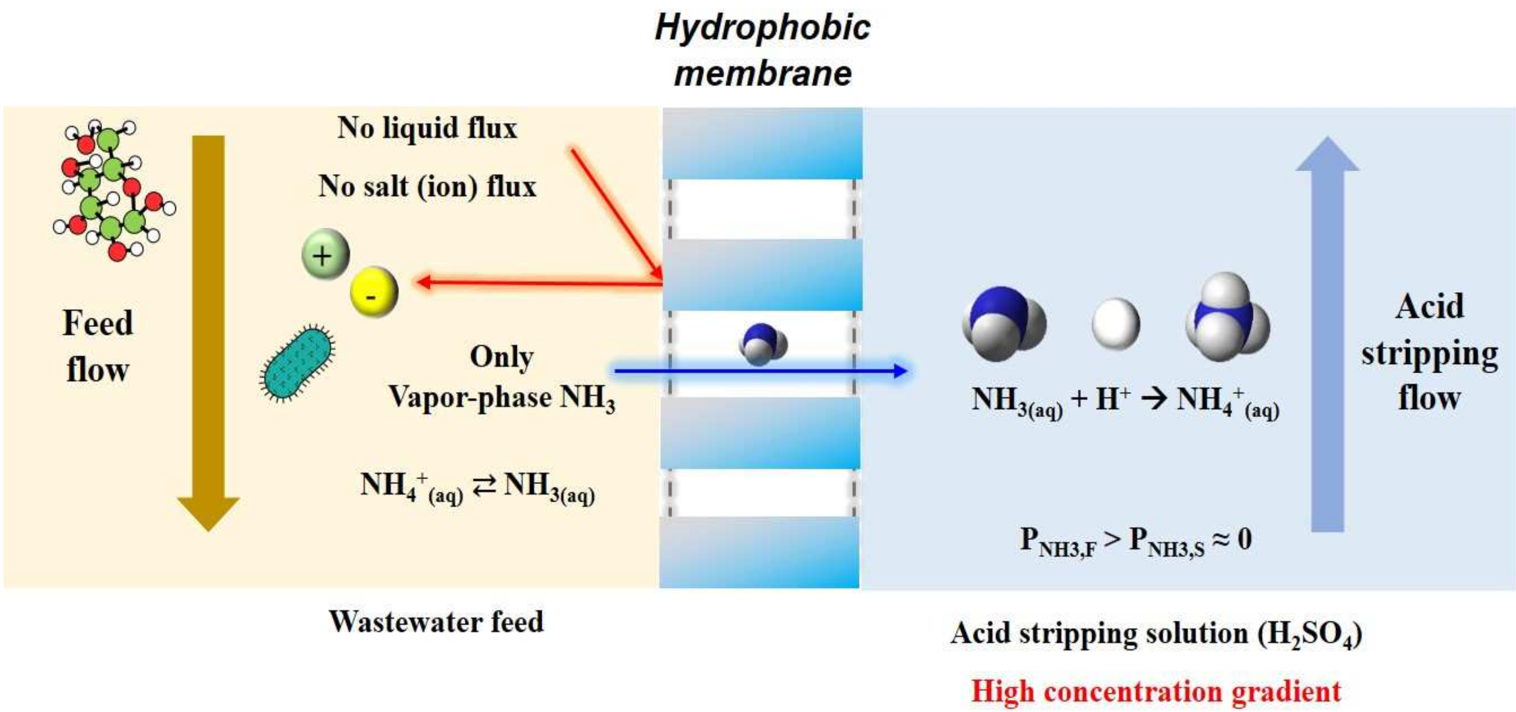
G-L mass transfer ex 3: Gas-permeable membrane

- 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 NH_3/NH_4^+ and CH_4 from wastewater



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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:

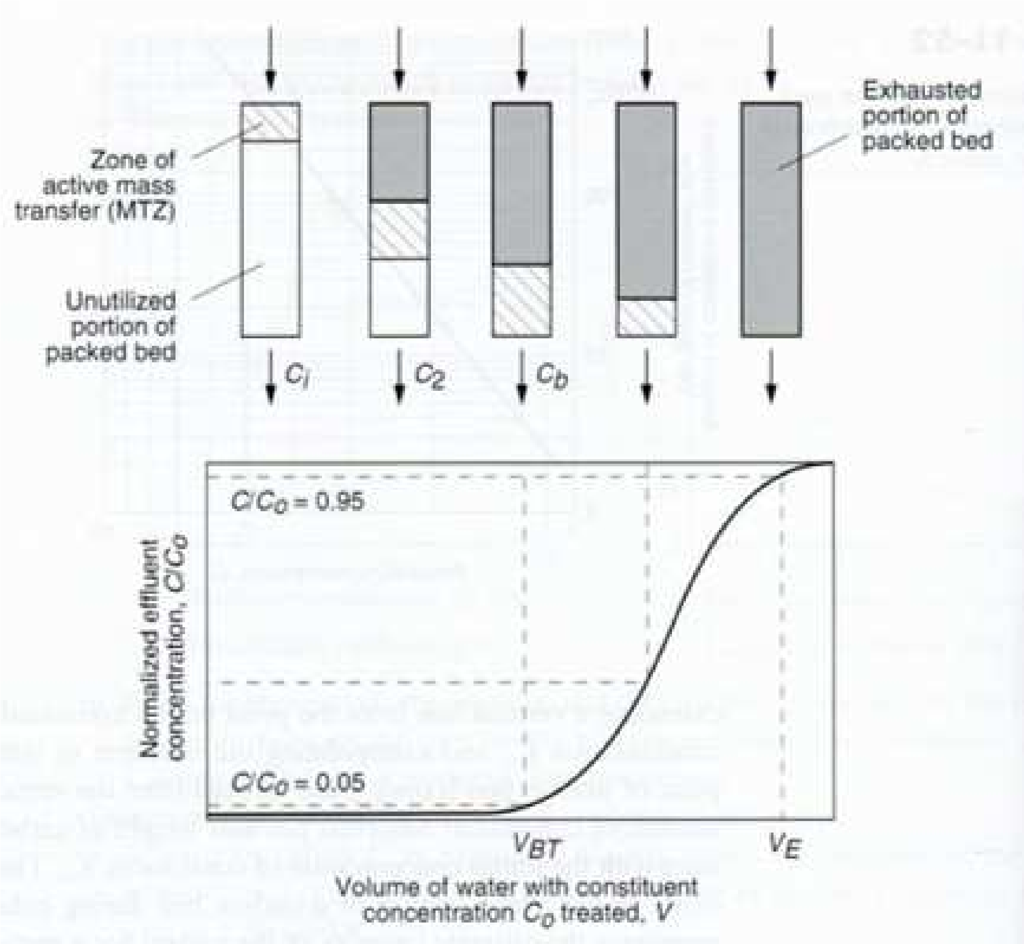
  - refractory organics
  - residual inorganic constituents (nitrogen, sulfides, heavy metals, etc.)
  - odor compounds

#5

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 CO_2 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



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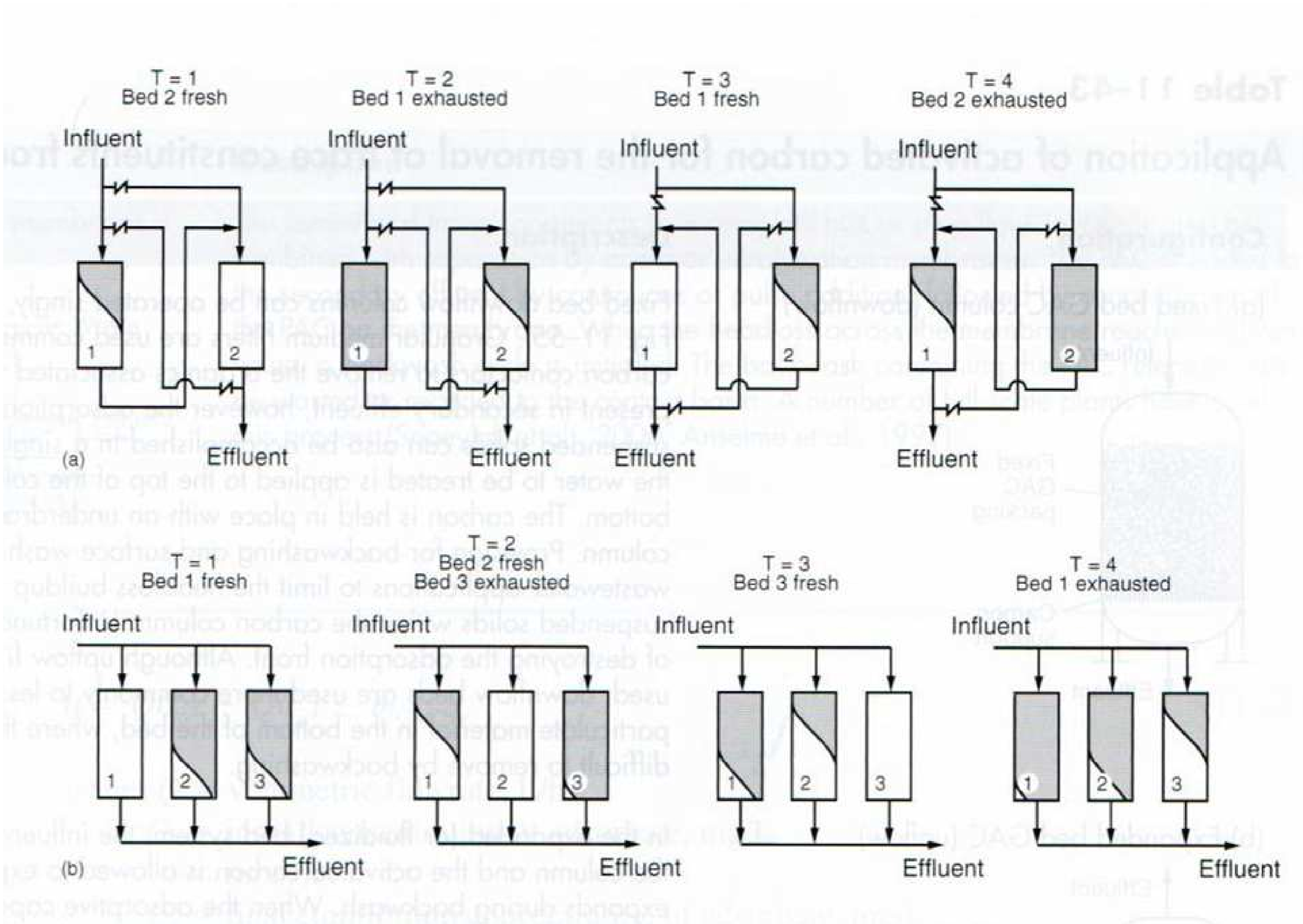
- **Mass transfer zone** (MTZ; dashed zone): adsorption is occurring, some adsorbate conc. in pore-water
- Grey zone: GAC exhausted (adsorption equilibrium with influent), no further adsorption
- **Breakthrough** occurs after adding V_{BT} of influent, but **want full usage of the column**!

GAC columns: configurations



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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, …)

References

#1) https://www.ysi.com/Product/id-7586200/Ceramic-Disc-Diffuser

#2, #3) Metcalf & Eddy, Aecom (2014) Wastewater Engineering: Treatment and Resource Recovery, 5th ed. McGraw-Hill, p. 343, 1247.

#4) Courtesy: Wooram Lee & SeonYoung An

#5) http://www.abbyoo.co.uk/knowledge-centre/activated-carbon

#6, #7) Metcalf & Eddy, Aecom (2014) Wastewater Engineering: Treatment and Resource Recovery, 5th ed. McGraw-Hill, p. 1234, 1235.