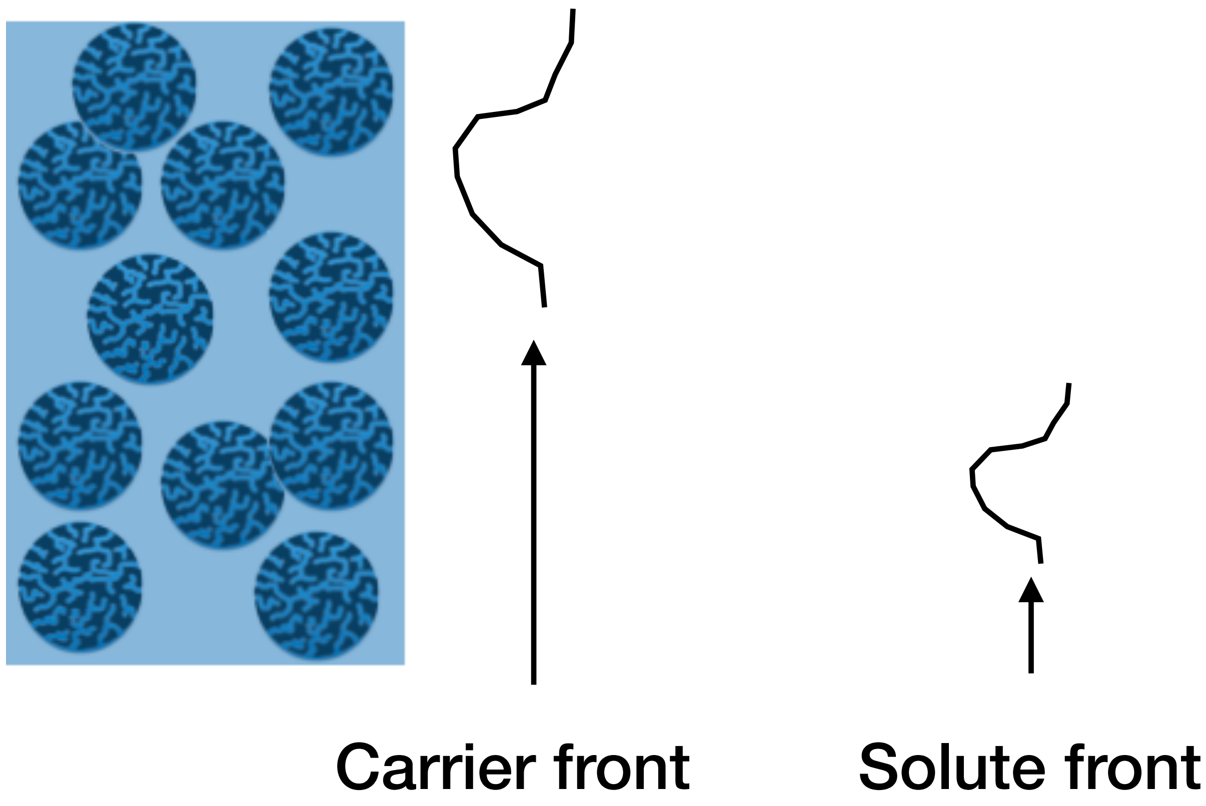
Lecture 11

Continuation of adsorption process

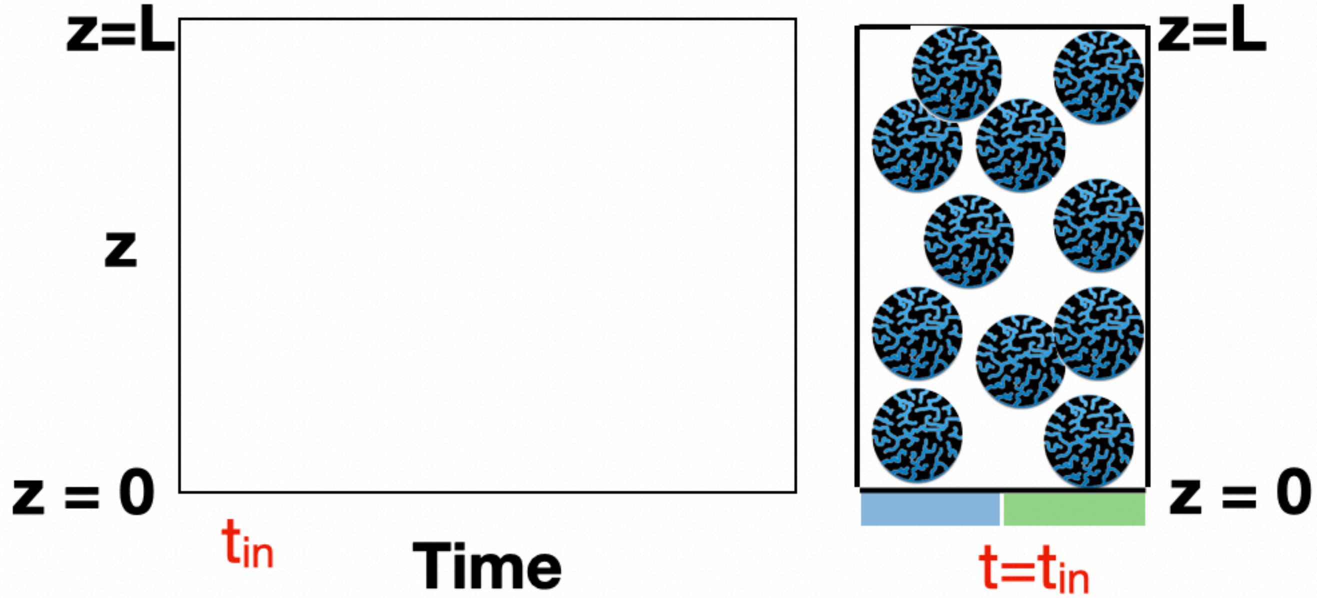
Movement of solute in a column

Why engineering solute velocity is important??

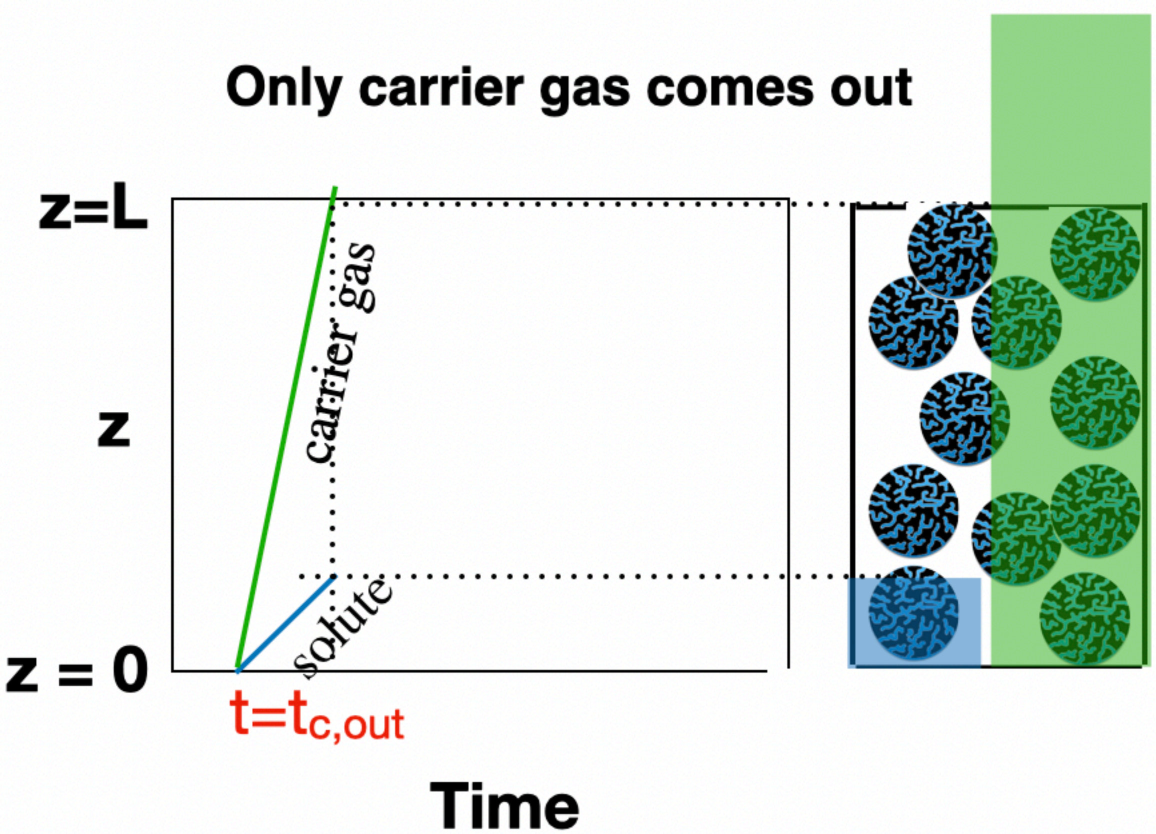
We want overall solute velocity to be smaller than the rest for separation.



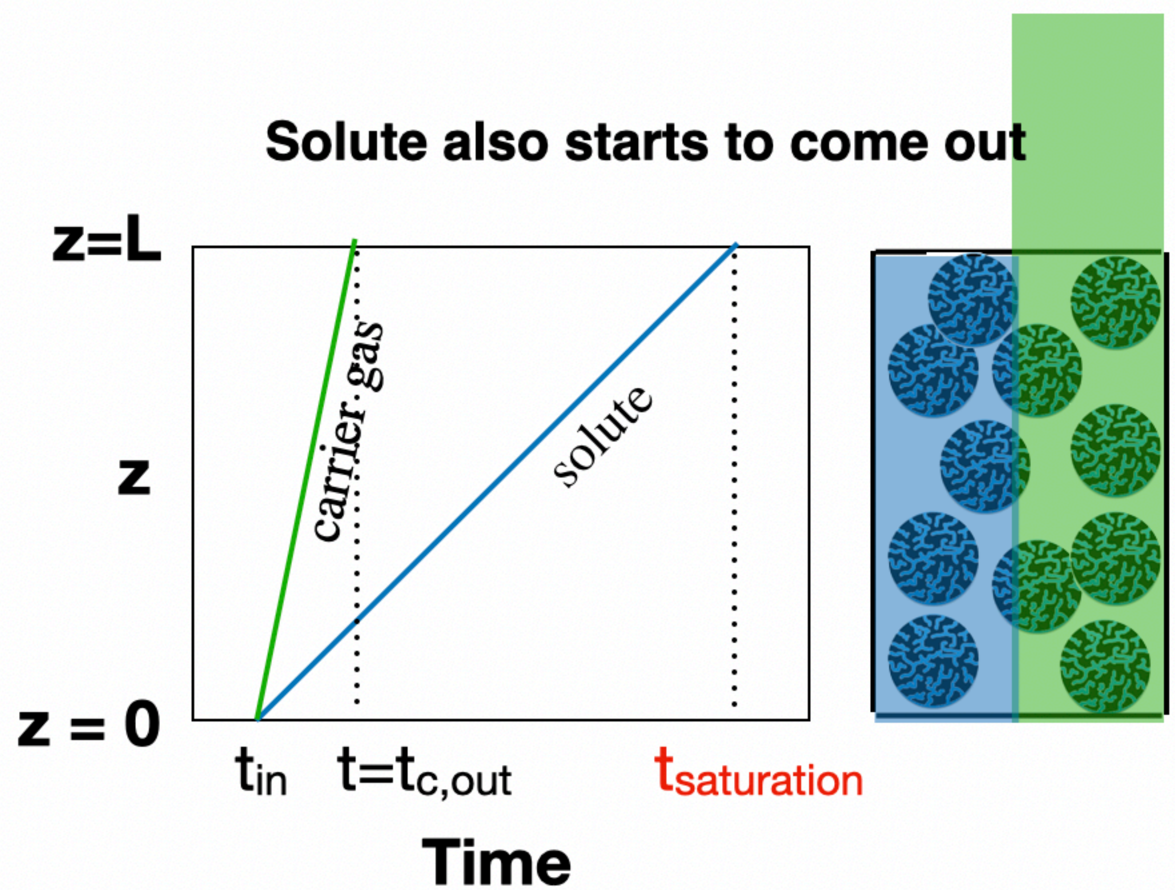
Why keeping track of solute movement is important?



Only carrier gas comes out



Solute also starts to come out



Understanding porosity

Total volume = $A_c L$

Volume available due to pellets packing (interparticle void) = $\varepsilon_e A_c L$

Total volume of pellets = $(1 - \varepsilon_e) A_c L$

Pellets are also porous, with porosity (intra-particle) ε_p,
so available volume in pellet

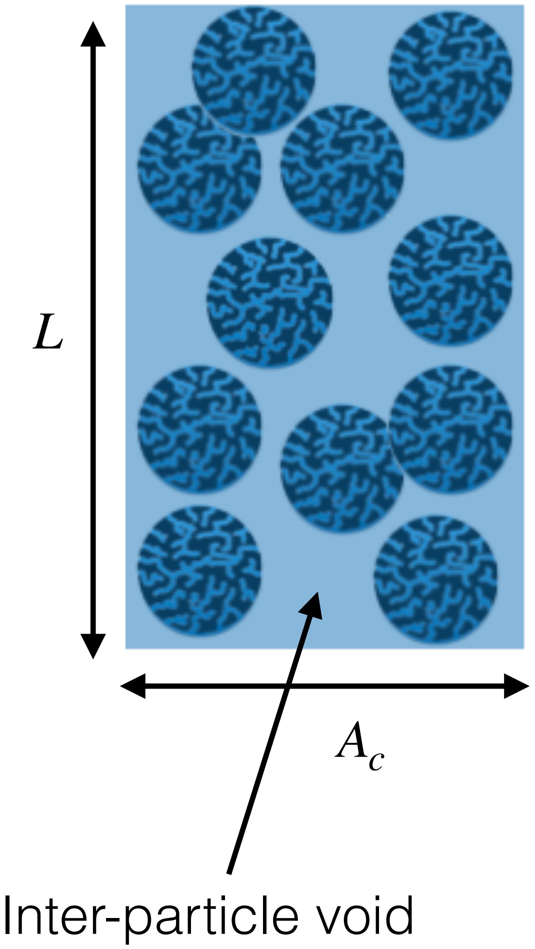
$$= \varepsilon_p (1 - \varepsilon_e) A_c L$$

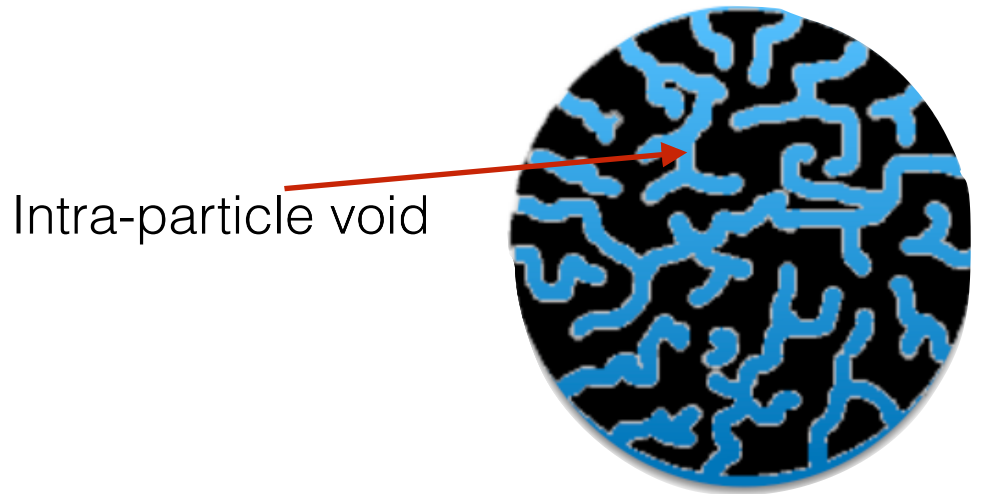
This is where molecules diffuse (gas or vapor phase) to adsorb

Nonporous volume of pellet =

$$(1 - \varepsilon_e) A_c L - \varepsilon_p (1 - \varepsilon_e) A_c L = (1 - \varepsilon_p)(1 - \varepsilon_e) A_c L$$

This is where molecules adsorb





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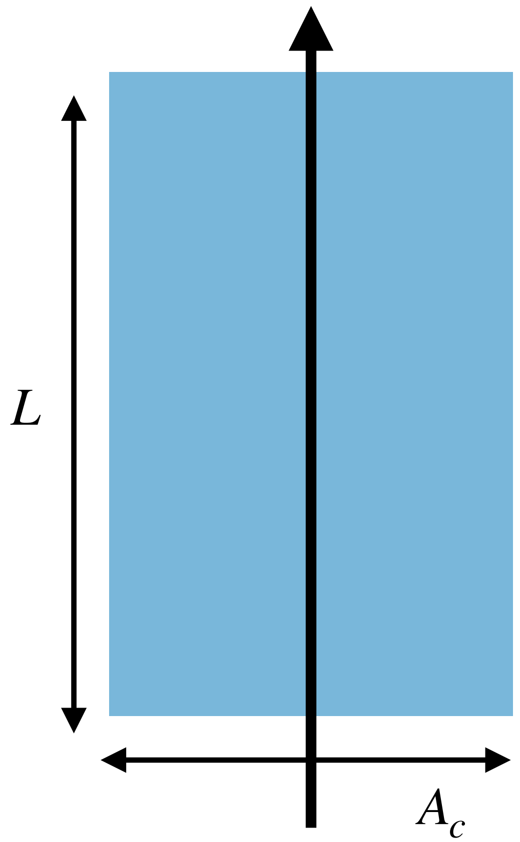
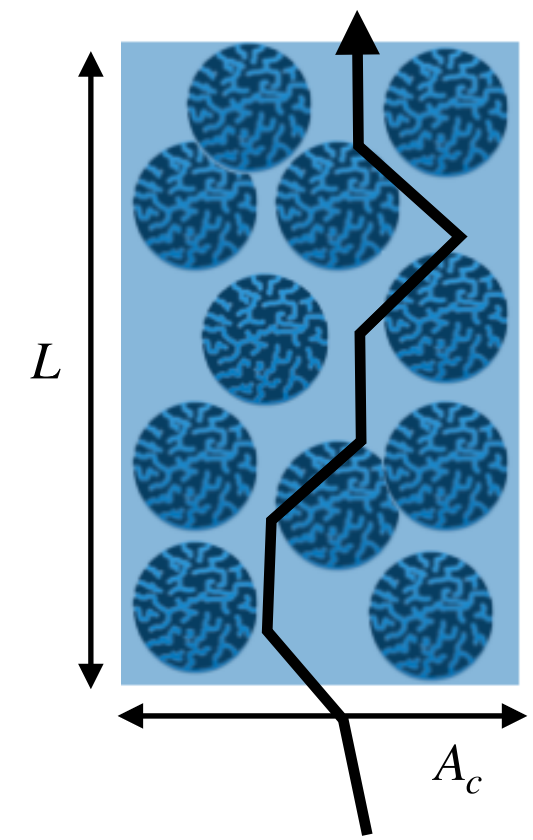
Role of velocity in adsorption process: Superficial and interstitial velocities



$\varepsilon_e = 1$
Empty container
(no adsorbent)



Superficial velocity

Effective cross–sectional area $= A_c$

$$v_{super} = \frac{Q}{A_c}$$

Interstitial velocity

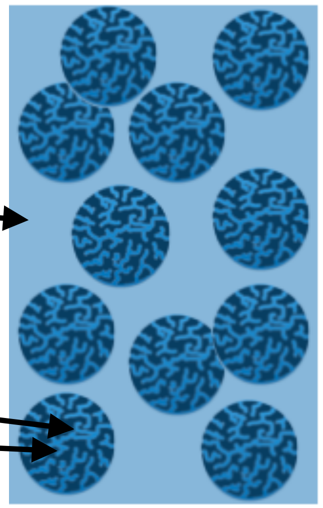
Effective cross–sectional area $= \varepsilon_e A_c$

$$v_{inter} = \frac{Q}{\varepsilon_e A_c}$$

Movement of solute in a column: average velocity

Solute position

1. Either in the inter particle void (between 2 particles) $v_{inter} = \frac{Q}{\varepsilon_e A_c}$
2. Or diffusing inside a particle $v \approx 0$
3. Or adsorbed in the particle pores $v = 0$



Average velocity of solute,

$$u_s = fraction\ of\ solute\ in\ void * v_{inter} + fraction\ of\ solute\ in\ particle * 0$$

$$\Rightarrow u_s = fraction\ of\ solute\ in\ void * v_{inter}$$

$$fraction\ of\ solute\ in\ void = \frac{amount\ in\ void}{amount\ in\ void + amount\ difusing\ in\ particle + amount\ adsorbed}$$

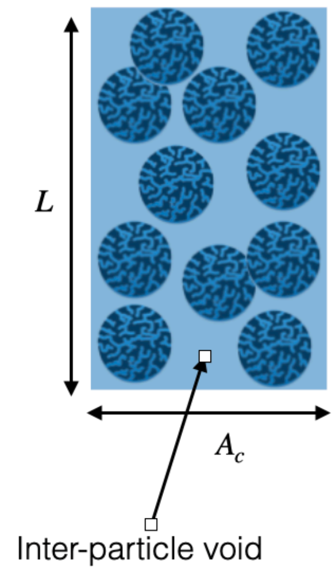
Movement of solute in a column

$$u_s = v_{inter} * \frac{amount\ in\ void}{amount\ in\ void + amount\ difusing\ in\ particle + amount\ adsorbed}$$

Let's increase concentration from c to c+Δc

$$q = f(P) = g(c)$$

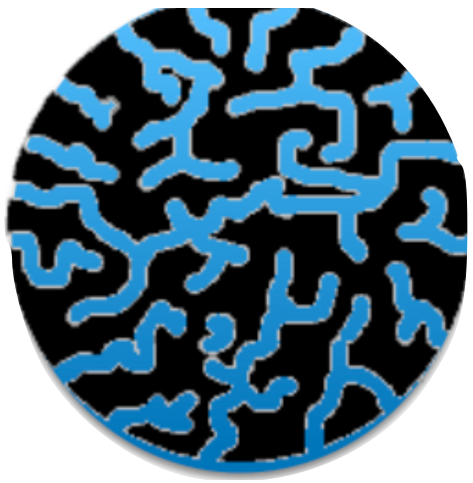
Adsorbed amount changes from q to q+Δq



Moles increased in inter-particle void = void volume * Δc = $(\varepsilon_e A_c L)\Delta c$

Moles increased inside particle (diffusing) $= \left[(1-\varepsilon_e)A_c L\right]\varepsilon_p * \Delta c$

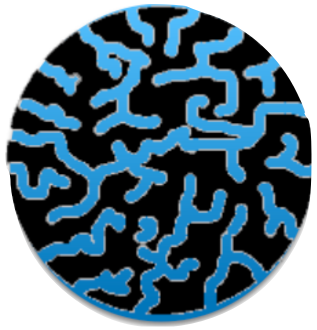
- Often, we have pore-size-distribution (small and large pores)
- Some molecules can not enter too small pore
- For this, a distribution coefficient is defined, K_d



Actual porosity in the particle $= K_d \varepsilon_p$

Moles increased inside particle (diffusing) $= \left[(1-\varepsilon_e)A_c L\right]K_d\varepsilon_p * \Delta c$

Movement of solute in a column



Moles increased in void = $(\varepsilon_e A_c L)\Delta c$

Moles increased in intra-particle pores (diffusing) $= [(1-\varepsilon_e)A_c L]K_d\varepsilon_p * \Delta c$

Nonporous volume of pellet = $(1-\varepsilon_p)(1-\varepsilon_e)A_c L$

Moles adsorbed $= (1-\varepsilon_p)(1-\varepsilon_e)A_c L\rho_{adsorbent}(\Delta q)$

Unit of q
mol solute/kg adsorbent

$$u_s = v_{inter} * \frac{amount\ in\ void}{amount\ in\ void + amount\ difusing\ in\ particle + amount\ adsorbed}$$

$$u_s = v_{inter} * \frac{\varepsilon_e * (A_c L) * \Delta c}{\varepsilon_e * (A_c L) * \Delta c + (1-\varepsilon_e)*(K_d\varepsilon_p)*(A_c L)*\Delta c + (1-\varepsilon_e)*(1-\varepsilon_p)*(A_c L)*\rho(\Delta q)}$$

Rearranging, we get

$$u_s = \frac{v_{inter}}{1 + \left(\frac{1-\varepsilon_e}{\varepsilon_e}\right)*(K_d\varepsilon_p) + \left(\frac{1-\varepsilon_e}{\varepsilon_e}\right)*(1-\varepsilon_p)*\rho\left(\frac{\Delta q}{\Delta c}\right)}$$

Movement of solute in a column: linear isotherm

$$u_s = \frac{v_{inter}}{1 + \left(\frac{1-\varepsilon_e}{\varepsilon_e}\right) * \left(K_d \varepsilon_p\right) + \left(\frac{1-\varepsilon_e}{\varepsilon_e}\right) * \left(1-\varepsilon_p\right) * \rho \left(\frac{\Delta q}{\Delta c}\right)}$$

At low pressure $1 + KP \approx 1$

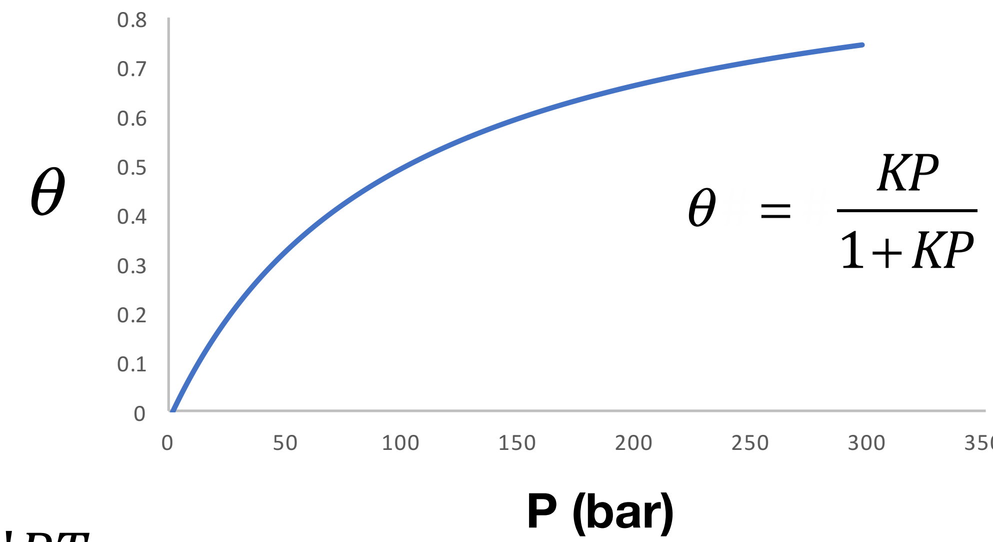
$$\theta = \frac{q}{q^{sat}} = KP$$

$$q = q^{sat} KP$$

$$\Delta q = q^{sat} K \left(\Delta P\right)$$

$$\frac{\Delta q}{\Delta c} = q^{sat} K \left(\frac{\Delta P}{\Delta c}\right) = q^{sat} K \left(RT\right) = q^{sat} KRT = K'RT$$

Langmuir isotherm



$$u_s = \frac{v_{inter}}{1 + \left(\frac{1-\varepsilon_e}{\varepsilon_e}\right) * \left(K_d \varepsilon_p\right) + \left(\frac{1-\varepsilon_e}{\varepsilon_e}\right) * \left(1-\varepsilon_p\right) * \rho K'RT}$$

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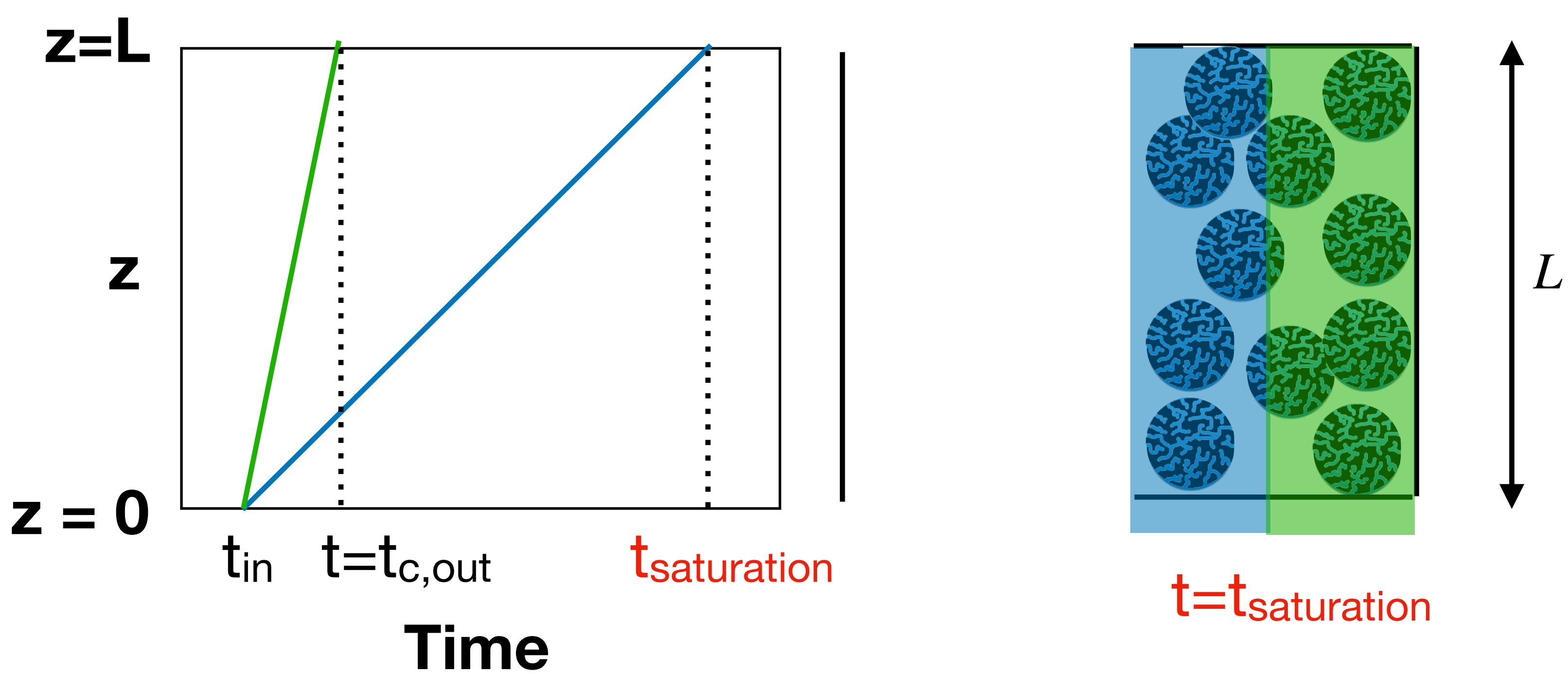
Operation window for adsorption: Breakthrough time

$$u_s = \frac{v_{inter}}{1 + \left(\frac{1-\varepsilon_e}{\varepsilon_e}\right) * \left(K_d \varepsilon_p\right) + \left(\frac{1-\varepsilon_e}{\varepsilon_e}\right) * \left(1-\varepsilon_p\right) * \rho \left(\frac{\Delta q}{\Delta c}\right)}$$

Breakthrough time: time when the solute first appears at the end of column



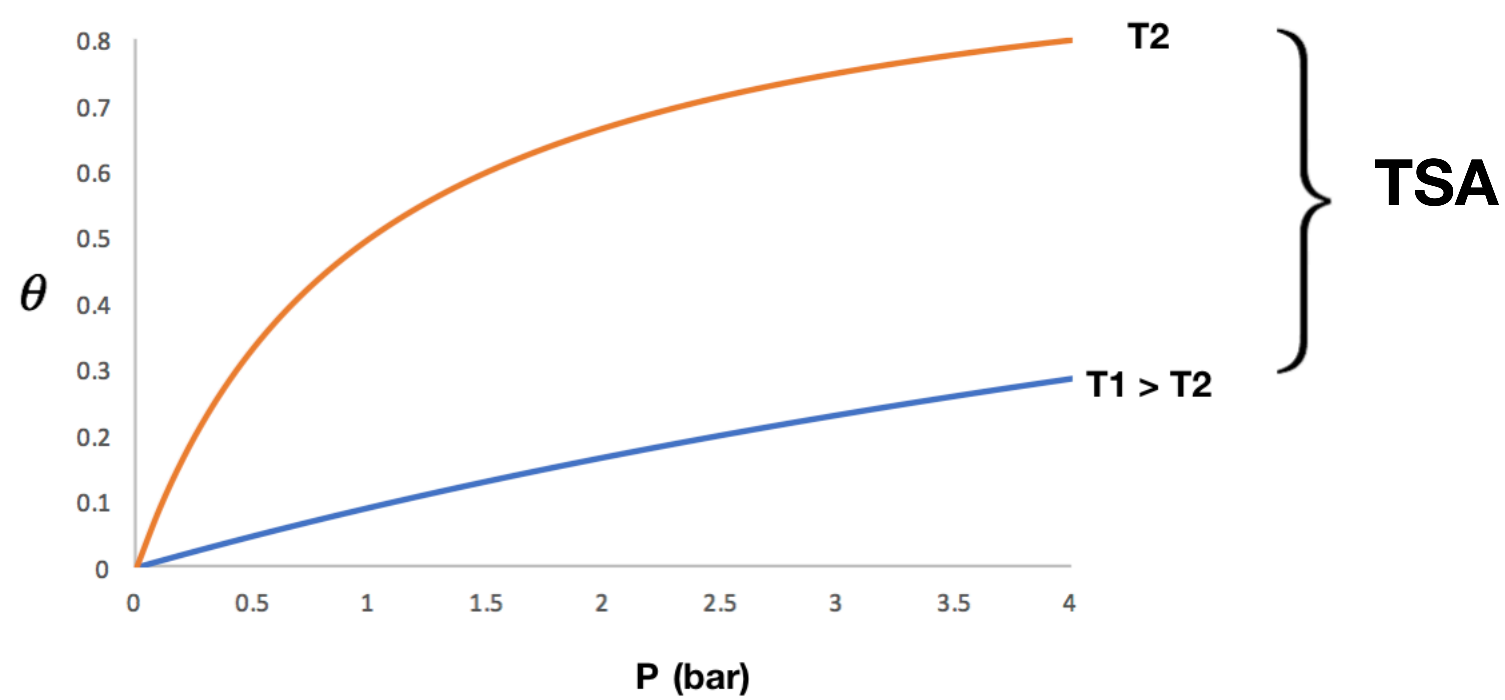
$$Breakthrough \;\; time = t_{saturation} - t_{in} = \frac{L}{u_s}$$

Breakthrough time

Do you want breakthrough time to be smaller or larger?

Temperature swing adsorption (TSA)

- Adsorption processes alternate between adsorption and desorption steps.
- Two popular methods of regeneration
    - Temperature swing adsorption (TSA)
    - Pressure swing adsorption (PSA)



Used for

- dilute feeds (longer feed period)
- adsorbates that are strongly adsorbed (high temperature needed to desorb)

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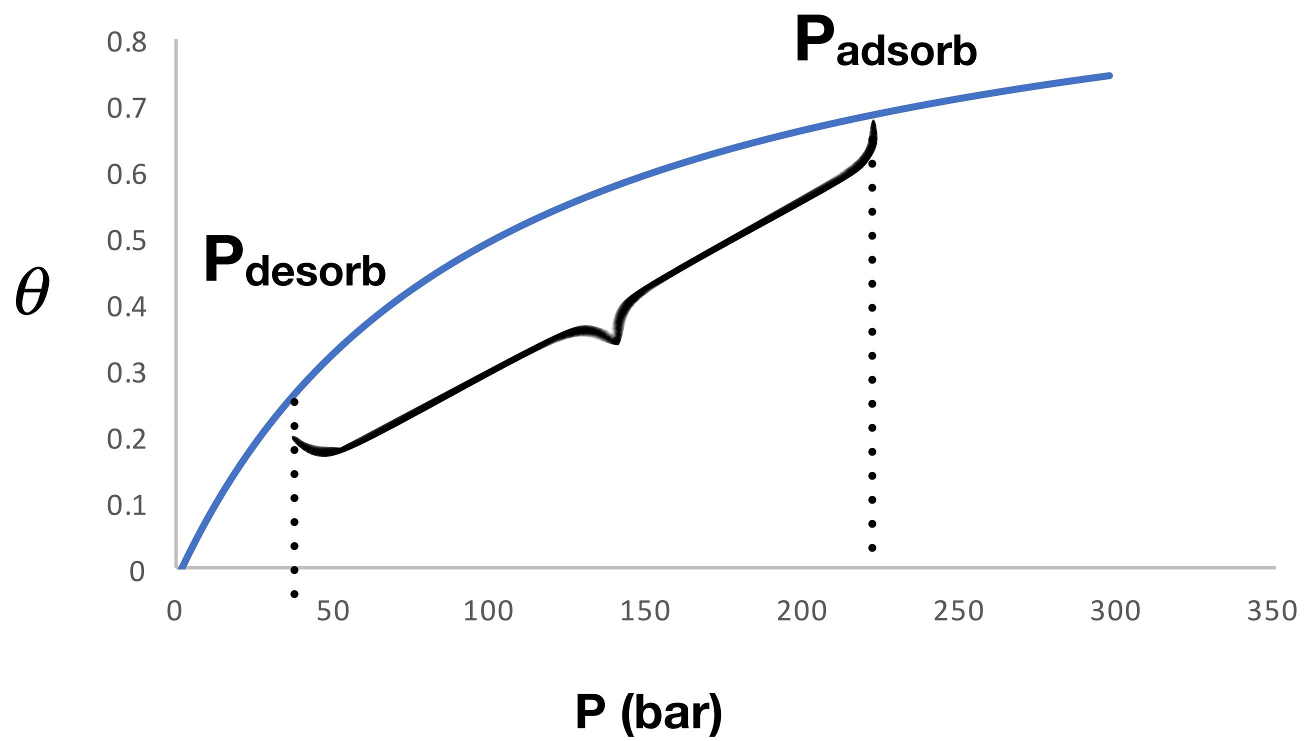
Pressure swing adsorption (PSA)



Used for

- concentrated feeds (shorter feed time is feasible)
- adsorbates that are not strongly adsorbed (no need for high temperature regeneration)

Membrane-based processes

Intended learning outcome

1. Understand difference and similarities between several kinds of membranes.
2. Understand key parameters for membrane separation.

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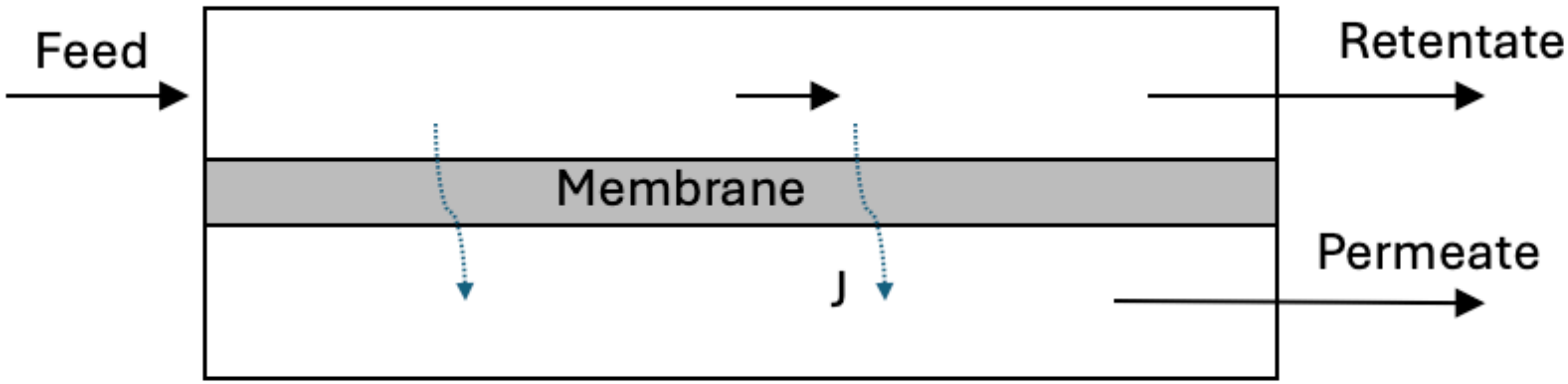
Membrane separation



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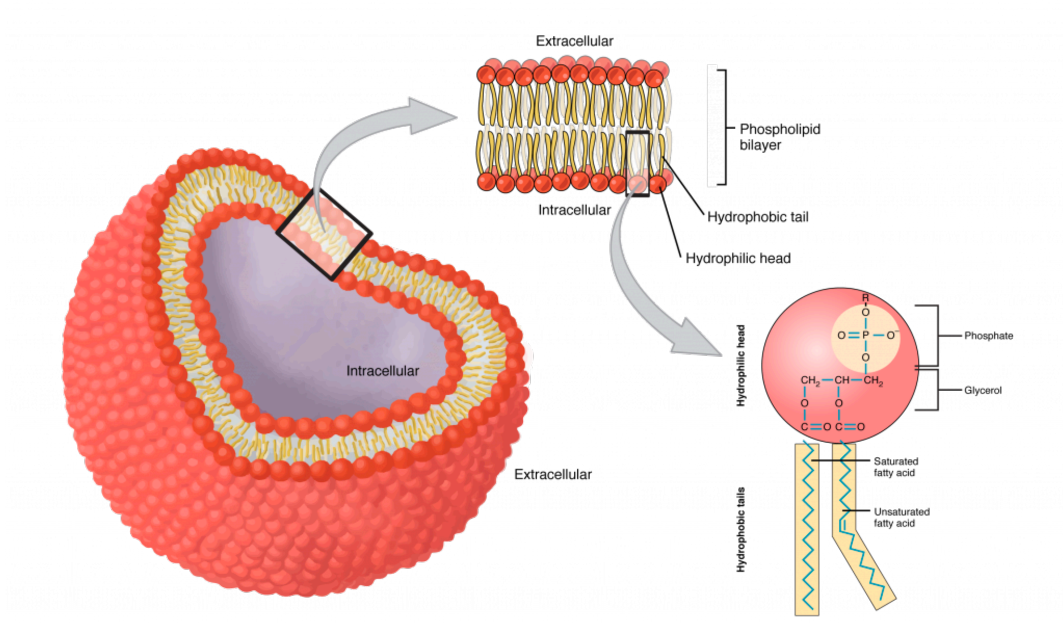
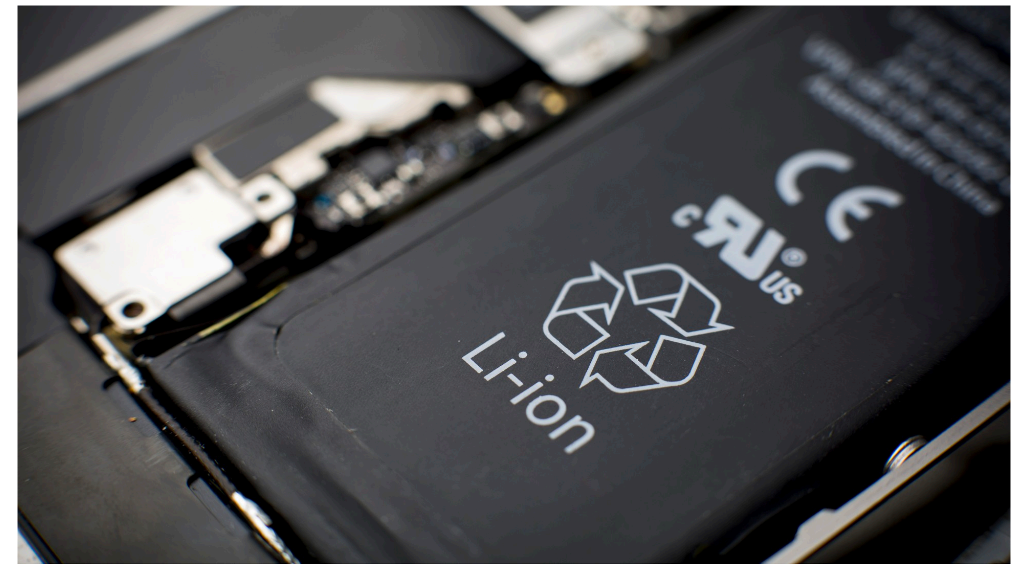
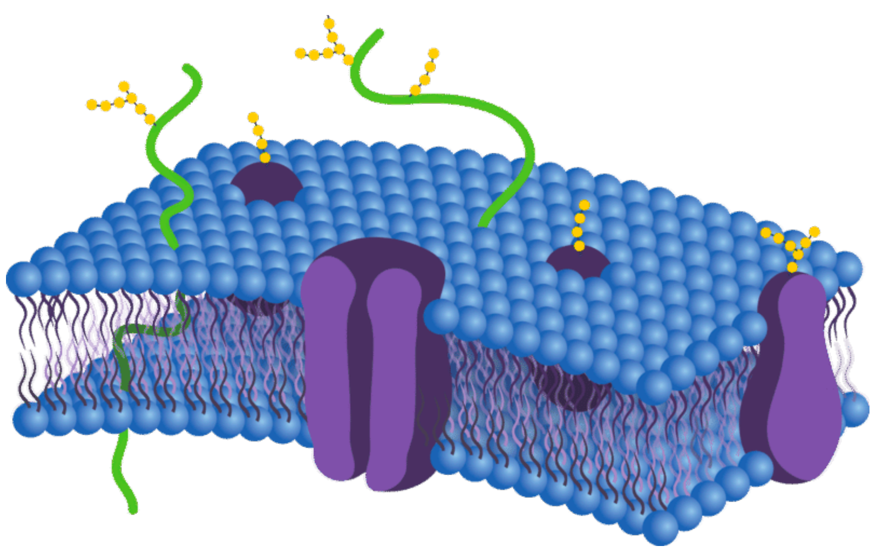
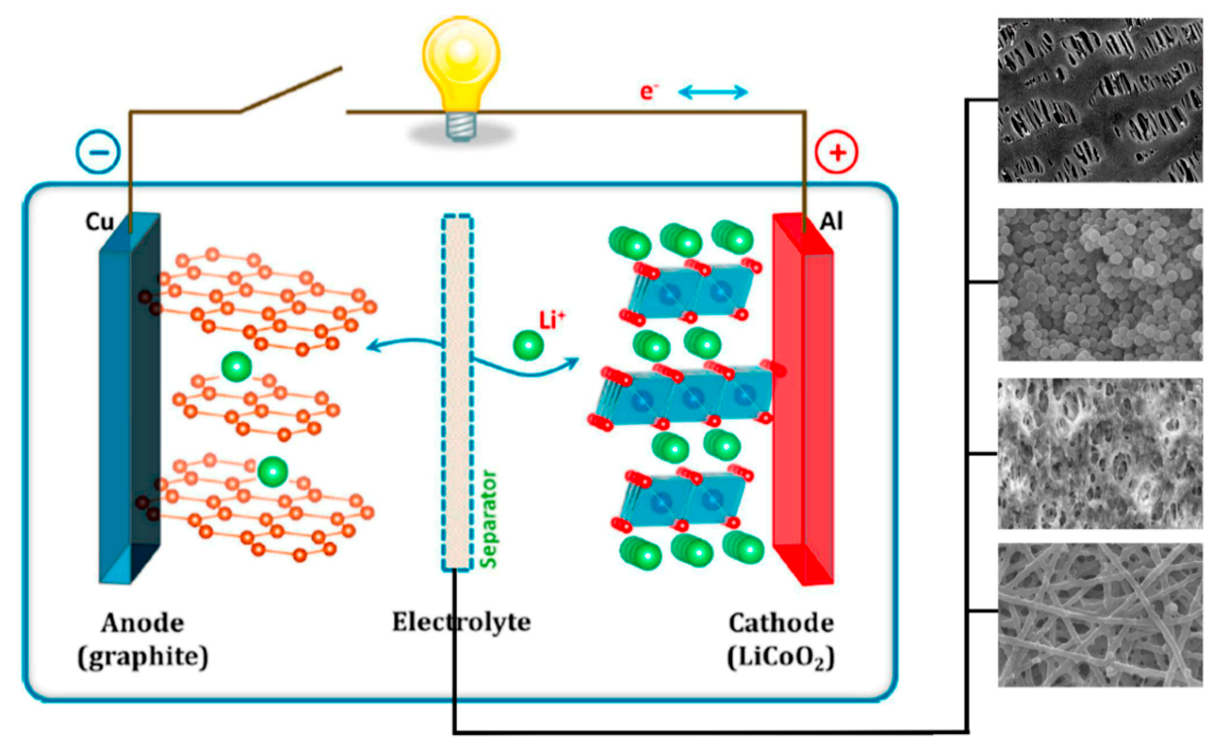
Where are membranes in our daily life







Cell membrane hosting selective water and ion channels.



Ion-exchange membrane in batteries

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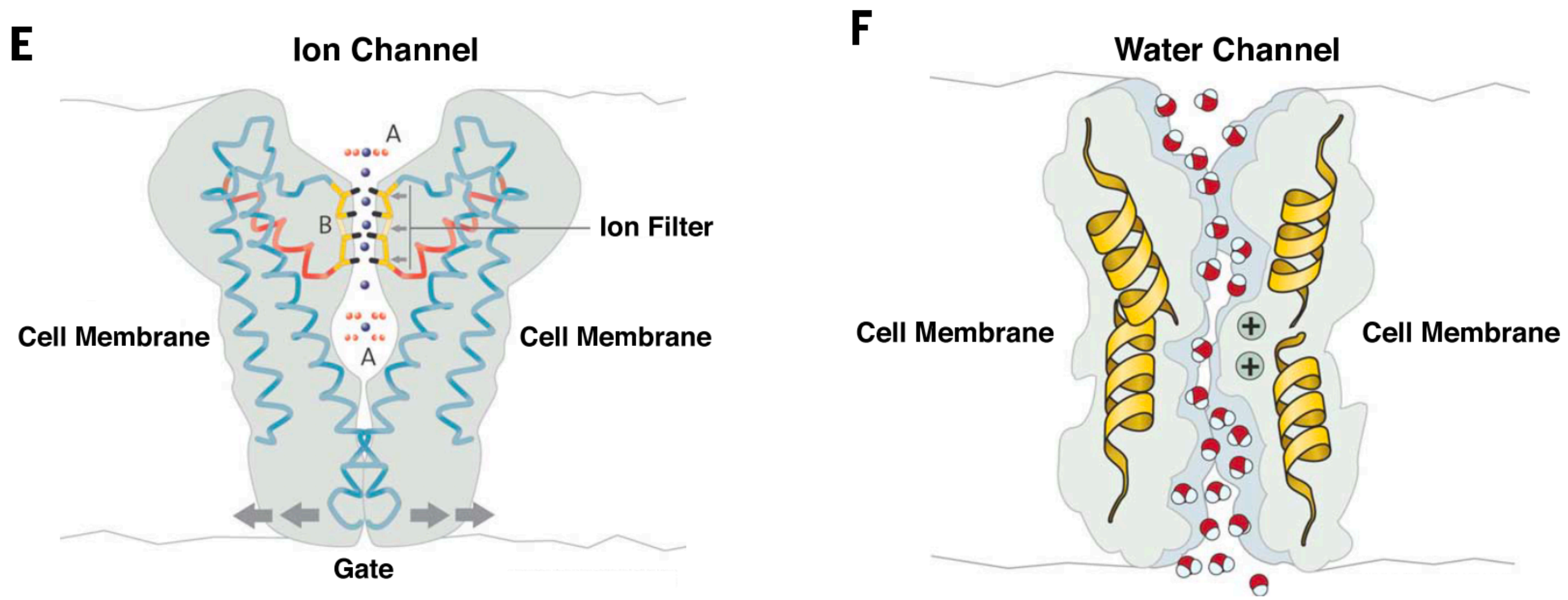
Ultimate limit of membrane (flux)



Nature does the perfect job in terms of membrane separation

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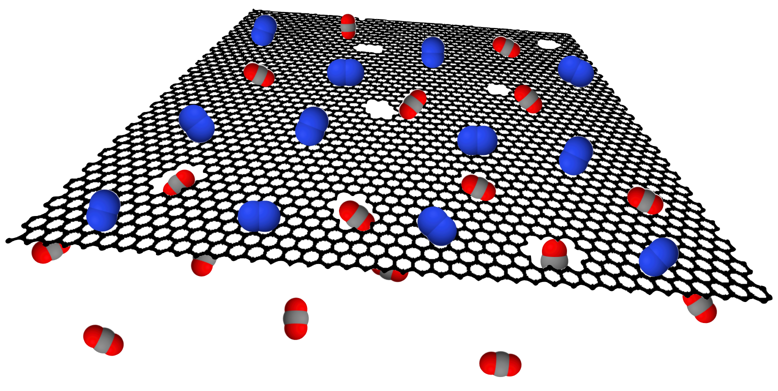

Even an atom-thick film can separate molecules

Membranes in industrial processes

Some examples

- **Gas/vapor separation**
  - CO_2/CH_4 (natural gas from wells)
  - CO_2/N_2 (carbon capture).
  - Water vapor dehydration.
- **Liquid separation**
  - Drinking water from seawater, brine,
  - Ethanol production (removal of water),
  - Nanofiltration (juice concentration)
- **Dialysis** (blood purification, removal of solutes).
- **Ion separation** (e.g., ions in electrochemical cells).

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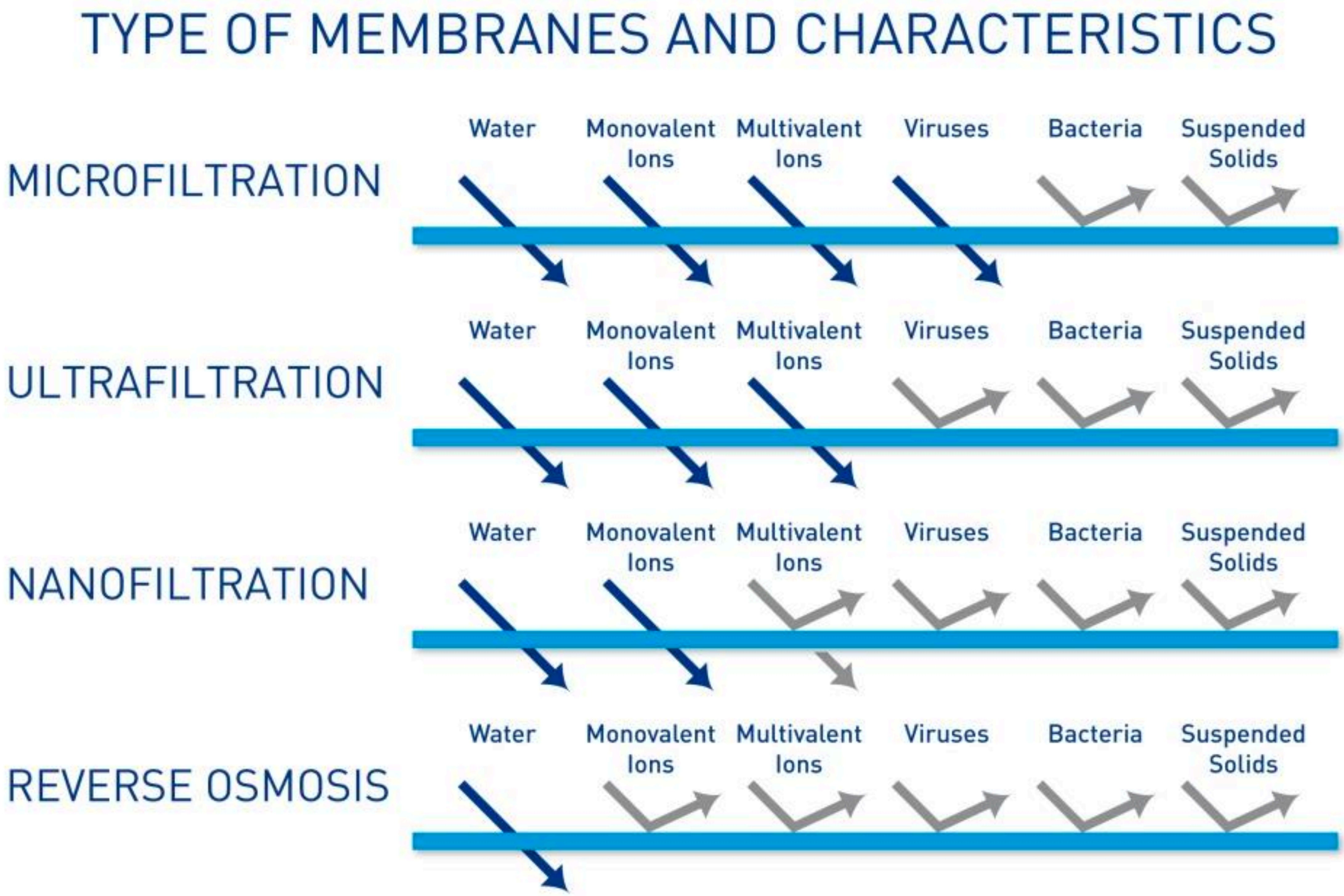
Water filtration at large scale is carried out by membranes



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Reverse osmosis

Extensive water and solvent purification applications:

- Potable water from sea or brackish water
- Ultrapure water for food processing and electronic industries
- Pharmaceutical grade water
- Water for chemical, pulp & paper industry
- Waste treatment

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A large-scale membrane plant for water purification

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Reverse Osmosis problem

If cost to purify saltwater water stream scales linearly with osmotic pressure (cost ∝ osmotic pressure), how much higher would be the cost to purify seawater (1 M NaCl) as compared to wastewater (0.1 M NaCl)?

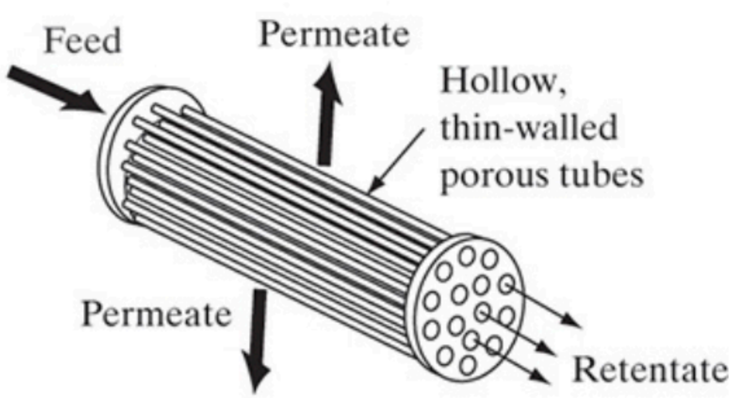
Correlation for osmotic pressure

$$\Pi = \frac{RT}{V_w} \ln \frac{1}{a_w} \qquad \Rightarrow \Pi = RTC_s$$

$$\frac{\Pi_{\text{wastewater}}}{\Pi_{\text{seawater}}} = \frac{C_{\text{wastewater}}}{C_{\text{seawater}}} = 0.1$$

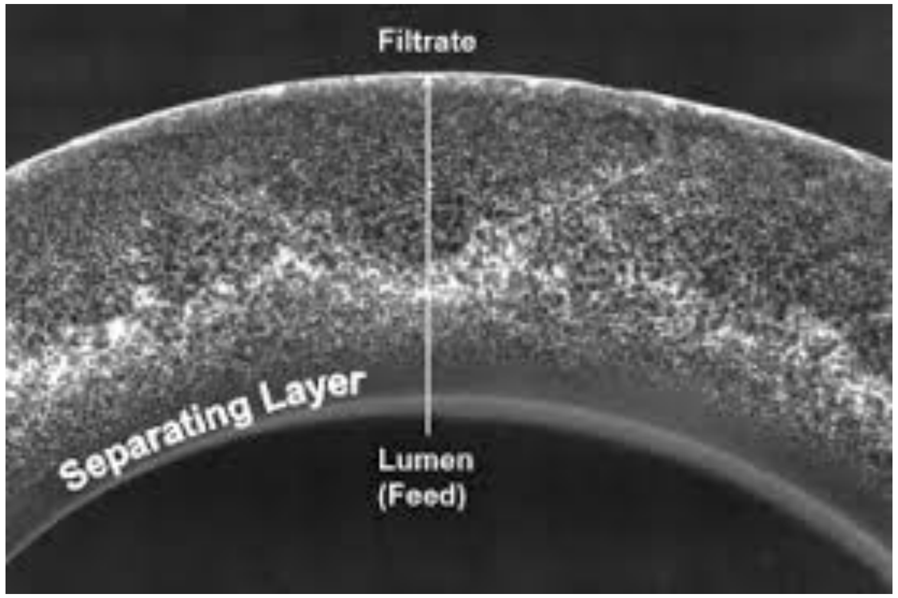
So it will take 10 times higher cost to purify seawater compared to wastewater !

Membrane configurations: hollow-fibre

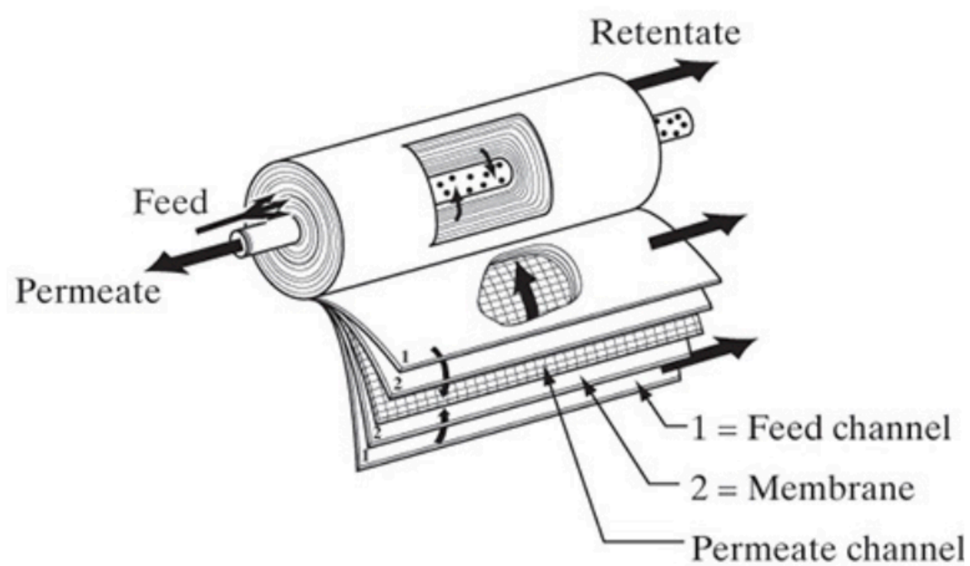


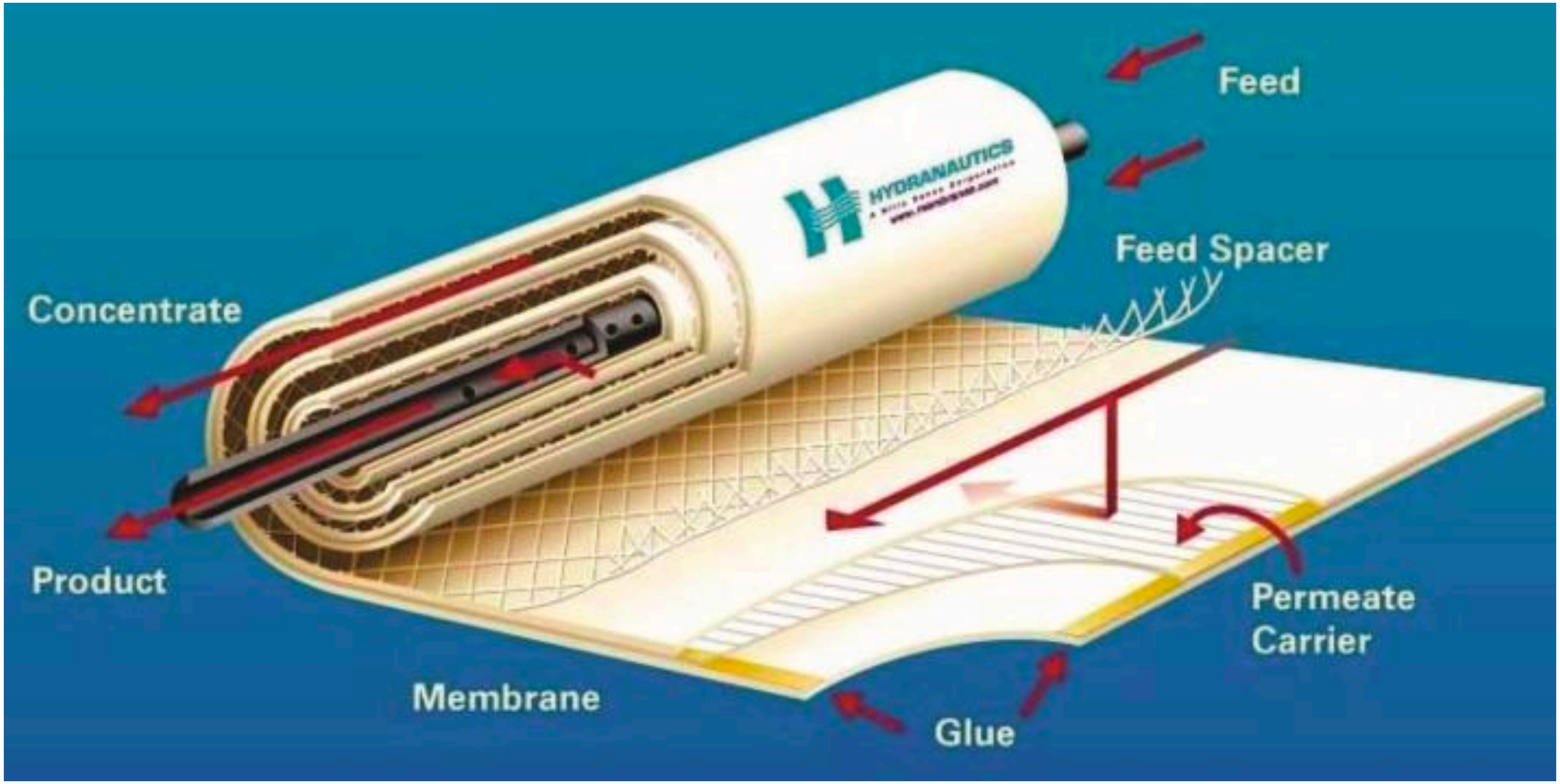
Hollow-fibre

(like shell and tube heat exchanger)

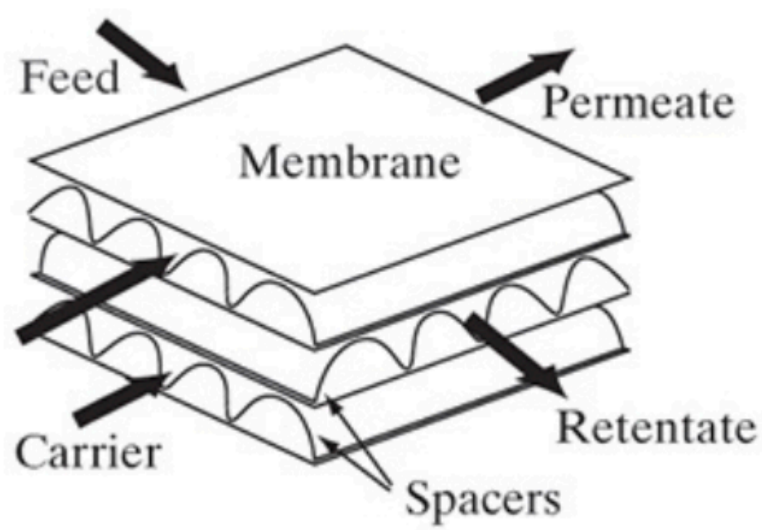


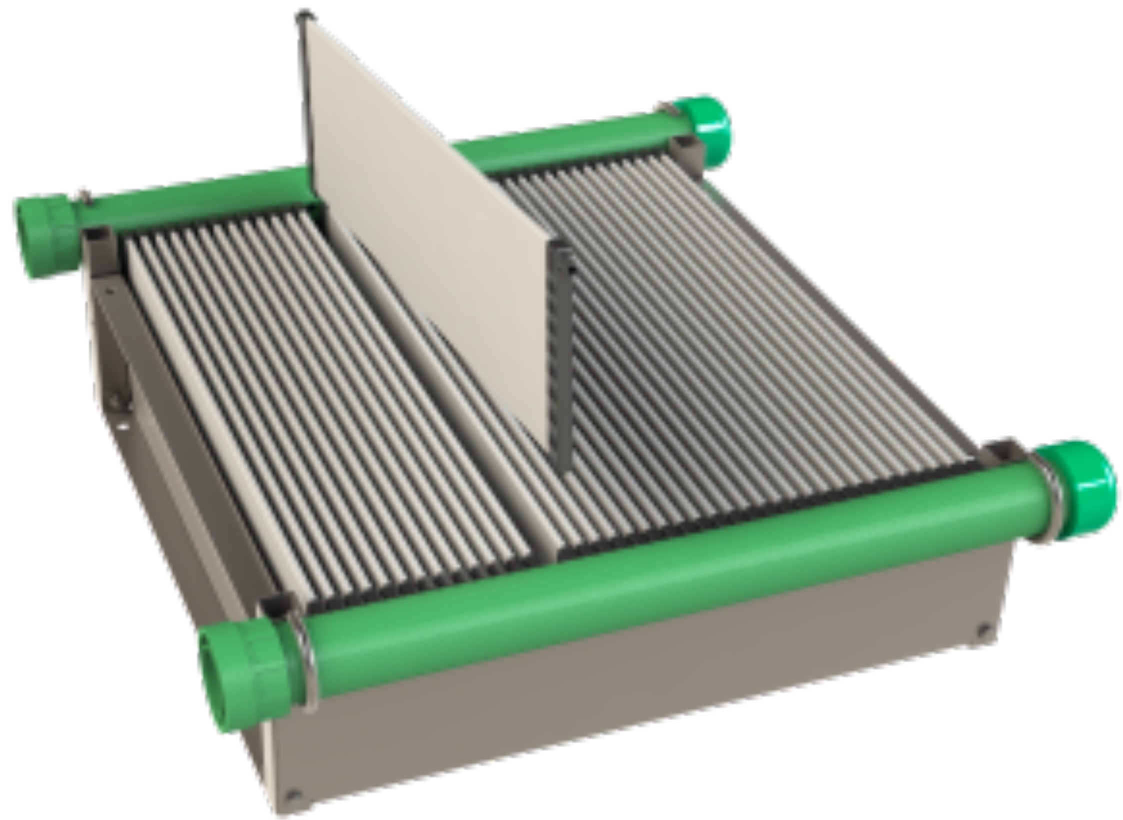
Membrane configurations: spiral-wound





Membrane configurations: plate and frame





Three popular membrane configurations

	Hollow fiber	Spiral wound	Plate and frame
Manufacturing cost	$	$$	$$$
Packing density (m2/m3)	10000	200-1000	50-100
Fouling (blocking of membrane)	High	medium	Low

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Membrane-based separation

Separation process	Equilibrium-stage	Steady-state
Distillation	Yes	Yes
Absorption	Yes	Yes
Liquid-Liquid Extraction	Yes	Yes
Membranes	No	Yes
Adsorption	No	No

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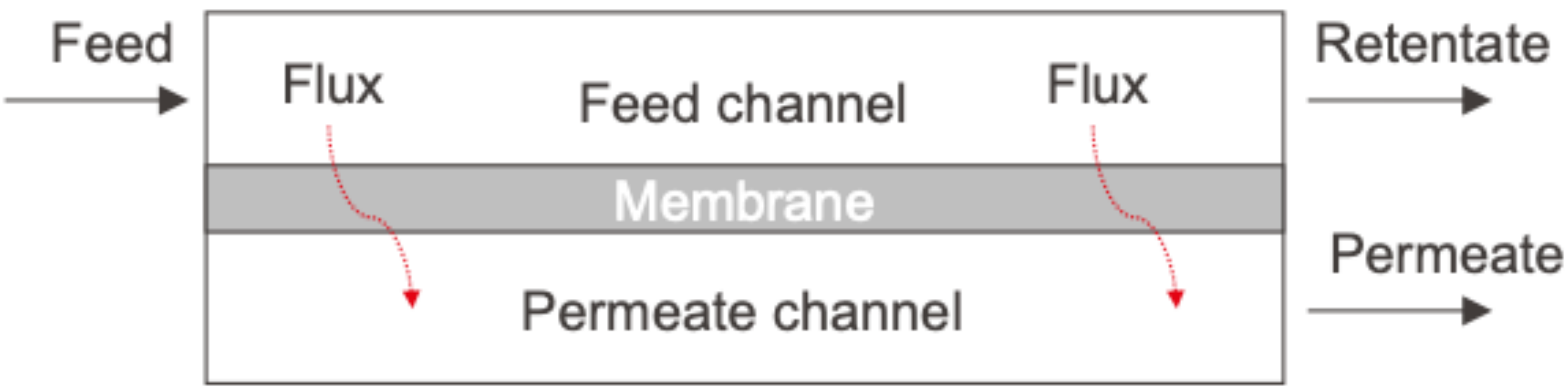
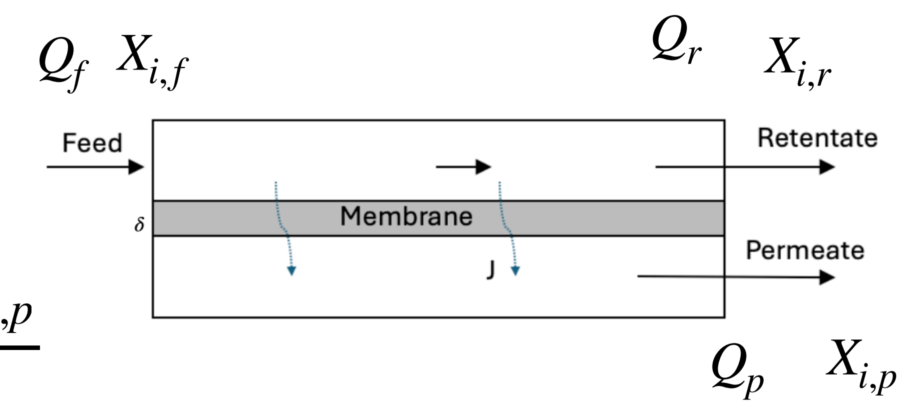
What are important parameters in membrane separation ?



Several important variables



$$J_1 = \text{flux of component 1} = \frac{\text{crossover of component 1}}{\text{membrane area}} = \frac{Q_{1,p}}{A} = \frac{Q_p * X_{1,p}}{A}$$

$$N_1 = \text{permeance of component 1} = \frac{\text{flux of component 1}}{\text{pressure difference}} = \frac{J_1}{\Delta P_1} = \frac{Q_{1,p}}{A \Delta P_1}$$

$$\bar{N}_1 = \text{permeability of component 1} = \text{permeance * thickness} = N_1 * \delta = \frac{J_1 \delta}{\Delta P_1} = \frac{Q_{1,p}\delta}{A \Delta P_1}$$

Permeability is material property

$$\alpha_{12} = \text{selectivity between components 1 and 2} = \frac{N_1}{N_2} = \frac{(J_1/\Delta P_1)}{(J_2/\Delta P_2)}$$

It is not the ratio of flux but permeance or permeability

Units used for gas separation membranes

Permeability

SI unit: mole m^{-1} s^{-1} Pa^{-1}

Popular unit: barrer

1 barrer = 3.35*10^{-16} mole m^{-1} s^{-1} Pa^{-1}

$$1 \ \ barrer \ = \ 10^{-10} \frac{cm^3_{STP} \ \ cm}{cm^2 \ \ s \ \ cmHg}$$

Richard Barrer

Permeance

SI unit: mole m^{-2} s^{-1} Pa^{-1}

Popular unit: Gas permeation Unit (GPU)

1 GPU = 3.35*10^{-10} mole m^{-2} s^{-1} Pa^{-1}

$$1 \ \ GPU \ = \ 10^{-6} \frac{cm^3_{STP}}{cm^2 \ \ s \ \ cmHg}$$

1 µm thick membrane with a permeability of 1 barrer will correspond to permeance of 1 GPU

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