Mass balance
Reactors I

Today's lecture

- Mass balance
  - Principle
  - Applications
  - Steady state
- State of mixing
- Reactor analysis using mass balance
  - Completely mixed batch reactor

Principle behind

- Conservation of matter: matter (atoms) can neither be created nor destroyed

  * exception (not relevant to this class!): $E = mc^2$

Mass balance without reactions

Simple accounting of materials:

(Accumulation) = (Input) – (Output)

like in your bank account (when interest rate=0),

balance = deposit - withdrawal

Mass balance: Time as a factor

[(Accumulation) = (Input) – (Output) **] / (time)**

$$\frac{dM}{dt} = \frac{d(in)}{dt} - \frac{d(out)}{dt}$$

rate of accumulation | rate of input | rate of output

- Solving a mass balance problem:

1) Draw schematics, make assumptions, & define control volume (system boundary)
2) Write a mass balance equation using time as a factor
3) Use mathematics to solve the equation

Solving a mass balance problem

Q: Prof. Choi purchases and brings into his house 20 kg of consumer goods every week. Of this amount, 50% is eaten by him as food and eventually leaves the house as CO_2 and other materials. The rest is produced as solid wastes except for 1 kg that accumulates in his house. The solid wastes are classified as non-recyclables and recyclables which are at a mass ratio of 1:1. How many 20-L non-recyclable waste plastic bags should Prof. Choi purchase every year? Assume a density of 1 kg/L for the non-recyclable waste.

Mass balance: substances in water

$$\frac{dM}{dt} = \frac{d(in)}{dt} - \frac{d(out)}{dt}$$

For substances homogeneously distributed in water or air, ***d(in)/dt*** and ***d(out)/dt*** can be calculated as:

$$\frac{Mass}{Time} = C \cdot Q = Mass\ flow\ rate$$

C = concentration **[M/L³]**

Q = flow rate **[L³/T]**

Accordingly,

$$\frac{dM}{dt} = C_{in} \cdot Q_{in} - C_{out} \cdot Q_{out}$$

Mass balance: including reactions

(Accumulation) = (Input) – (Output) + (Reaction)

$$\frac{dM}{dt} = \frac{d(in)}{dt} - \frac{d(out)}{dt} + R$$

R = rate of change in mass due to reaction [M/T]

= rV (V: volume)

reaction rate, $r = -kC^n$ [M/L^3/T] (n=reaction order)

for 1st order reaction, $r = -kC$

(most common in the environment)

Steady state

- $dM/dt = 0$
- No change in the amount of materials in the control volume, i.e., $M \neq f(t)$

  cf) transient state: $M = f(t)$

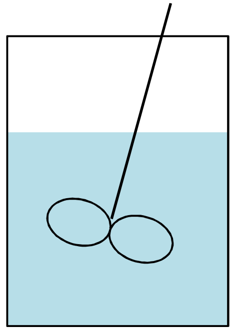
- The mass balance equation gets simpler! (No left-hand-side term)

Mass balance: including reactions

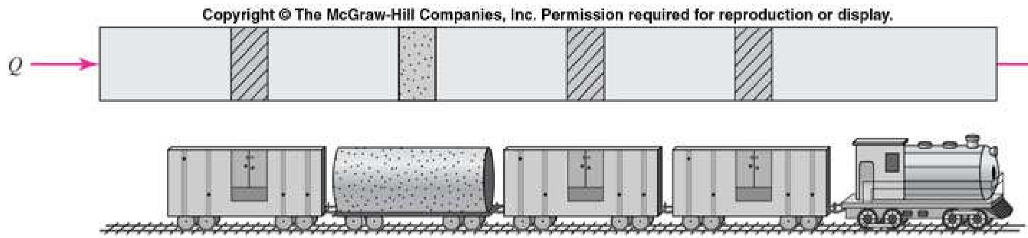
Q: A well-mixed sewage lagoon is receiving 430 m^3/d of untreated sewage. The lagoon has a surface area of 10 ha and a depth of 1.0 m. The pollutant concentration in the sewage discharging into the lagoon is 180 mg/L. The pollutants degrades in the lagoon according to first-order kinetics with a reaction rate constant of 0.70 d^{-1}. Assuming no other water losses or gains and that the lagoon is completely mixed, find the steady-state concentration of the pollutant in the lagoon effluent.

The state of mixing

- Ideal models for mixing
  - **completely mixed systems**: entire system is homogeneous



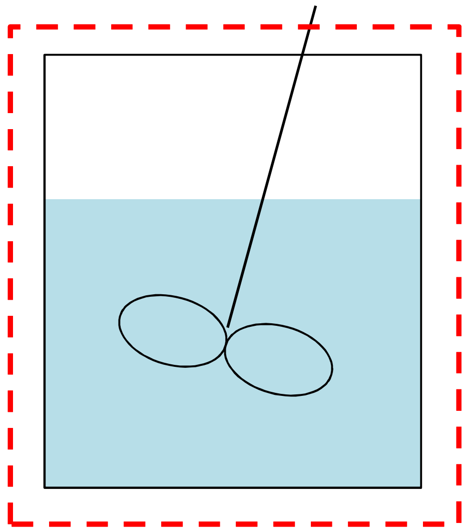
  - **plug flow systems**: no mixing in the direction of flow; homogeneous (completely mixed) in the direction perpendicular to the flow



(b)

Reactor analysis – CMBR, 1st order reaction

- **Completely mixed batch reactor (CMBR)**
  - Fill-and-draw type
  - No flow in or flow out



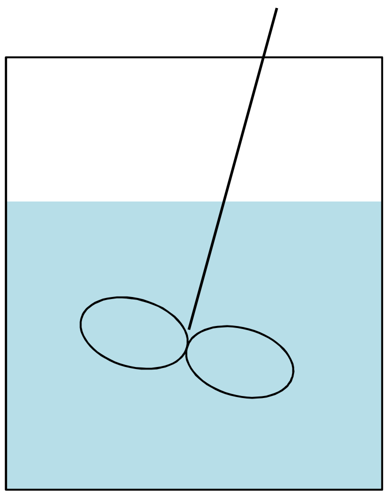
1) draw schematics, define CV

2) write a mass balance eq.

$$\frac{dM}{dt} = \frac{d(in)}{dt} - \frac{d(out)}{dt} + R$$

$$V\frac{dC}{dt} \qquad\qquad -kCV$$

Reactor analysis - CMBR, 1st order reaction



3) solve the equation

$$\frac{dC}{dt} = -kC$$

integrating over $t=0$ to t_{final}:

$$\frac{C_{final}}{C_{initial}} = e^{-kt_{final}}$$

Reactor analysis - CMBR, 1st order reaction

Q: A contaminated soil is to be treated in a completely mixed lagoon. To determine the time it will take to treat the soil, a laboratory completely mixed batch reactor is tested to gather the following data. Assuming a first-order reaction, estimate the rate constant, k, and determine the time to achieve 99% reduction in the original concentration.

Time (days)	Contaminant concentration (mg/kg)
1	280
16	132

Suggested readings

[ENG] pp. 152 – 165, 167 – 170

[KOR] pp. 146 – 161, 163 – 166

Next class

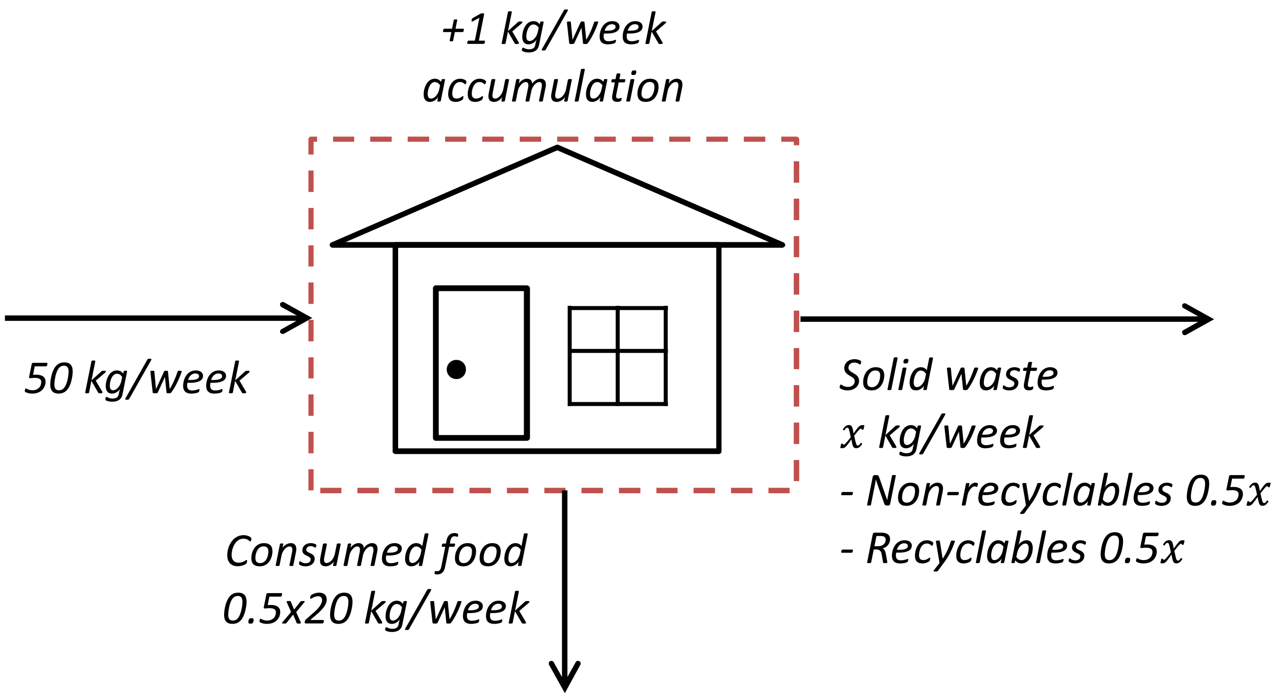
Reactors II

- More on reactor analysis – reactor with flow in & outs
- Hydraulic retention time
- Comparing the performance of different reactors

Slide#6 solution

i) Draw a schematic, make assumptions, define CV

Assume there's no inputs/outputs other than those given in the question.



ii) Write a mass balance eq.

$$\frac{dM}{dt} = \frac{d(in)}{dt} - \frac{d(out)}{dt}$$

iii) Arrange the eq. to a useful form

$$\frac{d(out)}{dt} = \frac{d(in)}{dt} - \frac{dM}{dt}$$

$$\frac{d(out)}{dt} = 20\ kg/week - 1\ kg/week = 19\ kg/week$$

$$= 0.5 \times 20\ kg/week + x$$

$$x = 9\ kg/week$$

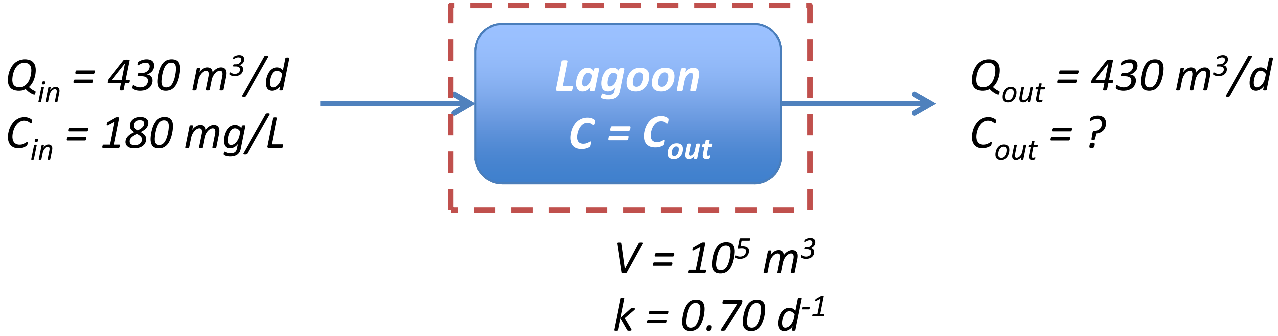
Non-recyclable waste produced every year

$$= 52\ weeks/year \times 0.5 \times 9\ kg/week = 234\ kg/year = 234\ L/year$$

Plastic bags to be purchased every year = $234\ L/(20\ L/bag) = \mathbf{11.7\ bags}$

Slide#10 solution

i) Draw a schematic diagram, make assumptions, define CV



ii) Write a mass balance eq.

$$\cancel{\frac{dM}{dt}}^{\,0} = Q_{in}C_{in} - Q_{out}C_{out} - kC_{out}V$$

iii) Arrange the eq. to a useful form

$$C_{out} = \frac{Q_{in}C_{in}}{Q_{out}+kV} = \frac{430\ m^3/d \times 180\ mg/L \times 10^3\ L/m^3}{430\ m^3/d + 0.70\ d^{-1} \times 10^5\ m^3} = 1100\ mg/m^3 = \mathbf{1.1\ mg/L}$$

Slide#14 solution

$$-kt = ln\frac{C_{final}}{C_{initial}}$$

$$k = -\frac{1}{t} \cdot ln\frac{C_{final}}{C_{initial}} = -\frac{1}{15\ d} \cdot ln\frac{132}{280} = 0.0501\ d^{-1}$$

$$t_{99\%} = -\frac{1}{k} \cdot ln\frac{C_{final}}{C_{initial}} = -\frac{1}{0.0501\ d^{-1}} \cdot ln0.01 = \mathbf{91.9\ days}$$

Reactors II

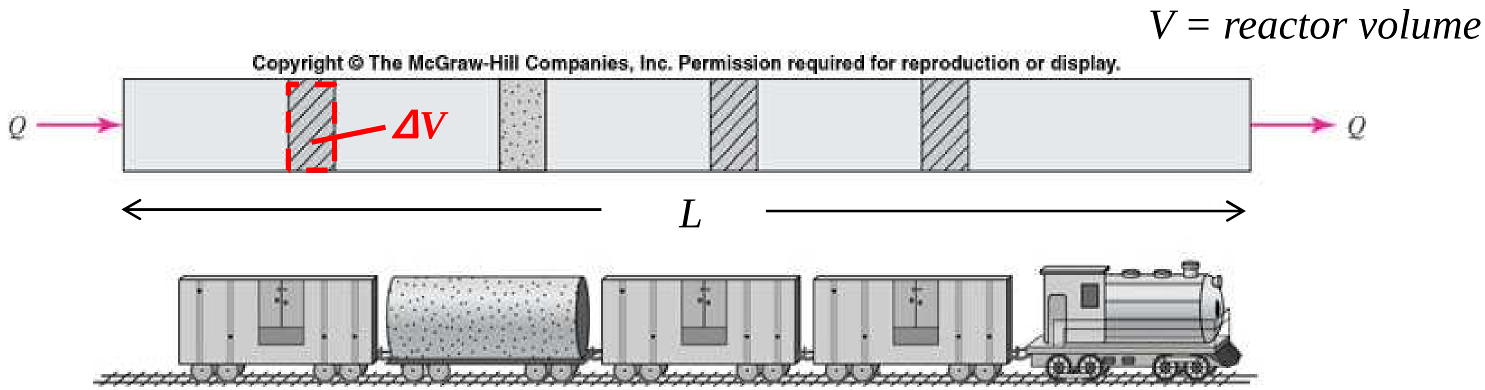
Today's lecture

- Reactor analysis using mass balance
  - Plug flow reactor
  - Completely mixed flow reactor

- Reactor analysis – wrapping up
  - Hydraulic retention time
  - PFR vs. CMFR

Reactor analysis – PFR, 1st order reaction

- Plug-flow reactor (PFR)



1) define control volume:

the moving "plug": a very thin, homogeneous plate moving in the direction of flow

Reactor analysis – PFR, 1st order reaction

2) write a mass balance eq.:

$$\frac{dM}{dt} = \frac{d(in)}{dt} - \frac{d(out)}{dt} + R$$

$\frac{dM}{dt} \leftarrow \Delta V \frac{dC}{dt}$

$R \leftarrow -kC\Delta V$ (1st order)

3) arrange the equation: $\frac{dC}{dt} = -kC$

integrating over $t=0$ to t_0 (= L/v_{flow} = V/Q):

$$\frac{C_{out}}{C_{in}} = e^{-kt_0}$$

→ same form as the batch reactor! (why??)

Reactor analysis – PFR, 1st order reaction

- Examples of PFRs

Disinfection

Rivers and streams

Reactor analysis - PFR

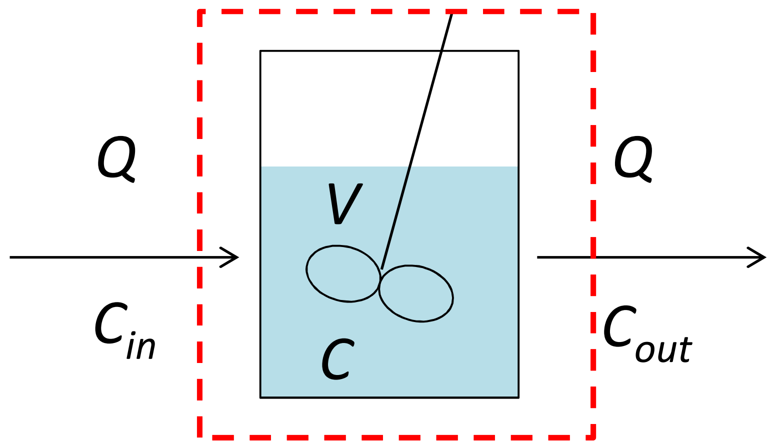
Q: In the U.S., a wastewater treatment plant must disinfect its effluent before discharging the wastewater to a stream. The wastewater contains 4.5 x 10^5 CFU/L of fecal coliform. The effluent standard for fecal coliform is 2 x 10^3 CFU/L. Assuming that the disinfection facility is a PFR, determine the length of pipe required if the velocity of the wastewater in the PFR is 0.75 m/s. Assume that the first-order reaction rate constant for destruction of the fecal coliforms is 0.23 min^{-1}.

Reactor analysis – CMFR, 1st order reaction

- Completely mixed flow reactor (CMFR) (continuous-flow stirred tank reactor, CSTR)

1) define control volume

2) write a mass balance eq.



$$\frac{dM}{dt} = \frac{d(in)}{dt} - \frac{d(out)}{dt} + R$$

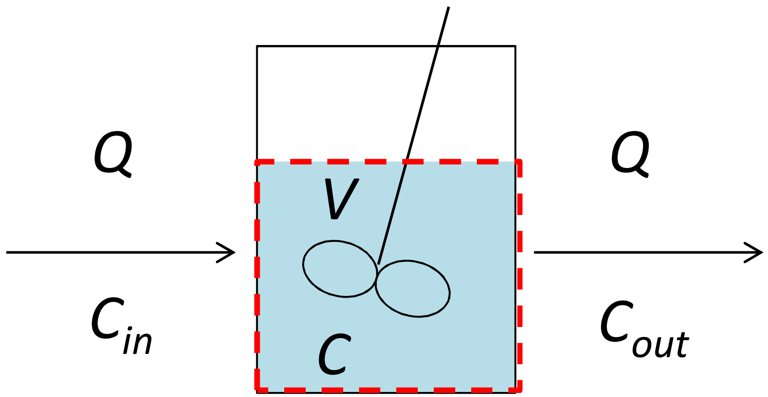
$\frac{dM}{dt}$ → $V\frac{dC}{dt}$

$\frac{d(in)}{dt}$ → $Q \cdot C_{in}$

$\frac{d(out)}{dt}$ → $Q \cdot C_{out}$

R → $-kCV$ (1st order)

Reactor analysis – CMFR, 1st order reaction



Because of homogeneous mixing, $C = C_{out}$

$$V\frac{dC_{out}}{dt} = QC_{in} - QC_{out} - kC_{out}V$$

Reactor analysis – CMFR, 1st order reaction

3) arrange the equation:

$$V\frac{dC_{out}}{dt} = QC_{in} - QC_{out} - kC_{out}V$$

Special case I. No reaction, initial concentration = C_0

$$V\frac{dC_{out}}{dt} = QC_{in} - QC_{out} - \cancel{kC_{out}V}$$

$$\frac{dC_{out}}{dt} = \frac{1}{t_o}(C_{in} - C_{out}) \qquad (t_0 = V/Q)$$

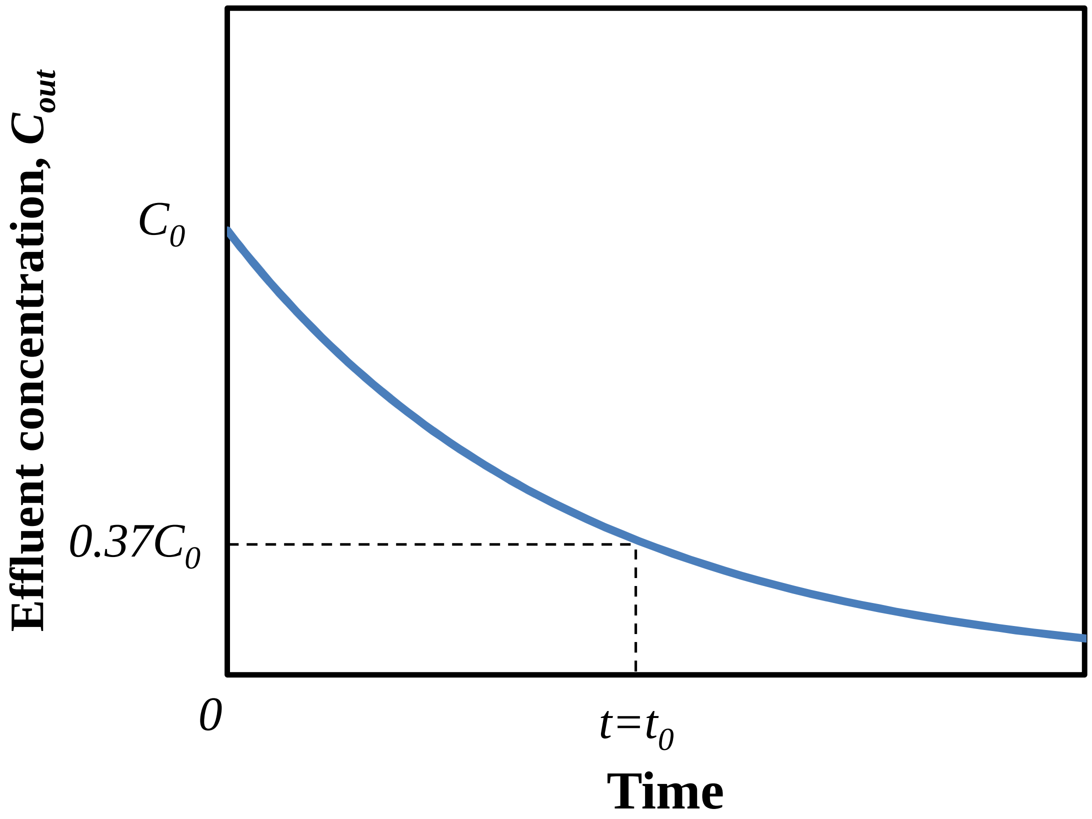
integrating over t=0 to t:

$$C_{out,t} = \boxed{C_o\left[exp\left(-\frac{t}{t_0}\right)\right]} + \boxed{C_{in}\left[1 - exp\left(-\frac{t}{t_0}\right)\right]}$$

Reactor analysis – CMFR, 1st order reaction

when $C_{in} = 0$,

$$C_{out,t} = C_o\left[exp\left(-\frac{t}{t_0}\right)\right]$$



Reactor analysis – CMFR, 1st order reaction

$$V\frac{dC_{out}}{dt} = QC_{in} - QC_{out} - kC_{out}V$$

Special case II. Steady state

$$V\frac{dC_{out}}{dt} = QC_{in} - QC_{out} - kC_{out}V$$

$$C_{out} = \frac{C_{in}}{1 + kt_0} \qquad (t_0 = V/Q)$$

→ influent concentration (C_{in}) is reduced in the effluent by a factor of ($1+kt_0$)

Reactor analysis – CMFR, 1st order reaction

- Examples of CMFRs

Biological wastewater treatment

Lake

Reactor analysis - CMFR

Q: Activated sludge is a key process for most wastewater treatment facilities. The process is often run as a CMFR. Assume a 400 m^3-sized CMFR for an activated sludge process receiving 2000 m^3/d of wastewater. If a terrorist dumped 10 kg of a non-biodegradable toxic chemical to the reactor, how long will it take for the toxic chemical concentration in the reactor to a safe level (1 mg/L)?

Reactor analysis - CMFR

Q: A chemical degrades in a steady-state CMFR according to first-order reaction kinetics. The upstream concentration of the chemical is 10 mg/L and the downstream concentration is 2 mg/L. Water is being treated at a rate of 29 m^3/min. The volume of the tank is 580 m^3. What is the rate of decay? What is the rate constant?

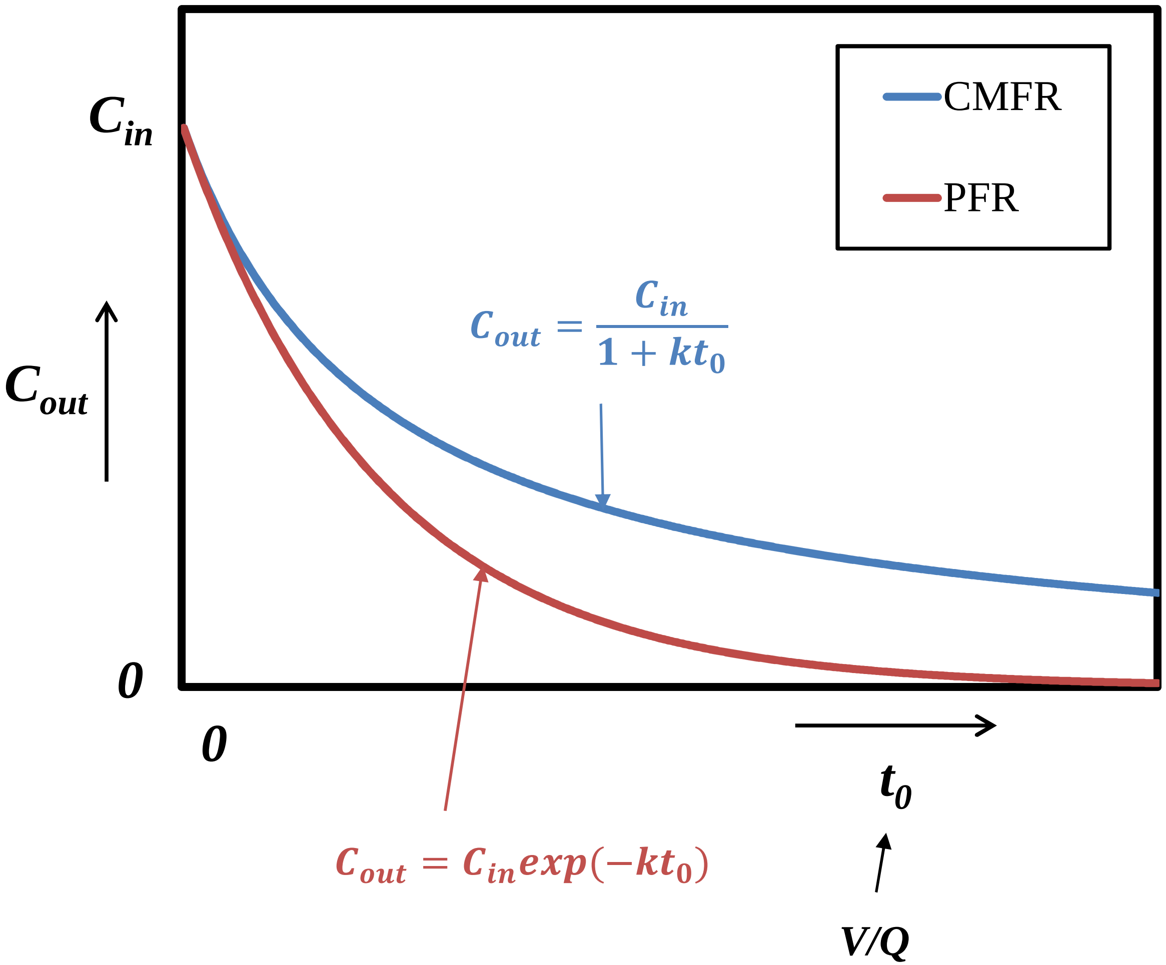
Hydraulic retention time

- Hydraulic retention time (HRT), t_0

  $t_0 = V / Q$

  - The average time the fluid particles spend in the reactor
  - PFR: the time that fluid particles spend in a reactor is the same (=t_0) for all particles
  - CMFR: the time that fluid particles spend in a reactor is different

PFR vs. CMFR



- At the same t_0, PFR shows better performance
- Advantage of using CMFR: less sensitive to shock loads and toxic compounds

Suggested readings

[ENG] pp. 165 – 176

[KOR] pp. 161 – 173

Next class

Ecosystem

- Fundamental characteristics of ecosystems
- Human impact
- Bioaccumulation of hazardous chemicals
- Nutrient cycle
- Lake ecosystem

Slide#6 solution

$$ln\frac{C_{out}}{C_{in}} = -kt_0 = -kL/v_{flow}$$

$$L = -\frac{v_{flow}}{k} \cdot ln\frac{C_{out}}{C_{in}} = -\frac{0.75\ m/s}{0.23\ min^{-1}} \times 60\ s/min \times ln\frac{2\times10^3\ CFU/mL}{4.5\times10^5\ CFU/mL}$$

$$= \mathbf{1060\ m}$$

Slide#13 solution

Non-biodegradable → no reaction

$$C_{out,t} = C_0 exp(-t/t_0)$$

$$t = -t_0 \cdot ln\frac{C_{out,t}}{C_0}$$

$$C_0 = \frac{10\ kg}{400\ m^3} \times 10^6\ mg/kg\ \times\ 10^{-3}\ m^3/L = 25\ mg/L$$

$$t_0 = \frac{V}{Q} = \frac{400\ m^3}{2000\ m^3/d} = 0.2\ d$$

$$t = -0.2\ d \cdot ln\frac{1\ mg/L}{25\ mg/L} = \mathbf{0.64\ day}$$

Slide#14 solution

$$C_{out} = \frac{C_{in}}{1+kt_0}$$

$$k = \frac{1}{t_0}\left(\frac{C_{in}}{C_{out}} - 1\right)$$

$$t_0 = \frac{580\ m^3}{29\ m^3/min} = 20\ min$$

$$k = \frac{1}{20\ min}\left(\frac{10\ mg/L}{2\ mg/L} - 1\right) = \mathbf{0.20\ min^{-1}}$$

rate of decay $= -r = -\left.\frac{dC}{dt}\right|_{reaction} = k \cdot C_{out}$

$$= (0.20\ min^{-1}) \cdot (2\ mg/L) = \mathbf{0.40\ mg/L - min}$$