Reactor analysis

Types of reactions

- **Homogeneous reactions**
  - Reactants are distributed uniformly throughout the fluid
  - Reaction rates are the same at any point within the fluid
  - ex: reaction between water-dissolved constituents
  - Reaction rates are usually a function of constituent concentration

- **Heterogeneous reactions**
  - Occur between one or more constituents that can be identified with specific sites
  - ex: reactions occurring at a solid surface, reactions that requires a solid-phase catalyst
  - Reaction rates are usually a function of surface area of a solid phase

Reaction rates

- **Reaction rate, r**

$$r = \pm \left. \frac{dC}{dt} \right|_{reaction}$$

- **Types of rate expressions**

$r = \pm k$	(zero-order)
$r = \pm kC$	(first-order)
$r = \pm k(C - C_s)$	(first-order)
$r = \pm kC^2$	(second-order)
$r = \pm kC_A C_B$	(second-order)
$r = \pm \dfrac{kC}{K + C}$	(saturation or mixed-order)
$r = \pm \dfrac{kC}{(1 + r_t t)^n}$	(first-order retarded)

Reaction rates

- **Examples of common rate expressions for selected processes**

Process	Rate expression	Comments
Bacterial conversion in natural systems	$r_c = -kC$	r_c = rate of conversion, M/L³/T k = first order reaction rate constant, 1/T C = concentration of organic material remaining, M/L³
Bacterial growth in bioreactors	$\mu = \dfrac{\hat{\mu}S}{K + S}$	μ = specific growth rate, 1/T $\hat{\mu}$ = maximum specific growth rate, 1/T S = concentration of substrate, M/L³
Chemical reactions	$r_c = \pm k_n C^n$	r_c = rate of conversion, M/L³/T k_n = reaction rate constant, (M/L³)$^{n-1}$/T C = concentration of constituent, M/L³ n = reaction order
Natural decay	$r_d = -k_d N$	r_d = rate of decay, #/T k_d = first order reaction rate constant, 1/T N = amount of organisms remaining, #

Reaction rates

- **Examples of common rate expressions for selected processes**

Process	Rate expression	Comments
Gas absorption	$r_{ab} = k_{ab} \dfrac{A}{V}(C_s - C)$	r_{ab} = rate of absorption, $M/L^3/T$ k_{ab} = coefficient of absorption, L/T r_{de} = rate of desorption, $M/L^3/T$ k_{de} = coefficient of desorption, L/T r_v = rate of volatilization, $M/L^3/T$
Gas desorption	$r_{de} = -k_{de} \dfrac{A}{V}(C - C_s)$	k_v = volatilization constant, $1/T$ C_s = saturation concentration of constituent in liquid, M/L^3 C = concentration of constituent in liquid, M/L^3 A = area, L^2
Volatilization	$r_v = -k_v(C - C_s)$	V = volume, L^3

Determination of rxn. rate coefficients

- Conduct reaction kinetic studies in a batch reactor to measure concentration changes of the target constituent over time (more than 4-5 time points)

- If the reaction rate expression is known, plot the results according to the corresponding rate expression; if the reaction rate expression is unknown, plot the results for various rate expressions to find the most appropriate one

- Find the best-fit value of k from the plot

Determination of rxn. rate coefficients

- Linear plots to determine reaction rate coefficients

| Type of reaction	Integrated form	Linearized plot
zero-order $r = -k$	$C = C_0 - kt$	C vs. t
first-order $r = -kC$	$-ln(C/C_0) = kt$	$-\ln(C/C_0)$ vs. t
second-order $r = -kC^2$	$1/C = 1/C_0 + kt$	$1/C$ vs. t
saturation $r = -kC/(K + C)$	$K \cdot ln(C_0/C) + (C_0 - C) = kt$	$(1/t)\ln(C_0/C)$ vs. $(C_0 - C)/t$

Determination of rxn. rate coefficients

Q: Following set of data was obtained using a batch reactor kinetic study. Determine the order of reaction that most appropriately describe the reaction kinetics. Determine the reaction rate coefficient.

Time, d	Concentration, mM
0	250
1	70
2	42
3	30
4	23
5	18
6	16
7	13
8	12

Determination of rxn. rate coefficients

C vs. t plot
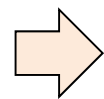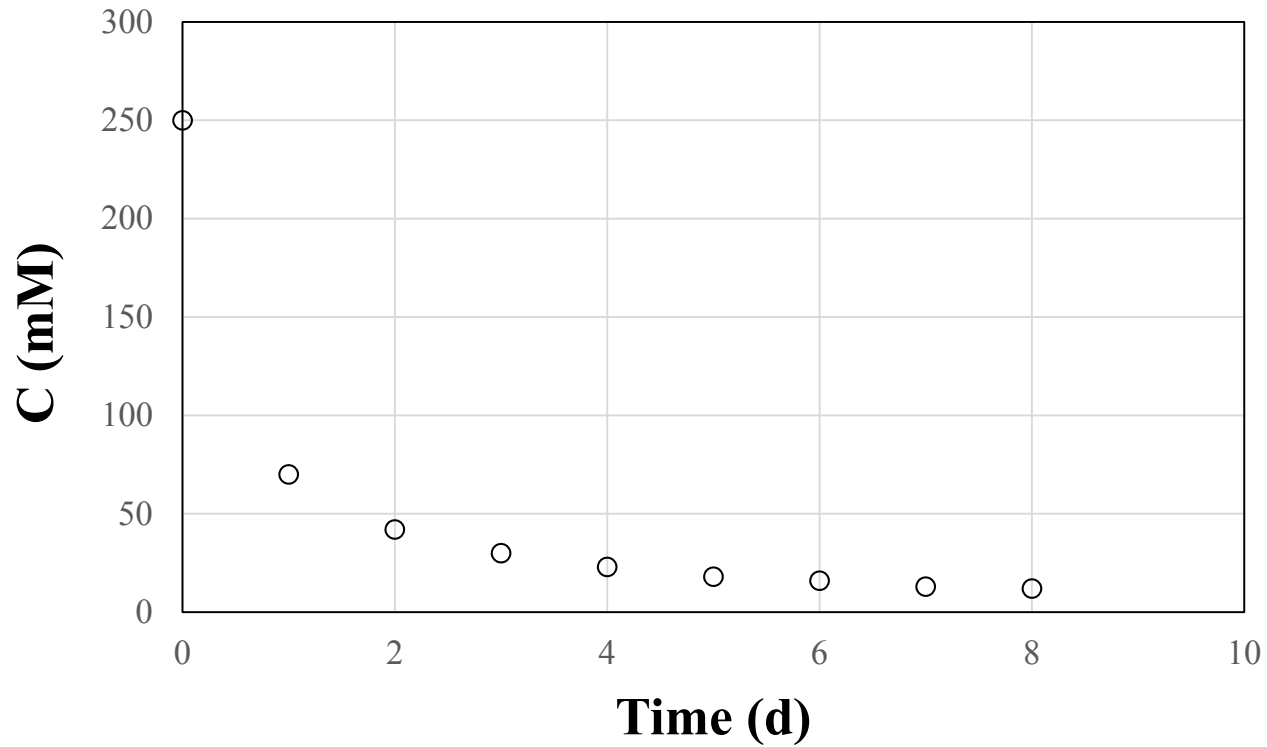
$\Rightarrow$ Maybe 1st or 2nd order

Determination of rxn. rate coefficients

Time, d	Concentration, mM	$-\ln(C/C_0)$	$1/C$
0	250	0	0.004
1	70	0.553	0.014
2	42	0.775	0.024
3	30	0.921	0.033
4	23	1.036	0.044
5	18	1.143	0.056
6	16	1.194	0.063
7	13	1.284	0.077
8	12	1.319	0.083

Determination of rxn. rate coefficients

1st order:

$-\log(C/C_0)$ vs. t
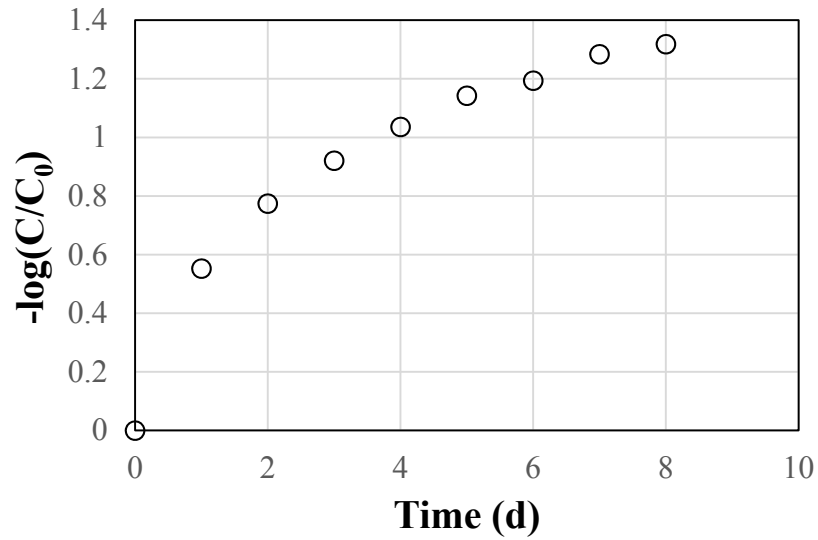
2nd order:

$1/C$ vs. t

Determination of rxn. rate coefficients


$$y = 0.0101\,x + 0.0038$$
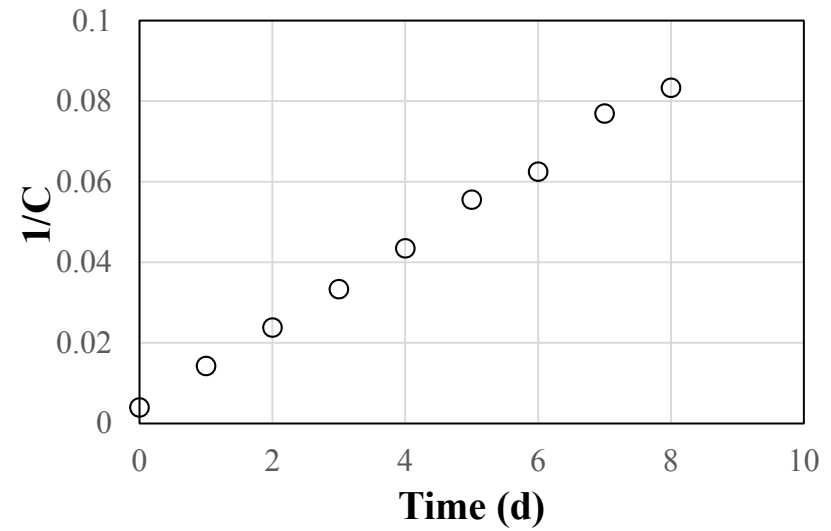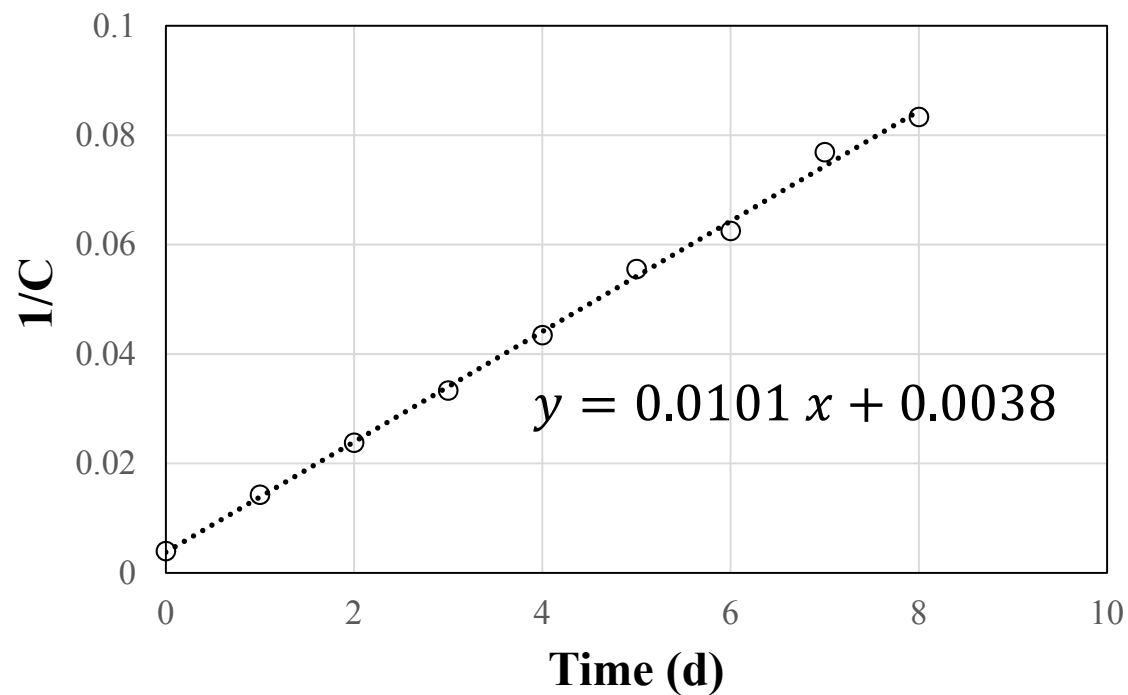
Types of reactors

- **Batch reactor**
  - No flow entering/leaving the reactor
  - The liquid contents are mixed completely
- **Continuous stirred-tank reactor (CSTR)**
  - Also known as completely-mixed flow reactor (CMFR)
  - Flow enters and leaves the reactor at a constant rate
 - The liquid contents are mixed completely
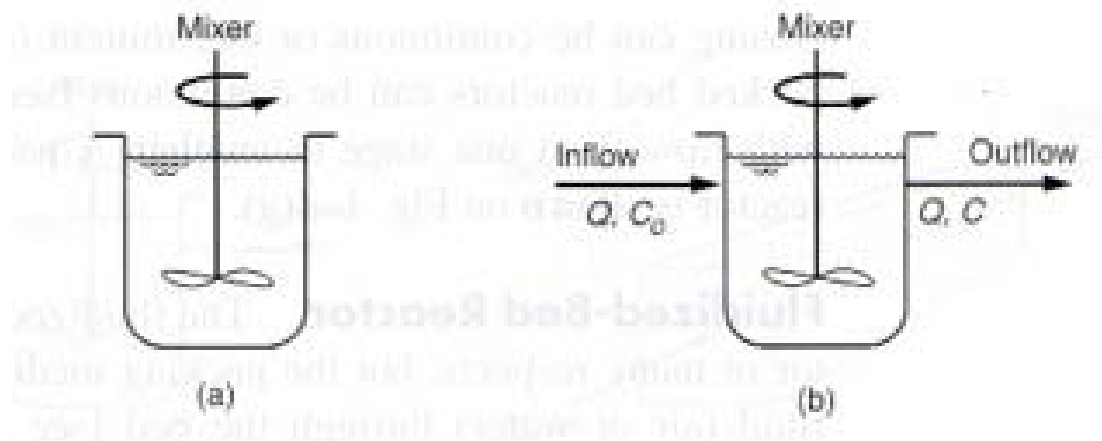
Types of reactors

- **Plug-flow reactor (PFR)**
  - Applies to reactors with high length-to-width ratio
  - Ideal PRF assumes no mixing in the direction of flow and complete mixing in the direction perpendicular to the flow
- **CSTRs in series**
  - Multiple CSTRs are connected in series
  - $n=1$: CSTR; $n=\infty$: PFR ($n=$number of CSTRs)
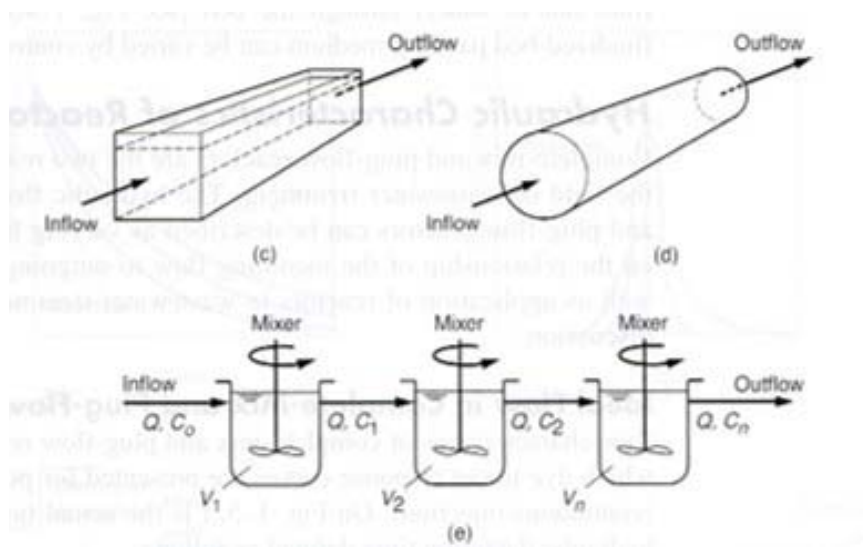
Types of reactors

- **Packed-bed reactors**
  - Filled with packing material (e.g., rock, slag, ceramic, plastics, etc.)
  - Operated in either the downflow or upflow mode
  - Continuous or intermittent dosing
- **Fluidized-bed reactors**
  - Similar to packed-bed reactors
  - Flow is applied in upflow mode, and the packing material is expanded by relatively high flow velocity
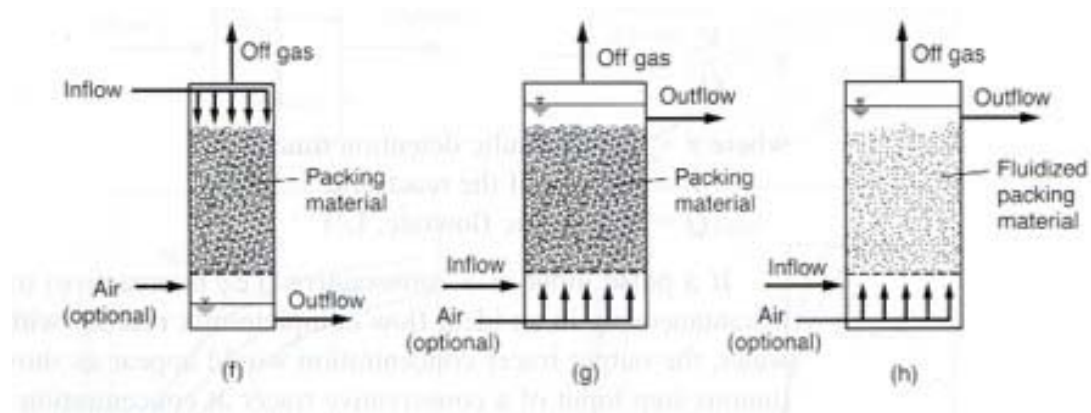
Mass balance analysis

(Reaction kinetics) + (Mass balance) = (Reactor analysis)

- **Applying mass balance**

1) Draw a simplified schematic of the system and identify the control volume (CV). Make assumptions if necessary.

2) Write a mass balance equation:

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

3) Solve or rearrange the equation to a useful form.

Mass balance analysis

- **Steady-state simplification**
  - In most applications in water/wastewater treatment, we are concerned with long-term operation → assume steady state
  - Steady-state: no accumulation in the CV (rate of accumulation = 0)

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

Ideal flow in CSTR & PFR – tracer response

- **Hydraulic retention time**

$$\tau = V/Q$$

τ = hydraulic retention time [T];   V = volume of the reactor [L^3]
*Q = flowrate [L^3/T]*

- **Conservative tracers**: substances that do neither chemically transform nor partition from water; used to analyze the flow characteristics either in natural/engineered systems

Ideal CSTR – tracer response

i) Draw schematic, identify CV

Assumptions:

- $C = 0$ at $t = 0$
- <u>Step input</u> of tracer: at $t \geq 0$ in the influent with a concentration of C_0
- Complete mixing in the reactor
- No reaction (conservative tracer)
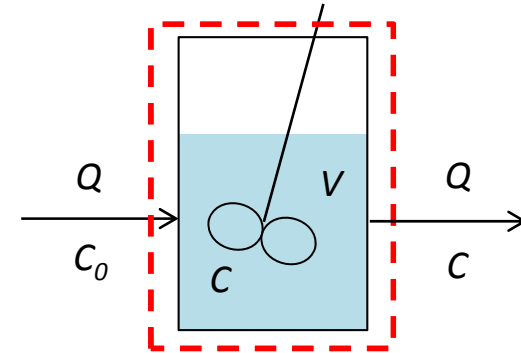
ii) Write mass balance eq.

(rate of accumulation)

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

iii) Solve the eq.

Ideal CSTR – tracer response

Solution (step input):

$$\frac{C}{C_0} = 1 - e^{-t/\tau}$$
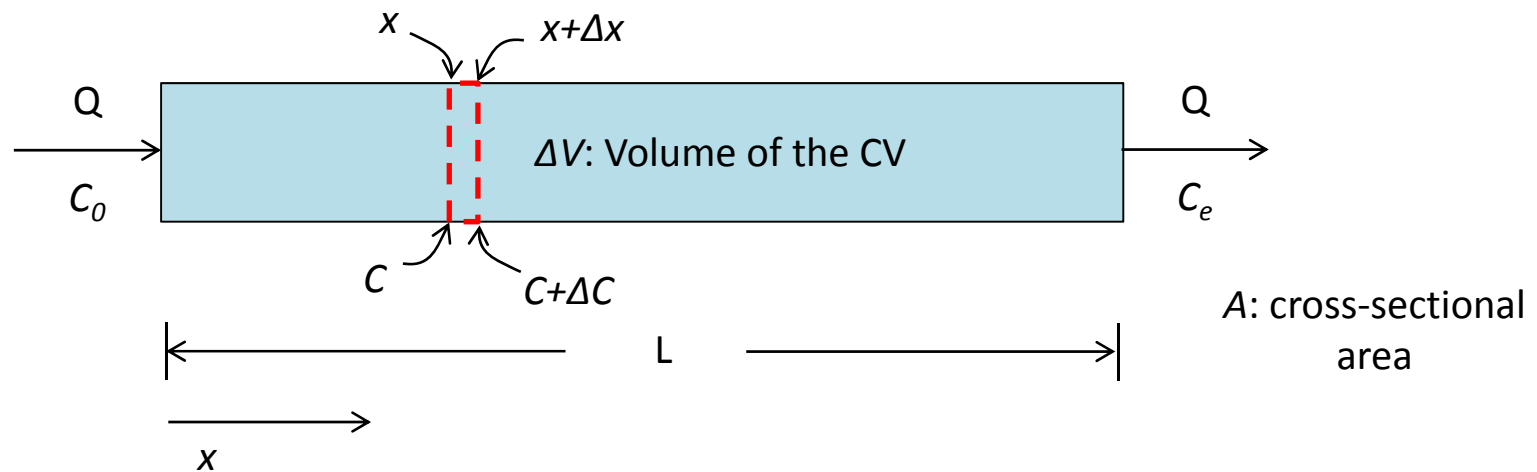
cf) solution (slug input):

$$\frac{C}{C_0} = e^{-t/\tau}$$

C_0 = concentration at t=0 due to slug input of tracer

Ideal PFR – tracer response

Assume any type of tracer input in the influent, described as $C_0=F(t)$

i) Draw schematic, identify CV

x $x+\Delta x$

Q ΔV: Volume of the CV   Q

C_0 C_e

C $C+\Delta C$

A: cross-sectional area

L

x

ii) Write mass balance eq.
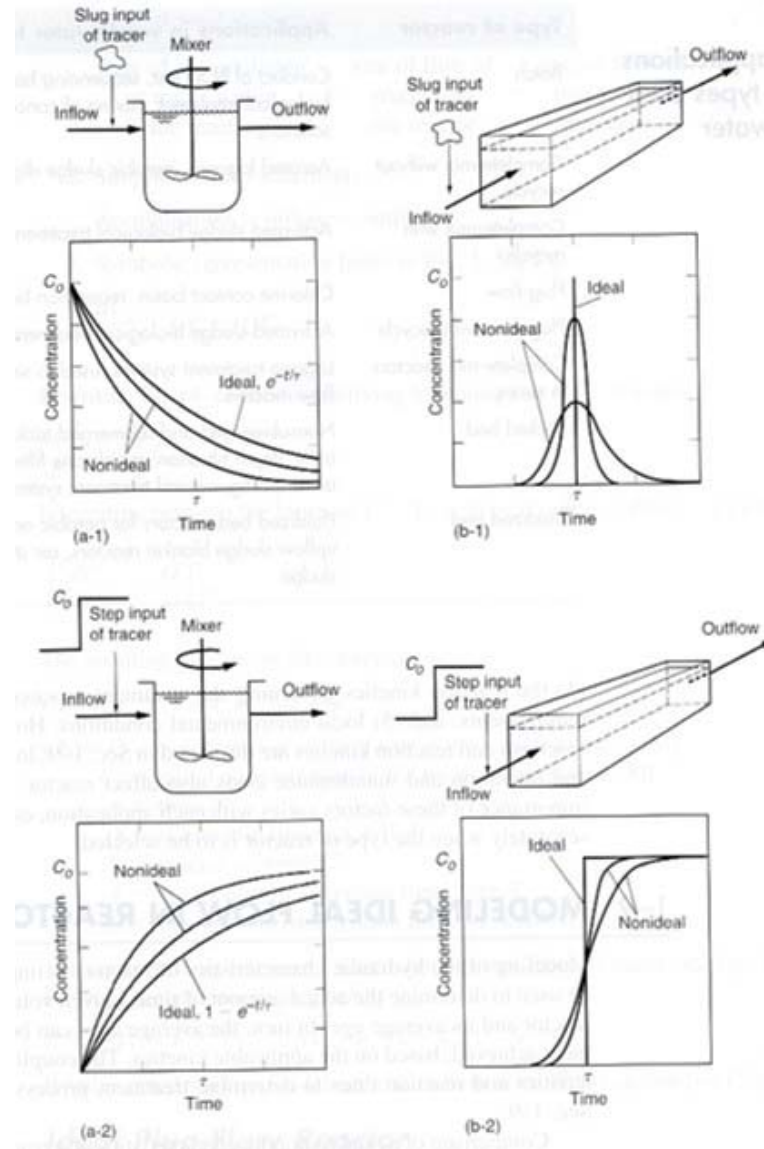## iii) Solve the eq.

Ideal PFR – tracer response

For any $C_0 = C(x = 0, t) = F(t)$:

$$C_e = C(x = L, t) = F(t - \tau)$$

For a PFR, the inflow concentration profile of a tracer is observed exactly the same in the outflow with a time shift of τ

Non-ideal flow in CSTR & PFR

- In practice, the flow in CMR and PFR is seldom ideal – there are some extent of deviations from the ideal cases

Non-ideal flow in CSTR & PFR

- Factors leading to non-ideal flow (short-circuiting)
  - **Temperature differences**: temperature difference developed within a reactor → density currents occur → water does not flow at a full depth
  - **Wind-driven circulation patterns**: wind creates a circulation cell which acts as a dead space
  - **Inadequate mixing**: insufficient mixing of some portions of the reactor
  - **Poor design**: dead zones developed at the inlet and the outlet of the reactor
  - **Axial dispersion in PFRs**: mechanical dispersion and molecular diffusion in the direction of the flow

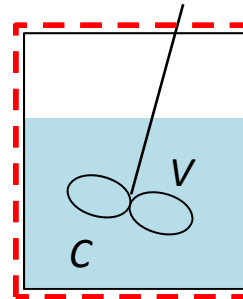# Reactor analysis - treatment processes

- Incorporate the reaction rate expression into the mass balance equation!

- Batch reactor with first-order reaction

    i) Draw schematic, identify CV
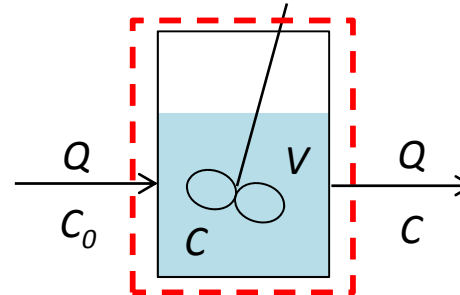
    ii) Write mass balance eq.

    iii) Solve the eq.

        Solution:

CSTR, 1$^{\text{st}}$ order reaction

i) Draw schematic, identify CV

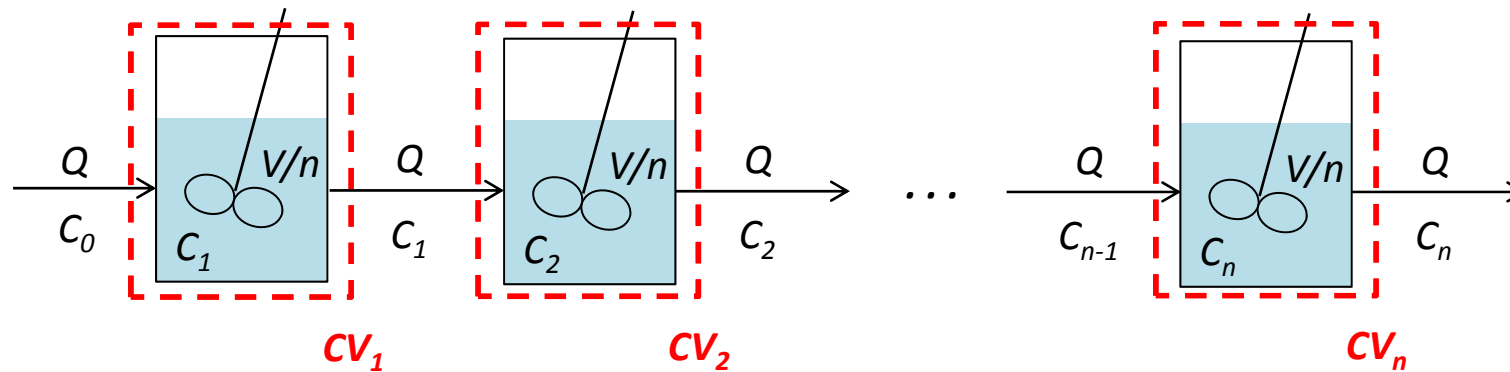**ii) Write mass balance eq.**

iii) Solve the eq.

General solution:

$$C/C_0 = \frac{1}{1+k\tau}\left(1 - e^{-(k+1/\tau)t}\right) + e^{-(k+1/\tau)t}$$
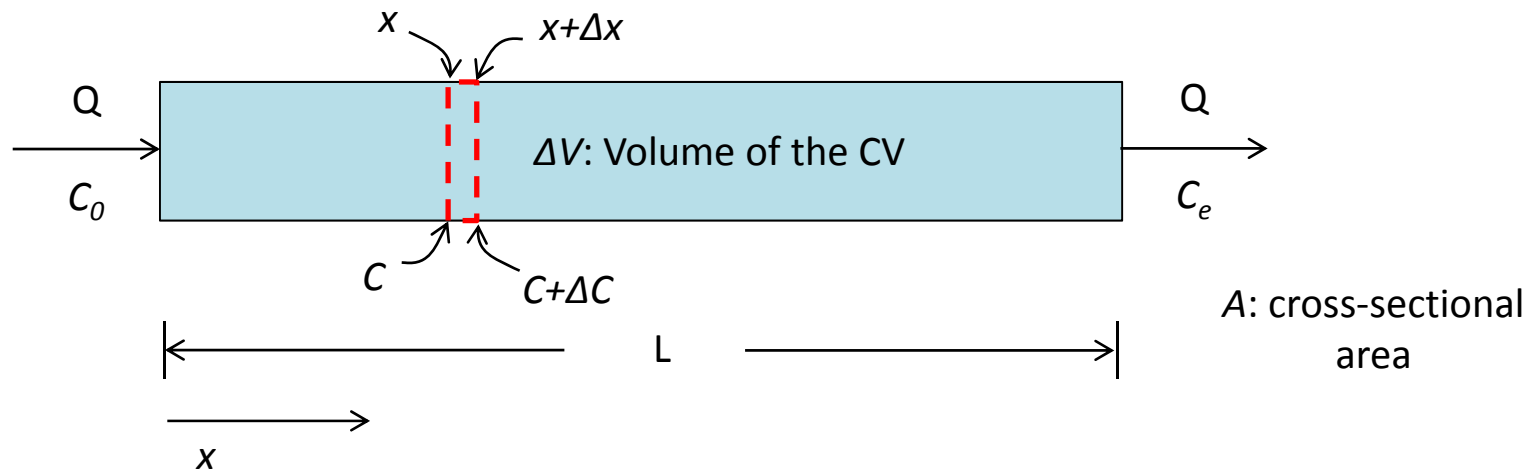
Steady-state solution:

CSTR in series, 1st order reaction

Steady-state solution:

PFR, 1st order reaction

Steady-state solution:

$$\frac{C_e}{C_0} = e^{-k\tau}$$

- Equivalent to the batch reactor solution (why??)

Treatment process modeling

Q: Compare the performance of i) a CSTR, ii) three CSTRs in series, and iii) a PFR having the same hydraulic detention time of 0.2 days when the first-order reaction rate coefficient, k, is 10 day^{-1}. Assume steady state.

CSTR vs. PFR