

Reactor analysis I

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**

$$r = \pm k \quad (\text{zero-order})$$

$$r = \pm kC \quad (\text{first-order})$$

$$r = \pm k(C - C_s) \quad (\text{first-order})$$

$$r = \pm kC^2 \quad (\text{second-order})$$

$$r = \pm kC_A C_B \quad (\text{second-order})$$

$$r = \pm \frac{kC}{K + C} \quad (\text{saturation or mixed-order})$$

$$r = \pm \frac{kC}{(1 + r_t t)^n} \quad (\text{first-order retarded})$$

Examples of common rate expressions

Process	Rate expression	Comments
Bacterial conversion in natural systems	$r_c = -kC$	$r_c = \text{rate of conversion, } M/L^3/T$ $k = \text{first order reaction rate constant, } 1/T$ $C = \text{concentration of organic material remaining, } M/L^3$
Bacterial growth in bioreactors	$\mu = \frac{\hat{\mu}S}{K + S}$	$\mu = \text{specific growth rate, } 1/T$ $\hat{\mu} = \text{maximum specific growth rate, } 1/T$ $S = \text{concentration of substrate, } M/L^3$
Chemical reactions	$r_c = \pm k_n C^n$	$r_c = \text{rate of conversion, } M/L^3/T$ $k_n = \text{reaction rate constant, } (M/L^3)^{n-1}/T$ $C = \text{concentration of constituent, } M/L^3$ $n = \text{reaction order}$
Natural decay	$r_d = -k_d N$	$r_d = \text{rate of decay, } \#/T$ $k_d = \text{first order reaction rate constant, } 1/T$ $N = \text{amount of organisms remaining, } \#$

Examples of common rate expressions

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

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

Linear plots to determine 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. $(C_0 - C)/t$

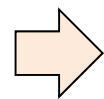
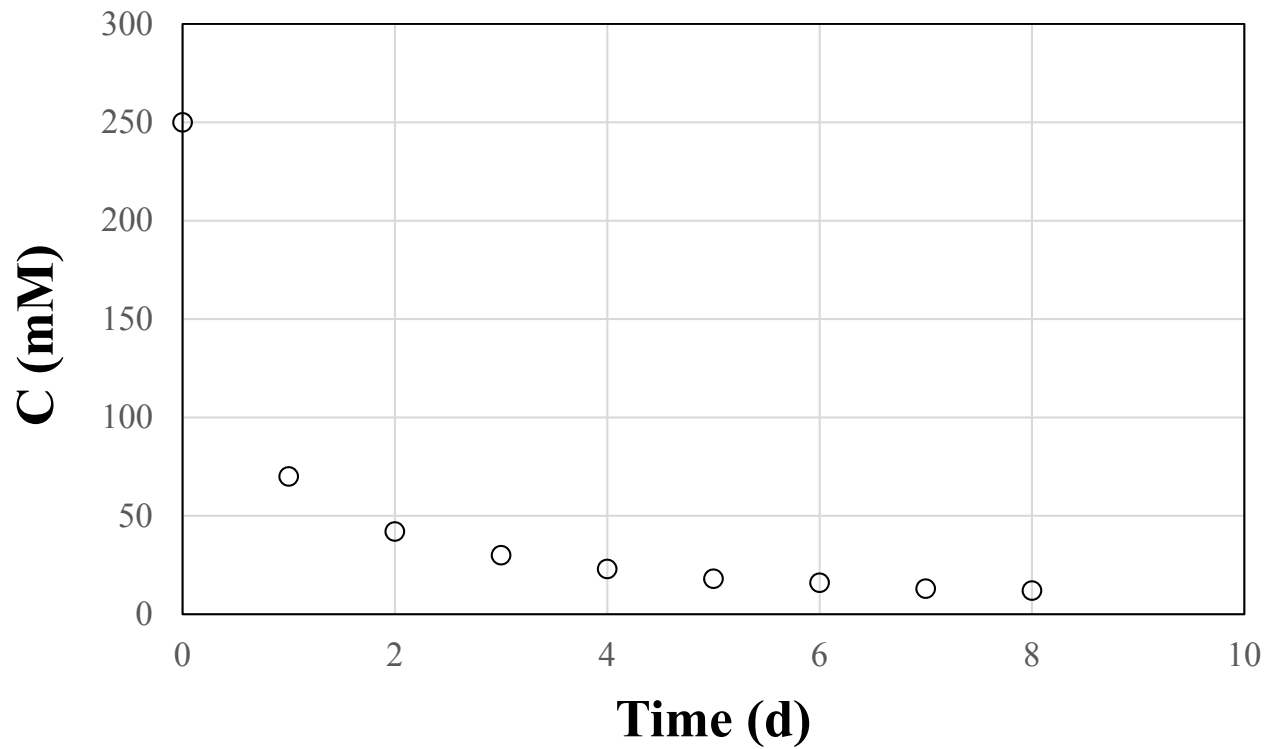
Determination of rxn. rate coefficients

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



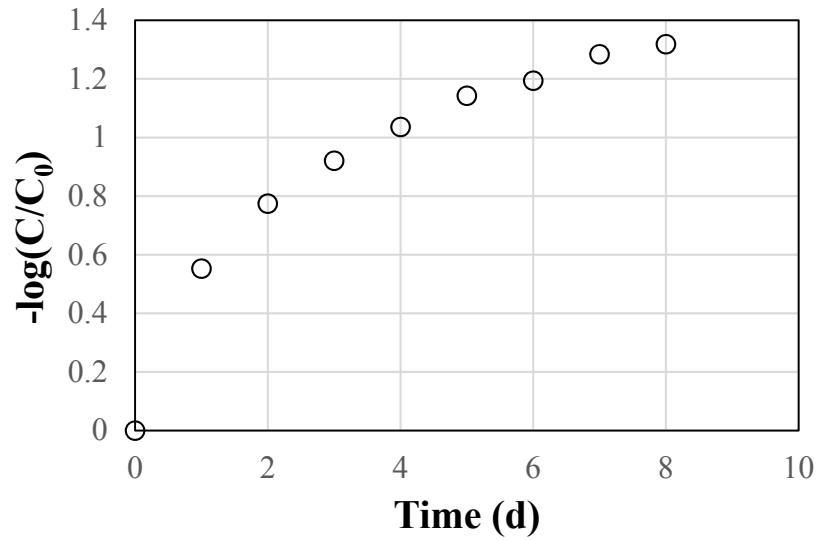
Maybe 1st or 2nd order

Determination of rxn. rate coefficients

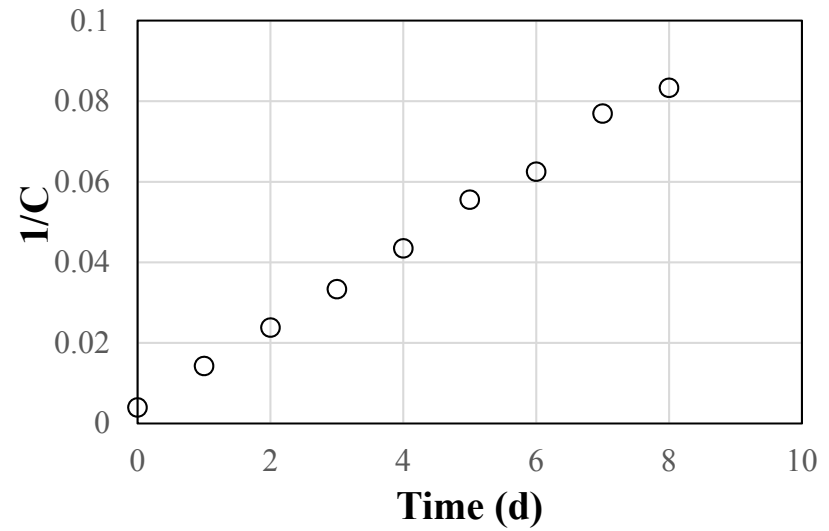
Time, d	Concentration, mM	$-\ln(C/C_0)$	$1/C$
0	250	0	0.004
1	70	0.553	0.014
2	42	0.775	0.024
3	30	0.921	0.033
4	23	1.036	0.044
5	18	1.143	0.056
6	16	1.194	0.063
7	13	1.284	0.077
8	12	1.319	0.083

Determination of rxn. rate coefficients

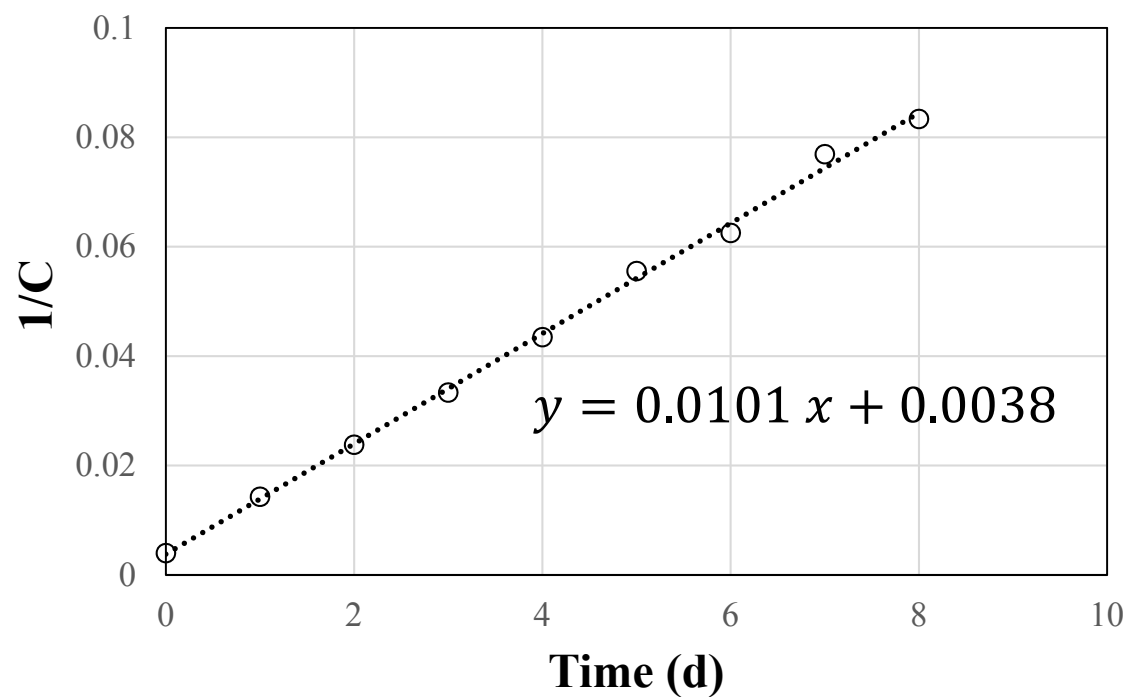
1st order:
 $-\log(C/C_0)$ vs. t



2nd order:
 $1/C$ vs. t

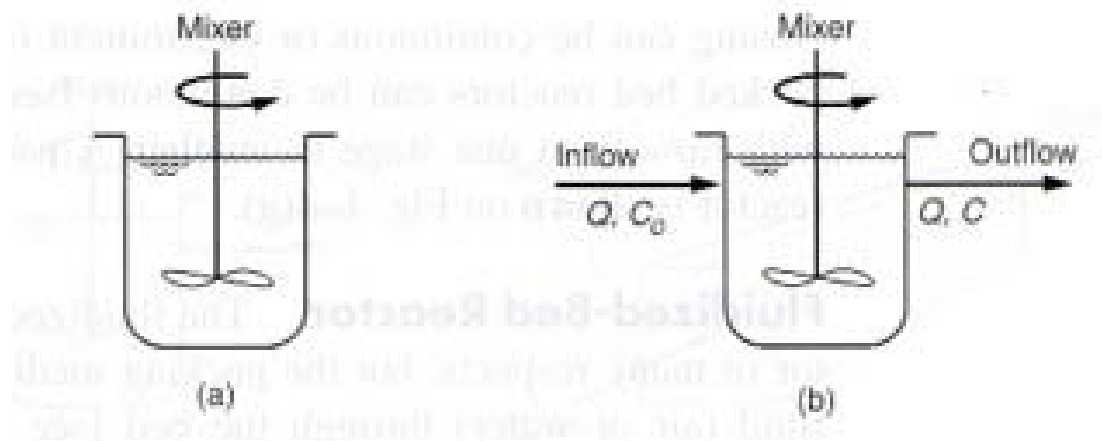


Determination of rxn. rate coefficients



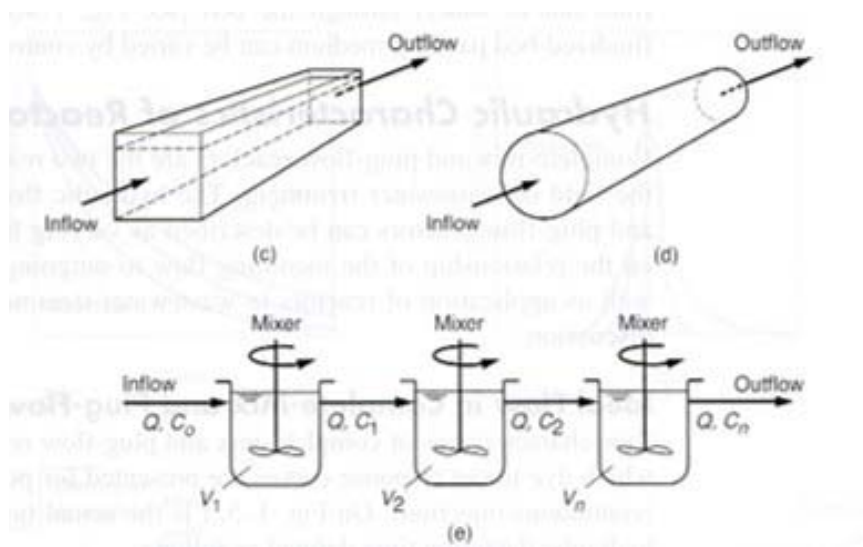
Types of reactors

- **Batch reactor**
 - No flow entering/leaving the reactor
 - The liquid contents are mixed completely
- **Continuously 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



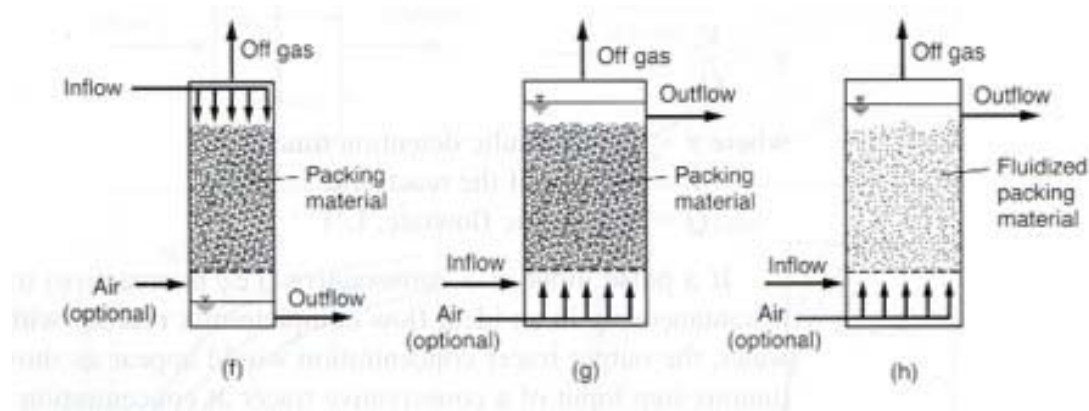
Types of reactors

- **Plug-flow reactor (PFR)**
 - Applies to reactors with high length-to-width ratio
 - Ideal PFR 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:

$$\textit{(rate of accumulation) = (rate of inflow) - (rate of outflow) + (rate of generation)}$$

- 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)

