Print version

CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #19

Chloramines Cont: Primary Literature
Enzyme Kinetics: basics
Brezonik, pp. 419-450

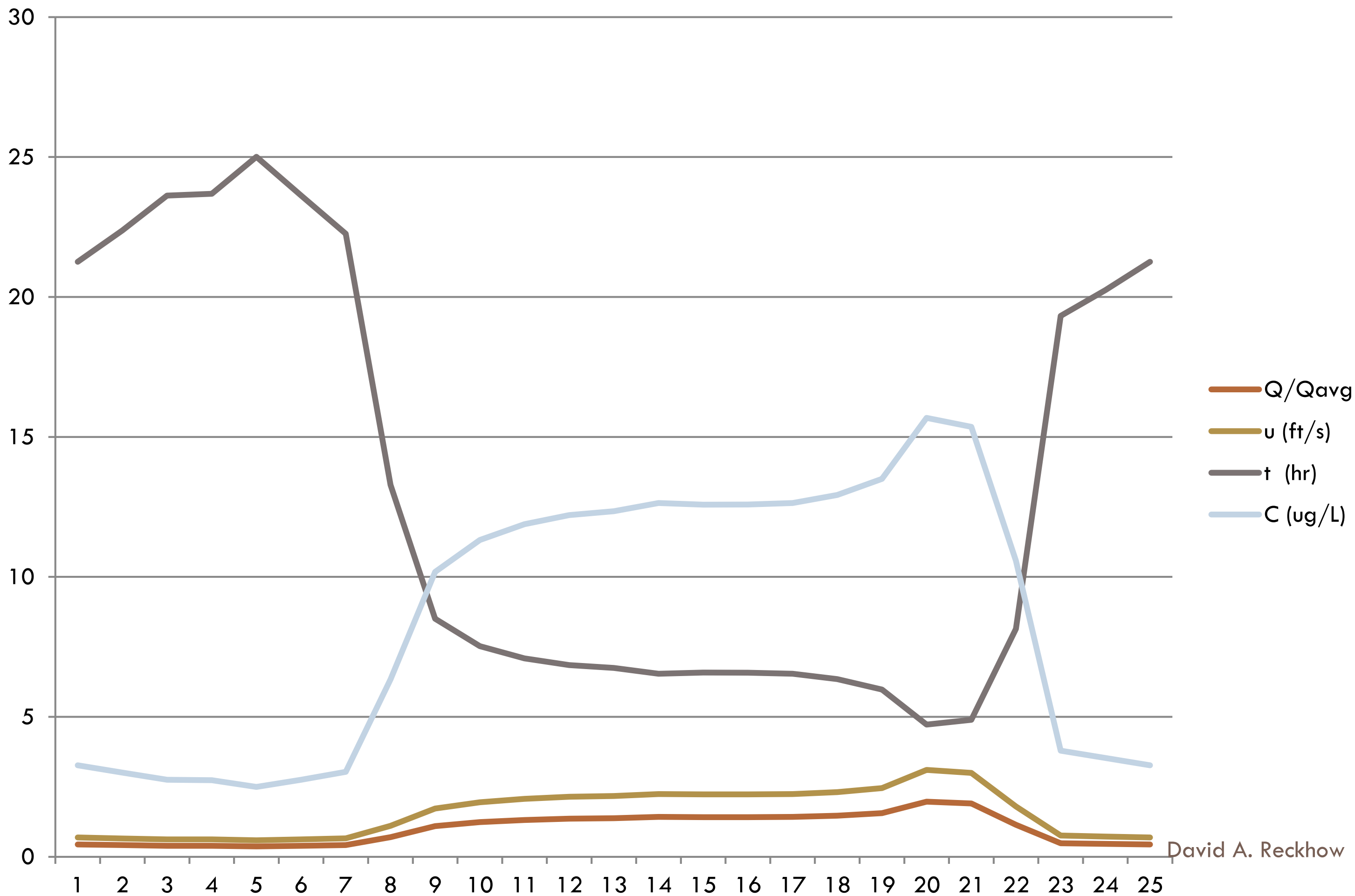
Conclusions

- *"Overall the model calculations suggest that biodegradation is…..not likely to play a major role in most water distribution systems"*
  - *"the conditions needed for significant HAA removals in a distribution system (i.e., total biomass densities > 10^5 cells/cm^2 over long distances of pipe) are unlikely in the US water distribution systems where total chlorine residuals typically are high and thus inhibit the development of biofilm on pipe walls"*

But this seems to contradict their introductory conclusion – how to reconcile?

What could they have concluded?

- Variability vs diurnal demand



David A. Reckhow

Objective/hypothesis

- Not really stated, but they did end the intro with:
  - *"In this work, computer simulations were performed to predict the fate of three HAAs (MCAA, DCAA, and TCAA) along a distribution system and within a biologically active filter. Sensitivity analyses were performed <u>to investigate the effects of physical parameters (e.g., fluid velocity) and biological parameters (e.g., biodegradation kinetics, biomass density) on HAA removal"</u>*

What could they have said?

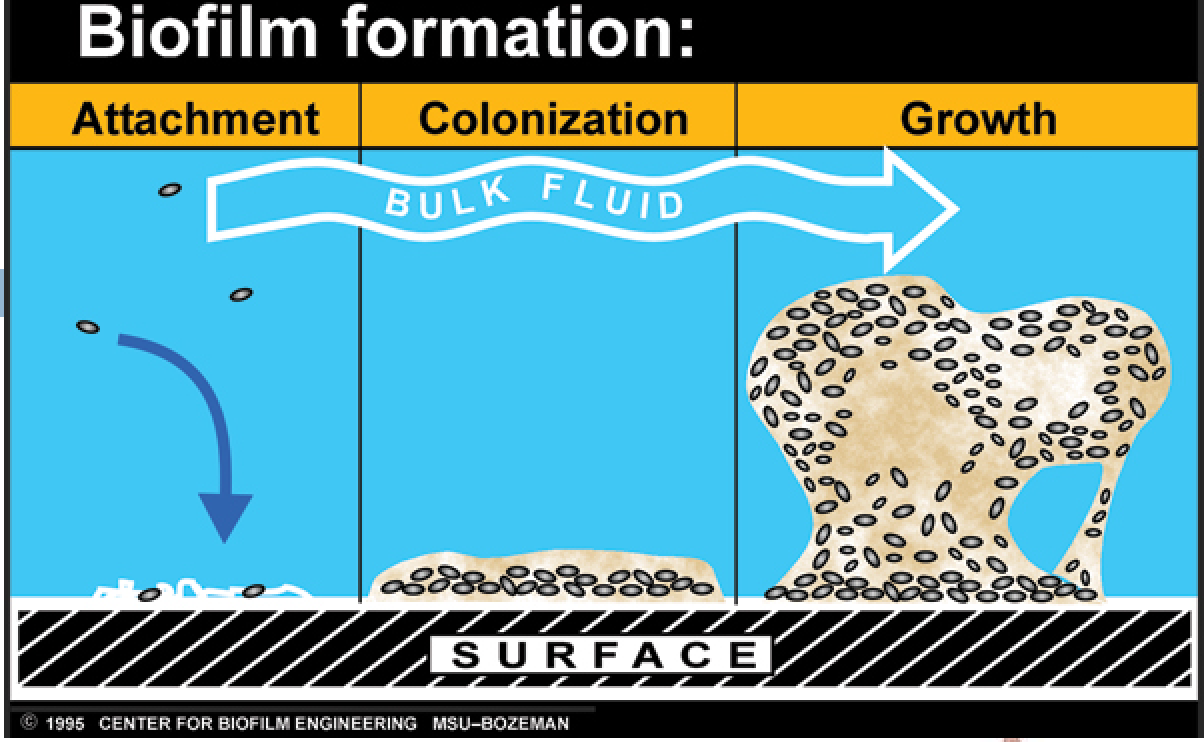
- To determined if observed HAA loss could be attributed to biodegradation on pipe walls given known physical and microbial characteristics of distribution systems
- To estimate spatial and temporal variability of HAA concentrations based on a rational physical model of biodegradation in distribution systems

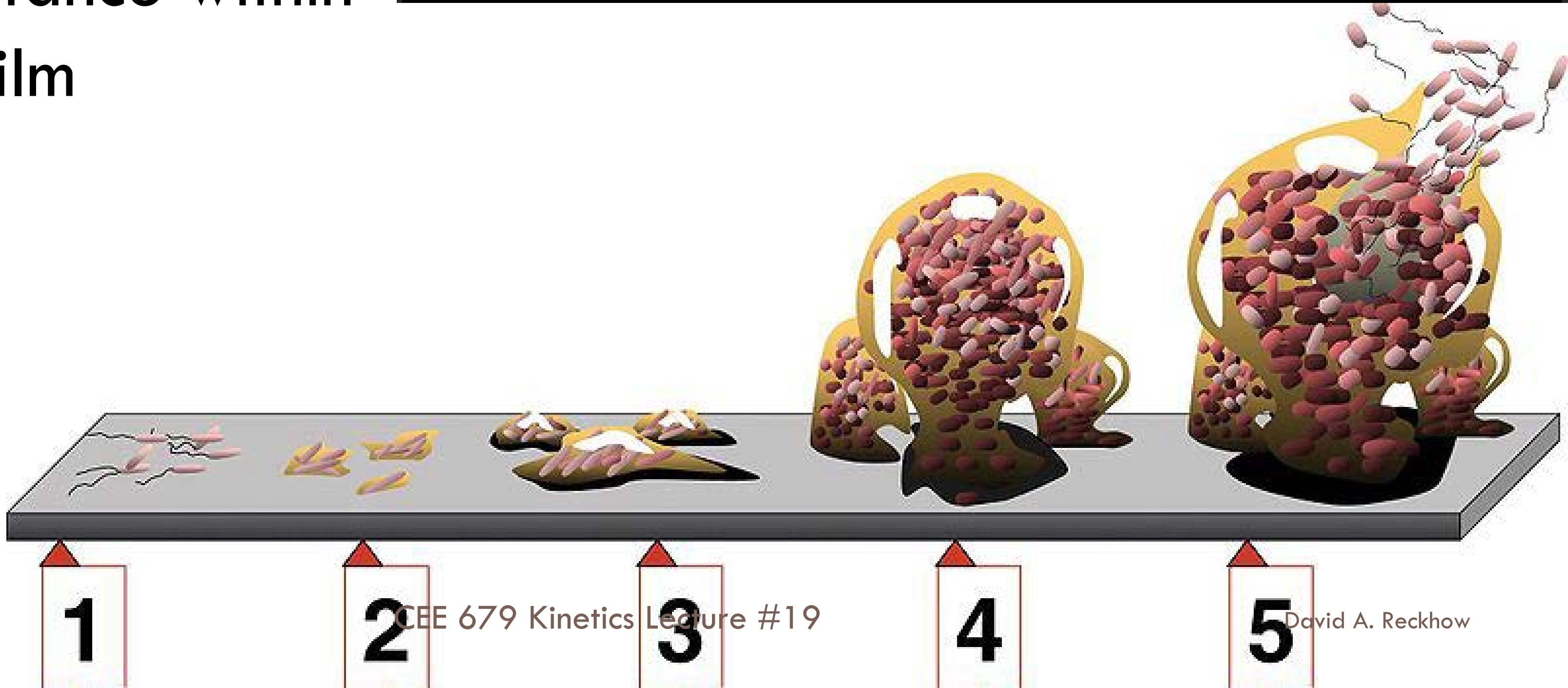
What could they have done?

- Find some direct evidence for biodegradation of HAAs in distribution systems
  - A product of the enzymatic reaction?
    - Chlorohydroxyacetate?
- Evidence of abiotic reactions?
  - Increase in MCAA?

What else?

- Consider mass transfer resistance within biofilm





What should be done next?

- Experimental Work
  - In-situ controlled study of flow velocity vs DCAA loss in a pipe segment?
  - Effect of biocide in above segment?
- Model Refinement
  - Account for internal mass transfer resistance
  - Combine with growth model for HAA degraders

SANCHO Model

- B1: biologically fixed bacteria
- B2: adsorbed bacteria

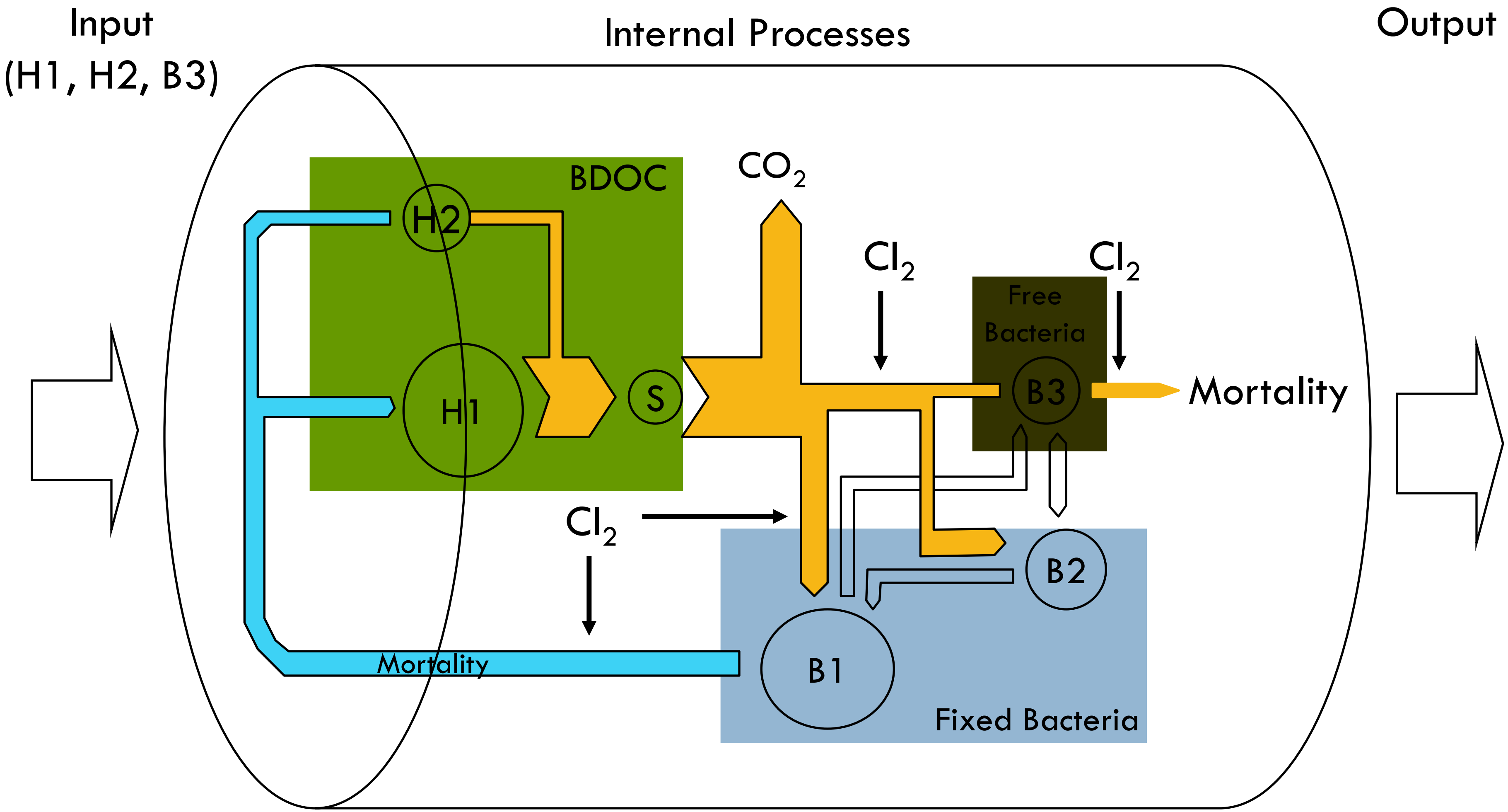


TABLE 2 Summary of equations used to compute the mass transfer rate constants for the distribution system and biologically active filter

Distribution System	Biologically Active Filter	Notation
$Sh = 0.023\ Re^{0.83}\ Sc^{0.33}$	$Sh = 1.09\epsilon^{-2/3}\ Re^{1/3}\ Sc^{1/3}$	d = pipe diameter
$k_m = \dfrac{ShD_w}{d}$	$k_m = \dfrac{ShD_w}{d_p}$	d_p = filter media grain diameter
$Sc = \dfrac{\mu_w}{\rho_w D_w}$	$Sc = \dfrac{\mu_w}{\rho_w D_w}$	D_w = solute diffusion coefficient in water
$Re = \dfrac{du\rho_w}{\mu_w}$	$Re = \dfrac{d_p v \rho_w}{(1-\epsilon)\mu_w}$	k_m = mass transfer rate constant
		Re = Reynolds number
		Sc = Schmidt number
		Sh = Sherwood number
		u = water flow velocity
		v = filtration rate
		ϵ = bed porosity
		μ_w = water viscosity at 20°C
		ρ_w = water density at 20°C

TABLE 3 General parameter values used for the model calculations

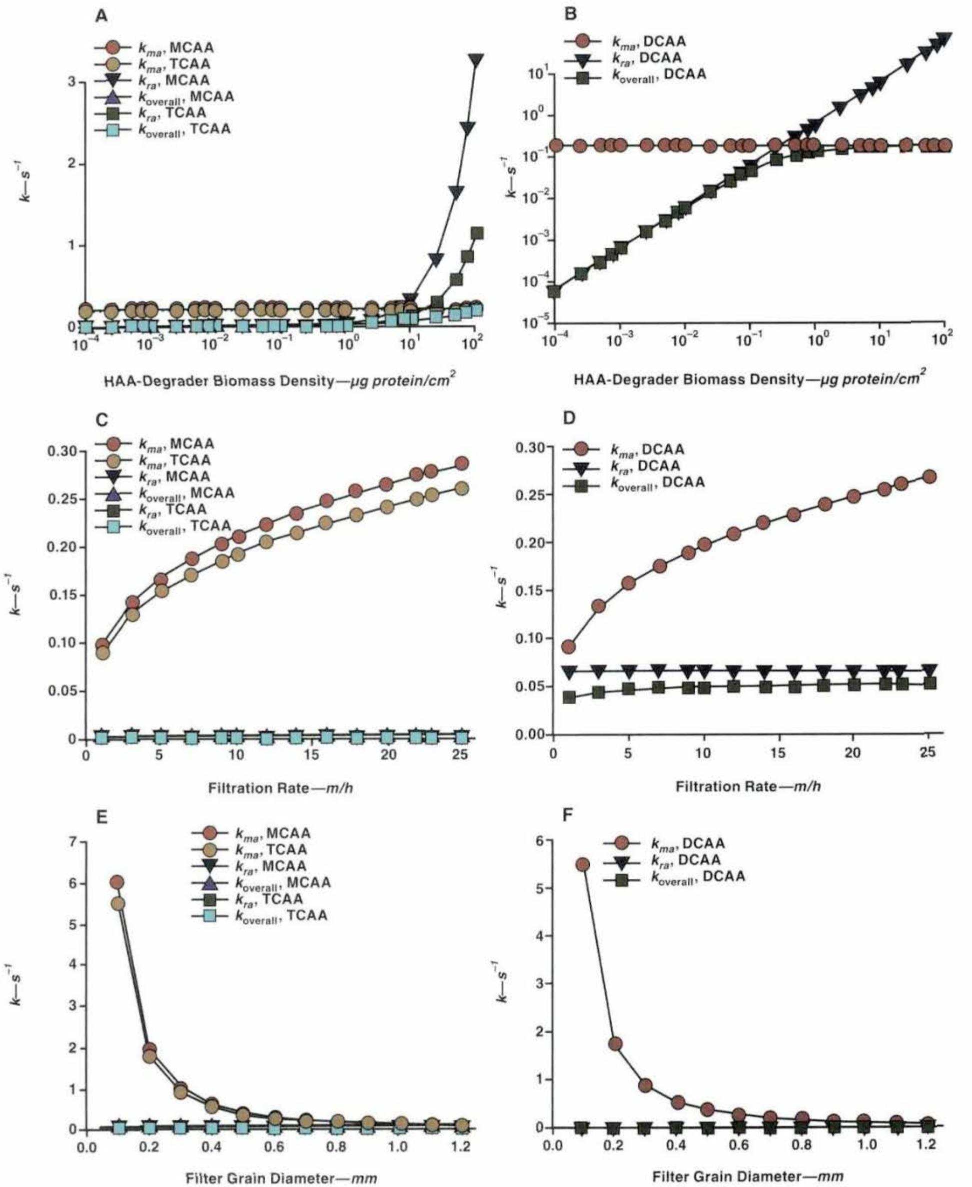
Parameter	Symbol	Value	References/Observations
Water temperature	T	20°C	Simulated summer conditions
Water viscosity	$\mu_{w,}20^{o}C$	1.0087×10^{-3} kg m^{-1} s^{-1}	Reynolds & Richards, 1996
Water density	$\rho_{w,}20^{o}C$	998.2 kg m^{-3}	Reynolds & Richards, 1996
Diffusion coefficient of MCAA in water	$D_{w,MCAA}$	1.12×10^{-9} m^2 s^{-1}	Zhang et al, 2004
Diffusion coefficient of DCAA in water	$D_{w,MCAA}$	1.02×10^{-9} m^2 s^{-1}	Zhang et al, 2004
Diffusion coefficient of TCAA in water	$D_{w,TCAA}$	9.75×10^{-10} m^2 s^{-1}	Zhang et al, 2004

DCAA—dichloroacetic acid, MCAA—monochloroacetic acid, TCAA—trichloroacetic acid

TABLE 4 Parameter values used to simulate the fate of haloacetic acids in water distribution systems

Parameter	Symbol	Range	References
Total bacterial density on the pipe wall	ρ	$10–10^8$ cells/cm^2; 10^7 cells/cm^2 for simulations *in* which other parameters were varied	Silhan et al, 2006; Lehtola et al, 2004; Chang et al, 2003; Ollos et al, 2003; Zhang et al,2002; Niquette et al, 2000; Donlan & Pipes, 1988; LeChevalier et al, 1987
Pipe diameter	d	2–36 in.; 6 in. for simulations in which other parameters were varied	McGhee, 1991; Rhoades, 1986
Water flow velocity	u	0.1–4 fps; 2 fps for simulations in which other parameters were varied	McGhee, 1991
Pipe distance	x	0–100 mi; 10 mi for simulations in which other parameters were varied	

FIGURE 4 Effect of HAA-degrader biomass density (A and B), filtration rate (C and D), and filter grain diameter (E and F) on the biodegradation rate constant k_{ra}, mass transfer rate constant k_{ma}, and the overall rate constant $k_{overall}$ for a biologically active filter



DCAA—dichloroacetic acid, HAA—haloacetic acid, MCAA—monochloroacetic acid, TCAA—trichloroacetic acid

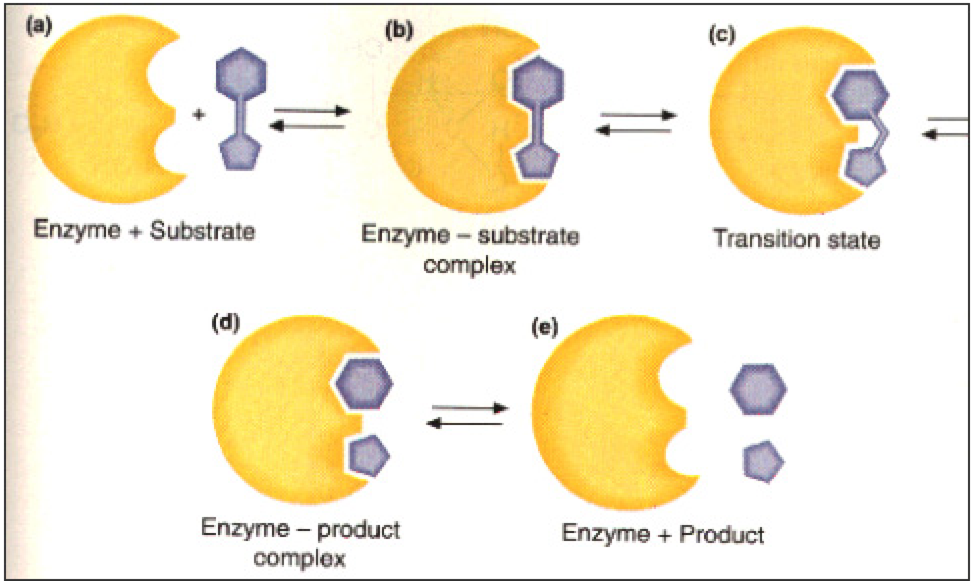
Simulations were performed using the kinetic parameters for Pennsylvania tap water enrichment cultures (i.e., PAWM, PAWD, PAWT). For parts A and B, the filtration rate was 10 m/h, and the filter grain diameter was 0.75 mm. For parts C and D, the HAA-degrader biomass density was 0.1 μg protein/cm^2 and the filter grain diameter was 0.75 mm. For parts E and F, filtration rate was 10 m/h, and the HAA-degrader biomass density was 0.1 μg protein/cm^2. For all simulations, the bed porosity was 40%.

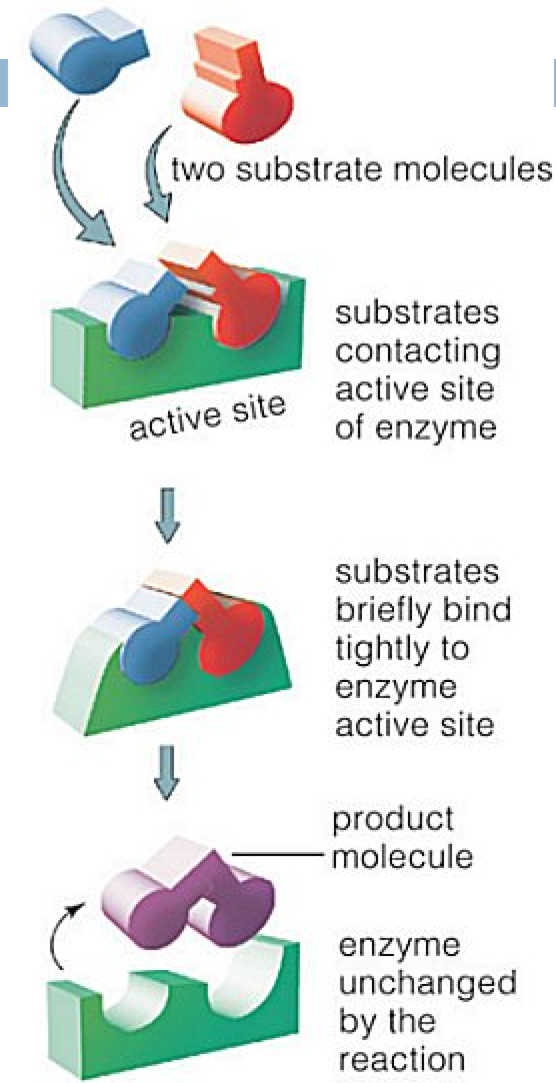
Effect of Zn on HAAs

- Effect of Zinc on the Transformation of HAAs in Drinking Water
  - Wei Wang and Lizhong Zhu
    - Journal of Hazardous Materials 174:40-46.

Enzymatic Reactions

- Many ways of illustrating the steps
  - Substrate(s) bond to active site
  - Product(s) form via transition state
  - Product(s) are released





Basic Enzyme Kinetics

Note that some references use k_2 for k_{-1}, and k_3 for k_2

- Irreversible

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} E + P$$

  - Single intermediate
    - The overall rate is determined by the RLS, k_2

$$r \equiv -\frac{d[S]}{dt} = \frac{d[P]}{dt} = k_2[ES]$$

    - But we don't know [ES], so we can get it by the SS mass balance

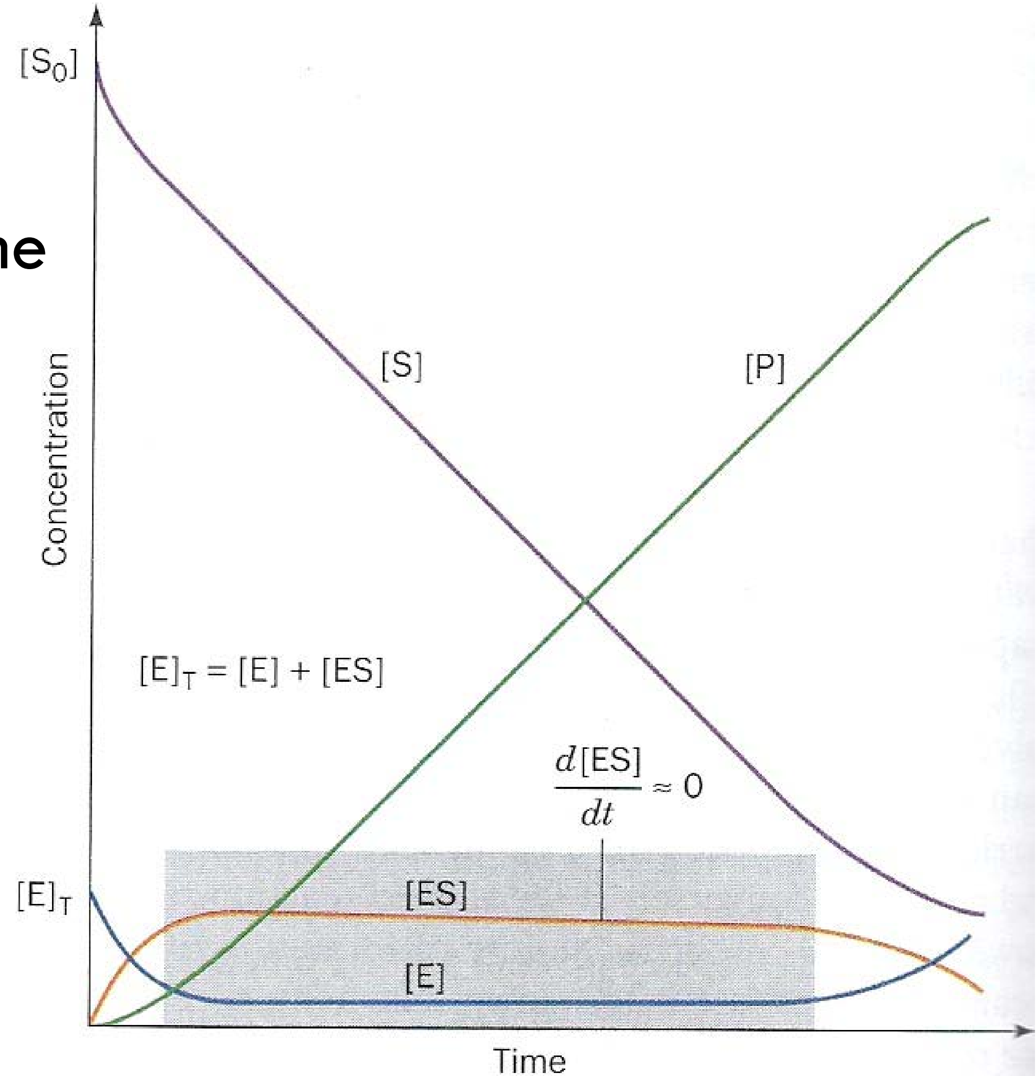
$$\frac{d[ES]}{dt} = 0 = k_1[E][S] - k_{-1}[ES] - k_2[ES]$$

    - Again, we only know $[E_o]$ or $[E_{tot}]$, not free [E], so:

$$0 = k_1([E_o] - [ES])[S] - k_{-1}[ES] - k_2[ES]$$

Reactants, products and Intermediates

- Simple Progression of components for simple single intermediate enzyme reaction
  - Shaded block shows steady state intermediates
  - Assumes $[S]>>[E]_t$
  - From Segel, 1975; Enzyme Kinetics



Basic Enzyme Kinetics II

- And solving for [ES],

$$k_1[ES][S]+k_{-1}[ES]+k_2[ES]=k_1[E_o][S]$$

$$[ES]=\frac{k_1[E_o][S]}{k_1[S]+k_{-1}+k_2}$$

$$[ES]=\frac{[E_o][S]}{[S]+\frac{k_{-1}+k_2}{k_1}}$$

David A. Reckhow

Michaelis-Menten

- Irreversible
  - Single intermediate

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} E + P$$

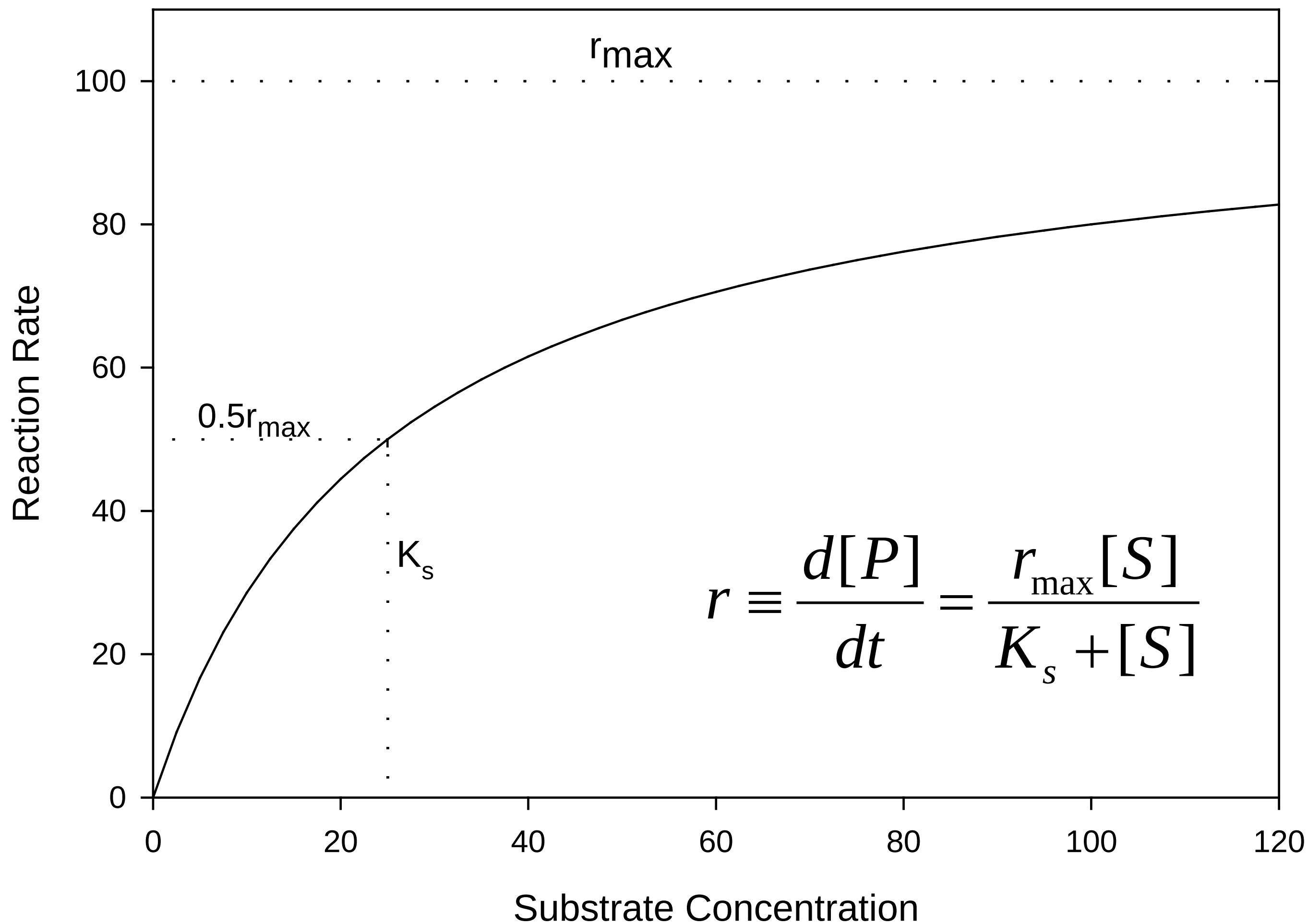
$$r \equiv \frac{d[P]}{dt} = k_2[ES]$$

$$[ES] = \boxed{\frac{[E_o][S]}{[S] + \frac{k_{-1}+k_2}{k_1}}}$$

$$r \equiv \frac{d[P]}{dt} = \frac{k_2[E_o][S]}{\frac{k_{-1}+k_2}{k_1} + [S]} = \frac{r_{max}[S]}{K_s + [S]}$$

Michaelis Menten Kinetics

- Classical substrate plot



Substrate and growth

- If we consider Y

$$r \equiv \frac{d[P]}{dt} = -\frac{d[S]}{dt} = \frac{1}{Y}\frac{dX}{dt}$$

- We can define a microorganism-specific substrate utilization rate, U

$$U \equiv \frac{r}{X} = \frac{dX}{dt} \Big/ YX \equiv \frac{\mu}{Y}$$

- And the maximum rates are then

$$U_{\max} \equiv k \equiv \frac{\mu_{\max}}{Y}$$

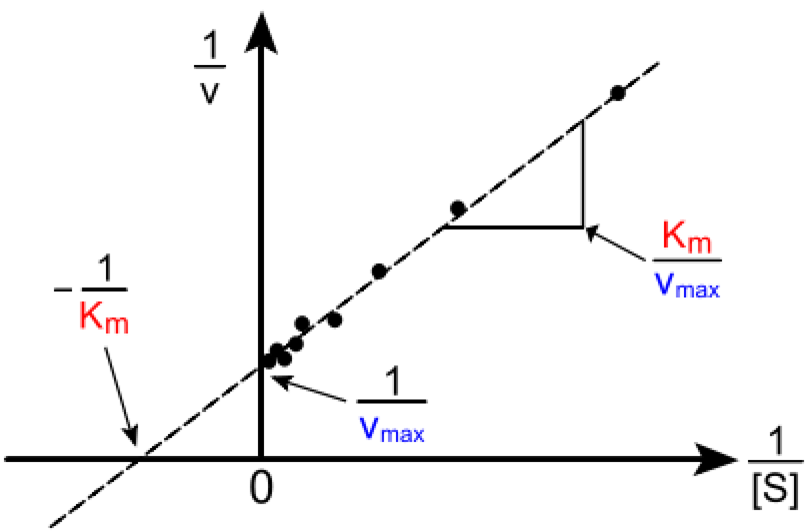
$$U \equiv \frac{1}{X}\frac{d[S]}{dt} = \frac{k[S]}{K_s + [S]}$$

and

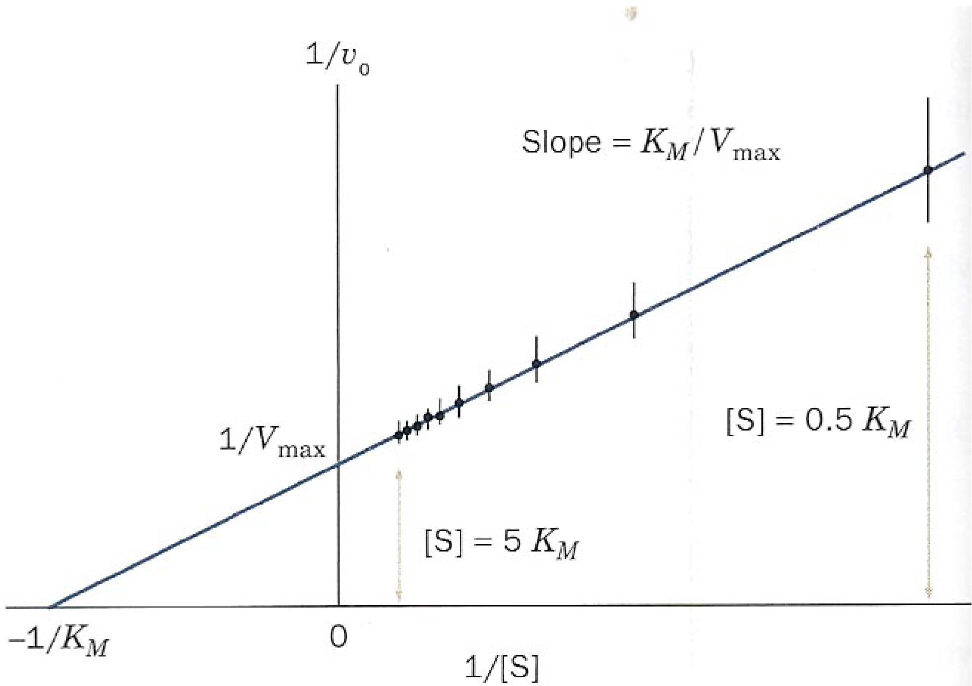
$$\mu \equiv \frac{1}{X}\frac{d[X]}{dt} = \frac{\mu_{\max}[S]}{K_s + [S]}$$

Linearizations

- Lineweaver-Burke
  - Double reciprocal plot



Wikipedia version

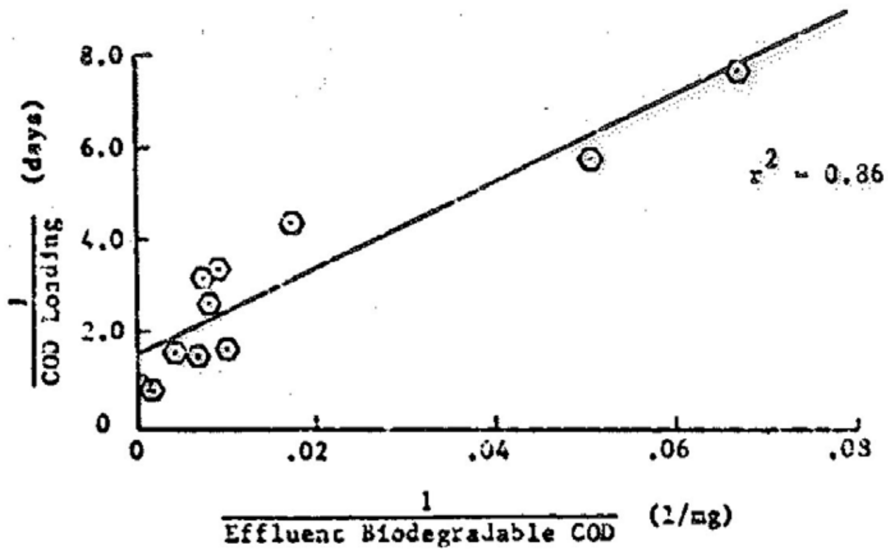


Voet & Voet version

- das

Lineweaver - Burk Plot

$$\frac{1}{U} = \frac{K_s}{k}\left(\frac{1}{S}\right) + \frac{1}{k}$$



$k = 0.64\ day^{-1}$

$K_s = 60\ mg/l$

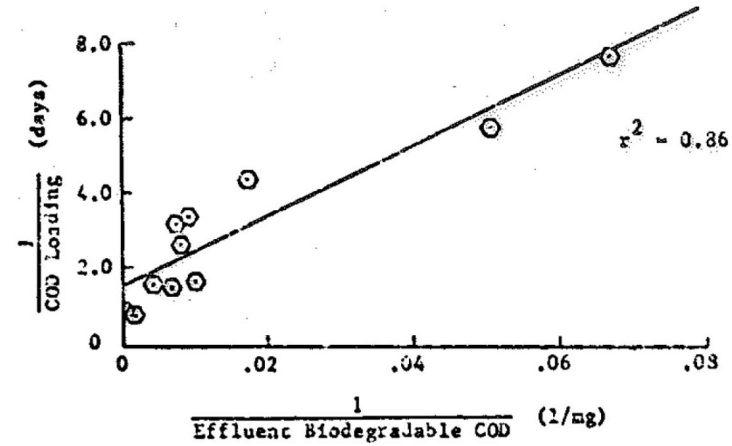
3 types

- Lineweaver Burk
- Hanes
- Eadie-Hofstee

Lineweaver - Burk

Plot

$$\frac{1}{U} = \frac{K_s}{k}\left(\frac{1}{S}\right) + \frac{1}{k}$$



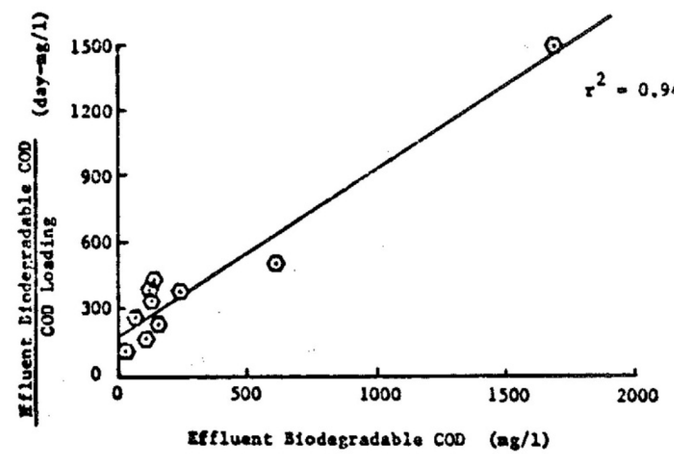
$k = 0.64\ day^{-1}$

$K_s = 60\ mg/l$

Hanes

Plot

$$\frac{S}{U} = \frac{1}{k}(S) + \frac{K_s}{k}$$



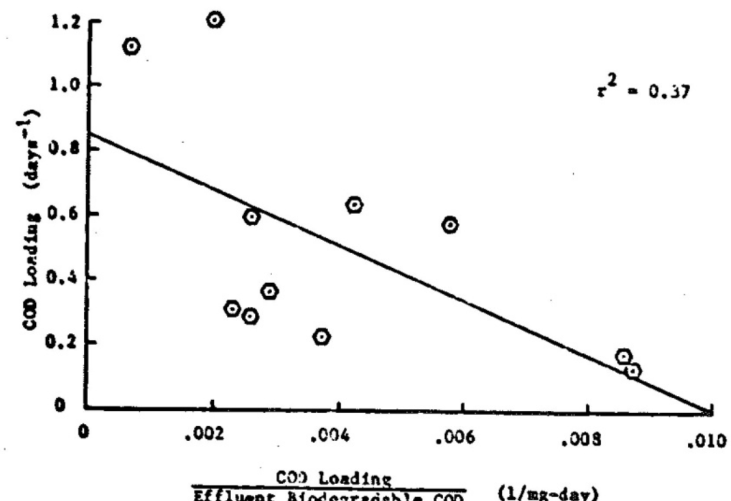
$k = 1.3\ day^{-1}$

$K_s = 238\ mg/l$

Eadie - Hofstee

Plot

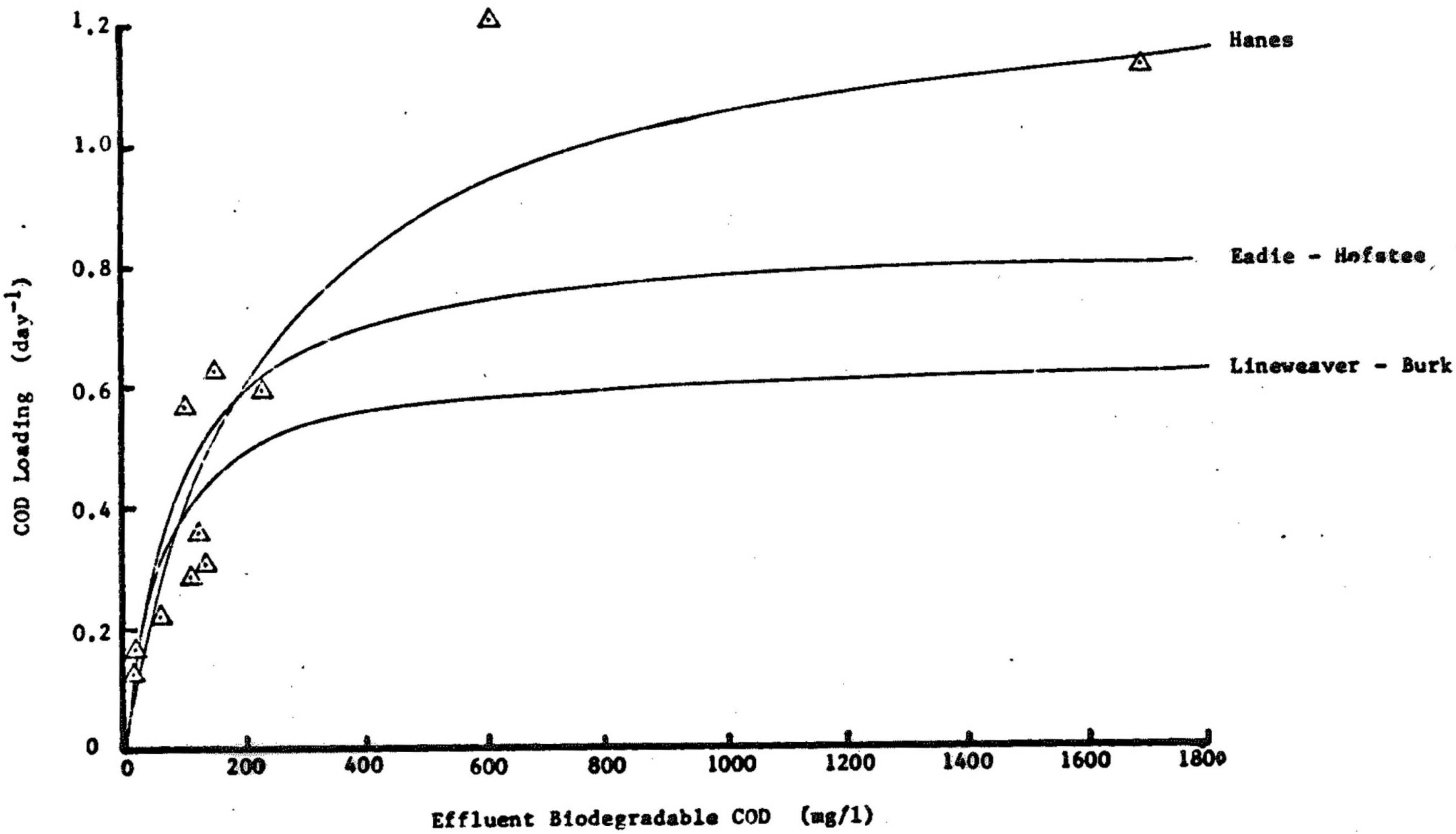
$$= -K_s\left(\frac{U}{S}\right) + k$$



$k = 0.86\ day^{-1}$

$K_s = 85\ mg/l$

Compare predictions



Multi-step

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} EP_2 \xrightarrow{k_3} 2E + P_2$$
$$\searrow P_1$$

- Double intermediate
  - Also gives:

$$r \equiv \frac{d[P]}{dt} = \frac{r_{\max}[S]}{K_s + [S]}$$

  - But now:

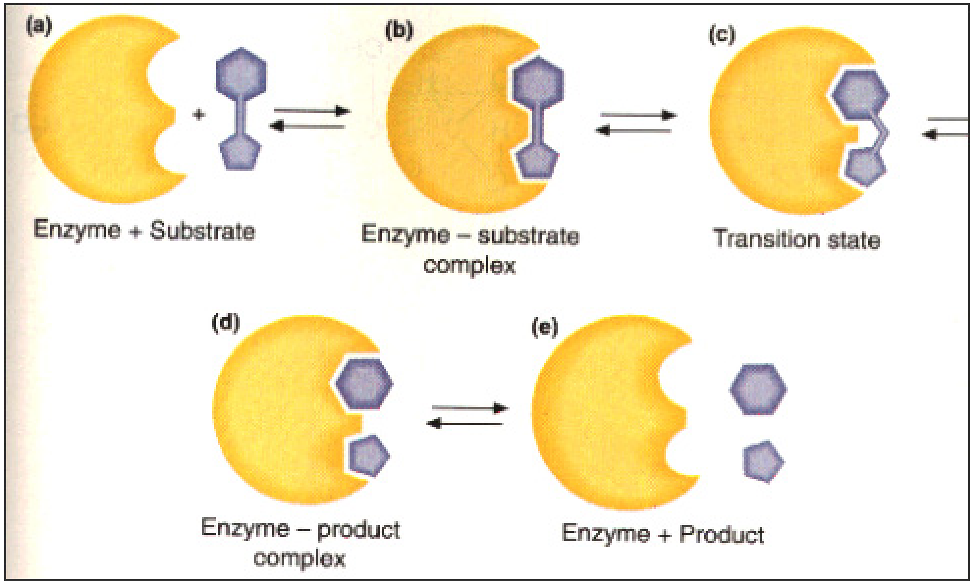
$$r_{\max} = \frac{k_2 k_3 [E_o]}{k_2 + k_3} \qquad K_s = \frac{k_3\left(k_{-1} + k_2\right)}{\left(k_2 + k_3\right)k_1}$$

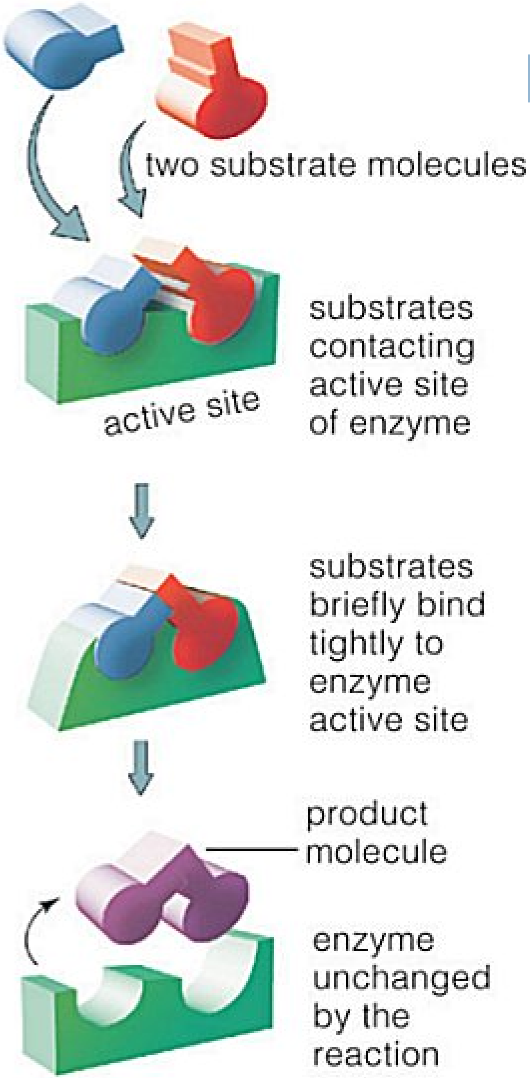
  - Note what happens when: $k_3 >> k_2$

- To next lecture

Enzymatic Reactions

- Many ways of illustrating the steps
  - Substrate(s) bond to active site
  - Product(s) form via transition state
  - Product(s) are released





Basic Enzyme Kinetics

Note that some references use k_2 for k_{-1}, and k_3 for k_2

- Irreversible

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} E + P$$

  - Single intermediate
    - The overall rate is determined by the RLS, k_2

$$r \equiv -\frac{d[S]}{dt} = \frac{d[P]}{dt} = k_2[ES]$$

    - But we don't know [ES], so we can get it by the SS mass balance

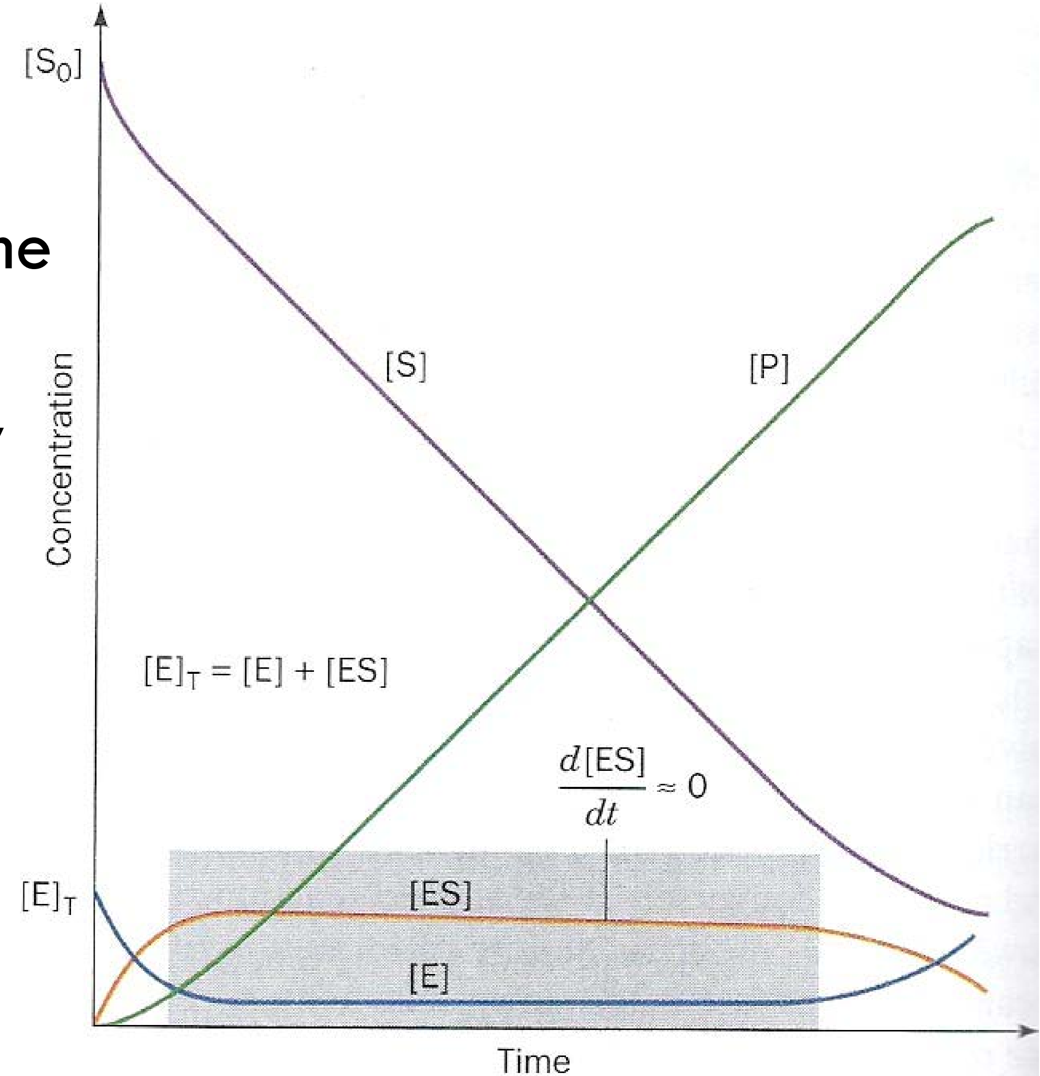
$$\frac{d[ES]}{dt} = 0 = k_1[E][S] - k_{-1}[ES] - k_2[ES]$$

    - Again, we only know $[E_o]$ or $[E_{tot}]$, not free [E], so:

$$0 = k_1\left([E_o] - [ES]\right)[S] - k_{-1}[ES] - k_2[ES]$$

Reactants, products and Intermediates

- Simple Progression of components for simple single intermediate enzyme reaction
  - Shaded block shows steady state intermediates
  - Assumes $[S] >> [E]_t$
  - From Segel, 1975; Enzyme Kinetics



Basic Enzyme Kinetics II

- And solving for [ES],

$$k_1[ES][S]+k_{-1}[ES]+k_2[ES]=k_1[E_o][S]$$

$$[ES]=\frac{k_1[E_o][S]}{k_1[S]+k_{-1}+k_2}$$

$$[ES]=\frac{[E_o][S]}{[S]+\frac{k_{-1}+k_2}{k_1}}$$

Michaelis-Menten

- Irreversible
  - Single intermediate

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} E + P$$

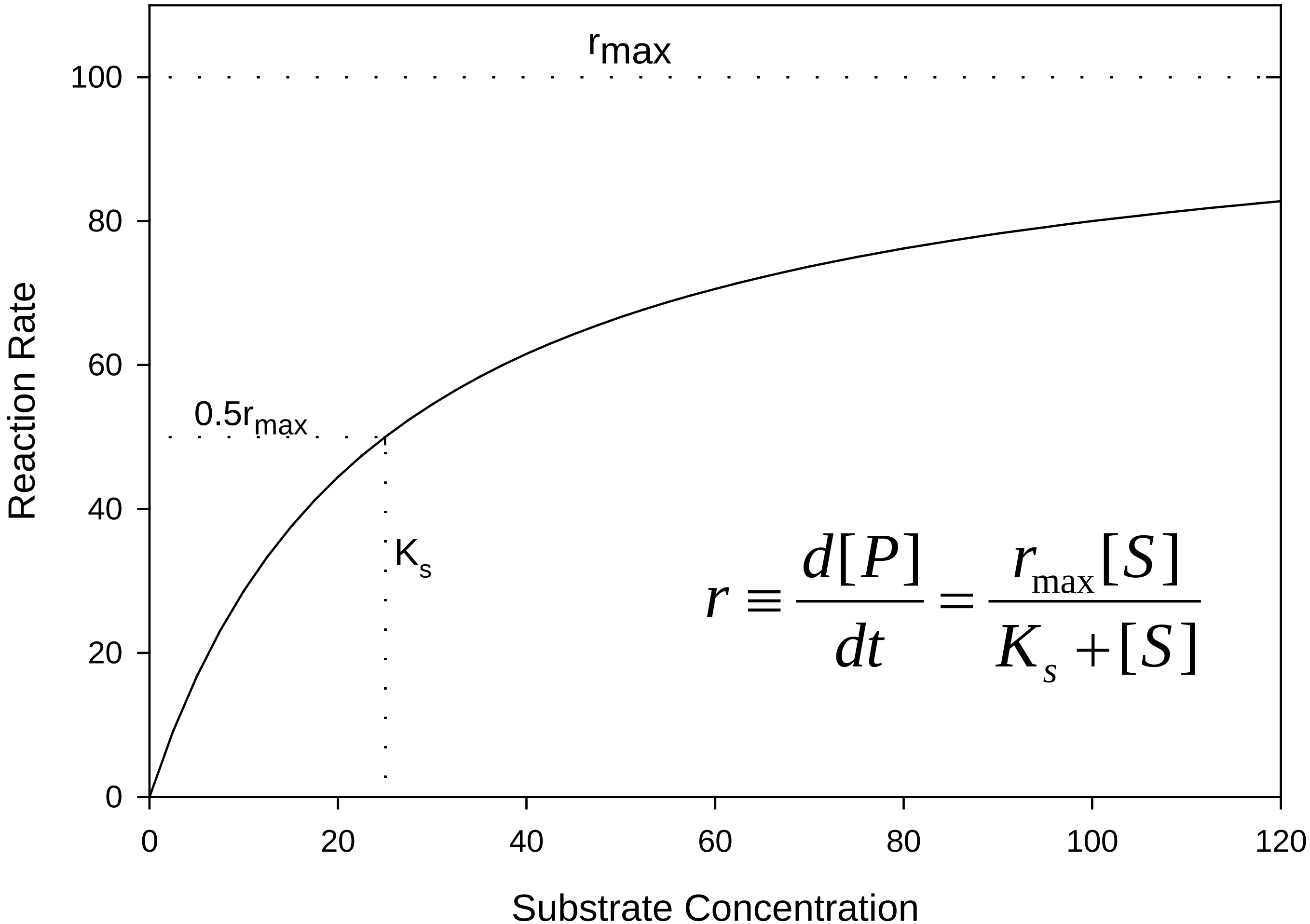
$$r \equiv \frac{d[P]}{dt} = k_2[ES]$$

$$\boxed{[ES] = \frac{[E_o][S]}{[S] + \frac{k_{-1}+k_2}{k_1}}}$$

$$r \equiv \frac{d[P]}{dt} = \frac{k_2[E_o][S]}{\frac{k_{-1}+k_2}{k_1} + [S]} = \frac{r_{max}[S]}{K_s + [S]}$$

Michaelis Menten Kinetics

- Classical substrate plot



Substrate and growth

- If we consider Y

$$r \equiv \frac{d[P]}{dt} = -\frac{d[S]}{dt} = \frac{1}{Y}\frac{dX}{dt}$$

- We can define a microorganism-specific substrate utilization rate, U

$$U \equiv \frac{r}{X} = \frac{dX}{dt} \Big/ YX \equiv \frac{\mu}{Y}$$

- And the maximum rates are then

$$U_{max} \equiv k \equiv \frac{\mu_{max}}{Y}$$

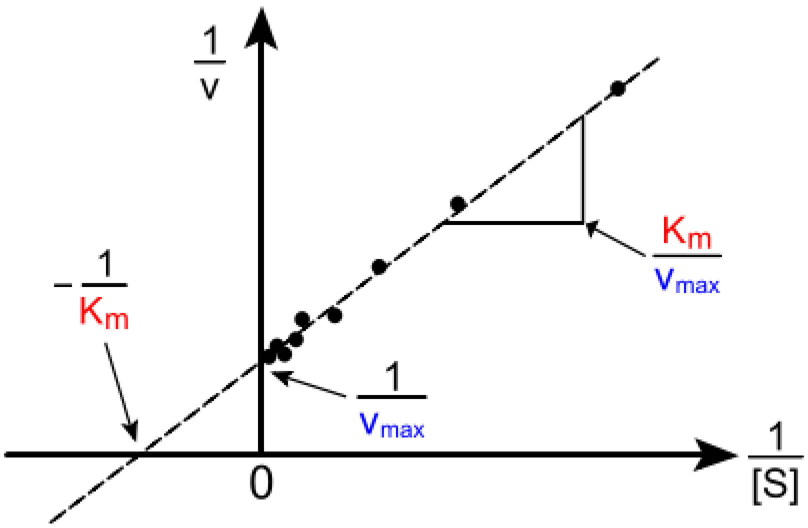
$$U \equiv \frac{1}{X}\frac{d[S]}{dt} = \frac{k[S]}{K_s + [S]}$$

and

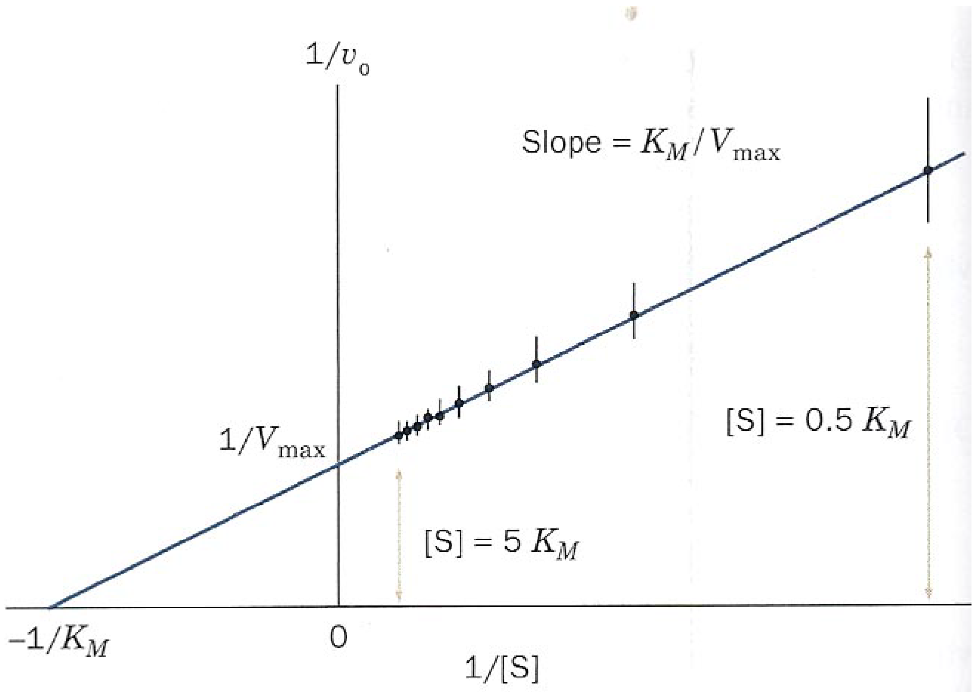
$$\mu \equiv \frac{1}{X}\frac{d[X]}{dt} = \frac{\mu_{max}[S]}{K_s + [S]}$$

Linearizations

- Lineweaver-Burke
  - Double reciprocal plot



Wikipedia version

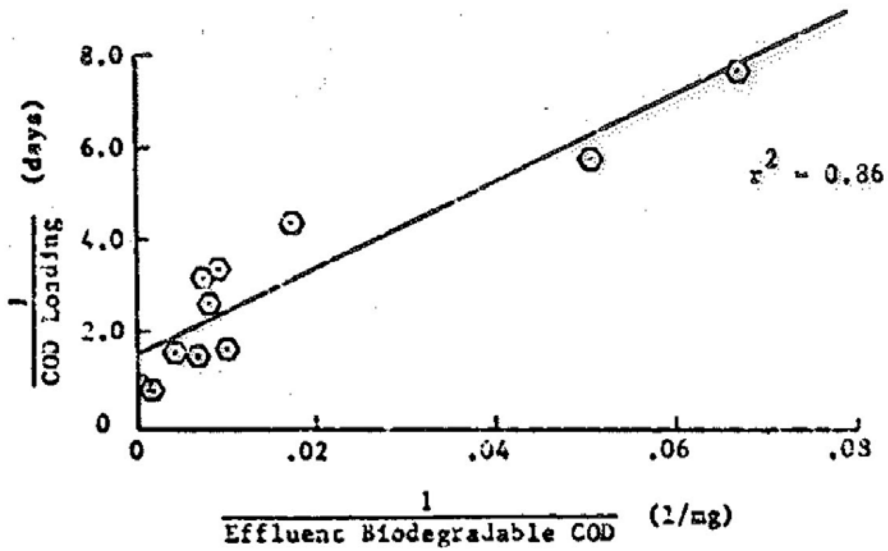


Voet & Voet version

- das

Lineweaver - Burk Plot

$$\frac{1}{U} = \frac{K_s}{k}\left(\frac{1}{S}\right) + \frac{1}{k}$$



$k = 0.64\ day^{-1}$

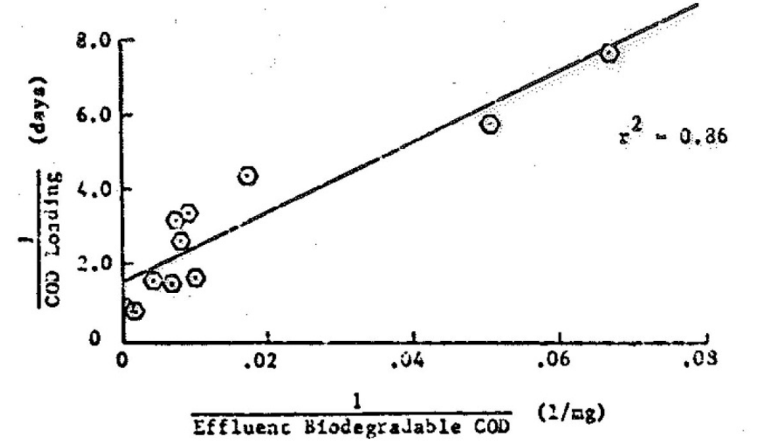
$K_s = 60\ mg/l$

3 types

Lineweaver - Burk

Plot

$$\frac{1}{U} = \frac{K_s}{k}\left(\frac{1}{S}\right) + \frac{1}{k}$$



$k = 0.64\ day^{-1}$

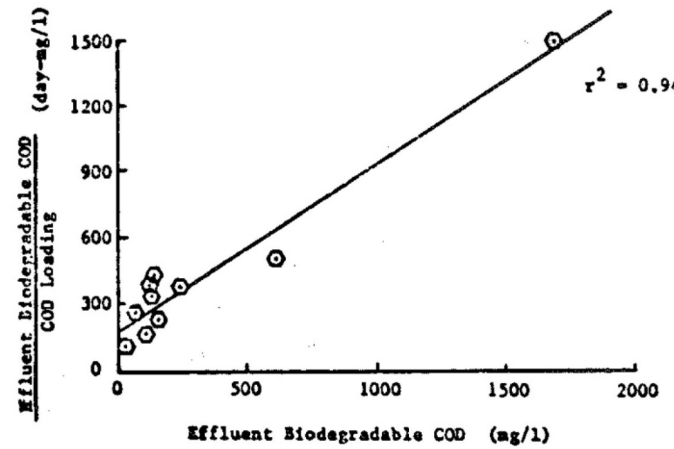
$K_s = 60\ mg/l$

- Lineweaver Burk

Hanes

Plot

$$\frac{S}{U} = \frac{1}{k}(S) + \frac{K_s}{k}$$



$k = 1.3\ day^{-1}$

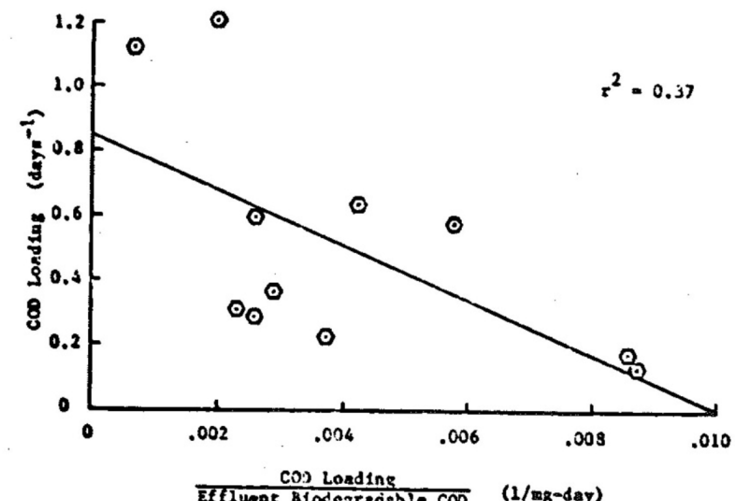
$K_s = 238\ mg/l$

- Hanes

Eadie - Hofstee

Plot

$$= -K_s\left(\frac{U}{S}\right) + k$$

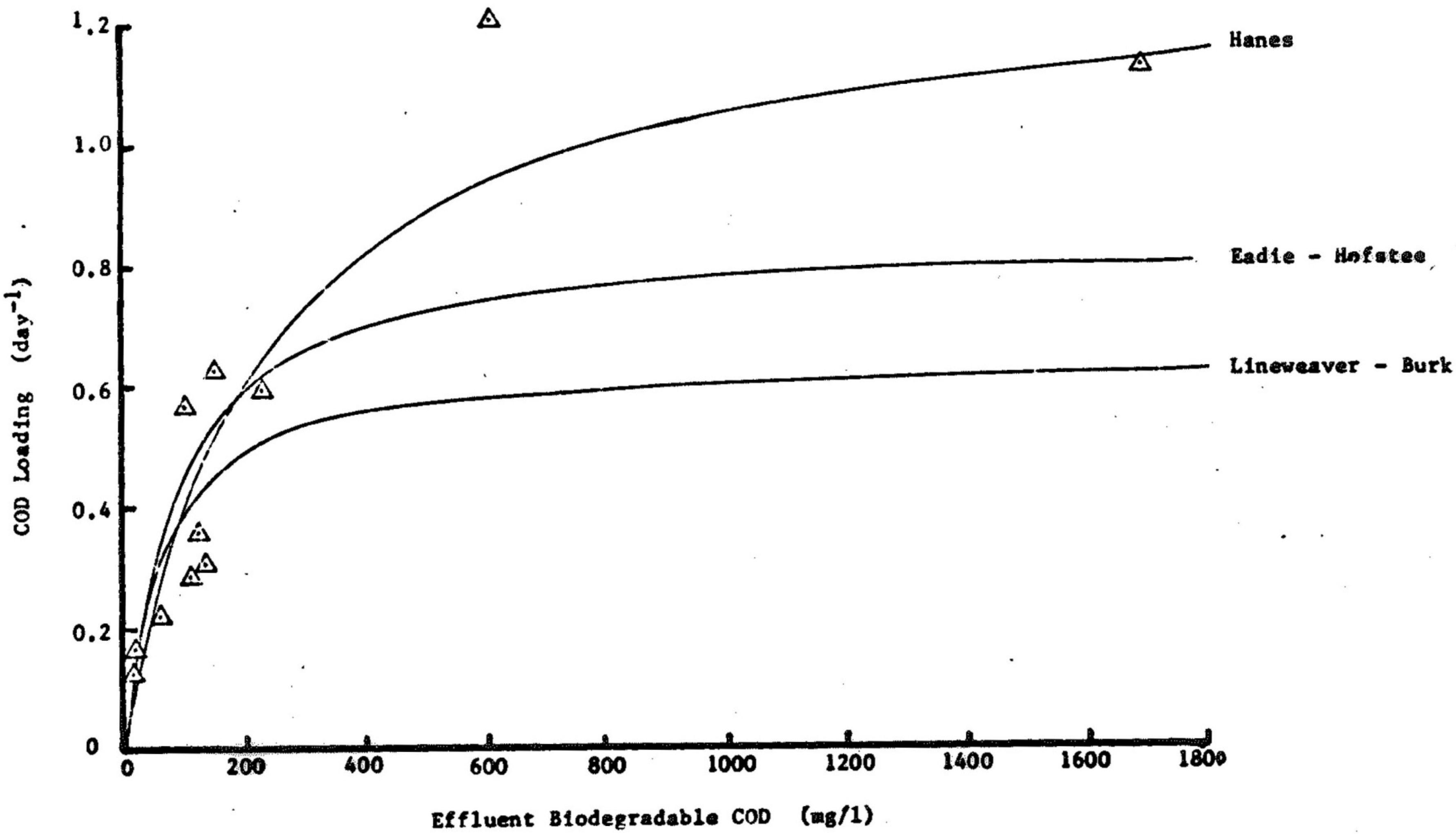


$k = 0.86\ day^{-1}$

$K_s = 85\ mg/l$

- Eadie-Hofstee

Compare predictions



Multi-step

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} EP_2 \xrightarrow{k_3} 2E + P_2$$
$$ES \searrow P_1$$

- Double intermediate
  - Also gives:

$$r \equiv \frac{d[P]}{dt} = \frac{r_{\max}[S]}{K_s + [S]}$$

  - But now:

$$r_{\max} = \frac{k_2 k_3 [E_o]}{k_2 + k_3} \qquad K_s = \frac{k_3\left(k_{-1} + k_2\right)}{\left(k_2 + k_3\right)k_1}$$

  - Note what happens when: $k_3 >> k_2$

- To next lecture