Lecture 15 - Biological Reaction Kinetics (continued)

We have addressed the "How?" and "How much?" of biological wastewater treatment. Need to also consider the "How fast?" (i.e. the kinetics)

Biological reactions generally involve enzymes to catalyse the reactions:

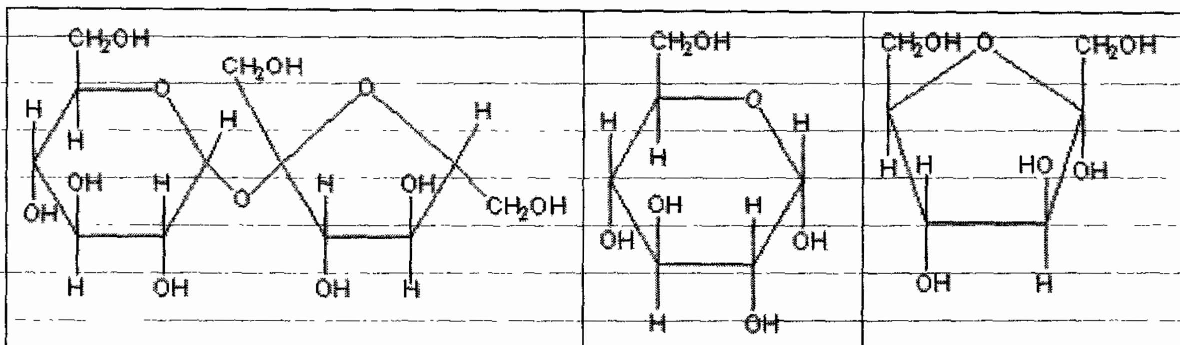
$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_4}{\overset{k_3}{\rightleftharpoons}} E + P$$

E - enzyme
S - substrate
P - products

Example from V & H, pg. 528

sucrose + invertase $\rightleftharpoons$ sucrose-invertase

$\rightarrow$ glucose + fructose + invertase



Sucrose | Glucose | Fructose

Anthony Carpi, Ph.D. "Carbohydrates," Visionlearning Vol. CHE-2 (5), 2003.
http://www.visionlearning.com/library/module_viewer.php?mid=61. Accessed April 2, 2005.

Michaelis and Menten (1913) proposed equation to determine kinetics of enzyme-catalysed reactions

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_3} E + P$$

Assume at start: $[E] = [E]_0$ $\quad [ES] = 0$ $\quad [S] \gg [E]$

$$\frac{d[ES]}{dt} = k_1[E][S] - k_2[ES] - k_3[ES] \approx 0$$ for reaction at uniform rate

Also $[E] + [ES] = [E]_0 \rightarrow [E] = [E]_0 - [ES]$

$$k_1\left([E]_0 - [ES]\right)[S] = (k_2 + k_3)[ES]$$

$$k_1[E]_0[S] = \left((k_2+k_3) + k_1[S]\right)[ES]$$

$$[ES] = \frac{k_1[E]_0[S]}{k_1[S] + (k_2+k_3)}$$

$$= \frac{[E]_0[S]}{[S] + \frac{k_2+k_3}{k_1}} = \frac{[E]_0[S]}{[S] + K_m}$$

K_m = Michaelis-Menton constant or half-velocity const or half-saturation const

Rate of product formation, r

$$r = \frac{d[P]}{dt} = k_3[ES]$$

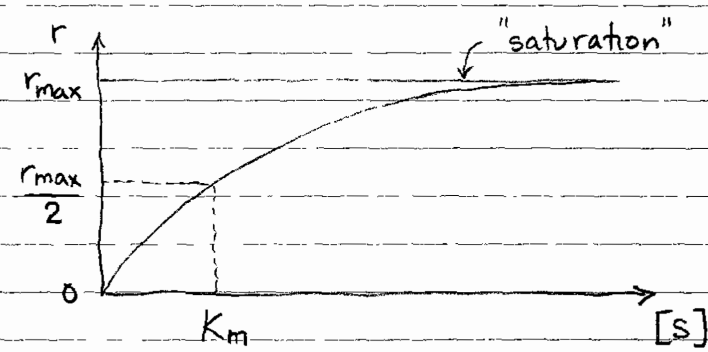
$$= \frac{k_3[E]_0[S]}{[S] + K_m}$$

$K_3 [E]_0$ is maximum rate of P formation, occuring when all E is in the form of ES

$$\left.\frac{d[P]}{dt}\right|_{max} = K_3 [ES]_{max} = K_3 [E]_0 = r_{max}$$

$\therefore$

$$r = r_{max} \frac{[S]}{[S] + K_m}$$



In lab experiments, Monod (1949) found similar behavior in growth of bacterial cultures

$$\mu_g = \mu_{max} \left(\frac{S}{K_s + S} \right)$$

S = substrate conc [M substrate / L^3]
K_s = half-saturation constant [M substrate / L^3]
μ_g = biomass specific growth rate $\left[\frac{\text{M new cells}}{\text{M cells} \cdot \text{T}} \right]$
μ_{max} = maximum specific growth rate

Goal of wastewater treatment is not to grow cells per se but for the microbiological culture to utilize substrate in the form of organic matter in wastewater.

Substrate utilization rate is closely related to biological growth and follows Monod-type equation:

Equation accounts for effect of substrate conc (S) as well as effect of biomass conc (X)

Rate of substrate utilization, r_{su} (< 0 to denote substrate is being reduced)

$$r_{su} = -\frac{kXS}{K_s + S}$$

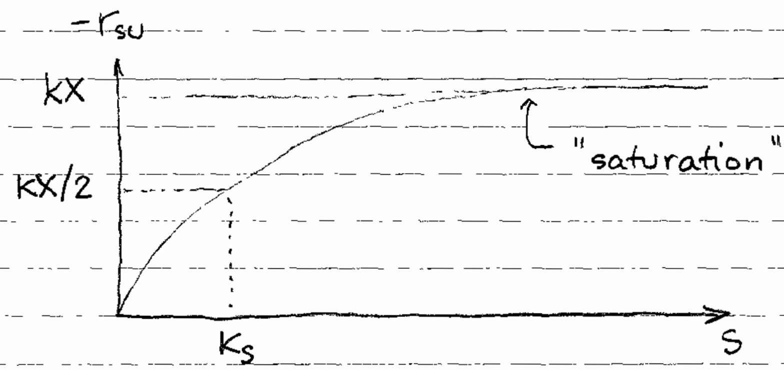
r_{su} = rate of substrate utilization $\left[\frac{M}{L^3 T}\right]$

k = maximum specific substrate utilization rate $\left[\frac{M\ \text{substrate}}{M\ \text{organism}\ T}\right]$

X = organism (biomass) conc $\left[\frac{M\ \text{organism}}{L^3}\right]$

S = concentration of growth-limiting substrate $\left[\frac{M\ \text{substrate}}{L^3}\right]$

K_s = half-saturation constant $\left[\frac{M\ \text{substrate}}{L^3}\right]$



Note that cell specific growth rate μ_g [Mass new cells / Mass cells · time] is related to substrate utilization rate r_{su} [Mass substrate / time] by cell yield [Mass new cells / Mass substrate] and cell conc X [Mass cells / vol]

$$-r_{su} = \frac{\mu_g}{Y} X \qquad -r_{su} = \frac{kXS}{K_s + S} = \frac{\mu_g}{Y} X = \frac{\mu_{max}\left(\frac{S}{K_s+S}\right)X}{Y}$$

and $$k = \frac{\mu_{max}}{Y}$$

k max spec substrate utilization rate

μ_{max} max spec growth rate

Actual bacterial growth is generally less than μ_m depending on substrate availability and endogenous respiration:

$$r_g = -Y r_{su} - K_e X$$

r_g = net biomass production (growth) rate $\left[\frac{M \text{ biomass}}{L^3 \ T}\right]$ usually $\left(\frac{g \text{ VSS}}{m^3 \cdot d}\right)$

K_e = endogenous decay coefficient $[T^{-1}]$

Endogenous decay includes:

- Cell material used to generate energy for cell maintenance
- Cell death
- Predation by protozoa and other organisms

Specific biomass growth rate (as opposed to cell growth rate)

$$\mu = \frac{r_g}{X} = -\frac{Y}{X} r_{su} - K_e$$

$$= + \frac{Y}{X} \frac{kXS}{K_s + S} - K_e$$

$$= Y \frac{kS}{K_s + S} - K_e$$

$$\mu = \mu_{max} \frac{S}{K_s + S} - k_e = \mu_g - k_e$$

= specific biomass growth rate $\left(\frac{g\ VSS}{g\ VSS \cdot d} \right)$

Typical values:

k 5 g bs COD/g VSS·d

↑ biodegradable soluble COD

K_s = 60 mg BOD/L
= 40 mg bsCOD/L

Y = 0.6 mg VSS/mg BOD
= 0.4 mg VSS/mg bs COD

k_e = 0.1 mg VSS/mg VSS·d

Rate of oxygen uptake

$$r_o = \overbrace{-r_{su}}^{>0} \overbrace{-1.42 r_g}^{<0}$$

r_o = oxygen uptake rate mg O_2/L·d

r_{su} in mg bs COD/L·d or mg BOD/L·d

r_g in mg VSS/L·d

1.42 = COD of cell tissue g bsCOD/g VSS

accounts for O_2 to oxidize substrate (r_{su})
less COD that goes into cell synthesis

Environmental factors affect growth

Temperature

		Overall range	Optimal range
Psychrophilic	(cold-loving)	10-30°	12-18
Mesophilic	(middle-loving)	20-50	25-40
Thermophilic	(heat-loving)	35-75	55-65

Growth rates vary with temp

$$K_T = K_{20}\,\Theta^{(T-20)}$$

K_T reaction rate at temp T in °C
K_{20} reaction rate at 20 °C
Θ temperature activity coeff

$\Theta = 1.047$ → growth doubles with $\Delta T = 15°C$
$\Theta = 1.072$ → growth doubles with $\Delta T = 10°C$

T temperature in °C

Low temps (5-10 C) requires extended detention and reduced loadings to compensate for lower biological activity

pH

4 to 9 OK 6.5 to 7.5 best

DO

Aerobic – DO > 1.5 to 2.0 mg/L
Anoxic – DO < 0.2 mg/L (denitrification)
Anaerobic – DO << 0.1 mg/L NO_3 < 1 mg/L