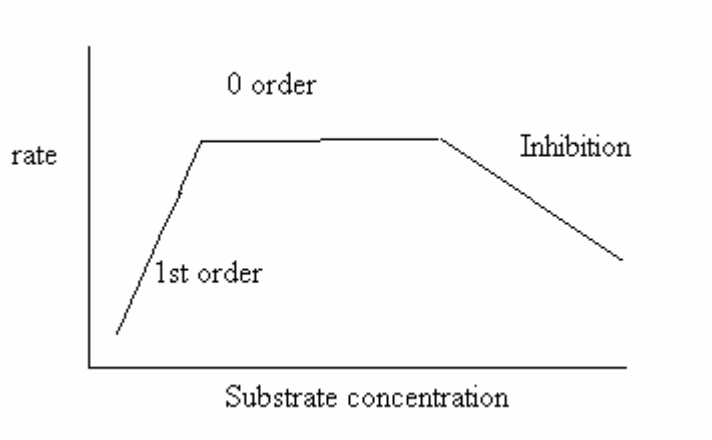
Inhibition of substrate degradation

When microbes are presented with a substrate a different type of kinetics may be observed due to toxicity or inhibition of the organisms or enzymes by the substrate. This can be depicted as drawn below.



The concentration may increase to a point where it becomes inhibitory to its own degradation or toxic to the microorganisms and thus slow the degradation down. Inhibition of degradation rate by high concentrations of the substrate can be described by the equation

$$v = \frac{V}{1 + \frac{K_m}{S} + \left(\frac{S}{K_i}\right)^n}$$

where the terms v, V, S and K_m are as used before, and
n = empirical constant describing the order of inhibition
K_i = the inhibition constant.

Another type of inhibition that can be observed in mixed waste streams is inhibition of the degradation of one substrate due to the degradation of another substrate. This type of inhibition can occur through three different mechanisms.

1. Competitive inhibition

Competitive inhibition occurs when two substrates are competing for the same enzyme. The substrates both bind reversibly to the enzyme active site, denying access to the site to each other. This causes a new K_m to be reached at higher concentrations than before but does not change V.

The equation that describes this inhibition is as follows.

$$v = \frac{VS}{S + K_m\left(1 + \frac{I}{K_i}\right)}$$

where

I = concentration of inhibiting chemical
K_i = inhibition constant (enzyme substrate dissociation constant)
The effects of this type of inhibition on the various plots for the data have been presented as handouts.

2. Uncompetitive inhibition

The inhibiting compound is not a substrate of the enzyme so does not bind to the free enzyme, but binds to the enzyme substrate complex. This causes a complete change in kinetics.

the V is decreased
a new K_m is found at a lower concentration (see next three pages)
The equation that describes this type of inhibition is as follows

$$v = \frac{VS}{K_m + S\left(1 + \frac{I}{K_i}\right)}$$

The terms are all as described previously. The effects of this type of inhibition on the various plots for the data have been presented as handouts.

3. Non competitive inhibition

This type of inhibition is complex. It is characterized by a random binding of the inhibitor to the enzyme or enzyme substrate complex. The effect is that the
K_m is unchanged
V is decreased
See last three of next six pages
The equation that describes this type of inhibition is as follows.

$$v = \frac{VS}{K_m\left(1 + \frac{I}{K_i}\right) + S\left(1 + \frac{I}{K_i}\right)}$$

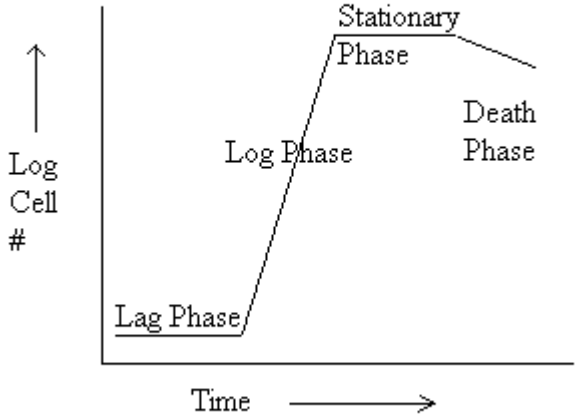
The effects of this type of inhibition on the various plots for the data have been presented as handouts.

By plotting the data as presented in the handouts, the type of inhibition can be determined.

Growth of Microbial Cultures

Microbial growth results in the doubling of the cell population in a specific time. This time depends on the type of organism and the substrate the organisms are growing on. The following diagram explains the usual stages of growth observed for experiments where organisms are exposed to substrates under batch incubation conditions. The stages of growth are as follows.

1) lag - very little growth or metabolism (acclimation or adaptation)
2) log - phase with logarithmic growth and high metabolic capabilities
3) stationary - phase where increase in cell number is balanced by cell death
4) death - phase where cell death overcome cell growth



When cells are grown under continuous culture, which describes most of our engineering practices except sequencing batch reactors (SBR), cells will be present in various stages of growth but we usually model it as a steady state. As a population, we assume that all cells are in log growth phase, but this is not true. To account for this a correction is made for the energy required for cell maintenance of non-actively growing cells. The term endogenous decay is used to lump together all of the factors that might cause a decrease in cell mass.

Endogenous decay formula $r_d = -k_d X$

where k_d = endogenous decay coefficient ($time^{-1}$)

X = concentration of cells (mass/vol.) (mg/L)

If we combine this into the other equations, we arrive at an equation for the net specific growth rate (μ').

$$\mu' = \mu_m \frac{S}{K_s + S} - k_d \qquad \text{or} \quad r'g = \frac{\mu_m XS}{K_S + S} - k_d X$$

If we use the substrate degradation kinetics linked to growth of the cells, then we can say

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

Where μ in this case is the specific growth rate g VSS/ g VSS d.

Typical Kinetic constants

Table 7-9 (overhead) presents some typical kinetic constants for aerobes (i.e. activated sludge). Note on measurement units. As described earlier we most often use measures of the gross organic content in wastewaters rather than try and account for every individual species. The measurements of COD and BOD (ultimate or at t=5) are the most commonly used. The text introduces $_{bs}$COD as a unit that means biodegradable soluble COD. This should be equal to the BOD ultimate and I will continue to use BOD instead of that term.

Rate of Oxygen Uptake

Since oxygen uptake is proportional to substrate degradation it can easily be calculated from the rate of substrate utilization. The amount of substrate used for cell growth must be subtracted from this since material that is incorporated into cell material does not exert the oxygen demand it would if it was converted to CO_2.

$$r_o = -r_{su} - 1.42 r_g$$

The 1.42 is the factor that accounts for the COD of cell tissue if it was oxidized to CO_2.

$$C_5H_7NO_2 + 5O_2 \Rightarrow 5CO_2 + NH_2 + 2H_2O$$

therefore

$$\frac{5 \text{ moles of } O_2}{1 \text{ mole of cells}} \text{ x } \frac{5(32 \text{ g/mol } O_2)}{113 \text{ g/mol Cells}} = 1.42 \text{ g } O_2 / \text{g Cells} \quad \text{(Equation 7-5 in text)}$$

Temperature effects

Biological reactions just like any other are temperature sensitive. The effect of temperature on biological reactions can be described by the following model.

$$r_{T1} = r_{T2} \theta^{(T1-T2)}$$

where

r_{T1}= reaction rate at one temp
r_{T2} = reaction rate at other temp
θ = temperature activity coefficient

T1 = temperature °C
T2 = second temp °C

Typical values for θ are 1.04 for activated sludge, 1.08 for aerated lagoons, and 1.035 for Trickling filters.

Biomass measures

As mentioned earlier the total volatile suspended solids measurement is often used as a measure of the biomass in the system. This is comprised of live cells, dead cells, cells debris and other solids from the influent. Some of the cell debris is not readily degradable. This amount has been estimated to be 10 to 15% of the total weight. Therefore the rate of production of non-degradable biomass can be predicted by the equation:

$r_{Xd} = f_d(k_d)X$ equation 7-25 in text

where r_{Xd} = rate of cell debris production
f_d = the fraction of the biomass that remains as cell debris (10 to 15%).

To predict the total VSS production rate you can use the following

$r_{XT\,VSS} = -Yr_{su} - k_dX + f_d(k_d)X + QX_{o,I}/V$ equation 7-26 in text

where
r_{XTVSS} = rate of total VSS production
$X_{o,I}$ = influent non biodegradable VSS
V = reactor volume
Q is the influent flow rate
the other terms have been defined previously.

In the case where specific populations of organisms are performing specific reactions or degrading specific substrates, we don't really care about the total VSS, but only the specific organisms that are doing the job we care about. This is especially important for nitrifying and some industrial reactors. One generalized equation that can be used to predict a specific population would be

$F_{X,\,act} = (-Yr_{su} - k_dX)/r_{XT,VSS}$ Equation 7-27 in text.

Where the r_{su} would be specific for that substrate.

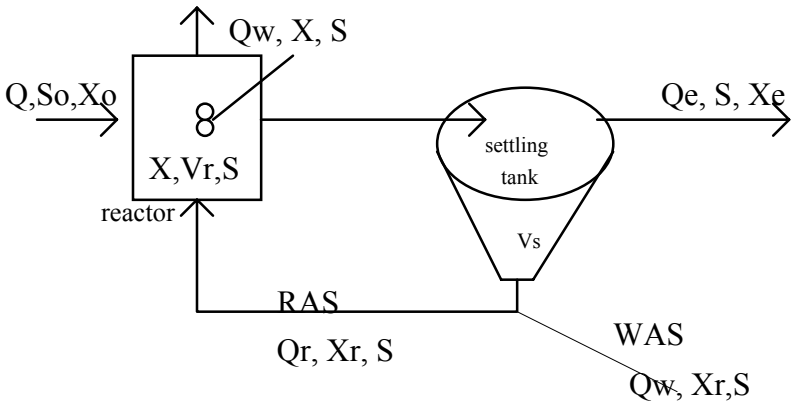
The last concept of biomass that you need to pick up is the observed yield. This relates the total amount of growth in a reactor to the total amount of substrate utilized (or relates the rates).
$Y_{obs} = -r_{XT,VSS}/r_{su}$

You can also use $Y_{obs} = X/(S_0-S)$

Modeling Suspended Growth Treatment Processes

Flow Scheme

Many different flow schemes can exist for suspended growth treatment processes. Depending on various design and space considerations the simplest flows are diagrammed below.



New terms

Q_w = waste flow
Qe = effluent flow = (Q-Q_w)
Q_r = sludge return flow
X_o = microorganisms in the influent
X_r = microorganism concentration in return sludge flow line
X_e = microorganism concentration in effluent
RAS = return activated sludge
WAS = waste activated sludge
So = Influent substrate concentration
S effluent substrate concentration

The mixing and aeration (if it is an aerobic process) are usually accomplished in one step. The pressure of the air input also mixes the system. The cells settle out of the MLSS in the settling tank where some of them are wasted (biological sludge) and some are recycled back into the reactor to maintain a good population of cells in the reactor.

In order to develop design or control parameters for this type of process we have to develop a model that provides the information we need to do the tasks.

Mass Balance Models

The majority of the models (or sets of equations that describe specific aspects of the process are developed from mass balance approaches. If you are good at mass balances you can solve any treatment process design or analysis questions. There are some typical relationships that are developed through the mass balance approach that we use more frequently than others. These are presented below.

Biomass Mass Balance

As with any mass balance a word statement should be developed to explain the inputs, changes and outputs of the commodity in question. It is very important in this system to define where the boundaries are. In most cases we will define the boundary to include both the reactor and the settler since these two function together to keep cells within the system.
In this case you would say as follows

Rate of accumulation = rate of input from flow + growth in the system – loss from the system.

To put it into mathematical terms that are easily developed

$$\frac{dX}{dt}V = QX_o - [(Q - Q_w)X_e - Q_w X_R] + r_g V$$ equation 7-32 from text.

if you wase from the recycle line

$$\frac{dX}{dt}V_r = QX_0 - [(Q - Q_w)X_e + Q_w X] + r_g V$$

if you waste from the reactor (not done all that much anymore so we won't do much with this)

At steady state dX/dt = 0 and if there are no bacteria in the influent then the equation (7-32) simplifies to

$(Q-Q_w)X_e + Q_wX_R = r_gV$ Equation 7-33 from text

By combining this with equation 7-21 (rate of growth) and dividng through by X then you get

$$\frac{(Q - Q_w)X_e + Q_w X_R}{VX} = -Y\frac{r_{su}}{X} - k_d$$ equation 7-34 from text

The inverse of the right hand side of this equation is defined as the solids retention time or SRT the denominator

$$SRT = \frac{VX}{(Q - Q_w)X_e + Q_w X_R}$$

To give this some meaning, you can look at it as the volume of cells in the reactor divided by the cells wasted (either intentionally or just lost to the effluent)

After some manipulation as discussed in the text we end up with a specific substrate utilization rate (U).

$$U = \frac{r_{su}}{X} = -Q\frac{(S_0 - S)}{VX} = -\frac{S_0 - S}{\tau X}$$ equation 7-38 in text

where (S_0-S) = mass concentration of substrate utilized

S_0 = substrate concentration in influent

S = substrate concentration in effluent

τ = hydraulic detention time

To determine the mass concentration of microorganisms the equation below can be used.

$$X = \frac{SRT}{\tau}\frac{Y(S_0 - S)}{(1 + k_d SRT)}$$ equation 7-43 in text

While effluent substrate concentration can be represented as

$$S = \frac{K_s(1 + k_d SRT)}{SRT(Yk - k_d) - 1}$$ equation 7-40 in text

The mixed liquor suspended solids concentration (MLVSS) includes the biomass plus the non degradable VSS and can be modeled using a mass balance approach resulting in the following equation:

$$X_T = \frac{(SRT)}{\tau}\left[\frac{Y(S_o - S)}{1 = (k_d)SRT}\right] + (f_d)(k_d)SRT + \frac{X_{o,i}SRT}{\tau}$$ equation 7-50 in text.

i.e. the total cells = biomass + cell debris +influent VSS

The solids production rate (P_x) can be determined by mass balance approach resulting in the following equation

$$P_{X,VSS} = \frac{QY(S_o - S)}{1 + k_d SRT} + \frac{(f_d)(k_d)YQ(S_o - S)SRT}{1 + k_d SRT} + QX_{0,i}$$ equation 7-52 in text

i.e. the total sludge produced = biomass produced +cell debris + influent VSS

Besides being a design item, the SRT is also an operational parameter. Figure 7-13 (overhead) shows the effects of too long or too short an SRT on the resultant cell concentration and the substrate concentration.

The observed yield can be calculated by

$$Y_{obs} = \frac{Y}{1 + k_d SRT} + \frac{(f_d)(k_d)(Y)SRT}{1 + k_d SRT} + \frac{X_{o,i}}{S_o - S}$$ equation 7-56 in text

You can get away without the last part since we most often that the amount of material in the influent is limited in comparison with what is in the reactor.

The reactor volume can be determined using the equation that has been obtained by rearranging one of the above equations.

$$V_r = \frac{(SRT)QY(S_o - S)}{X(1 + k_d SRT)}$$

Oxygen requirements

A mass balance for the degradation of carbonaceous material can be developed to give you the following equation

$R_O = Q(S_o\text{-}S) - 1.42\ P_x$

Where R_o is the oxygen required. (kg/d)

Example in text 7-6. Go through on your own, ask questions in class if you don't follow it.

Application Example 8-1 from old text. Next three pages this is not the same example as is in the current version of the text but I thought I would leave it in so you can have two examples of this type of problem I have copied it for you. The terminology is slightly different between the two books but you should be able to follow.

Another Example (Note the cell debris from some of equations has been omitted in this example, since it is from old material. The student could rework the problem using the cell debris parts of the equations as an exercise.

CFSTR with recycle
Q = 1650 m^3/d
r =0.6
S_o = 200 mg/L COD
S = 34 mg/L COD
X_e = 15 mg/L VSS
X_r = 5,000 mg/L
θ = 8 h = 0.33 d

fits Monod kinetics Rate constants as follows
k = 0.95 mgCOD/mg VSS/d K_s = 85 mg/L COD

Y = 0.48 mg VSS/mg COD $K_d = 0.07\ d^{-1}$

Determine
1. Total COD in effluent
2. Waste flow from underflow
3. Sludge age
4. MLVSS (X)

1. Total COD in effluent
34 mg/L + 15(1.42 mg COD/mf VSS) = 55 mg/L

4. $X = \frac{SRT}{\tau}\frac{Y(S_o - S)}{1 + K_d SRT}$ we need a SRT for this

or we can use

$$X = \frac{(So - S)(K_s + S)}{\tau k S} = \frac{(200\ mg/L - 34\ mg/L)(85\ mg/L + 34\ mg/L)}{(0.33\ d^{-1})(0.95\ d^{-1})(34\ mg/L)} = 1835\ mg/L$$

3. Sludge age
= 1/SRT
There are lots of ways to calculate SRT, the easiest for this purpose is:

$$\frac{1}{SRT} = \frac{YkS}{K_S + S} - k_d = \frac{(0.48)(0.95\ d^{-1})(34\ mg/L)}{85\ mg/L + (34\ mg/L)} - 0.07\ d^{-1} = 16.6\ d$$

2. Q_w Again there are many ways. Here is one way:

$$SRT = \frac{VX}{Q_w X_r + (Q - Q_w)X_e}$$

rewrite again
$SRT\ (Q_w X_r + (Q - Q_w)Xe) = VX$

Calculate $V = Q\tau = 1650\ m^3/d\ (0.33\ d) = 550\ m^3$

$(16.6\ d)\ (Q_w)(5{,}000\ mg/L) + 16.6\ d\ (1650 - Q_w)15 = 550\ m^3 \times 1850\ mg/L$

$Q_w = 7.33\ m^3/d$

Process Performance and Stability

Figure 7-14 in text. Overhead (In my overhead θ_c is used instead of SRT.

SRT_{min} = minimum solids retention time
below this value waste stabilization fails and cell washout occurs.

This can be approximated using equations 7-68 to 7-70

For design a good rule of thumb is to use an SRT of = 2 to 20 times SRT^M

Using Continuous Culture data to Determine Kinetic Constants

In many cases pilot scale or bench scale CFSTR reactor studies are performed with specific wastewaters to derive the kinetic constants Y, k, K_s, μ_m and k_d. The parameters that we can easily (and usually do) measure in these systems are S_o, S, SRT or τ, and X. These can be used to derive the necessary kinetic constants using the following two equations that have been derived from the equations presented previously. (see Handout)

$$\frac{X\tau}{S_o - S} = \frac{K_S}{k}\frac{1}{S} + \frac{1}{k}$$

and

$$\frac{1}{SRT} = -Y\frac{(S_o - S)}{X\tau} - k_d$$

Two plots are made

one $\frac{X\tau}{S_o - S}$ vs 1/S (the y intercept is 1/k, the slope is K_S/k)

and the other 1/SRT vs $\frac{(S_o - S)}{X\tau}$ (the slope is Y, the Y intercept is $-k_d$)

μ_m is determined by multiplying k x Y.

The handout goes through 1 example calculation.

Modeling Plug Flow reactors

A plug flow reactor (Figure 8-1 overhead) is one in which the influent wastewater is mixed with the return sludge and travels through the reactor as a plug. This results in more difficult to model conditions as the concentration of cells is theoretically increasing during the pass through the reactor and the concentration of the substrate to be removed is constantly decreasing through the pass. It can be modeled as a number of reactors in series or with a few assumptions can be treated more generally.

Assumptions to simplify plug flow modeling (my wording)

1. The change in concentration of organisms through the pass through the reactor is not significant to the model (SRT/τ >5d). The term $\overline{X}$ is used to represent this as the average concentration of organisms.
2. The rate of substrate utilization then becomes

$$r_{SU} = -\frac{kS\overline{X}}{K_S + S}$$

by integrating this equation over the length of the reactor and substituting in the equation that can be used to calculate X for $\overline{X}$ results in:

$$\frac{1}{SRT} = \frac{Yk(S_o - S)}{(S_o - S) + (1+\alpha)K_S \ln(S_i / S)} - k_d$$

True plug flow should be more efficient in that the organisms are (at least initially) seeing higher concentrations of the substrate, it is rare that we can operate at the peak efficiency. The plug flow reactor is also more sensitive to toxic inputs because they enter the reactor at higher concentrations than in complete mix reactors. The plug flow process can be altered to include step feed to help distribute the influent more evenly through the reactor.

Biological Denitrification

Main Forms of Nitrogen

In influent municipal waste water - NH_3, Urea, Amino acids (from proteins)

In effluent from biological treatment - NH_3, NO_3^-, NO_2^-,

Any of these and more can be in industrial waste e.g nitroaromatics, etc.

Why is it important that we treat them.

Nitrogen compounds are nutrients i.e. they will stimulate plant and algae growth as well as other autotrophs.

NH_3 - is a DO utilizer,
- is toxic at fairly low levels
- effects disinfection because it depletes Chlorine
- is regulated against

During the degradation of proteins, some sugars and nucleic acids, the nitrogenous components are released as ammonia. Some of the ammonia is used as a nitrogen source for growth, but in most municipal wastewater and some industrial wastewater there is excess ammonia produced. This will effect the pH of the wastewater as well as cause some toxicity problems.

The removal of ammonia is a 2 step process one group of organisms carries out the oxidation of ammonia to nitrite using O_2 as the electron acceptor.

1 st part

$NH_4^+ + 3/2\ O_2 \rightarrow NO_2^- + 2H^+ + H_2O$ $\Delta G^{\circ\prime} = -260.2$ kJ/rxn
-272 kJ/rxn

The group of bacteria that performs this is of the group *Nitrosomonas*.
They are common soil organisms
These organisms are Gram negative autotrophs

energy source (electron donor)	NH_4^+
electron acceptor	O_2
carbon source	CO_2

The cell yield is low because of these conditions; they produce very little energy during this process

The first reaction is catalyzed by the enzyme ammonia monooxegenase (AMO), this enzyme is membrane bound and is one of the reasons that the ammonia oxidizing organisms have lots of convoluted membrane systems.

$$NH_3 + O_2 + 2H^+ + 2e^- \rightarrow NH_2OH + H_2O$$

This reaction requires 2 e^- which are supplied by the next step.

The second reaction is catalyzed by the enzyme hydroxylamine oxidoreductase (HAO)
This is a periplasmic enzyme.

$$NH_2OH + H_2O \rightarrow HNO_2 + 4H^+ + 4e^-$$

Because this reaction produces four electrons two of which are recycled to AMO, two electrons are donated to the electron transport chain and are used to reduce O_2.

These reactions carried out by *Nitrosomonas* produce NO_2^- which is itself a toxic compound. Thus the *Nitrosomonas* live in close association with the next group of bacteria, which remove the nitrite by converting it to nitrate.

$NO_2 + 1/2\ O_2 \rightarrow NO_3^-$ $\Delta G^{\circ\prime} = -76$ kJ/rxn.

Since it take approximately 34 kJ to make ATP these organisms should be able to make two ATP per mole of NO_2. Experimental results show that only one ATP is actually made from each mole of nitrite. Thus the process is 50% efficient.

The organisms use a very short electron transport chain since the redox difference between nitrite and oxygen is only 0.43 V

The cells use the Calvin cycle for growth on CO_2 so require 18 mol of ATP to produce 1 six carbon unit.
The growth yields are very low for this group of organisms so they wash out of treatment systems very easy.

Overall yields for the complete conversion of ammonium to nitrate are around 0.2 mg VSS/ mg NH_4^+-N

Overall balanced reaction ($f_s = 0.05$)

$$NH_4^+ + 1.863\ O_2 + 0.098CO_2 \rightarrow 0.0196\ C_5H_7O_2N + 0.98\ NO_3^- + 0.0941\ H_2O + 1.98H^+$$

This results in a consumption of 4.25 g O_2/ g ammonium nitrogen, 0.16 g of new cells are formed and 7.07 g of alkalinity (as $CaCO_3$) are used.

The design of nitrification systems is based on ammonia oxidation kinetics (they are limiting)

$$\mu_n = \left(\frac{\mu_{nm} N}{K + N} \right) - k_{dn}$$

Where
μ_n = specific growth rate of nitrifying bacteria (g new cells/g cells d)
μ_{nm} = maximum specific growth rate of nitrifying bacteria (g new cells/g cells d)
N = nitrogen concentration (mg/L)
K_n = half velocity constant (mg/L)
K_{dn} = endogenous decay coefficient for nitrifying organisms (g VSS/g VSS d)

Various maximum growth rates have been observed usually ranging from 0.25-0.77 g VSS/g VSS d) much lower than that for heterotrophic organisms.

Factors Effecting Nitrification

1. Do concentration. These organisms are very sensitive to the O_2 concentration and cannot compete for O_2 well with heterotrophs. An equation for this limitation has been developed.

$$\mu_n = \left(\frac{\mu_{nm} N}{K + N} \right) \left(\frac{DO}{K_o + DO} \right) - k_{dn}$$

Where
DO = concentration of Dissolved Oxygen (should keep above 2 mg/L)
K_o = half saturation coefficient for DO (usually use 1.3 mg/L)

2. Temperature - nitrifying organisms are very temperature sensitive, appreciable rates are only achieved when temperatures are above 15°C. The following table provides some possible STR values for nitrifiers at different temperatures.

Temperature	SRT
10°C	10 to 20 d
20°C	4 to 7 d
>28	Kinetics change and NO_2^- ox must govern

3. NH_3 and NO_2^- concentrations

The concentrations of ammonium and nitrite will effect the maximum growth rate of the organisms involved. During start up and any process upset, nitrite might build up in the reactor, this is an item that must be watched.

4. pH - must have between a pH of 6.8 and 9.0. The removal of nitrogen means a removal of base so the pH tends to drop. The Alkalinity must be preserved. Model is as follows

$$\mu_{m_n} = \mu\,[1 - 0.833(7.2 - \mathrm{pH})]$$

5. Toxicity

These organisms are much more sensitive to toxic compounds (even some compounds that would not be toxic to any other organisms). Some of these are solvents, amines, proteins, tannins, phenolics, alcohols, cyanates, ethers, carbamates, benzene, metals (nickel, chromium, copper etc.) and un-ionized ammonia.

Biological Denitrification

Two processes

1. Assimilatory - nitrate is reduced to ammonium and taken up for cell growth. This can be accomplished by most bacteria and plants. It is not sufficient for an economical way to remove nitrate except in wetlands systems where you can get some removal with plant growth.

2. Dissimilatory - The removal of nitrate under anoxic conditions by facultative bacteria able to use nitrate as an electron acceptor.

Process: - organic material is used as a source of carbon and electrons with nitrate serving as the electron acceptor. This can only be carried out after the nitrifying organisms produce the nitrate. A source of organic carbon is also required. This would not be present if the waste came through a nitrification process.

Solutions (Figure 7-21 overhead).

1. add an external carbon source to provide energy for nitrate reduction (postanoxic)
2. play around with flow schemes (preanoxic).

Microbiology

A wide range of bacteria have been found to be able to reduce nitrate. The nitrate is used as an electron acceptor to receive electron from the oxidation of organic or inorganic compounds. Most nit4rate reducers can also use O_2 if it is present thus they are facultative aerobes. The organisms can be heterotrophic (use organic carbon) or autotrophic (use CO_2). One organism has been found that will both oxidize ammonia to nitrate and erduce nitrate to N_2 gas. *Parracoccus pantotropha* will reduce nitrate under aerobic conditions but needs something easy to degrade like acetate. *Nitrosomonnas europaea* can use nitrite to oxidize ammonia to nitrogen gas in the absence of O_2. The Annamox bacteria can also oxidize ammonia using nitrite, but it cannot use O_2. It is faster than *N. europaea.*

Stoichiometry

The overall reaction can be seen as a series of reactions

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2.$$

The first enzyme is nitrate reductase, the second nitrite reductase and so on. The enzymes are widespread in nature and differ slightly from species to species. In some cases they are present as a complex of enzymes that performs all of the functions. Some organisms do not carry out all of the steps in the process but after nitrite the products are all gasses and will be lost from the system.

Nitrate reductase is a membrane bound enzyme and is repressed in the presence of O_2 so the process only operates under anoxic conditions. The organisms also require a source of organic carbon for growth and energy generation.

The majority of nitrate reduction processes rely on the reduction of nitrate by heterotrophic species. These need an organic source of carbon and energy. This can be obtained from the BOD of the wastewater or can be added after wastewater treatment.

Wastewater

$$C_{10}H_{19}O_3N + 10\ NO_3^- \rightarrow 5N_2 + 10\ CO_2 + 3H_2O + NH_3 + 10\ OH^-$$

Where $C_{10}H_{19}O_3N$ is used to represent biodegradable component of wastewater.

Methanol

$$5CH_3OH + 6NO_3^- \rightarrow 3N_2 + 10CO_2^- + 7H_2O + 6OH^-$$

Acetate

$$5CH_3COOH + 8NO_3^- \rightarrow 4N_2 + 10CO_2 + 6H_2O + 8OH^-$$

Notice that each of these reactions produces alkalinity.

Another useful relationship is that 2.86 g O_2 can be viewed as equivalent to 1 g of NO_3-N. This can be used to help calculate the amount of BOD used by nitrate reduction. The text develops the relationship further:

$$\frac{bsCOD}{NO_3 - N} = \frac{2.86}{1 - 1.42Y_n}$$ where Y_n = net biomass yield on nitrate. (g VSS/g bsCOD)

Growth Kinetics

Typical Monod growth kinetics are modified for the lower utilization rate in the anoxic zone.

$$r_{SU} = -\frac{kXS\eta}{K_S + S}$$

where η = fraction of denitrifying bacteria in the biomass (varies from 0.2 to 0.8 (preanoxic) not necessary on postanoxic as these organisms dominate.

Since the substrate in the above equations is not nitrate the equation must be modified to include a nitrate limitation and an oxygen limitation is added since these organisms will usually not function in the presence of oxygen.

$$r_{SU} = -\left(\frac{kXS\eta}{K_S + S}\right)\left(\frac{NO_3^-}{K_{s,NO_3} + NO_3^-}\right)\left(\frac{K_o^{'}}{K_o^{'} + DO}\right)(\eta)$$

Biological Phosphorous Removal

Forms of phosphorous

basically only 2 organic and inorganic

Problems

Although phosphorous use in many products is now forbidden, phosphorous removal from wastewater is not regulated heavily. Regulations are anticipated due to the fact that phosphorous is a nutrient and will allow growth of organisms, thus creating the potential problems for watersheds.

Mechanism for removal

Biological phosphorous removal is accomplished by anoxic, aerobic cycling of the sludge and creates a side stream of aqueous phase highly concentrated with phosphorous or can be removed by sludge wasting. Figure 7-22 (overhead) shows an example reactor configuration.
Bacteria like *Acinetobacter* aer phosphorous accumulating organisms (PAO"S) and will absorb or concentrate phosphorous in the cells when exposed to anaerobic then aerobic conditions. They accumulate phosphorous under aerobic conditions then release it under anaerobic conditions when volatile fatty acids are present.
Example 7-8 (overhead) gives and example of how to calculate how much phosphorus will be removed.

Modeling the treatment of toxic and recalcitrant compounds.

In many industrial and some municipal systems specific organic compounds must be treated and can be modeled as separate from BOD or COD. The removal of many of these specific compounds can be due to adsorption to the floc and volatization as well as biological degradation. Your text covers the development of a set of equations that can be used to describe the combination of biotic and abiotic processes. P. 638-642. The resultant equation (7-127 to 7-129) are summarized below.

$$S_o = \left(\frac{1}{Y}\right)\frac{\mu_m S}{K_S + S}(X_S)\tau + K_p S X_T\left(\frac{\tau}{SRT}\right) + K_L a_S S(\tau) + S \quad \text{equation 7-127}$$

where
all symbols as defined previously except specific for the compound (and possibly the organism) and
K_p = partition coefficient (L/kg)
$K_L a_S$ = Mass transfer coefficient for volatilization of the compound.
X_T = total biomass
X_S = compound specific biomass which can be calculated using equation 7-128

$$X_S = \frac{Y(S_o - S) - K_p S X_T(\tau/SRT) - K_L a_S S(\tau)}{k_d(\tau) + (\tau/SRT)}$$

Equation 7-129 can be used when volatilization and adsorption can be neglected

$$S = \frac{K_S[1 + (k_d)SRT]}{SRT(\mu_m - k_d) - 1}$$

Example 7-10 demonstrates the use of this reasoning in the calculation of the fate of benzene in wastewater. (Overhead)

Chapter 8 Suspended Growth Treatment Processes

Read the introduction and sections that cover characterizing wastewater constituents on your own.

Activated sludge

Process

The activated sludge process consists of an aeration basin and a secondary clarifier. The waste flows into the aeration basin, is retained for a specific detention time and then flows into the secondary clarifier.

Aeration basin

The aeration basin is designed for the removal and transformation of soluble and particulate pollutants. The contents are known as mixed liquor.

The bacterial component known as mixed liquor suspended solids (MLSS) (or volatile solids). The microorganisms clump together in a floc. The soluble and suspended particles are removed by both adsorption onto the gel-like matrix of the floc and by metabolism by microorganisms. The microorganisms are recycled, so the population is enriched on the waste and degrade its substrates and grow very rapidly.\

The aeration basin may be designed to remove carbonaceous BOD as well as ammonia or nitrite BOD or both.

Secondary clarifier
The secondary clarifier is designed as a quiescent environment to allow sludge solids to separate by flocculation and gravity sedimentation.
The water goes over the top through a weir and is called the secondary effluent. The solids are removed from the bottom and are called return activated sludge or are wasted and called waste activated sludge.

The efficiency of the activated sludge process is effected by factors affecting biological oxidation and solids separation. When biological oxidation is affected, certain of the waste components may not be degraded. When solids separation is affected, the secondary effluent is not clear and organisms may wash out of the process leading eventually to complete failure.

Fundamentals of Process Analysis and Control

The selection of which type of suspended growth reactors is based upon 7 factors. (Table 8-4)

1. Effect of reaction kinetics
    a. Complete mix
    b. Plug flow

    These do not matter as much for straight BOD removal as the SRT is the more important design factor. For nitrification, plug flow or staged complete mix reactors are used. Table 8-5 (overhead) is a nice summary of kinetic equations used in suspended growth treatment calculations.

2. Oxygen transfer requirements
    a. Regular aeration – OK for complete mix or step feed
    b. Tapered aeration – best for plug flow to help meet increased demand at input

    Most aeration demands can be met by selecting more advanced aeration devices (more later).

3. Nature of Wastewater
    a. BOD, COD, pH, Alkalinity, very important for nitrification

4. Local Environmental Conditions
    a. Temperature
    b. Flowrates

5. Toxic or Inhibitory substances

a. More effect on nitrification than on BOD removal.
b. Complete mix can withstand shock loads better then plug flow
c. Step feed helps plug flow reactors handle shocks

6. Cost
    a. Construction
    b. Operation
    c. Must consider both the reactor and its associated clarifier

7. Future Needs
    a. Projected growth
    b. Projected legislation changes
    c. Projected water reuse needs

Solids retention Time

As described previously the solids retention time has a great bearing on the design and operation of an activated sludge process. Table 8-6 (overhead) lists some SRT values for use depending on the desired outcome of the treatment.

Food to Microorganism Ratio

The food to microorganism ratio (F/M) is a simple operational parameter that has a large effect on the performance of the organisms in the reactor. It can also be used as a rough design factor. It can be estimated as follows:

$$F/M = \frac{QS_O}{VX} \text{ or } \frac{S_O}{\tau X} \text{ or } \frac{\text{food applied}}{\text{biomass}}$$

This value can range from 0.04 g substrate/g biomass d (extended aeration) to 1 g substrate/g biomass d high rate processes.

Volumetric Organic Loading Rate

Another parameter used frequently for processes that we do not have a model or good kinetics for is the organic loading rate. This is the amount of BOD or COD applied per day.

$$L_{org} = \frac{QS_O}{V(10^3 \text{ g/kg})}$$

Sludge Production Rate

As discussed earlier the amount of sludge produced s always something that we care about. The equation below can be used to account for both growth on organic substrates and on nitrogen compounds.

$$P_{X,VSS} = \frac{QY(S_o - S)(1kg/10^3 g)}{1+(k_d SRT)} + \frac{(f_d)(k_d)QY(S_o - S)SRT(1kg/10^3 g)}{1+(k_d SRT)} +$$

$$\frac{QY_n(NO_x)(1kg/10^3 g)}{1+(k_{dn} SRT)} + Q(nbVSS)(1kg/10^3 g)$$

where NO_x is used to represent NH_3-N. To calculate the total solids instead of volatile solids we could label the four terms in the above equation A,B,C,and D and then use the following equation.

$$P_{X,TSS} = \frac{A}{0.85} + \frac{B}{0.85} + \frac{C}{0.85} + D + Q(TSS_o - VSS_o) \quad \text{equation 8-16.}$$

Oxygen Requirements

To add the oxygen required for nitrogen removal to the previous equations we end up with.

$R_o = Q(S_o\text{-}S)\text{-}1.42P_{X,bio} = 4.33Q(NO_x)$

Nutrient Requirements

The simplest way to calculate nutrient requirements is to use the cell formula provided earlier $C_5H_7NO_2$. This results in a need for 12.4 percent by weight of cell as nitrogen. So 100 grams of cells formed (P_X) would require 12.4 g of nitrogen-N. Another way to look at it is that as a general rule we assume that about 5 g of nitrogen and 1 g pf phosphate are needed for 100g of BOD used. This willusually provide excess nutrients so no organisms air limited.

Mixed Liqour Settling Characteristics and the Sludge Volume Index

This is a measure of the settleability and compactability of sludge. It is measured by a standard lab test in which mixed liquor is placed in a 1- or 2-L cylinder and allowed to settle for 30 min (usually). At the end of the settling period, the volume of sludge solids on the bottom of the cylinder is measured. The calculation relies on knowing the original density of the total suspended solids and the volume.

e.g. $SVI = \frac{y}{X_T V_c}(1{,}000 \text{ mg / g})$.

SVI = sludge volume index (mL/g)
y = volume of sludge after settling (mL)
X_T = TSS content of mixed liquor (mg/L)
V_c = Volume of cylinder (L)

A low SVI (100 or less) indicates that the sludge settles well above 150 means you have problems.

Secondary Clarification

The separation of the biomass from the treated wastewater is of utmost importance to providing a clear effluent as well as supplying activated biomass to the reactor. This will be covered in more detail later

Microbiology

The process is called activated sludge because some care is put into maintaining an active mass of microorganisms to degrade the waste. This is usually achieved through recycle of some of the sludge after it is settled from the wastewater. This sludge represents an acclimated population that are currently capable of degrading the waste in the water. We have already discussed most of the microbiology involved in this system. As a review we can list the genera of organisms involved in the process:

You will recall that there are several species of aerobes capable of degrading many compounds and that *Zooglea* is very important for maintaining a viable floc.

I would like to spend a while on some of the problem microorganisms that are often found associated with process upsets and in most cases the type of organism is indicative of the problem with the process. This lecture is from the book "Manual of Causes and Control of Activated Sludge Bulking and Foaming". by David Jenkins, Michael G. Richard and Glen T. Daigger.

Solids separation problems

There are several problems associated with solids separation. These problems are named in terms of the effect observed, so are general in nature. (Handouts Table, Figures)

Dispersed growth
viscous bulking (non-filamentous bulking) (slime formation)
Pinpoint floc
filamentous bulking
blanket rising
foaming/scum

There are several organisms involved in sludge bulking or foaming (Handout Table). The type of organism is often of use as a diagnostic technique to help determine the cause of the problem (handout table).

<u>Control and Problem Solving</u>

BULKING - When **filamentous** organisms proliferate and upset settling of sludge. Usually caused by a nutritional imbalance in the activated sludge reactor.

<u>control</u>
addition of Chlorine and H_2O_2 to RAS
alteration of DO level in reactor
increase F/M ratio.
add N and P
anoxic selector

SBR and Plug flow have better settling characteristics and are less susceptible to this.

RISING SLUDGE - caused by **denitrification**, N_2 formed is trapped by sludge, making it float. Can also often see bubbles associated with floating sludge.

control

1 increasing RAS withdrawal rate from the clarifier to reduce the detention time in the clarifier
2. decreasing flow into the clarifier
3. increase speed of the sludge collecting system
4. increase sludge wasting rate

these all decrease the amount of time spent under possible anaerobic conditions, therefore the possibility of denitrification occurring.

NOCARDIA FOAM - caused by growth of *Nocardia* usually due to low F/M in aeration tanks, high MLSS due to insufficient sludge wasting, operation in the sludge reaeration mode.

control

1. reducing sludge age (most common)
2. reduce air flow rate
3.adding a selector compartment (see below)
4. injecting mutant bacterial additive
5. chlorinating the RAS
6. chlorinate the foam directly
7. reduce pH of mixed liquor.

Expect a wait of at least 3 mean cell retention times (MCRT's) for the sludge to return to a settleable state. In some cases even longer times may be required.

Activated Sludge Selector Processes

The concept of selectors has been proposed as early as the 1970's. A selector is a small tank (20 to 60 min contact time) or a series of tanks in which the incoming wastewater is mixed with return sludge under aerobic, anoxic or anaerobic conditions (Figure 8-14 overhead). The selectors are designed to favor the growth of the floc forming bacteria over the filamentous bacteria (usually by exposing them to the high initial substrate concentrations they would not see in a large CFSTR.

Kinetic based selectors

The kinetic based selectors are designed to have a high F/M ratio's. This results in faster substrate uptake by the floc forming organisms which compete with the filaments well at only high F/M ratios.

Metabolic based selectors

These are anoxic or anaerobic in nature and are used to help select for organisms with the needed metabolic characteristics such as nitrat6e reduction, or phosphate removal.

The use of selectors helps maintain a sludge that settles well and can increase the efficiency of the activated sludge process by helping maintain a high MLVSS because the clarifier works better with sludge that settles well.

Process Descriptions

Table 8-15 lists several of the more common activated sludge processes that are used today.

Complete Mix

We have been discussing this all along. The main advantage is the dilution of shock loads into the reactor. The major disadvantage is that the substrate concentration is much more dilute than in other configurations and will have more problems with the growth of filamentous organisms etc. than others. Selectors should be used to help prevent this.

Plug flow

Plug flow reactors are advantageous in some circumstances, due to the fact that faster rates can be obtained at higher substrate concentrations. Initially a fast rate of metabolism and growth is present. As the plug proceeds the rate of metabolism of substrate is limited by concentration, but high numbers of microorganisms are present, so the observed rate might not be affected too much. It is be beneficial to use plug flow when intermediates are produced that interfere with degradation of the parent compound or when diauxie is observed. This allows high concentrations of each substrate to be present initially. Cannot handle shock loads, but has fewer problems with the growth of filamentous organisms.

Tapered aeration (diagram on board)

modification of plug flow
air is added depending on oxygen demand
more at head and less towards effluent end
use diffuser spacing to achieve this

Step-feed (diagram on board)

modification of plug flow in which wastewater is introduced at several points in the tank
equalizes F/M over reactor
has good flexibility of operation

Contact Stabilization (diagram on board)

plug flow
two tanks, one to stabilize and one to treat.
influent mixed with sludge (from stabilizer) in contact tank
goes into clarifier and then to stabilization tank
the return sludge is aerated while the rest is wasted unaerated
saves 50% on aeration volume requirements

Two Sludge (diagram on Board)

Two tanks are operated with clarifiers in between
One for BOD removal
The second for nitrification
each has its own sludge recycle
advantage is that the reactor sees the organisms needed and a really specialized population can develop. The reactors can be operated independently to keep the separate populations happy

High Purity Oxygen

Usually CFSTR in series
high purity O_2 is added to reactors instead of air
tanks must be covered so O_2 can be recovered and reused, some is wasted
can add 2-3x the amount of O_2 as when air is used
Usually generate high purity O_2 onsite
best for BOD removal, pH goes to low for nitrifiers (CO_2) accumulation.

Kraus process (Overhead)

variation of step aeration plug flow
good for low N levels
digestor supernatant is added as a nutrient source to portion of return sludge designed to nitrify
resulting mixed liquor is then added to main plug flow reactor

Extended Aeration

plug flow
low organic loading and a long aeration time.
good for small communities
Can get both BOD and ammonia removal
Sludge more digested than conventional so may have settling and compressibility problems later.

Oxidation ditch

plug flow
ring shaped channel with mechanical aerators
long detention times, long solids retention times
operate in extended aeration mode

Deep shaft

plug flow 400 to 500 ft deep
influent forced to go down and around metal annulus.
aeration occurs at about 1/2 way down.

Other proprietary processes are described in your text.

Table 8-16 (overhead) presents some typical design parameters for common activated sludge processes. Table 8-17 lists some advantages and limitations of these processes.

Activated Sludge Process Design

Typical kinetic coefficients for heterotrophic and nitrification organisms are found in tables 8-10 and 8-11 (overheads).

In order to design a process to treat a wastewater you first make sure that the process can be used to treat the waste (one thing your book rarely says is that a single AS reactor can only treat waste with a BOD in the 200-250 mg/L range (typical of municipal wastewater) for industrial waste with a higher BOD concentration you may have to use reactors in series or one of the processes to be discussed later.

Table 8-12 (overhead) presents a computational approach to the design of a CFSTR for both BOD and ammonia removal.
Example 8-2 (overhead many pages) presents an example process design.