glutamic acid.[21] This means that degradation of many biogenic substrates may behave in a zero-order manner over a broad range of substrate concentrations.

Wastewaters usually contain complex mixtures of organic compounds and the total concentration of biodegradable soluble organic matter is commonly characterized by the COD concentration. When K_S is measured on such mixtures using the COD concentration, the values are generally one to two orders of magnitude higher than they are for single substrates expressed as COD. For example, poultry and soybean processing wastewater have been reported to have K_S values of 500 and 350 mg/L as five day biochemical oxygen demand (BOD_5), which is another measure of biodegradable organic matter.[64] Thus, as a whole, overall removal of organic matter in wastewater treatment systems may behave in a first-order manner even though the removal of individual constituents may be zero-order.[121]

Domestic wastewater is perhaps the most common example of a complex substrate, and because of its ubiquity there has been considerable interest in characterizing its biodegradation kinetics. As one might expect from the discussion above, considerable variation in the parameter values has been reported, with $\hat{\mu}_H$ ranging from 0.12 to 0.55 hr^{-1} and K_S from 10 to 180 mg/L as COD.[54,55] An important characteristic of domestic wastewater that has only recently been recognized is that the organic component can be divided into readily and slowly biodegradable fractions, greatly improving the ability of mathematical models to mimic process performance.[26] Use of this division should decrease the range of values observed. As a consequence, values of 0.25 hr^{-1} and 20 mg/L as COD have been adopted as representative of the $\hat{\mu}_H$ and K_S values for the readily biodegradable fraction.[55]

The microbial communities in wastewater treatment systems are complex, containing many microbial species, and the relative predominance of the species depends on the physical configuration of the system. Therefore, since the values of $\hat{\mu}_H$ and K_S are species dependent, it follows that their values in mixed culture systems will depend on the bioreactor configuration. For example, reactors that subject the microorganisms to variations in substrate concentrations from very high to very low tend to select species that can grow rapidly (higher $\hat{\mu}_H$), whereas reactors which maintain a low, uniform substrate concentration throughout select microorganisms that are good scavengers of substrate (low K_S).[21,25] This complicates kinetic analysis and requires that experiments to determine kinetic parameters be conducted with systems that mimic the physical configuration to be employed in the full-scale facility. This topic is discussed in more detail in Chapter 8.

The biodegradation kinetics for many xenobiotic compounds can best be characterized by the Andrews equation (Eq. 3.39). Dividing both the numerator and denominator by K_S yields:

$$\mu = \hat{\mu} \frac{S_S/K_S}{1 + S_S/K_S + (S_S/K_S)^2(K_S/K_I)} \tag{3.49}$$

Expressing the equation in this manner emphasizes that the degree of substrate inhibition is determined by the ratio of K_S/K_I, rather than by K_I alone, as we saw with Eq. 3.40. Furthermore, Eq. 3.49 also makes it easy to see that the larger the ratio, the more inhibitory the substrate. 1,3- and 1,4-Dichlorobenzene are both moderately inhibitory compounds and have ratios of 0.14 and 0.08, respectively.[42]

In Section 3.2.9, the undesirability of oxygen being rate limiting was discussed, suggesting that knowledge of the oxygen half-saturation coefficient for heterotrophs,

$K_{O,H}$, is important. In spite of that, relatively little work has been done to estimate $K_{O,H}$ values for mixed microbial cultures, probably because population shifts occur in the community in response to changes in the dissolved oxygen concentration, making estimation of the value difficult. Nevertheless, limited pure culture data suggests that $K_{O,H}$ is very low. For example, values of 0.01, 0.08, and 0.15 mg O_2/L have been reported for *Sphaerotilus natans*[70] (a filamentous bacterium), *Candida utilis*[113] (a yeast), and *Citrobacter* sp.[70] (a floc-forming bacterium), respectively. This suggests that dissolved oxygen concentrations must be very low before they have serious impacts on the growth of heterotrophic bacteria, although they may influence the competition between filamentous and floc-forming bacteria. For depicting the impacts of dissolved oxygen on general heterotrophic biomass growth, one group adopted a value of 0.2 mg O_2/L for $K_{O,H}$.[55]

It will be recalled from Section 3.2.8 that many investigators use substrate removal, rather than biomass growth, as the primary event with which to characterize biochemical operations. In that case, the primary kinetic parameter is the maximum specific substrate removal rate, $\hat{q}$, rather than the maximum specific growth rate. Equation 3.44 defined $\hat{q}$ as $\hat{\mu}/Y$. Thus, $\hat{q}$ will be influenced by variations in Y as well as variations in $\hat{\mu}$. Like $\hat{\mu}$, Y is influenced both by the substrate being degraded and the microorganism performing the degradation (see Section 2.4.1). It should be noted, however, that Y is a reflection of the energy available in a substrate whereas $\hat{\mu}$ is a reflection of how rapidly a microorganism can process that energy and grow. Because they represent different characteristics, there is no correlation between the two parameters. For example, some substrates that are degraded very slowly (low $\hat{\mu}$) provide more energy to the degrading culture (i.e., higher Y) than do substrates that are degraded rapidly.[42] This suggests that deductions about the variability in $\hat{q}$ cannot be made from data on $\hat{\mu}$ alone, and vice versa. Knowledge of the true growth yield is also important. Typical Y values are discussed in Section 2.4.1.

Anoxic Growth of Heterotrophic Bacteria. As seen in Chapter 2, the only difference between aerobic and anoxic growth of heterotrophic bacteria on many substrates, such as biogenic organic matter, is the nature of the terminal electron acceptor and its impact on the amount of ATP that the cells can generate. Thus, for substrates for which this is true, we might expect the kinetic parameters describing growth under the two conditions to be very similar, and that is exactly what has been observed. When mixed microbial cultures were grown with excess oxygen or nitrate as the terminal electron acceptors and peptone as the rate-limiting substrate, the values of $\hat{\mu}_H$ and K_S were very similar, being 0.14 hr^{-1} and 67 mg/L as COD, respectively, under aerobic conditions and 0.13 hr^{-1} and 76 mg/L as COD under anoxic conditions.[79] Furthermore, as expected from the lower potential ATP formation under anoxic conditions, the anoxic yield was lower, being only 0.39 mg biomass COD/mg substrate COD versus a value of 0.71 aerobically. Consequently, $\hat{q}_H$ was almost twice as large under anoxic conditions. Although data directly comparing kinetic parameters under aerobic and anoxic conditions are limited, experience with treatment systems suggest that these findings are generally true.[79]

Anoxic growth conditions are generally imposed in biochemical operations for the purpose of reducing the nitrate concentration to low levels. Thus, there is a possibility that the terminal electron acceptor concentration will become rate limiting. Proper modeling of this situation requires knowledge of K_{NO}, the half-saturation

coefficient for nitrate. As with oxygen, the half-saturation coefficient for nitrate as the terminal electron acceptor has been found to be low, with values around 0.1 to 0.2 mg/L as N being reported.[20,33,93] Consequently, values in that range have been adopted by investigators conducting modeling studies.[11,25]

Another parameter required to fully define the kinetics of microbial growth under anoxic conditions is K_{IO}, the oxygen inhibition coefficient used in Eq. 3.48. If the cells are growing in a dispersed state so that all are exposed to the oxygen concentration in the bulk liquid, it appears that they do not denitrify when the dissolved oxygen concentration is above 0.1 to 0.2 mg/L.[101] However, when they grow as aggregates or films, the requirement for oxygen transport by diffusion allows biomass in the interior to be free of oxygen even when the bulk liquid contains it. Consequently, anoxic growth will occur even when the dissolved oxygen concentration in the bulk liquid exceeds 0.2 mg/L.[101] Thus, modelers have assumed values for K_{IO} ranging from 0.2[55] to 2.0[11] mg/L.

Aerobic Growth of Autotrophic Bacteria. The nitrifying bacteria are the most important aerobic autotrophs and for the nitrogen levels normally found in domestic wastewater the kinetics of their growth can be adequately represented by the Monod equation (Eq. 3.36). Because only a limited number of genera and species are involved, the variability in the values of the kinetic parameters is less than that associated with heterotrophs. The maximum specific growth rate coefficient for *Nitrosomonas* has been reported to lie between 0.014[71] and 0.092[109] hr^{-1}, with a value of 0.032 hr^{-1} considered to be typical at 20°C.[102] The half-saturation coefficient for ammonia has been reported to be between 0.06 and 5.6 mg/L as N,[109] but a commonly accepted value is 1.0 mg/L.[55,102] The maximum specific growth rate coefficient for *Nitrobacter* is similar to that for *Nitrosomonas*, having been reported to lie between 0.006[71] and 0.060[109] hr^{-1}. Likewise, the value considered to be typical,[102] 0.034 hr^{-1}, is similar to that for *Nitrosomonas*. The reported range of the half-saturation coefficient for *Nitrobacter* is slightly larger than that for *Nitrosomonas*, being 0.06 to 8.4 mg/L as nitrite-N,[109] as is the value thought to be typical, 1.3 mg/L.[102] The maximum specific growth rate coefficients for the autotrophic bacteria are considerably less than those for heterotrophic bacteria, reflecting their more restricted energy yielding metabolism and the fact that they must synthesize all cell components from carbon dioxide. This suggests that special consideration must be given to their requirements during design of reactors in which both carbon oxidation and nitrification are to occur. Although the half-saturation coefficients for the autotrophs are less than the reported values for heterotrophs growing on complex substrates, they are similar to the values reported for heterotrophs growing on single organic compounds. As a consequence of their small size, the kinetics of nitrification will behave in a zero-order manner over a broad range of ammonia and nitrite concentrations. As will be seen later, this has a significant impact on bioreactor performance.

A major difference in the growth characteristics of heterotrophic and autotrophic biomass is the greater sensitivity of the latter to the concentration of dissolved oxygen. Whereas the value of the half-saturation coefficient for oxygen is very low for heterotrophs, the values for the two genera of autotrophs are sufficiently high in comparison to typical dissolved oxygen concentrations that dual nutrient limitation as expressed by Eq. 3.46 should be considered to be the norm. For example, values of $K_{O,A}$ for both *Nitrosomonas* and *Nitrobacter* have been reported to lie between 0.3 and 1.3 mg/L.[109] Measurements which considered the effects of diffusional re-

sistance on half-saturation coefficients have suggested that the true values lie near the lower end of the range,[111,120] and values of 0.50 and 0.68 have been adopted as typical for *Nitrosomonas* and *Nitrobacter*, respectively, in systems in which some diffusional resistance will occur.[102]

Another difference between heterotrophic and autotrophic biomass is the greater sensitivity of the latter to changes in pH. Although all bacteria grow poorly outside of the normal physiological pH range of 6.0 to 8.0, nitrifying bacteria are particularly sensitive to pH, especially *Nitrosomonas*, as shown in Figure 3.4.[98] There it can be seen that the rate reaches a maximum at a pH of about 8, and declines sharply for lower pH values. A wide range of pH optima has been reported,[116] but most workers agree that as the pH becomes more acid the rate of ammonia oxidation declines.[93] Furthermore, if a culture is acclimated to a low pH the effect is less severe than if the pH is suddenly shifted. Siegrist and Gujer[111] have modeled the effect in Figure 3.4 with Eq. 3.50:

$$\hat{\mu}_A = \hat{\mu}_{Am}[1 + 10^{(6.5-pH)}]^{-1} \tag{3.50}$$

where $\hat{\mu}_{Am}$ is the maximum specific growth rate at the optimum pH. It should be

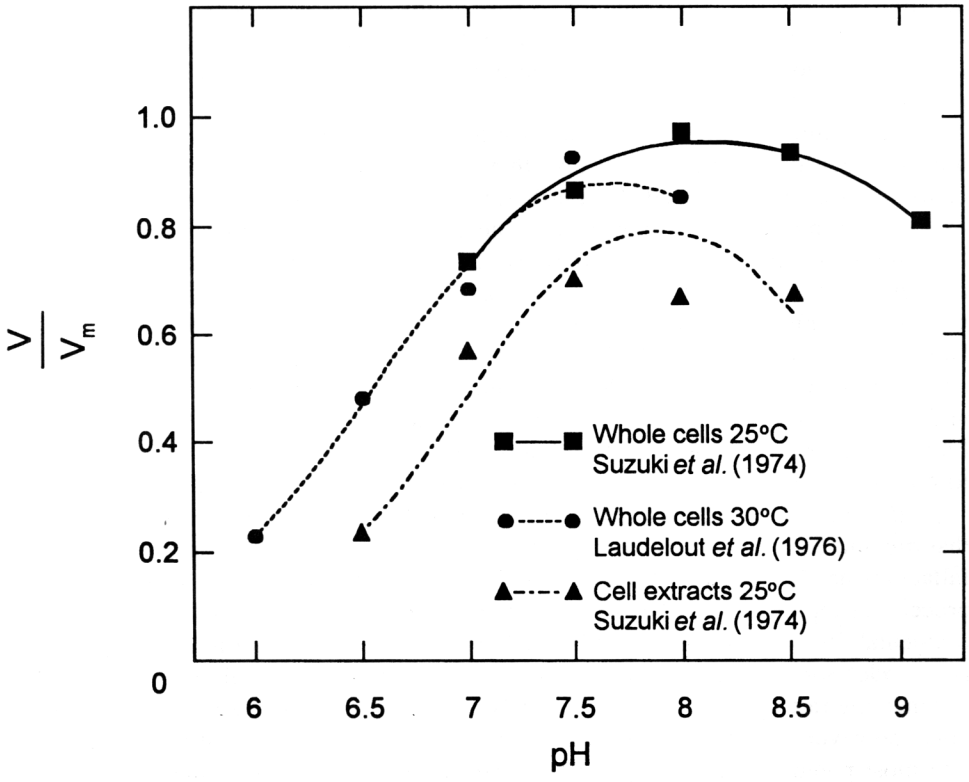

Figure 3.4 Effect of pH on the maximal activity of *Nitrosomonas*. The listed references are cited in 98. (From A. V. Quinlan, Prediction of the optimum pH for ammonia-N oxidation by *Nitrosomonas europaea* in well-aerated natural and domestic-waste waters. *Water Research* **18**:561–566, 1984. Copyright © Elsevier Science Ltd.; reprinted with permission.)

noted that this equation only predicts the decline in rate at low pH and does not predict the observed drop-off at pH above 8.5. This is not generally a problem, however, because the release of hydrogen ions during nitrification acts to depress the pH so that values in excess of 8.5 are seldom encountered. There is less agreement concerning the effects of pH on *Nitrobacter*. For example, Boon and Laudelot[13] have suggested that their maximum specific growth rate is independent of pH over the range between 6.5 and 9, whereas others[115] have shown a strong pH dependence. Because of this, and because the growth of *Nitrosomonas* is generally thought to be rate controlling, most investigators do not model the effect of pH on *Nitrobacter*.

The necessity for employing equations like 3.50 is due in part to the way in which the Monod equation is normally written for nitrifying bacteria. Although, ammonia and nitrite are both ionizable species, the Monod equation is normally written in terms of the total ammonia or nitrite concentration, without regard for the ionization state. However, the nonionized form of ammonia (free ammonia) is thought to be the actual substrate for *Nitrosomonas*,[98] and it is possible that undissociated nitrous acid is the substrate for *Nitrobacter*. For a given total ammonia concentration, the concentration of the nonionized form will change as the pH is changed, thereby making $\hat{\mu}$ as normally defined an apparent function of pH. A more direct approach would be to write the kinetic expression directly in terms of the true substrate and this has been done for *Nitrosomonas*.[98] However, because this approach is more complex than combining Eq. 3.36 with Eq. 3.50 to reflect the effect of pH, the latter is more commonly used at nitrogen concentrations normally found in domestic wastewaters.

Free ammonia and undissociated nitrous acid become more of a problem at high nitrogen concentrations because they both act as inhibitory substrates as their concentrations are increased.[1,4,13] Furthermore, free ammonia can also inhibit nitrite oxidation to nitrate.[4] This suggests that there are complex relationships between the total ammonia and nitrite concentrations, the pH, and the activity of both groups of nitrifying bacteria. Although these relationships become very important when wastewaters containing high concentrations of nitrogen are being treated, no kinetic relationships are available to depict all of the effects, although some are available for ammonia oxidation.[88] Nevertheless, it is important to recognize that the simple Monod equation is not adequate to depict the kinetics of nitrification when the concentration of ammonia exceeds that normally found in domestic wastewater (around 30 to 40 mg/L as N) and that alternative expressions should be sought.

Because of the autotrophic nature of nitrifying bacteria the concept developed that organic compounds display a general toxicity toward them. That this concept is fallacious has been demonstrated in pure[100] and mixed[58,60] cultures. Nitrification can proceed at rapid rates in the presence of organic matter, provided that other environmental factors, such as pH and dissolved oxygen concentration, are adequate. In fact, under some circumstances, the presence of biogenic organic matter can even enhance the rate of nitrification.[60] There are some organic compounds that are inhibitory, however, and act to decrease the specific growth rate of nitrifying bacteria. The most potent specific inhibitors of nitrification are compounds that chelate metals[60] and contain amine groups,[59] some of which are capable of decreasing the nitrification rate by 50% at concentrations of less than 1.0 mg/L. Furthermore, it appears that *Nitrosomonas* is the weak link in the nitrification chain, being more susceptible than *Nitrobacter* to organic inhibitors.[59] Many inhibitors have been shown to act in

a noncompetitive manner against nitrifiers,[91,92] allowing an equation like Eq. 3.48 to be used to depict their effect:

$$\mu_A = \hat{\mu}_A \left(\frac{S_{NH}}{K_{NH} + S_{NH}}\right)\left(\frac{K_I}{K_I + S_i}\right) \tag{3.51}$$

where S_{NH} is the ammonia-N concentration, K_{NH} is the half-saturation coefficient for ammonia-N, S_i is the concentration of the inhibitor, and K_I is the inhibition coefficient. As might be expected, K_I is very small for some compounds,[92] denoting extreme inhibition. Although many inhibitors of *Nitrosomonas* act in a noncompetitive manner, methane and ethylene act as competitive inhibitors.[65] This is because they are similar in size to ammonia and compete directly with it for the active site on the enzyme that initiates ammonia oxidation. Halogenated hydrocarbons act in a noncompetitive manner, but many are also reactive with the enzyme and can lead to products that damage the cell, thereby making their effects worse than simple inhibition.

There have also been suggestions in the literature that the presence of heterotrophic bacteria is deleterious to the activity of nitrifying bacteria, but this has been shown to be false.[12,60] Any effect of heterotrophs is indirect, such as a decrease in dissolved oxygen concentration or an alteration of pH. Because of the sensitivity of autotrophs to these factors, care must be given to the design of facilities in which autotrophs and heterotrophs share the same space.

Anaerobic Cultures. As discussed in Section 2.3.2 and seen in Figure 2.3, in anaerobic operations three groups of bacteria are involved in acidogenesis and two in methanogenesis. Fermentative bacteria convert amino acids and simple sugars to acetic acid, volatile acids, and a minor amount of H_2. Bacteria performing anaerobic oxidation convert long chain fatty acids and volatile acids to acetic acid and major amounts of H_2. Finally H_2-oxidizing acetogens form acetic acid from carbon dioxide and H_2, but they are considered to be of minor importance in anaerobic wastewater treatment operations and will not be considered here. The two groups of methanogens are aceticlastic methanogens, which split acetic acid into methane and carbon dioxide, and H_2-oxidizing methanogens, which reduce carbon dioxide.

To have a complete picture of the kinetics of microbial growth and substrate utilization in anaerobic systems, the kinetic parameters for all groups should be characterized. Unfortunately, because of the role of H_2 in regulating microbial activity and the close association between H_2-producing and H_2-consuming bacteria, this is not an easy task. For this reason and because the complex interactions among the microbial groups have only recently been recognized, most kinetic studies of anaerobic treatment processes have measured rates associated with entire communities rather than individual groups. That literature is too extensive to include here, but reviews[53,114] provide good summaries and the reader is encouraged to consult them for overall kinetic information.

As our understanding of the interactions in anaerobic processes has increased, engineers have sought to model anaerobic systems on a more fundamental level by including reaction steps for each important microbial group.[14,45] Although those efforts represent first attempts at expressing the kinetics of these complex systems, they provide information that is helpful in developing an appreciation of the kinetic characteristics of anaerobic bacteria. Because a temperature of 35°C is commonly

used for anaerobic operations, the following parameter values are for that temperature range. Fermentative bacteria (group 2 in Figure 2.3) grow relatively rapidly on amino acids and simple sugars, and their kinetics can be represented by the Monod equation (Eq. 3.36) with a $\hat{\mu}$ value on the order of 0.25 hr^{-1} and a K_S value around 20 to 25 mg/L as COD. Review of available data suggests that this reaction does not limit system performance.[45] The bacteria which oxidize long chain fatty acids (group 3 in Figure 2.3) grow more slowly than the fermentative bacteria and are subject to inhibition by H_2. The values of $\hat{\mu}$ and K_S depend on the degree of saturation of the fatty acid serving as growth substrate, with saturated acids having lower $\hat{\mu}$ and K_S values than unsaturated ones.[45] Nevertheless, Bryers[14] has adopted a $\hat{\mu}$ value of 0.01 hr^{-1} and a K_S value of 500 mg/L as COD as being representative of the entire group. Reaction 4 in Figure 2.3 represents the bacteria that degrade short chain fatty acids, such as propionic and butyric acids. Butyric acid appears to be degraded in a manner similar to that of the long chain fatty acids and bacteria growing on it have kinetic parameters similar to those in group 3. Propionic acid, on the other hand, is degraded by more specialized bacteria which grow more slowly. Gujer and Zehnder[45] reported $\hat{\mu}$ and K_S values of 0.0065 hr^{-1} and 250 mg/L as COD, respectively, whereas Bryers[14] chose values of 0.0033 hr^{-1} and 800 mg/L as COD based on other studies. Although the two sets of values differ somewhat in magnitude, they both suggest that growth on propionic acid is much slower than growth on other fatty acids. Aceticlastic methanogenesis (reaction 6 in Figure 2.3) is a very important reaction in anaerobic operations because it produces about 70% of the methane. Two major types of aceticlastic methanogenic bacteria can be present in anaerobic systems, but the one which predominates will depend on the bioreactor conditions imposed because their growth kinetics are quite different. *Methanosarcina* can grow rapidly, but do not have a high affinity for acetic acid. Representative parameter values for them are 0.014 hr^{-1} for $\hat{\mu}$ and 300 mg/L as COD of acetic acid for K_S.[106] *Methanosaeta* (formerly *Methanothrix*), on the other hand, grow more slowly, but have a higher affinity for acetic acid, as shown by a $\hat{\mu}$ value of 0.003 hr^{-1} and a K_S value of 30 to 40 mg/L as COD of acetic acid.[106] Finally, the H_2-oxidizing methanogens produce methane from H_2, thereby keeping the H_2 concentration low and allowing the H_2-producing reaction to proceed as discussed in Section 2.3.2. The kinetic parameters for their growth have been reported to be $\hat{\mu}$ = 0.06 hr^{-1} and K_S = 0.6 mg/L as COD of dissolved H_2,[45] although others have reported K_S to be in the range of 0.03–0.21 mg/L as COD of dissolved H_2.[128]

The pH of an anaerobic system has a strong impact on $\hat{\mu}$, with an optimum around pH 7. Just as with nitrifying bacteria, this is probably because the nonionized form of the substrate (fatty acids in this case) serves as the actual substrate for growth and the amount of nonionized form will depend on the pH. As a consequence, relationships between $\hat{\mu}$ and pH are needed for the major groups of bacteria. On the other hand, some[2,27] have modeled acetic acid utilization with the Andrews equation using nonionized acetic acid as the substrate, but it is unclear whether that equation should be used if $\hat{\mu}$ is made an explicit function of pH. In addition, the role of H_2 in regulating the utilization of propionic and butyric acids and the activity of the H_2-producing bacteria is very important, but is not reflected in the parameter values reported above, which are all for low H_2 levels. Bryers[14] has argued that the H_2 effect is based on thermodynamics, and as such, does not translate directly into kinetic expressions. Labib et al.,[69] on the other hand, have demonstrated inhibition of butyric

acid utilization by H_2 separate from the thermodynamic effects. Thus, even though information on the kinetic impacts of H_2 is very limited, it appears to be important, suggesting that additional studies are needed to allow development of appropriate rate expressions. In spite of these limitations, however, the kinetic parameters above provide a good sense of the relative capabilities of the microorganisms involved in anaerobic operations.

3.3 MAINTENANCE, ENDOGENOUS METABOLISM, DECAY, LYSIS, AND DEATH

As discussed in Section 2.4.2, a number of complex events interact to make the observed yield in biochemical operations less than the true growth yield and to cause only a fraction of the suspended solids to be active biomass. Even if our knowledge of all of those events was sufficient to allow mechanistically accurate kinetic models to be written, it is doubtful that they would be used in engineering practice because of their complexity. Consequently, as is common in engineering, simplified models have been adopted because of their utility and adequacy, and two will be reviewed in this section. The traditional approach has been in use for many years and has found many applications.[29,31,40,71,80] Its main attributes are its simplicity and familiarity. Its main weakness, however, is its inability to easily handle situations in which the nature of the terminal electron acceptor is changing. The second model addresses that situation.[25,26,54,55,73] It is called the lysis:regrowth approach.[26]

3.3.1 The Traditional Approach

In the traditional approach, all of the events leading to the reduction in yield and viability are expressed by the following stoichiometry:

$$\text{Biomass} + \text{electron acceptor} \rightarrow CO_2 + \text{reduced acceptor} + \text{nutrients} + \text{biomass debris} \tag{3.52}$$

The important concepts incorporated into this expression are that active biomass is destroyed as a result of "decay" and that the electrons removed as a result of the oxidation of the carbon to carbon dioxide pass to the electron acceptor. Furthermore, not all of the biomass is totally oxidized and a portion is left as biomass debris.[63,78,80] Although the debris is ultimately biodegradable,[37,90] its rate of biodegradation is so low that for all practical purposes it is inert to further biological attack in most biochemical operations, causing it to accumulate, reducing the fraction of active biomass in the suspended solids. Finally, nitrogen is released as ammonia-N, although some remains in the biomass debris. Figure 3.5 illustrates how these events are related to microbial growth in an aerobic environment.

If Eq. 3.52 is rewritten as a COD balance the result is:

$$\text{Biomass COD} + [-(1 - f_D)]O_2 \text{ equivalents of electron acceptor} \rightarrow f_D \text{ biomass debris COD} \tag{3.53}$$

where f_D is the fraction of the active biomass contributing to biomass debris, X_D. For the type of biomass normally found in biochemical operations for wastewater

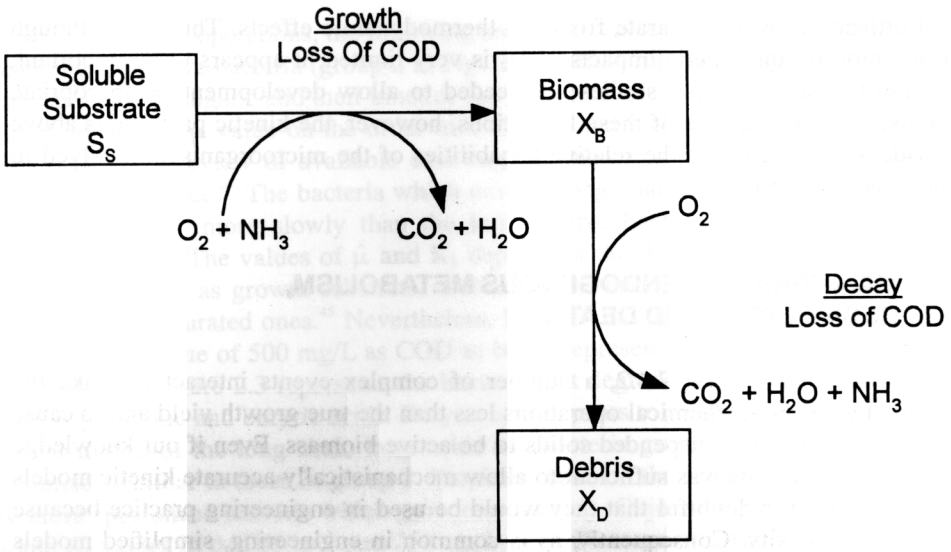

Figure 3.5 Schematic representation of the traditional approach to modeling biomass decay and loss of viability.

treatment it has a value of around 0.2.[25,78,81] Equation 3.53 shows that the utilization of oxygen or nitrate due to decay must equal the loss of active biomass COD minus the production of biomass debris COD.

Another important concept inherent in Eq. 3.52 is that nitrogen is released as ammonia as biomass is destroyed. If Eq. 3.52 were reformulated as a nitrogen based stoichiometric equation it would read:

$$\text{Biomass N} \rightarrow NH_3\text{-N} + \text{biomass debris N} \tag{3.54}$$

Since we have used biomass COD as the basic measurement of biomass, it would be convenient to write the nitrogen based stoichiometric equation in a way which linked it to biomass COD. This can be done by introducing two conversion factors, $i_{N/XB}$ and $i_{N/XD}$, which are respectively, the mass of nitrogen per mass of COD in active biomass and the mass of nitrogen per mass of COD in biomass debris. Their use leads to:

$$i_{N/XB} \cdot \text{Biomass COD} \rightarrow NH_3\text{-N} + i_{N/XD} \cdot \text{biomass debris COD} \tag{3.55}$$

Because the destruction of a unit mass of biomass COD leads to the generation of f_D units of biomass debris COD (Eq. 3.53), Eq. 3.55 tells us that the amount of ammonia-N released from the destruction of a unit mass of biomass COD is ($i_{N/XB} - i_{N/XD}f_D$). If $C_5H_7O_2N$ is representative of biomass, then $i_{N/XB}$ has a value of 0.087 mg N/mg biomass COD. The nature of biomass debris is less well characterized than active biomass and thus there is no generally accepted empirical formula from which $i_{N/XD}$ can be calculated. However, because many nitrogenous compounds serve as energy reserves that are destroyed during endogenous metabolism, it is likely that the nitrogen content of biomass debris is less than that of biomass. As a result, a value of 0.06 mg N/mg COD has been recommended for $i_{N/XD}$.[54,55]

The rate expression for decay of biomass is first order with respect to the biomass concentration:

$$r_{XB} = -b \cdot X_B \tag{3.56}$$

where b is the decay coefficient, with units of hr^{-1}. Employing the concept in Eq. 3.10, the rate of production of biomass debris can be seen to be:

$$r_{XD} = b \cdot f_D \cdot X_B \tag{3.57}$$

and the rate of oxygen (electron acceptor) utilization associated with biomass decay is:

$$r_{SO} = (1 - f_D)b \cdot X_B \text{ (COD units)} = -(1 - f_D)b \cdot X_B \text{ (O}_2\text{ units)} \tag{3.58}$$

The same equation would hold for utilization of nitrate expressed as oxygen equivalents, although the numerical value of the decay coefficient may well be different with alternative electron acceptors. Finally, the rate of ammonia-N release is:

$$r_{SNH} = (i_{N/XB} - i_{N/XD} \cdot f_D)b \cdot X_B \tag{3.59}$$

As might be expected from the discussion of parameter values in Section 3.2.10, the value of b is very dependent on both the species of organism involved and the substrate on which it is grown. The latter effect is probably due to the nature of the energy reserves synthesized during growth. Because Eq. 3.56 is an approximation describing very complex events, the value of b also depends to some extent on the rate at which the biomass is grown. Dold and Marais[25] have reviewed the literature concerning b and have concluded that in aerobic and anoxic wastewater treatment systems a typical value for heterotrophic biomass is 0.01 hr^{-1}. Others[10] have reported values as low as 0.002 hr^{-1} as being common in similar systems. Thus, it can be seen that quite a large range can exist. A large range of b values has also been reported for autotrophic nitrifying bacteria,[22] with values ranging from 0.0002 to 0.007 hr^{-1}. A value of 0.003 hr^{-1} is considered typical at 20°C.[55]

Decay also occurs in anaerobic systems, but the b values for such systems are lower than those for aerobic systems because the bacteria have much lower $\hat{\mu}$ values, and the two parameters appear to be correlated. For example, Bryers[14] has reported b values around 0.0004 hr^{-1} for bacteria carrying out anaerobic oxidations and methanogenesis and values around 0.001 hr^{-1} for fermentative bacteria.

3.3.2 The Lysis:Regrowth Approach

The most complete model depicting the loss of viability and biomass in biochemical operations was devised by Mason et al.[73] after an extensive review of the literature.[74] In that model, viable biomass can either die or be inactivated, leading to dead and nonviable biomass, respectively. Furthermore, all biomass can undergo lysis, although at different rates for different types, leading to soluble and particulate organic matter. The particulate organic matter is hydrolyzed to soluble organic matter, and the soluble organic matter from either source can be used by the viable biomass for new growth. Loss of viability is accounted for because the presence of dead biomass and particulate organic matter reduces the number of viable bacteria per unit mass of particulate material. Loss of biomass, i.e., decay, results from the fact that yield values are less than one so that the amount of biomass grown from the soluble