substrate released is always less than the amount destroyed by lysis, as discussed in Section 2.4.1.

A conceptually similar, but less complex, model was developed by Dold et al.[26] for use in modeling wastewater treatment systems containing both aerobic and anoxic zones. Only one type of biomass is considered to be present: active, viable biomass. However, it is viewed as continually undergoing death and lysis, yielding particulate substrate and biomass debris. As in the model of Mason et al.,[73] particulate substrate is hydrolyzed to soluble substrate, and the soluble substrate is used by the viable biomass for growth, yielding new cell material. However, as above, because biomass yield values are always less than one, the amount of new biomass formed is always less than the amount destroyed by death and lysis, resulting in a net loss of biomass from the system (i.e., decay). A loss of viability results from the accumulation of biomass debris and particulate substrate.

The model of Dold et al.[26] is simpler than that of Mason et al.,[73] yet appears to be adequate for modeling many important wastewater treatment systems.[25] Furthermore, it can account for differences in decay observed as bacteria are cycled through aerobic, anoxic, and anaerobic conditions, whereas those differences cannot be accounted for by the traditional decay approach.[123] Finally, it has been adopted for use in a general model of single-sludge processes[54,55] that has been shown to adequately represent the dynamic performance of full-scale systems.[8] Thus, it will be used herein as an alternative to the traditional approach. The events in it are depicted in Figure 3.6.

The COD-based stoichiometry of the lysis:regrowth approach of Dold et al.[26] is:

$$\begin{aligned}\text{Biomass COD} &\rightarrow (1 - f'_D)\ \text{particulate substrate COD}\\ &\quad + f'_D\ \text{biomass debris COD}\end{aligned} \tag{3.60}$$

where f'_D is the fraction of active biomass contributing to biomass debris. No COD is lost during death and lysis. Rather active biomass COD is simply converted into an equivalent amount of COD due to biomass debris and particulate substrate. As a

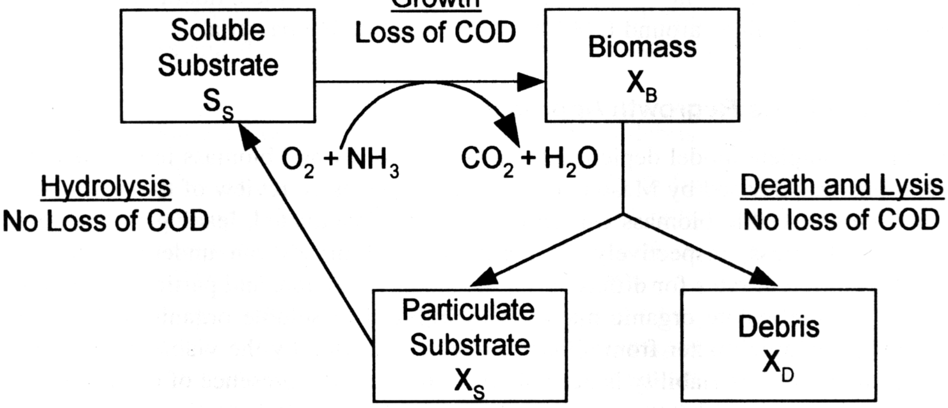

Figure 3.6 Schematic representation of the lysis:regrowth approach to modeling biomass decay and loss of viability.

consequence, no use of electron acceptor is directly associated with the loss of biomass, i.e., decay. Electron acceptor utilization occurs as soluble substrate, which arises from hydrolysis of particulate substrate, is used by active biomass for growth. As with the traditional approach, cell debris is assumed to be resistant to microbial attack within the time constraints of biochemical operations.

The nitrogen in the biomass is divided between biomass debris and particulate substrate, with the latter being called particulate biodegradable organic nitrogen. The nitrogen based stoichiometric equation depicting this is:

$$\text{Biomass N} \rightarrow \text{particulate biodegradable organic N} + \text{biomass debris N} \tag{3.61}$$

Giving the same meanings to $i_{N/XB}$ and $i_{N/XD}$ as given above, Eq. 3.61 can be rewritten in terms of biomass COD and biomass debris COD:

$$\begin{aligned} i_{N/XB}\cdot\text{Biomass COD} &\rightarrow \text{particulate biodegradable organic N} \\ &\quad + i_{N/XD}\cdot\text{biomass debris COD} \end{aligned} \tag{3.62}$$

Thus, each unit of biomass COD lost to decay yields $(i_{N/XB} - i_{N/XD}\cdot f'_D)$ units of particulate biodegradable organic nitrogen. This differs from the traditional approach which leads directly to soluble ammonia nitrogen.

As in the traditional approach, the rate of loss of biomass COD to death and lysis is considered to be first order with respect to the active biomass concentration:

$$r_{XB} = -b_L\cdot X_B \tag{3.63}$$

where b_L has units of hr^{-1}, just as b does. In a manner similar to the traditional approach, the rate of production of biomass debris COD is:

$$r_{XD} = b_L\cdot f'_D\cdot X_B \tag{3.64}$$

And the rate of production of particulate substrate COD (X_S) is:

$$r_{XS} = (1 - f'_D)b_L\cdot X_B \tag{3.65}$$

Note the similarity of this equation to Eq. 3.58, the equation for oxygen consumption in the traditional approach. This similarity arises from the retention in the particulate substrate of all electrons lost from active biomass, rather than their transfer to oxygen. Finally, the rate of production of particulate, biodegradable organic nitrogen (X_{NS}) is:

$$r_{XNS} = (i_{N/XB} - i_{N/XD}\cdot f'_D)b_L\cdot X_B \tag{3.66}$$

It is important to realize that b_L is conceptually and numerically different from b and that f'_D is numerically different from f_D. This follows from the cycling of COD that occurs in the lysis:regrowth approach. Biomass COD is lost, releasing particulate substrate COD, which is hydrolyzed to soluble substrate COD, which is degraded by active biomass yielding new biomass, which is lost by death and lysis giving particulate substrate COD, etc. The net effect of the two approaches is the same because a given amount of biomass will be lost from a bioreactor regardless of how we conceptualize the actual events occurring. Since it is necessary for carbon to cycle around the system several times in the lysis:regrowth conceptualization to achieve the same loss of biomass that the traditional approach achieves in one pass,

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b_L must be numerically larger than b. Likewise, since the same amount of biomass debris is ultimately formed from the loss of a given amount of biomass by decay, f'_D must be numerically smaller than f_D. In fact, the values of the four parameters are related:[26]

$$f'_D \cdot b_L = f_D \cdot b \tag{3.67}$$

Furthermore,

$$f'_D = \left(\frac{1 - Y}{1 - Y \cdot f_D}\right) f_D \tag{3.68}$$

It was stated above that f_D has a value around 0.2. Given the Y values associated with the biomass for which f_D was estimated, Eq. 3.68 suggests that the value of f'_D is around 0.08.[25] The values of f_D and f'_D are not likely to vary greatly, and thus those values will be adopted herein. It should be noted, however, that the relationship between b_L and b also depends on Y:[25]

$$b_L = \frac{b}{[1 - Y(1 - f'_D)]} \tag{3.69}$$

Although it is common during parameter evaluation studies to measure both Y and b, neither f_D nor f'_D is commonly measured. Since Y can influence the relationship between b_L and b, it is recommended that Eq. 3.69 be used instead of Eq. 3.67 to convert measured b values to b_L values.[55]

An important assumption implicit in the lysis:regrowth approach is that within a given culture, cell lysis occurs all of the time with the same value of the rate coefficient b_L, regardless of the rate at which the bacteria are growing. The validity of this assumption has been confirmed by measuring the release of nucleic acids as direct evidence of cell lysis.[95]

For autotrophic growth, the relationship between b_L and b is different.[54,55] This is because autotrophic organisms do not use organic matter for growth. Thus, death and lysis will not lead to additional autotrophic biomass growth. (The amount of autotrophic biomass that will grow from the nitrogen released is negligible.) Rather, heterotrophic biomass will grow on the organic matter released. As a consequence, the lysis:regrowth and traditional approaches are the same for autotrophic biomass; the result is that the two parameter values are equal.

3.4 SOLUBLE MICROBIAL PRODUCT FORMATION

As discussed in Section 2.4.3, soluble microbial products are thought to arise from two processes, one growth associated and the other non–growth-associated.[103]

Growth associated product formation results directly from biomass growth and substrate utilization. If soluble microbial product formation was occurring in appreciable amount, it would be necessary to modify the stoichiometric equation for microbial growth to account for it. Letting S_{MP} represent the concentration of soluble microbial products in COD units and Y_{MP} the product yield in units of product COD formed per unit of substrate COD used, Eq. 3.31 can be rewritten to account for soluble microbial product formation:

$$(1)S_S + [-(1 - Y_H - Y_{MP})]S_O \rightarrow Y_H X_{B,H} + Y_{MP} S_{MP} \tag{3.70}$$

This shows that less electron acceptor is used when soluble products are formed because part of the COD of the substrate remains in the medium as those products. Rewriting this equation in the form of Eq. 3.9 with biomass as the reference constituent gives:

$$\left(-\frac{1}{Y_H}\right) S_S + (-1)\left[-\left(\frac{1 - Y_H - Y_{MP}}{Y_H}\right)\right] S_O + X_{B,H} + \frac{Y_{MP}}{Y_H} S_{MP} = 0 \tag{3.71}$$

This tells us:

$$r_{SMP} = (Y_{MP}/Y_H) r_{XB} \tag{3.72}$$

Combining Eq. 3.72 with Eq. 3.35 for r_{XB} gives:

$$r_{SMP} = (Y_{MP}/Y_H)\mu \cdot X_{B,H} \tag{3.73}$$

The fact that r_{SMP} is proportional to μ shows that it is growth-associated.

Non–growth-associated product formation, also called biomass-associated product formation,[103] occurs as a result of cell lysis and decay. Rewriting Eq. 3.53 to incorporate soluble product formation into the COD-based stoichiometry of the traditional approach to decay gives:

$$\begin{aligned}&\text{Biomass COD} + [-(1 - f_D - f_{MP})]O_2 \text{ equivalents of electron} \\ &\quad \text{acceptor} \rightarrow f_D \text{ biomass debris COD} + f_{MP} \text{ soluble product COD}\end{aligned} \tag{3.74}$$

where f_{MP} is the fraction of active biomass contributing to biomass-associated products. Using this with Eq. 3.56 gives the rate of production of biomass-associated product:

$$r_{SMP} = b \cdot f_{MP} \cdot X_{B,H} \tag{3.75}$$

By analogy to biomass debris formation, a similar approach could be used to account for soluble microbial product formation in the lysis:regrowth approach, giving a parameter f'_{MP} which is smaller than f_{MP} in the same way that f'_D is smaller than f_D.

Combining Eqs. 3.73 and 3.75 suggests that the specific rate of soluble microbial product formation is linearly related to the specific growth rate. While such a relationship may be adequate for slowly growing cultures like those found in activated sludge systems, it is not adequate for more rapidly growing systems[49] and thus Eqs. 3.73 and 3.75 cannot be considered to be of general applicability to all systems. Although a relatively large body of research on soluble microbial product formation has been conducted,[49,103] it is still not sufficient to allow consensus on the rate expressions to be used. Thus, in spite of its known importance, soluble microbial product formation will not be incorporated into the models in Parts II and IV.

Insufficient information is available to provide typical values for f_{MP} and f'_{MP}, but, as indicated in Section 2.4.3, Y_{MP} values have been found to be less than 0.1.[42]

3.5 SOLUBILIZATION OF PARTICULATE AND HIGH MOLECULAR WEIGHT ORGANIC MATTER

The conversion of particulate and high molecular weight organic matter into forms small enough for bacteria to take up and degrade is an important step in biochemical operations for wastewater treatment because such materials are commonly present in wastewaters and also arise from lysis reactions as discussed previously. In spite of that, relatively few studies have focused on those reactions. Perhaps this is because many types of particulate materials are attacked by distinctly different mechanisms, even though they are collectively referred to as hydrolysis.

The stoichiometry of hydrolysis is thought to be very simple, with organic material simply changing form. Consequently, most investigators have assumed that COD is conserved, i.e., that no energy is consumed. This is indicated in Figure 3.6. Because no energy is consumed, no electrons are removed and no terminal electron acceptor is used. Thus, the stoichiometric equation is simply:

$$\text{Particulate substrate COD} \rightarrow \text{soluble substrate COD} \tag{3.76}$$

This means that the rate of formation of soluble substrate COD is equal to the rate of loss of particulate substrate COD.

In the face of complex situations in which reactions are ill defined, it is common for engineers to choose the simplest possible reaction rate expression, and that is what a number of investigators have done, assuming that hydrolysis is first order with respect to the concentration of particulate substrate, X_S.[14,15,28,44,73] This approach, however, ignores the effect that the biomass concentration will have on the rate.

One group[55] performed an extensive literature survey before adopting a kinetic expression for the hydrolysis of particulate organic matter patterned after that of Dold et al.,[26] which is based on the work of Stenstrom:[117]

$$r_{XS} = -k_h \left[\frac{X_S/X_{B,H}}{K_X + (X_S/X_{B,H})} \right] X_{B,H} \tag{3.77}$$

In this expression k_h is the hydrolysis coefficient (hr^{-1}) and K_X is a half-saturation coefficient (mg particulate substrate COD/mg active biomass COD). An important characteristic of this expression is that even though the rate is first order with respect to the heterotrophic biomass concentration, it is controlled by the ratio of particulate substrate concentration to heterotrophic biomass concentration, rather than by the particulate substrate concentration alone. This is necessary because the reaction is thought to be surface mediated, depending on the presence of extracellular enzymes whose quantity will be proportional to the biomass concentration.[26]

Data on the values of k_h and K_X are very limited. Based primarily on the recommendations of Dold and Marais,[25] one group[54] adopted a value of 0.092 hr^{-1} for k_h and a value of 0.15 for K_X.

The rate of hydrolysis will also be influenced by the electron acceptor concentration,[25,54,55] even though no electron acceptor is used in the reaction. Under aerobic conditions, an interactive, dual nutrient limitation expression has been adopted in a manner similar to that in Eq. 3.46. Under anoxic conditions, an expression similar to that in Eq. 3.48 has been found to be appropriate, with nitrate stimulating anoxic hydrolysis and oxygen inhibiting it. In both expressions, the effect of the particulate substrate should be given by Eq. 3.77. Under anaerobic conditions of short duration, hydrolysis is assumed to stop. While this would not be true for long term anaerobic conditions, it is consistent with observations in biochemical operations that cycle bacteria between aerobic and anoxic conditions.[25] It would probably be satisfactory to use Eq. 3.77 alone to describe hydrolysis under fully anaerobic conditions, but with a k_h value much smaller than that used for aerobic conditions.

As seen in Eq. 3.61, biomass decay results in the formation of particulate biodegradable organic nitrogen. In addition, organic nitrogen will be associated with the particulate organic matter in the wastewater. All of this material will be converted into soluble, biodegradable organic nitrogen, S_{NS}, (i.e., the nitrogen associated with amino acids and other soluble, nitrogen containing organic substrates) as the particulate substrate is hydrolyzed. The rate of generation of S_{NS} (r_{SNS}) is numerically equivalent to the rate of loss of particulate organic nitrogen (r_{XNS}), which is proportional to the hydrolysis rate of particulate organic matter:[25]

$$r_{SNS} = -r_{XNS} = -(X_{NS}/X_S)r_{XS} \tag{3.78}$$

where X_{NS} is the concentration of particulate, biodegradable organic nitrogen.

3.6 AMMONIFICATION AND AMMONIA UTILIZATION

Ammonification is the conversion of soluble organic nitrogen into ammonia-N that occurs as bacteria consume soluble organic matter containing nitrogen. Actually, the true rate of ammonification is difficult to measure because ammonia-N is being consumed by the bacteria as they grow, and the only measurable event is the net accumulation or loss of ammonia in the medium. If the amount of nitrogen available in the organic substrate is just sufficient to meet the biosynthetic needs of the new biomass, there will be no net change in the ammonia-N concentration in the medium. On the other hand, if that amount exceeds the need, the ammonia concentration in the medium will increase, whereas if that amount is less than the need, the ammonia concentration will decrease. It should be recognized, however, that whether organic nitrogen is incorporated directly into new biomass depends on its form. The nitrogen in simple compounds like amino acids may be incorporated directly as the amino acids are used for protein synthesis, while nitrogen in complex synthetic organic chemicals may be released to the medium as ammonia.

In an effort to make this complex situation mathematically tractable, most modelers assume that all nitrogen goes through the medium before being used. Thus, ammonification is assumed to release all organic nitrogen to the medium as ammonia, and nitrogen utilizing reactions are assumed to obtain their ammonia from the medium. Whether ammonia accumulates or is removed depends on the relative rates of its production and utilization.

Because ammonification occurs as heterotrophic biomass destroys nitrogen containing soluble organic matter, it is likely that its rate is proportional to the rate of soluble substrate removal. Relatively little work has been done to investigate the rate of ammonification in complex substrates in which only a part of the soluble organic matter contains nitrogen, and it is uncertain whether a direct proportionality can be assumed between soluble substrate removal and ammonification. Consequently, ammonification has been represented as a reaction that is first order with respect to both the heterotrophic biomass concentration and the concentration of soluble, biodegradable organic nitrogen:[25,54,55]

$$r_{SNS} = -k_a \cdot S_{NS} \cdot X_{B,H} \tag{3.79}$$

where k_a is the ammonification rate coefficient (L/(mg biomass COD · hr)). Very little information is available about its value. As discussed above, the assumed stoichiometry of ammonification is such that all nitrogen removed from nitrogen containing soluble organic matter is released as ammonia, although some may ultimately be used for biomass synthesis. Thus, the rate of production of ammonia nitrogen (S_{NH}) through ammonification is:

$$r_{SNH} = -r_{SNS} \tag{3.80}$$

Ammonia is removed from solution by two reactions. First, it is used in the synthesis of new biomass as seen in Eq. 3.6 and others presented in Section 3.2. Second, it is used as a substrate by autotrophic biomass. The rate expression for the second use is the same as any other substrate, as discussed in Section 3.2.6. The rate expression for the first use can be determined from the generalized rate expression and the stoichiometry of growth. Since $i_{N/XB}$ is the mass of nitrogen per unit of biomass COD, the rate of ammonia removal through biomass growth is simply:

$$r_{SNH} = -i_{N/XB} \cdot \mu \cdot X_B \tag{3.81}$$

Equation 3.81 is true for both heterotrophic and autotrophic growth, and thus the general symbol for biomass, X_B, has been used in it.

3.7 PHOSPHORUS UPTAKE AND RELEASE

Biological phosphorus removal is a complex process that is dependent on the growth of specialized phosphate accumulating organisms (PAOs), which store phosphorus as polyphosphate (poly-P), as discussed in Section 2.4.6. Because biological phosphorus removal is still the subject of active experimental investigation, there is little consensus concerning all of the rate expressions describing it. Furthermore, the microbial events involved are subject to complex control through the concentrations of several constituents. As a consequence, a discussion beyond the scope of this chapter would be needed to fully define the kinetics and stoichiometry of biological phosphorus removal. There are, however, two events that should be considered briefly because they are distinctly different from the events discussed above. These are the uptake and release of phosphorus by the PAOs.

It will be recalled from Section 2.4.6 that two conceptual models exist for biological phosphorus removal, the Comeau/Wentzel model and the Mino model, illustrated in Figures 2.5 and 2.6, respectively. The major difference between them is that the Mino model incorporates glycogen formation and utilization, whereas the Comeau/Wentzel model does not. In developing a mathematical model for biological phosphorus removal, one group decided that the introduction of a detailed mechanistically based mathematical model for the process was premature.[56] Rather, they preferred to recommend the simplest mathematical model that allows adequate prediction of biological phosphorus removal. Consequently, they basically followed the Comeau/Wentzel model. Furthermore, they assumed that PAOs cannot use nitrate as a terminal electron acceptor and that they can only grow on the PHB stored in the cell. Although these assumptions are severe restrictions, we have chosen to use activated sludge model (ASM) No. 2 as the basis for the rate expressions presented herein because it represents a consensus among several investigators in the field.[56] It should be recognized, however, that more complete expressions are likely to be developed as more research is done.

Under anaerobic conditions, PAOs do not grow, but store acetic acid as PHB through the cleavage of Poly-P with the associated release of soluble phosphate. (In the following equations, all phosphate concentrations are expressed as phosphorus, P, and all organic materials are expressed as COD). The rate of removal of acetic acid, r_{SA}, can be modeled with an interactive, dual limiting nutrient expression:

$$r_{SA} = -\hat{q}_A \left(\frac{S_A}{K_A + S_A}\right) \left[\frac{X_{PP}/X_{B,P}}{K_{PP} + (X_{PP}/X_{B,P})}\right] X_{B,P} \tag{3.82}$$

where $\hat{q}_A$ is the maximum specific rate of acetic acid uptake, hr^{-1}, S_A is the acetic acid concentration in COD units, K_A is a half-saturation coefficient for acetic acid, X_{PP} is the poly-P concentration in the biomass, expressed as a liquid phase P concentration, K_{PP} is a half-saturation coefficient for poly-P in the same units, and $X_{B,P}$ is the concentration of PAO biomass in COD units. The stoichiometry of the reaction is such that each mg/L of acetic acid COD removed from the medium forms a mg/L of PHB COD in the biomass. Thus, the rate expression for PHB (X_{PHB}) formation, r_{XPHB}, is:

$$r_{XPHB} = -r_{SA} \tag{3.83}$$

Furthermore, Y_P units of soluble phosphate, S_P, are released for each unit of acetic acid stored as COD, increasing S_P by an amount equal to the decrease in stored Poly-P concentration. Thus:

$$r_{SP} = -r_{XPP} = Y_P \cdot r_{XPHB} \tag{3.84}$$

The value of Y_P selected by Henze et al.[56] was 0.40 mg P/mg COD, reflecting the average stoichiometry for the process. The values of K_{SA} and K_{PP} were chosen to be small to make the parenthetical terms in Eq. 3.82 serve as switching functions that change rapidly from one to zero, thereby turning the reaction on and off. The value chosen for K_{SA} was 4.0 mg COD/L whereas the value chosen for K_{PP} was 0.01 mg P/mg PAO COD.

Under aerobic conditions, the PAOs grow by using the stored PHB as a carbon and energy source. This is assumed to be their only substrate for growth, even though they are capable of growth on soluble substrates. Because little soluble substrate is likely to be present in the aerobic portion of a biological phosphorus removal process, Henze et al.[56] ignored it to simplify the model. Furthermore, because the process can only occur under aerobic conditions, a switching function for oxygen was included to make the rate go to zero when oxygen is absent. Considering all of these factors, the rate of PAO growth can be described by:

$$r_{XBP} = \hat{\mu}_P \left[\frac{X_{PHB}/X_{B,P}}{K_{PHB} + (X_{PHB}/X_{B,P})}\right] \left(\frac{S_P}{K_P + S_P}\right) \left(\frac{S_O}{K_O + S_O}\right) X_{B,P} \tag{3.85}$$

where $\hat{\mu}_P$ is the maximum specific growth rate coefficient for PAOs, X_{PHB} is the stored PHB concentration in mg/L as COD, S_P is the soluble phosphate concentration