6

Multiple Microbial Activities in a Single Continuous Stirred Tank Reactor

In Chapter 5, we investigated the growth of aerobic heterotrophic bacteria in a single continuous stirred tank reactor (CSTR) receiving a soluble substrate. Through development of a simple model we saw that the SRT is an important determinant of bioreactor performance because it is related to the specific growth rate of biomass at steady-state. We also saw that there is a minimum SRT below which biomass growth cannot occur, as well as a minimum substrate concentration that can be achieved no matter how large the SRT. Finally, we saw how stoichiometry can be applied to determine the amount of electron acceptor required and the amount of excess biomass produced. All of these characteristics are of fundamental importance and apply to all types of biomass, both heterotrophic and autotrophic, in all types of environments, whether aerobic, anoxic, or anaerobic. Thus, even though the concepts in Chapter 5 are developed in the context of aerobic growth of heterotrophs, they are broadly applicable.

In spite of the broad utility of the concepts, the model developed in Chapter 5 has two characteristics that restrict its applicability in many wastewater treatment situations. One is that it is limited to soluble, readily biodegradable substrates, whereas most wastewaters contain particulate contaminants and soluble constituents of large molecular weight that must be reduced in size before they can be taken into the bacteria for biodegradation. If a model is to accurately depict the response of bioreactors receiving such wastewaters, it must include hydrolysis reactions. The other is that the biomass is assumed to be in a constant biochemical environment with no limitation by the electron acceptor. In many systems, however, limitations or alterations in the supply of electron acceptor cause shifts between aerobic and anoxic conditions, with short periods of anaerobiosis as well, and during these shifts the concentration of the electron acceptor may be limiting. Therefore, it would be desirable for a model to handle such situations.

In order to encourage practicing engineers to use modeling more extensively during the analysis of alternative wastewater treatment systems, in 1983 the International Association on Water Quality (IAWQ) [formerly the International Association on Water Pollution Research and Control (IAWPRC)] appointed a task group to review models for suspended growth cultures and to produce one capable of depicting the performance of wastewater treatment systems receiving both soluble and particulate substrates in which organic substrate removal, nitrification, and denitrification were all occurring. In other words, they were to consider most of the pro-

cesses discussed in Section 2.4. They completed their task in 1986 and submitted a report to IAWQ which was published in 1987,[17,18] outlining the major features of activated sludge model (ASM) No. 1. The task group was influenced by the published work of many researchers, but that of Marais and colleagues at the University of Cape Town in South Africa had a major impact on their thinking. A summary of much of the South African work can be found elsewhere.[12] Because ASM No. 1 is the result of the deliberations of several researchers with diverse opinions, and because it is capable of mimicking the performance of pilot[12] and full[3] scale systems, it will be adopted herein for investigating more fully the performance of suspended growth bioreactors. In this chapter, ASM No. 1 will be used to illustrate the impact in a single CSTR of the processes and events not covered in Chapter 5 and in Chapter 7 it will be used to investigate the performance of multiple bioreactor systems.

Because of the success of ASM No. 1, the IAWQ task group on mathematical modeling was reconstituted and asked to produce a consensus model capable of mimicking the performance of systems capable of performing organic substrate removal, nitrification, denitrification, and phosphorus removal. This was a complicated task because of the complexity of biological phosphorus removal and the evolving nature of our understanding of it. Nevertheless, they were successful, releasing their report in 1995,[19] calling the new model ASM No. 2. Use will be made of the model in Chapter 7, but it will not be explained in the same detail as ASM No. 1 because of the large number of components and processes involved. However, the major rate expressions associated with phosphorus removal in the model were presented in Section 3.7.

Modeling is now used extensively in biological wastewater treatment, in large part because of the success of ASM No. 1. Similar concepts have been applied to develop descriptive models for anaerobic wastewater treatment processes.[15,31] Space does not permit their investigation here, but the reader is encouraged to consult the primary literature concerning them.

6.1 INTERNATIONAL ASSOCIATION ON WATER QUALITY ACTIVATED SLUDGE MODELS

International Association on Water Quality ASM No. 1 is presented in matrix format in Table 6.1, where it can be seen to incorporate 8 processes and 13 components. Examination of the table reveals the utility of the matrix format, because application of the principles discussed in Section 5.1.2 allows immediate identification of the fate of each component and construction of the overall reaction rate term for it. It should be noted that components 1–8 are expressed in chemical oxygen demand (COD) units, whereas components 9–12 are given as nitrogen. The alkalinity is in molar units. These units are given in Table 6.2 along with the definition of each component.

6.1.1 Components in ASM No. 1

Components 1–5 and component 12 are all particulate. X_I is inert particulate organic material. The fact that there are no entries listed under it in Table 6.1 shows that it is neither generated nor destroyed in a biochemical reactor. However, if it is present

Table 6.1 Process Kinetics and Stoichiometry for Multiple Events in Suspended Growth Cultures as Presented by IAWQ Task Group on Mathematical Modeling[16,17]

Component[a] → i	1	2	3	4	5	6	7	8	9	10	11	12	13	
j Process ↓	X_I	X_S	$X_{B,H}$	$X_{B,A}$	X_D	S_I	S_S	S_O[b]	S_{NO}	S_{NH}	S_{NS}	X_{NS}	S_{ALK}	Process rate, r_j, $ML^{-3}T^{-1}$
1 Aerobic growth of heterotrophs			1				$-\frac{1}{Y_H}$	$\frac{1-Y_H}{Y_H}$		$-i_{N/XB}$			$-\frac{i_{N/XB}}{14}$	$\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_O}{K_{O,H}+S_O}\right)X_{B,H}$
2 Anoxic growth of heterotrophs			1				$-\frac{1}{Y_H}$		$-\frac{1-Y_H}{2.86\,Y_H}$	$-i_{N/XB}$			$\frac{1-Y_H}{14(2.86\,Y_H)}-\frac{i_{N/XB}}{14}$	$\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{K_{O,H}}{K_{O,H}+S_O}\right)\cdot\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\eta_g X_{B,H}$
3 Aerobic growth of autotrophs				1				$\frac{4.57-Y_A}{Y_A}$	$\frac{1}{Y_A}$	$-i_{N/XB}-\frac{1}{Y_A}$			$-\frac{i_{N/XB}}{14}-\frac{1}{7Y_A}$	$\hat{\mu}_A\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_O}{K_{O,A}+S_O}\right)X_{B,A}$
4 Death and lysis of heterotrophs		$1-f'_D$	-1		f'_D						$i_{N/XB}-f'_D i_{N/XD}$			$b_{L,H}X_{B,H}$
5 Death and lysis of autotrophs		$1-f'_D$		-1	f'_D						$i_{N/XB}-f'_D i_{N/XD}$			$b_{L,A}X_{B,A}$
6 Ammonification of soluble organic nitrogen										1	-1		$\frac{1}{14}$	$k_a S_{NS} X_{B,H}$
7 "Hydrolysis" of particulate organics		-1					1							$k_h\frac{X_S/X_{B,H}}{K_X+(X_S/X_{B,H})}\left[\left(\frac{S_O}{K_{O,H}+S_O}\right)+\eta_h\left(\frac{K_{O,H}}{K_{O,H}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\right]X_{B,H}$
8 "Hydrolysis" of particulate organic nitrogen											1	-1		$r_7(X_{NS}/X_S)$
Observed conversion rates, $ML^{-3}T^{-1}$								$r_i=\sum_{j=1}^{n}\Psi_{ij}r_j$						

[a]All organic compounds (1–7) and oxygen (8) are expressed as COD; all nitrogenous components (9–12) are expressed as nitrogen.
[b]Coefficients must be multiplied by −1 to express as oxygen.

Table 6.2 Definitions of Component Symbols in Table 6.1

Component number	Component symbol	Definition
1	X_I	Inert particulate organic matter, mg/L as COD
2	X_S	Slowly biodegradable substrate, mg/L as COD
3	$X_{B,H}$	Active heterotrophic biomass, mg/L as COD
4	$X_{B,A}$	Active autotrophic biomass, mg/L as COD
5	X_D	Debris from biomass death and lysis, mg/L as COD
6	S_I	Inert soluble organic matter, mg/L as COD
7	S_S	Readily biodegradable substrate, mg/L as COD
8	S_O	Oxygen, mg/L as COD
9	S_{NO}	Nitrate nitrogen, mg/L as N
10	S_{NH}	Ammonia nitrogen, mg/L as N
11	S_{NS}	Soluble biodegradable organic nitrogen, mg/L as N
12	X_{NS}	Particulate biodegradable organic nitrogen, mg/L as N
13	S_{ALK}	Alkalinity molar units

in the influent, it will accumulate with the degree being determined by the ratio of the SRT to the HRT (see Section 5.5.2). Component 2, X_S, is slowly biodegradable substrate. Although it is treated as a particulate constituent, its concentration in the influent to the bioreactor must be determined experimentally (see Chapter 8). It is destroyed by hydrolysis reactions, but is generated during biomass decay, which is modeled by the lysis:regrowth concept (see Section 3.3.2). Active heterotrophic biomass is depicted by $X_{B,H}$ whereas active autotrophic biomass (nitrifying bacteria) is given as $X_{B,A}$. Both are generated by growth on their respective substrates and both are lost by decay, leading to slowly biodegradable substrate and biomass debris, X_D. The latter is inert, and behaves in a manner similar to X_I. Component 12, X_{NS}, is particulate biodegradable organic nitrogen. It is formed by decay reactions since the slowly biodegradable substrate arising from biomass decay contains proteins and other nitrogen-containing organic compounds of high molecular weight. It is destroyed by hydrolysis.

Components 6–11 are all soluble, and with the exception of S_I, which is inert, are the constituents upon which the biomass acts. The presence of S_I in the matrix is simply to remind us that wastewaters contain nonbiodegradable soluble COD which passes through the bioreactor unaffected by biological activity (see Section 5.2.1). S_S is readily biodegradable substrate, which is removed by growth of heterotrophic biomass under aerobic or anoxic conditions and is generated by hydrolysis of slowly biodegradable organic matter. Its concentration in the wastewater entering a bioreactor must be determined experimentally, and the procedures for doing so are discussed in Chapter 8. Component 8 is oxygen, which is removed by aerobic growth of heterotrophic and autotrophic bacteria. The stoichiometric term for oxygen associated with heterotroph growth is the same as that in Table 5.1, but the term associated with autotroph growth contains the factor 4.57. That factor is required because ammonia is the substrate for autotrophic nitrifying bacteria and its concentration in the matrix (S_{NH}, component 10) is expressed as nitrogen, whereas oxygen is expressed as COD. Furthermore, Y_A has units of mg of biomass COD formed per mg

of nitrogen converted. Since the stoichiometric expression for oxygen in process 3 (autotrophic growth) comes from a COD-based stoichiometric equation, a factor must be included for the COD equivalents of ammonia-N in order to have consistent units. As discussed previously, the oxidation state of nitrogen is changed from −III to +V as nitrifiers form nitrate from ammonia. The amount of oxygen required to accept the electrons removed during this oxidation is 4.57 g O_2/g N, as indicated in Table 3.1. Thus, that factor must be included. Unlike the model in Table 5.1, which used the traditional approach to decay, no oxygen utilization is associated directly with biomass loss in Table 6.1 because it is modeled with the lysis:regrowth approach. Rather, the oxygen utilization associated with biomass loss occurs because of the use of readily biodegradable substrate generated by hydrolysis of the slowly biodegradable substrate formed by death and lysis. Component 9, S_{NO}, is nitrate-N. It is formed by aerobic growth of autotrophic bacteria and is lost as it serves as the electron acceptor for anoxic growth of heterotrophic bacteria. In the latter role, the oxidation state of the nitrogen is changed from +V to zero and the factor 2.86 appearing in the stoichiometric coefficient represents the oxygen equivalence of this change in units of g COD/g N, as shown in Table 3.1. Examination of column 10 shows that ammonia-N is involved in several reactions. Since ammonia is the preferred form of nitrogen for biomass growth, the term $-i_{N/XB}$ is included in rows 1–3 to represent the amount of nitrogen incorporated into new biomass. No provision is made in this model for reduction of nitrate-N to ammonia-N for incorporation into biomass in the event insufficient ammonia is present. This restriction should be recognized. Other models[11,33] allow use of nitrate-N for biomass synthesis. The second stoichiometric coefficient in column 10 for aerobic growth of autotrophic bacteria represents the use of ammonia as a substrate and is analogous to the coefficients used for readily biodegradable substrate (column 7) removal by heterotrophic biomass in rows 1 and 2. Ammonia is formed by ammonification of soluble organic nitrogen, S_{NS}, which is the last nitrogen based soluble constituent. It, in turn, is formed by hydrolysis of particulate organic nitrogen.

In Section 3.2.10 the sensitivity of autotrophic biomass to low pH is discussed. Furthermore, in Section 3.2.5 it is seen that alkalinity is destroyed during their growth. If the wastewater contains insufficient alkalinity, the growth of autotrophic biomass will cease because a needed nutrient (carbon) is missing and because the pH will drop, inhibiting their activity. Thus, the destruction of alkalinity by autotrophic bacterial growth is an important event that must be considered by the engineer. Another factor influencing alkalinity is denitrification, which produces it, and in properly configured systems, this production can offset somewhat its destruction. The coefficients in column 13 account for the changes in alkalinity, S_{ALK}, associated with nitrogen conversions in the bioreactor. Although the IAWQ task group did not attempt to model the effects of those changes on pH, they noted that when the alkalinity falls below 50 mg/L as $CaCO_3$, the pH becomes unstable and can fall well below 6,[35] thereby hindering nitrification.

6.1.2 Reaction Rate Expressions in ASM No. 1

The growth of heterotrophic bacteria with associated use of substrate and electron acceptor is given by processes 1 and 2 in Table 6.1 for the situation in which ammonia serves as the nitrogen source for synthesis of new cell material. Process 1 is

aerobic growth and its rate is given by Eq. 3.35 with substitution of Eq. 3.46 for μ, the specific growth rate coefficient. In this case, reactant 1 is readily biodegradable substrate and reactant 2 is dissolved oxygen. The main purpose of the dissolved oxygen term is to turn off aerobic growth as the dissolved oxygen concentration becomes low, and to allow anoxic growth to begin if nitrate is present, as suggested by the rate term for process 2. The specific growth rate coefficient in that rate term is of the same form as Eq. 3.48, with $K_{O,H}$ serving as the inhibition coefficient K_{IO}. By using $K_{O,H}$ in that capacity, the oxygen terms in the rate expressions for processes 1 and 2 compliment each other, with one approaching zero as the other approaches one (their sum always equals one). It should be noted that both heterotrophic rate expressions go to zero under totally anaerobic conditions, i.e., in the absence of both oxygen and nitrate. Given long term acclimation to anaerobic conditions, fermentative reactions would allow growth of facultatively anaerobic bacteria, but such acclimation is not likely to occur in the systems for which the model was developed. Nevertheless, this limitation should be recognized and the model should not be used to simulate bioreactors in which fully anaerobic conditions develop. Comparison of the rate term for process 2 to Eq. 3.48 reveals the presence of an additional parameter, η_g. It is a correction factor for growth under anoxic conditions. As seen in Section 3.2.10, the $\hat{\mu}_H$ and K_S values for cultures grown on the same substrate under totally aerobic and totally anoxic conditions are very similar, whereas the yield is lower under anoxic conditions.[24] This suggests that an appropriate way to model two separate biomasses grown in different environments would be to use the same values of the kinetic parameters under the two conditions, but to use different yield values. A major purpose of the model in Table 6.1, however, is to model a biomass that is alternated between aerobic and anoxic conditions. In that case, although the entire biomass will be capable of aerobic growth, only a portion of it may be able to grow under anoxic conditions. The purpose of η_g is to correct for this condition. Because only a portion of the biomass may be capable of denitrification, η_g takes on values less than one, with those values depending somewhat on the system configuration.[16] Because of the empirical nature of η_g, it also corrects for differences in the yield values under the two environmental conditions, and thus, ASM No. 1 uses a common yield value for aerobic and anoxic conditions.

Process 3 in Table 6.1 is aerobic growth of autotrophic bacteria, which is modeled with Eq. 3.46 in which reactant 1 is ammonia-N and reactant 2 is dissolved oxygen. Two important things should be noted about the way this process is modeled. The first is that nitrification is considered to occur in a single step, with nitrate-N arising directly from ammonia-N. This is a simplification, because, as seen in Section 2.3.1, nitrification is a two step process, with nitrite as an intermediate. As discussed in Section 3.2.10, the kinetic parameters for *Nitrosomonas* and *Nitrobacter* are similar. Consequently, under balanced growth conditions nitrite is used as fast as it is formed so that its concentration is usually very low and of little importance. Therefore, to reduce the number of equations and to simplify the model, ASM No. 1 uses a one-step approach. It should be noted, however, that nitrite can accumulate in suspended growth cultures, particularly during startup or following severe temperature changes when the two bacterial populations are not balanced.[1,30] Thus, the model is really only appropriate for bioreactors at steady-state or for those receiving dynamic loads no more severe than the diurnal flows and concentrations normally entering domestic wastewater treatment systems. Other models consider both steps

in nitrification, although they are more complicated.[33] The second important characteristic of the process rate expression for nitrification is that no consideration is given to substrate and product inhibition, which are known to occur at high nitrogen concentrations, as discussed in Section 3.2.10. These factors were not considered because of a lack of adequate kinetic relationships, as discussed earlier, and because they do not normally occur at the nitrogen levels commonly found in domestic wastewater. Consequently, ASM No. 1 should not be applied to simulate the treatment of wastewaters containing nitrogen concentrations greatly in excess of those levels.

Loss of heterotrophic biomass, process 4, is modeled by the lysis:regrowth approach discussed in Section 3.3.2. A primary reason for adopting this approach is that no use of electron acceptor is directly associated with it, thereby making it easier to express the effects of alternative electron acceptors in the overall model. The loss of heterotrophic biomass is thought to continue at the same rate, regardless of the electron acceptor available,[12] and is modeled by Eq. 3.63. Similarly, the formation of biomass debris, slowly biodegradable substrate, and particulate biodegradable organic nitrogen are modeled by Eqs. 3.64–3.66, respectively. The nature of the electron acceptor will influence the rates of utilization of these constituents, however, as reflected in the other process rate expressions.

Process 5, loss of autotrophic biomass, is also modeled by the lysis:regrowth approach, although the amount of autotroph regrowth is not really significant, as discussed previously. Rather, heterotrophs grow on the organic substrate resulting from death and lysis of the autotrophic bacteria. As a consequence, the magnitude of the loss coefficient for autotrophs is the same as that for the traditional decay approach.

As nitrogen containing organic compounds undergo biodegradation, the nitrogen in them is released as ammonia, as discussed in Section 3.6. This release is reflected in process 6, which is modeled with Eqs. 3.79 and 3.80. These expressions are approximate because of a lack of information about them, as discussed in Section 3.6. They should be satisfactory, however, within the constraints already established for the model.

An important contribution of ASM No. 1 is consideration of the fate of particulate and other slowly biodegradable substrate, as reflected in process 7, which is hydrolysis. Although the fate of such material in suspended growth cultures is important, relatively little research has been done from which a rate expression can be developed (see Section 3.5). Nevertheless, based on the limited literature available, ASM No. 1 uses Eq. 3.77 as the basic rate expression. Comparison of it to the expression in Table 6.1, however, reveals that it was extended to include the effects of the electron acceptor. First, it will be noted that another correction factor, η_h, is included to reflect a retardation of hydrolysis under anoxic conditions. Like η_g, this correction factor is empirical and the rationale for its use is the same. Second, the rate of hydrolysis is assumed to go to zero in the total absence of oxygen or nitrate. Although hydrolysis is known to occur in anaerobic bioreactors (see Section 2.3.2), adaptation of facultative bacteria is required and evidently does not occur when a predominately aerobic or anoxic culture is subjected to short periods of anaerobiosis, because hydrolysis stops under such conditions.[34] Because death and lysis are thought to continue at the same rate regardless of the nature of the electron acceptor, there will be an accumulation of slowly biodegradable substrate when suspended growth

cultures are subjected to short periods without either oxygen or nitrate. In spite of the lack of certainty associated with the rate expression for process 7, the patterns of oxygen and nitrate-N utilization predicted by ASM No. 1 have been found to mimic well the performance of both pilot-[12,13] and full-scale[3] suspended growth systems with a number of configurations. Thus, although additional research is needed on this important topic, use of the model depicted in Table 6.1 should be satisfactory for the purposes intended herein.

The final process in Table 6.1 is conversion of particulate, biodegradable organic nitrogen, X_{NS}, into soluble, biodegradable organic nitrogen, S_{NS}. This rate is assumed to be proportional to the rate of hydrolysis of slowly biodegradable organic matter, as is modeled with Eq. 3.78.

Two events discussed in Chapters 2 and 3 are not included in Table 6.1: (1) soluble microbial product formation, and (2) phosphorus uptake and release. The impact of soluble microbial product formation is minor, and acts primarily to raise the concentration of soluble organic matter in the effluent from a bioreactor, as discussed previously. It was excluded for the same reason it was excluded from the simple model in Chapter 5. Phosphorus uptake and release will occur only when anaerobic zones are included in systems to allow a selective advantage for phosphate accumulating organisms (PAOs), as discussed previously. As seen above, however, some of the rate expressions in Table 6.1 have questionable validity under anaerobic conditions. For this reason, and because a model for the growth of only PAOs requires a matrix larger than the one in Table 6.1,[11,19,33,36,37] this process was not included here. IAWQ ASM No. 2 utilizes an expanded matrix to incorporate phosphorus removal by PAOs.[19] We use it in Chapter 7 to see how reactor conditions affect phosphorus removal.

6.1.3 Representative Parameter Values

The model depicted in Table 6.1 contains a large number of kinetic and stoichiometric parameters which must be evaluated for use in simulations. Techniques for conducting those evaluations are discussed in Chapter 8. Although the model should be calibrated for each situation under study, it is acceptable to use typical parameter values to demonstrate fundamental principles concerning suspended growth cultures, provided the reader recognizes that the conclusions are general and not directly applicable to any specific situation. Typical parameter values for domestic sewage at neutral pH and 20°C were compiled for ASM No. 1.[17,18] Consideration of those values, as well as the values given in Chapter 3, has resulted in the list given in Table 6.3. They will be used here and in Chapter 7 to demonstrate several things about suspended growth cultures that could not be demonstrated with the simple model in Chapter 5.

6.1.4 ASM No. 2

Activated Sludge Model No. 2 incorporates all of the events included in ASM No. 1, plus biological phosphorus removal. The latter is very complex[11,33,36,37] and a large number of components must be included to model it adequately, as seen in Section 2.4.6 and Section 3.7. Consequently, ASM No. 2 is much larger than ASM No. 1

Table 6.3 Typical Parameter Values at Neutral pH and 20°C for Domestic Wastewater

Symbol	Units	Value
	Stoichiometric coefficients	
Y_H	mg biomass COD formed/mg COD removed	0.60
f'_D	mg debris COD/mg biomass COD	0.08
$i_{N/XB}$	mg N/mg COD in active biomass	0.086
$i_{N/XD}$	mg N/mg COD in biomass debris	0.06
Y_A	mg biomass COD formed/mg N oxidized	0.24
	Kinetic parameters	
$\hat{\mu}_H$	hr^{-1}	0.25
K_S	mg/L as COD	20
$K_{O,H}$	mg/L as O_2	0.10
K_{NO}	mg/L as N	0.20
$b_{L,H}$	hr^{-1}	0.017
η_g	dimensionless	0.8
η_h	dimensionless	0.4
k_a	L/(mg biomass COD · hr)	0.0067
k_h	mg COD/(mg biomass COD · hr)	0.092
K_X	mg COD/mg biomass COD	0.15
$\hat{\mu}_A$	hr^{-1}	0.032
K_{NH}	mg/L as N	1.0
$K_{O,A}$	mg/L as O_2	0.75
$b_{L,A}$	hr^{-1}	0.004

and considerably more complex, including 19 components and 19 process rate equations that require 22 stoichiometric coefficients and 42 kinetic parameters.[19] Because of its size, ASM No. 2 will not be described in detail herein. However, because we use it in Chapter 7, some of its major characteristics will be presented.[19]

Some processes that were explicitly modeled in ASM No. 1 were simplified in ASM No. 2 in order to minimize its size. For example, processes 6 and 8 in Table 6.1, ammonification of soluble organic nitrogen and hydrolysis of particulate organic nitrogen, were eliminated. Their functions were made implicit by assuming that they occurred in stoichiometric proportion to soluble substrate removal and hydrolysis of slowly biodegradable organic matter. This accomplished the same thing as ASM No. 1, but with fewer process rate expressions. Organic phosphorus conversion to soluble phosphate was handled in a similar manner.

The events occurring under anaerobic conditions are quite different in the two models. ASM No. 1 assumed that growth and hydrolysis stopped under anaerobic conditions, although microbial death and lysis continued. This was adequate for the processes ASM No. 1 depicts, but is entirely inadequate for biological phosphorus removal. Consequently, ASM No. 2 includes fermentation, uptake of acetate for formation of PHB and other polyhydroxyalkanoic acids (PHAs), and release of soluble phosphate from hydrolysis of polyphosphate. The inclusion of fermentation required the partitioning of readily biodegradable substrate into two components, readily fermentable substrate and fermentation products, represented by acetate. Ac-

etate is produced from readily fermentable substrate under anaerobic conditions and is taken up by the PAOs, as depicted by Eq. 3.82, forming PHB, as given by Eq. 3.83. Under anoxic conditions, i.e., when nitrate-N is present as an electron acceptor, fermentation decreases and the common heterotrophic biomass competes with the PAOs for acetate.

The scope of activities of the common heterotrophic bacteria was expanded. Under anaerobic conditions, they ferment readily fermentable substrate, producing acetate, but they cannot grow. They can only grow under aerobic and anoxic conditions, and can use both readily fermentable substrate and acetate for that purpose. Because heterotrophic growth cannot occur under anaerobic conditions, ASM No. 2 is not capable of modeling a totally anaerobic system. It can only mimic the performance of an anaerobic zone in a system with aerobic and anoxic zones.

Our knowledge of PAOs is still evolving. As a consequence, several simplifying assumptions were made in ASM No. 2 with respect to their growth. For example, they are assumed to grow only under aerobic conditions and can use only stored PHB as a growth substrate, as indicated in Eq. 3.85. They are assumed to be unable to use nitrate-N as an electron acceptor or to use any other electron donor, either stored in the cell or in the medium. These are reasonable assumptions, but exceptions to them are known to exist.[23,32] Thus, as we gain additional knowledge, it is very likely that ASM No. 2 will undergo revision. Nevertheless, even in its initial form it is a very powerful tool that allows engineers to explore the complex microbial events occurring in biological phosphorus removal systems.

6.1.5 Application of International Association on Water Quality Activated Sludge Models

Activated sludge models No. 1 and No. 2 are considerably more complex than the one used in Chapter 5 (Table 5.1). As a consequence, it is impossible to attain analytical solutions for the concentrations of the various constituents in a bioreactor, as was done in Chapter 5. Rather, matrix solutions and numerical techniques must be used, depending on the complexity of the system under study. Several organizations have developed computer codes for solving the simultaneous mass balance equations for the constituents in the models, allowing their application to a variety of bioreactor configurations. One such code is SSSP,[7] which was developed for implementation of ASM No. 1 on microcomputers. It is menu driven and may be used for both steady-state and dynamic simulations. It was used to perform the simulations for single CSTRs in this chapter and for multiple bioreactor systems in Chapter 7. Another is ASIM,[15] which implements both models, as well as several others. It was used for the some of the simulations in Chapter 7. Table 6.4 lists several computer codes that are available for using both IAWQ activated sludge models. In addition, Dold[10] has developed a code that extends ASM No. 1 to include phosphorus removal, but it differs somewhat from ASM No. 2.

6.2 EFFECT OF PARTICULATE SUBSTRATE

A major limitation of the model presented in Chapter 5 is that it does not consider the biodegradation of particulate organic material, which is an important class of

Table 6.4 Computer Codes Implementing IAWQ Activated Sludge Models

Code name	Features	Contact information
SSSP	Implements Model No. 1	C. P. Leslie Grady Jr., Environmental Systems Engineering, Rich Environmental Research Lab, Clemson University, Clemson, SC 29634-0919 USA
EFOR	Implements Model No. 1 plus a clarifier model	Jan Peterson, I. Kruger AS, Gladsaxevej 363, DK-2860 Soborg, Denmark
ASIM	A flexible modeling tool that implements both Model No. 1 and No. 2, as well as several others	Willi Gujer, EAWAG, Swiss Federal Institute for Environ. Science and Technology, CH-8600 Dübendorf, Switzerland
GPS-X	A general purpose simulator that implements both Model No. 1 and No. 2 plus other unit operations	Hydromantis, Inc., 1685 Main St. West, Suite 302, Hamilton, Ontario L8S 1G5 Canada
SBRSIM	Implements Model No. 1 for a sequencing batch reactor	Jürgen Oles, Technical University Hamburg-Harburg, Eissendorfer Strasse 42, 2100 Hamburg 90, Germany

organic substrate in many wastewaters. Thus a suitable application of the model in Table 6.1 would be to see how the nature of the substrate influences the performance of a single CSTR, such as that depicted in Figure 5.1. To do this, two situations were considered, one in which all influent organic matter was soluble, and the other in which it was all particulate. The total concentration was the same in both cases, 500 mg/L as COD, as was the flow rate, 1000 m^3/day (1.0 m^3 = 1000 L), giving a total COD mass input rate of 500 kg/day. The solids retention time (SRT)/hydraulic residence time (HRT) ratio was held constant at 20 while the SRT was varied. In other words, the reactor volume was increased in proportion to the increase in SRT. This was done to make it easier to visualize the fate of particulate material, as well as the relative importance of growth and decay as SRT is changed. When the SRT/HRT ratio is held constant, if particulate material does not undergo reaction it has a constant concentration in the system, regardless of the SRT. Furthermore, as growth occurs on particulate substrate, the concentration of suspended matter (particulate substrate plus biomass) will decrease because the yield is less than one. In addition, growth associated with increased soluble substrate removal in the bioreactor is reflected by an increase in biomass concentration, whereas an increase in the importance of decay is reflected by a decrease. The biomass separator was assumed to be perfect so that it removed all undegraded particulate substrate from the effluent and returned it to the bioreactor. Thus, undegraded particulate substrate was removed only through the wastage flow. The parameter values used to describe the reactions are those given in Table 6.3, with the exception of $\hat{\mu}_A$, the maximum specific growth rate for autotrophic bacteria, which was set equal to zero to eliminate them from

Table 6.5 Process Kinetics and Stoichiometry Adopted for Considering the Impact of Particulate Substrate on the Performance of an Aerobic CSTR. Lysis:Regrowth Model for Biomass Loss

	Component[a]					
Process	X_S	$X_{B,H}$	X_D	S_S	S_O[b]	Process rate, r_j
Growth		1		$-\frac{1}{Y_H}$	$\left(\frac{1-Y_H}{Y_H}\right)$	$\hat{\mu}_H \left(\frac{S_S}{K_S + S_S}\right)\left(\frac{S_O}{K_{O,H} + S_O}\right) K_{B,H}$
Death and lysis	$(1 - f'_D)$	-1	f'_D			$b_{L,H} \cdot X_{B,H}$
Hydrolysis	-1			1		$k_h \left(\frac{X_S/X_{B,H}}{K_X + (X_S/X_{B,H})}\right)\left(\frac{S_O}{K_{O,H} + S_O}\right) X_{B,H}$

[a]All components and coefficients are expressed as COD.
[b]Coefficient must be multiplied by -1 to express as oxygen.

consideration and limit the reactions to those associated with heterotrophs, as was done in Chapter 5. The influent contained sufficient ammonia-N for heterotrophic growth, but no nitrate-N, thereby eliminating nitrate-N, or reactions associated with it, from consideration as well. These selections simplified the model to include only processes 1, 4, and 7 and components 2, 3, 5, 7, and 8, as shown in Table 6.5. Finally, the dissolved oxygen concentration was held constant at 4.0 mg/L, which together with the $K_{O,H}$ value in Table 6.3, made the oxygen term in the rate expressions approach 1.0.

6.2.1 Steady-State Performance

Figure 6.1 shows the effect of SRT on the mixed liquor suspended solids (MLSS) concentration, the active fraction, and the oxygen requirement for bioreactors receiving the two types of substrate at a constant flow and concentration. The MLSS in the bioreactor receiving soluble substrate is composed of heterotrophic biomass and biomass debris, whereas the MLSS in the bioreactor receiving particulate substrate contains heterotrophic biomass, biomass debris, and unreacted particulate substrate, with the relative quantities depending on the SRT. The curves for the soluble feed are similar to those in Chapter 5 and can serve as a reference point with which to see the effect of particulate feed. The most obvious effect is that a longer SRT is required to get biomass growth on particulate substrate. As indicated by the oxygen requirement, washout occurs at an SRT of about 4.5 hr when the substrate is soluble, but at an SRT of about 26 hr when it is particulate. This reflects the fact that hydrolysis reactions are slow. At SRTs below 26 hr, nothing happens to the particulate substrate and it acts like inert material, giving a MLSS concentration equal to the influent concentration times the SRT/HRT ratio ($500 \times 20 = 10{,}000$) and an active fraction of zero, i.e., the MLSS is composed entirely of unreacted particulate substrate. As the SRT is increased past 26 hr, degradation of the particulate substrate begins, causing the MLSS concentration to drop and the active fraction and oxygen utilization to increase. In this region, the MLSS is composed of unreacted particulate substrate, active heterotrophic biomass, and some biomass debris. Eventually, at longer SRTs, bioreactor performance becomes independent of the feed type and is essentially the same for each. This occurs when both substrates are almost completely degraded so that system performance is governed primarily by biomass death and lysis, and the MLSS in each bioreactor is composed primarily of heterotrophic biomass and biomass debris.

Two significant points arise from Figure 6.1. The first is that long SRTs are required to achieve substantial degradation of particulate substrates. The second is that use of the process loading factor with a particulate substrate can be confusing. It will be recalled from Eq. 5.39 that the active fraction must be known before the process loading factor can be related to the specific growth rate of the biomass. Figure 6.1b, however, shows that the active fraction varies in a complex manner as the SRT is changed when the substrate is particulate. This is because the active fraction is the active biomass concentration divided by the MLSS concentration, which includes the undegraded particulate substrate. The SRT, on the other hand, is still related to the biomass specific growth rate by Eq. 5.12, and thus is more descriptive of process performance. Because most wastewaters contain some particulate

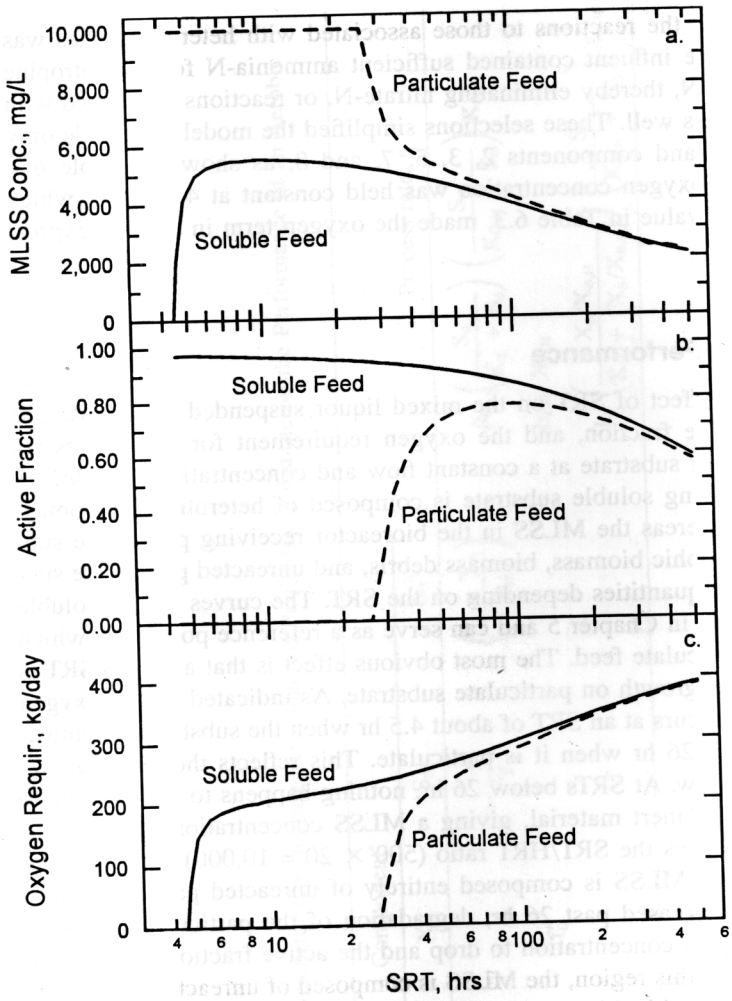

Figure 6.1 Effect of the nature of the organic matter in the feed on the performance of a CSTR with $\Theta_c/\tau = 20$. Influent biodegradable COD = 500 mg/L in each case. Flow = 1000 m^3/day. Particulate substrate was assumed to be removed by the biomass separator and retained in the reactor. Parameter values are listed in Table 6.3. $\hat{\mu}_A$ was set equal to zero.

substrate, SRT is preferable to process loading factor as a basic design and operational parameter for suspended growth bioreactors.

6.2.2 Dynamic Performance

So far we have only considered the steady-state performance of a CSTR, i.e., the performance that results when a bioreactor receives a constant influent flow at a constant concentration. Most wastewaters are subject to time dependent variability, however, and thus it would be beneficial to investigate the impact of the nature of the substrate under those conditions.

Because of variations in human activities, municipal wastewater treatment systems experience diurnal variations in the flow and concentration of the wastewater entering them. Figure 6.2 shows typical variations experienced over a 24 hr period, beginning at midnight as time 0. The patterns correspond to those observed at a large municipal plant in South Africa over a period of one week,[13] but the values have been normalized to a daily average flow of 100 m^3/day and a flow-weighted average concentration of 100 mg/L. The patterns are also typical of those experienced in the United States,[9] and will be adopted herein for demonstration purposes. As with kinetic and stoichiometric parameters, however, the necessity for determining the actual variations associated with a given wastewater cannot be overemphasized.

To determine the effect of the type of substrate on the dynamic response of a CSTR, the bioreactor in Figure 5.1 was subjected to the variations in flow and concentration shown in Figure 6.2. The flow values were adjusted to give a daily average flow of 1000 m^3/day and the biodegradable COD was adjusted to give a flow-weighted daily average concentration of 265 mg/L, a value commonly seen in United States domestic wastewater.[25] The SRT was set at 240 hr, a value sufficient to make the steady-state performance for the two substrate types essentially the same, as shown in Figure 6.1, while the HRT based on the daily average flow rate was set at 6 hr. As with the steady-state response, two situations were considered, one in which the organic matter was entirely soluble and one in which it was entirely particulate. All other constituents were assumed to be constant at concentrations sufficient to not limit the reactions. As before, the matrix in Table 6.5 described the system.

The response of the bioreactor is shown in Figure 6.3. Before considering the effect of the type of substrate on the bioreactor performance, we will examine only the soluble substrate case in order to understand why the bioreactor behaves as it does. Examination of the figure shows that the soluble substrate concentration has

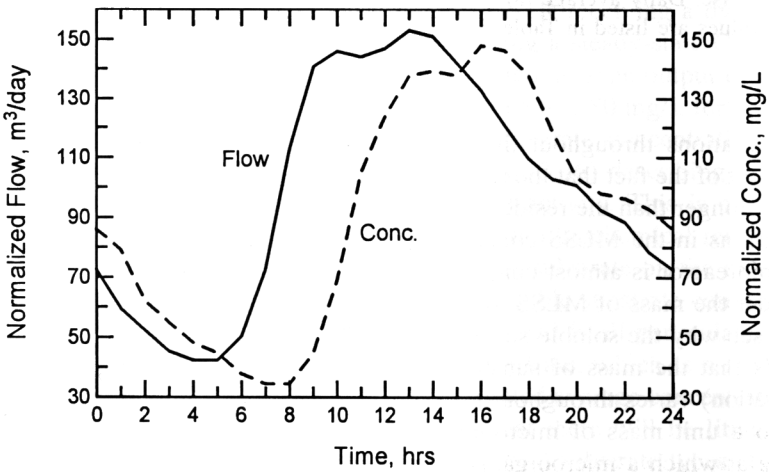

Figure 6.2 Typical diurnal patterns of wastewater flow and concentration for a community with little night time activity (after Dold and Marais[12]). The flow has been normalized to an average of 100 m^3/day. The concentration has been normalized to give a flow weighted average of 100 mg/L.

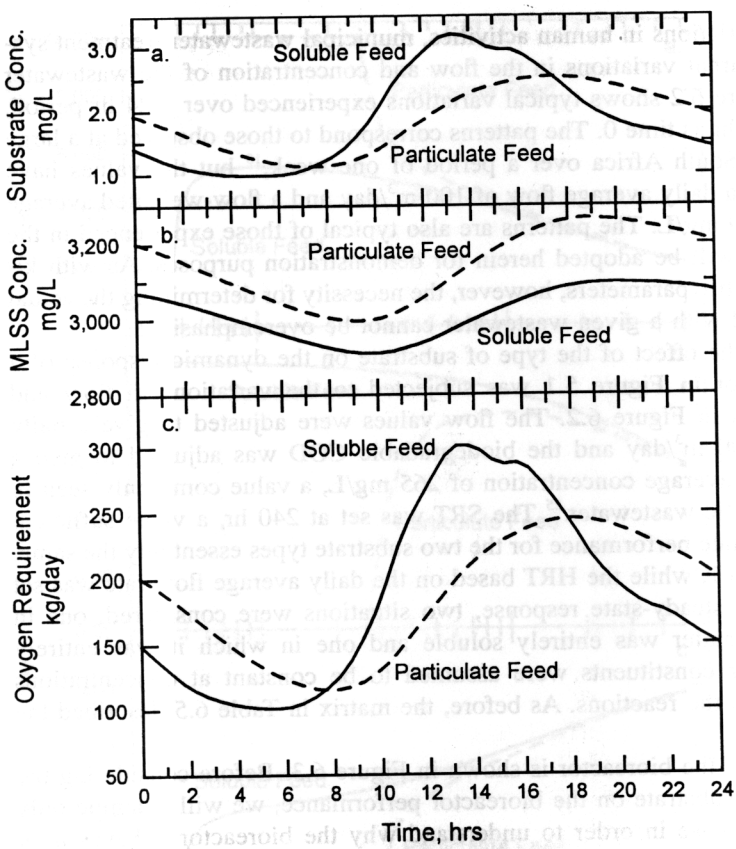

Figure 6.3 Effect of the nature of the organic matter in the feed on the response of a CSTR to the diurnal flow pattern in Figure 6.2. Flow weighted average influent biodegradable COD = 265 mg/L in each case. Daily average flow = 1000 m^3/day; SRT = 240 hrs; average HRT = 6 hrs. Parameter values are listed in Table 6.3. $\hat{\mu}_A$ was set equal to zero.

greater relative variations throughout the day than does the MLSS concentration. This is a direct result of the fact that the residence time of the MLSS in the bioreactor (the SRT) is much longer than the residence time of the soluble substrate (the HRT). As a result, variations in the MLSS concentration are dampened. In fact, the mass of MLSS in the bioreactor is almost constant throughout the day.

If we consider the mass of MLSS to be approximately constant throughout the day, we can then see why the soluble substrate concentration varies. Examination of Figure 6.2 reveals that the mass of substrate entering the bioreactor per unit time (flow × concentration) varies throughout the day. This means that the mass of substrate available to a unit mass of microorganisms also varies throughout the day. However, the rate at which a microorganism can remove substrate is controlled by the concentration of substrate surrounding it. Thus, as the mass flow rate of substrate into the bioreactor increases, the substrate concentration must rise to allow the microorganisms to remove substrate faster. Conversely, as the mass flow rate of substrate decreases, the microorganisms will drive the substrate concentration lower until

the rate of substrate removal is decreased to be consistent with the rate of input. Thus, the variation in substrate concentration is a direct consequence of the necessity for the microorganisms to vary their activity in response to the changing input rate of substrate. The variation in the oxygen requirement directly reflects that variation in activity.

The soluble substrate curves in Figure 6.3a also demonstrate an important point about the growth characteristics of the biomass in a CSTR receiving a time varying input; the specific growth rate is not constant over time. It will be recalled that the specific growth rate is controlled by the soluble substrate concentration, as expressed by the Monod equation (Eq. 3.36). Since the soluble substrate concentration is varying over time, so is the specific growth rate. This means that the bacteria are in a continually changing state. For the reactor configuration in Figure 5.1, the SRT is determined solely by the reactor volume and the wastage flow rate. Consequently, the SRT can be held constant, even though the specific growth rate of the bacteria is varying. In other words, the specific growth rate of the microorganisms in a CSTR that is not at steady-state is not fixed by the SRT. This can also be seen by performing a mass balance on heterotrophic biomass in the reactor. Such an exercise using the kinetics and stoichiometry in Table 6.5 reveals:

$$\mu_H = \frac{1}{\Theta_C} + b_{L,H} + \frac{1}{X_{B,H}} \frac{dX_{B,H}}{dt} \tag{6.1}$$

Since the heterotrophic biomass concentration varies over time in response to the changing input, so will the specific growth rate. It is important to recognize that the constant relationship between SRT and specific growth rate depicted in Eq. 5.12 is only valid for steady-state conditions.

Even though the specific growth rate is not determined solely by the SRT for a non–steady-state CSTR, the SRT is still a good indicator of average performance, with longer SRTs giving lower average substrate concentrations. Nevertheless, the average substrate concentration leaving a CSTR receiving a dynamic input will always be greater than the concentration leaving a steady-state CSTR. For the conditions imposed in Figure 6.3, the flow-weighted average output concentration for the soluble substrate case in 2.11 mg/L as opposed to 1.80 mg/L for a steady-state CSTR with the same SRT. The higher average substrate concentration results from the nonlinear nature of the Monod equation (Eq. 3.36) describing the relationship between substrate concentration and microbial activity. This is one reason why it is advantageous to practice equalization prior to a biochemical reactor.

Now consider the impact of the type of substrate on the dynamic behavior of the CSTR. Figure 6.3a shows the effluent soluble substrate concentrations resulting from the two feed types. When the influent feed is all particulate, soluble substrate arises from hydrolysis of the particulate substrate, which is a slow reaction. Thus, the response is dampened and the flow-weighted average concentration is lower (1.92 mg/L vs. 2.11 mg/L). Figure 6.3b shows that there will be little difference in the MLSS concentration or its variation for the two substrate types. The slightly higher concentration in the bioreactor receiving particulate substrate is because of a slight build up of that substrate in the system caused by the slow hydrolysis reactions, but the effect is small. Generally, one would not expect to be able to distinguish much difference in the amount of MLSS in the two systems.

The major impact of particulate substrate on the dynamic response of a CSTR is in the utilization of oxygen, as shown in Figure 6.3c. As might be expected from the previous discussion of the slow nature of hydrolysis, the impact of the presence of particulate substrate is to dampen the system response, thereby reducing the peak oxygen requirement. In addition, the need for hydrolysis to make substrate available causes a time lag in the occurrence of the maximum and minimum oxygen consumption rates. Examination of Figure 6.2 reveals that the minimum mass input rate occurs at about 6 hr and the maximum at about 13 hr, which correspond closely to the times of the minimum and maximum oxygen requirements in the bioreactor receiving soluble substrate, thereby demonstrating the rapidity with which biomass can respond to soluble substrate. In contrast, the need for hydrolysis of particulate substrate, in combination with the fact that its concentration does not vary rapidly because its residence time in the system is the SRT, delays the minimum response by about 3 hr and the maximum by about 5 hr. Since both systems use about the same amount of oxygen in a 24 hr period, this suggests that consideration must be given to the physical state of the substrate during design of the oxygen transfer system for a suspended growth bioreactor.

6.3 NITRIFICATION AND ITS IMPACTS

We see in Section 3.2.7 that the kinetics of growth of autotrophic nitrifying bacteria can be represented in the same manner as that of heterotrophic bacteria. Consequently, the general conclusions derived in Chapter 5 about biomass growth in CSTRs are equally applicable to them. We also see in Section 3.2.10 that the values of their kinetic coefficients are quite different from those for heterotrophs. This means that the specifics of their behavior in a given reactor environment will differ somewhat from that of the heterotrophs. In this section, we will investigate some of the characteristics of nitrifying bacteria that require special recognition and see how autotrophic and heterotrophic bacteria might influence one another when grown in the same bioreactor.

6.3.1 Special Characteristics of Nitrifying Bacteria

Comparison of the typical $\hat{\mu}$ values for heterotrophic and autotrophic bacteria in Table 6.3 shows that the value for autotrophs is almost an order of magnitude lower than that for heterotrophs, suggesting that the minimum SRT for nitrifying bacteria is almost an order of magnitude larger. As a consequence, they can be lost from bioreactors under conditions that allow heterotrophic bacteria to grow freely. This situation is aggravated by the fact that nitrifying bacteria are more sensitive to low temperatures and low dissolved oxygen concentrations, as will be discussed later in this section. Therefore, special consideration must be given to the choice of the SRT in systems containing autotrophic bacteria and it cannot be assumed that conditions suitable for the removal of soluble organic matter are suitable for the conversion of ammonia-N to nitrate-N.

Another characteristic of nitrifying bacteria is that their half-saturation coefficient is very low; the typical value given in Table 6.3 is 1.0 mg/L as N. It will be recalled that the half-saturation coefficient is the substrate concentration allowing

bacteria to grow at half of their maximal rate. This means that CSTRs containing autotrophic bacteria will have low ammonia-N concentrations even when the bacteria are growing relatively fast and that very low concentrations will result whenever the SRT is large enough to ensure stable growth. It also means that the ammonia-N concentration will rise rapidly as the SRT is decreased to the point of washout. As a consequence, nitrification has gained the reputation of being an all-or-none phenomenon. In other words, since the nitrogen concentration entering municipal wastewater treatment systems is on the order of 30 to 40 mg/L, the percent nitrification approaches 100 whenever the SRT is long enough to give stable growth and rapidly falls to zero as washout occurs. This is illustrated in Figure 6.4,[27] which includes data from the literature as well as the results of steady-state simulations with a model similar to the one employed herein.

There are some occasions in which the all-or-none phenomenon will not occur or will not be as drastic as that shown in Figure 6.4. One is when the bioreactor is subjected to diurnal loading, like that shown in Figure 6.2. It will be recalled from Section 6.2.2 that the flow-weighted average effluent substrate concentration from a CSTR receiving a diurnal input is not as low as the concentration from the same reactor receiving a constant input. The degree of difference between the two responses depends on the bioreactor SRT, as shown in Figure 6.5,[27] which was prepared by simulation with a model similar to the one presented herein. It also shows that complete nitrification can still be achieved in a CSTR receiving a diurnal input, but that longer SRTs are required. Another situation that can lead to incomplete nitrification is when the influent contains such a high ammonia-N concentration that both substrate and product inhibition can occur.[2,29] In that case the attainment of complete nitrification requires the use of multireactor systems in which denitrification can be used to reduce the product concentration, i.e., nitrite and nitrate. As pointed out earlier, substrate and product inhibition effects cannot yet be reliably modeled. Con-

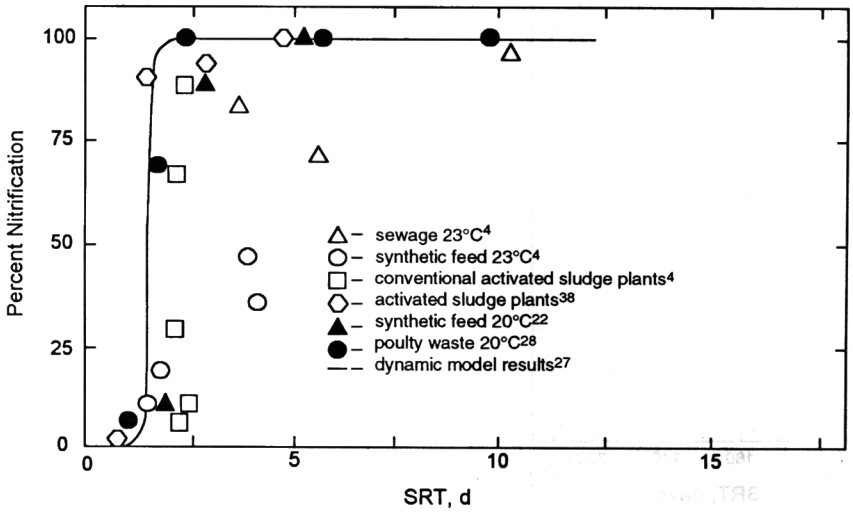

Figure 6.4 Effect of SRT on the steady state nitrification performance of a CSTR. The reference numbers refer to the sources of the data. (Adapted from Poduska and Andrews.[27])

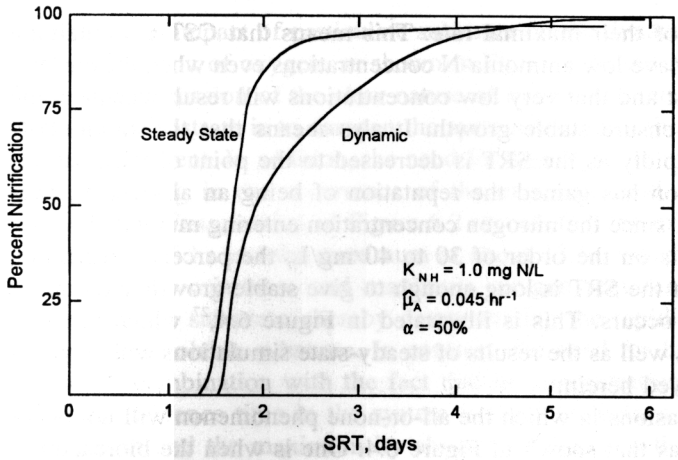

Figure 6.5 Comparison of steady state and dynamic performance of nitrification in a CSTR. (Adapted from Poduska and Andrews.[27])

sequently, pilot studies should always be run on wastes containing ammonia-N concentrations substantially higher than those found in domestic wastewater. A final circumstance in which a curve of a different shape may be obtained is when the wastewater contains chemicals inhibitory to the autotrophic bacteria. Such a curve is shown in Figure 6.6.[8] Inhibitory compounds can reduce $\hat{\mu}_A$ and increase K_{NH}, both of which reduce the percent nitrification achieved at a given SRT, making the curve

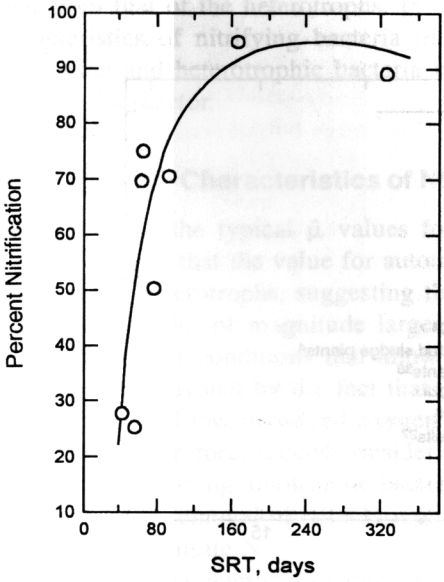

Figure 6.6 Effect of SRT on the performance of nitrification in a CSTR receiving a wastewater containing inhibitory compounds. (Adapted from Bridle et al.[8])

approach 100% more gradually. Both effects are illustrated in Figure 6.6, which was obtained with an industrial waste.[8]

Another important characteristic of nitrifying bacteria is their extreme sensitivity to the dissolved oxygen concentration, which necessitated the inclusion of a term for oxygen in the rate expression in Table 6.1. Examination of the values of K_O for autotrophs and heterotrophs in Table 6.3 shows that $K_{O,A}$ is much larger than $K_{O,H}$. This means that as the dissolved oxygen concentration is decreased, the term $S_O/(K_O + S_O)$ in the rate expression for autotrophs will become small more rapidly than the corresponding term in the rate expression for heterotrophs. Consequently, autotrophs will be affected by decreases in the oxygen concentration much more drastically than will heterotrophs. The importance of dissolved oxygen concentration to the growth of autotrophs is illustrated in Figure 6.7 where the minimum SRT required for their growth is plotted as a function of the oxygen concentration. The curve was generated with Eq. 5.16, with adjustment of $\hat{\mu}_A$ for the effects of oxygen as given by the rate expression in Table 6.1. The parameter values from Table 6.3 were used, as indicated in the figure. Examination of the figure shows that oxygen concentrations above 2.0 mg/L have little effect on the minimum SRT, and it is seldom necessary to maintain the concentration in excess of that value to get satisfactory nitrification. However, oxygen concentrations below 2.0 mg/L begin to have a strong effect and those below 0.5 mg/L have a drastic effect. A low dissolved oxygen concentration also diminishes the percent nitrification that can ultimately be achieved. Consequently, care in the specification of the oxygen transfer system is an important component of the design of a suspended growth bioreactor in which nitrification is to occur.

Nitrifying bacteria are also very sensitive to temperature, as reflected by the temperature coefficients in Section 3.9.2. Because $\hat{\mu}_A$ is small even at 20°C, low temperatures require bioreactors to have very long SRTs in order for nitrifying bacteria to grow. This is illustrated in Figure 6.8 which was generated with Eq. 5.16

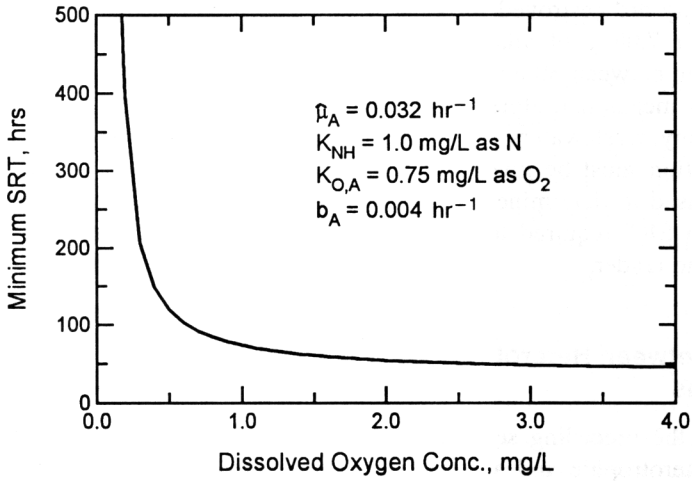

Figure 6.7 Effect of dissolved oxygen concentration on the minimum SRT required for nitrification in a CSTR receiving an ammonia-N concentration of 30 mg/L. Parameter values are for a temperature of 20°C.

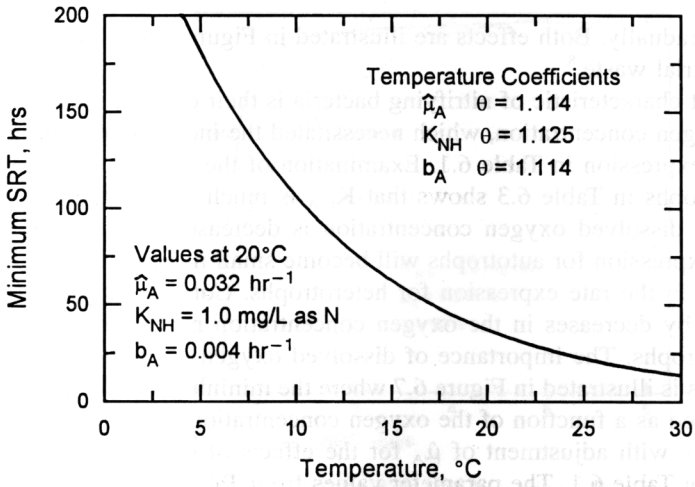

Figure 6.8 Effect of temperature on the minimum SRT required for nitrification in a CSTR receiving an ammonia-N concentration of 30 mg/L. The dissolved oxygen concentration is not limiting.

using kinetic parameters corrected for temperature with Eq. 3.95 and the coefficients shown in the figure. The dissolved oxygen concentration was assumed to be high enough to have no effect. Examination of the figure reveals that very large increases in the SRT are required to compensate for drops in temperature. This suggests that the choice of SRT for a nitrifying bioreactor must be made for the lowest temperature expected.

The model in Table 6.1 includes alkalinity as a component because of the sensitivity of nitrifying bacteria to low pH and the effect that the oxidation of ammonia-N has on alkalinity, and hence on pH. Equations 3.28 and 3.29 showed that 8.64 g of HCO_3^- alkalinity are destroyed for each g of nitrogen oxidized from ammonia-N to nitrate-N, or 7.08 g of alkalinity (as $CaCO_3$) per g of N. Domestic wastewaters often contain between 30 and 40 mg/L of nitrogen that can be oxidized during nitrification. This means that almost 300 mg/L of alkalinity (as $CaCO_3$) can be destroyed. Since many wastewaters do not contain this much alkalinity, it is apparent why consideration must be given to pH control in nitrifying bioreactors. Equation 3.50 may be used to determine the effect of pH on $\hat{\mu}_A$, with its resulting impact on the minimum SRT required to achieve nitrification. Such an activity is left as an exercise for the reader.

6.3.2 Interactions Between Heterotrophs and Autotrophs

From the discussion of the preceding section, it is apparent that there are several interactions between heterotrophic and autotrophic bacteria growing together in a CSTR. The most important concerns the dissolved oxygen concentration, which is why it is explicitly included in the model in Table 6.1. Because heterotrophic bacteria have larger $\hat{\mu}$ and smaller K_O values than autotrophs, they are capable of surviving

in bioreactors with SRTs and oxygen concentrations that would cause autotrophic bacteria to wash out. In other words, the heterotrophs control the dissolved oxygen concentration if the supply rate is insufficient to meet the needs of both groups. As a result, organic substrate removal can occur unimpeded under conditions that will not allow nitrification. Looked at another way, it is possible for a designer to choose an SRT and dissolved oxygen concentration that will allow only organic substrate removal or a combination that will allow both nitrification and organic substrate removal, but it is impossible to choose conditions that will allow nitrification without oxidation of any organic matter present. Since the designer can choose the conditions to be imposed on the bioreactor, he/she has control over the events that will occur in it, consistent with the kinetic characteristics of the organisms involved.

Simultaneous growth of heterotrophic and autotrophic bacteria need not be detrimental to the nitrifiers; it can be beneficial. As discussed previously, nitrifying bacteria are sensitive to inhibition by some organic compounds. If those compounds are biodegradable, it is possible to choose the SRT so that their concentrations in the bioreactor are too low to inhibit the nitrifiers, thereby allowing them to grow along with the heterotrophs destroying the inhibitors.[21] It is not necessary to perform nitrification in a separate bioreactor following destruction of the organic matter.

As stated before, domestic wastewater in the United States often contains about 265 mg/L of biodegradable COD and around 40 mg/L of reduced nitrogen.[25] Comparison of the Y_H and Y_A values in Table 6.3 in light of these concentrations reveals that the amount of autotrophic biomass formed in a bioreactor receiving such a feed will be small relative to the amount of heterotrophic biomass formed. Furthermore, when consideration is given to the fact that the MLSS in a suspended growth bioreactor contains inert particulate organic matter as well as biomass debris, it is likely that the contribution of the autotrophic bacteria to the MLSS concentration will be very small. That this is indeed the case is illustrated in Figure 6.9a. The curves in this figure were generated with the model in Table 6.1 using as input a feed with the characteristics listed in Table 6.6, which are considered to be representative of a domestic wastewater in the United States following primary sedimentation.[7] The curve without nitrification was obtained by setting $\hat{\mu}_A$ equal to zero during the simulation.

Unlike their effect on the MLSS concentration, however, nitrifying bacteria have a major impact on the amount of oxygen required in a CSTR receiving a feed like domestic wastewater. This can be seen by considering the stoichiometry of microbial growth as reflected by the coefficients in Table 6.1. For the true growth yields in Table 6.3, the oxygen utilization associated with heterotrophic growth (exclusive of biomass death and lysis) is $1 - 0.60$, or 0.40 g O_2/g COD removed, whereas that associated with autotrophic growth is $4.57 - 0.24$, or 4.33 g O_2/g N oxidized. Death and lysis makes the utilization greater for the heterotrophs, perhaps around 0.65 g O_2/g COD removed for a typical SRT, but have little impact on the autotrophic oxygen utilization because the value of the true growth yield (0.24) is small relative to 4.57. Given the concentrations of the two substrates in the influent, these values suggest that the autotrophs require around 173 g of oxygen (40×4.33) for each liter of influent whereas the heterotrophs require around 172 g (265×0.65). Thus, even though the concentration of reduced nitrogen entering the bioreactor is much less than the concentration of biodegradable COD entering, the large change in oxidation state of nitrogen associated with the production of nitrate, in combina-

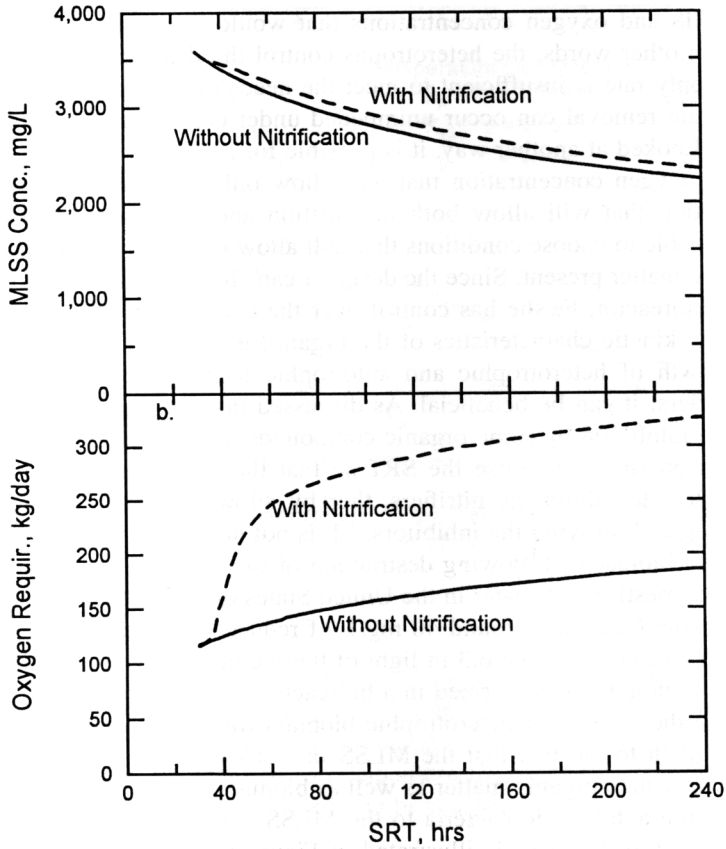

Figure 6.9 Effects of SRT and nitrification on the MLSS concentration and oxygen requirement in a CSTR with $\Theta_c/\tau = 20$. Parameter values are given in Table 6.3 and the influent conditions are given in Table 6.6. The value of $\hat{\mu}_A$ was set equal to zero to eliminate nitrification in one case. The dissolved oxygen concentration was fixed at 4.0 mg/L.

Table 6.6 Characteristics Considered to Be Representative of a United States Domestic Wastewater Following Primary Sedimentation[7]

Component	Concentration
Inert particulate organic matter	35.0 mg/L as COD
Slowly biodegradable substrate	150.0 mg/L as COD
Readily biodegradable substrate	115.0 mg/L as COD
Oxygen	0.0 mg/L as O_2
Soluble nitrate nitrogen	0.0 mg/L as N
Soluble ammonia nitrogen	25.0 mg/L as N
Soluble biodegradable organic nitrogen	6.5 mg/L as N
Particulate biodegradable organic nitrogen	8.5 mg/L as N
Alkalinity	5.0 mM/L

tion with the differences in biomass yield, means that similar amounts of oxygen are required by the two groups of microbes. This can be seen clearly in Figure 6.9b. Failure to consider this effect during bioreactor design will lead to an inability to transfer sufficient oxygen, with resulting impairment of nitrification performance, as discussed previously.

Because of the important effect of nitrification on the oxygen requirement in a bioreactor, there are circumstances in which it would be advantageous to be able to calculate it explicitly. This can be done by using the simple model in Chapter 5 with minor modification. For the simple decay model, an equation analogous to Eq. 5.33 can be used by recognizing that the factor 1.0 must be replaced with 4.57, as discussed in Section 6.1.1:

$$RO_A = F(S_{NHO} - S_{NH}) \left[4.57 - \frac{(1 + f_D \cdot b_A \cdot \Theta_c) Y_A}{1 + b_A \cdot \Theta_c} \right] \tag{6.2}$$

where S_{NHO} represents the ammonia-N concentration in the feed that is available to the nitrifiers, i.e., the amount remaining after consideration of the amount used by the heterotrophs for biomass synthesis.

6.3.3 Effects of Nitrification in Bioreactors Receiving Only Biomass

In Section 5.4.2 and Figure 5.10, we investigate the performance of a CSTR receiving only biomass in the feed. Because the model in Chapter 5 considered only the growth of heterotrophic biomass, the discussion was limited to the fate of only heterotrophic bacteria under such circumstances. However, if the SRT of the bioreactor is sufficiently long, autotrophic bacteria will also grow, with an important impact on system performance. As expected from the preceding discussion, the major impacts of autotrophs on a bioreactor receiving only biomass in its feed are on the oxygen requirement and the pH. If f_D is 0.20, the destruction of 100 g of biomass COD will lead to the release of 20 g of biomass debris COD and the consumption of 80 g of oxygen. As reflected by $i_{N/XB}$ and $i_{N/XD}$, the nitrogen contents of biomass and biomass debris are around 0.086 and 0.06 g N/g biomass COD, respectively. Consequently, destruction of 100 g of biomass will also lead to the release of 7.4 g of ammonia-N (100[0.086–(0.20·0.06)]), which can act as substrate for autotrophic bacteria. If the oxygen requirement associated with oxidation of the ammonia-N is 4.33 g O_2/g N, growth of the autotrophs will increase the reactor's oxygen requirement by 40%. This can have a substantial impact on the amount of oxygen that must be supplied. Furthermore, oxidation of the nitrogen released by destruction of the biomass will result in the destruction of 52.4 g of alkalinity (as $CaCO_3$) for each 100 g of biomass COD destroyed. Since it is not unusual for the feedstream entering such a reactor to contain 4000 mg/L of biomass COD and for 50% of it to be destroyed, one can see that the occurrence of nitrification in the reactor will destroy substantial quantities of alkalinity. Consequently, it is often necessary to control pH in such systems. Failure to do so will create an unstable environment in which the pH oscillates, thereby hindering system performance.

6.4 DENITRIFICATION AND ITS IMPACTS

In the context of biochemical operations, anoxic growth of heterotrophic bacteria is simply an alternative mode of growth in response to the absence of oxygen and the presence of nitrate-N as the terminal electron acceptor. Because the resulting reduction of nitrate-N to N_2 removes nitrogen from the wastewater undergoing treatment, the process is also referred to as denitrification. Generally, it occurs when the appropriate conditions are purposely established in bioreactors, but as the rate expression in Table 6.1 suggests, it will occur any time the oxygen concentration is low, the nitrate concentration is high, and organic matter is present as an electron donor. This means that the potential for its occurrence exists in all biochemical reactors. It should be included as a possible reaction in any complete system model.

6.4.1 Characteristics of Denitrification

In Section 2.4.1, we see that four enzymes are involved in the reduction of nitrate-N to N_2: nitrate reductase, nitrite reductase, nitric oxide reductase, and nitrous oxide reductase. Nevertheless, just as nitrification was treated as a single step process in ASM No. 1, so is denitrification. This simplification will not seriously restrict the results of simulations and is necessary because insufficient information is available about the factors influencing each of the individual reaction rates to allow all of them to be included in a system model, although preliminary attempts have been made to model them in simple systems.[6] One modification of ASM No. 1 allows for direct use of nitrite during denitrification,[33] but the rate is not linked to the nitrite concentration, which could lead to erroneous results.

Denitrification is usually practiced to remove nitrogen from a wastewater, but that is not the only reason for including it in a treatment system.[13] In the previous section we saw that the inclusion of nitrification in a biochemical reactor requires that substantial amounts of oxygen be supplied. The electron accepting potential of that oxygen is not entirely lost, however, because much of it still resides in the nitrate produced. For example, 4.57 g O_2 are needed to convert a g of ammonia-N to nitrate-N through nitrification, but each g of nitrate-N has the electron accepting capacity of 2.86 g O_2 as shown in Table 3.1. Thus, if there were ways to use that electron accepting capacity in the oxidation of some of the organic matter in the wastewater, almost 63% of the energy expended in converting the ammonia-N to nitrate-N could be recovered. The development of treatment systems in which this can be done has been a major focus of environmental engineering during the past decade. We also see in the previous section that nitrification results in the destruction of substantial quantities of alkalinity, 7.08 g (as $CaCO_3$) per g of ammonia-N oxidized. Denitrification, on the other hand, destroys hydrogen ions and produces carbon dioxide, as shown in Eq. 3.22. This has the net effect of increasing alkalinity. As can be seen from the stoichiometric coefficient for alkalinity production in Table 6.1, approximately $(1-Y_H)/14$ moles of alkalinity will be produced for each gram of nitrate-N reduced to N_2. For a typical Y_H value, this amounts to approximately 3.5 g of alkalinity (as $CaCO_3$) per g of nitrate-N. Thus, about half of the alkalinity lost through the oxidation of ammonia-N to nitrate-N can be recovered during the subsequent reduction of nitrate-N to N_2. Through appropriate configuration or operation

of the bioreactor it is possible to make use of this to reduce the amount of chemical that must be purchased for pH control.[13] We will see later how this can be done.

6.4.2 Factors Affecting Denitrification

Even though denitrification is usually practiced as part of a treatment system within which the nitrate is formed by nitrification, it is easier to understand the unique characteristics of denitrification if it is considered in isolation. Such a consideration is not artificial because some industrial wastewaters contain high concentrations of nitrate and biological treatment is one option open to the engineer for its removal. In this section we will consider the growth of biomass in a CSTR receiving an influent containing nitrate. We will assume that the influent also contains sufficient ammonia-N to meet the biosynthetic needs of the biomass so that the only role of the nitrate-N is as the terminal electron acceptor. This means that the stoichiometry depicted in Table 6.1 is applicable.

Comparison of process 1 in Table 6.1, aerobic growth of heterotrophs, with process 2, anoxic growth of heterotrophs, reveals that the COD-based stoichiometry is the same. This was also seen in Chapter 3 when Eq. 3.24 was compared to Eq. 3.8. Thus, for the utilization of a given amount of organic matter in a CSTR, the amount of electron acceptor used (on a COD basis) will be the same for both growth conditions. This suggests that the oxygen requirement curves that we have looked at in preceding sections can also be expressed as nitrate-N requirement curves, as long as the nitrate-N is expressed on a COD or O_2 equivalent basis through use of the factor 2.86 g O_2/g N (or −2.86 g COD/g N) as shown in Table 3.1. This, in turn, tells us that the amount of nitrate-N that will be removed by growth on a given amount of influent substrate will depend on the SRT of the bioreactor. The longer the SRT, the greater the fraction of the electrons in the substrate that will go to the acceptor, and the greater the amount of nitrate-N that will be reduced. Thus, one factor affecting the removal of nitrate-N through denitrification is the SRT of the reactor in which the biomass is growing.

When considering denitrification it is necessary to reverse your thinking. During aerobic growth of heterotrophs, the goal is removal of the organic substrate and the electron acceptor is supplied in excess. However, during anoxic growth of heterotrophs, the goal is the removal of the electron acceptor, and sufficient organic substrate, i.e., electron donor, must be supplied to accomplish this. Consequently, engineers focus on the $\Delta S/\Delta N$ ratio, the amount of substrate COD that must be supplied to remove a given amount of nitrate-N, rather than on the electron acceptor requirement as was done for aerobic bioreactors. Consideration of the factors discussed in the preceding paragraph suggest that $\Delta S/\Delta N$ varies with SRT in a manner opposite to the way in which the oxygen requirement varies with the SRT in an aerobic bioreactor. Returning to Chapter 5, in which the traditional approach to decay was used, Eq. 5.33 allowed calculation of the amount of oxygen (electron acceptor) used:

$$RO = F(S_{SO} - S_S)\left[1 - \frac{(1 + f_D \cdot b_H \cdot \Theta_c)Y_H}{1 + b_H \cdot \Theta_c}\right] \tag{5.33}$$

Since RO represents the amount of electron acceptor used, and since each g of

nitrate-N can accept as many electrons as 2.86 g of oxygen, the equation can be rewritten as:

$$2.86 \cdot F(S_{NOO} - S_{NO}) = F(S_{SO} - S_S)\left[1 - \frac{(1 + f_D \cdot b_H \cdot \Theta_c)Y_H}{1 + b_H \cdot \Theta_c}\right] \tag{6.3}$$

Recognition that $F(S_{NOO} - S_{NO})$ is ΔN and that $F(S_{SO} - S_S)$ is ΔS, gives the following expression for $\Delta S/\Delta N$ using the traditional approach to decay:

$$\frac{\Delta S}{\Delta N} = \frac{2.86(1 + b_H \cdot \Theta_c)}{1 + (b_H \cdot \Theta_c) - Y_H(1 + f_D \cdot b_H \cdot \Theta_c)} \tag{6.4}$$

Because of the cycling of carbon in the lysis:regrowth approach to decay, it is not possible to derive an analogous expression using that approach, but the same principles apply and thus Eq. 6.4 is important for showing that $\Delta S/\Delta N$ varies with SRT in a manner opposite to that of the oxygen requirement. In other words, the amount of electron donor required to remove a given amount of nitrate-N will decrease as the SRT is increased. This happens because the increased importance of decay at longer SRTs allows a greater fraction of the electrons available in the donor to go to the acceptor rather than into biomass. Furthermore, it can be seen that the magnitude of this effect depends on the values of the kinetic and stoichiometric coefficients describing the system. The effect of SRT is illustrated in Figure 6.10[14] with data collected from a CSTR receiving methanol as the electron donor. Although ΔS was expressed as the mass of methanol rather than as the mass of COD, it is clear that the observations confirm the theory.

The calculation of the $\Delta S/\Delta N$ ratio above is based on the assumption that nitrate-N is the only available electron acceptor. In practice, however, it is difficult to totally eliminate the entrance of oxygen into a bioreactor. Since oxygen is the preferred electron acceptor, any entering the bioreactor will increase the amount of

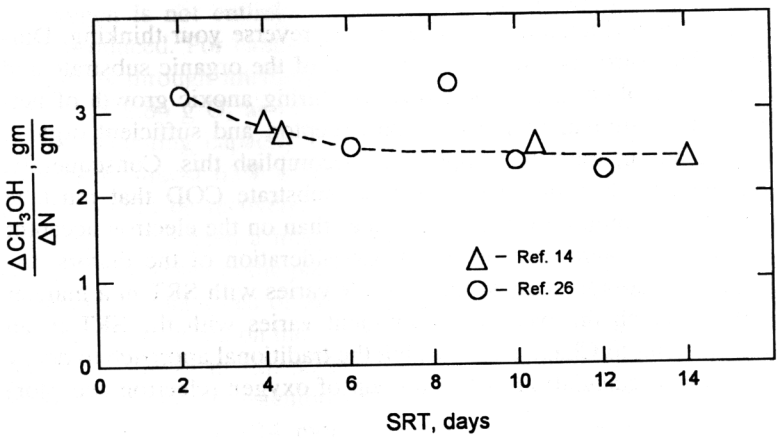

Figure 6.10 Effect of SRT on the $\Delta S/\Delta N$ ratio. The reference numbers refer to the sources of the data. (From D. J. Engberg and E. D. Schroeder, Kinetics and stoichiometry of bacterial denitrification as a function of cell residence time. *Water Research* **9**:1051–1054, 1975. Copyright © Elsevier Science Ltd.; reprinted with permission.)

electron donor that must be added to reduce a given amount of nitrate-N. In other words, it will increase the $\Delta S/\Delta N$ ratio.

The impact of the input of oxygen into a denitrification reactor can best be seen through use of the model in Table 6.1 because it considers both aerobic and anoxic growth of the heterotrophic bacteria and the effect of dissolved oxygen on each. To illustrate this point, a wastewater like that in Table 6.6 was assumed to be entering a CSTR operated at an SRT of 240 hr. The kinetic and stoichiometric coefficients describing the biomass in the bioreactor were assumed to have the values given in Table 6.3, except for $\hat{\mu}_A$ which was set equal to zero to ensure only heterotrophic reactions. Two situations were considered. In one, the influent nitrate-N concentration was set equal to 50 mg/L, which gave a mass input rate equivalent to 143 kg/day of oxygen. Given the values of the stoichiometric coefficients in Table 6.3, the amount of biodegradable COD entering the bioreactor (265 kg/day) was in excess of that needed to meet the required $\Delta S/\Delta N$ ratio. This case is called the excess COD case. In the other, the influent nitrate-N concentration was set equal to 60 mg/L, giving a mass input rate equivalent to 172 kg/day of oxygen, which was more than could be completely removed by the available COD. This is called the limiting COD case. Simulations were then conducted in which the rate of oxygen transfer into the bioreactor was set at various values and the results are shown in Figure 6.11. For the excess COD case, the input of a significant amount of oxygen could be tolerated without having an effect on the effluent nitrate-N concentration because the oxygen simply acted to allow more removal of COD. Eventually, however, a point was reached at which nitrate-N removal deteriorated because the total input of electron acceptor, i.e., nitrate-N plus oxygen, exceeded the amount of electrons available from the donor. For the limiting COD case, the entrance of even a small amount of oxygen caused the nitrate-N concentration to increase because any oxygen entering the bioreactor accepted electrons that otherwise would have gone for nitrate-N

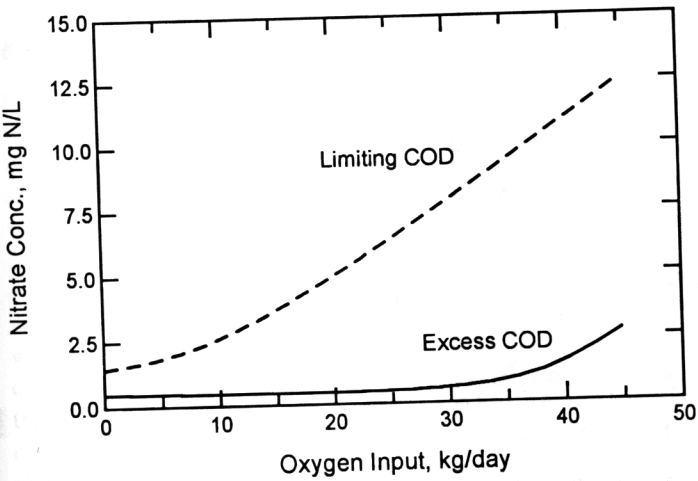

Figure 6.11 Effect of oxygen input rate on denitrification in a CSTR operated at an SRT of 240 hrs. Parameter values are given in Table 6.3 and the influent conditions are given in Table 6.6. For the limiting COD case the influent nitrate-N concentration was 60 mg/L whereas in the excess COD case it was 50 mg/L. The influent flow was 1000 m^3/day.

reduction. Although the magnitudes of the values given in Figure 6.11 are specific for the reactor conditions and parameter values used in the simulations, the results show clearly the importance of controlling the entrance of oxygen into a bioreactor in which denitrification is occurring.

The $\Delta S/\Delta N$ ratio is calculated from process stoichiometry, and simply tells us how much of one reactant will be removed in proportion to another. If the mass input rate of biodegradable COD into a denitrifying bioreactor is greatly in excess of that needed to remove the nitrate-N present, then the effluent biodegradable COD will be high (because there is insufficient acceptor to which to transfer electrons) and the nitrate-N concentration will be low and rate controlling. In other words, the term $S_S/(K_S + S_S)$ in the rate expression for process 2 in Table 6.1 will approach 1.0 and the term $S_{NO}/(K_{NO} + S_{NO})$ will be small. Conversely, if the input rate of biodegradable COD is less than that needed to remove the nitrate-N, then the effluent nitrate-N concentration will be high (because there is insufficient donor to provide the needed electrons) and the biodegradable COD concentration will be low and rate controlling. In other words, $S_{NO}/(K_{NO} + S_{NO})$ will approach 1.0 and $S_S/(K_S + S_S)$ will be small. The only way for both concentrations to be low and for both to simultaneously influence the rates of activity in the bioreactor is for the influent concentrations to closely match the required $\Delta S/\Delta N$ ratio. Given the influence of the entrance of small amounts of oxygen, as discussed above, and the variability associated with the values of the stoichiometric and kinetic coefficients in mixed microbial communities such as those used in wastewater treatment, this is difficult to achieve. For example, Figure 6.12[39] presents results from a study in which the relative amounts of biodegradable COD and nitrate-N (expressed as the carbon:nitrogen ratio) in the influent to a CSTR were varied. There it can be clearly seen that there was only a small range of influent ratios over which the effluent concentrations of both constituents were low. To overcome this problem, it is common practice to add the

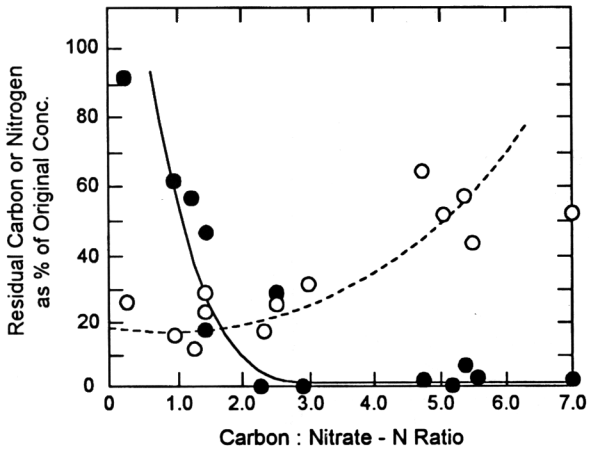

Figure 6.12 Effect of S_{SO}/S_{NOO} (expressed as C/N ratio) on the removal of carbon (○) and nitrogen (●) in a CSTR operated under anoxic conditions. (From K. Wuhrmann, Discussion of 'Factors affecting biological denitrification of wastewater' by R. N. Dawson and K. L. Murphy. *Advances in Water Pollution Research, Jerusalem, 1972*, 681–682, 1973. Reproduced by permission of Dr. K. L. Mechsner.)

organic substrate in slight excess of the amount required to remove the nitrate-N, and then to pass the effluent from the anoxic bioreactor through a small aerobic bioreactor in which any residual electron donor can be removed with oxygen as the electron acceptor.

6.5 MULTIPLE EVENTS

The purpose for development of the model in Table 6.1 was to allow engineers to simulate biochemical reactors in which all of the listed processes are occurring. Thus, it would be instructive to use it to investigate such a situation in a single CSTR. It is apparent, by now, however, that the conditions required for anoxic growth of heterotrophs and aerobic growth of autotrophs are mutually exclusive, since both are controlled by the dissolved oxygen concentration, but in the opposite manner. Consequently, if a CSTR is receiving a constant input and is operating at steady-state with a constant dissolved oxygen concentration, it is impossible for significant amounts of both nitrification and denitrification to occur. However, observations of treatment systems receiving diurnal variations in flow and concentration suggested that when the input was low, resulting in a high dissolved oxygen concentration, nitrification occurred, but when the input was high, driving the dissolved oxygen to very low concentrations, nitrification ceased and denitrification began, destroying part of the nitrate-N formed during the aerobic period. This made the daily average effluent total nitrogen concentration lower than in a system receiving adequate oxygen, suggesting that it might be possible to purposefully design a system in which the dissolved oxygen concentration varied sufficiently to allow both reactions to occur. In addition to reducing the amount of nitrogen discharged, this would reduce the amount of alkalinity destroyed and the amount of oxygen required, as discussed previously. Let us now consider each situation for a typical domestic wastewater.

6.5.1 Effects of Diurnal Variations in Loading

Figure 6.13 shows the simulated performance of a CSTR containing a biomass with the kinetic and stoichiometric coefficients in Table 6.3 and receiving an input with the variations shown in Figure 6.2. The average daily flow rate was 1000 m^3/day and the reactor volume was 500 m^3, giving an average HRT of 12 hr. The flow-weighted average concentrations of the various influent components were as shown in Table 6.6. The influent alkalinity, however, was assumed to have a constant concentration because it is influenced primarily by the characteristics of the carriage water. Two situations were considered. In one, the dissolved oxygen concentration was held constant at 2.0 mg/L throughout the entire 24 hr period. Given the value of $K_{O,H}$ in Table 6.3, this effectively eliminated denitrification. In the other, the mass transfer rate for oxygen was sufficient to maintain a dissolved oxygen concentration of 2.0 mg/L if the bioreactor received the daily average flow and concentrations. As shown in Figure 6.13a, however, because of the variable input, this resulted in excessive oxygen concentrations during periods of low loading, but inadequate concentrations during high loading. Under those conditions, significant denitrification occurred, as shown in Figure 6.13c. Comparison of the solid and dashed curves in parts b and d of the figure shows that while the lack of oxygen had only a minor

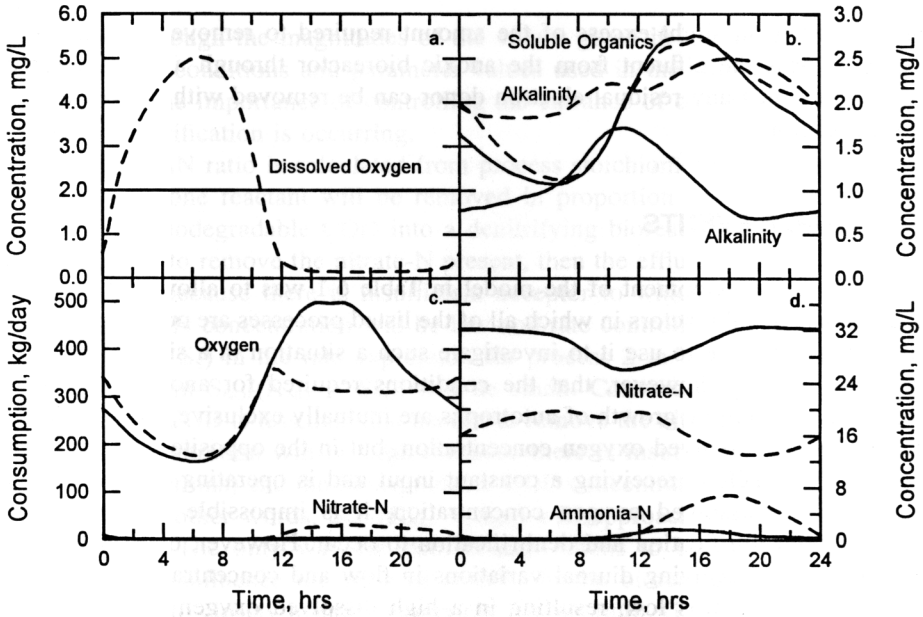

Figure 6.13 Response of a CSTR to a diurnal input. The input patterns are like those in Figure 6.2, but the flow weighted average concentrations are those given in Table 6.6. The daily average flow rate was 1000 m^3/day. The solid curves are for a reactor in which the dissolved oxygen concentration was held constant at 2.0 mg/L. The dashed curves are for a reactor in which the mass transfer coefficient for oxygen was held constant at 3.83 $hr.^{-1}$ The average HRT = 12 hrs and the SRT = 240 hrs. The parameter values are given in Table 6.3.

effect on the concentration of soluble organic matter in the effluent, it significantly lowered the nitrate-N concentration and raised the ammonia-N concentration. The raising of the ammonia-N concentration was due to retardation of nitrification, but the decrease in the nitrate-N concentration was caused by a combination of less production from nitrification and more consumption by denitrification. Nevertheless, it is apparent that less nitrogen was discharged from the system that had limited oxygen transfer capacity. Furthermore, less alkalinity was destroyed.

While it is not desirable to design a supposedly aerobic system with inadequate oxygen transfer capacity, the results from the simulation show clearly that all events can occur in a single biomass provided that the SRT of the system is sufficiently long to allow the nitrifying bacteria to grow during the aerobic period. This suggests that it should be possible to design a system in a way that maximizes nitrogen removal by controlling the periods with and without oxygenation. Such a system would have minimal power input as well as minimal alkalinity destruction.

6.5.2 Intermittent Aeration

Batchelor[5] was among the first to use simulation to investigate the possibility of using intermittent aeration to achieve both nitrification and denitrification in a single CSTR receiving a constant influent. His study was conducted with a model that was conceptually similar to the one in Table 6.1, although it differed somewhat with

respect to both the kinetics and stoichiometry employed. In addition, the values of the kinetic and stoichiometric parameters were slightly different from those in Table 6.3. Nevertheless, the results of his simulations illustrate some important concepts regarding the major variables influencing the performance of such systems.

The situation considered by Batchelor[5] was of a wastewater containing 200 mg/L of biodegradable COD and 30 mg/L of ammonia-N, entering a CSTR with an SRT of 240 hr and an HRT of 4.3 hr. The bioreactor was operated with a cycle time (the time between initiations of aeration) of 0.5 hr while the aeration fraction (the fraction of time that the bioreactor was aerobic) was varied. In each case, the effluent nitrogen concentrations from the bioreactor achieved a stable oscillation and the average concentrations of ammonia-N, nitrate-N, and total nitrogen were calculated. Figure 6.14 shows clearly that at low aeration fractions, the average ammonia-N concentration rises whereas at high aeration fractions the average nitrate-N concentration rises. Furthermore, an optimum exists at which the discharge of nitrogen is minimized. This result is consistent with our previous discussions. At aeration fractions in excess of the optimum, nitrification is complete, but the anoxic period is insufficient to allow much reduction of nitrate-N. Conversely, at aeration fractions less than the optimum, the aerobic period becomes insufficient for growth of the nitrifying bacteria. If the aeration fraction is made so low that the product of the aeration fraction and the SRT is below the minimum SRT for the nitrifiers, they will wash out and no nitrogen removal will be achieved, other than that associated with incorporation of nitrogen into the heterotrophic biomass via synthesis. For the kinetic parameters used by Batchelor,[5] the minimum SRT for nitrification was 52.6 hr. Since the system SRT was 240 hr, this suggests that total process failure would occur at an aeration fraction of 0.22. The fraction of the SRT that is aerobic is called the aerobic SRT and it is now recognized as an important parameter in the design of systems in which both nitrification and denitrification are occurring.

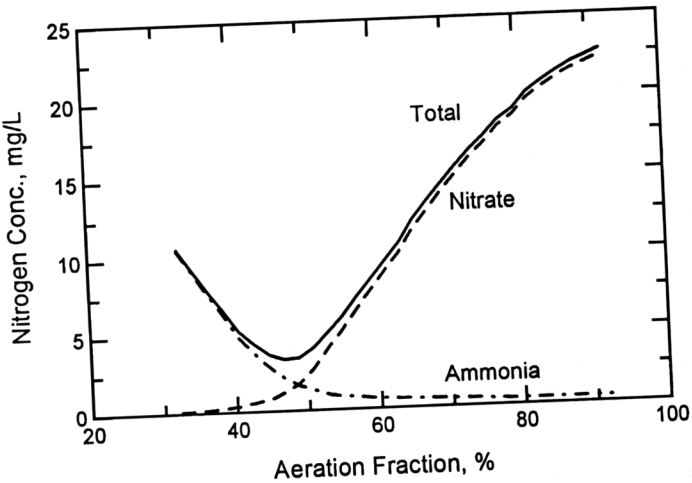

Figure 6.14 Effect of aeration fraction on the concentrations of ammonia-N, nitrate-N, and total-N in a CSTR operated with intermittent aeration at a cycle time of 0.5 hr. The HRT = 4.3 hrs and the SRT = 240 hrs. The influent biodegradable COD = 200 mg/L and the influent nitrogen concentration = 30 mg/L. (Adapted from Batchelor.[5])

The optimal aeration fraction in Figure 6.14 is 47%, but since the minimum allowable aeration fraction depends on the system SRT and the degree of denitrification also depends on the system SRT, we might expect the optimum aeration fraction to depend on the SRT as well. That this is the case is shown by the dark circles in Figure 6.15. The vertical bars in the figure indicate the range of aeration fractions at each SRT which results in total nitrogen concentrations within 1.0 mg/L of the minimum. That range is seen to broaden as the SRT is increased, suggesting that longer SRTs provide more latitude in operation of the bioreactor to achieve optimal nitrogen removal.

Both Figure 6.14 and Figure 6.15 were prepared from simulations conducted with a cycle time of 0.5 hr. However, we might also expect the cycle time to influence the degree of nitrogen removal. During aerobic periods, the ammonia concentration will fall and the nitrate-N concentration will rise as nitrification occurs. Conversely, during anoxic periods, denitrification will cause the nitrate-N concentration to fall while the continued influx of ammonia in the absence of nitrification will cause the ammonia concentration to rise. The longer the cycle time, the greater the amplitude of the cycles because a longer time will be available for each reaction. Since the effluent concentration is characterized by the daily average concentration, longer cycle times result in higher average nitrogen concentrations. On the other hand, as the cycle time is shortened, a point will be reached at which it is difficult for the biomass to shift rapidly enough from aerobic to anoxic metabolism, and vice versa. Consequently, there is also an optimum cycle time associated with each SRT and aeration fraction. At this time our understanding of the metabolic controls acting on the synthesis and activity of denitrifying enzymes is not sufficient to allow the optimum cycle time to be selected by simulation. Nevertheless, experimental studies have shown that cycle times on the order of 20 to 45 min work well.[20]

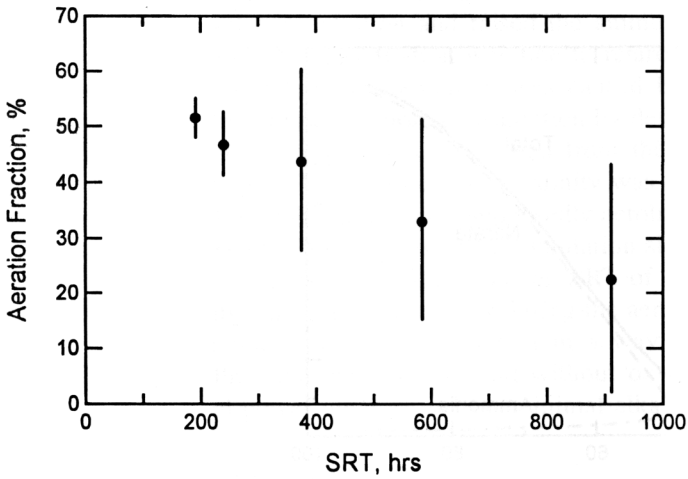

Figure 6.15 Effect of SRT on the optimal aeration fraction (dots) and the range of near optimal aeration fractions (lines) in a CSTR operated with intermittent aeration. The influent biodegradable COD = 200 mg/L and the influent nitrogen concentration = 30 mg/L. The dissolved oxygen concentration was fixed at 2.0 mg/L when the aeration was on and 0.0 mg/L when it was off. (Adapted from Batchelor.[5])

6.5.3 Closure

The important point to gain from the preceding is that engineers can exert control over the environment in biochemical reactors, thereby allowing processes to occur in a single system that would not otherwise occur together. This suggests that the engineer has considerable latitude in system design. The complexity of the interactions, however, makes it impossible to intuitively predict the outcome of all possible systems that the engineer might conceive. This, in turn suggests why it is necessary to work with models like those in Table 6.1. Through their application, engineers can explore large numbers of possible bioreactor systems to see how system layout and environment influence the outcome of the possible reactions.

It is apparent that the number of options available during design of a single CSTR is very limited. Thus, most biochemical operations employ reactors with spatial gradients in them, usually through use of reactors with large length to width ratios, but also through use of compartmentalized reactors. Since both can be modeled as tanks in series systems, in the next chapter we will apply ASM No. 1 to study the performance of a number of such systems.

6.6 KEY POINTS

1. International Association on Water Quality activated sludge model No. 1 incorporates eight processes acting on thirteen components. The processes are aerobic and anoxic growth of heterotrophic biomass, aerobic growth of autotrophic bacteria, decay of both heterotrophic and autotrophic biomass, ammonification of soluble organic nitrogen, and hydrolysis of both particulate organic substrate and particulate organic nitrogen.
2. The thirteen components incorporated into ASM No. 1 include six particulate and seven soluble ones. The particulate ones are inert organic matter, slowly biodegradable substrate, heterotrophic biomass, autotrophic biomass, biomass debris, and organic nitrogen. The soluble ones are inert organic matter, readily biodegradable substrate, dissolved oxygen, nitrate-N, ammonia-N, organic nitrogen, and alkalinity.
3. In ASM No. 1, biomass growth is expressed by a double Monod equation in which both the electron donor and acceptor are considered, biomass loss is modeled by the lysis:regrowth approach, ammonification is considered to be first order with respect to the soluble organic nitrogen concentration, and hydrolysis is modeled by a surface mediated reaction term in which the rate is controlled by the slowly biodegradable substrate to biomass ratio and the electron acceptor concentration.
4. Activated sludge model No. 2 includes biological phosphorus removal in addition to carbon oxidation, nitrification, and denitrification. Because biological phosphorus removal is a complicated process, ASM No. 2 is considerably more complex than ASM No. 1.
5. Because hydrolysis is a slow reaction, long SRTs are required to obtain substantial degradation of particulate substrate.
6. The major impact of the presence of particulate substrate in the feed to a CSTR receiving a dynamic input is to dampen the variability in the

oxygen requirement, thereby decreasing the peak requirement and delaying the occurrence of the maximum and minimum values.

7. Because the half-saturation coefficient for nitrifying biomass is very small relative to the concentration of ammonia-N in most wastewaters, nitrification behaves in an all-or-none manner in which nitrification is either almost complete or washout occurs. Furthermore, the washout SRT is very sensitive to the dissolved oxygen concentration and the temperature.
8. Because of the kinetics and stoichiometry of nitrification, the growth of autotrophic bacteria in a CSTR in which heterotrophs are growing can have a major impact on the amount of oxygen required while having little effect on the MLSS concentration.
9. The release of ammonia-N as the result of biomass destruction in a CSTR receiving a feed containing only biomass provides a significant amount of substrate for nitrifying bacteria. Growth of those bacteria will have a substantial impact on the oxygen requirement in the bioreactor as well as on the amount of alkalinity destroyed.
10. Denitrification can have several benefits: it can remove nitrogen by converting nitrate-N to nitrogen gas; it can recover approximately 63% of the energy expended during nitrification by using the resulting nitrate-N as a terminal electron acceptor for organic substrate removal; and it can recover about half of the alkalinity destroyed during nitrification.
11. The $\Delta S/\Delta N$ ratio is an important characteristic of denitrifying bioreactors because it determines how much electron donor must be provided to convert a given amount of nitrate-N to nitrogen gas. However, because the ratio is influenced by factors such as the SRT and the presence of oxygen, it is not generally possible to operate a CSTR so that the effluent concentrations of both the electron donor and nitrate-N are low. Consequently, the electron donor is usually provided in excess and any residual is removed in a small aerobic bioreactor with oxygen as the electron acceptor.
12. If a CSTR with an SRT sufficient for nitrification receives influent that follows typical diurnal patterns of flow and concentration, it is possible for denitrification to occur during periods of peak loading if the input rate of oxygen is insufficient to maintain significant concentrations of dissolved oxygen.
13. By subjecting a CSTR to intermittent aeration, it is possible to have both nitrification and denitrification occur in a single bioreactor receiving a constant input. Under those circumstances, the fraction of time that the system is aerobic is an important determinant of system performance, and there will be an optimum fraction that minimizes the effluent nitrogen concentration.

6.7 STUDY QUESTIONS

1. What are the thirteen components and the eight processes considered in IAWQ ASM No. 1? Construct a matrix that indicates which processes act on which components, using a plus sign to indicate when the concentra-

tion of a component is increased by the process and a negative sign to indicate when it is decreased.

2. What are the eight processes considered in ASM No. 1 and how is each modeled?
3. Simplify the matrix representing ASM No. 1 for the following situations:
   a. A totally aerobic bioreactor receiving only soluble constituents in the feed.
   b. A totally aerobic bioreactor receiving only particulate constituents in the feed.
   c. A totally anoxic bioreactor receiving particulate organic constituents and soluble nitrate and ammonia nitrogen.
   d. A totally aerobic bioreactor receiving ammonia-N as the only electron donor.
4. Draw a sketch comparing the steady-state performance of CSTRs receiving soluble and particulate substrates, and use it to contrast the usefulness of the process loading factor and SRT as design and operational parameters for bioreactors receiving particulate substrate.
5. Draw a sketch contrasting the response to typical diurnal loading patterns of the oxygen requirement in CSTRs receiving soluble and particulate substrates? Why do the two reactors behave differently?
6. What is meant by the statement that nitrification behaves in an all-or-none fashion? Why does it do so? What are the impacts of temperature and dissolved oxygen concentration on nitrification?
7. What are the effects of nitrification in a CSTR receiving an influent with the characteristics of typical domestic wastewater? Why do they occur?
8. Using a computer code for IAWQ ASM No. 1 and typical temperature coefficients for the growth of heterotrophic and autotrophic biomass, investigate the effects of temperature (10° to 35°C) and SRT (48 to 360 hr) on the effluent concentrations of ammonia-N and readily biodegradable substrate from a CSTR receiving an influent with the characteristics given in Table 6.6. Use your results to discuss what is likely to happen to the performance of such a bioreactor throughout the year as the temperature changes and how SRT can be used to influence that performance.
9. What are the effects of nitrification in a CSTR receiving an influent containing heterotrophic biomass as its major constituent? What are the implications of those effects to the design and operation of such a reactor?
10. What is meant by the term $\Delta S/\Delta N$ ratio, how is it used in characterizing the performance of an anoxic CSTR, and why does it decline as the SRT of the bioreactor is increased?
11. Why is it difficult to operate an anoxic CSTR in a way that will ensure that the effluent concentrations of both the organic substrate and nitrate-N are low?
12. When a single CSTR receiving influent at a constant rate is subjected to intermittent aeration, the fraction of time that the system is aerobic will affect the effluent nitrogen concentration. Draw a sketch showing the effect of aeration fraction on the effluent nitrogen concentrations from such a system. Why does it look as it does?

13. For the situation described in Study Question 12, why does the optimal aeration fraction decrease as the SRT of the bioreactor is increased? Why does the range of near optimal aeration fractions increase?

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