10
Biological Nutrient Removal

10.1
Introduction

Nutrient compounds frequently present in wastewater are valuable substances which act as fertilizers. They are becoming increasingly significant in water and wastewater management because the discharge of nutrients such as nitrogen and phosphorus into rivers and lakes can cause adverse influences on our environment and life. An excessive increase in the quantities of these nutrients in the aquatic surroundings disturbs the ecological balance, resulting in severe damage to environment (e.g. eutrophication).

It is probable that either nitrogen or phosphorus will be the limiting nutrient controlling eutrophication because of the relatively large quantities required for biomass growth compared to other nutrients, such as sulfur, potassium, calcium and magnesium.

Nitrogen is dissolved in water as ammonia, nitrite and nitrate and is present in organic molecules such as amino acids, which are formed by the hydrolysis of proteins and are transformed to ammonia during biodegradation. Ammonia and organic nitrogen compounds are most closely associated with plants and animals. An example of an organic nitrogen compound is urea (NH_2CONH_2), which is a major chemical component of urine. Urea is produced from ammonia in fauna and converted to ammonium by hydrolysis.

Several problems result from discharging wastewater with ammonia and nitrate into rivers and lakes:

- Ammonia is oxidized by bacteria to nitrite and nitrate, leading to a decrease in the dissolved oxygen concentration and to fish killing.
- Uncontrolled nitrification of ammonia causes a decrease in pH in the receiving stream.
- Ammonia and ammonium are in chemical equilibrium; with increasing temperature and pH more and more ammonia is produced which is toxic to fish.
- Nitrate stimulates the growth of algae, contributing to the eutrophication of open bodies of water.

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- Nitrite and nitrate may reach groundwater resources which are used for producing drinking water. High concentrations of nitrate and nitrite in drinking water cause methemoglobinemia in babies and promote the formation of carcinogenic nitrosamines. As a result, the water must be denitrified in drinking water plants.
- In oxygen-free soil layers, denitrification can cause sludge build-up and anaerobic decomposition, resulting in the generation of methane.

In order to solve these problems, nitrogen must be removed from water. Biological nitrification and denitrification are an alternative.

Phosphorus is a key element in all known forms of life and a common earth element which can be induced into aquatic ecosystems by natural and human-caused erosion of soil materials and by human activity, e.g. the use of fertilizer in agriculture. It exists in different forms, such as dissolved inorganic orthophosphate, dissolved organic phosphorus found in algae, dissolved inorganic polyphosphate and non-dissolved particulate phosphorus (Fig. 10.1):

- Dissolved organic phosphorus is found as a lysis product of algae and bacteria in water and is used for industrial products like pesticides, complex binders and antiknock agents. They are difficult to biodegrade and pass through bank filtration and the filtration of water purification plants (Klinger 1999).

- Two types of dissolved inorganic phosphates are orthophosphate and polyphosphate. Orthophosphate takes the form of PO_4^{3-}, HPO_4^{2-} or $H_2PO_4^-$, depending on the pH value. PO_4^{3-} plays a major role in organic molecules such as DNA and RNA, where it forms part of their structural backbone (see Fig. 3.8 in Chapter 3). Living cells also utilize phosphate to transport cellular energy via adenosine triphosphate (ATP; see Fig. 3.15). Existing orthophosphate facilitates algal growth. This is followed by algal death, lysis of algae and biodegradation by aerobic bacteria, which leads to oxygen depletion in lakes (eutrophication). Orthophosphate is stored in algae as polyphosphate. Polyphosphate is formed by polymerization of orthophosphate linked between hydroxyl groups and hydrogen atoms.

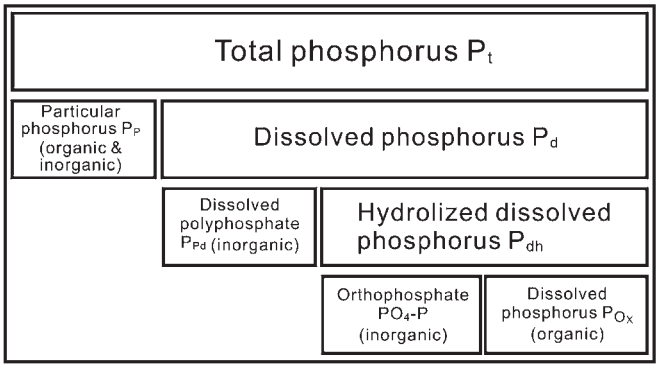

Fig. 10.1 Different forms of phosphorous in wastewater (Klein 1988; DIN 38405, D11).

- Non-dissolved organic phosphorus particles are found in organisms and their cell refuse. A part of these phosphorus particles is separated by sedimentation and filtration; the colloid particles are eliminated only after flocculation and membrane processes.

To avoid problems with nitrogen and phosphorus, more and more limitations are being placed on the discharge permits of WWTP.

The minimum requirements for the discharge of municipal wastewater into inshore waters are laid down by the Wastewater Framework Regulation (Abwasserverordnung: Verordnung über Anforderungen an das Einleiten von Abwasser in Gewässer) of the Federal Republic of Germany from 17 June 2004 (AbwV 2004) which was recently renewed, going into effect from 1 January 2005.

The NH_4-N concentration of a 2-h mixed sample of domestic and municipal wastewater must be less than 10 mg L^{-1} NH_4-N for BOD_5 loads greater than 300 kg d^{-1} (Appendix 1 in AbwV 2004). That means that all treatment plants with flow rates greater than 4000 m^3 d^{-1} have to be expanded to include a nitrification stage. An expansion is made necessary by the limit on the total inorganic nitrogen content (ammonia, nitrite and nitrate) and total phosphorus content. For BOD_5 loads from 600 kg d^{-1} to 6000 kg d^{-1}, the total N and P concentrations of a 2-h mixed sample must be less than 18 mg L^{-1} N and 2 mg L^{-1} P respectively. For BOD_5 loads greater than 6000 kg d^{-1}, both limit values are even lower, i.e. 13 mg L^{-1} N and 1 mg L^{-1} P (see Table 2.9).

The German Wastewater Framework Regulation also sets limits for industrial effluents for their direct discharge into inshore waters. The limit for total N ranges from 18 mg L^{-1} N for the food industry to 70 mg L^{-1} N for landfill leachate water. The limits for phosphorus and ammonium nitrogen are mostly fixed at 2 mg L^{-1} P_t and 10 mg L^{-1} NH_4-N, respectively (Table 10.1).

The different limits for various branches of industry depend on the raw materials used. For example, most food producers have the same limits of total N and P concentration as those for domestic and municipal wastewater at the 6000 kg d^{-1} BOD_5 level.

The European Union passed Directive 91/676/EEC (EU 1991a) concerning the protection of waters against pollution caused by nitrates from agricultural sources to reduce or prevent water pollution. The member states are obliged to take measures against the discharge of nitrate into surface waters and groundwater. Moreover, a framework for European Community action in the field of water policy was established in the form of Directive 2000/60/EC from 23 October 2000 which aims at maintaining and improving the aquatic environment in the EC. It was completed and amended by Decision No. 2455/2001/EC from 20 November 2001 to establish a list of priority substances (Annex X) in the field of water policy.

In addition, Directive 91/271/EEC (EU 1991b) requires the collection and treatment of wastewater, with P removal in sensitive areas and effectively in almost all large urban areas. Application of this Directive is essential to protect the quality of surface waters (see Chapter 2 for regulations concerning wastewater and Chapter 12 for hygienic standards for bathing water).

Table 10.1 German legal requirements for direct discharge of specific industrial effluents to inshore waters regarding nitrogen, phosphorus, COD and BOD_5 (AbwV 2004).

Industry/products	S_{NH4-N} (mg L^{-1} N)	S_{Nt} (mg L^{-1} N)	S_{Pt} (mg L^{-1} P)	S (mg L^{-1} COD)	S (mg L^{-1} BOD_5)
Food production[a)]	10	18	2	110	25
Sugar production	10	30	2	200	25
Edible oil refinery	–	30	4.5	200	38
Leather production	10	–	2	250	25
Biological treatment of waste	–	70	3	200	20
Meat meal industry	–	50	–	150	25
Cellulose production	–	10	2	25	30
Gelatine production	10	30	2	110	25
Paper production	–	10	2	50	25
Textile production	10	20	2	160	25
Petroleum processing	–	40	1.5	82	25
Laundry	–	20	2	100	25
Animal and plant production	–	–	2	110	25

[a)] This includes milk, brewery, potatoes, meat, fish, drinks, alcohol and alcoholic drinks, fruits and vegetables.

In domestic wastewater, one major problem is that the ratios of N:C and P:C of many organic compounds in wastewater are much higher than those needed by heterotrophic bacteria for catabolism and anabolism. Therefore, inorganic and organic N and P compounds are left in the treated wastewater. The processes for nitrogen and phosphorus removal are generally applied for domestic wastewater treatment. In industrial effluents, the contents of N and/or P are usually too low, so that N and/or P must be supplemented via additives. If the wastewater has a high N concentration, it is removed by stripping with steam or air at higher pH which must be cleaned afterwards, e.g. by absorption and reaction in sulfonic acid. The process of nitrification and denitrification has been used here only seldom.

The typical mean NH_4-N and total N concentrations in raw municipal wastewater range is 44.5–75.9 mg L^{-1} NH_4-N and 74.5–103.5 mg L^{-1} N in Berlin wastewater (WWTP Ruhleben). The total P concentrations range is 11.7–18.9 mg L^{-1} P (BWB 2004; see also Table 2.3). But sometimes industrial effluents are heavily loaded with ammonia; and its concentration varies depending on the production processes responsible (see Table 2.4).

Chemical systems have frequently been used to remove phosphorus in wastewater treatment. Biological processes to remove nitrogen and phosphorus from wastewater have become more or less standard technology in wastewater treatment. The utilization of biological nutrient removal processes for the treatment of wastewater has environmental, economical and operational benefits. We will return to this topic later.

10.2
Biological Nitrogen Removal

10.2.1
The Nitrogen Cycle and the Technical Removal Process

The relationship between the various nitrogen compounds and their transformation is presented in Fig. 10.2 as the nitrogen cycle. The transformation reactions include fixation, ammonification, assimilation, nitrification and denitrification. The principle compounds in the nitrogen cycle are nitrogen gas, ammonium, organic nitrogen and nitrate (De Renzo 1978).

The atmosphere serves as a reservoir of N_2 gas which is naturally transformed by electrical discharge (lightning) and by nitrogen-fixing organisms. Moreover, N_2 gas is fixed by a technical manufacturing process known as the Haber–Bosch synthesis process since 1915. Industrial fixation was initially developed for the production of fertilizers and explosives:

$$N_2 + 3H_2 \rightarrow 2NH_3 \tag{10.1}$$

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O \tag{10.2}$$

$$C_6H_5CH_3{}^{1)} + 3\,HNO_3 \rightarrow C_6H_2CH_3(NO_2)_3{}^{2)} + 3\,H_2O \tag{10.3}$$

In the fixed state, nitrogen can continue through various reactions. Nitrogen gas is returned to the atmosphere by an explosive reaction of a mixture from $NaNO_3$ and $Ca(NO_3)_2$ with NH_4Cl to N_2 gas (Foerst 1965). Nitrogen gas is also formed by the biological reduction through denitrification. The nitrogen cycle is applicable to surface water and the soil/groundwater environment, where many transforming reactions can occur. Nitrogen can be added by precipitation and dustfall, surface runoff, artificial fertilizers and the direct discharge of wastewater (Fig. 10.2).

Domestic wastewater contains organic nitrogen compounds and ammonium. These originate from protein metabolism in the human body. In fresh domestic wastewater, approximately 60% of the nitrogen is in the organic and 40% is in the inorganic form, such as NH_4^+. The organic compounds include amino acids, proteins, ADP/ATP and urea as the basic organic sources of nitrogen and phosphorus.

Biological nitrification and denitrification together make up the most useful processes to remove nitrogen. During nitrification, ammonium is first oxidized to nitrite or nitrate by aerobic chemolitho-autotrophic bacteria. Nitrite and nitrate are then reduced to N_2 gas in the denitrification process by chemoorgano-heterotrophic denitrifying bacteria under anoxic conditions. Nitrification and denitrification occur inside living bacteria in nature and in biological wastewater treatment processes.

In Sections 10.2.2 to 10.2.5 we discuss the microbiology, basic reactions, kinetics and performance of biological nitrogen removal processes by nitrification and denitrification.

[1)] Toluene, [2)] TNT = 2,4,6-Trinitrotoluene

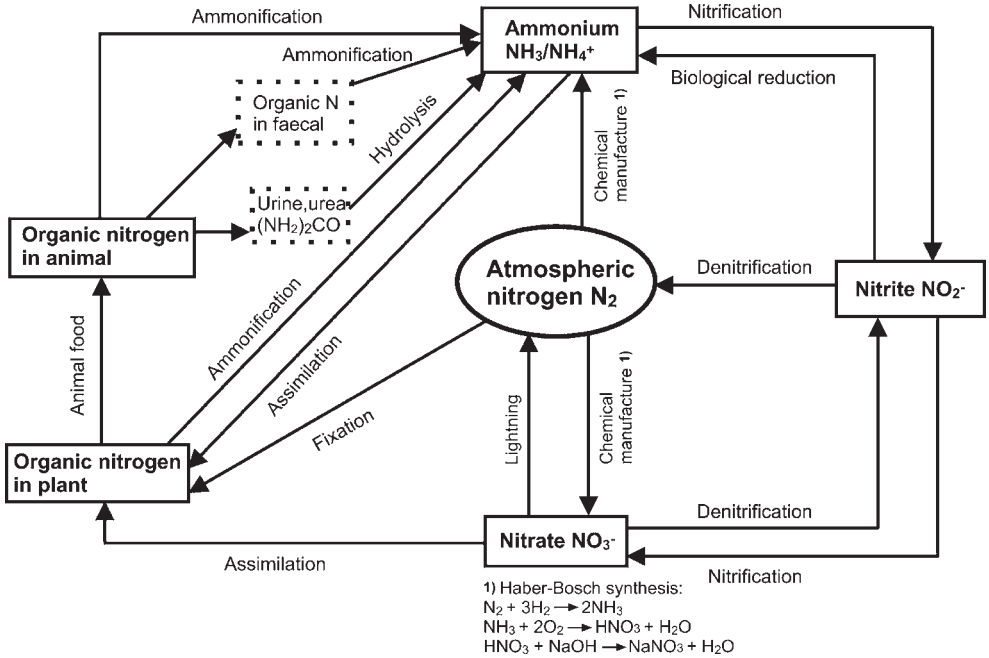

Fig. 10.2 Principal compounds in the nitrogen cycle are nitrogen gas, ammonium, organic nitrogen and nitrate.

10.2.2 Nitrification

10.2.2.1 Nitrifying Bacteria and Stoichiometry

The autotrophic bacteria oxidize inorganic nitrogen components to obtain energy for growth and maintenance, while they obtain carbon for cell building by the reduction of CO_2. The principal genera in the activated sludge process, *Nitrosomonas* and *Nitrobacter*, are responsible for the oxidation of ammonium to nitrite (nitritification) and of nitrite to nitrate (nitratification), respectively.

Basic physiological and structural characteristics of *Nitrosomonas* and *Nitrobacter* are presented in Table 10.2.

The stoichiometry for catabolism of NH_4 and NO_2 oxidation are:

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+ + \Delta G^o \quad (10.4)$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- + \Delta G^o \quad (10.5)$$

with $\Delta G^o = -240 \ldots -350$ kJ mol^{-1} for *Nitrosomonas* and $\Delta G^o = -65 \ldots -90$ kJ mol^{-1} for *Nitrobacter* (Halling-Sørensen and Jørgensen 1993; Wiesmann and Libra 1999).

Table 10.2 Basic comparison between nitrifying and denitrifying bacteria (Gerardi and Michael 2002; Halling-Sørensen and Jørgensen 1993).

Indication	Nitrifiers		Denitrifiers
	Nitrosomonas	*Nitrobacter*	
Carbon source	Inorganic (CO_2)	Inorganic (CO_2)	Organic carbon
Cell shape	Coccus (spherical)	Bacillus (rod-shaped)	–
Cell size	1.0 · 1.5 µm	0.5 · 1.0 µm	–
O_2 requirement	Strictly aerobic	Strictly aerobic	Facultative aerobic
pH range	5.8–8.5	6.5–8.5	6.5–8.5
t_G	8–36 h	12–60 h	0.25–0.5 h
Growth range of temperature	5–30 °C	5–40 °C	

The overall oxidation of ammonium by both groups is obtained by adding Eqs. (10.4) and (10.5):

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \tag{10.6}$$

in which a large amount of oxygen is needed and the pH decreases in water with low buffer capacity if no pH control is performed.

Compared to the catabolism of nitrification, anabolism has more complex stoichiometric reactions. Due to the use of carbon dioxide as the carbon source, a much lower growth rate of nitrifying biomass results and it is difficult to study cell-building compared to aerobic heterotroph growth, especially if the cell-building of both nitrifying genera must be determined separately. Therefore, there are significant deviations among equations describing the metabolism of nitritification and nitratification (Sherrad 1977; Dombrowski 1991; US EPA 1993; Grady et al. 1999; Henze et al. 2002).

The stoichiometric reactions for the anabolism of NH_4^+ and NO_2^- oxidation are as follows, assuming that the empirical formulation of bacterial cells is $C_5H_7O_2N$ (Halling-Sørensen and Jørgensen 1993; Henze et al. 2002):

$$13NH_4^+ + 15CO_2 \rightarrow 10NO_2^- + \underset{\text{bacteria}}{3C_5H_7O_2N} + 23H^+ + 4H_2O \tag{10.7}$$

$$10NO_2^- + 5CO_2 + NH_4^+ + 2H_2O \rightarrow 10NO_3^- + \underset{\text{bacteria}}{C_5H_7O_2N} + H^+ \tag{10.8}$$

When compared to the catabolism of NH_4^+, less energy is available for the growth of *Nitrobacter* in comparison to *Nitrosomonas* (see Eqs. 10.4 and 10.5). Both anabolic reactions usually take place at $5.5 < pH < 8.3$; therefore, Eq. (10.9) must be considered (see also Section 4.3):

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \tag{10.9}$$

The stoichiometric reactions of NH_4^+ and NO_2^- oxidation for catabolism and anabolism applied to 1 mol NH_4^+ and NO_2^- are given by Eq. (10.10) and Eq. (10.11) respectively (Wiesmann and Libra 1999):

$$NH_4^+ + 1.98HCO_3^- + 1.3O_2 \rightarrow 0.0182C_5H_7O_2N + 0.98NO_2^- + 1.04H_2O + 1.89H_2CO_3 \quad (10.10)$$

$$NO_2^- + 0.02H_2CO_3 + 0.48O_2 + 0.005NH_4^+ + 0.005HCO_3^- \rightarrow 0.005C_5H_7O_2N + NO_3^- + 0.015H_2O \quad (10.11)$$

Ammonium and nitrite are used as energy sources and CO_2 as a carbon source for nitrifying bacteria. Ammonium is oxidized to nitrite over three steps and the oxidation of nitrite to nitrate is a single step (Eq. 10.12). The intermediate between hydroxylamine and nitrite is not known (Henze et al. 2002).

$$NH_4^+ \xrightarrow{a} NH_2OH \xrightarrow{b} NOH? \xrightarrow{c} NO_2^- \xrightarrow{d} NO_3^- \quad (10.12)$$

It is assumed that, for every reaction step, almost the same amount of energy is produced. The energy produced by the oxidation from ammonium to nitrite is a factor of about 3.0–3.8 greater than that of the transformation from nitrite to nitrate (see Eqs. 10.4 and 10.5). Based on this fact, the biomass yield coefficient of Y^o_{XA/NH_4} or Y^o_{XA/NO_2} has to correspond to this relation (see Eqs. 10.18 and 10.19). Many authors have measured the growth of *Nitrosomonas* and *Nitrobacter* and described its stoichiometry, but the values are very different. The growth of new cells in the activated sludge process is referred to as an increase in the mixed liquor volatile suspended solids (MLVSS). Nitrifying bacteria obtain a relatively small amount of energy from the oxidation of ammonium and nitrite, resulting in long generation times and a small population MLVSS.

The specific growth rate of the nitrifying bacteria in activated sludge is much lower than that of aerobic organo-heterotrophs. Nitrifiers' poor ability to form flocs and the risk of being washed out of the system with their low growth rate can be overcome by the likelihood that they are adsorbed onto the surface of other floc particles. This characteristic is normally used for nitrification in biofilm reactors (see Chapter 7). Using membrane bioreactors (see Chapter 12) for nitrification is also very beneficial. The growth of nitrifying bacteria is affected by a number of environmental parameters such as dissolved oxygen concentration c′, pH and the presence of inhibitors (see Section 10.2.2.3).

In order to determine the rate of NH_4 oxidation in a CSTR, assuming steady state, the following expressions are used:

$$0 = Q_0 (S_{NH_4-N,0} - S_{NH_4-N}) - r_{NH_4-N} V \quad (10.13)$$

$$r_{NH_4-N} = \frac{\mu_A X_A}{Y^o_{XA/NH_4-N}} \quad (10.14)$$

$$r_{O_2} = \frac{\mu_A X_A}{Y^o_{XA/O_2}} \quad (10.15)$$

In the next section, the yield coefficients and specific growth rate of nitrifying bacteria μ are discussed.

10.2.2.2 Stoichiometry and Kinetics of Nitrification

From the catabolic stoichiometric reactions Eqs. (10.4) and (10.5) for *Nitrosomonas* and *Nitrobacter* respectively, the true yield coefficients are:

$$Y^{\circ}_{O_2/NH_4-N} = 1.5\,\frac{M_{O_2}}{M_N} = 1.5\,\frac{32\ \text{g mol}^{-1}\ O_2}{14\ \text{g mol}^{-1}\ N} = 3.43\,\frac{\text{g } O_2}{\text{g N}} \tag{10.16}$$

$$Y^{\circ}_{O_2/NO_2-N} = 0.5\,\frac{M_{O_2}}{M_N} = 0.5\,\frac{32\ \text{g mol}^{-1}\ O_2}{14\ \text{g mol}^{-1}\ N} = 1.14\,\frac{\text{g } O_2}{\text{g N}} \tag{10.17}$$

The stoichiometric coefficients show the true oxygen requirements, with the exception of the amount for endogenous respiration. From the sum of both coefficients we obtain $Y^{\circ}_{O_2/N} = 4.57\ \text{g } O_2\ (\text{g N})^{-1}$. Thus, 4.57 g O_2 are required for each g NO_3-N produced (see Section 11.3.3). If anabolism is considered, the yield coefficients are only a little lower.

The true yield coefficients follow directly from Eqs. (10.10) and (10.11):

$$Y^{\circ}_{XA/NH_4-N} = \frac{0.0182\ M_{C_5H_7O_2N}}{M_{NH_4-N}} = \frac{0.0182 \cdot 115\ \text{g mol}^{-1}\ C_5H_7NO_2}{14\ \text{g mol}^{-1}\ NH_4-N} = 0.147\,\frac{\text{g MLVSS}}{\text{g N}}\ ^{1)} \tag{10.18}$$

$$Y^{\circ}_{XA/NO_2-N} = \frac{0.005\ M_{C_5H_7NO_2}}{M_{NO_2-N}} = \frac{0.005 \cdot 113\ \text{g mol}^{-1}\ C_5H_7O_2N}{14\ \text{g mol}^{-1}\ NO_2-N} = 0.04\,\frac{\text{g MLVSS}}{\text{g N}} \tag{10.19}$$

The total yield values without accumulation of NO_2^- for the growth of *Nitrosomonas* and *Nitrobacter* are 0.187 g MLVSS per g NH_4-N oxidized or g NO_3-N produced. Lindemann (2002) and Choi (2005) presented and compared some yield coefficients. Averaged values of Y°_{XA/NH_4-N} and Y°_{XA/NO_2-N} were calculated from values of different authors, as follows (Larsen-Vefring 1993):

$$Y^{\circ}_{XA/NH_4-N} \approx 0.142\ \text{g MLVSS}\ (\text{g } NH_4\text{-N})^{-1}$$

$$Y^{\circ}_{XA/NO_2-N} = 0.02 \text{ to } 0.084 \approx 0.048\ \text{g MLVSS}\ (\text{g } NO_2\text{-N})^{-1}$$

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1) The total parameter MLVSS (mixed liquor volutile suspended solids) includes here only the mass of Nitrosomonas or Nitrobacter, respectively.

The influence of the decay rate (death and endogenous respiration) was not considered. The yield coefficients for the growth of nitrifyers with respect to oxygen consumption are calculated as follows:

$$Y^{o}_{XA/O_2} = \frac{Y^{o}_{XA/NH_4-N}}{Y^{o}_{O_2/NH_4-N}} = \frac{0.147}{3.43} = 0.043 \frac{\text{g MLVSS}}{\text{g } O_2} \tag{10.20}$$

$$Y^{o}_{XA/O_2} = \frac{Y^{o}_{XA/NO_2-N}}{Y^{o}_{O_2/NO_2-N}} = \frac{0.04}{1.14} = 0.035 \frac{\text{g MLVSS}}{\text{g } O_2} \tag{10.21}$$

As the yield coefficients show, nitrification is characterized by high oxygen consumption and low biomass production. From Eqs. (10.20) and (10.21) it can be seen that almost the same amounts of oxygen are used for the cell multiplication of *Nitrosomonas* and *Nitrobacter*.

Ammonia and nitric acid are believed to be the real electron donor (substrate) of *Nitrosomonas* and *Nitrobacter*, respectively, because less energy is required for its transport into the cell compared to the transport of an ionised molecule like NH_4^+ or NO_2^- (Suzuki et al. 1974; Bergeron 1978; Wiesmann 1994). NH_3 and HNO_2 are formed by dissociation which can be described based on a dissociation equilibrium depending on pH and temperature:

$$NH_4^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_3 + H^+ \tag{10.22}$$

$$NO_2^- + H^+ \underset{k_4}{\overset{k_3}{\rightleftharpoons}} HNO_2 \tag{10.23}$$

The concentration of NH_3 and NH_4^+ can be expressed via the dissociation constant $K_{D,NH_3} = k_2/k_1$ from Eq. (10.22) as follows:

$$K_{D,NH_3} = \frac{S_{NH_4^+-N}}{S_{NH_3-N} \cdot S_{H^+}} \tag{10.24}$$

with:

$$S_{NH_4^+-N} + S_{NH_3-N} = S_{NH_4-N,\Sigma} \tag{10.25}$$

Introduction of Eq. (10.25) into Eq. (10.24) gives:

$$K_{D,NH_3} = \frac{S_{NH_4-N\Sigma} - S_{NH_3-N}}{S_{NH_3-N} \cdot S_{H^+}} \tag{10.26}$$

or:

$$S_{NH_3-N} = \frac{S_{NH_4-N\Sigma}}{1 + K_{D,NH_3} \cdot 10^{-pH}} \tag{10.27}$$

where:

$$pH = -\log S_{H^+};\ S_{H^+} = 10^{-pH}$$

Note, that $S_{NH_4^+-N,\Sigma}$ is approximately the same as $S_{NH_4^+-N}$ for 6.0 < pH < 7.8, the pH range at which wastewater is usually treated. Finally, this results in (Anthonisen et al. 1976; Wiesmann 1994):

$$S_{NH_3-N} = \frac{S_{NH_4^+-N}}{1 + K_{D,NH_3} \cdot 10^{-pH}} \tag{10.28}$$

with:

$$K_{D,NH_3-N} = \exp\left(\frac{6344}{273 + T}\right) \tag{10.29}$$

The concentration of HNO_2-N is described using a similar calculation method:

$$S_{HNO_2-N} = \frac{S_{NO_2-N}}{1 + K_{D,HNO_2} \cdot 10^{pH}} \tag{10.30}$$

with:

$$K_{D,HNO_2} = \exp\left(-\frac{2300}{273 + T}\right) \tag{10.31}$$

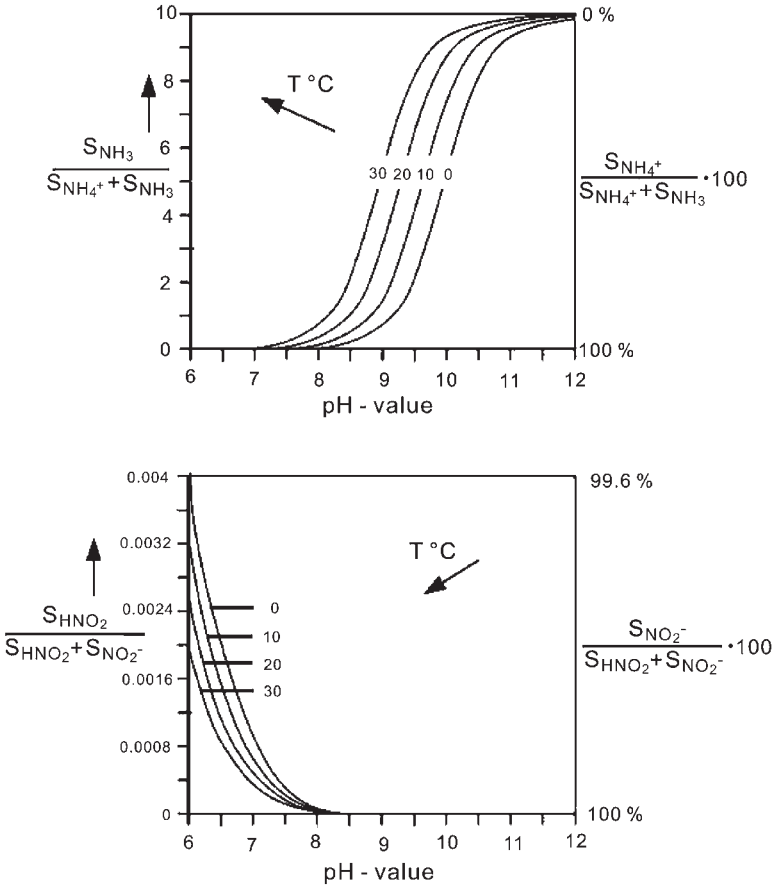

Fig. 10.3 Influence of the temperature and pH value on the dissociation equilibrium of NH_3 and HNO_2.

The dissociation equilibria of $NH_3/NH_4^+ + S_{NH_4}$ and $HNO_2/NO_2^- + S_{HNO_2}$ with regard to the influence of temperature and pH are presented in Fig. 10.3.

It is very important to recognize that S_{NH_3} increases and S_{HNO_2} decreases with increasing pH.

A kinetic description of nitrification is proposed based on Haldane kinetics. Both equations are valid for ammonium and nitrite-rich wastewater where both ammonium and nitrite oxidations are inhibited by substrate surplus (see Eq. 10.32 and Eq. 10.33).

$$\mu_{NS} = \mu_{max,NS} \cdot \frac{S_{NH_3-N}}{K_{S,NH_3} + S_{NH_3-N} + \frac{S^2_{NH_3-N}}{K_{iH,NS}}} \cdot \frac{c'}{K'_{NS} + c'} \tag{10.32}$$

$$\mu_{NB} = \mu_{max,NB} \cdot \frac{S^3_{HNO_2-N}}{K_{S,HNO_2} + S_{HNO_2-N} + \frac{S^2_{HNO_2-N}}{K_{iH,NB}}} \cdot \frac{c'}{K'_{NB} + c'} \tag{10.33}$$

For higher values of $S^3_{NH_3-N}$ (higher pH) or $S^3_{HNO_2-N}$ (lower pH) the reactions are inhibited.

For lower values of S_{NH_3-N} or S_{HNO_2-N}, e.g. in municipal wastewater treatment plants, the inhibition according to Haldane kinetics can be neglected. Oxygen limitation can be disregarded for $c' \gg K'$. According to these assumptions, Eqs. (10.32) and (10.33) result in simplified kinetic descriptions which are used for nitrification in the WWTP loaded with a low ammonia and nitrite concentration, respectively:

$$\mu_{NS} = \mu_{max,NS} \cdot \frac{S_{NH_3-N}}{K_{S,NS} + S_{NH_3-N}} \tag{10.34}$$

$$\mu_{NB} = \mu_{max,NB} \cdot \frac{S_{HNO_2-N}}{K_{S,NB} + S_{HNO_2-N}} \tag{10.35}$$

Table 10.3 presents the kinetic and yield coefficients of nitrification.

Usually, ammonium oxidation to nitrite is regarded as the bottleneck of nitrification to nitrate. However at low pH, low c' and low temperature, the oxidation rate of NO_2^- is considerably lower than that of NH_4^+. NO_2^- accumulation can be observed (see Section 10.2.4). It is beneficial if NH_4^+ is oxidized only to NO_2^-, which is subsequently denitrified in biological nitrogen-removal systems. Nitrogen removal via the nitrite pathway is also an environmentally cleaner process which reduces the cost of aeration and carbon sources (e.g. methanol as an electron donor). Moreover, it has been reported that denitrification rates with nitrite are 1.5–2.0 times faster than with nitrate (Abeling and Seyfried 1992). The concept of nitrogen removal via nitrite accumulation will be explained in Section 10.2.4 in detail.

If CO_2 is added as the carbon source in effluents with low concentrations of organics resulting in low CO_2 formation, its concentration may be a rate-limiting factor, especially if high NH_4^+ concentrations are to be oxidized in higher pH regions (Green et al. 2002; Carrera et al. 2003).

Table 10.3 Kinetic and yield coefficients of autotrophic nitrification.

Reference	T (°C)	μ_{max} (h^{-1})	$K_{NH_4\text{-}N}$ (mg L^{-1} N)	K_{iH} (mg L^{-1} N)	K′ (mg L^{-1} O_2)	$Y^{\circ}_{X_{A/N}}$ [a]
NH_4 oxidation						
Knowles et al. (1965)	30	0.0822	0.084	–	–	–
Bergeron (1978)	25	0.0064	0.138	35	1.8	–
Nyhius (1985)	15–17	0.04	0.056	33	0.5	–
Dombrowski (1991)	20	0.0138	0.714	540	0.29	–
Wiesmann (1994)	20	0.032	0.028	540	0.3	0.147
Horn and Hempel (1996)	20–22	0.0063	0.5	–	0.5	0.062
Pirsing (1996)	25	0.038	0.03	200	0.3	0.142
Lindemann (2002)	22.5	0.0074	0.079	16.5	0.25	0.142
NO_2 oxidation						
Knowles et al. (1965)	30	0.058	$1.9 \cdot 10^{-4}$	–	–	–
Bergeron (1978)	25	0.005	$2.5 \cdot 10^{-4}$	35	1.4	–
Nyhius (1985)	15–17	0.016	$1.7 \cdot 10^{-4}$	0.15	0.75	–
Dombrowski (1991)	25	0.019	$0.39 \cdot 10^{-4}$	0.25	1.1	–
Wiesmann (1994)	20	0.045	$0.32 \cdot 10^{-4}$	0.26	1.1	0.042
Okabe et al. (1995)	20	0.034	$0.94 \cdot 10^{-4}$	–	0.68	0.083
Pirsing (1996)	25	0.041	$0.55 \cdot 10^{-4}$	0.1	1.3	0.048
Lindemann (2002)	22.5	0.019	$3.0 \cdot 10^{-4}$	0.26	1.27	0.048

[a] For NH_4 oxidation: g MLVSS (g NH_4-N)$^{-1}$; for NO_2 oxidation: g MLVSS (g NO_2-N)$^{-1}$.

10.2.2.3 Parameters Influencing Nitrification

There are several parameters which influence the ability of a population of nitrifying bacteria to perform nitrification, such as c′, pH, T, t_R and t_{RX}. Of all these parameters, c′ and pH are the most important.

Nitrifying bacteria are strict aerobes. The nitrification rate is limited entirely if oxygen is not supplied. Equations (10.32) and (10.33) show the influence of oxygen on the nitrification rate. For example, the region of oxygen limitation can be estimated using K'_{NB} = 1.1 mg L^{-1} O_2 (see Table 10.3). The point of limitation may be given as $\mu = 0.9\ \mu_{max}$ (90% of maximal growth rate) which is already reached at c′ = 9.9 mg L^{-1} O_2 (see also Eq. 6.11). This means that there is always a limiting effect of the oxygen concentration on the nitrification rate when aerating with air.

For effective nitrification, the amount of c′ maintained in the aeration tank should be monitored as a control parameter to ensure permanent effluent concentrations for NH_4^+, NO_2^- and NO_3^-. The practice of over-aeration is expensive and can even contribute to shearing of nitrifying bacterial flocs and/or enhance foam production.

A relationship between growth rate and pH was given by Eqs. (10.28) and (10.32) for ammonium oxidation and by Eqs. (10.30) and (10.33) for nitrite oxidation. The optimum pH for the growth of nitrifying bacteria is generally assumed to be pH 7.2–8.0, depending on S_{NH_4} (see Eq. 10.28). If the pH of the aeration tank drops

below pH 5.5 or goes above pH 9.0, a significant decrease in nitrification occurs as a result of protein damage. A low wastewater pH has the primary effect of inhibiting nitrifiers' enzymatic activity and has a secondary effect on the availability of alkalinity.

A drop in temperature results in a remarkable reduction in the growth rate of nitrifying bacteria. Some authors (Hopwood and Downing 1965; Knowles et al. 1965; Painter and Loveless 1983) described the temperature dependence of nitrification. To describe the influence of temperature on nitrification as well as denitrification, we use the Arrhenius equation for biochemical reactions (see Eq. 3.1).

The temperature dependence of the maximum growth rate during nitrification was already published by Knowles et al. (1965):

$$\mu_{max,NS} = 0.042 \exp(0.0351\,T - 2.174) \tag{10.36}$$

$$\mu_{max,NB} = 0.042 \exp(0.0587\,T - 1.13) \tag{10.37}$$

The nitrification rate is a function of temperature between 8 °C and 30 °C. Low wastewater temperatures in winter negatively affect the nitrification. Therefore, many regulatory agencies in temperate regions have different ammonia discharge limits according to the season.

Figure 10.4 shows the optimal range of nitrification with respect to the growth rate of nitrifying bacteria in relation to pH and temperature (Larsen-Vefring 1993).

Excursions to low temperatures, temporary and long-term drops in c′ and/or extreme pH values lead to incomplete nitrification which results in operational disruptions.

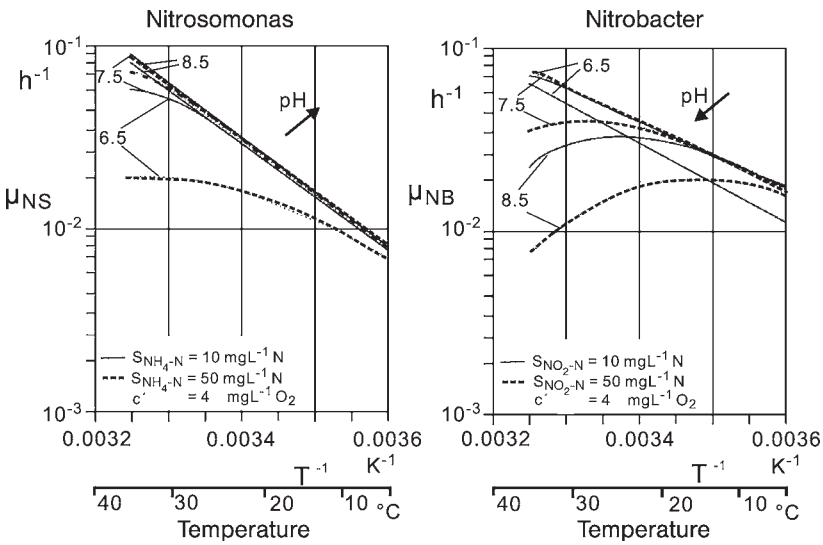

Fig. 10.4 Specific growth rate of nitrifying bacteria in relation to pH and temperature (Larsen-Vefring 1993, calculated).

Table 10.4 Operational parameters influencing nitrification.

Parameters	Optimal range/value and comments
c'	2–3 mg L^{-1} O_2, c' limits nitrification
pH	pH 7.2–8.0, pH <5.5 and >9.0 critical
Temperature	T = 28–32 °C, T <5 °C and >40 °C critical
S_{NH3}	Inhibits *Nitrosomonas* >10 mg L^{-1}, *Nitrobacter* >0.1 mg L^{-1}
S_{HNO2}	Inhibits *Nitrosomonas* and *Nitrobacter* >1.0 mg L^{-1}
S_{NH4}	inhibits nitrification > 400–500 mg L^{-1}
t_{RX}	> 4–6 days, increases with decreasing temperature
t_R	> 10 h at low temperatures
X	> 2 g L^{-1} MLVSS
Ratio of FM[a)]	~ 0.5 g NH_4-N (g MLVSS)$^{-1}$ recommended

[a)] Ratio of feed to biomass.

Table 10.4 summarizes the operational parameters favoring nitrification. Generally, increasing T, t_R, S_N and a sufficiently high t_{RX} are beneficial for nitrifying bacteria. They result in sufficient MLVSS. A sludge age of t_{RX} > 4–6 days is needed to achieve nitrification. The presence of healthy and adequate nitrifying bacteria is the basic requirement for successful nitrification. The influences of t_R and t_{RX} on removal or removal rate are discussed in Chapter 6.

10.2.3 Denitrification

10.2.3.1 Denitrifying Bacteria and Stoichiometry

Denitrifying bacteria are capable of removing oxidized nitrogen from wastewater by converting it to N_2 gas which escapes to the atmosphere. Most denitrifying organisms are facultative aerobic chemoorgano-heterotrophic bacteria which make up approximately 80% of the bacteria within an activated sludge environment. Under anoxic conditions nitrite and nitrate serve as electron acceptors instead of O_2 and organic substrates as electron donors for ATP production at very low oxygen concentration.

Denitrifying bacteria are common soil and water microorganisms and are associated with fecal waste. They enter an activated sludge process as fecal organisms in domestic wastewater and use free molecular oxygen if it is available. The energy produced with O_2 as the electron acceptor is only 7% more than with NO_2^- and NO_3^- if the same C source is used (McKinney and Conway 1957).

Besides heterotrophic denitrification, denitrification can also be performed by chemolitho-autotrophic bacteria with H_2 or with reduced sulfate compounds as electron acceptors (Lompe 1992; Beller et al. 2004). Kuai and Verstraete (1998) showed the occurrence of oxygen-limited autotrophic nitrification–denitrification. The reduction of NO_2^- and NO_3^- to gases such as NO, N_2O or N_2 in suspended sludge or biofilm under low c' and/or anoxic condition is possible, even in the ab-

sence of organic carbon as endogeneous denitrification (Bernet et al. 2001). Autotrophic denitrification is used in some waterworks for treating groundwater containing NO_3^-/NO_2^- (Lompe 1992). We will not discuss these processes here.

There are five main nitrogenous compounds in denitrification (see Eq. 10.38). Nitrate is the initial substrate for denitrification and molecular N_2 is the end-product. Other intermediates like NO and N_2O can be emitted if incomplete denitrification occurs due to very high nitrate concentrations and relatively low organic substrate concentrations (Sümer et al. 1996).

$$NO_3^- \xrightarrow{1} NO_2^- \xrightarrow{2} NO \xrightarrow{3} N_2O \xrightarrow{4} N_2 \tag{10.38}$$

The reduction of NO_3^- is carried out by one organism in four steps. Each step can conditionally be inhibited; and intermediate products can escape by being dissolved in water and by being subsequently desorbed and transported by mass transfer into gas bubbles and then into the air. The kinetics of the intermediate steps are still not known in detail. Until now, no exact nitrogen balance has been able to show how much NO and N_2O are built. It is very important to balance exactly by measurements, but it is very difficult to perform.

Nearly all denitrifiers are able to use NO_2^- and NO_3^-. The catabolism of denitrification that provides two growth- and energy-yielding steps is described in simplified form using methanol as the energy source (Halling-Sørensen and Jørgensen 1993; Lawrence and McCarty 1969):

$$6NO_3^- + 2CH_3OH \rightarrow 6NO_2^- + 2CO_2 + 4H_2O \tag{10.39}$$

$$6NO_2^- + 3CH_3OH \rightarrow 3N_2 + 3CO_2 + 3H_2O + 6OH^- \tag{10.40}$$

$$6NO_3^- + 5CH_3OH \rightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^- + \Delta G^0 \tag{10.41}$$

with $\Delta G^0 = -783$ kJ mol^{-1}.

However, this is in contrast to aerobic catabolism, during which the hydroxyl ion is not produced:

$$3O_2 + 2CH_3OH \rightarrow 2CO_2 + 4H_2O \tag{10.42}$$

The organic substrate is completely oxidized to CO_2 and H_2O. The produced OH^- (see Eqs. 10.40 and 10.41) is alkaline; and some of the CO_2 produced is returned to the nitrification tank. The ion is compensated in part or completely depending on NH_4^+ influent concentration and is consumed during nitrification of soft water.

In order to maintain adequate alkalinity in the activated sludge, various chemicals or alkalics can be added to the water. These chemicals include bicarbonates (HCO_3^-), carbonates (CO_3^{2-}) and hydroxides (OH^-) of calcium, magnesium and sodium. The following chemicals for buffering alkalinity are commonly added: sodium bicarbonate ($NaHCO_3$), calcium carbonate ($CaCO_3$), sodium carbonate (Na_2CO_3), calcium hydroxide ($Ca(OH)_2$) and sodium hydroxide (NaOH). Sometimes this is not needed if, for example, hard water such as the water from Berlin (Beelitzhof) is being treated, which has a total hardness of 15.3 °dH and a carbonate hardness of 10.8 °dH (BWB 2004).

10.2.3.2 Stoichiometry and Kinetics of Denitrification

Nearly all organics can be used as substrate. For this discussion of stoichiometry for catabolism and anabolism methanol is suitable. Related to one C atom of methanol, we can write (Lawrence and McCarty 1969):

$$0.926\,NO_3^- + CH_3OH + 0.22\,H_2CO_3 \rightarrow 0.051\,C_5H_7O_2N + 0.435\,N_2 + 0.926\,HCO_3^- + 1.56\,H_2O \quad (10.43)$$

$$1.49\,NO_2^- + CH_3OH + 0.79\,H_2CO_3 \rightarrow 0.059\,C_5H_7O_2N + 0.72\,N_2 + 1.49\,HCO_3^- + 1.84\,H_2O \quad (10.44)$$

In accordance with Eq. (10.13), the substrate utilization and denitrification rates are calculated as:

$$r_{NO_3\text{–}N} = \frac{\mu X}{Y^{\circ}_{XC/NO_3\text{–}N}} \quad (10.45)$$

$$r_{SD} = \frac{\mu X}{Y^{\circ}_{XC/SC}} \quad (10.46)$$

The corresponding equations for NO_2 can be obtained.

From Eq. (10.43) the true yield coefficients $Y^{\circ}_{XC/SC}$ and $Y^{\circ}_{SC/NO_3\text{–}N}$ follow:

$$Y^{\circ}_{XC/SC} = \frac{0.051\,M_{XC}}{M_{SC}} = \frac{0.051 \cdot 12 \cdot 5\ g\ mol^{-1}\ C_5H_7O_2N\text{–}C}{1.0 \cdot 12\ g\ mol^{-1}\ CH_3OH\text{–}C} = 0.255\,\frac{gXC}{gSC} \approx 0.51\,\frac{gMLVSS^{1)}}{gDOC} \quad (10.47)$$

$$Y^{\circ}_{SC/NO_3\text{–}N} = \frac{M_{SC}}{0.926\,M_{NO_3\text{–}N}} = \frac{1.0 \cdot 12\ g\ mol^{-1}\ CH_3OH\text{–}C}{0.926 \cdot 14\ g\ mol^{-1}\ NO_3\text{–}N} = 0.89\,\frac{gSC}{gNO_3\text{–}N} \quad (10.48)$$

From Eq. (10.47) and Eq. (10.48), then Eq. (10.49) follows:

$$Y^{\circ}_{XC/NO_3\text{–}N} = Y^{\circ}_{XC/SC} \cdot Y^{\circ}_{SC/NO_3\text{–}N} = \frac{gXC}{gNO_3\text{–}N} \approx 0.454\,\frac{gMLVSS}{gNO_3\text{–}N} \quad (10.49)$$

and, respectively, for NO_2 from Eq. (10.44):

$$Y^{\circ}_{XC/NO_3\text{–}N} = Y^{\circ}_{XC/SC} \cdot Y^{\circ}_{SC/NO_2\text{–}N} = \frac{gXC}{gNO_3\text{–}N} \approx 0.34\,\frac{gMLVSS}{gNO_3\text{–}N} \quad (10.50)$$

[1)] It is assumed that the MLVSS consists of 50% carbon.

Table 10.5 Kinetic and yield coefficients of heterotrophic denitrification (Wiesmann 1994).

Symbol	Unit	NO_3 reduction	NO_2 reduction
μ_{max}	d^{-1}	2.6	1.5
$Y^{o}_{X/S}$	g MLVSS (g DOC)$^{-1}$	1	1
$Y^{o}_{X/N}$	g MLVSS (g NO_X-N)$^{-1}$	1.2	0.8
k_d	d^{-1}	0.1	0.1
K_S	mg L^{-1} DOC	62.5	–
$K_{NO_X\text{-}N}$	mg L^{-1} NO_X-N	≤ 0.14	≤ 0.12

Thus, 0.454 g MLVSS is produced for 1 g NO_3-N removed by denitrification; and 25.5% of the CH_3OH-C is used for anabolism and 74.5% for catabolism (see Eq. 10.49). However, the production of biomass depends on substrate used, resulting in different $Y^{o}_{X/N}$. Denitrifying bacteria can use most organic compounds commonly found in domestic wastewater. Several organic substrates such as methanol, acetic acid, ethanol, glucose, molasses or a part of the influent wastewater are often added to a denitrification tank if post-denitrification is run (see Section 10.4.2).

Table 10.5 presents some kinetic and yield coefficients of denitrification.

The specific growth rate of bacteria is influenced by both the concentration of the organic substrate and the concentration of NO_2^- or NO_3^-. The kinetics of denitrification can be described by a double Monod kinetic model and an additional term to include the inhibiting effect of dissolved O_2 concentration on denitrification for NO_3^- (Batchelor 1982; IAWPRC 1986):

$$\mu_{NO_3\text{–}N} = \mu_{max,NO_3\text{–}N} \frac{S}{K_S + S} \cdot \frac{S_{NO_3}}{K_{NO_3} + S_{NO_3}} \cdot \frac{K_{iO_2}}{K_{iO_2} + c'} \tag{10.51}$$

and for NO_2^-:

$$\mu_{NO_2\text{–}N} = \mu_{max,NO_2\text{–}N} \frac{S}{K_S + S} \cdot \frac{S_{NO_2}}{K_{NO_2} + S_{NO_2}} \cdot \frac{K_{iO_2}}{K_{iO_2} + c'} \tag{10.52}$$

Note that all three saturation coefficients can differ if different substrates are used.

10.2.3.3 Parameters Influencing Denitrification

From the kinetic observation in Eqs. (10.51) and (10.52) it can be seen that denitrification needs certain favorable conditions, such as the presence of organic substrate, very low c′ ($c' \approx 0$), correct pH and T.

Sufficient organic substrate is one of the main control parameters for denitrification. From Eq. (10.48) the optimal ratio of organic carbon to nitrate is approximately $Y^{o}_{SC/NO_3\text{-}N}$ = 0.89 g DOC (g NO_3-N)$^{-1}$ where complete denitrification is possible. For lower ratios, the NO_3 effluent concentration is increased. The value for NO_2 is somewhat lower at $Y^{o}_{SC/NO_2\text{-}N}$ = 0.58 g DOC (g NO_2-N)$^{-1}$. This is one of the advantages of nitrification via NO_2 accumulation (see Section 10.2.4). A high denitrification rate can be achieved if the concentration of readily biodegradable organic matter is controlled.

Free molecular oxygen inhibits denitrification because the oxygen suppresses the formation of the enzyme nitrate reductase (Payne 1973). Wheatland et al. (1959) found that the denitrification rate at $c' = 0.2$ mg L^{-1} was about one-half of the rate at $c' = 0$ mg L^{-1} ($K_{iO} = 0.2$ mg L^{-1} O_2).

Denitrification results in an increase in the alkalinity. The OH^- produced in Eqs. (10.40) and (10.41) is used for building H_2O with the H^+ produced during nitrification. Denitrification can occur over a wide range of pH values. Most studies show the highest rates of denitrification occurring at pH 7.0–7.5 (Halling-Sørensen and Jørgensen 1993).

The growth rate of the organism and removal rate of nitrate are both affected by temperature. For wastewater below 5 °C, denitrification is highly limited because biological metabolism is too slow. Table 10.6 summarizes the operational factors favoring denitrification.

Within a redox potential range of +50 mV to –50 mV, oxygen is either absent or present only at a relatively small concentration. Above +50 mV, aerobic conditions dominate.

If it is possible for the carbon source for denitrification to be depleted, endogenous denitrification can occur. Adam (2004) observed a constant denitrification rate over a long time (>30 h) in a post-denitrification process without Bio-P organisms. This means that the kind of carbon source was not changed and/or depleted during this experiment. This is a typical characteristic of endogenous denitrification. Based on Eq. (10.51), r_{NO_3} can be described to reflect endogenous respiration:

$$r_{NO_3} = \mu_{NO_3-N} X + k_e X \approx k_e X \tag{10.53}$$

where: $\mu_{NO_3-N} X \approx 0$

Endogenous denitrification rates are normally lower than when using external carbon sources. However, if the bacterial concentration in the anoxic zone is increased, the denitrification rate increases as a result (Adam 2004). The increase in ammonium concentration and decrease in bacterial concentration could be observed during endogenous denitrification and bacterial lysis.

Table 10.6 Operational parameters influencing denitrification.

Parameters	Optimal range/value and comments
Organic carbon	Main control parameter, ratio of 3 : 1 (organics as COD to NO_2 and NO_3) is optimal for complete denitrification, and above 3:2 causes increase in NO_2 and NO_3.
c'	Inhibits denitrification, obvious inhibition of denitrification at $c' > 0.2$ mg L^{-1} O_2.
pH	Affects enzymatic activity of denitrifying bacteria, 7.0 < pH optimum <7.5.
Temperature	Denitrification rate increases with increasing T, until T=35 °C; very low rate below 5 °C.
Redox potential	+50 to –50 mV, above +50 mV aerobic conditions dominate.

10.2.4
Nitrite Accumulation During Nitrification

Nitrite is accumulated under certain process conditions which promote the ammonium oxidation rate to a point that it exceeds the nitrite oxidation rate. Finding and optimizing these process conditions are the key points for nitrite accumulation. The following parameters are favorable for high nitrite concentrations:

- Limited dissolved oxygen concentrations due to a lower $K'_{NS} = 0.3$ mg L^{-1} O_2 for *Nitrosomonas* compared with $K'_{NB} = 1.1$ mg L^{-1} O_2 for *Nitrobacter* (see Table 10.3).
- Controlling the pH to obtain certain concentration levels of HNO_2 and NH_3 (see Section 10.2.2.2).
- Higher temperature favors *Nitrosomonas* (T = 28–35 °C; see Section 10.2.5).

The different K′ values of *Nitrosomonas* and *Nitrobacter* (Dombrowski 1991; Wiesmann 1994; Pirsing 1996) show that nitrite oxidation to nitrate is more limited at low oxygen concentrations than ammonium oxidation. In aerobic biofilm reactors with high biomass concentrations, the conversion rate is usually limited by the oxygen transfer from liquid to biofilm (see Chapter 7). The limited oxygen transfer to a biofilm causes a very low dissolved oxygen concentration at the surface of the biofilm, so that the nitrite oxidation to nitrate is limited more effectively due to the lower K′ values of *Nitrosomonas* compared to *Nitrobacter*. To take advantage of this characteristic, most research done on nitrite accumulation has centered on biofilm reactors (Abeling and Seyfried 1992; Garrido et al. 1997; Bernet et al. 2001; Antileo et al. 2003).

In some cases the oxidation of ammonia stops at the nitrite stage, even though c′ is high enough not to limit nitrite oxidation. This can be explained by the fact that nitrite accumulation is also linked to inhibition by ammonia. Anthonisen et al. (1976) found that ammonia inhibition of *Nitrosomonas* first becomes evident at concentrations of 8–124 g m^{-3} NH_3-N (see Eq. 10.28), while the selective inhibition of *Nitrobacter* by HNO_2 already occurs at concentrations of 0.1–1.0 g m^{-3} NH_3-N.

By using both the characteristics of low oxygen concentration and the different ammonia inhibitions of *Nitrosomonas* and *Nitrobacter*, 74% nitrite accumulation was observed in a suspended membrane bioreactor (Choi 2005).

Figure 10.5 shows the schematic of nitrification and denitrification for achieving nitrite accumulation.

Sustained nitrite accumulation via the nitrite pathway ($NH_4^+ \rightarrow NO_2^- \rightarrow N_2$) offers several benefits for nitrogen removal of wastewater, compared to the nitrate pathway ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^- \rightarrow NO_2^- \rightarrow N_2$):

- faster kinetics of the nitrification and denitrification processes,
- up to 25% energy savings during aeration,
- up to 40% savings from reduced demand for organic substrate,
- a higher rate of denitrification,
- lower biomass production (up to one third of former amount).

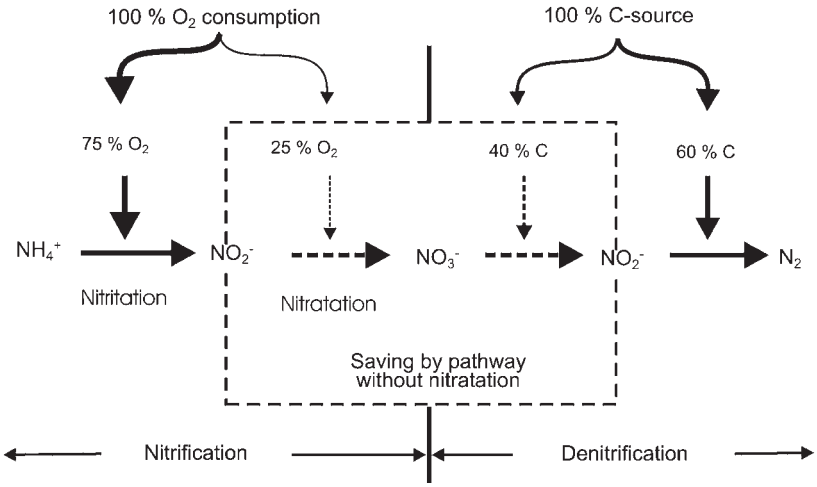

Fig. 10.5 Schematic for the accumulation of nitrite by nitrification and denitrification.

As disadvantages it can be mentioned:

- nitrification must be operated and controlled precisely,
- automatic measurement of NO_2 concentration in effluent of the anoxic step results in increasing operating costs.

10.2.5
New Microbial Processes for Nitrogen Removal

The ANAMMOX process – an acronym for *an*aerobic *amm*onium *ox*idation – has been described as a new way for biological nitrogen removal. Certain chemolithoautotrophic bacteria are capable of oxidizing the electron donor ammonium to nitrogen gas, with nitrite as the electron acceptor under anoxic conditions (Mulder 1992; Mulder et al. 1995; Jetten et al. 1998; Helmer et al. 2001):

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O + \Delta G^0$$

where: $\Delta G^0 = -359$ kJ ... -380 kJ $(\text{mol } NH_4^+)^{-1}$

The bacteria belong to the rare order of the Planctomycetes, of which *Planctomyces* and *Pirellula* are the most important members. Current genera are *Brocadia* and *Kuenenia* (both freshwater species) and *Scalindua* (marine species). The bacteria catalyzing the ANAMMOX reaction are autotrophic, which means the conversion of nitrite to N_2 proceeds without the use of organic carbon. The process is characterized by low sludge production and a substantial reduction in aeration energy by 60% and chemicals for neutralization. The net CO_2 emissions are strongly reduced. The cost reduction compared to conventional N removal should be considerable (Van Dongen et al. 2001).

The SHARON process (acronym for *s*ingle reactor system for *h*igh activity *a*mmonia *r*emoval *o*ver *n*itrite) was conceived to promote biological nitrogen removal over nitrite in concentrated wastewater (Van Dongen et al. 2001) and provides several advantages (see Section 10.2.2). Its pH control is very important. Nitrite oxydation can be inhibited in regions of lower pH (higher HNO_2 concentration) and limited in regions of lower oxygen concentration (Van Kempen et al. 2001). The process is operated at high temperatures (>25 °C), which selectively promote the fast-growing ammonium oxidizers, while *Nitrobacter* can be washed out of the system. It is characterized by a complete absence of sludge retention ($t_{RX} = t_R$), because the growth and washout of sludge are in equilibrium (Hellinga et al. 1998; Van Kempen et al. 2001).

Processes based on this autotrophic nitrogen removal concept have been described and investigated intensively in a sequencing batch reactor SBR (Strous et al. 1998; Fux et al. 2002), in a continuous flow moving-bed pilot plant (Helmer et al. 2001), in a fluidized-bed reactor (Van de Graaf et al. 1996) and in suspended SHARON–ANAMMOX systems (Hellinga et al. 1998; Van Dongen et al. 2001). This combined new way for nitrogen elimination can be applied technically to industrial wastewater with high ammonium concentrations but no DOC.

Cost estimates for the classic method of autotrophic nitrification/heterotrophic denitrification and for partial nitritation/autotrophic anaerobic ammonium oxidation (ANAMMOX) with anaerobic sludge digestion demonstrate that partial nitritation/ANAMMOX is more economical than classic nitrification/denitrification (Fux and Siegrist 2004). A full-scale cost estimation of different techniques for N removal from rejection water was carried out based on STOWA (1996) for WWTP capacity of 500 000 inh.

10.3 Biological Phosphorus Removal

10.3.1 Enhanced Biological Phosphorus Removal

Enhanced biological phosphorus removal in activated sludge systems was first reported in the late 1960s (Vacker et al. 1967). *Acinetobacter* sp. and especially the strain *L. woffii* were identified as the organisms responsible for accumulating excess phosphates in their cells, if they have short-chain volatile fatty acids (VFAs) available, especially acetate, as feed stock (Fuhs and Chen 1975).

Biological phosphorus removal is realized by creating conditions favorable for the growth of phosphate-accumulating organisms (PAOs). An initial anaerobic zone allows the PAOs to take up VFAs into their cells and store them as poly-β-hydroxybuterate (PHF). The polyphosphate stored just prior to this is oxidized and used as an energy source, producing ATP; and it is thereby released into the liquid phase (Fig. 10.6). The anaerobic uptake of organic matter is inherently related to the accumulated polyphosphate.

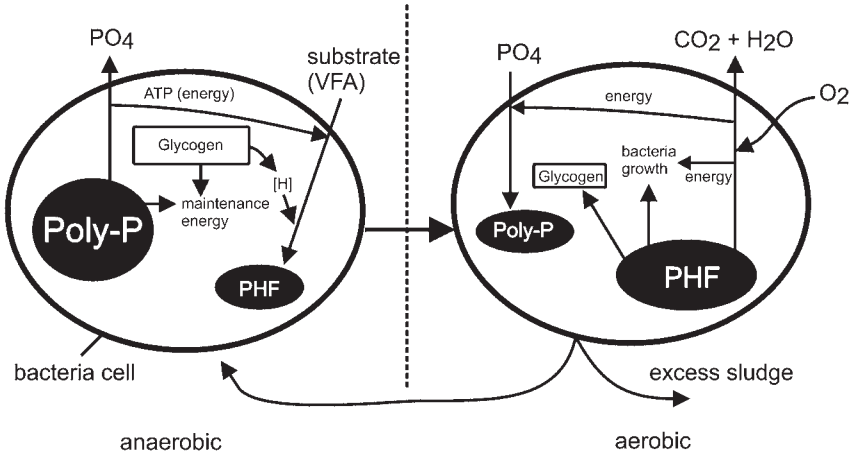

Fig. 10.6 Mechanism of enhanced biological phosphorus removal; shown is each time the beginning of the process (Wentzel et al. 1991).

After the mixed liquor reaches the aerobic zone, the stored PHF is used by the PAOs for cell growth and to provide energy for reforming polyphosphate from all the available orthophosphate and also for the synthesis of polyglucose (glycogen). By going through both anaerobic and aerobic conditions, PAOs are adequately established and become predominant in the biomass community after several weeks. The PAO's are the only bacteria being able to store substrate in a first anaerobic reactor and to oxidize them in a second aerobic reactor. This is only possible by enrichment of the Poly–P storage. This enrichment of the PAOs containing a high concentration of polyphosphate leads to the establishment of biological phosphorus removal. The net elimination of the process results from the bacterial cell growth and the removal of surplus sludge at the point when the phosphate is taken up to a higher level than that released in the anaerobic stage (see Fig. 10.7, below).

10.3.2 Kinetic Model for Phosphorus Removal

10.3.2.1 Preliminary Remarks

Obtaining kinetic and stoichiometric information requires that we make some assumptions, as follows:

- the reactors are operated as CSTRs (see Section 6.2.2),
- the process is in steady state,
- acetate is used as the substrate.

The biochemical pathway of the organic substrate metabolism is closely associated with polyphosphate storage. There is an apparent relationship between two parameters: organic substrate and polyphosphate. Substrate uptake and phosphorus release in the anaerobic phase can be described by the balances of acetate and PO_4-P (Fig. 10.7).

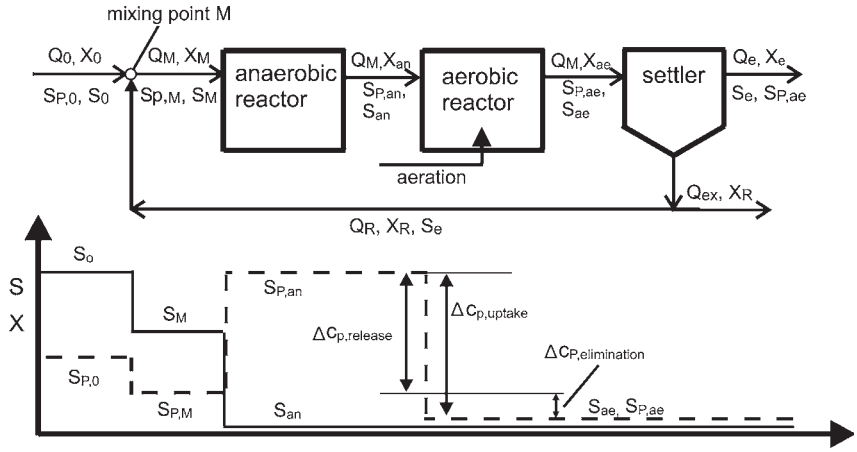

Fig. 10.7 Two-stage biological phosphorus removal in CSTR (AO process, Phoredox) with concentration profiles for phosphorus and substrate.

The process diagram is expanded compared to Fig. 6.3 by installing an anaerobic reactor in front of the aerobic one.

10.3.2.2 Anaerobic Zone

The following balances are valid for an anaerobic CSTR volume V_{an}:

for acetate S:

$$0 = Q_M (S_M - S_{an}) - r_{S,an} V_{an} \tag{10.54}$$

for PO_4-P:

$$0 = Q_M (S_{P,M} - S_{P,an}) + \frac{r_{S,an}}{Y^o_{SC/PO_4-P}} V_{an} \tag{10.55}$$

for biomass X:

$$0 = Q_M (X_M - X_{an}) + \frac{r_{S,an}}{Y^o_{SC/XC}} V_{an} \tag{10.56}$$

with:

$$Y^o_{SC/PO_4-P} = \frac{S_M - S_{an}}{S_{P,an} - S_{P,M}} = \frac{S_M - S_{an}}{S_{PP,an} - S_{PP,M}} \tag{10.57}$$

and:

$$Y^o_{XC/SC} = \frac{X_{an} - X_M}{S_M - S_{an}} \tag{10.58}$$

where S_M is the concentration of acetate after mixing with returned sludge, S_{an} is the concentration of acetate in the anaerobic reactor, $S_{P,an}$ is the concentration of PO_4-P in the anaerobic reactor, $S_{P,M}$ is the concentration of PO_4-P after mixing with returned sludge, $r_{S,an}$ is the rate of acetate uptake, $S_{PP,an}$ is the concentration

of polyphosphate in bacterial cells in the anaerobic reactor and $S_{PP,M}$ is the concentration of polyphosphate in bacterial cells after mixing with returned sludge.

In order to determine $S_{P,an}$ with a known reactor volume V_{an} and flow rate Q_M, it is first necessary to know the dependency of the substrate conversion rate $r_{S,An}$ on the concentrations of acetate S_{an} and orthophosphate-P $S_{P,an}$ in the anaerobic stage. The specific maximum growth rate μ_{max} and yield coefficient $Y^{\circ}_{XC/SC}$ are replaced by the rate coefficient k. The modified double-Monod kinetics could be verified by experiments (Wentzel et al. 1987; Gao 1995; Romanski 1999):

$$r_{S,An} = \frac{\mu_{max}}{Y^{\circ}_{XC/SC}} X_{an} \frac{S_{an}}{K_S + S_{an}} \frac{n_{PP}}{K_{PP} + n_{PP}} \tag{10.59}$$

with:

$$n_{PP} = \frac{S_{PP,an}}{X_{an}} \tag{10.60}$$

If $n_{PP} = 0$, no substrate can be taken up. For $n_{PP} \gg K_{PP}$, the acetate uptake rate $r_{S,an}$ is only a function of S_{an} and X_{an}; and for $S_{an} \gg K_S$ it depends only on X_{an}.

10.3.2.3 Aerobic Zone

The following balances are valid for an aerobic CSTR volume V_{ae}:

for acetate S:

$$0 = Q_M (S_{an} - S_{ae}) - r_{S,ae} V_{ae} \tag{10.61}$$

for PO_4-P:

$$0 = Q_M (S_{P,an} - S_{P,ae}) - \frac{r_{S,ae}}{Y^{\circ}_{SC/PO_4-P}} V_{ae} \tag{10.62}$$

for biomass X:

$$0 = Q_M (X_{an} - X_{ae}) + \frac{r_{S,ae}}{Y^{\circ}_{SC/XC}} V_{ae} \tag{10.63}$$

with:

$$Y^{\circ}_{SC/PO_4-P} = \frac{S_{an} - S_{ae}}{S_{P,ae} - S_{P,an}} = \frac{S_{an} - S_{ae}}{S_{PP,ae} - S_{PP,an}} \tag{10.64}$$

and:

$$Y^{\circ}_{XC/SC} = \frac{X_{ae} - X_{an}}{S_{an} - S_{ae}} \tag{10.65}$$

In the aerobic zone, phosphorus uptake and substrate transformation rates are influenced by orthophosphate in the liquid phase and by the carbon source stored as PHB in bacterial cells. They are very closely connected with each other and it is assumed that the bacterial growth occurs based on intracellular PHB:

$$r_{P,ae} = \frac{\mu_{max}}{Y^{o}_{XC/PO_4-P}} X_{ae} \frac{S_{P,Ae}}{K_{P,Ae} + S_{P,Ae}} \frac{n_{PHB}}{K_{PHB} + n_{PHB}} \frac{c'}{K' + c'} \quad (10.66)$$

$$r_{S,ae} = -\frac{\mu_{max}}{Y^{o}_{XC/PHB}} X_{ae} \frac{S_{P,ae}}{K_{P,ae} + S_{P,ae}} \frac{n_{PHB}}{K_{PHB} + n_{PHB}} \frac{c'}{K' + c'} \quad (10.67)$$

with:

$$n_{PHB} = \frac{S_{PHB}}{X_{an}} \quad (10.68)$$

Note that the substrate is now stored as PHB inside the cells.

Various models have been developed for the biological phosphorus removal by several authors (Wentzel et al. 1986; Tsuno et al. 1987; Ante and Voß 1995; Gao 1995; Henze et al. 1995; Romanski 1999). But today there is no standard model to describe the kinetics of biological phosphorus removal. Its rate depends primarily on the concentration of polyphosphate-accumulating bacteria in both anaerobic and aerobic reactors and the concentrations in the Eqs. (10.59), (10.66) and (10.67). These equations have not been sufficiently validated and further investigations are needed.

10.3.3
Results of a Batch Experiment

Figure 10.8 shows concentration profiles of S and S_P in a batch experiment, presenting a net elimination of phosphorus (Romanski 1999).

In the anaerobic period, the obligatorily aerobic poly-P bacteria (PAOs) take up substrate (e.g. acetate) and store it as lipid reserve material (PHB). Simultaneous-

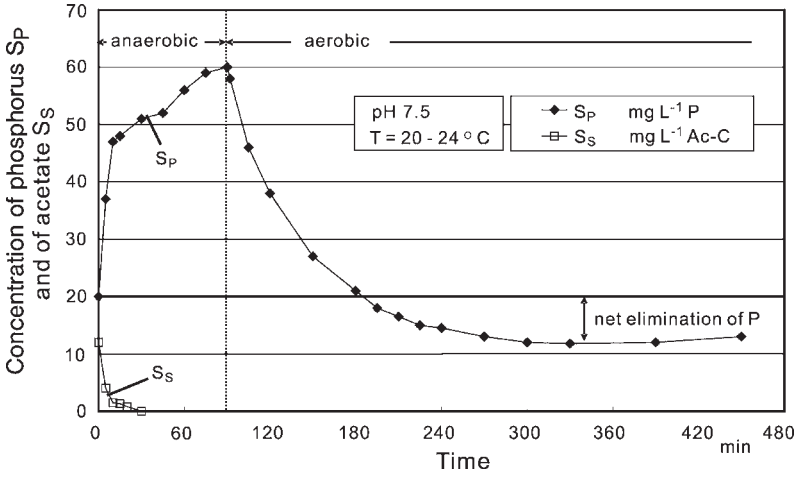

Fig. 10.8 Concentration profiles of S_S and S_P in a batch experiment (Romanski 1999).

ly, the polyphosphate in the cells is partly utilized as an energy source and is released, resulting in an increase in S_P from 20 mg L^{-1} to 60 mg L^{-1} PO_4-P, which is closely correlated with the synthesis of PHB. The polyphosphate is released with a high rate as long as the acetate exists. Afterwards, other substrates being formed by lysis of bacteria are partly converted into lower fatty acids, resulting in a slower P-release.

In the following aerobic phase, the orthophosphate is taken up into the bacterial cells while the PHB is utilized for growth. The orthophosphate concentration S_P decreases from the initial concentration of 20 mg L^{-1} at the beginning of the anaerobic batch test down to 12 mg L^{-1} PO_4-P. The difference of 8 mg L^{-1} PO_4-P is the net elimination of phosphorus. More phosphate is taken up aerobically than is released anaerobically because it is enriched in the biomass due to bacterial growth which is removed with the excess sludge.

10.3.4
Parameters Affecting Biological Phosphorus Removal

An adequate supply of VFAs is one of the key factors for successful biological phosphorus removal, due to its very strong relation to polyphosphate release or phosphate uptake. VFAs either are a part of the readily biodegradable substrate in the influent or are formed from it by fermentation in the anaerobic zone by facultative aerobic bacteria. In comparison, methanogenic bacteria are not able to grow in a system with changes from anaerobic to aerobic conditions.

If adequate dissolved oxygen is present, PAOs can grow in the aerobic zone at adequate rates. But the introduction of O_2 or NO_2 and NO_3 to the anaerobic zone should be minimized because it is used preferentially as a terminal electron acceptor, which reduces the amount of VFAs available for uptake by the PAOs (Hascoet and Florentz 1985). As a result, phosphate uptake in the aerobic zone is reduced.

The solid retention time t_{RX} must be adequate to allow PAOs to grow and can remarkably affect the phosphorus removal rate. Increasing the anaerobic t_{RX} will allow increased fermentation of organic matter, resulting in increased production of VFAs and total removal rate. A low hydraulic retention time t_R is beneficial in optimizing the process. The main parameters affecting biological phosphorus removal performance are summarized in Table 10.7.

Decreasing temperature in the anaerobic zone reduces the rate of fermentation. PAOs are less affected by decreasing pH than nitrifying bacteria are (US EPA 1993). Overall phosphate removal may fall with decreasing pH values because more energy is needed to take up acetates against a higher H^+ concentration, because the concentration of undissociated acetate decreases.

The phosphorus content of the bacteria n_{PP} may have a remarkable influence on the phosphorus removal rate because it is very closely linked to the capacity of PAOs for P release and uptake. The typical average n_{PP} value is 5–7% of the bacterial mass and values as high as 12–15% are obtained in some cases, depending on the process configuration. The n_{PP} for conventional activated sludge will typically range from 1.5% to 2.0% (Grady et al. 1999).

Table 10.7 Parameters affecting BPR process.

Parameters	Optimal range/value and comments
Concentration of VFAs[a)]	Adequate concentration of VFAs is beneficial. Low VFA concentration reduces the P release in anaerobic zone resulting in corresponding low P uptake in aerobic zone.
t_{RX}	t_{RX} = 1.0–1.5 d is recommended for a growing of PAOs.
c′	c′ limits the formation of VFAs because VFAs are properly formed under strictly anaerobic conditions.
Temperature	Low temperatures can reduce the formation of VFAs and the activity of PAOs.
pH	PAOs are less sensitive to pH changes than nitrifying bacteria. Decreasing pH adversely affects the P removal rate.
Presence of NO_3	NO_3 in anaerobic zone reduces P release resulting in decreasing P uptake in aerobic zone.
P content of MLSS	Very closely connected with capacity of PAOs for P-release and uptake.

[a)] Volatile fatty acids.

10.4 Biological Nutrient Removal Processes

10.4.1 Preliminary Remarks

Biological nutrient removal processes are modifications of the activated sludge process that combine anoxic and/or anaerobic zones with aerobic zones to provide nitrogen and/or phosphorus removal. Many configurations are possible, resulting in a wide range of performance capabilities and operational characteristics, which are presented in Table 10.8.

This section describes and discusses biological removal systems which provide removal of either nitrogen or phosphorus, or both components.

10.4.2 Nitrogen Removal Processes

The primary process for biological nitrogen removal consists of an aerobic stage for nitrification and an anoxic stage for denitrification. Figure 10.9a shows a two-stage biological nitrogen removal system (Ludzack and Ettinger 1962) called a modified Ludzak–Ettinger (MLE) process. They were the first to propose a single sludge nitrification–denitrification process using biodegradable organics in the influent wastewater.

Table 10.8 Characteristics of different zones in the biological nutrient removal process.

Zone	Biochemical transformation	Function	Removed component
Anaerobic	Phosphorus release	Enrichment of PAOs[a)]	Phosphorus
	Formation of readily biodegradable organic matter by fermentation		Carbon
	Uptake and storage of volatile fatty acids by PAOs		
Anoxic	Denitrification	Reduction of NO_3-N to N_2	Nitrogen
	Metabolism of exogenous substrate by facultative heterotrophs	Selection of denitrifying bacteria	Carbon
	Production of alkalinity	Uptake of PO_4[b)]	Phosphorus
Aerobic	Nitrification	Oxidation of NH_4-N to NO_2-N and/or NO_3-N	Nitrogen
	Consumption of alkalinity	Nitrogen removal via gas stripping	
	Phosphorus uptake	Formation of polyphosphate	Phosphorus
	Metabolism of stored and exogenous substrate by PAOs	Uptake of PO_4[c)]	
	Metabolism of exogenous substrate by heterotrophs		Carbon

[a)] Phosphate-accumulating organism.
[b)] In the presence of easily biodegradable organics, nearly all the PO_4-P is taken up.
[c)] If all the easily biodegradable organics are used in the anoxic stages without complete PO_4-P uptake, additional PO_4-P is removed within the aerobic stage using organic lysis product.

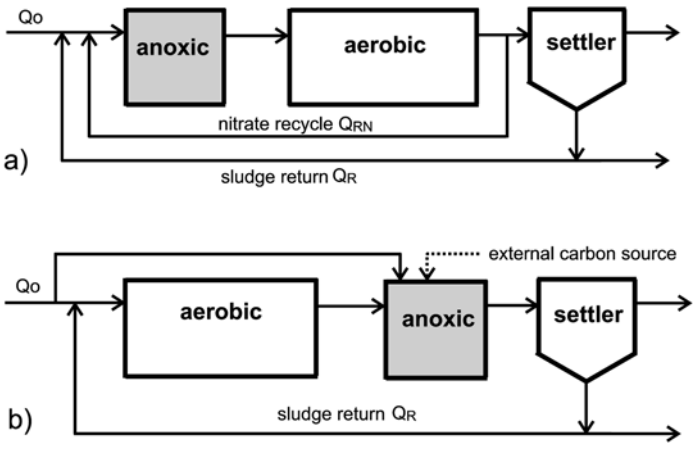

Fig. 10.9 Biological nitrogen removal process for (a) pre-denitrification and (b) post-denitrification.

The anoxic stage for denitrification is located in front of the aerobic stage where NO_3^- is formed. Both recycle streams Q_{RN} and Q_R have the target effluent amount of nitrate which restrains the possible amount of the denitrification. The real effluent nitrogen concentration is determined by the total nitrogen influent concentration to the process and the relation of total recycle flow Q_{Rt} to the influent flow Q_0 as n_{RN}.

It is advantageous that the organic matter contained in the wastewater is consumed while no additional organic substrate is added. One drawback of this process is the remaining NO_3^- which is discharged after formation because a typical maximum recycle flow rate is $Q_{RN} \approx 5\,(Q_0 + Q_R)$. At higher Q_{RN}, the energy consumption for pumping is too high, resulting in high operational costs without a noticeable increase in N removal. This process enables excellent nitrification and a good degree of denitrification down to $S_N \approx 4$–8 mg L^{-1} N_t. In order to increase removal efficiency down to effluent levels of $S_N < 3.0$ mg L^{-1} N_t, the MLE process was developed further, yielding the four-stage Bardenpho process by Bardard (1973). It involves the expansion of the process by a secondary anoxic and a small aerobic reactor.

In contrast to the MLE process (Fig. 10.9a), the aerobic zone is located in front of the anoxic zone (Fig. 10.9b). To use the biodegradable organic matter in the wastewater, a part of the influent bypasses the first stage and is introduced to the anoxic stage. Only the sludge is returned to the initial aerobic process. The energy consumption for pumping Q_{RN} is saved. If in some cases sufficient organic matter is not present in the influent or in the effluent from the aerobic nitrifying stage, a supplemental N-free carbon source, such as methanol or acetate, is added to the anoxic stage. This configuration may be useful if the price of added supplemental substrate is low and very low NH_4 concentrations are required. This configuration can be expanded beyond the anoxic stage by a smaller aerobic zone to remove the remaining carbon and NH_4 (in the case of a bypass of wastewater) from the anoxic stage. The addition of a supplemental N-free carbon source results in an improvement in the process efficiency, but increases chemical costs.

10.4.3 Chemical and Biological Phosphorus Removal

Before discussing the biological P removal process, we will briefly explain chemical P elimination by precipitation. The main part of phosphorus in domestic wastewater is orthophosphate PO_4-P (Fig. 10.1). It can be separated from wastewater by precipitation with Al^{3+} and Fe^{3+} salts. Mostly two different processes are used: simultaneous precipitation occurs in the aerobic tank of an activated sludge plant, where Fe^{3+} is produced by the very fast oxidation of the cheaper Fe^{2+}. If $FeSO_4$ is applied, we write:

$$PO_4^{3-} + FeSO_4 \rightarrow FePO_4 \downarrow + SO_4^{2-} + e^- \qquad (10.69)$$

The insoluble $FePO_4$ forms flocs mostly inside the activated sludge particles and can be separated as excess sludge.

In some northern countries, post-precipitation is preferred behind the secondary clarifier, using a reactor for precipitation and a settler for floc separation. The reactor is not aerated. Therefore instead of Fe^{2+} salts, Al^{3+} and Fe^{3+} salts are applied. If $Fe_2(SO_4)_3$ is used, we write:

$$2PO_4^{3-} + Fe_2(SO_4)_3 \rightarrow 2FePO_4 \downarrow + 3SO_4^{2-} \quad (10.70)$$

To obtain larger flocs with higher settling rate, polymers as flocculation aids are added.

As shown in Table 10.1, dissolved inorganic polyphosphates and organic phosphorus as well as particulate phosphorus are further components of municipal wastewater. They can only be separated partly by adsorption and co-precipitation.

The anaerobic and aerobic (or oxic) process (AO process, also called Phoredox) is a method for biological phosphorus removal (see Fig. 10.7). The placement of an anaerobic reactor in front of the conventional activated sludge process leads to the use of influent organic matter for the anaerobic formation of PHB. High rates of phosphorus removal are obtained by minimizing nitrification and maximizing the production of poly-P-storing bacteria. High solids production is beneficial if usage in agriculture is planned because the production of high phosphorus content biomass is maximized. The anaerobic zone is contained in the main process stream and is thus regarded as a mainstream biological phosphorus removal process.

10.4.4 Processes for Nitrogen and Phosphorus Removal

10.4.4.1 Different Levels of Performance

Many configurations have been developed as combined processes for biological nitrogen and phosphorus removal, including anaerobic, anoxic and aerobic zones. Due to the negative influence of nitrate on phosphorus removal, recycling of the nitrate into the anaerobic zone should be minimized and controlled; it is a key consideration in the selection and design of these processes.

The AAO process (Fig. 10.10a) is a combination of the anoxic and oxic MLE process (Fig. 10.9a) for nitrogen removal and the anaerobic and oxic Phoredox process (see Fig. 10.7) for phosphorus removal. The internal recycle flow rate is usually $Q_{RN} \approx (2\text{–}4) \cdot (Q_0 + Q_R)$. The nitrogen removal rate is similar to that of the MLE process, but the phosphorus removal is sometimes a little lower than that of the AO Phoredox process.

Some nitrate is introduced with the return sludge into the anaerobic zone, resulting in an adverse impact on the phosphorus removal if Q_{RN} is too low. The greatest influence on the phosphorus removal is the organics content of the influent. If the organics content is high enough for both phosphorus and nitrogen removal, then the nitrate recycle will only have a slight impact on effluent quality, but if it is low then there would be serious influence on the removal rate. Denitrification for conversion of nitrate to N_2 can be also carried out in part within a sludge blanket in the settler, which reduces the nitrate recycle to the anaerobic zone and leads to bacterial flocs being washed out of the system. Improper design of the

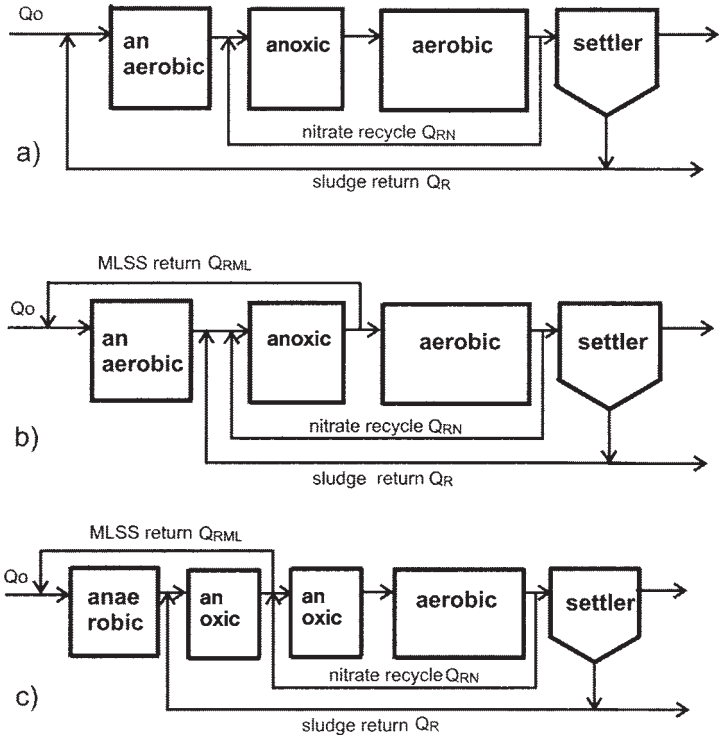

Fig. 10.10 Processes for removal of both nitrogen and phosphorus: (a) the AAO process; (b) sludge return only into the anoxic stage, partly return of O_2- and AlO_3-free activated sludge from the anoxic to the anaerobic stage; (c) two anoxic stages.

sludge blanket can lead to bulking, clumping and floating sludge, which reduces system effectiveness.

In order to eliminate the negative influences of the nitrate recycling to the phosphorus removal rate, a process was developed where the sludge was only returned to the anoxic stage in order to avoid the input of some oxygen into the anaerobic stage (Fig. 10.10b). Behind the anoxic stage a partial flow with NO_3-free, non-thickened sludge was recycled into the anaerobic stage.

In addition to that, the anoxic zone can be divided into two (up to four) reactors (Fig. 10.10c). The first anoxic reactor receives and denitrifies the return sludge stream and the second receives and denitrifies the nitrate recirculation stream. The denitrified mixed liquor is recirculated from the effluent of the first anoxic reactor to the anaerobic zonein order to provide the influent wastewater with bacteria. The advantage is the protection of the second anoxic stage for influences of recycled nitrate with sludge return.

Many other biological nutrient removal processes for both nitrogen and phosphorus have been developed (Randall et al. 1992; Grady et al. 1999). The kind of pro-

cess and plant design used depends on the treatment goal, the legislation, the composition of the wastewater to be treated and the costs for operation as well as the costs for the modification of the existing plant.

10.4.4.2 WWTP Waßmannsdorf

The primary principle of the AAO process is applied in the Waßmannsdorf wastewater treatment plant near Berlin, Germany (Schuchardt 2005). This WWTP eliminates organic substrate, nitrogen and phosphorus. Figure 10.11 presents the layout and sampling points of the WWTP.

The influent wastewater has about 100 mg L^{-1} DOC, 56 mg L^{-1} NH_4-N and 9.5 mg L^{-1} PO_4-P (Fig. 10.12), which fluctuate according to a daily cycle.

In the anaerobic zone, approximately half of the DOC is removed when the PAOs take up PHB into the bacterial cells (see Fig. 10.6). The PHF is used for the reduction of nitrate in the anoxic zone. The measured DOC concentration of 16 mg L^{-1} in the effluent from the aerobic stage corresponds to the inert organic matter.

The change in the orthophosphate concentration shows the typical course of biological P elimination. It increases in the anaerobic stage due to the PO_4-P release from the Bio-P bacterial cells, the uptake of PO_4-P begins in the anoxic zone by denitrification with polyphosphate uptake and continues in the aerobic zone. No PO_4-P is detected in the aerobic effluent. Phosphorus precipitants are dosed as needed at the beginning of the third aerobic zone to compensate for the extreme daily fluctuations in phosphorus loads and also the high flows associated with storm drainage.

First, in the aerobic zone, the NH_4-N concentration is decreased in the course of nitrification. Its effluent concentration is about 0.81 mg L^{-1} NH_4-N and a nearly complete nitrification to nitrate is observed already in the first and/or second aerobic zone (Fig. 10.13).

The amount of aeration following the first and/or second aerobic zone can be reduced if, for example, precise measurement of the nitrogen fractions is used to control c′ exactly, depending on the time of day (see Problem 10.2).

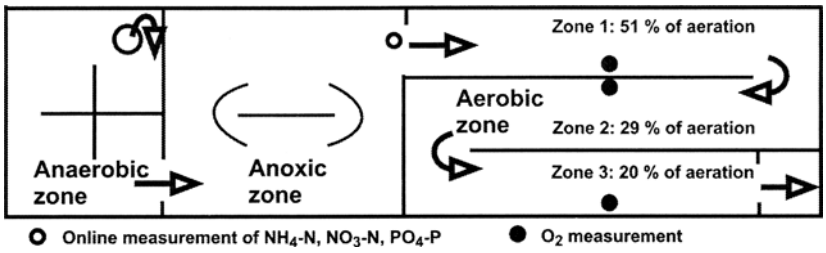

Fig. 10.11 Processes for removal of organics, nitrogen and phosphorus by the AAO process in WWTP Waßmannsdorf near Berlin (Schuchardt 2005).

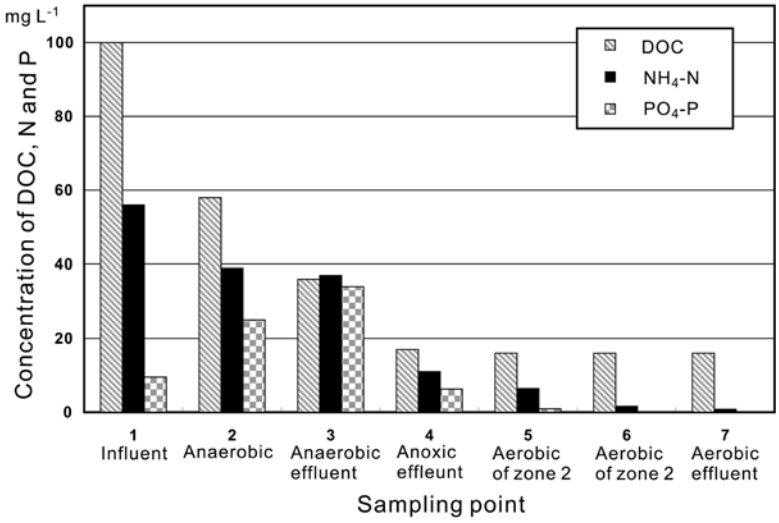

Fig. 10.12 Concentration profiles of DOC, ammonium and phosphate in WWTP Waßmannsdorf, 3.5.2000 (13^{00}–16^{50}) (Schuchardt et al. 2002).

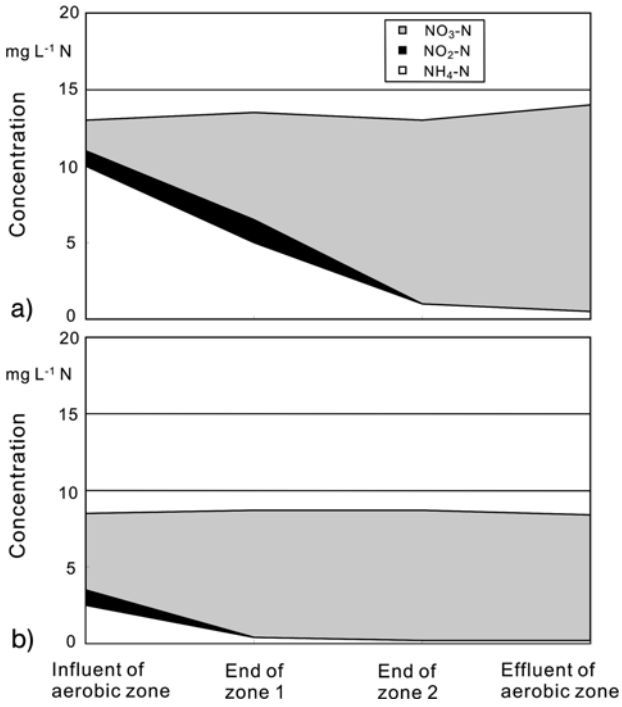

Fig. 10.13 Concentrations of nitrogen fractions in the aerobic zone of basin BB-K in WWTP Waßmannsdorf (Schuchardt 2005).
a) 14.11.2001, 14^{20}–16^{05}; b) 15.11.2001, 6^{15}–8^{05}.

10.4.4.3 Membrane Bioreactors (MBR)

The process of biological removal of nitrogen and phosphorus has been adapted to MBR technology. Modern membrane applications allow us to carry out the process without secondary clarifiers and to increase the sludge concentration to values of 10–20 g L^{-1} MLVSS, which cannot be attained by sedimentation, resulting in high sludge ages, higher metabolic rates and better nutrient removal.

Although they have increased energy consumption, higher initial investment costs and operating costs, various accounts of practical experience and data are available on MBR processes and increasing numbers of full-scale plants are going into operation. Recently, post-denitrification and enhanced biological phosphorus removal have emerged in the form of MBR processes (Kraume et al. 2005). A MBR bench-scale plant was successfully operated performing biological phosphorus removal in both pre- and post-denitrification configurations without additional carbon and with different sludge retention time t_{RX} values of 15 d and 26 d (Adam et al. 2002; Lesjean et al. 2003).

Chapter 12 presents the principles and applications of membrane technology in biological wastewater treatment.

10.5 Phosphorus and Nitrogen Recycle

10.5.1 Recycling of Phosphorus

High-grade deposits of phosphate rock are utilized as the main source for the production of fertilizers and other industrial phosphates. Until now, phosphorus has been utilized as a non-renewable resource. The end-products of the phosphate industry are introduced in the environment via sewage and manure with hardly any of it being reused. It is clear that known reserves have a limited lifetime of about 50–100 years (Steen 1998). If the current practice does not change, we may face the depletion of one of the most important elements of all living beings. This problematic situation could be prevented by the recycling of phosphates into the agricultural fertilizer industry and/or the phosphate industry. Closing the phosphorus cycle is the answer.

With the focus on wastewater treatment, there are various methods to recycle phosphorus, such as biological P removal and spreading sludge in agriculture, as well as chemical P precipitation.

Bio-P-containing sludges have average phosphorus concentrations of 2.9% (STOWA 2001), which can be increased by the incineration process (up to 8% P in ash). In spite of the increase in P concentration achieved, the quality is still not sufficient for use in the phosphorus industry because of the levels of impurities such as copper and zinc (Lijmbach et al. 2002).

The most widely developed techniques for recovering phosphorus are calcium phosphate formation and precipitation of struvites (i.e. magnesium ammonium phosphates, MAP, or potassium ammonium phosphates; CEEP 1998).

First, the formation of calcium phosphate can be induced with high calcium concentrations and elevated pH by the addition of lime. Up to 80% P recovery has been achieved, but 50–60% may be more common. The calcium phosphate formed is very similar to mined phosphate rock and can readily be used in the manufacture of agricultural fertilizers or by the phosphate industry. But the main disadvantage of this technique is the low efficiency of P formation compared to the calcium input.

The MAP process is suitable for high-strength wastewater, like digester supernatant or manure wastewater (Lijmbach et al. 2002). Magnesium forms a relatively insoluble complex together with ammonium and phosphate (MAP). The formation reaction is well known for analyzing magnesium:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} \rightarrow MgNH_4PO_4 \tag{10.71}$$

Normally, struvites produced by precipitation can be used as an agricultural fertilizer; and recycling is possible in certain phosphate industry processes, such as in phosphorus furnaces (CEEP 1998). A number of full-scale struvite recovery plants are operating in Japan, producing material that is sold to the local fertilizer industry (Ueno and Fujii 2001).

The struvite technique is characterized not only by removing PO_4 and NH_4 from the wastewater but also by its reuse.

10.5.2 Recycling of Nitrogen

Wastewater with high NH_4 concentration can be treated according to the reaction in Eq. (10.71) (Schulze-Rettmer 1993). To reduce the consumption of magnesium and phosphate, magnesium must be recycled. Struvite is treated by heat drying and by injecting steam under basic conditions in the presence of NaOH:

$$MgNH_4PO_4 + NaOH \rightarrow MgNaPO_4 + NH_3 + H_2O \tag{10.72}$$

The concentrated ammonia from Eq. (10.72) is separated and reused, while the $MgNaPO_4$ can be used again for precipitation of the NH_4 in the MAP process:

$$NH_4^+ + MgNaPO_4 + OH^- \rightarrow MgNH_4PO_4 + NaOH \tag{10.73}$$

The MAP process is suitable for high-strength ammonium-rich wastewater (see Table 2.4) and operates at high efficiency of ammonium elimination (up to 99%; Schulze-Rettmer 1993). Moreover, there are various possible techniques to recycle ammonium nitrogen from wastewater, such as the application of biosolids (sludge from WWTP) in agriculture, adsorption of ammonium by zeolites, stripping of ammonia and chemical precipitation in the MAP process (Maurer et al. 2002). The produced NH_3 in Eq. (10.72) can be further used for the synthesis of nitrate (see Eqs. 10.2 and 10.3).

PROBLEM 10.1

Domestic wastewater containing ammonium is to be treated. An effluent total nitrogen concentration of $S_{Nt,e} = 10$ mg L^{-1} is given. A pre-denitrification step (Fig. 10.14) is available for the removal of ammonium.

It is assumed that 99% of the ammonium is oxidized to nitrate without nitrite accumulation. Enough carbon is available to ensure complete denitrification (100%). The anoxic and aerobic reactors are completely mixed and operated in steady state.

The following conditions and data are given: no additional formation of NH_4 during the anoxic and aerobic process, wastewater influent flow rate $Q_0 = Q_R = 100$ m^3 d^{-1}, $Q_{RN} = 4\ Q_0$ resulting in $n_{RN} = 4$, $S_{NH_4\text{-}N,0} = 50$ mg L^{-1} before mixing point, $S_{NO_3\text{-}N,ax} = 1$ mg L^{-1}; and the bacterial concentration is $X_{NS} = 0.05$, respectively $X_D = 0.2$ g L^{-1} MLVSS.

Calculate the volumes of the anoxic and aerobic reactors.

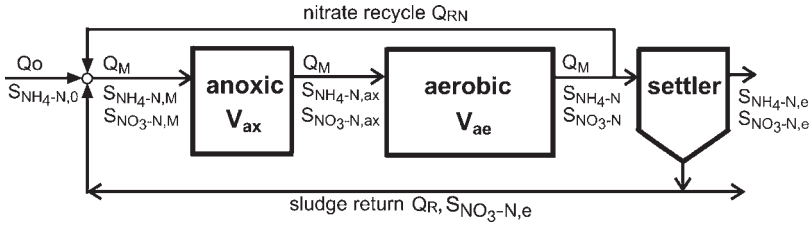

Fig. 10.14 Configuration for post-denitrifification with internal recycle.

Solution

First, we obtain the following values from known data above:

$Q_{RN} = 4\ Q_0 = 4 \cdot 100$ m^3 $d^{-1} = 400$ m^3 d^{-1}

$Q_M = Q_0 + Q_R + Q_{RN} = 100 + 100 + 400$ m^3 $d^{-1} = 600$ m^3 d^{-1}

$Q_M \equiv$ flow rate after mixing point

$S_{NH_4\text{-}N} = S_{NH_4\text{-}N,e} = 0.5$ mg L^{-1} due to the 99% degree of ammonium oxidation

$S_{NO_3\text{-}N} = S_{NO_3\text{-}N,e} = 9.5$ mg L^{-1} based on $S_{Nt,e} = 10$ mg L^{-1} N $= S_{NH_4\text{-}N,e} + S_{NO_3\text{-}N,e}$

The following coefficients are valid:

$\mu_{max,NS} = 0.48$ d^{-1}

$\mu_{max,D} = 2.6$ d^{-1}

$K_{NH_4\text{-}N} = 0.5$ mg L^{-1} N

$K_{NO_3\text{-}N} = 0.14$ mg L^{-1} N

$Y^{o}_{XA/NH_4\text{-}N} = 0.142$ g MLVSS (g NH_4-N)$^{-1}$

$Y^{o}_{XH/NO_3\text{-}N} = 1.2$ g MLVSS (g NO_3-N)$^{-1}$

1. Calculation of the volume of the aerobic reactor.

The ammonium balance at the mixing point M (see Fig. 10.14) is:

$$Q_0 \cdot S_{NH_4\text{–}N,0} + Q_R \cdot S_{NH_4\text{–}N} + Q_{RN} \cdot S_{NH_4\text{–}N} = Q_M \cdot S_{NH_4\text{–}N,M} \tag{10.74}$$

$S_{NH_4\text{–}N,M} = 8.75$ mg L^{-1} N.

In the anoxic reactor there is no oxidation of ammonium, so we balance ammonium on the aerobic reactor:

$$0 = Q_M \cdot S_{NH_4\text{–}N,M} - Q_M \cdot S_{NH_4\text{–}N} - \frac{\mu_{max,NS} X_{NS}}{Y^{o}_{XA/NH_4\text{–}N}} \cdot \frac{S_{NH_4\text{–}N}}{K_{NH_4\text{–}N} + S_{NH_4\text{–}N}} V_{ae} \tag{10.75}$$

Applying the given coefficients, we obtain the aerobic reactor volume:

$$\begin{aligned} V_{ae} &= (Q_M \cdot S_{NH_4\text{–}N,M} - Q_M \cdot S_{NH_4\text{–}N}) \cdot \frac{Y^{o}_{XA/NH_4\text{–}N}}{\mu_{max} X_{NS}} \cdot \frac{K_{NH_4\text{–}N} + S_{NH_4\text{–}N}}{S_{NH_4\text{–}N}} \\ &= (600 \cdot 0.00875 - 600 \cdot 0.0005) \cdot \frac{0.142}{0.48 \cdot 0.05} \cdot \frac{0.5 + 0.5}{0.5} = 58.6 \text{ m}^3 \end{aligned} \tag{10.76}$$

Equation (10.76) results in the hydraulic retention time t_R of the aerobic reactor related to the influent flow rate Q_0:

$$t_R = \frac{V_{ae}}{Q_0} = \frac{58.6}{100} \frac{\text{m}^3}{\text{m}^3\,\text{d}^{-1}} = 0.586 \text{ d} = 14 \text{ h} \tag{10.77}$$

2. Calculation of the volume of the anoxic reactor.

From the nitrate balance at the mixing point M:

$$Q_0 \cdot S_{NO_3\text{–}N,0} + Q_R \cdot S_{NO_3\text{–}N,e} + Q_{RN} \cdot S_{NO_3\text{–}N,e} = Q_M \cdot S_{NO_3\text{–}N,M} \tag{10.78}$$

$S_{NO_3\text{–}N,M} = 7.9$ mg L^{-1} N

We balance nitrate on the anoxic reactor:

$$0 = (Q_M \cdot S_{NO_3\text{–}N,M} - Q_M \cdot S_{NO_3\text{–}N,ax}) - \frac{\mu_{max,D} X_D}{Y^{o}_{XH/NO_3\text{–}N}} \cdot \frac{S_{NO_3\text{–}N,ax}}{K_{NO_3\text{–}N} + S_{NO_3\text{–}N,ax}} V_{ax} \tag{10.79}$$

Applying the given coefficients, we obtain the anoxic reactor volume:

$$V_{ax} = (600 \cdot 0.0079 - 600 \cdot 0.001) \cdot \frac{1.2}{2.6 \cdot 0.2} \cdot \frac{0.14 + 1}{1} = 10.9 \text{ m}^3 \tag{10.80}$$

Equation (10.80) results in hydraulic retention time t_R of the anoxic reactor:

$$t_R = \frac{V_{ax}}{Q_0} = \frac{10.9}{100} \frac{\text{m}^3}{\text{m}^3\,\text{d}^{-1}} = 0.109 \text{ d} = 2.61 \text{ h} \tag{10.81}$$

Note: In this system without aerobic C removal, the concentration of denitrifying bacteria is relativ low, resulting in a relative large denitrification hydraulic retention time.

PROBLEM 10.2

At the WWTP Waßmannsdorf (schematic in Fig. 10.11a), the ammonium loads show a pronounced daily variation. In the morning, the load of ammonium is lower than in the afternoon. For both cases, the ammonium is already completely oxidized to nitrate in the first or second aerobic zone with only a very low amount of nitrite accumulation (Fig. 10.13). Now we consider the aeration efficiency of the aerobic zone. As shown in Fig. 10.15, the dissolved oxygen concentration fluctuates in the aerobic zones.

There is potential to save energy consumed for aeration. What measures could improve this? Discuss the possibilities to improve the efficiency and to save operating costs.

Solution

There are four possible improvements:

1. Reducing energy costs for aeration. The cost of aeration is the main factor determining the operating costs of a WWTP. At the concentrations occurring in the morning, ammonium is completely oxidized to nitrate after the first aerobic zone, which means that no aeration is necessary after this point. A remarkable energy savings for aeration in the second and third aerobic zones is be expected. This is also true for the afternoon.

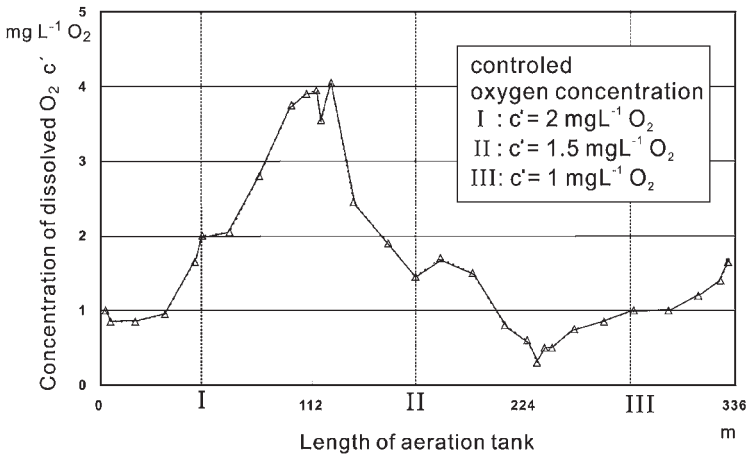

Fig. 10.15 Oxygen concentration profiles in aerobic zones of BB-M (I), WWTP Waßmannsdorf, 23.2.2000, 14^{50}–15^{40}, O_2 concentration is automatically controlled at three points I, II and III (Schuchardt 2005).

2. Online measurement of ammonium and nitrate is needed to control their concentration profiles and to regulate the aeration accordingly.
3. Precise regulation of dissolved oxygen concentration c′ is necessary (Fig. 10.15). The number of c′ control points should be increased through all zones.
4. Higher c′ can not only cause high energy costs but also reduce the specific oxygenation capacity described by the constant $k_L a$ (see Eq. 5.10).

Do you have further ideas to improve the process control and to optimize the process?

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