

4.2.3 Determination of nitrification kinetics

In the previous section the equation of Downing et al (1964) was used to model the growth of nitrifiers with a Monod relationship:

$$(dX_n/dt) = Y_n \cdot r_n = [\mu_m \cdot (N_a / (N_a + K_n)) - b_n] \cdot X_n \quad (4.28)$$

Where:

(dX_n/dt)	= growth rate of the nitrifying bacteria (mg VSS.l ⁻¹ .d ⁻¹)
r_n	= nitrification rate (mg N.l ⁻¹ .d ⁻¹)
Y_n	= yield coefficient of nitrifiers (mg VSS.mg ⁻¹ N)
μ_m	= maximum specific growth constant of nitrifiers (d ⁻¹)
N_a	= ammonium concentration (mg N.l ⁻¹)
K_n	= half saturation constant for ammonium (mg N.l ⁻¹)
b_n	= autotrophic decay constant (d ⁻¹)
X_n	= nitrifier concentration (mg VSS.l ⁻¹)

Stenstrøm and Poduska (1980) have shown that the dissolved oxygen concentration has an effect on the nitrifier growth. This effect can also be described with a Monod expression. As explained in Appendix 1, the effect is caused by oxygen limitation inside the sludge floc that will occur when the bulk dissolved oxygen concentration decreases below the critical concentration. In the general model this has not been included, as oxygen concentration is considered more as an operational than a design parameter: typically a (bulk) dissolved oxygen concentration around 2 mg.l⁻¹ O₂ is assumed, which is sufficient for nitrification. However, during an OUR test the effect of a low oxygen concentration cannot be ignored. Thus for nitrifiers (i.e. Nitrosomonas being responsible for the rate limiting step):

$$dX_n/dt = r_n \cdot Y_n = [\mu_m \cdot N_a / (N_a + K_n) \cdot (DO / (DO + K_o)) - b_n] \cdot X_n \quad (A4.1)$$

Where:

μ_{max}	= the maximum specific growth rate for nitrifiers
K_o	= half saturation constant of dissolved oxygen for nitrification

Three different approaches have been developed to determine the value of the kinetic parameters of nitrification:

- (1) A method in which the sludge age of an activated sludge system is gradually lowered while observing the resulting change in the ammonium concentration in the effluent. This method is not particularly accurate and is very laborious; it may take several weeks or even months to obtain reliable values for the constants.
- (2) A method proposed by Van Haandel and Marais (1981), in which an activated sludge process operating under constant flow and load conditions was submitted to alternating anoxic- and aerobic periods. During the aerobic periods the variation of the nitrate concentration was determined and used to calculate the nitrification constants. This method is much more accurate, but it still requires significant effort to carry out.
- (3) The third method uses respirometrics. Oxygen uptake rate (OUR) tests are extremely simple to carry out. The experimentally determined OUR is taken as a measure for the nitrification rate and from it the nitrification constants can readily be calculated. When the OUR determination is repeated at different dissolved oxygen concentrations, the half saturation value for dissolved oxygen may also be determined.

Only the respirometric method will be discussed here. Stoichiometrically there is a consumption of two moles of oxygen per mole of nitrified ammonium or (equivalent) per mole of produced nitrate. Hence there is a proportionality of 4.57 mg O₂ per mg nitrate N produced, so that:

$$\text{OUR}_n = 4.57 \cdot r_n = [\mu_m \cdot N_a / (N_a + K_n) \cdot \text{DO} / (\text{DO} + K_o) - b_n] \cdot X_n / Y_n \quad (\text{A4.2})$$

Where OUR_n = oxygen uptake rate for nitrification

As a prerequisite for the determination of the nitrification kinetics, first a nitrifying sludge must be generated under steady state conditions, which allows the nitrifier concentration of the sludge to be determined. The concentration of nitrifiers is given by Marais and Ekama, (1976):

$$X_n = Y_n \cdot R_s \cdot N_c / ((1 + b_n \cdot R_s) \cdot R_h) \quad (\text{A4.3})$$

Where N_c = nitrified ammonium concentration (nitrification capacity) of the activated sludge system under consideration

A nitrifying sludge batch is aerated (without feed) until the OUR has declined to a more or less constant value, equivalent to the endogenous respiration rate. In general this takes about 0.5 to 1 hour. At this point a known quantity of ammonium is added, e.g. in the form of an ammonium chloride solution. As a result of the ammonium addition, the OUR will increase steeply. After some time the OUR will decrease again to approximately the same value as before the ammonium addition. Fig. A4.1 represents a typical curve of the OUR after addition of a batch-load of ammonium. This curve can be used to determine the kinetic nitrification constants as will be explained in the subsequent sections.

(1) Mass balance check

The area between the OUR curve and the base endogenous respiration line represents the oxygen consumption per litre of reactor resulting from the addition of ammonium. When the surface area is determined, it can be compared with the observed nitrate concentration increase. If the oxygen consumption is approximately 4.57 times higher than the produced nitrate concentration (in mg NO₃-N.l⁻¹), then it can be concluded that the experimental data are reliable and may be used for calculation of the kinetic constants.

(2) Estimate of the maximum specific growth rate constant μ_m

From the observation that the OUR is almost constant during the period directly after the addition of ammonium, it can be concluded that during this phase no ammonium limitation exists and that nitrification is proceeding at the maximum rate (i.e. $N_a \gg K_n$). With the aid of Eq. (A4.3) the concentration of nitrifiers can be calculated. The maximum specific growth rate μ_m can be determined from:

$$\text{OUR}_m = 4.57 \cdot r_n = 4.57 \cdot (\mu_m - b_n) \cdot X_n / Y_n \quad (\text{A4.4})$$

Where OUR_m = maximum OUR due to nitrification during the test

In general, the numerical value of the maximum specific growth rate μ_m is much larger than the value of the decay constant b_n , so that a good approximation is $(\mu_m - b_n) \approx \mu_m$.

(3) Half saturation constant of ammonium

To determine the value of the half saturation constant of ammonium K_n , once again the OUR profile is evaluated. When the OUR starts to decrease, ammonium is becoming a rate limiting factor. In accordance with Monod kinetics, when the OUR is equal to half the maximum OUR value, the ammonium concentration at that particular moment is equal to the value of K_n . Hence K_n is determined as follows:

1. When it is observed that the OUR for nitrification is reduced to half of the maximum OUR value, a sample is withdrawn and the ammonium concentration is determined. ATU (Allyl-Thio-Ureum) is added to suppress further nitrification in the sample;
2. Alternatively the oxygen consumption for nitrification is determined in the time period required to decrease the OUR from $0.5 \cdot \text{OUR}_m$ to OUR_{en} : the amount of oxygen consumed is equivalent to the grey area indicated in Fig. A4.1. The ammonium concentration present in the batch at the moment that the OUR was equal to $0.5 \cdot \text{OUR}_m$, can be estimated by dividing the oxygen consumption by 4.57.

(4) Half saturation constant of dissolved oxygen

To evaluate the effect of dissolved oxygen limitation on the nitrification rate, several batch tests are carried out, each at a different dissolved oxygen concentration. For each of these tests, the μ_m value is calculated by the procedure outlined above. The values of μ_m are plotted as a function of the average dissolved oxygen concentration in the different batch tests (see Fig. A4.2).

From the observation that the μ_m value increases at higher dissolved oxygen concentrations, it is concluded that the oxygen concentration is a limiting factor in the nitrification rate. A true maximum value for the specific growth rate of nitrifiers (μ_{max}) can now be calculated using Eq. (A4.5):

$$\text{OUR}_m = 4.57 \cdot r_{Nm} = 4.57 \cdot \mu_m \cdot [\text{DO}_{av} / (\text{DO}_{av} + K_o)] \cdot X_n / Y_n \quad (\text{A4.5})$$

Or $\mu_{max} = \mu_m \cdot [\text{DO}_{av} / (\text{DO}_{av} + K_o)]$. As both the μ_m and the DO_{av} concentration is different for each the batch tests, the best estimate for μ_{max} is the mean of all values calculated from Eq. (A4.5) for a particular K_o value.

For different values of K_o a plot is made of μ_m as a function of the dissolved oxygen concentration. The K_o value that results in the closest correlation between the experimental values and the theoretical curves is selected. This will be explained in detail in Section A4.2. Note that in the model presented in this book, K_o has not been included as a parameter, as in the optimised design procedure the applied oxygen concentration is assumed to be higher than the critical concentration, i.e. oxygen limitation will not occur.

(5) Determination of the decay constant

The decay rate of nitrifiers is small and for that reason the test to determine the value of b_n is time consuming as well. A nitrifying sludge batch is aerated without feed for a period sufficient to remove any remaining substrate from the sludge batch and to ensure the virtual elimination of heterotrophic biomass (as heterotrophs have a much higher decay rate than nitrifiers). The decay of the heterotrophic biomass may take between 2 to 6 weeks, depending on the temperature of the sludge batch. When the decay of the heterotrophs is virtually complete, the decay rate of nitrifiers can be evaluated by adding ammonium chloride at regular intervals (several days) and observe the decrease in OUR_m in time.

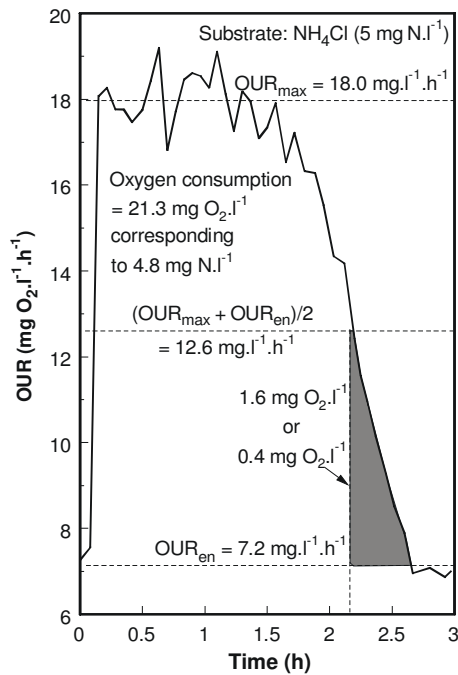


Figure A4.1
Typical respirogram after feeding of a sludge batch with ammonium chloride

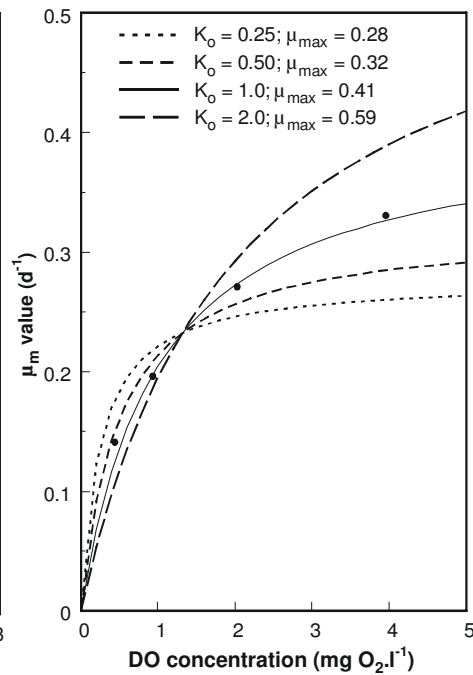


Figure A4.2
Theoretical curves and experimental values of μ_m of the nitrifiers as a function of the dissolved oxygen concentration

An alternative is to feed the sludge batch with ammonium only, and to periodically discharge excess sludge. After a period equal to two or three sludge ages, the elimination of heterotrophic biomass can be considered almost complete. Theoretically there should be an exponential decay of OUR_m with time, as the concentration of nitrifiers decreases exponentially. Hence there will be a linear relationship between $\ln(OUR_m)$ and time and the slope of the straight line is equal to the decay constant b_n . As the decay rate of nitrifiers is very slow, the test will take at least a month. In practice it is not very important to know the exact value of the decay constant, as invariably $\mu_m \gg b_n$ and for that reason the influence of b_n on nitrification kinetics is very limited. For practical purposes one can adopt a value already reported by other authors, for example: $b_n = 0.04 \cdot 1.03^{(T-20)}$ (Marais and Ekama, 1976).