

4.3.3 Denitrification kinetics

Marais and his group of research workers developed an empirical model for the kinetics of denitrification. This model is an extension to the model for the removal of organic material presented in the chapter 3.

4.3.3.1 Sludge production in anoxic/aerobic systems

When the data published on sludge production in aerobic/anoxic systems is compared, it can be concluded that sludge production is not affected by the presence of anoxic zones and is equivalent to that of a purely aerobic system. In this context the data collected by Sutton et al (1979) during their experiments are possibly the most illustrative. In Fig. 4.14 these data are presented. The organic sludge mass per unit mass of daily applied COD (mX_v) is plotted as function of the sludge age for different anoxic sludge mass fractions, temperatures and sludge ages (both pre-D and post-D systems).

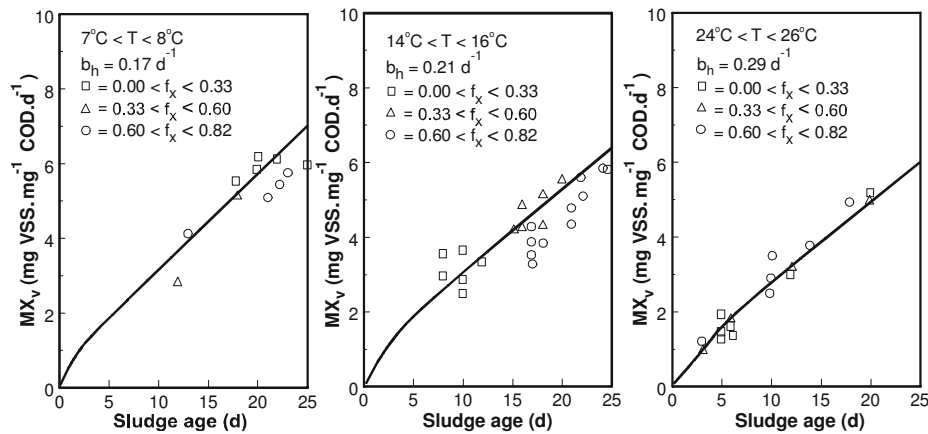


Figure 4.14 Theoretical and experimental values of the organic sludge mass produced per unit mass of daily applied COD (mX_v)

There is a close correlation between the experimental data and the theoretical curves of mX_v , which have been drawn using Eq. (3.69), derived in Chapter 3 for completely aerobic systems:

$$mX_v = (1 - f_{ns} - f_{np}) \cdot (1 + f \cdot b_h \cdot R_s) \cdot C_r + f_{np} \cdot R_s / f_{cv} \quad (3.50)$$

In the example presented in Fig. 4.14, the closest correlation between the data of Sutton et al (1979) and theory is obtained for $f_{ns} = 0.11$ and $f_{np} = 0.25$. The correlation between experimental data and theory is close over a wide range of temperatures (7 to 26°C), sludge ages (3 to 35 days) and anoxic sludge mass fractions ($0.00 < f_x < 0.82$). On the basis of the data by Sutton et al (1979) and others, it is concluded that all the parameters and constants that determine the sludge production in an aerobic activated sludge process can be applied unchanged in processes with anoxic zones, i. e.: $Y = 0.45 \text{ mg VSS} \cdot \text{mg}^{-1} \text{ COD}$; $f = 0.2$; $f_{cv} = 1.5 \text{ mg COD} \cdot \text{mg}^{-1} \text{ VSS}$ and $b_h = 0.24 \cdot (1.04)^{T-20} \text{ d}^{-1}$.

4.3.3.2 Denitrification rates

Denitrification rates can be conveniently determined in an anoxic plug flow reactor. A true plug-flow reactor is characterised by the fact that no back-mixing occurs: the mixed liquor flows as a “piston” from the inlet to the outlet of the reactor. In Fig. 4.15 the experimental set up of a system with an anoxic plug flow reactor is shown.

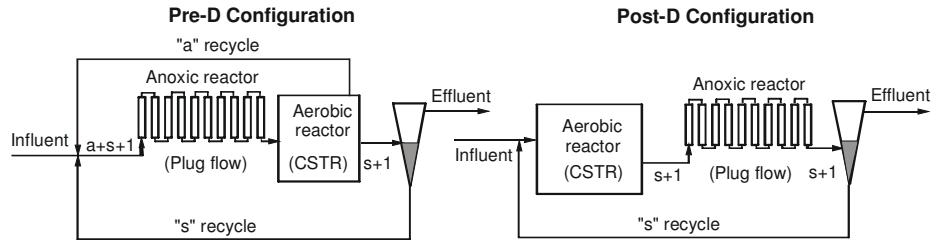


Figure 4.15 Schematic representation of the experimental set-up for the determination of the denitrification kinetics

The retention time in the anoxic reactor increases proportionally with its volume (length). Hence by withdrawing samples at different points, it is possible to obtain a nitrate concentration profile in the anoxic reactor as a function of the contact time. The denitrification rate at any moment is given by the gradient of the nitrate concentration profile. Typical nitrate concentration profiles as observed in pre-D and post-D reactors are presented in Fig. 4.16. The decrease of the nitrate concentration tends to be linear with time. This indicates that nitrate removal is a zero order process with respect to the concentration of nitrate. The nitrate concentration profile in a pre-D reactor indicates that two phases can be distinguished:

- A primary phase with a short duration (of only a few minutes) with a high denitrification rate;
- A secondary phase during the remaining of the anoxic retention time, with a constant but lower denitrification rate.

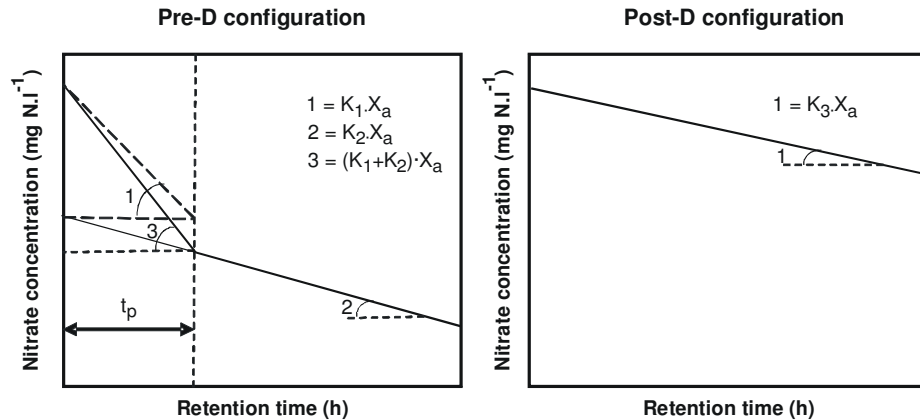


Figure 4.16 Nitrate concentration profiles in anoxic plugflow reactors for pre-D and post-D reactors

In the post-D reactor there is also a linear profile of the nitrate concentration as a function of retention time, but the denitrification rate in the post-D reactor is always smaller than in the secondary phase of a pre-D reactor. From the data obtained with plug flow reactors by Stern et al (1974), Wilson et al (1976) and Marsden et al (1974), it can be calculated that the denitrification rate is proportional to the active sludge concentration and can be expressed as:

$$r_D = (dN/dt) = -K \cdot X_a \quad (4.45)$$

K = denitrification constant ($\text{mg N} \cdot \text{mg}^{-1} X_a \cdot \text{d}^{-1}$)

The denitrification behaviour in the pre-D reactor can be described using two constants: K_1 for the primary phase and K_2 for the secondary phase. It can be imagined that during the primary phase two denitrification processes develop simultaneously and that only one of these two continues during the secondary phase as indicated by the interrupted lines in Fig. 4.16. In that case one would have: $K = K_1 + K_2$ in the primary phase and $K = K_2$ in the secondary phase.

Van Haandel et al (1981) showed that the high value of the denitrification rate during the primary phase could be associated with the simultaneous utilisation of both easily and slowly biodegradable material. In the secondary phase the easily biodegradable material is depleted and the denitrification rate is only due to the utilisation of slowly biodegradable material. The rate of denitrification can be written as:

$$r_D = (dN/dt) = r_{Ds} + r_{Dp} = (K_1 + K_2) \cdot X_a \quad (t < t_p) \text{ and}$$

$$r_D = (dN/dt) = r_{Dp} = K_2 \cdot X_a \quad (t > t_p) \quad (4.46)$$

Where:

r_{Ds} / r_{Dp} = denitrification rate associated with the utilisation of easily/slowly biodegradable material

K_1 / K_2 = denitrification constant for easily/slowly biodegradable organic material ($\text{mg N} \cdot \text{mg}^{-1} X_a \cdot \text{d}^{-1}$)

t_p = duration of the primary phase (d)

In the post-D reactor, denitrification is only associated with the utilisation of slowly biodegradable material. Since this concentration in a post-D reactor will be smaller than in a corresponding pre-D reactor, the denitrification rate will also be smaller. The rate of nitrate removal in a post-D reactor can be expressed as:

$$r_D = dN/dt = K_3 \cdot X_a \quad (4.47)$$

The kinetic expressions for denitrification in Eqs. (4.46 and 4.47) are all zero order equations: in a steady state situation, the denitrification rate does not change with time as the active biomass can be considered to be constant. Therefore the above expressions can be used to calculate nitrate removal in anoxic reactors, independent of its hydraulic regime, and may also be applied to completely and partially mixed reactors.

Van Haandel et al (1981) calculated the values of the denitrification rate constants K_1 , K_2 and K_3 from the experimental results obtained by several authors, all using municipal waste water as influent.

From the data obtained by Stern et al (1974), Wilson et al (1976), Marsden et al (1974), Van Haandel et al (1981), Nichols (1981) in South Africa; Sutton et al (1969) in Canada; Heide (1975) in the Netherlands and Heidman (1979) in the United States, the following average values were calculated for the range of temperatures from 12 to 26°C:

$$\begin{aligned} K_1 &= 0.72 \cdot 1.2^{(T-20)} \\ K_2 &= 0.10 \cdot 1.08^{(T-20)} \\ K_3 &= 0.08 \cdot 1.03^{(T-20)} \end{aligned} \quad (4.48)$$

Research that has not yet been published, using municipal waste water from Campina Grande (Brazil), shows that the formulas in Eq. 4.48 remain valid for temperatures up to 28°C. In all cases the data were obtained with waste waters containing only minor industrial contributions. It is possible that in waste waters with a significant or predominant industrial contribution the constants have different values due to the presence of toxic materials.

4.3.3.3 Minimum anoxic mass fraction in the pre-D reactor

In the previous section it was shown that the denitrification rate in the pre-D reactor is high, as long as easily biodegradable organic material is present. As the objective of the anoxic reactors is to remove nitrate, it is important that the denitrification rate is kept as high as possible. Therefore it is necessary that the retention time in the pre-D reactor is sufficiently long to guarantee complete utilisation of the easily biodegradable material. To determine the minimum retention time, the removal rate of the easily biodegradable material is compared with the feeding rate to the pre-D reactor. The feeding rate of easily biodegradable material can be expressed as:

$$r_{sbs} = S_{bsi}/R_1 = f_{sb} \cdot S_{bi}/R_1 \quad (4.50)$$

Where:

r_{sbs} = feeding rate of easily biodegradable material to the pre-D reactor
 R_1 = hydraulic retention time in the pre-D reactor = V_1/Q_i (d)
 V_1 = volume of the pre-D reactor

The utilisation rate of easily biodegradable material is proportional to the associated denitrification rate $r_{Ds} = K_1 \cdot X_a$ (Eq. 4.46). In the process of utilisation, a fraction of $(1 - f_{cv} \cdot Y)$ is oxidised.

As stoichiometrically 1 mg $\text{NO}_3\text{-N}$ equals 2.86 mg O_2 , the utilisation rate of easily biodegradable material can be expressed as:

$$r_{Ds} = (1 - f_{cv} \cdot Y)/2.86 \cdot r_{us} = f_{dn} \cdot r_{us} \quad (4.51)$$

Where:

$f_{dn} = (1 - f_{cv} \cdot Y)/2.86$ = denitrification constant
 r_{Ds} = denitrification rate due to the utilisation of easily biodegradable material
 r_{us} = utilisation rate of easily biodegradable material

Now the minimum required retention time in the pre-D reactor to remove the easily biodegradable organic material can be calculated by the condition:

$$r_{sbs} = r_{us} \quad (4.52)$$

Using Eqs. (4.50 and 4.51) in Eq. (4.52) one has:

$$\begin{aligned} f_{sb} \cdot S_{br} / R_{min} &= r_{Ds} \cdot f_{dn} \\ &= K_1 \cdot X_a \cdot f_{dn} \end{aligned} \quad (4.53)$$

R_{min} = minimum retention time required for complete utilisation of the easily biodegradable material in the pre-D reactor (d)

Substituting for X_a from Eq. (3.29) and rearranging:

$$R_{min} / R_h = f_{dn} \cdot f_{sb} / (K_1 \cdot C_r) \quad (4.54)$$

The minimum retention time R_{min} is associated to a minimum sludge mass fraction in the pre-D reactor. Since $R_{min} = V_{min} / Q_i$, one has:

$$R_{min} / R_h = (V_{min} / Q_i) / (V_r / Q_i) = (V_{min} / V_r) = f_{min} \text{ or } f_{min} = f_{dn} \cdot f_{sb} / (K_1 \cdot C_r) \quad (4.55)$$

Where:

V_{min} = minimum pre-D reactor volume required for complete utilisation of easily biodegradable material

f_{min} = minimum sludge mass fraction in the pre-D reactor

For “normal” values of f_{sb} , K_1 and C_r , the minimum fraction f_{min} is always very small and the anoxic sludge mass fraction in a full-scale activated sludge process will be invariably much larger than f_{min} . It can be concluded that the utilisation of easily biodegradable material can be considered complete in the pre-D reactor, provided that sufficient nitrate is available.