

# Chapter 10. Denitrification

All the figures and tables in this material are from the reference below unless specified otherwise.
Reference: Bruce E. Rittmann and Perry L. McCarty, "Environmental Biotechnology: Principles and Applications", McGraw-Hill, 2001.

***Changha Lee***

**School of Chemical and Biological Engineering**

**Seoul National University**

# Intro: Denitrification

## √ Denitrification :

Dissimilatory reduction of $NO_3^-$ and $NO_2^-$ into $N_2$ gas

($NO_3^-$ and $NO_2^-$ are electron acceptors used in energy generation )

- Denitrification is widespread among heterotrophic and autotrophic bacteria.
  (many of which can switch between oxygen respiration and nitrogen respiration)
- Denitrification is applied when the complete removal of N is required to prevent eutrophication.
- In order to have denitrification, the nitrogen must be of its oxidized forms, $NO_3^-$ and $NO_2^-$.
  So denitrification is frequently is coupled to nitrification
- Tertiary denitrification : the water does not contain the necessary electron donor and thus an **exogenous** electron donor must be provided.
- One-sludge denitrification : the water contains an electron donor that can drive denitrification.

# 10.1 Physiology of Denitrifying Bacteria

## √ Denitrification process

- It proceeds in a stepwise manner:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

$NO_3^- + 2e^- + 2H^+ = NO_2^- + H_2O$ *Nitrate* Reductase

$NO_2^- + e^- + 2H^+ = NO + H_2O$ *Nitrite* Reductase

$2NO + 2e^- + 2H^+ = N_2O + H_2O$ *Nitric Oxide* Reductase

$N_2O + 2e^- + 2H^+ = N_2 + H_2O$ *Nitrous Oxide* Reductase

- Very low concentrations of electron donors or too high DO can lead to accumulation of denitrification intermediates. ($NO_2^-$, NO and $N_2O$)

  i) Low concentrations of electron donors limit the supply of electrons to drive the reductive half-reactions.
  ii) A high DO level tends to repress the nitrite and nitrous oxide reductases before the nitrate reductase is suppressed.

# 10.1 Physiology of Denitrifying Bacteria

- **pH values out of the optimal range of 7 – 8 can lead to accumulation of intermediates.**

  - In low acidity waters, the pH control can be an issue because the denitrification produces strong bases.

$$CH_3COOH + \frac{8}{5}NO_3^- + \frac{4}{5}H_2O \rightarrow \frac{4}{5}N_2 + 2H_2CO_3 + \frac{8}{5}OH^-$$

$$4H_2 + \frac{8}{5}NO_3^- \rightarrow \frac{4}{5}N_2 + \frac{8}{5}OH^- + \frac{16}{5}H_2O$$

  - 8/5 Equivalents of strong base produced when 8/5 mol of $NO_3^-$-N is reduced.

  - An alkalinity increase of (50)/(14) = 3.57 g as $CaCO_3$ /g $NO_3^-$-N consumed.

  - For the acetate case, the effect is altered slightly because 2 mol of a weaker acid ($H_2CO_3$, pKa ≈ 6.3) replace 1 mol of a weak acid ($CH_3COOH$, pKa = 4.3)

# 10.1 Physiology of Denitrifying Bacteria

## √ Stoichiometric and kinetic parameters for denitrifiers

- In the early application of denitrification, intensive study was conducted for systems with relatively high $NO_3^-$-N (electron acceptor) or little BOD (electron donor) levels such as agricultural runoff (high $NO_3^-$-N) and advanced treatment of secondary effluent (little BOD).

- Thus, research addressed exogenous electron donnors and carbon sources.

- Because methanol was relatively inexpensive, a very large database on methanol has been developed.

  But the large database on methanol cannot be applied directly for situations in which another organic molecule is the donor.

# 10.1 Physiology of Denitrifying Bacteria

**Table 10.1** Representative stoichiometric and kinetic parameters for denitrifiers ($T$ = 20 °C)

| Electron Donor | Methanol | Heterotrophs BOD | $H_2$ | Autotrophs $S^0$ |
|---|---|---|---|---|
| C-source | methanol | BOD | $CO_2$ | $CO_2$ |
| $f_s^0$ | 0.36 | 0.52 | 0.21 | 0.13 |
| $Y$, g $VSS_a$/g donor | 0.27 | 0.26 | 0.85 | 0.10 |
| g $VSS_a$/g OD | 0.18 | 0.26 | 0.11 | 0.07 |
| $\hat{q}$, g donor/g $VSS_a$-d | 6.9 | 12 | 1.6 | 8.1 |
| g OD/g $VSS_a$-d | 10.4 | 12 | 11.8 | 11.2 |
| $K$, mg donor/l | 9.1 | 1 | 1 | ? |
| mg OD/l | 13.7 | 1 | 0.13 | ? |
| $b$, $d^{-1}$ | 0.05 | 0.05 | 0.05 | 0.05 |
| $[\theta_x^{min}]_{lim}$, d | 0.55 | 0.33 | 0.76 | 1.3 |
| $S_{min}$, mg donor/l | 0.25 | 0.017 | 0.04 | ? |
| mg OD/l | 0.38 | 0.017 | 0.005 | ? |
| $D$, $cm^2/d$ | 1.3 | 1.0 | 0.9 | — |
| $J_R$, kg OD/1,000 $m^2$-d | 1.5 | 0.5 | 1.2 | ? |
| $S^*_{min}$ (no detachment) | 0.027 | 0.017 | 0.040 | 0.066 |
| ($b_{det}$ = 0.2/d) | 0.15 | 0.087 | 0.23 | 0.45 |
| $K^*$ | 1.8 | 0.4 | 2.2 | ? |

Notes: For $K^*$, $L$ = 40 $\mu m$, $D_f/D$ = 0.8, and $X_f$ = 40 mg $VSS_a/cm^3$. ? = not yet determined —not applicable.

# 10.1 Physiology of Denitrifying Bacteria

√ **Table 10.1**

- While the $f_s^0$ value for heterotrophs using general $BOD_L$ is only slightly smaller than $f_s^0$ for aerobic heterotrophs (around 0.6 e- eq synthesis/e- eq donor), the $f_s^0$ values for the two autotrophs are much smaller, similar to nitrifiers (why?). The $f_s^0$ value for the one-carbon oxidizers that consume methanol is lower than for other heterotrophs.
  True yield values parallel the $f_s^0$ values.

- Since $\hat{q}$ and b values are roughly similar (i.e., 12 g OD/g VSSa-d and 0.05/d), $[\theta_\chi^{min}]_{lim}$ is controlled mainly by Y.

$$[\theta_\chi^{min}]_{lim} = \frac{1}{Y\hat{q} - b}$$

- $S_{min}$ values are less than 1 mg OD/l, which means that high residuals of BOD in the effluent are not a special problem.

- While high DO is required for maximum nitrification, high DO slows or stop denitrification. Therefore, the process design and operation must reconcile these conflicting physiological characteristics.

# 10.1 Physiology of Denitrifying Bacteria

$$f_s^0 = \frac{1}{1 - \frac{\Delta G_s}{\varepsilon \Delta G_r}}$$

$$\Rightarrow f_s^0 = \frac{1}{1 + \frac{\Delta G_s}{-\varepsilon \Delta G_r}}$$

$-\Delta G_r \uparrow \Rightarrow f_s^0 \uparrow$

$\Delta G_s \uparrow \Rightarrow f_s^0 \downarrow$

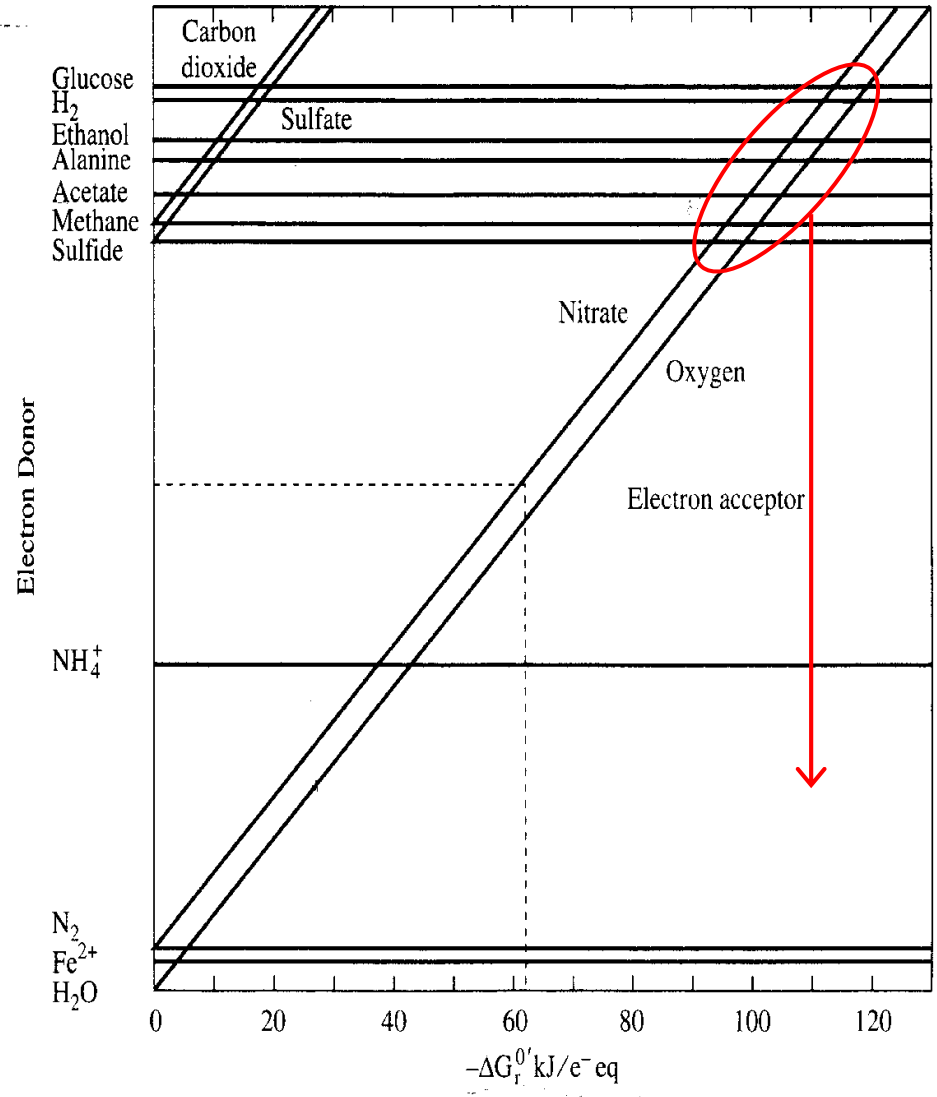



**Figure 2.2** Relationship between various electron donors and acceptors and resulting reaction free energy.

# 2.7 Yield Coefficient and Reaction Energetics

√ **Let's review Sec. 2.7**

$$\Delta G_s = \frac{\Delta G_p}{\varepsilon^n} + \frac{\Delta G_{pc}}{\varepsilon}$$

$$\Delta G_p = 35.09 - \Delta G_c^{0'}$$

$\Delta G_{pc}$ = [an estimated value of 3.33 kJ/g cell (McCarty, 1971)] x [5.65 g/e$^-$ eq]

**from Table 2.4, ammonium as Nitrogen source, 113.8/20 = 5.65*

= 18.8 kJ/e$^-$ eq

***e.g., Heterotrophic bacterial growth using organics***

***- Acetate (carbon & e- source)***

$\Delta G_c^{0'}$ = 27.40 (Table 2.3), $\Delta G_p$ = 35.09 – 27.40 = 7.69 kJ/e- eq

***- Glucose (carbon & e- source)***

$\Delta G_c^{0'}$ = 41.35 (Table 2.3), $\Delta G_p$ = 35.09 – 41.35 = –6.26 kJ/e- eq

**Table 2.3** Organic half-reactions and their Gibb's free energy

| Reaction Number | Reduced Compounds | Half-reaction | $\Delta G^{0'}$ kJ/e$^-$ eq |
|---|---|---|---|
| O-1 | Acetate: | $\frac{1}{8}\,CO_2 + \frac{1}{8}\,HCO_3^- + H^+ + e^- = \frac{1}{8}\,CH_3COO^- + \frac{3}{8}\,H_2O$ | 27.40 |
| O-2 | Alanine: | $\frac{1}{6}\,CO_2 + \frac{1}{12}\,HCO_3^- + \frac{1}{12}\,NH_4^+ + \frac{11}{12}\,H^+ + e^- = \frac{1}{12}\,CH_3CHNH_2COO^- + \frac{5}{12}\,H_2O$ | 31.37 |
| O-3 | Benzoate: | $\frac{1}{5}\,CO_2 + \frac{1}{30}\,HCO_3^- + H^+ + e^- = \frac{1}{30}\,C_6H_5COO^- + \frac{13}{30}\,H_2O$ | 27.34 |
| O-4 | Citrate: | $\frac{1}{6}\,CO_2 + \frac{1}{6}\,HCO_3^- + H^+ + e^- = \frac{1}{18}\,(COO^-)CH_2COH(COO^-)CH_2COO^- + \frac{4}{9}\,H_2O$ | 33.08 |
| O-5 | Ethanol: | $\frac{1}{6}\,CO_2 + H^+ + e^- = \frac{1}{12}\,CH_3CH_2OH + \frac{1}{4}\,H_2O$ | 31.18 |
| O-6 | Formate: | $\frac{1}{2}\,HCO_3^- + H^+ + e^- = \frac{1}{2}\,HCOO^- + \frac{1}{2}\,H_2O$ | 39.19 |
| O-7 | Glucose: | $\frac{1}{4}\,CO_2 + H^+ + e^- = \frac{1}{24}\,C_6H_{12}O_6 + \frac{1}{4}\,H_2O$ | 41.35 |
| O-8 | Glutamate: | $\frac{1}{6}\,CO_2 + \frac{1}{9}\,HCO_3^- + \frac{1}{18}\,NH_4^+ + H^+ + e^- = \frac{1}{18}\,COOHCH_2CH_2CHNH_2COO^- + \frac{4}{9}\,H_2O$ | 30.93 |
| O-9 | Glycerol: | $\frac{3}{14}\,CO_2 + H^+ + e^- = \frac{1}{14}\,CH_2OHCHOHCH_2OH + \frac{3}{14}\,H_2O$ | 38.88 |
| O-10 | Glycine: | $\frac{1}{6}\,CO_2 + \frac{1}{6}\,HCO_3^- + \frac{1}{6}\,NH_4^+ + H^+ + e^- = \frac{1}{6}\,CH_2NH_2COOH + \frac{1}{2}\,H_2O$ | 39.80 |
| O-11 | Lactate: | $\frac{1}{6}CO_2 + \frac{1}{12}\,HCO_3^- + H^+ + e^- = \frac{1}{12}\,CH_3CHOHCOO^- + \frac{1}{3}\,H_2O$ | 32.29 |
| O-12 | Methane: | $\frac{1}{8}\,CO_2 + H^+ + e^- = \frac{1}{8}\,CH_4 + \frac{1}{4}\,H_2O$ | 23.53 |
| O-13 | Methanol: | $\frac{1}{6}\,CO_2 + H^+ + e^- = \frac{1}{6}\,CH_3OH + \frac{1}{6}\,H_2O$ | 36.84 |
| O-14 | Palmitate: | $\frac{15}{19}\,CO_2 + \frac{1}{92}\,HCO_3^- + H^+ + e^- = \frac{1}{92}\,CH_3(CH_2)_{14}COO^- + \frac{31}{92}\,H_2O$ | 27.26 |
| O-15 | Propionate: | $\frac{1}{7}\,CO_2 + \frac{1}{14}\,HCO_3^- + H^+ + e^- = \frac{1}{14}\,CH_3CH_2COO^- + \frac{5}{14}\,H_2O$ | 27.63 |
| O-16 | Pyruvate: | $\frac{1}{5}\,CO_2 + \frac{1}{10}\,HCO_3^- + H^+ + e^- = \frac{1}{10}\,CH_3COCOO^- + \frac{2}{5}\,H_2O$ | 35.09 |
| O-17 | Succinate: | $\frac{1}{7}\,CO_2 + \frac{1}{7}\,HCO_3^- + H^+ + e^- = \frac{1}{14}\,(CH_2)_2(COO^-)_2 + \frac{3}{7}\,H_2O$ | 29.09 |
| O-18 | Domestic Wastewater: | $\frac{9}{50}\,CO_2 + \frac{1}{50}\,NH_4^+ + \frac{1}{50}\,HCO_3^- + H^+ + e^- = \frac{1}{50}\,C_{10}H_{19}O_3N + \frac{9}{25}\,H_2O$ | * |
| O-19 | Custom Organic Half Reaction: | $\frac{(n-c)}{d}\,CO_2 + \frac{c}{d}\,NH_4^+ + \frac{c}{d}\,HCO_3^- + H^+ + e^- = \frac{1}{d}\,C_nH_aO_bN_c + \frac{2n-b+c}{d}\,H_2O$ where, $d = (4n + a - 2b - 3c)$ | * |
| O-20 | Cell Synthesis: | $\frac{1}{5}\,CO_2 + \frac{1}{20}\,NH_4^+ + \frac{1}{20}\,HCO_3^- + H^+ + e^- = \frac{1}{20}\,C_5H_7O_2N + \frac{9}{20}\,H_2O$ | * |

# 10.1 Physiology of Denitrifying Bacteria

- **The denitrifying bacteria often use $NO_3^-$ or $NO_2^-$ as the N source for cell synthesis.**

  - The extra electron cost increase $f_s^0$ and probably reduces Y.

$$f_s^0 = \frac{1}{1 + \frac{\Delta G_s}{-\varepsilon \Delta G_r}} \qquad Y = \frac{f_s^0 (M_c)}{(n_e)(8)}$$

$$\Delta G_s = \frac{\Delta G_p}{\varepsilon^n} + \frac{\Delta G_{pc}}{\varepsilon}$$

$\Delta G_{pc}$ = [an estimated value of 3.33 kJ/g cell x [113.8 g/ n $e^-$ eq]

| | | |
|---|---|---|
| C-1 | $\frac{1}{5}CO_2 + \frac{1}{20}HCO_3^- + \frac{1}{20}NH_4^+ + H^+ + e^-$ | $= \frac{1}{20}C_5H_7O_2N + \frac{9}{20}H_2O$ |
| Nitrate as Nitrogen Source | | |
| C-2 | $\frac{1}{28}NO_3^- + \frac{5}{28}CO_2 + \frac{29}{28}H^+ + e^-$ | $= \frac{1}{28}C_5H_7O_2N + \frac{11}{28}H_2O$ |
| Nitrite as Nitrogen Source | | |
| C-3 | $\frac{5}{26}CO_2 + \frac{1}{26}NO_2^- + \frac{27}{26}H^+ + e^-$ | $= \frac{1}{26}C_5H_7O_2N + \frac{10}{26}H_2O$ |
| Dinitrogen as Nitrogen Source | | |
| C-4 | $\frac{5}{23}CO_2 + \frac{1}{46}N_2 + H^+ + e^-$ | $= \frac{1}{23}C_5H_7O_2N + \frac{8}{23}H_2O$ |

# 10.2 Tertiary Denitrification

## √ Denitrification processes

- Tertiary denitrification : exogenous electron donors are needed (added).
- One sludge denitrification : electron donors are already present in the wastewater

## √ Tertiary denitrification

- **Used for water and wastewater containing $NO_3^-$ or $NO_2^-$ , but little or no electron donors.**

i) Agricultural runoff contaminated with nitrogen fertilizers

ii) Drinking water supplies in agricultural regions (high N-contaminated raw water)

iii) Effluent from aerobic biological process (i.e., secondary treatment)

# 10.2 Tertiary Denitrification

- Electron donor: the rate limiting step in almost all circumstances

  i) Organic electron donor

  - Most commonly supplied
  - They promote the accumulation of heterotrophic denitrifiers.
  - In terms of physiology and kinetics, very similar to the aerobic heterotrophs used for BOD oxidation → Similar design criteria
  - Historically methanol was chosen for its economic benefits, not because it is a better "exogenous" electron donor than any other choice.

$$0.1667CH_3OH + 0.1561NO_3^- + 0.1561^+ \rightarrow 0.00954C_5H_7O_2N + 0.0733N_2 + 0.3781H_2O + 0.119CO_2$$

- Concentrated organic wastes are good $e^-$-donors

- Waste streams from the food processing and beverage industry are good choice because of high BOD concentration & very high C/N ratio.

  → low N is desirable because the goal of denitrification is total removal of N.

# 10.2 Tertiary Denitrification

ii) Inorganic electron donor

**- $H_2$ is an excellent electron donor for autotrophic denitrification**

→ low cost per electron equivalent compared to organic compounds

→ less biomass production than heterotrophs

→ no reduced nitrogen ($NH_4^+$) added (organic $e^-$-donors may contain reduced N)

→ lack of safe and efficient $H_2$ transfer system (disadvantage)

**- Reduced sulfur**

→ Most common of reduced S is elemental sulfur, $S_{(s)}$.

→ Normally embedded in a solid matrix that includes a solid base, such as $CaCO_3$, because the oxidation of $S_{(s)}$ generates strong acid.

$$S(s) + \frac{6}{5}NO_3^- + \frac{2}{5}H_2O \rightarrow SO_4^{2-} + \frac{3}{5}N_2 + \frac{4}{5}H^+$$

# 10.2 Tertiary Denitrification

## √ Example 10.1

**STOICHIOMETRY OF DENITRIFICATION REACTIONS** Three different denitrification schemes are being tested: heterotrophic with methanol as the donor, heterotrophic with acetate as the donor, and autotrophic with $H_2$ as the donor. From Table 10.1, we use $f_s^0$ values of 0.36, 0.52, and 0.21, respectively. Each reactor is operated with an SRT of 15 d. We are to compute the overall stoichiometric reaction for each system under the operating conditions.

**Denitrification schemes**

- Heterotrophic with methanol
- Heterotrophic with acetate
- Autotrophic with $H_2$

**Parameters**

- $f_s^0$ : **0.36, 0.52, 0.21**
- $\theta_x$ : **15 days**

**Compute the overall Stoichiometric reactions for each system !**

# 10.2 Tertiary Denitrification

**Table 10.1** Representative stoichiometric and kinetic parameters for denitrifiers ($T$ = 20 °C)

| Electron Donor | Methanol | BOD | $H_2$ | $S^0$ |
|---|---|---|---|---|
| C-source | methanol | BOD | $CO_2$ | $CO_2$ |
| $f_s^0$ | 0.36 | 0.52 | 0.21 | 0.13 |
| $Y$, g $VSS_a$/g donor | 0.27 | 0.26 | 0.85 | 0.10 |
| g $VSS_a$/g OD | 0.18 | 0.26 | 0.11 | 0.07 |
| $\hat{q}'$, g donor/g $VSS_a$-d | 6.9 | 12 | 1.6 | 8.1 |
| g OD/g $VSS_a$-d | 10.4 | 12 | 11.8 | 11.2 |
| $K$, mg donor/l | 9.1 | 1 | 1 | ? |
| mg OD/l | 13.7 | 1 | 0.13 | ? |
| $b$, $d^{-1}$ | 0.05 | 0.05 | 0.05 | 0.05 |
| $[\theta_x^{min}]_{lim}$, d | 0.55 | 0.33 | 0.76 | 1.3 |
| $S_{min}$, mg donor/l | 0.25 | 0.017 | 0.04 | ? |
| mg OD/l | 0.38 | 0.017 | 0.005 | ? |
| $D$, $cm^2$/d | 1.3 | 1.0 | 0.9 | — |
| $J_R$, kg OD/1,000 $m^2$-d | 1.5 | 0.5 | 1.2 | ? |
| $S^*_{min}$ (no detachment) | 0.027 | 0.017 | 0.040 | 0.066 |
| ($b_{det}$ = 0.2/d) | 0.15 | 0.087 | 0.23 | 0.45 |
| $K^*$ | 1.8 | 0.4 | 2.2 | ? |

Notes: For $K^*$, $L$ = 40 $\mu m$, $D_f/D$ = 0.8, and $X_f$ = 40 mg $VSS_a/cm^3$. ? = not yet determined —not applicable.

# 10.2 Tertiary Denitrification

√ **Example 10.1**

From Ch. 3

$$f_s = f_s^0 \frac{1+(1-f_d)b\theta_x}{1+b\theta_x}$$

1. Calculate $f_s$, $f_e$
2. Define cell synthesis equation ($R_c$) ( Equation C-2, Table 2.4, same for all)
3. Define acceptor equation ($R_a$) (Equation I-7, Table 2.2, same for all )
4. Define donor equation ($R_d$) (methanol, acetate, $H_2$, Table 2.3)
5. Compute the overall stoichiometric equation

$$R = f_e R_a + f_s R_c - R_d$$

# 10.2 Tertiary Denitrification

i) Heterotrophic with Methanol

b = 0.05/day (Table 10.1) , $f_d$=0.8 for all system

$$f_s = f_s^0 \frac{1+(1-f_d)b\theta_x}{1+b\theta_x}$$

1. Calculate $f_s$, $f_e$

| $f_s$ | $f_e$ |
|---|---|
| 0.267 | 0.733 |

2. Cell synthesis equation

$$\frac{1}{28}NO_3^- + \frac{5}{28}CO_2 + \frac{29}{28}H^+ + e^- \rightarrow \frac{1}{28}C_5H_7O_2N + \frac{11}{28}H_2O$$

3. Acceptor equation

$$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- \rightarrow \frac{1}{10}N_2 + \frac{3}{5}H_2O$$

4. Donor equation

$$\frac{1}{6}CO_2 + H^+ + e^- \rightarrow \frac{1}{6}CH_3OH + \frac{1}{26}H_2O$$

# 10.2 Tertiary Denitrification

5. Overall equation

$$f_s R_c \quad 0.267\times\left(\frac{1}{28}NO_3^- + \frac{5}{28}CO_2 + \frac{29}{28}H^+ + e^- \rightarrow \frac{1}{28}C_5H_7O_2N + \frac{11}{28}H_2O\right)$$

$$f_e R_a \quad 0.733\times\left(\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- \rightarrow \frac{1}{10}N_2 + \frac{3}{5}H_2O\right)$$

$$-R_d \quad \frac{1}{6}CH_3OH + \frac{1}{26}H_2O \rightarrow \frac{1}{6}CO_2 + H^+ + e^-$$

$$0.1667CH_3OH + 0.1561NO_3^- + 0.1561H^+ \rightarrow 0.00954C_5H_7O_2N + 0.0733N_2 + 0.3781H_2O + 0.119CO_2$$

# 10.2 Tertiary Denitrification

**i) Heterotrophic with methanol**

$$0.1667CH_3OH + 0.1561NO_3^- + 0.1561H^+ \rightarrow 0.00954C_5H_7O_2N + 0.0733N_2 + 0.3781H_2O + 0.119CO_2$$

**ii) Heterotrophic with acetate (homework)**

$$0.125CH_3COO^- + 0.1438NO_3^- + 0.1438H^+ \rightarrow 0.0122C_5H_7O_2N + 0.0658N_2 + 0.125HCO_3^- + 0.0639CO_2 + 0.1542H_2O$$

**iii) Autotrophic with $H_2$ (homework)**

$$0.5H_2 + 0.1773NO_3^- + 0.0246CO_2 + 0.1773H^+ \rightarrow 0.00493C_5H_7O_2N + 0.00862N_2 + 0.5714H_2O$$

# 10.2 Tertiary Denitrification

**Table 10.2** Summary of stoichiometry for various denitrification reactions at $T = 20\ ^{\circ}C$ (Example 10.1)

| Reaction Type | Heterotrophic with Methanol | Heterotrophic with Acetate | Autotrophic with $H_2$ |
|---|---|---|---|
| $f_s$ | 0.267 | 0.342 | 0.138 |
| Electron equivalents in donor | 1 | 1 | 1 |
| Electron equivalents in biomass | | | |
| Total ($= f_s$) | 0.267 | 0.342 | 0.138 |
| in C ($= \frac{20}{28} \cdot f_s$) | 0.191 | 0.244 | 0.099 |
| in N ($= \frac{8}{28} \cdot f_s$) | 0.076 | 0.098 | 0.039 |
| $NO_3^-$ consumed | | | |
| mol | 0.1561 | 0.1438 | 0.1773 |
| $e^-$ eq as acceptor ($= f_e$) | 0.733 | 0.658 | 0.862 |
| $e^-$ eq as N source | 0.076 | 0.098 | 0.039 |
| $e^-$ eq total | 0.809 | 0.756 | 0.901 |
| Net $H^+$ consumed | | | |
| $H^+$ equivalents | 0.1561 | 0.1438 | 0.1773 |
| Key ratios | | | |
| g OD/g $NO_3^-$-N | 3.66 | 3.97 | 3.22 |
| g alk as $CaCO_3$/g $NO_3^-$-N | 3.57 | 3.57 | 3.57 |
| g VSS/g $NO_3^-$-N | 0.490 | 0.685 | 0.224 |
| g VSS/g OD ($= Y_n$) | 0.135 | 0.172 | 0.0696 |

$e^-$-donor

(= C/N ratio)

(= buffer requirement)

(=sludge wasting rate)

# 10.3 One-Sludge Denitrification

## √ One-sludge denitrification

the water contains an electron donor that can drive denitrification.

- One-sludge denitrification (= single-sludge = combined denitrification) uses the BOD in the influent of a wastewater to drive denitrification

- For one-sludge denitrification, the aerobic process (the influent) should

1) Provide good aerobic conditions that allow full nitrification
2) Reserve BOD (organic electron donor) for anoxic denitrification.

*1) and 2) seems to conflict with each other, but they should be done simultaneously . Consequently, the task is to how to reconcile them.

# 10.3 One-Sludge Denitrification

- **Benefits :**

  - No exogenous electron donor needs to be added.
    → chemical costs are reduced over tertiary denitrification.

  - Some of the influent BOD is oxidized with nitrate as the electron acceptor (not $O_2$).
    → aeration costs are reduced compared to alternative systems that oxidize all BOD and nitrify the reduced-nitrogen forms in the influent with $O_2$ .

  - Full or nearly full N removal is achieved → protecting receiving waters at the risk of cultural eutrophication. (Low $S_{min}$)

# 10.3.1 Basic One-Sludge Strategies

- Influent wastewater contains TKN.

- In one sludge denitrification (not one reactor), the TKN must be oxidized to $NO_3^-$-N without oxidizing all the BOD before denitrification takes place.

  Total Kjeldahl nitrogen (TKN) = organic BOD and reduced nitrogen (NH4+)

- Despite a wide range of engineering configurations, all one-sludge processes rely on one or more of three basic strategies.

- Three basic strategies for reserving organic electron donor while nitrification takes place :

  1) **Biomass storage and decay**
  2) **Classical predenitrification**
  3) **Simultaneous nitrification with denitrification**

# 10.3.1 Basic One-Sludge Strategies

## √ Biomass storage and decay

- The synthesis of biomass stores electron equivalents that originally came from the BOD and can be released through endogenous respiration to drive denitrification.

TKN → $NO_3^-$-N
BOD: partly oxidized and partly stored (synthesis)

$NO_3^-$-N → $N_2$
Biomass as electron donor (endogenous respiration)

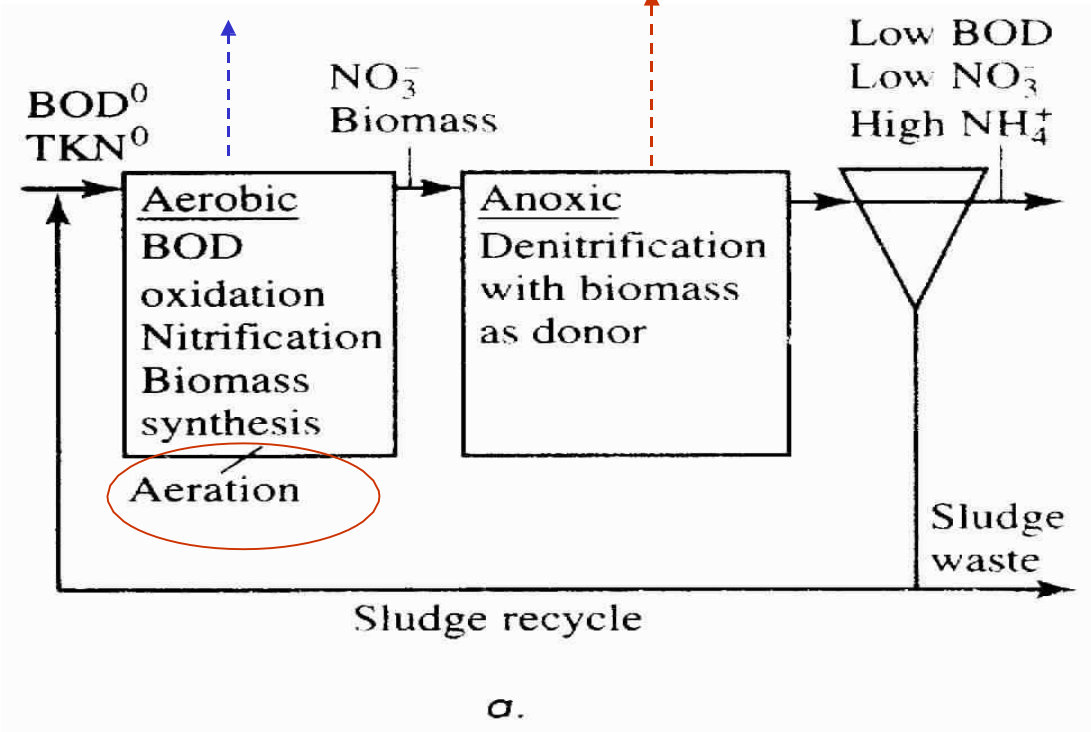



**Fig.10.1 (a) biomass storage and decay**

# 10.3.1 Basic One–Sludge Strategies

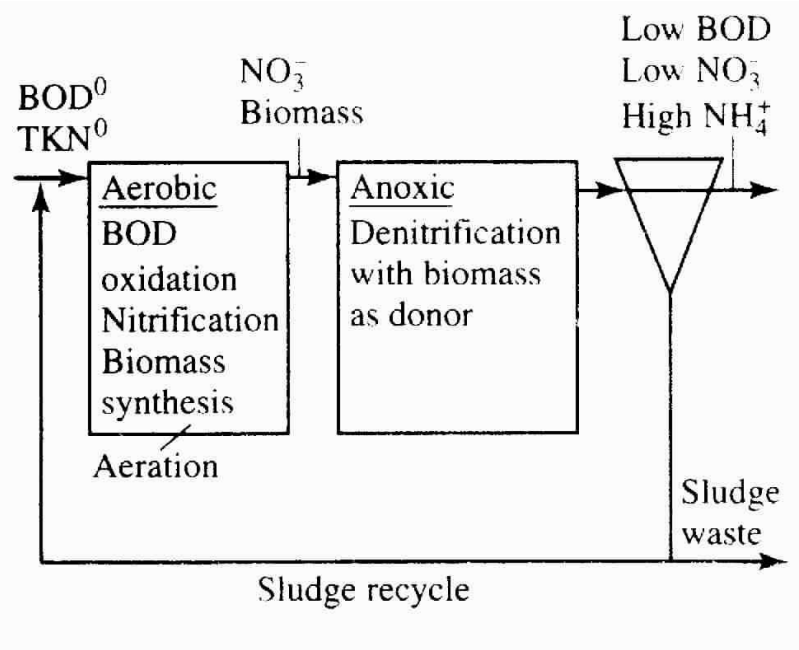
- It is called *Wuhrmann biomass decayer* (*Swiss engineer* K. Wuhrmann, 1964)

- Biomass storage and decay has limited applicability by itself and is not often employed as a stand-alone process due to two shortcomings:

  1) Endogenous respirations has slow kinetics (*b = 0.05/d*)

     → a high conc. of MLVSS (*operating problems with settler and recycle*) and a long HRT in a anoxic tank
     → high capital costs are necessary

  2) The decay of biomass always releases $NH_4^+$-N from the anoxic step



# 10.3.1 Basic One-Sludge Strategies

## √ Classical predenitrification

- The first tank (anoxic); the influent BOD (electron donor) is directlyutilized for denitrification.
- The second tank (aerobic); the influent TKN is nitrified to $NO_3^-$ and any remained BOD is oxidized.
- The nitrate formed in the aerobic tank is recycled to an anoxic tank.

Directly utilizes the influent BOD (electron donor) for denitrification

TKN → $NO_3^-$-N
Remained BOD: aerobically consumed

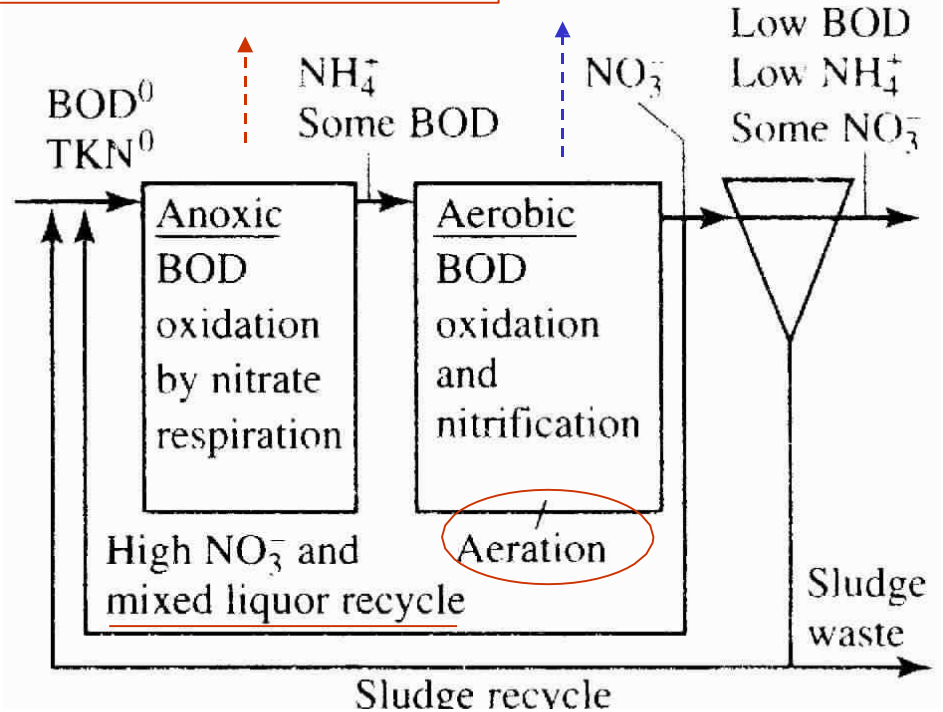



Fig.10.1
(b) classical predenitrification

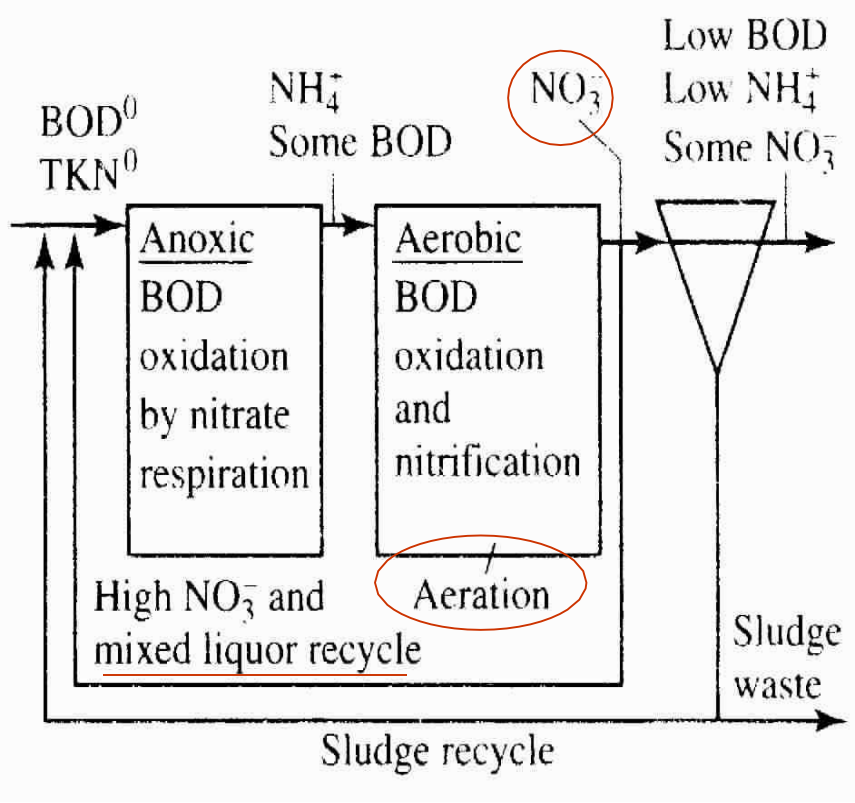
# 10.3.1 Basic One-Sludge Strategies

- Fractional removal of N = ~ $\frac{Q^{r2}}{Q + Q^{r2}}$

$Q$ : flow rate
$Q^{r2}$ : mixed-liquor recycle flow rate

- The large recycle flow of $NO_3^-$ from the second to the first tank is necessary, because $NO_3^-$ not recycled leaves in the effluent.

- **Recycle ratios of 400 percent or more** are employed to bring enough $NO_3^-$ back to the anoxic tank so that total N removals are substantial.



# 10.3.1 Basic One-Sludge Strategies

## √ Classical predenitrification

Widespread use worldwide

- ***Advantages:***

  i) Direct use of influent BOD for denitrification
  → reduces aeration costs for the removal of BOD
  ii) Faster kinetics than with *biomass storage and decay*
  iii) No release of $NH_4^+$-N in the effluent

- ***Disadvantage:***

  i) large mixed-liquor recycle rate
  → increases costs of piping and pumping

# 10.3.1 Basic One-Sludge Strategies

## √ Simultaneous nitrification with denitrification

- Various nitrogen reductases using N as e$^-$acceptor are repressed only when the DO concentration is well above 1 mg/L.
- However, inhibition of the nitrogen reductase is not severe when the DO concentration is less than 1 mg/L.
- DO concentration is depressed inside the aggregates that normally form in treatment systems; thus, denitrification can occur inside the floc (or biofilm), as long as the electron donor (BOD) penetrates inside.

- When D.O. concentration is poised at a suitably low level (< ~ 1 mg/L), anoxic denitrification can occur in parallel to the aerobic reactions of nitrification and aerobic BOD oxidation.

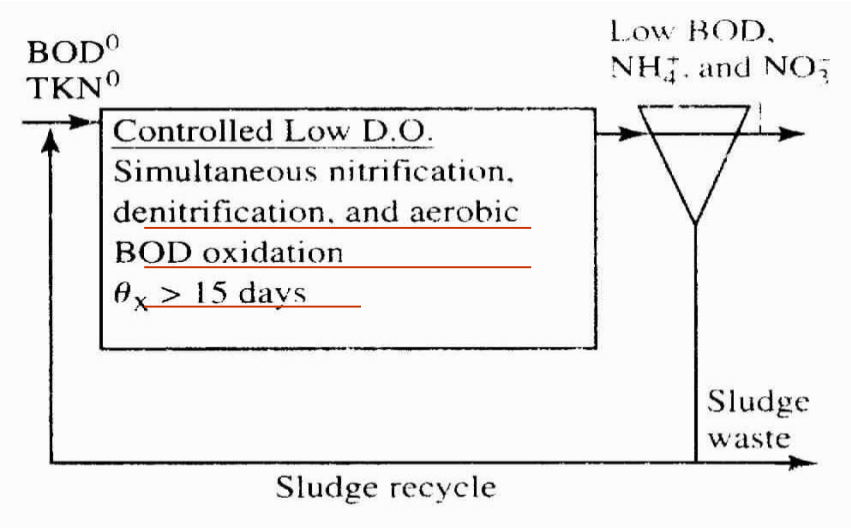



**Fig.10.1**
**(c) Simultaneous nitrification with denitrification**

# 10.3.1 Basic One-Sludge Strategies

- 100% N removal by simultaneous nitrification with denitrification has been documented (*Rittmann and Langeland, 1985*), and small amounts of denitrification probably occur in most activated sludge systems that nitrify and have DO. conc. below saturation (*deSilva, 1997*)

- Simultaneous nitrification with denitrification offers all the advantages of predenitrification, but overcomes the main disadvantage, the high recycle rate.

- Maintaining a low DO concentration throughout one reactor creates an infinitely high recycle ratio and allows essentially 100% N removal.

- ***Drawback***
  : We do not yet know the combinations of SRT, HRT, and DO. conc. that guarantee reliability.

# 9.3 Activated Sludge Nitrification : One-Sludge Versus Two-Sludge

**Different combinations are possible.**

**(Aerobic BOD oxidation + Nitrification + Denitrification)**

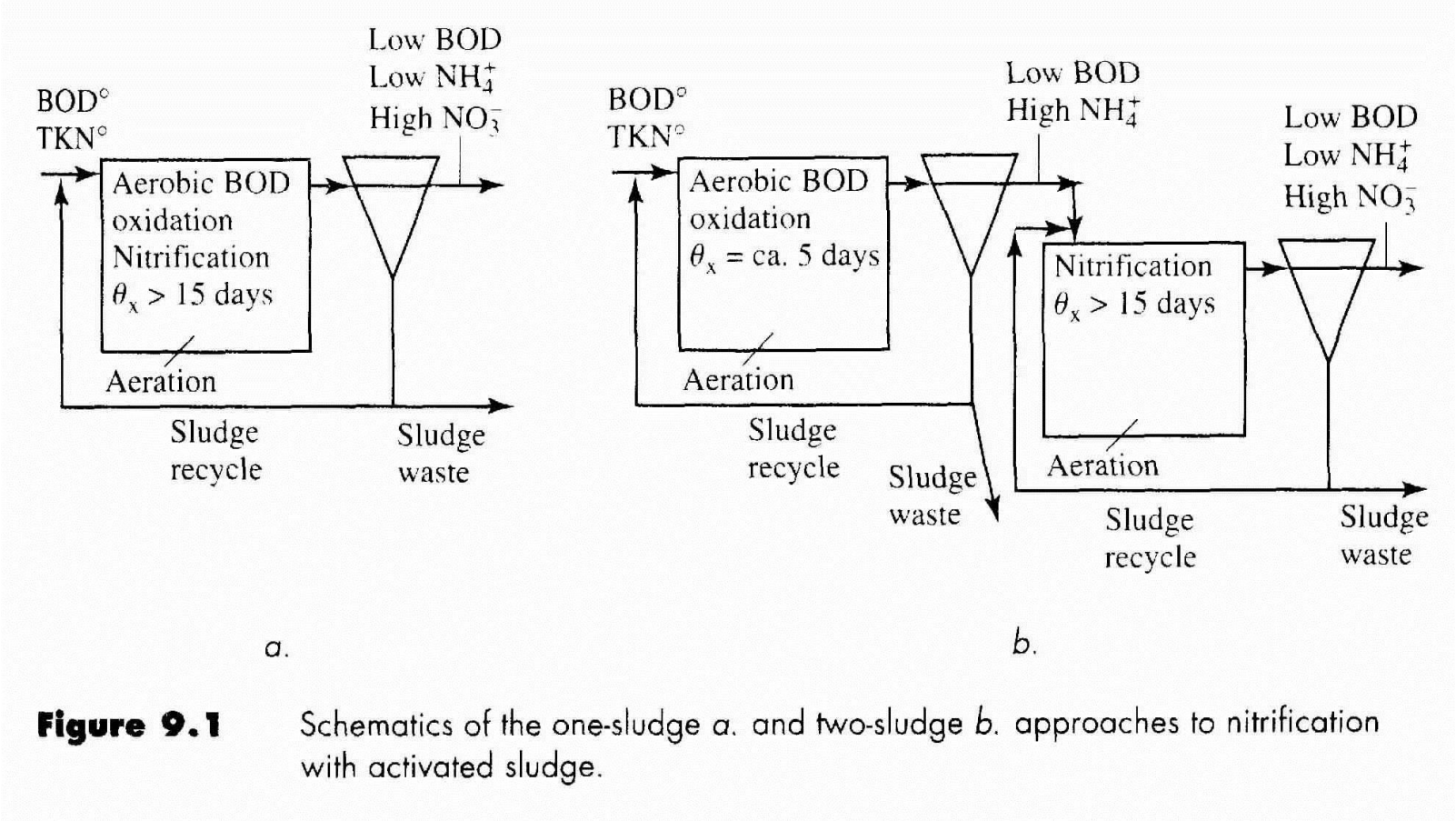



**Figure 9.1** Schematics of the one-sludge *a.* and two-sludge *b.* approaches to nitrification with activated sludge.

# 10.3.1 Basic One-Sludge Strategies

## √ Common features of all one-sludge processes

- One community (or one sludge) of microorganisms carries out all the reactions.
- The heterotrophs switch back and forth between aerobic and anoxic (*endogenous*) respiration, or they do both simultaneously.
- Because the nitrifiers are slow growing autotrophs, their growth rate controls the SRT needed. SRTs greater than 15 days are required in most cases, sometimes much longer SRTs are used.
- The longer SRTs provide an added safety factor for the nitrifiers who experience periods of low or zero DO.
- The long SRTs mean that accumulation of inert suspended solids is important.

# 10.3.1 Basic One-Sludge Strategies

## √ Common features of all one-sludge processes

- A practical outcome of a long SRT is that the HRT (in settler) needs to increase in order to keep the MLSS conc. within reasonable limits dictated by settler performance. That's why settler parameters for one-sludge denitrification is similar to those used for extended aeration activated sludge.

- HRTs for predinitrification and simultaneous nitrification with denitrification are at least 10 h for typical sewage, and 24 h or greater are used in some instances.

- To overcome the limitations of one-sludge denitrification, the Barnard process, sequencing batch reactor (SBR), and biofilm systems are developed.

# 10.3.2 Variations on the Basic One-Sludge processes

## √ **Barnard process (1975)** *by Dr. J. Barnard of South Africa*

- Influent TKN : 50 mg/L
- recycle ratio ($Q^{r2}$) from reactor 2 to 1 : 400 %
- **Reactor** 1: denitrification rate is 100% of recycled input, or 80 % of the influent TKN

- **Reactor 2**

  $NO_3^-$-N/L leaving : 10 mg/L (20%)

- **Reactor 3** :endogenous decay of cells

- 0.3 mg $NH_4^+$-N is released per mg $NO_3^-$-N due to endogenous cell decay

-Because 10 mg/L of $NO_3$-N is converted to $N_2$ gas, Reactor 3 releases 3mg $NH_3$-N/L

- **Reactor 4** releases 3 mg $NO_3$-N/L

**Final effluent TKN : 3 mg $NO_3$-N/L**
**Total removal rate : 94 %**

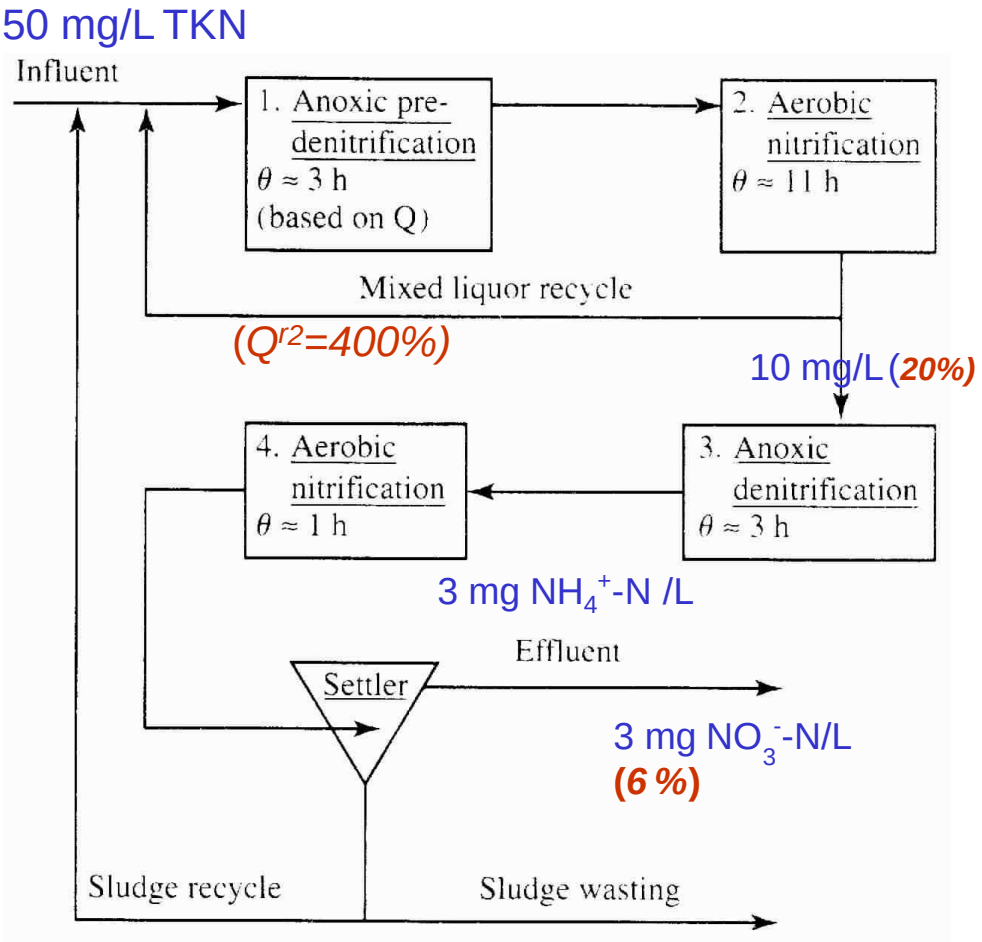



**Fig.10.2 Schematic of the Barnard process**

# 10.3.2 Variations on the Basic One-Sludge processes

## √ Barnard process

- Well established worldwide one-sludge denitrification process **(> 90% N removal)**

- Drawbacks
  - need many tanks
  - long HRT
  - significant mixed-liquor recycle (400%) between reactors 2 and 1

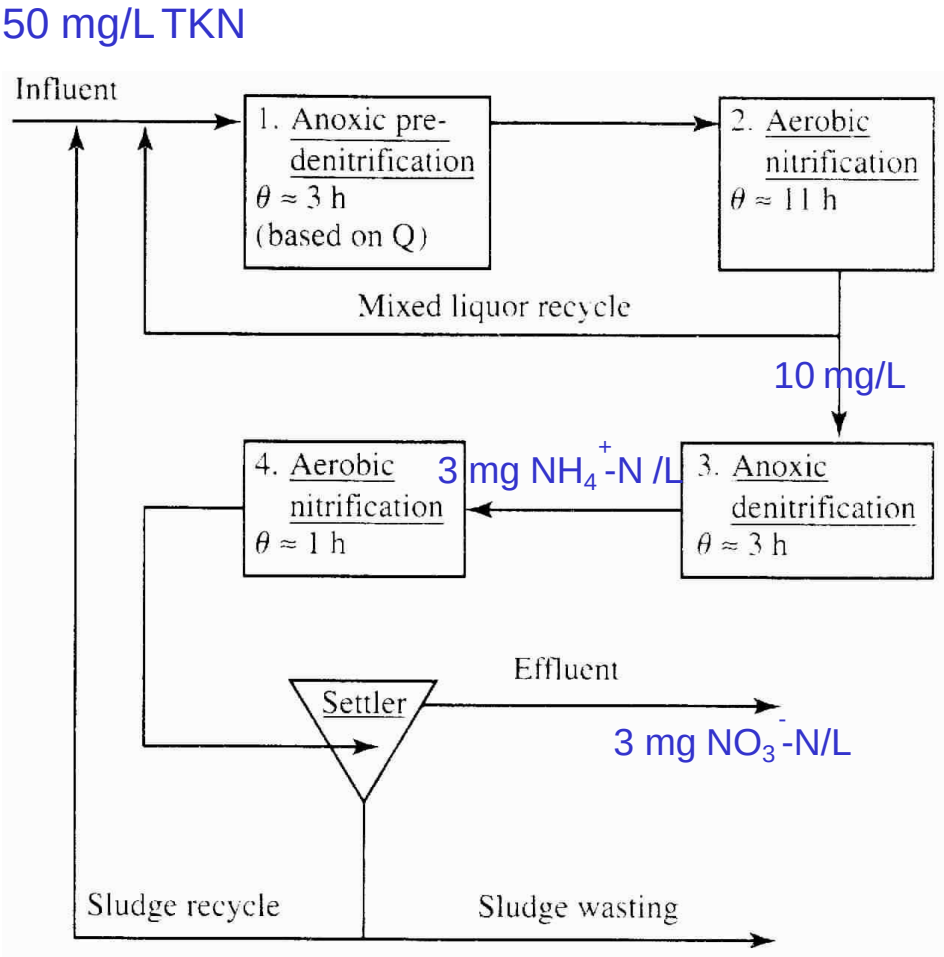



**Fig.10.2 Schematic of the Barnard process**