Example 10.1  Stoichiometry of denitrification reactions

Denitrification scheme

- Heterotrophic with methanol
- Heterotrophic with acetate
- Autotrophic with $\text{H}_2$

Parameters

- $f^0$s values: 0.36, 0.52, 0.21
- SRT: 15 days

Compute the overall Stoichiometric reactions for each system
Example 10.1  Stoichiometry of denitrification reactions

1. Calculate the $f_s$, $f_e$

2. Cell synthesis ($R_c$) with NO$_3$ (Equation C-2, Table 2.4, same for all)

3. Acceptor equation ($R_a$) (Equation I-7, Table 2.2, same for all)

4. Donor equation ($R_d$) (methanol, acetate, H$_2$, Table 2.3)

5. Compute the stoichiometric equation

\[
 f_s = f_s^0 \frac{1 + (1 - f_d^0) b \theta_x}{1 + b \theta_x} \quad [3.33]
\]

\[
 R = f_e R_a + f_s R_c - R_d \quad [2.37]
\]
Example 10.1 Stoichiometry of denitrification reactions

i) Heterotrophic with Methanol

Assumption: \( b = 0.05 \text{/day (Table 10.1)} \), \( fd = 0.8 \) for all system

1. Calculate \( fs, fe \)

<table>
<thead>
<tr>
<th></th>
<th>( fs )</th>
<th>( fe )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.267</td>
<td>0.733</td>
</tr>
</tbody>
</table>

2. Cell synthesis equation

\[
\frac{1}{28} \text{NO}_3^- + \frac{5}{28} \text{CO}_2 + \frac{29}{28} \text{H}^+ + \text{e}^- \rightarrow \frac{1}{28} \text{C}_5\text{H}_7\text{O}_2\text{N} + \frac{11}{28} \text{H}_2\text{O}
\]

3. Acceptor equation

\[
\frac{1}{5} \text{NO}_3^- + \frac{6}{5} \text{H}^+ + \text{e}^- \rightarrow \frac{1}{10} \text{N}_2 + \frac{3}{5} \text{H}_2\text{O}
\]

4. Donor equation

\[
\frac{1}{6} \text{CO}_2 + \text{H}^+ + \text{e}^- \rightarrow \frac{1}{6} \text{CH}_3\text{OH} + \frac{1}{26} \text{H}_2\text{O}
\]
Example 10.1 Stoichiometry of denitrification reactions

\[ f_{sR_c} \quad 0.267 \times (\frac{1}{28} \text{NO}_3^- + \frac{5}{28} \text{CO}_2 + \frac{29}{28} \text{H}^+ + \text{e}^- \rightarrow \frac{1}{28} \text{C}_5\text{H}_7\text{O}_2\text{N} + \frac{11}{28} \text{H}_2\text{O}) \]

\[ f_{eR_a} \quad 0.733 \times (\frac{1}{5} \text{NO}_3^- + \frac{6}{5} \text{H}^+ + \text{e}^- \rightarrow \frac{1}{10} \text{N}_2 + \frac{3}{5} \text{H}_2\text{O}) \]

\[ - R_d \quad \frac{1}{6} \text{CH}_3\text{OH} + \frac{1}{26} \text{H}_2\text{O} \rightarrow \frac{1}{6} \text{CO}_2 + \text{H}^+ + \text{e}^- \]

\[ 0.1667 \text{CH}_3\text{OH} + 0.1561 \text{NO}_3^- + 0.1561 \text{H}^+ \]
\[ \rightarrow 0.00954 \text{C}_5\text{H}_7\text{O}_2\text{N} + 0.0733 \text{N}_2 + 0.3781 \text{H}_2\text{O} + 0.119 \text{CO}_2 \]
Example 10.1 Stoichiometry of denitrification reactions

i) Heterotrophic with methanol

\[ 0.1667 \text{CH}_3\text{OH} + 0.1561 \text{NO}_3^- + 0.1561 \text{H}^+ \rightarrow 0.00954 \text{C}_5\text{H}_7\text{O}_2\text{N} + 0.0733 \text{N}_2 + 0.3781 \text{H}_2\text{O} + 0.119 \text{CO}_2 \]

ii) Heterotrophic with acetate

\[ 0.125 \text{CH}_3\text{COO}^- + 0.1438 \text{NO}_3^- + 0.1438 \text{H}^+ \rightarrow 0.0122 \text{C}_5\text{H}_7\text{O}_2\text{N} + 0.0658 \text{N}_2 + 0.125 \text{HCO}_3^- + 0.0639 \text{CO}_2 + 0.1542 \text{H}_2\text{O} \]

iii) Autotrophic with \( \text{H}_2 \)

\[ 0.5 \text{H}_2 + 0.1773 \text{NO}_3^- + 0.0246 \text{CO}_2 + 0.1773 \text{H}^+ \rightarrow 0.00493 \text{C}_5\text{H}_7\text{O}_2\text{N} + 0.00862 \text{N}_2 + 0.5714 \text{H}_2\text{O} \]

Table 10.2.
### Summary of Example 10.1

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

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Heterotrophic with Methanol</th>
<th>Heterotrophic with Acetate</th>
<th>Autotrophic with $H_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_s$</td>
<td>0.267</td>
<td>0.342</td>
<td>0.138</td>
</tr>
<tr>
<td>Electron equivalents in donor</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Electron equivalents in biomass Total ($= f_s$)</td>
<td>0.267</td>
<td>0.342</td>
<td>0.138</td>
</tr>
<tr>
<td>$\text{in } C$ ($= \frac{20}{28} \cdot f_s$)</td>
<td>0.191</td>
<td>0.244</td>
<td>0.099</td>
</tr>
<tr>
<td>$\text{in } N$ ($= \frac{8}{28} \cdot f_s$)</td>
<td>0.076</td>
<td>0.098</td>
<td>0.039</td>
</tr>
<tr>
<td>$\text{NO}_3^-$ consumed mol</td>
<td>0.1561</td>
<td>0.1438</td>
<td>0.1773</td>
</tr>
<tr>
<td>$e^- \text{ eq as acceptor } (= f_o)$</td>
<td>0.733</td>
<td>0.658</td>
<td>0.862</td>
</tr>
<tr>
<td>$e^- \text{ eq as N source}$</td>
<td>0.076</td>
<td>0.098</td>
<td>0.039</td>
</tr>
<tr>
<td>$e^- \text{ eq total}$</td>
<td>0.809</td>
<td>0.756</td>
<td>0.901</td>
</tr>
<tr>
<td>Net $H^+$ consumed $H^+$ equivalents</td>
<td>0.1561</td>
<td>0.1438</td>
<td>0.1773</td>
</tr>
<tr>
<td>Key ratios</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>g OD/g $\text{NO}_3^-$-N</td>
<td>3.66</td>
<td>3.97</td>
<td>3.22</td>
</tr>
<tr>
<td>g alk as CaCO$_3$/g $\text{NO}_3^-$-N</td>
<td>3.57</td>
<td>3.57</td>
<td>3.57</td>
</tr>
<tr>
<td>g VSS/g $\text{NO}_3^-$-N</td>
<td>0.490</td>
<td>0.685</td>
<td>0.224</td>
</tr>
<tr>
<td>g VSS/g OD ($= Y_n$)</td>
<td>0.135</td>
<td>0.172</td>
<td>0.0696</td>
</tr>
</tbody>
</table>
Summary of Example 10.1

1. The observed yield of denitrifiers \( f_s \) declines significantly from acetate to methanol to \( \text{H}_2 \) as the donor.

2. \( 4.3 \sim 13 \% \) of e\(-\) eq of \( \text{NO}_3^- \)-N consumed is used as the N source in synthesis.

   The great % (13 %) is associated with the greatest \( f_s \) (0.342).

   For acetate, e\(-\) eq as N-source = 0.342 x (8/28) = 0.098 (eqns. at p.502)

   \[
   \% \text{ of e\(-\) eq} = \left( \frac{0.098}{0.756} \right) \times 100 = 13 \%.
   \]

3. 28.6 % of the oxygen demand of the biomass is invested in reducing the N-source (\( \text{NO}_3^- \)) to the -3 oxidation state.

4. For heterotrophic nitrification with acetate requires an input of

   \( \sim 4 \text{g BOD}_L / \text{g NO}_3^- -\text{N} \) and produces \( \sim 0.69 \text{ g VSS of biomass (sludge wasting rate)} \) and 3.6 g as \( \text{CaCO}_3 \) of alkalinity (= buffer requirement).
10.3 One-Sludge Denitrification

**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.

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

- Two goals in one-sludge denitrification:
  1) Providing aerobic conditions that allow full nitrification
  2) Providing anoxic conditions and Reserving BOD (organic electron donor) for 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 risk from cultural eutrophication.
10.3.1 Basic One-Sludge Strategies

• Influent wastewater contains TKN. In one sludge denitrification, the TKN must be oxidized to NO$_3^-$ - N without oxidizing all the BOD before denitrification takes place.

\[
\text{Total Kjeldahl nitrogen (TKN) = organic BOD and reduced nitrogen (NH4+)}
\]

• 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 1) **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.

\[
\text{TKN} \rightarrow \text{NO}_3^- \text{-N} \\
\text{BOD: partly oxidized and partly stored (synthesis)}
\]

\[
\text{NO}_3^- \text{-N} \rightarrow \text{N}_2 \\
\text{Biomass as electron donor (endogenous respiration)}
\]

![Fig.10.1 (a) biomass storage and decay](image)
10.3.1 1) **Biomass storage and decay**

- 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 an anoxic tank
     - high capital costs are necessary

  2) the decay of biomass always releases \( \text{NH}_4^+ \)-N from the anoxic step although at concentrations lower than in the influent.
10.3.1 **Classical predenitrification**

- The first tank (anoxic); the influent BOD (electron donor) is directly utilized 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 a anoxic tank ($Q_r^2$; large)

**Fig. 10.1**
(b) classical predenitrification

Directly utilizes the influent BOD (electron donor) for denitrification

TKN $\rightarrow$ NO$_3^-$ N
Remained BOD: aerobically consumed
10.3.1 **Classical predenitrification**

-Fractional removal of N = $\frac{Q_r^2}{Q + Q_r^2}$

$Q$: plant flow rate  
$Q_r$: 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 Classical predenitrification

Widespread use worldwide;

- **Advantages:**
  
  i) direct use of influent BOD for denitrification  
     \[\rightarrow\text{reduces aeration costs for the removal of BOD}\]
  ii) faster kinetics than with *biomass storage and decay*
  iii) no release of \(\text{NH}_4^+\)-N in the effluent

- **Disadvantage:**
  
  i) large mixed-liquor recycle rate  
     \[\rightarrow\text{increases costs of piping and pumping}\]
10.3.1 Simultaneous nitrification with denitrification

Three factors allow all reactions to occur simultaneously.

1) Various nitrogen reductases using N as e⁻ acceptor are repressed only when the D.O. conc. is well above 1 mg/L.

2) However, inhibition of the nitrogen reductase is not severe when the D.O. conc. is less than 1 mg/L.

\[ \text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2 \]

\[ \text{NO}_3^- + 2e^- + 2H^+ = \text{NO}_2^- + H_2O \quad \text{Nitrate Reductase} \]
\[ \text{NO}_2^- + e^- + 2H^+ = \text{NO} + H_2O \quad \text{Nitrite Reductase} \]
\[ 2\text{NO} + 2e^- + 2H^+ = \text{N}_2\text{O} + H_2O \quad \text{Nitric Oxide Reductase} \]
\[ \text{N}_2\text{O} + 2e^- + 2H^+ = \text{N}_2 + H_2O \quad \text{Nitrous Oxide Reductase} \]
10.3.1 Simultaneous nitrification with denitrification

Three factors allow all reactions to occur simultaneously.

3) D.O. conc. 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*.

![Diagram of simultaneous nitrification with denitrification](image)
10.3.1 *Simultaneous nitrification with denitrification*

- 100 percent 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 D.O. 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 D.O. conc. throughout one reactor creates an infinitely high recycle ratio and allows essentially 100 percent N removal.

- **Drawback**

  : We do not yet know the combinations of SRT, HRT, and D.O. conc. that guarantee reliability.
Epilog for One-Sludge Processes

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 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 Epilog for One-Sludge Processes

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.
### Variations on the Basic One-Sludge processes

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

- **Influent TKN**: 50 mg/L
- **Recycle ratio** ($Q_r^2$) from reactor 2 to 1: 400%

**Reactor 1**: denitrification rate is 100% of recycled input and 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 3 mg 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