CE421/521 Environmental Biotechnology

Nitrogen and Phosphorus Cycles
Lecture 9-26-06
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Nitrification Kinetics

\[
\mu = \frac{\mu_{\text{max}} S_{\text{NH}_4}}{K_S + S_{\text{NH}_4}} \cdot \frac{S_{O_2}}{K_O + S_{O_2}}
\]

where
\(\mu_{\text{max}}\) = maximum specific growth rate, h\(^{-1}\)
\(K_S\) = half saturation coefficient for ammonia, mg/L as NH\(_4\)-N
\(K_O\) = half saturation coefficient, mg/L as O\(_2\)
Yield = mg biomass formed/mg ammonia utilized
## Nitrification Kinetics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nitrosomonas Range</th>
<th>Typical (@ 20°C)</th>
<th>Nitrobacter Range</th>
<th>Typical (@ 20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{max}}$</td>
<td>0.014 - 0.092</td>
<td>0.032</td>
<td>0.006 - 0.06</td>
<td>0.034</td>
</tr>
<tr>
<td>$K_S$</td>
<td>0.06 - 5.6</td>
<td>1.0</td>
<td>0.06 - 8.4</td>
<td>1.3</td>
</tr>
<tr>
<td>$K_O$</td>
<td>0.3 - 1.3</td>
<td>0.5</td>
<td>0.3 - 1.3</td>
<td>0.68</td>
</tr>
<tr>
<td>Yield</td>
<td>0.04 - 0.13</td>
<td>0.1</td>
<td>0.02 - 0.07</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Optimum pH for nitrifiers is around 8.0, range 7.5 - 8.5 (higher than for most other biological processes).
Nitrifiers are sensitive to

\[ \mu = \frac{\mu_{\text{max}} S_{\text{NH4}}}{K_S + S_{\text{NH4}}} \cdot \frac{K_I}{K_I + I} \]

where \( I \) = concentration of inhibitor, mg/L
\( K_I \) = inhibition coefficient, mg/L
Effects of Temperature

- derivation of the
- A____________ equation

\[ k = Ae^{\frac{-\mu}{RT}} \]

\[ k_2 = k_1 \theta (T_2 - T_1) \]

- where \( k_{1,2} = \text{reaction rate coefficient at temperature } T_{1,2} \)
- \( \theta = t_____________ c_____________ \)
## Typical Theta Values

<table>
<thead>
<tr>
<th>theta values</th>
<th>Nitrosomonas</th>
<th>Nitrobacter</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{mx}$</td>
<td>1.098 - 1.118</td>
<td>1.068 - 1.112</td>
</tr>
<tr>
<td>$K_s$</td>
<td>1.125</td>
<td>1.157</td>
</tr>
<tr>
<td>$k_d$</td>
<td>1.029 - 1.104</td>
<td>1.029 - 1.104</td>
</tr>
</tbody>
</table>

![Graph showing ln k vs ln θ relationship with points and a line indicating the trend. Temp (deg C or K) is on the x-axis, while ln k and ln θ are on the y-axis.](image-url)
Calculating Theta

given the following measured data, calculate the theta value

<table>
<thead>
<tr>
<th>T, °C</th>
<th>b, h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0037</td>
</tr>
<tr>
<td>20</td>
<td>0.0095</td>
</tr>
<tr>
<td>30</td>
<td>0.0229</td>
</tr>
<tr>
<td>40</td>
<td>0.0372</td>
</tr>
</tbody>
</table>
DENITRIFICATION

1. A _______________________ nitrate reduction:
   NO₃⁻ → NH₄⁺ nitrate is incorporated into cell
   material and reduced inside the cell

2. D ________________________ nitrate reduction
   (denitrification)
   - NO₃⁻ serves as the t______________
     e______________ a______________ (TEA) in an
     anoxic (anaerobic) environment

   nitrate reductase  nitrite r.  nitric oxide r.  nitrous oxide r.
   NO₃⁻ → NO₂⁻ → NO → N₂O → N₂

   summarized as:
   NO₃⁻ → NO₂⁻ → N₂
DENITRIFICATION

- requires o______________
m_________________(example: methanol)

- kinetics for denitrification similar to those for heterotrophic aerobic growth

\[
\mu = \frac{\mu_{\text{max}} S}{K_S + S} \cdot \frac{NO_3^-}{K_{NO_3} + NO_3^-}
\]
DENITRIFICATION

$$6\text{NO}_3^- + 5\text{CH}_3\text{OH} \rightarrow 3\text{N}_2 + 5\text{CO}_2 + 7\text{H}_2\text{O} + 6\text{OH}^-$$

- calculate COD of methanol:

- calculate alkalinity:
Nitrogen Removal in Wastewater Treatment Plants

- Total Kjeldahl Nitrogen (TKN) = o___________ n_____________ + a______________
  (measured by digesting sample with sulfuric acid to convert all nitrogen to ammonia)
- TKN ~ 35 mg/L in influent
- p____________ t____________ removes approximately 15%
- additional removal with biomass w_________________
Methods for Nitrogen Removal

1. Biological
   - ANAMMOX: ammonium is the electron donor, nitrite is the TEA
   
   \[
   \text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + 2 \text{H}_2\text{O}
   \]
   Suitable for high ammonia loads (typically greater than 400 mg/L) and low organic carbon

2. Chemical/Physical
   1. air
   2. breakpoint c
   3. ion e
   4. reverse o
Concerns for nitrogen discharge:

1. T_____________________
2. D____________________ of DO
3. E_______________________
4. Nitrate in d______________ water – causes methemoglobinemia (blue baby) oxidizes hemoglobin to methemoglobin
System Configurations

- Completely mixed activated sludge (CMAS)
- Conventional activated sludge (CAS)
- Sequencing Batch Reactor (SBR)
- Extended aeration, oxidation ditch, others
Activated Sludge Wastewater Treatment Plant

Influent Force Main

Bar Rack/Screens

Grit Tank

Primary Settling Tank

Secondary Settling Tank

Activated Sludge Aeration Basin

Air or Oxygen

Diffusers

Screenings

Grit

Primary Sludge

Waste Activated Sludge (WAS)

Tertiary Filtration (Optional)

Return Activated Sludge (RAS)

Chlorine Contact Basin (optional)

Cl₂

to receiving stream

wastewater flow

residuals flow
Completely Mixed Activated Sludge (CMAS)
Completely Mixed Activated Sludge (CMAS)
Conventional (plug flow) Activated Sludge (CAS)
Conventional Activated Sludge
Conventional Activated Sludge
Step Feed Activated Sludge
CMAS with Selector

High F/M Selector

Low F/M

CMAS with Selector
Sequencing Batch Reactor

WASTEWATER

AIR

FILL

REACT

SETTLE

DECANT

TREATED EFFLUENT

Sludge wastage at end of decant cycle
Phosphorus

- limiting n___________________ in algae
  (at approximately 1/5 the nitrogen requirement)
- 15% of population in US discharges to wastewater discharge contains approximately 7-10 mg/L as P
- wastewater discharge contains i__________________
- o__________________
- i______________: orthophosphate
Removal of Phosphorus

- Chemical precipitation:
  - traditional precipitation reactions
    \[ \text{Al}^{+3} + \text{PO}_4^{-3} \rightarrow \text{AlPO}_4 \]
    \[ \text{Fe}^{+3} + \text{PO}_4^{-3} \rightarrow \text{FePO}_4 \]
  - as solid (magnesium ammonium phosphate, MAP)
    \[ \text{Mg}^{+2} + \text{NH}_4^+ + \text{PO}_4^{-3} \rightarrow \text{MgNH}_4\text{PO}_4 \]
Struvite as a problem

- Scale build-up chokes pipelines, clogs aerators, reduces heat exchange capacity
- Canned king crab industry
- Kidney stones
Struvite as a Fertilizer

- Nonburning and long lasting source of nitrogen and phosphorus
- Found in natural fertilizers such as guano
- Heavy applications have not burned crops or depressed seed germination (Rothbaum, 1976)
- Used for high-value crops

For ISU study on removing ammonia from hog waste see: www.public.iastate.edu/~tge/miles_and_ellis_2000.pdf
Full Scale ASBR

- 2300 head operation in central Iowa, USA
- methane recovery for energy generation
- site for full-scale study for struvite precipitation
Biological P Removal

- Discovered in plug flow A.S. systems
- Requires anaerobic (low DO and NO$_3^-$) zone and aerobic zone
- Biological “battery”
- Grow phosphate accumulating organisms (PAO) with 7% P content
- Need to remove TSS
Key Reactions in Anaerobic Environment

- Uptake of acetic acid
- Storage polymer (PHB) is formed
- Polyphosphate granule is consumed
- Phosphate is released
Key Reactions in Aerobic Environment

- Energy (ATP) is regenerated as bacteria consume BOD
- Phosphorus is taken into the cell and stored as poly-P granule
- When BOD is depleted, PAO continue to grow on stored reserves (PHB) and continue to store poly-P
Anaerobic Zone (initial)

H$_3$CCOOH → H$_3$CCOO$^-$ + H$^+$ → ATP → ADP + Pi → ADP + Pi → Pi

Polyphosphate Granule

PHB polymer

ATP

H$^+$ → ATP
Anaerobic Zone (later)

\[ H_3C\text{COO}^- + H^+ \rightarrow \text{ATP} \]

Polyphosphate Granule

\[ \text{ADP} + P_i \rightarrow \text{ATP} \]

\[ \text{ADP} + P_i \rightarrow \text{ATP} \]

\[ H^+ \rightarrow \text{ATP} \]

PHB polymer

\[ \text{ADP} + P_i \rightarrow \text{ATP} \]
Aerobic Zone (initial)
Aerobic Zone (later)

\[ \text{Polyphosphate Granule} \]

\[ \text{PHB polymer} \]

\[ \text{CO}_2 + \text{NADH} \rightarrow \text{ATP} \]

\[ \text{ADP} + \text{P}_i \]

\[ \text{H}^+ \]

\[ \text{2H}^+ + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \]

\[ \text{ATP} \]

\[ \text{NAD} \]

\[ \text{H}_2\text{O} \]

\[ \text{ADP} + \text{P}_i \]

\[ \text{P}_i \]
Bio-P Operational Considerations

- Need adequate supply of acetic acid
- Nitrate recycled in RAS will compete for acetic acid
- May need a trim dose of coagulant to meet permit
- Subsequent sludge treatment may return soluble phosphorus to A.S.
A/O EBPR

Phosphate Storage “Battery”

<table>
<thead>
<tr>
<th>Anaerobic Selector</th>
<th>Aeration Basin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Release of phosphorus</td>
<td>Uptake of phosphorus</td>
</tr>
<tr>
<td>Uptake of acetic acid</td>
<td>Formation of phosphorus storage</td>
</tr>
<tr>
<td></td>
<td>granules (up to 7% P)</td>
</tr>
<tr>
<td>ATP → ADP</td>
<td>ADP → ATP</td>
</tr>
</tbody>
</table>

air

Alum, Fe³⁺ (optional)

waste activated sludge (WAS)

return activated sludge (RAS)
Combined N and P Removal

- Competition between bio-P and denitrification
- BOD becomes valuable resource
  - required for both N and P removal
- Operation depends on treatment goals
- One reaction will limit
  - difficult to eliminate all BOD, N, and P
- Commercial models (BioWin, ASIM, etc.) useful to predict performance
Combined Biological Phosphorus & Nitrogen Removal

- Anaerobic Selector
- Anoxic Selector
- Aeration Basin (nitrification zone)
- Secondary Settling Tank
- Return activated sludge (RAS)
- Nitrate rich recirculation
- Air
- Waste activated sludge (WAS)

A²O
Combined EBPR & Nitrogen Removal

5-Stage Bardenpho
Combined Biological Phosphorus & Nitrogen Removal

- Anaerobic Selector
- First Anoxic Tank
- Second Anoxic Tank
- Aeration Basin
- Secondary Settling Tank
- Modified UCT

Flow:  
- Nitrate free recirculation from Anaerobic Selector to First Anoxic Tank
- Nitrate rich recirculation from Second Anoxic Tank to Aeration Basin

Other Flows:  
- Return activated sludge (RAS)
- Waste activated sludge (WAS)
- Air into Aeration Basin
Combined Biological Phosphorus & Nitrogen Removal

Aeration Basin (nitrification zone)

Nitrate free recirculation

Anaerobic Selector

Anoxic Selector

Nitrate rich recirculation

Secondary Settling Tank

Return activated sludge (RAS)

Waste activated sludge (WAS)

Air

Virginia Initiative Plant (VIP)
Sulfur

- **inorganic:** \( \text{SO}_4^{-2} \quad \text{S}^{\circ} \quad \text{H}_2\text{S} \)
- **organic:** \( \text{R} \quad - \quad \text{O} \quad - \quad \text{SO}_3^{-2} \)

**four key reactions:**

1. \( \text{H}_2\text{S} \quad \text{oxidizes} \quad \text{S}^{\circ} \)
   - \( \text{Thiobacillus thioparus} \) oxidizes \( \text{S}^{\circ} \) to \( \text{S}^{\circ} \)
   - \( \text{S}^{-2} + \frac{1}{2} \text{O}_2 + 2\text{H}^+ \rightarrow \text{S}^{\circ} + \text{H}_2\text{O} \)
   - phototrophs use \( \text{H}_2\text{S} \) as electron donor

- filamentous sulfur bacteria oxidize \( \text{H}_2\text{S} \) to \( \text{S}^{\circ} \) in sulfur granules: \( \text{Beggiatoa, Thiothrix} \)
2. Oxidation of E___________ Sulfur (Thiobacillus thiooxidans at low pH)

\[
2S^0 + 3O_2 + 2H_2O \rightarrow 2H_2SO_4
\]

3. A________ sulfate reduction: proteolytic bacteria breakdown organic matter containing sulfur (e.g. amino acids: methionine, cysteine, cystine)

4. D___________ sulfate reduction: under anaerobic conditions

\[
SO_4^{-2} + \text{Organics} \rightarrow S^{-2} + \text{Organics} \rightarrow S^{-2} + 2H^+ \rightarrow H_2S
\]

- *Desulvibrio* and others
- Sulfate is used as a TEA & l_____ m____________ w___________ organics serve as the electron donors
- Low cell y____________
- P____________ of SRB depends on COD:S ratio, particularly readily degradable (e.g., VFA) COD
- SRB compete with m____________ for substrate: high COD:S favors methanogens, low COD:S favors SRB
Crown Sewer Corrosion

**FIGURE 15.3** Cross section showing microbial involvement in the corrosion of a concrete sewer pipe. (Adapted from Sydney et al., 1996.)