Lecture 12 - Nutrient removal

Nitrogen and phosphorus are essential nutrients for aquatic plant growth.

When available in excess in a water body, the water body can become "eutrophic" - literally "well fed."

Algae can be represented as $C_{106}H_{263}O_{110}N_{16}P_1$.

Algal growth requires $C : N : P = 106 : 16 : 1$ in moles

$\approx 40 : 7 : 1$ in weight.

Liebig's Law of the Minimum states that growth will be limited by the nutrient that is least available relative to the organisms' needs.

$P$ is usually limiting in fresh water.

$N$ is usually limiting in estuaries and coastal waters.

In water bodies where eutrophication is a problem, the nutrient load from wastewater must be controlled.

Typical concentrations in wastewater (USEPA, 1997)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Total N (mg/L)</th>
<th>Total P (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw wastewater</td>
<td>50 (15-100)</td>
<td>10 (4-15)</td>
</tr>
<tr>
<td>Primary treatment</td>
<td>~40</td>
<td>~7</td>
</tr>
<tr>
<td>Secondary treatment</td>
<td>25-30</td>
<td>~6</td>
</tr>
<tr>
<td>Biological N removal</td>
<td>5-8</td>
<td></td>
</tr>
<tr>
<td>Biological P removal</td>
<td></td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
Nitrogen removal

Nitrification - conversion of ammonia to nitrate.

Two-step process: (see MFE, Fig. 7-21, pg 3)

1. Oxidation of ammonium, $\text{NH}_4^+$, to nitrite, $\text{NO}_2^-$

$$2 \text{NH}_4^+ + 3\text{O}_2 \rightarrow 2\text{NO}_2^- + 4\text{H}^+ + 2\text{H}_2\text{O}$$

2. Oxidation of nitrite, $\text{NO}_2^-$ to nitrate, $\text{NO}_3^-$

$$2 \text{NO}_2^- + \text{O}_2 \rightarrow 2\text{NO}_3^-$$

Nitrification is slightly less thermodynamically favorable than oxidation with oxygen, but both can proceed in biological treatment such as AST.

Nitrifying bacteria grow more slowly than heterotrophic bacteria and have lower cell yield - longer detention times needed to achieve nitrification in AST.

Overall reaction: $\text{NH}_4^+ + 2\text{O}_2 \rightarrow 2\text{H}^+ + \text{H}_2\text{O} + \text{NO}_3^-$

1 gram N uses 4.57 grams O$_2$ based on stoichiometry.

In actuality, less O$_2$ is needed since C is generated by fixing CO$_2$ and N into cell mass. This uses [AIE]:

$$\text{NH}_4^+ + 2\text{HCO}_3^- + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{CO}_2 + 3\text{H}_2\text{O}$$

1 gram N uses 7.14 g AIE as CaCO$_3$. 
Organic Nitrogen (proteins; urea) → Ammonia Nitrogen → Nitrate (NO$_2^-$) → Nitrate (NO$_3^-$)

Bacterial Decomposition → Assimilation → Organic Nitrogen (bacterial cells) → Organic Nitrogen (net growth)

Nitrification

O$_2$ → Lysis and Autooxidation → Organic Carbon → Denitrification

Nitrogen Gas (N$_2$)
Both reactions actually contribute. Overall reaction is estimated as:

\[
\text{NH}_4^+ + 1.863 \text{O}_2 + 0.098 \text{CO}_2 \rightarrow 0.0196 \text{C}_6\text{H}_7\text{NO}_2 + 0.98 \text{NO}_3^- + 0.0941 \text{H}_2\text{O} + 1.98 \text{H}^+
\]

For each gram of N, 4.25 g O\text{2} used, 0.16 g new cells formed, 7.07 g Alk as CaCO\text{3} used.

Denitrification

Bacteria oxidize organic substrate using nitrate/nitrite as electron acceptor.

Nitrate goes as: \(\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2\)

Organic substrate may be wastewater:

\[
\text{C}_{10}\text{H}_{19}\text{O}_3\text{N} + 10\text{NO}_3^- \rightarrow 6\text{N}_2 + 10\text{CO}_2 + 3\text{H}_2\text{O} + \text{NH}_3 + 10\text{OH}^-
\]

Occurs under anoxic conditions in pre-anoxic process.

Sometimes called "substrate-driven" denitrification.

Wastewater is electron donor.
Postanoxic denitrification:

Called "endogenous driven"

Endogenous decay of cells supplies electron donors ⇒ slower rate of reaction, requires longer retention times.

Sometimes supplementary source of carbon (electron donor) added: methanol or acetate

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

Acetate: $5\text{CH}_3\text{COOH} + 8\text{NO}_3^- \rightarrow 4\text{N}_2 + 10\text{CO}_2 + 6\text{H}_2\text{O} + 8\text{OH}^- \uparrow$

Conditions: DO < 0.2 mg/L in bulk liquid

Actual DO in floc can be less than bulk liquid and nitrification and denitrification may proceed simultaneously.

Addition of an external carbon source:

- Methanol: \[5\text{CH}_3\text{OH} + 6\text{NO}_3^- \rightarrow 3\text{N}_2 + 5\text{CO}_2 + 7\text{H}_2\text{O} + 6\text{OH}^- \uparrow\]
- Acetate: \[5\text{CH}_3\text{COOH} + 8\text{NO}_3^- \rightarrow 4\text{N}_2 + 10\text{CO}_2 + 6\text{H}_2\text{O} + 8\text{OH}^- \uparrow\]
Other options include a "two-sludge" system:

Race-track oxidation ditch.

Same in principle as preanoxic system.

Rate processes:

Reactions are represented in same general form:

\[ \mu = \frac{\mu_{\text{max}}}{S + K_s} \]

Coefficient values differ:

<table>
<thead>
<tr>
<th>Substrate</th>
<th>( \mu_{\text{max}} )</th>
<th>( K_s )</th>
<th>( Y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heterotrophes</td>
<td>3.13</td>
<td>5 - 40</td>
<td>0.3 - 0.5</td>
</tr>
<tr>
<td>Nitrification</td>
<td>0.2 - 0.9</td>
<td>0.5 - 1.0</td>
<td>0.1 - 0.15</td>
</tr>
<tr>
<td>Denitrification</td>
<td>3.2</td>
<td>9</td>
<td>0.4</td>
</tr>
<tr>
<td>w/methanol</td>
<td>0.6 - 2</td>
<td>9 - 13</td>
<td>0.17</td>
</tr>
</tbody>
</table>
Phosphorus removal

Phosphorus in wastewater treatment plant effluents is a concern because P is usually the limiting nutrient in fresh water bodies. P in effluent can therefore cause eutrophication of lakes and rivers.

Typical P concentrations:
- Untreated domestic wastewater: 10 mg/L, 7 mg/L
- After primary treatment: 8 mg/L, 7 mg/L
- After secondary treatment: 7 mg/L, 7 mg/L

Typical removal in secondary biological treatment is 10 to 30% of total P.

In water-quality limited streams, effluent limits for P are set at 0.1 to 2 mg/L
(0.5 was once used as a generic limit but no longer)

Phosphorus chemistry:

Phosphorus analytical chemistry is tricky because there are not analytical methods to quantitatively measure all the forms of P important for biota.

Ironically, P cycling through organisms is well understood because there are radioactive isotopes of P that can be used as tracers.

Analytically determined P forms:
- Total P (TP)
  - Particulate P: trapped by 0.45-μm filter
  - Soluble P: passes thru' filter
- Soluble reactive P: measured by molybdate blue method (without acid digestion) = ortho-P
- Soluble unreactive P: remainder
Forms of phosphorus available to microorganisms:

- Soluble reactive P
  - = orthophosphate $\text{PO}_4^{3-}$

Polyphosphates from detergents are also a concern:
- e.g., sodium tripolyphosphate $\text{Na}_8\text{P}_3\text{O}_{10}$

Boil in $\text{H}_2\text{SO}_4$ for 90 min. Acid digestion of sample causes polyphosphates to break down to orthophosphates - then measure with molybdate blue method to get total inorganic P = ortho-P + polyphosphate

In environment, polyphosphates hydrolyze to form ortho-P over time.

Strong acid digestion (nitric or perchloric acid) of unfiltered sample breaks down organic particulates to ortho-P - then measure with molybdate blue to get total P = total inorganic P + organic P

Summary:
- No digestion = ortho-P
- $\text{H}_2\text{SO}_4$ acid digestion = Inorganic P = ortho-P + poly-P
- Strong acid digestion = Total P = inorganic P + organic P

Above can be done on filtrate of 0.45-μm filter to get soluble fraction or on unfiltered sample to get totals.
Biological P removal systems are designed to create conditions favorable to Phosphorus Accumulating Organisms (PAOs) - see pg 10 and 11.

Certain bacteria (e.g. Acinetobacter) synthesize polyphosphates and store it in their cellular material - process is sometimes called "luxury uptake".

PAOs are favored by alternating aerobic/anaerobic conditions. First step is anaerobic:
Available carbon and electrons are stored in polyhydroxybutyrate (PHB) and other volatile fatty acids. This storage is not done if electron acceptors like O₂ or NO₃ are present, hence the need for anaerobic conditions. Simultaneously, polyphosphate is broken down and ortho-P is released to mixed liquor (see Figure 1-23 from M4E, pg 12).

Next step is aerobic or anoxic (denitrifying):
Bacteria metabolize stored PHB, uptake ortho-P, stored as poly-P within cell material. Cells become enriched in polyphosphates.

Last step is removal of P-enriched cells in wasted sludge - P is removed along with cells.

Key to success of P removal is encouraging the growth of the particular types of bacteria that accumulate P.

The anaerobic reactor causes fermentation that breaks down COD to acetate, a substrate preferred by PAOs. This step is sometimes called the "selector" since it favors (selects for) PAOs.
Removal mechanisms for excess biological phosphorus (COD = chemical oxygen demand, PHB = poly-β-hydroxybutyrate).

Figure by MIT OCW.
Bacteria absorb BOD by releasing phosphorus

\[ \text{ATP} \rightarrow \text{ADP} + \text{PO}_4 + \text{energy} \]

Bacteria store phosphorus during growth to compete for BOD when they get back to anaerobic zone.

Stored phosphorus in bacteria is removed in waste sludge.

Typical profile of soluble phosphorus concentrations in a biological nutrient removal process (ATP = adenosine triphosphate, ADP = adenosine diphosphate).

Fate of soluble BOD and phosphorus in nutrient removal reactor.

Figure by MIT OCW.
Configurations for biological P removal

**Pre-denitrification** (also called A2O process)

1. Influent from primary treatment
2. Anaerobic
3. Anoxic (denitrification)
4. Aerobic
5. Secondary Clarifier
6. Effluent
7. Sludge recycle
8. Sludge wasting

**Pre-anoxic nitrogen removal process**

**Bardenpho process**:

1. Influent from primary treatment (~8 mg/L P)
2. Anaerobic
3. Anoxic
4. Aerobic
5. Anoxic
6. Aerobic
7. Secondary Clarifier
8. Effluent (1-2 mg/L phosphorus)
9. Sludge recycle
10. Achieves added N removal

Removes 93% total N, 65% total P
ProStrip process:

Influent from primary reactor
nB mg/l P

Aerobic

Secondary clarifier

Effluent (<1 mg/l P)

Sludge recycle

 lime

"Side-stream P-stripping"

Anaerobic reactor

High-P supernatant
30-70 mg/l P

Low-P anaerobic recycle

Chemical P precipitation

Precipitate to waste

Hydrolysis in anaerobic reactor releases poly-P to water (supernatant) - 30-70 mg/l P

Addition of lime to precipitator tank raises pH to ~11, causes Ca₃(PO₄)₂ (s) to precipitate

Requires more sophisticated operation than alternatives above
Sequencing batch reactor (SBR)

Rather than continuous flow through sequence of tanks for different treatment steps, all steps are done sequentially in a single tank.

For conventional AST:

Step 1 - Fill
(add substrate)

Step 2 - React

Step 3 - Settle

Step 4 - Draw
(decant effluent)

Step 5 - Idle
(waste sludge)

SBRs are very flexible as to steps, making it possible to add anoxic and anaerobic steps to the sequence for N or P removal.
SBR for P removal

Step 1 - Fill

Step 2 - Anaerobic react
(tank is mixed but without aeration)

Step 3 - Aerobic react

Step 4 - Anoxic react (denitrification)
(Note: steps 3 and 4 may be repeated)

Step 5 - Settle

Step 6 - Decant

Step 7 - Idle (waste sludge)
SBR WITH BIOLOGICAL PHOSPHORUS REMOVAL

Step 1: Fill

Step 2: Anaerobic React

Step 3: Aerobic React

Step 4: Anoxic React (denitrification)

Step 5: Settle

Step 6: Decant

Figure by MIT OCW

Chemically-enhanced primary treatment (CEPT)

Also called: Advanced primary treatment
Chemically assisted primary treatment
Chemically assisted settling

Improves removal rates in primary treatment by enhancing settling.
Also very effective for P removal, odor control

Chemicals used:

- Metal salt (usually ferric chloride, FeCl₃, sometimes alum, Al₂(SO₄)₃, others - see pg 19.

- Anionic polymer

Typical concentrations:

- FeCl₃ - 20-30 mg/L
- Polymer - 0.25 mg/L

Phosphorus removed by chemical precip.:

\[
\text{FeCl}_3 + \text{H}_2\text{PO}_4^- + 2\text{HCO}_3^- \rightarrow \\
\text{FePO}_4 \downarrow + 3\text{Cl}^- + 2\text{CO}_2 + 2\text{H}_2\text{O}
\]

Coagulant action of ferric salts and polymer increases settling of solids - see pg 20

Very effective as technique to upgrade existing treatment plants - see page 21

- Allows increased wastewater flow rate to be treated - see page 22
# Inorganic Chemicals Used Most Commonly for Coagulation and Precipitation Processes in Wastewater Treatment

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Molecular Weight</th>
<th>Equivalent Weight</th>
<th>Form</th>
<th>Percent</th>
<th>Equivalent Weight</th>
<th>Form</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum</td>
<td>Al₂(SO₄)₃·18H₂O#</td>
<td>666.5</td>
<td></td>
<td>Liquid</td>
<td>8.5 (Al₂O₃)</td>
<td></td>
<td>Liquid</td>
<td>17 (Al₂O₃)</td>
</tr>
<tr>
<td></td>
<td>Al₂(SO₄)₃·14H₂O#</td>
<td>594.4</td>
<td>114</td>
<td>Liquid</td>
<td>8.5 (Al₂O₃)</td>
<td></td>
<td>Liquid</td>
<td>17 (Al₂O₃)</td>
</tr>
<tr>
<td>Aluminum Chloride</td>
<td>AlCl₃</td>
<td>133.3</td>
<td>44</td>
<td>Liquid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium Hydroxide (lime)</td>
<td>Ca(OH)₂</td>
<td>56.1 as CaO</td>
<td>40</td>
<td>Lump</td>
<td>63-73 as CaO</td>
<td></td>
<td>Powder</td>
<td>85-99</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>Slurry</td>
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<td>15-20</td>
</tr>
<tr>
<td>Ferric Chloride</td>
<td>FeCl₃</td>
<td>162.2</td>
<td>91</td>
<td>Liquid</td>
<td>20 (Fe)</td>
<td></td>
<td>Liquid</td>
<td>20 (Fe)</td>
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<tr>
<td>Ferric Sulfate</td>
<td>Fe₂(SO₄)₃</td>
<td>400</td>
<td>51.5</td>
<td>Granular</td>
<td>18.5 (Fe)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ferrous Sulfate (copperas)</td>
<td>FeSO₄·7H₂O</td>
<td>278.1</td>
<td>139</td>
<td>Granular</td>
<td>20 (Fe)</td>
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<tr>
<td>Sodium Aluminate</td>
<td>Na₂Al₂O₄</td>
<td>163.9</td>
<td>100</td>
<td>Flake</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

# Number of bound water molecules will typically vary from 14 to 18

Figure by MIT OCW.

Adapted from: Metcalf, and Eddy. 2003
North Budapest Wastewater Treatment Plant
Comparison of Influent vs. Pre-aeration Raw Water

COD Influent Conc. = 515 mg/l
COD Pre-aeration Conc. = 594 mg/l

Topolcany Wastewater Treatment Plant
BOD and COD % Removal vs. Ferric Chloride Concentration

Figure by MIT OCW.
Adapted from: Murcott, and Hurleman. 1994, p. 24
a. Existing primary treatment plant

b. CEPT (left) and primary precipitation (right)

c. Preprecipitation (or CEPT) followed by ASP

d. Preprecipitation with ASP and postdenitrification

Multi-stage upgrading of an existing primary treatment plant
Overflow Rate Verses TSS Removal for Sarnia Treatment Plant

Figure by MIT OCW.