Chapter 4: Advanced Wastewater Treatment for Phosphorous Removal

Winter 2011
Faculty of Engineering & Applied Science
4.1 Phosphorus in wastewaters

1. Common forms of phosphorous in wastewaters

- **organic phosphorus** $\Rightarrow$ bacterial decomposition of organic phosphorus can release orthophosphate

\[
\text{organic P} \xrightarrow{\text{bacteria}} \text{decomposition} \rightarrow \text{PO}_4
\]

- **polyphosphates** (polymers of phosphoric acid) $\Rightarrow$ molecules with 2 or more P atoms, oxygen and in some cases hydrogen atoms combine in a complex molecule $\Rightarrow$ gradually hydrolyze in water and convert to the soluble ortho form

\[
\text{polyphosphates} \xrightarrow{\text{hydrolysis in water}} \text{PO}_4
\]

- **orthophosphates** ($\text{H}_2\text{PO}_4^-, \text{HPO}_4^{2-}, \text{PO}_4^{3-}$) $\Rightarrow$

\[
\text{PO}_4 + \text{NH}_3 + \text{CO}_2 \xrightarrow{\text{sunlight}} \text{green plants}
\]
2. Phosphorous analysis in wastewaters

- ortho-P \( \Rightarrow \) measured by molybdate blue method

- total inorganic P = ortho-P + polyphosphates \( \Rightarrow \) measured by (1) acid digestion of sample (boil in \( \text{H}_2\text{SO}_4 \) for 90 min) to break down polyphosphates to ortho-P, (2) then with molybdate blue method

- total P = organic-P + total inorganic P \( \Rightarrow \) measured by (1) strong acid digestion of sample (boil in nitric or perchloric acid for 90 min) to break down organic-P to ortho-P, (2) then with molybdate blue method
- total P = particulate P + soluble P
- particulate P \(\xrightarrow{}\) trapped by 0.45\(\mu\)m filter
- soluble P = soluble reactive P + soluble unreactive P
  \(\xrightarrow{}\) passes through the 0.45\(\mu\)m filter

- ✔ soluble reactive P \(\xrightarrow{}\) forms of P available to microorganisms = ortho-P
- ✔ soluble unreactive P \(\xrightarrow{}\) reminder
3. Phosphorous sources in wastewaters

- Phosphorus in surface water ➔ human-generated wastes and land runoff
- Non-point sources in surface drainage ➔ vary from 0 to 15 b of P/ac/yr
- Domestic waste contains ➔ approximately 2 b (0.9 kg) of P/cap/yr
- P in wastewater treatment plant effluents ➔ a concern because P is usually the limiting nutrient in fresh water bodies ➔ P in effluent can therefore cause eutrophication of lake and rivers
4. Phosphorous removal in conventional treatment

<table>
<thead>
<tr>
<th></th>
<th>Before Sedimentation</th>
<th>After Sedimentation</th>
<th>Biologically Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids</td>
<td>800</td>
<td>680</td>
<td>530</td>
</tr>
<tr>
<td>Total volatile solids</td>
<td>440</td>
<td>340</td>
<td>220</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>240</td>
<td>120</td>
<td>30</td>
</tr>
<tr>
<td>Volatile suspended solids</td>
<td>180</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>BOD</td>
<td>200</td>
<td>130</td>
<td>30</td>
</tr>
<tr>
<td>Ammonia nitrogen as N</td>
<td>22</td>
<td>22</td>
<td>24</td>
</tr>
<tr>
<td>Total nitrogen as N</td>
<td>35</td>
<td>30</td>
<td>26</td>
</tr>
<tr>
<td><strong>Soluble phosphorus as P</strong></td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>Total phosphorus as P</strong></td>
<td>7</td>
<td>6</td>
<td>5</td>
</tr>
</tbody>
</table>

(Viessman et al., Water Supply and Pollution Control, 2009)
Primary sedimentation in conventional treatment only settles a small percentage of P in wastewater since the majority (ortho-P) in dissolved and in solution. P removed by primary sedimentation is limited to 16% P content in the primary sedimentations of 1 liter of wastewater is about 1.1 mg (organic-P removed). P removal by subsequent biological treatment is another 18% (organic-P removed).

Total P removal by conventional treatment is about 34%.
66% of P left for advanced wastewater treatment
4.2 Phosphorous removal by biological processes

- In the biological removal of phosphorous, the phosphorous in the influent wastewater is incorporated into cell biomass which is subsequently removed from the process as a result of sludge wasting.
- The reactor configuration provides the Phosphorous accumulating organisms (PAOs) with a competitive advantage over other bacteria. PAOs are encouraged to grow and consume phosphorous.
- The reactor configuration is comprised of an anaerobic tank and an activated sludge activated tank.
The retention time in the anaerobic tank is about 0.50 to 1.00 hours and its contents are mixed to provide contact with the return activated sludge and influent wastewater.
- Step I $\Rightarrow$ in the anaerobic zone

- Under anaerobic conditions, PAO assimilate fermentation products (i.e. volatile fatty acids $\Rightarrow$ carbon source) into storage products within the cells $\Rightarrow$ generate energy

- Acetate ($\Rightarrow$ the substrate) is produced by fermentation of bsCOD, which is dissolved degradable organic material that can be easily assimilated by the biomass

- Using energy available, the PAO assimilate acetate and produce intracellular polyhydroxybutyrate (PHB) storage products $\Rightarrow$ carbon and electrons are stored in PHB

- Concurrent with the acetate uptake is the broken-down of polyphosphates within the cells and release of ortho-P, as well as Mg, K, Ca cations $\Rightarrow$ The PHB content in the PAO increases as the polyphosphate decreases
Step II ➔ in the aerobic zone
- Bacteria metabolize stored PHB ➔ providing energy and carbon for new cell growth
- PHB oxidation process uptakes ortho-P, stores it as polyphosphate within cell material
- The soluble ortho-P is removed from solution and cells become enriched in polyphosphates

Step III ➔ P removal
- P-enriched cells will be removed as waste sludge
- P is removed along with cells
Removal mechanisms for excess biological phosphorus (COD = chemical oxygen demand, PHB = poly-β-hydroxybutyrate).

(Shanahan, Water and Wastewater Treatment Engineering, 2006)
Bacteria absorb BOD by releasing phosphorus

Ortho Phosphorus

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

Influent ortho phosphorus concentration

Stored phosphorus in bacteria is removed in waste sludge

ADP + PO₄ → ATP

energy

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

(Shanahan, Water and Wastewater Treatment Engineering, 2006)
4.3 Phosphorous removal by chemical-biological processes

- Chemical precipitation is used to remove the inorganic forms of phosphate by the addition of a coagulant (e.g., alum or iron and a mixing of wastewater and coagulant.
- Popular coagulants include metal salts such as aluminum sulfate (alum) and ferric chloride \(\Rightarrow\) ferrous chloride, lime, and various polymers are also used.
- Ortho-P is combined with metal cation and removed.
- Poly-P and organic-P are removed by being entrapped or adsorbed in the floc particles.
<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Molecular Weight</th>
<th>Equivalent Weight</th>
<th>AVAILABILITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum</td>
<td>Al₂(SO₄)₃·18H₂O#</td>
<td>666.5</td>
<td></td>
<td>Liquid 8.5 (Al₂O₃)</td>
</tr>
<tr>
<td></td>
<td>Al₂(SO₄)₃·14H₂O#</td>
<td>594.4</td>
<td>114</td>
<td>Liquid 8.5 (Al₂O₃)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lump 17 (Al₂O₃)</td>
</tr>
<tr>
<td>Aluminum Chloride</td>
<td>AlCl₃</td>
<td>133.3</td>
<td>44</td>
<td>Liquid</td>
</tr>
<tr>
<td>Calcium Hydroxide (lime)</td>
<td>Ca(OH)₂</td>
<td>56.1 as CaO</td>
<td>40</td>
<td>Lump 63-73 as CaO</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Powder 85-99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Slurry 15-20</td>
</tr>
<tr>
<td>Ferric Chloride</td>
<td>FeCl₃</td>
<td>162.2</td>
<td>91</td>
<td>Liquid 20 (Fe)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lump 20 (Fe)</td>
</tr>
<tr>
<td>Ferric Sulfate</td>
<td>Fe₂(SO₄)₃</td>
<td>400</td>
<td>51.5</td>
<td>Granular 18.5 (Fe)</td>
</tr>
<tr>
<td>Ferrous Sulfate (copperas)</td>
<td>FeSO₄·7H₂O</td>
<td>278.1</td>
<td>139</td>
<td>Granular 20 (Fe)</td>
</tr>
<tr>
<td>Sodium Aluminate</td>
<td>Na₂Al₂O₄</td>
<td>163.9</td>
<td>100</td>
<td>Flake 46 (Al₂O₃)</td>
</tr>
</tbody>
</table>

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

(Shanahan, Water and Wastewater Treatment Engineering, 2006)
P removal by Alum

- Alum ions combine with P ions

\[
\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} + 2\text{PO}_4^{3-} = 2\text{AlPO}_4\downarrow + 3\text{SO}_4^{2-} + 14\text{H}_2\text{O}
\]

- The molar ratio for Al to P is 1 to 1 and the weight ratio of commercial alum to phosphorus is 9.7 to 1

- Excess alum ions is recommended to precipitate P from wastewater ➔ P reductions of 75%, 85% and 95% require alum to P weight ratios of about 13 to 1, 16 to 1, and 22 to 1, respectively

- Excess alum may decrease the natural alkalinity

\[
\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} + 6\text{HCO}_3^- = 2\text{Al(OH)}_3\downarrow + 3\text{SO}_4^{2-} + 6 \text{CO}_2 + 14\text{H}_2\text{O}
\]
P removal by ferric chloride

- Iron coagulants precipitate ortho-P in wastewater

\[
\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{PO}_4^{3-} = \text{FePO}_4\downarrow + 3\text{Cl}^- + 6\text{H}_2\text{O}
\]

- The molar ratio for Fe to P is 1 to 1
- Excess Fe ions is recommended to precipitate P from wastewater ➔ without coagulation aids, Fe to P dosages should be 1.8 to 1.0 or greater
- Excess Fe ions may decrease the natural alkalinity

\[
\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + 3\text{HCO}_3^- = \text{Fe(OH)}_3\downarrow + 3\text{Cl}^- + 3\text{CO}_2 + 6\text{H}_2\text{O}
\]

- Coagulation aids (e.g., lime) may be applied to raise pH and supply alkalinity

\[
2\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + 3\text{Ca(OH)}_2 = 2\text{Fe(OH)}_3\downarrow + 3\text{CaCl}_2 + 6\text{H}_2\text{O}
\]
Three P removal schemes:

(a) Chemical precipitation with biological treatment → most frequently employed alternative

(b) Lime precipitation in primary sedimentation followed by secondary completely mixed activated sludge

(c) Tertiary treatment by chemical precipitation

(Viessman et al., Water Supply and Pollution Control, 2009)
Viessman et al., Water Supply and Pollution Control, 2009

Influent

Primary

- BOD = 200 mg/l
- SS = 240 mg/l
- oP = 3.0 mg/l
- iP = 4.0 mg/l
- tP = 7.0 mg/l

Settled wastewater

Aeration

- BOD = 130 mg/l
- SS = 120 mg/l
- oP = 1.9 mg/l
- iP = 4.0 mg/l
- tP = 5.9 mg/l

Alum = 110 mg/l

Final

- BOD = 10 mg/l
- SS = 15 mg/l
- oP = 0.02 * 15 = 0.3 mg/l
- iP = 0.7 mg/l
- tP = 1.0 mg/l

Effluent

Primary sludge per liter of wastewater

- SS = 120 mg
- oP = 0.009 * 120 = 1.1 mg

Waste chemical–biological sludge per liter of wastewater

- SS = 65 + 15 = 80 mg
- oP = 0.02 * 80 = 1.6 mg
- P = 7.0 - 3.7 = 3.3 mg

(Viessman et al., Water Supply and Pollution Control, 2009)
Example 4-1 Calculate the theoretical sludge production for the hypothetical chemical-biological plant diagrammed in last Figure. Assume the influent wastewater characteristics listed in the Figure, primary removals of 50% SS and 35% BOD, an operating F/M in the activated-sludge process of 0.4, fraction of applied BOD that appears as excess biological growth in waste-activated sludge is 0.5, an alum dosage of 80 mg/l, 15 mg/l of effluent SS, and an effluent phosphorous concentration of 1.0 mg/l.

\[
\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} + 2\text{PO}_4^{3-} = 2\text{AlPO}_4\downarrow + 3\text{SO}_4^{2-} + 14\text{H}_2\text{O}
\]

\[
\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} + 6\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3\downarrow + 6\text{H}^+ + 3\text{SO}_4^{2-} + 14\text{H}_2\text{O}
\]
k = fraction of influent BOD that becomes excess biomass in secondary treatment, assuming about 30 mg/l of BOD and SS remaining in the secondary effluent.