Overview of Supplemental Carbon Sources for Denitrification and Enhanced Biological Phosphorus Removal

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Speakers

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Our Company

EOSi Company Background

- Founded in 2003. Based in Bourne, MA (Cape Cod). 31 Employees
- Focus – Deliver sustainable contaminant removal solutions through green chemicals and expert technical services
- Two U.S. patents, one in Japan, two in Canada, EU patent pending

Customer and Supply Chain Snapshot

- 550+ Customers in 40 States, and 5 countries
- 53% Municipal – 32% Industrial – 14% Decentralized
- 20 Manufacturing Locations across the United States
Agenda

- Why Nitrogen and Phosphorus Removal?
- Sources of Carbon – Internal vs. External
- Nitrogen Removal Basics
  - Nitrification
  - Denitrification
- Denitrification Case Study
- Inherent Characteristics of Primary Carbon Sources
- Enhanced Biological Phosphorus Removal (EBPR)
- EBPR Case Study
Why Nitrogen and Phosphorus Removal?

- Nitrogen and phosphorus are nutrients that are natural parts of the ecosystem and promote growth of algae and aquatic plants for food and habitat of aquatic organisms
- Too much N and P causes algae to grow faster than ecosystem can handle
- Large growths of algae (algal blooms) severely reduce oxygen in water
  - Toxicity to fish and aquatic life
  - Eutrophication
  - Blue Baby Syndrome
When Do You Need a Carbon Source?

- Low Nitrogen and/or Phosphorus Limits
- Low BOD/TKN ratio in raw influent
- Low F:M ratios
- Inefficient Process Configuration
- Short retention times – need faster kinetics
- Cold weather operation
## Raw Wastewater Characteristics

### Common Parameters

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weak</td>
</tr>
<tr>
<td>--------------</td>
<td>------</td>
</tr>
<tr>
<td>TSS</td>
<td>100</td>
</tr>
<tr>
<td>VSS</td>
<td>80</td>
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<tr>
<td>BOD</td>
<td>110</td>
</tr>
<tr>
<td>COD</td>
<td>250</td>
</tr>
<tr>
<td>Ammonia</td>
<td>12</td>
</tr>
<tr>
<td>Organic N</td>
<td>8</td>
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<tr>
<td>Nitrite</td>
<td>0</td>
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<tr>
<td>Nitrate</td>
<td>0</td>
</tr>
<tr>
<td>TP</td>
<td>4</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>50</td>
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</table>
Carbon Sources

- **Internal**
  - Influuent COD load
  - Endogenous respiration
  - Endogenous
    - Natural lysis leads to cell rupture and COD release
  - Lysis products
    - Enhanced lysis. Cells are stressed using oxidative, thermal, electrical or mechanical means to induce cell rupture and COD release

- **External**
  - Pure or manufactured compounds
    - e.g. methanol, MicroC®
  - Co-products
    - e.g., crude glycerin, molasses,
  - Waste products
    - e.g. Cheese Whey Bev Waste
Biological Nutrient Removal Overview

• Secondary Treatment (Biological)
  – Use of microorganisms to remove contaminants
  – Tank or lagoon-based treatments
• Biological Nutrient Removal (N and P Removal)
  – Biological Nitrogen
    • Nitrification
    • Denitrification
  – Effluent Quality:
    • BOD < 10 mg/L
    • TN < 10 mg/L
    • TP < 1 mg/L
Nitrification

• Two-step process oxidizing ammonia to nitrite and then to nitrate under aerobic conditions

• Involves two specific groups of autotrophic bacteria
  – Ammonium Oxidizing Bacteria (AOB’s)
  – Nitrite Oxidizing Bacteria (NOB’s)
Nitrification Stoichiometry

• First step is the oxidation of ammonium to nitrite by AOB’s through the following stoichiometric equation:
  \[ \text{NH}_4^+ + 1.5\text{O}_2 \rightarrow \text{NO}_2^- + 2\text{H}^+ + \text{H}_2\text{O} \]

• Second step is further oxidation of nitrite to nitrate by NOB’s through the following stoichiometric equation:
  \[ \text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 2\text{H}^+ \]

Adequate alkalinity is required as pH decreases through nitrification. 7 mg of alkalinity is consumed per mg ammonia oxidized.
Microorganisms Required for BOD Removal & Nitrification

• Heterotrophic Bacteria
  – Utilize carbon for formation of new biomass
  – Responsible for BOD removal

• Autotrophic Bacteria
  – Utilize carbon from carbon dioxide for formation of new cells
  – Also utilizes ammonia as the electron donor for formation of nitrite and nitrate
Aerobic, Heterotrophic Metabolism

- Synthesis reaction to grow new cells
- Energy reaction to produce CO$_2$ and H$_2$O

Aerobic, Autotrophic Metabolism

- CO$_2$ used for synthesis of making new cells
- Ammonia used as energy source to produce nitrite and nitrate
Denitrification

• Involves the biological reduction of nitrate and/or nitrite to nitrogen gas in the absence of dissolved oxygen (anoxic conditions)

• Involves use of heterotrophic bacteria when present. Otherwise various organic carbon sources need to be used
Why Denitrify?

• Meet permit limits for total nitrogen (TN)
• Removal of nitrates required for Bio-P to occur
• Minimizes rising sludge in clarifiers
• Alkalinity recovery from nitrification
• Reduces energy use
Heterotrophic Metabolism in Anoxic Conditions

• Heterotrophic bacteria use carbon for the formation of new biomass
• Use nitrate/nitrite instead of oxygen as electron donor although oxygen is preferred
Primary Carbon Sources Used for Denitrification

- Acids – Acetic Acid/Acetate
- Carbohydrates
- Glycerin – MicroC® 2000
- Methanol
Safety Cost Matrix

- **Acetate**
- **Dilute Acetic Acid**
- **Waste Products**
  - Crude glycerin based mixtures
- **100% Acetic Acid**
- **Ethanol**
- **MicroC® 2000**
- **MicroC® 3000**
- **Methanol**

**COST $/lb of Nitrogen Removed**

- **Most Safe**
  - Acetate
  - Dilute Acetic Acid
  - Waste Products
- **Least Safe**
  - 100% Acetic Acid
  - Ethanol

- **Most Expensive**
- **Least Expensive**
## Comparison of the Primary Carbon Sources

<table>
<thead>
<tr>
<th>Carbon Source</th>
<th>Methanol</th>
<th>Acetic Acid 56%</th>
<th>Acetic Acid 20%</th>
<th>MicroC® 1000</th>
<th>MicroC® 2000</th>
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</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>1,185,000</td>
<td>617,000</td>
<td>216,000</td>
<td>670,000</td>
<td>1,100,000</td>
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<tr>
<td>Specific Gravity</td>
<td>0.79</td>
<td>1.03</td>
<td>1.01</td>
<td>1.22</td>
<td>1.22</td>
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<tr>
<td>Bulk Density lbs/gal</td>
<td>6.59</td>
<td>8.59</td>
<td>8.42</td>
<td>10.17</td>
<td>10.17</td>
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<tr>
<td>Ib COD/gal substrate</td>
<td>9.88</td>
<td>5.15</td>
<td>1.80</td>
<td>5.62</td>
<td>8.67</td>
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<tr>
<td>Theoretical COD:N (g COD/gNO3-N)</td>
<td>2.86</td>
<td>2.86</td>
<td>2.86</td>
<td>2.86</td>
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<tr>
<td>Yield g COD/ g COD</td>
<td>0.41</td>
<td>0.53</td>
<td>0.53</td>
<td>0.53</td>
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<tr>
<td>Total COD/N</td>
<td>4.85</td>
<td>6.09</td>
<td>6.09</td>
<td>6.09</td>
<td>6.09</td>
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<tr>
<td>Total Dose (g substrate/g NO3-N)</td>
<td>3.19</td>
<td>10.16</td>
<td>28.44</td>
<td>11.13</td>
<td>7.32</td>
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<tr>
<td>Total Dose (gal substrate/lb NO3-N)</td>
<td>0.48</td>
<td>1.18</td>
<td>3.38</td>
<td>1.09</td>
<td>0.70</td>
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<tr>
<td>Carbon Source</td>
<td>Advantages</td>
<td>Disadvantages</td>
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<td>-----------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------</td>
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<tr>
<td><strong>Acids – Acetic/Acetate</strong></td>
<td>• Can be used for EBPR&lt;br&gt;• Readily available</td>
<td>• Potentially Flammable&lt;br&gt;• Requires large storage volume&lt;br&gt;• Lower COD&lt;br&gt;• Corrosive</td>
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<tr>
<td><strong>Methanol</strong></td>
<td>• Highest COD&lt;br&gt;• Low freezing point&lt;br&gt;• Typically most economical on $/gal basis&lt;br&gt;• Lowest Yield</td>
<td>• Flammable&lt;br&gt;• Requires expensive capital for storage and feed system&lt;br&gt;• Price volatility&lt;br&gt;• Only utilizes methylotrophic bacteria&lt;br&gt;• Slow denitrification kinetics in colder weather&lt;br&gt;• Slow acclimation period</td>
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<tr>
<td><strong>Glycerin – MicroC® 2000</strong></td>
<td>• Non-hazardous&lt;br&gt;• Lower capital cost compared to methanol&lt;br&gt;• Can be used for EBPR</td>
<td>• Can get viscous in colder weather&lt;br&gt;• Impurities and handling challenges with crude glycerin&lt;br&gt;• MicroC® 2000 more expensive on a $/gal basis than commodities</td>
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<tr>
<td><strong>Carbohydrates</strong></td>
<td>• Can use waste or by-products – may be cheapest option&lt;br&gt;• Readily biodegradable&lt;br&gt;• Promote biological diversity (small facilities)</td>
<td>• If waste product, product quality and consistency may not be optimal&lt;br&gt;• Lower COD Values typically&lt;br&gt;• Potential for fermentation/ degradation in storage&lt;br&gt;• Insects</td>
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Supplemental Carbon Dosing Points for Denitrification

Diagram:
- Influent → Primary clarifier → Anoxic → Aerobic → Anoxic → Secondary clarifier → Effluent
- Nitrate removal (1)
- Nitrate recycle
- Return Activated Sludge (RAS)
- Waste Activated Sludge (WAS)
- Solids Handling / Sludge Disposal
Nitrogen Removal Flowsheet

Nitrogen removal process involves the conversion of nitrogen compounds through various biochemical processes. The process begins with the hydrolysis of organic nitrogen (Organic N) to ammonium ($NH_4^+$). Ammonium can be assimilated into the biomass of bacteria (Organic N (bacterial cells)), or further oxidized to nitrite ($NO_2^-$) and nitrate ($NO_3^-$) through the process of nitrification. Nitrite and nitrate can be further reduced to nitrogen gas ($N_2$) through denitrification, which involves the consumption of oxygen ($O_2$) and other electron acceptors such as nitrate and nitrite. Alkalinity plays a role in maintaining the pH balance, which is crucial for the survival of microorganisms in these processes.
UAJA was exploring upgrading existing plant configuration in order to meet incoming permit. The authority had elected to try MicroC® 2000 as a supplemental carbon source to meet their limits and forgo an expensive capital upgrade.

**Plant Characteristics**

- **A2/O Process** (anaerobic, anoxic, aerobic)
- **Flow Design/Flow Actual**: >8 MGD/ >4 MGD
- **TN Discharge Permit**: 6.0 mg/L (annual basis)
Current Plant Configuration

- Screens
- Grit Removal
- Primary Clarifiers
- BNR Tanks
- Final Clarifiers
- Alum
- Tertiary Filters
- U.V.
- Filter Backwash
- W.A.T.
- Reject Water
- Maintenance
- Plant Drain Pump Station
- Biofilter
- AWT
- Composting
- Mix Tank
- Centrate
- Aerated Solids Storage
- WAS
- RAS

EOSi
Green Solutions For Achieving Your Limits
UAJA Pilot Results

Figure 1. Nitrate concentrations in the anoxic zone effluent during pilot testing.

MicroC 2000™ feed begins
Feed point adjusted
UAJA Case Study Conclusions

- Decrease in effluent TN of 40%
- No infrastructure improvements were implemented, saved the Authority millions of dollars
- Glycerin-based carbon sources demonstrated ability to quickly enhance denitrification for carbon-limited BNR systems
- Dosing point, feed rate, and internal recycle rate optimized for nitrogen removal
- Now receives nitrogen credits which they can save/sell
Phosphorus Removal Techniques

• Chemical removal
  – Uses the insolubility properties of Phosphorus compounds
  – Chemical addition (calcium, aluminum, iron) to precipitate out P

• Conventional Biological Phosphorus Removal
  – Biomass takes up P as an essential cell component during BOD oxidation
  – Removes 10-30% of the influent P

• **Enhanced Biological Phosphorus Removal (EBPR)**
  – A sequence of anaerobic and aerobic zones selects organisms that are capable of taking phosphorus at levels beyond stoichiometric requirements
  – Removes 2.5-4 times more P than conventional activated sludge
EBPR

- Phosphate-accumulating organisms (PAOs)
  - Store orthophosphate (ortho-P) in excess of their biological growth requirements
  - Heterotrophic organisms that use organic carbon (rbCOD)
  - Must be first in an anaerobic environment followed by aerobic environment
    - Allows PAOs to gain advantage to grow and function
    - PAOs release phosphorus in favor of up-taking Volatile Fatty Acids (VFA) in anaerobic conditions
    - PAOs adsorb more phosphorus than they release under aerobic conditions
    - The result is excessive accumulation of orthophosphate in mixed liquor

- Phosphorus laden PAOs settle in secondary clarifier and with proper wasting, phosphate removal can be achieved
EBPR Requirements

- For biological phosphorus removal to occur
  - Biomass first needs to pass through an anaerobic phase,
  - Then enter a phase where an electron acceptor is present, i.e. an anoxic phase where nitrate is present or an aerobic phase where oxygen is present
Supplemental Carbon Dosing Points for EBPR

- Methanol does **NOT** support EBPR
EBPR Case Study – Ballenger-McKinney Wastewater Treatment Plant
Ballenger-McKinney Plant Characteristics

- MBR following BNR process
- 5-stage Bardenpho
- Design flow: 15 MGD
- Yearly TP and TN discharge limit corresponding to daily concentrations of 0.15 mg/L TP and 4.1 mg/L TN
Drivers to Pursue EBPR Through MicroC® 2000

- Improve denitrification process
- Lower cleaning, chemical, and maintenance costs
- Lower chemical usage
  - Feeding 700 GPD Ferric Chloride for chemical precipitation
  - Ferric Chloride consistently clogged membrane filters so 300 GPW Citric Acid was used to clean filters
  - Citric Acid was being purchased at a premium cost
  - Feeding 560 GPD Methanol for only denitrification as Methanol doesn’t facilitate EBPR
- MicroC® 2000 Trial for EBPR
  - MicroC® 2000 was selected to provide a viable carbon source to enhance phosphorus release when BOD:TP is not adequate
  - Glycerol readily ferments to VFA that are utilized to support PAO enrichment
  - Glycerol is non-flammable and non-hazardous, making for easy use without special handling and storage conditions
EBPR Strategies

• Development of a baseline characterization
• Nutrient profiling and Phosphorus Uptake Rate (PUR) conducted
• MicroC® 2000 was added to Reactor (pre-anoxic)
• Aerobic zone in Reactor 5a was converted to an intermittently aerated basin (18 hours of air-off and 6 hours of air-on)
• Nutrient profiling also conducted after acclimation of the process
  – Phosphorus release was observed in Reactor 4
  – 80% of phosphorus removal was achieved biologically
Nutrient Profiling and PUR

**PUR Test**
- Prior to MicroC injection, PUR tests were conducted in three different HRT w and w/o adding MicroC2000
- No phosphorus uptake/release were observed

**Nutrient Profiling**
- Oxygen profiling demonstrated that DO in the anoxic and anaerobic tanks were never below 0.1 mgO2/L
- The effluent concentration of NOx is around 2 mgN/l. This value does not decrease below 0.5 mgN/L before recycling to the anaerobic phase.

Both NOx and DO concentration make a threshold in promoting EBPR. Lack of biological phosphorus uptake & release is presented in this graph.
EBPR Results

FeCl₃ in ML1
TP EFF Composite
TP Eff Ave Probe

FeCl₃ (GPD)
mg P/L

MeOH Total
MeOH PreANX
NOₓ EFF Composite

MeOH (GPD)
mg N/L

30-Apr
20-May
9-Jun
29-Jun
19-Jul
8-Aug
28-Aug
17-Sep
7-Oct
27-Oct
16-Nov
6-Dec
30-Apr
20-May
9-Jun
29-Jun
19-Jul
8-Aug
28-Aug
17-Sep
7-Oct
27-Oct
16-Nov
6-Dec
### Plant Performance Before and After EBPR Trial

<table>
<thead>
<tr>
<th></th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric Chloride (GPD)</td>
<td>700</td>
<td>&lt;200</td>
</tr>
<tr>
<td>Methanol (GPD)</td>
<td>560</td>
<td>220</td>
</tr>
<tr>
<td>MicroC® 2000 (GPD)</td>
<td>0</td>
<td>250</td>
</tr>
<tr>
<td>Citric Acid (GPW)</td>
<td>300</td>
<td>&lt;150</td>
</tr>
<tr>
<td>Effluent NOx (mg N/L)</td>
<td>1.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Effluent TP (mg P/L)</td>
<td>0.32</td>
<td>0.2</td>
</tr>
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</table>

- Lower cleaning, chemical, and maintenance costs with lowered usage of FeCl₃, Methanol, and Citric Acid
- Yearly savings in chemical costs of $108,000/year
- TN and TP removal efficiencies increased to 98.3% and 97%, respectively
- Plant still using MicroC® 2000 for EBPR and working together with technical staff at EOSi to further optimize process
- Ballenger is now eligible for $180,000 grant for maintaining low TN and TP effluent
References

• Process Control for Biological Nutrient Removal, Jeanette Brown, Water Environment Federation, May 29th, 2013
Questions?