1\textsuperscript{st} Annual Innovative Wastewater Technologies Seminar

Innovations in Nitrogen and Phosphorus Removal

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Brown and Caldwell
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Vision of WRRF

- Recovery of key resources
- Energy neutral or positive treatment
- Public and private sector partnerships
- Optimal integration of sources

AND: Always ensure protection of public health
Innovation
Nutrient Removal Basics

• Nitrogen Removal
  • Nitrification requires oxygen
    = energy for blowers/aerators
  • Denitrification requires carbon
    = organics needed; organics that could have been used for energy production

• Phosphorus Removal
  • Phosphorus Accumulating Organisms (PAO) require soluble carbon
    = competition with denitrification for organics; organics could have been used for energy production
Required and Available Energy for Wastewater Treatment, Exclusive of Heat Energy

- Energy required for secondary wastewater treatment
  - 1,200 to 2,400 MJ/1000 m³

- Energy available in wastewater for treatment
  - 5,850 MJ/1000 m³ (@ COD = 500 mg/L)

- Energy available in wastewater is 2 to 4 times the amount required for treatment
Organic Carbon vs. Energy

- 1.3 MJ/person per day ($0.01/person/day)
- Can be readily recovered as energy
- Can also be recovered as value added carbon ($0.05-$0.5/person/day)
  - methane generated from anaerobic digestion
  - bioplastics (i.e., PHA) via activated sludge
  - alginate/biogels via granular sludge
  - soluble organics via fermentation
Estimated Capital and Operating Costs for Each Treatment Level

Capital costs ($/gpd)

Operating costs ($/MG treated)

1: No N/P removal
2: 8 to 10 mg/l N
3: 8 to 10 mg/l N; 1 mg/l P
4: 6 mg/l N; 0.5 mg/l P
5: 3 mg/l N; 0.1 mg/l P
6: 3 mg/l N; 0.05 mg/l P
7: 2 mg/l N; 0.05 mg/l P
8: 1 mg/l N; 0.05 mg/l P

Example greenfield Level 2 plant (24 mgd design flow) with NO solids handling (sludge discharged to sewer) was $2.45/gpd.
Nitrogen Removal Processes
## Carbon Requirements for Mainstream Biological Nitrogen Removal Processes

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Nitrification-denitrification</th>
<th>Nitritation-denitrification</th>
<th>Partial nitritation-deammonification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon required for nitrogen removal (mg COD /mg N)</td>
<td>6.0 – 10.0</td>
<td>3.0 – 5.0</td>
<td>1.0 – 3.0</td>
</tr>
<tr>
<td>Net Process Oxygen Requirement (mg O₂/mg N Converted to N₂)</td>
<td></td>
<td></td>
<td>1.71</td>
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</tbody>
</table>

- Influent COD:N Ratio often 10 – 13 mgCOD/mgN
- Opportunities available to divert COD out of the plant and use it for energy generation
- The conundrum of aerobic treatment is that electrical energy is needed to destroy chemical energy (COD)
- Process units available to redirect Carbon for energy generation
Conventional Nitrogen Removal Processes

Electricity (e.g., aeration, pumping)

Infrastructure (facility footprint)

Chemicals (e.g., external carbon, alkalinity, polymers)

TN 8 - 10 mg/L

TN 3 - 5 mg/L
Conventional Nitrification-Denitrification

Autotrophic Bacteria
Aerobic Environment

1 mole Ammonia
\((NH_3/\text{NH}_4^+)\)

Nitrite Oxidizing
Bacteria (NOB)

1 mole Nitrite
\((\text{NO}_2^-)\)

25% \(O_2\) (energy)

75% \(O_2\) (energy)
~100% Alkalinity

Ammonia Oxidizing
Bacteria (AOB)

1 mole Nitrite
\((\text{NO}_2^-)\)

1 mole Nitrate
\((\text{NO}_3^-)\)

Heterotrophic Bacteria
Anoxic Environment

1 mole Nitrite
\((\text{NO}_2^-)\)

\(\frac{1}{2}\) mol Nitrogen Gas
\((N_2)\)

40% Carbon (BOD)

60% Carbon (BOD)
Advances in Nitrogen Removal
Recent Advances in N Removal started with Sidestream Treatment

Centrate NH₄

AOB
NH₄ + O₂ → NO₂⁻

Alkalinity

Methanol or other carbon source

Mostly NO₂

NO₂ Denite

Centrate with low Effluent NH₄ and NOₓ

Centrate with high NO₂ to headworks for odor control?

N₂

Denitrification

Nitritation

Nitritation

Anammox

NH₃

NO₂⁻

NO₃⁻

Typical Energy Demand Ranges

- Nitrification / Denitrification
- Nitritation / Denitrification
- Deammonification
Anammox Bacteria

- Very Slow Growth
  - 10 day doubling time at 20°C
  - SRT (30 - 50 days)

- Sensitive to:
  - Nitrite
    - causes irreversible loss of activity
    - toxicity based on concentration & exposure time
    - $\text{NH}_4^+:\text{NO}_2^-$ ratio 1 : 1.3
  - DO - reversible inhibition
  - Free ammonia (<10 mg/l)
  - Temperature >30°C preferred
  - pH (neutral range)

1 Gallon
80 Gallons
635 Gallons
132,000 Gallons

Bernhard Wett, 2005
Coupled Aerobic-Anoxic Nitrous Decomposition Operation (CANDO)

- Couples nitritation (NH$_3$ conversion to NO$_2$) followed be incomplete denitrification (NO$_2$ conversion to N$_2$O)
- N$_2$O is captured and can be used for combustion (e.g., biogas engine or boiler)
- Increase power output making the net energy recovery much more favorable

Gao, Scherson and Wells 2014
Denitrifying anaerobic methane oxidation (DAMO)

Still under development at lab-scale, very slow bacterial growth but could have good potential in conjunction with anaerobic and anammox processes.
From Green House Gas to Green Biofuel

**CARBON RECOVERY?**

$\text{CH}_4 \quad \text{CH}_3\text{OH}$

**NH$_3$**

**NH$_2$OH**

**NO$_2^-$**

**NO$_3^-$**

**ANAEROBIC DIGESTION**

**NITRIFICATION**

SRB Process

Su et al., 2015
C:N ratio into the bioreactor may be a key control factor in defining predominant pathway for TN removal

Control denitrification by heterotrophic organisms

- **Higher C:N ratio**
  - 6 - 10 :1 range?
  - Heterotrophs Outcompete

- **Medium C:N**
  - 3 - 5 :1 range?

- **Lower C:N ratio**
  - 1 - 3 :1 range?
  - Anammox Outcompete

**Wastewater C:N Ratio**

- If C/N ratio is sufficient for conventional nitrification/denitrification, opportunity to:
  - Reduce C:N ratio by CEPT and HRAS and reduce Energy needed for nitrogen removed
  - Divert carbon to anaerobic digestion to both recover energy (CHP system)
Resource Efficient Recycling Options

Stage 1: Carbon Removal and Recovery

Stage 2: Nitrogen Removal

Stage 3: P Removal/Recovery

Water Reuse
Biosolids
Energy Generation
Fertilizer
By-Products

By-Products
Carbon Removal Processes

Anaerobic - UASB

Physical - Primary Settling

Physical - Micro-Sieves and Micro-Filters

Activated Sludge / A-Stage
Nitrite Shunt/
Mainstream Deammonification
Low DO Operation Nitrite-Shunt Process

Jimenez et al. (2014)
Ammonia vs NOx control

DO = set point

DO Controller/PLC

Aerobic Duration Controller/PLC

NH4-N - NOx-N = setpoint

N Species

SecEff Ammonia N
SecEff Nitrite + Nitrate
SecEff Total inorganic N

D.O., NO2-N, NO3-N

CONC. (mgN/L)

Air

Regmi et al., 2014
Nitrite Shunt through FNA Production

Zhiguo Yuan, The University of Queensland
Approaches to Mainstream Deammonification

- Small Flocculant & Suspended Growth Anammox Granules
  e.g. Activated Sludge Systems

- Large Anammox Granules
  e.g. granular sludge systems

- Hybrid Suspended & Attached Growth
  e.g. IFAS

- Attached Growth Biofilm
  e.g. RBC, MBBR, Biofilter

Increasing diffusivity or mass transfer resistance

- DC Water, USA
- HRSD, USA
- AIZ Strass/ARA Consult, Austria
- Glarnarland/Cyklar-Stulz, Austria
- Changi WRP, Singapore PUB
- Beijing Technical University, China
- Beijing Drainage Group, China
- Harbin IT, China
- Delft Technical University / Paques / WSHD - Dokhaven, Netherlands
- Veolia Water, France
- Ghent University RBC
  Veolia Water, France
Integrated Anaerobic/Aerobic Treatment

Influent → Preliminary Treatment → Anaerobic Process → N Removal → Effluent

Disintegration of Sewage Sludge

Biogas

Waste sludge

Dewatering

Sludge Disposal

DAMO

CH₄ → e⁻ → NO₃ → e⁻ → NO₂ → NH₄⁺ → CO₂ → N₂ → NO₃

Anammox
Energy neutrality or self sufficiency

- Harness energy content of wastewater (14 MJ/kg COD)
- While performing nitrogen removal

Strass WWTP, Austria
HRSD’s Approach

Carbon redirection
Nitrite-shunt
Nitrogen Polishing

Pilot Plant is Located in Hampton Roads Sanitation District’s Chesapeake Elizabeth Treatment Plant, Virginia Beach.

Regmi et al. (2014)
Enhanced Mainstream Nitrogen Removal

Zhiguo Yuan, The University of Queensland
What about P Removal?
Some Traditional Flow Diagrams for Bio-P

5-Stage Bardenpho

Johannesburg (JHB) Process

Modified JHB Process

UCT Process

Modified UCT Process

Westbank Process

Barnard (2011)

Anaerobic

Anoxic
Issues with Bio-P and N Removal

- Bio-P becomes less stable when applied in conjunction with N removal processes due:
  - competition with GAOs
  - introduction of nitrate/nitrite to anaerobic zone
  - competition for carbon
- N removal via denitrification becomes carbon limited due to bio-P
- Supplemental carbon is added to enhance denitrification and/or bio-P
- PAOs that can use nitrate/nitrite as an electron acceptor instead of O₂ to be highly desirable pathway for both N and P removal
Biological Advances

Denitrifying Phosphorus Removal

Y. Ma et al, 2009
Biological Advances

Nitrite Shunt and Bio-P (DPAO?)

Effluent Quality, mg/L

- TN
- TP

11/01/14, 11/15/14, 11/29/14, 12/13/14, 12/27/14, 01/10/15, 01/24/15, 02/07/15

Effluent Quality, mg/L
Ballasted-Flocculation with Magnetite

Figure 1: CoMag Process Flow Diagram
Bionanotechnological phosphate removal system with thermostable ferritin

BiAqua Technology: Biobased adsorbents

We have designed the product to suit typical conditions in MMF. This means it can be retrofit into the large installed base of MMF.

After the adsorption phase, the adsorbent is regenerated.
1) Iron and phosphate are washed from the filter
2) The iron nanoparticle is reformed in the ferritin
Struvite Crystallization Processes for Bio-P Plants

- **Liquid technologies:**
  - Crystalactor®
  - Ostara Pearl®
  - PHOSPAQ™
  - Multiform Harvest

- **Solids technologies:**
  - AirPrex®
Vision of WRRF

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**AND: Always ensure protection of public health**
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HRSD Mainstream Nitrite-Shunt + Anammox Polishing

• Nitrogen removal in nitrite-shunt

• Anammox Polishing
Energy Balance of WRRF

aerobic metabolism \[ \text{CH}_2\text{O} + \text{O}_2 \xrightarrow{\text{activated sludge}} \text{CO}_2 + \text{H}_2\text{O} + E_T + E_S \]

anaerobic metabolism \[ \text{CH}_2\text{O} \xrightarrow{\text{digester}} 0.5*\text{CH}_4 + 0.5*\text{CO}_2 + (E_T+E_S) \]

cogeneration in CHP \[ 0.5*\text{CH}_4 + \text{O}_2 \xrightarrow{\text{CHP}} 0.5*\text{CO}_2 + \text{H}_2\text{O} + E_T + E_E \]

\( E_T \) - thermal energy \quad \( E_S \) - syntheses energy \quad \( E_E \) - electricity
P recovery from Iron Phosphate Sludge

Waste Water → Primary Treatment → Secondary Treatment → P removal → RO Treatment → Drinking water

Stage I: FeS precipitation process
Stage II: Electrochemical process

FeCl₃ > FePO₄ > FeSₓ > PO₄³⁻ in solution

NaCl → Na₂S

Fe³⁺, S⁰ → Fe²⁺, S²⁻ → ANODE

HS⁻ → CATHODE

Jurg Keller, The University of Queensland
Anoxic P removal possible by denitrifying PAOs (DPAOs)
Carbon and oxygen requirements are curbed
PHA stored by PAOs in anaerobic conditions can be used for denitrification and P uptake in anoxic conditions
DPAOs activity over nitrite is of interest when integrating bio-P in a shortcut N removal system.
Bio-P and denitrifying dephosphatation with advanced biological nitrogen removal processes.