SOLID PHASE DENITRIFICATION, A SUSTAINABLE TECHNOLOGY FOR REDUCING NITRATE AND PHOSPHATE CONCENTRATIONS

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INTRODUCTION

Recirculating Aquaculture Systems

Increased System Size + Decreased Water Exchange + Increased Feeding = Higher Nitrates

• Discharge of Nitrate has negative environmental impact, especially in saltwater ecosystems

• Elevated system Nitrate = STRESS On the Animals
We propose that there needs to be a change in thinking from **Dilution** of Nitrate to **Removal** of Nitrate!
Denitrification is defined as the removal of NITRATE and is not the specific mechanism.
Hypothesis:

A Biodegradable Biopolymer such as Polyhydroxyalkanotes (PHAs) can be used as both the carbon source and substrate for denitrification in both freshwater and marine systems, referred to as Solid Phase Denitrification (SPD).
POLYHYDROXYALKANOTES (PHAs)

Family of biodegradable bioplastic polymers, produced from sugar fermentation.

- Specifically Developed for Aquatic Systems
- 100% Natural
- Pure – no fillers; no chemicals
- Produced from Sustainable Source
- ASTM D7081 Certified Marine Biodegradable
DENITRIFICATION

Two Biological Mechanisms for Removal of Nitrate Using SPD

1. Aerobic Assimilation
   \[ \text{NO}_3^- - N + P \rightarrow \text{Bacterial Biomass} \]

2. Anaerobic
   Nitrate (NO$_3^-$) →
   Nitrite (NO$_2^-$) →
   Nitric oxide (NO) →
   Nitrous oxide (N$_2$O) →
   Nitrogen gas (N$_2$)
**MONOD FORMAT- SATURATION EQUATION**

\[
VDR = VDR_{\text{max}} \left( \frac{C_{NO_3-N}}{C_{NO_3-N} + K_{1/2}} \right)
\]

- \( VDR \) = Volumetric Denitrification Rate \([\text{kg/m}^3 \text{ day}]\)
- \( VDR_{\text{max}} \) = maximum reaction rate \([\text{kg/m}^3 \text{ day}]\)
- \( K_{1/2} \) = half-saturation coefficient for Nitrate \([\text{mg NO}_3-N/\text{L}]\)
- \( C_{NO_3-N} \) = nitrate-nitrogen \([\text{mg NO}_3-N]\)
1. Aerobic Biomass Assimilation

- Assumes systems are Organic Carbon Limited
- Introduction of an Organic Carbon source promotes heterotrophic bacterial growth
- Bacteria assimilate nitrate and phosphate into biomass
- Physical removal of biomass via LSS filtration
- Presence of DO prevents hydrogen sulfide production
AEROBIC ASSIMILATION
(DENITRIFICATION)
PHA STOICHIOMETRY

\[ \text{NO}_3^- + 2.39 \text{C}_4\text{H}_6\text{O}_2 + 3.59 \text{O}_2 \rightarrow \text{C}_5\text{H}_7\text{O}_2\text{N} + 3.18 \text{H}_2\text{O} + 3.56 \text{CO}_2 + \text{HCO}_3^- \]

VDR\text{\textsubscript{AER}}: \quad \sim 0.150 – 0.250 \text{ g NO}_3^-\text{N} / \text{L PHA} / \text{day}

Consumption of PHA: \quad 14.7 \text{ g PHA} / \text{g NO}_3^-\text{N}

Production of Solids: \quad 8.1 \text{ g VSS} / \text{g NO}_3^-\text{N}

Production of CO\text{\textsubscript{2}}: \quad 11.2 \text{ g CO}_2 / \text{g NO}_3^-\text{N}

Overall Aerobic Reaction is Slower with Higher PHA Consumption
and Greater CO\text{\textsubscript{2}} Production than Anaerobic Reaction
2. Anaerobic (Anoxic) Conditions

- \( \text{NO}_3^- \text{N} \rightarrow \text{N}_2 \)
- Low Oxygen Conditions ([DO] < 1.0 mg/L)
- Utilizes Solid Organic Carbon Source (PHA)
- PHA Also Provides Surface Area for Bacterial Attachment
- Alkalinity Production
- Risk of Hydrogen Sulfide Production!
**Anaerobic (Anoxic) Denitrification PHA Stoichiometry**

\[
\text{NO}_3^- + 0.39 \text{C}_4\text{H}_6\text{O}_2 \rightarrow 0.088 \text{C}_5\text{H}_7\text{O}_2\text{N} + 0.456 \text{N}_2 + \text{HCO}_3^- \\
+ 0.121 \text{CO}_2 + 0.363 \text{H}_2\text{O}
\]

- **VDR\textsubscript{ANA} (4x higher):** ~1.0–3.5 g NO\textsubscript{3}-N / L PHA /day
- **Consumption of PHA (6x lower):** 2.4 g PHA / g NO\textsubscript{3}-N
- **Production of Solids (11x lower):** 0.71 g VSS / g NO\textsubscript{3}-N
- **Production of Alkalinity:** 3.57 g Alk / g NO\textsubscript{3}-N
Solid Phase Denitrification
Lab-Scale Fluidized-Bed Bioreactors

Representative of a saltwater broodstock holding system or marine aquarium system

- High Salinity (28+ppt)
- Low BOD
- Spike with NO$_3$-N to 50 mg/l & KH$_2$PO$_4$ to 8 mg/l
- No Hydrogen Sulfide Production below 5 mg/l NO$_3$-N.
- Phosphate = 0= VDR
Mirel™ Bioplastics PHA media – 10 L/min
Research Results: Fluidized-Bed Bioreactors

Dissolved Oxygen: Influent & Effluent
Three Fluidized-Bed Bioreactors

Mirel™ Bioplastics PHA media 10 L/min
Research Results: Fluidized-bed Bioreactors

Phosphorus: Influent & Effluent
Three Fluidized-Bed Bioreactors

Mirel™ Bioplastics PHA media 10 L/min
SOLID PHASE DENITRIFICATION

PROTOTYPE ANAEROBIC BIOREACTOR

Representative of Marine Recirculating Aquarium and Aquaculture Systems

Marine Aquarium/Aquaculture Systems

• High Salinity (28+ ppt)
• Low/Medium BOD
• NO₃-N spiked/fed to 30-250 mg/L
• Hydrogen Sulfide detected NO₃-N levels below 100 mg/L.
Research Results: Optimized SPD PolyGeysers

VDR vs. Loading Rate
(NO₃-N range 40–150 mg/L @ variable flow rates)

Safety Factor = 2

Average over testing range

R² = 0.58583

VDR (mg NO₃ removed / L media / day)

NO₃ Loading rate (mg NO₃ / L media / d)
Anaerobic (Anoxic) Denitrification: Oxygen Inhibition/Limitation

$$VDR \times V_b = (VDR_{max} \times V_b - K_c \times Q \times C_i) \times \Theta^{T-20} \times Q \times N_i/(K_N \times V_b + Q \times N_i)$$
ANAEROBIC (ANOXIC) DENITRIFICATION: OXYGEN INHIBITION/LIMITATION

\[ VDR \times V_b = (VDR_{max} \times V_b - K_c \times Q \times C_i) \times \Theta^{T-20} \times Q \times N_i/(K_N \times V_b + Q \times N_i) \]
SPD Reactor Application
Two Operating Modes

- Anaerobic SPD
  - Anaerobic, pulsed packed -bed bioreactor
  - Reduction of NO$_3$-N to N$_2$ gas
  - Faster removal process than aerobic
  - Biomass capture and removal via LSS
  - Risk of sulfide production at low NO$_3$ concentrations

- Aerobic SPD
  - Aerobic, fluidized-bed bioreactor
  - Biomass capture and removal via LSS
  - Primarily for maintenance and/or phosphate removal
  - No sulfide production
Required Information:

- System volume: 400 m³ exhibit
- Current nitrate concentration: 450 mg/L
- Target nitrate concentration: 100 mg/L
- Max daily feed rate: 5 kg/day
  - Wet feed (fish, squid, etc) @ 25% DW, 65% protein
- Target drawdown time: 10 months

Approach: break the problem into two parts

- Drawdown (Anaerobic): \([\text{NO}_3\text{-N}] \geq 100 \text{ mg/L}\)
- Maintenance (Aerobic): \([\text{NO}_3\text{-N}] \leq 100 \text{ mg/L}\)

Initial reactor size based on drawdown
Maintenance reactor size based on feed rate
REACTOR SIZING EXAMPLE: ANAEROBIC DRAWDOWN (3 STEPS)

Step 1: Determine daily nitrate production from feed

\[
\{\text{Change in NO}_3\} = \{\text{NO}_3 \text{ addition}\} - \{\text{NO}_3 \text{ removal}\} = 0
\]

{\text{NO}_3 \text{ addition}}:

5 kg feed / day * 25 % dry weight * 65% protein * 0.092 kg NH\textsubscript{3} / kg protein = 75 g NH\textsubscript{3} / day

Assume all ammonia is oxidized into nitrate = 75 g NO\textsubscript{3} / day

{\text{NO}_3 \text{ removal}}

(Assume VDR of 1.0 g N removed / L\textsubscript{media} / day):

\[
\frac{75 \text{ g NO}_3/\text{day}}{1.0 \text{ g} / \text{L media} / \text{day}} = 75.0 \text{ L}_\text{media} 52 \text{ kg}
\]

(0.687 kg PHA / L PHA)
Reactor Sizing Example: Anaerobic Drawdown (3 Steps)

Step 2: Account for daily nitrate change based on system volume

\[
\text{NO3 mass} = \{[\text{NO3}]\} \times \{\text{Tank Volume}\} - \{\text{Change in [NO3]}\}
\]

Mass of nitrate to be removed:
\[
\text{NO3 mass} = (450 \text{ mg/L} - 100 \text{ mg/L}) \times 400 \text{ m}^3 = 140 \text{ kg NO}_3-\text{N}
\]

Daily removal rate:
\[
\{\text{Change in NO}_3\} = \frac{140 \text{ kg NO}_3}{305 \text{ days}} = 459 \text{ g NO}_3 \text{ per day}
\]

**SPD PolyGeyser Volumetric Denitrification Rate (VDR): 1.0 g NO}_3/L_{media}/day**

\[
(459 \text{ g NO}_3 / \text{day}) / (1.0 \text{ g NO}_3/L_{media}/\text{day}) = \frac{459 \text{ L}_{media}}{315 \text{ kg}}
\]

Step 3: Combine media volumes from Step 1 and Step 2

Drawdown reactor size = 75 L_{media} + 459 L_{media} = \boxed{534 L_{media}}

367 kg
Reactor Sizing Example: Aerobic Maintenance

Determine required daily nitrate change based on feed rate

\[
\{\text{Change in NO}_3\} = \{\text{NO}_3 \text{ addition}\} - \{\text{NO}_3 \text{ removal}\} = 0
\]

\{\text{NO}_3 \text{ addition}\}:

5 kg feed / day * 25 % dry weight * 65% protein * 0.092 kg NH$_3$ / kg protein = 75 g NH$_3$ / day

Assume all ammonia is nitrified into nitrate = 75 g NO$_3$ / day

\{\text{NO}_3 \text{ removal}\} (Assume VDR of 0.25 g N removed / L$_{\text{media}}$ / day):

\[
(75 \text{ g NO}_3 / \text{day}) / (0.25 \text{ g} / \text{L media} / \text{day}) = \frac{300 \text{ L}_{\text{media}}}{\text{L}_{\text{media}}} = 206 \text{ kg PHA}
\]

**If you want drawdown in 1 yr to 50 mg/L nitrate, aerobic reactor size is ~2x greater than maintenance at 100 mg/L**
Anaerobic Drawdown (w/ feed inputs)

- 367 kg PHA for reactor
- 10 month drawdown (305 days) to 100 mg/L
- \( (140 \text{ kg } \text{NO}_3 + 0.075 \text{ kg } \text{NO}_3/\text{d} \times 305 \text{ d}) \times 2.9 \text{ kg PHA/kg } \text{NO}_3 \)
- = 472 kg PHA CONSUMED

- Total PHA Consumed = 839 kg
SPD Reactor Application Treatment Cost Estimates

- Aerobic Maintenance
  - 206 kg PHA for reactor
  - $75 \text{ g NO}_3/\text{d} \times 14.7 \text{ g PHA/g NO}_3 = 1.6 \text{ kg PHA/d} \times 365 \text{ d}$
  - $= 584 \text{ kg PHA CONSUMED}$
  - Total PHA Consumed $= 790 \text{ kg}$
Option 1
- Drawdown with Anaerobic reactor to 100 mg NO₃/L
- Aerobic maintenance @ 100 mg/L
- Yearly average media cost based on 5 year operating time:
  - $0.0194 / L; $0.073 / gal; $19.41 / m³

Option 2
- Drawdown with Anaerobic reactor to 100 mg NO₃/L
- Anaerobic maintenance @ 100 mg/L
- Yearly average media cost based on 5 year operating time:
  - $0.0076 / L; $0.029 / gal; $7.59 / m³