LOW SUBSTRATE NITRATE KINETICS UTILIZING PASSIVE SELF-REGULATING DENITRIFICATION TECHNOLOGY

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Introduction

Increased Density + Higher Nitrates Nitrate Toxicity (Marine Systems) Nitrate – Environmental Impact

Change thinking from conversion of nitrogen to removal of nitrogen!

Denitrification

Engineering Overview

- Fundamentals of Denitrification
 - Stoichiometry & Kinetics
- Tertiary Denitrification
 - Exogenous electron donor
- One-sludge Denitrification
- Other Options

Denitrification

(Bacteria widespread in the environment)

Facultative aerobic bacteria

• Shift to NO₃⁻ or NO₂⁻ when O₂ limited

Chemotrophic

- Heterotrophic organic electron donor
- Autotrophic $-H_2$ or reduced sulfur

Heterotrophic Denitrification

- Low BOD treated wastewater external carbon source
 - methanol, acetate, glucose, ethanol, starch cheap, bulk quantities
- High BOD wastewater endogenous respiration

Denitrification

Nitrate $(NO_3^-) \Rightarrow$ Nitrite $(NO_2^-) \Rightarrow$ Nitric Oxide $(NO) \Rightarrow$ Nitrous Oxide $(N_2) \Rightarrow$ Nitrogen Gas (N_2)

$$NO_3 + \frac{5}{6}CH_3OH \rightarrow \frac{1}{2}N_2 + \frac{5}{6}CO_2 + \frac{2}{3}H_2O + OH^-$$

Denitrification

Optimal Conditions

- Low redox potential
 - ORP > -200 mV incomplete denitrification NO_2^- , NO_2 and N_2O
 - ORP < 400 mV production of hydrogen sulfide (H_2S)
- Low Oxygen Levels (anoxic)
 - High DO \Rightarrow accumulation of intermediates, NO₂⁻, NO₂ and N₂O
- pH: 7 to 8
- Alkalinity 3.57 g CaCO₃/ g NO₃—N consumed

Denitrification Classifications

Wastewater Treatment Industry

- Tertiary external carbon source
 - methanol, acetate, glucose, ethanol, starch cheap, bulk quantities
- One-sludge / single sludge BOD

Tertiary Treatment



Tertiary Treatment

- Organic donors \Rightarrow heterotrophic denitrification
 - "Methanol" historical, cheap, readily available

 $NO_3^{-} + 1.07 CH_3OH + H^+ \Rightarrow 0.061 C_4H_7O_2N + N_2 + 2.42 H_2O + 0.76 CO_2$

- Inorganic donors \Rightarrow autotrophic denitrification
 - hydrogen gas H₂

 $H_2 + 0.35 \text{ NO}_3^- + 0.05 \text{ CO}_2 + 0.35 \text{ H}^+ \Rightarrow 0.01 \text{ C}_4 \text{H}_7 \text{O}_2 \text{N} + 0.17 \text{ N}_2 + 1.14 \text{ H}_2 \text{O}_2 \text{N}$

• Reduced sulfur - SO₄²⁻

 $S + 1.2 \text{ NO}_3^- + 0.4 \text{ H}_2\text{O} \Rightarrow \text{SO}_4^{2-} + 0.60 \text{ N}_2^- + 0.80 \text{ H}^+$

Tertiary Treatment

Activated Sludge

- SRT = 5 days
- 0.75 g VSS/g NO₃-N removed

• Biofilms

- Submerged Fixed Films
- Fluidized Media
- MBBR
- Membrane Bioreactors

Single-sludge Denitrification (preanoxic denitrification)



Advantages: direct use of influent BOD, faster kinetics, low TAN discharge

Single-sludge Denitrification (biomass storage & decay or postanoxic denitrification)



Problems: slow kinetics of endogenous respiration, release of TAN from decaying sludge

Single-sludge Denitrification

- BOD supplies organic carbon source
- Integrated into biofilter
 - Aerobic: oxidation of BOD & nitrification
 - Anoxic: denitrification
- Advantages
 - No chemicals reduces cost, danger of under /overdosing
 - BOD removed as part of denitrification process
 - High percentage of nitrogen removed

AST Research Areas

preanoxic denitrification –single sludge

PolyGeyser[®] Bead Filter

postanoxic denitrification – Tertiary treatment

PolyGeyser[®] Bead Filter

DOC/NOAA Phase I SBIR

Concurrent Clarification and Biological Nitrification/Denitrification in a Single Floating Bead Bioclarifier to Simplify Nitrogen Management in Recirculating Aquaculture Systems

Phase I Technical Objectives

Characterize the volumetric denitrification capacity, using captured solids, in AST's drop filter configuration
Determine the effects of the sludge retention time and backwash frequency on the denitrification process within these filters
Conduct basic reactor modeling to project PolyGeyser denitrification performances for a variety of applications

PolyGeyser[®] Bead Filter

preanoxic denitrification

Aerobic Reactor





Anoxic Reactor

Anoxic Conditions in the Sludge Zone



Dissolved Oxygen concentrations across the drop zone and in sludge zone of the DF-3 PolyGeyser[®] at backwash intervals of 1.9, 5.5, and 9.1 hrs.

Water Quality across DF-3 PolyGeyser®



Nitrate-nitrogen concentrations across the drop zone and in sludge zone of the DF-3 PolyGeyser[®] at backwash intervals of 1.9, 5.5, and 9.1 hrs.

Water Quality across DF-3 PolyGeyser[®]



Alkalinity concentrations across the drop zone and in sludge zone of the DF-3 PolyGeyser[®] at backwash intervals of 1.9, 5.5, and 9.1 hrs

USDA Phase I SBIR

Passive Self-Regulating Denitrification Technology for Aquaculture

Phase I Technical Objectives

- Characterize the volumetric denitrification capacity of floating PHA pellets in AST's PolyGeyser[®] configuration
- Determine the effect of hydraulic loading rates on denitrification performance
- Conduct basic reactor modeling to project PolyGeyser[®] denitrification performances for a variety of applications

PolyGeyser[®] Bead Filter





Polyhydroxyalkanotes (PHAs)

Family of bioplastic polymers, produced from sugar fermentation

- Low Maintenance
- Cost effective
- Carbon source
- Substrate for Bacteria



Denitrification – PHA Stoichiometry

NO₃⁻ + 0.39 C₄H₆O₂ → 0.088 C₅H₇O₂N + 0.456 N₂ + HCO₃⁻ + 0.121 CO₂ + 0.363 H₂O

Polyhydroxyalkanotes (PHAs)

 excessive biofloc formation at high Nitrate-nitrogen loading & high BOD





Construction of Lab-Scale Experimental PolyGeyser[®]





Construction of Small-Scale Experimental BioReactors





Water Quality Sampling

Parameter	Method / Range
DO / Temperature	YSI Model 58 Dissolved Oxygen Meter
Salinity / Conductivity	YSI Model 33 S-C-T Meter
Nitrogen – Ammonia	Hach Method 8038 Nessler Method $0 - 2.50 \text{ mg/L NH}_3$ -N
Nitrogen –Nitrite	Hach Method 8507 Diazotization Method $0 - 0.300 \text{ mg/L NO}_2^-$ -N
Nitrogen -Nitrate	Hach Method 8039 Cadmium Reduction Method $0.0 - 10.0 \text{ mg/L NO}_3^-$ - N
Alkalinity	Standard Methods 2320B as CaCO ₃

PolyGeyser[®] - Backwash



Solids Removal



Acclimation of Experimental Denitrification Units at High Nitrate-nitrogen



150 mL/min Flow Rate

Acclimation of Experimental Denitrification Units at High Nitrate-nitrogen



Alkalinity / NO_3 -N = 3.77

Acclimation of Experimental Denitrification Units at High Nitrate-nitrogen



Marine Lab-Scale BioReactors





- Salinity 10 to 32 ppt
- Low BOD
- Low TSS
- Nitrate 50 to 250 mg/L-N

Nitrate-nitrogen Across BioReactors



Alkalinity Across BioReactors



Volumetric Nitrification Removal Rate





- Three lab-scale denitrification BioReactor were designed, constructed and operated
- Three lab-scale PolyGeyser[®] denitrification unit was designed, constructed and are operating
- "proof of-concept"

Questions?







Acknowledgements

Research was supported by the United States Department of Agriculture, SBIR Program under Agreement No. 59-1930-1-130

Research was supported by the Department of Commerce, SBIR Program under Agreement No. DG133R05-CN-1208

Opinions, conclusions, and recommendations are of the authors and do not necessarily reflect the view of the USDA or DOC.