Hydrogel Immobilizations for Anammox Enrichment

H.B.S. Thesis Defense

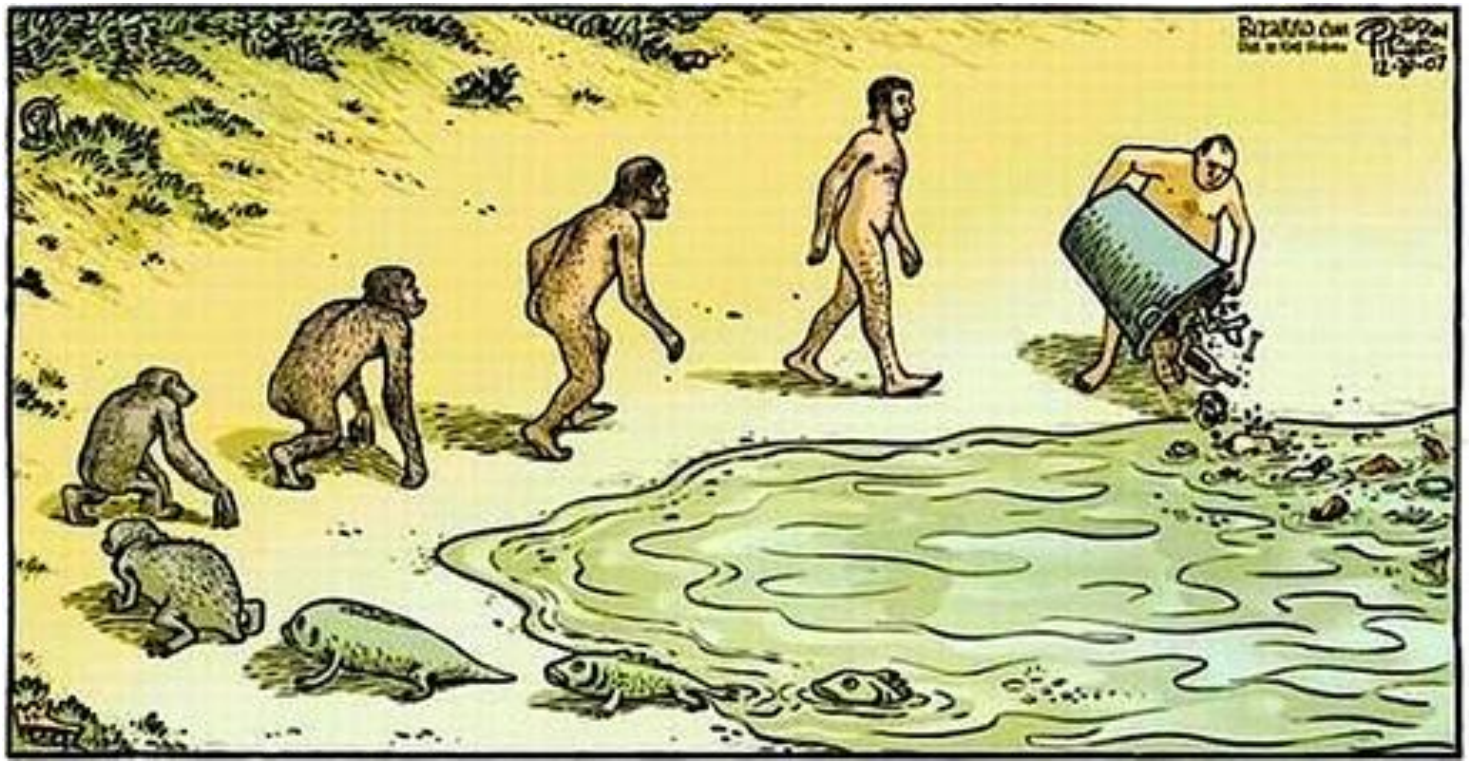
Grant Stein

Dr. Tyler Radniecki

June 7, 2017

Background

Why Nitrogen Removal?



Why Nitrogen Removal?

Source: https://www.nature.com/scitable/knowledge/library/eutrophication-causes-consequences-and-controls-in-aquatic-102364466

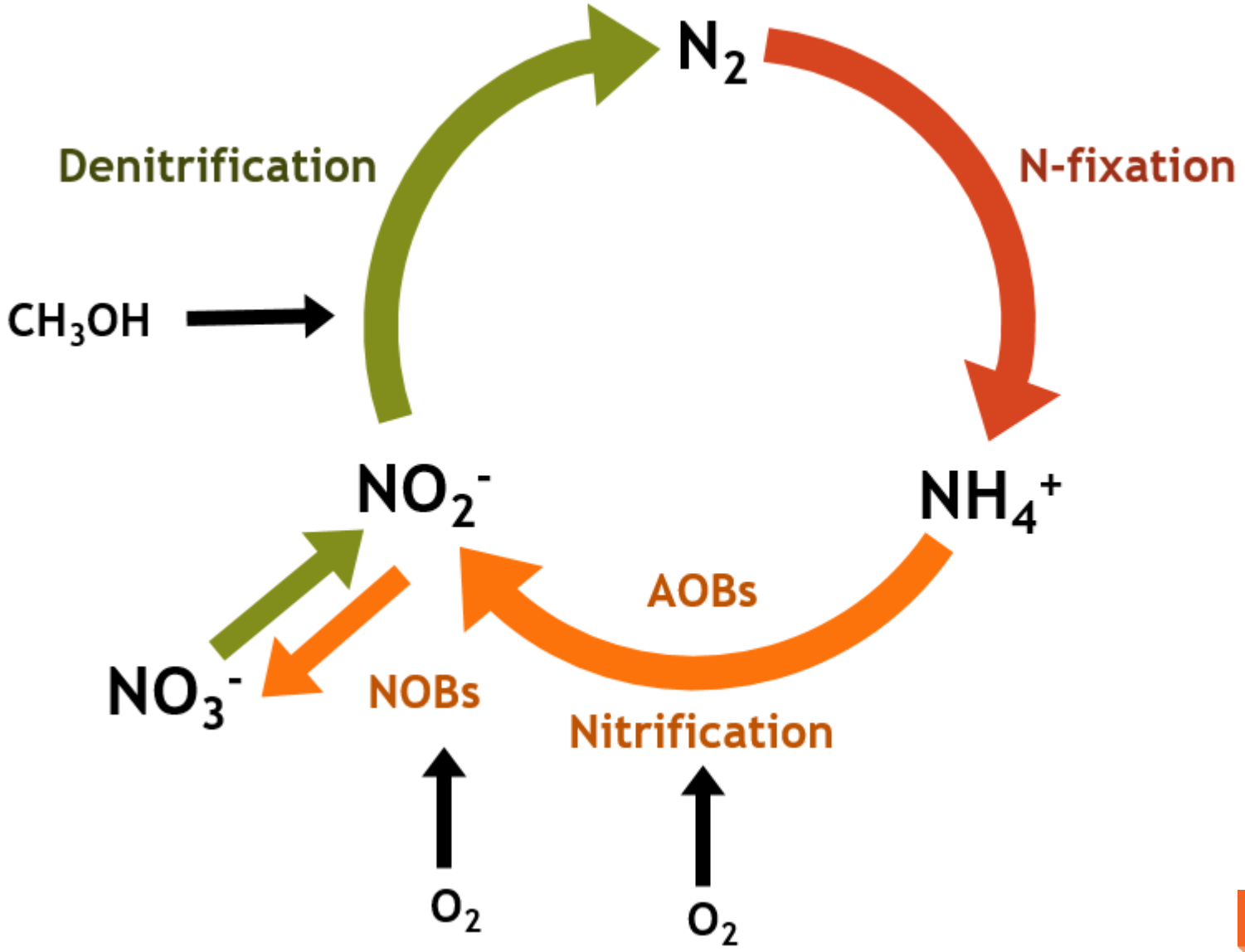
Why Nitrogen Removal?

Source: http://www.eniscuola.net/en/2016/11/03/what-is-eutrophication-causes-effects-and-control/

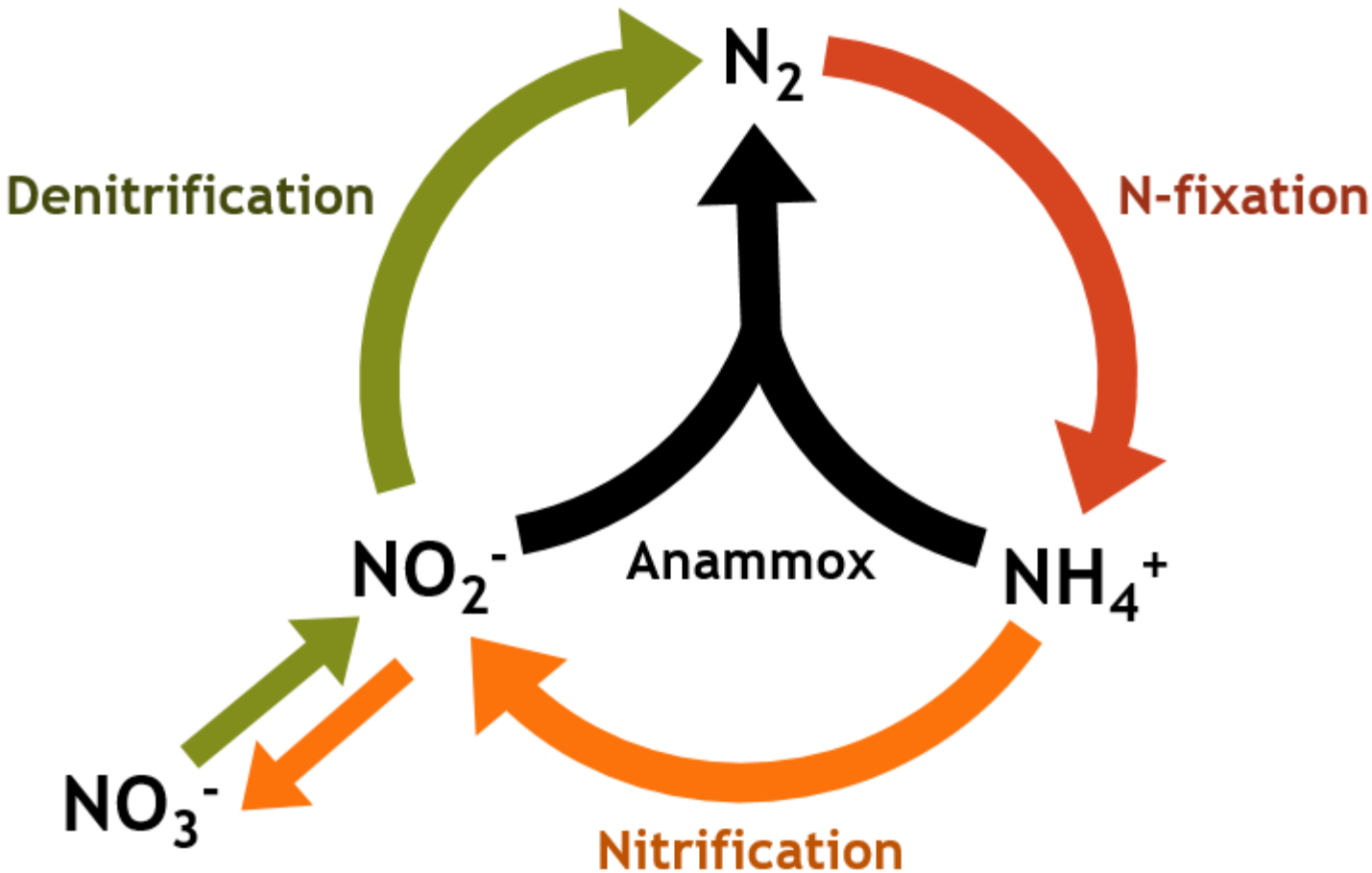
Conventional Treatment

- Aerobic Nitrification
  - AOB $$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O$$
  - NOB $$NO_2^- + 0.5O_2 \rightarrow NO_3^-$$
- Anaerobic Denitrification

$$NO_3^- + 0.833CH_3OH \rightarrow 0.8333CO_2 + 0.5N_2 + 1.167H_2O + OH^-$$

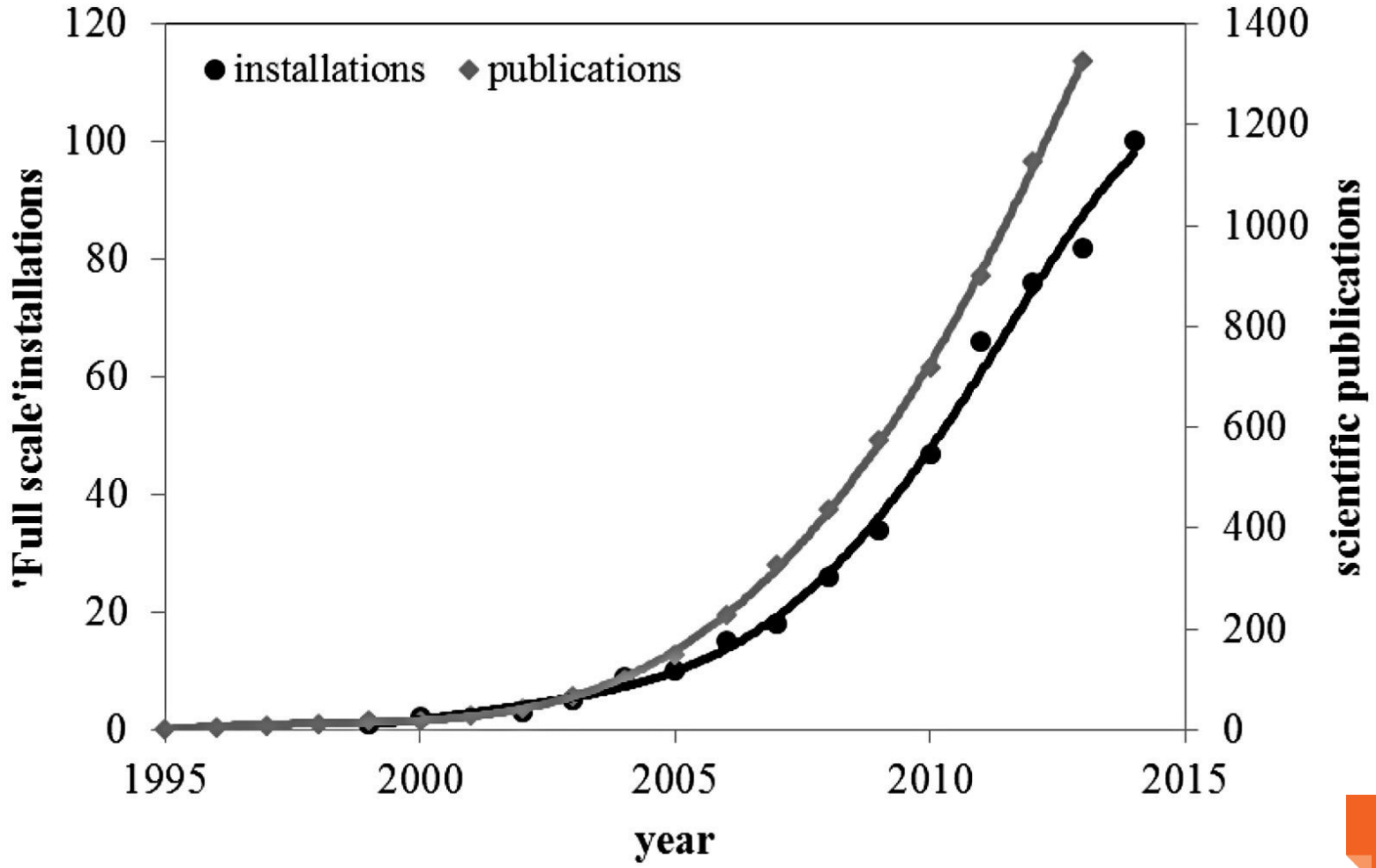

N_2
Denitrification
N-fixation
CH_3OH
NO_2^-
NH_4^+
AOBs
NO_3^-
NOBs
Nitrification
O_2
O_2

$$\textbf{\textit{Anammox}}: \quad NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$$



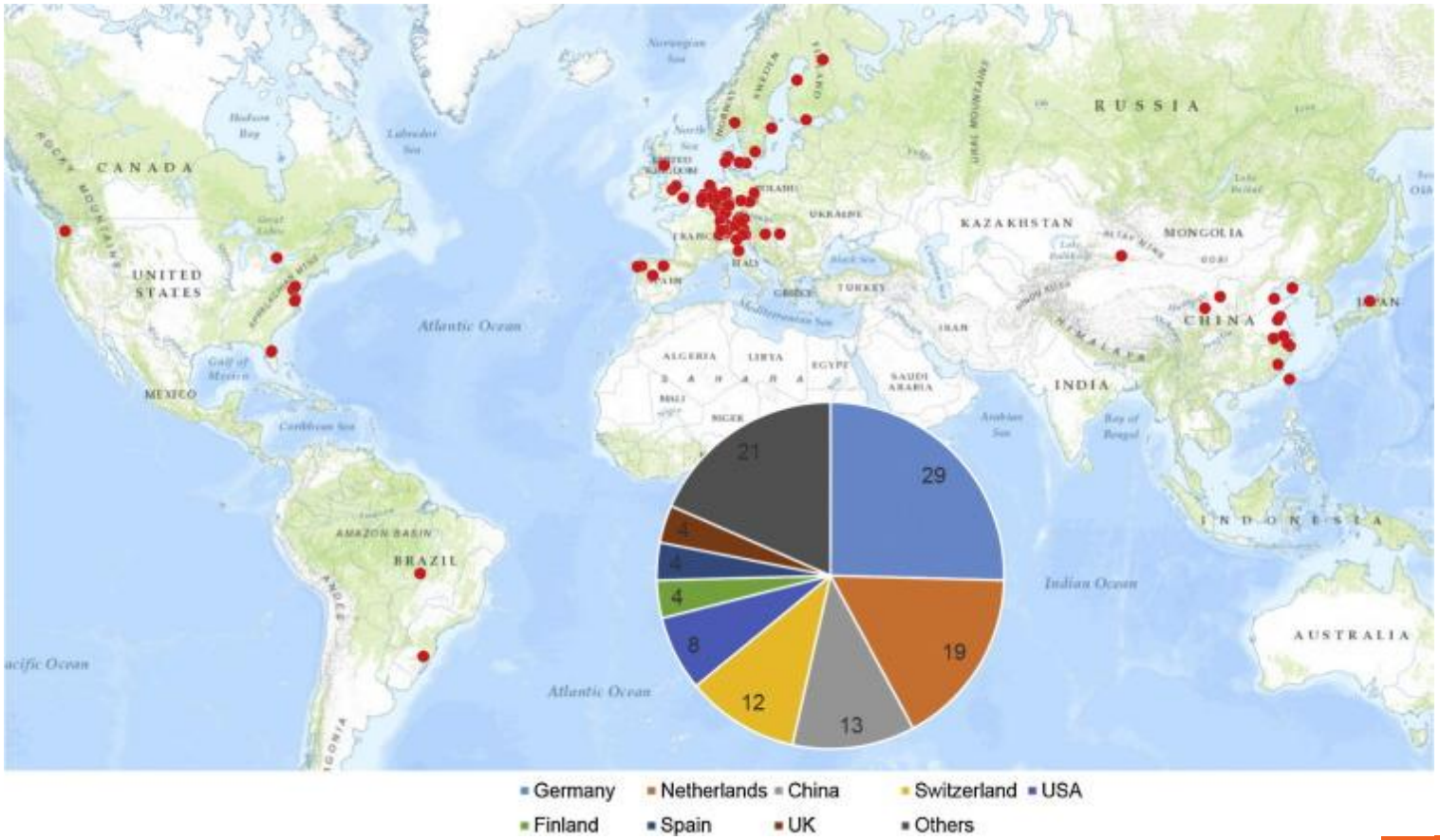
Anammox: "***An***aerobic ***Amm***onium ***Ox***idation"

Anammox: Current Trends



Source: https://www.researchgate.net/publication/260759243_Full-scale_partial_nitritationanammox_experiences_-_An_application_survey

Anammox at Work



Source: https://doi.org/10.1016/j.chemosphere.2015.06.094

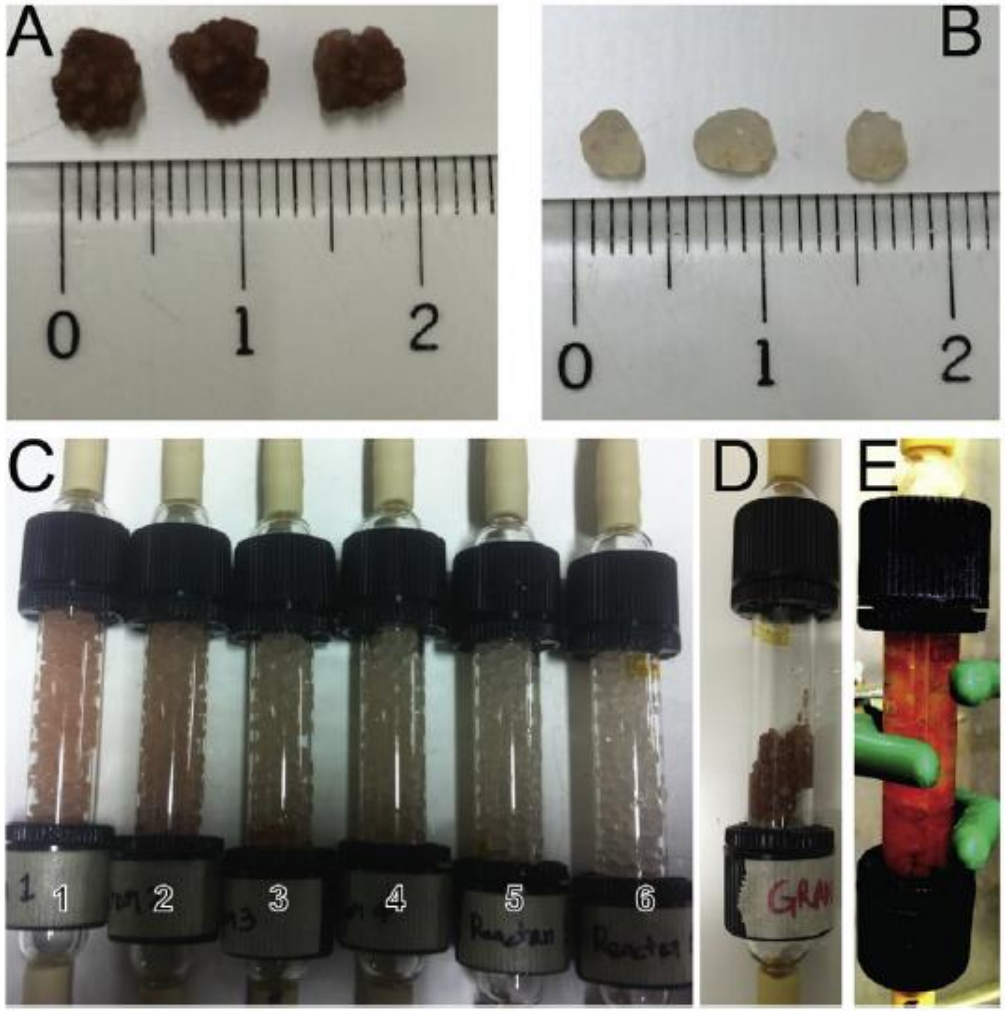
Current Challenges

(Sultana, 2016)

(a) (b)

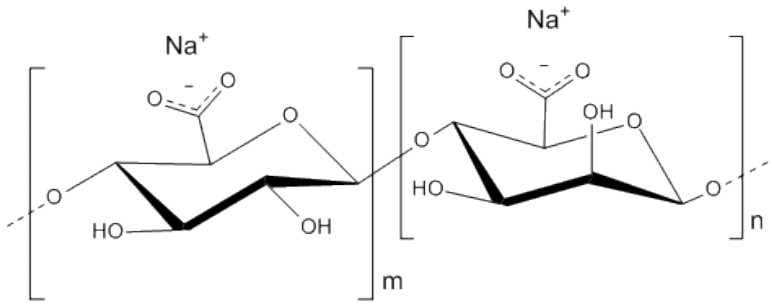
(Ali *et al.*, 2015)

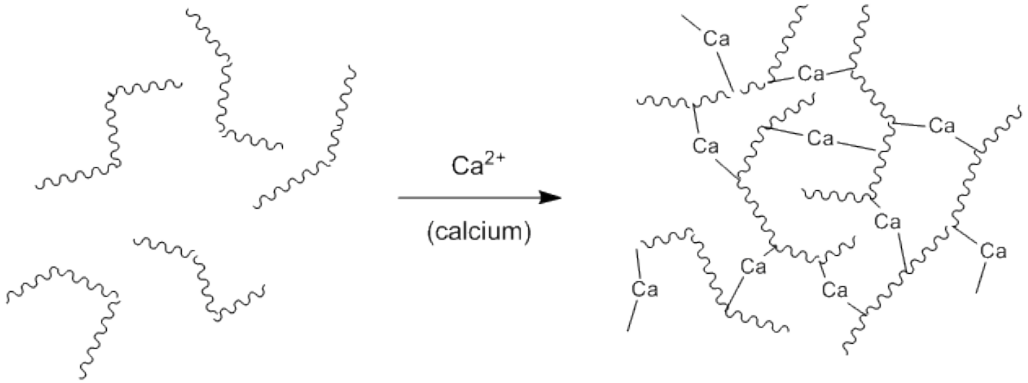
Immobilizations for Enrichment



(Ali *et al.*, 2015)

Calcium Alginate





http://www.fooducation.org/2009/02/my-first-spherification.html

Polyvinyl Alcohol

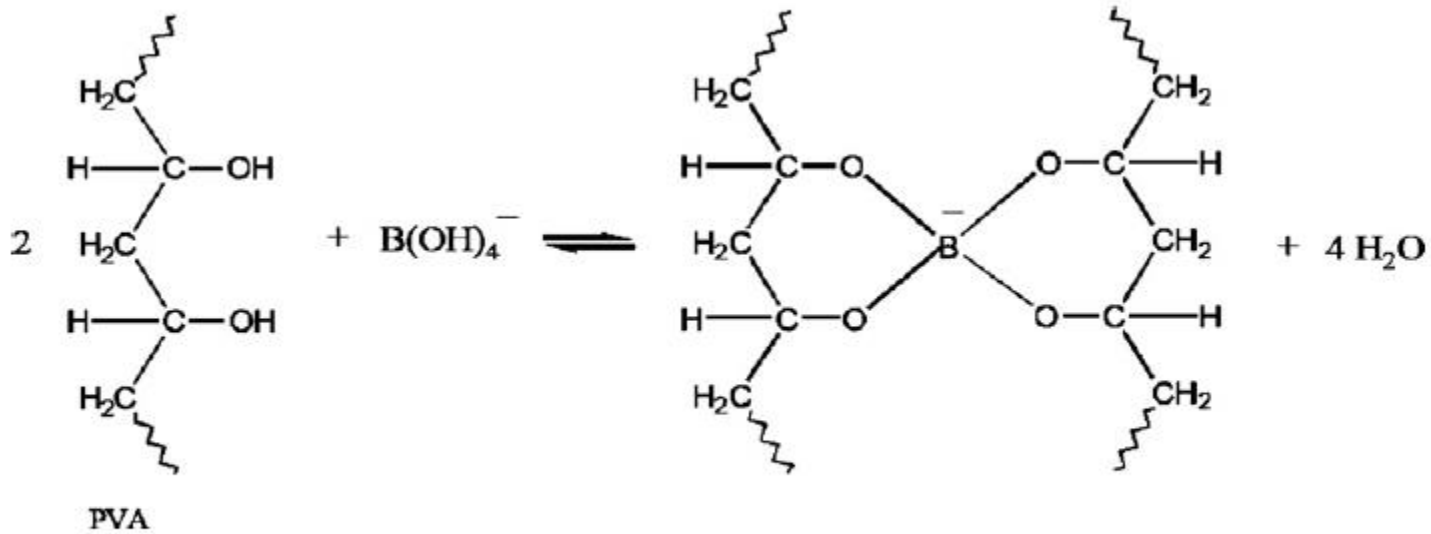


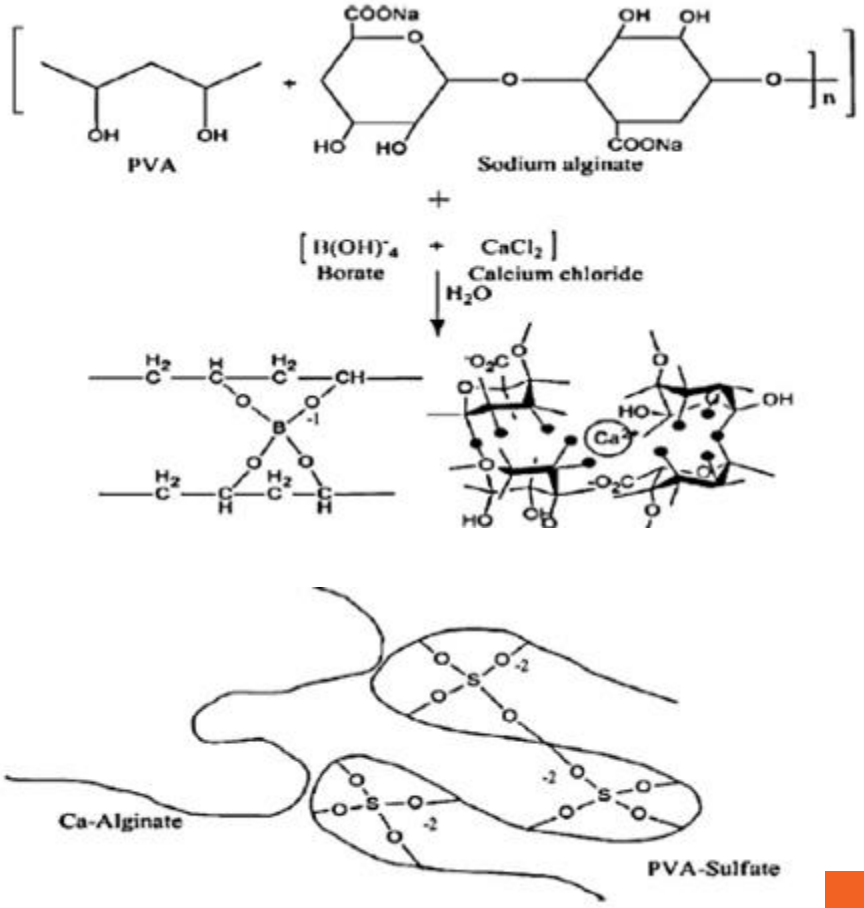
Fig. 2. Crosslinking process of PVA with tetrahydroxyborate ion.

(Zain and Idris., 2011)

Copolymers

1. PVA + Alginate

2. Crosslinking
   - $B(OH)_4^-$
   - $CaCl_2$
   - Na_2SO_4



(Zain and Idris., 2011)

Hypothesis

- Immobilizations for Enrichment
  - Stability from PVA
  - Porosity from Alginate
- Ideal Ratio of PVA-Alginate
- 3% PVA, 1% Alginate is Best

Materials & Methods

Research Plan

1. Immobilize Sludge
2. Characterize Enrichment

Research Plan

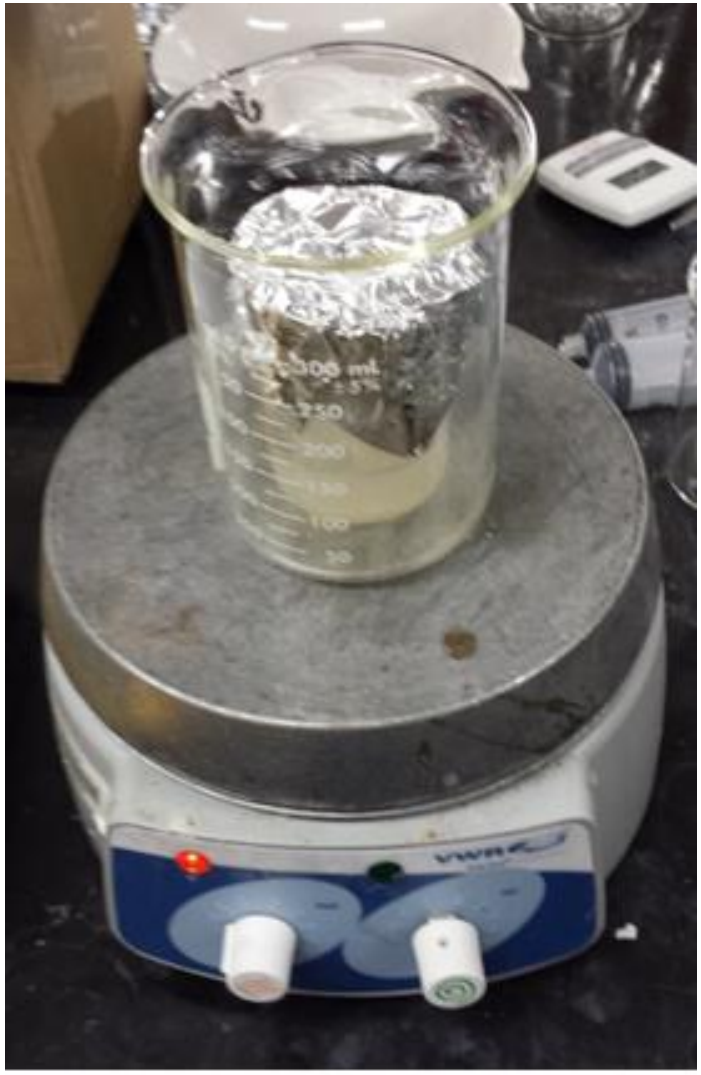
1. Immobilize
   - 10% PVA
   - 10% PVA, 1% Alginate
   - 3% PVA, 1% Alginate
   - 2% Alginate
   - K1 Media

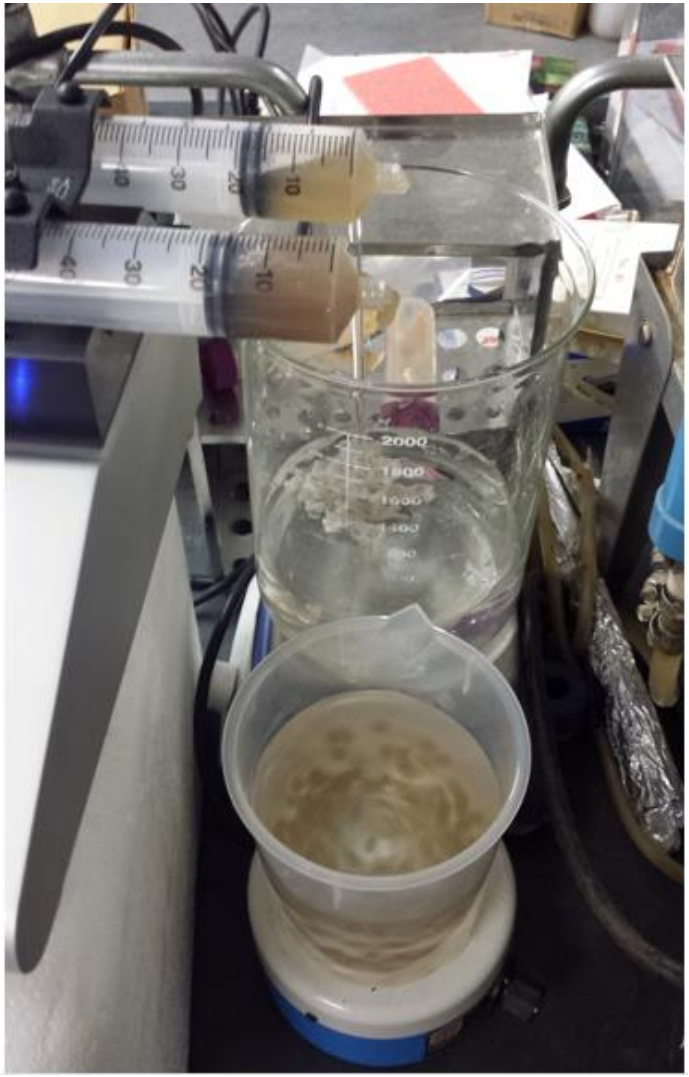
K1 Media

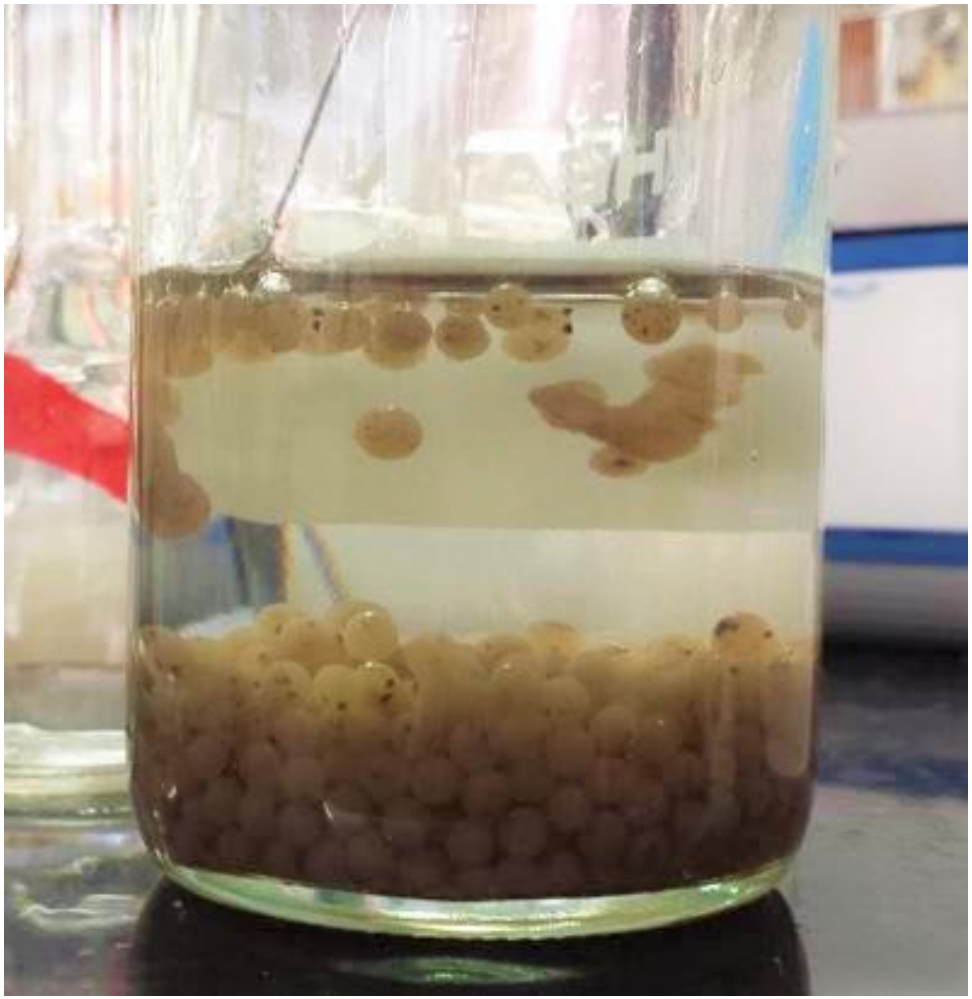
https://fischer.en.alibaba.com/product/1593091541-219596289/China_manufacturer_MBBR_filter_media_Moving_Bed_Bio_Filter_Media_Kaldnes_K1_media.html

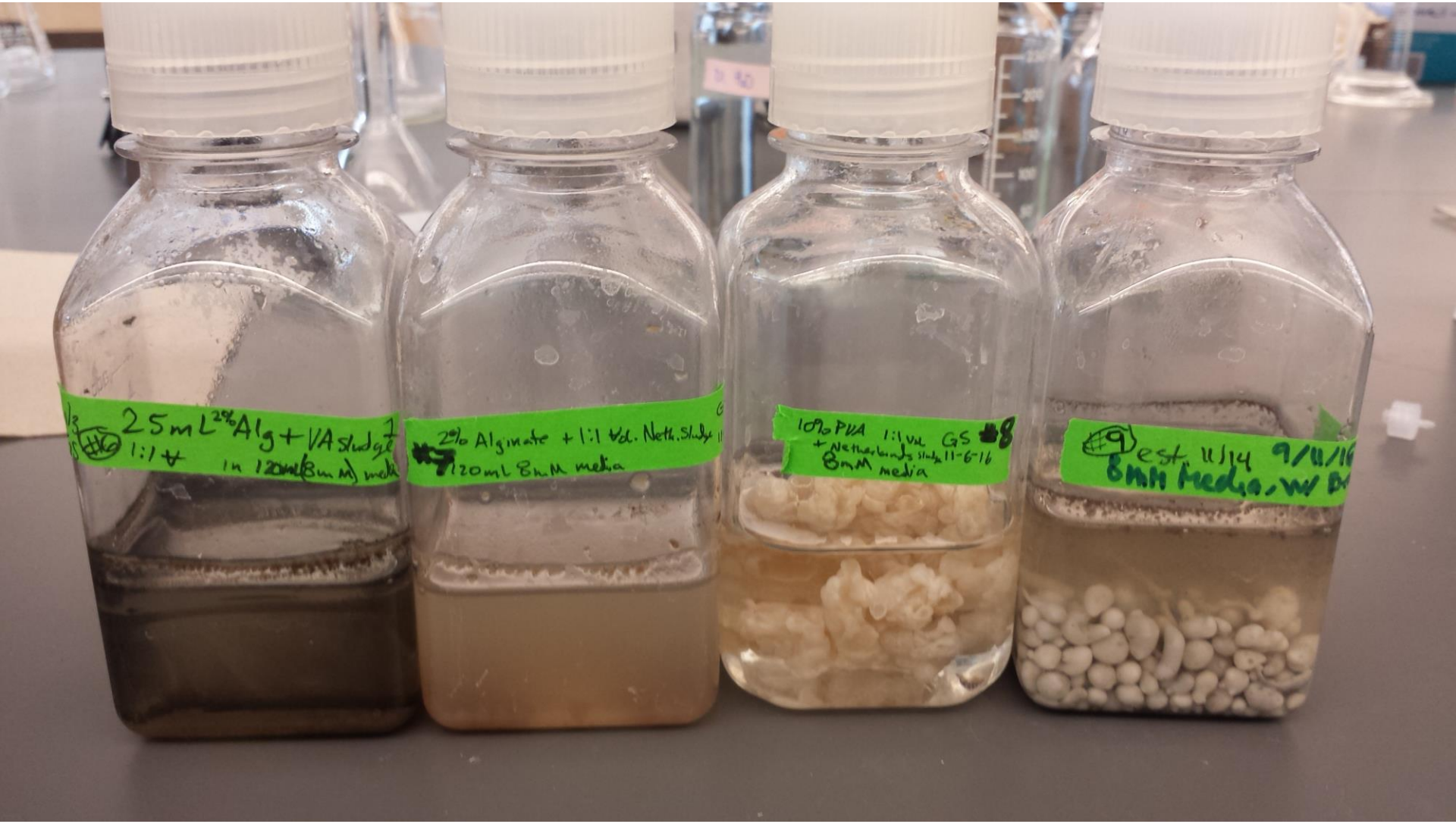
Research Plan

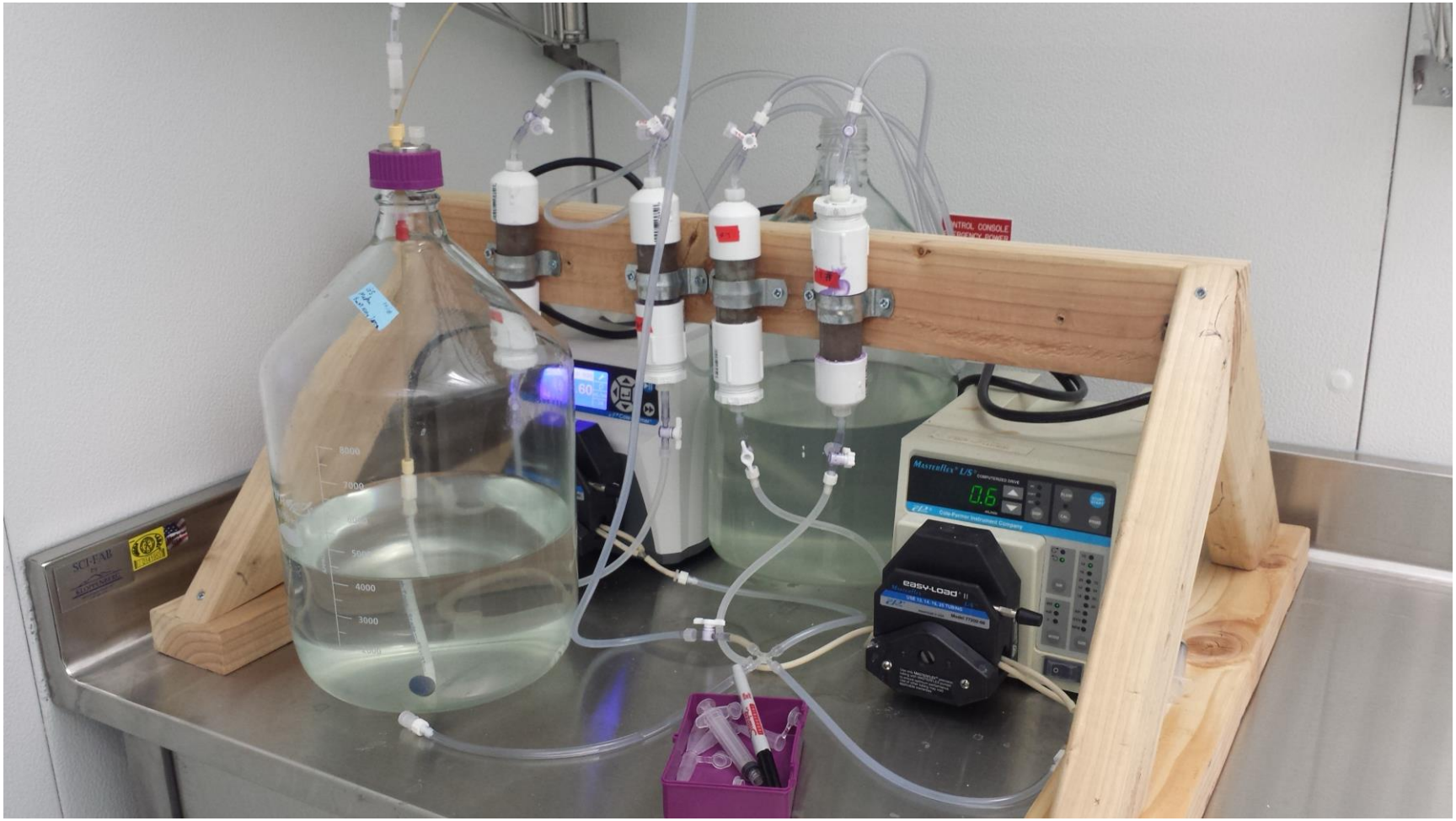
2. Characterize
   - Nitrogen Species
     - NH_4, NO_2, NO_3
   - Nitrogen Removal Rate
   - Removal Efficiency
   - Metabolic Ratios


VWR






2% Alginate + 1:1 Vol. Neth. Sludge
120ml 8mM media
10% PVA 1:1 vol GS #8
+ Netherlands sludge 11-6-16
8mM media
#9 est. 11/14 9/11/16
8mM media, w/


SCI-FAB
8000
7000
4000
3000
Masterflex L/S
0.6
easy-load II

Analysis

- Nitrogen Removal Rate (NRR)

$$NRR = \frac{([NO_2^-] + [NH_4^+])_{in} - ([NO_2^-] + [NH_4^+])_{out}}{\theta_H}$$

- Nitrogen Removal Efficiency (NRE)

$$NRE = \frac{([NO_2^-] + [NH_4^+])_{in} - ([NO_2^-] + [NH_4^+])_{out}}{([NO_2^-] + [NH_4^+])_{in}} \times 100\%$$

Analysis

$$\boldsymbol{NH_4^+} + 1.32\boldsymbol{NO_2^-} + 0.066\boldsymbol{HCO_3^-} + 0.13\boldsymbol{H^+} \rightarrow 1.02\boldsymbol{N_2} + 0.26\boldsymbol{NO_3^-} + 2.03\boldsymbol{H_2O} + 0.066\boldsymbol{CH_2O_{0.5}N_{0.15}}$$

(Strous *et al.*, 1998)

- Nitrite-Ammonium Removal Ratio (NARR)
  - Ideal: 1.32

$$NARR = \frac{[NO_2^-]_{in} - [NO_2^-]_{out}}{[NH_4^+]_{in} - [NH_4^+]_{out}}$$

- Nitrite-Nitrate Ratio (NNR)
  - Ideal: 5.08

$$NNR = \frac{[NO_2^-]_{in} - [NO_2^-]_{out}}{[NO_3^-]_{out} - [NO_3^-]_{in}}$$

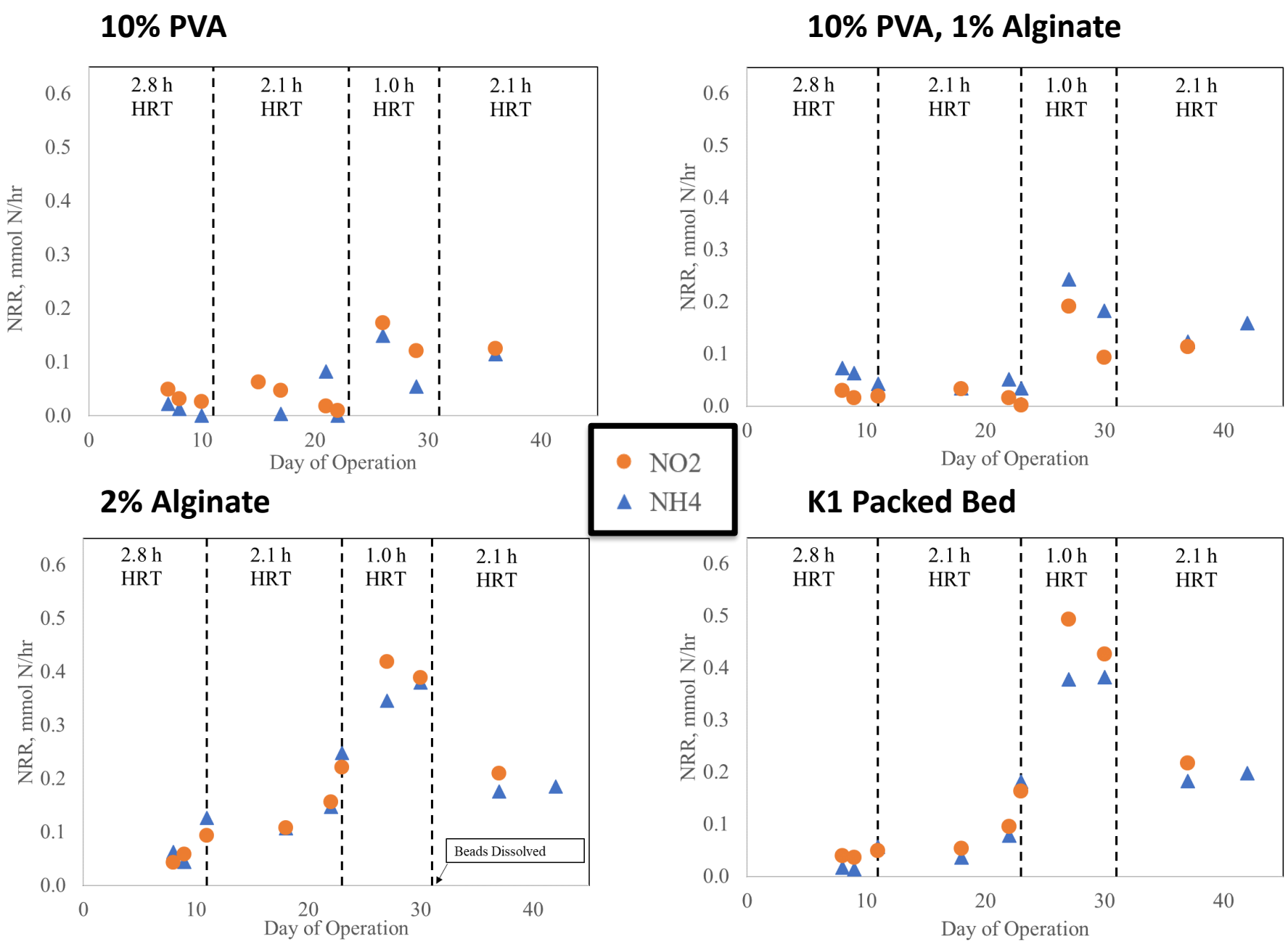
Results & Discussion

First Immobilizations

Analysis

- Nitrogen Removal Rate (NRR)

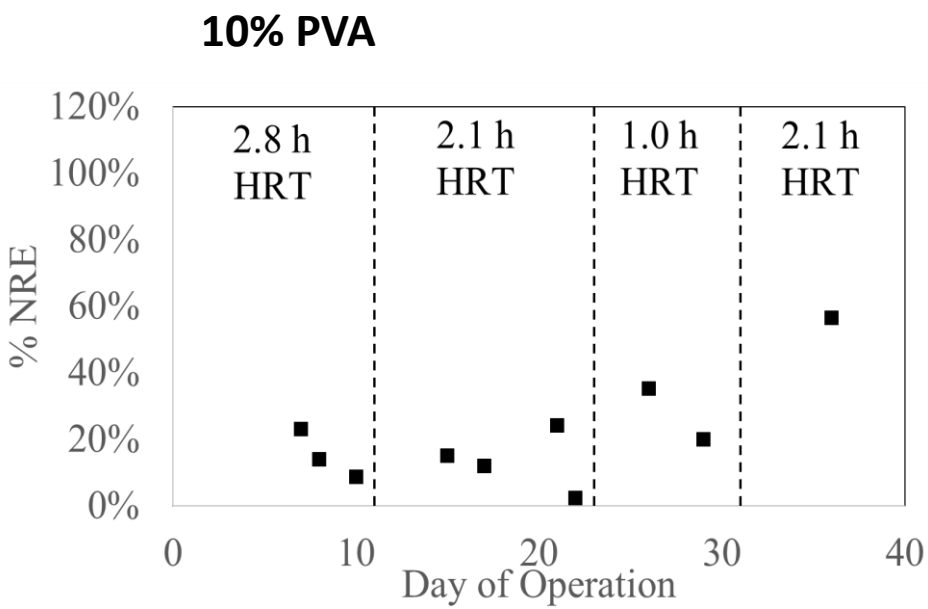
$$NRR = \frac{([NO_2^-] + [NH_4^+])_{in} - ([NO_2^-] + [NH_4^+])_{out}}{\theta_H}$$

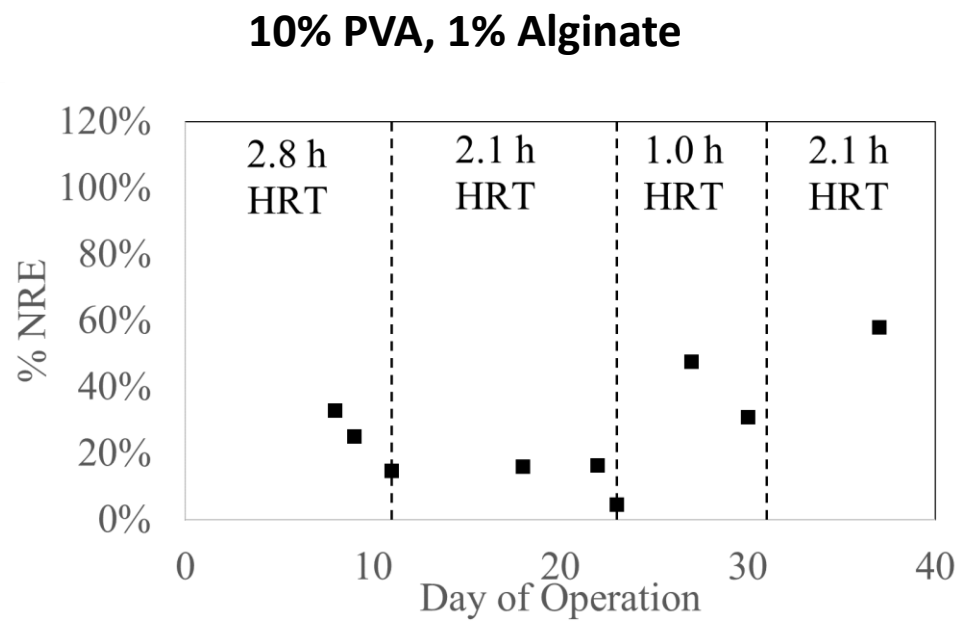

10% PVA
10% PVA, 1% Alginate
2% Alginate
K1 Packed Bed
2.8 h HRT
2.1 h HRT
1.0 h HRT
2.1 h HRT
NRR, mmol N/hr
Day of Operation
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0
10
20
30
40
NO2
NH4
Beads Dissolved

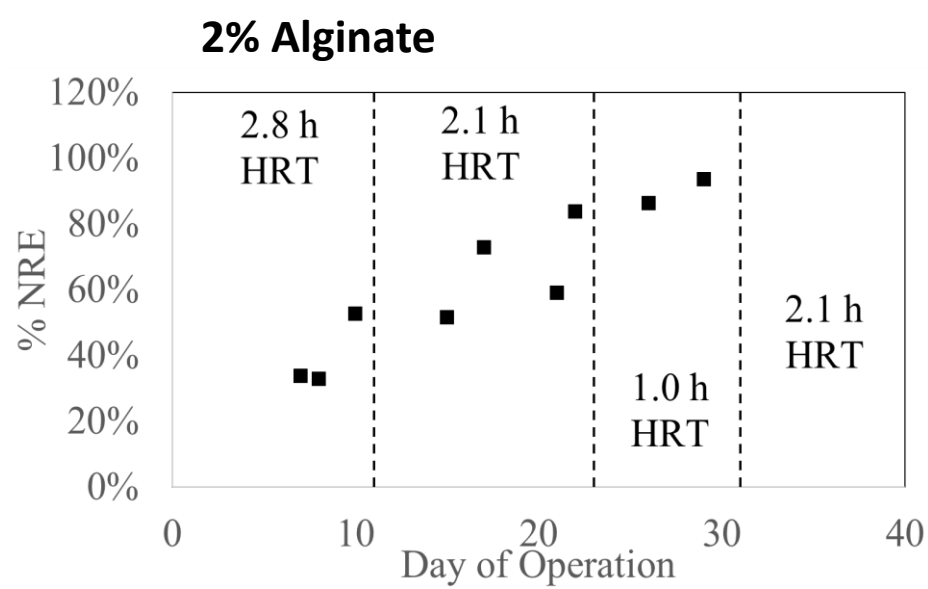
Analysis

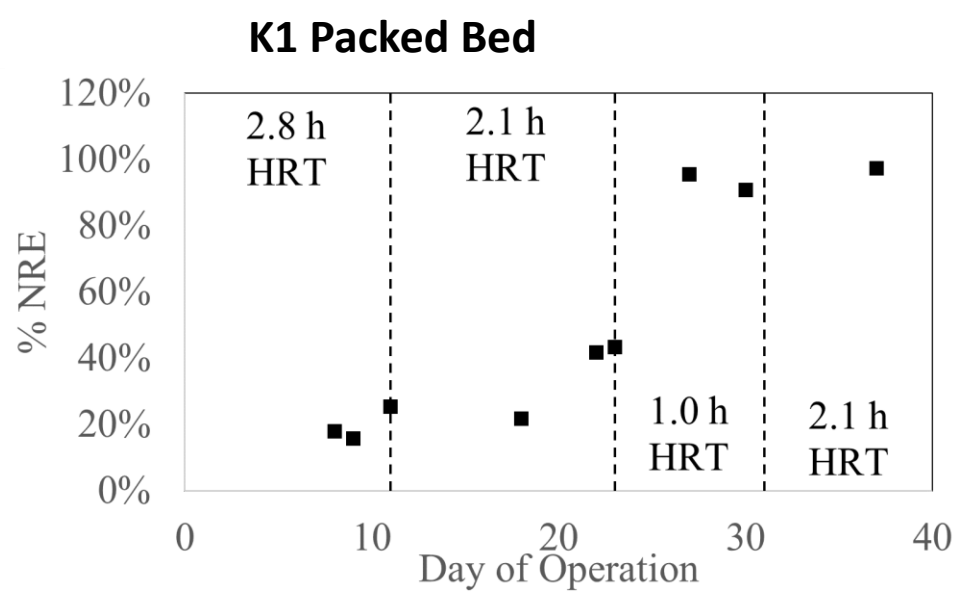
- Nitrogen Removal Efficiency (NRE)

$$NRE = \frac{([NO_2^-] + [NH_4^+])_{in} - ([NO_2^-] + [NH_4^+])_{out}}{([NO_2^-] + [NH_4^+])_{in}} \times 100\%$$


10% PVA
120%
100%
80%
60%
40%
20%
0%
% NRE
2.8 h HRT
2.1 h HRT
1.0 h HRT
2.1 h HRT
0
10
20
30
40
Day of Operation


10% PVA, 1% Alginate
120%
100%
80%
60%
40%
20%
0%
% NRE
2.8 h HRT
2.1 h HRT
1.0 h HRT
2.1 h HRT
0
10
20
30
40
Day of Operation


2% Alginate
120%
100%
80%
60%
40%
20%
0%
% NRE
2.8 h HRT
2.1 h HRT
1.0 h HRT
2.1 h HRT
0
10
20
30
40
Day of Operation


K1 Packed Bed
120%
100%
80%
60%
40%
20%
0%
% NRE
2.8 h HRT
2.1 h HRT
1.0 h HRT
2.1 h HRT
0
10
20
30
40
Day of Operation

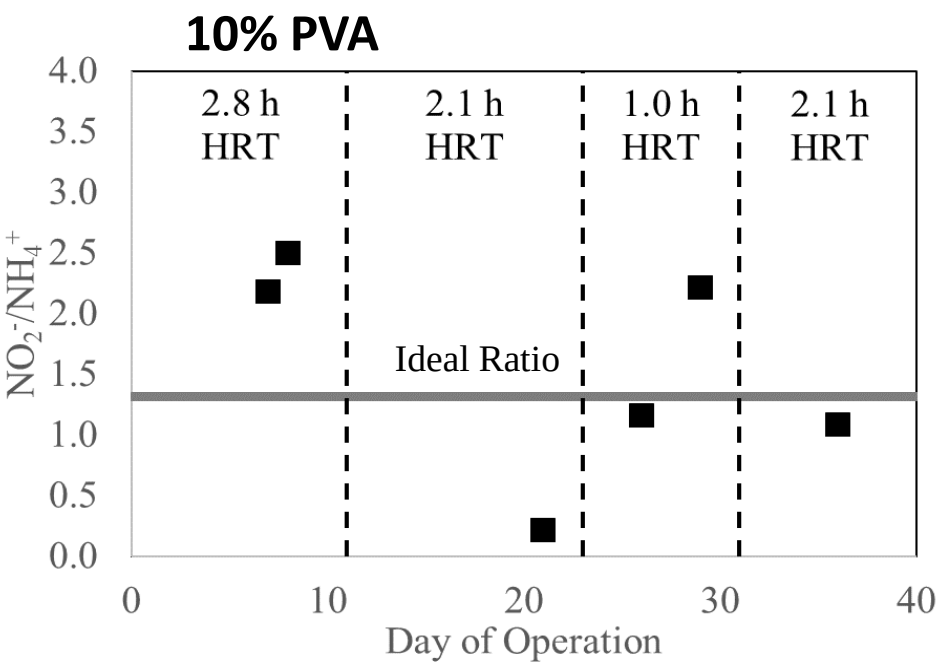
Analysis

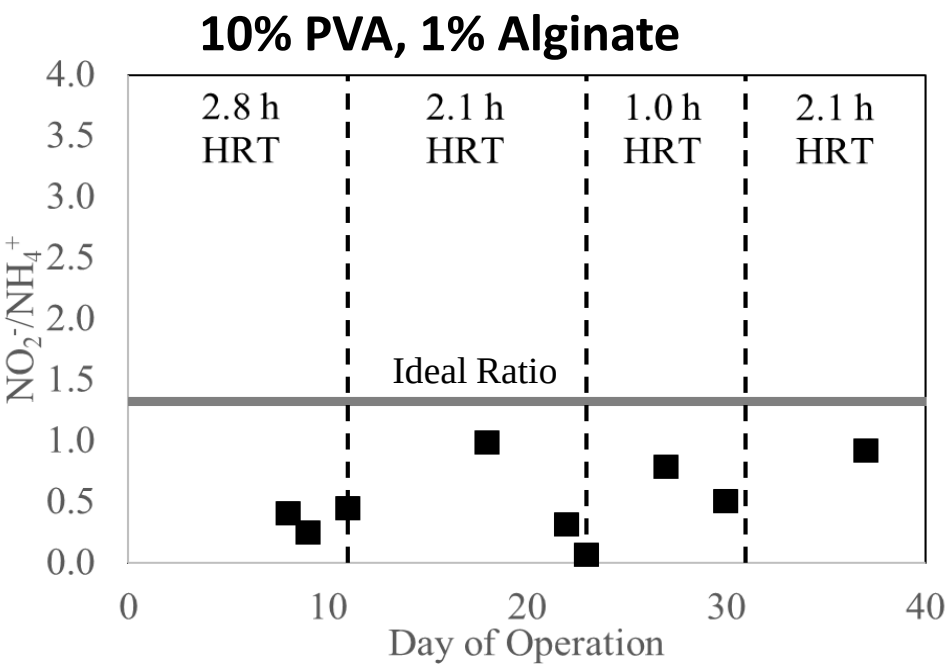
- Nitrite-Ammonium Removal Ratio (NARR)
  - Ideal: 1.32

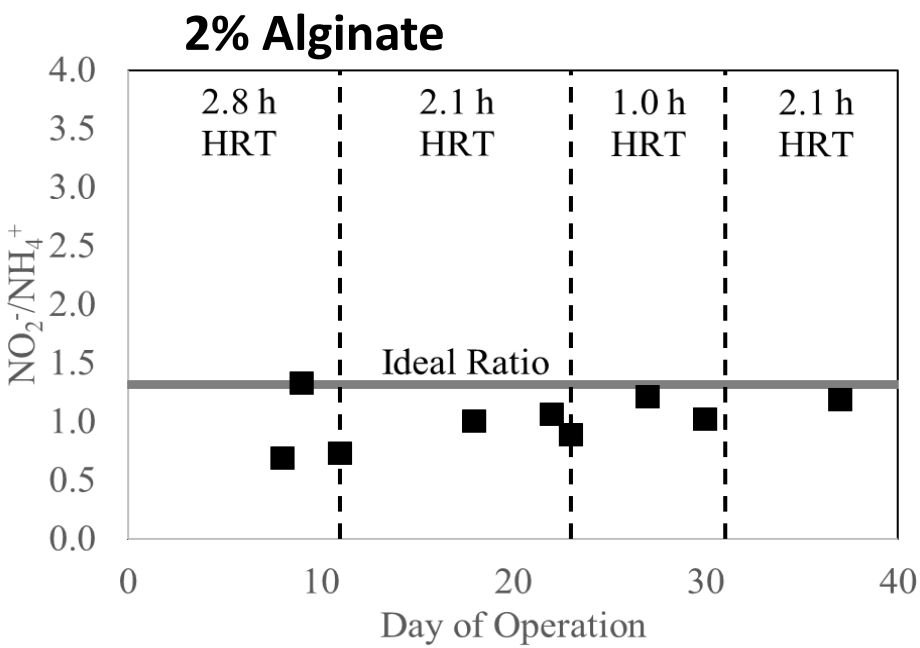
$$NARR = \frac{[NO_2^-]_{in} - [NO_2^-]_{out}}{[NH_4^+]_{in} - [NH_4^+]_{out}}$$

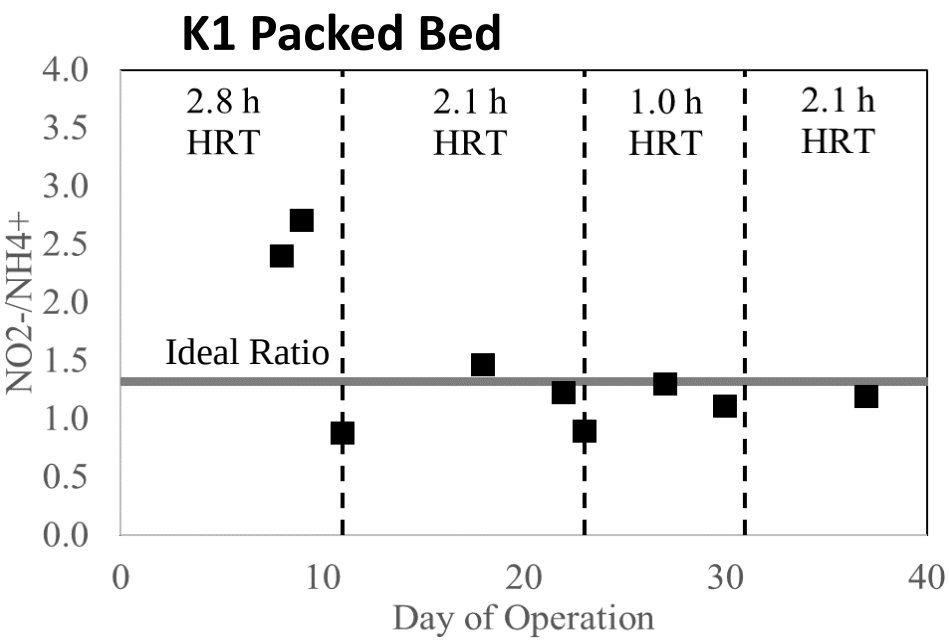
$$\boldsymbol{NH_4^+} + 1.32\boldsymbol{NO_2^-} + 0.066\boldsymbol{HCO_3^-} + 0.13\boldsymbol{H^+}$$
$$\rightarrow 1.02\boldsymbol{N_2} + 0.26\boldsymbol{NO_3^-} + 2.03\boldsymbol{H_2O} + 0.066\boldsymbol{CH_2O_{0.5}N_{0.15}}$$

(Strous *et al.*, 1998)


10% PVA
2.8 h HRT
2.1 h HRT
1.0 h HRT
2.1 h HRT
Ideal Ratio
NO_2^-/NH_4^+
Day of Operation
0
10
20
30
40
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0

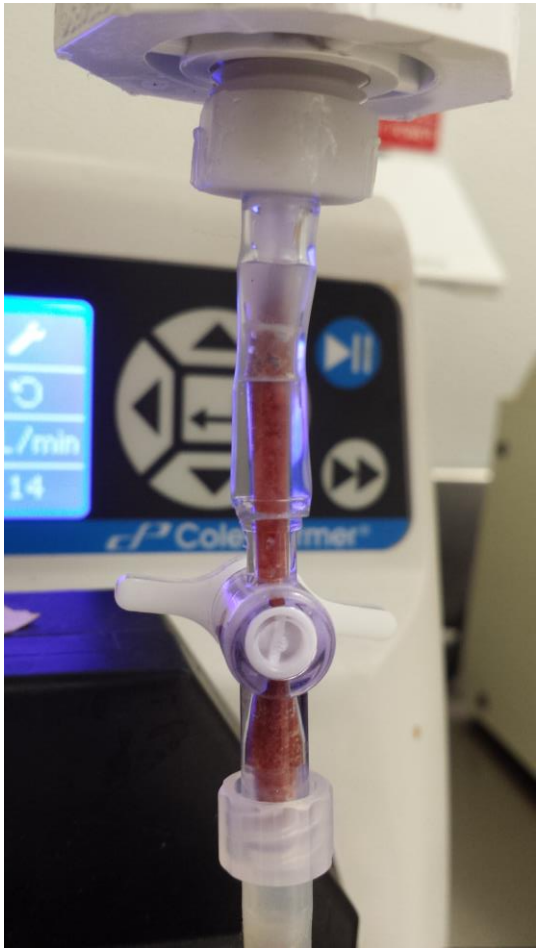

10% PVA, 1% Alginate
2.8 h HRT
2.1 h HRT
1.0 h HRT
2.1 h HRT
Ideal Ratio
NO_2^-/NH_4^+
Day of Operation
0
10
20
30
40
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0

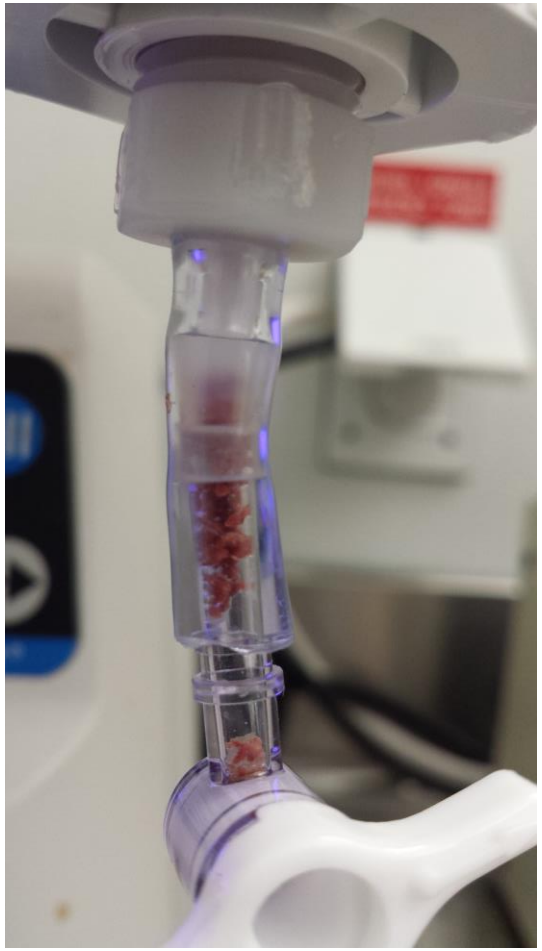

2% Alginate
2.8 h HRT
2.1 h HRT
1.0 h HRT
2.1 h HRT
Ideal Ratio
NO_2^-/NH_4^+
Day of Operation
0
10
20
30
40
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0


K1 Packed Bed
2.8 h HRT
2.1 h HRT
1.0 h HRT
2.1 h HRT
Ideal Ratio
NO2-/NH4+
Day of Operation
0
10
20
30
40
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0

Graphic Image Up Next

500
400
300
200
100





Results & Discussion

Second Immobilizations

Second Immobilizations

10% PVA, 1% Alginate

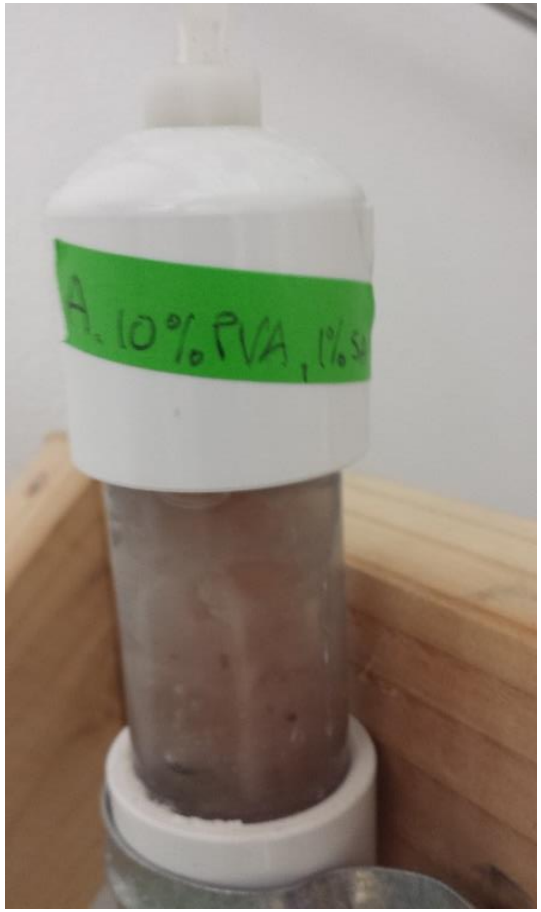
3% PVA, 1% Alginate

2% Alginate

K1 Packed Bed

Day 2

Day 15



Day 30

10% PVA, 1% Alginate

Day 2

Day 15

Day 30

3% PVA, 1% Alginate

Day 2

Day 15

Day 30

2% Alginate

Day 2

Day 15

Day 30

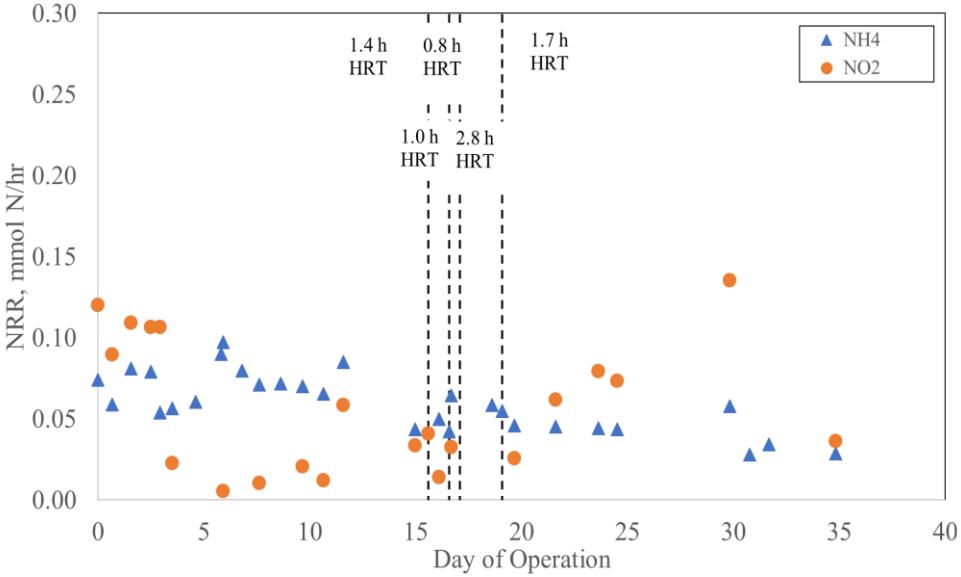
K1 Packed Bed

Analysis

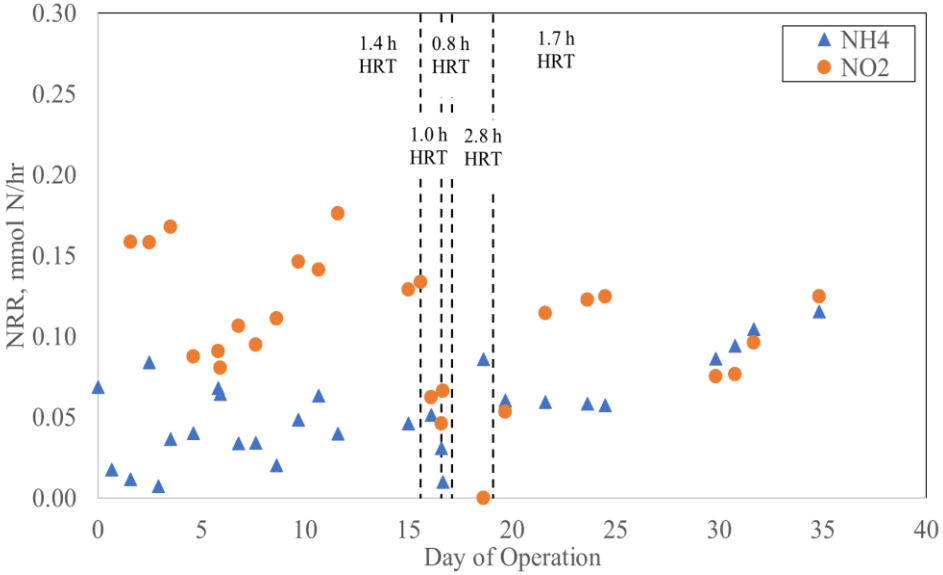
- Nitrogen Removal Rate (NRR)

$$NRR = \frac{([NO_2^-] + [NH_4^+])_{in} - ([NO_2^-] + [NH_4^+])_{out}}{\theta_H}$$

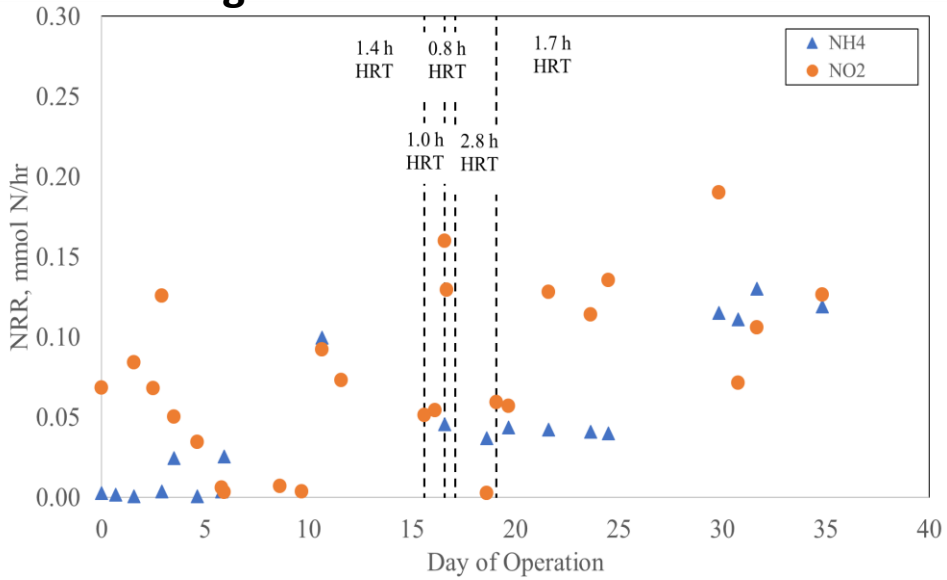
10% PVA, 1% Alginate



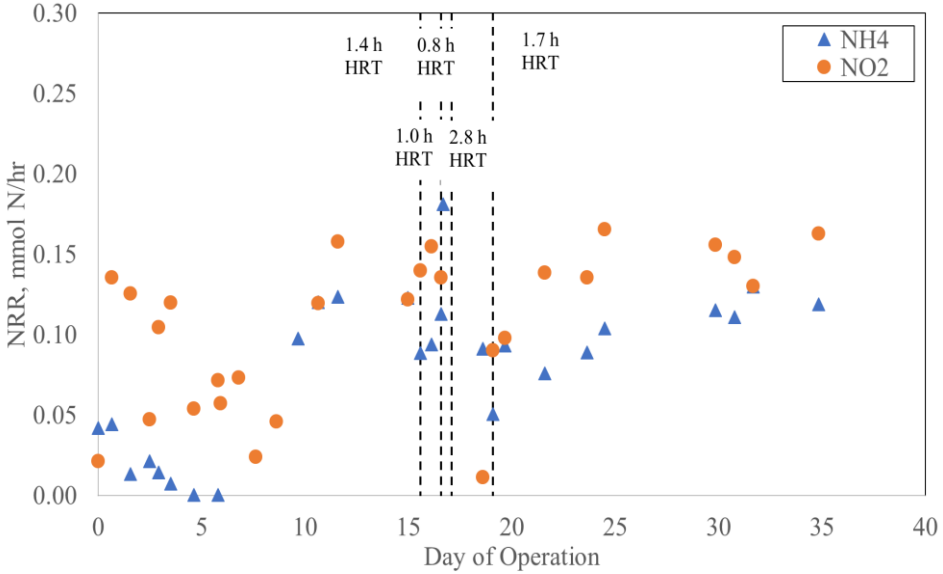
3% PVA, 1% Alginate



2% Alginate



K1 Media

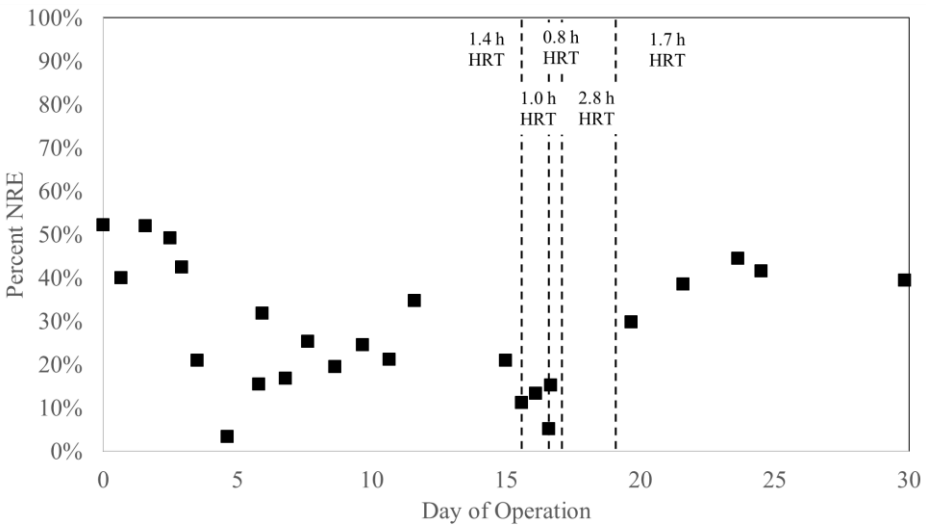


Analysis

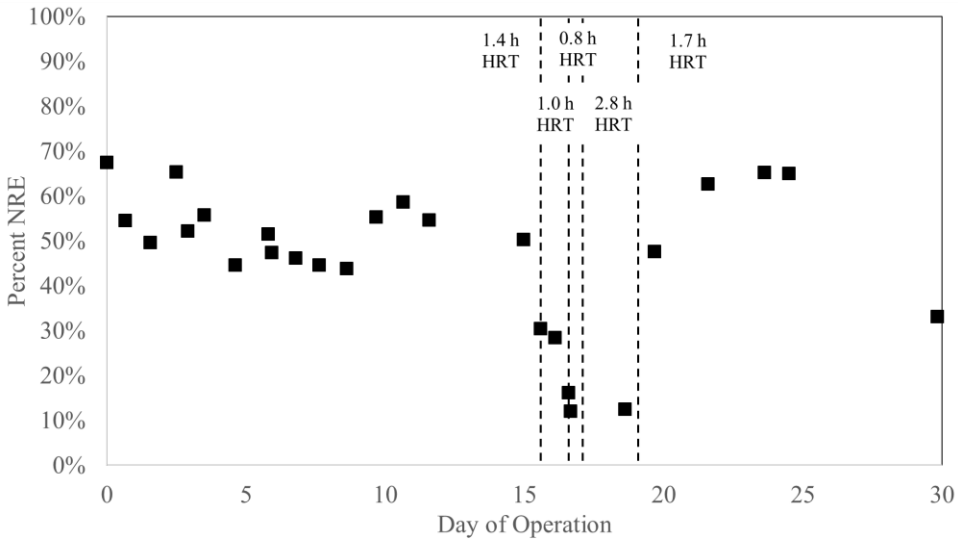
- Nitrogen Removal Efficiency (NRE)

$$NRE = \frac{([NO_2^-] + [NH_4^+])_{in} - ([NO_2^-] + [NH_4^+])_{out}}{([NO_2^-] + [NH_4^+])_{in}} \times 100\%$$

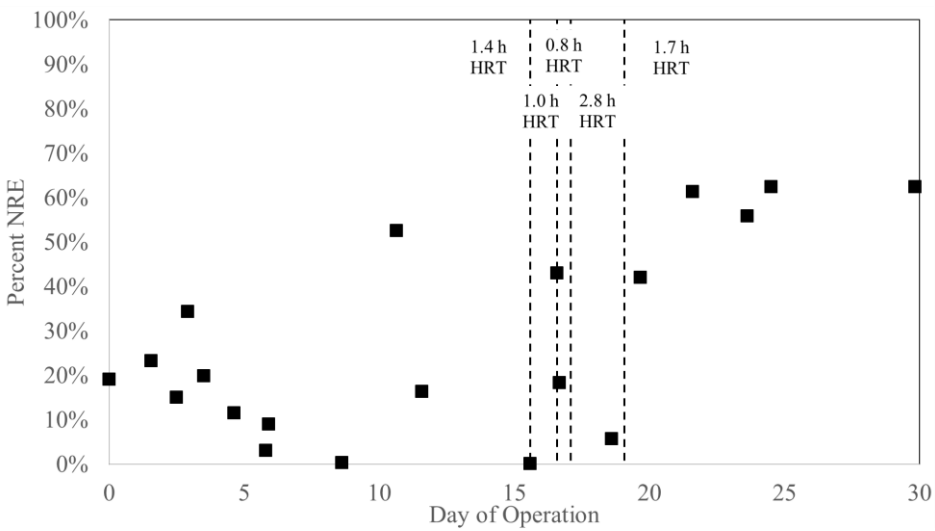
10% PVA, 1% Alginate



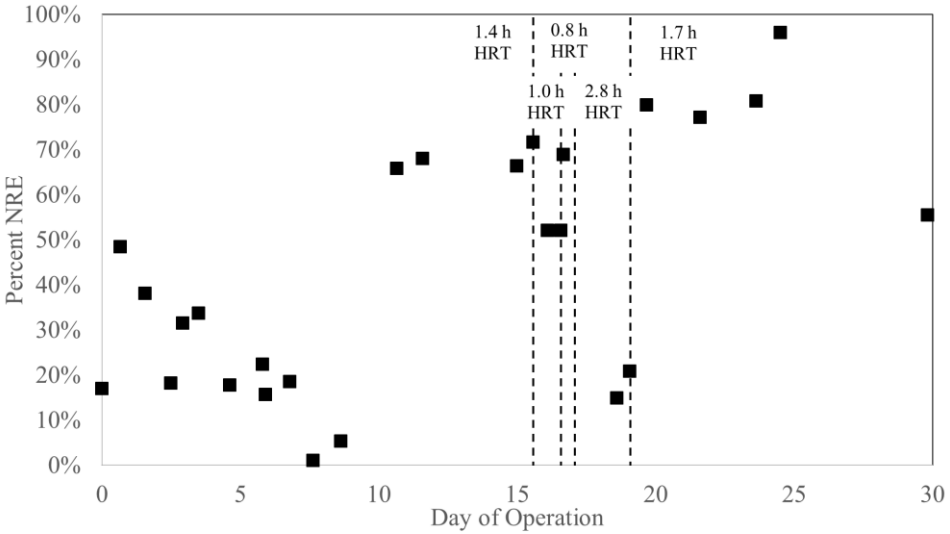
3% PVA, 1% Alginate



2% Alginate



K1 Media



Analysis

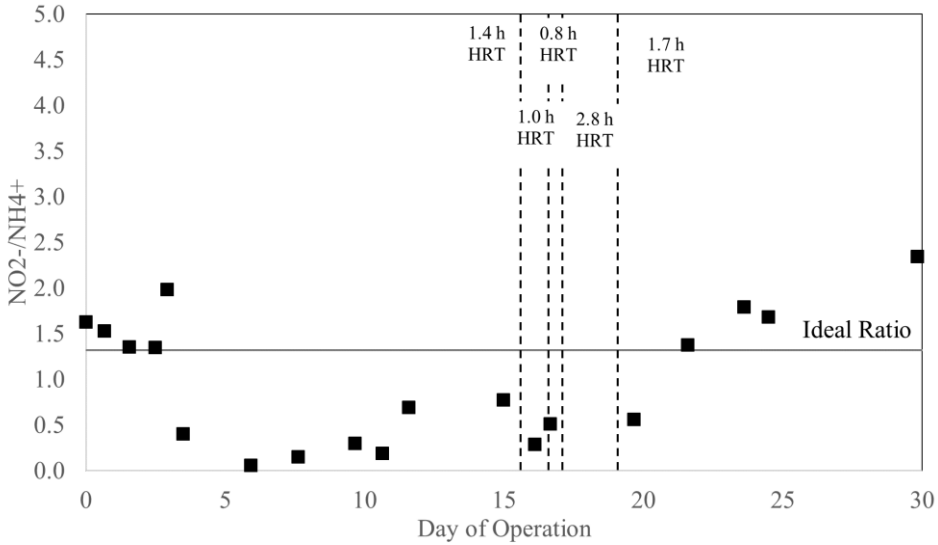
- Nitrite-Ammonium Removal Ratio (NARR)
  - Ideal: 1.32

$$NARR = \frac{[NO_2^-]_{in} - [NO_2^-]_{out}}{[NH_4^+]_{in} - [NH_4^+]_{out}}$$

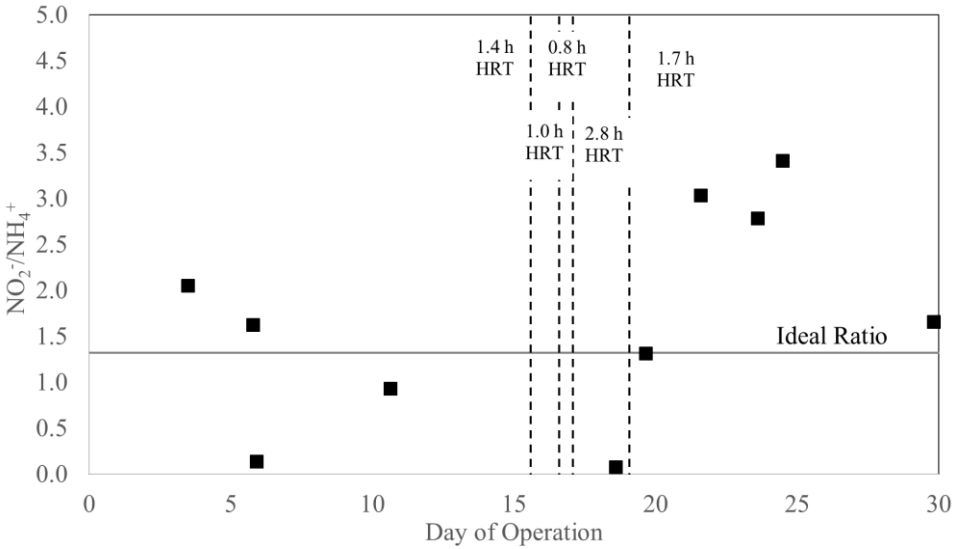
$$\boldsymbol{NH_4^+} + 1.32\boldsymbol{NO_2^-} + 0.066\boldsymbol{HCO_3^-} + 0.13\boldsymbol{H^+}$$
$$\rightarrow 1.02\boldsymbol{N_2} + 0.26\boldsymbol{NO_3^-} + 2.03\boldsymbol{H_2O} + 0.066\boldsymbol{CH_2O_{0.5}N_{0.15}}$$

(Strous *et al.*, 1998)

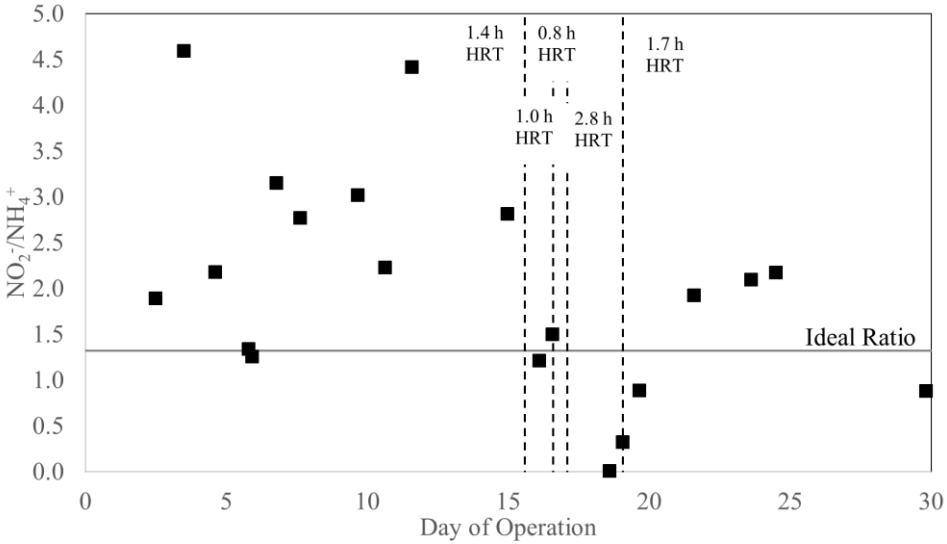
10% PVA, 1% Alginate



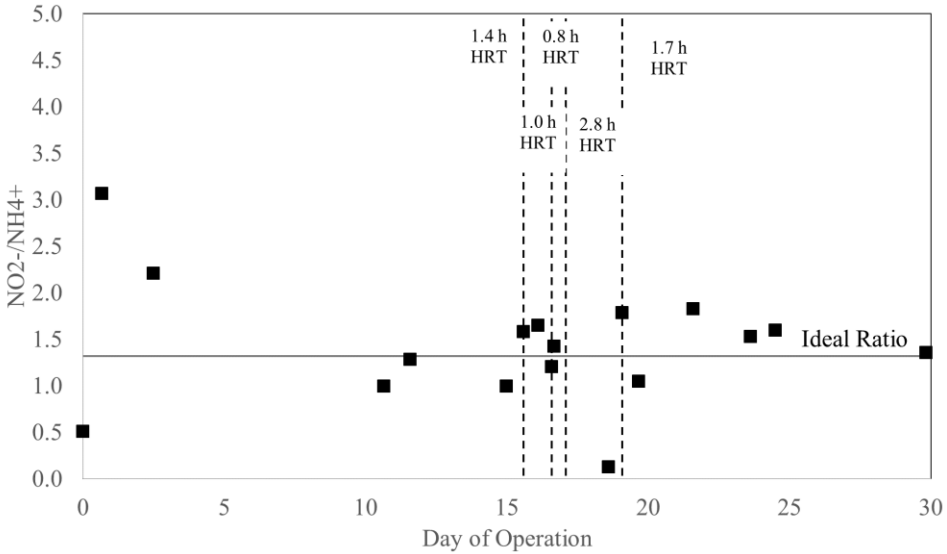
3% PVA, 1% Alginate



2% Alginate



K1 Media



Analysis

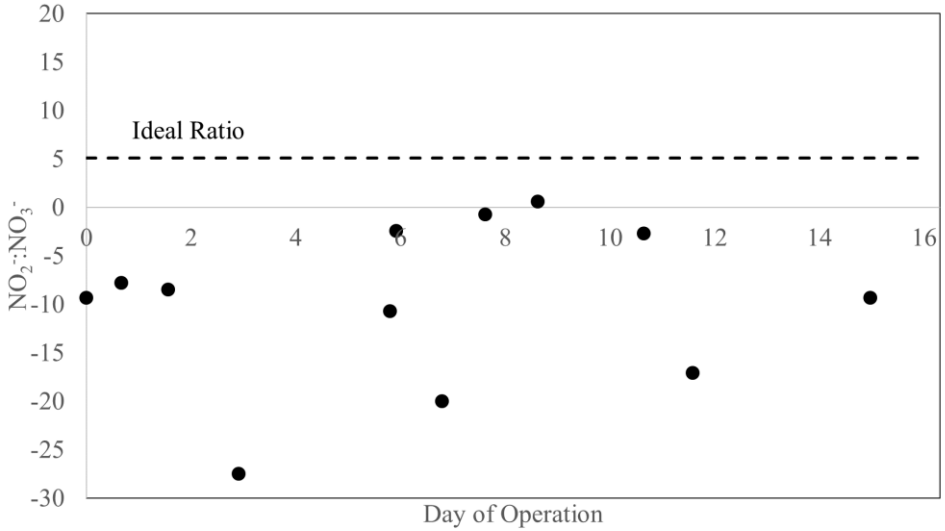
- Nitrite-Nitrate Ratio (NNR)
  - Ideal: 5.08

$$NNR = \frac{[NO_2^-]_{in} - [NO_2^-]_{out}}{[NO_3^-]_{out} - [NO_3^-]_{in}}$$

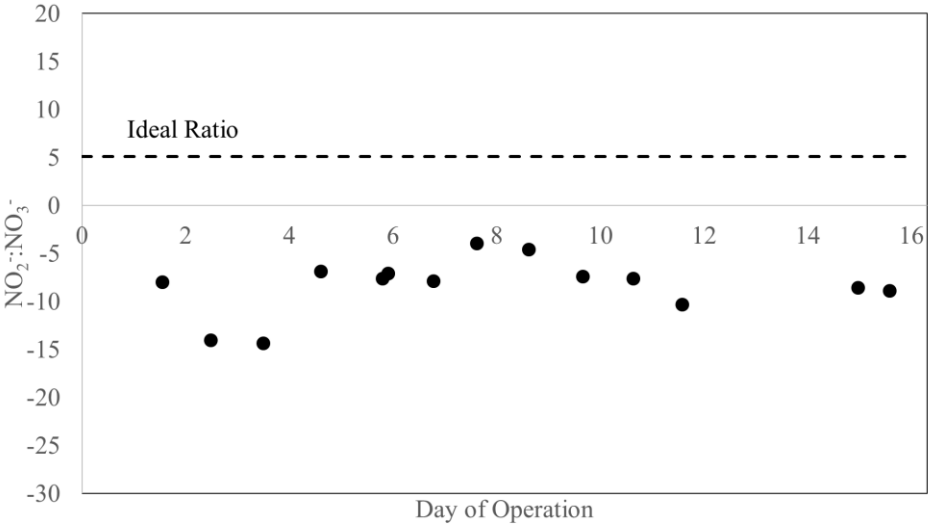
$$\boldsymbol{NH_4^+} + 1.32\boldsymbol{NO_2^-} + 0.066\boldsymbol{HCO_3^-} + 0.13\boldsymbol{H^+}$$
$$\rightarrow 1.02\boldsymbol{N_2} + 0.26\boldsymbol{NO_3^-} + 2.03\boldsymbol{H_2O} + 0.066\boldsymbol{CH_2O_{0.5}N_{0.15}}$$

(Strous *et al.*, 1998)

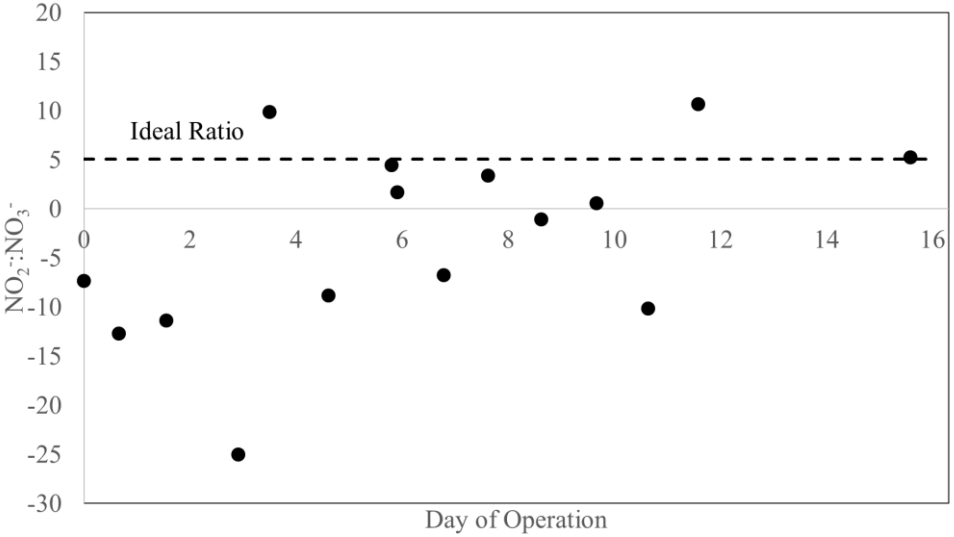
10% PVA, 1% Alginate



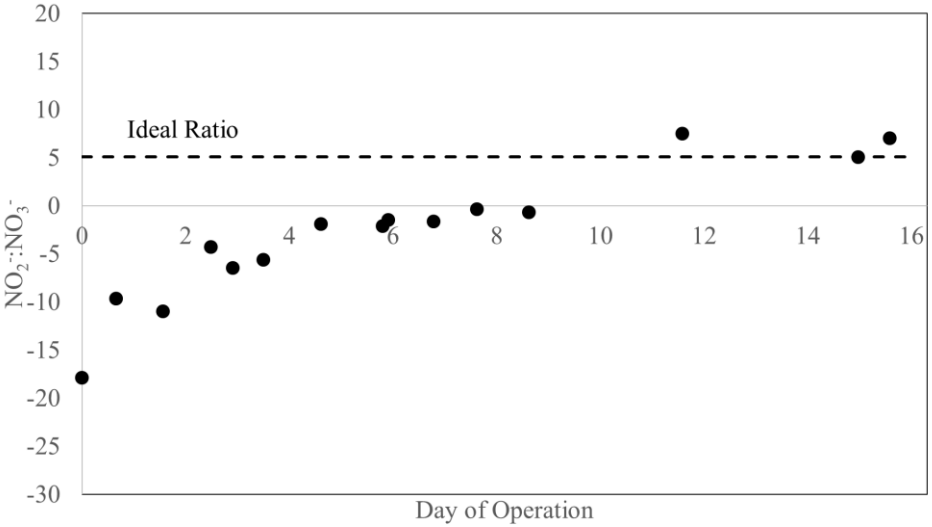
3% PVA, 1% Alginate



2% Alginate



K1 Media



Conclusions

Conclusions

- Anammox was Enriched
- Alginate
  - Weak, Dissolves
  - Good Diffusion
- PVA
  - Dense, Swells
  - Bad Diffusion
- Copolymer
  - 3% PVA, 1% CA most stable
- K1 Packed Bed
  - Good Diffusion
  - Some washout

Future Work

- Alginate as organic carbon source?
  - Heterotrophic Denitrification
- What causes most gel degradation?
  - Sheer
  - Microbial Growth
  - Gas Generation
- Resistance of Anammox to Nutrient Shock

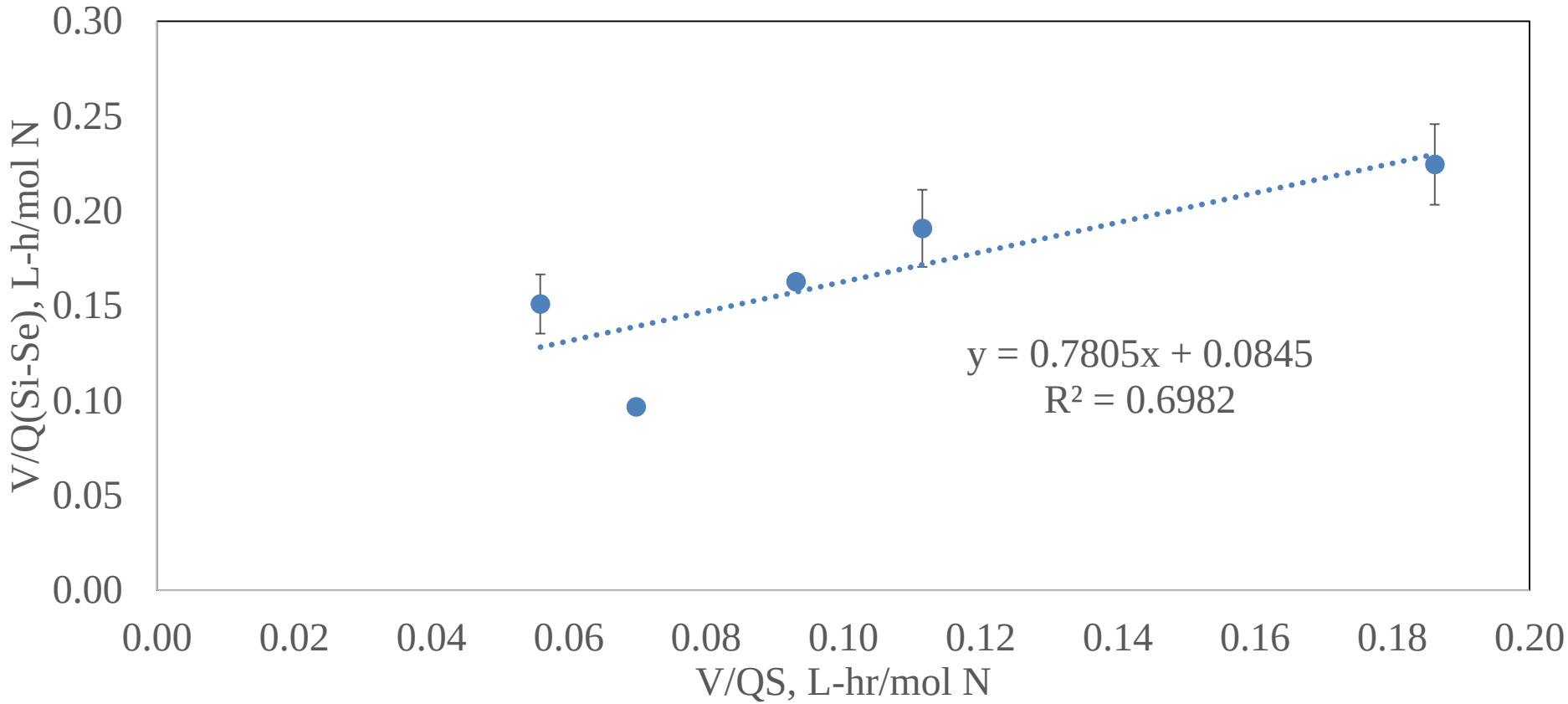
Applications

- Transportation of Anammox
- Improved Diffusion vs. Anammox Granules
  - Better Enrichment
- Combine Anammox with other nitrogen removal technologies

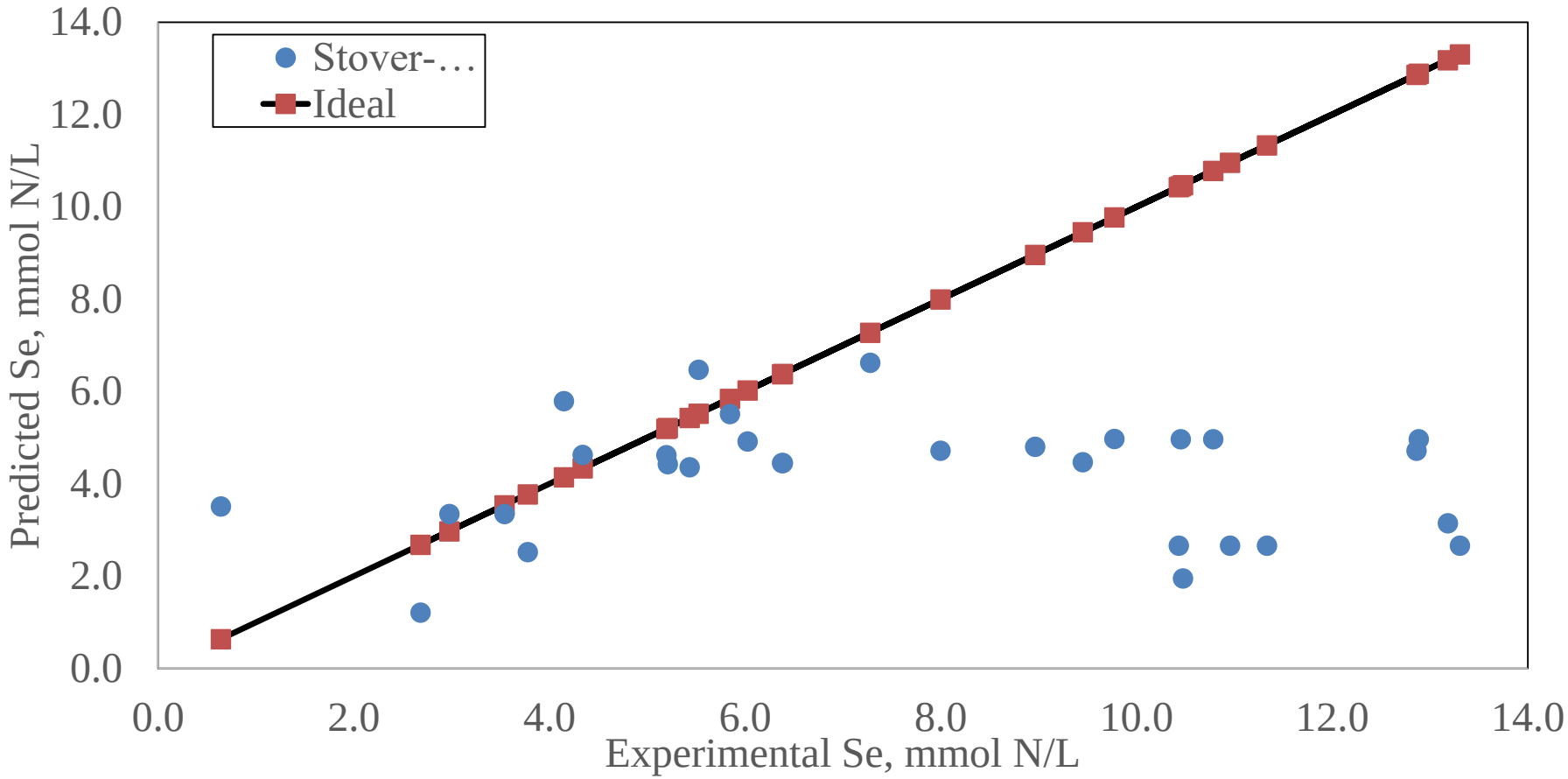
Acknowledgements

- Dr. Tyler Radniecki, (mentor)
- Dr. Joe McGuire, Dr. Kari van Zee, (committee)
- Sharmin Sultana, Rich Hilliard
- Sarah Gilroy, Silvia Colussi-Pelaez

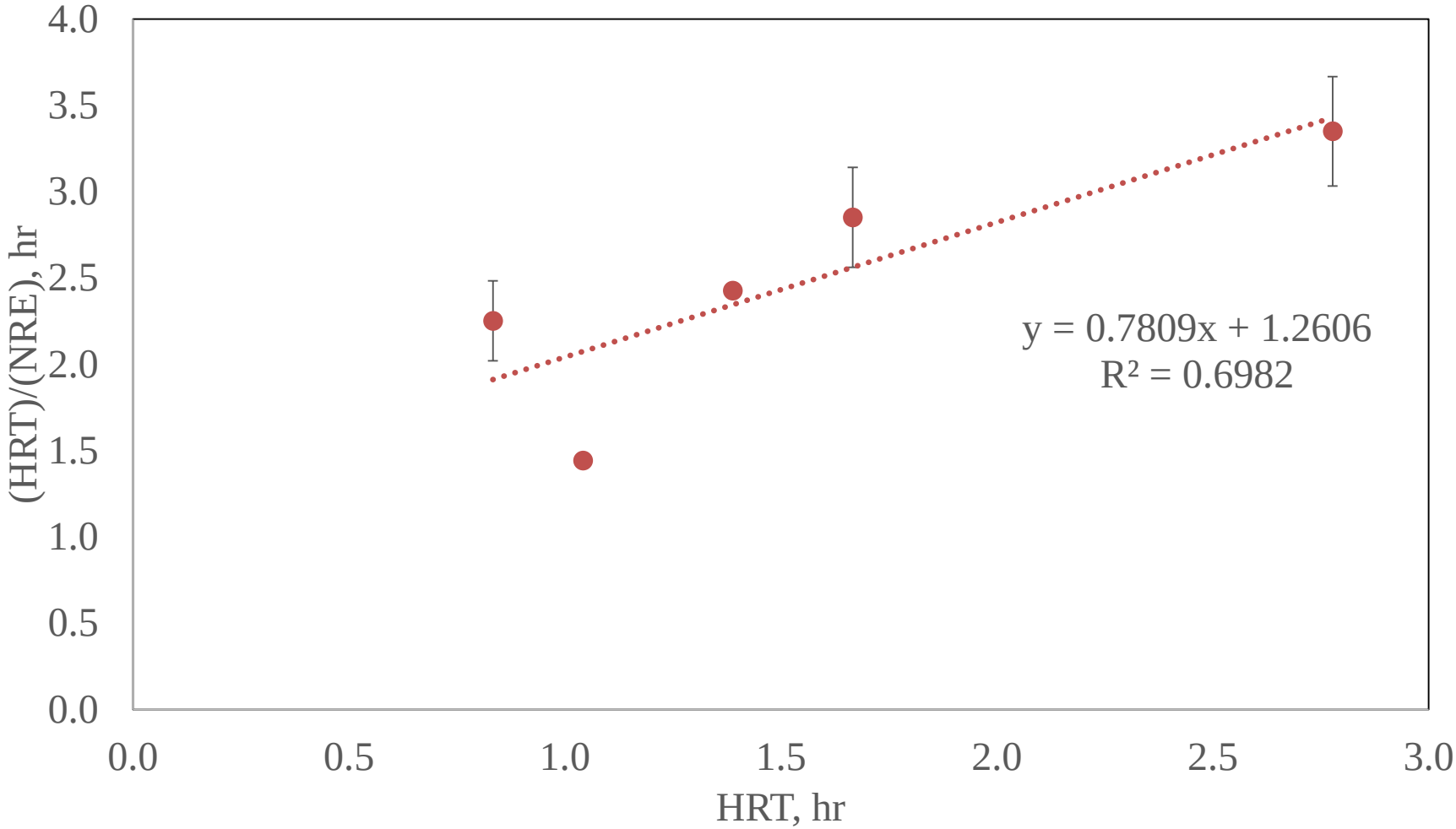
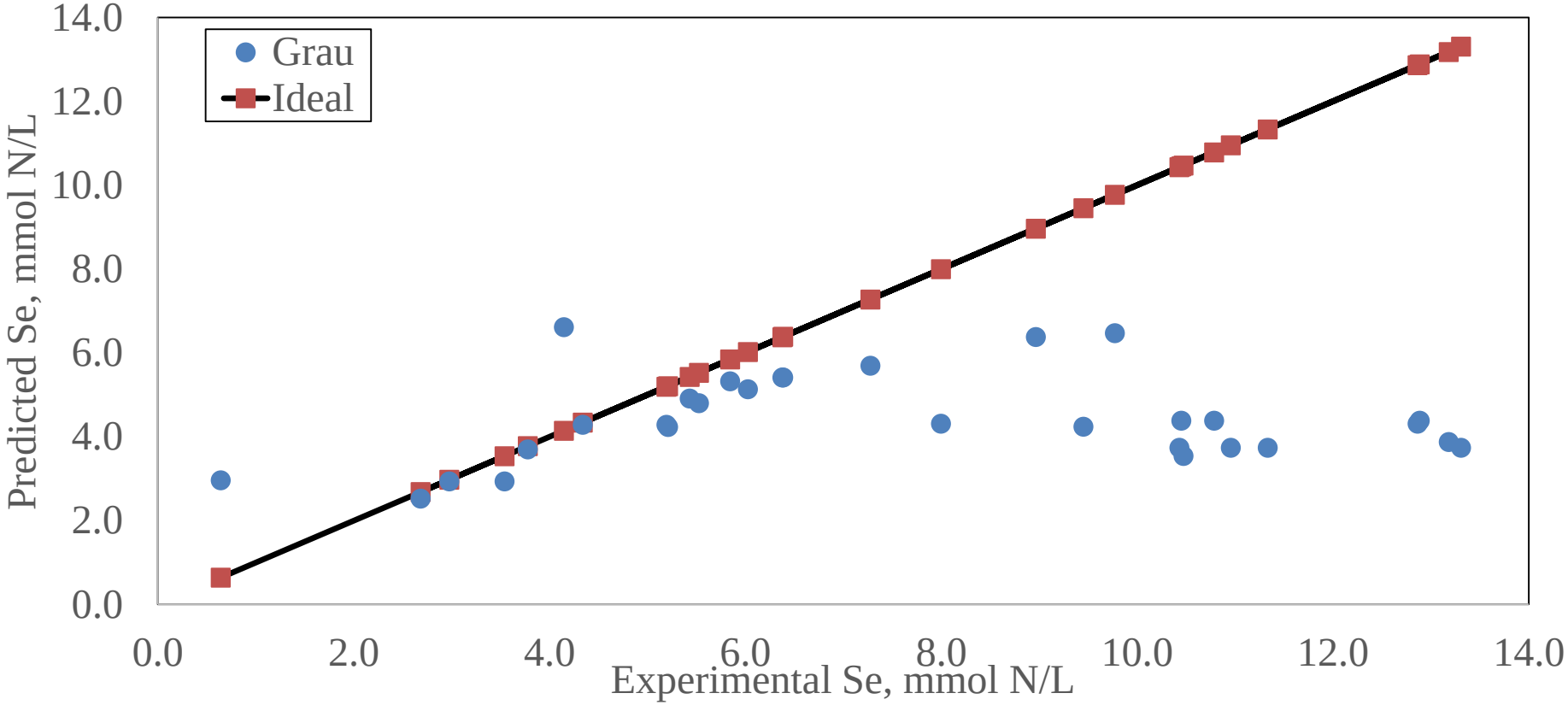
Kinetics: Stover-Kincannon



Kinetics: Stover-Kincannon



Kinetics: Grau Second-Order



Kinetics: Grau Second-Order