Alkaline Hydrolysis of NC fines and comparative evaluation of post-hydrolysis techniques for nitrogen removal

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NEWEA 2022
Annual Conference
Jan 23-26, Boston, MA

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Alkaline Hydrolysis (AH) of waste NC fines

<u>Outline</u>

1. *Kinetics of alkaline hydrolysis (AH) for degradation of NC fines (pure/waste) at bench scale*
2. *Pilot scale testing of AH-liquor*
3. *Evaluation of post-hydrolysis techniques for nitrogen removal from AH-liquor*
4. *Nitrogen removal from post-AH NC liquor with bimetals reduction*
5. *Nitrogen removal from post-AH NC liquor with conventional denitrification with BOD assessment of post-AH NC liquor*

Nitrocellulose (NC) fines

- Generated through nitration of cellulose ester polymer
- Used in production of propellants, smokeless gunpowder, and some explosives[1]
- Self ignition stability is directly related to degree of nitrogen purity[1]
- Higher nitration – more unstable
- Insoluble in water[2]
- Solubility in other liquids depends on nitrogen content
- Low nitrogen mixtures soluble in acetone and Ether-alcohol mixtures[3]
- High nitrogen mixtures soluble in acetone

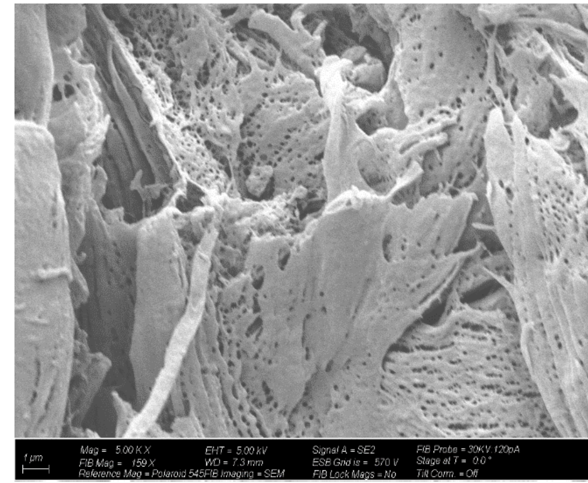
NC	
N Content	12.6-14%
Flash point	12.8 °C
Melting and ignition	160-170 °C
Specific Gravity	1.66
m.w.	504.3

1. Kim, Byung J, and Jae K Park. Comprehensive Evaluation and Development of Treatment Technologies for Nitrocellulose Fines and Process Wasterwaters. U.S. Army, 1993.
2. Weston, Roy F. Composting Nitrocellulose Fines - Hazard Analysis. Weston, Inc, 1995.
3. López-López, María, et al. "New Protocol for the Isolation of Nitrocellulose from Gunpowders: Utility in Their Identification." Talanta, Elsevier, 25 Mar. 2010.

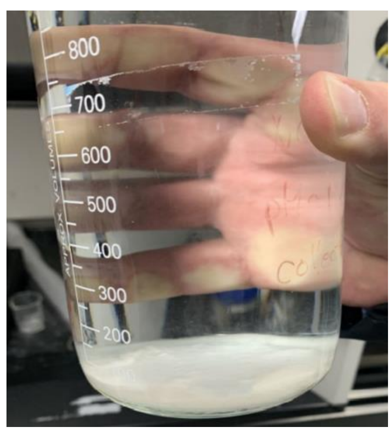
Nitrocellulose (NC) fines

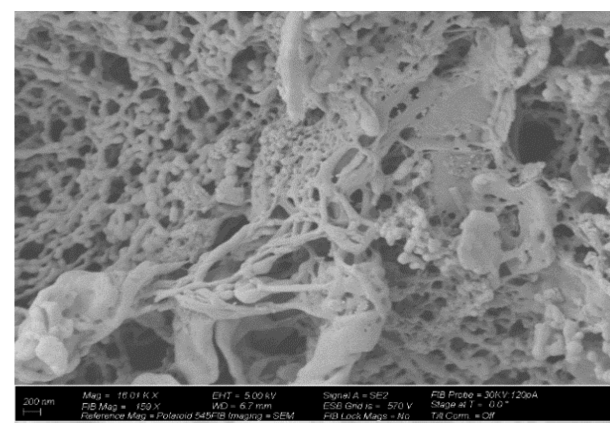
- Production grade NC fines [NC (p)]

NC(p)	
Water %	40-50
Elemental analysis	
C%	25.43
H%	2.49
N%	12.75



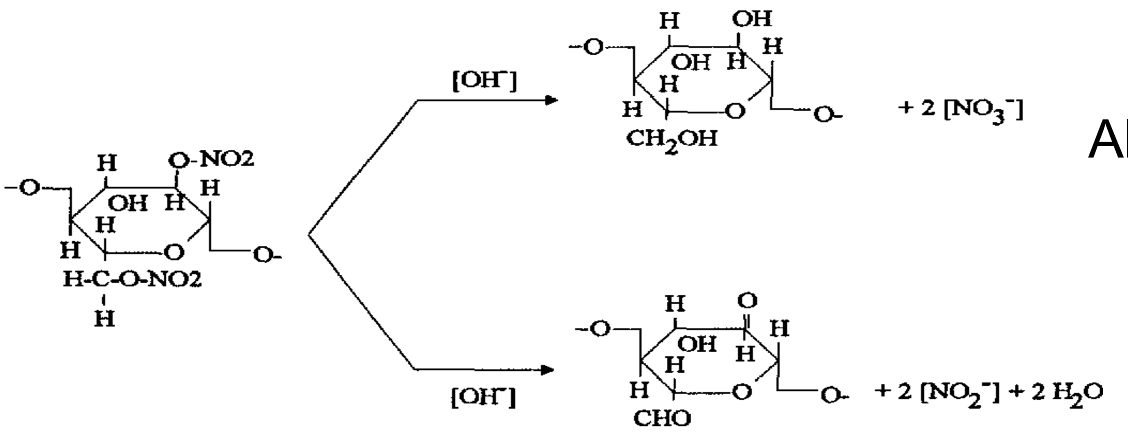
- NC fines from wastewater stream [NC(w)]





Alkaline hydrolysis (AH): kinetic study

- NC wastewater with 3% solids concentration
- AH is a resilient technique proved for degradation of NC
- AH can achieve denitration of NC while also decomposing the primary cellulose backbone



Alkaline driven mechanism for NC decomposition

(Christodoulatos et al., 2001)

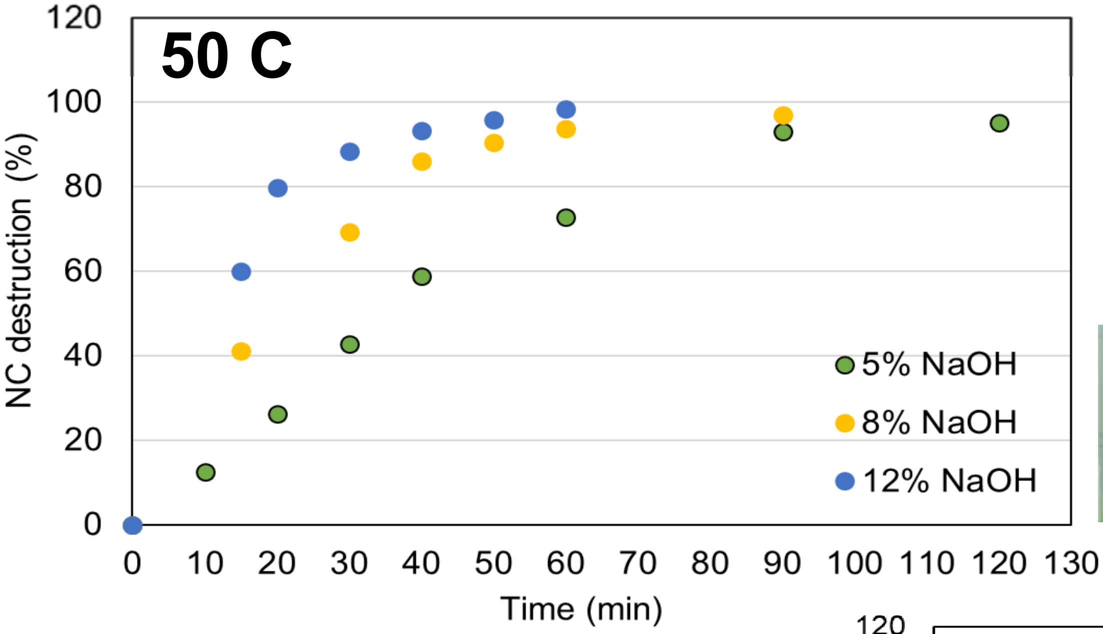
Testing conditions with NC(p)

Parameter	Value
Temperature (C)	50,70,90
NaOH (%)	1,2, 3, 5, 8, 12
NC (%)	3

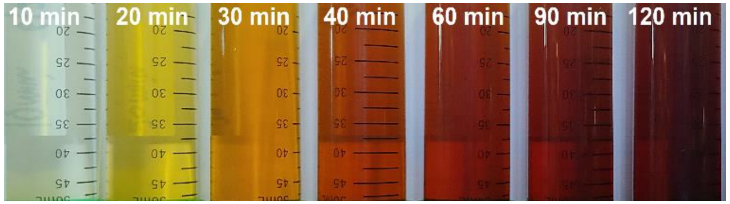
Bench scale testing

- Sodium Hydroxide as alkaline medium
- One flask (250 ml Erlenmeyer flasks, 100 ml reaction volume) for each sampling point sacrificed at specific time intervals

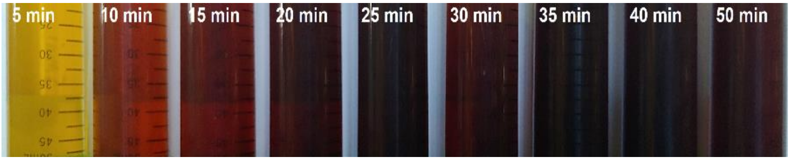
AH of NC(p)



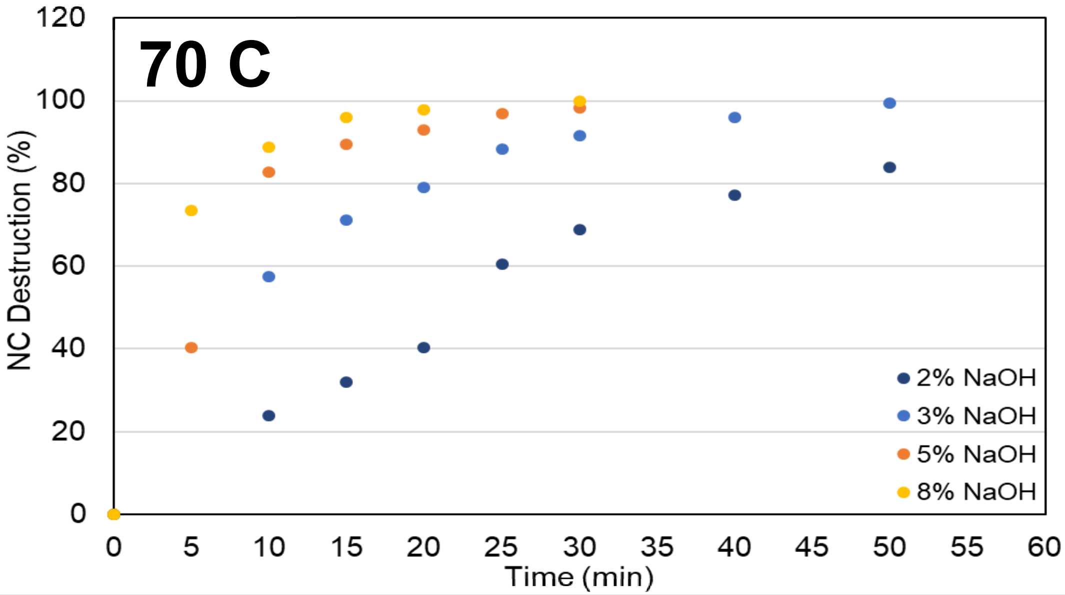
50 C
NC destruction (%)
Time (min)
0
20
40
60
80
100
120
0
10
20
30
40
50
60
70
80
90
100
110
120
130
5% NaOH
8% NaOH
12% NaOH



10 min
20 min
30 min
40 min
60 min
90 min
120 min

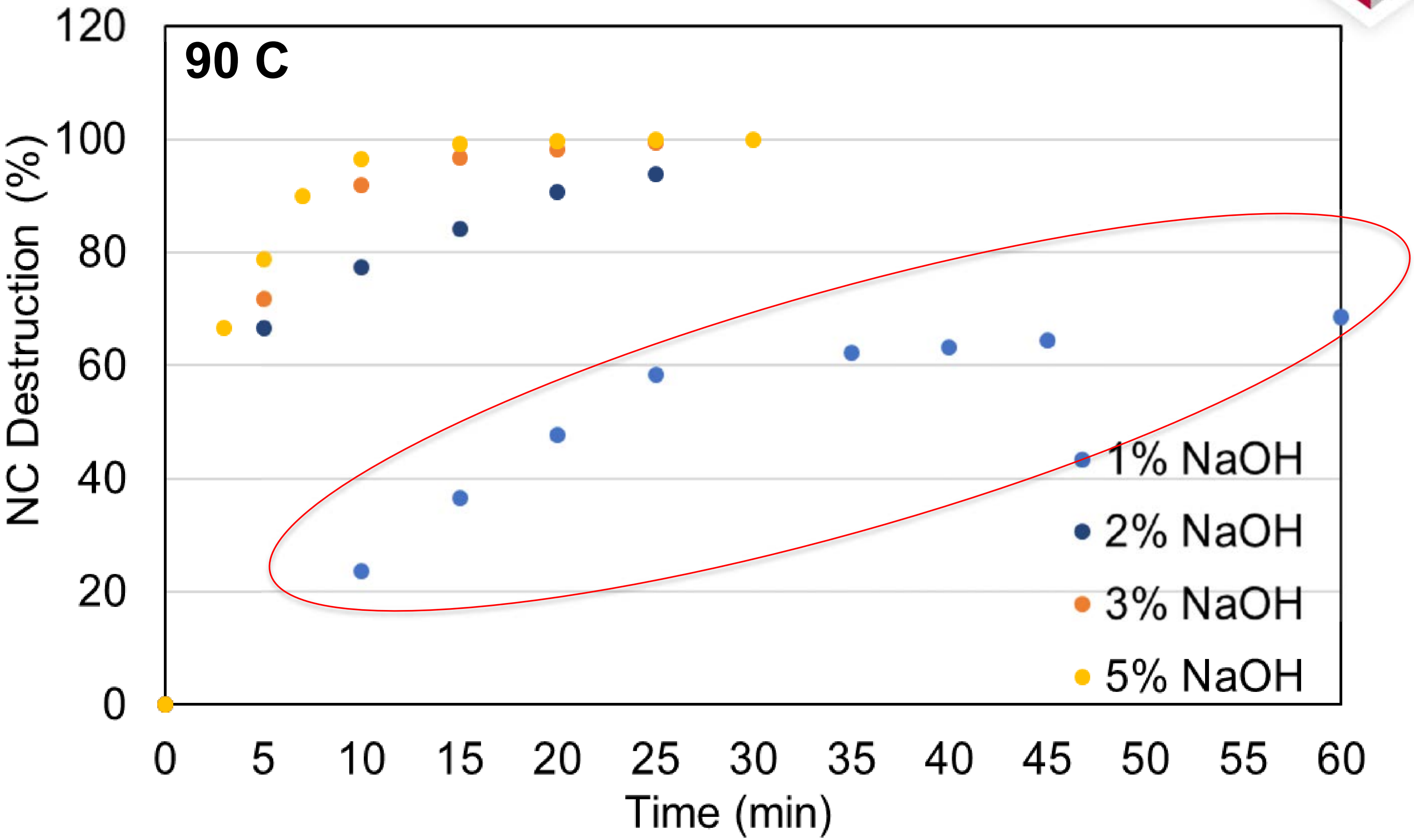


5 min
10 min
15 min
20 min
25 min
30 min
35 min
40 min
50 min



70 C
NC Destruction (%)
Time (min)
0
20
40
60
80
100
120
0
5
10
15
20
25
30
35
40
45
50
55
60
2% NaOH
3% NaOH
5% NaOH
8% NaOH

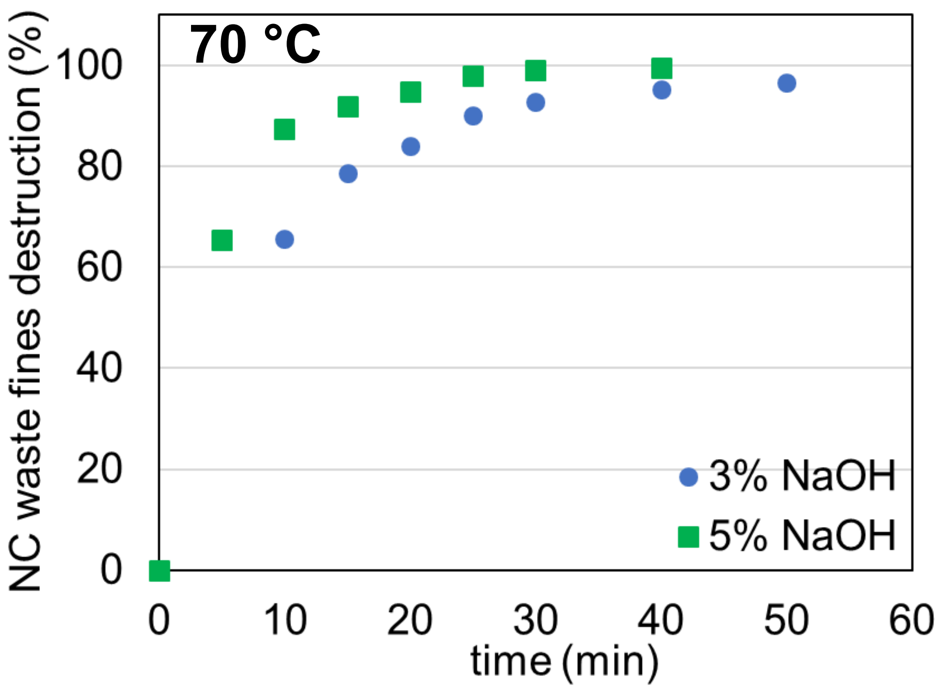
AH of NC(p)

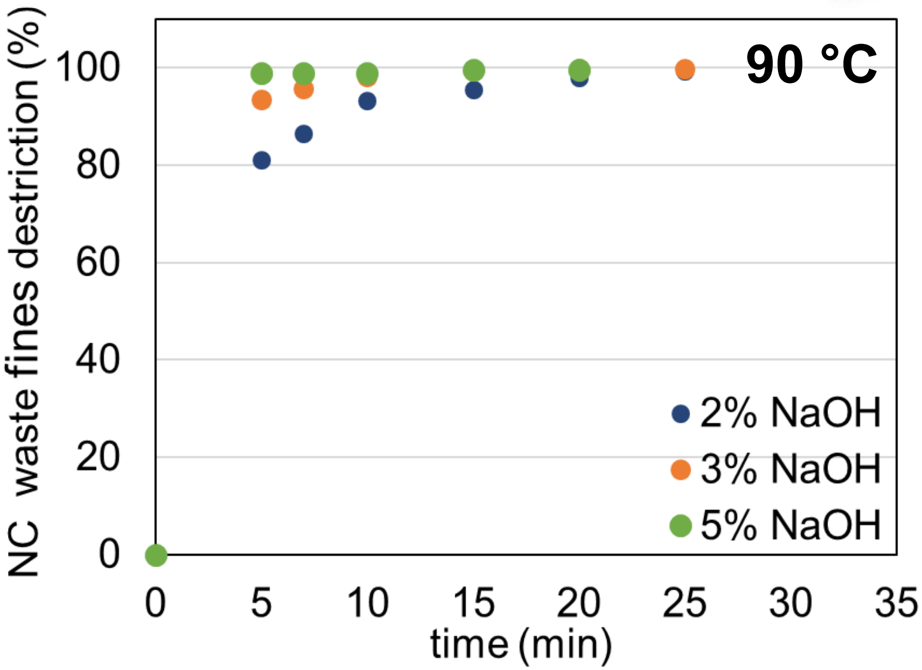


Average time to reach 99% destruction ≥ 25 min

AH of NC(w)

Testing 3% solids content with waste NC fines from wastewater stream





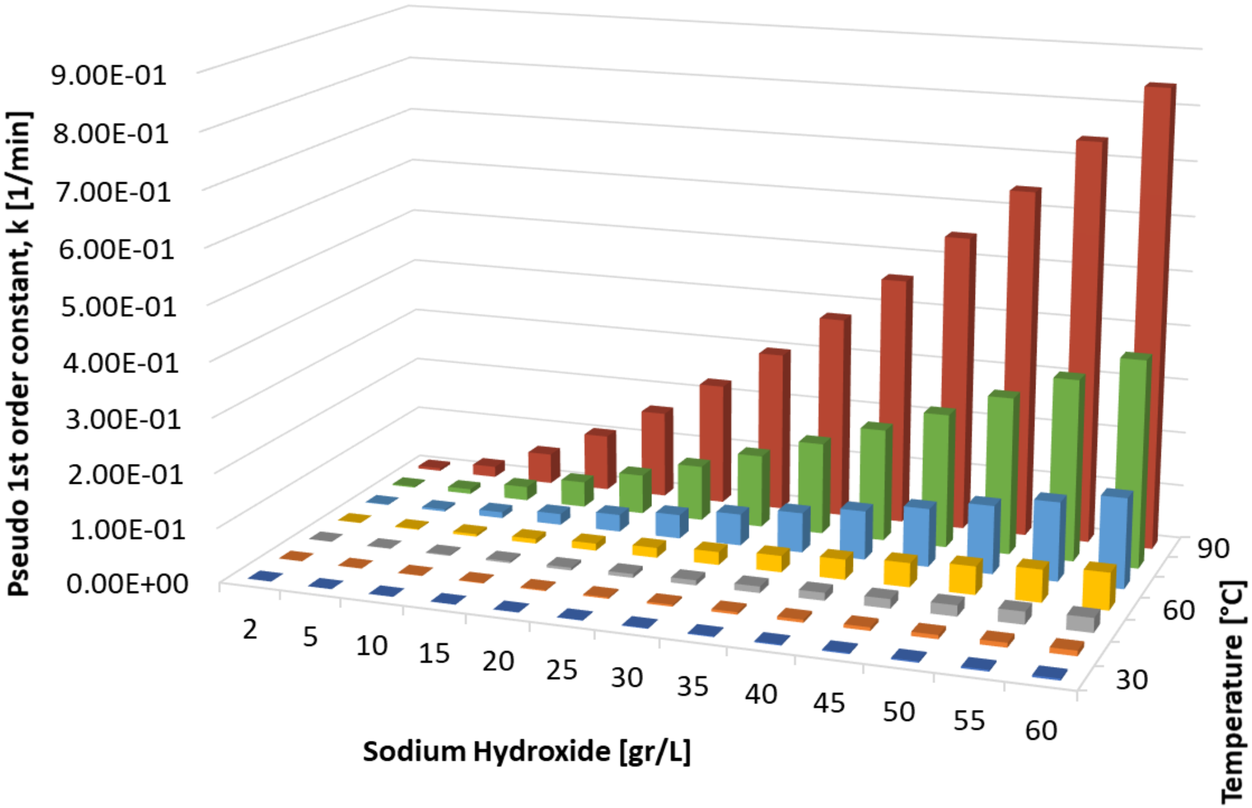
NC:NaOH solids ratio of 1:1 will obtain 99% destruction within 30-60 min for with 90-70 °C

AH kinetic study

Kinetic model for degradation of NC fines

$$C_{NC} = C_{NC}^{0} \exp\left[\left(-2.44 \times 10^{9} (C_{NaOH}^{0})^{1.5} \exp\left(-\frac{10152}{T}\right)\right) t\right] \text{ for } [NaOH] \left[\frac{gr}{L}\right]$$

Estimated AH
__Pseudo First Order Constants (k)__
for NC fines degradation as a function of NaOH (g/L) and Temperature

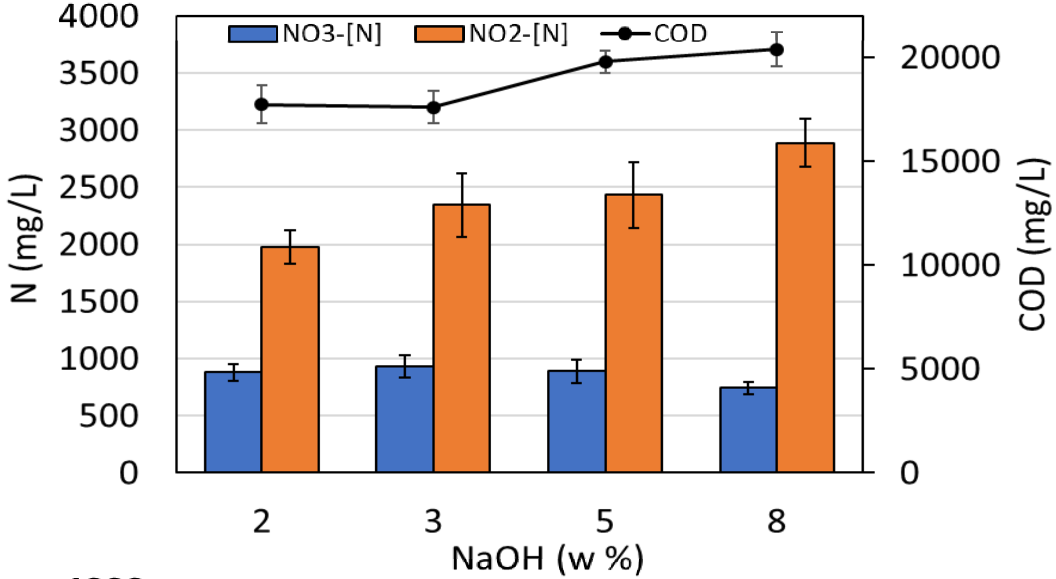


Characterization of post-AH NC liquor

- *Extremely dark color*
- *High pH*
- *Inorganic nitrogen load up to 4000 mgN/L*
- *Organic carbon load up to 18 g/L*

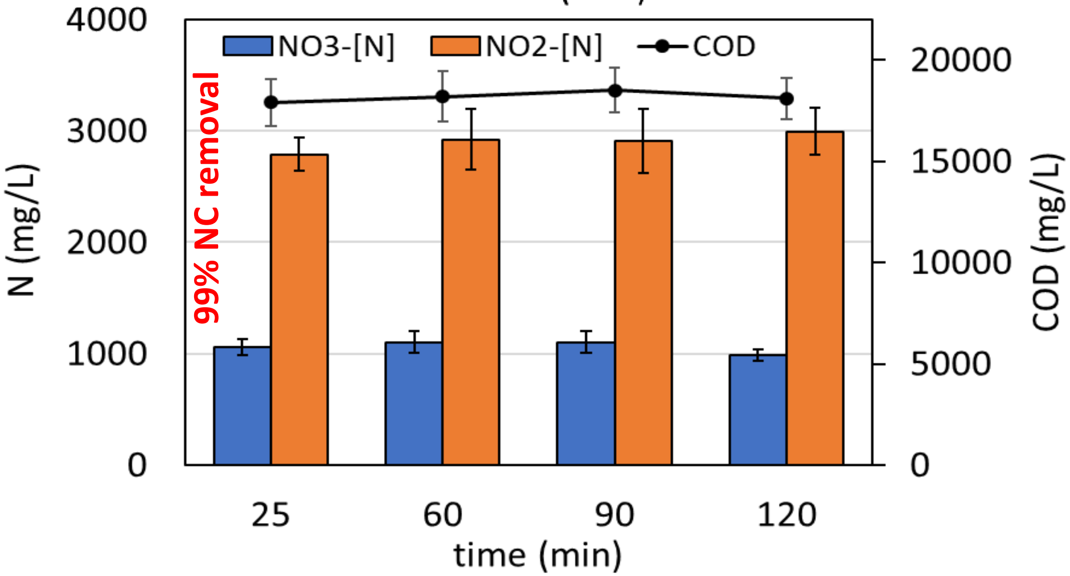
pH (f)	NO_3-N (mg/L)	NO_2-N (mg/L)	NO_2/NO_3	COD (g/L)
13.25±0.1	1025±50	2860±50	2.8±0.1	18±5

Characterization of post-AH NC liquor



Effect of caustic strength

- Fix NCw 3%
- Fix T (90 C)



Effect of AH time

- Fix NaOH 3%
- Fix T (90 C)
- Fix NCw 3%

Alkaline hydrolysis (AH): parametric study

Pilot scale testing

USA Lab-30FS reactor

- Condenser with collection flask
- T monitor and mix controller
- 30 L volume reactor vessel
- Working volume 10 L
- mixing speed fixed to 180±5 rpm

Testing conditions with pure NC fines

Parameter	Value
Temperature (C)	90, 70
NaOH (%)	3
NC (%)	3

AH pilot scale for NC(p) fines

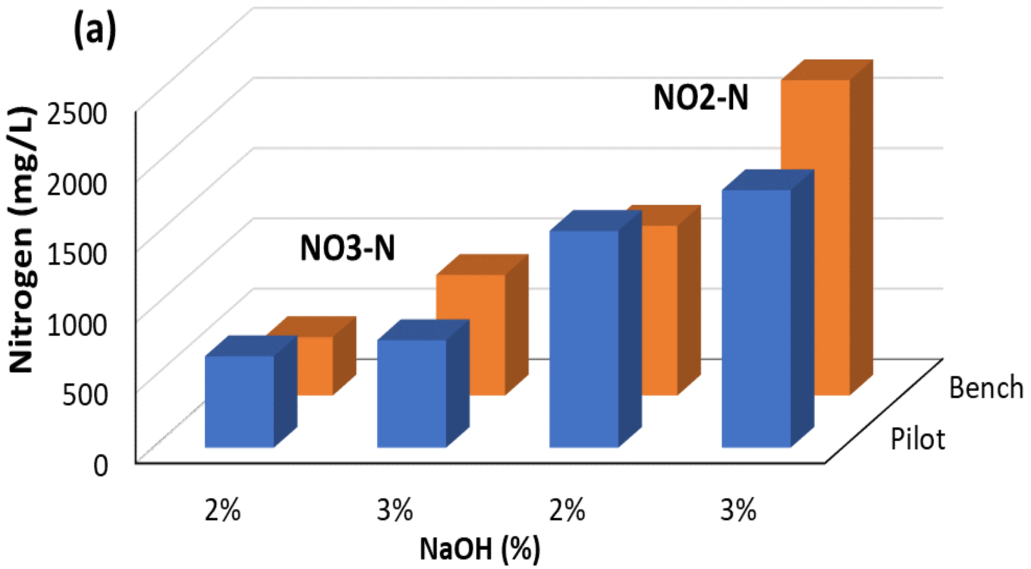
T=5 min *T=30 min* *T=1 h*

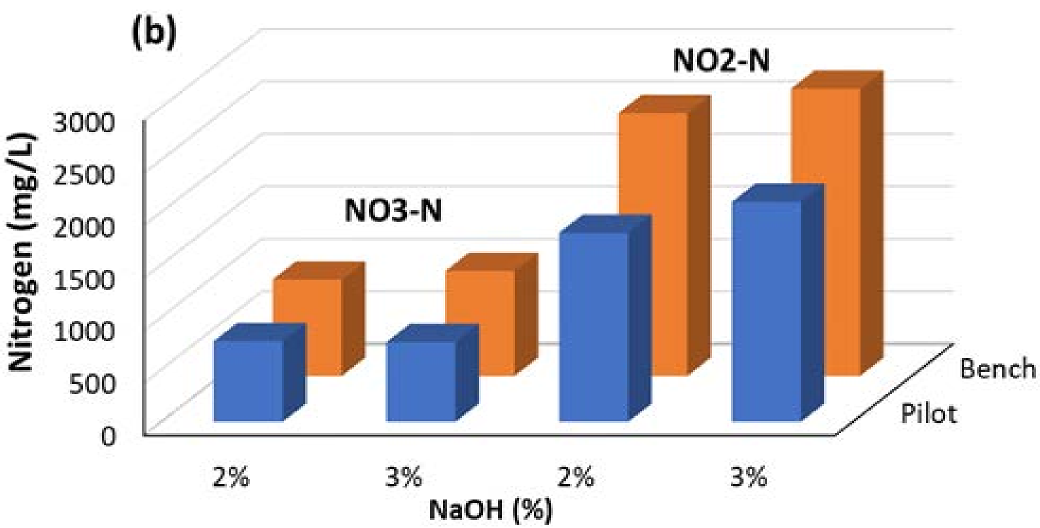
Parameter	Value
Temperature (°C)	70
Time (min)	60
NC removal	99%
COD (mg/L)	19010

T=5 min *T=15 min* *T=25 min*

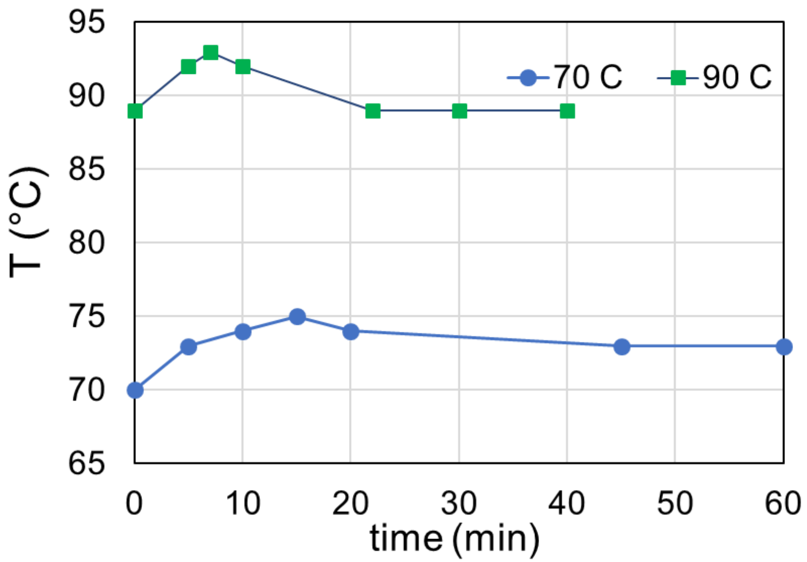
Parameter	Value
Temperature (°C)	90
Time (min)	30
NC removal	99%
COD (mg/L)	19500

AH pilot scale for NC fines





Nitrate and nitrite concentrations as nitrogen from bench and pilot scale tests at (a) 70 °C and (b) 90 °C



AH kinetic study

Summary

- AH is confirmed effective in degradation of targeted NC fines from wastewater
- NC: NaOH solids ratio of 1:1 at 90 °C will achieved 99% destruction within 30 min
- An equation for modeling of NC fines degradation was obtained using non linear regression and pseudo first order approximation
- Higher temperature play a significant role in enhancing kinetic rate of reaction compared to caustic strength
- Optimal conditions from bench scale tests compare well with outcomes from AH tests at larger scale

NO_3-N (g/L)	NO_2-N (g/L)	COD (g/L)
1.02±5	2.86±5	18±5

How to address nitrogen and COD in post-hydrolysis liquor?

Nitrogen removal in post-AH NC liquor

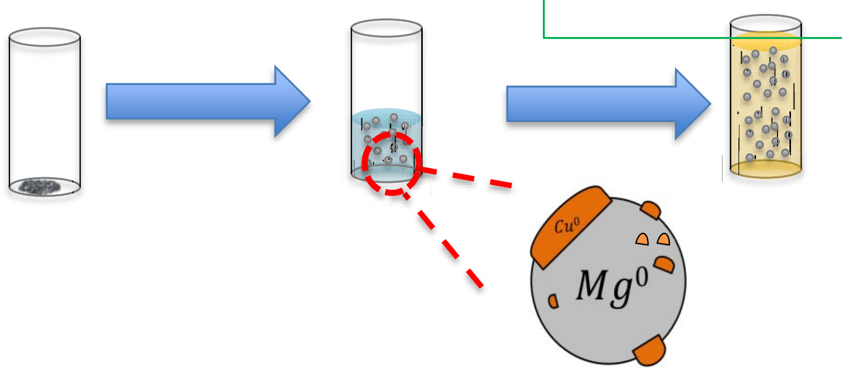
Physicochemical process

Bimetals reduction

ZVMg$_{(solid)}$

+ $CuCl_2$ Solution
5 min mixing time
Mg/Cu forms

Addition of post-AH liquor

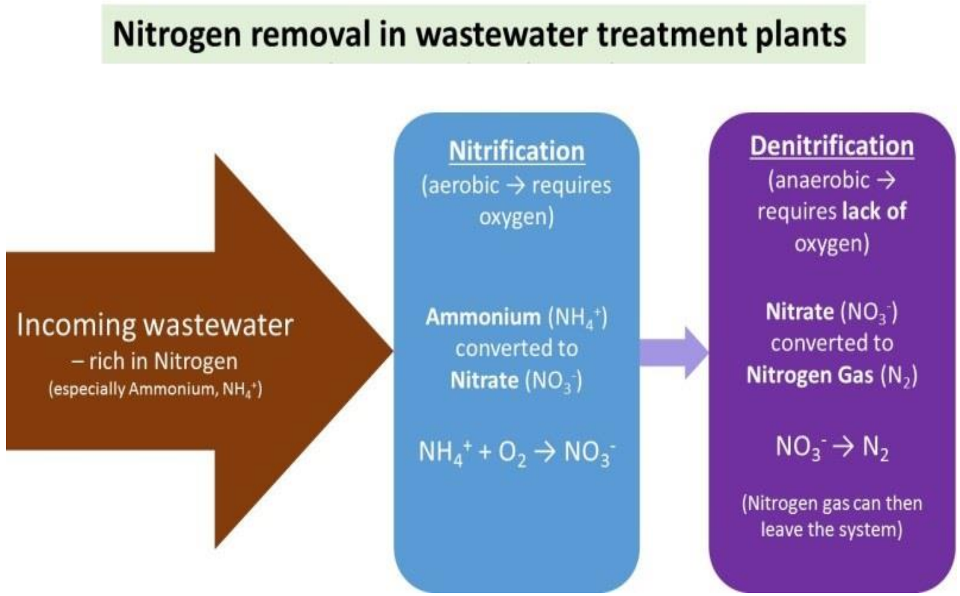


NO_3^- **reduction** → NO_2^- → NH_4^+ / $N_{2\,(g)}$

Parallel reactions

Biological process

Heterotrophic denitrification (HDN)



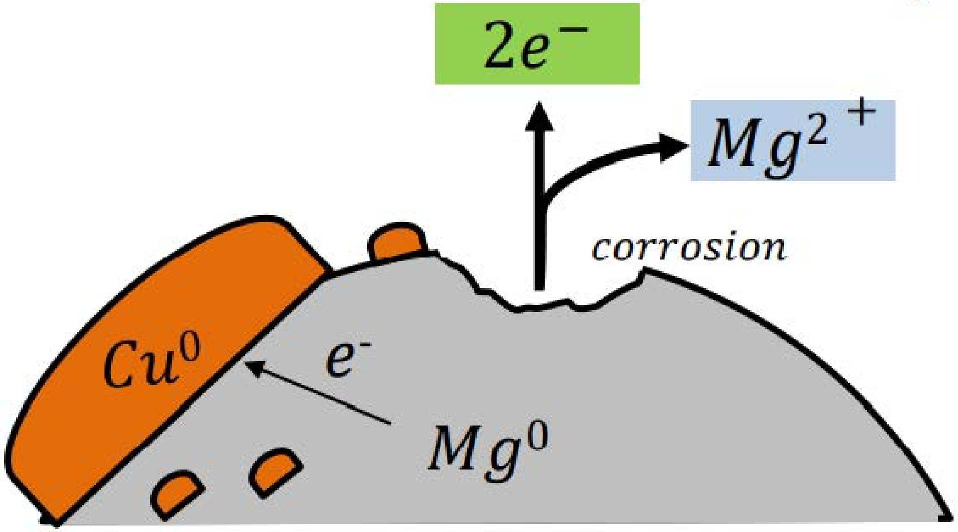
Bimetals reduction for post-AH liquor

- Zero valent iron (ZVI) widely used for environmental remediation
- Process enhanced by

1. metals with higher reduction potential (Mg)

$$Mg^0 \rightarrow Mg^{2+} + 2e^- \qquad ; E^0 = -2.37\,V$$
$$Fe^0 \rightarrow Fe^{2+} + 2e^- \qquad ; E^0 = -0.44\,V$$

2. Bimetals contact (galvanic corrosion)

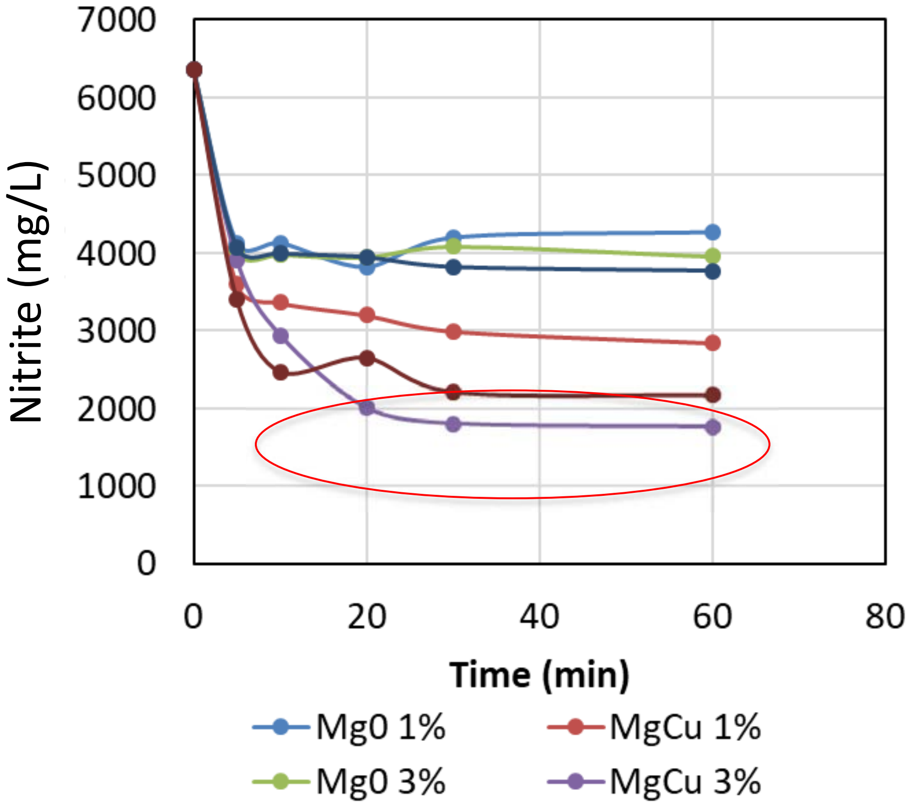


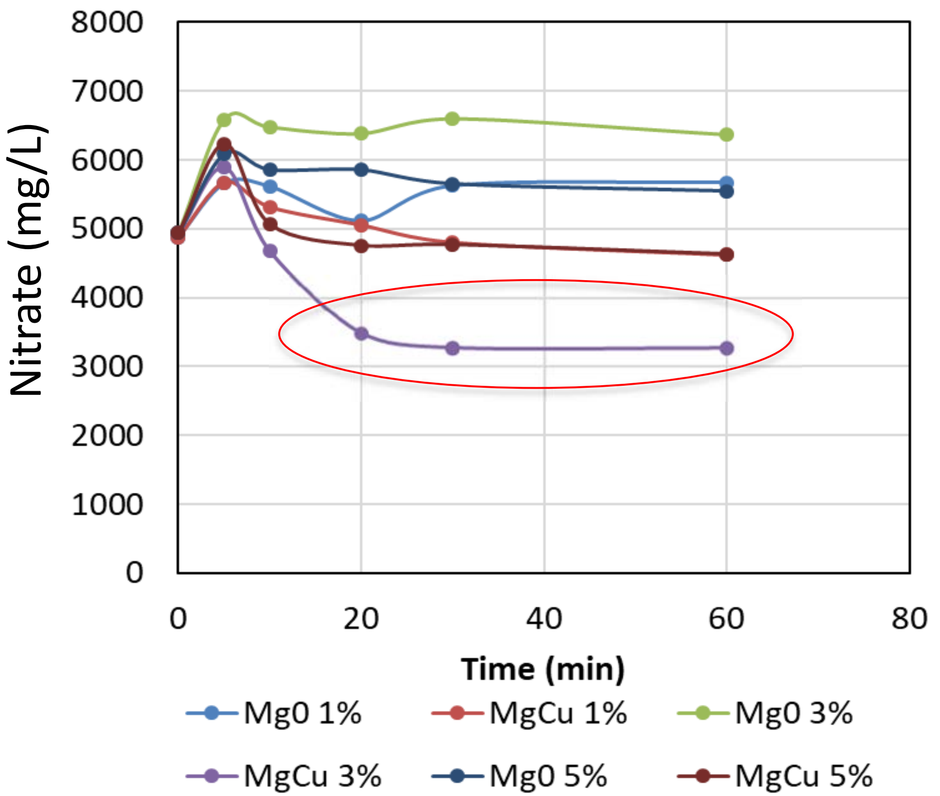
Bimetals reduction for post-AH liquor

Testing Conditions:

- ZvMg only
- Mg/Cu at 10:1 ratio
- Initial pH of post-AH liquor adjusted to ≤2.0

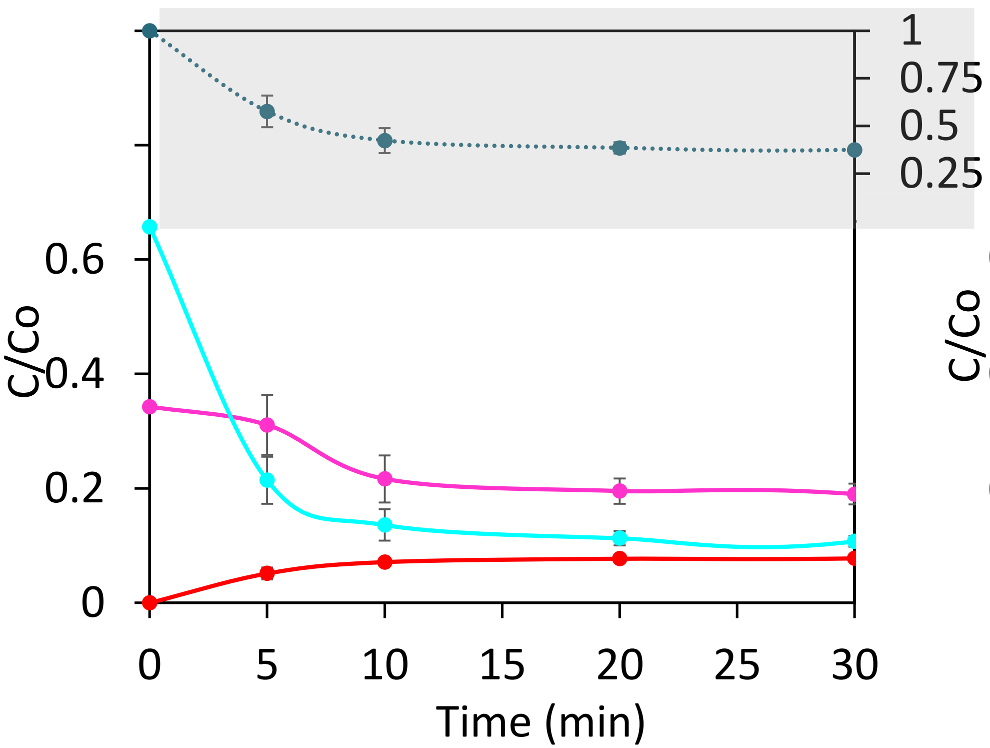
Solids to liquid (S/L) percentages ratio 1-5%



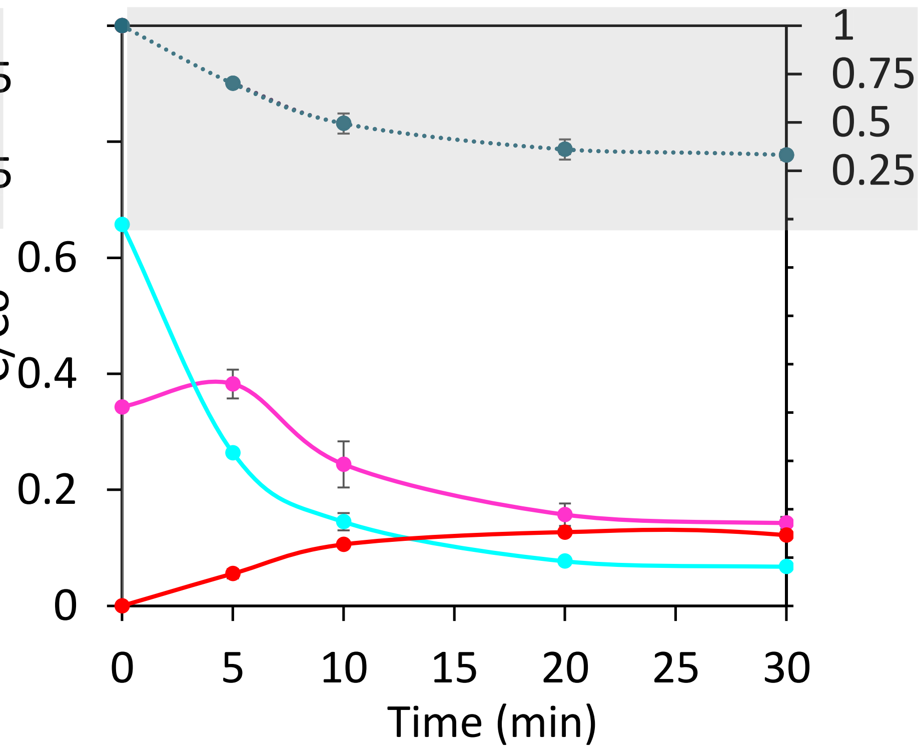


Bimetals reduction for post-AH liquor

Nitrogen removal from post-AH liquor at 3% S/L



Undiluted AH liquor



2x Dilution AH-liquor

Total N | NO_3-N | NO_2-N | NOH_3-N

Nitrogen removal from post-AH liquor at 60-70%

Bimetals reduction for post-AH liquor

COD removal from post-AH liquor at 3% S/L

Target AH liquor	Dilution AH liquor	% COD Removal
AH-liquor from NC(p)	2X	77.5
	4X	79.1
AH-liquor from NC(w)	2X	83.0

post-AH liquor before and after treatment with Mg/Cu

Heterotrophic Denitrification (HDN) of post-AH liquor

Dissolved Oxygen ≤ 0.5 mg/L

In anoxic environment, heterotrophic bacteria will use the oxygen from nitrates as they assimilate BOD, producing nitrogen gas.

Denitrification Reaction Sequence

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$$

Nitrate → Nitrite → Nitric Oxide → Nitrous Oxide → Nitrogen Gas

HDN of post-AH NC liquor

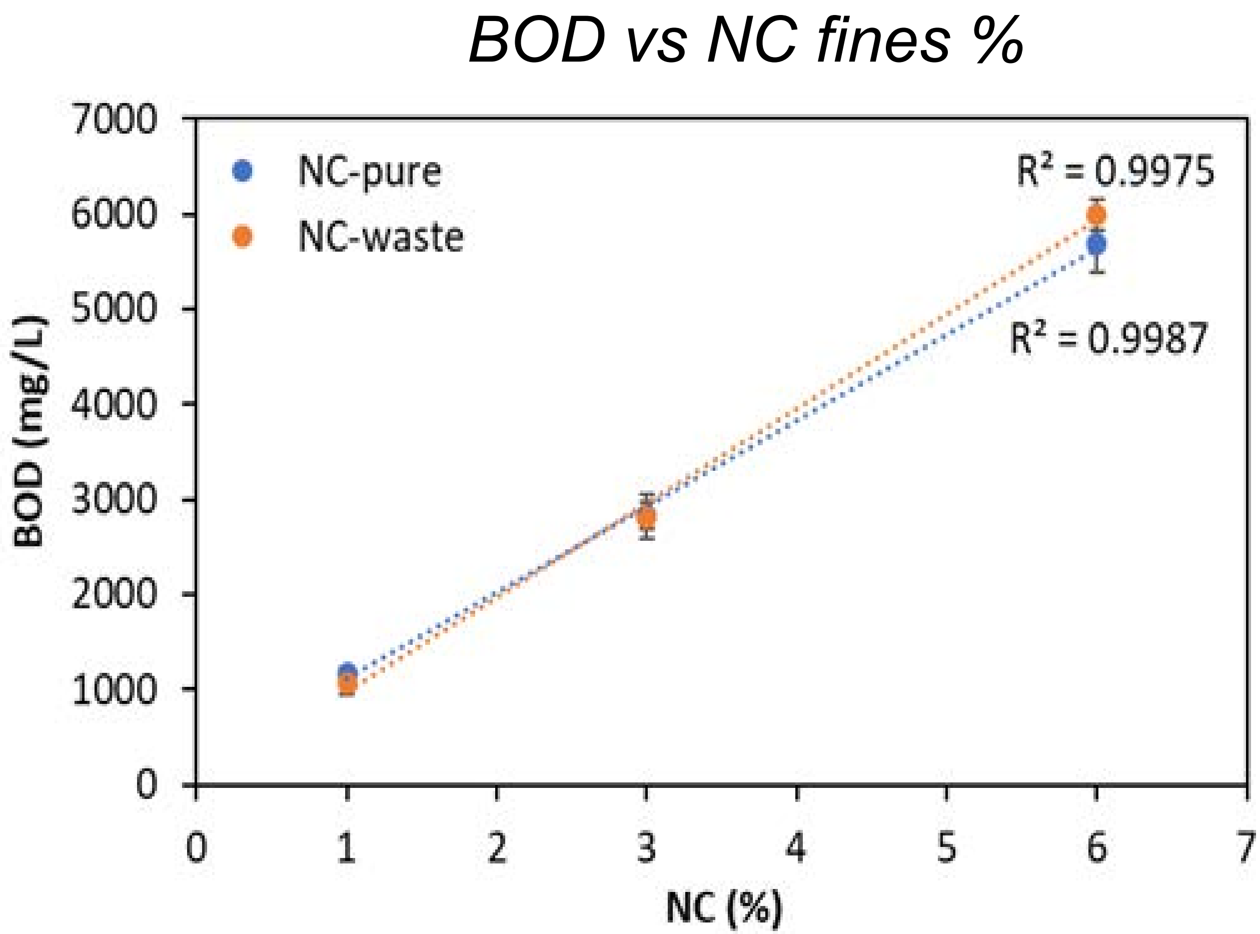
Requirements for HDN

- Biochemical Oxygen Demand (BOD)/ to nitrous oxygen (NOx-[N]) of min 2.5-max 5
- A COD/BOD ratio ≤ 2
- 99% transformation of 3% NC solids generate about 3800 mg/L of NO_x-N
- Identify BOD/NO_x-N and COD/BOD ratios in post-hydrolysis NC liquor

NC (w) %	COD (g/L)	ΣNOx-N (g/L)
1	6.82	1.50
3	16.8	3.73
6	32.1	6.09
NC (p) %	**COD (g/L)**	**ΣNOx-N (g/L)**
1	6.20	1.50
3	16.2	3.73
6	29.9	6.09

Characterization of post-AH liquor for different NC %

BOD in post-AH NC liquor



AH of NC fines yield of 1000 mg BOD/g NC hydrolyzed

HDN of post-AH NC liquor

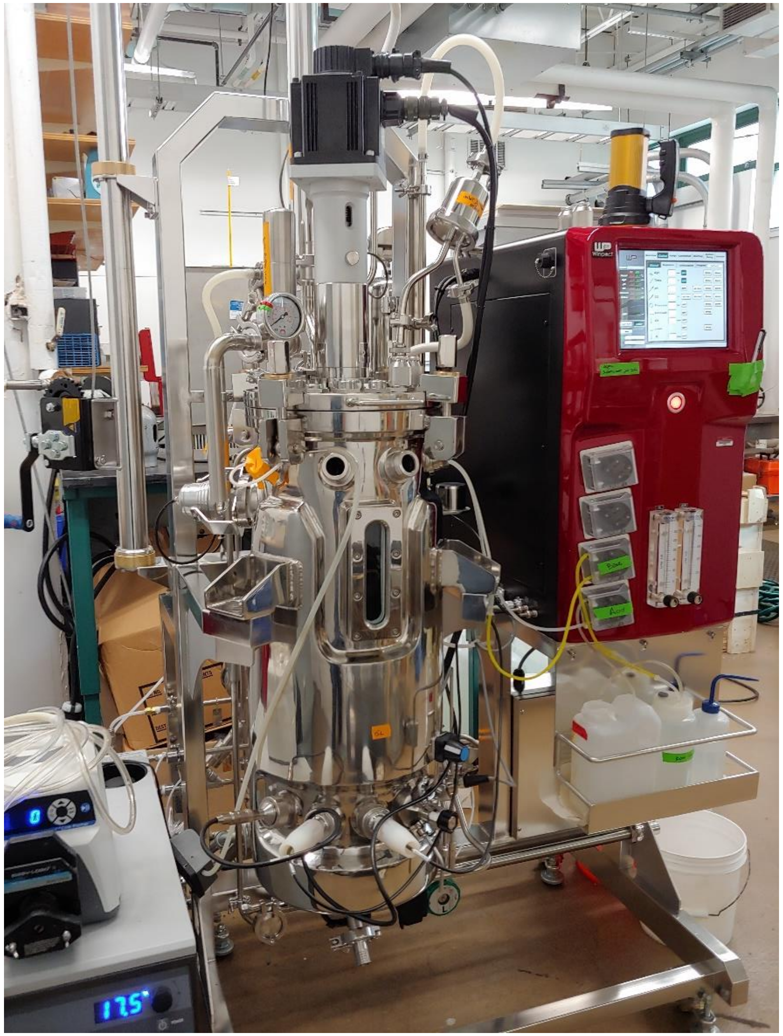
BOD Requirements for HDN

- Based on BOD assessment and characterization of post-AH liquor

NC (w) %	COD/BOD	BOD/ΣNOx-N
1	5.79	0.78
3	5.94	0.76
6	5.65	0.93
NC (p) %	**COD/BOD**	**BOD/ΣNOx-N**
1	5.81	0.78
3	5.75	0.85
6	4.99	0.99

- Ratios for NC(w) do not meet the standard criteria for HDN
- In WWTP, HDN is downstream to aerobic treatments
- Addition of organic carbon to sustain HDN is common
- Methanol selected for external supply to post-AH liquor

HDN experimental set up



Winpact Evo System
Controller and bioreactor

30 L reactor capacity, recirculation jacket with heating/cooling system; online DO, pH, ORP probes with online pH adjustment

Operating Parameter	Value
Temperature (C)	30
AH liquor dilution	8x
Flow (L/d)	8
Working volume (L)	15
HRT (d)	1.8
Total Influent N (mg/L)	430±10
Influent NO2-N (mg/L)	323±5
Influent NO3-N (mg/L)	107±10

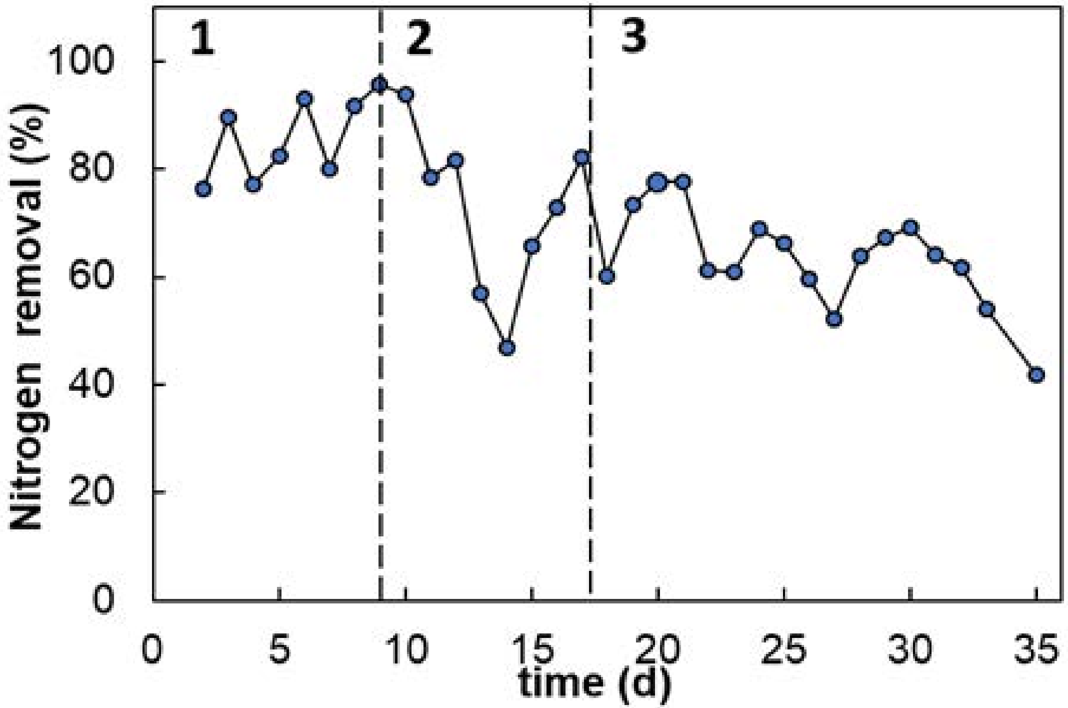
HDN of post-AH liquor

Operating conditions by influent nitrogen

Phase	Influent Nitrogen progression	Time (d)
1	100% NO_3 synthetic solution	8
2	25% NO_3, 75% NO_2 synthetic solution	8
3	Diluted AH liquor (8X) from NC(p)	20

Activated Sludge from local wastewater treatment plant (Bergen County Utility Authority) utilized as initial inoculum acclimated for a period of 2 weeks

HDN of post-AH NC liquor

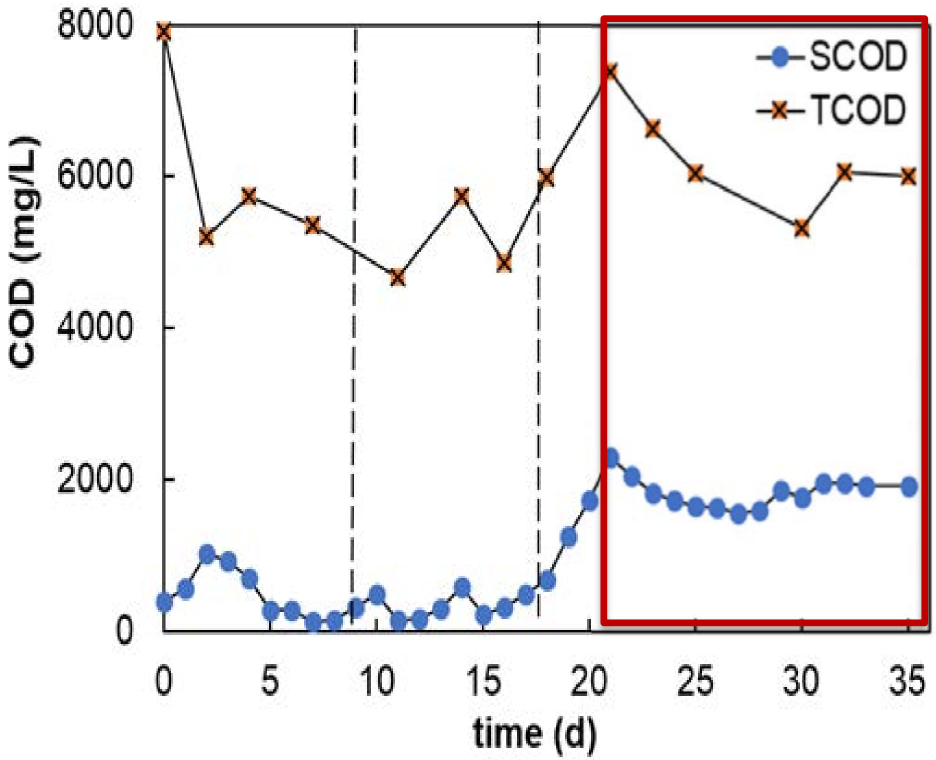


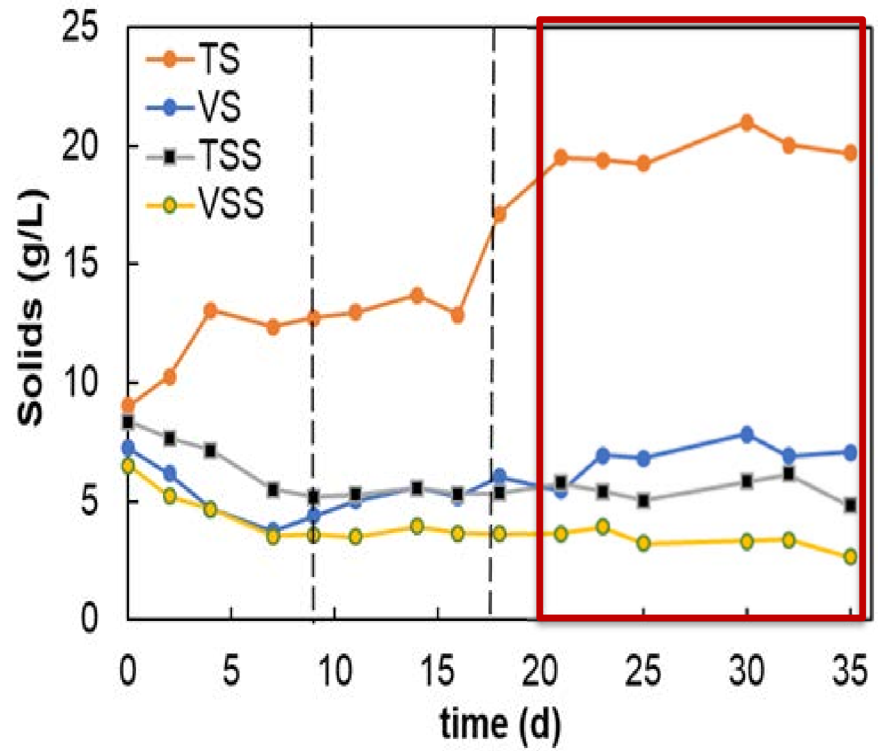
Average performance parameters

- **Avg MLVSS (g/L)** 1.81±0.05
- **Avg TSS/VSS ratio** 0.50
- **Avg COD removal** 57%
- **Avg N** removal 60%

Phase	Influent Nitrogen progression	Time (d)	Supplied MeOH (mg/L)	Influent pH
1	100% NO_3 synthetic solution	8	1060	7.55
2	25% NO_3, 75% NO_2 synthetic solution	8	765	7.60
3	Diluted AH liquor (8X) from NC(p)	20	460	8.40

HDN of post-AH NC liquor





- Inhibition of denitrifiers activity over time
- Decline of COD removal
- Gradual decline in VSS which indicate biomass loss
- Induced toxicity may derive by synergistic effect between salts accumulation and COD in post-AH liquor

Comparison of Nitrogen removal in post-AH NC liquor

Summary and conclusions

- Bimetals reduction and HDN were both effective in reducing the concentrations of nitrate and nitrite in the post-AH liquor
- Both processes required dilution of initial AH-liquor due to COD and nitrogen overload
- Reduction with bimetals (Mg/Cu) achieved higher inorganic nitrogen and COD removal (≥70%) with less dilution and faster kinetic compared to HDN (≤ 60%)
- Bimetals obtained also de-coloration of AH liquor (i.e. clear color)
- Denitrifies bacteria in HDN process showed toxicity inhibition from AH-liquor which may result in higher complications for large scale applications

Thank you for your attention!

Questions?