Problem of low-cost ammonium removal in drinking and wastewaters in Vietnam

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Cao The Ha, PhD. Assoc. Prof.

Center for Env. Tech. & Sust. Dev. (CETASD)

Hanoi University of Science (HUS) – VNU HN

Brief Content

1. Author Introduction
2. Country Conditions (regarding to water issues)
3. Situation/Problems in supplied/drinking water
4. Situation/Problems in wastewater
5. Conclusions

CV

1. Full Name: Cao The Ha, Born: 1952
2. Major: Physical Chemist (Kinetics-Catalysis-Adsorption)
3. Became environmentalyst: 1994, 2000
4. Present Duties:
   - Teaching: Phys. Chem. for Chem. Faculty

     Env. Tech. for Env. Faculty
   - Research:
     - Water Technologies
     - 3R
     - Energy – Material - Environment

Country Conditions

1. Vietnam has long S-shape, ¾ area is covered by mountain/highland, a tropical, agricultural country, doing “renovation” of economy
   - A lot of rivers, water is abundant, BUT monsoon
   - 70% population occupied in agr., low income (~ $700/p.a)
   - Changing fast: ~ 8%/a
2. University & Res. Institutes System:
   - Separate, mostly National
   - 2 National Univ. + others (belonging to MoET)
3. VN Nat. Univ., HN: 2 “Univ.” + 3 Schools
   - HUS = the oldest & largest (former Hanoi University)

Location: in South East region of Asia. $23^{o}23$-$8^{o}34$N latitudes; and $102^{o}10$-$109^{o}24$E longitude

Area: 329,247 km^2 and about 1 Mio. 200 miles^2 Sea

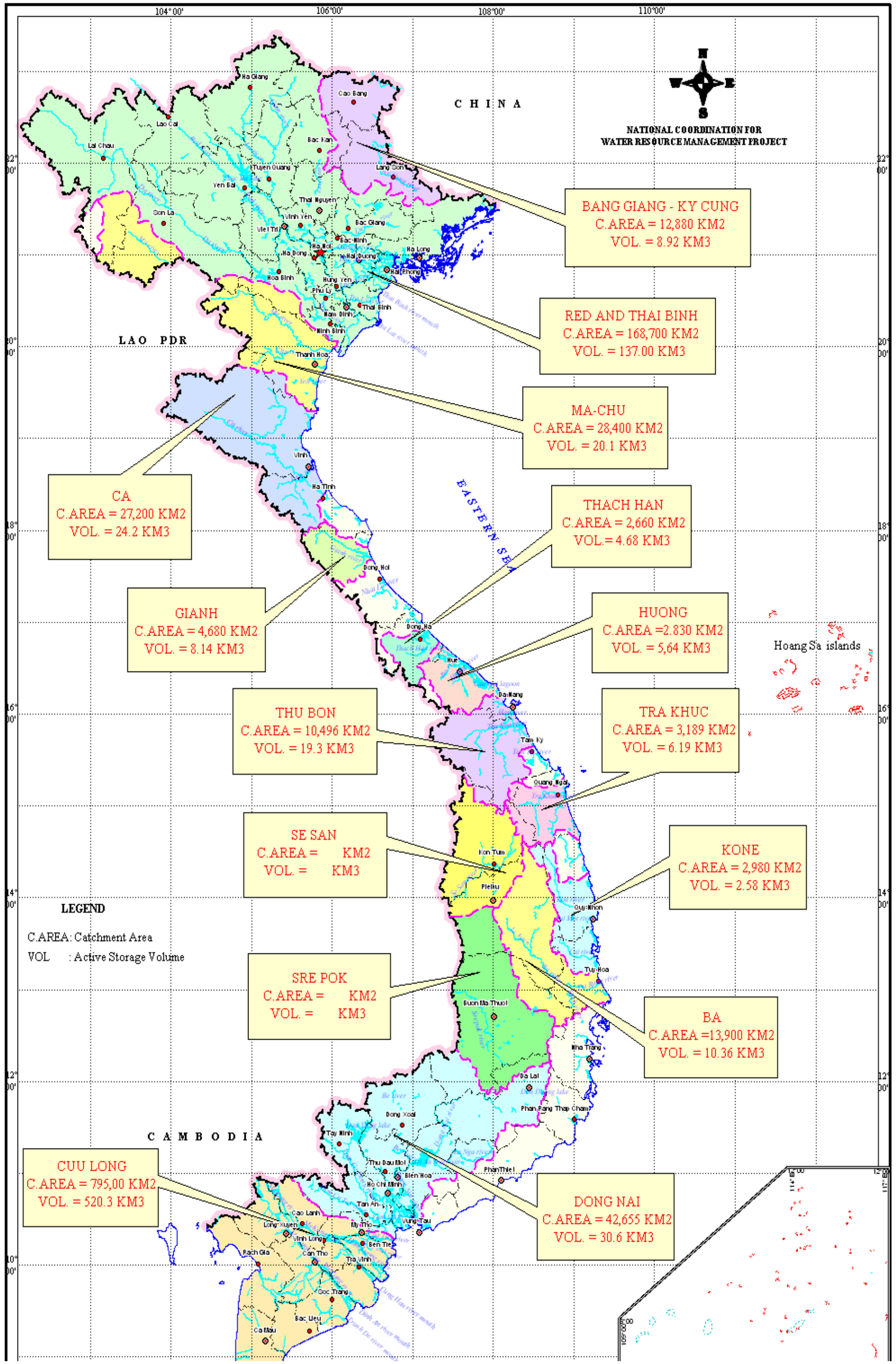
Long: 1650 km (about 15^{o} latitude)

Costal line: 3,260 km long in the East and South

Border line: 4,550 km long with China (North); Laos and Cambodia (West & South)

Climate: tropical, strong monsoon

Slop: West to East



VIETNAM NATIONAL UNIVERSITY, HANOI
(VNU HN)

- **HANOI UNI. OF SCIENCE** (HUS)
- **HNU OF SOC. SCIENCE AND HUMANITY**
- **SCHOOL OF TEACHER TRAINING**
- **SCHOOL OF ENG. & OTHERS**

A 15-YEAR PLAN (2003-2018) WAS APPROVED BY VN GOV. MAIN FUTURES:

LOCATION:	30 km FROM HANOI
AREA:	1000 ha
No STUDENTS:	20 – 30 K
COST:	US$ 500 M

VIETNAM NATIONAL UNIVERSITY, HANOI
(VNU HN)

HANOI UNI. OF SCIENCE
(HUS)

HNU OF SOC. SCIENCE AND HUMANITY

SCHOOL OF TEACHER TRAINING

SCHOOL OF ENG. & OTHERS

FACULTIES OF SCIENCE
(MATH, PHYS., CHEM. etc.)

RESEARCH CENTERS
(eg. CETASD)

Hanoi University of Science, Center for Env. Tech. & Sus. Dev. (CETASD), Block T3, 334 Nguyen Trai Str., Thanh Xuan Dist., Hanoi
Tel. (084) 4 858 7964/858 9213; Fax. (084) 4 858 8152; E-mail: cetasd@fpt.vn/caotheha@gmail.com

Problem in WS & WW

1. Supply Water
   - 30% is groundwater
   - Hanoi (urban population 2 Mio.): 100% groundwater

Problems:

- 60% Cities & Towns have WP, 80% population has tape water (75-150 L/p.d.)
- 40-60% rural pop. has clean water (50 L/p.d.)

(*Source: VN Env.Outlook, 2005*)

- Quality: Fe, Mn, Hd, As, NH_4^+, F^- ???

Problem in WS & WW

2. Wastewaters

- Domestic & Municipal WW: a few facilities in Cities, mostly septic tanks
- Industrial WWs: mostly Primary & Secondary treatment
- Technology: neutralization, coagulation, settling, CAS, TF, UASB, SBR

- 4.26% treated IWW get VN standards
- No attention on N, P removal

SOLUTION

1. **Our Goal:**
    - N removal
    - For IWW: Low-Cost
    - Resource saving, GHGs emission mitigation
2. Review of N removal, Method selection
3. Results in drinking water treatment
    - Nitrification + Denitrification & Annamox process
    - Nitrification + Denitrification without carbon source
4. Situation & Proposals for Agro-Industrial WW

2. Review of N-removal (biol.) (1/7)

1. Conventional: Nitrification $\rightarrow$ Denitrification

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + 2H_2O \quad (1)$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \quad (2)$$

$$2NO_3^- + 10H^+ + 10e^- \rightarrow N_2 + 2OH^- + 4H_2O \quad (3)$$

$$2NO_2^- + 6H^+ + 6e^- \rightarrow N_2 + 2OH^- + 2H_2O \quad (4)$$

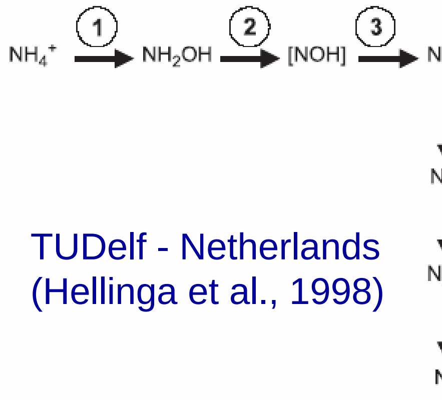
Drawback:

(1) Larger V for nitrification

(2) A lot of O_2 required: 4.2 g O/1 g N-ammonium

(3) Needs in e-donor (eg. MeOH) supply: 2.47 g MeOH/1 g N-nitrate

2. SHARON (single reactor sys. for high ammonia removal over nitrite proc.)



TUDelf - Netherlands
(Hellinga et al., 1998)

Demands 25% less aeration energy; 40% less added carbon.

Difficult to conduct (1) reac. (chemostat conditions)

2. Review of N-removal (biol.) (2/7)

3. ANAMMOX (anaerobic ammonium oxidation via nitrite)

Anammox was predicted by (Broda, 1977):

$5NH_4^+ + 3NO_3^- \rightarrow 4N_2 + 9H_2O + 2H^+$ ΔG^0 = -297 kJ/mol (1)

$NH_4^+ + 1.5O_2 \rightarrow 3NO_2^- + 2H^+ + H_2O$ ΔG^0 = -275 kJ/mol (2)

$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$ ΔG^0 = -349 kJ/mol (3)

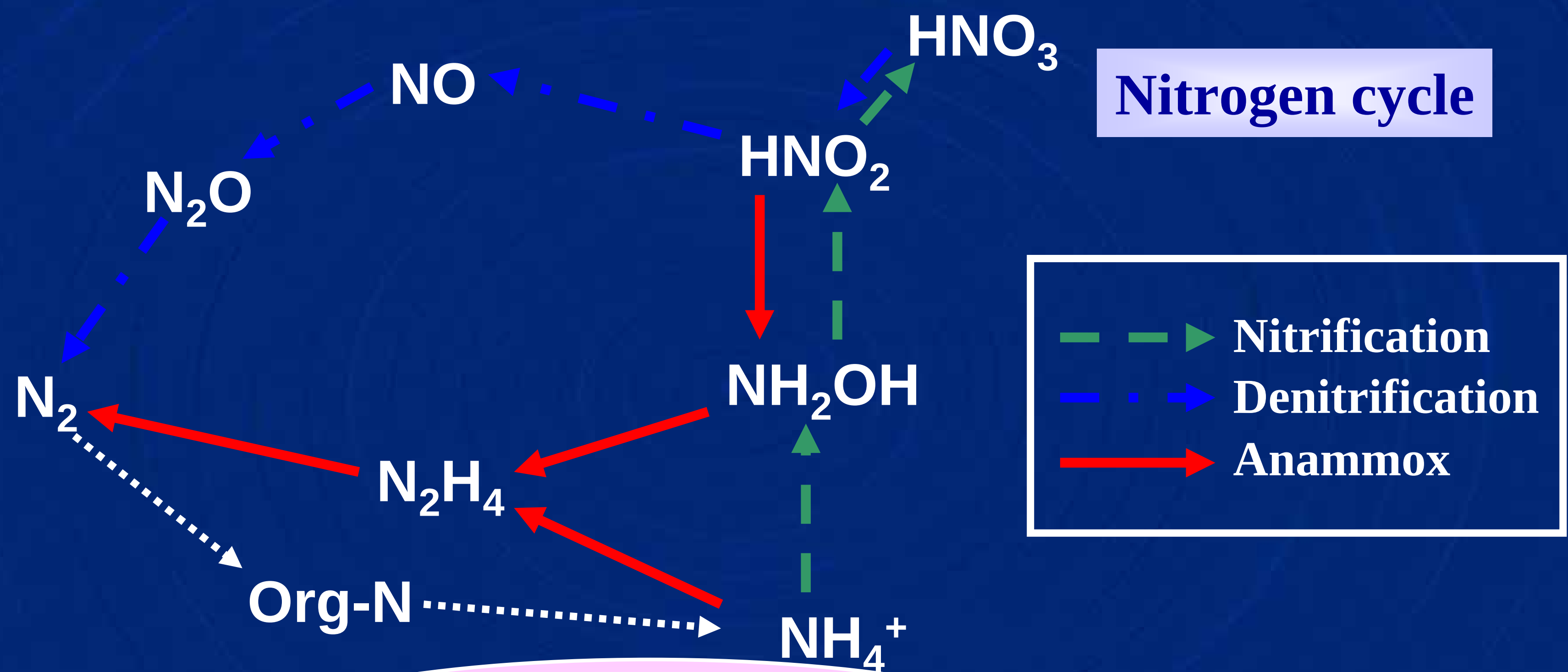
Actual Evidence:

1994 Mulder et al. observed simultaneous elimination of both N-ammonium and N-nitrite in anaerobic denitrification reactor for treatment of supernatant from sludge digester in Gist-brocades (Delft, Netherlands) (*Mulder et al., 1995*).
This discovery triggered off a change of studies in TU of Delft (*van de Graaf et al., 1995, 1996, 1997*). After TU-Delft: (*Schmid et al., 2000*); (*Furukawa et al., 2000*); (*Egli et al., 2001*); (*Pynaert et al., 2002*); (*Schmid et al., 2003*).

Found in nature: in Baltic Sea sediment (*Thamdrup & Dalsgaard, 2002*); in anoxic zone in the bottom of Costa Rica Sea (*Dalsgaard et al., 2003*); of Black Sea (*Kuypers et al., 2003*).

2. Review of N-removal (biol.) (3/7)

3. ANAMMOX (anaerobic ammonium oxidation via nitrite)



Anammox

$$NH_4^+ + NO_2^- \longrightarrow N_2 + 2H_2O$$

$$NH_4^+ + 1.31NO_2^- + 0.066HCO_3^- + 0.13H^+ \longrightarrow 1.02N_2 + 0.26NO_3^- + 0.066\text{Biomass} + 2.03H_2O$$

(*Strous, 1998; K. Furukawa, 2005*)

2. Review of N-removal (biol.) (4/7)

3. ANAMMOX (anaerobic ammonium oxidation via nitrite)

Advantage:

(1) Reduce energy for O_2 supply

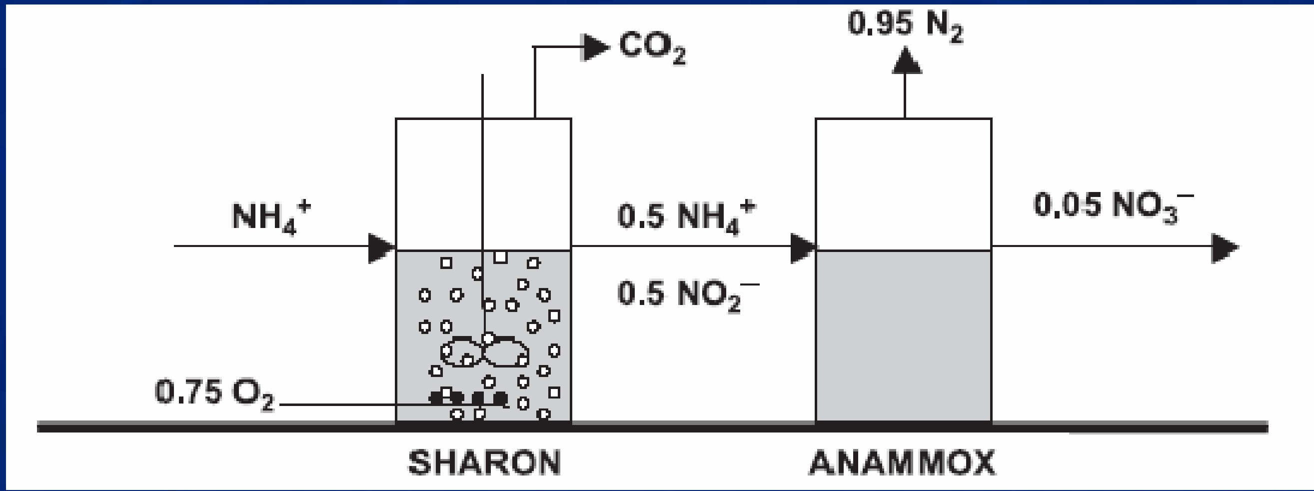
(2) No need in external carbon source

Drawback:

(1) Low grow rate $\rightarrow$ long starting-up period

2. Review of N-removal (biol.) (5/7)

4. The combined SHARON & ANAMMOX



(Jetten et al., 1997)

In the First Reactor:

$$NH_4^+ + HCO_3^- + 0.75O_2 \rightarrow 0.5NH_4^+ + 0.5NO_2^- + CO_2 + 1.5H_2O$$

Advantage:

- Saves 50% on required oxygen,
- No need in the external carbon source
- Reduces CO_2 emission by more than 100% (the combined process actually consumes CO2) (*van Loosdrecht & Jetten, 1997*)
- Overall, the combined process is 90% less expensive than the conventional processes (*Dijkman & Strous, 1999*).

TUDelft - Netherlands (Hellinga et al., 1998)

2. Review of N-removal (biol.) (6/7)

5. Other Processes

CANON process = completely autotrophic nitrogen removal over nitrite (*Dijkman & Strous, 1999*)

Under oxygen-limited conditions (< <u>0.5% air saturation</u>) a **coculture** of aerobic & anaerobic ammonium-oxidizing bacteria (*Nitrosomonas-like* aerobic bacteria and *Planctomycete-like* anaerobic ammonium-oxidizing bacteria-ANAMMOX (*Third et al., 2001*)) can be established (*Strous, 2000*).

First, under oxygen-limited condition, ammonium is oxidized to nitrite by aerobic nitrifiers, such as *Nitrosomonas* & *Nitrososira* (*Hanaki et al., 1990*):

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O$$

Second, anaerobic ammonium oxidizers *Planctomycete-like* ANAMMOX bacteria convert ammonium with the produced nitrite to dinitrogen gas and trace amounts of nitrate (*Strous, 2000*):

$$NH_4^+ + 1.3NO_2^- \rightarrow 1.02N_2 + 0.26NO_3^- + 2H_2O$$

TUDelf - Netherlands
(Hellinga et al., 1998)

The combination (*Strous, 2000*):

$NH4+ + 0.85O2 \rightarrow 0.435N2 + 0.13NO3– + 1.3H2O + 1.4H+$

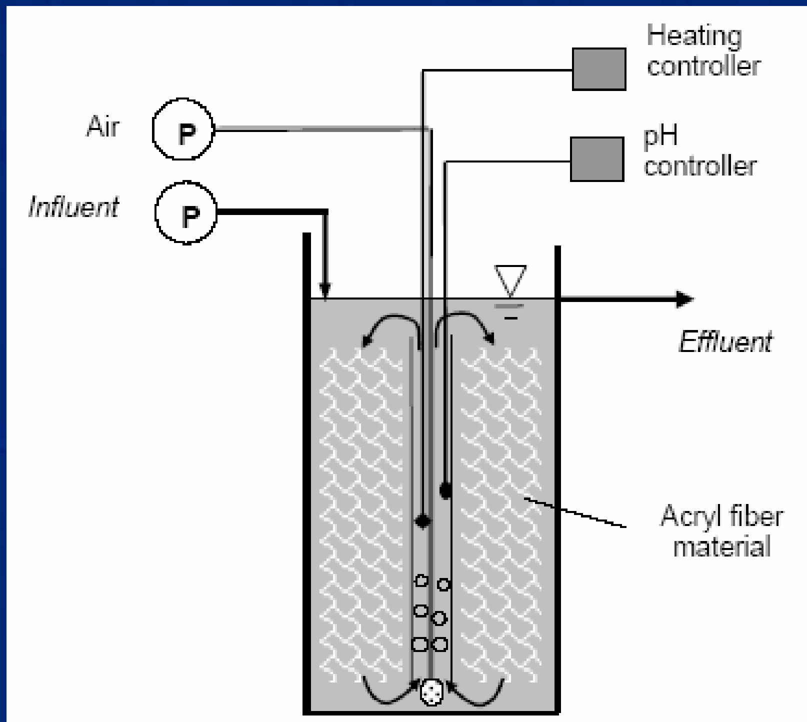
2. Review of N-removal (biol.) (7/7)

5. Other Processes

OLAN process = Oxygen-Limited Autotrophic Nitrification-Denitrification (*Kuai & Verstraete, 1998; Pynaert et al., 2003*)

SNAP process = Single-stage Nitrogen removal using Anammox & Partial nitritation (*Furukawa & Lieu et al., 2005a,b*)

TUDelf - Netherlands
(Hellinga et al., 1998)



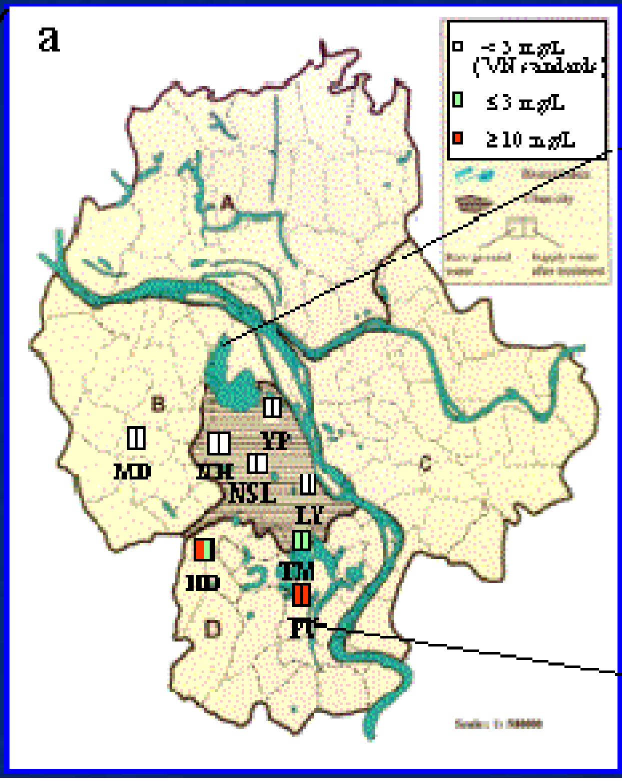
3. Results in Drinking Water Treatment in VN (1/11)

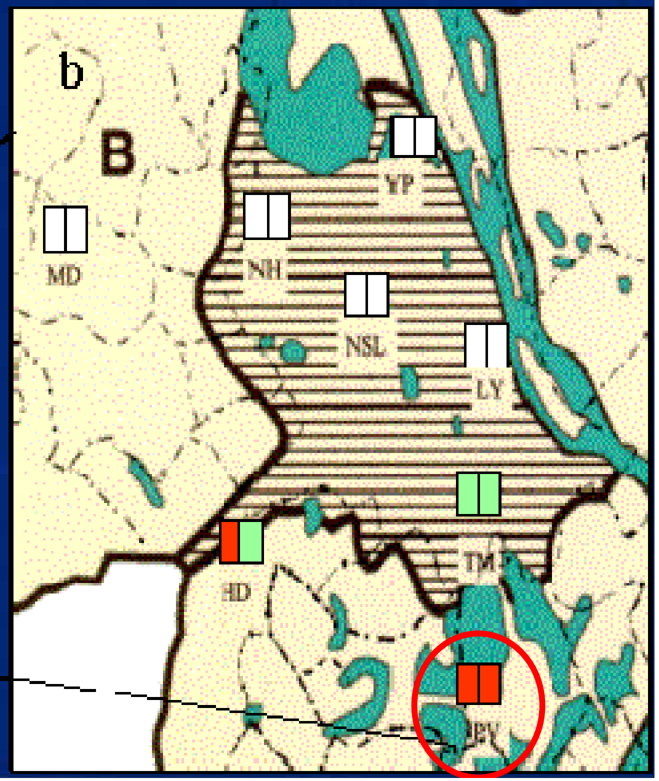
Why do we have to remove N?

Water plants in South Hanoi: Phap Van, Ha Dinh, Tuong Mai & some other smaller stations have high ammonium concentration ranging from 10 to more than 20 mg N/L.

VN standard = WHO, $NH_4^+ \leq 1.5$ mg/L; EU ≤ 0.5 mg/L

$\Sigma(NO_3+NO_2) \leq 50$ mg/L ($NO_2 \leq 3$ mg/L)

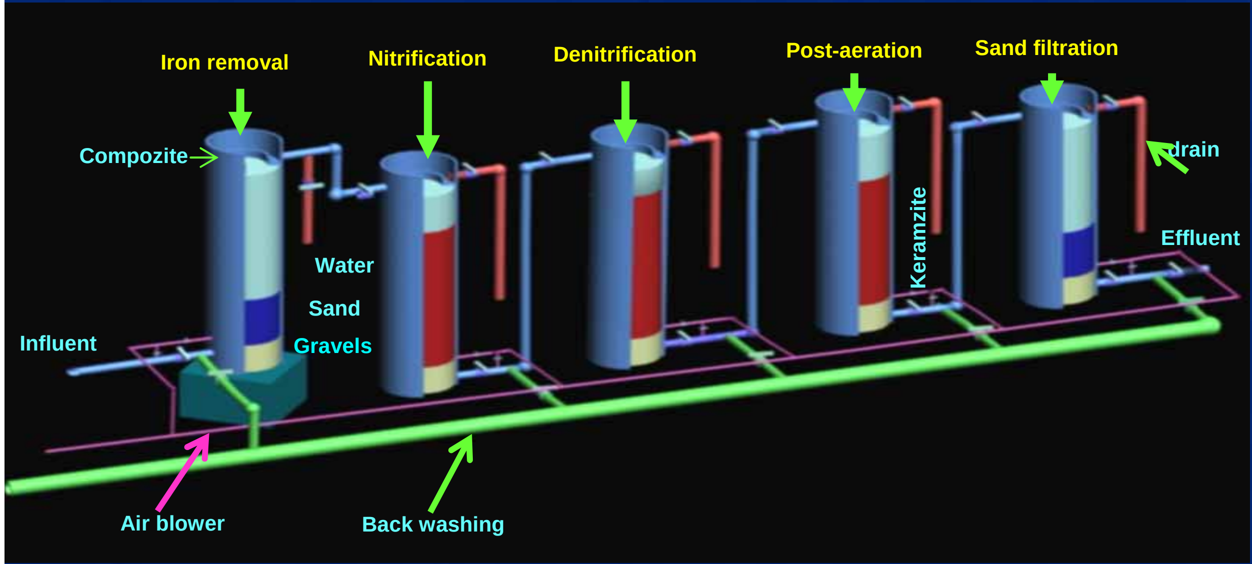


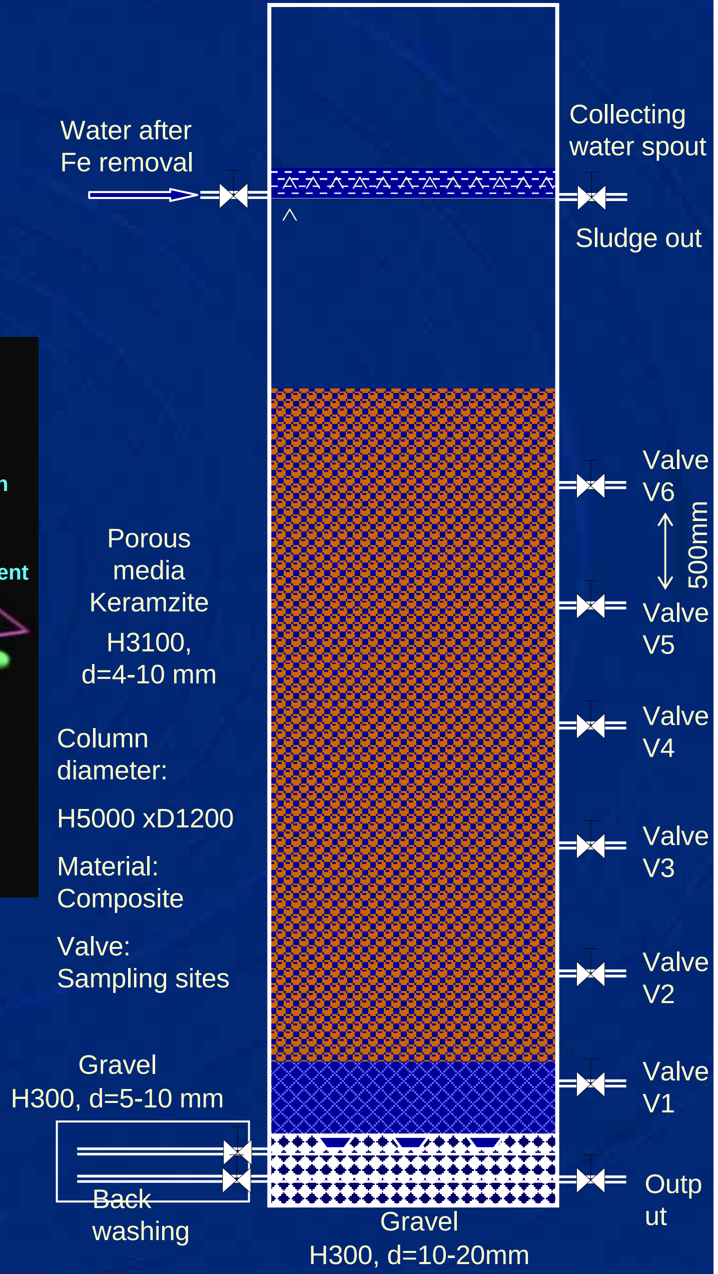


The Target: Phap Van WP
$N\text{-}NH_4^+ \sim 20$ mg/L

3. Results in Drinking Water Treatment in VN (2/11)

Experiment Setup





3. Results in Drinking Water Treatment in VN (3/11)

How to remove ammonium-N biologically?

1. Nitrification:

$$1.02NH_4^+ + 1.89O_2 + 2.02HCO_3^- \rightarrow 0.021C_5H_7O_2N + 1.0NO_3^- + 1.92H_2CO_3 + 1.06H_2O$$

2. Denitrification - DeNR:

$$6NO_3^- + 5CH_3OH \rightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^- \quad (1)$$

$$12NO_3^- + 5C_2H_5OH \rightarrow 6N_2 + 10HCO_3^- + 9H_2O + 2OH^- \quad (2)$$

$$8NO_3^- + 5CH_3COOH \rightarrow 4N_2 + 10CO_2 + 6\ H_2O + 8OH^- \quad (3)$$

3. And Post-aeration

3. Results in Drinking Water Treatment in VN (4/11)

Photos of the pilot plant for Fe and ammonium removal in Phap Van, Hanoi

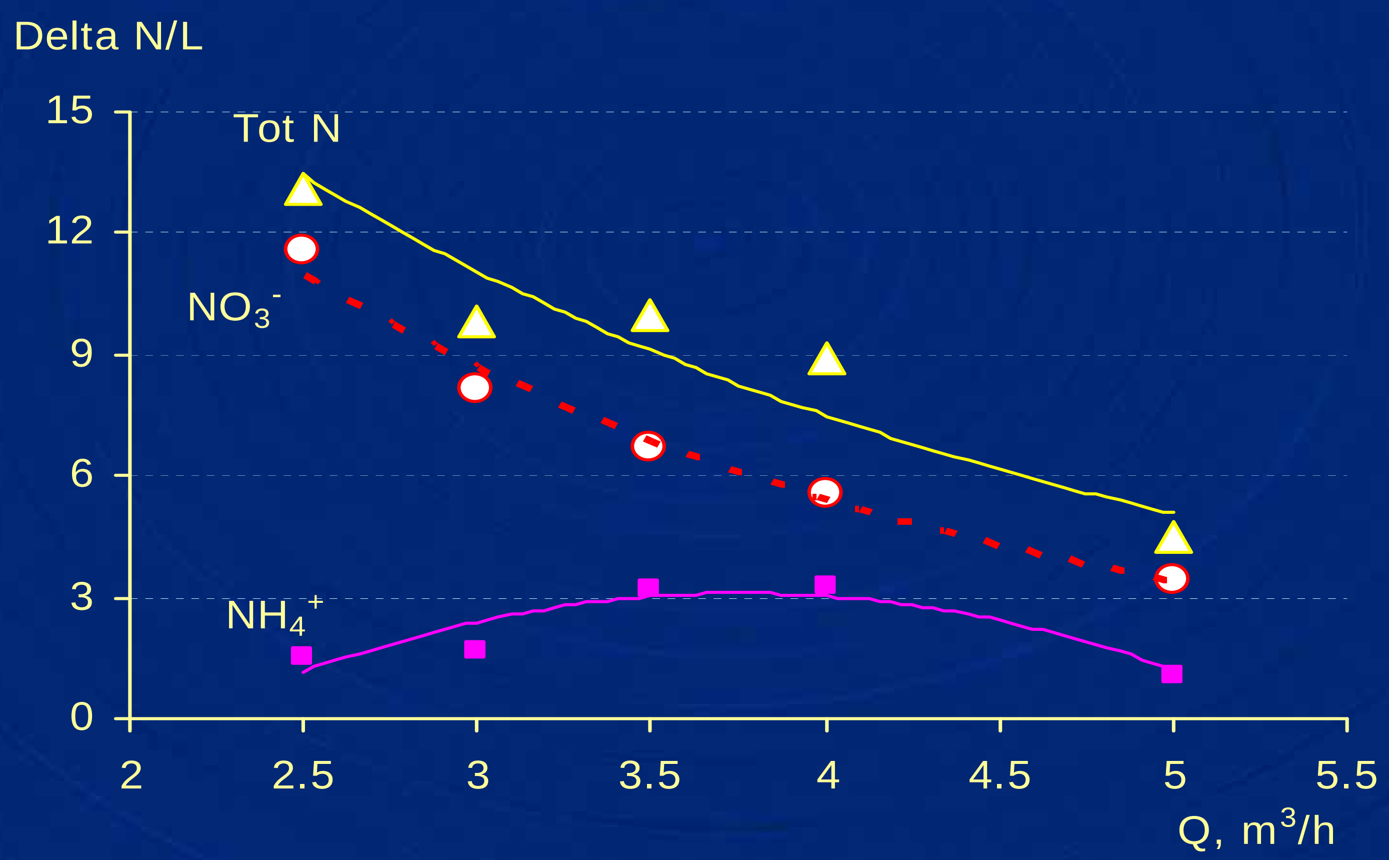
3. Results in Drinking Water Treatment in VN (5/11)

Effluent Quality:

Vietnamese Standards and WHO guidelines of 1.5 mg NH_4^+/L (< 1.17 mg N/L) and < 50 mg/L nitrate (or 11.3 mg N-NO_3^-/L)

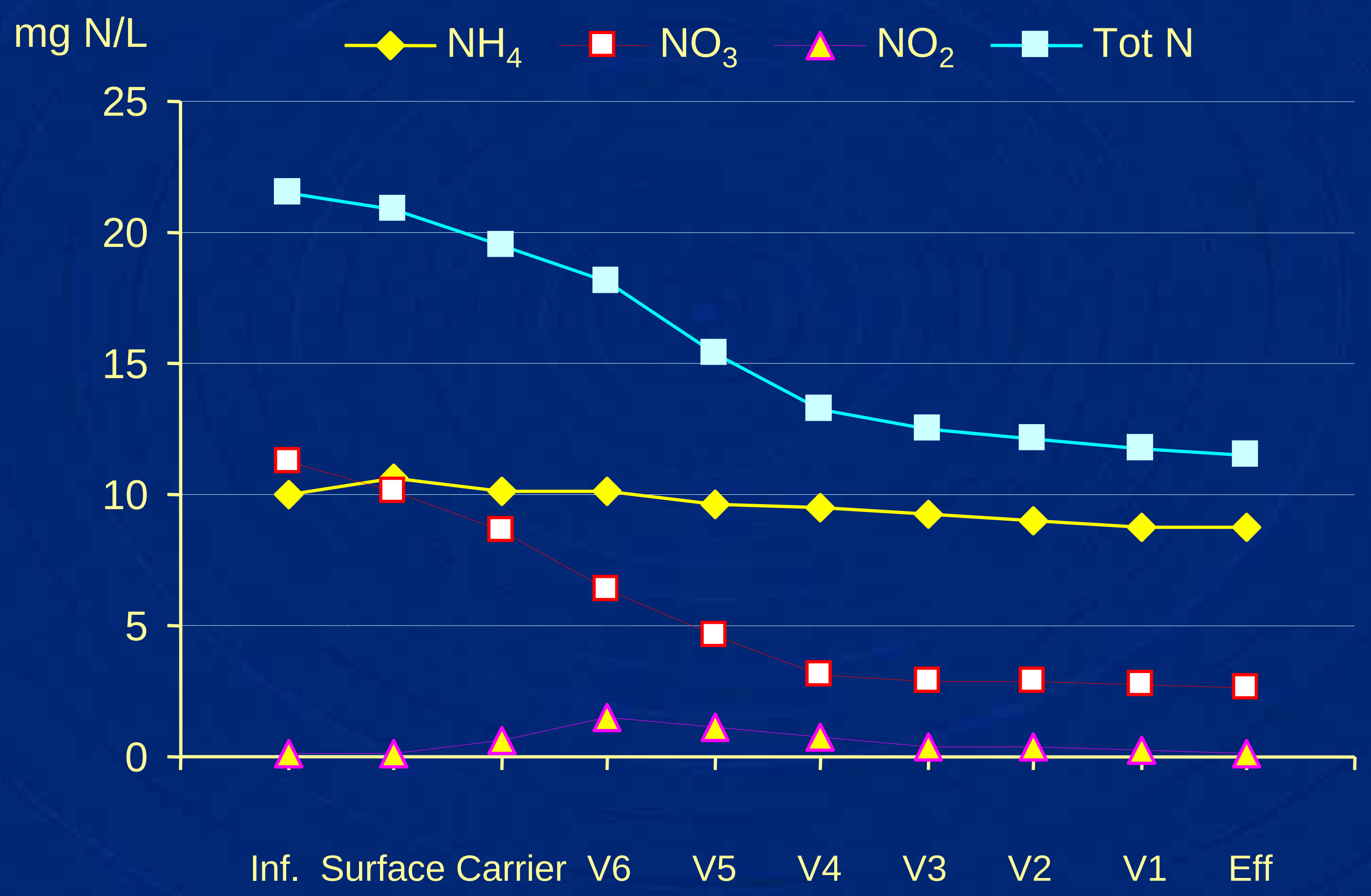
3. Results in Drinking Water Treatment in VN (6/11)

Dependence of nitrogen losses on flow rate



3. Results in Drinking Water Treatment in VN (7/11)

N-concentrations profiles along DENR



3. Results in Drinking Water Treatment in VN (8/11)

– Organic carbon source is acetate or ethanol, theoretical COD/N-NO_3^- ratio = 2.86.

– Actual COD/N-NO_3^- ratio < theoretical,

– Nitrate-N removed always > Total N removed

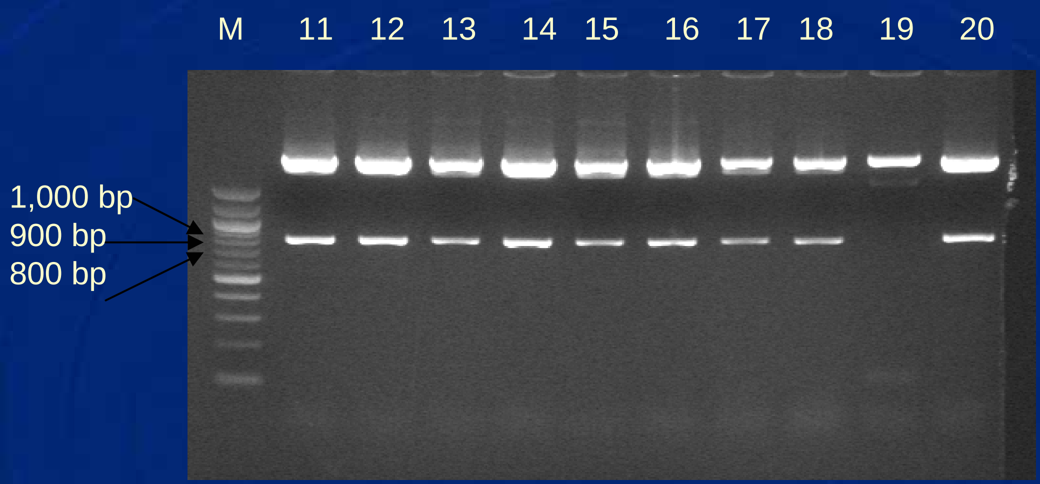
– A part of ammonium-N was also removed along with nitrite formation.

Hypothesis: along with the conventional denitrification there was also ammonium removal via anoxic oxidation by nitrite (*Anammox*) [*Strous et al., 1999*]:

$$NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H^+ \rightarrow$$

$$1.02N_2 + 0.26NO_3^- + 0.066\text{Biomass} + 2.03H_2O \quad (4)$$

3. Results in Drinking Water Treatment in VN (9/11)



M：100 bp DNA ladder
11~20：Plasmid extraction 5 uℓ migration it did the clone sample which does.

Insertion check of figure 4 latter half part

16S rDNA Analysis

The germ whose homology is high	Similarity
Uncultured planctomycetales bacterium (AB176696.1)	95 %
Uncultured anoxic sludge bacterium KU1 (AB054006.1)	94 %
Candidatus brocadia Anammoxidans (AF375994.1)	94 %

Profs. Fuji (Sojo Uni.); Prof. Furukawa & PhD. Lieu (Kumamoto Uni.)

3. Results in Drinking Water Treatment in VN (10/11)

Proposed N-removal mechanisms

Raw water after Fe removal, partially nitrified
NH_4^+ (10.05 mg N/L); NO_3^- (11.29 mg N/L)

COD/NO_3^--N = 2.86

Phase 1:
before valve 5-6

NH_4^+ conversion = 0
NO_3^- + C-organic → NO_2^- accumulation (max N-NO_2^- = 1.5 mg N/L)
NO_3^- + C-organic → N_2 + CO_2 (eqns.1-3)

Phase 2:
After valve 5-6

NH_4^+ + NO_2^- → N_2 + NO_3^- (13.5% Total N removal) (eqn. 4)
NO_3^- (6.4 mgN/L) + C-organic → N_2 + CO_2 (eqns.1-3)

NO_3^- (effluent) = 2.65 mg N/L
Total N removal = 47%

3. Results in Drinking Water Treatment in VN (11/11)

The second N-removal scheme

Fe(II) removal $\rightarrow$ Nitrification $\rightarrow$ Denitrification
(without C, by Slow Sand Filter) ???

$Q = 15\ m^3/h$

$[NH_4^+]_{in} = 18$ mg/L

$[NH_4^+]_{eff} \leq 0.5$ mg/L

TN removal ~ 60%

Xuan Truong
Seafood Export Co.

4. Problem of N-removal in WW Treatment (1/4)

Why N-removal ?

- VN is an agricultural country: ~ 30% GDP; 70% population
- Agri-products processing WW has very high COD, N
- Treatment Cost ust be limited
- Examples: (1) Fishery; (2) Rubber Latex; (3) Animal Farms; (4) Slaughterhouse; (5) Landfil Leachate etc.

Industry	Production Rate, t/a	Volume of Wastewater, m^3/t	Waste Loadings, t/t		Waste Loading, t/a	
			COD	TN	COD	TN
Fishery	3,300,000	80	0.120	0.016	396,000	52,800
Rubber Latex	635,000	20	0.160	0.008	101,600	5,080

4. Problem of N-removal in WW Treatment (2/4)

Current Technology

- Primary treatment (particulate removal)
- Anaerobic (UASB) $\rightarrow$ Aerobic
- Primary Treat. $\rightarrow$ CAS/or Ponds
- Never get eff. Standard, costly
- Waste of Energy & Nutrient
- Causing GHGs emission

4. Problem of N-removal in WW Treatment (3/4)

Current Technology (cont.)

4. Problem of N-removal in WW Treatment (4/4)

Proposal

- Integrated Approach, eg.:

(1) Anaerobic (UASB) $\rightarrow$ 80-90% COD removal; Utilization of CH_4

(2) Aerobic treatment for odor control, partial COD removal

(3) Removal of nutrients by aquatic plants, incl. algae

(4) Biomass utilization as animal/fish/shrim feed (VN has to import “oil cake” for animal feed production, PARADOX !!!)

CONCLUSION

(1) Solving problem of N-removal means “complete” purification of WW

(2) There are many things worth to be recovered: Energy, Materials

(3) Recovery & Reutilization are the future of WW treatment

Thank You
for your attention!!