

Innovative N Removal Technologies

Why we want to remove N?

- Nitrate in drinking water → Blue-baby syndrome
- Nitrogen in water bodies \rightarrow Eutrophication
- Ammonia & Nitrate \rightarrow Highly toxic to fish life
- Because of their negative effects on both humans and environment, reducing nitrogen levels before the discharge is neccesary.

How do we remove nitrogen?

Nitrogen Removal Intro

- There are a number of technologies capable of removing nitrogen:
 - Breakpoint chlorination of ammonia
 - Ion exchange (ammonia or nitrate)
 - Air stripping of ammonia
 - Biological removal
- How is nitrogen removed in biological systems?
 - A certain amount of nitrogen is required for biomass growth
 - By nitrification / denitrification
 - By deammonification (Anammox)

Main N-cycle transformations



Nitrogen Cycle



NITROGEN REMOVAL IN SIDE STREAMS NEW PROCESS DEVELOPED IN COLLABORATION WITH INDUSTRY: Single reactor system for High activity Ammonium Removal Over Nitrite Simple system for N-removal over nitrite

> ANAMMOX Fully autotrophic N-removal

CANON

Combination of nitritation and Anammox

BABE

Bio-augmentation with endogenous nitrifiers

Anammox

The electron donor is ammonium, the electron acceptor is nitrite.

Ammonium (ox. state -3) gets *oxidised* to N2 (0), and nitrite (+3) is *reduced* to N2.

Autotrophic \rightarrow avoids the need for addition of a carbon source, which is sometimes a cost in conventional systems.

All original attempts to isolate the responsible microorganism failed; organism grows extremely slowly (μ max = 0.003 h-1), probably lives in nature at the oxic/anoxic interface.



ANAMMOX equation

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1 \text{ NH}_{4}^{+} + 1.32 \text{ NO}_{2}^{-} + 0.066 \text{ HCO}_{3}^{-} + 0.13 \text{ H}^{+} = 1.02 \text{ N}_{2} + 0.26 \text{ NO}_{3}^{-} + 0.066 \text{ CH}_{2}\text{O}_{0.5}\text{N}_{0.15} + 2.03 \text{ H}_{2}\text{O}
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ANAMMOX® characteristics

- Anaerobic
- Autotrophic





- Biomass yield: 0.05 kg VSS/kg N
- Conversion rate: 1 kg N/kg VSS.d
- Min. doubling time: 11 days (biomass retention is important!)

Characteristics of Anammox Bacteria



Characteristics of Anammox Bacteria

• Anammox culture has a brownish-red color, probably due to a high cytochrome content











Environmental Factors Affecting Anammox Process

 Maximum activity of Anammox biomass is observed between 35 & 40 °C, while a temperature of 45 °C causes an irreversible decrease of the Anammox activity due to biomass lysis

 \rightarrow can be successfully operated at 18 °C.

When temperature is decreased to 15 °C, the maximum capacity of the reactor also decreased and the system turned unstable due to nitrite accumulation

Environmental Factors Affecting Anammox Process

- Ammonia and nitrate do not inhibit the anammox process until a certain concentration but anammox bacteria are very sensitive to oxygen and nitrite.
- The process is inhibited by nitrite concentrations higher than 20 mM. When the nitrite concentration is more than 5 mM for a longer period (12 h), anammox activity is completely lost.
- Oxygen concentration as low as 20µM inhibit the anammox activity completely but reversibly.
- Phosphate has also strong inhibition of Anammox activity between the concentrations 5 mM and 50 mM

Start-up of the Anammox Process

- Because of low biomass yield → Using a system that avoids biomass wash-out with the effluent and maximises the biomass concentration in the system is very important
- Even a slight loss of biomass supposes a delay in the time required to obtain the desired loading rate.

Role in nature



Did you know?

•That most of the air we breathe is made by ANAMMOX bacteria?



Anammox

Process only known from one species:

chemolitho-autotrophic planctomycete Brocadia anammoxidans

Energy generation:

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

Carbon fixation:

 $CO_2 + 2 NO_2^- + H_2O \rightarrow CH_2O + 2 NO_3^-$

Measured overall growth at r = 0.0014 h⁻¹ (Strous, 2000):

 $1 \text{ NH}_4^+ + 1.32 \text{ NO}_2^- + 0.066 \text{ HCO}_3^- + 0.13 \text{ H}^+ \rightarrow$

 $1.02 \text{ N}_2 + 0.26 \text{ NO}_3^- + 0.066 \text{ CH}_2\text{O}_{0.5}\text{N}_{0.15} + 2.03 \text{ H}_2\text{O}$ Known:

 N_2 comes from NH_4^+ and NO_2^- N in biomass comes from NH_4^+



ANAMMOX® vs Conventional

	Conventional treatment	ANAMMOX®	
Power	3 - 5	1 - 2	kWh/kg N
Methanol	2.5 - 3	0	kg/kg N
Sludge production	0.5 – 1.0	0.1	kg VSS/kg N
CO ₂ emission	> 4.7	0.7	kg/kg N
Total Costs ¹	3 – 5	1 – 2	€/kg N

¹Total Costs includes both operational cost and capital charge

Advantages ANAMMOX[®] process

- Most cost effective
- No external C-source (methanol) required
- Power consumption reduced by ~ 60%
- CO₂ emission reduced by ~ 90 %
- Limited production of excess sludge
- Compact

- Anammox process can be used for all types of influents with a high ammonium concentration (NH₄+-N > 100 mg/l)
 - Municipal wwtp (rejection water from a sludge digester)
 - Organic solid waste treatment
 - Food industries
 - Manure processing industries
 - Fertilizer industries
 - (Petro)chemical industries
 - Metallurgical industries
 - Mining industries

HISTORY AND STATUS ANAMMOX





Research & process scale-up

ATKINS

SHARON

- The Netherlands: Rotterdam, Utrecht, Zwolle, Beverwijk, Garmerwolde and Den Haag (total capacity 2,740,000 PE)
- USA: New York (3,000,000 PE)
- Switzerland: Zurich (?)

ANAMMOX

- The Netherlands: Rotterdam
- Germany: Hattingen
- Sweden: Stockholm



ATKINS

The first full-scale Anammox reactor, Rotterdam, the Netherlands.

It works at design load and removes over 500 kg N/day.

Photo: Paques BV

Source: anammox.com

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SHARON PROCESS

NITRITIFICATION

- Nitrification 2 step process
 Ammonium → Nitrite → Nitrate
- By denitrifying nitrite instead of nitrate big advantage possible
- Need: Preferential selection for ammonium oxidisers

Competing out nitrite oxidisers

• Strong Factors Effect of Temperature on Growth Rate

T < 20 C: Nitrite Oxidation faster T > 20 C: Ammonium Oxidation faster

At higher temperature a growth rate or sludge age exists where ammonium is oxidised but nitrite is not converted

High Ammonium content or Nitrite content <u>in</u> reactor > 3-5 gN/L



NITRITATION

CONVENTIONAL AMMONIUM REMOVAL:

Nitrification: $2 \text{ NH}_4^+ + 4 \text{ O}_2 \rightarrow 2 \text{ NO}_3^- + 4 \text{ H}^+ + 2 \text{ H}_2\text{O}$ Denitrification: $2 \text{ NO}_3^- + 8\text{g} \text{ COD} + 2 \text{ H}^+ \rightarrow \text{N}_2 + 3\text{g} \text{ SLUDGE}$

 $2 \text{ NH}_4^++4 \text{ O}_2^+8 \text{ COD} \rightarrow \text{N}_2^+2 \text{ H}^++3\text{g} \text{ SLUDGE}$

NITRITATION:

Nitritification: $2 \text{ NH}_4^+ + 3 \text{ O}_2 \rightarrow 2 \text{ NO}_2^- + 4 \text{ H}^+ + 2 \text{ H}_2\text{O}$ Denitritification: $2 \text{ NO}_2^- + 4.8\text{g} \text{ COD} + 2 \text{ H}^+ \rightarrow \text{N}_2 + 1.8\text{g} \text{ SLUDGE}$

 $2 \text{ NH}_4^++3 \text{ O}_2^-+4.8 \text{ COD} \rightarrow \text{N}_2^+2 \text{ H}^++1.8 \text{g} \text{ SLUDGE}$

Wastewater treatment plant:



NITROGEN REMOVAL IN SIDE STREAMS

CHARACTERISTICS. HIGH CONCENTRATION → SMALL TANK VOLUME HIGH TEMPERATURE

SHORT SRT POSSIBLE 10-30 % OF THE LOAD TO WWTP SMALL VOLUME NO ABSOLUTE NEED FOR GOOD EFFLUENT → POTENTIAL TO REMOVE NITROGEN IN COMPACT REACTOR BY ALTERNATIVE METHODS



Short-Circuited Nitrification/Denitrification Pathway

The SHARON Process



- continuous stirred tank reactor (= CSTR)
- no biomass retention: sludge retention time = hydraulic retention time
- pH=7 ; T = 35°C :

ammonium oxidizers grow faster than nitrite oxidizers

- \Rightarrow nitrite oxidizers are washed out by keeping retention time low
- \Rightarrow partial nitritation to nitrite is achieved

The

Anammox process



Simplified reaction:

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

The SHARON-Anammox process



nitrite:ammonium ≈ 1:1 produced by SHARON

if bicarbonate:ammonium \approx 1:1 in SHARON influent

Simplified reaction:

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

⇒ Optimal ratio nitrite:ammonium = 1:1

Rotterdam WWTP

Combination Sharon-Anammox



CANON

Completely Autotrophic Nitrogen Removal Over Nitrite

CANON

- Removes ammonia
 - in a single step
 - Oxygen limited environment
- CANON process relies on cooperation of
 - *Nitrosomonas*-like aerobic + *Planctomycete*-like ANAMMOX bacteria
 - If the balance is disturbed \rightarrow it may interefere with N removal.
- German researchers call such a single-stage conversion of ammonium into molecular nitrogen →deammonification
- Another name for CANON: OLAND (oxygen-limited autotrophic nitrification-denitrification
- Little practical experience is available for the Canon process
- A proper Oxygen condition in a bulk liquid was found as the most important factor affecting the process.

Canon

CANON (Completely Autotrophic Nitrogen removal Over Nitrite)

Cooperation between aerobic and anaerobic ammonium oxidisers under oxygen limitation.

Completely autotrophic \rightarrow promising opportunity for wastewaters with a very low organic carbon content (eg. landfill leachates, aquaculture waste).

• Ammonium is oxidised to nitrite by aerobic ammonium oxidisers (Nitrosomonas, Nitrosospira etc.);

 $\mathsf{NH4+} + 1.5 \text{ O2} \rightarrow \mathsf{NO2-} + 2 \text{ H} + \text{ H2O}$

- The nitrite produced can be used by anammox; NH4+ + 1.3 NO-2- \rightarrow N2 + 2 H2O
- Overall nitrogen removal by CANON:

 $1 \text{ NH4+} + 0.75 \text{ O2} \rightarrow 0.5 \text{ N2} + 1.5 \text{ H2O} + \text{H+}$

Advantages of CANON system; low aeration costs (60% less than traditional systems), requires no addition of a carbon source (process is autotrophic) and the only end product is N2.

