The EU funded SWIM-SM: developing capacity for Sustainable and Integrated Wastewater Treatment and Reuse

Online Course on Natural Treatment Systems: Denitrification

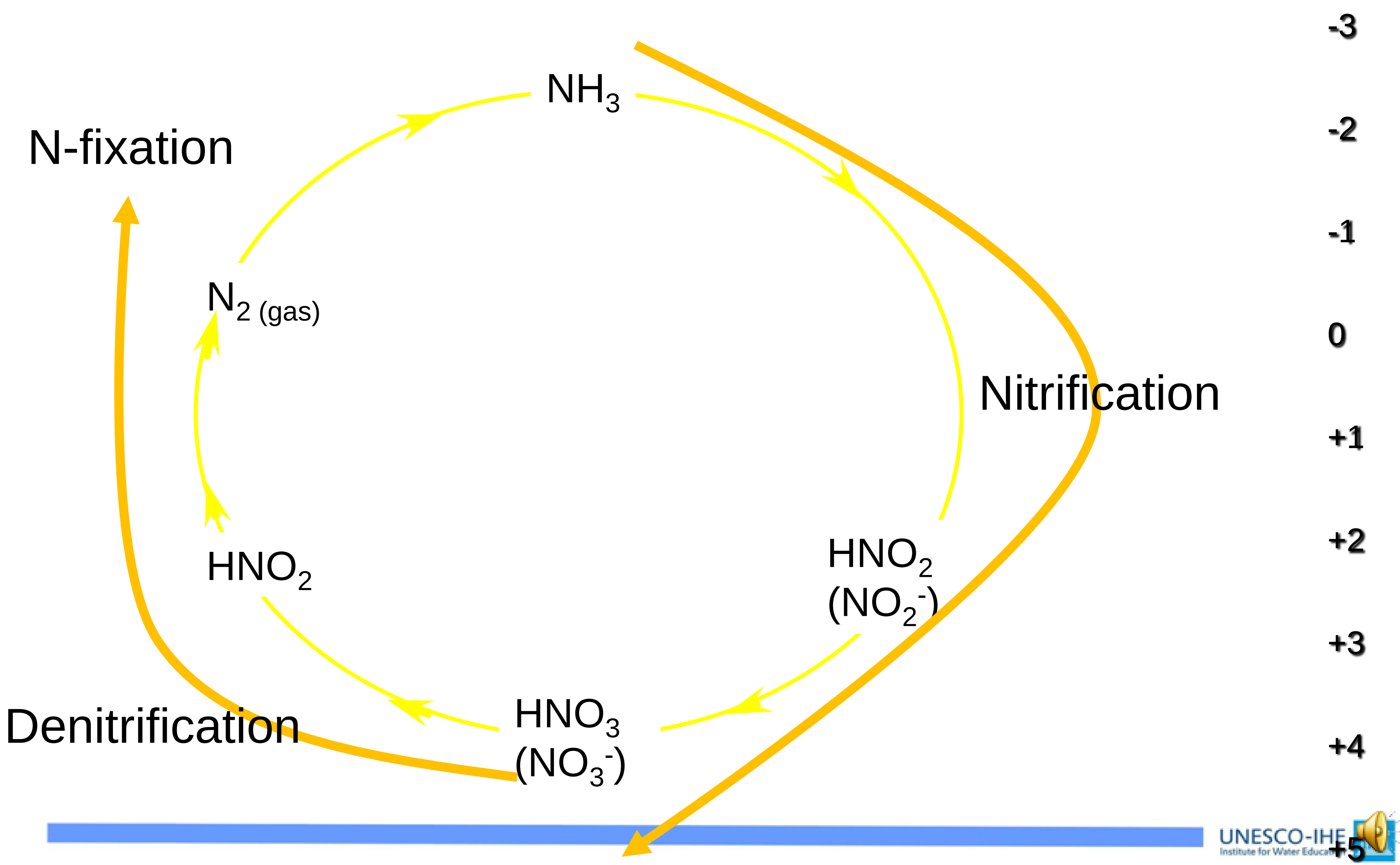
Denitrification

SWIM OLC

on

Natural Treatment Systems

TEXT BOOK N-CYCLE



N-removal in natural systems

- Ammonia stripping! (does not deplete the ozone layer and does not contribute to global warming)
- **Nitrification-denitrification**
- Methane and nitrous oxide emissions!
- Ammonia and nitrate assimilation by algae (exit with effluent)
- Assimilation by plants
- Sedimentation of particulate organic N

De-nitrification

The biological reduction of nitrate (NO_3) by facultative heterotrophic organisms.

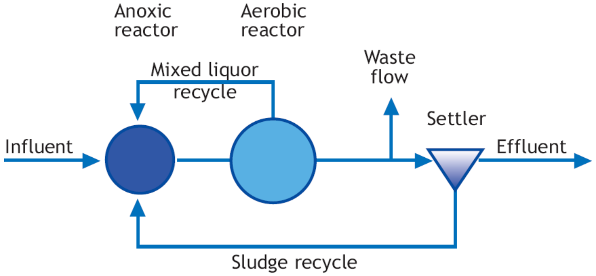
Catabolism:

Nitrate reduction to N_2 gas (anoxic):

$$NO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}N_2 + 3H_2O + \text{Energy}$$

Benefits

- Reduction in effluent nitrate conc
- Reduction of rising sludge in SSTs
- Reduction in oxygen demand
- Recovery of alkalinity
- Higher reactor pH
- Reduced aggression to concrete



Whenever nitrification is possible, include denitrification even if not required!

Disadvantage

- Will require longer sludge age to ensure nitrification. With denitrification..
  - …reactor volume is larger
  - …less WAS produced but more stable
- Mixed liquor recycle pumps
- Slightly more complex system

Benefits of denitrification far outweigh disadvantages!

Design principle

- Need to calculate mass of electron donors (organics, COD) required for utilization of known mass of electron acceptors (nitrate).

Design principle

- Calculation for nitrate removal is essentially a reconciliation of electron acceptors (nitrate) and donors (WW or dosed organics, COD) taking due consideration of ...

(1) Biological kinetics of denitrification,

(2) System operating constraints (anoxic reactor size and recycle ratios).

N-removal from WW

Two main processes of N removal:

(1) Sludge production – N incorporated in AS and removed via waste activated sludge (WAS)

(2) Biological denitrification –

$NO_3^- \rightarrow N_2$ gas.

N REMOVAL VIA WAS

- N content of WAS ≈ 0.10 mgN/mgVSS.
- Includes N in active (X_{BH}), endogenous (X_E) and inert solids (X_I) of WAS.
- Removes 15-20% of influent TKN

Stoichiometry: catabolism

Nitrate to nitrite:

$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$ + Energy

Nitrite to nitrogen gas:

$NO_2^- + 4H^+ + 3e^- \rightarrow \frac{1}{2}N_2 + 2H_2O$ + Energy

Usually nitrate is reduced directly to N_2 gas:

$NO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}N_2 + 3H_2O$ + Energy

$5H^+$ and $5e^-$ supplied by organics.

O_2 equivalent of NO_3^-

Nitrate reduction to N_2 gas (anoxic):

$NO_3^- + 6H^+ + 5e^- \rightarrow ½N_2 + 3H_2O$ + Energy

Oxygen reduction to water (aerobic):

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

So e^- accepting capacity of nitrate

= (32/4) / (14/5) → 2.86 mgO/mgNO_3^-N

(Organics are e^- donor)

Impact on oxygen demand

- Nitrification consumes 4.57 mgO/mgN
- Denitrification recovers 2.86 mgO/mgN
- So 2.86/4.57 = 63% oxygen recovered!

Impact on alkalinity

$NO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}N_2 + 3H_2O$ + Energy

($5H^+$ from organics + $1H^+$ from bulk liquid)

= (1*50)/14 = 3.57 mg/l $CaCO_3$ generated per mgNO_3-N/l denitrified.

Nitrification consumes 7.14 mg/l $CaCO_3$.

So denitrification recovers half the alkalinity lost in nitrification.

Comparison: nitrification vs denitrification

Compound:	NH^+_4	N_2	NO^-_2	NO^-_3
Oxidation state:	-3	0	+3	+5

Nitrification (oxidation)

8 e^- atom N = 4.57 mgO_2/mgN

Net loss

Denitrification (reduction)

5 e^- atom N = 2.86 mgO_2/mgN

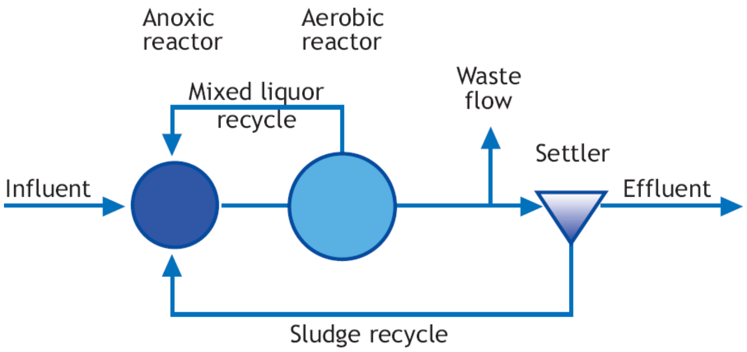
Nitrification: 4.57 $mgO_2/mgNH_4$-N nitrified to NO_3–N

Denitrification: 2.86 mgO_2 recovered/mg NO_3-N denitrified to N_2 gas

Therefore, denitrification allows at best 62.5% (5/8 or 2.86/4.57) recovery of the nitrification oxygen demand

Requirements for denitrification

- Presence/input of nitrate
- Absence of DO (unaerated zone)
- Facultative heterotrophic biomass
- Suitable electron donor (organics).



Absence of DO

DO is inhibitory on denitrification

DO = 0 mg/l -- Denitrification 100%

DO = 0.5 mg/l – Denit < 10%

Even if DO conc is zero in reactor, DO entering reactor is used first, reducing the nitrate removal by the reactor.

Facultative biomass

- Ability to denitrify widespread among OHOs
- In AS systems, significant number of OHOs are facultative (can denitrify).

Electron donor

- Organics serve as electron donor (ED).
- Sources of organics are:
  - (1) Internal ED – present in wastewater
  - (2) Self generated (ED) - via endogenous respiration
  - (3) External (ED) – dosed to system e.g. methanol or other organics.

Denitrification kinetics

- $d(NO_3\text{-}N)/dt = -K\,X_{BH}$ $mgNO_3\text{-}N/(L.d)$

  K = specific denitrification rate

  $mgNO_3\text{-}N/(mgOHOVSS.d)$

- X_{BH} obtained from steady state model.
- K rates now more consistent with sludge age (R_s).

Denitrification k rates

- Large data base of profiles at 14 and 20°C:

$K_1 = 0.72\ (1.2)^{(T-20)}$ (halves in 4°C)

$K_2 = 0.101\ (1.08)^{(T-20)}$ (halves in 9°C)

$K_3 = 0.072\ (1.03)^{(T-20)}$ (halves in 23°C)

Note units of K: $mgNO_3$-N/(mgOHOVSS.d)

Summary

Effect of denitrification on system:

- Sludge age will be longer since nitrification is obligatory – larger reactor volume.
- Reduction in oxygen demand over fully aerobic system with nitrification.
- Increase in alkalinity and pH.

Denitrification should always be included where nitrification is possible.