Wastewater treatment processes overview II

Today's lecture

- Biological nutrient removal (BNR) processes
 - Nitrification: oxidation of ammonia-N
 - Denitrification: reduction of nitrate-N to N₂
 - Anammox
 - Enhanced biological P removal

Biological oxidation of nitrogen

- Necessity for NH₄-N & NO₂-N oxidation
 - The effect of ammonia on receiving water with respect to DO concentrations and fish toxicity
 - The need to provide nitrogen removal to control eutrophication
 - The need to provide nitrogen control for water-reuse applications

Nitrification

- Two-step biological process: NH_4 -N → NO_2 -N & NO_2 -N → NO_3 -N
- − The first step $[NH_4-N \rightarrow NO_2-N]$ is termed as "nitritation"
- Different type of microorganisms are involved for each step

Nitrification – processes & microbiology

Process

- Both suspended & attached growth applicable
- Suspended growth nitrification processes
 - Note nitrifying bacteria are less competent than aerobic heterotrophs

 need maintaining low BOD conc. to activate them!
 - So: operate the reactor at higher SRT than what's needed for BOD removal

Microbiology

- Ammonia-oxidizing bacteria (AOB) & nitrite-oxidizing bacteria
 (NOB) --- aerobic chemoautotrophs
- AOBs: Nitrosomonas (+Nitrosospira)
- NOBs: Nitrobacter (+Nitrococcus, Nitrospina, Nitrospira)

Nitrification stoichiometry

AOB (nitration): $2NH_4^+ + 3O_2^- + 2NO_2^- + 4H^+ + 2H_2O$

NOB: $2NO_2^- + O_2 \rightarrow 2NO_3^-$

Overall: $NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$

Note: This is the stoichiometry for energy reaction (NOT considering biomass growth)

- Oxygen requirement: 2 mole $O_2/1$ mole NH_4^+ = 4.57 g O_2/g NH_4 -N oxidized
- Alkalinity consumption: 2 eq alkalinity/1 mole NH_4^+ = 7.14 g Alk as $CaCO_3/g NH_4-N$ oxidized
- Nitrification cell yield: 0.10~0.15 for AOB & 0.04~0.07 for NOB
- Considering biomass production, the O₂ requirements and alkalinity consumption is slightly less than the calculated values above (<u>why??</u>)

Nitrification stoichiometry

ex) Assuming Y=0.12 g VSS/g NH_4 -N for AOB and Y=0.04 g VSS/g NO_2 -N for NOB, the overall stoichiometry is:

$$NH_4(HCO_3) + 0.9852Na(HCO_3) + 0.0991CO_2 + 1.8675O_2 \rightarrow$$

$$0.01982C_5H_7O_2N + 0.9852NaNO_3 + 2.9232H_2O + 1.9852CO_2$$

→ 1.8675 mole $O_2/1$ mole NH_4^+ 1.9852 eq Alk/1 mole NH_4^+

Environmental factors affecting nitrification

DO concentration

- Nitrifying bacteria are more sensitive to DO than heterotrophs
- Nitrite oxidation is inhibited more at low DO than ammonia oxidation
 → elevated NO₂-N concentration at low DO

pH

- Optimum at pH of 7.5~8.0
- Ammonia oxidation rate reduces significantly at pH<7.0
- Possibly due to the reduction of free ammonia (NH₃) concentration
- Sufficient alkalinity is needed!
- For wastewater with high NH₄⁺ concentrations and low alkalinity,
 addition of alkalinity may be needed (lime, soda ash, NaHCO₃, ...)

Environmental factors affecting nitrification

Toxicity

- AOB is sensitive to a wide range of organic & inorganic compounds
- Show significantly reduced ammonia oxidation rate in the presence of toxic substances

Free ammonia & nitrous acid inhibition

- NH₃-N & HNO₂
- High pH: NH_3 -N \uparrow / low pH: $HNO_2 \uparrow$

Denitrification

Biological reduction of nitrate (NO₃-) or nitrite (NO₂-) to nitrogen gas (N₂)

Denitrification required

- To complete the biological nitrogen removal process
- Otherwise, <u>accumulation of NO₃-N</u>: health threats!
- "Blue baby syndrome"
- Korean regulation: < 10 mg NO₃-N/L

Usually by heterotrophic bacteria

- Wide range of heterotrophs mostly facultative aerobes
- Some autotrophs are capable of nitrate/nitrite reduction
 - Use Fe⁰, Fe²⁺, S²⁻, S⁰, ..., or NH₄⁺

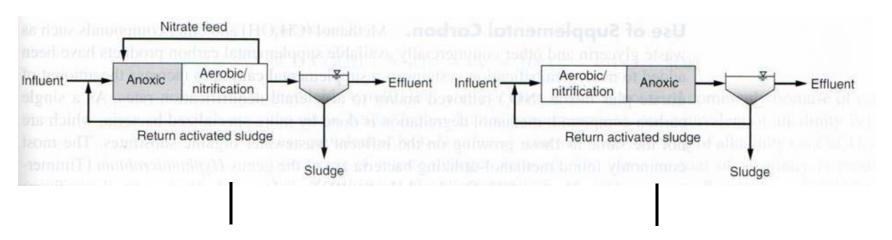


Denitrification

- Two modes of nitrate removal in biological processes
 - Assimilatory nitrate reduction
 - Reduction of NO₃-N to NH₄-N for use in cell synthesis when NH₄-N is not available
 - Independent of DO concentration
 - Dissimilatory nitrate reduction: much more significant!
 - Nitrate/nitrite serves as an electron acceptor
 - When DO is absent or limited
 - Mostly facultative bacteria
 - Nitrate reduction proceeds through a series of intermediate products:

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

Denitrification processes



Preanoxic denitrification

- Electron donor provided by influent
- MLE (Modified Ludzak-Ettinger) process: most common for biological nitrogen removal in municipal wastewater treatment

Postanoxic denitrification

- BOD not available in anoxic reactor: denitrification by endogenous decay
- Much slower rate than preanoxic
- Often external carbon source is added (e.g. methanol, acetate)

Denitrification Stoichiometry

Wastewater: $C_{10}H_{19}O_3N + 10NO_3^- \rightarrow 5N_2 + 10CO_2 + 3H_2O + NH_3 + 10OH^-$

Methanol: $5CH_3OH + 6NO_3^- \rightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^-$

Acetic acid: $5CH_3COOH + 8NO_3^- \rightarrow 4N_2 + 10CO_2 + 6H_2O + 8OH^-$

Production of alkalinity

- 3.57 g Alk as CaCO₃ produced per g NO₃-N (or NO₂-N) reduced
- 50% of alkalinity consumed by nitrification can be recovered

DeN - Organic substrate requirements

- A sufficient amount of organic substrate (e⁻ donor) should be available
 - bsCOD or BOD as an important design parameter
 - Sources of e⁻ donor for denitrification
 - 1) bsCOD in the influent
 - 2) bsCOD produced during biological hydrolysis
 - 3) bsCOD produced during endogenous decay
 - 4) External source such as methanol or acetate
 - ~4 g BOD required per g NO₃-N reduced
 - actual requirement depending on operating conditions and the type of edonor
 - Especially important to determine the BOD requirements when external carbon source is provided

Simultaneous nitrification and denitrification

- In activated sludge floc (suspended growth) or biofilm (attached growth)
- Local conditions in the floc or biofilm may be different from bulk liquid
- High DO at the exterior and low DO inside

 conditions for nitrification and denitrification may develop in a single floc or biofilm
- Can be significant if optimal conditions are developed

Anammox process

- Anaerobic ammonia oxidation
- Anaerobic oxidation of ammonia to produce nitrogen gas

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

 $e^- donor \quad e^- acceptor$

- Requires aerobic nitritation of ammonia to NO_2^- for the process to occur (~55% conversion of NH_4 -N to NO_2 -N)
- By autotrophic bacteria
 - → No organic carbon consumption during the process

Anammox process

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

- Proposed metabolic model (Van de Graaf et al., 1997)
 - Reduction of nitrite to hydroxylamine (NH₂OH)
 - 2) Condensation of hydroxylamine with ammonium to hydrazine (N₂H₄)
 - 3) Oxidation of hydrazine to nitrogen gas
- Some formation of NO₃-N from NO₂-N
 - To provide the reducing power to fix CO₂

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

• Overall reaction (Strous et al., 1999)

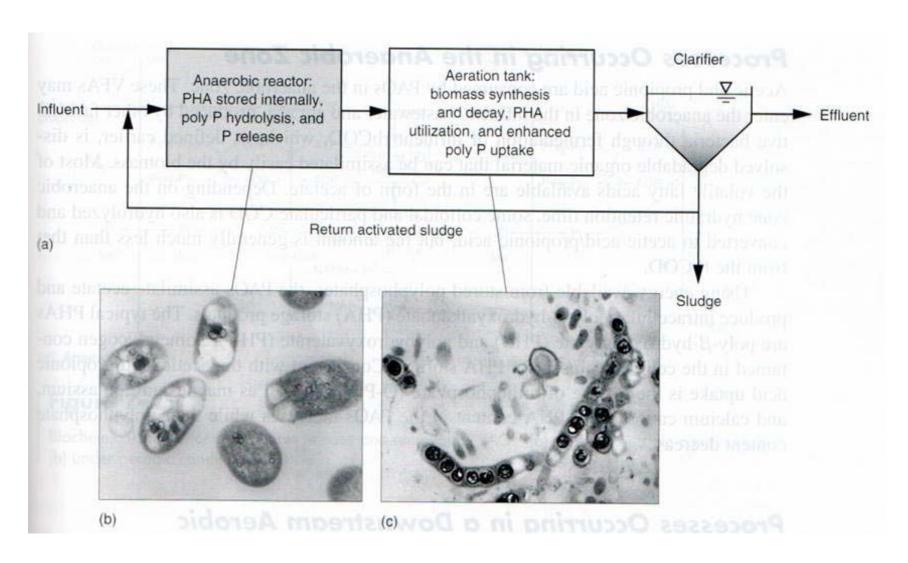
$$1.0NH_4^{+} + 1.32NO_2^{-} + 0.066HCO_3^{-} + 0.13H^{+}$$

$$\rightarrow 1.02N_2 + 0.26NO_3^{-} + 0.066CH_2O_{0.5}N_{0.021} + 2.03H_2O_{0.00}$$

Enhanced biological P removal

- Involves incorporation of P in the biomass produced in the treatment system and subsequent removal of the biomass as waste sludge
- Biomass of heterotrophic bacteria contains ~0.015 g P/g VSS
 - Insufficient to remove P from influent wastewater (only 10~20% of total)
- Use phosphorus accumulating organisms (PAOs) for enhanced biological phosphorus removal (EBPR)
- Reduced chemical costs and less sludge production compared to chemical precipitation

Enhanced biological P removal



EBPR – Process description

- Place an anaerobic tank ahead of the aeration tank
 - Provide <u>selectivity</u> for growth of PAOs
- In the anaerobic tank, PAOs consume energy stored in the form of polyphosphates
 - The energy generated is used to convert volatile fatty acids into carbohydrate storage products (PHA)
- In the aerobic tank, PAOs consume COD & stored PAH for biomass growth
 - Use some of the energy for enhanced P uptake to store polyphosphates
- So:
 - Anaerobic tank: PHA accumulation & P release
 - Aerobic tank: <u>excessive P uptake & PHA utilization</u>
- PAOs form very dense floc with good settleability additional benefit

EBPR – Process description

Process occurring in the anaerobic zone

- Volatile fatty acids (VFAs) are produced by fermentation
- VFAs are assimilated by PAOs into PHAs by energy available from stored polyphosphates
 - Typical PHAs: poly-β-hydroxybutyrate (PHB) & polyhydroxyvalerate (PHV)
 - Some glycogen contained in the cell is also used

Processes occurring in the aerobic/anoxic zone

- Stored PHA is metabolized to provide energy for cell growth
- Some glycogen is produced from PHA metabolism
- Soluble orthophosphate in solution in taken up by PAOs to form polyphosphates in the existing cells and the new cells
- Portion of the biomass is wasted → P removal
- The process can occur in the anoxic zone as well $(NO_3^- \text{ or } NO_2^- \text{ as } e^- \text{ acceptors})$