

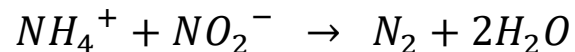
Biological nutrient removal

Today's class

- Oxidation of ammonia ($\text{NH}_4^+/\text{NH}_3$): **nitrification**
- Reduction of nitrate (NO_3^-): **denitrification**
- **Enhanced biological P removal**

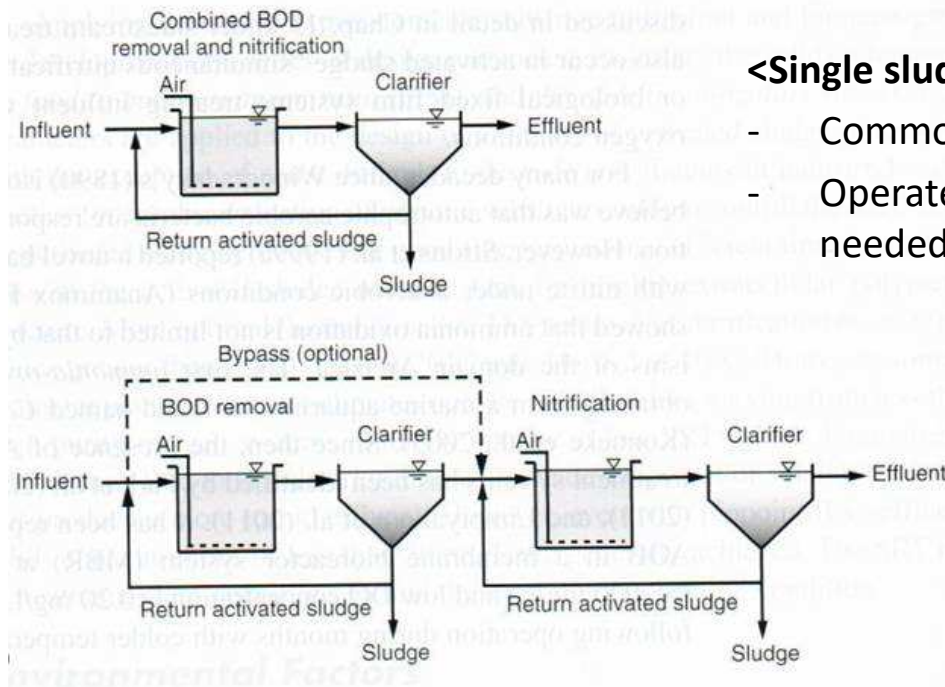
Biological oxidation of nitrogen

- Necessity for $\text{NH}_4\text{-N}$ & $\text{NO}_2\text{-N}$ 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: $\text{NH}_4\text{-N} \rightarrow \text{NO}_2\text{-N}$ & $\text{NO}_2\text{-N} \rightarrow \text{NO}_3\text{-N}$
 - The first step [$\text{NH}_4\text{-N} \rightarrow \text{NO}_2\text{-N}$] is termed as “nitritation”
 - Different type of microorganisms are involved for each step
- **Anammox process**
 - Anaerobic Ammonia Oxidation
 - Some bacteria can oxidize ammonia with nitrite under anaerobic conditions:



Nitrification processes

- Both suspended & attached growth applicable
- Suspended growth nitrification processes
 - Note nitrifying bacteria are less competent than aerobic heterotrophs → need maintaining low BOD concentration to activate them!



<Single sludge suspended growth system>

- Common
- Operate at high SRT than what's needed for BOD removal

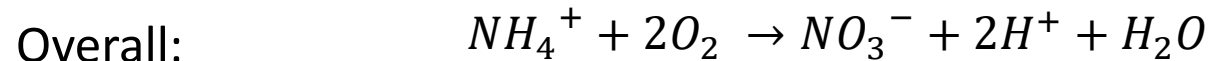
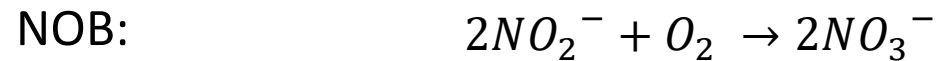
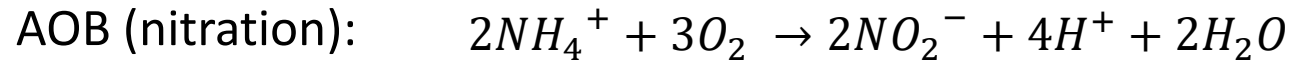
<Two-sludge suspended growth system>

- Good for wastewater containing toxic substances
- 1st unit operated at short SRT for BOD removal (+toxic removal)
- 2nd unit for nitrification at low BOD

Microbiology of nitrification

- Ammonia-oxidizing bacteria (AOB) & nitrite-oxidizing bacteria (NOB)
- Aerobic chemoautotrophs
- Major AOB: *Nitrosomonas* (+*Nitrospira*)
- Major NOB: *Nitrobacter* (+*Nitrococcus*, *Nitrospina*, *Nitrospira*)

Stoichiometry of nitrification

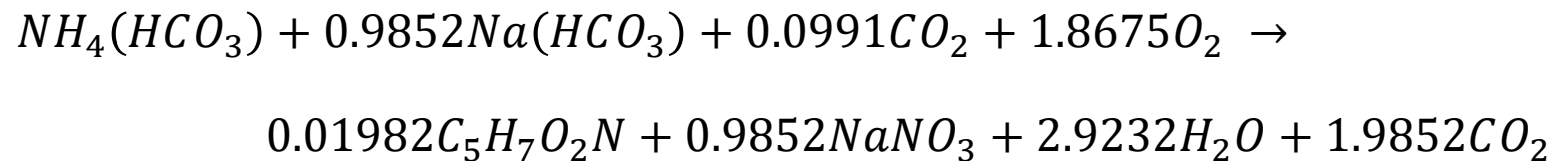


*Note: This is stoichiometry **NOT** considering biomass production*

- 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 O_2 requirements and alkalinity consumption is slightly less than the calculated values above (**why??**)

Stoichiometry of nitrification

ex) Assuming $Y=0.12$ g VSS/g $\text{NH}_4\text{-N}$ for AOB and $Y=0.04$ g VSS/g $\text{NO}_2\text{-N}$ for NOB, the overall stoichiometry is:



→ 1.8675 mole O_2 /1 mole NH_4^+

1.9852 eq Alk/1 mole NH_4^+

Nitrification kinetics

- Monod equation applicable
- AOBs & NOBs are more sensitive to DO than heterotrophs
 - In most cases DO should be treated as one of the major limiting substrate

$$\mu_{AOB} = \mu_{max,AOB} \left(\frac{S_{NH}}{S_{NH} + K_{NH}} \right) \left(\frac{S_o}{S_o + K_{o,AOB}} \right) - b_{AOB}$$

$$\mu_{NOB} = \mu_{max,NOB} \left(\frac{S_{NO}}{S_{NO} + K_{NO}} \right) \left(\frac{S_o}{S_o + K_{o,NOB}} \right) - b_{NOB}$$

μ_{AOB} = specific growth rate of AOB, 1/d

μ_{NOB} = specific growth rate of NOB, 1/d

$\mu_{max,AOB}$ = maximum specific growth rate of AOB, 1/d

$\mu_{max,NOB}$ = maximum specific growth rate of NOB, 1/d

b_{AOB} = decay coefficient of AOB, 1/d

b_{NOB} = decay coefficient of NOB, 1/d

S_{NH} = NH_4 -N concentration, mg/L

K_{NH} = half-velocity constant for NH_4 -N, mg/L

S_o = DO concentration, mg/L

$K_{o,AOB}$ = half-velocity constant for DO for AOB, mg/L

K_{NH} = half-velocity constant for NH_4 -N, mg/L

S_{NO} = NO_2 -N concentration, mg/L

K_{NO} = half-velocity constant for NO_2 -N, mg/L

$K_{o,NOB}$ = half-velocity constant for DO for NOB, mg/L

- NOBs are more sensitive to DO than AOBs
 - $K_{o,NOB} \approx (2\sim3) \times K_{o,AOB}$
 - Elevated NO_2 -N concentration at low DO

Environmental factors affecting nitrification

- **Dissolved oxygen (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, ...)
- **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: NH₃-N ↑ / low pH: HNO₂ ↑

Requirements for denitrification

- By nitrification, NO_3^- is produced
- Denitrification ($\text{NO}_3^- \rightarrow \text{N}_2$) should follow to complete the biological nitrogen removal process
 - To complete the biological nitrogen removal process
 - Otherwise, accumulation of NO_3^- -N: health threats!
 - “Blue baby syndrome”
 - Korean regulation: $< 10 \text{ mg NO}_3^- \text{-N/L}$



Typical nitrate (NO_3^-) removal mechanisms

- **Assimilatory nitrate reduction**

- Reduction of $\text{NO}_3\text{-N}$ to $\text{NH}_4\text{-N}$ for use in cell synthesis when $\text{NH}_4\text{-N}$ is not available
- Independent of DO concentration

- **Dissimilatory nitrate reduction**

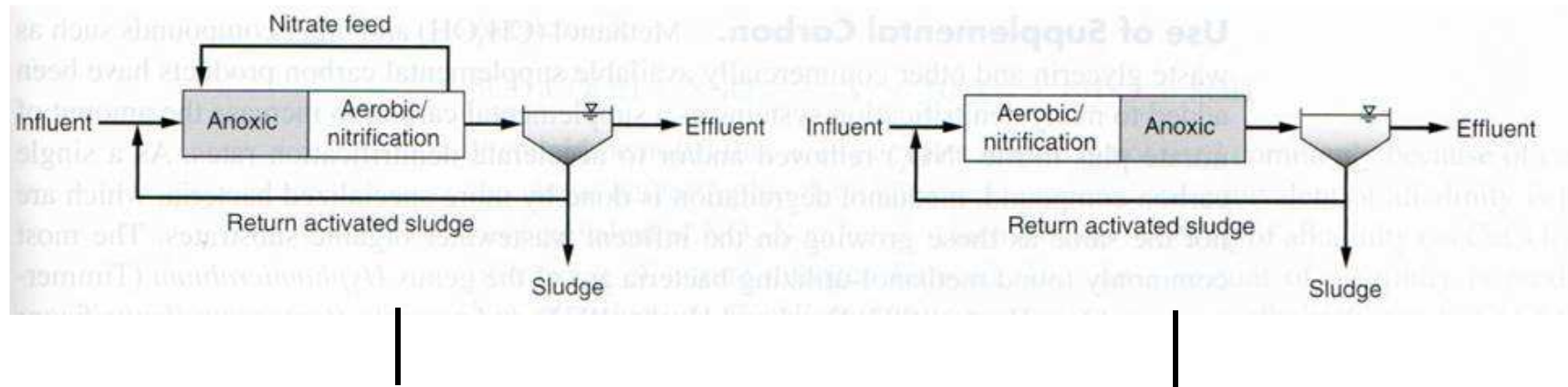
- Nitrate/nitrite serves as an electron acceptor
- When DO is absent or limited
- Nitrate reduction proceeds through a series of intermediate products:



Denitrifying microorganisms

- **Wastewater denitrification process is usually performed by heterotrophic bacteria**
- **Wide range of heterotrophs are facultative aerobes**
 - Switch their e^- acceptor from O_2 to NO_3^- or NO_2^- at **anoxic** conditions
 - NO_3^- & NO_2^- are quite good e^- acceptors; utilizes good e^- donors (organics)
 - Allows high energy gain for bacteria → high Y
- **Some autotrophs are capable of nitrate/nitrite reduction**
 - Use Fe^0 , Fe^{2+} , S^{2-} , S^0 , ..., or NH_4^+ (Anammox – will discuss later)

Denitrification processes



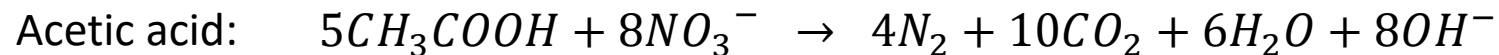
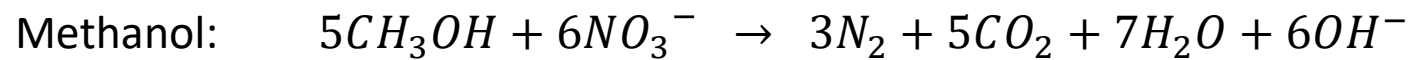
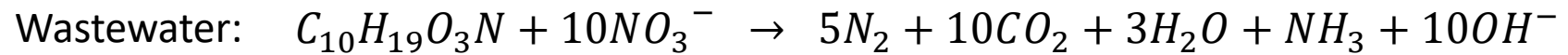
- **Preanoxic denitrification**

- 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)

Stoichiometry



– Production of alkalinity

- 3.57 g Alk as $CaCO_3$ produced per g NO_3^- -N (or NO_2^- -N) reduced
- 50% of alkalinity consumed by nitrification can be recovered

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 $\text{NO}_3\text{-N}$ reduced
 - actual requirement depending on operating conditions and the type of e^- donor
 - 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

GHG from biological N removal

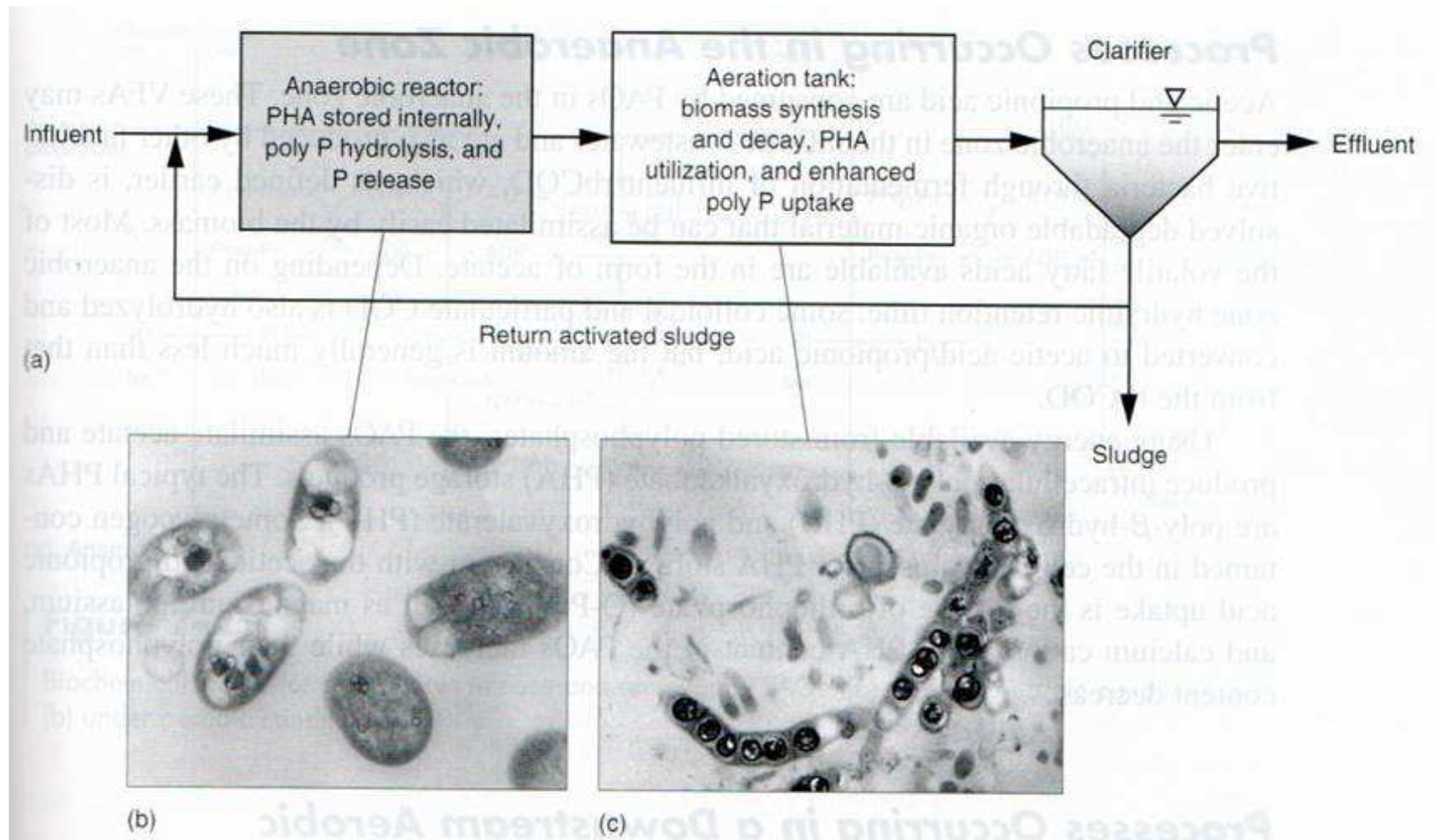
- **Nitrous oxide (N₂O)**
 - A potent greenhouse gas (GHG): 300 times greater potency than CO₂
 - Agriculture is the major source of N₂O emission

- N₂O emissions by wastewater treatment
 - Contributes 3% of total global emissions
 - N₂O emissions greater in the aerobic zones than the anoxic zones
 - **From heterotrophic denitrification**
 - Not produced significantly at steady-state operations, but can be significant at transient state
 - **From ammonia oxidation (AOBs)**
 - By hydroxylamine oxidation: $\text{NH}_2\text{OH} \rightarrow \text{NOH}\cdot \rightarrow \text{NO} \rightarrow \text{N}_2\text{O}$
 - By nitrite reduction: AOBs can use hydroxylamine, H₂, and NH₄⁺ as e⁻ donors for NO₂⁻ reduction

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



Enhanced biological P removal

- **Process description**

- Place an anaerobic tank ahead of the aeration tank
 - Provide selectivity 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: excessive P uptake & PHA utilization
- PAOs form very dense floc with good settleability – additional benefit

Enhanced biological P removal

- **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 is taken up by PAOs to form polyphosphates in the existing cells and the new cells
 - Portion of the biomass is wasted \rightarrow P removal
 - The process can occur in the anoxic zone as well (NO_3^- or NO_2^- as e^- acceptors)

Enhanced biological P removal

- **Environmental factors**
 - Competition with GAOs
 - Glycogen accumulating organism (GAO): glycogen storage under aerobic condition & VFA uptake in the anaerobic tank to store PHA under anaerobic condition
 - Higher GAO population results in reduced P removal efficiency
 - Factors affecting the competition between PAOs & GAOs
 - pH > 7.0 favorable for PAO growth over GAOs (pH~7.5 optimum)
 - PAOs dominate GAOs below 15°C & above 30°C
 - Low aerobic tank SRT favorable for PAOs
 - Alternating VFA feed between acetate and propionate can eliminate GAOs

Key references

- Textbook sec 7-9, 7-10, 7-12, 7-13

Next class

- Practical applications of biological treatment (secondary wastewater treatment)
 - Secondary clarifier settling problems
 - Suspended growth processes for BOD removal & nitrification
 - Suspended growth processes for N & P removal
 - Attached growth processes, hybrid processes