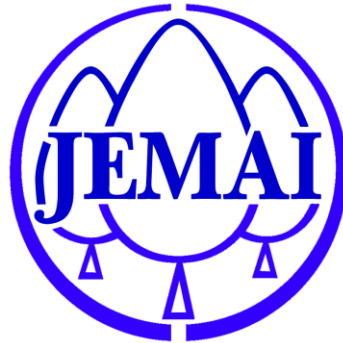


# **Water Pollution / Equipment for water pollution control (7)**

## **Removal of nitrogen from waste water**



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**Japan Environmental Management Association for Industry  
(JEMAI)**

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# 1. Mechanism of biological removal of nitrogen

## 1. 1 Early stage denitrification technology

- Physico - chemical process

Ammonia stripping method

Zeolite adsorption method

- Use of microorganisms widely distributed in nature

Biological nitrification-denitrification process

# 1. 2 Biological nitrification and denitrification

## 1. 2. 1 Nitrification

- Principle

Oxidation process of ammonium nitrogen to nitrite nitrogen or nitrate nitrogen by the reaction under aerobic condition.

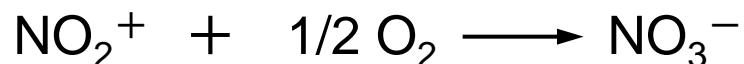
- Microorganisms in nitrification process

Autotrophic bacteria which get energy from oxidation of ammonium nitrogen or nitrite nitrogen and multiply by using inorganic compounds.

Oxidation of ammonium nitrogen: Nitrosomonas sp., etc

Oxidation of nitrite nitrogen: Nitrobacter sp., etc

- Reaction formula



## 1. 2. 2 Denitrification

- Principle

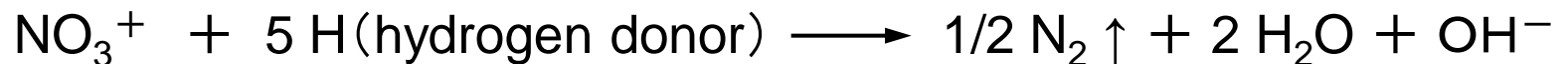
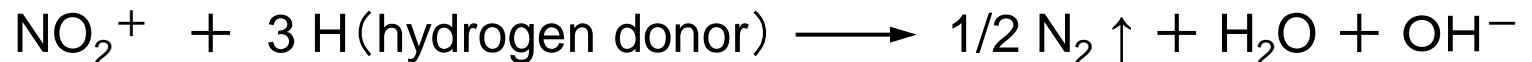
Removal process of nitrite nitrogen or nitrate nitrogen as nitrogen by reduction treatment by treating treated water of nitrification step under anaerobic condition.

- Microorganisms in denitrification process

Heterotrophic bacteria which need organic compounds for multiplication exist by aerobic respiration under aerobic condition and can also exist as facultative anaerobic bacteria by nitrate respiration under anaerobic condition which use nitric acid or nitrous acid as electron acceptor.

→ *Pseudomonas denitrificans*, *Ps. stutzeri* etc

- Reaction formula

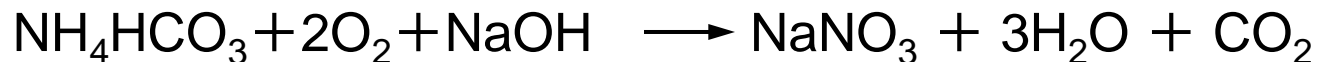


## 1. 2. 3 Summary

- The amount of 4.6kg of O<sub>2</sub> is required to oxidize NH<sub>4</sub>—N to NO<sub>3</sub>—N.
- Proton (H<sup>+</sup>) generates by oxidation of NH<sub>4</sub>—N to NO<sub>2</sub>—N.

→Ph adjustment by adding alkaline is required to prevent pH decrease in treatment vessel.

Ex: Required amount of NaOH for nitrification of digestion liquor of human excreta to keep pH in vessel as 7.0 is 2.86kg per 1kg of NH<sub>4</sub>—N.



- Hydrogen donor is required to reduce NO<sub>2</sub>—N and/or NO<sub>3</sub>—N to nitrogen and pH in treatment vessel raise because of OH<sup>-</sup> generation.
- Methanol, acetates or BOD in waste water are generally used as a hydrogen donor.

# Equivalent in chemical reaction of denitrification

	Partial reaction	Change of amount of chemical substances by 1 mmol transfer of electron
Oxidation formula :		
(a) Methanol	$1/6\text{CH}_3\text{OH} + 1/6\text{H}_2\text{O} = 1/6\text{CO}_2 + \text{H}^+ + \text{e}^-$	2 mg/L Organic carbon
(b) Acetate	$1/8\text{CH}_3\text{COO}^- + 3/8\text{H}_2\text{O} = 1/4\text{CO}_2 + 1/8\text{OH}^- + \text{H}^+ + \text{e}^-$	3 mg/L Organic carbon
(c) Ethanol	$1/12\text{CH}_3\text{CH}_2\text{OH} + 1/4\text{H}_2\text{O} = 1/6\text{CO}_2 + \text{H}^+ + \text{e}^-$	2 mg/L Organic carbon
(d) Aceton	$1/16\text{CH}_3\text{COCH}_3 + 5/16\text{H}_2\text{O} = 3/16\text{CO}_2 + \text{H}^+ + \text{e}^-$	9/4 mg/L Organic carbon
(e) Sucrose	$1/48\text{C}_{12}\text{H}_{22}\text{O}_{11} + 13/48\text{H}_2\text{O} = 1/4\text{CO}_2 + \text{H}^+ + \text{e}^-$	3 mg/L Organic carbon
Reduction formula :		
(f) Oxygen	$1/4\text{O}_2 + \text{H}^+ + \text{e}^- = 1/2\text{H}_2\text{O}$	8 mg/L Oxygen
(g) Nitrate	$1/5\text{NO}_3^- + \text{H}^+ + \text{e}^- = 2/5\text{H}_2\text{O} + 1/10\text{N}_2 + 1/5\text{OH}^-$	14/5 mg/L $\text{NO}_3\text{-N}$
(h) Nitrate	$1/2\text{NO}_3^- + \text{H}^+ + \text{e}^- = 1/2\text{H}_2\text{O} + 1/2\text{NO}_2^-$	7 mg/L $\text{NO}_3\text{-N}$
(i) Nitrite	$1/3\text{NO}_2^- + \text{H}^+ + \text{e}^- = 1/3\text{H}_2\text{O} + 1/6\text{N}_2 + 1/3\text{OH}^-$	14/3 mg/L $\text{NO}_3\text{-N}$
Cell synthesis :		
(j) Cell	$5/28\text{CO}_2 + 1/28\text{NO}_3^- + 29/28\text{H}^+ + \text{e}^- = 1/28\text{C}_5\text{H}_7\text{O}_2\text{N} + 11/28\text{H}_2\text{O}$	15/7 mg/L Organic carbon

[McCarty (1969)]

- Required amount of methanol to denitrify 1 mol of  $\text{NO}_2^-$  or  $\text{NO}_3^-$  are 1/2 mol or 5/6 mol. In case of acetate 3/8mol or 5/8mol.
- In case of using BOD in waste water which composition is unknown, as 1 mol of  $\text{NO}_3^-$  is equivalent to 1.25 mol of  $\text{O}_2$  from the relationship between (f) and (g) equations the required BOD to reduce 1mg/L  $\text{NO}_3^-$ -N is 2.86mg/L of  $\text{O}_2$  as theoretical oxygen demand under the condition that BOD is completely oxidized.
  - $1(\text{mg/L}) \div 14(\text{mg/mol}) \times 1.25 \times 32(\text{mg/mol}) = 2.86\text{mg/L}$

## 2 Organization of process

### 2.1 Trend of process

Three phase system :

BOD oxidation → Nitrification → Denitrification

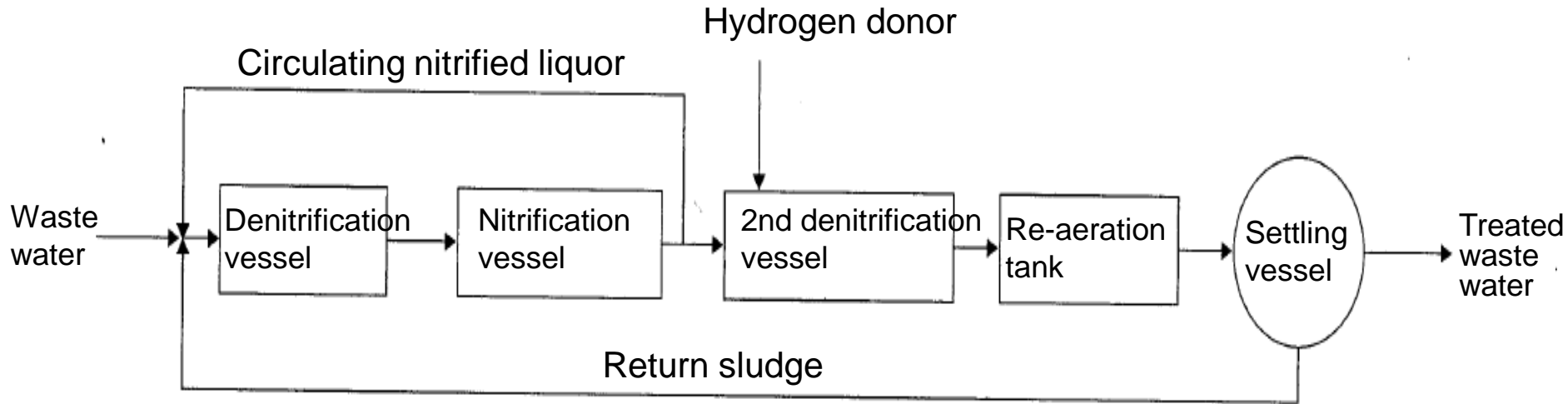
Two phase system :

Aerobic condition (BOD oxidation+ Nitrification)  
→ No oxygen condition (Denitrification)

Single phase system :

Mixture system (BOD oxidation+ Nitrification + Denitrification)

## 2. 2 Circulating nitrification and denitrification (single phase system)



- Waste water flowed into denitrification vessel is mixed with return sludge and circulating nitrified liquor.
- Denitrification vessel is operated under no oxygen condition with stirring to proceed denitrification in parallel with multiplication of bacteria by using BOD in waste water to change nitrous acid and nitric acid to nitrogen gas in nitrified liquor.

- In nitrification vessel remained BOD is removed and ammonia is oxidized to nitrous acid and nitric acid.
  - Most part of nitrified liquor is circulated to denitrification vessel and remained part of nitrified liquor flows into second denitrification vessel.
- The denitrification efficiency in denitrification vessel is determined by the circulation ratio of nitrified liquor and generally 50~70% of nitrified liquor is circulated.
- In second denitrification vessel remained nitrous acid and nitric acid are removed.
  - Denitrification by endogenous respiration is available but in order to increase denitrification efficiency denitrification in parallel with multiplication of bacteria is mainly adopted.

- Re-aeration vessel is installed to remove remained added-hydrogen donor and increase efficiency of solid-liquid separation at settling vessel.
- As denitrification process there are other processes such as biological slime process based on same principle and combination process of floating organism method and biological slime process except nitrification-denitrification process by floating organism method.

### 3. Basic operation condition

#### 3.1 Nitrification

##### (1) Sludge retention time (SRT)

- Multiplication rate of nitrifying bacteria (autotrophic bacteria) for nitrification reaction is 1/10 of heterotrophic bacteria for oxidation of BOD.
- The larger value of SRT the smaller volume of generation of excess sludge because of proceeding of endogenous respiration. On the other hand the smaller value of SRT the larger volume of generation of excess sludge.
- The relationship between specific growth rate  $\mu$  of activated sludge and SRT is mostly,

$$\mu = \frac{1}{\text{SRT}}$$

- To hold enough amount of nitrifying bacteria in a vessel which multiplication rate is very low SRT needs to be set at large value. Generally SRT is set for 7~10 days or more.

## (2) pH

- Multiplication rate of nitrifying bacteria is largely affected by pH.  
The most suitable pH → Nitrosomonas sp. pH8.0~8.5  
Nitrobacter sp. pH7.0~8.0
- As pH affects generation of free ammonia, concentration of nitrous acid and alkalinity which are toxic substances for microorganisms  
pH is preferable to be kept at neutral.

## (3) Temperature

- Multiplication rate of nitrifying bacteria is largely affected compared with BOD oxidizing bacteria.
- Nitrification rate decreases extremely under 15°C.

## (4) Toxic substances

- In general the sensitivity of nitrifying bacteria against toxic substances is higher than that of BOD oxidizing bacteria.

## (5) Dissolved oxygen

- Nitrifying bacteria is more affected by dissolved oxygen than BOD oxidizing bacteria.
- From the point of nitrification rate of nitrifying bacteria the concentration of oxygen in a vessel is preferably 2~3mg/L .  
But in actual operation many cases operate at 1mg/L or more oxygen concentration in case of keeping MLSS at high level.

MLSS: Mixed Liquor Suspended Solid

## 3.2 Denitrification

### (1) Anaerobic condition (Completely no oxygen)

- Denitrification is normally proceeded within an airtight container.
- If molecular oxygen exists, aerobic respiration proceeds before nitrate respiration. Therefore Nitrate nitrogen is used as assimilative substance and is restricted to be used as disassimilate one (denitrification).
- In many cases oxidation-reduction potential of mixture solution in denitrification vessel exists between  $-200 \sim -300\text{mV}$ .

### (2) Hydrogen donor

- Refer to 1.2.2