Nitrogen Control in Wastewater Treatment Facilities using ORP

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Why Control Nitrogen?

• Operating permit requirements becoming increasingly strict
• Nitrogen is a nutrient that promotes the growth of algae in receiving waters
• Toxicity towards aquatic life
• Presents a public health hazard
Duckweed
Secondary Treatment Standards

• CBOD$_5$ - annual average
  – 20 mg/L

• TSS - annual average
  – 20 mg/L

• Fecal coliform - annual average
  – 200 #/100mL
Advanced Treatment Standards

- Groundwater dischargers
  - $\text{NO}_3^- - \text{N} \ - \ 12 \text{ mg/L - maximum}$

- Surface water
  - TKN parameters
  - Unionized ammonia - 0.02 mg/L
• CBOD$_5$ - annual average
  – 5 mg/L

• TSS - annual average
  – 5 mg/L

• Total Nitrogen - annual average
  – 3 mg/L

• Total P - annual average
  – As low as 0.2 mg/L
Reuse Standards

• TSS < 5.0 mg/L
  – turbidity/TSS correlation for reject (2.0 – 2.5 ntu)

• Normally no nutrient parameters

• Fecal coliform
  – 75th (or 90th) percentile of samples - no detected fecal coliform
  – 25 /100 mL single sample maximum
Upcoming Numeric Nutrient Criteria!

- Nitrogen as low as
  - 0.28 mg/L (Estuaries)
  - 0.67 mg/L (Freshwater)
- Phosphorus as low as
  - 0.014 mg/L (Estuaries)
  - 0.06 mg/L (Freshwater)
Nitrogen

- Nitrogen compounds like ammonia ($\text{NH}_3$) are toxic in high concentrations

- Other nitrogen compounds like cyanide ($\text{CN}^-$) are lethal in small quantities

- Nitrogen oxides are one cause of acid rain
The Nitrogen Cycle

In the beginning

forms of nitrogen make their way into our collection systems.
It begins the journey from our homes, offices, school or just about anywhere during our daily routines.
The Nitrogen Cycle

• Fresh wastewater is high in organic nitrogen and ammonia from urea.

• Total Kjeldahl Nitrogen (TKN) is the sum of organic nitrogen and ammonia.

• Domestic wastewater contains 30 – 80 mg/L of TKN
Ammonification

• During its travel to our wwtp, animal and plant waste material is converted to ammonia and ammonium through biological decomposition.

Organic nitrogen + Microorganisms = NH$_3$ / NH$_4$
NITRIFICATION
Nitrification

- Nitrification is the biological oxidation of ammonium to nitrate.
- Two groups of bacteria are responsible for this: *Nitrosomonas* and *Nitrobacter*
Nitrifying Organisms

- *Nitrosomonas* can oxidize ammonium to nitrite, but cannot complete oxidation to nitrate.

- *Nitrobacter* are limited to oxidizing nitrite to nitrate.
Nitrifying Organisms

• Both groups are strict aerobes

• Approximately 4.6 pounds of oxygen are needed for complete nitrification
Results of Nitrification

• Approximately 0.1 grams of new nitrifiers are produced per gram of ammonium oxidized

• Approximately 7.1 grams of alkalinity (as CaCO$_3$) are destroyed per gram of ammonium oxidized
Summary of Factors Effecting Nitrification

• Process Temperature
  – Optimum 30 -35 °C

• Concentration of ammonia-N
  – Affects nitrifier growth rate - Last 0.5 mg/L is hardest to remove

• Dissolved Oxygen
  – Minimum of 1 mg/L, average of 2 mg/L,
  – 4.6 lbs O₂ required to oxidize 1 lb NH₃
Summary of Factors Effecting Nitrification

• Influent and process pH
  – Optimum range is 7.5 to 9.0

• Influent and Process Alkalinity
  – 7.1 lbs of alkalinity is destroyed for every 1.0 lb of ammonia-N oxidized

• Oxic SRT
  – Dependent on D.O., pH, temperature and target removal rate
Summary of Factors Effecting Nitrification

• Toxicants
  – Heavy metals, cyanide and some organic chemicals can inhibit nitrification rate

• F/M Ratio
  – Higher D.O.s are required at lower F/M and SRTs
DENITRIFICATION
Denitrification

• Denitrification is result of the biological reduction of nitrate to nitrite, then ultimately, to nitrogen gas.

• Denitrification occurs in the absence of molecular oxygen (anoxic conditions).
Denitrifying Organisms

• A relatively broad range of organisms can accomplish denitrification

• These are facultative organisms that can use either oxygen or nitrate as an electron acceptor
Electron Acceptors

Systems within bacteria ensure the most efficient form of energy is utilized

- If oxygen is present, it will be used preferentially over nitrate
- If oxygen is not present, nitrate will be used preferentially over sulfate
Figure 3-6: ORP & Metabolic Processes

1. Organic Carbon Oxidation
2. Polyphosphate Development
3. Nitrification
4. Denitrification
5. Polyphosphate Breakdown
6. Sulfide Formation
7. Acid Formation
8. Methane Formation
Results of Denitrification

• Nitrate that is potentially objectionable is converted to nitrogen gas that has no significant effect on the environment

• Process benefits include development of alkalinity, reduction of $O_2$ demand, and produces a sludge with better settling characteristics
Conditions Required for Denitrification

• Anoxic environment

• Carbon source

• Proper range for other environmental factors (pH, temperature, SRT)
Anoxic Environment

- Dissolved oxygen level below 0.2 mg/L
- Nitrate must be present
- Oxidation Reduction Potential (ORP) of between +50mv and –50mv
- Mixing is important
- Watch dissolved oxygen in return streams
Carbon Sources

• Raw Wastewater
• Endogenous carbon
• Methanol
• Acetic acid
• Dog food
A Cheap Carbon Source
Factors Effecting Denitrification

- **pH**
  - 7.5 - 9.0

- **Temperature and SRT**
  - Longer SRT and higher MLSS during periods of low temperature

- **Anoxic conditions**
  - D.O. less than 0.2 mg/L or
  - ORP in +50 to -50 mV range
Factors Effecting Denitrification

• Carbon Source
  – Relative to process temperature
  – Endogenous carbon may not be enough during periods of low temperature
  – Quality and quantity of carbon available strongly influences denitrification rate
Post-denitrification (Wuhrman Process)

- OXIC (nitrification)
- POST-ANOXIC

Organic Matter
Wuhman process used at a school WWTP
Process control tests for Denitrification

- Dissolved oxygen
- ORP
- NO$_3$ - N - colorimetric or electrometric
- Settleability
- pH and alkalinity
- COD or TOC
- SRT
Oxidation Reduction Potential

Using a pH meter with an ORP probe (or a specific ORP meter), you can determine if a system is Aerobic, Anoxic or Anaerobic
Oxidation Reduction Potential

• Oxygen represents the upper end of the ORP scale

• Readings in the +50 to +225 mV range indicate presence of oxygen

• Readings in +200 to +400 mV range indicate oxygen and nitrate
Aerobic Environment
Oxidation Reduction Potential

- Readings of +50 to –50 mV indicates anoxic conditions

- Nitrate is the best available electron acceptor, but will use sulfate and then CO2
Anoxic Environment
Oxidation Reduction Potential

- Readings below –50 indicate sulfate and carbonaceous organics are the electron acceptors

- Fermentative anaerobic conditions prevail
Oxidation Reduction Potential

• At small wastewater treatment plants where a DO meter is not available, ORP can be used to evaluate the treatment zones.

• DO meters typically operate best above 0.5 mg/L.
Oxidation Reduction Potential

• In true anoxic zones or cycles, DO must be below 0.2 mg/L

• ORP can be used to determine if zone is anoxic
Oxidation Reduction Potential

• With ORP, operators can determine aeration or blower operation

• Blowers can be cycled on and off according to ORP readings to achieve energy savings and improved effluent
DO and ORP Relationship
DO and ORP Relationship
Aeration Timer

- Out = Off
- In = Run
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Questions?

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