NITROGEN REMOVAL
GUIDE FOR WASTEWATER OPERATORS

THE WATER PLANET COMPANY
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FORMS OF NITROGEN OF INTEREST TO WASTEWATER OPERATORS

Nitrogen exists in several forms. The principal nitrogen types of concern to wastewater treatment are listed below. The relationships of the various forms are important for operators to understand.

Ammonia (NH_3). Nearly all of the nitrogen in raw wastewater is ammonia. (Technically it is mostly ammonium (NH_4^+) but the difference is meaningless to most operators.) Not counting the nitrogen that is removed at the same time as BOD is removed and bacteria are grown, nitrogen is removed from wastewater as follows. Ammonia is converted to nitrate (nitrification) and nitrate is converted to nitrogen gas (denitrification) and the nitrogen gas bubbles out of the wastewater into the atmosphere.

Nitrate (NO_3). Nitrate is created as ammonia is removed in oxygen-rich conditions and removed in oxygen-poor conditions.

Nitrite (NO_2). Nitrite is formed as ammonia is converted to nitrate. The nitrite to nitrate conversion generally happens quickly and completely, leaving very little nitrite in the wastewater. Municipal wastewater effluents generally contain less than 0.5 mg/L nitrite (NO_2). Greater concentrations are found when a facility is partially nitrifying. Nitrite (NO_2) uses up a lot of chlorine and interferes with disinfection in plants using chlorine gas or hypochlorite.

Nitrogen Gas (N_2). When nitrogen is removed from wastewater, it is removed as nitrogen gas. The gas goes into the atmosphere. The air we breathe is 78% nitrogen gas (N_2) and only 21% oxygen. The remaining one percent is argon and other inert materials.

Total Kjeldahl Nitrogen (TKN). TKN is made up of Ammonia (NH_3) and organic-Nitrogen.

organic-Nitrogen (org-N). Except for the organic-nitrogen contained in effluent TSS (some 10-12% of effluent TSS is organic-N), operators don't have much control over organic-N. A small fraction, typically one or two milligrams per liter, of soluble organic-Nitrogen passes through treatment facilities unchanged.

total-Nitrogen (total-N). To determine the total-Nitrogen concentration, laboratory testing of TKN, Nitrate (NO_3) and Nitrite (NO_2) is generally required. The results of the three tests are added together. Many labs perform a cost saving nitrite + nitrate test that doesn't differentiate between nitrate and nitrite.

$$\text{total-N} = \text{TKN} + NO_3 + NO_2$$

NITROGEN REMOVAL FROM WASTEWATER: OVERVIEW

Municipal wastewater treatment plants biologically remove nitrogen in two ways.

ONE. Something on the order of 10 mg/L of the nitrogen in the raw wastewater (influent) is taken in by bacteria as BOD is removed.

TWO. The remaining 20 mg/L or so of incoming nitrogen is converted to nitrogen gas in a three-step biological process, two of which are concern to operators: nitrification and denitrification.

> Step 1. Organic-nitrogen is converted to ammonia-nitrogen (NH_3) by a mostly anaerobic process called Ammonification; a process over which operators have very little control.
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> Step 2. Ammonia-nitrogen (NH_3) is converted to nitrate-nitrogen (NO_3) by an aerobic biological process called nitrification.
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> Step 3. Nitrate-nitrogen (NO_3) is converted to nitrogen gas biologically in a low-oxygen (anoxic) environment. During denitrification, nitrogen gas bubbles harmlessly out of wastewater into the atmosphere.

AMMONIFICATION. The majority of the nitrogen contained in raw sewage (urea and fecal material) is converted from organic-nitrogen to ammonia (NH_3) as it travels through sewer pipes. As a result, most of the influent nitrogen is ammonia (NH_3), although some organic-nitrogen remains. Ammonification is mostly an anaerobic process. It is sometimes called hydrolysis.

NITRIFICATION. Ammonia removal requires oxygen – lots of it. Nitrification is a strictly aerobic biological process. Technically, bacteria convert ammonia (NH_3) to nitrite (NO_2) and then to nitrate (NO_3); it isn't really "removed."

Nitrifying bacteria are slower growing and more sensitive to environmental upset than BOD removing bacteria. Generally, nitrification occurs only under aerobic conditions at dissolved oxygen levels of more than 1.0 mg/L. In activated sludge facilities, nitrification requires a long retention time, a low food to microorganism ratio (F:M), a high mean cell residence time (measured as MCRT or Sludge Age), and a pH of over 6.5 in the aeration tank.

The nitrification process produces acid. The acid lowers the pH of the aeration tank and – unless alkalinity is present to buffer the pH loss – ammonia removal will shut down as the pH drop is toxic to the nitrifying bacteria. An aeration tank (or trickling filter) alkalinity of at least 60 mg/L is generally required.

Water temperature also affects the rate of nitrification. At temperatures below 20 degrees C, nitrification proceeds at a slower rate, but will continue at temperatures below 10^oC. However, if nitrification is lost at low temperature, it will not resume until the temperature increases to close to 15^oC.

DENITRIFICATION. Wastewater cannot be denitrified unless it is first nitrified (nitrate cannot be removed unless it is first created!). The biological reduction of nitrate (NO_3) to nitrogen gas is performed by bacteria that live in a low-oxygen environment. To thrive, the bacteria need BOD – soluble BOD. Particulate BOD needs to be broken down into solution before it is of value.

Denitrifying organisms are generally less sensitive to toxic chemicals than nitrifiers, and recover from toxic shock loads quicker than nitrifiers. However, most facilities have more difficulty maintaining consistent nitrate (NO_3) removal (denitrification) than ammonia (NH_3) removal.

NITROGEN REMOVAL FROM WASTEWATER: MORE DETAILED INFORMATION

NITRIFICATION. Nitrification is a two-step process. Bacteria known as *Nitrosomonas* (and others) convert ammonia (NH_3) to nitrite (NO_2). Next, bacteria called *Nitrobacter* (and others) finish the conversion of nitrite (NO_2) to nitrate (NO_3). The reactions are generally coupled and precede rapidly to the nitrate (NO_3) form; therefore, nitrite (NO_2) levels at any given time are usually below 0.5 mg/L.

These bacteria, known as "nitrifiers," are strict "aerobes;" meaning, they must have free dissolved oxygen to perform their work. Nitrification occurs only under aerobic conditions with a sufficiently positive oxidation reduction potential (ORP). Nitrification requires a long retention time, a low food to microorganism ratio (F:M), a high mean cell residence time (measured as MCRT or Sludge Age), and adequate buffering (alkalinity). Temperature, as discussed below, also plays a role.

The nitrification process produces acid. This acid formation lowers the pH of the biological population in the aeration tank and, because it is toxic to nitrifiers – particularly those that convert nitrite (NO_2) to nitrate (NO_3) – can cause a reduction of the growth rate of nitrifying bacteria. The optimum pH for *Nitrosomonas* and *Nitrobacter* is between 7.5 and 8.5; however most treatment plants are able to effectively nitrify with a pH of 6.5 to 7.0. Nitrification becomes inhibited at a pH of 6.5. The nitrification reaction (that is, the conversion of ammonia (NH_3) to nitrate (NO_3) consumes 7.1 mg/L of alkalinity (as $CaCO_3$) for each mg/L of ammonia (NH_3) nitrogen oxidized. An alkalinity of 60 mg/L in the aeration tank is needed to insure adequate buffering.

Water temperature also affects the rate of nitrification. Nitrification reaches a maximum rate at temperatures between 30 and 35 degrees C (86^oF and 95^oF). At temperatures below 20 degrees C, nitrification proceeds at a slower rate, but will continue at temperatures of less than 10 degrees C but will not resume if nitrification is lost until the wastewater temperature increases to around 15^oC.

For every pound of ammonia (NH_3) removed: 4.18 pounds of oxygen and 7.14 pounds of alkalinity are consumed.

DENITRIFICATION. The biological reduction of nitrate (NO_3) to nitrogen gas (N_2) in a low oxygen, BOD-rich environment is called denitrification.

Denitrification occurs when oxygen levels are depleted and nitrate (NO_3) becomes the primary oxygen source for microorganisms. The process is performed under anoxic conditions; that is, when the dissolved oxygen concentration is less than 0.5 mg/L, ideally less than 0.2. A better measure is ORP, with -100 mV or lower being ideal. When bacteria break apart nitrate (NO_3) to gain the oxygen (O_2), the nitrate (NO_3) is reduced to nitrogen gas (N_2). Since nitrogen gas doesn't dissolve in water, it escapes to the atmosphere as gas bubbles. Free nitrogen is the major component of air; thus, its release does not cause any environmental concern.

A carbon source is required for denitrification to occur; some 5 to 10 times as much BOD as nitrate (NO_3). pH is not a concern because denitrification produces alkalinity which beneficially raises wastewater pH. Approximately 3.6 mg/L of alkalinity is produced for every 1 mg/L of nitrate (NO_3) removed, thereby returning one-half of the alkalinity lost during nitrification.

Denitrifying bacteria will breathe either dissolved oxygen or nitrate (NO_3). If dissolved oxygen and nitrate (NO_3) are present, bacteria will use the dissolved oxygen first and will not remove nitrate (NO_3). Denitrification occurs only under anoxic, low-oxygen conditions.

Another important aspect of denitrification is the requirement for carbon; there needs to be enough soluble organic matter to drive the denitrification reaction. Organic matter may be in the form of raw wastewater, or it can be added as an alcohol, acetic acid (vinegar), or some other form of supplemental carbon.

Denitrifying organisms are generally less sensitive to toxic chemicals than nitrifiers, and recover from toxic shock loads quicker than nitrifiers.

NITROGEN REMOVAL FROM WASTEWATER: TIPS FOR OPERATORS

At little to no cost, most treatment plants can make process changes to provide nitrogen removal. A discussion of various strategies follows.

Enhanced Ammonification. Because effluent organic-nitrogen concentrations are typically quite low (generally less than 2 mg/L), few treatment plants seek to reduce organic-N.

Nonetheless, treatment facilities with total-Nitrogen limits can oftentimes – with little effort and little cost – improve ammonification to provide an extra 0.5 to 1.5 mg/L reduction in total-Nitrogen.

This is done by creating a BOD-rich anaerobic zone at the front end of the treatment plant. We've done it in MLE (Modified Ludzack-Ettinger) activated sludge plants by converting pre-anoxic denitrification tanks to fully anaerobic conditions by reducing the internal recycle rate and managing the dissolved oxygen (DO) in the aeration tanks. Another tactic is to organically overload primary clarifiers so that they ferment wastewater. We've also recycled material from gravity thickeners and sludge storage tanks.

Enhanced Nitrification. Nitrification needs a lot of air, not necessarily the 2 mg/L that is often recommended, but a goodly amount. Our favored approach is to monitor aerobic conditions with ORP but adjust aeration using DO. Once consistent ammonia removal has been achieved, we slowly make small reductions in the DO setting until we see an adverse impact on ammonia removal. We then restore complete nitrification, establish an ORP target, and forever monitor ORP and adjust aeration to maintain our minimum target ORP.

Nitrifiers grow slowly. Textbooks, design manuals, and state guidance documents list minimum hydraulic retention times; can't say as we've found a magic number. A hydraulic retention time of 6 hours should, however, be more than enough. Perhaps even more important than retention time is mixed liquor concentration. Ammonia removal requires a high mean cell residence time (sludge age); typically, an MCRT of 8 days or more. Our experience: the higher the better for ammonia removal (nitrate removal too!).

Nitrification needs alkalinity; if there isn't enough alkalinity in the raw wastewater to maintain a pH of 6.5 and an alkalinity of 60 mg/L, alkalinity has to be added.

To implement ammonia removal, the first consideration – in an activated sludge plant – is mixed liquor concentration: which, as a general rule, we like to raise as high as can be maintained given existing conditions (e.g., clarifier blankets). The second is oxygen: which, as a general rule, we like to keep as low as possible – just enough to support complete ammonia removal. The third is alkalinity / pH. Every mg/L of ammonia converted to nitrate consumes 7.1 mg/L of alkalinity. The least expensive way of adding alkalinity is to create it during denitrification. Denitrification adds back about 50% of the alkalinity removed during nitrification. In instances where the conditions are favorable for nitrification, but the reaction is incomplete, ammonia removal might be improved by generating alkalinity by cycling the air off in order to create periods of anoxic conditions. Caution: If dissolved oxygen or retention time is limiting nitrification, this strategy will worsen, not improve nitrification.

In small treatment facilities, 50-pound bags of baking soda (sodium bicarbonate) can be mixed with 100 or more gallons of water in day tanks and pumped into the wastestream using chemical feed pumps. In larger plants, tanker truck deliveries of liquid magnesium hydroxide can be transferred to holding tanks and pumped into the wastestream with chemical feed pumps. Chemicals such as sodium hydroxide are widely used but do present safety concerns.

Nitrification design standards are generally very conservative. It is good to recognize and understand them, but don't allow the textbook "requirements" inhibit experimentation. Can't think of one treatment plant that we've worked with that wasn't able to achieve consistent ammonia removal; whether designed to nitrify or not.

In order to establish and maintain nitrification it is important to monitor Dissolved Oxygen (DO), Alkalinity, and Ammonia daily. Same day results are important! The daily use of test strips such as those manufactured by Hach may be sufficient. The ideal monitoring practice is to use in-line instrumentation connected to a SCADA system.

Regardless of how the data is collected, it won't be of much value unless it is regularly reviewed and used in making process adjustments.

It has been our experience that once a plant has been set up to effectively nitrify, it continues to do so unless (a) a toxin is discharged into the sanitary sewers, (b) equipment failure, or (c) temperatures fall very low. Facilities that struggle with consistent nitrification are those very few with influent nitrogen concentrations of 75 mg/L or more, or facilities where the basics – e.g., air, alkalinity – are ignored.

Denitrification. For denitrification to occur, nitrified wastewater needs to reside 1-2 hours in a low-oxygen, high BOD environment. The easiest way to create such a space is to cycle the aeration tank air so that it is off for a couple of hours. Another way is to create a low oxygen area of sufficient size ahead of the aeration tank(s) and to pipe all return activated sludge to the inlet end of the anoxic tank so that it mixes with the incoming wastewater. Plants that are set up to co-settle sludge in their primary clarifiers can readily convert one or more primary clarifiers to pre-anoxic tanks for nitrate removal

The two key parameters for denitrification are low DO (less than 0.5 mg/L) and surplus BOD (5-10 mg/L of soluble BOD per mg/L of nitrate produced during nitrification). It is not nearly as important to mix the contents of the anoxic tank as the textbooks say, but it helps to do so. If aeration is cycled off for denitrification, there is no need for mixing; the contents will become re-suspended with the air is turned back on.

In pre-anoxic tanks, mechanical mixing is desired, but often not necessary. Oftentimes, it is possible to sufficiently mix the contents by simply directing the flow in such a way as to keep solids in suspension. If a primary clarifier is converted to a pre-anoxic tank and RAS is pumped back to the tank, the sludge blanket can be allowed to build enough to allow mixed liquor to flow out of the tank and back into aeration; without mixing of any sort.

Two factors govern he effectiveness of pre-anoxic denitrification tanks: (a) the volume of nitrates that are recycled back and (b) the amount of BOD available to drive nitrate removal. Any number of strategies are available to improve BOD availability.

Contrary to textbook reporting, our experience with recycling is this. We've found that most (but not all!) plants work best when the RAS plus internal recycle flow is equal to two times the influent flow. If less than 2Q, too few nitrates are pumped back to the pre-anoxic tank and therefore aren't removed. If more than 2Q, too much high DO water is brought back from the aeration tank and the pre-anoxic tank doesn't effectively remove all of the nitrates that it receives. To dial in nitrate removal, we recommend finding the optimal ORP for nitrate removal (typically, around -100 mV) and adjust recycle rates to maintain optimal denitrification. And/or monitor the nitrate concentration in both the final effluent and the water leaving the pre-anoxic tank and establish an anoxic tank effluent nitrate target that provides the best final effluent nitrate concentration. (Note: The anoxic tank nitrate concentration can be brought down very low by reducing recycle rates to near zero – but – doing so will raise the effluent nitrate concentration because very few of the nitrates produced in the aeration tank are returned to the pre-anoxic tank for removal.) The goal is optimizing the EFFLUENT nitrate concentration.

Influent (raw wastewater) usually contains enough BOD to support denitrification. But, primary clarifiers often remove so much of the influent BOD that there isn't enough left in the wastewater to support complete denitrification. If too much BOD is being removed during primary treatment, better results can be obtained by taking one or all of the primary clarifiers out of service.

If enough BOD exists, but it is largely insoluble (denitrifiers don't do well with the BOD that is part of TSS), it may be necessary to provide a short period of aeration prior to the anoxic stage. The pre-aeration period will allow for the particulate BOD to be made soluble and therefore available to the denitrifying bacteria.

If there isn't enough BOD coming in to satisfy demand, it may be possible to supplement using internal waste streams. The most common sources of fermented waste are primary gravity thickeners and recycled waste sludge from sludge holding tanks. If either of these are done, the sludge wasting rate will need to increase to make up for the additional solids load.

Another excellent source is septage. Septage contains a significant quantity of volatile fatty acids. Volatile fatty acids (VFAs) are not only good food for denitrifying bacteria, VFAs promote biological phosphorus removal. Treatment facilities that receive septage take in a BOD source that is well suited to denitrification. The challenge is to pace the septage flow and to divert it to where it is most needed.

It has been our experience that effective denitrification enhances operations. It almost always creates a mixed liquor with less foaming, and a bacterial population that settles better in clarifiers. Many plants find that they can increase their mixed liquor concentrations significantly.

In doing so, they reduce the amount of sludge that needs to be wasted because more of it is digested in the mainstream flow. The sludge, however, does not dewater as well. At some plants this can be a major issue.

Denitrification adds back alkalinity, which in turns assists nitrification, particularly in soft waters: plants with influent alkalinities of under 200 mg/L.

Although a hardier biochemical process, we've found that the denitrification process in many facilities requires more day-to-day fine tuning than nitrification. A loss of denitrification – unlike restoring nitrification, a process than can take weeks to accomplish – can typically be remedied in two or three days' time.

Notes:

The information contained in this guide is a result of Water Planet's experience. We've worked with operators to optimize nitrogen removal at over 50 wastewater treatment plants.

To make the guide readable, we generalized. For most every number, for most every recommendation, there is an exception. Operators are advised to keep this in mind. Please call or email us with questions or comments.

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