Nitrogen Removal from Wastewater

Nitrogen Chemistry

An overview of the chemical reactions that describe biological nitrogen removal in municipal wastewater treatment plants follows.

Ammonification. While traveling through sewer pipes, the majority of the nitrogen contained in raw sewage (urea and fecal material) is converted from organic-nitrogen to ammonia through a process called hydrolysis. The process is anaerobic and is described by the simplified equation below.

$$NH_2COHN_2 + H_2O + 7H^+ \longrightarrow 3NH_4^+ + CO_2$$

The equation shows the conversion of urea to ammonium, not ammonia. The ratio of ammonia (NH_3) versus ammonium (NH_4^+) is affected by pH and temperature. At conditions typical for most municipal wastewater treatment plants (pH of 6 to7, and temperatures of 10 to 20 degrees Celsius), far more ammonium than ammonia is produced. Since ammonia and ammonium behave similarly, this fact is of no real consequence to treatment plant designers and operators.

Nitrification. The biological conversion of ammonia/ammonium to nitrate is called Nitrification. Nitrification is a two-step process. Bacteria known as *Nitrosomonas* convert ammonia and ammonium to nitrite. Next, bacteria called *Nitrobacter* finish the conversion of nitrite to nitrate. The reactions are generally coupled and proceed rapidly to the nitrate form; therefore, nitrite levels at any given time are usually low.

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 at dissolved oxygen levels of 1.0 mg/L or more. 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, 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 stops at a pH below 6.0. The nitrification reaction (that is, the conversion of ammonia to nitrate) consumes 7.1 mg/L of alkalinity (as $CaCO_3$) for each mg/L of ammonia nitrogen oxidized. An alkalinity of no less than 50-100 mg/L in the aeration tank is generally required 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 of 40^oC (104^oF) and higher, nitrification rates fall to near zero. At temperatures below 20 degrees C, nitrification proceeds at a slower rate, but will continue at temperatures of 10 degrees C and less. However, if nitrification is lost in low temperature wastewater, it will not resume until the temperature increases to well over 10^oC.

Some of the most toxic compounds to nitrifiers include cyanide, thiourea, phenol and heavy metals such as silver, mercury, nickel, chromium, copper and zinc. Nitrifying bacteria can also be inhibited by nitrous acid and high concentrations of free ammonia.

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The following equations describe the nitrification process. Organic-nitrogen must first be converted to ammonia/ammonium to be nitrified. Unless converted to ammonia/ammonium, organic-nitrogen will pass through a treatment plant unchanged.

<u>Alkalinity buffering equation</u>

$$H_20 + CO_2 \leftrightarrow H_2CO_3 \leftrightarrow HCO_3 + H^+ \leftrightarrow CO_3 + 2H+$$

<u>Nitrification equations</u>

$$NH_4^+ + 1.5O_2 \longrightarrow 2H^+ + 2H_2O + NO_2^-$$

$$NO_2^- + 0.5O_2 \longrightarrow NO_3^-$$

$$NH_4^+ + 1.83\ O_2 + 1.98\ HCO3^- \longrightarrow 0.021\ C_5H_70_2N + 0.98\ NO_3^- + 1.041\ H_2O + 1.88\ H_2CO_3^-$$

$$NH_4+ + 1.9O_2 + 2HCO3^- \longrightarrow 1.9\ CO_2 + 2.9\ H_2O + 0.1\ CH_2$$

From the above equations, it can be calculated that for every pound of ammonia oxidized to nitrate, the following occurs:

4.18 pounds of oxygen are consumed and

7.14 pounds of alkalinity are consumed measured as calcium carbonate ($CaCO_3$) – or – 12 pounds of alkalinity measured as sodium bicarbonate ($NaHCO_3$)

Denitrification. The biological reduction of nitrate (NO_3^-) to nitrogen gas (N_2) by facultative heterotrophic bacteria is called Denitrification. "Heterotrophic" bacteria need a carbon source as food to live. "Facultative" bacteria can get their oxygen by taking dissolved oxygen out of the water or by taking it off of nitrate molecules.

Denitrification occurs when oxygen levels are depleted and nitrate 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. When bacteria break apart nitrate (NO_3^-) to gain the oxygen (O_2), the nitrate is reduced to nitrous oxide (N_2O), and, in turn, nitrogen gas (N_2). Since nitrogen gas has low water solubility, it escapes into the atmosphere as gas bubbles. Free nitrogen is the major component of air, thus its release does not cause any environmental concern.

The formula describing the denitrification reaction follows:

$$6NO_3- + 5CH_3OH \longrightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH'$$

A carbon source (shown in the above equation as CH_3OH) is required for denitrification to occur. Optimum pH values for denitrification are between 7.0 and 8.5. Denitrification is an alkalinity producing process. Approximately 3.0 to 3.6 pounds of alkalinity (as $CaCO_3$) is produced per pound of nitrate, thus partially mitigating the lowering of pH caused by nitrification in the mixed liquor.

Since denitrifying bacteria are facultative organisms, they can use either dissolved oxygen or nitrate as an oxygen source for metabolism and oxidation of organic matter. If dissolved oxygen and nitrate are present, bacteria will use the dissolved oxygen first. That is, the bacteria will not lower the nitrate concentration. Denitrification occurs only under anaerobic or anoxic conditions.

Another important aspect of denitrification is the requirement for carbon; that is, the presence of sufficient soluble organic matter to drive the denitrification reaction. Organic matter may be in the form of raw wastewater, or supplemental carbon.

The carbon – typically measured as BOD – needs to be in a readily digestible form. Not all BOD is the same. Denitrifying bacteria need the BOD to be in a soluble form; short-chained carbon molecules are preferred to complex, long-chained compounds.

Conditions that affect the efficiency of denitrification include nitrate concentration, anoxic conditions, presence of organic matter, pH, temperature, alkalinity and the effects of trace metals. Denitrifying organisms are generally less sensitive to toxic chemicals than nitrifiers, and recover from toxic shock loads quicker than nitrifiers.

Temperature affects the growth rate of denitrifying organisms, with greater growth rate at higher temperatures. Denitrification can occur between 5 and 30^{o}C (41^{o}F to 86^{o}F), and these rates increase with temperature and type of organic source present. The highest growth rate can be found when using methanol or acetic acid. A slightly lower rate using raw wastewater will occur, and the lowest growth rates are found when relying on endogenous carbon sources at low water temperatures.

Wastewater cannot be denitrified unless it is first nitrified, and organic-nitrogen must be converted to ammonia in order to be nitrified.