Nitrification (Ammonia Oxidation) In Wastewater Treatment Plants

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Introduction

Biological nitrification is the microbe-mediated process of oxidizing ammonia to remove nitrogenous compounds from wastewaters. Domestic sewage typically contains 20 to 40 mg/L (ppm) of ammonia nitrogen (NH_4-N). Organic matter containing nitrogen, e.g., protein and nucleic acid, also biodegrades to release ammonia. Releasing this ammonia into receiving streams has a direct toxic effect on fish and other animals and, in addition, causes significant oxygen depletion as illustrated in the following equation.

Nitrification Process (oxidation of ammonium ions to nitrate)

$$2NH_4^+ + 3O_2 ® 2NO_2^- + 4H^+ + 2H_2O$$

$$2NO_2^- + O_2 ® 2NO_3^-$$

The net effect is that it takes 4.5 mg of oxygen to fully oxidize one mg of ammonia-N. Therefore even small concentrations of ammonia can cause significant deterioration to the flora and fauna in the body of water receiving it. Thus, many domestic and industrial wastewater treatment plants are required to remove the ammonia before discharge of the treated water.

The Microbial Populations

As shown in the nitrification process equations, ammonia is first oxidized to nitrite ions, then the nitrite ions are oxidized to nitrate ions. Each oxidation is carried out by a different group of bacteria, the ammonia oxidizing bacteria (AOB) and the nitrite oxidizing bacteria (NOB). Each group of bacteria has multiple species and a wastewater treatment process may contain several species of each group. In fact, the process may also include Archaea which are distinct from the bacteria but function similarly in many cases.

Most textbook descriptions of the nitrification process, however, refer to Nitrosomonas species as the AOB and Nitrobacter species as the NOB and this simplification can serve the process operator and troubleshooter well as the two groups have well characterized growth conditions. Nitrifying bacteria are autotrophs, they use inorganic sources of carbon (such as carbon dioxide and carbonate ion) to produce biomass in contrast to the great majority of the other microbes in the system (heterotrophs) which typically use a variety of organic substances both as an energy and carbon source . The autotrophs grow and reproduce much more slowly than the heterotrophs, e.g. Nitrosomonas may reproduce (divide) once in eight hours compared to a fast-growing heterotroph that may divide every 20 minutes. In addition, the autotrophs are more sensitive to the growth conditions such as pH, temperature and the presence of toxic compounds.

To maintain nitrifying microbes in a process, the sludge age must be kept high enough to retain a sufficient population of these organisms. Under toxic and/or cold-weather conditions, the growth rate of natural nitrifying populations tends to slow appreciably, causing nitrifiers to wash out of the system. Thus, it can be a problem to maintain ammonia removal if such conditions persist.

Optimal Conditions for Nitrification

The optimal conditions for nitrification are shown in the following table.

CONDITION	ACCEPTABLE RANGE	OPTIMUM RANGE
Dissolved Oxygen, ppm	>1	>2
pH	6.5 – 9.0	7.5 – 8.0
Temperature, °C	10 – 40	20 - 35
Toxic Heavy Metals, ppm	<0.1	None
Toxic Organics, ppm	Trace	None
Alkalinity, ppm as $CaCO_3$	>40	>100

Proper nutrition for nitrifying bacteria also requires other elements as shown in the following table[1].

Element	Optimum Concentration (mg/L)	Concentration Inhibitory to Nitrosomonas
Calcium	0.5	
Copper	0.005-0.03	0.1-0.5
Chromium	Not required	0.25
Iron	7.0	
Magnesium	0.03-12.5	
Molybdenum	0.001-1.0	
Nickel	0.1	0.25-3.0
Phosphorus	310	
Zinc	1.0	3.0

Note that while copper, nickel and zinc are required, there is a narrow range between optimum and toxic concentrations. Ammonium ion (NH_4^{+}) is in equilibrium with free (unionized) ammonia (NH_3) at normal process pH and free ammonia can be toxic to a variety of bacteria but especially Nitrobacter. At a pH of 6, total ammonium-N can be over 200 mg/L and tolerated by Nitrobacter, while at pH 8, total ammonium-N should be kept below 20. The nitrite ion (NO_2^-) is also in equilibrium with free nitrous acid (HNO_2) which is toxic to NOB. At pH 6 nitrite-N should be less than 300 while at pH 7 nitrite-N may be as high as 3000 mg/L (see C.W. Randall and D. Buth, 1984. Nitrite Buildup in Activated Sludge Resulting From Combined Temperature and Toxicity Effects. J.WPCF 56:1045ff.).

Maintaining optimal conditions is not always practical since it can be cost prohibitive. Instead, several measures can be used to help maintain the nitrifying populations in the face of deteriorating conditions. These include:

- Maintaining a higher than normally desired biomass concentration in the biotreater aeration zone, and then building up an even higher sludge concentration in the biotreater to help hold the slow growing autotrophs in the system under anticipated adverse conditions (like colder weather).

- Using bioaugmentation with separately grown, concentrated microbial inocula to augment the natural seeding and growth of the autotrophs in the system.

- Keeping tight control over the pH of the system. Lower pH's (acidic conditions) are particularly adverse.

- Maintaining excess dissolved oxygen in the aeration zone at all times. The autotrophs compete with heterotrophs for dissolved oxygen and the heterotrophs are more efficient at scavenging oxygen at low concentration. A dissolved oxygen concentration of 2 mg/L should be maintained.

- Keeping high concentrations of substances known to be toxic to the autotrophs such as excessively high ammonia concentrations or toxic heavy metal ions such as copper and chromium out of the wastewater entering the system. This can be helpful in industrial settings such as petroleum refineries where relatively high concentrations of ammonia are present in the untreated wastewater and where separation of side streams is more feasible.

- Enforcing industrial pretreatment standards for domestic sewer discharges of substances known to negatively affect the slower growing nitrifiers.

Following is a partial list of compounds known to inhibit nitrification (from EPA WWTP Operation Manual or A. B. Hooper and K. R. Terry, 1973. Specific Inhibitors of Ammonia Oxidation in Nitrosomonas. J. Bact. 115:480-485.):

Pollutant	Inhibitory Concentration (mg/L)	Pollutant	Inhibitory Concentration (mg/L)
Cadmium	5-9	Nickel	0.25-5
Chloride	180	Silver	0.25
Chromium Total	0.25-1	Zinc	0.01-1
Copper	0.05-0.5	Sulfide	4
Cyanide	0.3-20	Methanol	160
Lead	0.5-1.7	Methylamine	330
Magnesium	50	Ethanol	414
Mercury	2-12.5		

An extensive measurement of toxicity to groups of microbes (aerobic heterotrophs, Nitrosomonas, and methanogens) by organic compounds is available. See Diane J. W. Blum and R. E. Speece, 1991. A database of chemical toxicity to environmental bacteria and its use in interspecies comparisons and correlations. Res. J. WPCF 63:198-207.