N_2O Formation

The formation of N_2O occurs during the transformation of ammonium/ammonia (NH_4^+/NH_3) present in wastewater into nitrogen gas (N_2) via the nitrification and denitrification processes.

Nitrification

Nitrification is the first process of biological nitrogen removal. It consists of the oxidation of NH_3 to nitrate (NO_3^-) carried out by two groups of autotrophic microorganisms: the ammonium oxidizing bacteria (AOB, Ammonia Oxidizing Bacteria) responsible for the oxidation of NH_3 to hydroxylamine (NH_2OH) and subsequently to nitrite (NO_2^-) and the nitrite oxidizing bacteria (NOB, Nitrite Oxidizing Bacteria) responsible for the oxidation of NO_2^- to NO_3^- (Figure 62.1).

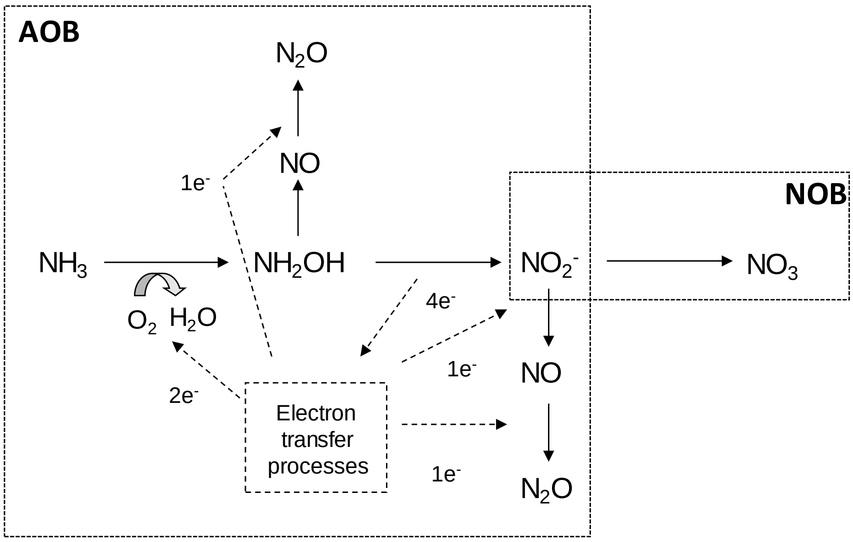

Figure 1. Schematic representation of the nitrification process carried out by AOB and NOB bacteria. Only the AOB can form N_2O through two distinct pathways as shown in the figure (adapted from Kim et al., [1]).

Although N_2O is not produced during the main NH_3 oxidation pathway, it can originate by activating two secondary metabolic pathways in the AOBs during the first nitrification step: i) hydroxylamine oxidation and ii) nitrifying denitrification. Under normal conditions, hydroxylamine oxidation should only result in nitrite formation. However, under certain conditions, nitric oxide (NO) is also produced and passes to N_2O. Some conditions that facilitate the activation of this N_2O production route are the transition from a period of AOB inactivity (e.g. anaerobic or anoxic conditions) to a period of maximum activity (aerobic conditions with the presence of NH_3).

The other metabolic pathway for the production of N_2O in AOB is the process known as nitrifying denitrification. In this case, N_2O is produced from the reduction of NO_2^- produced by the AOBs. This metabolic pathway in AOB is only activated when there is an accumulation of NO_2^- and low oxygen concentrations. Under normal nitrification conditions, NO_2^- rarely accumulates as NOB rapidly oxidizes it to NO_3^-. However, new processes trying to optimize the supply of oxygen in WWTPs promote that nitrification ends in NO_2^-, which is known as partial nitrification and has considerable savings in oxygen supply. This, however, could increase N_2O emissions from this production route.

Denitrification

The denitrification process consists of the reduction of NO_3^- to N_2 linked to the oxidation of organic or inorganic substrates under anoxic conditions through the action of different groups of denitrifying bacteria (Figure 2).

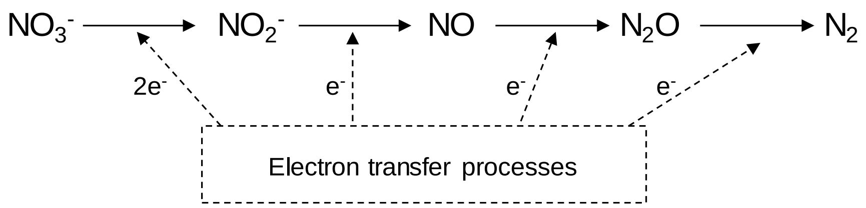

Figure 2. Schematic representation of the denitrification process.

One of the intermediates of this process is N_2O, which under normal conditions is reduced to N_2 and does not usually accumulate. However, there are several factors that affect the reduction process of N_2O to N_2 and consequently favor the accumulation of N_2O. Some of the most important are: i) presence of oxygen, ii) presence of nitrite and iii) limitation of COD. The presence of dissolved oxygen inhibits the denitrification process. The step that is most susceptible to oxygen inhibition is the reduction of N_2O. Therefore, small amounts of dissolved oxygen may favor the accumulation of N_2O. It has also been shown that the presence of nitrite can cause greater inhibition in N_2O reduction than in the other denitrification steps. This inhibition is more relevant when operating at slightly acid pH (pH 6.5-7) since the compound that causes this inhibition is nitrous acid, the protonated species of nitrite. Finally, a limitation of COD during the denitrification process results in a limitation of electrons to carry out the reduction of NO_3^- to N_2. It seems that denitrifying microorganisms prioritize the reduction of NO_3^- and NO_2^- as it is energetically more favorable than the reduction of N_2O, leading to an accumulation of this compound.

In any case, it is important to highlight that, in most WWTPs, the highest N_2O emissions are detected during the aeration stages and are due to the nitrification process. AOB bacteria do not have the capacity to consume the N_2O they form, being emitted directly during the aeration stage.