

4.1 FUNDAMENTALS OF NITROGEN REMOVAL

4.1.1 Forms and reactions of nitrogenous matter

Nitrogenous matter in waste waters is mainly composed of ammonium nitrogen (which can be present as gaseous (NH_3) and ionic form (NH_4^+)) and organic nitrogen (urea, amino acids and other organic compounds with an amino group). Sometimes waste waters contain traces of oxidised forms of nitrogen, mainly nitrite (NO_2^-) and nitrate (NO_3^-). Different to organic matter, nitrogenous matter can be defined quantitatively and unequivocally by one parameter: the nitrogen concentration in its different forms. In practice, spectrophotometric tests and specific ion electrodes are used to determine the concentrations of ammonium, nitrate and nitrite. Organic nitrogen can be determined after its conversion to ammonium nitrogen by chemical digestion. The sum of the organic and ammonium concentrations is called Total Kjeldahl Nitrogen, TKN.

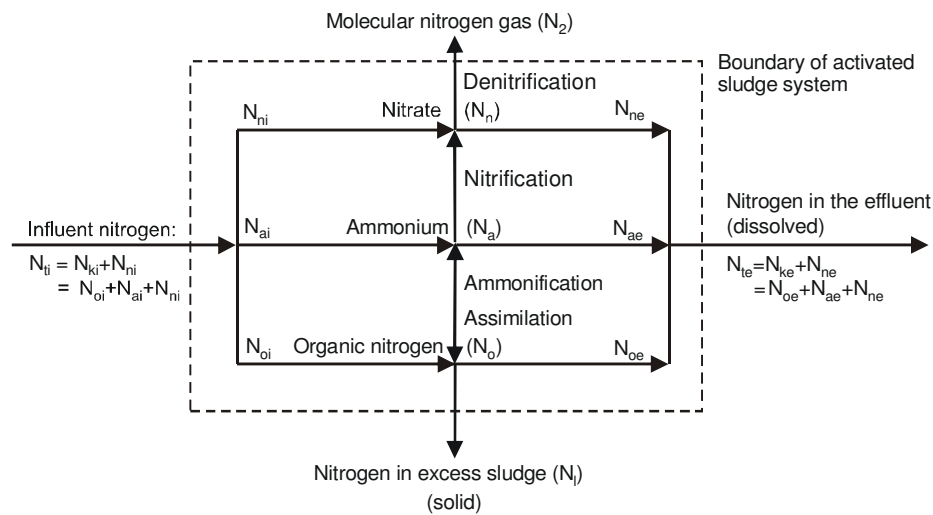


Figure 4.1 Schematic representation of the forms of nitrogenous material and their reactions in the activated sludge process

In the activated sludge process several reactions may occur, that change the form of nitrogenous matter. Figure 4.1 shows the different possibilities: (a) ammonification or the inverse: ammonium assimilation by the organisms, (b) nitrification and (c) denitrification.

(a) Ammonification/assimilation

Ammonification is the conversion of organic nitrogen into ammonium, whereas the inverse process, the conversion of ammonium into organic nitrogen, is called bacterial anabolism or assimilation. Considering that the pH in mixed liquor is typically near the neutral point of $\text{pH} = 7$, ammonium will be present predominantly in its ionic form (NH_4^+) and the following reaction equation may be written:



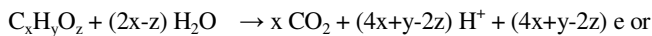
(b) Nitrification

Nitrification is the biological oxidation of ammonium, with nitrate as the end product. The reaction is mediated by specific bacteria and is a two-step process: in the first step ammonium is oxidised to nitrite by bacterial species such as Nitrosomonas spp. The complementary step, oxidation of nitrite to nitrate, is mediated by species such as Nitrobacter spp. Both Nitrosomonas and Nitrobacter can only develop biochemical activity in an environment containing dissolved oxygen. The two steps can be written as:

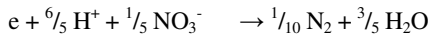
**(c) Denitrification**

Denitrification is the biological reduction of nitrate to molecular nitrogen, with organic matter used as a reductor. For organic matter with a general structural formula $\text{C}_x\text{H}_y\text{O}_z$, the half reactions of this redox process can be expressed as:

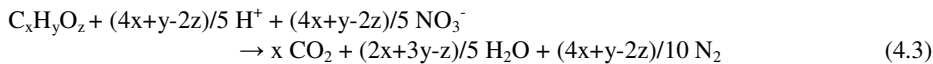
Oxidation reaction:



Reduction reaction:



Overall redox reaction:



The TKN concentration in municipal sewage typically is in the range of 40 to 60 mg $\text{N}\cdot\text{l}^{-1}$, i. e. a fraction in the range of 0.06 to 0.12 of the influent COD. About 75 percent of the total TKN concentration is ammonium nitrogen and the remaining 25 percent is predominantly organic nitrogen.

In the activated sludge process, organic nitrogen is converted rapidly and almost quantitatively to ammonium nitrogen (ammonification). If nitrification occurs and the oxygenation capacity is sufficient, the oxidation of ammonium nitrogen will be almost complete. If after nitrification the formed nitrate is removed by denitrification, the total nitrogen concentration in the effluent is in general smaller than 5 to 10 mg $\text{N}\cdot\text{l}^{-1}$, with a nitrogen removal efficiency of 90 percent or more.