Conversion processes of organic and inorganic matter

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Characterization of substrate and solids

- The microbial action starts in the sewerage system and reaches its maximum in the sewage treatment works.

- In treatment plants, the conversion of organic matter to more oxidized or reduced forms takes place.

- Under aerobic conditions there is the oxidation of the organic matter (carbonaceous matter), that is, the organic carbon is converted into its most oxidized form (CO_2: carbon in the oxidation state of 4+).

- Under anaerobic conditions, the conversion reaction of the organic matter leads to the most oxidized form of carbon (CO_2), but also to its most reduced form (CH_4: carbon with an oxidation state of 4−).

- In sewage treatment under aerobic conditions, the conversion of ammonia (nitrogenous matter) into more oxidized forms of nitrogen (NO^{3-}) can take place, and, under anoxic
- conditions, the subsequent conversion of these to reduced forms (N^2) can also happen.

Characterisation of the carbonaceous matter

The carbonaceous matter (based on organic carbon) present in the wastewater to be treated can be divided in terms of biodegradability into

- The **inert organic matter** (non-biodegradable) passes through the treatment system without changing its form. Two fractions can be identified with respect to the physical state:
  - **Soluble.** The non-biodegradable soluble organic matter does not undergo transformations and leaves the system with the same concentration that it entered.
  - **Particulate.** The non-biodegradable particulate organic matter (suspended) is involved by the biomass and is removed together with the sludge (excess sludge or the sludge that settles at the bottom of the reactors).

- The **biodegradable organic matter** is changed in its passage through the system. Two fractions can be identified, related to the biodegradability, which is also dependent on the physical state:
  - **Rapidly biodegradable.** This fraction is usually in a soluble form and consists of relatively simple molecules.
  - **Slowly biodegradable.** This fraction is usually in a particulate form, although slowly biodegradable soluble organic matter may be present. The slowly-biodegradable matter consists of relatively complex molecules that are not directly used by the bacteria. For this to occur, the conversion into soluble matter is necessary, through the action of extracellular enzymes. This conversion mechanism, called hydrolysis, does not involve the use of energy, but results in the delay in the consumption of the organic matter.

Characterisation of the nitrogenous matter

- **The inorganic nitrogen** is represented by ammonia, either in its free form (NH_3) or in its ionized form (NH^{+4}). Ammonia is present in the influent sewage because the hydrolysis and ammonification reactions have already started in the sewerage system.

- **The organic nitrogen** is divided in a similar form to the carbonaceous matter, as a function of the biodegradability: (a) inert and (b) biodegradable.
  - **Inert.** The inert fraction is divided into two fractions, according to the physical state:
    - – Soluble. This part is usually negligible and does not need to be considered.
    - – Particulate. This part is associated with the non-biodegradable carbonaceous organic matter, being involved by the biomass and removed with the excess sludge.
  - **Biodegradable**. The biodegradable fraction can be subdivided into the following three components:
    - – Rapidly biodegradable. The rapidly-biodegradable organic nitrogenous matter is in a soluble form and is converted by heterotrophic bacteria into ammonia, through the process of ammonification.
    - – Slowly biodegradable. The slowly-biodegradable organic nitrogenous matter is in a particulate form, being converted into a soluble form (rapidly biodegradable) through hydrolysis. This hydrolysis occurs in parallel with the hydrolysis of the carbonaceous matter.
    - – Ammonia. Ammonia (inorganic nitrogen) results from the hydrolysis and ammonification processes described above. Ammonia is used by heterotrophic and autotrophic bacteria.

Suspended and attached biomass growth

- Dispersed growth: the biomass grows in a dispersed form in the liquid medium, without any supporting structure Systems:
  - stabilization ponds and variants
  - activated sludge and variants
  - upflow anaerobic sludge blanket reactors (receiving wastewaters containing suspended solids)

- Attached growth: the biomass grows attached to a support medium, forming a biofilm. The support medium can be immersed in the liquid medium or receive continuous or intermittent liquid discharges. The support medium can be a solid natural (stones, sand, soil) or artificial (plastic) material or consist of an agglomerate of the biomass itself (granules).

  Systems with a solid support for attachment:
  - trickling filters
  - rotating biological contactors
  - submerged aerated biofilters
  - anaerobic filters
  - land disposal systems

Representation of the biomass

- Not all the solids mass participates in the conversion of the organic substrate, as there is an inorganic fraction that does not play an active role in biological treatment.

- The unit of mass of the microbial cells is normally expressed in terms of suspended solids (SS), since the biomass consists of solids that are suspended in the reactor (in the case of dispersed growth).

- The biomass is frequently expressed in terms of volatile suspended solids (VSS). These represent the organic fraction of the biomass – the organic matter can be volatized, that is, converted into gas by combustion (oxidation).

- The volatile suspended solids can be divided into an active and an inactive fraction. The active fraction is that which has the real participation in the conversion of the substrate

Representation of the organic matter/ Substrate

- Influent substrate So (influent BOD_5 or COD). Represents the total BOD_5 (soluble BOD + particulate BOD) or total COD (soluble COD + particulate COD) influent to the biological reactor.
  - ✓ Even in systems with primary sedimentation, around 1/3 of the suspended solids are not removed in this stage and enter the biological reactor.
  - ✓ In the reactor, suspended solids are adsorbed by the biomass and are converted into soluble solids by hydrolysis mechanisms, after which they undergo the conversion reactions. Therefore, in the influent to the reactor, the soluble substrate as well as the particulate substrate must be computed as the influent substrate to be removed.

- Effluent substrate S (effluentBOD_5 or COD). Represents the effluent soluble BOD_5 or soluble COD from the reactor.
  - ✓ Even though the effluent from the reactor could contain a high concentration of suspended solids (biological solids that compose the biomass), these solids are largely removed in the subsequent settling stage, when existent (e.g. secondary sedimentation tank or sedimentation lagoons).
  - ✓ The quality of the final effluent from the treatment plant depends on the (a) soluble BOD or COD: reactor performance; (b) particulate BOD or COD: performance of the final settling unit (when existent).

Conversion of the carbonaceous matter

Aerobic conversion

- Stabilization of the organic matter (conversion to inert products, such as carbon dioxide and water).
- Utilization of oxygen.
- Production of carbon dioxide.
- Release of energy.

$$\underset{\text{organic matter}}{C_6H_{12}O_6} + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O + \text{Energy}$$

$$C_xH_yO_z + \frac{1}{4}(4x + y - 2z)\,O_2 \rightarrow x\,CO_2 + \frac{y}{2}H_2O$$

Anaerobic conversion

- Non-exclusivity of the oxidation. The carbon of CO_2 is present in its highest state of oxidation (+4). However, the opposite occurs with CH_4, in which the carbon is in its most reduced state (−4), subsequently being able to be oxidized (for example, by combustion – methane is inflammable).
- No utilization of oxygen.
- Production of methane and carbon dioxide.
- Release of energy (less than in aerobic respiration).

$$\underset{\text{organic matter}}{C_6H_{12}O_6} \longrightarrow 3\,CH_4 + 3\,CO_2 + \text{Energy}$$

$$C_xH_yO_z + \frac{4x - y - 2z}{4}H_2O \rightarrow \frac{4x - y + 2z}{8}CO_2 + \frac{4x + y - 2z}{8}CH_4$$

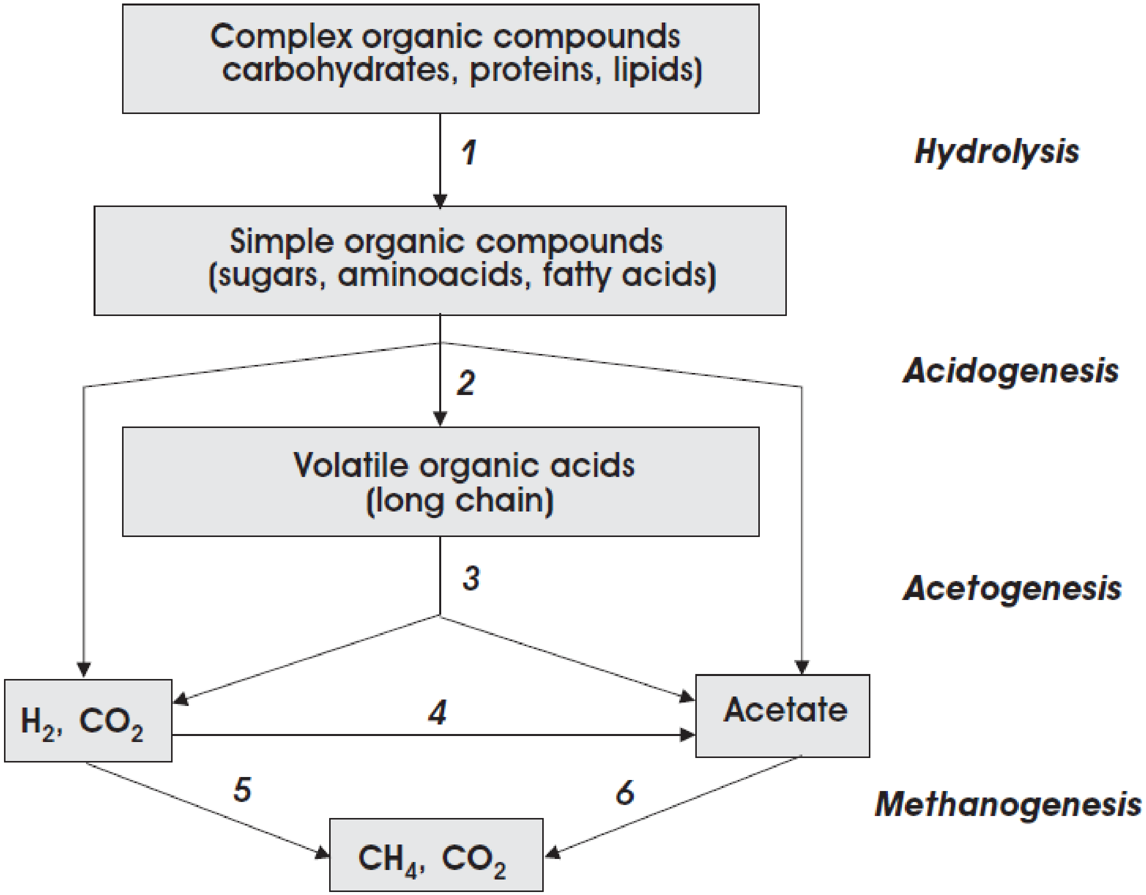
The anaerobic conversion occurs in two stages:

- Acidogenic phase: conversion of the organic matter into organic acids by acidogenic organisms (acid-forming organisms). In this stage, there is only the conversion of organic matter, but no removal.

- Methanogenic phase: conversion of the organic acids into methane, carbon dioxide and water by methanogenic organisms (methane-forming organisms). The organic matter is converted again, but because CH_4 is transferred to the atmosphere, there is the removal of the organic matter.

Before the acidogenesis stage, the complex organic compounds (carbohydrates proteins, and lipids) need to be converted into simple organic compounds, through the mechanism of hydrolysis.

Metabolic sequences and microbial groups



1, 2: hydrolytic fermentative organisms
3: hydrogen-producing acetogenic organisms
4: hydrogen-consuming acetogenic organisms
5: hydrogen-utilising methanogenic organisms
6: acetoclastic methanogenic organisms

Conversion of nitrogenous matter

Oxidation of ammonia (nitrification)

- In domestic sewage, the organic nitrogen is converted into ammonia, through the process of **ammonification**. This process does not change the quantity of nitrogen (TKN) in the wastewater, has no consumption of oxygen, and starts in the sewerage system itself, continuing in the primary and biological treatment units. In the end of the treatment, the quantity of organic nitrogen is small.

- An important oxidation reaction that occurs in some wastewater treatment processes is the **nitrification**, in which the ammonia is transformed into nitrites and these nitrites into nitrates. Only some treatment processes are able to support a significant nitrification, because of their capacity of maintaining sufficient concentrations of the nitrifying bacteria.

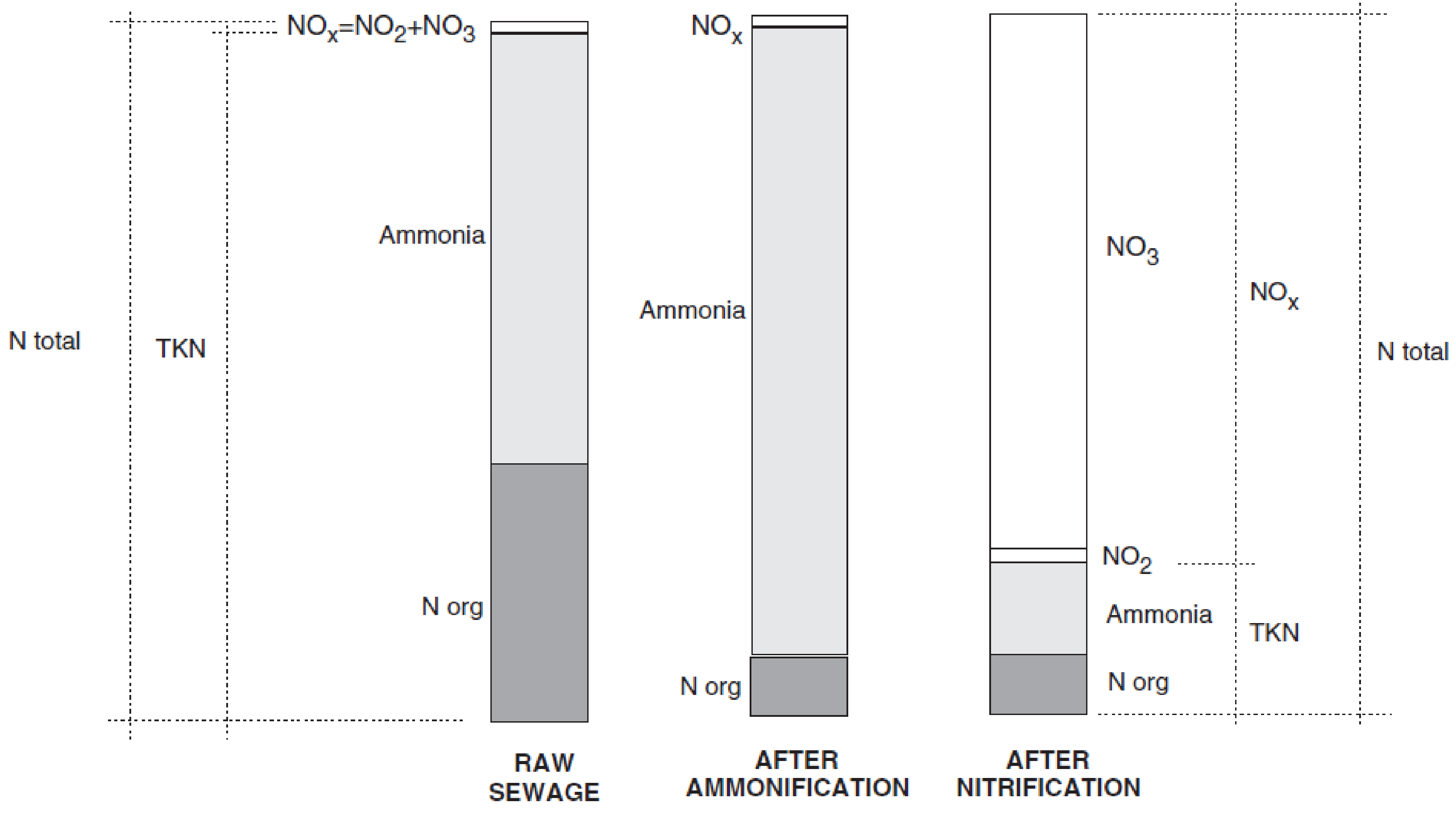
$$2NH_4^+ + 3O_2 \xrightarrow{Nitrosomonas} 2NO_2^- + 4H^+ + 2H_2O$$

$$2\ NO_2^- + O_2 \xrightarrow{Nitrobacter} 2\ NO_3^-$$

Global reaction

$$NH_4^+ + 2\ O_2 \longrightarrow NO_3^- + 2\ H^+ + H_2O$$

Distribution of nitrogen in a treatment system with nitrification



- The oxidized forms of nitrogen (nitrites and nitrates) are collectively called NOx.
- It is seen that with nitrification there is no removal of nitrogen (total nitrogen remains the same), but only conversion of the nitrogen forms.

Reduction of nitrate (denitrification)

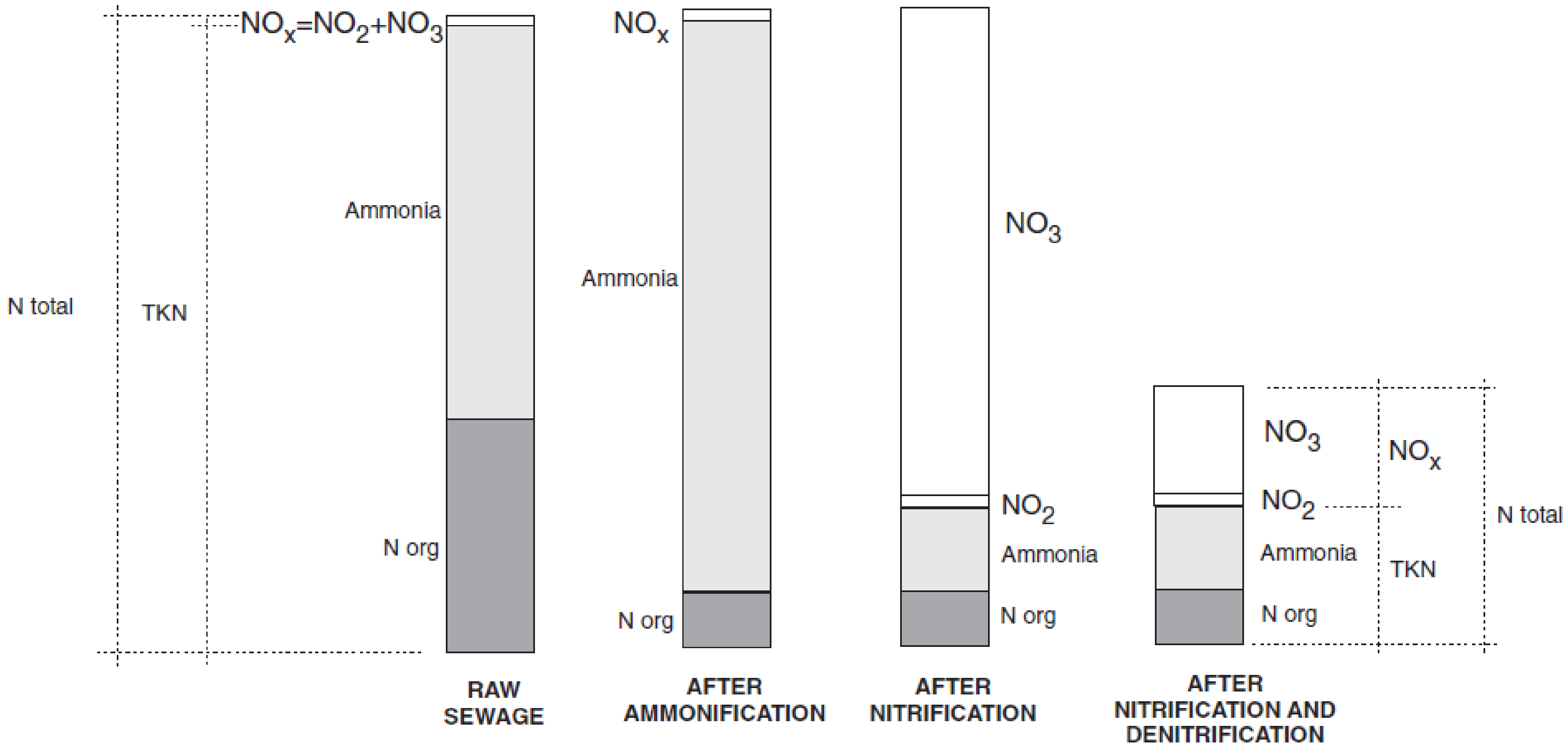
- In anoxic conditions (absence of oxygen, but in the presence of nitrates), the nitrates are used by heterotrophic organisms as an electron acceptor instead of oxygen. In this process, called denitrification, nitrate is reduced to nitrogen gas:

$$2\ NO_3^- + 2\ H^+ \longrightarrow N_2 + 2.5\ O_2 + H_2O$$

With the denitrification reaction, the following points should be noted:

- Economy of oxygen (the organic matter can be stabilized in the absence of oxygen)
- Consumption of H+, implying an economy of the alkalinity and an increase in the buffer capacity of the medium

Distribution of nitrogen in a treatment system with nitrification and denitrification

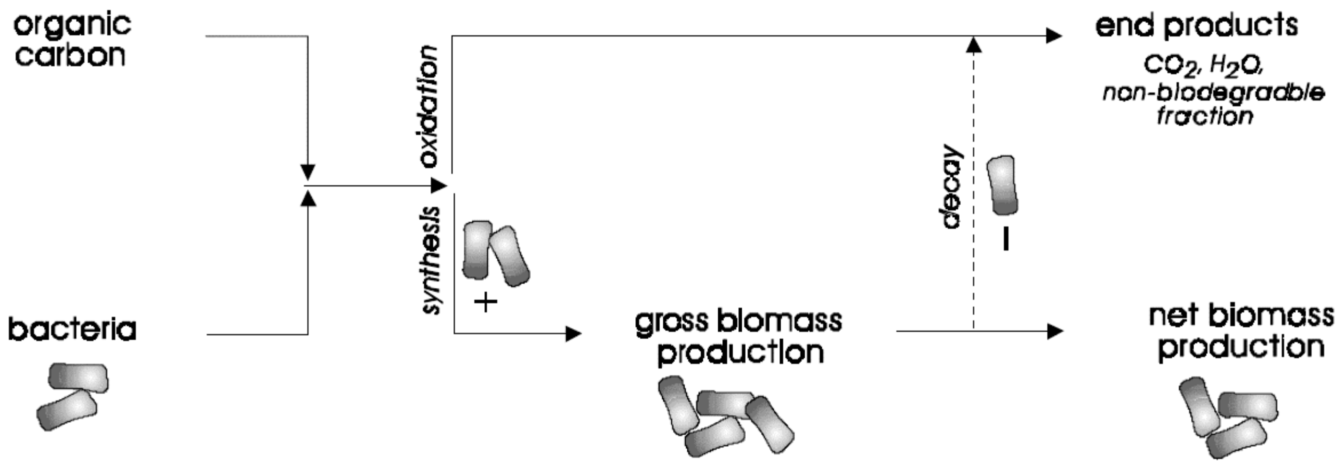


Besides the conversion in the forms of nitrogen, there is also the removal of nitrogen (total nitrogen is decreased). In other words, denitrification leads to an effective removal of nitrogen from the liquid, corresponding to the nitrate that is converted to nitrogen gas, which escapes to the atmosphere.

Principles of Bacterial Growth

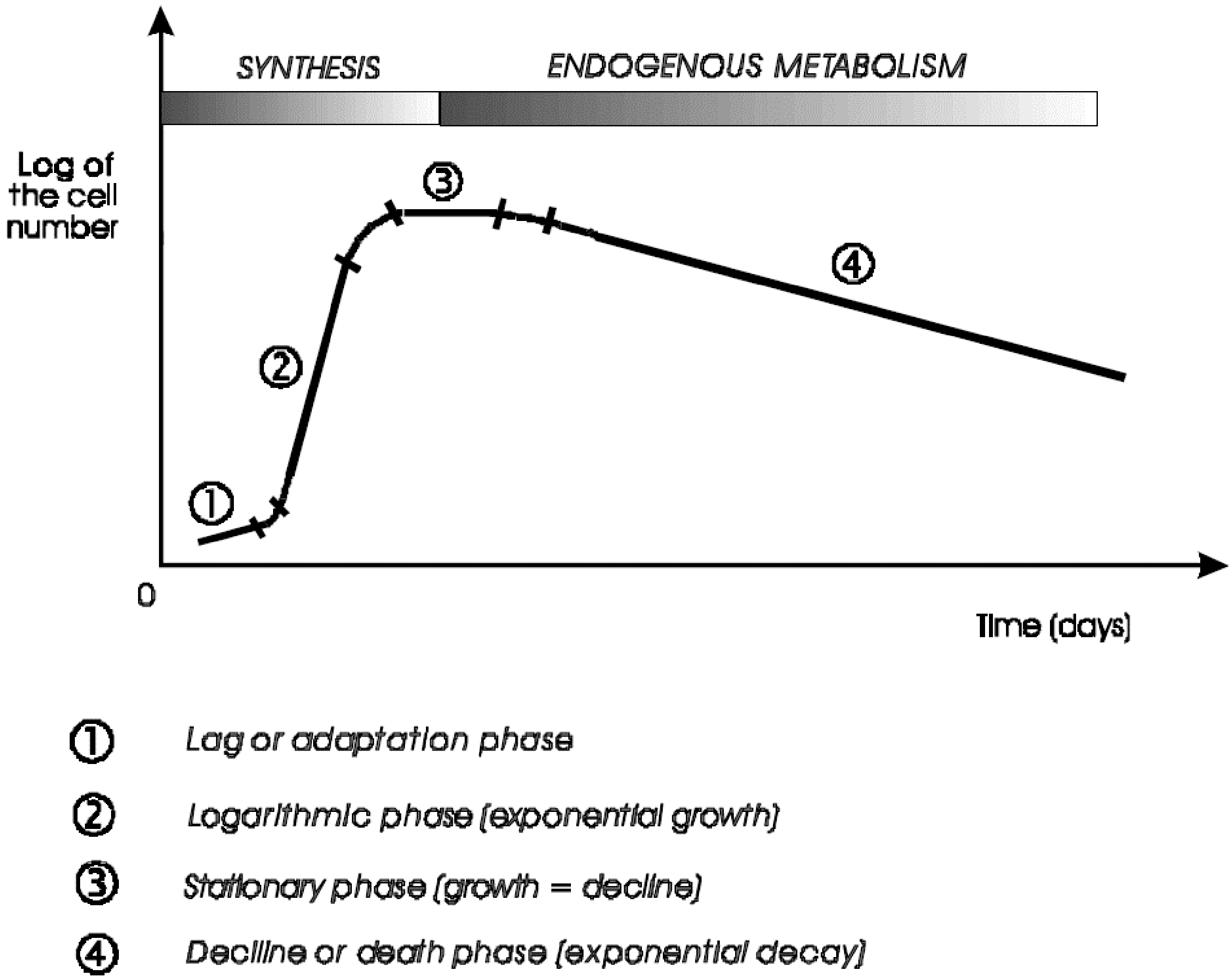
Bacterial-growth curve

- The main reproduction mode for bacteria is by binary fission, in which, when the cell reaches a certain size, it splits into two cells, which will subsequently generate four new cells and so on.
- Thus, after n divisions the number of cells formed is 2^n.



Typical bacterial-growth curve

When inoculating a liquid volume with a certain initial quantity of bacterial cells and a limited quantity of substrate, the number of bacteria will progress with time according to the typical bacterial growth-curve



Bacterial-growth phases

- **Lag phase.** The lag phase is a period for enzymatic adaptation of the bacteria to the new substrate supplied. This phase can be reduced in the case of typical domestic sewage, in which the bacteria have already acquired the necessary enzymatic equipment.

- **Exponential-growth phase**. In the exponential growth phase the cells divide themselves at a constant rate. Plotted on a logarithmic scale, the number of cells grows linearly, justifying the alternative designation of *logarithmic phase*. There is an excess of the substrate in the medium, allowing the growth rate to reach its maximum, with the only limitation by the microorganisms' capacity to process the substrate. In parallel with the maximum growth rate, there is also the maximum substrate removal rate.

- **Stationary phase.** The stationary phase is when the food starts to be scarce in the medium, and the bacterial growth rate is equal to the death rate. Therefore, the number of cells is maintained temporally constant.

- **Decline or decay phase.** In the decline or decay phase, the availability of the substrate in the medium is reduced. In these conditions, *endogenous respiration* prevails, and the bacteria are forced to use their own cellular protoplasm as a substrate source. The dying cells allow their nutrients to diffuse into the medium, serving as food to other cells. The death rate is exponential and constant, leading to a straight line on the logarithmic scale.

Kinetics of bacterial growth

Specific gross bacterial growth

- The bacterial growth can be expressed as a function of the bacteria concentration at a given time in the reactor.
- The net growth rate is equal to the gross growth rate minus the bacterial decay rate.
- The growth rate of a bacterial population is a function of its number, mass or concentration at a given time. Mathematically, this relation can be expressed as:

$$\frac{dX}{dt} = \mu.X$$

where:

X = concentration of the microorganisms in the reactor, SS or VSS (g/m^3)

μ = specific growth rate (d^{-1})

t = time (d)

- The bacterial growth is a function of the availability of the substrate in the medium. When the substrate is present at a low concentration, the growth rate is proportionally low.
- In sewage treatment, the carbonaceous matter is usually the limiting growth factor.

- The specific growth rate μ must be therefore expressed as a function of the substrate concentration. Monod presented this relation according to the following empirical formula:

$$\mu = \mu_{max} \cdot \frac{S}{K_s + S}$$

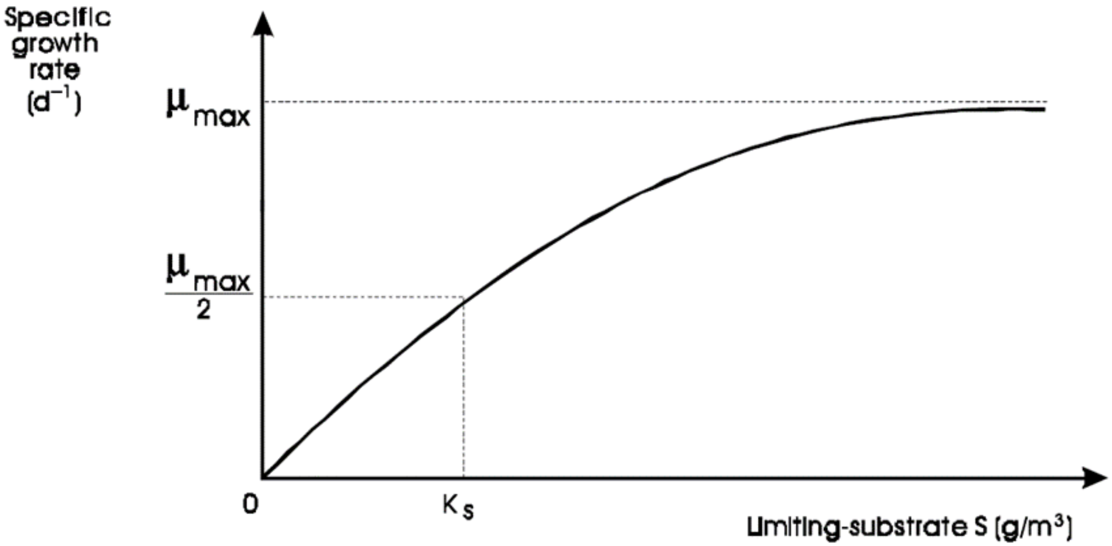
where:

μ_{max} = maximum specific growth rate (d^{-1})
S = concentration of the limiting substrate or nutrient (g/m^3)
K_s = half-saturation coefficient, which is defined as the substrate concentration for which $\mu = \mu_{max}/2$ (g/m^3)

Two constants are used to describe the growth rate:

- μ (mg/L) is the maximum growth rate constant (the rate at which the substrate concentration is not limiting)

- K_s is the half-saturation constant (mg/L) (i.e., concentration of S when μ = μ/2



Values of K_s and μ_{max} in the following ranges have been reported:

- *Aerobic treatment (Metcalf & Eddy, 1991):*

$$\mu_{max} = 1.2 \text{ to } 6\ d^{-1}$$

$$K_s = 25 \text{ to } 100\ \text{mg}\ BOD_5/l$$
or
$$K_s = 15 \text{ to } 70\ \text{mgCOD}/l$$

- *Anaerobic treatment (van Haandel and Lettinga, 1994; Chernicharo, 1997):*

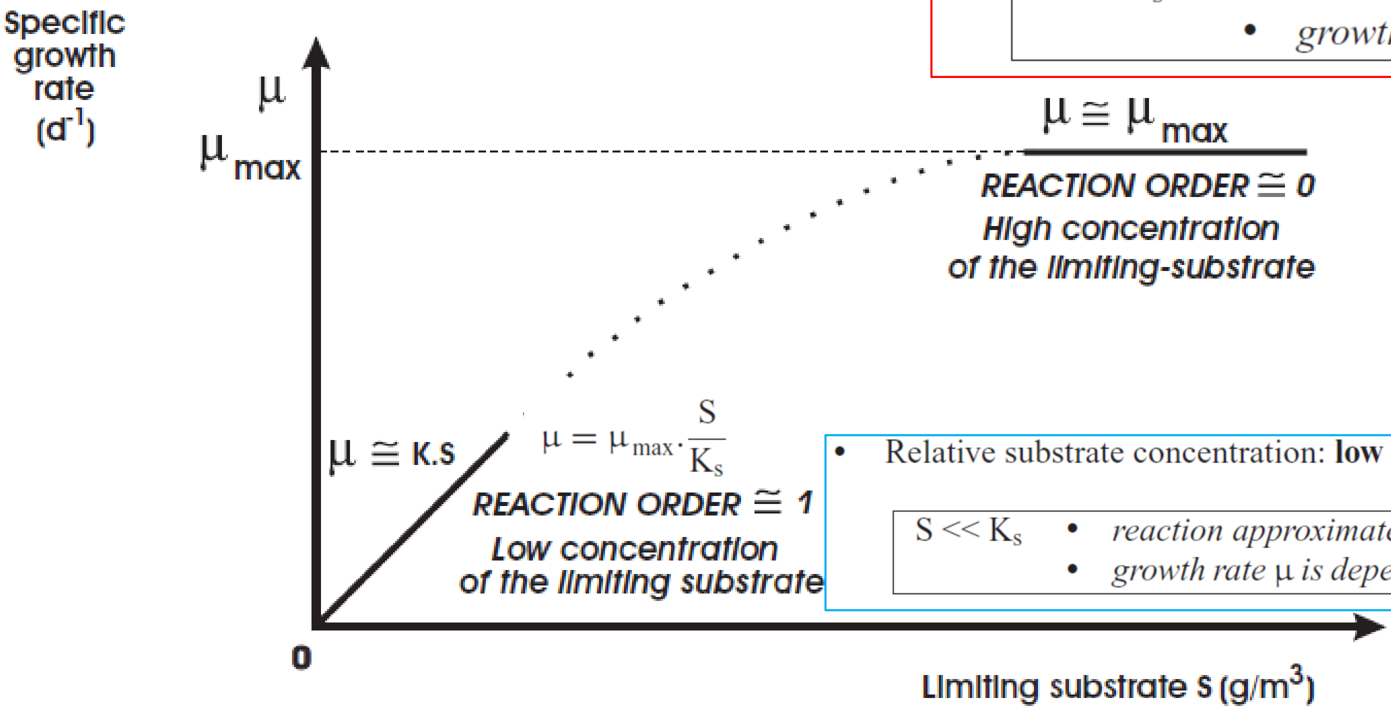
$$\mu_{max} = 2.0\ d^{-1} \text{ (acidogenic organisms)}$$
$$\mu_{max} = 0.4\ d^{-1} \text{ (methanogenic organisms)}$$
$$\mu_{max} = 0.4\ d^{-1} \text{ (combined biomass)}$$

$$K_s \approx 200\ \text{mgCOD}/l \text{ (acidogenic organisms)}$$
$$K_s \approx 50\ \text{mgCOD}/l \text{ (methanogenic organisms)}$$

Extreme conditions in the saturation reaction (Monod kinetics)

- Relative substrate concentration: **high**

$S >> K_s$	• *reaction approximately zero order* • *growth rate μ independent of S*



- Relative substrate concentration: **low**

$S << K_s$	• *reaction approximately first order* • *growth rate μ is dependent on S (directly proportional)*

Example

Express μ as a function of μ_{max} for the following conditions:

- domestic sewage; $S = 300$ mg/L (adopt $K_s = 40$ mg/L)

Domestic sewage ($S = 300$ mg/L)
From Equation 3.13:

$$\mu = \mu_{max} \cdot \frac{S}{K_s + S} = \mu_{max} \cdot \frac{300}{40 + 300} = 0.88\mu_{max}$$

Hence, $\mu = 0.88\ \mu_{max}$

In these conditions, in which S is large in comparison with K_s, the growth rate μ is close to μ_{max}. There is a great availability of the limiting nutrient and the population presents a high growth rate. The reaction is approximately zero order. This situation is not very frequent in the treatment of domestic sewage and occurs at the head of a plug-flow reactor, where the substrate concentration is still high.

Bacterial decay

- The decay rate can be expressed as a first-order reaction:

$$\frac{dX}{dt} = -K_d.X$$

where:

K_d = endogenous respiration coefficient, or bacterial decay coefficient (d^{-1})

- For typical domestic sewage, K_d varies in the following ranges:
  - *Aerobic treatment:*

$K_d = 0.04$ to 0.10 mgVSS/mgVSS.d (base: BOD_5) (Metcalf & Eddy, 1991; von Sperling, 1997)
or
$K_d = 0.05$ to 0.12 mgVSS/mgVSS.d (base: COD) (EPA, 1993; Orhon and Artan, 1994)

  - *Anaerobic treatment:*
    The values available in the literature appear to be not very reliable (Lettinga, 1995), although the value of 0.02 mgVSS/mgVSS.d (base: COD) has been cited by Lettinga et al (1996).

Net bacterial growth

$$\frac{dX}{dt} = \mu.X - K_d.X$$

$$\frac{dX}{dt} = \mu_{max} \cdot \frac{S}{K_s + S}.X - K_d.X$$

Gross biological solids production

- Bacterial growth, that is, biomass production, can be also expressed as a function of the substrate used.
- The greater the substrate assimilation, the greater the bacterial growth rate.
- This relation can be expressed as:

Growth rate = Y (Substrate removal rate)

$$\frac{dX}{dt} = Y\frac{dS}{dt}$$

where:

X = concentration of microorganisms, SS or VSS (g/m^3)
Y = yield coefficient, or coefficient of biomass production; biomass (SS or VSS) produced per unit mass of substrate removed (BOD or COD) (g/g)
S = concentration of BOD_5 or COD in the reactor (g/m^3)
t = time (d)

- The value of Y can be obtained in laboratory tests with the wastewater to be treated.
- For the biological treatment of domestic sewage, the Y value for the bacteria responsible for the removal of the carbonaceous matter varies between:

  - *Aerobic treatment:*

$Y = 0.4$ to 0.8 g VSS/g BOD_5 removed (Metcalf & Eddy, 1991)
or
$Y = 0.3$ to 0.7 g VSS/g COD removed (EPA, 1993; Orhon and Artan, 1994)

  - *Anaerobic treatment:*

$Y \approx 0.15$ gVSS/gCOD (*acidogenic bacteria*) (van Haandel and Lettinga, 1994)
$Y \approx 0.03$ gVSS/gCOD (*methanogenic archaea*) (van Haandel and Lettinga, 1994)
$Y \approx 0.18$ gVSS/gCOD (*combined biomass*) (Chernicharo, 1997)

Net solids production

✓ When including the endogenous respiration, the net solids production becomes:

$$\frac{dX}{dt} = Y\frac{dS}{dt} - K_d.X$$

Substrate removal rate

The substrate removal is associated with the gross biomass growth

$$\frac{dS}{dt} = \frac{1}{Y}.\frac{dX}{dt}$$

Substituting dX/dt for μ.X

$$\frac{dS}{dt} = \frac{\mu}{Y}.X$$

or (expressing μ)

$$\frac{dS}{dt} = \mu_{max}.\frac{S}{K_s + S}.\frac{X}{Y}$$