



16

Anaerobic Wastewater Treatment

Jules B. van Lier, Nidal Mahmoud and Grietje Zeeman

16.1 SUSTAINABILITY IN WASTEWATER TREATMENT

16.1.1 Definition and environmental benefits of anaerobic processes

The fermentation process in which organic material is degraded and biogas (composed of mainly methane and carbon dioxide) is produced, is referred to as anaerobic digestion. Anaerobic digestion processes occur in many places where organic material is available and redox potential is low (zero oxygen). This is typically the case in stomachs of ruminants, in marshes, sediments of lakes and ditches, municipal land fills, or even municipal sewers.

Anaerobic treatment itself is very effective in removing biodegradable organic compounds, leaving mineralised compounds like NH_4^+ , PO_4^{3-} , S^{2-} in the solution. Anaerobic treatment can be conducted in technically plain systems, and the process can be applied at any scale and at almost any place. Moreover the amount of excess sludge produced is very small and well stabilised, even having a market value when the so-called granular anaerobic sludge is produced in the bioreactor. Moreover, useful energy in the form of biogas is produced instead of high-grade energy

consumed. Accepting that anaerobic digestion in fact merely removes organic pollutants, there are virtually few if any serious drawbacks left, even not with respect to the rate of start-up of the system. Figure 16.1 shows the fate of carbon and energy in both aerobic and anaerobic wastewater treatment (AnWT) assuming that the oxidation of 1 kgCOD requires 1 kWh of aeration energy. In contrast to anaerobic treatment, aerobic treatment is generally characterised by high operational costs (energy), while a very large fraction of the waste is converted to another type of waste (sludge). Aerobic treatment in a conventional activated sludge process yields about 50% (or more) new sludge from the COD converted, which requires further treatment, e.g. anaerobic digestion, before it is reused, disposed off or incinerated. The carbon/energy flow principles of aerobic and anaerobic bio-conversion largely affect the set up of the corresponding wastewater treatment system. Not surprisingly, to date, AnWT has evolved into a competitive wastewater treatment technology. Many different types of organically polluted wastewaters, even those that were previously believed not to be suitable for AnWT, are now treated by anaerobic high-rate conversion processes.

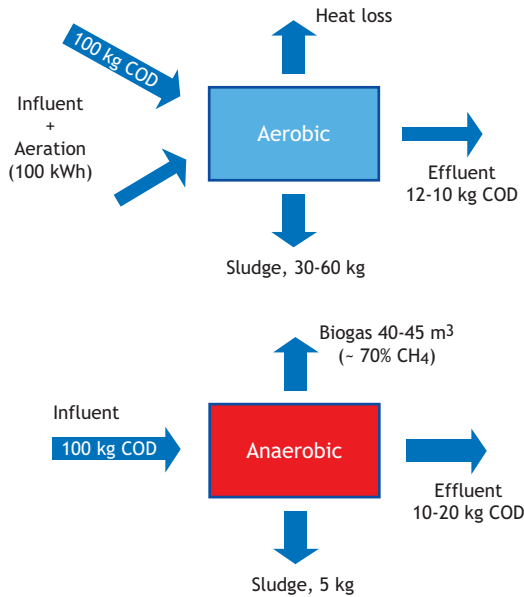


Figure 16.1 Fate of carbon and energy in aerobic (above) and anaerobic (below) wastewater treatment

In countries like the Netherlands, almost all agro-industrial wastewaters are presently treated with anaerobic reactor systems. The application potential, e.g. in the petro-chemical industries, is rapidly growing. Figure 16.2 shows the gradual increase in the number of anaerobic high-rate reactors from the mid seventies onwards.

At present, a total number of 2,266 registered full scale installations are in operation, which are constructed by renowned companies like Paques, Biothane, Biotim, Enviroasia, ADI, Waterleau, Kurita,

Degremont, Envirochemie, GWE, Grontmij as well as other local companies. To this number an estimated number of 500 ‘homemade’ reactors can be added which are constructed by very small local companies or by the industries themselves but which do not appear in the statistics.

Analysing the reasons why the selection for AnWT was made, the following striking advantages of AnWT over conventional aerobic treatment systems can be given:

- reduction of excess sludge production up to 90%.
- up to 90% reduction in space requirement when using expanded sludge bed systems.
- high applicable COD loading rates reaching 20-35 kg COD per m³ of reactor per day, requiring smaller reactor volumes.
- no use of fossil fuels for treatment, saving about 1 kWh/kgCOD removed, depending on aeration efficiency.
- production of about 13.5 MJ CH₄energy/kgCOD removed, giving 1.5 kWh electricity (assuming 40% electric conversion efficiency).
- rapid start up (< 1 week), using granular anaerobic sludge as seed material.
- no or very little use of chemicals.
- plain technology with high treatment efficiencies.
- anaerobic sludge can be stored unfed, reactors can be operated during agricultural campaigns only (e.g. 4 months per year in the sugar industry).
- excess sludge has a market value.
- high rate systems facilitate water recycling in factories (towards closed loops).

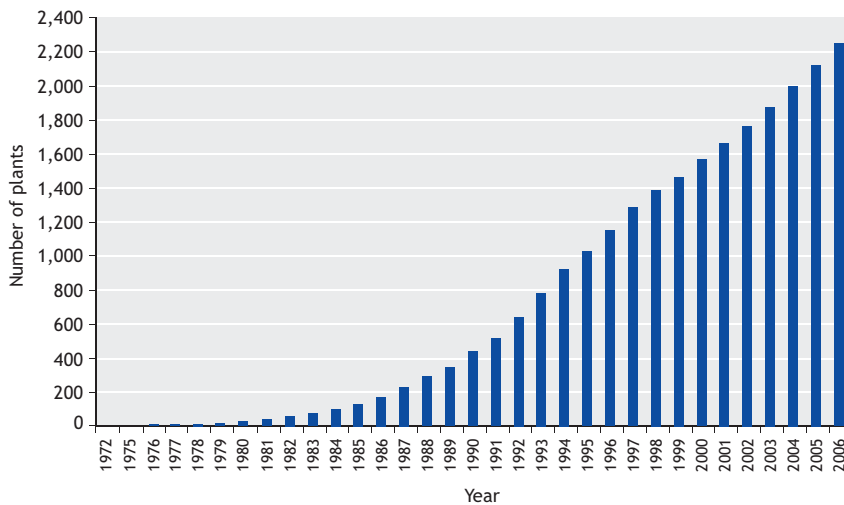


Figure 16.2 Increase in number of world wide installed anaerobic high-rate reactors in the period 1972-2006

Obviously, the exact ranking of the above advantages depends on the local economic and societal conditions. In the Netherlands, excess sludge handling is the cost-determining factor in operating wastewater treatment systems. Since land filling is no option for excess sewage sludge and biowastes, while prices for incineration reach €500/ton wet sludge or more, the low sludge production in anaerobic reactors is an immediate economic benefit. The system compactness, another important asset of AnWT, can be illustrated by a full-scale example, where an anaerobic reactor with a 6 m diameter and a height of 25 m, suffices to treat up to 25 tons of COD daily. The produced sludge, which is less than 1 Ton dry matter per day in this example, is not a waste product, but is marketed as seed sludge for new reactors. Such compactness makes the system suitable for implementation on the industry premises or sometimes even inside the factory buildings. The latter is of particular interest in densely populated areas and for those industries aiming to use anaerobic treatment as the first step in a treatment for reclaiming process water.

The renewed interest in the energy aspects of AnWT directly results from the ever rising energy prices and the overall concern on global warming. The above 25 Tons COD/d of agro-industrial waste(water) can be converted in 7,000 m³CH₄/d (assuming 80% CH₄ recovery), with an energy equivalent of about 250 GJ/d. Working with a modern combined heat power (CHP) gas engine, reaching 40% efficiency, a useful 1.2 MW electric power output can be achieved (Table 16.1). The overall energy recovery could even be higher (reaching up to 60%) if all the excess heat can be used on the industry premises or direct vicinity. Assuming that full aerobic treatment would require about 1 kWh/kgCOD removed, or 1 MW installed electric power in the above case, the total energy benefit of using AnWT over the activated sludge process is 2.2 MW. At an energy price of 0.1 €/kWh this equals about 5,000 €/d. Apart from the energy itself, current drivers include the carbon credits that can be obtained by generating renewable energy using AnWT (Table 16.1). For an average coal-driven power plant, the generation of 1 MW electricity emits about 21 tonCO₂/d, whereas for a natural gas-

driven plant it is half that value. At a foreseen stabilised price of €20/ton CO₂, the above exemplified industry could earn €500/d on carbon credits (based on a coal powered plant), whereas no fossil fuels are used for treating the wastewater. Although this amount is negligible in industrialised countries, it could provide a real incentive in developing countries to start treating the wastewater using high-rate AnWT, and thereby protecting the local environment. The carbon credit policy can, therefore, be regarded as a Western subsidy for implementing AnWT systems in less prosperous countries.

Table 16.1 gives a summary of the expected energy output as well as the predicted CO₂ emission reduction (if the produced CH₄ is converted to electricity) of an anaerobic reactor, operated at commercially available organic loading rates.

16.2 MICROBIOLOGY OF ANAEROBIC CONVERSIONS

16.2.1 Anaerobic degradation of organic polymers

The anaerobic degradation pathway of organic matter is a multi step process of series and parallel reactions. This process of organic matter degradation proceeds in four successive stages, namely: (i) hydrolysis, (ii) acidogenesis, (iii) acetogenesis, and (iv) methanogenesis. These are discussed below.

Methanogenic bacteria are located at the end of the anaerobic food chain and, partly thanks to their activity, no large quantities of organic matter accumulate in anaerobic environments, where this matter is inaccessible to aerobic organisms. The anaerobic digestion process involves a complex food web, in which organic matter is sequentially degraded by a wide variety of micro-organisms. The microbial consortia involved jointly convert complex organic matter and ultimately mineralize it into methane (CH₄), carbon dioxide CO₂, ammonium (NH₃), hydrogen sulphide (H₂S) and water (H₂O).

Table 16.1 Energy output and CO₂ emission reduction applying anaerobic high-rate wastewater treatment systems

Loading capacity (kgCOD/m ³ .d)	5 – 35
Energy output (MJ/m ³ reactor installed per d)	55 – 390
Electric power output (kW/m ³ reactor installed)	0.25 – 1.7
CO ₂ emission reduction (tonCO ₂ /m ³ .y, based on coal-driven power plant)	1.9 – 13

Assumptions: 80% CH₄ recovery relative to influent COD load and 40% electric conversion efficiency using a modern combined heat power generator.

The anaerobic ecosystem is the result of complex interactions among microorganisms of several different species. The major groupings of bacteria and reaction they mediate are: (i) fermentative bacteria, (ii) hydrogen-producing acetogenic bacteria, (iii) hydrogen-consuming acetogenic bacteria, (iv) carbon dioxide-reducing methanogens, and (v) aceticlastic methanogens. The reactions they mediate are presented in Figure 16.3.

The digestion process may be subdivided into the following four phases:

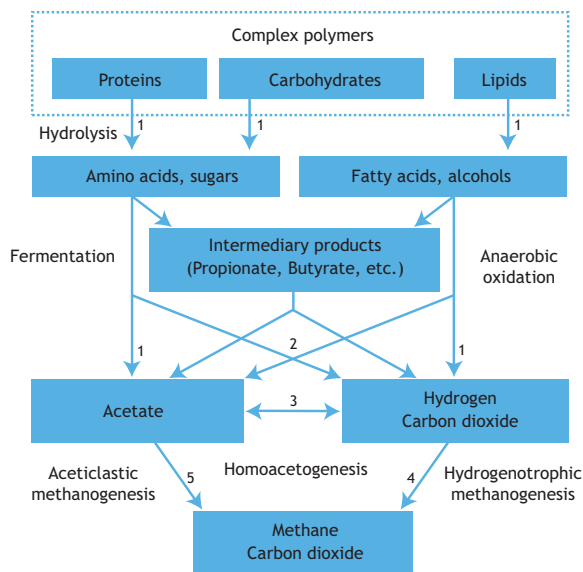


Figure 16.3 Reactive scheme for the anaerobic digestion of polymeric materials. Numbers indicate the bacterial groups involved: 1. Hydrolytic and fermentative bacteria, 2. Acetogenic bacteria, 3. Homo-acetogenic bacteria, 4. Hydrogenotrophic methanogens, 5. Aceticlastic methanogens (Gujer and Zehnder, 1983)

- 1) *Hydrolysis*, where enzymes excreted by fermentative bacteria (so-called ‘exo-enzymes’) convert complex, undissolved material into less complex, dissolved compounds which can pass through the cell walls and membranes of the fermentative bacteria.
- 2) *Acidogenesis*, where the dissolved compounds present in cells of fermentative bacteria are converted into a number of simple compounds which are then excreted. The compounds produced during this phase include volatile fatty acids (VFAs), alcohols, lactic acid, CO_2 , H_2 , NH_3 and H_2S , as well as new cell material.
- 3) *Acetogenesis* (intermediary acid production) where digestion products are converted into acetate, hydrogen (H_2) and CO_2 , as well as new cell material.

- 4) *Methanogenesis*, where acetate, hydrogen plus carbonate, formate or methanol are converted into methane, CO_2 and new cell material.

In this global scheme, the following sub-processes can be distinguished (Figure 16.3):

- 1) Hydrolysis of biopolymers:
 - hydrolysis of proteins
 - hydrolysis of polysaccharides
 - hydrolysis of fats
- 2) Acidogenesis/fermentation:
 - anaerobic oxidation of amino acids and sugars
 - anaerobic oxidation of higher fatty acids and alcohols
- 3) Acetogenesis:
 - formation of acetic acid and H_2 from intermediary products (particularly VFAs)
 - homoacetogenesis: the formation of acetic acid from H_2 and CO_2
- 4) Methanogenesis:
 - methane formation from acetic acid
 - methane formation from hydrogen and carbon dioxide

Figure 16.3 gives the unidirectional degradation of organic matter to the end products CH_4 and CO_2 . The homoacetogenic process illustrates the inter conversion of acetate, the major CH_4 precursor and H_2/CO_2 . In practice, other back reactions may occur also, e.g. the formation of higher VFA or alcohols out of acetate and propionate. These back reactions are of particular importance in case of malfunctioning or perturbation of the anaerobic reactor or when a specific reaction is deliberately pursued. Under normal AnWT applications, i.e. stable reactor performance under mesophilic conditions, acetate is the major precursor of CH_4 (about 70% of the COD flux). Interesting to observe is that there is only COD conversion and no COD destruction. COD removal takes place owing to the fact that the end product of the reaction chain, CH_4 , is gaseous and highly insoluble in water.

In the case of the presence of alternative electron acceptors, like NO_3^- and SO_4^{2-} , other bacterial groups will be present in the anaerobic reactor as well, such as denitrifiers and sulphate reducers (see Section 16.4).

16.2.1.1 Hydrolysis

Since bacteria are unable to take up particulate organic matter, the first step in anaerobic degradation consists of the hydrolysis of polymers. This process is merely a

surface phenomena in which the polymeric particles are degraded through the action of exo-enzymes to produce smaller molecules which can cross the cell barrier. During the enzymatic hydrolysis process, proteins are hydrolyzed to amino acids, polysaccharide to simple sugars and lipids to long chain fatty acids (LCFA). Hydrolysis is in most cases, notably with (semi-) solid substrates and wastewaters with a high suspended solids (SS)/COD ratio, rate-limiting for the overall digestion process. Moreover, the hydrolysis process is very sensitive to temperature and temperature fluctuations. For that reason, the design of anaerobic digesters for (semi-) solid substrates and wastewaters with a high SS/COD ratio, such as distillery slops and low temperature sewage, is usually based on the hydrolysis step.

Hydrolysis can be defined as a process in which complex polymeric substrates, particulate or dissolved, are converted into monomeric and dimeric compounds which are readily accessible for the acidogenic bacteria. During anaerobic digestion of complex substrates hydrolysis is usually the first step. Although in some cases a preparatory step, i.e. physico-chemical pre-treatment or comminution, is needed to make hydrolysis possible. With the digestion of biological sludges, such as waste activated sludge, the hydrolysis of the sludge is preceded by death and lysis of the biomass. The hydrolysis is accomplished by exo-enzymes which are produced by the acidogenic bacteria. The products of the hydrolysis are the substrates for the acidogenic bacteria. A schematic presentation of the hydrolysis of lipids into LCFAs is given in Figure 16.4.

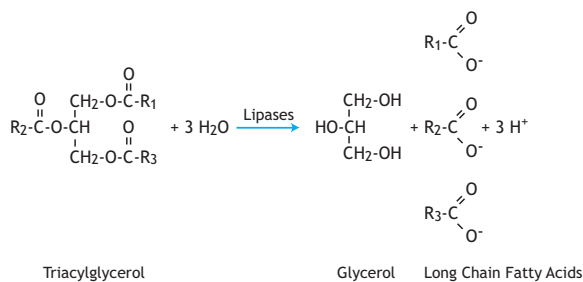


Figure 16.4 The hydrolysis of lipids

As mentioned, hydrolysis is generally considered to be the rate-limiting step during the anaerobic digestion of complex substrates. However, usually this is not due to a lack of enzyme activity but to the availability of free accessible surface area of the particles and the overall structure of the solid substrate (Zeeman *et al.*, 1996, Chandler *et al.*, 1980). Even in dilute wastewaters such as low temperature domestic sewage,

hydrolysis may determine the overall process and thereby determining the required reactor design. It must be noted that 45–75% of domestic sewage, and 80 % in primary sludge consists of suspended matter. The main biopolymers in sewage are proteins, carbohydrates and lipids.

16.2.1.2 Acidogenesis

During the acidogenesis step, the hydrolysis products (amino acids, simple sugars, LCFAs), which are relatively small soluble compounds, are diffused inside the bacterial cells through the cell membrane and subsequently fermented or anaerobically oxidized. Acidogenesis is a very common reaction and is performed by a large group of hydrolytic and non-hydrolytic microorganisms. About 1% of all known bacteria are (facultative) fermenters. The acidification products consist of a variety of small organic compounds, mainly VFAs, i.e. acetate and higher organic acids such as propionate and butyrate, as well as H₂, CO₂, some lactic acids, ethanol and ammonia (Figure 16.3).

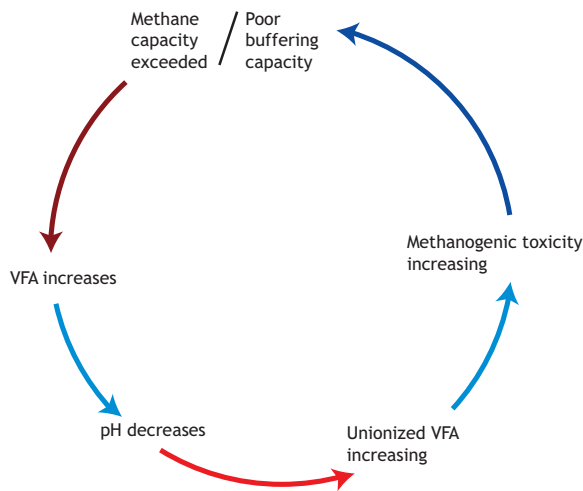
Characteristically, neutral compounds such as sugars and proteins are converted into VFAs and carbonic acid, being the main end products. Therefore, fermentative organisms are usually designated as acidifying or acidogenic microorganisms, and the process is therefore indicated by acidogenesis. Table 16.2 lists several acidogenic reactions starting from sucrose and generating different amounts of VFAs, HCO₃⁻, H₂, H⁺. Apparently, the type of end products depends on the conditions in the reactor medium. From Table 16.2 it follows that the ΔG^{o'} of the less energetic acidogenic reactions with sucrose as the substrate strongly depends on the prevailing H₂ concentrations. If H₂ is effectively removed by H₂ scavenging organisms such as methanogens, acetate will be the main end product. However, if methanogenesis is retarded and H₂ accumulates, more reduced products such as propionate and butyrate are likely to appear and possibly the even more reduced compounds lactate and alcohols. Therefore, effluents of overloaded or perturbed anaerobic reactors (or reactors designed as acidifying reactors in an anaerobic two-step process) often contain these more reduced intermediate products.

Acidogenesis is the most rapid conversion step in the anaerobic food chain. The ΔG^{o'} of acidifying reactions is highest of all anaerobic conversions, resulting in ten to twentyfold higher bacterial growth rates, and fivefold higher bacterial yields and conversion rates

Table 16.2 Acidogenic reactions with sucrose as the substrate and the corresponding free energy change (ΔG°) at 25°C

Reactions	ΔG° (kJ/mol)	Eq.
$C_{12}H_{22}O_{11} + 9H_2O \rightarrow 4CH_3COO^- + 4HCO_3^- + 8H^+ + 8H_2$	- 457.5	(16.1)
$C_{12}H_{22}O_{11} + 5H_2O \rightarrow 2CH_3CH_2CH_2COO^- + 4HCO_3^- + 6H^+ + 4H_2$	- 554.1	(16.2)
$C_{12}H_{22}O_{11} + 3H_2O \rightarrow 2CH_3COO^- + 2CH_3CH_2COO^- + 2HCO_3^- + 6H^+ + 2H_2$	- 610.5	(16.3)

compared to methanogens (Table 16.3). For that reason, anaerobic reactors are subjected to souring, i.e. a sudden pH drop, when reactors are overloaded or perturbed by toxic compounds. Once alkalinity is consumed by the produced acids the pH starts to drop, resulting in a higher concentration of non-dissociated VFAs, leading to a more severe inhibition of methanogens. The latter, obviously leads to an even quicker accumulation of VFAs and subsequent pH drop (Figure 16.5).

**Figure 16.5** Reactor pH drop as a result of methanogenic overloading and accumulating VFAs

The fact that acidifiers are active even at low pH (4), means the reactor souring to pH 4 to 5 can and will occur when the methanogenic capacity of the system is trespassed.

The acidogenic conversion of amino acids generally follows the Stickland reaction, in which an amino acid is de-ammonified by anaerobic oxidation yielding also VFA and H_2 , in conjunction with the reductive de-ammonification of other amino acids consuming the

produced H_2 . From both reactions NH_3 is released and subsequently acts as a proton acceptor, thus leading to a pH increase. In this reaction there is no net proton production and there is no chance of reactor pH drop.

16.2.1.3 Acetogenesis

The short chain fatty acids (SCFA), other than acetate, which are produced in the acidogenesis step are further converted to acetate, hydrogen gas and carbon dioxide by the acetogenic bacteria. The most important acetogenic substrates are propionate and butyrate, key-intermediates in the anaerobic digestion process. But also lactate, ethanol, methanol and even H_2 and CO_2 are (homo)acetogenically converted to acetate as shown in Figure 16.3 and Table 16.4. LCFAs are converted by specific acetogenic bacteria following the so-called β -oxidation in which acetate moieties are split from the aliphatic chain (Table 16.4). LCFAs with uneven C atoms also yield propionate next to acetate. Non-saturated LCFAs like oleate and linoleate are firstly saturated by H_2 addition prior to the β -oxidation. The acetogenic bacteria are obligate hydrogen producers and their metabolism is inhibited by hydrogen, which immediately follows from the stoichiometric conversion reaction, such as for propionate:

$$\Delta G' = \Delta G'_0 + RT \ln \frac{[Acetate] \cdot [CO_2] \cdot [H_2]^3}{[Propionate]} \quad (16.4)$$

Studies carried out on acetogenic conversions have elucidated the required narrow associations between the H_2 -producing acetogenic bacteria and the H_2 -consuming methanogenic bacteria, thereby regulating the H_2 level in their environment. This is of vital importance as these reactions are thermodynamically unfavourable, indicated by the positive ΔG° in Table 16.4. From this table it follows that the reactions for ethanol, butyrate,

Table 16.3 Averaged kinetic properties of acidifiers and methanogens

Process	Conversion rate gCOD/gVSS.d	Y gVSS/gCOD	K_s mgCOD/l	μ_m 1/d
Acidogenesis	13	0.15	200	2.00
Methanogenesis	3	0.03	30	0.12
Overall	2	0.03-0.18	-	0.12

propionate and the LCFAs palmitate will not occur under standard conditions, as the ΔG° is positive, and thus the bacterial energy yield is negative.

However, under stabilised digestion conditions the hydrogen partial pressure is maintained at an extremely low level. This can be achieved by an effective uptake of the hydrogen by methanogens or sulphate reducing bacteria. Methanogenic bacteria usually utilize molecular hydrogen in the anaerobic digester so rapidly that the hydrogen partial pressure drops below 10^{-4} atm, which is enough to ensure the actual occurrence of the hydrogen producing acetogenic reaction (Figure 16.6).

This interdependence means that the degradation of higher fatty acids and alcohols largely depends on the activity of electron scavenging organisms such as methanogenic bacteria. Microbial associations in which a H_2 -producing organism can grow only in the presence of a H_2 -consuming organism are called syntrophic

associations. The coupling of formation and use of H_2 is called interspecies hydrogen transfer. In a properly functioning methane-producing installation, the partial hydrogen pressure will not exceed 10^{-4} atm and is usually between 10^{-4} - 10^{-6} atm. At such a low hydrogen concentration, the degradation of ethanol, butyrate or propionate becomes exergonic and will yield energy for the acetogens.

Similar to the other acetogenic substrates, LCFA conversion is highly endergonic and often limits the entire digestion process (Novak and Carlson, 1970). Trials with upflow anaerobic sludge blanket (UASB) reactors were only partly successful as LCFA tend to absorb to the sludge forming fatty clumps of biomass with little if any methanogenic activity. Expanded bed reactors, in which the LCFA is more evenly distributed over the available biomass were more successful (Rinzema, 1988). Other authors propose in fact to use the absorptive capacity of the sludge and periodically

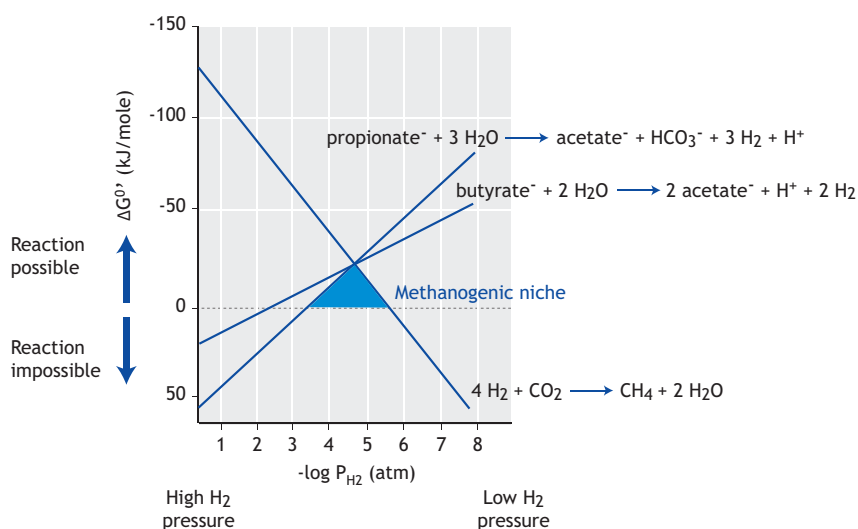


Figure 16.6 Free energy change as a function of the H_2 partial pressure. A negative ΔG° indicates possible occurrence of the mentioned reaction

Table 16.4 Stoichiometry and change of free energy (ΔG°) for some acetogenic reactions, assuming neutral pH, a temperature of $25^{\circ}C$ and a pressure of 1 atm (101 kPa). Water is regarded as a pure liquid, and all soluble compounds have an activity of 1 mol/kg

Compound	Reaction	ΔG° (kJ/mol)	Eq.
Lactate	$CH_3CHOHCOO^- + 2H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 2H_2$	-4.2	(16.5)
Ethanol	$CH_3CH_2OH + H_2O \rightarrow CH_3COO^- + H^+ + 2H_2$	+9.6	(16.6)
Butyrate	$CH_3CH_2CH_2COO^- + 2H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2$	+48.1	(16.7)
Propionate	$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 3H_2$	+76.1	(16.8)
Methanol	$4CH_3OH + 2CO_2 \rightarrow 3CH_3COOH + 2H_2O$	-2.9	(16.9)
Hydrogen-CO ₂	$2HCO_3^- + 4H_2 + H^+ \rightarrow CH_3COO^- + 4H_2O$	-70.3	(16.10)
Palmitate	$CH_3-(CH_2)_{14}-COO^- + 14H_2O \rightarrow 8CH_3COO^- + 7H^+ + 14H_2$	+345.6	(16.11)

load the sludge with LCFA after which solid state digestion will convert the absorbed matter to CH_4 (Pereira *et al.*, 2004). Such a sequencing bed mode of operation requires multiple reactors to treat a continuous flow wastewater.

16.2.1.4 Methanogenesis

Methanogenic bacteria accomplish the final stage in the overall anaerobic conversion of organic matter to methane and carbon dioxide. During this fourth and last stage of anaerobic degradation of organic matter, a group of methanogenic archaea both reduce the carbon dioxide using hydrogen as electron donor and decarboxylate acetate to form CH_4 (Figure 16.3). It is only in this stage when the influent COD is converted to a gaseous form that automatically leaves the reactor system. Methanogens are obligate anaerobes, with a very narrow substrate spectrum. Some can only use certain determined substrates such as acetate, methylamines, methanol, formate, and H_2/CO_2 or CO . For engineering purposes, methanogens are classified into two major groups: the acetate converting or aceticlastic methanogens and the hydrogen utilising or hydrogenotrophic methanogens (Table 16.5). Generally, about 70 % of the produced methane originates from acetate as the main precursor. The rest mainly originates from H_2 and CO_2 . The growth rate of the aceticlastic methanogens is very low, resulting in doubling times of several days or even more. The extremely low growth rates explain why anaerobic reactors require a very long start-up time with unadapted seed material and why high sludge concentrations are pursued. Hydrogenotrophic bacteria have a much higher maximum growth rate than the acetoclastic bacteria with doubling times of 4 to 12 hours. Because of this feature and despite the very delicate acetogenic reaction step discussed in the previous section, anaerobic high-rate reactor systems exert a remarkable stability under varying conditions.

Table 16.5 lists two types of aceticlastic methanogens with very different kinetic characteristics.

Also the morphological characteristics of both methanogenic genera are very different as indicated by Figure 16.7.

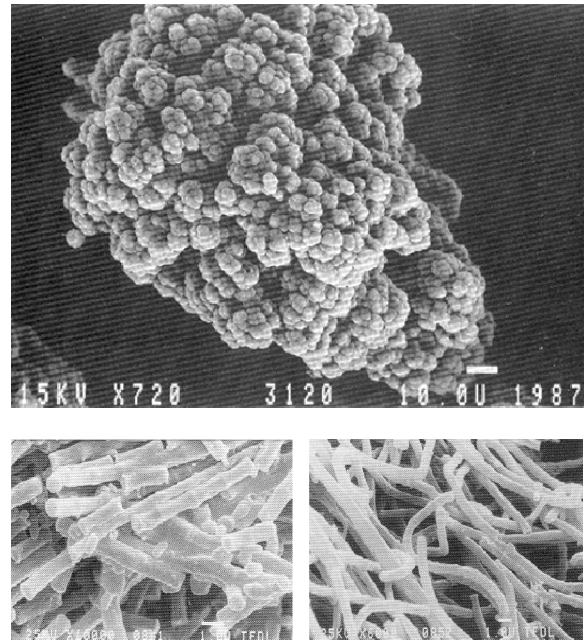


Figure 16.7 Morphology and appearance of the most important acetotrophic methanogens belonging to the genera *Methanosarcina* (above) and *Methanosaeta* (below)

Methanosarcina spp. are characterised by a coccoid shape, appearing in small grape-like clumps, and have a relative wide substrate spectrum as they can convert a.o. acetate, H_2/CO_2 , methylamines, methanol, and formate. They have a relatively high μ_{max} and relative low substrate affinity. *Methanosaeta* spp. are filamentous, appear in large spaghetti like conglomerates can only convert acetate and are kinetically characterised by a low μ_{max} and a very high substrate affinity. Although the μ_{max} of the latter organism is significantly lower, *Methanosaeta* spp. are the most common acetotrophic methanogens in anaerobic high rate systems based on high solids retention times, such as sludge bed systems and anaerobic filters. The reason for this phenomenon can be attributed to the fact that wastewater treatment

Table 16.5 Most important methanogenic reactions, the corresponding free energy change (ΔG°) and some kinetic properties

Functional step	Reaction	ΔG° kJ/mol	μ_{max} 1/d	T_d d	K_s mgCOD/l	Eq.
Acetotrophic methanogenesis*	$\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightarrow \text{CH}_4 + \text{HCO}_3^-$	-31	0.12 ^a 0.71 ^b	5.8 ^a 1.0 ^b	30 ^a 300 ^b	(16.12)
Hydrogenotrophic methanogenesis	$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-131	2.85	0.2	0.06	(16.13)

* Two different methanogens belonging to ^a*Methanosarcina* spec. and ^b*Methanosaeta* spec.

systems always aim at the lowest possible effluent concentrations, while substrate concentrations inside biofilms or sludge granules of the mentioned anaerobic systems approaches 'zero' when bulk liquid concentrations are low. Under such conditions, *Methanosaeta* spp. species have a clear kinetic advantage over the *Methanosarcina* spp. (Figure 16.8).

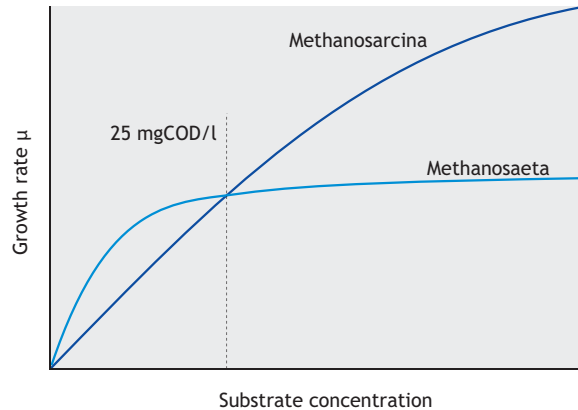


Figure 16.8 Monod growth curves of the acetotrophic methanogens *Methanosarcina* spp. and *Methanosaeta* spp. Both μ_{\max} and the Monod half saturation constant (K_s) of both genera is given in Table 16.5

Once the *Methanosaeta* spp. dominate the sludge bed, a very effective wastewater treatment system is obtained, reaching extremely low effluent acetate concentrations. Considering the inferior kinetic properties at low substrate concentrations and the inferior adherence properties of *Methanosarcina* spp., it is advised to keep the effluent acetate concentrations at a very low level during the first start-up of an anaerobic reactor with unadapted seed material.

16.3 PREDICTING THE CH₄ PRODUCTION

The organic pollution can be classified on the basis of solubility (soluble and insoluble organic matter) and/or on the basis of biodegradability.

Both are of great importance for the treatment process. Regarding the enormous variety of organic compounds generally present in wastewater it is impractical and generally also impossible to determine these compounds separately. In order to quantify the organic pollution in practice, use is being made of the fact that these contaminants can be oxidised by strongly oxidizing agents. In wastewater treatment engineering practice two standard tests based on the oxidation of organic material are applied: the biochemical oxygen

demand (BOD) and the chemical oxygen demand (COD) tests (Chapter 3). In both tests, the organic material is oxidised and the amount of oxygen consumed stands for the value of the parameter. In the BOD test it concerns the biochemical amount of oxygen required by the aerobic organisms to oxidize the organic matter. The BOD value therefore is closely related to the biodegradability. For application of anaerobic treatment, it is preferable to use some kind of standardized anaerobic biodegradability test instead of the conventional aerobic BOD test. In such an anaerobic test a sample of the wastewater is exposed to an available amount of anaerobic sludge and the total amount of CH₄ produced after termination of the digestion process is determined and then related to the amount of organic matter present in the sample. As a certain amount of CH₄ is equivalent to a certain amount of COD, we in fact determine the BOD_{anaerobic}.

Since generally not all organic pollutants are biodegradable and also part of the organic substrate will be used for cell synthesis, the BOD value generally is substantially lower than the COD value. Latter is particularly the case for the conventional aerobic BOD test, much less for the anaerobic BOD test because of the significantly lower growth yield under anaerobic conditions. Efforts for standardisation are currently being done including ring tests in various laboratories.

In the standardized COD test, which generally uses bichromate as oxidizing medium at an elevated temperature (150°C), almost all organic pollutants are completely converted into CO₂ and H₂O. On the other hand organic nitrogen present in the contaminants is converted into NH₃, whereas organic matter containing quaternary ammonium salts like betaine (trimethyl glycine) stay as well reduced and are 'invisible' in the COD test.

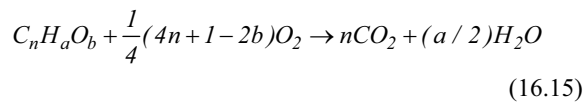
The total organic carbon (TOC) is another measurement used, but it is a much less useful parameter. The organic carbon concentration is measured in the form of carbon dioxide after incineration of the organic material present in a waste water sample. Correction must be made for inorganic carbon, originally present in the sample. The theoretical value of a pure compound follows from Eq. 16.14:

$$TOC_t = 12n / (12n + a + 16b + 14d) \quad (\text{gTOC/gC}_n\text{H}_a\text{O}_b\text{N}_d) \quad (16.14)$$

16.3.1 COD

The COD undoubtedly represents the most important parameter for the concentration of contaminants in wastewater, particularly for industrial wastewaters. This feature in which organic matter is almost completely oxidized makes the COD test very suitable for assessment of COD balances. Calculation of the substrate COD and the theoretical quantity of methane produced is presented below.

The COD of an organic compound $C_nH_aO_b$ can easily be calculated on the basis of the chemical oxidation reaction, assuming a complete oxidation:



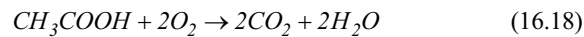
Eq. 16.15 shows that 1 "mol" of organic material demands $1/4(4n+a-2b)$ moles O_2 or $8(4n+a-2b)$ g O_2 . Hence the theoretical oxygen demand of organic material can be expressed as:

$$COD_t = 8(4n+a-2b) / (12n+a+16b) \quad (\text{gCOD/gC}_n\text{H}_a\text{O}_b) \quad (16.16)$$

Obviously, with nitrogen containing compounds (proteins and amino acids) Eq. 16.16 needs to be corrected for the number of electrons that will stay with N and the total weight of N in the compound.

$$COD_t = 8(4n+a-2b-3d) / (12n+a+16b+14d) \quad (\text{gCOD/gC}_n\text{H}_a\text{O}_b\text{N}_d) \quad (16.17)$$

From the chemical-oxidation equation for acetic acid,



follows that 1 mol (60 grams) of acetic acid (oxidation number of the C atom is 0) requires 2 moles (64 grams) of oxygen. This means that 1 gram of acetic acid requires 64/60 (1.067) grams of oxygen, consequently 1 gram of acetic acid corresponds to 1.067 gram COD.

The ratio between the COD and TOC values is calculated from:

$$COD / TOC = 8(4n+a-2b-3d) / (12n) = 8/3 + 2(a-2b-3d) / (3n) \quad (16.19)$$

Table 16.6 summarizes the calculated theoretical values of the COD per unit mass for a number of organic compounds of the type $C_nH_aO_bN_d$. The COD per unit mass may be very different for different chemical compounds. In the case of strongly reduced compounds, for example methane, this COD is high, by using Eq. 16.2 for methane (CH_4 i.e. $n=1$, $a=4$, $b=0$, $d=0$) in Eq. 16.4 one calculates:

$$COD_{CH_4} = 8(4 \cdot 1 + 4 - 2 \cdot 0 - 3 \cdot 0) / (12 \cdot 1 + 4 + 16 \cdot 0 + 14 \cdot 0) = 4 \text{ gCOD} / \text{gCH}_4 \quad (16.20)$$

It is clear that the ratio of COD and TOC differs substantially for the various compounds. This is explained by the differences in the average oxidation state of the organic carbon. The carbon oxidation state (C-ox. state) of carbon can vary from -4 (the most reduced state of carbon, as found in CH_4) to +4, the most oxidized as found in CO_2 . Figure 16.9 depicts for a number of compounds their mean C-ox. state in relation to the theoretical composition of the biogas produced which obviously yields a linear correlation (Table 16.6).

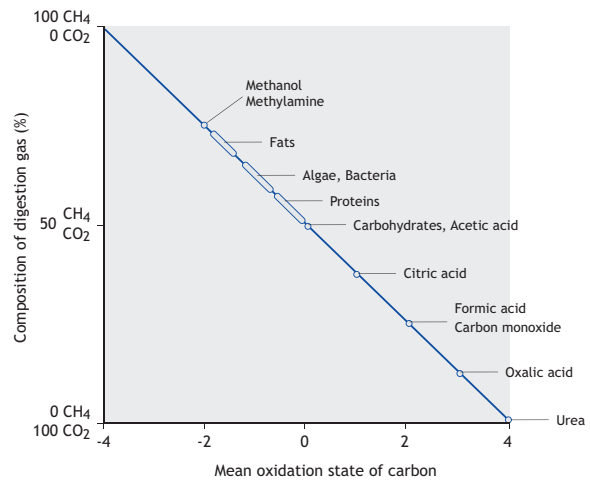


Figure 16.9 Theoretical composition of the biogas produced in relation to the mean oxidation state of the carbon in specific substrates, assuming complete mineralization of the substrate

The lower the average oxidation state of the carbon in a compound (i.e. the more negative), the more oxygen can be bound by the compound, and consequently the higher is its COD value.

Since organic-N is converted into NH_3 -N in the COD test (consequently the amount of N in the compound should be accounted for as being in its reduced form, i.e. having taken up 3 electrons), and one atom of H

Table 16.6 Stoichiometric values of COD and TOC per unit mass for different pure organic compounds $C_nH_aO_bN_d$, the COD/TOC values and the mean carbon oxidation state for these compounds and the estimated CH_4 % in the biogas

Compound	n	a	b	d	gCOD/ g $C_nH_aO_bN_d$	gTOC/ g $C_nH_aO_bN_d$	COD/ TOC	C-ox. state	CH ₄ %
Methane	1	4	0	0	4	0.75	5.33	-4	100
Ethane	2	6	0	0	3.73	0.8	4.67	-3	87.5
Methanol	1	4	1	0	1.5	0.38	4	-2	75
Ethanol	2	6	1	0	2.09	0.52	4	-2	75
Cyclohexane	6	12	0	0	3.43	0.86	4	-2	75
Ethylene	2	4	0	0	3.43	0.86	4	-2	75
Palmitic acid	16	32	2	0	3.43	0.75	3.83	-1.75	72
Acetone	3	6	1	0	2.21	0.62	3.56	-1.33	67
Ethylene glycol	2	6	2	0	1.29	0.39	3.33	-1	62.5
Benzene	6	6	0	0	3.08	0.92	3.33	-1	62.5
Betaine	5	11	2	1	1.64 ^a	0.51	3.2	-0.8	60
Glycerine	3	8	3	0	1.22	0.39	3.11	-0.67	58
Phenol	6	6	1	0	2.38	0.77	3.11	-0.67	58
Lysine	6	14	2	2	1.53	0.49	3.11	-0.67	58
Phenyl alanine	9	11	2	1	1.94	0.65	2.96	-0.44	56
Insuline	254	377	75	65	1.45	0.53	2.72	-0.08	51
Glucose	6	12	6	0	1.07	0.4	2.67	0	50
Lacitic acid	3	6	3	0	1.07	0.4	2.67	0	50
Acetic acid	2	4	2	0	1.07	0.4	2.67	0	50
Citric acid	6	8	7	0	0.75	0.38	2	1	37.5
Glycine	2	5	2	1	0.64	0.32	2	1	37.5
Formic acid	1	2	2	0	0.35	0.26	1.33	2	25
Oxalic acid	2	2	4	0	0.18	0.27	0.67	3	12.5
Carbondioxide	1	0	2	0	0	0.27	0	4	0

^a Calculated COD. Theoretical: with standardised bi-chromate COD test no COD will be measured

provides one electron and one atom of O will take up two electrons, the average oxidation number of the C atom in a compound $C_nH_aO_bN_d$ follows from:

$$C - ox.state = (2b - a + 3d) / n \quad (16.21)$$

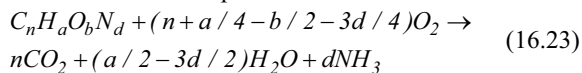
The number of electrons made free per atom C in the complete oxidation of $C_nH_aO_bN_d$ amounts to:

$$4 - (2b + 3d - a) / n = 4 + (a - 2b - 3d) / n \quad (16.21)$$

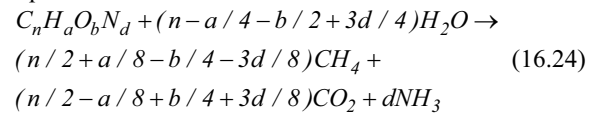
Consequently the number of molecules O_2 required for the oxidation amounts to:

$$n + 1 / 4a - 1 / 2b - 3 / 4d \quad (16.22)$$

Therefore the equation for complete chemical oxidation of this compound is:



In case the compound ($C_nH_aO_bN_d$) is completely biodegradable and would be entirely converted by the anaerobic organisms (no sludge yield) into CH_4 , CO_2 and NH_3 , the theoretical amount of methane gas (and CO_2) produced can be calculated using the Buswell equation:



The COD provides the correct information concerning the oxidation state of the compound, consequently the amount of methane that can be produced from it (Table 16.6, Figure 16.9). The only exceptions are the quaternary ammonium salts such as the already mentioned betaine, which stays reduced in the laboratory COD test. Therefore, the COD is generally accepted as the most adequate parameter to quantify the concentration of organic material and certainly not the TOC. For predicting the relative

amount of CH_4 in the produced biogas when the exact composition of the organic matter is unknown, the COD/TOC ratio is a very useful tool. The latter is based on the linear correlation between the mean oxidation state and the COD/TOC ratio (Figure 16.10).

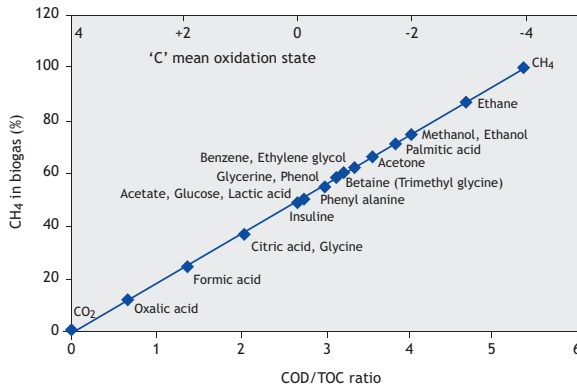
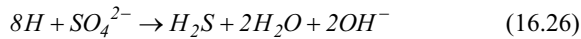
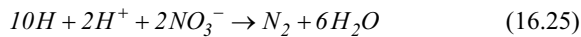


Figure 16.10 Expected CH_4 % in the produced biogas as a function of the COD/TOC ratio: $\text{CH}_4\% = 18.75 \cdot \text{COD/TOC}$

In the presence of specific inorganic electron acceptors like nitrate, sulphate or sulphite, the production of methane will decrease, due to the occurrence of a.o. the following reactions:



For wastewaters containing an excess of organic electron acceptors with respect to the amount of nitrate (NO_3^-), nitrite (NO_2^-), sulphate (SO_4^{2-}) or sulphite (SO_3^{2-}) present, a complete removal of these electron acceptors (oxygen donors) may occur. Since the solubility of H_2S in water considerably exceeds that of CH_4 , a substantial lower COD removal from the water phase will be obtained in case the wastewater contains sulphate.

The quantity of CO_2 present in the biogas produced generally is significantly lower than follows from the Buswell equation or the COD/TOC ratio as depicted in Figure 16.10. This is because of (a) the relatively high solubility of CO_2 in water and (b) because part of the CO_2 may become chemically bound in the water phase due to the formation of ammonia in the anaerobic conversion of nitrogen containing organic compounds and cations which were present in the wastewater as salts of VFA, SO_4^{2-} , NO_3^- .

16.4 IMPACTS OF ALTERNATIVE ELECTRON ACCEPTORS

16.4.1 Bacterial conversions under anoxic conditions

Anaerobic digesters contain mixed microbial communities. Besides the methanogenic association described before, other bacteria are present which can compete with the methanogens for methanogenic substrates (Table 16.7). The listed bacteria have different microbial respiration systems and can use different electron acceptors such as oxygen (O_2) by (facultative) aerobic bacteria, nitrate (NO_3^-) by denitrifiers, sulphate (SO_4^{2-}) or sulphite (SO_3^{2-}) by sulphate reducing bacteria and iron (Fe^{3+}) by iron reducers. Anoxic means that oxygen in the form of oxygen gas (O_2) is not available as an electron acceptor.

16.4.1.1 Sulphate reduction

In the presence of sulphate, sulphite or thiosulphate, sulphate reducing bacteria (SRB), which have a much wider substrate spectrum, are able to use several intermediates of the anaerobic mineralisation process (Table 16.7). These bacteria convert sulphate into hydrogen sulphide. Besides the direct methanogenic substrates such as molecular hydrogen (H_2), formate, acetate, methanol and pyruvate, SRB can also use propionate, butyrate, higher and branched fatty acids, lactate, ethanol and higher alcohols, fumarate, succinate, malate and aromatic compounds (Colleran *et al.* 1995). Hence, the main intermediary products of the anaerobic degradation process ($\text{H}_2/\text{CH}_3\text{COO}^-$) can be converted by both SRB, methanogens and/or obligate hydrogen producing bacteria (OHPB). Because these three groups of bacteria operate under the same environmental conditions (pH, temperature), they will compete for the same substrates. The outcome of this competition depends on the conversion kinetics (see Section 16.10).

If organic material is oxidised via sulphate reduction, 8 electrons can be accepted per molecule of sulphate. Since one molecule of oxygen can only accept 4 electrons, the electron accepting capacity of 2 moles of O_2 equals 1 mol of SO_4^{2-} , equivalent to 0.67 g of O_2 per g SO_4^{2-} . This means that for waste streams with a COD/sulphate ratio of 0.67, there is theoretically enough sulphate available to completely remove the organic matter (COD) via sulphate reduction. For COD/sulphate ratios lower than 0.67, the amount of organic matter is insufficient for a complete reduction of the sulphate present and extra substrate then should be

Table 16.7 Stoichiometry and change of free energy ΔG° (kJ/mol substrate) of hydrogen and acetate conversion under different conditions

Reaction	ΔG° (kJ/mol substrate)	Eq.
Aerobes		
$H_2 + 0.5 O_2 \rightarrow H_2O$	-237	(16.27)
$CH_3COO^- + 2 O_2 \rightarrow 2 HCO_3^- + H^+$	-844	(16.28)
Denitrifiers		
$H_2 + 0.4 NO_3^- + 0.4 H^+ \rightarrow 0.2 N_2 + 1.2 H_2O$	-224	(16.29)
$CH_3COO^- + 1.6 NO_3^- + 0.6 H^+ \rightarrow 2 HCO_3^- + 0.8 N_2 + 0.8 H_2O$	-792	(16.30)
Fe³⁺ reducing bacteria		
$H_2 + 2 Fe^{3+} \rightarrow 2 Fe^{2+} + 2 H^+$	-228	(16.31)
$CH_3COO^- + 4 Fe^{3+} + 4 H_2O \rightarrow 4 Fe^{2+} + 5 H^+ + 2 HCO_3^-$	-352	(16.32)
Sulphate reducing bacteria		
$H_2 + 0.25 SO_4^{2-} + 0.25 H^+ \rightarrow 0.25 HS^- + H_2O$	-9.5	(16.33)
$CH_3COO^- + SO_4^{2-} \rightarrow HS^- + 2 HCO_3^-$	-48	(16.34)
Methanogens		
$H_2 + 0.25 HCO_3^- + 0.25 H^+ \rightarrow 0.25 CH_4 + 0.75 H_2O$	-8.5	(16.35)
$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$	-31	(16.36)

added if removal of sulphate is the objective of the treatment. On the contrary, for wastewaters with a COD/sulphate ratio exceeding 0.67, a complete removal of the organic matter can only be achieved if, in addition to sulphate reduction, methanogenesis also occurs.

In the presence of sulphate, organic matter is not necessarily degraded less easily, but compared to methane, hydrogen-sulphide has the great disadvantage that it dissolves much better in water than methane. This means that, for the same degree of organic waste degradation, a lower quantity of COD will be reduced in wastewater containing sulphate. Sulphide production can further cause the following process technical problems during anaerobic digestion:

- H₂S is toxic to methanogenic bacteria (MB), acetogenic bacteria (AB) and SRB. In case of methanogenic treatment of the waste-stream, some of the organic compounds in the wastewater will be used by SRB rather than MB and are therefore not converted into methane. This results in a lower methane yield per unit of degraded organic waste and, therefore, negatively affects the overall energy balance of the process. Moreover, the quality of the biogas is reduced since a part of the produced sulphide ends up as H₂S in the biogas. Removal of H₂S from the biogas is therefore usually required.
- The produced sulphide has a bad smell and can cause corrosion problems to pipes, engines and boilers. Thus, the maintenance costs of the installation

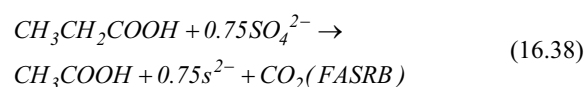
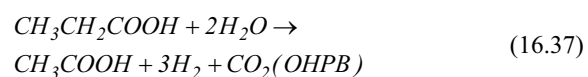
increase and extra investment costs are necessary to avoid these problems.

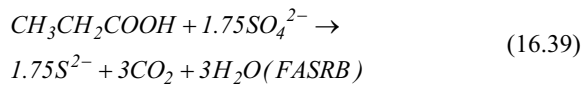
- Part of the sulphide will be present in the effluent of the anaerobic reactor. As mentioned above, this results in a lower overall treatment efficiency of the anaerobic reactor system, as sulphide contributes to the wastewater COD (per mole of sulphide two moles of oxygen are required for a complete oxidation into *sulphate*). Moreover, sulphide can upset the treatment efficiency of the aerobic post treatment system, e.g. algal blooming in lagoons or activated sludge bulking. Thus, an extra post treatment system to remove the sulphide from the wastewater may be required.

Based on their substrate consumption, SRB may be classified into the following three groups:

- 1) hydrogen oxidising SRB (HSRB)
- 2) acetic acid oxidising SRB (ASRB)
- 3) fatty acids oxidising SRB (FASRB)

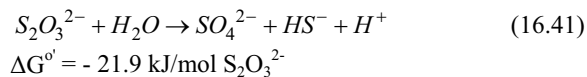
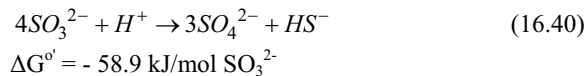
In the last group, two oxidation patterns can be distinguished:





Some SRB are capable of completely oxidising VFA to CO₂ and sulphide as end products. Other SRB lack the tricarboxylic acid cycle and carry out an incomplete oxidation of VFA with acetate and sulphide as end-products. In the latter case, acetic acid is excreted in the medium. It should be further noticed that incomplete oxidation of propionic acid by an SRB yields the same degradation products as the conversion by the OHPB and HSRB. Hence, it is not possible to deduce from mass balances which bacteria carry out this conversion.

In addition to the reduction of sulphate, reduction of sulphite and thiosulphate is also very common among SRB (Widdel and Hansen, 1992). *Desulfovibrio* strains have been reported to be able to reduce di-, tri- and tetra-thionate (Fitz and Cypionka, 1990). A unique ability of some SRB, e.g. *Desulfovibrio dismutans* and *Desulfobacter curvatus*, is the dismutation of sulphite or thiosulphate (Widdel and Hansen, 1992):



The microbial ecology of SRB has been studied by various novel analytical techniques, e.g. by applying sulfide microelectrodes, ¹³C and ³¹P nuclear magnetic resonance (NMR, Santos *et al.*, 1994) and 16S ribosomal RNA (rRNA) based detection methods (Raskin *et al.*, 1995). Some SRB were found to be able to respire oxygen, despite being classified as strict anaerobic bacteria. The ability of SRB to carry out sulphate reduction under aerobic conditions (Canfield and Des Marais, 1991, Frund and Cohen, 1992) is very intriguing and could be of engineering significance.

In the absence of an electron-acceptor, SRB are able to grow through a fermentative or acetogenic reaction. Pyruvate, lactate and ethanol are easily fermented by many SRB (Widdel *et al.*, 1988; Dolfig, 1987). An interesting feature of SRB is their ability to perform acetogenic oxidation in syntrophy with hydrogenotrophic MB (HMB), as described for co-cultures of HMB with *Desulfovibrio* sp. using lactate and ethanol (Widdel *et al.*, 1988; Oude Elferink *et al.*,

1994) or with *Desulfobulbus*-like bacteria using propionate (Wu *et al.*, 1991).

Acetogenic oxidation of propionate by *Desulfobulbus* sp. has also been reported in UASB (Wu *et al.*, 1992), fluidized bed (Heppner *et al.*, 1992) and fixed bed (Zellner and Neudörfer, 1995) reactors. In the presence of sulphate, however, these bacteria behave as true SRB and metabolise propionate as electron-donors for the reduction of sulphate.

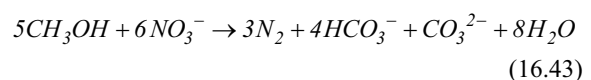
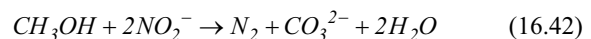
If SO₄²⁻ is present in the wastewater, SO₄²⁻ reduction by SRB cannot be prevented. Several attempts were made to try to steer the competition in a single reactor system but were unsuccessful. On the other hand, several technological solutions are available on the market that are directed to lower the H₂S concentration in the anaerobic reactor to minimise the toxicity of the MB (Figure 16.11).

16.4.1.2 Denitrification

In general, no denitrification occurs during anaerobic purification and digestion. Organically bound nitrogen will be converted into ammonium. Denitrification can only be expected if the influent contains nitrate (see Chapter 5).

Denitrification is mediated by denitrifying micro-organisms, i.e. chemoheterotrophic bacteria which are capable of oxidising organic matter with nitrate. Nitrate is then converted via nitrite and nitrogen oxide into N₂ gas. Generally, denitrifying micro-organisms prefer oxygen as an electron acceptor, as the latter compound yields more energy (Table 16.7). In aerobic purification processes, they start to use nitrate as soon as O₂ is depleted to cope with the organic load. In an activated-sludge plant, denitrification will normally occur only at a dissolved O₂ concentration of 1 mg/l or below.

Denitrification is a heterotrophic process requiring an electron donor. The stoichiometry of methanol oxidation with nitrate and nitrite occurs according to the following reaction equation:



These reaction equations show that denitrification will result in a pH increase (carbonate production).

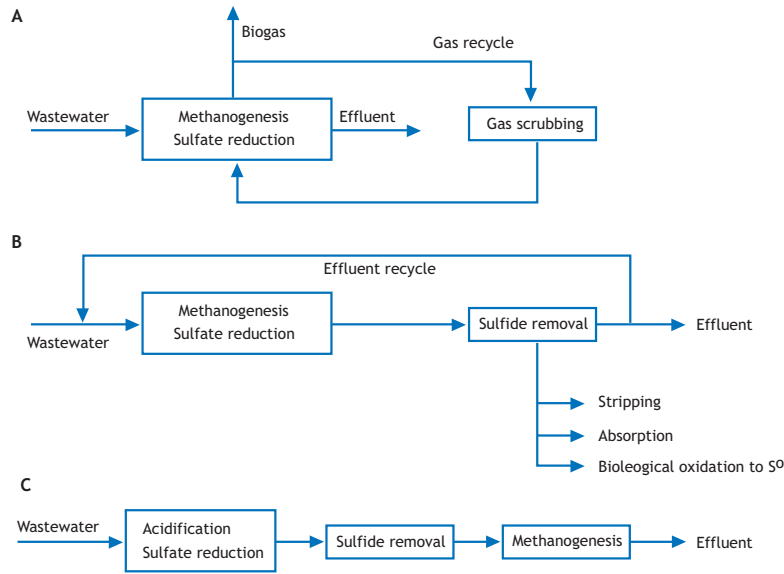


Figure 16.11 Technological solutions to decrease the H₂S concentration in the anaerobic reactor. (A) enhanced H₂S stripping by biogas recycling and sulphide stripping in the gas line, (B) H₂S removal in a (micro)aerobic post treatment system and recirculation of the treated effluent to the anaerobic reactor influent for dilution, (C) combined pre-acidification and sulphate reduction with sulphide removal step for lowering the S content in the anaerobic reactor. In the latter approach most of the H₂S will be stripped in the acidification step owing to the low prevailing pH

16.5 WORKING WITH THE COD BALANCE

Like any biological system an anaerobic treatment process must be monitored for relevant parameters, and measurements must be evaluated for adequate operation and control. Section 16.3 discusses the usefulness of the COD as the control parameter for anaerobic systems. The reason for this is that in contrast to aerobic systems there is no COD destruction in an anaerobic reactor. During anaerobic treatment the COD is only 're-arranged'. Complex organic compounds are broken down in more simple intermediates and eventually mineralised to CH₄ and CO₂. All COD that entered the system ends up in the end-product CH₄, minus the COD that is incorporated in the new bacterial mass. Since a perfect mass balance can be made by only using the COD as a parameter, the COD is therefore generally taken as a control tool to operate an anaerobic system:

$$COD_{in} = COD_{out} \quad (16.44)$$

For practical purposes Eq. 16.44 should be expanded to the various outlets of the anaerobic reactor as depicted in Figure 16.12.

For identifying the fate of COD in an anaerobic reactor detailed analyses of the gaseous, liquid and solid outlets should be performed (Table 16.8).

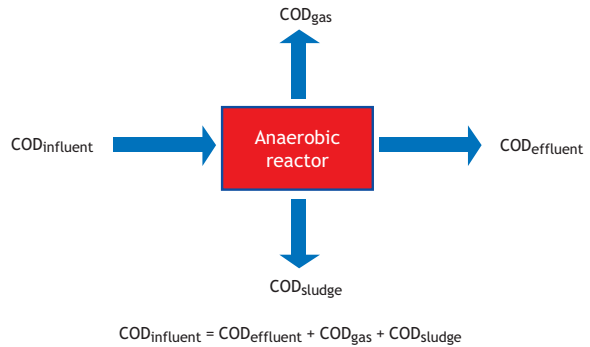
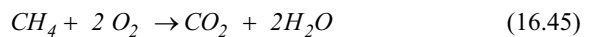


Figure 16.12 COD balance of an anaerobic reactor. By differentiating the COD fractions of gas, liquid and solids, the missing parameters can be estimated from the more easily measurable parameters

Based on the basic influent characteristics, i.e. flow rate and COD concentrations, and information on the biodegradability of the COD, the expected CH₄ production rate can be easily estimated. From section 16.3.1. we can derive that:



which means that 22.4 m³ CH₄ (STP) requires 2 moles of O₂ (COD), which equals 64 kg COD. Therefore, theoretically, 1 kg COD can be converted in 0.35 m³ CH₄.

Similarly, the theoretical COD equivalent for 1 kg 'bacterial VSS', with an estimated composition of $C_5H_7O_2N$, can be calculated as 1.42 kgCOD/kgVSS. Having both the final products CH_4 and newly grown bacteria expressed as COD, the balance can be made if influent and effluent are properly measured.

Often 'gaps' in the COD balance occur which can be attributed mostly to the 'loss of electrons' when these are channelled to oxidised anions like SO_4^{2-} and NO_3^- , as explained in section 16.4. Therefore, in this case, for closing the COD balance either all reduced gases should be taken into account or the concentration of electron acceptors needs to be measured. It should be realised that soluble COD containing gases like H_2S , will be present in the effluent. In this example, organic COD is converted into inorganic COD of which a pH dependent fraction will end in the biogas while the remainder will stay in the effluent.

Another frequently cited cause for a COD gap is the entrapment or accumulation of COD in the sludge bed, sometimes drastically changing the stoichiometric value of 1.42 kgCOD/kgVSS. The latter is particularly true during the treatment of fat- or LCFA-containing wastewater. With these substrates, COD removal efficiencies are generally very high, but low CH_4 production rates lead to huge gaps in the balance. In this example, the COD gap indicates severe long-term operational problems. The accumulating solids will deteriorate the SMA of the sludge, finally resulting in a complete failing of the anaerobic process.

Operating an anaerobic reactor using the COD balance as a tool to monitor reactor performance gives the operator vital information about the functioning of

the system. Adequate action can be undertaken before irreversible deterioration occurs. Also, the impact of alternative electron acceptors on the CH_4 production rate can be easily assessed while based on the gas production and effluent COD values, an estimate can be made of the amount of newly grown and entrapped biomass.

16.6 IMMOBILISATION AND SLUDGE GRANULATION

The key for modern high-rate biotechnology, whatever systems will be considered, is the immobilization of proper bacteria. The required high sludge retention in anaerobic treatment systems is based on immobilization, though it is not just a matter of immobilizing bacteria but of well balanced bacterial consortia. Regarding the occurrence of various syntrophic conversion reactions in the anaerobic conversion of most organic compounds, the detrimental effect of higher concentrations of specific intermediates and the strong effect of environmental factors like pH and redox potential, the development of balanced bacterial consortia is a prerequisite for a proper anaerobic treatment system. Significant progress in the knowledge of the fundamentals of the immobilisation process has been made since the development and successful implementation of high rate anaerobic treatment systems in the seventies. Immobilisation may occur on inert support material mounted in a fixed matrix in so-called anaerobic filters (AF), which are operated both in upflow and in downflow mode. The matrix can also be free floating like in moving bed bioreactors and fluidized bed (FB) systems. If no inert support material is used, a so-called 'auto-immobilisation' will occur, which is understood as the immobilisation of bacteria on

Table 16.8 Various COD fractions and their fate in an anaerobic reactor system. Number of dots indicates the relative importance of the indicated COD fraction in the respective compartment (influent, effluent, sludge, biogas)

COD fraction	Influent	Effluent	Sludge	Gas
Soluble organic	•••	•••	•	
Soluble inorganic	•	••	•	
Suspended organic	•••	••	••	
Suspended inorganic		•	•	
Colloidal	•	••	•	
Absorbed	•		•••	
Entrapped			•••	
CH_4		•		•••
H_2				•
H_2S	•	••		•
N_2				•
Newly grown biomass		••	••	

themselves in bacterial conglomerates, or on very fine inert or organic particles present in the wastewater. The bacterial conglomerates will mature in due time and form round shape granular sludge.

With respect to immobilization, particularly the phenomenon of granulation has puzzled many researchers from very different disciplines. Granulation in fact is a completely natural process. It will proceed in all systems where the basic conditions for its occurrence are met, i.e. on mainly soluble substrates and in reactors operated in an up-flow manner with hydraulic retention times (HRT) lower than the bacterial doubling times. Owing to the very low growth rate of the crucial acetoclastic MB, particularly under sub-optimal conditions, the latter conditions are easily met. Sludge granulation also was found to occur in reversed flow Dorr Oliver Clarigesters applied in South Africa since the fifties of the last century. However, this only became apparent by observation of sludge samples taken from such a digester in 1979. Surprisingly enough no attention was given to the characteristics of the Clarigester sludge such as size, form and the mechanical strength, density and porosity of sludge flocs/aggregates. Despite all the efforts made to develop systems with a high sludge retention nobody apparently noticed that major part of the sludge consisted of a granular type of sludge. While studying the start-up and feasibility of anaerobic upflow filters, Young and McCarty (1969) already recognized the ability of anaerobic sludge to form very well settleable aggregates. These granules were as large as 3.1 mm in diameter and settle readily. In AF experiments with potato starch wastewater and methanol solutions conducted in the Netherlands similar observations were made (Lettinga *et al.*, 1972, 1979). Whereas the interest in AnWT in USA and South Africa diminished, large emphasis on developing industrial scale systems was put in the Netherlands, where the instalment of new surface water protection acts coincided with the world energy crises of the seventies. As a result, increasing emphasis could be afforded on applied and fundamental research in this field, particularly also on the phenomenon of sludge granulation. A worldwide growing interest occurred from both the engineering and the microbiological field. As a result, the insight in the mechanism of the sludge granulation process for anaerobic treatment has been elucidated sufficiently, at least for practical application (e.g. de Zeeuw, 1982; 1987; Hulshoff Pol and Lettinga, 1986; Hulshoff Pol *et al.*, 1987, 2004; Dolfing, 1987; Beefink and Staugard, 1986; Wiegant and de Man, 1986; Grotenhuis, 1992;

Wu, 1987; Wu *et al.*, 1991; Van Lier *et al.*, 1994; Thaveesri *et al.*, 1994; Fang *et al.*, 1994). Granulation can proceed under mesophilic, thermophilic and psychrophilic conditions. It is of huge practical importance to improve the insight in fundamental questions concerning the growth of mixed balanced cultures. This will lead very likely to the application of the process for the degradation of a large variety of (difficult) chemical compounds. These challenging questions need to be attacked jointly through the efforts of process scientists and microbiologists.

16.6.1 Mechanism underlying sludge granulation

In essence, sludge granulation finds its ground in the fact that bacterial retention is imperative when dilution rates exceed the bacterial growth rates. Immobilization further requires the presence of support material and/or specific growth nuclei. The occurrence of granulation can be explained as follows:

- 1) Proper growth nuclei, i.e. inert organic and inorganic bacterial carrier materials as well as bacterial aggregates, are already present in the seed sludge.
- 2) Finely dispersed matter, including viable bacterial matter, will become decreasingly retained, once the superficial liquid and gas velocities increase, applying dilution rates higher than the bacterial growth rates under the prevailing environmental conditions. As a result film and/or aggregate formation automatically occurs.
- 3) The size of the aggregates and/or biofilm thickness are limited, viz. it depends on the intrinsic strength (binding forces and the degree of bacterial intertwining) and the external forces exerted on the particles/films (shear stress). Therefore at due time, particles/films will fall apart, evolving the next generation. The first generation(s) of aggregates, indicated by Hulshoff Pol *et al.* (1983) as 'filamentous' granules mainly consist of long multi-cellular rod shaped bacteria. They are quite voluminous and in fact more flock than granule.
- 4) Retained secondary growth nuclei will grow in size again, but also in bacterial density. Growth is not restricted to the outskirts, but also proceeds inside the aggregates. At due time they will fall apart again, evolving a third generation, etc.
- 5) The granules will gradually 'age' or 'mature'. As a result of this process of maturing the voluminous 'filamentous granules', predominating during the initial stages of the granulation process, will disappear and become displaced by dense 'rod'

granules. In a matured granular sludge, filamentous granules generally will be absent.

During the above described selection process, both organic and hydraulic loading rates gradually increase, increasing the shear stress inside the system. The latter results in firm and stable sludge aggregates with a high density and a high superficial velocity. Figure 16.13 pictures the course in time of the in-reactor sludge concentrations, expressed as gVSS/l, and the applicable organic loading rate. The start is accomplished when the design loading rate is reached. For mainly soluble wastewaters which are partly acidified, granular sludge will be easily cultivated.

Table 16.9 lists some common characteristics of methanogenic granular sludge.

With respect to the granulation process, essentially there do not exist any principle differences between a UASB reactor, seeded with digested sewage sludge, and an upflow reactor with inert free floating support material like the FB reactor, which uses sand particles or pumice as carrier material for the in-growing biomass. Granulation indeed can proceed quite well in a FB system, provided the reactor is operated with a moderate shear on the particles, i.e., in such a mode that biofilms can grow sufficiently in thickness and/or different

particles can grow together. Full scale experiences have shown that complete fluidization is not required and is in fact detrimental in achieving stable and sufficiently thick biofilms. At present the expanded granular sludge bed (EGSB) reactors are of much interest for commercial applications than the more expensive FB systems (see also Section 16.7.2.4).

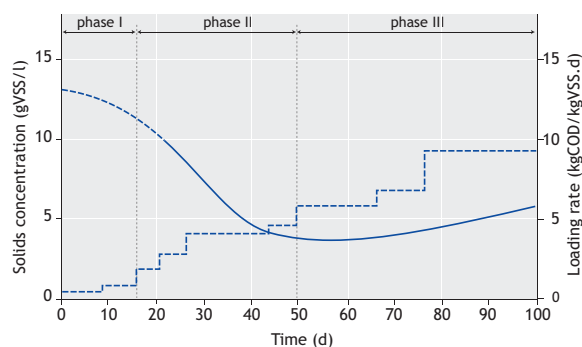

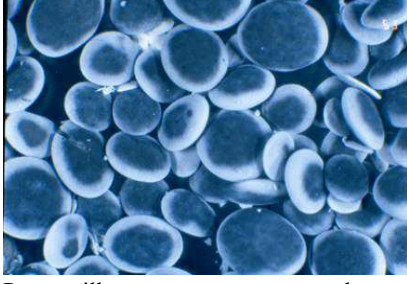


Figure 16.13 Sludge dynamics during the first start-up of a UASB reactor. Phase I: Applied loading rate < 3 kgCOD/m³.d, expansion of the sludge bed and wash-out of colloidal sludge fraction, flotation layer may occur and the specific methanogenic activity starts to increase. Phase II: heavy sludge wash-out while selection between heavy and light sludge, strong increase in loading rate and formation of dense aggregates. Phase III: increase in total sludge concentration, increase in granular sludge quantity, loading rate can be further increased

Table 16.9 Proposed definition and characteristics of good quality granular sludge (photos: Biothane B.V.)

Granular sludge examples	'Good quality granule' characteristics
	Metabolic activity: Specific methanogenic activity range of granular sludge: 0.1 – 2.0 kgCOD-CH ₄ / kgVSS.d Typical values for industrial wastewater : 0.5 – 1.0 kgCOD-CH ₄ / kgVSS.d
Potato wastewater grown granules	
	Settleability and other physical properties:
Paper mill wastewater grown granules	<ul style="list-style-type: none"> • settling velocities: 2–100 m/h, typically: 15-50 m/h • density: 1.0 –1.05 g/l • diameter: 0.1–8 mm, typically: 0.15–4 mm • shape: spherical formed and well defined surface • color: black / gray / white

Definition: Dense spherical-shaped microbial conglomerate, consisting of microorganisms, inert material, and extracellular polymeric substances (EPS), and which is characterised by a 'high metabolic activity' and a 'high settle ability'.

16.7 ANAEROBIC REACTOR SYSTEMS

Anaerobic reactors are in use since the 19th century, when Mouras and Cameron developed the automatic scavenger and the septic tank to reduce the amounts of solids in the sewerage system. Although at a very poor rate, the first anaerobic stabilisation processes occurred in the tanks that were designed for intercepting the black-water solids. The first anaerobic reactor was developed in 1905 when Karl Imhoff designed the Imhoff tank, in which solids sediments are stabilised in a single tank. The actual controlled digestion of entrapped solids in a separate reactor was developed by the Ruhrverband, Essen-Relinghausen in Germany.

In the same decades, Buswell started to adopt the same technology for treating liquid wastes and industrial wastewater. All these systems can be characterised as low rate systems since no special features were included in the design to augment the anaerobic catabolic capacity. The process feasibility of these systems was very much dependent on the growth rate of the anaerobic consortia. As a result, reactors were very big and very fragile in operation. In the final decades of the 19th century also some first trials of upward flow fixed film reactors were performed, but it was too early to make these systems successful (McCarty, 2001). Also the anaerobic pond can be regarded as a low loaded anaerobic treatment system. Anaerobic ponds are often constructed in conjunction with facultative and maturation ponds. The applied loading rate to anaerobic ponds ranges between 0.025–0.5 kgCOD/m³.d, while using pond depths of 4 m. The big disadvantages of anaerobic ponds are problems related to odour as these systems easily become overloaded. Also the loss of energy rich CH₄ to the atmosphere is a recognised disadvantage.

16.7.1 High-rate anaerobic systems

One of the major successes in the development of anaerobic wastewater treatment was the introduction of high-rate reactors in which biomass retention and liquid retention are uncoupled. Contrary to aerobic processes, in an anaerobic or anoxic (denitrification) process, the maximum permissible load is not governed by the maximum rate at which a necessary reactant can be supplied (e.g. oxygen during aerobic processes), but by the amount of viable anaerobic biocatalysts or the anaerobic bacteria which are in full contact with the wastewater constituents. In anaerobic high-rate systems, high sludge concentrations are obtained by physical retention and or immobilisation of anaerobic

sludge. High biomass concentrations enable the application of high COD loading rates, while maintaining long SRTs at relatively short HRTs. Different high-rate systems were developed over the last three decades including the anaerobic contact process (ACP), anaerobic filters, the UASB, FB and EGSB reactors and the baffled reactors.

To enable an anaerobic reactor system to accommodate high organic loading rates for treating a specific wastewater, the following conditions should be met:

- *High retention of viable sludge in the reactor under operational conditions.* The higher the amount of sludge retained, the higher will be the loading potential of the system. Therefore, it is necessary to cultivate a well settleable or immobilized biomass, and that the sludge will not deteriorate in this respect.
- *Sufficient contact between viable bacterial biomass and waste water.* In the case where part of the sludge retained in the reactor remains deprived of substrate, this sludge is of little if any value.
- *High reaction rates and absence of serious transport limitations.* It is clear that the kinetics of the degradation processes are a factor of great importance. It is essential that metabolic end-products can easily escape from the aggregate. The size of the biofilms should remain relatively small and the accessibility of the organisms inside the biofilm should be high.
- *The viable biomass should be sufficiently adapted and/or acclimatized.* For any wastewater subjected to treatment, the sludge should be enabled to adapt to the specific characteristics of the concerning wastewater.
- *Prevalence of favourable environmental conditions for all required organisms inside the reactor under all imposed operational conditions, focusing on the rate limiting steps.* It should be emphasized here that this condition doesn't mean that the circumstances should be similar at any location within the reactor and at any instant. As a matter of fact even the contrary is true. Regarding the fact that a large variety of different organisms are involved in the degradation of more complex compounds, the existence of micro-niches within the system is an absolute pre-requisite. Only in this way can the required flourishing growth of the required very different organisms be achieved. It should be noticed that particularly in the interior of biofilms and

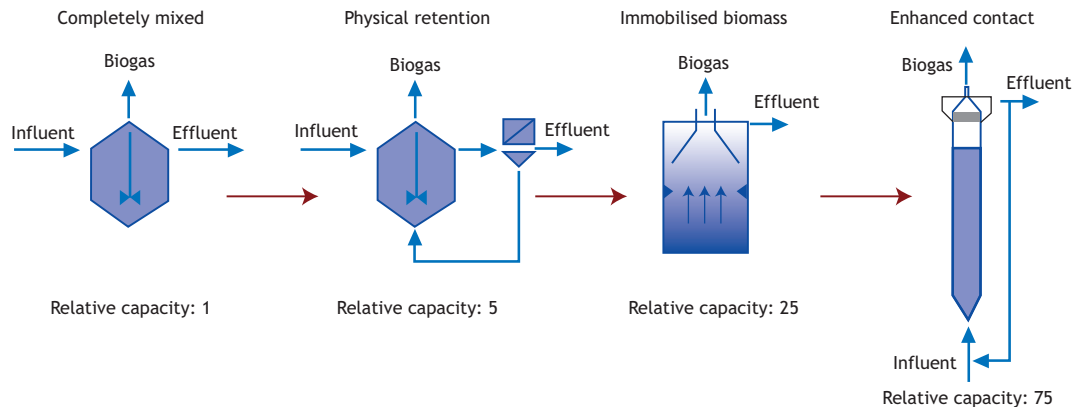


Figure 16.14 Relative loading capacity of different AnWT systems. Maximum applied loading rates under full scale conditions reach about 45 kgCOD/m³.d applying enhanced contact in EGSB type systems

granules, the concentration of substrates and metabolites are low enough to allow even the very endergonic acetogenic reactions to proceed, e.g. the oxidation of propionate at the very low hydrogen concentrations.

As mentioned above, Stander in South Africa and Schroefer and coworkers were amongst the first to recognize the importance of maintaining a large population of viable bacteria in the methanogenic reactor. On the other hand the idea certainly was not completely new at that time, because the need of the presence of a high viable biomass concentration already was applied in full scale aerobic treatment systems in use in the early fifties and before. It therefore could be expected that supporters of the 'anaerobic concept' would try out the 'aerobic activated sludge' concept for anaerobic wastewater treatment. The anaerobic contact process by Schroefer *et al.* (1955) indeed turned out to be reasonably successful for the treatment of higher strength industrial wastewaters. With a few exceptions, hardly any at that time would think that anaerobic treatment ever could become feasible for low strength wastewaters. Regarding the problems experienced with

the various versions of the anaerobic contact process, only very few even believed anaerobic treatment could become applicable for treating medium strength wastewater. However in the sixties and seventies the situation changed rapidly, and in the nineties the anaerobic treatment concept even was shown feasible for very low strength wastewaters at low ambient temperatures. These unforeseen developments can be attributed to superior methods of sludge retention, based on sludge immobilization. Figure 16.14 illustrates the development of high rate reactor systems and the impact of improved sludge retention and enhanced contact on the applicable organic loading rates. While the first trials of Buswell did not reach loading rates of 1 kgCOD/m³.d, modern AnWT systems are sold on the market with guaranteed loading rates exceeding 40 kgCOD/m³.d.

At present, most applications of AnWT can be found as end-of-the-pipe treatment technology for food processing wastewaters and agro-industrial wastewater. Table 16.10 lists the various industrial sectors where the surveyed 2,266 reactors are installed. It should be noticed that the number of anaerobic applications in the

Table 16.10 Application of anaerobic technology to industrial wastewater. Total number of registered worldwide installed reactors = 2,266, census January 2007, after van Lier (2007) (see also Figure 16.2)

Industrial sector	Type of wastewater	Nr. of reactors	%
Agro-food industry	Sugar, potato, starch, yeast, pectin, citric acid, cannery, confectionary, fruit, vegetables, dairy, bakery	816	36
Beverage	Beer, malting, soft drinks, wine, fruit juices, coffee	657	29
Alcohol distillery	Can juice, cane molasses, beet molasses, grape wine, grain, fruit	227	10
Pulp and paper industry	Recycle paper, mechanical pulp, NSSC, sulphite pulp, straw, bagasse	249	11
Miscellaneous	Chemical, pharmaceutical, sludge liquor, landfill leachate, acid mine water, municipal sewage	317	14

non-food sector is rapidly growing. Common examples are the paper mills and the chemical wastewaters, such as those containing formaldehyde, benzaldehydes, terephthalates, etc. (Razo-Flores *et al.*, 2006). The latter is surprising since it is particularly difficult for the chemical industries to enter with anaerobic technology, owing to the general prejudices against biological treatment and anaerobic treatment in particular. With regard to the chemical compounds it is of interest to mention that certain compounds, such as poly chloro-aromatics and poly nitro-aromatics as well as the azo-dye linkages can only be degraded when a reducing (anaerobic) step is introduced in the treatment line. Anaerobics are then complementary to aerobics for achieving full treatment.

Only very recently, high-rate AnWT systems were developed for treating cold and very low strength wastewaters. In addition to municipal sewage, many industrial wastewaters are discharged at low temperatures, e.g. beer and maltery wastewaters. Full scale results so far show that any of the cited wastewaters are anaerobically treated using common seed materials, illustrating the robustness and flexibility of the anaerobic process.

16.7.2 Single stage anaerobic reactors

16.7.2.1 The Anaerobic Contact Process (ACP)

As explained in section 16.7.1, processes employing external settlers and sludge return are known as the anaerobic contact process (ACP), see Figure 16.15.

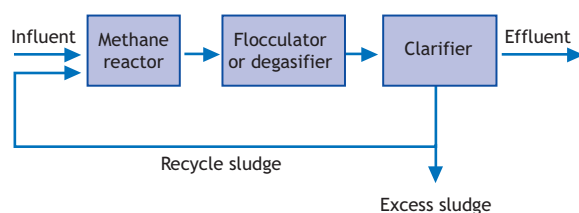


Figure 16.15 Anaerobic contact process, equipped with flocculator or a degasifier unit to enhance sludge sedimentation in the secondary clarifier

The various versions of the first generation of 'high rate' anaerobic treatment systems for medium strength wastewaters were not very successful. In practice, the main difficulty appeared to be the separation of the sludge from the treated water. These difficulties can be mainly due to the fact that a too intensive agitation in the bio-reactor was considered necessary. The idea was that the more intensive the mixing, the better would

become the contact between sludge and wastewater. However, in that time no consideration was given to the quite detrimental effect of intensive mixing on the sludge structures, viz. its settleability and the negative impact on the presence of balanced micro-ecosystems, i.e., syntrophic associations (Section 16.2.1.3).

Various methods for sludge separation have been tested and/or employed in the different versions of the ACP. These methods include vacuum degasification in conjunction with sedimentation, the addition of organic polymers and inorganic flocculants, centrifugation and even aeration (in order to stop digestion). However, the results were usually unsatisfactory. At present, with the current knowledge on anaerobic digestion technologies, a more gentle and intermittent mode of mixing is applied. With such an approach, the sludge will acquire and keep excellent sedimentation properties, and the anaerobic contact process can certainly make a valuable contribution to environmental protection and energy recovery, particularly with wastewaters containing high fractions of suspended solids and semi liquid wastes. If well designed, modern ACP may reach organic loading rates of 10 kgCOD/m³.d.

16.7.2.2 Anaerobic Filters (AF)

The modern version of upflow anaerobic filter (UAF) was developed in the USA by Young and McCarty (1964, 1982) in the late sixties. The sludge retention of the UAF is based on:

- the attachment of a biofilm to the solid (stationary) carrier material,
- the sedimentation and entrapment of sludge particles between the interstices of the packing material, formation of very well settling sludge aggregates.

Initially, a suitable carrier material for the systems was hard to find (Young, 1991). Various types of synthetic packing have been investigated and natural materials such as gravel, coke and bamboo segments as well. It turned out that the shape, size and weight of the packing material are important aspects. Also the surface characteristics with respect to bacterial attachment is important. Moreover, it was found that the bed should remain open of structure, viz. providing a large void fraction. Applying proper support material AF systems are rapidly started, owing to the efficient adherence of anaerobic organisms to the inert carrier. The ease of starting up the system was the main reason for its popularity in the eighties and nineties. Problems with UAF systems in particular generally occur during long-

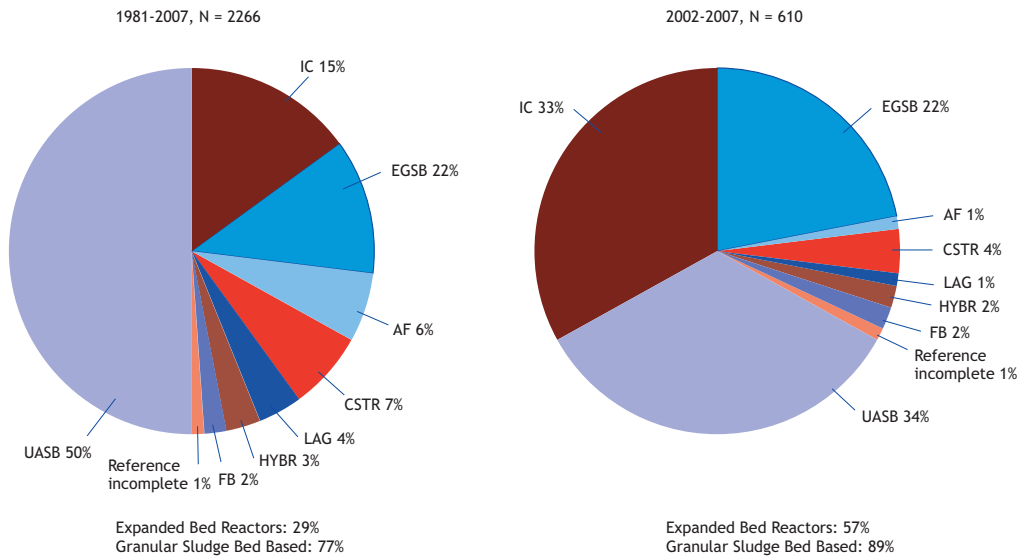


Figure 16.16 Implemented anaerobic technologies for industrial wastewater pictured for the period 1981-2007 (left) and the period 2002-2007 (right). UASB: upflow anaerobic sludge blanket, EGSB: expanded granular sludge bed, IC®: internal circulation reactor, type of EGSB system with biogas-driven hydrodynamics, AF: anaerobic filter, CSTR: continuous stirred tank reactor, Lag.: anaerobic lagoon, Hybr.: combined hybrid system with sludge bed at the bottom section and a filter in top, FB: fluidized bed reactor (van Lier 2007)

term operation. The major disadvantage of the UAF concept is the difficulty of maintaining the required contact between sludge and wastewater, because clogging of the 'bed' easily occurs. This particularly is the case for partly soluble wastewaters. These clogging problems obviously can be overcome (at least partly) by applying a primary settler and/or a pre-acidification step (Seyfried, 1988). However, this would require the construction and operation of additional units. Moreover, apart from the higher costs, it would not completely eliminate the problem of short-circuiting (clogging of the bed) flows, leading to disappointing treatment efficiencies.

Since 1981, about 140 full scale UAF installations have been put in operation for the treatment of various types of wastewater, which is about 6% of the total amount of installed high-rate reactors (Figures 16.2 and 16.15). The experiences with the system certainly are rather satisfactory, applying modest to relatively high loading rates up to 10 kgCOD/m³.d. The UAF system will remain attractive for treatment of mainly soluble types of wastewater, particularly when the process of sludge granulation will not proceed satisfactory. On the other hand, long term problems related to system clogging and the stability of filter material caused a decline in the number of installed full scale AF systems. In the last 5 years only 6 new and registered AF systems were constructed which is about 1% of the total amount of newly installed AnWT systems (Figure 16.16).

In order to minimise clogging and sludge accumulation in the interstices of the filter material anaerobic filters are sometimes operated in a downflow mode, the so-called down-flow fixed film reactors. Various modes of operation and filter material were investigated but full-scale application is rather disappointing. The limiting factor is the applicable low organic loading rate owing to the limited amount of biomass that can be retained in such a system as it is primarily based on attachment of biomass to the surface of the packing material. In UAF filters the majority of the anaerobic activity is found in the non-attached biomass.

16.7.2.3 Anaerobic Sludge Bed Reactors (ASBR)

The anaerobic sludge bed reactors (ASBR) undoubtedly are by far the most popular AnWT systems so far. The sludge retention in such a reactor is based on the formation of easily settling sludge aggregates (flocs or granules), and on the application of an internal gas-liquid-solids separation system (GLSS device).

By far the best known example of this concept is the upflow anaerobic sludge bed reactor (UASB), which was developed in the Netherlands in the early seventies (Lettinga *et al.*, 1976, 1980). In view of its prospects, and the fact that almost 90% of the newly installed high-rate reactors are sludge bed systems (Figure 16.16), the UASB process will be elaborated in more detail than the other systems (Section 16.8). At the start of 2007, about

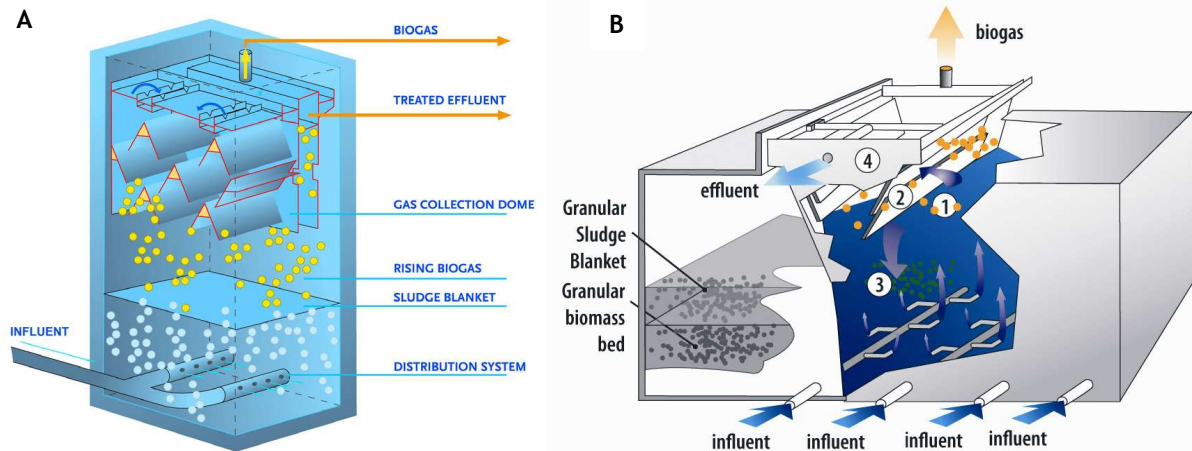


Figure 16.17. UASB reactors of the major anaerobic system manufacturers: (A) Paques B.V. and (B) Biothane B.V.

1,750 full-scale UASB installations have been put into operation. Most of these full scale reactors are used for treating agro-industrial wastewater, but its application for wastewater from chemical industries and sewage is increasing (Table 16.10). Figure 16.17 shows a schematic representation of a UASB reactor. Two examples of a full-scale UASB instalations are shown in figure 16.18.

Similar to the UAF system the wastewater moves in an upward mode through the reactor. However, contrary to the AF system generally no packing material is present in the reactor vessel. The sludge bed reactor concept is based on the following ideas:

1) Anaerobic sludge has or acquires good sedimentation properties, provided mechanical mixing in the reactor remains gentle and the process is operated

correctly. For that reason, but also because it reduces the investment and maintenance costs, mechanical mixing is not applied in UASB reactors. Because of the excellent settling characteristics of the sludge, high superficial liquid velocities can be applied without any risk of considerable sludge wash-out.

2) The required good contact between the sludge and wastewater in UASB-systems generally is accomplished (i) by feeding the wastewater as uniformly as possible over the bottom of the reactor, or (ii) as a result of the agitation caused by the production of biogas.

3) Particularly with low strength wastewater, reactors with a high height-diameter ratio are used reaching heights of 20-25 m (see section 16.7.2.4). A low surface area will facilitate the feeding of the system, whereas the accumulating biogas production over the height of the tower reactor will cause a turbulent



Figure 16.18 UASB installations for treatment of (A) agro-industrial and (B) dairy wastewater in Indonesia (photo: Paques B.V. and Biothane B.V. respectively)

flow. Also the increased upflow velocity results in a better contact between the sludge and the pollutants. With wastewaters containing biodegradable additionally achieved by applying a liquid recirculation flow. As a result, a more completely mixed flow pattern is acquired and stratification of the substrate and intermediate products over the height of the reactor is minimised, thereby minimising potential inhibition.

4) The washout of sludge aggregates is prevented by separating the produced biogas using a gas collection dome installed at the top of the reactor. In this way a zone with relatively little turbulence is created in the uppermost part of the reactor, consequently the reactor is equipped with an in-built secondary clarifier. The gas collection dome acts like a three phase GLSS. The GLSS device constitutes an essential part of a UASB reactor and serves to:

- a) Collect, separate and discharge the produced biogas. For a satisfactory performance the gas-liquid surface area within the device should be sufficiently large, so that gas can evade easily. This is particularly important in case scum layers should develop. Sufficient mixing by biogas turbulence should prevail at the gas-liquid interface in order to combat this phenomenon. Since the formation of scum layers is a very complex phenomenon with a wide diversity of appearance, it is impossible to give unified and clear guidelines for the dimensions of the gas-liquid interface.
- b) Reduce liquid turbulences in the settler compartment for enhancement of sludge settling, resulting from the gas production. In order to prevent biogas bubbling to the settling zone at the top, one or more baffles should be installed beneath the aperture between the gas domes as well as between gas dome and reactor wall.
- c) Remove sludge particles by a mechanism of sedimentation, flocculation and/or entrapment in a sludge blanket (if present in the settler). The collected sludge can slide back into the digestion compartment, in case the sludge bed does not reach into the settler, or can be discharged occasionally together with excess sludge from the digester compartment.
- d) Limit the expansion of the sludge bed in the digester compartment. The system more or less acts as a barrier against excessive expansion of the lighter part of the sludge bed. In case the sludge bed expands into the settler, the sludge will tend to thicken (because the gas has been separated). This

thickened, heavier sludge, present in the settler, lays on the top of the more voluminous sludge blanket that tends to move into the settler.

- e) Reduce or prevent buoying sludge particles of being rinsed out from the system. For this purpose a skim layer baffle should be installed in front of the effluent weir of the overflow. Such a baffle particularly is essential for treating very low strength wastewaters, because wash out of viable biomass then should be kept at very low levels.
- f) Accomplish some polishing of the wastewater with respect to suspended matter.

Some researchers and practitioners suggest replacing the GLSS device by a packed bed in the upper part of the reactor. This so-called upflow hybrid reactor is a merge between the UASB and the UAF reactors. In some designs the packing material is mounted only in the settling compartment leaving the GLSS at its original position. About 2 to 3% of all anaerobic reactors installed are hybrid reactors (see Figure 16.16). In most applications, the majority of organic matter conversion is located in the sludge bed section whereas the removal of a specific fraction of pollutants is located in the filter area at the top. Specific chemical wastewaters show better treatment efficiencies for all compounds using hybrid systems compared to UASB reactor. The most known example is the treatment of purified terephthalic acid (PTA) wastewater (Kleerebezem, 1999a,b). Results showed that the conversion of terephthalic acid to benzoate is only possible at low concentrations of acetate and benzoate. By applying a hybrid system, the latter two are converted in the sludge bed area whereas, terephthalic acid is then converted in the hybrid section, where specific flora is retained for degrading the refractory compound. The most known disadvantage of hybrid reactors is the deterioration of the filter section after prolonged periods of operation. Hybrid reactors are also advantageous for achieving enhanced effluent polishing as colloidal matter is entrapped at the top part of the system. In fact, trials with domestic sewage showed improved removal of both suspended solids and colloidal matter (Elmitwalli *et al.*, 2002). Biomass accumulating in the packing material ensures a prolonged contact of wastewater with viable bacterial matter, in the absence of packing material little viable biomass will be present in the upper part of the reactor due to the sludge discharge regime generally applied in anaerobic sewage treatment plants. The packing material furthermore enhances flocculation of the finer suspended solids fraction present in the wastewater.

16.7.2.4 Anaerobic expanded and fluidized bed systems (EGSB and FB)

Expanded bed and fluidized bed systems are regarded as the second generation of sludge bed reactors achieving extreme organic loading rates (exceeding 30 to 40 kgCOD/m³.d). The FB process is based on the occurrence of bacterial attachment to mobile carrier particles, which consist, for example, of fine sand (0.1-0.3 mm), basalt, pumice, or plastic. The FB system can be regarded as an advanced anaerobic technology (Li and Sutton, 1981; Heijnen, 1983, 1988), that may reach loading rates of 50-60 kgCOD/m³.d. However, long-term stable operation appears to be problematic. The system relies on the formation of a more or less uniform (in thickness, density, strength) attached biofilm and/or particles. In order to maintain a stable situation with respect to the biofilm development, a high degree of pre-acidification is considered necessary and dispersed matter should be absent in the feed (Ehlinger, 1994). Despite that, an even film thickness is very difficult to control and in many situations a segregation of different types of biofilms over the height of the reactor occurs. In full scale reactors often bare carrier particles segregated from the biofilms leading to operational problems. In order to keep the biofilm particles in the reactor, flow adjustments are necessary after which the support material will start to accumulate in the lower part of the reactor as a kind of stationary bed, whereas light fluffy aggregates (detached biofilms) will be present in the upper part. The latter can only be accomplished when the superficial velocity remains relatively low, which in fact is not the objective of a FB system.

Modern FB systems like the Anaflux system (Holst *et al.*, 1997), rely on bed expansion rather than on bed fluidization. As bed expansion allows a much wider distribution of prevailing biofilms, the system is much more easy to operate. As in the conventional AF systems an inert porous carrier material (particles <0.5 mm, density about 2) is used for bacterial attachment in the Anaflux system. The Anaflux reactor uses a triple phase separator at the top of the reactor, more or less similar to the GLSS device in UASB and EGSB reactors. When the biofilm layer attached to the media becomes excessively over-developed, and the concerning (lighter) aggregates then tend to accumulate in the separator device, the material is periodically extracted from the reactor by an external pump in which it is subjected to the application of sufficient shear to remove part of the biofilm. Then both the media and detached biomass are returned to the reactor, and the

free biomass is then allowed to be rinsed out from the system. In this way the density of the media is controlled and a more homogeneous reactor bed is created. Up to 30-90 kgVSS/m³ reactor can be retained in this way and because of the applied high liquid upflow velocities, i.e. up to 10 m/h) an excellent liquid-biomass contact is accomplished. The system is applicable to wastewaters with a suspended solids concentration <500 mg/l. At present, about 50 full-scale anaerobic FB reactors are installed (Figure 16.16) of which most are Anaflux processes.

The EGSB system employs granular sludge, which is characterised by good settling characteristics and a high methanogenic activity (see also Table 16.9). When extreme sludge loading rates are applied the settle ability will be less owing to the biogas hold-up in the granules. Because of the high settleability of the sludge, high superficial liquid velocities, i.e. exceeding 6 m/h, can be applied. These high liquid velocities, together with the lifting action of gas evolved in the bed, leads to a slight expansion of the sludge-bed. And as a result of that, an excellent contact between sludge and wastewater prevails in the system, leading to significantly higher loading potentials compared to conventional UASB installations. In some expanded bed systems, e.g. the Biopaques IC[®] reactor (Figure 16.19), the net liquid flow velocities, resulting from both hydraulic and gas flows, may range from 25-30 m/h, causing an almost complete mixing of the reactor medium with the available biomass.

Contrary to the Anaflux FB system there generally does not exist a need to control the size of the biomass, although in specific cases it was observed that the granular size tends to become too large. The EGSB systems rely on a complete retention of the granular sludge. Excellent results have been obtained with modern full-scale EGSB installations using various kinds of wastewaters, reaching organic loading rates of up to 40-45 kgCOD/m³.d. Interestingly, by applying EGSB reactor system several other types of wastewaters can be treated which cannot be treated using conventional UASB systems such as:

- 1) Wastewaters containing biodegradable compounds. Full scale reactors show stable performance over many years treating methanol formaldehyde wastewaters characterised by 10 g/l formaldehyde (Zoutberg and Frankin, 1996).
- 2) Cold (even < 10°C) and dilute (COD << 1 g/l) wastewaters, i.e. when specific gas production is

very low and biogas mixing is absent (Rebac *et al.*, 1998). EGSB reactors are characterised by an improved hydraulic mixing, independent from the biogas production. In contrast to UASB systems all retained sludge is employed, while small inactive particles are rinsed from the system.

- 3) Wastewaters containing long chain fatty acids (Rinzema, 1988). At low upflow velocities (UASB), LCFA tend to absorb to the sludge and form inaccessible fatty clumps. At high upflow velocities (EGSB) the substrate is introduced at a lower concentration and is more evenly distributed to the biomass.
- 4) Wastewaters with foaming problems in UASB systems.

Owing to the success of these 'super' high-rate anaerobic systems, at present the large companies sell more EGSB than UASB systems (Figure 16.19).

A special version of the EGSB-concept is the so-called Internal Circulation (IC[®]) reactor (Vellinga *et al.*, 1986). In this type of reactor, the produced biogas is separated from the liquid halfway the reactor by means of a gas/liquid separator device and conveyed upwards through a pipe to a degasifier unit or expansion device. Here, the separated biogas is removed from the system, whereas the sludge-water mixture drops back to the

bottom of the reactor via another pipe. In fact, the lifting forces of the collected biogas are used to bring about a recirculation of liquid and granular sludge over the lower part of the reactor, which results in improved contact between sludge and wastewater. The extent of liquid/sludge recirculation depends on the gas production. The most common EGSB systems are presented in Figure 16.20. Full scale examples of IC and EGSB systems are shown in Figure 16.21.

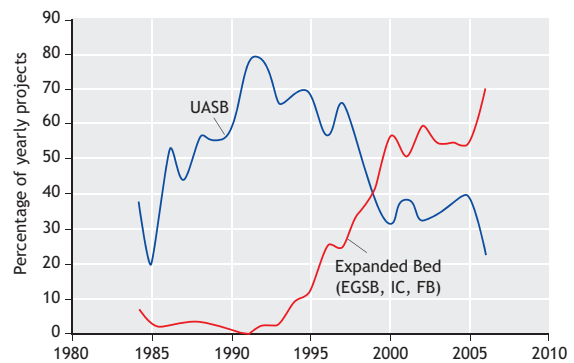


Figure 16.19 Share of UASB and EGSB systems in the full-scale anaerobic treatment systems installed in the period 1984-2007. The EGSB reactors included EGSB, IC[®], and FB systems.

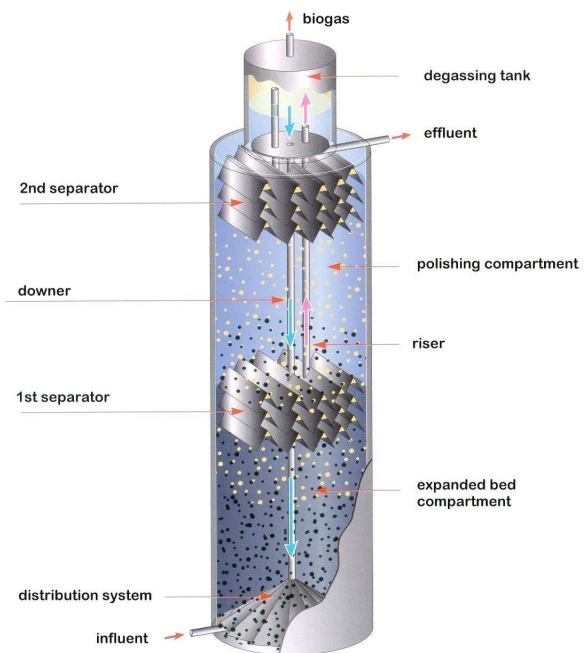
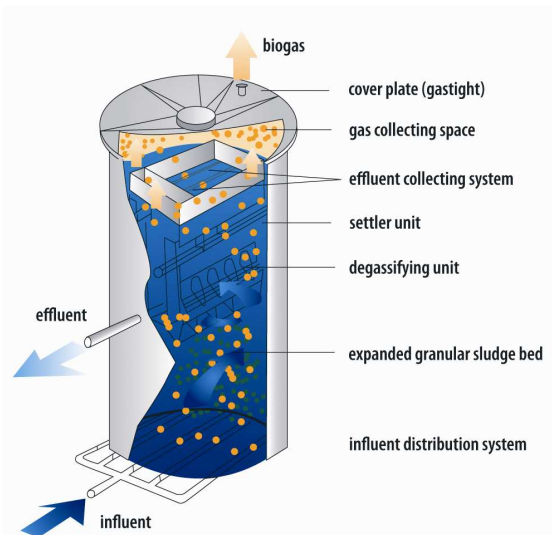


Figure 16.20 EGSB and IC[®] reactor of the major anaerobic system manufacturers Biothane B.V. (left) and Paques B.V. (right)



Figure 16.21 (A) IC installation for treatment of @ and (B) EGSB installation for treatment of (photo: Paques B.V. and Biothane B.V. respectively)

The extreme COD loading rates of EGSB type systems result in extreme biogas loading rates. Efficient biomass retention is acquired applying specifically designed GLSS units. In such conditions, conventionally designed GLSS devices are of no use (Section 16.8.2).

16.7.2.5 Other anaerobic high rate systems

Where ACP, UASB and EGSB reactors are based on a mixed to completely mixed reactor content, various designs have been tested which employ *staging* of the various phases of anaerobic treatment (van Lier *et al.*, 2001). An extreme example is the two stage process where the acidification step is completely separated from the methanogenic step (see section 16.7.2.6). Horizontal staging is obtained in anaerobic baffled reactors (ABR), which is best characterised as a series of serially operated UASB units.

Although some larger scale applications were made on domestic sewage, the reactor is not further developed. The major problem is the hydrodynamic limitation giving constraints to the achievable SRT in the system, since the superficial liquid velocity in a baffled system is substantially higher than in a single step sludge bed reactor. As a logic results, most of the sludge will move with the liquid through the various compartments and then has to be separated after the last compartment in a settler and then returned to the head of the reactor. Vertically staged reactors like the upflow staged sludge bed system (van Lier *et al.*, 1994, 2001, Tagawa *et al.*, 2001) were specifically developed for high temperature treatment. Although the staged reactor concept showed very promising results on a pilot scale so far no full scale reactors were developed.

Very interesting possibilities may exist for anaerobic sequencing batch reactor (ASBR) which consists of a set of anaerobic reactors operated in a batch mode using a 'fill and draw' method. A certain amount of the raw wastewater is supplied to the anaerobic reactor, after the supernatant liquid of a previous batch has been discharged. Then a 'gentle' type of mixing of the reactor contents is started in order to enable the settled viable sludge to contact the wastewater and to eliminate the biodegradable organics. After a sufficient period of reaction time, the sludge is allowed to settle and the supernatant solution is discharged. The next cycle is then started. Granulation proceeds well in an ASBR on dilute wastewaters, also at lower ambient temperatures (Banik *et al.*, 1997). ASBR systems were shown to be of particular interest for LCFA containing wastewaters (Alves *et al.*, 2001). During the filling period, LCFAs absorb to the anaerobic sludge after which a gentle digestion period proceeds in which the absorbed sludge is stabilised and completely regenerated to high active methanogenic biomass..

More recently anaerobic membrane bioreactors (AMBR) are intensively researched (Liao *et al.*, 2006, Jeison and van Lier, 2006). Membrane technology can be considered an interesting option in those cases where established technologies may fail. This likely is the case when extreme conditions prevail, such as high temperatures and high salinity, or wastewaters with refractory and/or toxic compounds. Full-scale experiences have demonstrated that under those conditions sludge immobilization by granule formation does not develop successfully, negatively affecting sludge retention. The requirements of wastewater treatment under extreme conditions is expected to

become more and more common, following the current trend of closing industrial process water cycles. Under such conditions, MBR systems are very effective in the retention of specifically required micro-organisms which are needed for the removal of accumulating refractory compounds in closed cycle industrial processes. At present only a few full scale AMBR systems are in operation. Considering the sharp drop in membrane prices an increase in this emerging technology is expected.

16.7.2.6 Acidifying and hydrolytic reactors

Except for well stirred tank reactors no specific reactor concepts have been developed for acidogenesis so far. The process of acidogenesis generally proceeds sufficiently fast in a stirred tank reactor and in practice there generally does not exist any real need for a complete acidogenesis. Moreover, nowadays it is fully understood that joint acidification with methanogenesis is beneficial for granule formation (Verstraete *et al.*, 1996). Furthermore, it is increasingly accepted that the presence of higher concentrations of acidifying organisms in the feed of the methanogenic reactor is quite detrimental for the granular methanogenic sludge present in that reactor. The latter means that the sludge retention of an acidogenic reactor needs to be improved.

Acidifying reactors can be combined with solids entrapments systems, safeguarding the methanogenic reactor from too high SS loading. Trials were made combining primary clarification with anaerobic stabilisation on domestic sewage. Although Wang (1994) implemented some full scale systems in China, no large implementations have been implemented so far.

16.8 UPFLOW ANAEROBIC SLUDGE BLANKET (UASB) REACTOR

16.8.1 Process description

The UASB reactor is the most widely and successfully used high rate anaerobic technology for treating several types of wastewater (Figure 16.17). The success of the UASB reactor can be attributed to its capability for retaining a high concentration of sludge, meanwhile efficient solids, liquids and water phase separation is attained. The UASB reactor consists of a circular or rectangular tank in which waste (water or sludge) flows in an upward direction through an activated anaerobic sludge bed which occupies about half the volume of the reactor and consists of highly settleable granules or flocs (Figure 16.17). During the passage through the

anaerobic sludge the treatment process takes place by solids entrapment and organic matter conversion into biogas and sludge. The produced biogas bubbles automatically rise to the top of the reactor, carrying water and solid particles, i.e. biological sludge and residual solids. The biogas bubbles are (via baffles) directed to a gas-liquid surface at the upper part of the reactor, leading to an efficient GLSS. The solid particles drop back to the top of the sludge blanket, while the released gases are captured in an inverted cone or related structure, located at the top of the reactor. Water passes through the apertures between the baffles carrying some solid particles which settle in the settling area because of the drop in upward velocity owing to the increase in the cross sectional area. After settling the solids slide back to the sludge blanket, while water leaves the settlers over overflow weirs.

16.8.2 Design considerations of the UASB reactor

16.8.2.1 Maximum hydraulic surface loading

The methanogenic conversion capacity of UASB reactors, expressed in kgCOD/m³.d, is directly related to the amount of retained viable biomass and the specific methanogenic activity of the accumulated sludge. In addition to the quantity and quality of the retained sludge, the maximum organic loading potentials also depend on the proper mixing of the sludge with the incoming wastewater. The required sludge retention time (SRT) sets limits to applicable upward liquid velocities (V_{upw}) as well as to the specific biogas loading resulting from the anaerobic conversion process (Lettinga and Hulshoff Pol, 1991). The design of the UASB reactor combines the features of a high-rate bioreactor with those of an in-built secondary clarifier at the top. Therefore, average V_{upw} in the UASB reactor's cross sectional area and the clarification section at the top are in the range of 0.5 – 1.0 m/h. Higher hydraulic loadings may lead to non-desired loss of biomass if flocculent type of sludge accumulates during reactor operation. The latter may happen, for instance, during the first start-up when the reactor is seeded with non-adapted seed material like digested sewage sludge or during the anaerobic treatment of domestic sewage. The V_{upw} can be calculated using the average flow and the reactor's cross sectional area, A (Eq. 16.46).

$$V_{upw} = \frac{Q_{inf}}{A} \quad (\text{m/h}) \quad (16.46)$$

where:

Q_{inf} influent flow rate

With the growth and accumulation of thick flocculent sludge, or granular sludge, much higher hydraulic loadings are admissible in the reactor. High V_{upw} values are applied in expanded bed reactors reaching values up to 8-10 m/h.

Based on the maximum allowable V_{upw} , the minimum surface dimensions can be calculated (Eq. 16.47).

$$A_{min} = \frac{Q_{inf}}{V_{upw,max}} \quad (m^2) \quad (16.47)$$

At a given hydraulic retention time (HRT, Θ), the maximum upward velocity determines the H/A ratio, in which H is the reactor height according to Eq. 16.48.

$$\Theta = \frac{A_{min} \cdot H_{max}}{Q} \quad (h) \quad (16.48)$$

$$V_{reactor} = \Theta \cdot Q \quad (m^3) \quad (16.49)$$

For any situation in which the organic loading capacity is not restrictive, Eq. 16.49 gives the volume of the required UASB reactor. The latter is only the case with diluted wastewaters, such as with most domestic wastewaters in the tropical zone of Latin America having COD values < 1,000 mg/l. Here, the hydraulic load fully determines the accumulating sludge quantity, whereas the in-reactor methanogenic capacity generally exceeds the applied organic loading rates.

16.8.2.2 Organic loading capacity

In most cases UASB reactors are used for the treatment of more concentrated wastewaters (Table 16.10). The volumetric conversion capacity or organic loading rate (OLR) in kgCOD/m³ reactor.d is then dependent on the:

- quantity of accumulated biomass, X, in kg volatile suspended solids VSS/m³ reactor.
- specific methanogenic activity (SMA) of the sludge in kgCOD/kgVSS.d.
- the contact factor (f_c), between 0 and 1.

The OLR can be calculated using Eq. 16.50, based on Monod kinetics:

$$OLR = r_v = f_c \cdot \mu \cdot X = f_c \left(\frac{V_{max} \cdot S}{K_m + S} \right) \cdot X \cdot T \quad (kgCOD/m^3) \quad (16.50)$$

The conversion rate V_{max} , and/or the SMA depends on several factors such as:

- temperature
- presence of inhibitory or toxic compounds
- biodegradability of the substrate
- presence of suspended solids (SS) in the influent
- degree of wastewater pre-acidification.

In UASB reactors the amount of anaerobic sludge generally is in the range 35-40 kgVSS/m³ reactor volume (settler included). The contact factor (f_c) depends on the effectiveness and evenness of the feed distribution and the applied organic loading rate with the resulting biogas production largely contributing to the reactor mixing.

Considering the number of unknown factors, a thorough wastewater characterisation is indispensable prior to designing a UASB reactor. In addition, reactor pilot trials are generally performed to achieve a better insight into the growth and development of the anaerobic sludge on a specific wastewater. Based on a large number of pilot trials in the past decades and the subsequent large number of full scale experiences, a table of allowable organic loading rates in dependence to the reactor temperature has been developed (Table 16.11). When the allowable OLR or r_v is known, the required UASB reactor volume can be easily calculated from the influent flow rate and its concentration (Eq. 16.51):

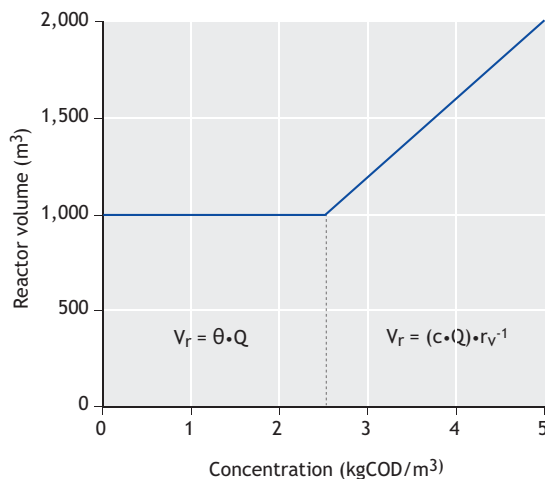
$$V_{reactor} = \frac{C_{inf} \cdot Q_{inf}}{r_v} \quad (16.51)$$

A UASB reactor is either hydraulically or organically limited in which the volume of a UASB reactor is calculated by either Eq. 16.49 or 16.51. If the actual situation is not known, generally the volume is calculated based on both considerations after which the largest volume suggested by either equation is taken as the design volume. Figure 16.22 depicts the impact of the wastewater concentration (in kgCOD/m³) on the required reactor volume. Assuming a minimum HRT of 4 h for preventing sludge wash out, the minimum required reactor volume will be at least 1,000 m³, irrespective of the concentration of the wastewater. At high influent COD concentrations, obviously, the required reactor volume directly depends on the wastewater concentration since the admissible organic loading rate is fixed.

Table 16.11 Permissible organic loads in single-step UASB reactors for various types of wastewater in relation to the applied operating temperature. The biomass consists of granular sludge

Temperature (°C)	Organic loading rate (kgCOD/m ³ .d)			
	VFA wastewater	non-VFA wastewater	Wastewater with < 5% SS-COD	Wastewater with 30-40 % SS-COD
15	2 - 4	1.5 - 3	2 - 3	1.5 - 2
20	4 - 6	2 - 4	4 - 6	2 - 3
25	6 - 12	4 - 8	6 - 10	3 - 6
30	10 - 18	8 - 12	10 - 15	6 - 9
35	15 - 24	12 - 18	15 - 20	9 - 14
40	20 - 32	15 - 24	20 - 27	14 - 18

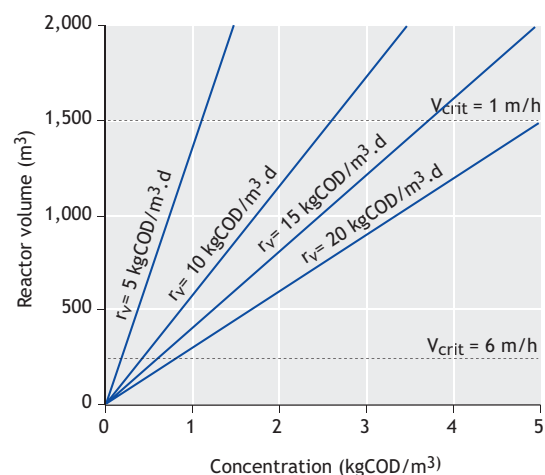
Often the great unknown is the maximum hydraulic loading potential or the minimum HRT. It is impossible to give hard numbers since it directly depends on the sludge that will be cultivated on that specific wastewater. Generally, for UASB reactors, and particularly those operating with non-granular sludge, a maximum upflow velocity of 1 m/h is considered. Figure 16.23, shows the impact on the required reactor volume when upflow velocities of 6 m/h can be tolerated as is the case when good quality granular sludge is cultivated. In the example the same height of the reactor is taken. Effectively, reactor volumes can be reduced by a factor of 6.

**Figure 16.22** Calculating the required UASB reactor volume using the following assumptions: $\Theta_{\min} = 4\text{h}$, $Q = 250\text{ m}^3/\text{h}$, $r_v = 15\text{ kgCOD}/\text{m}^3\cdot\text{d}$, $T = 30^\circ\text{C}$. The volume is determined by either the hydraulic or organic loading rate (after Lettinga and Hushoff Pol, 1991)

In addition to liquid velocities, high loaded reactors are also limited by the turbulence brought about by the produced biogas. The biogas upward velocity (V_{biogas}) can be calculated using Eq. 16.52.

$$V_{\text{biogas}} = \text{COD}_{\text{conc}} \cdot \frac{E_{\text{ff-meth}}}{100} \cdot \frac{0.35}{F_{\text{meth-biogas}}} \cdot \frac{(T + 273)}{273} \cdot V_{\text{upw,liquid}} \quad (16.52)$$

In which $E_{\text{ff-meth}}$ is the % of the COD (in kg/m^3) converted to CH_4 , T is temperature in $^\circ\text{C}$, and $F_{\text{meth-biogas}}$ is fraction of CH_4 in biogas (generally between 0.6 and 0.9 for wastewaters). It must be noted that the actual value of $F_{\text{meth-biogas}}$ will be higher than the theoretical estimate using $18.75/100 \cdot \text{COD}/\text{TOC}$ (Figure 16.10), owing to the high solubility of CO_2 in the medium and chemically binding of HCO_3^- to cations like Na^+ , K^+ , and NH_4^+ (section 16.3.1.). With conventionally designed GLSS devices the maximum allowable V_{biogas} is between 2 and 3 m/h.

**Figure 16.23** Calculating the required UASB reactor volume using the following assumptions: $Q = 250\text{ m}^3/\text{h}$, reactor height = 6 m, $T = 30^\circ\text{C}$. The volume is determined by either the hydraulic or organic loading rate. V_{crit} determines the 'cut-off' level for the minimum required reactor volume based on hydraulic limitations (after Lettinga and Hushoff Pol, 1991)

Particularly with reactors characterised by a very high height/diameter ratio, special care is given to the detailed design of the gas/liquid separator as can be viewed in Figure 16.17.

16.8.2.3 Reactor internals

The most important UASB reactor internals that require careful consideration are the feed inlet distribution, the effluent outlet, and the GLSS device. Most constructors and contractors apply their own -often patented- design. It goes beyond the purpose of this chapter to address in details the design feature of these internals. Some general remarks are given in Section 16.11, where some general design features of anaerobic sewage treatment reactors are given.

Of crucial importance is the evenness and density of the feed distribution system, particularly when the UASB system is applied at low loading rates, i.e. when turbulence brought about by biogas production is limited. Table 16.12 gives some indicative values applicable to UASB reactors operated with either flocculent or granular sludges. Full scale experiences show that at organic loading rates exceeding 5 kgCOD/m³.d, biogas induced reactor turbulence is sufficient for adequate mixing, decreasing the mass transfer rate to an appropriate level. Compared to UASB reactors, the influent distribution systems in EGSB reactors are less critical owing to the relative small reactor surfaces.

The tentative design guidelines for conventional GLSS devices in UASB reactors are given in Table 16.13. Further design features are explained in detail by e.g. van Haandel and Lettinga (1994) and most critical parameters for the construction of a UASB reactor for domestic sewage treatment are shown in Figure 16.25.

Table 16.12 Required area (m²) per feed inlet of a UASB reactor, in dependence to type of sludge and applied loading rate

Type of sludge	Loading rate (kgCOD/m ³ .d)	Surface area per feed inlet (m ²)
Medium thick flocculant (20-40 kgTS/m ³)	< 1 – 2	1 – 2
	> 3	2 – 5
Dense flocculant (> 40 kgTS/m ³)	< 1	0.5 – 1
	1 – 2	1 – 2
	> 2	2 – 3
Granular sludge	< 2	0.5
	2 – 4	1 – 2
	> 4	> 2

16.8.3 UASB septic tank

The UASB septic tank is a novel reactor system of particular interest for application in decentralised sanitation concepts. Influent to these reactors may consist of relatively diluted domestic wastewaters or concentrated waste streams, such as separately collected black water. Similar to the UASB reactor, the reactor is operated in an up-flow mode, whereas up-flow velocities are very low, ranging from about 0.01 m/h for black water systems to 0.20 m/h for diluted domestic waters. Because of the low hydraulic loadings, improved solids separation is obtained. In fact UASB-Septic Tank systems function as an accumulation and stabilisation system for solids and a methanogenic reactor for soluble organic compounds. In contrast to UASB reactors, the UASB septic tank can be equipped with a central 'stirrer' for periodic and very gentle movements of the sludge bed.

Table 16.13 Summary of tentative guidelines for the design of the gas-liquid-solids-separator device

UASB – GLSS device	
1	The slope of the settler bottom (i.e. the inclined wall of the gas collector) should be between 45-60°.
2	The surface area of the apertures between the gas collectors should be 15-20% of the reactor surface area.
3	The height of the gas collector should be between 1.5-2 m at reactor heights of 5-6 m.
4	To facilitate the release and collection of gas bubbles and to combat scum layer formation, a liquid-gas interface should be maintained in the gas collector.
5	To avoid up-flowing gas bubbles to enter the settler compartment, the overlap of the baffles installed beneath the apertures should be 15-20 cm.
6	Generally, scum layer baffles should be installed in front of the effluent weirs.
7	The diameter of the gas exhaust pipes should be sufficient to guarantee the easy removal of the biogas from the gas collection cap, particularly in case of foaming.
8	In the upper part of the gas cap, anti-foam spray nozzles should be installed in the case the treatment of the wastewater is accompanied with heavy foaming.

Table 16.14 Kinetic parameters of main substrates / intermediate products in the anaerobic conversion process (after Batstone *et al.*, (2000). Data from various types of digestion systems. Table presents cited literature review data only if available, otherwise most typical are taken. All substrate and VSS related weights are expressed as COD equivalents

Substrate	Uptake rate kg/kgVSS.d	μ_{\max} 1/d	Y kgVSS/kg	K_s kg/m ³	K_d 1/d
Hydrogen	2-65	0.02-12	0.014-0.183	0.00002-0.0006	0.009
Acetate	3-18	0.05-1.4	0.014-0.076	0.011-0.930	0.004-0.036
Propionate	0.16-0.31	0.004-0.016	0.025-0.05	0.06-1.15	0.01-0.04
Butyrate	5-14	0.35-0.90	0.066	0.012-0.30	0.027
Valerate	15-19	0.86-1.20	0.058-0.063	0.062-0.36	0.01-0.03
LCFA	1.4-37	0.10-1.65	0.045-0.064	0.06-2.0	0.01-0.20
Amino acids	36-107	2.36-16	0.06-0.15	0.05-1.4	0.01-3.2
Monosaccharides	29-125	0.41-21.3	0.01-0.17	0.022-0.63	0.02-3.2

16.9 ANAEROBIC PROCESS KINETICS

Bacterial conversion rates, including anaerobic processes, are generally described as applying Monod kinetics for substrate conversion (see Chapter 2). Anaerobic conversion kinetics, including all kinetic parameters, have been recently and extensively reviewed by Batstone *et al.* (2002) who presented a unified anaerobic digestion model, denominated as ADM1 in analogy with the ASM1 for activated sludge. ADM1 evolved from a number of different anaerobic models which have been presented in literature in the past decades. For the same convenience as explained in section 16.3 and 16.5, the ADM1 model also makes use of the COD balance for describing the flow of electrons during the anaerobic conversion process. Striking are the large variations in the cited assessed kinetic parameters for the specific conversion reactions, see Table 16.14, after Batstone *et al.* (2000). This means that process configuration, exact prevailing microbial flora, and actual operation of the system largely determine the applicable kinetic parameters.

So far, ADM1 is a very useful tool for describing existing systems giving insights into the process dynamics and the impact of changing process parameters such as feed concentration, substrate flow, temperature, etc. on the overall digestion process. Using actual reactor data, the kinetic parameters can be adjusted for realistically predicting the reactor performance on COD removal and CH₄ production. Also, for teaching purposes, ADM1 is a valuable tool giving insight in the importance of specific conversion steps in the entire chain of consecutive reactions. On the other hand, ADM1 still lacks biofilm kinetics and system hydrodynamics which may largely determine the actual kinetics in high-rate anaerobic treatment systems.

For instance, in a 3 phase system where convective mass transport on a micro and macro level, which is induced by the gaseous end-products, may largely affect the kinetic parameters and actual system dynamics may fully overrule the model input parameters. Therefore, and so far, as a design tool, ADM1 is of no use and the current challenge is to combine the biological ADM1 model with other hydrodynamic and chemical models for creating a comprehensive design tool or operation support tool when operating an anaerobic system in a dynamic environment.

16.10 ANAEROBIC TREATMENT OF DOMESTIC AND MUNICIPAL SEWAGE

Municipal wastewaters is in quantity the most abundant type of wastewater on earth. Discharge of non-treated wastewaters to surface waters has a huge environmental impact and poses serious health concerns to the population. Minimising both the human health risks and environmental risks were the main incentives for developing adequate treatment technologies for addressing these wastewaters in Western societies (see Chapter 1) In many less prosperous countries financial constraints restrict application of these technologies and alternatives are searched for. AnWT offers a cost effective alternative which was already recognised in the mid seventies of the last century by e.g. Lettinga and co-workers. High-rate anaerobic wastewater, however, was developed for the treatment of high strength industrial wastewaters, whereas domestic sewage and municipal wastewaters are characterised as a very dilute type of wastewaters. In large parts of the world the COD concentrations of municipal sewage is <1,000 mg/l and often even below 500 mg/l. According to Figure 16.22, anaerobic treatment of these type of wastewater is limited by the hydrodynamic constraints

in the system rather than the organic conversion capacity. However, sewage temperatures are often lower than industrial wastewaters. Only under tropical climate conditions can municipal wastewaters reach temperatures ideal for AnWT (van Haandel and Lettinga, 1994). The first experiences with compact/high-rate anaerobic treatment using UASB reactors for sewage treatment started during the early eighties in Cali, Colombia (van Haandel and Lettinga, 1994). The results obtained from the operation of the 64 m³ pilot UASB reactor showed the feasibility of the system under the prevailing environmental and sewage characteristics. The initial trials were rapidly followed by full scale reactors in Colombia, Brasil and India. Table 16.15 lists some of the results of these full scale sewage UASB reactors. Since the early nineties, hundreds of full scale UASB reactors have been constructed from 50–50,000 m³ in volume (von Sperling and Chernicharo 2005), particularly under (sub)-tropical conditions (Draaijer *et al.*, 1992; Schellinkhout and Osorio, 1994). Generally, a reduction in the BOD between 75 and 85% is realized, with effluent BOD concentrations of less than 40–50 mg/l. Total removal rates with regard to COD and TSS are up to 70–80% and sometimes even higher (von Sperling and Chernicharo, 2005; Van Haandel and Lettinga, 1994). In order to comply with local regulations for discharge, the UASB system is generally accompanied by a proper post-treatment system, such as: facultative ponds, sand filtration, constructed wetlands, trickling filters, physico-chemical treatment, and activated sludge treatment (Schellinkhout and Osorio, 1994; von Sperling and Chernicharo, 2005).

The UASB reactor and the post-treatment step can be implemented consecutively or in a more integrated set-up. Table 16.16 lists the most important features of high-rate anaerobic sewage treatment. Most of the advantages are in agreement with advantages listed for industrial anaerobic reactors (Section 16.1.1).

During the early development of anaerobic sewage treatment some of the constraints, however, were simply ignored or not taken into consideration in the full scale design because of financial limitations. This however, results in negative experiences and is a bad advertisement. Nowadays, uncontrolled greenhouse gas emissions should be avoided and non-flaring of captured CH₄ should be prohibited. If instead all the energy is used, and with increasing energy prices and tradable CO₂ credits (section 16.1.1), anaerobic sewage treatment may even become an affordable investment for many developing countries. For most of the listed constraints technical solutions are available, or at least in development, e.g. recovery of the methane from effluents seems feasible using air which subsequently is directed to the flare or the furnace as burning air for the captured CH₄. With all constraints addressed, anaerobic sewage treatment has very big potentials to solve the major wastewater related problems in developing countries.

The simplicity of the system also follows from Figure 16.24, which compares the functional units of an activated sludge process with that of an anaerobic high-rate system. The single step UASB reactor in fact comprises 4 functional units:

- 1) *Primary clarifier*: removal/entrapment of (non)biodegradable suspended solids from the influent
- 2) *Biological reactors (secondary treatment)*: Removal of biodegradable organic compounds by converting them into methane.
- 3) *Secondary clarifier*: clarifying the treated effluent in the settler zone at the top part of the UASB reactor.
- 4) *Sludge digester*: stabilisation (digestion) and improving the dewatering characteristics of the retained sludge.

Table 16.15 Treatment performance of the first full scale UASB plants treating municipal sewage. COD refers to total COD of the raw wastewater (after van Haandel and Lettinga 1994)

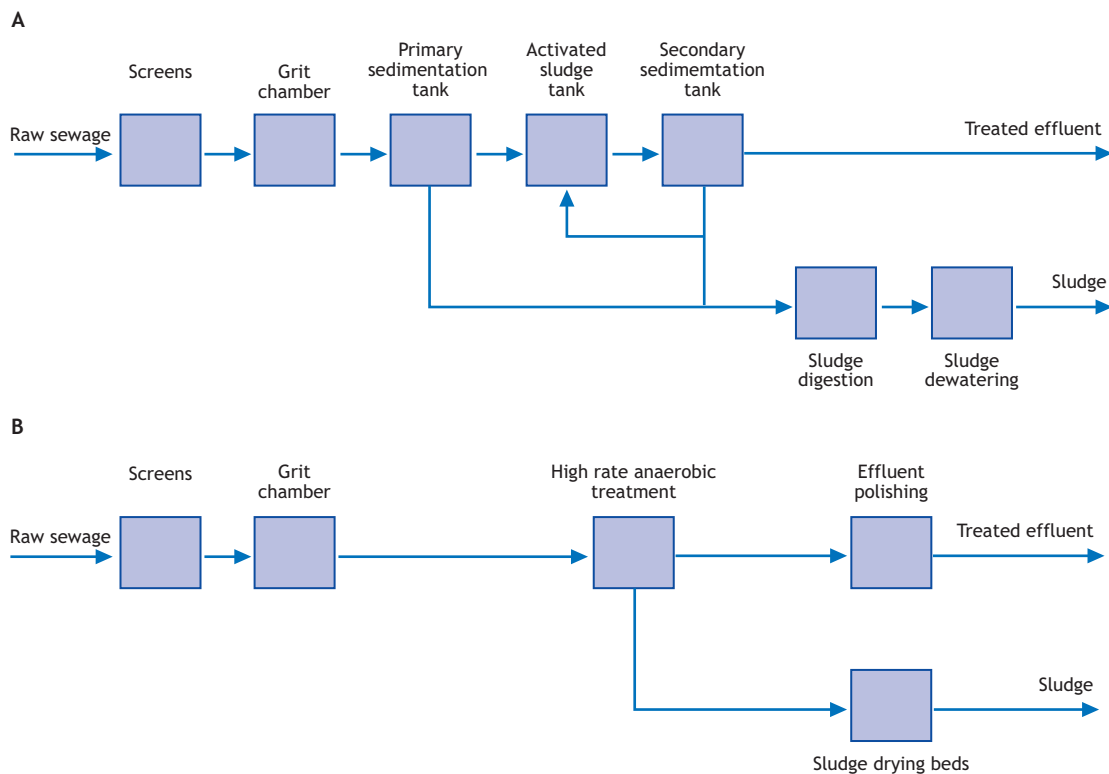
Country	Volume m ³	Temperature °C	HRT h	Influent COD mg/l	Effluent COD ^a mg/l	% Removal COD
Colombia	64	24-26	4-6	267	110	65
Colombia	6,600	25	5.2	380	150	60-80
Brazil	120	23	4.7-9	315-265	145	50-70
Brazil	67.5	23	7	402	130	74
Brazil	810	30	9.7	563	185	67
India	1,200	20-30	6	563	146	74

^a Calculated from the influent COD and removal efficiency

Table 16.16 Main advantages and constraints^a of anaerobic sewage treatment in anaerobic high rate systems

Advantages
<ul style="list-style-type: none"> • Substantial savings, reaching 90%, in operational costs as no energy is required for aeration. • 40-60% reduction in investment cost as less treatment units are required • If implemented at appropriate scale, the produced CH₄ is of interest for energy recovery or electricity production • The technologies do not make use of high-tech equipment, except for main headwork pumps and fine screens. Treatment system is less dependent on imported technologies. • The process is robust and can handle periodic high hydraulic and organic loading rates. • Technologies are compact with average HRTs between 6 and 9 h and are, therefore, suitable for application in the urban areas, minimising conveyance costs • Small scale applications allow decentralisation in treatment, making sewage treatment less dependent on the extent of the sewerage networks. • The excess sludge production is low, well stabilized and easily dewatered so it does not require extensive post treatment. • The valuable nutrients (N and P) are conserved which give high potential for crop irrigation. • A well designed UASB filters Helminth's eggs from the influent, a prerequisite prior to agricultural reuse
Constraints
<ul style="list-style-type: none"> • Anaerobic treatment is a partial treatment, requiring post-treatment for meeting the discharge or reuse criteria. • The produced CH₄ is largely dissolved in the effluent (depending on the influent COD concentration). So far no measures are taken to prevent CH₄ escaping to the atmosphere. • The collected CH₄ is often not recovered nor flared. • There is little experience with full-scale application at moderate to low temperatures. • Reduced gases like H₂S, that are dissolved in the effluent may escape causing odour problems.

^a Compared to activated sludge processes

**Figure 16.24** Functional units of a sewage treatment plant, comparing activated sludge (A) and UASB technology (B)

Obviously, the head-works, i.e. pump pits and pumps if gravity cannot be used, screens and sand and grit removal are needed for any compact treatment system. Anaerobic sewage treatment generally requires fine screens, < 8-10 mm clear distance between bars, after the coarse screens to minimise operational problems, such as influent clogging. In most cases the fine screen is the most expensive part of the treatment system. The sludge from an anaerobic sewage treatment reactor is well stabilised owing to the long SRTs and can be dried by applying sludge drying beds. No smell arises from the sludge drying beds.

According to Figure 16.22, the design of a sewage treatment UASB reactor is relatively simple as only the hydraulic criteria are of importance. Volumetric sizing of a UASB reactor fed with moderate sewage of 500 mgCOD/l can be calculated using Eq. 16.49, applying an HRT of about 8 h. Taking a height of 5 m the required area can be roughly estimated.

The most critical design aspects are pictured in Figure 16.25 and are well explained by van Haandel and Lettinga (1994) and von Sperling and Chernicharo (2005). Table 16.17 provides some key numbers based on the various full scale reactors in Latin America.

Although domestic sewage is a dilute type of wastewater, it is also characterised as a complex type of wastewater, with a relative high content of suspended solids, i.e. a low $COD_{soluble}/COD_{total}$ ratio and a low temperature. The suspended solids may constitute 50-65% of the total COD. Therefore, total COD conversion is largely limited by hydrolysis of particulate matter.

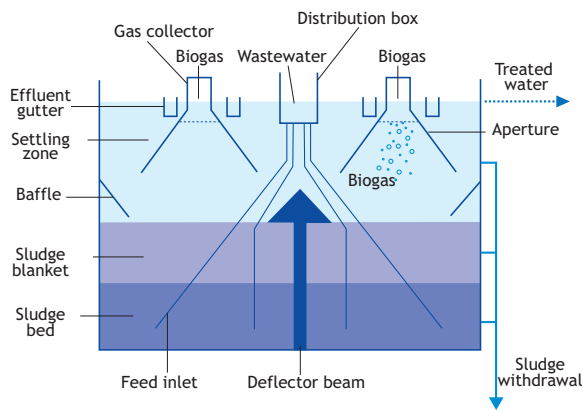


Figure 16.25 Schematic representation of a UASB reactor for treating domestic sewage. Most important design aspects are indicated

Table 16.17 Some design criteria of UASB reactors treating sewage in tropical countries

Parameter	Value
Min. average HRT	4 h
height	4-5 m
Feed inlet points	1 inlet per 1 to 4 m ²
Feed distribution	Each inlet pipe from a separate compartment
Static pressure in feed inlet box	Up to 50 cm
Upflow velocity in aperture	Average daily 4 m/h During 2-4 hrs 8 m/h
Upflow velocity	0.5-0.7 m/h

Particularly when the sewage temperature drops to < 20°C, the biological conversion capacity will determine the overall COD removal rather than the prevailing hydrodynamic conditions. In fact, because of the low temperature and the high TSS/COD ratio, the range in which the HRT (Θ) determines the volumetric sizing of the UASB reactor, viz. $V_r = \Theta \cdot Q$ (Eq. 16.49), is distinctly smaller than the range indicated in Figure 16.20. When temperature drops and non-digested sludge starts to accumulate in the sludge bed, the hydrolytic and methanogenic capacity of the sludge will gradually decrease, deteriorating both particulate and soluble COD removal, and eventually leading to reactor failure.

Apparently, the prime design criterion, even with dilute domestic sewage, is the reactor solids retention time (SRT), which should be above a minimum value in order to maintain the methanogenic conversion capacity of the sludge. With dilute domestic sewage under tropical conditions, $COD < 1,000$ mg/l and $t > 20^\circ C$, this condition will always be met. The prevailing SRT depends on various sewage characteristics such as:

- sewage temperature.
- influent suspended solids concentration.
- rate of solids digestion in the reactor.
- filtering capacity of the sludge bed, which are determined by the applied upflow velocities and sludge characteristics.
- growth and decay of new sludge.
- sludge retention in the settler, determined by the applied liquid velocities.
- withdrawal of excess sludge.

The SRT can be calculated using Eq.16.19,

$$SRT = \frac{X_{reactor} \cdot V_{reactor}}{Q_{effl} \cdot X_{effl} + Q_{excess - sludge} \cdot X_{excess - sludge}} \quad (16.53)$$

where:

- X concentration of viable biomass (kg/m^3)
 V reactor volume (m^3)
 Q flow (m^3/d)

As a rule of thumb, the minimum SRT should always be more than 3 times the doubling time (T_d) of the biomass, responsible for the rate limiting step. With dilute domestic sewage under tropical conditions, these are the methanogens, with an estimated T_d at 25°C of about 10 days. Therefore, SRTs of existing full scale sewage treatment systems will never be below 30 days. The impact of temperature on the required SRT in the UASB reactor is depicted in Figure 16.26.

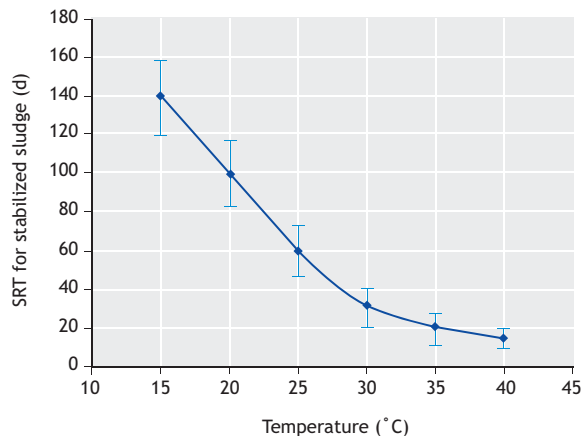


Figure 16.26 Required SRT for domestic sewage treatment as a function of temperature

Realising the importance of the SRT it becomes clear that the conventional UASB reactor design for municipal wastewater needs reconsideration when temperature drops and COD concentrations exceed 1,000 mg/l. In many arid climate countries with limited water supply, sewage concentrations range between

1,000–2,500 mgCOD/l, e.g. Middle East, Northern Africa, Arabic peninsula, etc. Furthermore, the temperate climates in the Middle East and Northern Africa are characterised by cold winters, particularly in mountainous areas.

Recent experiences in Jordan and Palestine, show municipal sewage COD concentrations reaching 2,500 mgCOD/l at TSS/COD ratio's of 0.6 (Mahmoud *et al.*, 2003), whereas winter temperatures may drop to 15°C. Applying the conventional UASB reactor design, the HRT needs to be increased reaching values of 20–24 hours (Hallalsheh, 2002). This, obviously, will affect the hydrodynamics of the system requesting changes in influent distribution for preventing short-circuiting. Alternatively, the large suspended solids load can be addressed in separate reactor units such as a primary clarifier or enhanced solids removal in upflow filter systems, coupled to a sludge digester (Elmitwalli, 2000). A novel approach is to link the UASB reactor to a coupled digester with sludge exchange (Mahmoud, 2002; Mahmoud *et al.*, 2004). With the latter system, accumulating solids will be digested at higher temperatures, whereas the methanogenic activity in the reactor will be increased by a return digested sludge flow.

At present, the first full scale reactor in the Middle East region is under commissioning in the Fayoum, south of Cairo, Egypt. The design is based on the conventional approach taking into account the relatively high strength of the sewage, resulting in a somewhat higher HRT with an average of 12 h. Pilot trials in Amman showed the feasibility of the system as an ideal pre-treatment method for a low cost reduction in the COD load, while generating energy for post-treatment. Table 16.18 briefly summarises the most important results (Hallalsheh *et al.*, 2005).

Although the prospects for a full scale application in Amman look very promising (Table 16.18), decisions

Table 16.18 UASB pilot reactor trials at the Amman – Zarqa, waste stabilisation pond site 'Khirbet As Samra', Jordan

Average influent characteristics		Treatment performance (including post-clarification)	
Flow	180,000 m^3/d	COD removal:	up to 80%
BOD	500–700 mg/l	BOD removal:	up to 85%
COD	1,500 mg/l	TSS removal:	up to 80%
TSS	600–700 mg/l	Pathogens:	negligible
$\text{NH}_4^+ - \text{N}$	70–130 mg/l	CH_4 production:	0.15 $\text{Nm}^3 \text{CH}_4/\text{kgCOD}_{\text{removed}}$
TKN	90–200 mg/l	Potential CH_4 production:	27,000 m^3/d , equivalent to a potential power supply of ≈ 5 MW (assuming 40% CHP efficiency).
P_{tot}	10–40 mg/l		
T	16–28 °C		

were recently made to change the existing pond system into a modern activated sludge plant. With regard to sustainability in domestic sewage treatment this decision is considered a wasted opportunity. Particularly since the more concentrated municipal wastewaters are in fact ideal for anaerobic pre-treatment. The recovered energy can then be beneficially used on the site for extensive treatment up to discharge or reuse standards. Any excess energy may serve as a power supply for e.g. irrigation pumps or for settlements in the vicinity of the plant.

Considering the present concern with fossil fuel consumption, anaerobic sewage treatment offers a feasible alternative for treating the huge flow of domestic and municipal wastewaters in many parts of the world. In light of the current green house gas discussion, recovery of all produced CH₄ should be an

intrinsic part of the treatment plant design. Owing to its compactness, high-rate anaerobic sewage treatment can be applied in urban areas as well. The latter will lead to huge costs reductions in constructing sewerage networks, pumping stations, and conveyance networks. It must be realised that only 35% of the produced municipal wastewaters in Asia are treated, whereas in Latin America this value is only 15% (WHO/UNICEF 2000). In Africa, the generated wastewaters are hardly collected and sewage treatment, with the exception of the Mediterranean part and South Africa, is nearly absent. With an increase in the basic understanding of the anaerobic process and an increase in the number of full scale experiences at any scale, anaerobic treatment will undoubtedly become one of the prime methods for treating organically polluted wastewaters streams.

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NOMENCLATURE

Symbol	Description	Unit
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Abbreviation	Description
AB	Acetogenic bacteria
ABR	Anaerobic baffled reactors
ACP	Anaerobic contact process
AF	Anaerobic filters
AMBR	Anaerobic membrane bioreactors
AnWT	Anaerobic wastewater treatment
ASBR	Anaerobic sludge bed reactors
ASRB	Acetic acid oxidising sulphate reducing bacteria
CHP	Combined heat power
EGSB	Expanded granular sludge bed
FASRB	Fatty acids oxidising sulphate reducing bacteria
FB	Fuidized bed
GLSS	Gas-liquid-solids separation system
HMB	Hydrogenotrophic methanogenic bacteria
HSRB	Hydrogen oxidising sulphate reducing bacteria
HRT	Hydraulic retention time
IC	Internal circulation
LCFA	Long chain fatty acid
MB	Methanogenic bacteria
NMR	Nuclear magnetic resonance
OHPB	Obligate hydrogen producing bacteria
OLR	Organic loading rate
PTA	Purified therephthalic acid
SCFA	Short chain fatty acid
SMA	Specific methanogenic activity
SRB	Sulphate reducing bacteria
SRT	Sludge retention time
UAF	Upflow anaerobic filter
UASB	Upflow anaerobic sludge blanket reactor
VFA	Volatile fatty acid

Subscript	Description
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Greek symbol	Description	Unit
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