8
Anaerobic Degradation of Organics

8.1
Catabolic Reactions – Cooperation of Different Groups of Bacteria

8.1.1
Survey

In contrast to most widely propagated aerobic degradation processes, the anaerobic conversion of organics down to methane and carbon dioxide is limited to the work of three different groups of bacteria (see Table 8.1 and Fig. 8.1 in the sections below):

1. *Acidogenic* bacteria produce extracellular enzymes (exoenzymes) for the hydrolysis of all organic solid particles and those dissolved colloids and molecules which are too large to diffuse through cell walls and membranes. Carbonhydrates are hydrolyzed down to mono- and disaccharides, proteins into amino acids and lipids into fatty acids. These compounds are transformed to acetate and longer chain fatty acids as well as CO_2 and H_2.
2. *Acetogenic* bacteria transform lower fatty acids such as butyrate and propionate into acetate, CO_2 and H_2. It is of great importance that H_2 is oxidized by other anaerobic bacteria. Otherwise, propionate concentrations would continually increase.
3. Therefore, hydrogen and acetate must be utilized by *methanogenic* bacteria. They exhibit two main products of catabolic metabolism. Methane is not very soluble in water and carbon dioxide is in equilibrium with HCO_3^- and CO_3^{2-} as a function of pH (see Fig. 4.2). Most of the CO_2 and nearly all the methane produced are desorbed, forming biogas bubbles which can be recovered for utilization.

8.1.2
Anaerobic Bacteria

8.1.2.1 Acidogenic Bacteria

The most important organics in wastewater are proteins, lipids and hydrocarbons. All can be utilized by acidogenic bacteria, which encompass a very large group of different, mostly facultative anaerobic bacteria.

Fundamentals of Biological Wastewater Treatment. Udo Wiesmann, In Su Choi, Eva-Maria Dombrowski

ISBN: 978-3-527-31219-1

Proteins are hydrolyzed into amino acids by proteases which function as exo-enzymes. The amino acids can be taken up by diffusion through cell walls and membranes at a relatively high rate. This process is not rate-limiting for subsequent reactions (Seyfried 1979). A small amount of amino acids is used directly for growth (anabolism), while a large amount is converted to lower fatty acids, CO_2, H_2 as well as NH_4^+ and is excreted (catabolism).

Lipids are esters formed from glycerine, an alcohol with three valences, and fatty acids. These have been hydrolyzed previously by lipase enzymes. Glycerine can be partially used for anabolic reactions and is converted in part to lower alcohols (catabolism). The fatty acids cannot be used by acidogenic bacteria and are excreted.

Polymeric *hydrocarbons* are hydrolyzed into monomers (glucose and other sugars) by most facultative anaerobic bacteria via exo-enzymes (McInerney and Bryant 1981). One part is totally used for protein synthesis and bacterial growth, while another part is converted into lower fatty acids. An example is presented by Eq. (8.1), see Fig. 8.1:

$$C_6H_{12}O_6 \rightarrow CH_3CH_2COOH + CH_3COOH + CO_2 + H_2 \quad (8.1)$$

This first reaction step results in a reduction of DOC (16.7%) and the formation of CO_2 as well as H_2. Mosey (1983) proposed a mechanism for the formation of fatty acids from glucose (Fig. 8.2).

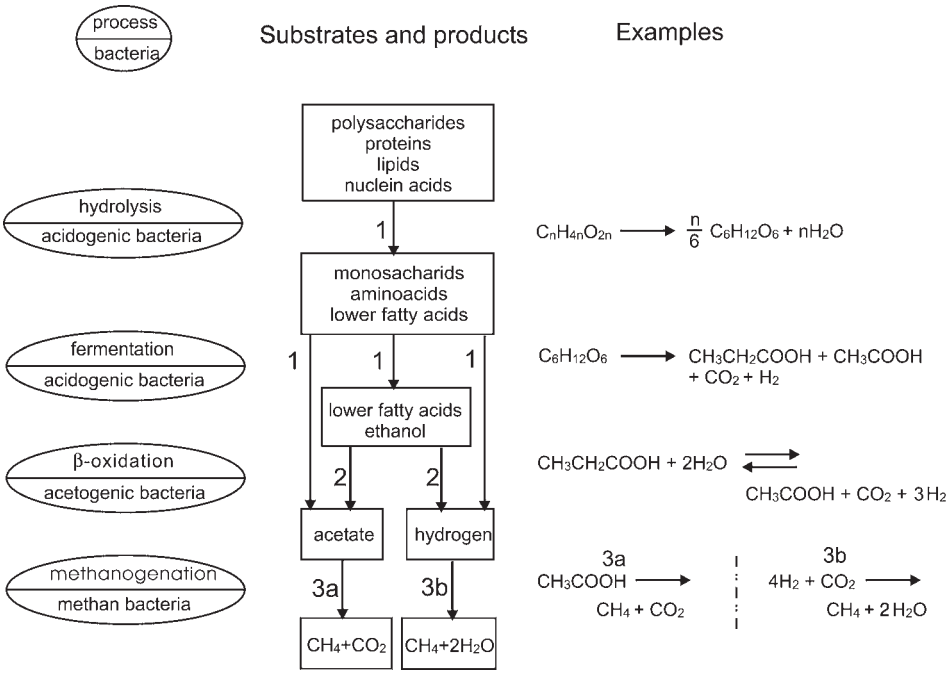


Fig. 8.1 Anaerobic metabolism.

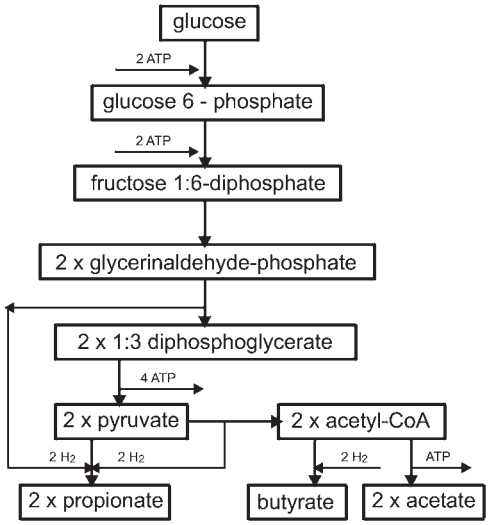


Fig. 8.2 Fermentation of 1 mol glucose to lower fatty acids and the production of 1 mol ATP (Mosey 1983).

The conversion of chemical energy into ATP during anaerobic fermentation is very low and only 1 mol ATP per 1 mol glucose is converted for growth.

8.1.2.2 **Acetogenic Bacteria**

Only a part of acetate is formed directly during fermentation. Most of it is formed by synthrophic reactions (McInerney 1999). Until now, only a few cultures have been isolated which are capable of this.

Synthrophobacter wolinii was described by Boone and Bryant (1980) and is able to convert propionate to acetate.

$$CH_3CH_2COO^- + 3\ H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 3\ H_2$$
$$\Delta G^\circ = 76.1\ \text{kJ mol}^{-1} \qquad (8.2)$$

Synthrophomonas wolfeii was first described by McInerney et al. (1979). Butyrate is transformed to acetate:

$$CH_3CH_2CH_2COO^- + 2\ H_2O \rightarrow 2\ CH_3COO^- + H^+ + 2\ H_2$$
$$\Delta G^\circ = 48.1\ \text{kJ mol}^{-1} \qquad (8.3)$$

In both reactions hydrogen is formed. However, problems arise at higher H_2 concentrations, as discussed in Section 8.1.3.

8.1.2.3 **Methanogenic Bacteria**

Lower fatty acids such as butyrate and propionate can only be mineralized if two catabolic products of acetogenic bacteria, i.e. hydrogen and acetate, are consumed by methanogenic bacteria.

$$CH_3COOH + H_2O \rightarrow CH_4 + HCO_3^- + H^+ \quad \Delta G^\circ = -31 \text{ kJ mol}^{-1} \tag{8.4}$$

$$4\ H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3\ H_2O \quad \Delta G^\circ = -135.6 \text{ kJ mol}^{-1} \tag{8.5}$$

The methanogens are very old microorganisms, living on earth since before the oxygen-rich atmosphere was formed. *Methanosarcina* and *Methanothrix* are able to grow using acetate for catabolism; and 70% of the methane formed in digestion processes and elsewhere in nature is produced via Eq. (8.4) (Jeris and McCarty 1965). *Methanosarcina* spp are the most versatile methanogens producing ATP from acetate (Eq. 8.4) and hydrogen (Eq. 8.5). Methanol and methyl amine (Weimer and Zeikus 1978) are further intermediate products which can be biodegraded down to CH_4 and CO_2.

Four spherical cell species of *Methanosarcina barkeri* often grow in a close community (Fig. 8.3a). In contrast with *Methanosarcina, Methanotrix* does not use H_2. It was first isolated by Zehnder et al. (1980) and is rod-shaped, similar to *Methanobacterium bryantii* (Fig. 8.3d). *M. ruminantium* (Fig. 8.3b) and *M. bryantii* (Fig. 8.3d)

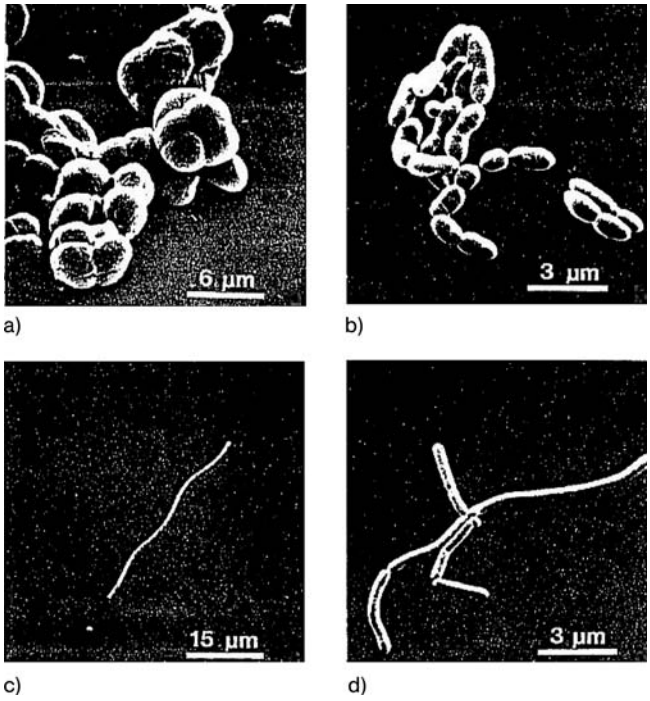


Fig. 8.3 Electron microscopic photographs of methanogenic bacteria. (a) *Methanosarcina barkeri*; (b) *Methanobacteria ruminantium*; (c) *Methanospirillum hungatii*; (d) *Methanobacterium bryantii* (Zehnder and Wuhrmann 1977).

are able to produce ATP using H_2/CO_2 and formicate HCOOH, but both do not grow on acetate (Balch et al. 1979). H_2/CO_2-using Methanobacteria produce considerably more ATP than bacteria using acetate. They have a correspondingly higher maximum growth rate.

Although only about 30% of all CH_4 is produced from H_2/CO_2, Methanobacteria are very important for the regulation of anaerobic wastewater treatment processes. This will be explained in the next section.

Detailed information about anaerobic bacteria has been published by Zehnder and Wuhrmann (1977) and by Zehnder (1988).

8.1.3
Regulation of Acetogenics by Methanogenics

Table 8.1 presents several catabolic reactions which yield acetate and H_2. First we shall have a look at Eq. (8.2), the degradation of propionate to acetate. It is interesting to note how far the concentration of hydrogen must be decreased to make the degradation of propionate possible.

This makes it necessary to study the equilibrium of Eq. (8.2). First, we write for the equilibrium constant:

$$K_e = \frac{S_{Pr^-} S^3_{H_2O}}{S_{Ac^-} S_{HCO_3^-} S_{H^+} \cdot c^3_{H_2}} \tag{8.6}$$

Table 8.1 Arrangement of some important catabolic anaerobic reactions for oxidation (electron-donating reaction) and respiration (electron-accepting reaction). In part from Harper and Pohland (1986) and Pohland (1992).

Process	Reaction	ΔG° (kJ mol^{-1})
Fermentation by acidogenic bacteria	$C_6H_{12}O_6 \rightarrow CH_3CH_2COOH + CH_3COOH + CO_2 + H_2$ $C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2\ CO_2 + 2\ H_2$	
β-Oxidation by acetogenic bacteria (synthrophic reactions)	$CH_3CH_2CH_2COO^- + 2\ H_2O \rightarrow 2\ CH_3COO^- + H^+ + 2\ H_2$ $CH_3CH_2COO^- + 3\ H_2O \rightarrow CH_3COO^- + H^+ + HCO_3^- + 3\ H_2$ $CH_3CH_2OH + H_2O \rightarrow CH_3COO^- + H^+ + 2\ H_2$ $CH_3CHOH\ COO^- + 2\ H_2O \rightarrow CH_3COO^- + H^+ + HCO_3^- + 2\ H_2$	48.1 76.1 9.6 –4.2
CH_4 formation by methanogenic bacteria	$HCO_3^- + H^+ + 4\ H_2 \rightarrow CH_4 + 3\ H_2O$ $CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$	–135.6 –31.0
Further respiration reactions	$2\ CH_3CHOH\ COO^- + SO_4^{2-} \rightarrow 2\ CH_3COO^- + 2\ HCO_3^- + 2\ H^+ + S^{2-}$ $CH_3COO^- + SO_4^{2-} \rightarrow 2\ HCO_3^- + H^+ + S^{2-}$ $4\ H_2 + SO_4^{2-} \rightarrow 2\ H_2O + S^{2-}$ $2\ NO_3^- + 5\ H_2 + 2\ H^+ \rightarrow N_2 + 6\ H_2O$	–1120.5

After introducing partial pressures for:

$$c_{H2} = \frac{p_{H_2}}{RT} \tag{8.7}$$

$$K_c = (RT)^3 \frac{S_{Pr^-} S^3_{H_2O}}{S_{Ac^-} S_{HCO_3^-} S_{H^+} \cdot p^3_{H_2}} \tag{8.8}$$

$$K_c = (RT)^3 \, k \frac{S_{Pr^-}}{S_{Ac^-} S_{HCO_3^-} S_{H^+} \cdot p^3_{H_2}} \tag{8.9}$$

where R is the ideal gas constant and:

$$k = S^3_{H_2O} \tag{8.10}$$

The equilibrium constant is a function of the free enthalpies of reaction:

$$K_c = \exp\left(-\frac{(\Delta G^\circ - \Delta G)}{RT}\right) \tag{8.11}$$

where ΔG is the free enthalpy of reaction and ΔG° is the standard free enthalpy for T = 0 K.

From Eqs. (8.9) and (8.10), it follows that:

$$\Delta G = \Delta G^\circ + RT\,(3 \ln RT + \ln k + \ln S_{Pr^-} - \ln S_{Ac^-} - \ln S_{HCO_3^-} - \ln S_{H^+} - 3 \ln p_{H_2}) \tag{8.12}$$

For given values of S_{Pr^-}, S_{Ac^-}, $S_{HCO_3^-}$, pH and T, the reaction enthalpy can be calculated as a function of p_{H_2} (McInerney and Bryant 1981; Pohland 1992; McInerney 1999). Curve 1 in Fig. 8.4 presents some results.

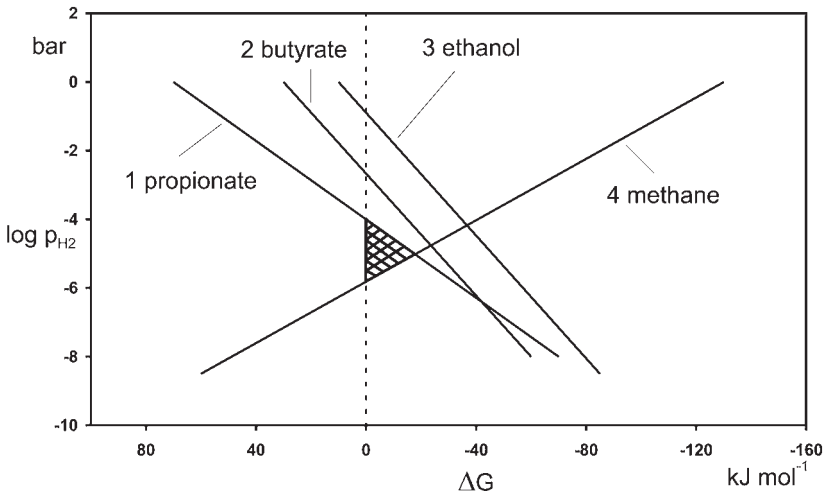


Fig. 8.4 Influence of hydrogen partial pressure p_{H2} on free enthalpy ΔG for anaerobic degradation of propionate (curve 1), butyrate (curve 2), ethanol (curve 3) and for CH_4-formation from H_2 (curve 4). Curve 1 is calculated from Eq. (8.12) using S_{Pr^-} = 1 mmol L^{-1}, S_{Ac^-} = 1 mmol L^{-1}, $S_{HCO_3^-}$ = 50 mmol L^{-1}, pH 7, T = 25 °C (McInerney and Bryant 1981).

Only at partial pressures $p_{H_2} < 10$ Pa or $p_{H_2} < 10^{-4}$ bar is ΔG negative at the given conditions and the equilibrium constant K_c increases, resulting in a higher rate of propionate conversion. Compared with that, for $p_{H_2} > 10$ Pa or $p_{H_2} > 10^{-4}$ bar ΔG is positive, K_c decreases and the propionate concentration increases. But there is an important catabolic reaction utilized by some methanogenic bacteria which produces CH_4 from H_2 (see Eq. 8.5).

This cooperation of acetogenic bacteria which produces H_2 from butyrate and propionate (Eqs. 8.2 and 8.3), but which is not able to transfer hydrogen to other β-oxidation products and methanogenics using H_2 is called β-oxidation (Stronach et al. 1986).

If the thermodynamic equilibrium is calculated using the same method as described above, a straight line with a positive slope follows, resulting from the negative free enthalpy $\Delta G° = -135.6$ kJ mol^{-1} (Fig. 8.4, curve 2).

For $p_{H_2} = 2 \cdot 10^{-6}$ bar, the difference of reaction enthalpies is nearly zero. Methane cannot be produced via the reaction in Eq. (8.5) and p_{H_2} must increase. The reaction can only "move along the two sides of the triangle" formed by curves 1, 4 and the vertical line for $\Delta G = 0$. But for other T, pH and concentrations of propionate, acetate and CO_2, the triangle with the two paths of reaction is moved somewhat and a somewhat higher or lower p_{H2} must be reached.

Following the same thermodynamic consideration, curve 2 can be obtained for butyrate and curve 3 for ethanol. For given conditions (not shown here) ΔG is already negative for $p_{H_2} \approx 10^{-1}$ bar (ethanol) and $p_{H_2} \approx 10^{-3}$ bar (butyrate). The fermentation of butyrate or ethanol, in each case by a pure culture, is inhibited by higher partial pressures of H_2. However, for experiments with mixed cultures the lowest value of $p_{H_2} = 10^{-4}$ bar is crucial for the whole process. In nature this problem was solved billions of years ago by forming communities which included methanogenic bacteria able to use H_2 and acetate.

8.1.4
Sulfate and Nitrate Reduction

Sulfate-reducing bacteria of the genera *Desulfovibrio* and *Desulfotomaculum* grow in anaerobically treated wastewater that contains sulfate (Zeikus 1979). Several organic compounds can be mineralized or partly used with lactate, i.e. *Desulfovibrio desulfuricans* (Gottschalk 1986; Yoo 2000):

$$2\ CH_3CHOHCOO^- + SO_4^{2-} \rightarrow 2\ CH_3COO^- + 2\ HCO_3^- + 2\ H^+ + S^{2-} \qquad (8.13)$$

and acetate by *Desulfobacter postgateii* (Widdel and Pfennig 1981):

$$CH_3COO^- + SO_4^{2-} \rightarrow 2\ HCO_3^- + H^+ + S^{2-} \qquad (8.14)$$

Beside these chemoorganoheterotrophic sulfate reducers even chemolitho-autotrophics have been isolated (Brandis and Thauer 1981; Nethe-Jaenchen and Thauer 1984):

$$4\ H_2 + SO_4^{2-} \rightarrow 4\ H_2O + S^{2-} \qquad (8.15)$$

Depending on the pH, the sulfur exists mainly in the form of S^{2-} (high pH) or H_2S (low pH):

$$S^{2-} + H^+ \rightleftarrows HS^- \quad (8.16)$$

$$HS^- + H^+ \rightleftarrows H_2S \quad (8.17)$$

The formation of H_2S is a serious problem because of its corrosive effects and its smell. Therefore, it must be separated from biogas, e.g. by reaction with iron sharings. Another disadvantage of sulfate reduction is the consumption of acetate (Eq. 8.14) and hydrogen (Eq. 8.15). Via these reactions, sulfate-reducing and some denitrifying bacteria compete with the methanogenic bacteria for hydrogen:

$$2\ NO_3^- + 5\ H_2 \rightarrow N_2 + 2\ OH^- + 4\ H_2O \quad (8.18)$$

and the CH_4 content of the biogas is reduced.

8.2 Kinetics – Models and Coefficients

8.2.1 Preface

We must distinguish between the hydrolysis of solids and that of dissolved organics. The anaerobic treatment process of solids and sludge stabilization are frequently used in municipal WWTPs in order to obtain residual solids which cannot be utilized further by microorganisms as their carbon and energy source. It is to a large extent odorless and can be dewatered easily. About 25–30% of dry mass is converted thereby into sludge gas containing CH_4. Therefore, it can be used as a form of gaseous energy. This process will not be discussed here in detail.

The hydrolysis of dissolved organics is the first step of anaerobic wastewater treatment. Higher-loaded wastewater, such as that generated by breverage and food industries, offers the possibility to separate, concentrate and recycle the anaerobic bacteria from the treated wastewater or to immobilize the bacteria on solid support materials (Section 8.4). The efficiency of these processes can be increased and the processes can be optimized considerably. Micro- and macrokinetics are the foundation of process construction and control. In the next section we will discuss the present knowledge of anaerobic microkinetics.

8.2.2 Hydrolysis and Formation of Lower Fatty Acids by Acidogenic Bacteria

The formation rate of amino acids from proteins, glycerine and fatty acids from lipids and monosaccharides from higher hydrocarbons depends on:

- the mole mass of polymers,
- their stability during hydrolysis,
- the portion of colloids,
- the concentration of enzymes.

Normally, a high enzyme concentration is assumed in relation to the total amount of substrates, measured as COD or DOC, resulting in a first-order reaction with regard to substrate concentration:

$$r_H = k_H S \text{ mg (L h)}^{-1} \text{ COD} \tag{8.19}$$

where k_H is the rate coefficient (h^{-1}) and S is the polymer concentration (mg L^{-1} COD).

For most types of wastewater, hydrolysis and the formation of lower fatty acids by acidogenic bacteria are not rate-limiting for the total process. This follows from kinetic studies of hydrolysis of polymers and glucose fermentation to lower fatty acids (Table 8.2).

A relatively high amount of energy can be supplied for ATP production and anabolism. A yield coefficient $Y^{\circ}_{X/S}$ = 0.162–0.310 g MLSS (g COD)$^{-1}$ has been measured. The mean value of $Y^{\circ}_{X/S}$ = 0.236 is about 50% of that for the aerobic mineralization of glucose. The influence of the glucose concentration on the growth rate is described by Monod kinetics:

$$r_X = \mu_{max} X \frac{S}{K_S + S} - k_d X \tag{8.20}$$

with μ_{max} = 10.9–64.8 d^{-1}

Values of K_S = 24.1 mg L^{-1} COD and 73.4 mg L^{-1} COD were obtained for the saturation coefficient, which points to the useable range of substrate limitation. Only one K_S value is very high and could be confirmed by other measurements. These degradation reactions of hydrolysis products (i.e. glucose) to butyrate and propionate are called fermentation. These coefficients and others from the literature are compiled in Table 8.2.

8.2.3
Transformation of Lower Fatty Acids by Acetogenic Bacteria

In order to study the formation of acetate from butyrate and propionate by acetogenic bacteria, it is necessary to reduce the partial pressure of H_2 down to p_{H2} = 10^{-3} bar (butyrate) or between 10^{-4} bar and $2 \cdot 10^{-6}$ bar (propionate; Fig. 8.4). It is useful to investigate the growth of *Synthrophobacter wolinis* on *n*-butyrate (Eq. 8.2) or the growth of *Synthrophomonas wolfeii* on propionate (Eq. 8.3) in mixed culture with methanogenic bacteria, as they reduce the p_{H_2} (Eq. 8.5) and the acetate concentration (Eq. 8.4). The removal of acetate is absolutely necessary to prevent product inhibition. Two results of butyrate transformation to acetate in experiments are presented in Table 8.2. The yield coefficient $Y^{\circ}_{X/S}$ = 0.0094 ... 0.022 = 0.014 g MLSS (g COD)$^{-1}$ and the maximum specific growth rate μ_{max} = 0.17 ... 0.39 = 0.28 d^{-1} are considerably lower than those of acidogenic bacteria: the μ_{max} is lower by a factor of about 100 and $Y^{\circ}_{X/S}$ by a factor of about 15. From these values, the following specific maximal substrate removal rates are obtained for butyrate:

$$r_S/X = \mu_{max}/Y^{\circ}_{XS} = 0.28/0.014 = 20 \text{ g COD (g MLSS} \cdot \text{d)}^{-1}$$

Table 8.2 Fermentation, β-oxidation and methanization – stoichiometric and kinetic coefficients.

Bacterial substrate	Ref.	Reactor (pH)	T (°C)	$Y^{\circ}_{X/S}$ [a]	μ_{max} [b]	K_S [c]	K_{SH} [d]	K_{iH} [e]	k_d [b]
Fermentation of glucose to lower fatty acids by acidogenics	Ghosh and Pohland (1974)	Chemostat	35	0.162	30.1	24.1			1.06
	Massey and Pohland (1978)	Chemostat	35	0.31	64.8	2583			1.56
	Hanaki et al. (1985)	Chemostat	35	0.212	10.9	73.4			4.13
β-Oxidation of *n*-Butyrate	Lawrence and McCarty (1969)	Chemostat (pH 7.0)	35	0.0094	0.39	48.3			0.027
	Chang (1982)	Batch	35	0.022	0.17	47.0			0.005
β-Oxidation of propionate to acetate and H_2 by acetogenics	Andrews (1969)	Chemostat (pH 7.0)	38	0.05	0.4		3	60	
	Lawrence and McCarty (1969)	Chemostat (pH 7.0)	35		0.4		0.36		
	Gujer and Zehnder (1983)	Chemostat (pH 7.0)	33	0.025	0.155	248			
Methanization from H_2	Shea et al. (1968)	Chemostat pH 7.8)	37	0.043	1.06	556[f]			0.009
	Zehnder and Wuhrmann (1977)	Chemostat (pH 7.0)	33		1.4				
	Bryer (1985)		55	0.038	1.4	37.5			0.1
Methanization from acetate	Graef and Andrews (1973)	Chemostat (pH 7.0)	38	0.057	0.4		2.13	42.7	
	Carr and O'Donell (1977)		35	0.027	0.11		1.15	35.6	0.006
	Bolle et al. (1986)	Chemostat (pH 7.0)	35	0.037	0.038		2.1	16.9	0.0036

[a] g MLSS (g COD)$^{-1}$, [b] d^{-1}, [c] mg L^{-1} COD, [d] mg L^{-1} COD, [e] mg L^{-1} COD, [f] µmol L^{-1}.

and for propionate:

$$r_S/X = 0.0028/0.001 = 2.8 \text{ g COD (g MLSS)}^{-1}$$

if the results of three studies are considered (Table 8.2). The maximum specific removal rate of propionate is lower than that of butyrate nearly by a factor of 7. But in reality, the reaction in Eq. (8.2) is very sensitive to the following influences:

- As mentioned in Section 8.13, p_{H2} must be reduced by methanogenic bacteria down to 10^{-4} bar.
- The conversion of propionate to acetate can be inhibited by higher concentrations of non-ionized propionate S_{HPr}. As shown by several authors, the influence of S_{HPr} on the specific growth rate can be described by Haldane kinetics (Andrews 1969; Attal et al. 1988; Fukuzaki et al. 1990):

$$\mu = \mu_{max} \frac{S_{HPr}}{K_{SH} + S_{HPr} + S_{HPr}^2/K_{iH}} \tag{8.21}$$

- In addition to S_{HPr}, the concentration of non-ionized acetate S_{HAC} influences μ by non-competitive inhibition (Mosey 1983; Denac 1986; Fukuzaki et al. 1990; Kus 1993):

$$\mu = \mu_{max} \frac{S_{HPr}}{K_{SH} + S_{HPr} + S_{HPr}^2/K_{iH}} \cdot \frac{K_{iH}}{K_{iH} + S_{HAc}} \tag{8.22}$$

Therefore, the formation of methane from H_2 and acetate should not be disturbed. Otherwise, propionate and butyrate cannot be biodegraded.

8.2.4
Transformation of Acetate and Hydrogen into Methane

As described by Fig. 8.4, the hydrogen partial pressure must be reduced down to $p_{H_2} < 10^{-4}$ bar by *Methanosarcina* and *Methanobacterium* to enable conversion of propionate to acetate (see Section 8.1.3). The specific growth rate was described using Monod kinetics (Table 8.2). If the rate of H_2 oxidation is measured as COD, the mean specific removal rate follows as:

$$r_S/X = \mu_{max}/Y^\circ_{X/S} = 32.5 \text{ g COD (g MLSS d)}^{-1}$$

with mean values of $\mu_{max} = 1.3\ d^{-1}$ and $Y^\circ_{X/S} = 0.04$ g MLSS (g COD)$^{-1}$. This specific rate is higher than that of propionate degradation (see Section 8.2.3). If there are no toxic effects from heavy metal ions, these bacteria grow rapidly and propionate degradation is not inhibited by higher p_{H_2}.

Methane formation from acetate by *Methanosarcina* and *Methanotrix* (Eq. 8.4) is a much slower reaction. From three studies (Table 8.2), a mean specific removal rate can be calculated as:

$$r_S/X = \mu_{max}/Y^\circ_{X/S} = 4.9 \text{ g COD (g MLSS d)}^{-1}$$

with $\mu_{max} = 0.18\ d^{-1}$ and $Y^{\circ}_{X/S} = 0.037$ g MLSS (g COD)$^{-1}$. This is low compared to acetate formation from propionate. Therefore, it is the most important step of anaerobic digestion and is more frequently studied. All authors mentioned in Table 8.2 considered Haldane kinetics with non-ionized acetate as the substrate:

$$\mu = \mu_{max} \frac{S_{HAc}}{K_{SH} + S_{HAc} + S^2_{HAc}/K_{iH}} \tag{8.23}$$

The frequently observed disruption of digestion processes with sinking pH and enrichment of lower fatty acids can be explained in part by substrate inhibition. As shown in Eq. (8.22), some authors observed an inhibition of methane formation by propionate described as a non-competitive inhibition.

Because we have to distinguish three totally different groups of anaerobic bacteria, we actually have to measure the concentration of these groups X. This is very difficult and often not realized although it is a requirement for correct determinations of μ_{max} values. Normally, the unit g L^{-1} MLSS or MLVSS (mixed liquid volutile suspended solids) is used (Table 2.6).

8.2.5 Conclusions

The anaerobic degradation of organics is a rather complicated process. Even if we only wish to discuss the digestion of glucose, we must take into account three different groups of bacteria. It is not easy to separate them and, in the case of conversion of propionate to acetate and hydrogen, the acetogenic and methanogenic bacteria are dependant upon each other. Although it is important to know the value of X, the bacterial concentration responsible for one interesting catabolic reaction, measurements are frequently impossible and X must be obtained by calculations using mass balances.

In many studies the concentrations:

$$S_{Ac} = S_{HAc} + S_{Ac^-} \quad \text{and} \quad S_{Pr} = S_{HPr} + S_{Pr^-}$$

are used in Monod or Haldane kinetics instead of c_{HAc} and c_{HPr} in recent publications.

Let us write:

$$\mu_{max} \frac{S_{Ac}}{K_S + S_{Ac} + S^2_{Ac}/K_i} = \mu_{max} \frac{S_{HAc}}{K_{SH} + S_{HAc} + S^2_{HAc}/K_{iH}} \tag{8.24}$$

and $CH_3COOH \leftrightarrow CH_3COO^- + H^+$

Then, respectively:

$$K = \frac{S_{Ac^-}\, S_{H^+}}{S_{HAc}} \tag{8.25}$$

as well as:

$$S_{Ac} = S_{Ac^-} + S_{HAc} \tag{8.26}$$

and:

$$S_{HAc} = \frac{S_{Ac}}{1 + K\,10^{pH}} \tag{8.27}$$

After introducing Eq. (8.27) into Eq. (8.24), we obtain:

$$K_{SH} = \frac{K_S}{1 + K\,10^{pH}} \tag{8.28}$$

and:

$$K_{iH} = \frac{K_i}{1 + K\,10^{pH}} \tag{8.29}$$

Note that, in contrast to K_S and K_i, K_{SH} and K_{iH} are *not* functions of pH, because of Eq. (8.25), which yields:

$$K = \frac{S_{Ac^-}}{S_{HAc} \cdot 10^{pH}} \tag{8.30}$$

The next important point is to calculate how much methane is produced if 1 mol CH_3COOH or 1 mol $C_6H_{12}O_6$ is degraded anaerobically. We can compare both substrates according to their COD. Let us start with CH_3COOH.

For chemical oxidation of CH_3COOH we write:

$$CH_3COOH + 2\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O$$

and therefore 1 mol CH_3COOH needs 2 mol O_2; or 60 g HAc give 64 g COD.

Methane production from CH_3COOH can be calculated using:

$$CH_3COOH \rightarrow CH_4 + CO_2$$

giving a yield coefficient of:

$$Y^{o}_{CH_4/HAc} = \frac{r_{CH_4}}{r_{HAc}} = \frac{1\ \text{mol}\ CH_4}{1\ \text{mol HAc}} = \frac{22.4}{64}\ \frac{Nm^3}{kg}\ \frac{CH_4}{COD} = 0.35\ Nm^3\ (\text{kg COD})^{-1} \tag{8.31}$$

Now we calculate the yield of CH_4 from glucose: for the chemical oxidation of $C_6H_{12}O_6$, it follows that:

$$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O$$

Therefore, 1 mol $C_6H_{12}O_6$ needs 6 mol O_2; or 180 g $C_6H_{12}O_6$ is equivalent to 192 g COD.

Methane production from $C_6H_{12}O_6$ can be calculated by summarizing Eqs. (8.1), (8.2), (8.4) and (8.5)

$$C_6H_{12}O_6 \rightarrow 3\ CH_4 + 3\ CO_2$$

giving a yield coefficient of:

$$Y^{o}_{CH_4/C_6H_{12}O_6} = \frac{r_{CH_4}}{r_{Glu}} = \frac{3\ \text{mol}\ CH_4}{1\ \text{mol}} = \frac{22.4}{64}\ \frac{Nm^3\ CH_4}{kg \cdot COD} \tag{8.32}$$

$$= 0.35\ Nm^3\ CH_4\ (kg\ COD)^{-1}$$

Conclusion: from wastewater loaded with hydrocarbons (CH_2O) and a given reaction rate of kg COD $(m^3\ d)^{-1}$, which can be mineralized by anaerobic processes (digestion), the maximum rate of methane production can be calculated using Eq. (8.31):

$$r_{CH_4} = 0.35\ r_{COD}\ Nm^3\ CH_4\ (kg\ COD)^{-1}$$

regardless of whether polysaccharides, monosaccharides or acetate are present in the wastewater.

8.3 Catabolism and Anabolism

The catabolic conversion of acetate into CH_4 and CO_2 (Eq. 8.4) is a very simple reaction. We will use the method realized by methanogenic *Methanotrix* bacteria as an example for the evaluation of the stoichiometric equation describing catabolism and anabolism.

Starting from a general form considering only carbon, hydrogen and oxygen as elements of bacterial mass, we do not need to add nutrients and we can write:

$$CH_{SH}O_{SO} \rightarrow Y^{o}_{X-C/S-C}CH_{BH}O_{BO} + Y^{o}_{CH_4-C/S-C}CH_4 + Y^{o}_{CO_2-C/S-C}CO_2 + Y^{o}_{H_2O-H/S-C}H_2O \tag{8.33}$$

Note that the substrate molecule and the "bacteria molecule" are each standardized relative to one carbon atom, resulting in the yield coefficients, three of which can be measured:

$$Y^{o}_{XC/SC} \equiv \frac{\text{C for growth}}{\text{C of total substrate removal}}$$

$$Y^{o}_{CH_4-C/SC} \equiv \frac{\text{C for } CH_4 \text{ formation}}{\text{C of total substrate removal}}$$

$$Y^{o}_{CO_2-C/SC} \equiv \frac{\text{C for } CO_2 \text{ formation}}{\text{C of total substrate removal}}$$

According to these formulas, the content of hydrogen and oxygen in the substrate molecule and the "bacteria molecule" are given by SH and SO as well as BH and BO, respectively. Now, we already know that we will obtain three mass balances for the three elements C, H and O. Therefore, we can calculate only three of the four yield coefficients. In order to complete the stoichiometric equations describing catabolism and anabolism, one of the four yield coefficients must be measured (however, see Section 4.2.1).

Let us use acetate as the substrate with CH_2O (CH_3COOH, written as $C_2H_4O_2$ and divided by two, gives CH_2O) and $CH_{1.8}O_{0.5}$ as a mean composition for the bacterial mass. Instead of Eq. (8.33), we now write:

$$CH_2O \rightarrow Y^{o}_{XC/SC}CH_{1.8}O_{0.5} + Y^{o}_{CH_4-C/SC}CH_4 + Y^{o}_{CO_2-C/SC}CO_2 + Y^{o}_{H_2O-H/SC}H_2O \tag{8.34}$$

The balances for each of the three elements are:

$$\text{C balance: } 1 = Y^{o}_{XC/SC} + Y^{o}_{CH_4-C/SC} + Y^{o}_{CO_2-C/SC} \tag{8.35}$$

$$\text{H balance: } 2 = 1.8\, Y^{o}_{XC/SC} + 4\, Y^{o}_{CH_4-C/SC} + 2\, Y^{o}_{H_2O-H/SC} \tag{8.36}$$

$$\text{O balance: } 1 = 0.5\, Y^{o}_{XC/SC} + 2\, Y^{o}_{CO_2-C/SC} + Y^{o}_{H_2O-H/SC} \tag{8.37}$$

From these three balances, three of the four yield coefficients can be calculated. To find the stoichiometry of Eq. (8.34), one of these yields must be measurable. Let us assume that we measure $Y^{o}_{CH_4-C/S-C}$ and we obtain:

$$Y^{o}_{CH_4-C/SC} = 0.48 \text{ mol } CH_4 \text{ (mol C)}^{-1}$$

Remember that, for catabolism alone, we would write $Y^{o}_{CH_4-C/SC} = 0.5$ and $Y^{o}_{CO_2-C/SC} = 0.5$. The solution of the three balances gives:

$$Y^{o}_{XC/SC} = \frac{1 - 2\,Y^{o}_{CH_4-C/SC}}{1.2} = 0.03 \text{ mol X–C (mol S–C)}^{-1}$$

$$Y^{o}_{CO_2-C/SC} = 0.167 + 0.67\, Y^{o}_{CH_4-C/SC} = 0.49 \text{ mol } CO_2 \text{ (mol S–C)}^{-1}$$

$$Y^{o}_{H_2O-H/SC} = 0.01 \text{ mol } H_2O\text{–H (mol S–C)}^{-1}$$

The reaction describing the elements used for anabolism and catabolism is obtained after multiplying by a factor of two, considering the 2 C atoms in one acetate molecule:

$$CH_3COOH \rightarrow 0.060\, CH_{1.8}O_{0.5} + 0.96\, CH_4 + 0.98\, CO_2 + 0.026\, H_2O \tag{8.38}$$

Only 3% of the acetate carbon is used for growth!

8.4 High-rate Processes

8.4.1 Introduction

Compared with anaerobic sludge treatment, anaerobic wastewater treatment allows us to increase the concentration of bacteria remarkably, resulting in an increase in reaction rate (high-rate processes). Three different mechanisms are effective at increasing the bacterial concentration:

- Sedimentation of floc-forming bacteria and recycling of the thickened sludge into the bioreactor.
- Sedimentation and suspension of particles formed from bacteria and minerals inside the bioreactor.
- Immobilizing the bacteria at the surface of either fixed or suspended solid materials, as well as at rotating solid plates.

Comparing the specific maximum removal rate:

$$\frac{r_{s\,max}}{X} = \frac{\mu_{max}}{Y^{\circ}_{X/S}} \tag{8.39}$$

for an aerobic and an anaerobic process (degradation of acetate by methanogenic bacteria) and using mean values for μ_{max} and $Y^{\circ}_{X/S}$ from Table 6.2 (aerobic bacteria) and Table 8.2 (methanogenic bacteria) for unlimited substrate removal, we obtain for aerobics:

$$\frac{r_{s\,max}}{X} = \frac{\mu_{max}}{Y^{\circ}_{X/S}} = \frac{12}{0.6} = 20 \text{ g COD (g MLSS d)}^{-1}$$

and for anaerobics:

$$\frac{r_{s\,max}}{X} = \frac{\mu_{max}}{Y^{\circ}_{X/S}} = \frac{0.2}{0.04} = 5 \text{ g COD (g MLSS d)}^{-1}$$

This real difference of only a factor of four is remarkably low because:

- The higher sludge density results in a higher bacterial concentration inside anaerobic reactors.
- There is less influence from mass transfer and diffusion than in aerobic aerated reactors, which can be limited by low dissolved oxygen levels.

Some effective and economical high-rate anaerobic treatment processes which take advantage of these benefits have gone into operation over recent decades (Dauber 1993).

In all these high-rate processes, the temperature is increased to about 35 °C. It is therefore absolutely necessary to construct the bioreactor with a thermal insulation and a preheating system for the inflowing and recycled wastewater and the settled

sludge, especially in northern climates. The biogas produced should be used nearly completely and only a very low amount should be burned off in a bypass flame.

The lowest substrate concentrations which can be reduced anaerobically in an economical way are about S_o = 2000–3000 mg L^{-1} COD.

About 80–90% of the BOD_5 can be removed:

$$\alpha = \frac{S_o - S_1}{S_o} \cdot 100 = 80 - 90\%$$

If it is intended to discharge the treated water into surface water, it must be treated aerobically in a second stage to adhere to local legislation.

8.4.2 Contact Processes

In the anaerobic contact process, the higher bacterial concentration is most often obtained in an incompletely mixed tank reactor (suspended growth) as a result of recycling sludge after settling in a sedimentation tank (Fig. 8.5), similar to an activated sludge reactor.

The reactor is mixed using:

- stirrers,
- the distribution of recycled external wastewater near the reactor bottom,
- the recycling of compressed biogas (not presented in Fig. 8.5).

In some reactors, two or three of these mixing processes are applied. Nevertheless, the case of nearly ideal mixing is rarely obtainable. It is absolutely necessary to install a system for degasifying the mixed liquor, i.e. the treated wastewater, suspended bacterial flocs and gas bubbles, before sedimentation. Several methods are available. In most degasifying systems, the water flows through tanks kept under a partial vacuum. In addition, the mass transfer rate and the gas/liquid interfacial surface are increased by the use of rotating stirrers or the formation of falling drops or trickling films. Temperatures fall during the degasification, resulting in lower CH_4 and CO_2 production rates and higher saturation concentrations of both gases. This significantly reduces the amount of gas bubbles which form during sedimentation.

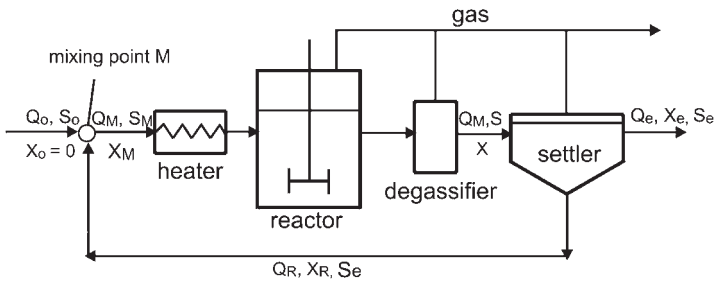


Fig. 8.5 Contact process.

An anaerobic wastewater treatment process can be calculated easily if the following conditions are met:

- The process is controlled by acetate degradation.
- It is a steady-state process.
- The reactor is completely mixed.
- The surplus bacteria are removed with the overflow.
- Bacterial decay is neglected.

We want to estimate the acetate concentration S_e depending on the mean hydraulic retention time t_R. Looking at Fig. 8.5, we write the bacterial balance for the reactor:

$$0 = Q_M\,(X_M - X) + \mu\,X\,V \tag{8.40}$$

For the bacterial concentration at mixing point M, we obtain:

$$X_M = X_R\,\frac{n_R}{1+n_R} \tag{8.41}$$

with:

$$n_R = \frac{Q_R}{Q_0} \text{ as the sludge recycle ratio} \tag{6.39}$$

The concentration of bacteria in the recycled sludge X_R must be calculated from the balance of a settler:

$$(Q_0 + Q_R)\,X = Q_0 X_e + Q_R X_R \tag{8.42}$$

with $Q_0 X_e$ as the overflow mass flow rate and $Q_R X_R$ as the mass flow rate of recycled sludge.

It is useful to define β, the separation coefficient of the settler:

$$\beta = \frac{(Q_0+Q_R)\,X - Q_0 X_e}{(Q_0+Q_R)\,X} \tag{8.43}$$

and considering Eq. (6.39):

$$\beta = \frac{(1+n_R)\,X - X_e}{(1+n_R)\,X} \tag{8.44}$$

then, respectively:

$$X_e = X\,(1-\beta)\,(1+n_R) \tag{8.45}$$

which is introduced into Eq. (8.43):

$$X_R = X\beta\,\frac{1+n_R}{n_R} \tag{8.46}$$

Eq. (8.47) in Eq. (8.41) gives:

$$X_M = \beta\,X \tag{8.47}$$

introducing this into the balance of the reactor (Eq. 8.40) and considering $Q_M = Q_0 + Q_R$, we can write:

$$0 = (1 + n_R)\,(\beta - 1) + \mu\, t_R \tag{8.48}$$

Using Monod kinetics:

$$\mu = \mu_{max}\frac{S}{K_S + S} \tag{6.1}$$

The acetate concentration in the effluent is represented by:

$$S_e = \frac{K_S\,(1-\beta)\,(1+n_R)}{\mu_{max}\,t_R - (1-\beta)\,(1+n_R)} \tag{8.49}$$

and the critical mean retention time follows for $S_e = S_0$:

$$t_{RC} = \frac{(1-\beta)\,(1+n_R)\,(K_S + S_0)}{\mu_{max}\,S_0} \tag{8.50}$$

For $\beta = 0$, $n_R = 0$, $S_0 \gg K_S$, we obtain the simple solution valid for a chemostat:

$$t_{RC} = \frac{1}{\mu_{max}} \tag{6.26}$$

In large-scale contact reactors, the mixing energy is not sufficient to realize locally constant conditions (concentrations, temperature, pH), which means that considerable discrepancies exist between theory and practice. Nevertheless, the influence of t_R, β and n_R can be discussed fundamentally and can often be compared successfully with operational data.

Two-stage anaerobic contact processes can be advantageous, with a first stage predominately for the formation of lower fatty acids at a lower pH 5.5–6.5 and a second stage predominately for the methanization process at a higher pH 6.5–7.5. Because of the higher yield coefficient of acidogenic bacteria (Table 8.2; $Y^{\circ}_{X/S}$ = 0.23 g MLSS (g COD)$^{-1}$) compared with that of methanization ($Y^{\circ}_{X/S}$ = 0.04 g MLSS (g COD)$^{-1}$) and the higher reaction rate in the first stage, sludge concentrations are frequently high enough and must not be increased by sedimentation and sludge recycle.

In all systems described below, the bacteria are retained directly inside the reactor.

8.4.3
Upflow Anaerobic Sludge Blanket

In the upflow anaerobic sludge blanket (UASB) type of reactor, the gas/solid/liquid separation system is integrated into the vessel (Fig. 8.6).

This reactor can only be used if large, dense, readily settleable particles are formed – a granular sludge which allows high concentrations of suspended solids between 20 g L^{-1} MLSS and 30 g L^{-1} MLSS (Lettinga and Hueshoff 1991, 1992).

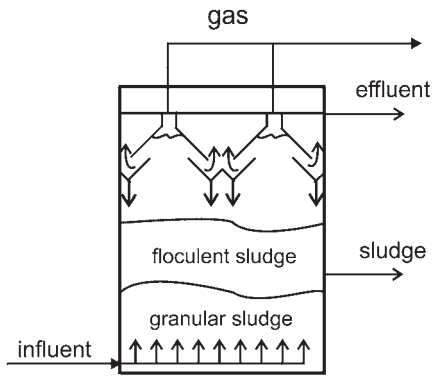


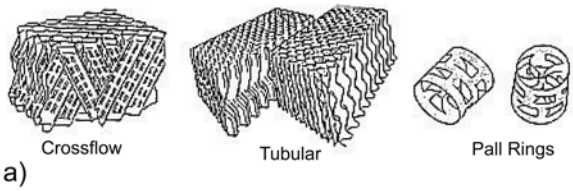
Fig. 8.6 Upflow anaerobic sludge blanket.

The influent wastewater is distributed at the bottom by a system of tubes which provides a flow through a blanket of granular sludge. Inside these porous particles, fatty acids and biogas are formed. The reaction rate of the process is controlled by diffusion, convection and reaction inside the pores. Ascending biogas bubbles keep the particles partially fluidized. Depending on the kind of wastewater, the sludge tends to be more or less flocculating, which determines how well it is suspended in the fluidized sludge (Fig. 8.6). At the top of the UASB, the gas bubbles are separated from the water in hoods and the rising flocs which show a lower settling rate are carried up by the gas/liquid flow. Gas is collected in the hoods and removed. Liquid/solid separation takes place in the settler section. The treated water flows over weirs while discharging into a wastewater canal system for further treatment either together with municipal wastewater or directly by subsequent dedicated processes, such as aerobic purification. The mass of flocculent and granular sludge must be controlled by siphoning off excess sludge. Depending on the wastewater, hydraulic retention times of t_R = 0.2–2.0 d are typical for a load of B_V = 2–25 kg COD m^{-3} d^{-1} (Grady et al. 1999).

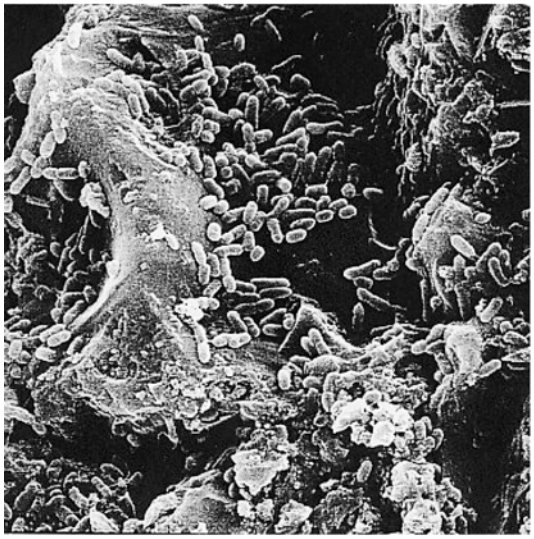
8.4.4
Anaerobic Fixed Bed Reactor

A fixed bed reactor is filled with solid media to facilitate the formation of biofilms with anaerobic bacteria. Frequently, the synthetic media used are the same as those in trickling filters (Fig. 8.7a; Young 1991) or, alternatively, they are porous polyurethane particles with a diameter between 0.3 cm and 1.0 cm and are used with inner surfaces for bacteria immobilization (Fig. 8.7b; Spieß 1991; Kus 1993).

Examples of such support materials are shown in Fig. 8.7. The surface area for bacterial growth is about 100 m^2 m^{-3} with a void volume fraction of 90–95% (Grady et al. 1999). The formation of biofilms and the two-phase flow must facilitate liquid/gas separation and must avoid blockage by thick biofilms or large suspended sludge particles. For these reasons, the wastewater is recycled to increase the flow rate and shear stress inside the fixed bed (Fig. 8.8a).



a)



b)

Fig. 8.7 Media for immobilization of anaerobic bacteria.
(a) Non-porous synthetic media (Young 1991).
(b) Immobilized bacteria on porous polyurethane particle.

Excess sludge is normally rinsed out with the effluent. If blockages occur, the flow rate of the recycle flow must be increased temporarily.

In some cases, the advantages of the UASB and the fixed bed reactor – the establishment of high bacteria concentrations by granular particles and the formation of biofilms near the effluent to reduce the loss of bacteria – are combined (Fig. 8.8b).

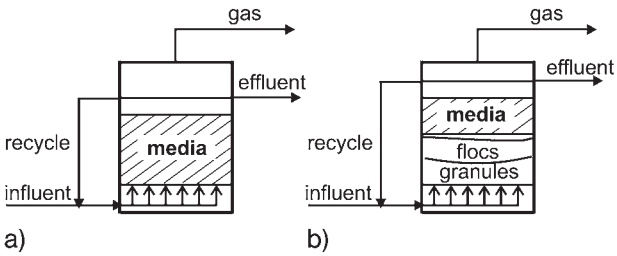


Fig. 8.8 Anaerobic fixed bed reactor (a), Hybrid USAB (b).

On the top of an UASB, a fixed bed reactor with a relatively short bed of synthetic media is installed (hybrid UASB).

8.4.5 Anaerobic Rotating Disc Reactor

Anaerobic rotating disc reactors (RDR) are characterized by a horizontal wheel that, on a technical scale, can have a diameter of up to 2 m and a length of about 5 m (Fig. 8.9). With a plate spacing of 5 cm, about 100 plates can be installed, giving a total surface area of about 630 m^2.

An anaerobic RDR has a double wall for heating and temperature control, has a closed top and is combined with a gas collection system. The plates are completely submerged in the wastewater. Surplus sludge is collected at the bottom and must be removed periodically. The discs rotate with a speed of 0.5–2.0 min^{-1}.

Several authors have published results obtained by laboratory-, pilot- and large-scale studies (Tait and Friedman 1980; Laquidara et al. 1986; Ware and Pescod 1989; Ware et al. 1990; Breithaupt 1997; Breithaupt and Wiesmann 1998).

Breithaupt (1997) used plates with a covering made from a synthetic structural material which made it possible to form biofilms with a higher area and thickness. In these anaerobic RDR both a high total COD removal and a high COD removal rate could be realized for wastewater with high acetate concentrations.

The reactor is not completely mixed: the concentration of immobilized bacteria increases in the first 25% of the total length up to 10 g L^{-1} MLSS and decreases in the last 75% down to 2.5 g L^{-1} MLSS. The pH increases due to the methanization of acetate. Using an acetate balance and considering axial dispersion, Haldane kinetics and the influence of locally changing pH, mathematical models were used to calculate the acetate concentration profile (Breithaupt 1997).

Anaerobic RDRs are particularly suitable for moderate amounts of highly loaded wastewater. Low amounts of <10 m^3 d^{-1} wastewater are more appropriate for aero-

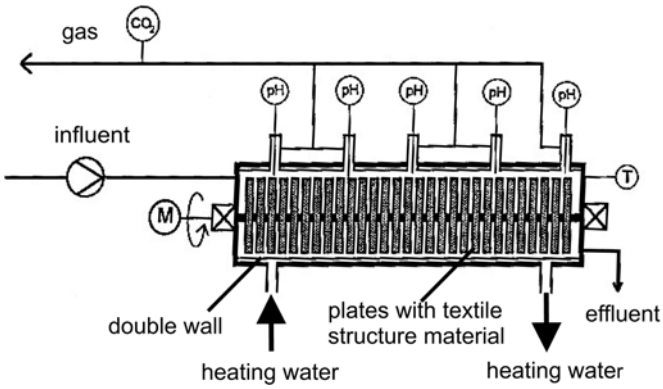


Fig. 8.9 Anaerobic rotating disc reactor (Breithaupt 1997).

bic treatment; and high amounts of >10^3 m^3 d^{-1} should be treated by using one of the other anaerobic processes described above.

8.4.6
Anaerobic Expanded and Fluidized Bed Reactors

In both systems, small particles are used as carriers for biofilms (bioparticles). Frequently, silica sand with a diameter of 0.2–0.5 mm and a specific density of 2.65 g cm^{-3} or activated carbon particles with somewhat higher diameters and a lower density are used. The upward flow rate must be high enough to expand the bed and the wastewater must be recycled at a much higher rate than in fixed bed reactors (Fig. 8.10).

Expanded beds are expanded by 15–30% and fluidized beds by 30–300%, relative to the volume at rest. Because of the very high surface area of the biofilms (9000–11 000 m^2 m^{-3}), their low thickness and the high mass transfer rate in the mobile bed, the biogas production rate is very high and the mean retention time of the wastewater is often only about 6 h and sometimes remarkably lower.

High biomass concentrations of 15–35 g L^{-1} MLSS are possible, similar to those achieved with the UASB process (Hall 1992), but the load rates achieved of more than 20 kg COD m^{-3} d^{-1} can be significantly higher than that of the UASB process (2–25 kg COD m^{-3} d^{-1}; Grady et al. 1999) because of the reduced limitation of mass transfer by diffusion and convection. The upper segment of the reactors above the expanded and fluidized beds serves to separate the gas bubbles from the water (which is recycled to a large degree) and from the bacterial flocs which have sheared off the biofilms.

In recent times, new anaerobic systems have been investigated and proposed for technical use which are equipped with integrated membranes for retaining and increasing the amount of bacteria.

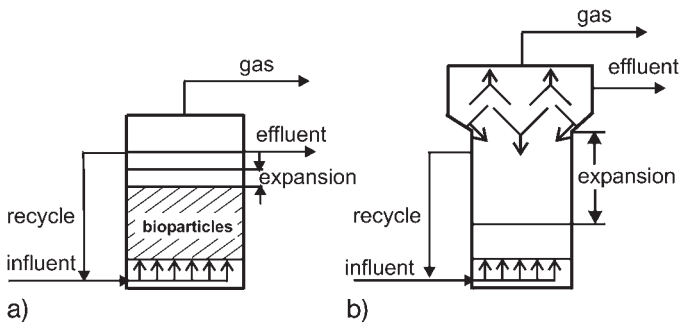


Fig. 8.10 Anaerobic expanded and fluidized bed reactors: (a) expanded bed, (b) fluidized bed

PROBLEM

An industrial wastewater with a substrate concentration of $S_o = 2000$ mg L^{-1} DOC = 5000 mg L^{-1} COD and a flow rate of $Q_o = 1000$ m^3 d^{-1} is to be treated anaerobically by a one-stage contact process at steady state for a temperature of 35 °C, with a removal efficiency of 90% and a concentration of X = 1 g L^{-1} MLSS methanogenic bacteria. The wastewater is free of SO_3^{2-} and NO_3^-. The reaction is neither limited nor inhibited by low or high concentrations of acetate.

Given coefficients:

$\mu_{max} = 0.18\ d^{-1}$

$Y^{\circ}_{X/S} = 0.037$ g MLSS (g COD)$^{-1}$

Calculate:
1. The necessary volume of the bioreactor V.
2. The volume of methane produced daily r_{CH_4} V in $Nm^3\ d^{-1}$.

Solution

1. First we have to balance the substrate. As demonstrated in Section 8.2.4, the organics and the CO_2 formed are all converted into acetate. Although intermediate compounds are formed by other bacteria, they do not reduce the COD or DOC.

$$0 = Q_0(S_0 - S) - \frac{\mu_{max} X \cdot V}{Y^{\circ}_{X/S}}$$

$$V = \frac{Q_0(S_0 - S)\,Y^{\circ}_{X/S}}{\mu_{max} X} = \frac{10^3 \cdot 4.5 \cdot 10^3 \cdot 0.037}{0.18 \cdot 1} = 925\ m^3$$

2. As demonstrated in Section 8.25, the yield is:

$Y^{\circ}_{CH_4/S} = 0.35\ Nm^3\ CH_4$ (kg COD)$^{-1}$

or: $r_{CH_4} = 0.35\ r_S\ Nm^3\ CH_4$ (kg COD)$^{-1}$

$$r_S = \frac{Q_0(S_0 - S)}{V} = \frac{10^3 \cdot 4.5 \cdot 10^3}{925}\ g\ (dm^3)^{-1} = 4.86\ kg\ COD\ (m^3\ d)^{-1}$$

$r_{CH_4} = 0.35 \cdot 4.86\ Nm^3\ CH_4\ (m^3\ d)^{-1} = 1.70\ Nm^3\ CH_4\ (m^3\ d)^{-1}$

$r_{CH4} \cdot V = 925 \cdot 1.70 = 1.572\ Nm^3\ d^{-1}$

References

Andrews, J.F. **1969**, Dynamic model of the anaerobic digestion process, *Am. Soc. Civil Eng.* 95, 95–116.

Attal, A.; Ehlinger, F.; Audic, J.M.; Faup, G.M. **1988**, pH-Inhibition mechanism of acetogenic, acetoclastic and hydrogenophilic populations, Proc. Int. Symp. Anaerobic Digestion, 5, 22–26.

Balch, W.E.; Fox, F.E.; Magrum, L.J.; Woese, C.R.; Wolfe, R.S. **1979**, Methanogens: reevaluation of an unique biological group, *Microbiol. Rev.* 43, 260–296.

Bolle, W.L.; Breugel, J.; Gils, W. **1986**, Kinetics of anaerobic purification of industrial wastewater, *Biotechnol. Bioeng.* 28, 542–548.

Boone, D.R.; Bryant, M. **1980**, Propionate degrading bacterium *Synthrophobacter wolinii* sp. nov. gen. nov. from methanogenic ecosystem, *Appl. Environ. Microbiol.* 40, 626–632.

Brandis, A.; Thauer, R.K. **1981**, Growth of *Desulfovibrio* species on hydrogen and sulfate as sole energy source, *J. Gen. Microbiol.* 126, 249–252.

Breithaupt, T. **1997**, Rotationsscheibenreaktor für die aerobe, anoxische und anaerobe Abwasserreinigung. Praktische Einsatzmöglichkeiten und mathematische Modellierung, *VDI-Forschungsberichte, Reihe 15*, 197.

Breithaupt, T.; Wiesmann, U. **1998**, Konzentrationsprofile in Rotationsscheibenreaktoren und deren Modellierung am Beispiel des anaeroben Acetatabbaus mit experimenteller Überprüfung, *Acta Hydrochem. Hydrobiol.* 26, 288–295.

Bryer, J.D. **1985**, Structured modelling of the anaerobic digestion of biomass particulates, *Biotechnol. Bioeng.* 27, 638–649.

Carr, A.D.; O'Donell, R.C. **1977**, The dynamic behavior of an anaerobic digester, *Prog. Water Technol.* 9, 727–738.

Chang, J. **1982**, *Studies On Methanogenic Phase In Anaerobic Digestion*, PhD thesis, Tohoku University, Tohoku.

Dauber, S. **1993**, in: *Anaerobtechnik*, ed. B. Böhnke, W. Bischofsberger, S.F. Seyfried, Springer-Verlag, Berlin.

Denac, M. **1986**, *Anaerober Abbau gelöster organischer Stoffe in Festbett- und Wirbelschichtreaktoren*, PhD thesis, ETH Zurich.

Fukuzaki, S.; Nishio, N.; Nagai, S. **1990**, Kinetics of the methanogenic fermentation of acetate, *Appl. Environ. Microbiol.* 56, 3158–3163.

Ghosh, S.; Pohland, F.G. **1974**, Kinetics of substrate assimilation and product formation in anaerobic digestion, *J. W.P.C.F.* 46, 748–759.

Gottschalk, G. **1986**, *Bacterial Metabolism*, 2nd edn, Springer-Verlag, Berlin.

Grady, C.P.L. Jr.; Daisser, G.T.; Lin, H.C. **1999**, *Biological Wastewater Treatment*, 2nd edn, Marcel Dekker, New York, p. 611.

Graef, S.P.; Andrews, J.F. **1973**, Mathematical modelling and control of anaerobic digestion, *AIChE Symp. Ser.* 70, 101–131.

Gujer, W.; Zehnder, A.J.B. **1983**, Conversion processes in anaerobic digestion, *Water Sci. Technol.* 15, 127–167.

Hall, E.R. **1992**, Anaerobic treatment of wastewaters in suspended growth and fixed film processes, in: *Design of Anaerobic Processes for the Treatment of Industrial and Municipal Wastes*, ed. Malina, J.F. Jr.; Pohland, F.G., Technomics Publishing, Lancaster, Penn., p. 41–118.

Hanaki, K.; Noike, T.; Matsumoto, J. **1985**, Mathematical modelling of the anaerobic digestion process, in: *Mathematical Models in Biological Waste Water Treatment*, ed. Jörgensen, S.E.; Gromiec, M.J., Elsevier-Verlag, Berlin, p. 41–118.

Harper, S.R.; Pohland, F.G. **1986**, Recent developments in hydrogen management during anaerobic biological wastewater treatment, *Biotechnol. Bioeng.* 27, 585–602.

Jeris, J.S.; McCarty, P.C. **1965**, Biochemistry of methane fermentation using ^{14}C tracers, *J. W.P.C.F.* 37, 178.

Kus, F. **1993**, Kinetik des anaeroben Abbaus von Essig- und Propionsäure in Bioreaktoren mit immobilisierten Bakterien, *VDI-Forschungsberichte, Reihe 15*, 115.

Laquidara, M.J.; Blanc, F.C.; O'Shaughnessy, J.C. **1986**, Developtment of biofilm, operating characteristics and operational control in the anaerobic rotating biological contactor process, *Water Pollut. Control Fed.* 58, 107–114.

Lawrence, A.W.; McCarty, P.L. **1969**, Kinetics of methane fermentation in anaerobic treatment, *J. W.P.C.F.* 41, 2.

Lettinga, G.; Hulshoff, L.W. **1991**, UASB process design for various types of wastewaters, *Water Sci. Technol.* 24, 87–108.

Lettinga, G.; Hulshoff, L.W. **1992**, UASB process design for various types of wastewaters, in: *Design of Anaerobic Processes for the Treatment of Industrial and Municipal Wastes*, ed. Malina, J.F. Jr.; Pohland, F.G., Technomics Publishing, Lancaster, Penn., p. 119–145.

Massey, M.L.; Pohland, F.G. **1978**, Phase separation of anaerobic stabilization by kinetic controls, *J. W.P.C.F.* 50, 2204–2222.

McInerney, M.J. **1999**, Anaerobic metabolism and its regulation, *Biotechnology* 11a, 455–478

McInerney, M.J.; Bryant, M.P. **1981**, Review of methane fermentation fundamentals, in: *Fuel Gas Production from Biomass*, ed. Wise, D.L., CRC Press, Boca Raton, p. 19–46.

McInerney, M.J.; Bryant, M.P.; Pfennig, N. **1979**, Anaerobic bacterium that degrades fatty-acids in syntrophic association with methanogenes, *Arch. Microbiol.* 122, 129–135.

Mosey, F.E. **1983**, Mathematical modelling of the anaerobic digestion process: regulatory mechanisms for the formation of short chain volatile acids from glucose, *Water Sci. Technol.* 15, 209–232.

Nethe-Jaenchen, R.; Thauer, R.K. **1984**, Growth yields and saturation constant of *Desulfovibrio vulgaris* in chemostat culture, *Arch. Microbiol.* 137, 236–240.

Pohland, F.G. **1992**, Anaerobic treatment: fundamental concepts, applications, and new horizons, in: *Design of Anaerobic Processes for the Treatment of Industrial and Municipal Wastes*, ed. Malina, J.F.; Pohland, F.G., CRC Press, London, p. 1–33.

Seyfried, C.F. **1979**, Reinigung organisch hochverschmutzter Abwässer mit dem anaeroben Belebungsverfahren am Beispiel von Abwässern aus der Nahrungsmittelherstellung, Veröffentlichung des Instituts für Siedlungswasserwirtschaft, Universität Hannover.

Shea, T.G.; Pretorius, W.A.; Cole, R.D.; Pearson, E.A. **1968**, Kinetics of hydrogen assimilation in the methane fermentation, *Water Res.* 2, 833–848.

Spieß, A. **1991**, Anaerobe Abwasserreinigung in neuen Bioreaktoren mit Polyurethanpartikeln zur Immobilisierung der Bakterien, *VDI-Forschungsberichte, Reihe 15*, 85.

Stronach, S.M.; Rudd, T.; Lester, J.N. **1986**, *Anaerobic Digestion Processes in Industrial Wastewater Treatment*, Springer-Verlag, Berlin, p. 32–33.

Tait, S.J.; Friedman, A.A. **1980**, Anaerobic rotating biological contactor for carbenous wastewater, *J. W.P.C.F.* 52, 2256–2269.

Ware, A.J.; Pescod, M.B. **1989**, Full-scale studies with an anaerobic/aerobic RBC unit treating brewery wastewater, *Water Sci. Technol.* 21, 197–208.

Ware, A.J.; Pescod, M.B.; Storch, B. **1990**, Evaluation of alternatives to conventional disc support media for rotating biological contactors, *Water Sci. Technol.* 22, 113–117.

Weimer, P.J.; Zeikus, J.G. **1978**, Acetate metabolism in *Methanosarcina barceri*, *Archiv. Microbiol.* 119, 175–182.

Widdel, F.; Pfennig, N. **1981**, Studies on dissimilatory sulfate reducing bacteria that decompose fatty acids I. Isolation of new sulfate reducing bacteria enriched with acetate from saline environments. Description of *Desulfobacter postgatei* gen. nov., sp. nov., *Arch. Microbiol.* 129, 395–400.

Yoo, E.S. **2000**, *Biological and Chemical Mechanisms of Reductive Decolorization of Azo Dyes*, PhD thesis, TU Berlin.

Young, J.C. **1991**, Factors effecting the design and performance of up flow anaerobic filters, *Water Sci. Technol.* 24, 133–156.

Zehnder, A.J. **1988**, *Biology of Anaerobic Microorganisms*, John Wiley & Sons, New York.

Zehnder, A.J.; Wuhrmann, K. **1977**, Physiology of a Methanobacterium Strain AZ, *Arch. Microbiol.* 111, 119.

Zehnder, A.J.; Huser, B.A.; Brock, T.D.; Wuhrmann, K. **1980**, Characterisation of an acetic-decaroxylation, non-hydrogen-oxidizing methane bacteria, *Arch. Microbiol.* 124, 1–11.

Zeikus, J.G. **1979**, Microbial populations in digesters, in: *Proc. 1st Int. Symp. Anaerobic Digestion*, Applied Science Publications, London.