

ANAEROBIC WASTEWATER TREATMENT

Anaerobic treatment, being a biological treatment, bears many similarities to aerobic treatment. This chapter develops the concepts of anaerobic treatment in light of previous discussions for aerobic treatment given in Chapter 17, pointing out the distinguishing features of anaerobic treatment in comparison to aerobic treatment.

Until recently "biological treatment" has meant an aerobic process in which oxygen is supplied by aeration to allow aerobic bacteria to break down and assimilate the wastes. The supply of air is a major operational expense of this process. Large quantities of sludge are also produced, which may or may not have resale value. If no resale opportunity exists, sludge disposal is another major expense associated with the process.

Anaerobic treatment, in contrast to aerobic treatment, does not require air input and generates considerably smaller quantities of sludge. The sludge produced has approximately the same fertilizer value per unit weight as sludge produced in an aerobic process. Anaerobic treatment may require substantial quantities of heat energy input but this energy penalty may be completely offset by the methane produced. There are also other methods or circumstances that reduce the heat energy requirement. The biogas (methane) feature of anaerobic treatment has been promoted as a solution to energy problems in various articles and, although claims may be exaggerated in some circumstances, many industrial wastes provide opportunities for realization of these benefits. The food and beverage industry, for example, produces wastes that are often rich in organic content and have temperatures above the ambient temperature.

In recent decades, several developments have occurred that have greatly increased energy efficiency and attractiveness of anaerobic waste treatment. Research groups throughout the world have developed anaerobic reactors to treat wastes more quickly, more reliably, and with a greater net production of methane gas. Full-scale implementations of these developments have met with success and competitive installations will continue to take advantage of the new technologies.

History

The production of biogas, consisting primarily of methane and carbon dioxide, was discovered in the seventeenth century after scientists observed "marsh gas" burning on the surface of swamps. Marsh gas is methane, a product of anaerobic biological degradation of organic materials. Mass transfer of oxygen from the atmosphere is unable to maintain measurable concentrations of oxygen under stagnant water conditions and high concentrations of organic matter. Under anaerobic conditions algae, which produce oxygen, are unable to survive.

Wastewaters, unless applied to a broad surface area or supplied from artificial aerators, naturally give rise to anaerobic treatment. Not necessarily by design, anaerobic treatment occurs in any holding tank for wastewater, including cesspools and septic tanks, which are among the first "treatments" applied to wastewater. Solids are metabolized and solubilized in anaerobic treatment. Solids are easily collected to form a highly concentrated waste and solids reduction was the primary application of anaerobic treatment until modern times. Research and implementation of engineered anaerobic treatment processes for solids reduction have been in progress for over a century.

Ironically, this oldest form of wastewater treatment was not developed and was applied only circumstantially in ponds for high-strength wastewaters. Reasons for this will become clear as concepts in this chapter are developed. But domestic wastewater, particularly in North America, is dilute and anaerobic treatment of low-strength wastewaters remains a challenge today.

Except for anaerobic ponds, the first application of anaerobic treatment to raw wastewaters was in the 1950s, when the anaerobic contact process, which is a configuration similar to a recycle activated sludge process, was developed. Industrial wastewaters often have organics concentrations high enough to make anaerobic treatment feasible and this process proved to be successful. Since then at least five major options have been developed for anaerobic waste treatment and most of these have lowered the organic strength threshold at which a waste can be treated anaerobically.

18.1 ANAEROBIC METABOLISM

There is no oxygen present or consumed in an anaerobic process. In the fermentation that occurs, a portion of the energy-rich organic compounds are oxidized but other organic compounds or inorganic carbon dioxide are used as the electron (hydrogen) acceptors. The transfer of electrons does release relatively small amounts of chemically bound energy (reduction in free energy) which is used for growth by the anaerobes. Because the energy yield of anaerobic fermentation is only about one seventh of the yield for aerobes (Zoetemeyer, 1982), the growth of anaerobes is slow. However, this does not mean that their rate of processing substrate is low.

Because there is no oxygen consumed in the process there is no reduction in COD in an anaerobic process. The removal of COD is accomplished by the conversion of organics into methane, which is a relatively insoluble gas (see Henry's law constants in Table 1.4). There will also be a significant production of CO_2 . The production of hydrogen and other gases also occurs but it is small enough to be negligible. Anaerobic treatment is realized in the final conversion of metabolic intermediates to methane. If the process is stopped short of this step, the effluent contains soluble products from intermediate stages of metabolism with the same oxygen demand as the initial material.

Anaerobic digestion involves a complex consortium of microorganisms. Toerien et al. (1970) suggested that the biochemical processes as well as the microbial species involved could be divided into three categories. A schematic of the reaction steps is outlined in Fig. 18.1.

1. Hydrolysis

Large molecules and suspended solids cannot be directly metabolized by anaerobes. When their concentrations are significant, hydrolysis reactions become an important first stage of anaerobic metabolism. Hydrolysis is the breakdown of large, complex soluble and insoluble molecules into smaller molecules that can

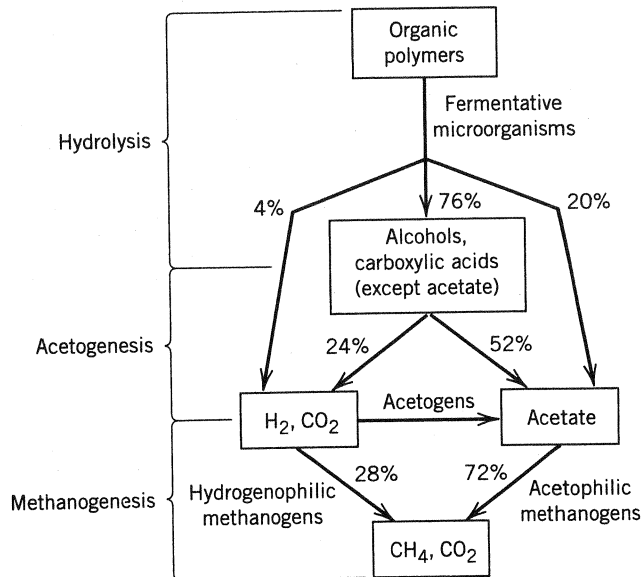


Figure 18.1 Anaerobic decomposition of organic matter. From Zehnder et al. (1982).

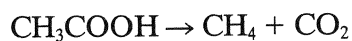
be transported into the cells and metabolized. Extracellular enzymes associated with the primary fermentative microorganisms are used to accomplish the task. There is an expenditure of energy in hydrolysis reactions. The energy for hydrolysis and synthesis is obtained from the catabolism of the smaller molecules resulting from hydrolysis. The fermentative microorganisms responsible for this step do not form methane.

2. Acetogenesis and Acid Formation

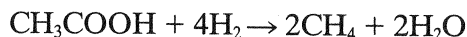
The same microorganisms that perform hydrolysis reactions carry the fermentation through this stage. The end products of hydrolysis are fermented into organic acids, other low molecular weight compounds, hydrogen, and carbon dioxide. The primary product of this fermentation is acetic acid. As shown in Fig. 18.1, microbial degradation of hydrolysis products is accompanied by a significant amount of hydrogen production. Bacteria that produce acetic acid and hydrogen are acetogenic bacteria. Other acid forming bacteria form butyric and propionic acid as well as other low molecular weight compounds. These microorganisms are relatively hardy and can tolerate a wide range of environmental conditions. The acid formers have an optimal pH between 5–6. Digesters are normally operated at a pH near 7 but their metabolic rates at this pH are still favorable compared to the methane formers responsible for the final conversion of organics into methane. Without proper operation of the process, particularly pH control, the acid formers can create highly unfavorable conditions for the methane formers.

3. Methanogenesis

The formation of methane, which is the ultimate product of anaerobic digestion, occurs by two major routes. The primary route is the fermentation of the major product of the acid forming phase, acetic acid, to methane and carbon dioxide. Bacteria that utilize acetic acid are acetoclastic (or acetophilic) bacteria. The overall reaction is

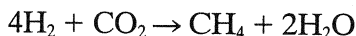


Based on thermodynamic considerations and from experimental data, Zeikus (1975) proposed the following reaction for acetate conversion to methane:



The most common acetoclastic methanogens in reactors treating wastes with a high volatile fatty acid content are from the genera *Methanosarcina* and *Methanosaeta* (formerly *Methanothrix*¹). *Methanosarcina* spp. are coccoid bacteria with doubling times near 1.5 d, and *Methanosaeta* spp. are sheathed rods, sometimes growing as long filaments with doubling times near 4 d (Zinder, 1988). These doubling times occur at optimal conditions for the methane formers. Even though *Methanosaeta* spp. grow more slowly, they are most frequently the dominant genus.

Some methanogens are also able to use hydrogen to reduce carbon dioxide to methane (hydrogenophilic methanogens) with an overall reaction of



There is a synergistic relation between the hydrogen producers and the hydrogen scavengers. Subtle changes in hydrogen conditions can change the end products of the acid forming phase. Furthermore, as the hydrogen partial pressure rises, hydrogen oxidation becomes more thermodynamically favorable than acetate degradation and acetate production is increased (Harper and Pohland, 1987). Alcohol degradation is also inhibited by high hydrogen levels. As noted earlier the net hydrogen production from the two phases is very small but it is an important intermediate in the metabolic processes.

It is recommended that overall hydrogen partial pressures be below 10^{-4} atm (corresponding to approximately a 10^{-8} M solution) for stability and good performance in anaerobic systems. At these hydrogen levels continuous production of acetic acid from influent and intermediate organics is assured and acetate utilization capacity is not inhibited (Harper and Pohland, 1987). These recommendations are based on thermodynamic considerations and the assumption of equilibrium between the liquid and the gas phase for hydrogen. Equilibrium between liquid and gas phases is not achieved, even in active reactors (Pauss and Guiot, 1993). Hydrogen concentrations in the liquid are higher than the equilibrium value because of mass transfer limitations. More research is required to understand hydrogen dynamics.

The methane formers are much more fastidious in their environmental requirements than the acid formers. Their rates of metabolism are also lower than the rates of the acid formers and therefore methane production is generally the rate-limiting step in anaerobic digestion. The optimal pH for methane formers is around 7.0 and their activity drops to very low values when the pH falls outside of the range of 6.0–8.0.

Inhibition of the methanogens can exacerbate deteriorating conditions. The methane formers fail to remove the organic acids produced in the initial stages of metabolism while the acid formers continue acid production. This adds more environmental stress on the methane formers. The process “pickles” itself, with no removal of COD. However, there are measures that can be taken to guard against this situation.

18.2 PROCESS FUNDAMENTALS

The design and operation of anaerobic processes must be cognizant of the characteristics of microorganisms and features of their metabolic pathways outlined in Section

¹The original culture used to define the type species *Methanothrix soehngenii* was based on a mixed culture (Patel and Sprott, 1990).

18.1. The most important considerations for operation of anaerobic processes are discussed next.

18.2.1 Environmental Variables

Both physical and chemical variables influence the habitat of the microorganisms in the reactor. Oxidation–reduction potentials in anaerobic reactors are usually below -350 mV.

Temperature

As temperature increases the rate of reaction generally increases. For biological systems the rate increases are usually not as great as for chemical reactions.

There are two optimal ranges for process operation to produce methane: 30 – 40°C (the mesophilic range is from 15 to 40°C) and 50 – 60°C (the thermophilic range is for temperatures above 40°C). The psychrophilic range is temperatures below 15 – 20°C . Methane has been produced at temperatures down to 10°C or lower, but for reasonable rates of methane production, temperatures should be maintained above 20°C . Rates of methane production approximately double for each 10°C temperature change in the mesophilic range. Loading rates must decrease as temperature decreases to maintain the same extent of treatment. Operation in the thermophilic range is not generally practical because of the high heating energy requirement. A stable temperature is more conducive to stable operation than any specific temperature.

pH

The most important process control parameter is pH. The optimum pH range for all methanogenic bacteria studied by Zehnder et al. (1982) was between 6 and 8 but the optimum pH for the group as a whole is near 7.0. The lower growth rates of the methanogens require that the process be run at conditions most favorable to them. Numerous references report that the pH required in anaerobic systems for good performance and stability is in the range of 6.5–7.5, although stable operation has been observed outside this range. The system must contain adequate buffering capacity to accommodate the production of volatile acids and carbon dioxide that will dissolve at the operating pressure. Excess alkalinity or ability to control pH must be present to guard against the accumulation of excess volatile acids.

Anaerobic processes can operate over a wide range of volatile acids concentrations (from less than 100 mg/L to over $5\,000$ mg/L) if proper pH control is practiced. A constant pH lends stability to the process. Automatic pH control is often the most economical means of pH control because less chemicals are consumed. The alkalinity requirement varies with the waste, system operation, and type of process.

The three major chemical sources of alkalinity are lime, sodium bicarbonate, and sodium carbonate. Sodium hydroxide, which is often used in vegetable and fruit peeling operations, is also an important source of alkalinity. Other substances that produce alkalinity are soaps or other salts of organic acids.

Mixing

Septic tanks, Imhoff tanks, and sludge digesters were the first anaerobic treatment operations. All of these processes employed single-tank anaerobic reactors. In septic tanks incoming solids are settled and digested in the same compartment. An additional compartment may be included for polishing of the effluent but the first compartment

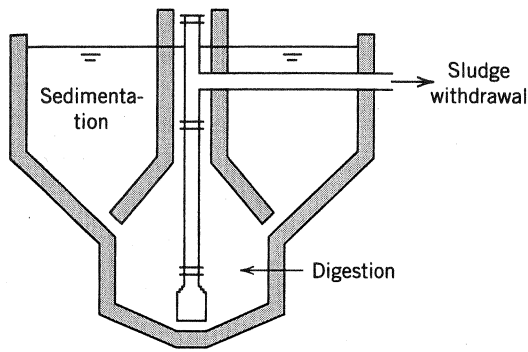


Figure 18.2 Imhoff tank.

is the essential digestion chamber. The Imhoff tank (Fig. 18.2) which is a two-story treatment system, consists of a sedimentation basin with a compartment below for digestion of the settled solids. This system is primitive by modern standards. Inadequate mixing is one reason for poor performance. Mixing of the digestion chamber is accomplished only by the evolution of gas.

Early single-tank anaerobic sludge digesters may have been mixed mechanically or with other methods. The importance of mixing for improved anaerobic process performance was recognized in the 1940s (Babbitt and Baumann, 1958). The separation of digestion from other processes and the application of mixing were the first major advancements in anaerobic treatment.

Mixing is an important factor in pH control and maintenance of uniform environmental conditions. Without adequate mixing, unfavorable microenvironments can develop. Mixing distributes buffering agents throughout the reactor and prevents local buildup of high concentrations of intermediate metabolic products that can be inhibitory to methanogens.

Ammonia and Sulfide Control

Free ammonia can inhibit anaerobic metabolism at high concentrations. Anaerobes can acclimatize to high ammonia concentrations but large fluctuations can be deleterious to the process. Free ammonia, which is much more toxic than the ammonium ion, is more prevalent at high pH. Both elevated pH and NH_3 levels contribute to process failure but the situation can be controlled by addition of acid.

Wastes high in protein content will produce significant amounts of ammonia, which increases alkalinity. It is often desirable to recycle effluent from a reactor receiving proteinaceous waste to add alkalinity to the influent. The protein content of most wastes is usually not high enough to cause ammonia toxicity problems. However, wastes containing blood can produce enough ammonium bicarbonate to elevate pH beyond the optimal range without acid addition.

Sulfate can be used as an electron acceptor under anaerobic conditions, resulting in sulfide production. Sulfides are inhibitory to methanogens and sulfate reducers themselves. Wastes high in sulfate can be prone to sulfide toxicity. Metals will precipitate sulfides; iron can be added to eliminate sulfide toxicity when sulfide concentrations are inhibitory (Gupta et al., 1994).

Nutrient Requirements

The low growth yields of anaerobes (both groups) from a given amount of substrate result in lower nutrient requirements compared to aerobes. The normal composition

of microorganisms (both aerobic and anaerobic) is usually assumed to be $C_5H_7NO_2$. Phosphorus content is about one fifth of nitrogen content on a weight basis. The quantity of sludge or volatile suspended solids (VSS) produced depends on process operating conditions and is also related to influent waste strength measured on a COD basis (assuming all other growth requirements are in excess). For a typical activated sludge process, this results in a COD:N:P requirement of 100:5:1 on a mass basis. Anaerobic systems produce 20% or less of the amount of sludge produced in aerobic systems for the same substrate and the N and P requirements should decrease proportionately. The COD:N ratio has been observed to be as high as 700:5. A value of 250:5 is reasonable for highly loaded processes (0.8–1.2 kg COD/kg VSS/d); for processes operating at a lower loading rate the ratio can conservatively increase from 250:5 by multiplying it by a factor equal to the loading rate divided by 1.2 kg COD/kg VSS/d (Henze and Harremoës, 1983).

There are a number of trace elements required for successful anaerobic digestion. Nickel and cobalt have been shown to promote methanogenesis (Murray and van den Berg, 1981). For typical wastes, these substances will normally be present in excess.

18.2.2 Solids Yield and Retention Time

The most important advancement in the field of anaerobic treatment has been recognition of the central role of sludge age or solids retention time (SRT) in controlling the process. The SRT is the average time that a solid particle, particularly a biological particle, stays in the reactor (Sections 17.6 and 17.8.1). In suspended growth processes SRT is the same for all solid particles, whether they are of biological origin or not, but in other processes this is not the case. Conventional anaerobic sludge digestion reactors with artificial mixing are suspended growth reactors.

The importance of increasing SRT by solids recycle in activated sludge systems was recognized from the development of the process, but similar approaches for anaerobic systems were not implemented until the 1950s, when the anaerobic contact process (a suspended growth sludge recycle process) was developed. In a suspended growth reactor without recycle, the SRT and hydraulic retention time (HRT) are the same. This places a severe constraint on an anaerobic process because of the slow growth rates of the anaerobes. Very large reactors are required.

The new anaerobic process modifications either control SRT independently of HRT or by process design promote occurrence of very high SRTs, which is desirable. An increase in SRT will produce an increase in sludge (microorganism) concentration in the reactor. A minimum SRT must be maintained to allow the working microorganisms to reproduce themselves before being washed out and wasted from the system. The equation that defines SRT has already been given in Chapter 17. It is

$$\theta_x = \frac{\text{Mass of sludge in the reactor}}{\text{Mass removal rate of sludge from the reactor}} \quad (18.1)$$

The sludge of interest in an anaerobic reactor is specifically the anaerobic biomass. The concentration and ease of substrate degradation, concentration of microorganisms, and HRT interact to determine the amount of substrate removal. In a suspended growth reactor, the parameters in the equation for sludge age are readily formulated. The development is exactly the same as the development for activated sludge processes in Chapter 17 (Eqs. 17.21–17.23 and 17.27–17.28).

$$\frac{1}{\theta_x} = \frac{Q_w X_w}{V X_v} \quad (18.2)$$

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where

θ_x is SRT

Q_w is volumetric flow rate of waste solids from the system

X_w is VSS concentration in Q_w

V is the volume of the reactor

X_V is the average concentration of VSS in the reactor

The waste flow, Q_w , is usually equal to the influent flow rate, Q , except in systems that employ recycle of biological solids. If there is more than one solids removal stream from the suspended growth system, then the solids removed in all streams must be taken into account in the materials balance. The application of Eq. (18.1) to other systems is not straightforward because of the difficulty of measuring biomass in the reactor in these systems. A brief discussion of some ramifications of changes in SRT is given here. The discussion overlaps with material in Chapter 17, which the reader is advised to review.

Below the minimum SRT it is impossible to obtain any treatment; beyond this point, an increase in SRT will produce an increase in removal of substrate. Each incremental increase in SRT beyond the minimum will produce a diminishing improvement in treatment. The amount and concentration of sludge in the reactor are approximately directly proportional to the SRT. Higher SRT will result in an excess of sludge in the reactor. The excess sludge inventory aids in keeping the process stable because this reserve biomass allows the system to cope with changes in influent quality and quantity. If a toxicant appears that inactivates a portion of the biomass, the reserve biomass is able to maintain reasonable treatment.

From laboratory studies of many wastes the minimum reproduction time (SRT) for methane formers is 3–5 days at 35°C. All biological systems require a safety factor of from 3 to 20 times the minimum SRT for successful operation (Lawrence and McCarty, 1969).

There are four methods of maintaining and increasing the amount of biological solids in an anaerobic reactor:

1. Separation of solids from the reactor effluent and recycle of these solids to the reactor
2. Provision of fixed surfaces on which bacteria grow and are retained in the system
3. Development of a dense sludge blanket, which results in holdup of solids in the system
4. Operation of the system at long hydraulic detention times

The fourth method is used in conventional sludge digestion units and is not suitable for lower strength wastes because of the large reactor volumes required and the difficulty of concentrating soluble wastes. Regarding methods 1 and 3, it is not possible to separate biological solids from inert organic or inorganic solids in the liquid. Increasing the SRT by these methods will increase the concentration of all types of particles and inhibitory levels of inert solids may be reached that ultimately limit the maximum SRT which can be maintained.

Bacteria attach to and grow on the surfaces mentioned in method 2. The tenacity with which the bacteria adhere to the surfaces in these types of reactors can allow very high SRTs to be attained. The first three methods have been implemented with notable success in the more recent reactor designs that are discussed in detail in Section 18.5. Methods 1 and 2 are used in familiar aerobic processes, activated sludge units and trickling filters, respectively. Method 3 is unique to anaerobic systems. Under

proper conditions dense granules containing biomass form in this system. In methods 2 and 3 the density of biomass in the reactor is variable.

18.2.3 Biogas Potential

Assays analogous to the BOD test have been devised to assess the potential for a waste to be treated under anaerobic conditions.

Biochemical Methane Potential and Anaerobic Toxicity Assay

The methane potential of a waste is related to the concentration of organics (COD) in it and the efficiency of treatment. The 5-d biochemical oxygen demand (BOD_5) is also a common parameter used to measure waste strength. A BOD_5 value can be conservatively converted to a COD value by multiplying BOD_5 by 1.5. The maximum theoretical yield of methane, M , is $0.35 \text{ m}^3 \text{ CH}_4/\text{kg COD}$ ($5.6 \text{ ft}^3/\text{lb}$) removed as shown in Example 18.1.

The maximum methane potential of a waste may not be realized in a treatment process for reasons such as toxicity or the refractory nature of some of the organics. In 1979 a procedure named the biochemical methane potential (BMP) test, analogous to the BOD test, was defined to assess the methane potential of a waste. The procedure is readily modified to a toxicity assay (Owen et al., 1979). Although these procedures have not been incorporated into *Standard Methods* (1992), they are widely used in the field.

In the BMP test a sample is inoculated with an active culture and supplemented with growth requirements to provide optimal conditions for anaerobic metabolism. Stock solutions containing minerals, nutrients, vitamins, and other growth factors are prepared. The appropriate sample volume is anaerobically transferred to a serum bottle. The prepared solutions are combined, inoculum is added, and the mixture is transferred to the serum bottle. Anaerobic transfers prevent oxygen toxicity. The tubing and flasks used to transfer the sample, medium, and inoculum are flushed with 70:30 nitrogen:carbon dioxide gas before a transfer is made. One of the prepared solutions contains sodium sulfide to provide a reducing environment and another solution contains resazurin, an indicator that turns pink when it is oxidized, which indicates the presence of oxygen.

The serum bottle is capped after all solutions are added and incubated at the desired temperature, which is usually 35°C . Gas production and composition are monitored over time. The incubation period is typically 30 d or the time for gas production to cease. Gas volume produced is monitored with a glass syringe that is allowed to equilibrate with atmospheric pressure after the needle is inserted into the serum bottle. Samples for analysis of gas content are also taken with a syringe.

The anaerobic toxicity assay uses the procedure for BMP except that an acetate-propionate spike is added to the serum bottle to provide a readily degradable substrate. Methane production from various sample sizes (and dilutions in the serum bottle) is compared to gas production from a control to assess the toxicity of the sample.

Methane Production in Anaerobic Treatment

The normal composition of biogas from anaerobic processes ranges from 60 to 70% methane (CH_4) and a balance of 30–40% carbon dioxide. Small amounts of hydrogen and traces of hydrogen sulfide (H_2S), ammonia, water vapor, and other gases are also present. The energy content is entirely associated with methane, which has an energy

content of 37 MJ/m³ (994 Btu/ft³). The presence of carbon dioxide in biogas reduces its energy content to the range of 22–26 MJ/m³ (591–698 Btu/ft³).

Because of its corrosive nature, H₂S is an undesirable component of biogas. It can be removed by passing the gas over iron filings, which are easily regenerated by exposure to air.

Water vapor in biogas may also present a problem. Gas leaving the digester is saturated with water vapor that may condense in pipe lines, causing blockage. Moisture may be removed by using condenser traps that are periodically drained.

The BMP procedure indicates the maximum potential methane production from a wastewater. The rate of methane production is related to the flow rate and substrate removal by Eq. (18.3).

$$Q_m = Q(S_{T0} - S_{Te})M = QEMS_{T0} \quad (18.3)$$

where

Q_m is the quantity of methane per unit time

Q is influent flow rate

S_{T0} is the total influent COD (suspended + soluble)

S_{Te} is the total effluent COD (suspended + soluble)

E is an efficiency factor (dimensionless, ranging from 0 to 1)

M is the volume of CH₄ produced per unit of COD removed

Environmental conditions in a treatment process and losses will decrease the yield of methane from the theoretical or BMP values. A conservative value for M is 0.20 m³/kg (3.2 ft³/lb). Observed M values in the literature range from 0.10 to 0.35 m³/kg (1.6 to 5.6 ft³/lb) COD removed. Part of the deviation from theoretical values may result from gas leakage or the conversion of some substances to compounds that are not oxidized under conditions of the COD test. Some of the COD removed is converted to biomass. The COD balance must compare the total COD input to the process against the total COD, both soluble and suspended, accumulating in the reactor and exiting from the process. If only effluent soluble COD is accounted for and the net accumulation of biomass in the reactor is ignored, the calculated M values will definitely be less than the theoretical maximum. In some processes it is difficult to monitor the accumulation of solids in the reactor over short periods of time (which may be a few months).

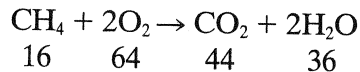
The efficiency factor is related to overall treatment efficiency (in terms of COD removed from the wastewater) and the concentration of nonbiodegradable components in the influent. It is typically in the range of 0.6–0.9. The influent COD originating from components such as seeds and skins is practically nonremovable. In general, soluble components in the influent are readily removed and solid components are removed to an intermediate degree. Laboratory treatability studies are needed to define E .

There is a practical minimum limit of 1 000 mg/L on the influent COD concentration needed to obtain successful anaerobic treatment, although some studies have successfully treated waste at lower COD concentrations (Droste et al., 1988). The low amount of synthesis of anaerobes makes control of solids losses from the reactor critical at low substrate concentrations. As influent substrate concentration increases, the efficiency of any biological process improves. Also, as influent concentration increases, reactor loadings can be increased within limits while maintaining suitable HRTs. In anaerobic treatment this means a larger output of methane per unit volume of reactor per unit time.

■ Example 18.1 Methane Yield

Prove that the maximum yield of CH_4 is $0.35 \text{ m}^3 \text{ CH}_4/\text{kg COD}$ ($5.6 \text{ ft}^3/\text{lb}$). Also calculate the daily volume of methane produced from a waste containing a COD of $3\,000 \text{ mg/L}$ if 80% of the waste is degraded and the wastewater flow rate is $675 \text{ m}^3/\text{d}$ (0.178 Mgal/d).

Because all COD removed in an anaerobic process is converted to methane, it is necessary to determine the COD equivalence of methane. This is done, as outlined in Chapter 5, by calculating the amount of oxygen required to completely oxidize 1 mole of CH_4 at STP. The balanced reaction is



The COD of methane is $64 \text{ g O}_2/16 \text{ g CH}_4$ or 4.00 g/g . The complete metabolism of 1.00 kg of COD will produce 0.25 kg of CH_4 . The number of moles of CH_4 produced will be $250 \text{ g}/16 \text{ g} = 15.6 \text{ moles}$. The volume of 1 mole of gas is 22.4 L . The total volume of gas produced is

$$V = 22.4 \frac{\text{L}}{\text{mole}} \times 15.6 \text{ moles} = 349 \text{ L} = 0.35 \text{ m}^3$$

Equation (18.3) is used to determine the methane volume produced from a waste containing $3\,000 \text{ mg/L COD}$ at a flow rate of $675 \text{ m}^3/\text{d}$ with 80% COD removal.

$$\begin{aligned} Q_m &= QEMS_{T0} = \left(675 \frac{\text{m}^3}{\text{d}}\right)(0.80)\left(0.35 \frac{\text{m}^3 \text{CH}_4}{\text{kg}}\right)\left(3\,000 \frac{\text{mg}}{\text{L}}\right)\left(\frac{1 \text{ kg}}{10^6 \text{ mg}}\right)\left(\frac{1\,000 \text{ L}}{1 \text{ m}^3}\right) \\ &= 567 \text{ m}^3/\text{d} \end{aligned}$$

In U.S. units:

$$\begin{aligned} Q_m &= \left(0.178 \times 10^6 \frac{\text{gal}}{\text{d}}\right)(0.80)\left(0.35 \frac{\text{m}^3 \text{CH}_4}{\text{kg}}\right)\left(3\,000 \frac{\text{mg}}{\text{L}}\right)\left(\frac{1 \text{ kg}}{10^6 \text{ mg}}\right)\left(\frac{3.79 \text{ L}}{\text{gal}}\right)\left(\frac{35.3 \text{ ft}^3}{\text{m}^3}\right) \\ &= 20\,000 \text{ ft}^3/\text{d} \end{aligned}$$

Note: The total volume of gas produced will depend on the volume of CO_2 produced. If the $\text{CH}_4:\text{CO}_2$ ratio is 2:1 on a volumetric basis, the total volume of gas produced will be $851 \text{ m}^3/\text{d}$ ($30\,030 \text{ ft}^3/\text{d}$).

18.3 PROCESS ANALYSIS

The complexity of the anaerobic process makes it difficult to model. Models developed here are restricted to suspended growth processes because they are most easily modeled. An overall model is developed for the process before a detailed model is developed that takes into consideration each of the major phases of anaerobic decomposition. A model should be applied consistently with the assumptions and conditions for which it has been developed.

The developments follow the principles given in Chapter 17, which the reader is advised to consult.