doi: 10.2166/9781789063479_0167

Chapter 6

Maximizing sustainability by energy recovery in anaerobic treatment systems

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ABSTRACT

Traditionally, wastewater treatment systems require considerable energy input, but this has changed since modern anaerobic treatment systems were developed in the second half of the last century. The production of biogas opens the possibility to produce electric power, which may make these systems independent of external energy and may even become net energy producers. A second source of energy production in wastewater treatment systems is sludge production. After drying the sludge its combustion can generate energy, though less than the energy potential from biogas, not only due to the reduced sludge mass, but also because solid fuel has a lower conversion efficiency than gaseous fuel. It has been demonstrated that in an efficient anaerobic treatment system operating under favourable conditions (warm climate, low-sulphate concentration in the influent) $\sim$1/6 of the influent organic material is converted into sludge whereas 4/6 is converted into biogas and 1/6 leaves the anaerobic treatment system with the treated effluent. Normally, the production of electric power from the biogas is more than sufficient to run the treatment system and an external source energy is not required. However, this does not mean that energy production is always a sound economic solution. Economic feasibility depends on the price of electric power and generally requires the operation of a large treatment system. In this chapter, equations are derived to estimate the composition of biogas and sludge in anaerobic wastewater treatment systems and specifically the influence of sulphate in the influent is discussed. Moreover, the processes for collection and treatment of biogas and sludge are presented. The potential for useful energy generation from anaerobic treatment systems is analysed and several examples are presented in order to highlight the feasibility of the energy recovery under different operating conditions.

Keywords: anaerobic wastewater treatment, biogas production and composition, electric power from biogas and sludge, influence of sulphate in the influent, volatile solids production.

6.1 INTRODUCTION

All biological wastewater treatment systems seek to reduce the concentration of organic material since its presence is highly undesirable. When raw wastewater is discharged on surface water, it leads to consumption of dissolved oxygen, and, depending on the ratio between surface water flow and organic

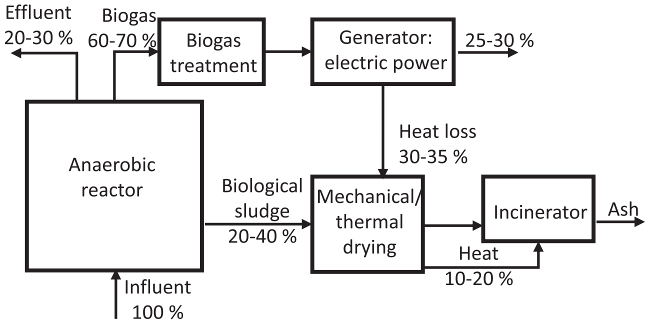


Figure 6.1 Distribution of organic material of influent wastewater in anaerobic treatment systems. Numbers indicate the estimated fractions under normal operational conditions.

load, it can cause death of microorganisms. Conventional aerobic wastewater treatment systems are energy consumers, but anaerobic treatment systems offer the possibility of recovering the energy content of the influent organic matter, which can be profitably employed in wastewater treatment plants or sold as electric energy. As shown in Figure 6.1 the organic material of wastewater after the anaerobic treatment is distributed in three fractions: (1) a gaseous fraction composed of biogas, (2) a solid fraction composed of biological sludge and (3) a fraction dissolved in the effluent. In this distribution, the largest fraction is biogas, in which methane is the main component and can be used for electric energy generation. Sludge combustion can provide useful energy production after separation from the liquid phase and drying. The residual organic material in the effluent is composed of a biodegradable and a non-biodegradable fraction. The biodegradable components can be removed in a post-treatment unit as activated sludge or polishing ponds (see Chapter 5) whereas the non-biodegradable fraction will only be removed if the production of high-quality water is an objective of the treatment system. In that case advanced processes such as reverse osmosis can be used to produce water without impurities.

In this chapter, an estimate is made of the composition of biogas and sludge as well as the potential for useful energy generation from these in anaerobic treatment systems. Moreover, the processes for collection and treatment of biogas and sludge are presented.

6.2 ENERGY RECOVERY IN ANAEROBIC TREATMENT SYSTEMS

The production of biogas is the most characteristic feature of the anaerobic treatment. Biogas is composed mainly of methane and carbon dioxide, which are decomposable products of organic material and have a limited solubility in water. There are other components, whose magnitude depends on the operating conditions in digesters and the characteristics of wastewater. In this chapter, it will be shown that for sewage treatment contributions of nitrogen and water vapour in biogas may exceed that of carbon dioxide. If sulphate is present in wastewater hydrogen sulphide will also be formed, which generally has a low concentration, but is nonetheless important because it can cause several problems in anaerobic digesters as it will be reported in detail in Section 6.4.7.

The destination of biogas depends on the produced quantity and the quality. If high amounts are available, it is possible to use biogas in a productive way, generating electricity and heat in combined heat and power units or refining and pressurizing it for subsequent use, for example for automotive purposes or injection in the gas grid. The technical feasibility of using biogas for power generation is not in question: there are many manufacturers who produce generators specifically designed for the use of biogas as fuel, with power generation ranging from 30 kW to over 5 MW. The transformation efficiency of these units is in the range of 35–40%. For very large biogas flows (production $>5\ \mathrm{MW_{el}}$) there is the possibility of using gas turbines, which have a high initial cost, but with an efficiency of $\geq 50\%$.

A more complicated application is the upgrading of biogas for producing pure methane. In this case, the purified biogas must be compressed to a pressure high enough for grid injection (16 bar) or to a high pressure of 200–250 atm to be used in cars which are adapted for use of compressed natural gas. The upgrading of biogas into methane has also been demonstrated, but the feasibility of this alternative depends on the price of conventional fuel, which is too low for widespread application.

Raw biogas treatment processes are well established and the economic feasibility depends mainly on the benefit of the productive use, that is, the cost of fuel that otherwise would have to be purchased. In small treatment systems, it is usually not economically convenient using the biogas for energy production and it is preferable to burn it with a flare. It is worth noting that the combustion is important, and that omission of this step can result in the generation of greenhouse gases (GHG) by the anaerobic treatment higher than the one derived by the aerobic. The methane is a potent GHG with a carbon equivalence of 25:1, that is 1 mol of methane gas is 25 times more harmful than carbon dioxide.

Example 6.1

Estimate the per capita production of gases contributing to the greenhouse effect in aerobic and anaerobic systems for a per capita contribution of 100 g chemical oxygen demand (COD)/day and making the following assumptions:

(1) Aerobic: oxygen consumption: 0.72 g O_2/g COD; aeration efficiency: 1 kWh/kg O_2; fuel consumption for power generation: 0.2 kg CH_4/day/kW of electric power.
(2) Anaerobic: anaerobic digestion efficiency: 70%
(3) Average elemental composition of sewage is C_2H_2O, close to the value of $C_2H_{19/9}ON_{1/9}$ determined by Henze and Harremoes (2001).

Solution

Assuming that carbon dioxide is produced in equimolar ratio with the consumption of oxygen in the aerobic system, it follows that the oxygen consumption of 72 g O_2/inh/day or $72/32 = 2.25$ mol/inh/day generates 2.25 mol/inh/day of CO_2. On the contrary, the energy consumed in oxygen transfer (1 kWh/kg O_2) will be ~72 Wh/day or 3 W. For power generation of 1 W, consumption of 5 g CH_4/day is required and this generates $5/16 = 0.31$ mol/day CO_2 (other fuels have roughly the same contribution). For a power generation of 3 W, the production of CO_2 is therefore 0.93 mol/inh/day leading to a total of $2.25 + 0.93 = 3.2$ mol CO_2/inh/day in aerobic systems.

In anaerobic systems the per capita production is $0.7 \times 100/4 = 17.5$ g CH_4/day or $17.5/16 = 1.1$ mol CH_4/day. If this amount is not burned, fatally it escapes into the atmosphere as a contributor to the GHG effect. Not considering the production of CO_2 in anaerobic digestion (its major fraction does not pass into the atmosphere but remains dissolved), methane production is equivalent to $21 \times 1.1 = 23$ mol CO_2/inh/day, a factor $23/3.2 = 7$ times greater than the calculated value for the aerobic generation system! By burning the methane production of biogas, the CO_2 production will be 1.1 mol/inh/day, ~1/3 of the production in aerobic systems.

If methane in the biogas is burnt, there is still the dissolved CH_4, with amounts to ~20 mg CH_4/L generating from the digestion of 80 mg COD/L. If the dissolved CH_4 is not metabolized, for example by methanotrophic bacteria it will eventually be released into the atmosphere. If a per capita contribution of 120 L/day is assumed, the dissolved methane would be $20/16 \times 120 = 150$ mmol CH_4/inh equivalent to 3.1 mol CO_2/inh, equal to the production in aerobic systems.

It can be concluded that even if all the biogas produced is burnt, the CO_2 production of the burnt biogas and the release of dissolved methane leads to at least the same contribution of GHGs by anaerobic and aerobic treatment systems. Therefore, the sustainability of anaerobic systems for sewage treatment is actually questionable, due to the unavoidable release of GHGs into the atmosphere. In the above analysis, anaerobic digestion of aerobic sludge is not considered, but in reality, ~30% of the organic influent load to aerobic systems is converted into methane and will increase the output of GHGs, so that in the end the two systems produce practically equivalent amounts of GHGs. If methane can be productively used, anaerobic systems become more attractive in terms of sustainability, because they reduce the use of fossil fuels.

6.3 SOLUBILITY OF GASES

Biogas is a mixture of various gases and vapours that desorb from the liquid phase in an anaerobic digester because of the limited solubility of these products in water. To estimate the flow of biogas, it is necessary to know the production and solubility of its components. Calculation requires a first assumption of equilibrium conditions between the gaseous phase (biogas) and liquid phase in a bioreactor whose composition is assumed to be equal to one of the effluents, and that there is a uniform composition in both phases. In good approximation, this will normally be the case, even though the solid phase in the reactor can be highly stratified (Cozma *et al.*, 2013).

The solubility of gases in the liquid phase can be expressed with Henry's law, stating that if a liquid and a gaseous phase are in equilibrium, there is proportionality between the saturation (maximum) concentration of a gas component in the liquid phase and its concentration in the gas phase:

$$C_s = k_d C_g \tag{6.1}$$

where C_s = saturation concentration of the dissolved gas (mg/L or mmol/L); C_g = gas concentration in the gas phase (mg/L or mmol/L) and k_d = distribution coefficient (dimensionless).

The distribution coefficient indicates the solubility of a gas: the higher the coefficient, the higher the solubility. The value of this coefficient has been determined and tabulated for the most important volatile compounds. Table 6.1 shows the values of the distribution coefficients for different temperatures of gases which can be biogas components. Concentrations may be expressed in any unit (g/L, mol/L, etc.).

Equation (6.1) can also be written in a different form:

$$C_s = k_h P_p \tag{6.2}$$

where k_h = Henry's constant; P_p = partial pressure of the component in the biogas (g/(m^3 Pa) or g/J).

The relationship between the distribution coefficient and the Henry constant is:

$$k_h = k_d W_m / RT \ (\mathrm{g/J}) \tag{6.3}$$

where W_m = molar weight of the gas; R = universal gas constant = 8.3 J/kmol; T = temperature (K).

Table 6.1 Distribution coefficients of several biogas components.

Gas	Formula	Molecular Weight (g/mol)	Temperature (°C)		
			k_{d20}	k_{d25}	k_{d30}
Methane	CH_4	16	0.034	0.032	0.031
Carbon dioxide	CO_2	44	0.94	0.83	0.74
Nitrogen	N_2	28	0.017	0.016	0.015
Oxygen	O_2	32	0.034	0.032	0.030
Ammonium	NH_3	17	0.76	0.71	0.67
Hydrogen sulphide	H_2S	34	2.87	2.55	2.27

6.4 BIOGAS FLOW

To estimate the flow of biogas generated in anaerobic treatment, firstly it is necessary to evaluate the volumetric flow of its components. In Figure 6.2 the gases normally present in biogas are presented. Along with methane, which is the main component, significant contributions of carbon dioxide, water and nitrogen are expected. In addition, there are other compounds which are less bulky, but whose presence is important because of their nature: O_2, NH_3 and H_2S (Van Haandel & van der Lubbe, 2019).

Regarding hydrogen sulphide, the contribution of this component depends on the concentration of sulphate in the water supply generating the sewage. Usually, this concentration will be small but there are regions where water resources with a high-sulphate concentration are the only source for public water supply. In these cases, sulphide production may still not be high, but due to sulphate reduction, there is a consumption of organic matter and methane production may be strongly reduced. Nitrogen, oxygen and ammonium are dissolved in influent whereas methane, carbon dioxide and hydrogen sulphide gas are generated in the anaerobic treatment unit. Being a vapour and not a gas at ambient temperature, the partial pressure of H_2O is constant for a given temperature and is independent of the pressure of the gas phase.

6.4.1 Production potential of methane

Methane production depends directly on the applied organic load and digestion efficiency. Stoichiometric production is calculated as 0.25 kg of CH_4/kg digested COD. When it is assumed that ~10% of influent COD is transformed into volatile solids, the production of methane can be calculated from the applied organic load if the removal efficiency of the organic material is known. The removal efficiency depends on a variety of factors: the nature of the organic material, environmental conditions, operating conditions and reactor characteristics in terms of design and construction. The daily mass of methane produced may be expressed as

$$M_{CH_4} = (MS_{ta} - MS_{te} - MS_{xv}) / 4 \tag{6.4}$$

As a first estimate of the methane production, it can be assumed that all produced methane desorbs from the liquid phase. Knowing that the molar volume of a gas at atmospheric pressure is given by

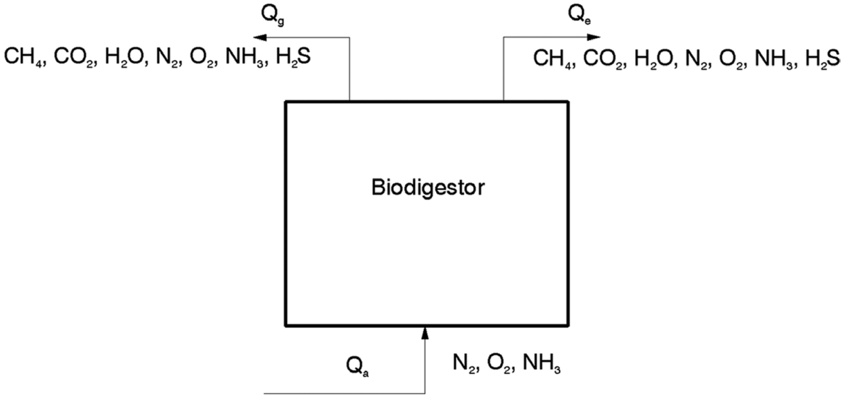


Figure 6.2 Schematic representation of the different components of biogas and the equilibrium between the gas and liquid phases.

22.4 × (273 + T)/273 (T in °C) and 1 mol of methane has a mass of 16 g, the produced methane volume is calculated as

$$\begin{aligned} V_{CH_4} &= 22.4 \times (273 + T)/273 \times M_{CH_4}/16 \\ &= 22.4(273 + T)/273(MS_{ti} - MS_{te} - MS_{xv})/64 \end{aligned} \tag{6.5}$$

where V_{CH_4} = first estimate of methane volume in the biogas (L/day); M_{CH_4} = mass of the produced methane (g/day); MS_{ti} = mass of applied COD (g/day); MS_{te} = mass of COD in the effluent (g/day); MS_{xv} = COD mass converted into volatile sludge (g/day).

Example 6.2

Determine the potential for per capita methane production from sewage by anaerobic digestion, making the following assumptions: (1) per capita organic matter production: 100 g COD/inh/day, (2) the organic material removal efficiency: 80%, (3) conversion into volatile solids: 10%.

Solution

From Equation (6.4):

$$\begin{aligned} M_{CH_4} &= (MS_{ti} - MS_{te} - MS_{xv})/4 \\ &= (100 - 20 - 10)/4 = 17.5\,\text{g}\,CH_4/\text{inh/day}. \end{aligned}$$

From Equation (6.5) at a temperature of 25°C:

$$\begin{aligned} V_{CH_4} &= 22.4 \times (273 + T)/273 \times M_{CH_4}/16 \\ &= 22.4 \times (273 + 25)/273 \times 17.5/16 \\ &= 26.7\,L_{CH_4}/\text{inh/day}. \end{aligned}$$

However, the estimated volume of the produced methane is not precise since part of the methane produced will remain dissolved in the liquid phase. The solubility of methane is low (as shown in Table 6.1) being the distribution coefficient $k_d = 0.03$. To make a first estimate of dissolved methane concentration can be assumed that biogas is composed by only methane. As 1 mol of methane (or any other gas) has a volume of 24.4 L at a temperature of 25°C and atmospheric pressure, its concentration is 1/24.4 mmol/L = 41 mmol/L. Now, applying Equation (6.1) for the case of having only methane in the biogas is: $C_s = 41 \times 0.03 = 1.2$ mmol/L = 20 mg/L. Thus, it is estimated that the dissolved methane is 20 mg CH_4/L. As is known that for producing 1 mg CH_4, about a mass of 4 mg of COD must be digested, it is estimated that a maximum of 80 mg COD/L will be found as dissolved methane after anaerobic digestion. This concentration is not negligible in the case of municipal sewage, which normally has a concentration of digestible COD in the range of 300–500 mg/L. In Example 6.2, for a per capita contribution of 120 L/day, methane loss in the effluent would be 0.020 g CH_4/L × 120 L/inh/day = 2.4 g CH_4/inh/day or 2.4/17.5 = 14%. So the best estimate of CH_4 production in the biogas would be M_{CH_4} = 17.5 − 2.4 = 15.1 g/inh/day, whereas the per capita volume is V_{CH_4} = 22.4 × (273 + 27)/273 × 15 1/16 = 23.1 CH_4/L/day. It is important to notice that as the temperature becomes lower, the digested COD becomes smaller and the dissolved methane concentration becomes higher. As a result, the dissolved fraction increases and may be as high as 50% in case with a low influent COD and a low temperature.

Example 6.3

Estimate the fraction of the produced methane that remains dissolved in a upflow anaerobic sludge blanket (UASB) reactor operating at a temperature of 15°C and a sludge age of 75 days, treating sewage with a COD of 500 mg/L in the influent.

Solution

The fractions of the influent COD which are discharged in the effluent (f_s) and transformed into sludge (f_x) can be estimated (from Equations (5.1) and (5.2)) as $f_s = 0.22$ and $f_x = 0.11$ (see also dos Santos, 2013). Hence, the digested fraction is $f_d = 1 - f_s - f_x = 0.67$. Therefore, the digested COD is $0.67 \times 500 = 330$ mg/L, equivalent to $330/4 = 82$ mg CH_4/L. On the contrary, at 15°C the solubility of methane in water at 15°C is ~23 mg/L ($k_d = 0.036$), so that a fraction of $23/82 = 28\%$ is retained in the liquid phase and 72% is released into the biogas. Figure 6.3 shows the methane fraction in the gas phase for different temperatures and influent COD concentration as a function of the sludge age.

To make a more accurate estimate of the biogas volume and the partial pressures of methane and other components in the biogas, it is necessary to apply an iterative calculation, taking into account also the contributions of other gases. Firstly, the contribution of each component will be individually evaluated and then the iterative calculation procedure will be applied.

6.4.2 Carbon dioxide

The presence of CO_2 in the biogas is due to its production in the anaerobic digestion process. It can be assumed that the CO_2 production in molar terms is equivalent to the methane production, considering an average carbon oxidation number close to zero for organic matter, accordingly with the elemental composition of sewage used for Example 6.1, but its presence in the gas phase is much smaller because of its greater solubility. The partial CO_2 pressure can be estimated from the equilibrium of the carbonic system:

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \tag{6.6a}$$

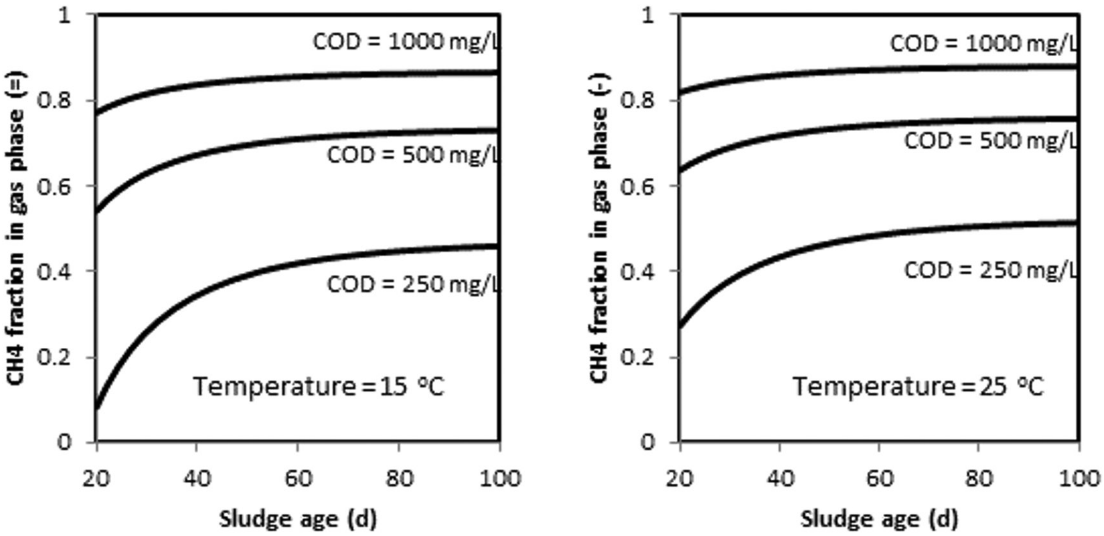


Figure 6.3 Fraction of the methane production that desorbs from the liquid phase as a function of the sludge age for different temperatures and influent COD concentrations.

or

$$\left[\mathrm{HCO_3^-}\right]\left[\mathrm{H^+}\right]/\left[\mathrm{CO_2}\right] = k_1 \qquad (6.6b)$$

or

$$\left[\mathrm{HCO_3^-}\right]\left[\mathrm{H^+}\right]/\left(k_d\left[\mathrm{CO_2}\right]_g\right) = k_1 \qquad (6.6c)$$

By applying Equation (6.3) this can also be written as

$$p_{\mathrm{CO_2}} = \left[\mathrm{HCO_3^-}\right]10^{(\mathrm{p}k_1+\mathrm{p}K_\mathrm{H}-\mathrm{pH})} \qquad (6.7a)$$

where $pX = -\log[X]$; k_1 = first dissociation constant of the carbonic system $= 4.6 \times 10^{-7}$; k_H = Henry constant for CO_2 = 0.034 mol/L/atm at 25°C; that is, $\mathrm{p}K_\mathrm{H} = 1.47$ (Loewenthal & Marais 1976).

Since at pH ≈ 7 the alkalinity is practically equal to the concentration of bicarbonate, Equation (6.7a) can also be written as

$$p_{\mathrm{CO_2}} = \mathrm{Alc.} \times 10^{(\mathrm{p}k_1+\mathrm{p}K_\mathrm{H}-\mathrm{pH})} \qquad (6.7b)$$

It is concluded that in the case of sewage treatment the CO_2 partial pressure will be low: for instance for an alkalinity of 350 ppm or 7 meq/L (normal for domestic wastewater) and a pH = 7.0 a partial pressure of only 0.04 at 25°C is calculated. The CO_2 pressure can be calculated provided there are data of alkalinity and pH, as well as for temperature. The presence of CO_2 in the biogas normally is not problematic. In contrast dissolved CO_2 in the liquid phase results in aggressive water, which can lead to serious concrete corrosion problems.

6.4.3 Water vapour

The pressure of water vapour is directly related to the temperature. At 25°C, the water saturation pressure is 23.7 mm of mercury (3.1 Pa), or at a pressure of 760 mm or 1.013 kPa partial pressure is 0.031. Table 6.2 shows some values of water vapour pressure for different temperatures. The presence of water vapour in the biogas can cause problems, particularly when the ambient temperature greatly varies. During periods of low ambient temperature, water may condensate in biogas piping, because the biogas is generated in the relatively warm liquid phase. The biogas will have water vapour at the pressure of the liquid phase in the reactor, but out of the treatment system the biogas temperature decreases and water vapour will tend to become supersaturated and condensate. Apart from causing blockages, the condensed water tends to cause corrosion problems, especially if hydrogen sulphide is also present in the biogas. For those reasons, there will usually be a condensate retention device in the biogas transport system, which may be the hydraulic seal of the UASB reactor, if located at the lowest point of biogas piping.

Table 6.2 Values of the saturation pressure of water vapour at different temperatures.

Temperature (°C)	Saturation Pressure		Temperature (°C)	Saturation Pressure	
	mm Hg	Partial Pressure		mm Hg	Partial Pressure
0	4.6	0.006	20	17.5	0.023
5	6.5	0.009	**25**	**23.7**	**0.031**
10	9.2	0.012	30	31.7	0.042
15	12.8	0.017	35	41	0.054

6.4.4 Nitrogen

In many cases, it may be assumed that wastewaters are saturated with atmospheric nitrogen (which has a partial pressure of 0.8 atm). In that case, the saturation concentration is 14.8 mg/L at 25°C (Table 6.1). If it is assumed that nitrogen is not produced or lost during anaerobic treatment, the influent nitrogen will leave the system in the biogas and in the effluent, thus from the mass balance:

$$Q_l C_a = Q_l C_s + Q_g C_g \tag{6.8a}$$

or

$$C_a = C_s + \left(Q_g / Q_l\right) C_g \tag{6.8b}$$

Hence

$$C_g = C_a / \left(k_d + \left(Q_g / Q_l\right)\right) \tag{6.8c}$$

and

$$C_s = k_d C_a / \left(1 + \left(Q_g / Q_l\right)\right) \tag{6.8d}$$

where C_a = nitrogen concentration in the influent; C_g = nitrogen concentration in the gas phase; Q_g/Q_l = ratio between the biogas and wastewater flow.

In order to calculate nitrogen in the effluent and in the biogas, it is necessary to know the concentration in the influent and the ratio of the flows of biogas and wastewater.

Example 6.4

For the conditions of Example 6.2 and having a per capita sewage contribution of 120 L/day, estimate the partial pressure of nitrogen on the biogas.

Solution

The concentration of nitrogen in the influent is estimated from the distribution constant ($k_d = 0.016$, Table 6.1). At a partial pressure of 0.8 bar, the concentration of nitrogen in the air is $41 \times 0.8 = 34$ mmol/L. Now the saturation concentration of nitrogen is calculated as

$$C_s = 0.016 \times 34 = 0.54\,\text{mmol/L and } C_a = 14.8\,\text{mg N/L}$$

Since $Q_g/Q_l = 26.7/120 = 0.22$ (Example 6.2), the nitrogen concentration in the biogas is

$$\begin{aligned} C_g &= C_a/\left(k_d + \left(Q_g/Q_a\right)\right) \\ &= 14.8/\left(0.016 + 0.22\right) = 63\,\text{mg/L or } 63/28 = 2.2\,\text{mmol/L.} \end{aligned}$$

Hence

$$C_s = k_d C_g = 0.016 \times 63 = 1.0\,\text{mg/L.}$$

The calculations indicate that nitrogen is efficiently removed by stripping in the anaerobic digester and almost all transferred to the gas phase, due to its very low solubility.

At a temperature of 25°C and a pressure of 1 bar the concentration of a gas is 41 mmol, so that when the nitrogen has a concentration of 2.2 mmol/L in the gas phase, its partial pressure is $2.2/41 = 0.05$ atm. Comparing the calculation results of the partial pressure of carbon dioxide, water and nitrogen (Sections 6.4.2 and 6.4.3), surprisingly it is observed that for anaerobic digestion of normal sewage in the produced biogas, the partial pressures for carbon dioxide, nitrogen and water vapour are all of the same order of magnitude.

6.4.5 Oxygen

Different from the case of nitrogen, the oxygen concentration in the influent is generally low, because microorganisms can consume the oxygen transferred from the atmospheric gas to the liquid phase of the bioreactor. Oxygen consumption can occur or not during the permanence of the wastewater in the sewerage network, but, in any case, its utilization by facultative hydrolytic and acidogenic bacteria in the anaerobic reactor will cause its rapid depletion. In case of feeding devices causing air dragging into the digester, it is possible to observe a reduction in methane production because the organic material will be selectively oxidized by oxygen and subtracted to methanogenesis. Therefore, it is important to avoid air dragging into the feeding system.

6.4.6 Ammonium

Ammonium is present in the influent and also generated in the anaerobic digester as a result of mineralization of organic nitrogen. In sewage normally the concentration is in the range of 40–60 mg N/L or 3–4 mmol/L. As in the case of nitrogen, ammonium is distributed between the gas and liquid phases. The ratio between the number of moles per day, leaving the system in the gas and liquid phases can be expressed as

$$N_g / N_e = \left(Q_g C_g\right) / \left(Q_l C_s\right) \tag{6.9a}$$

Combining the previous equation with Equation (6.1) it is obtained:

$$N_g / N_e = \left(Q_g / Q_l\right) / k_d \tag{6.9b}$$

where N_g and N_e = the number of moles of NH_3 in the biogas and in the effluent, respectively.
For a ratio of gas and liquid flows $(Q_g/Q_e) = 0.22$ from the previous example, and knowing the value of the distribution coefficient ($k_d \approx 0.7$ in Table 6.1) it is estimated that

$$N_g/N_e = 0.19/0.7 = 0.3$$

On the contrary, in the neutral pH range the fraction that gaseous ammonium (NH_3) in the liquid phase is small (1%, since $pK_{NH_3} = 9.1$ at 25°C); almost all ammonium (~99% at a neutral pH) is in the ionic form (NH_4^+). Therefore, the ammonium fraction in the biogas will be small of the order of 0.3% of the total ammonium mass in the system. Thus, for practical purposes it can be considered that ammonium practically remains in the liquid phase in anaerobic reactors. Even in concentrated wastes where ammonium and the ratio (Q_g/Q_l) are high, the ammonium fraction in the biogas remains low. For example, in the case of anaerobic digestion of manure or sludges, ammonium concentrations of $C_l = 3$ g N/L and $(Q_g/Q_l) = 3$ may be found, so that $N_g/N_l = 3/0.7 = 4.3$ and $N_g = 4.3N_l$. The NH_3 concentration in the effluent will be 1% of the total ammonium: $N_l = 0.03$ g/L and the concentration in the biogas $4.3 \times 0.03/3 = 0.043$ g/L = 3 mmol/L. This means that still almost all ammonium is in the liquid phase, but the partial pressure of ammonium is no longer negligible: $p_{NH_3} = 3/41 = 0.07$.

6.4.7 Hydrogen sulphide

Sulphate reduction by sulphate-reducing bacteria (SRBs) is a microbiological process, which occurs in anaerobic reactors and usually predominates over methanogenesis. Sulphate reduction in anaerobic systems may have advantages and disadvantages (Lens & Hulshoff Pol, 2000). Drawbacks are as follows:

(1) Hydrogen sulphide is a strong toxic gas, dangerous to human life at concentrations as low as 100 ppm in air.

(2) It has unpleasant odour of rotten eggs, detectable by nose at concentrations as low as 0.5 ppb, thus increasing odour problems in sewage treatment plants (STPs).
(3) At high concentrations, it is a toxic compound for methanogens and other microorganisms.
(4) It could cause the corrosion of concrete and steel of the infrastructure.
(5) Upon biogas combustion hydrogen sulphide may be converted into sulphuric acid, which corrodes metals in internal combustion engines.
(6) After combustion, it enters the atmosphere as sulphur dioxide, a harmful gas.
(7) Increased BOD and COD of the effluent because of the oxygen demand of sulphide.
(8) In the event of considerable presence of metals, inorganic sludge accumulation occurs in the form of precipitated sulphides.
(9) Deterioration of aerobic post-treatment (filamentous sludge, nitrification inhibition).

Among potential advantages that sulphate reduction can bring about are as follows:

(1) Removal of sulphate and biological transformation into sulphur and water recovery.
(2) Degradation of xenobiotic compounds that otherwise could not be removed biologically.
(3) Possibility of removal and recovery of heavy metals from the liquid phase.
(4) The precipitated metal sulphide may serve as granulation nucleus.

The sulphide generated in anaerobic reactors is physically distributed into three phases: (1) in the biogas, (2) in the anaerobic effluent and (3) in the emissions from the surface of anaerobic reactors or other points of escape. To prevent odour from spreading due to release of gas from the surface, anaerobic reactors can be covered while a partial vacuum (1–2 cm water column) applied by forced ventilation, which removes the gas phase including desorbing biogas. This mixture must be treated to remove hydrogen sulphide. In quantitative terms the mass of hydrogen sulphide in the contaminated air is small.

The formed sulphide in a digester is distributed among the three forms of reduced sulphur: dissolved hydrogen sulphide (H_2S), bisulphide (HS^-) and sulphide ions (S^{2-}) which can be estimated from the below chemical equilibrium:

$$H_2S \leftrightarrow HS^- + H^+ \leftrightarrow S^{2-} + 2H^+ \tag{6.10}$$

Hydrogen sulphide is a weak acid, as its dissociation constants are: $pK_1 = 7.0$ and $pK_2 = 14.0$. As the dissociation constants are known, the relative concentrations of the three species can be calculated. In Figure 6.4a, the profile distribution of sulphide, bisulphide and sulphide in water is plotted as a function of pH. Figure 6.4b shows the corresponding pH–pX diagram. It can be observed that in water

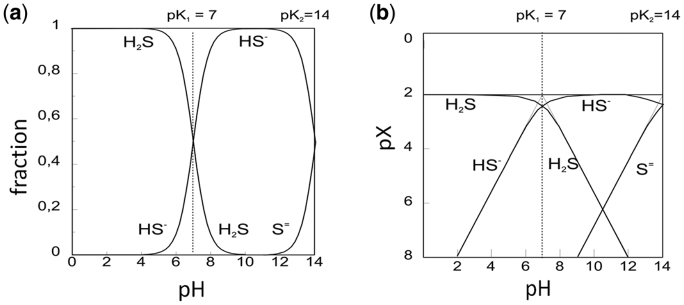


Figure 6.4 (a) Fractions of hydrogen sulphide, bisulphide and sulphide as a function of pH and (b) pX–pH plot for a sulphidric system (10 mmol/L of reduced sulphur).

the form of non-dissociated hydrogen sulphide prevails when the pH is below the neutral value. The form of sulphide ion (S^{2-}) only appears in a significant way when the pH is extremely high (pH >12).

The ratio of the concentration of dissolved hydrogen sulphide and dissociated bisulphide can be calculated by the below dissociation equation:

$$C_{\mathrm{be}}/C_{\mathrm{he}} = 10^{(\mathrm{pH}-\mathrm{p}K_1)} \tag{6.11}$$

where C_{be}, C_{he} = concentration of bisulphide and dissolved hydrogen sulphide in the effluent (and in the liquid phase of a digester).

Hydrogen sulphide gas, being a volatile compound, tends to establish an equilibrium between the fraction dissolved in the liquid phase (the content of a reactor) and the gas phase (biogas). When it is assumed that the biogas produced and the digester contents are in equilibrium according to Henry's law (Equation (6.1)), the concentration of hydrogen sulphide (H_2S without the dissociated forms HS^- and $S^=$) can be calculated as:

$$C_{\mathrm{s}} = \left(N_{\mathrm{he}}/Q_{\mathrm{e}}\right) = k_{\mathrm{d}}C_{\mathrm{g}} = k_{\mathrm{d}}\left(N_{\mathrm{g}}/Q_{\mathrm{g}}\right) \tag{6.12a}$$

or

$$N_{\mathrm{g}}/N_{\mathrm{he}} = \left(Q_{\mathrm{g}}/Q_{\mathrm{e}}\right)/k_{\mathrm{d}} \tag{6.12b}$$

where N_{he}, N_{g} = flux (daily number of moles) of H_2S in the effluent and the biogas.

Hence the ratio between the flows of H_2S in the biogas and in the effluent depends on two factors:

(1) the $Q_{\mathrm{g}}/Q_{\mathrm{l}}$ ratio and
(2) the value of the distribution coefficient.

In Figure 6.5 the division between species of sulphide has been plotted as a function of the $Q_{\mathrm{g}}/Q_{\mathrm{l}}$ ratio for different pH values in the liquid phase. It shows that the fraction of the sulphide that is in the biogas depends heavily on the $Q_{\mathrm{g}}/Q_{\mathrm{l}}$ ratio. In the case of wastewaters with a low concentration of organic material like sewage ($Q_{\mathrm{g}}/Q_{\mathrm{l}} \approx 0.2$) almost all sulphide remains dissolved, but in concentrated wastes ($Q_{\mathrm{g}}/Q_{\mathrm{l}} \approx 10$) a large fraction of sulphide migrates to the gas phase. The curves were built according to the following equations:

$$N_{\mathrm{be}}/N_{\mathrm{he}} = 10^{(\mathrm{pH}-\mathrm{p}K_1)}$$

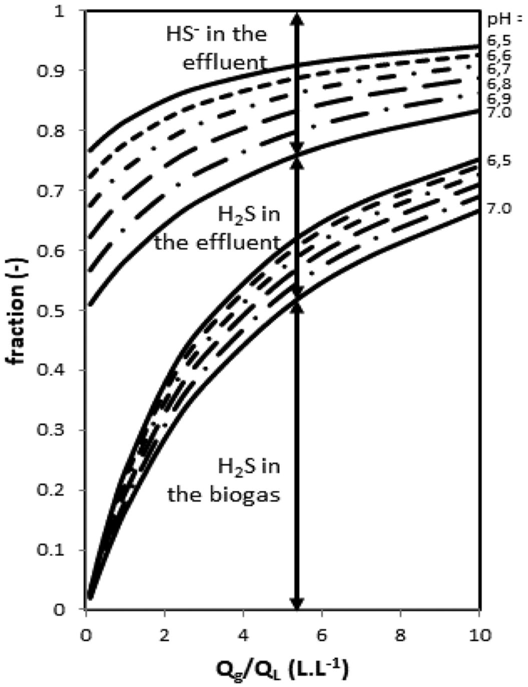
$$N_{\mathrm{g}}\,/\,N_{\mathrm{he}} = \left(Q_{\mathrm{g}}\,/\,Q_{\mathrm{e}}\right)/\,k_{\mathrm{d}}$$

$$\begin{aligned} N_{\mathrm{t}} &= N_{\mathrm{g}} + N_{\mathrm{he}} + N_{\mathrm{be}} \\ &= N_{\mathrm{g}} + N_{\mathrm{he}}\left(1+10^{(\mathrm{pH}-\mathrm{p}K_1)}\right)N_{\mathrm{he}}\left[\left(Q_{\mathrm{g}}/Q_{\mathrm{e}}\right)/k_{\mathrm{d}} + 1 + 10^{(\mathrm{pH}-\mathrm{p}K_1)}\right] \end{aligned}$$

$$N_{\mathrm{he}}\,/\,N_{\mathrm{t}} = 1/\left[\left(Q_{\mathrm{g}}\,/\,Q_{\mathrm{e}}\right)/\,k_{\mathrm{d}} + 1 + 10^{(\mathrm{pH}-\mathrm{p}K_1)}\right]$$

$$N_{\mathrm{g}}\,/\,N_{\mathrm{t}} = \left(Q_{\mathrm{g}}\,/\,Q_{\mathrm{e}}\right)/\,k_{\mathrm{d}}\,/\left[\left(Q_{\mathrm{g}}\,/\,Q_{\mathrm{e}}\right)/\,k_{\mathrm{d}} + 1 + 10^{(\mathrm{pH}-\mathrm{p}K_1)}\right]$$

$$N_{\mathrm{be}}/N_{\mathrm{t}} = 1 - \left(N_{\mathrm{g}}/N_{\mathrm{t}}\right) - \left(N_{\mathrm{he}}/N_{\mathrm{t}}\right)$$



.

$N_{be}/N_{he} = 10^{(pH - pK1)}$

$N_g/N_{he} = (Q_g/Q_e)/k_d$

$N_t = N_g+N_{he}+N_{be} = N_g+N_{he}(1+10^{(pH-pK1)})$

$N_{he}[(Q_g/Q_e)/k_d+1+10^{(pH - pK1)}]$

$N_{he}/N_t = 1/[(Q_g/Q_e)/k_d+1+10^{(pH-pK1)}]$

$N_g/N_t=(Q_g/Q_e)/k_d/[(Q_g/Q_e)/k_d+1+10^{(pH-pK1)}]$

$N_{be}/N_t = 1- (N_g/N_t) – (N_{he}/N_t)$

$N_e/N_t = (N_{be}+N_{he})/N_t =$

$=(1+10^{(pH-pK1)})/[(Q_g/Q_e)/k_d+1+10^{(pH-pK1)}]$

Where:

N_t = total number of reduced sulphur moles

N_g = H_2S in biogas

N_{he} = H_2S in the effluent

N_{be} = HS^- in the effluent

Figure 6.5 Fraction of the sulphide species as a function of the Q_g/Q_l ratio for different pH values.

$$\begin{aligned} N_e/N_t &= \left(N_{be}+N_{he}\right)/N_t \\ &= \left(1+10^{(pH-pK_1)}\right)/\left[\left(Q_g/Q_e\right)/k_d+1+10^{(pH-pK_1)}\right] \end{aligned}$$

where N_t = total number of reduced sulphur moles; N_g = H_2S in biogas; N_{he} = H_2S in the effluent; N_{be} = HS^- in the effluent.

Example 6.5

For the conditions of Examples 6.2, estimate the fraction of the generated hydrogen sulphide gas remaining in the effluent when the sulphate concentration in the influent is 20 mg S/L and all sulphate in a digester is reduced.

Solution

It was estimated that the ratio $(Q_g/Q_l) = 23/120 = 0.19$ and for a distribution coefficient $k_d = 2.5$ (Table 6.1) it is calculated that:

$$N_g / N_e = \left(Q_g / Q_e\right) / k_d = 0.19 / 2.5 = 0.08$$

Therefore, the number of moles of hydrogen sulphide in the biogas is 8% of the number of H_2S moles in the effluent. On the contrary, in the liquid phase the pH is approximately neutral, so that there is a partial dissociation of the hydrogen sulphide gas to bisulphite:

$$H_2S \leftrightarrow HS^- + H^+ \left(pK_1 = 7 \text{ at } 25°C\right)$$

For pH = 7, the number of moles of dissolved hydrogen sulphide will be equal to the number of moles of disulphide. Thus the fraction of hydrogen sulphide in the biogas is estimated as:

$$\begin{aligned} f_g &= N_g/N_t = N_g/\left(N_g + 2N_e\right) \\ &= N_g/N_e/\left(N_g/N_e + 2\right) = 0.08/2.08 = 0.04 \end{aligned}$$

and

$$f_l = 1 - f_g = 0.96$$

Therefore, for a generated sulphide concentration in the digester of 20 mg S/L, the concentration of sulphide in the effluent will be 20 × 0.96 = 19.2 mg/L. The concentration of hydrogen sulphide in the biogas $C_g = C_s/k_d = 0.5 \times 19.2/2.5 = 3.8$ mg/L or 3.8/32 = 0.12 mmol/L. As in the biogas total concentration of the components is 41 mmol/L, the partial pressure of hydrogen sulphide is $p_{H_2S} = 0.12/41 = 0.003$.

Example 6.6
For the conditions of Example 6.4 but with a ratio $Q_g/Q_l = 10$, estimate the fraction of the hydrogen sulphide gas which remains in the effluent generated when the sulphate concentration in the influent is 20 mg S/L and all the sulphate in the digester is reduced (pH = 6.8).

Solution
For $(Q_g/Q_a) = 10$ and a distribution coefficient $k_d = 2.5$ (Table 6.1) it is calculated that

$$N_g / N_l = (Q_g / Q_l) / k_d = 10 / 2.5 = 4$$

Hence, the number of moles per day in the biogas is four times larger than the number in the effluent. On the contrary, for pH = 6.8 with Equation (6.10): $N_{be} = 0.63N_{he}$ and one can estimate the fraction of sulphide ions in the biogas as

$$\begin{aligned} f_g &= N_g / N_t = N_g / \left(N_g + 1.63N_l\right) \\ &= \left(N_g / N_l\right) / \left(N_g / N_l + 1.63\right) = 4 / \left(4 + 1.63\right) = 0.70 \end{aligned}$$

and

$$f_l = 1 - f_g = 0.30$$

Hence, for a generated sulphide concentration of 20 mg S/L in the digester, the concentration of sulphide in the effluent will be 20 × 0.3 = 6 mg/L. The concentration of hydrogen sulphide in the biogas is: $C_g = C_s/k_d = 0.5 \times 6/2.5 = 1.2$ mg/L or 1.2/32 = 0.04 mmol/L. As the total concentration is 41 mmol/L in the biogas, the partial pressure of hydrogen sulphide is $p_{H_2S} = 0.04/41 = 0.001$.

Note that much more H_2S is stripped from the liquid phase than in Example 6.5 (70% against 4%), but the partial pressure is actually smaller (0.001 vs 0.003), that is, the biogas is 'cleaner' because there is so much more methane and carbon dioxide produced.

Although some production of sulphide may be occurred due to the mineralization of proteins, generally the major part comes from sulphate reduction by organic material:

$$8e + 8H^+ + SO_4^{2-} \rightarrow S^{2-} + 4H_2O$$

In this half reaction, sulphate acts as an oxidant in the oxidative catabolic reaction in a similar way to oxygen in an aerobic environment:

$$4e + 4H^+ + O_2 \rightarrow 2H_2O$$

It is concluded that 1 mol of sulphate (32 g) has the same oxidation capacity as 2 mol of oxygen (64 g), that is, 1 g of sulphur in the sulphate form is equivalent to 2 g of oxygen and can therefore oxidize 2 g of COD, when it is reduced to hydrogen sulphide. As 2 g of COD have the potential of producing 0.5 g CH_4 it follows that, per mg of formed sulphide, there is a reduction of methane production of 0.5 mg.

The sulphate concentration in natural waters and therefore in municipal wastewater, varies widely from <10 mg S/L to more than 100 mg S/L. This has a very important effect on anaerobic treatment: not only is the methane production potential is half reduced, but the concentration of hydrogen sulphide in the biogas will increase, making its productive use more complicated. The presence of hydrogen sulphide in the liquid phase is not only potentially toxic to methanogens, but the sulphide in the effluent is also toxic to many aquatic organisms and consumes oxygen in the oxidation of sulphur to sulphate, which may reduce the dissolved oxygen in the receiving water body. Thus, the post-treatment of the effluent to remove or reduce sulphide concentration is usually necessary when the sulphate concentration in sewage is high. The recovery of sulphur from the effluent may be interesting if water must be reused in industrial processes such as cellulose pulp production.

6.5 ITERATIVE CALCULATION PROCEDURE FOR BIOGAS PRODUCTION AND COMPOSITION

In the previous sections, estimates were made of the partial pressure of different components of biogas. In these preliminary calculations there are two flaws: (1) it was tacitly admitted that the methane fraction in the biogas was very high and (2) it was supposed sulphide formation did not have a significant effect on the methane production potential. In this section, an iterative calculation procedure is developed that corrects these inaccuracies, considers the fraction of methane in the biogas is variable and accounts that a considerable oxidation of the organic material by sulphate reduction instead of methane production can occur. This requires iterative calculations according to the below procedures. One can distinguish essentially two cases: (1) the sulphate concentration is low and its reduction does not significantly affect the methane production or (2) the sulphate concentration is high and has a significant effect on the entire process of anaerobic digestion.

Some waters have naturally a much higher sulphate concentration (e.g. >100 or even >300 mg S/L and this may seriously limit the applicability of anaerobic digestion of sewage. Another source of high sulphate may be infiltration of sea water that sometimes may occur.

6.5.1 Low-sulphate concentration

In this case, it is not necessary to consider the reduction in methane production due to oxidation of organic material by sulphate, which simplifies the calculations. The iterative calculation procedure for estimating the biogas composition is as follows (data of Examples 6.2, 6.4 and 6.5):

(a) New estimate of the biogas composition
Having estimated the partial pressures of CO_2 (0.04), H_2O (0.03) and N_2 (0.06), a new estimate can be made of the methane pressure. In the previous examples:

$$p_{CH_4} = 1 - p_{CO_2} - p_{H_2O} - p_{N_2} = 1 - 0.04 - 0.03 - 0.06 = 0.87 \qquad (6.13)$$

(b) New estimate of the methane production in the biogas
The new estimate of the methane partial pressure leads to a new estimate of the dissolved methane in the liquid phase. In the example above the partial pressure was 0.87 and the

methane gas concentration in the biogas is now 0.87 × 41 = 36 mmol/L, whereas the saturation concentration in the liquid phase will be $C_s = 0.03 \times 36 = 1.08$ mmol/L or 17 mg/L. Therefore, the COD concentration of digested organic material, which is found as dissolved methane in the liquid phase, is 4 × 17 = 68 mg COD/L. For a per capita contribution of 120 L/day, a mass of 68 × 120 = 8160 mg COD/day, equivalent to $M_{CH_4} = 8.16/4 = 2$ g CH_4/day, remains in the effluent. Moreover, for the assumed sulphate concentration of 20 mg S/L, the oxidation of 2 × 20 = 40 mg COD/L or 0.04 × 120 = 4.8 g COD/day is used for sulphate reduction, which reduces the production of methane by 4.8/4 mg CH_4/L or 1.2 g CH_4/day. Therefore, the mass of methane in the biogas can now be expressed as:

$$\begin{aligned} M_{CH_4} &= \left(MS_{ti} - MS_{te} - MS_{xv} - MS_{CH4d} - MS_{oxi}\right)/4 \\ &= \left(100 - 20 - 10 - 8.2 - 4.8\right)/4 = 57/4 = 14.25\,\text{g}\,CH_4/\text{inh/day} \end{aligned} \tag{6.14a}$$

The new volume can now be calculated, duly not accounting the dissolved methane and the methane, which is not produced due to oxidation of organic material by sulphate:

$$\begin{aligned} V'_{CH_4} &= 22.4 \times \left(273 + t\right)/273 \times M_{CH_4}/16 \\ &= 22.4\left(273 + t\right)/273 \times 14.25/16 = 23.2\,\text{L/inh/day} \end{aligned} \tag{6.14b}$$

(c) New estimate of the biogas/effluent flow ratio
Once the new estimates of the methane flow and partial pressure are obtained, the biogas/effluent flow ratio, Q_g/Q_a, can be calculated as

$$Q_g = V'_{CH_4}/p_{CH_4} = 23.2/0.87 = 26.7\,\text{L/inh/day} \tag{6.14c}$$

and

$$Q_g/Q_l = 26.7/120 = 23.8/0.87/120 = 0.22\,\text{L/L} \tag{6.14d}$$

(d) New estimate of the partial pressure of nitrogen
Having a new estimate for the Q_g/Q_l ratio, the new values for the partial pressure of nitrogen is obtained, using the same procedure as in Example 6.3:

$$p_{N_2} = C_a/\left(k_d + \left(Q_g/Q_l\right)\right)/28/41 = 0.05$$

(e) Compare the recalculated value of the composition and flow of the biogas with the values obtained in the previous iteration.
Knowing that the values of the partial pressures of CO_2 (=0.04) and H_2O (=0.03) remain the same because they depend only on the pH + alkalinity and the temperature respectively, the new values of the partial pressure of CH_4 (=1 − 0.04 − 0.03 − 0.05 = 0.87) and the biogas volume (=26.7 L/inh/day) are now compared with the values of the previous iteration (1 and 26.7 L/inh/day respectively). It can be observed that these values are different and, for this reason, a new calculation cycle is repeated from steps (a) to (d) and this procedure iterated until the calculated values of two successive iterations are very close, that is, different only for an established acceptable error.

(f) Continue iteration calculations until a constant value is obtained for the variables
Normally, two or three iterations are sufficient. Table 6.3 shows a series of iterative calculations relative to the data of Examples 6.2 and 6.4. It can be noted that the values become constant after the third iteration (bold), when four decimal numbers are used. The values of the partial pressures of CH_4 and N_2 show the slowest convergence.

Table 6.3 Interactive calculations to establish the values of the volume and composition of biogas if there is little sulphate reduction.

Iteration	p_{CH_4}	M_{CH_4}	Q_g	Q_g/Q_a	p_{N_2}
0	1	17.5	26.6875	0.222396	0.052616
1	0.8732	14.2500	21.7313	0.2074	0.0562
2	0.8697	14.2500	21.7313	0.2082	0.0559
3	**0.8699**	**14.2500**	**21.7313**	**0.2082**	**0.0560**
4	0.8699	14.2500	21.7313	0.2082	0.0560

A_q = 120 L/inh/day, temp = 25°C, MS_{inh} = 100 g COD/day (70% digestion), methane production = 17.5 g CH_4/inh/day, p_{CO_2} = 0.04, p_{H_2O} = 0.03.

6.5.2 High-sulphate concentration

When the sulphate concentration is high, the methane production is affected because the organic material will be preferentially oxidized. In that case, the above iterative calculation procedure is extended in two aspects:

(a) Methane production is now estimated by decreasing the availability of organic material for anaerobic digestion of 2 mg COD/mg S. For example, at a concentration of 100 mg/L of SO_4–S or 120/1000 × 100 = 12 g S/inh/day:

$$V''_{CH_4} = 22.4(273+T)/273(MS_{ti} - MS_{te} - MS_{xv} - 2MS_{SO_4})/64$$
$$= 24.6 \times (100 - 20 - 10 - 2 \times 12) = 17.7\ \text{L/inh/day}.$$

(b) Part of the formed hydrogen sulphide will pass to the gas phase, but the magnitude of this part depends on the ratio between the established biogas flow and the effluent flow. Figure 6.4 clearly shows that the fraction of hydrogen sulphide in the biogas depends on Q_g/Q_l ratio and pH. Once the sulphide fraction which migrates to the gaseous phase is established, the volume and the partial pressure of hydrogen sulphide can be calculated as well as the concentration of this component in the effluent.

Example 6.7

Estimate for the data in previous examples the production of methane and biogas and the residual sulphide concentration in the liquid phase as a function of the sulphate concentration over the range from 0 to 200 mg S/L.

Solution

For each sulphate concentration, the problem requires an iterative calculation procedure that consists of the following steps:

(1) Initially, it is assumed that the sulphate is converted to sulphide, the organic material demand to effect this redox process is estimated and the corresponding reduction in methane production is calculated (column 2 of Table 6.4):

$$MS_{oxid} = 2MSO_4$$
$$MS_{CH_4tot} = (MS_{ti} - MS_{te} - MS_{xv} - MS_{oxid})/4$$

In reality, this estimate is imperfect because SRBs will grow and in this anabolic process SRBs, being heterotrophic, use organic material. At high-SO_4 concentrations, this growth will not be insignificant because oxidative catabolism occurs, which generates much energy and thus anabolism is considerable.

(2) Estimate the partial pressure of methane in the biogas using the values of the partial pressures of CO_2, H_2O, N_2 and H_2S. For N_2 and H_2S this will require an iterative calculation procedure.
(3) Estimate the methane mass in the effluent as the difference between the total methane production and the mass that is transferred to the gaseous phase (column 4):

$$\mathrm{MS}_{\mathrm{CH_4,efl}} = \mathrm{MS}_{\mathrm{CH_4tot}} - p_{\mathrm{CH_4}} \times 0.020 \times 120$$
$$\mathrm{MCH}_{4,\mathrm{efl}} = \mathrm{MS}_{\mathrm{CH_4,efl}} / 4$$

(4) Estimate the methane volume corresponding to the daily mass of the produced methane in the gas phase (column 5):

$$V_{\mathrm{CH_4}} = 22.4(273+t)/273\left(\mathrm{MS}_{\mathrm{CH_4tot}} - \mathrm{MS}_{\mathrm{CH_4,efl}}\right)/64$$

(5) With the aid of the estimates of the pressure and volume of methane, calculate the ratio between the gas and liquid flows, Q_g/Q_l (column 6):

$$Q_g / Q_l = \left(V_{\mathrm{CH_4}} / p_{\mathrm{CH_4}}\right) / Q_l$$

(6) Obtaining the Q_g/Q_l ratio, calculate the partial pressure of nitrogen and hydrogen sulphide (columns 7 and 8).
(7) Knowing that the partial pressures of CO_2 and water vapour do not depend on the flow of biogas, calculate the partial pressure of these two components.
(8) Now, having the estimates for the partial pressures of CO_2, H_2O, N_2 and H_2S calculate a new estimate for the partial pressure of CH_4.
(9) With the aid of the new $p_{\mathrm{CH_4}}$, for each sulphate concentration repeat steps 2–8 until the same result is obtained in two consecutive iterations. At the end of each iterative calculation the flow and composition of the biogas are obtained.

Table 6.4 shows the results of the iterative calculations for different sulphate to sulphide conversions. Figures 6.6 and 6.7 are graphical presentations of Table 6.4. When analysing the values in Table 6.4 and Figures 6.6 and 6.7, the dramatic influence of sulphate reduction on the production of methane and biogas composition can be noted: the mass of the produced methane is reduced by a factor of 4 when the concentration of sulphate is increased from 0 to 200 mg S/L. For the admitted values of 100 g COD/inh/day and a per capita volume of 120 L/day the calculated COD of the influent is 100/120 = 0.833 g/L and a biodegradable concentration of 0.7 × 833 = 583 (70% efficiency). The data indicate that for a ratio S-SO_4/COD in the influent greater than 200/583 ≈ 1/3 mg S/mg COD methane production is not feasible, which has also confirmed by the practical experience. Under these conditions, all the organic material is used for sulphate reduction.

As for the estimation of concentration of hydrogen sulphide in the liquid phase, firstly the mass of sulphur in the biogas is calculated: for fixed influent concentration of 200 mg S/L, the partial pressure of H_2S is 0.0275 and the concentration in the gas is 41 × 0.0275 = 1.15 mmol/L or 37 mg/L biogas. The ratio biogas/influent flow rate is $Q_g/Q_l = 0.048$ (column 6 of Table 6.4), thus the daily production per capita is 0.048 × 120 = 5.8 L/inh/day with a sulphur mass of 37 × 5.8 = 213 mg S/day. This is <1% of the influent sulphur mass (calculated by 213/(120 × 200)). For this reason, the mass of sulphur in the effluent, in good approximation, will be equal to the mass of sulphide generated in the anaerobic reactor or present in influent: 200 mg S/L. The concentration of 200 mg/L in the effluent will produce bisulphide and hydrogen sulphide gas. For a pH = 7.0 this ratio is equal, that is, $C_{\mathrm{H_2Se}} = C_{\mathrm{HS^-}} = 100$ mg/L. The concentration of hydrogen sulphide in the effluent and the reactor is very high: many researchers (Buisman & Lettinga, 1990; Rinzema, 1988) have shown that a

Table 6.4 Estimates of the production of biogas and the partial pressures of methane, nitrogen and hydrogen sulphide as functions of the reduced sulphate concentration for the same suppositions as in Table 6.3.

1	2	3	4	5	6	7	8
$SO_4^=$ mg S/L	MS_{CH_4tot} g/inh/day	p_{CH_4} (dimensionless)	MS_{CH_4g} g/inh/day	V_{CH_4} L/inh/day	Q_g/Q_a (dimensionless)	p_{N_2} (dimensionless)	p_{H_2S} (dimensionless)
0	17.5	0.873	15.40	23.54	0.1962	0.0569	0.0000
20	16.3	0.866	14.22	21.73	0.1811	0.0613	0.0026
40	15.1	0.858	13.04	19.93	0.1661	0.0663	0.0053
60	13.9	0.849	11.86	18.12	0.1510	0.0723	0.0079
80	12.7	0.840	10.68	16.33	0.1361	0.0794	0.0106
100	11.5	0.828	9.51	14.53	0.1211	0.0881	0.0134
120	10.3	0.815	8.34	12.75	0.1063	0.0988	0.0161
140	9.1	0.798	7.18	10.98	0.0915	0.1123	0.0189
160	7.9	0.778	6.03	9.22	0.0768	0.1301	0.0217
180	6.7	0.751	4.90	7.48	0.0624	0.1541	0.0246
200	5.5	0.714	3.79	5.79	0.0482	0.1881	0.0275

concentration of 100 mg/L H_2S severely inhibits methane production in anaerobic digesters. Thus, the production of methane could be even less than the calculations indicate since it was evaluated without considering the toxic effect of hydrogen sulphide gas.

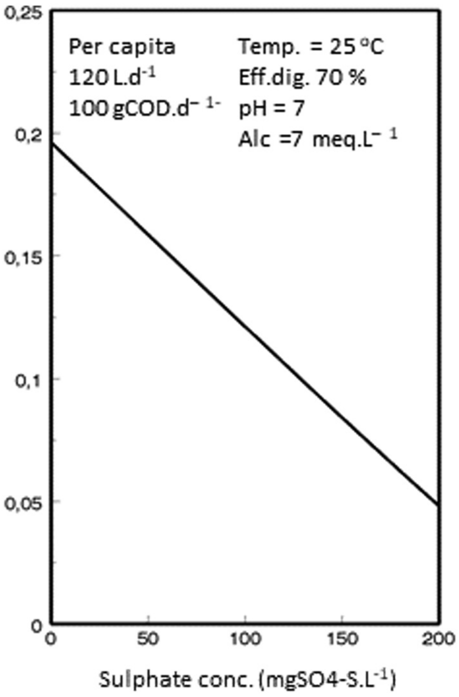


Figure 6.6 Influence of the sulphate concentration on the biogas production (see also Table 6.4).

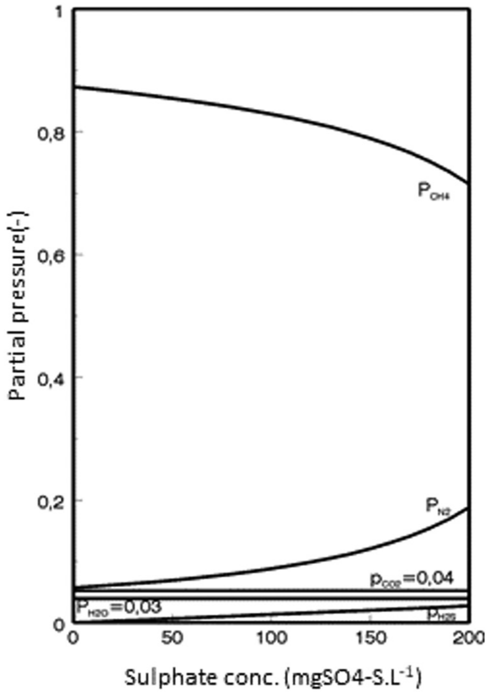


Figure 6.7 Influence of the sulphate concentration (reduced to sulphide) on production and composition of biogas (see also Table 6.4).

Example 6.8

A system composed of two UASB reactors, with a total volume of 7500 m^3 treats municipal sewage. The water supply system is precarious and for that reason, the population tends to use also ground water, which is very rich in sulphate (1 g/L). As a result the average concentration of sulphate in the sewage is 200 mg/L (as $SO_4^=$) or 67 mg S/L. Table 6.5 shows operational data. Evaluate the influence of sulphate on the methane production.

Solution

To estimate the effective production of biogas, it must be considered that the organic material of the influent is distributed into four fractions in the UASB reactor:

(1) not removed and released into the effluent
(2) transformed into volatile solids and released as such in excess sludge
(3) oxidized in the redox process with sulphate reduction
(4) digested forming methane.

Therefore, one can calculate the methane production potential as:

$$CH_4 = S_d / 4 = \left(S_{ti} - S_{te} - S_{xv} - S_{ox}\right) / 4 \qquad (6.15)$$

where CH_4 = mass of the produced methane per L of influent (mg CH_4/L); S_d = concentration of digested COD (mg COD/L); S_{ti} = influent COD concentration (mg COD/L); S_{te} = effluent COD

Table 6.5 Operational data of an anaerobic treatment system for sewage with 200 mg/L of sulphate in the influent.

Variable	Unit	Value
Population	Inh	90,000
Flow	m^3/day	9000
Organic load	kg COD/day	6300
Influent COD concentration	mg/L	650
Effluent COD concentration	mg/L	307
Sludge production	kg TSS/day	1200
Volatile fraction in the sludge	mg SO_4/L	0.67
Sulphate in the effluent		≈0

concentration (mg COD/L); S_{xv} = COD transformed into volatile sludge in the UASB reactor (mg COD/L); S_{ox} = oxidized COD by sulphate (mg COD/L).

If there is 200 mg SO_4^{2-}/L or 200/3 = 67 mg S-SO_4^{2-}/L in the influent, with an oxidation capacity of 2 × 67 = 133 mg COD/L, it can prevent the production of 133/4 = 33 mg CH_4/L.

The S_{xv} concentration is estimated knowing that 1 g of volatile sludge has a COD of ~1.5 g. According to Table 6.5, there is a production of 1200 kg Total Suspended Solids (TSS) sludge per day for an organic load of 6300 kg COD/day. Table 6.5 also shows that the anaerobic sludge has a volatile fraction of 2/3 so that the sludge production, in terms of Volatile Suspended Solids (VSS), is 2/3 × 1200 = 800 kg VSS/day, representing 1.5 × 800 = 1200 kg COD/day. As the applied load is 6300 kg COD/day the COD incorporated into the sludge is a fraction of 1200/6300 = 0.19 of the COD input, so it accounts for 0.19 × 650 = 124 mg/L. In the absence of sulphate in the influent, the expected anaerobic sludge production would be lower, since the sludge yield coefficient generated from the sulphate reduction is much greater (due to the oxidative catabolism).

Hence, the methane production can now be calculated as:

$$\begin{aligned} CH_4 &= S_d/4 = \left(S_{ta} - S_{te} - S_{xv} - S_{ox}\right)/4 \\ &= \left(650 - 307 - 124 - 133\right)/4 = 86/4 = 22\,\text{mg}\,CH_4/L \end{aligned}$$

However, not all of the methane produced will desorb: methane solubility in water is ~20 mg/L when the partial pressure of methane in the gas phase is 1 atm. Therefore, in that case the concentration of methane that could desorb is only:

$$CH_{4g} = CH_4 - 20 = 22 - 20 = 2\,\text{mg/L}$$

Knowing that the density of methane is ~2/3 kg CH_4/m^3, the produced methane is calculated:

$$V_{CH_4} = 1.5 \times CH_{4g} = 3\,\text{mL}_{CH_4}\,/\,\text{L influent.}$$

It can be concluded that there is practically no biogas production, not only due to the direct cause, the oxidation of organic material by sulphate, but also due to indirect reasons. The first one is that organic material is also lost to the higher sludge production. Another indirect effect of the presence of sulphate and the consequent reduction of biogas production is that the mixing of the bioreactor is reduced because the contribution of rising biogas bubbles is absent. The generation of biogas is actually the main driver of the reactor mixing and facilitates uniform distribution of influent organic material and contact between the biomass and the substrate. Since there is no contribution of biogas to mix

Table 6.6 Comparison between the performance of UASB reactors treating sewage with and without the presence of 67 mg S-SO_4^{2-}/L in the influent, assuming 100% SO_4 conversion.

Mass of COD	Sulphate: 67 mg S/L		No Sulphate		Assumptions
	kg COD/day	Fraction	kg COD/day	Fraction	
In the influent	6300	1	6300	1	
In the effluent	2980	0.47	1575	0.25	Efficiency = 75%
In the sludge	1200	0.19	630	0.10	Sludge production = 10%
Dissolved CH_4	720	0.11	720	0.11	20 mg/L of CH_4
Oxidized	1200	0.19	0	0.00	2 kg COD/kg S
In the biogas	200	0.03	3375	0.54	
Methane mass (kg/day)	50		844		0.25 kg CH_4/kg COD
Vol CH_{4g} (m^3/day)	75		1265		1.5 m^3/kg CH_4
Electric energy (kW)	10		169		0.2 kW/(kg CH_4/day)

the reactor and thus to improve the contact between sludge mass and incoming organic material, it is conceivable that preferential channels will be formed, resulting in hydraulic short circuits. Under these conditions the fraction of the sludge present in stagnant zones receives little substrate and operates below its full capacity, whereas in other zones, where the flow of the liquid phase is accelerated, overload can occur. Both features tend to give a reduction of the organic material removal efficiency and particularly of methanogenesis. On the contrary, the concentration of 67 mg/L of sulphide itself can be toxic for methanogens, especially if the pH is slightly reduced, which again would lead to a decrease of methanogenic activity.

It is concluded that the presence of 200 mg/L of sulphate has a disastrous effect on the efficiency of anaerobic sewage digesters. The problems extend beyond the performance of UASB reactors: post-treatment in either polishing ponds or aerobic reactors is very complicated. The high-sulphide concentration makes algae growth in polishing ponds almost impossible and exerts a large oxygen demand in aerobic reactors, thus increasing energy consumption. In fact, if aerobic post-treatment is applied, it would be preferable not to use the first anaerobic step and apply the aerobic treatment directly to the influent.

Table 6.6 and Figure 6.8 show the dramatic influence of a high-sulphate concentration on anaerobic sewage treatment. Although without sulphate at least 65% of the influent COD is converted into methane with 11% remaining as dissolved methane in the liquid phase, with the high-sulphate concentration there is virtually no biogas production.

6.6 TREATMENT OF SULPHIDE PRODUCED IN ANAEROBIC DIGESTERS

It is apparent from Figure 6.8 that the division of reduced sulphur mass depends primarily on the ratio Q_g/Q_l and also on the pH in the digester. As the ratio Q_g/Q_l depends on the concentration of the influent organic matter, this will be the main factor that determines whether the generated sulphide is found predominantly in the liquid phase or in the gas phase. Depending on the organic load, it can be necessary to remove the sulphide from the biogas or the effluent. These two alternatives will be discussed below. The removal of sulphide from contaminated gas above the liquid surface in the digester is also discussed. Figure 6.9 shows schematically the auxiliary units of the anaerobic digester to treat reduced sulphur that is generated in the anaerobic reactor. For the treatment of biogas three methods are distinguished: biological (Lin *et al.*, 2018), physical and chemical (Zhang & Zhang, 2002). For removal of sulphide in the liquid phase the same methods can be applied.

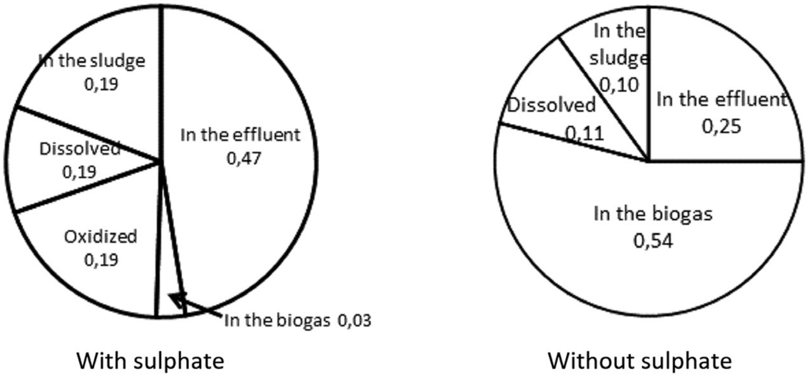


Figure 6.8 Distribution of the influent COD in different fractions with (left) and without (right) sulphate.

6.6.1 Sulphide in biogas

The most widely applied unit for hydrogen sulphide removal from biogas is probably the Thiopaques process in which the hydrogen sulphide is transformed into elemental sulphur. The process consists of three steps (see Figure 6.9):

(1) In a counter current scrubber the biogas is placed in contact with an alkaline solution and the H_2S in the biogas is absorbed and dissociates:

$$H_2S + OH^- \rightarrow HS^- + H_2O \tag{6.16a}$$

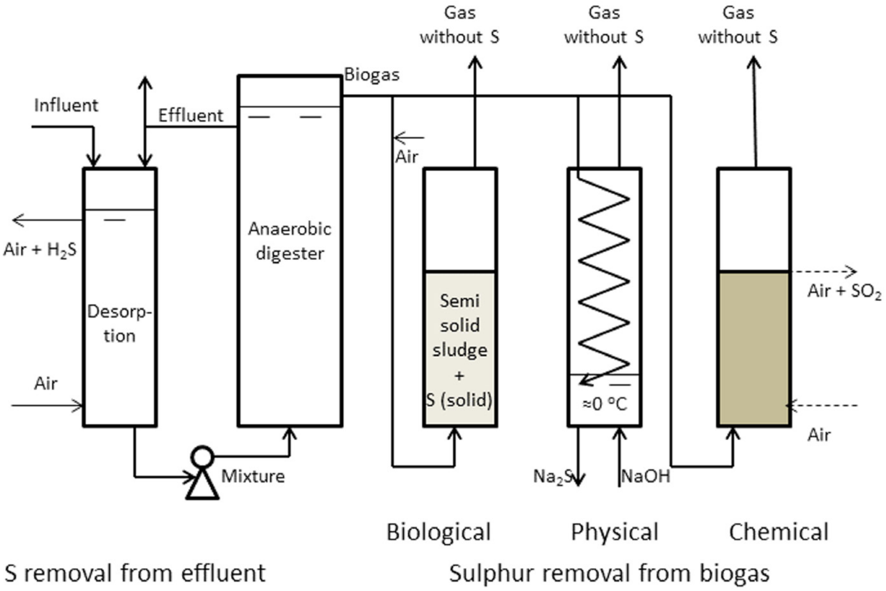


Figure 6.9 Schematic representation of an anaerobic digestion system with possible auxiliary units for sulphide removal from biogas.

(2) In a biological unit and a controlled aerobic environment HS^- is oxidized to sulphur:

$$HS^- + 0.5O_2 \rightarrow S\downarrow + OH^- \tag{6.16b}$$

(3) The solid sulphur is separated from the liquid phase and becomes available as a nutrient or raw material.

An alternative to remove smaller quantities of hydrogen sulphide in biogas is to add a small amount of oxygen to the mixture of biogas and then pass it through a unit operated with attached sulphide-oxidizing bacteria able to convert aerobically the H_2S in the biogas into sulphur. Physically, this biological unit can be located in the biogas accumulation zone above the liquid phase in the digester. This option is sometimes used for cleaning biogas in manure digesters, where biogas may be used directly to power generators for electricity production. Support media with a rough surface and high superficial area for better adhesion of biomass are employed for biogas treatment. The sulphide absorbed onto the solid surface accommodating the biomass will be oxidized by oxygen.

The formed sulphur accumulates onto the solid surface and occasionally chunks of sulphur fall off and can be withdrawn for use of recovered sulphur or mixed with the effluent for agricultural reuse. Care must be taken not to add too much oxygen since it can make a potentially explosive mixture with the biogas when the volumetric ratio O_2/CH_4 is above 1:15–1:20. It is worth noting that the oxygen demand for the sulphide removal from the biogas is much smaller than this critical ratio.

To inoculate biomass for the process, the solid surface can be covered with liquid manure, which always contains bacteria that oxidize hydrogen sulphide. The size of the hydrogen sulphide oxidation unit is small relative to the size of the digester. For a 1000 m^3 digester, just a few square metres are enough to remove the hydrogen sulphide in the biogas.

Physical removal of sulphides is possible because the hydrogen sulphide solubility in water increases with decreasing temperature. When the water vapour in the biogas has to be removed, the biogas may be cooled to $\sim 0°C$: condensation of water will occur and hydrogen sulphide from the biogas will tend to dissolve in the formed liquid phase. To facilitate this dissolution, alkalinity is added to the condensed water. This alternative is attractive in regions with a cold climate, where ambient temperature is low for most of the year.

In the chemical removal process (iron sponges process) the principle of operation is based on the reaction between iron oxide and hydrogen sulphide producing ferrous sulphide. In a reactor with partially oxidized iron filings the following reaction occurs:

$$FeO + H_2S \rightarrow FeS + H_2O \tag{6.17a}$$

When the removal capacity is exhausted, due to the conversion of ferrous oxide to ferrous sulphide, it can be regenerated by oxidation with air as indicated in Figure 6.10:

$$FeS + 3/2O_2 \rightarrow FeO + SO_2\uparrow \tag{6.17b}$$

Other oxidants may also be used for chemical treatment of the biogas, for example hypochlorite solutions, but in these cases, regeneration is usually not possible.

6.6.2 Sulphide removal from the effluent

The methods employed to remove hydrogen sulphide from the effluent, as already mentioned, are biological, physical or chemical. A biological method consists of the oxidation of sulphide to sulphur with oxygen. A physical method is based on the application of a desorption unit to transfer the hydrogen sulphide dissolved in the effluent to air in an open tank or in a closed unit with air in counter current.

For sulphide oxidation in an anaerobic reactor, it is possible to add oxygen directly to the reactor bulk phase through micro-aeration. In this case, a population of sulphide-oxidizing bacteria (*Thiobacillus*

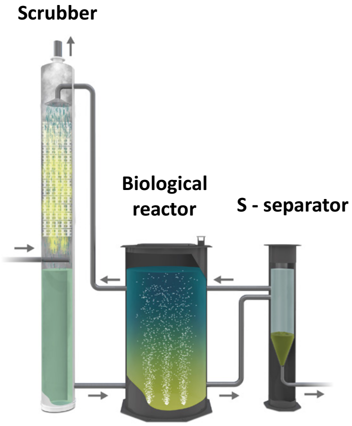


Figure 6.10 Removal of H_2S from biogas by absorption and partial oxidation.

sp.) is established, and the sulphide in the liquid phase is oxidized to sulphur. The sulphur suspension is mixed with the sludge mass in the reactor and then discharged with the excess sludge. In this way, accumulation of a considerable concentration of sulphide in the liquid phase is avoided and thus indirectly the desorption of hydrogen sulphide to biogas will be limited. This method is particularly useful if much of the sulphur remains in the liquid phase, that is, when ratio Q_g/Q_l is small and when the sulphate concentration is high.

An alternative is to operate a separate reactor where a low concentration of dissolved oxygen is maintained. Under these conditions a specific bacterial population (*Thiobacillus* sp.), which generates a suspend sulphur from sulphide will develop. Control of the dissolved oxygen concentration must be accurate to avoid oxidation to sulphate, which requires four times more oxygen (and therefore energy) and does not remove the sulphur from the liquid phase. Janssen *et al.* (1999) demonstrated the advantage of using the redox potential of the reactor to control the concentration of dissolved oxygen. If the oxygen transfer is carried out in such a way that there is not high turbulence, sulphur aggregates in large flocs that are removable by simple settling. Marked turbulence tends to generate a colloidal suspension and separation of the sulphur from the liquid phase may become problematic.

The removal of the liquid phase can also be effected by desorption, a physical process taking place in a separate unit, where the digester effluent is transferred and placed in a counter current flux in the presence of air. This method is particularly effective when the influent has a low pH. In that case, mixing effluent (neutral pH) and influent (acid conditions) produces a mixture with low pH, in which hydrogen sulphide ion is converted into H_2S. Like carbon dioxide, hydrogen sulphide gas is supersaturated in the mixture and it is transferred to the air phase. An industrial unit (tray aerator or scrubber) or simply an accumulation tank can be used to mix influent and effluent. Mechanical stirring or bubble aeration may be applied to accelerate desorption of volatile supersaturated compounds (CO_2 and H_2S). In case of a high-sulphide concentration in the effluent, the desorption unit may be closed to avoid spreading of bad odours. This implies that a solution must be given for the hydrogen sulphide transferred to the air. In the desorption unit there is also air oxygen transfer to the liquid phase of the mixture. This micro-aeration can facilitate sulphide oxidation in the digester itself when the influent and recirculation mixture is introduced. Sulphur in colloidal form, which may be formed, will be extracted with the effluent or with excess sludge.

Chemical removal of sulphide from the liquid phase has been applied mostly for wastewaters with high-sulphate concentration (Song *et al.*, 2004). Ferric chloride may be added to the influent and used to precipitate sulphur as ferrous sulphide and, in addition, it will act as a coagulant improving the settleability of the anaerobic sludge.

6.6.3 Hydrogen sulphide in air used for odour collection

An important source of odour due to hydrogen sulphide can be the liquid surface of UASB reactors, where gas may escape from the liquid phase. For this problem, sometimes UASB reactor is covered. In this case it is possible to apply a small under pressure (1–2 mbar) and treat the air containing desorbed biogas. The amount of air required to reduce odour depends on the under pressure that it is applied but it should not be >1% of the wastewater flow. A small motor can pump the air to the odour removal unit. Another important source of odour problems is the discharge of effluent, especially if this discharge leads to turbulence due to pressure drops.

The treatment of the contaminated air essentially consists of H_2S removal. There are different mechanisms to achieve odour elimination: (1) use of contaminated air as part of the oxidation air for the combustion of the biogas, (2) use of biological odour control systems to promote sulphide abatement, (3) use of iron oxide for sulphide oxidation and (4) use of limestone (seashells).

In the first option, air is mixed with the biogas for its combustion. This option is particularly attractive when using a flare for burning biogas rather than its use as fuel. In this case, the hydrogen sulphide in the biogas and the contaminated air will be oxidized to sulphur dioxide (SO_2):

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O \tag{6.18}$$

This option is less suitable in case of productive use of biogas because it introduces a certain amount of sulphide (though not too high), which tends to accelerate corrosion of the generator engine.

The oxidation of sulphide gas using biological odour control systems can be carried out using three different kinds of bioreactor configurations (Cooper & Alley, 2011): biofilters; biotrickling filters and bioscrubbers. Among them, biofilters are probably the most popular, in which a fixed bed with a porous biofiltering material of 1–1.5 m depth is used to support a wet biofilm. Natural porous media such as wooden chips, bark, peat or bagasse are used as media to develop a specific bacterial mass under adequate conditions of humidity. The solid medium itself should contain trace inorganic compounds and nutrients as nitrogen and phosphorus, to support biological sulphide oxidation. Biological oxidation generates sulphuric acid; thus, a pH buffer should be provided to avoid pH drop and loss of biological activity of the biofilter. Therefore, the production of some leachate is desired to avoid sulphate salt accumulation in the solid media. Biofilters are simple and compact and can handle more than 10 m^3/h of air per m^3 reactor. To inoculate the bed material with a population of oxidizing bacteria it can be mixed with manure or wetted with treated sewage or secondary sludge.

Chemical oxidation of hydrogen sulphide with iron oxide is a spontaneous process that occurs at ambient temperature when biogas passes through a solid which contains iron oxide (FeO) for example the oxidized form of iron filings or soil containing iron oxide (Equation (6.16a)). The oxidation capacity of the unit can be recovered by flowing air (oxygen) through the solid, thus oxidizing sulphide to SO_2. The experience of a full-scale system with a soil rich in iron at Pirassununga (Brazil) is that it requires a very small area (~100 m^2 for 100,000 inhabitants), obtaining a removal of more than 90% of H_2S and practically eliminating the problem of odours which was serious at the plant site. The soil depth is 0.5 m and air is introduced by perforated polyvinyl chloride (PVC) pipes placed with a spacing of 0.5 m. Another original method was applied successfully in Bucaramanga (Colombia), where seashells in a suspension were used to fix H_2S. The oxygen in air oxidizes the hydrogen sulphide to sulphuric acid and the acid reacts with the calcium carbonate that is the main component of seashells, forming gypsum:

$$H_2S + 2O_2 + CaCO_3 \rightarrow CaSO_4 + H_2O + CO_2 \tag{6.19}$$

The only operation in this case is the occasional withdrawal of $CaSO_4$ to replace it with seashells. Regardless of the manner of removing odours from air in the case of sewage treatment, a large part of sulphide will not desorb from the liquid phase and eventually it will be discharged from UASB reactors with the reactor effluent for the post-treatment, which can be aerobic. In this case, the formed sulphide will be oxidized back to sulphate. This oxidation is rapid and complete. If ponds are used for post-treatment, the presence of sulphide may reduce the growth of algae and hence the photosynthetic production of oxygen, which is an essential aspect of the pond performance as has been shown in Chapter 5. On the contrary, under normal conditions the produced oxygen in the pond will oxidize the sulphide forming sulphur or sulphate.

6.7 BIOGAS COLLECTION

The biogas generated in an UASB reactor has a pressure of ~0.3–0.5 m water column (30–50 mbar), which is normally sufficient for direct use in power generators. A gas collection system in each phase separator element is composed of a network of rigid PVC pipes with diameters much larger than necessary for the biogas transport, but necessary to avoid blockages due to introduction of solid particles from the reactor into the collection system. For this reason, it is important that the biogas outlet from the gas chamber is situated as far as possible from the gas–liquid interface in the phase separator. It is convenient that washing of the pipes is foreseen to remove solids periodically from the interior of the pipes.

The biogas pressure is usually controlled by a hydraulic seal, used to set the level of the liquid–gas interface in the separator elements as shown in Figure 6.11a: the height *H* of the water column above the point of biogas release in hydraulic seal sets the biogas pressure in the gas chamber and sets the level difference between the level of the gas–liquid interface in the separator elements and the free surface of the UASB reactor. The biogas pressure can be read on the gauge as shown in Figure 6.11a. The hydraulic seal can also be used to retain condensed water that is in the biogas when the temperature of the UASB is higher than environmental temperature (the water in the seal). The condensed water is automatically drained from a siphon placed at the desired pressure level. In Figure 6.11b, a hydraulic seal for 10,000 m^3/day of biogas is shown.

In the case of domestic sewage treatment, biogas is normally burned in a flare, which can be a single unit as shown in Figure 6.12a. The flare in Figure 6.12a is designed to burn biogas generated in a system for 70,000 inhabitants. It is concluded that it is a small unit of low cost.

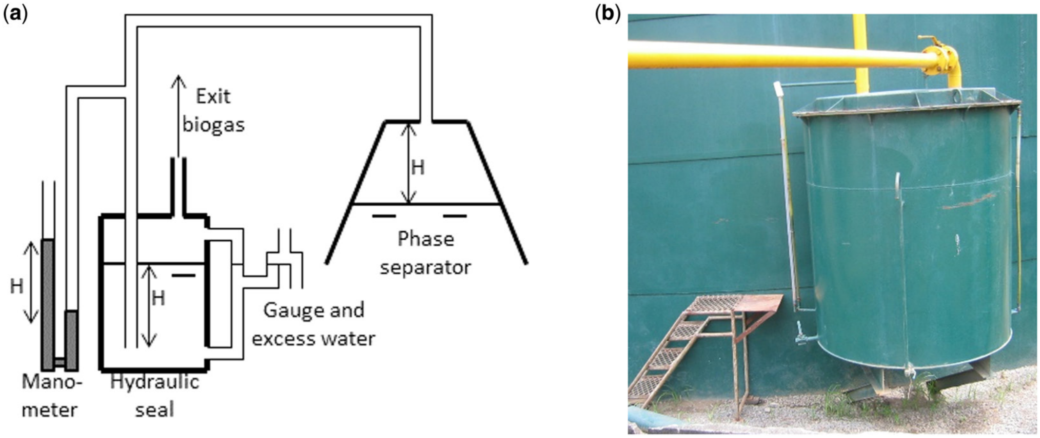


Figure 6.11 (a) Schematic representation of gas withdrawal from the anaerobic reactor and (b) constructed hydraulic seal with manometer and gauge to read the biogas pressure.

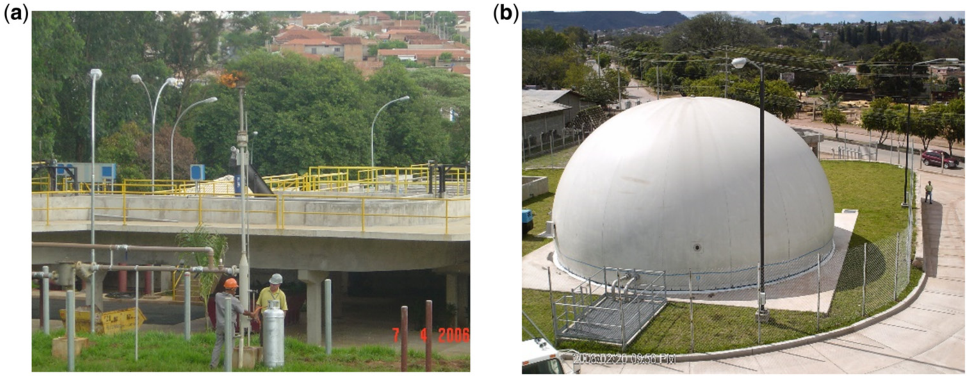


Figure 6.12 (a) Flare of the UASB reactor in Matão (SP, Brazil) and (b) plastic semi-sphere for biogas accumulation in Tegucigalpa (Honduras).

If the goal is to use biogas for the production of electric energy, it is advisable to install a biogas storage unit to accommodate the daily variations in production rate. The volume of this unit should be such that it can store at least 1 h of gas production. Traditionally, biogas has been stored in a gasholder which was constructed by polyester reinforced with fibreglass or steel covered with material to resist corrosion. These units are rigid and the gas volume varies with changing production and usage rates. On top of the gasholder a weight was placed so that the desired pressure is automatically set. Nowadays, semi-spheres of inflatable plastic material ('biogas balloons') are used more frequently as they have a lower construction cost. These units have an outer layer that is inflated by a small fan to the desired pressure (typically 30 mbar) and an inner gas membrane impermeable for CH_4. This inner membrane fluctuates with the biogas production variations. Figure 6.12b shows the biogas storage unit.

6.8 GENERATION OF ELECTRIC ENERGY FROM BIOGAS

Ideally, all produced biogas should be used in generators, but it is difficult to continuously operate generators and use exactly the amount of biogas that is produced. Therefore, it is realistic to expect that the average biogas production rate will be higher than the average consumption rate by generators. In this case, it is necessary to have a flare to burn the excess production. This unit must have a device to automatically initiate combustion every time biogas starts to flow through it. The flare may be made using masonry or stainless steel. Its burning capacity should be enough to burn all biogas, when no electric energy is generated.

Power generation from biogas produced in the treatment plant is particularly attractive because the cost of generation will be low. Normally, the major cost generation is the operational, that is, the cost of acquisition of a generator. In the case of biogas generation in a wastewater treatment system, in principle, the fuel is free. Energy production becomes particularly interesting when there is a direct use in the treatment system, for example to drive pumps or aerators in post-treatment units. Also there is a strong incentive for electricity production if the legislation that regulates sale of electricity to distributors and is favourable for the producers or if carbon credits can be obtained.

The potential of electric power production is directly proportional to the methane production, which in turn depends on the organic load and the efficiency of anaerobic digestion. To calculate the potential of power generation the lower combustion heat is used, which is the combustion energy required when it is considered that the water formed in the oxidation is not condensed and therefore the condensation energy is lost. The amount of methane combustion heat is 50 MJ/kg CH_4 or

50,000/3600 = 13.9 kWh/kg CH_4. However, only part of the methane combustion energy is effectively converted into electrical energy in a power generator. The most widely used type of generator for power generation is a gas motor in which biogas and air are directly injected. Modern units have a power conversion efficiency of 35 (small units) to 40% (units for more than 1 MW). For this range the efficiency of electricity production is 4.9–5.6 kWh/kg CH_4.

Example 6.9

Estimate the per capita production potential of electric energy with the aid of the following data:

(1) Contribution per capita: 100 g COD/day, 120 L/day
(2) Anaerobic digestion efficiency: 80% of the COD (70% digested and 10% transformed into sludge)
(3) Losses due to dissolved methane: 20 mg/L effluent
(4) Biogas losses due to collection, transport and storage: 30%
(5) Conversion efficiency of the generator: 40%

Solution

Methane production is one-fourth of the digested COD mass, so the per capita production of methane: $0.7 \times 100/4 = 17.5$ g CH_4/day. For a per capita contribution of 120 L/day the dissolved methane is $20 \times 0.120 = 2.4$ g CH_4/day. Hence, the biogas production will be $17.5 - 2.4 = 15.1$ g CH_4/inh/day. Now, taking into account the loss of 30%, the available production for generating energy is $0.7 \times 15.1 = 10.6$ g CH_4/inh/day.

For a generator efficiency of 40%, the energy production is estimated to be 5 kWh/kg CH_4 or 5 Wh/g CH_4. As there is a per capita production of 10.6 g CH_4/day, per capita energy production will be $10.6 \times 5 = 53$ Wh/day, that is, there is a potential to produce a power of $53/24 = 2.2$ W/inh. This power is usually sufficient to meet the entire demand of a treatment system, including aerobic post-treatment.

On the contrary, the energy produced may not be enough for a water company economic convenience, unless for very large systems. One of the largest anaerobic sewage treatment systems in the world is the Onça plant at Belo Horizonte with a volume of 48,000 m^3. This system operates with a residence time of 8 h so the treated volume is close to 150,000 m^3/day with an organic load estimated at 120 t COD/day (assumed COD = 800 mg/L). Considering that 60% of this load will be effectively used for power generation one would have a mass of $0.6 \times 80/4 = 12$ t CH_4/day or ~60,000 kWh/day, that is, power of $60{,}000/24 = 2500$ kW. An analysis will be needed to evaluate if the generation of this power is economically feasible. In many cases, smaller systems probably do not have economic feasibility in the Brazilian context, where the price for energy is low, thanks to ample possibility hydropower generation.

6.9 SLUDGE MANAGEMENT STRATEGIES

6.9.1 Sludge composition

The sludge generated in anaerobic reactors is characterized by the accumulation of inorganic solids, with a 55–70% of volatile solids. This value is slightly lower than the 60–85% observed for aerobic activated sludge systems. The wasted anaerobic sludge contains a moderate amount of nitrogen, ~3–6%, and phosphorus, 1–2%. The concentration of certain chemical elements in sludge, such as metals and metalloids, is often regulated for its application as agricultural fertilizer in different countries (Table 6.7).

When comparing the results of metal analyses, it is observed that anaerobic sludge is characterized by a high iron and zinc content. This is probably due to the abundance of these elements in raw wastewater and the precipitation of insoluble Fe and Zn sulphides in anaerobic bioreactors. In

Table 6.7 Presence of metals and metalloids in the sludge generated in different anaerobic STPs (columns 1–3) as well as the sludge generated in the 40 largest cities of China, using aerobic-based processes (column 4). dw: Dry Weight.

	Metals and Metalloids in STP Sludge (mg/kg dw)				Legal Requirements (mg/kg dw)	
	(1)	**(2)**	**(3)**	**(4)**	**Brazil (5)**	**Europe (6)**
Cd	0.74 ± 0.02			1.66 ± 2.07	39	20–40
Cu	707 ± 37	714	161 ± 10	163 ± 140	1500	1000–1750
Ni	38 ± 3	157 ± 60	53.9 ± 3.4	51.1 ± 76.9	420	300–400
Pb	110 ± 1	28 ± 3.1	6.8 ± 1	44.5 ± 28.1	300	750–1200
Zn	3048 ± 853	1300 ± 1210	1400 ± 98	609 ± 372	2800	2500–4000
Hg	2.1 ± 0.1	–	–	2.84 ± 2.88	17	16–25
Cr	720 ± 19	132 ± 42	–	180 ± 555	1000	–
As	11 ± 1	–	–	20.8 ± 14.4	41	–
Se	–	21 ± 1.1	–	–	100	–
Fe	11,766 ± 684	10,560 ± 2900	31,500 ± 1900	–	–	–
Mn	162 ± 10	98 ± 12	200 ± 6	–	–	–

(1) De la Varga *et al.* (2013); one anaerobic UASB pilot plant treating sewage, Spain.
(2) Braga *et al.* (2017); six full-scale anaerobic STP, Brazil.
(3) Lombardi and Garcia (2002) and Souza *et al.* (2014); Campinas full-scale anaerobic STP, Brazil.
(4) Geng *et al.* (2021); sludge from 40 different STP representing 22% of the China population.
(5) Brasil (2006) Conselho Nacional do Meio Ambiente. Resoluçao n 375.
(6) Council Directive 86/278/EEC of 12 June 1986; European Union limits for metals in STP sludge.
Furthermore, this information is complemented with the legal limits in Brazil (5) and Europe (6) for the safe use of sewage sludge in agriculture.

general, and except for zinc that is higher, the metal content of anaerobic STP sludge is not very different from the sludge generated in aerobic processes. The presence of heavy metals in waste sludge is influenced by the discharge of industrial wastewaters into sewerage systems, especially from the metallurgy and metalworking industry, as well as urban runoff, carrying pollutants from diffuse sources such as the ones originated from the washout of roads. In fact, particles emitted from wear and tear of brakes contain Fe, Cu, Zn, Sn, Zr and Sb, among others (Grigoratos & Martini, 2014) which may end up in sewage.

6.9.2 Quantities of generated sludge

Sludge management in STPs is usually one of the three main operational cost items, along with personnel and energy costs. One of the main advantages of anaerobic sewage treatment, in comparison to the aerobic alternative, is the lower amount of sludge generated, which reduces the costs associated with sludge disposal. Typically, the observed yields in anaerobic UASBs are between 0.1 and 0.18 g TSS/g COD, which are much lower than the values observed in aerobic sewage treatment, that is, 0.3–0.5 g TSS/g COD. Additionally, the purged solids' concentration from anaerobic UASB systems is between 3 and 6% TSS, a value much higher than that of 0.4–1.2% reported for aerobic systems. This reduces the amount of the sludge stream to be treated in the sludge line.

6.9.3 Sludge dewatering and drying

One of the main characteristics of waste sludge from anaerobic UASB reactors is the high solids' concentration. Additionally, due to the high sludge residence times applied, the waste sludge becomes stabilized, and can be easily dewatered, diminishing its fermentation potential and simplifying sludge treatment. For these reasons, thickening and stabilization operations, common for primary or secondary aerobic sludge treatment, are not required. The percentage of solids in waste anaerobic sludge can be increased to 20–45% in terms of dry solid percentage using mechanical dewatering processes or sludge-drying beds.

Dewatering is a physical operation employed to remove the excess water from the thickened sludge, producing a residue with high solid content known as 'cake'. If mechanical operational units are used, a liquid contaminated stream will be generated, which has to be returned to the water line to be treated adequately. There are many reasons to obtain the cake with high solids' concentration in STPs:

(1) Sludge transportation costs are substantially decreased.
(2) The dewatered cake is easier to handle and transport.
(3) Dewatering is required if the sludge cake is to be landfilled, thus diminishing the potential of leachate production.
(4) The dewatered cake has a higher calorific value when incineration is the destination for the sludge, as water is eliminated. In any case, it is very important to reduce the moisture as much as possible to increase the calorific value of the sludge. Sludge cakes with over 50% volatile solids can often be incinerated without auxiliary fuel.
(5) Dewatering is required if the sludge cake is to be composted.

Dewatering the waste sludge generated by anaerobic bioreactors can be accomplished utilizing different technologies such as filter presses, screw presses, belt-filters and centrifuges (Metcalf & Eddy, 2014). The efficiency of sludge dewatering in these technologies could be improved by adding inorganic coagulants as aluminium sulphate, ferric chloride or poly-aluminium chloride, and especially synthetic polymeric flocculants, such as cationic polyacrylamide, or natural flocculants derived from starch, chitosan, cellulose or tannin, in which the chemical structure of the natural product was partially modified to improve the product performance. Doses between 2 and 15 g of polymer per kg of dehydrated TSS are normally used for this purpose.

6.9.3.1 Filter presses

Filter presses are equipment that operates intermittently, with sequential stages of sludge loading, pressure filtration, discharge of the dehydrated cake and a final idle stage until the cycle is restarted again. During the operation, the sludge to be dewatered is introduced into the plates, on which filter cloths have been arranged and fitted. In the first stage, the increase in pressure, resulting from pumping, forces the water to be filtered through the filter cloths. In the second stage, the compression caused by a hydraulic cylinder helps to achieve higher degrees of dehydration. With filter presses, very high solids' concentrations can be achieved, which can exceed 35% TSS. Unlike the other sludge dewatering technologies, polymers are barely used for sludge conditioning whereas inorganic coagulants, ferric chloride or aluminium sulphate are usually preferred. In some cases, lime is added after the coagulant to improve the filtration capacity. The energy requirement of this technology is between 20 and 40 kWh/t TSS.

6.9.3.2 Screw presses

A screw press is a unit that operates at low speed and consists of an Archimedean screw rotating at a low speed inside a metal screen confined in a cylindrical casing. The aperture of the screen is below 0.5 mm, using normally wedge-wire metal filter. The whole device is usually inclined to facilitate the separation of the sludge cake from the drained water. Once chemically conditioned, the sludge is fed at low pressure into one end of the unit. The rotating action of the screw causes the sludge to advance forward upwards. The friction forces originated during the slow transport of the sludge, between the Archimedean screw and the screen, create a pressure that facilitates water filtering, collecting the cake at the opposite end to the feeding side.

Screw press systems can directly dewater sludge without requiring any previous thickening stage, which could result in substantial reductions in capital and operating expenses. However, this is not an advantage for dewatering anaerobic sludge, as it does not require any thickening step, unlike conventional waste activated sludge. In contrast to other mechanical dewatering technologies, this technology exhibits lower dry solid content in the cake (17–25%). Nevertheless, it provides several benefits, including reduced energy consumption, lower operational and maintenance costs, compactness and decreased noise levels.

6.9.3.3 Belt filters

Belt filters operate continuously and consist of three sections: a gravity drainage section, in which water is removed by gravity, a second section where moderate pressure is exerted, as the sludge is confined between the band cloths and finally, a high-pressure area where the sludge is subjected to higher pressures as the force exerted by the cloths and the rollers increases, thus generating a cake of dehydrated sludge. The solid content in these systems can achieve between 20 and 28% TSS. The energy requirement of this technology is between 10 and 25 kWh/t TSS, being lower than that required for centrifuges or filter presses.

6.9.3.4 Centrifuges

Centrifugation process is widely used in STPs to separate excess water and generate a thickened cake with a higher solid content using bowl centrifuges. A polymer-conditioned sludge stream is constantly fed into a rotating bowl, where a solid cake and a diluted liquid stream are produced. The separated liquid, called centrate, must be returned to the STP water line, while the thickened sludge cake has a solids' concentration often ranging between 20 and 30%. The energy requirement of this technology is between 30 and 60 kWh/t TSS.

6.9.3.5 Sludge-drying beds

A sludge-drying bed is one of the oldest and simplest units for sludge dewatering and it has been applied to dewater the sludge purged from anaerobic sewage bioreactors (Figure 6.13). It gradually dewaters the sludge over the periods of several weeks by evaporation from the sludge surface in contact with the air and by drainage, using a system composed by a sand and gravel layer with drainage tubing located at the bottom of the bed. The collected water is usually recycled to the water line of the STP. The sludge to be dried is placed on the system in a 200–300 mm depth layer. Once dried, the solids are transported out of the STP to be used in agriculture or are landfilled. Conventional drying beds typically have rectangular shapes, with outer walls normally constructed with concrete blocks. Although the use of

Figure 6.13 Sludge-drying bed in a municipal STP containing fresh sludge (left) and with dehydrated sludge (right).

drying beds is associated with small plants in areas where cheap land is available and with hot or dry climates, it is possible to use them in temperate climates, always considering the rainfall in the area.

Odour generation is usually very low when anaerobic sludge from UASB reactors is processed in drying beds since the sludge is stabilized as a result of the high sludge age in anaerobic bioreactors. Drying periods of 30–45 days can be applied, and the solids' concentration generally lies between 30 and 45% and may achieve more than 50–60% TSS under dry climate conditions, attaining a partial sludge sanitization in terms of microbial indicators (Lopes *et al.*, 2020). This technology requires more time and is less compact than mechanical devices. However, operational and maintenance costs are very low, its operation is simple and the percentage of solids in the dehydrated sludge is very high.

6.9.3.6 Sludge-drying lagoons

Similar to drying beds, lagoons can be viewed as a cost-effective sludge dewatering technology in regions characterized by hot and dry climates, low population density and with cheap land availability. While it shares similarities to drying beds in terms of requiring vast land areas and labour-intensive mechanical removal of dewatered solids, its construction is simpler due to the absence of the need for filtrate drainage. However, drying lagoons are significantly less utilized than drying beds to treat digested sludge. The depth of the lagoon commonly ranges between 0.75 and 1.25 m. The main difference between this process and drying beds lies in the fact that evaporation is the primary mechanism driving the dewatering process, since no drainage can occur. This results in the need for longer drying times, ranging from several months to more than a year. Typically, the cake is removed with a concentration in the range of 25–30% of TSS (Table 6.8).

Table 6.8 Comparison among the most common technologies used for dewatering waste sludge.

	Filter Press	Screw Press	Belt Filter	Centrifuge	Drying Beds	Lagoons
Consumption (kWh/t TSS)	20–40	5–15	10–25	30–60	–	–
Land occupied	Low	Low	Low	Low	High	High
Cake solids (%)	Up to 35	17–25	20–28	20–30	50–60	25–30
Operation mode	Discontinuous	Continuous	Continuous	Continuous	Discontinuous	Discontinuous
Operational complexity	High	Intermediate	Intermediate	Intermediate	Low	Low
Capital costs	Intermediate	Low	Intermediate	High	Low	Low
Dewatering time	Intermediate	Short	Short	Short	Long	Very Long
Maintenance	High	Low	High	Intermediate	Low	Low
Chemical requirements	High	High	High	High	Low or none	–
Odour problems	–	–	–	–	Potential	Potential
Weather impact	–	–	–	–	High	High
Groundwater pollution	Low	Low	Low	Low	Intermediate	High
Noise	Intermediate	Low	Intermediate	High	–	–

Source: Adapted from Von Sperling and Chernicharo (2005), and Metcalf and Eddy (2014).

6.10 ENERGY GENERATION FROM SLUDGE COMBUSTION

Sludge generation in anaerobic treatment systems has a production of ~0.15 kg TSS/kg COD applied, with an organic fraction of 55–70% and a concentration of 50–80 g TSS/L. The produced sludge may be separated from the water by mechanical processes (filtration, centrifugation), whereupon it becomes a semi-solid cake with a solid fraction of ~20% and thus a residual humidity of ~80%. If further drying is desired, thermal processes such as sludge-drying beds or external heat application must be applied.

Depending on the use of the dried sludge and the cost of providing a final destination of the dried sludge it may be interesting to increase the solid fraction beyond the value that can be achieved by mechanical methods (15–25%). If the area for drying beds is not available, thermal drying may be applied, which is a process that produces a final sludge with no or very little water. It requires an external energy source, which can supply the heat required to evaporate the water from a sludge cake. Thermal drying can be completed with combustion of the dried sludge with air in an incinerator; in that case the energy source of the process is the combustion heat of the volatile sludge itself (see Figure 6.1). In that case, an important issue to be considered for sewage sludge incineration is the emission of toxic pollutants, due to the potential emission, among others, of dioxins, furans and nitrogen oxides, making the in-situ sludge incineration unaffordable. For this reason, centralized sludge incineration or co-incineration plants are used in many European countries, USA, and Japan.

The possibility of producing electric energy from the dried sludge is limited based on the following analysis: in anaerobic treatment systems roughly 2/3 of the influent organic material are transformed into biogas and the remaining fraction (1/3) is equally divided between organic material residual in the effluent and organic material transformed into sludge, both accounting for a fraction of 1/6 of the influent organic load. Thus, the fraction of the organic material transformed into biogas (methane) is of the order of four times greater than the fraction transformed into volatile sludge ((2/3)/1/6) = 4). When it is desired to use energy to generate a usable product e.g. electric energy the difference becomes even greater for two reasons:

(1) The biogas transformation efficiency is greater than that of sludge, because biogas is a gaseous fuel that can be used in an Otto-type explosion generator, characterized by an efficiency of 35–40%. In the case of sludge combustion, it is necessary to use a combination of a boiler to generate steam and a turbine to generate electricity. The efficiency of the boiler–turbine combination is at most ~15%. Knowing that the chemical energy per unit mass of COD is ~13.7 MJ, it is estimated that per unit mass of COD of the influent the potential of electricity generation is:

$$2/3 \times (0.35 \text{ to } 0.40) \times 13.7 \approx 3.4 \text{ MJ/kg COD}$$

whereas the energy generated from the sludge is no more than

$$1/6 \times 0.15 \times 13.7 = 0.34 \text{ MJ/kg COD.}$$

Therefore, it is estimated that the potential of electric energy generation from the biogas is ~10 times higher than the one generated from the sludge combustion.

(2) The sludge combustion energy is even lower because the sludge after drying still has residual humidity, which must be removed and it requires ~2.5 MJ/kg H_2O. Thus, if the sludge after drying has a humidity U_e and a volatile fraction f_v, and knowing that $f_{cv} = 1.5$ g VSS/g COD, it is calculated that the generation of the combustion heat is given by

$$Q_c = (1 - U_e)\, f_v f_{cv} 13.7/6 \text{ MJ/kg COD} \tag{6.20}$$

On the contrary, the value to evaporate water from the dried sludge with a residual humidity U_e is given by

$$Q_e = 2.5U_e / 6 / (1 - f_v)\,\text{MJ} / \text{kg COD} \tag{6.21}$$

In Figure 6.14, the values of heat production by combustion (Q_c) and the heat demand by water evaporation (Q_e) are plotted as functions of the residual humidity U_e for organic sludge fractions of 60 and 70%. In the figure, an 80% heat utilization efficiency as well as the difference between the effective heat generated and the heat demand for evaporation are also reported. It can be seen that the difference is positive for a residual humidity of ~60%, that is, the heat generated is sufficient to sustain sludge combustion when the residual moisture is <60%. This value can be easily obtained in drying beds, but not with the aid of mechanical methods of sludge dehydration.

Example 6.10

Evaluate if the biogas production in a UASB reactor is sufficient to dry the produced sludge after mechanical dehydration to 80% humidity. Assume a sludge production of 0.1 g VSS/g COD, a VSS/TSS ratio of 0.67 for the sludge and a digestion efficiency of 70%. Evaporation heat of water is 2.5 MJ/L and combustion heat is 13.7 MJ/kg COD

Solution

Since 1 g VSS has 1.5 g TSS and the humidity is 80%, the sludge production is 0.1 g VSS or 0.15 g TSS per g COD with 0.15/0.8 = 0.19 kg of wet sludge per kg COD. The required heat for evaporation of (0.19 − 0.15) = 0.04 kg H_2O/kg COD is 0.04 × 2.5 = 0.1 MJ/kg COD. On the contrary, the digested COD is 0.7 g/g COD with a combustion heat for the formed methane of $0.7 \times 13.7 \approx 10$ MJ/kg COD. However, only ~50% of this biogas is actually captured and used, so that a more realistic energy production of 5 MJ/kg COD is estimated. It is concluded that the combustion heat of the biogas is ~50 times greater than the energy demand for evaporation of the water in the sludge cake, so that even with low heat transmission efficiency, it should be possible to dry the sludge using only the combustion heat of the biogas to dry sludge, even though this does not seem to be applied in practice.

Example 6.11

Evaluate if the heat production of sludge combustion from a UASB reactor is enough to have auto-sufficiency in an incinerator. Adopt the same assumptions as in the previous example.

Solution

The required heat for evaporation is the same as in the previous example. The combustion heat depends on the volatile fraction of the sludge. In Figure 6.13, the evaporation heat and the combustion heat are

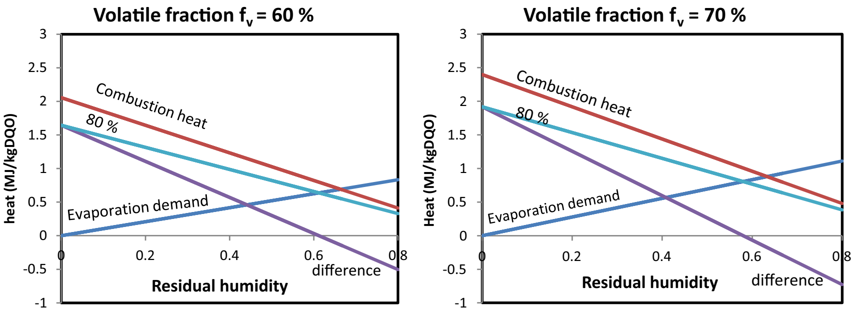


Figure 6.14 Evaporation and combustion energy upon combustion of sludge cake as a function of humidity. The energy balance for 80% efficiency is also indicated, showing the need for external energy for humidity of $\lesssim$ 60%.

shown as functions of sludge humidity for volatile sludge fractions of 0.6 and 0.7. In Figure 6.13 also shown is the energy balance for an assumed energy transmission efficiency of 80%. The figure shows that under these conditions the maximum humidity of the sludge is ~60%, depending on the VSS/TSS ratio, which is much less than the humidity obtained from mechanical dehydration, so that some external energy must be supplied, if it is desired that completely dry sludge is produced for maximum heat production by combustion. This external energy can be biogas in which case the energy balance is positive even for a very high initial humidity of the sludge.

Example 6.12

Dry sludge is produced, and combustion is applied to generate steam to feed a turbine to produce electric energy. Estimate the production potential per capita using a top-quality boiler–turbine combination, which has an efficiency of 16%. The combustion heat of volatile sludge is 13.7 MJ/kg COD = 20 MJ/kg VSS. Volatile sludge production is 0.1 g VSS/g COD. Per capita contribution: 100 g COD/day.

Solution

The volatile sludge production per capita is 100 × 0.1/1000 = 0.010 kg VSS/inh/day with a per capita combustion heat of 20 × 0.01 = 0.2 MJ/day = 2.3 W. If the conversion efficiency is 16%, the per capita production potential is 0.16 × 2.3 = 0.37 W. This production potential is much smaller than the potential from gas, not only because the organic material is much smaller (16% of the influent COD for volatile sludge against 68% for methane), but also because the conversion efficiency of the solid fuel (16% for dry sludge) is much smaller than that for the gaseous fuel (40% for methane).

6.11 NUTRIENT RECOVERY FROM SLUDGE AND WASTEWATER STREAMS

Phosphorus and nitrogen compounds are essential nutrients required by modern agriculture to improve yields. The world's population increased from 2.5 billion inhabitants in 1950 to 8 billion at the end of 2022, and it is expected that it will reach 9.8 billion by around 2050. A large fraction of the phosphorus used in agriculture worldwide is obtained from a non-renewable resource, phosphate rock, mostly mined in Morocco (including Western Sahara), China, the USA, and Russia. In contrast, the production of nitrogen fertilizers is not restricted to a small number of countries and depends on the availability of energy to produce them through the Haber–Bosch and Ostwald processes. A large part of the developing countries is currently facing a great challenge: the increase in the prices of phosphorus fertilizers is limiting their use in agriculture and impacting food production in these regions (Brownlie *et al.*, 2023). Thus, the recovery of nutrients from STPs and other waste resources would be important to guarantee the necessary food for the entire world population.

Example 6.13

Estimate the phosphorus and nitrogen daily loads in a 90,000 inhabitants anaerobic STP and determine the fractions associated with the treated effluent and the anaerobic sludge generated. Consider a generation of 100 g COD/day, 10 g total nitrogen (TN)/day and 1.2 g total phosphorus (TP)/day and 100 L/day of sewage produced. Sludge yields 0.1 g TSS/g COD removed, COD removal percentage is 80. Nutrient content in the sludge is 0.05 kg N/kg TSS and 0.015 kg P/kg TSS.

Solution

Considering the above indicated figures, the amount of the incoming mass of TN and TP present in the raw sewage is (daily basis)

$$TN_{in} = 90{,}000\,\text{inh} \times 10\,\text{g TN / inh/day} = 900{,}000\,\text{g TN/day or } 900\,\text{kg TN/day}$$

$$TP_{in} = 90{,}000\,\text{inh} \times 1.2\,\text{g TP/inh/day} = 108{,}000\,\text{g TP/day or } 108\,\text{kg TP/day}$$

For anaerobic sewage treatment, the only mechanism contributing to N and P removal from wastewater is associated with the sludge formation. Thus, N and P associated with sludge generation should be:

$$\begin{aligned} \mathrm{MS_X} &= 0.8\,\mathrm{g\,COD(removed)} \times \mathrm{g\ COD(fed)} \times 0.1\,\mathrm{g\,TSS/g\,COD(removed)} \times 90{,}000\,\mathrm{inh} \\ &= 720{,}000\,\mathrm{g\,TSS/day} \approx 720\,\mathrm{kg\,TSS/day} \end{aligned}$$

$$\mathrm{TN_X} = 0.05\,\mathrm{kg\,N/kg\,TSS} \times 720\,\mathrm{kg\,TSS/day} = 36\,\mathrm{kg\,TN/day}$$

$$\mathrm{TP_X} = 0.012\,\mathrm{kg\,P/kg\,VSS} \times 720\,\mathrm{kg\,TSS/day} = 10.8\,\mathrm{kg\,TP/day}$$

where $\mathrm{MS_X}$ = anaerobic sludge generation (kg TSS/day); $\mathrm{TN_{SV}}$ = total nitrogen in the sludge (kg N/day); $\mathrm{TP_{XV}}$ = total phosphorus in the sludge (kg P/day).

The percentage of TN and TP associated with the sludge formation represents 4 and 10% of the daily nutrient load, respectively. In those STPs using anaerobic technologies, the recovery of phosphorus or nitrogen associated with the sludge is low, due to the low biomass yield of the process. In any case, the sludge generated in anaerobic STPs contains all the nutrients removed from the treated sewage. In fact, the use of sludge from STPs as agricultural fertilizer is a common practice in many countries around the world.

Anaerobic sewage treatment is not the adequate solution to remove nutrients from the water phase. In recent years, many studies have tried to improve the removal of nutrients in these systems. One approach is the promotion of struvite precipitation, a phosphate salt containing ammonia and magnesium ions ($MgNH_4PO_4 \cdot 6H_2O$). This strategy is only effective when the treated wastewater contains high concentrations of orthophosphate ions, as is often the case with black water. The precipitation of struvite only compensates if the phosphorus concentration greatly exceeds 100 mg P/L, a level far from that of 5–15 mg P/L observed in sewage.

In Table 6.9, the calculated concentrations of pollutants of raw and treated sewage for the analysed scenario are shown. As indicated, the calculated nutrient concentrations in the effluent and raw sewage are similar. In fact, there are many studies in the literature indicating that the observed removal of nitrogen and phosphorus in anaerobic bioreactors is almost negligible.

Most of the nutrients contained in anaerobically treated sewage, without further post-treatment, remain in the effluent. The eutrophication of the receiving water bodies is one of the main problems of the discharge of anaerobically treated sewage. Nutrients contained stimulate algae blooms, harming water life. An alternative to take advantage of the nutrients and the water itself could be to store the treated waters in accumulation ponds, and use them for agricultural irrigation, as long as the distance between the fields and the STP does not make this application unfeasible. Water reuse is treated in Chapter 8, and could be a way to recover nutrients, and diminishing the use of chemical fertilizers. This practice, as well as the use of sewage sludge as fertilizer, is regulated by law in several countries.

The World Health Organization publishes guidelines for the safe use of wastewater in agriculture (WHO 2006), to reduce the risks associated with the presence of pathogens and certain chemical compounds associated with wastewater and sewage sludge. For these reasons, in most cases, anaerobically treated sewage should undergo post-treatments to ensure adequate water quality, including a partial reduction of nutrients, especially nitrogen compounds, to guarantee a good food crop.

Table 6.9 COD, TN and TP concentrations and nutrients loads of the analysed scenario.

	mg COD/L	mg TN/L	mg TP/L	kg TN/day	kg TP/day
Raw	833.3	83.3	10.0	900	108
Effluent	166.7	80.0	9.0	864	97

One of the questions that could be raised is the comparison of the amounts of nutrients present in sewage, with the amount of fertilizer consumed. According to the International Fertilizer Association (IFA, 2023) during 2020, 21.8 and 112.3 Mt of phosphorous- and nitrogen-based fertilizers were consumed worldwide, which implies an average annual consumption per world inhabitant of 2.8 kg P and 14.4 kg N. It can be quickly calculated for our case study that an inhabitant generates 0.438 kg P and 3.65 kg N annually. Assuming that all nutrients from wastewater could be effectively reused, ideally 15% of P and 25% of N could be recovered, thereby reducing the consumption of chemical fertilizers. This is obviously a very simple calculation; surely the real figures that can be achieved are more modest, highlighting the great potential associated with the nutrients contained in urban wastewater.

6.12 CONCLUDING REMARKS

It has been shown that anaerobic wastewater systems can be operated without the need of external energy, even when wastewater is diluted such as the case of sewage. The required energy for anaerobic treatment is obtained by using its organic material as an energy source. In the case of sewage ~2/3 of the influent organic material is converted into methane and may be used for energy generation. About 1/6 of the influent organic material is converted into organic sludge and 1/6 is discarded in the effluent. Organic sludge may be incinerated to produce electric energy and heat, but the alternative of using it as an organic fertilizer (after drying) may be more attractive from the economic point of view.

Nitrogen and phosphorus recovery from anaerobically treated wastewater can be carried out by using the reclaimed water and sludge generated in agriculture, according to local regulations. In most cases anaerobically treated sewage should undergo further treatment to ensure adequate water quality to guarantee a good crop.

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