ΠΑΝΕΠΙΣΤΗΜΙΟ ΠΑΤΡΩΝ
UNIVERSITY OF PATRAS

ΑΝΟΙΚΤΑ ακαδημαϊκά μαθήματα ΠΠ

Περιβαλλοντική Βιοτεχνολογία-Environmental Biotechnology

Ενότητα 8: Anaerobic Digestion

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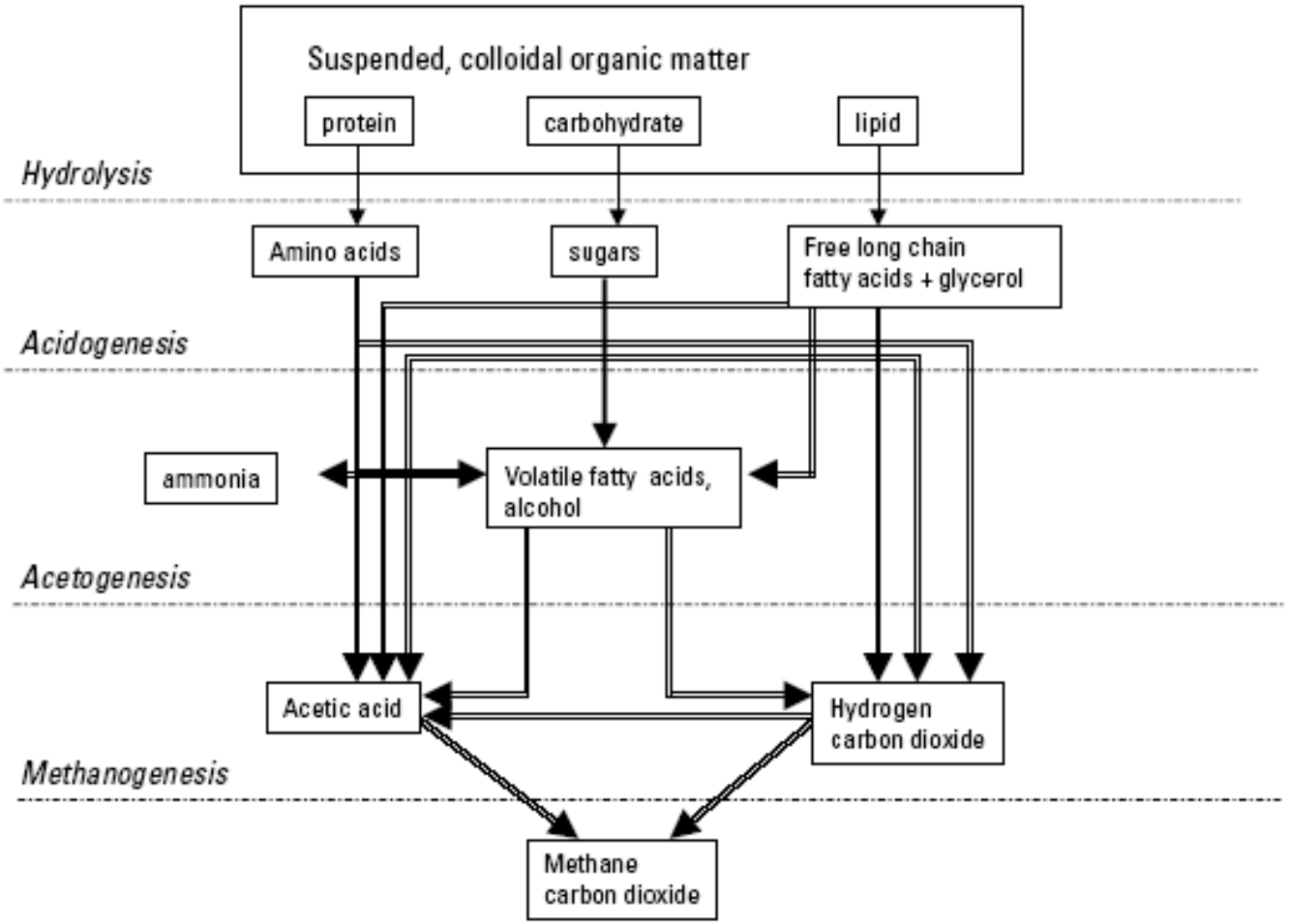
Description of the process



Description of the process

Methanogenesis refers to an anaerobic process in which the electron equivalents in organic matter (BOD_L) are used to reduce carbon to its most reduced oxidation state, -4, in CH_4, or methane. Methane is a poorly soluble gas that evolves from the water.

Kinetic Parameters

	Acetate Fermenters	**Hydrogen Oxidizers**
Electron Donors	Acetate	H_2 and Formate
Electron Acceptors	Acetate	CO_2
Carbon Sources	Acetate	CO_2
f_s^0	0.05	0.08
Y	0.04 g VSS_a/g Ac	0.45 g VSS_a/g H_2
$\hat{q}$ (at 35°C)	7 g Ac/g VSS_a-d	3 g H_2/g VSS_a-d
K	400 mg Ac/l	?
b	0.03/d	0.03/d
$(\vartheta_x^{min})lim$	4 d	0.76/d
S_{min}	48 mg Ac/l	?

Thus, the BOD_L is removed from the water by directing electron equivalents to CH_4, a result that we call waste stabilization. Each mole of CH_4 contains 8 electron equiv., or 64 g of BOD_L or COD. At standard temperature and pressure (i.e., STP = 0°C and 1 atm), each mole of CH_4 has a volume of 22.41. **Thus, each g of BOD_L stabilized generates 0.351 of CH_4 gas at STP**.

Application process

The process can be applied in the treatment of both municipal and industrial waste.
Non-extensive application because:
-lack of understanding of chemistry and microbiology
-presence of toxic components
-high requirements for reliable operation due to the risk management of biogas

Advantages
1. Low production of waste biological solids
2. Low nutrient requirements
3. Methane is a useful end product
4. Generally, a net energy producer
5. High organic loading is possible
Disadvantages
1. Low growth rate of microorganisms
2. Odor production
3. High buffer requirement for pH control
4. Poor removal efficiency with dilute wastes

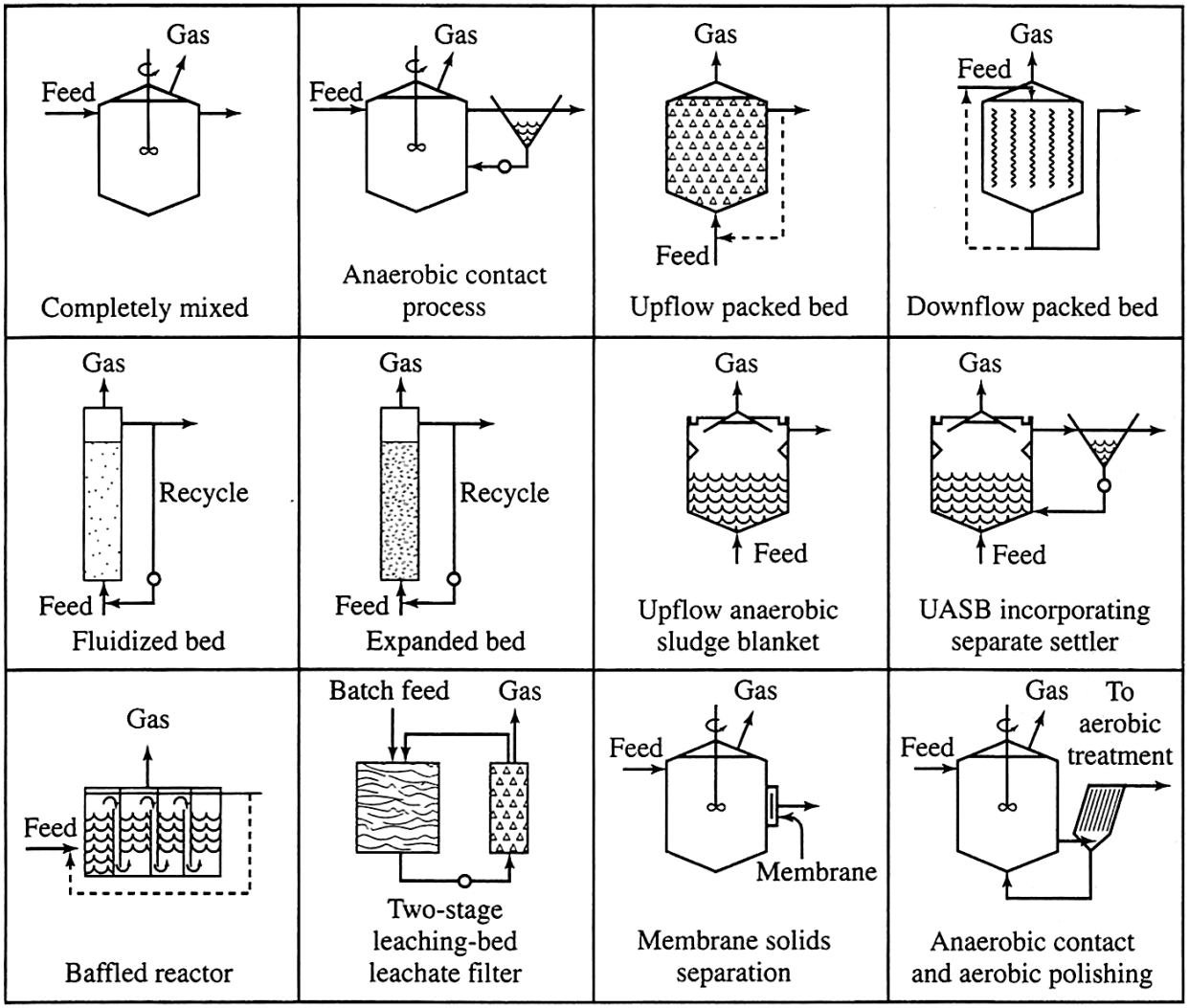
5-15% of BOD_L converted into sludge
less biomass → less nutritious

35.8 KJ/l at STP the calorific value of CH_4

The typical load in AD is 5-10 Kg COD/d*m^3 of reactor, while 1 Kg COD/d*m^3 in aerobic systems, which are limited by the transport of O_2. The AD is particularly useful for waste treatment with COD 5,000 mg/l or higher.

Reduction of 1 g S requires 2 g BOD_L and leads to loss of 0.7 L CH_4.

Reactor configurations



Reactor configurations (CSTR)

Detention times are commonly **15-25 d**, which is well above $[\vartheta_x^{min}]_{lim}$ of about 4 d at that temperature for the critical acetate-using methanogens. Thus, washout of the critical organisms is avoided by using an implied safety factor, based on $\vartheta_x/[\vartheta_x^{min}]_{lim}$, of about 4 to 6.

Municipal primary and secondary sludges entering an anaerobic sludge digester normally have concentrations from 2.5 to 15% total solids. With a detention time of about 20 d, the organic loading to a well-mixed digester of the continuous flow stirred-tank reactor (CSTR) type is **1 to 4 kg biodegradable COD per d per m^3 of digester volume**. This is a loading comparable to, but higher than the volumetric loading achieved in aerobic systems. In addition, the digester produces energy, rather than consuming it. It is easy to see why so many municipal treatment plants employ anaerobic treatment for waste sludges.

Reactor configurations (anaerobic contact)

The **anaerobic contact process** is an analogy to the aerobic activated sludge system. The first such system was developed and described in 1955 by Schroepfer and his co-workers (Schroepfer et aI., 1955) for the treatment of relatively dilute packing house wastes with COD of about 1,300 mg/I. By adding a settling tank and recycle of the biomass back to the reactor, they separated ϑ_x from ϑ and achieved a hydraulic detention time of about **0.5 d**, which is significantly less than the 4-d $[\vartheta_x^{min}]_{lim}$ of the acetoclastic methanogens. They **obtained 91 to 95 percent BOD removals at loading rates of 2 to 2.5 kg/m^3 -d**.

Although the anaerobic contact process has seen many applications, one recurring problem is a **tendency for the biosolids in the settling tank to rise due to bubble generation and attachment in the settling tank**.

Reactor configurations
(upflow & downflow packed bed)

The **upflow packed bed process**, also commonly called the **anaerobic filter**, was developed through laboratory studies in the late 1960_s. This system is similar to a trickling filter system in that, originally, a rock medium was used for attaching the biosolids. The anaerobic filter was used for treating soluble substrates with COD from **375 to 12,000 mg/l** and had detention times of **4 to 36 h**.

The anaerobic filter is excellent for the retention of biosolids and has seen wide application. The main concern with this system is **clogging by biosolids, influent suspended solids, and precipitated minerals**. Because of this potential problem, packed-bed systems work best for wastewaters containing few suspended solids, as these are likely to be removed by the process and clog pore spaces.

Reactor configurations
(upflow & downflow packed bed)

An alternative to the upflow packed-bed system is the **downflow packed bed**. Reasons why the downflow system might be superior are quite subtle. With the downflow system, the solids tend to accumulate more near the top surface, where substrate concentration and biological growth are higher. This may make it easier to achieve solids removal from the top by gas recirculation. Another possible advantage of the downflow system is that sulfide produced through sulfate reduction may be stripped from the liquid in the upper part of the column. Normally, the sulfate-reducing population resides in the upper levels of the reactor, while the methanogenic population is at lower levels. **Hydrogen sulfide can be toxic to the methanogens**, and stripping H_2S before it reaches the methanogenic part of the reactor can reduce toxicity to the methanogens.

Inf. CODs are in the 2,500 to 10,000 mg/l range, although some applications are for CODs over 100,000 mg/l. Design loading often is in the **10 to 16 kg/m^3 -d** range, more than tenfold higher than for normal aerobic processes.

Reactor configurations
(Upflow Anaerobic Sludge Blanket)

Lettinga, van Velsen, de Zeeuw, and Hobma (1979) developed an important new anaerobic reactor, the **upflow anaerobic sludge blanket reactor** (UASBR), which has had wide application for the treatment of industrial wastewaters and has been used to some extent for the treatment of relatively dilute municipal wastewaters as well.

Stander found that his system tended to improve its performance over time, an effect that he described as "maturing." Lettinga much later found a phenomenon that is perhaps related to this maturing: With time, the biosolids form what Lettinga called **"granules"**. These granules, which naturally form after several weeks of reactor operation, are compact spherical gray-white particles about 0.5 mm in diameter. They have a small ash content, about 10%, and consist primarily of a dense mixed population of bacteria that are required to carry out the overall methane fermentation of substrates. Microorganisms found to dominate in granules are acetate-utilizing methanogens, especially *Methanothrix* and *Methanosarcina*. Settled granules can attain concentrations between 1 and 2%, and the specific activity of the particles can be on the order of **1 to 2 g COD/g VSS-d**.

Reactor configurations
(Upflow Anaerobic Sludge Blanket)

The formation of granules depends upon **characteristics of the waste stream, the substrate loading, and operational details, such as the upward fluid velocity**. Serious problems that occur at times are the formation of granules that float and the lack of granule formation, both of which result in loss of biomass from the system. Thus, a knowledge of factors affecting granulation is key to successful use of the UASB system.

Many UASB systems are being used with a great deal of success on many food-processing industry wastewaters, as well as on wastewaters from the paper and chemical industries. Design loading typically is in the range of **4 to 15 kg COD/m^3-d**. Because the UASB system at times forms granules or biosolids that do not settle well within the reactor, a separate settler can be provided as a safeguard against excessive loss of biosolids from the reactor.

Microbiology of the process

The consortia of microorganisms involved in the overall conversion of complex organic matter to methane begins with bacteria that hydrolyze complex organic matter such as carbohydrates, proteins, and fats-into simple carbohydrates, amino acids, and fatty acids. The simple carbohydrates and acids are then utilized to obtain energy for growth by fermenting bacteria, producing **organic acids** and **hydrogen** as the dominant intermediate products. The organic acids are then partially oxidized by other fermenting bacteria, which produce additional H_2 and acetic acid. H_2 and acetic acid are the main substrates used by archaeI methanogens, which convert them into methane. H_2 is used as an electron donor, with carbon dioxide as an electron acceptor to form methane, while acetate is cleaved (the acetoclastic reaction) to form methane from the methyl group and carbon dioxide from the carboxyl group in a fermentation reaction.

Microbiology of the process

The microorganisms involved in the first step grow relatively rapidly, because the fermentation reactions give a greater energy yield than the reactions that lead to methane formation. For this reason, **the methanogens are more slowly growing and tend to be rate-limiting in the process**. This generalization is true with domestic wastewater organic matter, municipal sludges, and most industrial wastewaters. However, with certain organic materials, for example the anaerobic decomposition of lignocellulosic materials such as grasses, agricultural crop residues, or newsprint, the hydrolysis step may be very slow and rate-limiting.

Microbiology of the process

Reactor start-up

The successful start-up and operation of an anaerobic system requires that a proper balance be maintained between the hydrolytic and fermentative organisms involved in the first step and the methanogenic organisms responsible for the second step. This balance is accomplished through proper **seeding**, as well as through control of **organic-acid production and pH during the start-up**, when the microbial populations are establishing themselves. Ideally, an anaerobic reactor is seeded with digested sludge or biosolids from an active anaerobic treatment system. This kind of balanced, active seeding is necessary because of the slow doubling time (ca. 4 d at 35°C) of the critical microorganisms involved in the second step. If the seed contains only a small number of methanogens, the start-up time may be long. For example, about **10^8 to 10^9 of the critical microorganisms are required per ml of reactor volume** to ensure successful operation of an anaerobic treatment system.

Microbiology of the process

Reactor start-up

During reactor start-up, the operator must maintain a sufficiently small loading on the reactor so that organic acids produced by the much faster growing fermentative bacteria do not exceed the buffering capacity of the system. Ift his occurs, the pH will drop, and the methanogenic population can be killed. The crucial steps during start-up are: **(1)** begin with as much good anaerobic seed as possible, **(2)** fill the digester with this seed and water, **(3)** bring the system to temperature, **(4)** add buffering material in the form of a chemical such as sodium bicarbonate to protect against pH drop, and **(5)** add a small amount of organic waste sufficient to let the organic acid content from fermentation reach no more than about 2,000 to 4,000 mg/l, while keeping pH between 6.8 and 7.6. These organic acids are the food source required for the methanogenic population to grow.

Microbiology of the process

Volatile Acids

The organic acid concentration is a key indicator of system performance. The question then is what organic acids should be measured on a routine basis, and how can this be accomplished? The key organic acids are the series of short chain fatty acids and which vary in chain length from formic acid with one carbon per mole to octanoic acid with eight carbon atoms per mole. These acids have been termed **volatile acids** because, in their unionized form, they can be distilled from boiling water. This meaning of the term volatile is different from its meaning in volatile organic compounds (VOCs), a term generally used to describe organic compounds that are readily removed from water by simple air stripping.

The volatile acids that are generally found present in highest concentrations as intermediates during start-up of an anaerobic system or during organic overload are **acetic, propionic, butyric, and isobutyric acids**. These comprise the bulk of the organic acids found in anaerobic systems. Other non-volatile organic acids also are formed as intermediates of waste organic degradation (**e.g., lactic, pyruvic, and succinic acids**)

Stoichiometry of the process

While some intermediate products remain after treatment, most of the organic matter consumed by the microorganism is converted to the main end products: carbon dioxide, methane, water, and biomass. If other elements, such as nitrogen and sulfur, are part of the consumed organic matter, then they are converted to inorganic form, generally **ammonium** and **sulfides**. On this basis, the end products of methanogenic treatment of an organic waste can be determined readily using the procedures for writing stoichiometric equations. For example, we consider the empirical molecular formula for the organic matter (and electron donor, or BOD_L) to be $C_nH_aO_bN_c$. A certain portion of its electron equivalents, is, is (net) synthesized into biomass, and ammonium is the source of cell nitrogen.

While CO_2 is not the true acceptor for the acetoclastic methanogens, the exact pathway by which compounds are converted to end products is not important for maintaining a mass balance. This can be illustrated by writing out the conversion of acetate to methane, **which we know takes place through the** acetoclastic reaction:

$$CH_3 : COO^- + H_2O \rightarrow CH_4 + HCO_3^-$$

Stoichiometry of the process

$$-R_d : \frac{1}{8}CH_3COO^- + \frac{3}{8}H_2O \rightarrow \frac{1}{8}CO_2 + \frac{1}{8}HCO_3^- + H^+ + e^-$$

$$R_a : \frac{1}{8}CO_2 + H^+ + e^- \rightarrow \frac{1}{8}CH_4 + \frac{1}{4}H_2O$$

$$R : \frac{1}{8}CH_3COO^- + \frac{1}{8}H_2O \rightarrow \frac{1}{8}CH_4 + \frac{1}{8}HCO_3^-$$

$$C_nH_aO_bN_c + (2n + c - b - \frac{9df_s}{20} - \frac{df_e}{4})H_2O \rightarrow$$

$$\frac{df_e}{8}CH_4 + (n - c - \frac{df_s}{5} - \frac{df_e}{8})CO_2 + \frac{df_s}{20}C_5H_7O_2N$$

$$+ (c - \frac{df_s}{20})NH_4^+ + (c - \frac{df_s}{20})HCO_3^-$$

Stoichiometry of the process

The value f_s represents the fraction of waste organic matter synthesized or converted to cells, while f_e represents the portion converted for energy, such that $f_s + f_e = 1$. The value for f_s depends on the energetics of the cell's energy generation and synthesis reactions, as well as the decay rate (b) and ϑ_x. For a reactor operating at steady state, f_s can be estimated:

$$f_s = f_s^0 \left[\frac{1 + (1 - f_d) b \vartheta_x}{1 + b \vartheta_x} \right]$$

The f_s^0 values include the methanogens and all bacteria needed to convert the original organic matter to acetate and hydrogen.

Requirements of pH and alkalinity

The **desired pH** for anaerobic treatment is **between 6.6 and 7.6**. Values outside this range can be quite detrimental to the process, particularly to methanogenesis. The **biggest problem** generally is to maintain the **pH above 6.6**, because organic acids produced as intermediates in the process during start-up, overload, or other unbalance can cause a rapid pH drop and cessation of the methane production.

The main chemical species controlling pH in anaerobic treatment are those related to the carbonic acid system, as governed by the following reactions:

$$CO_2(aq) = CO_2(g)$$
$$CO_2(aq) + H_2O = H_2CO_3$$
$$H_2CO_3 = H^+ + HCO_3^-$$
$$HCO_3^- = H^+ + CO_3^{2-}$$
$$H_2O = H^+ + OH^-$$

The equilibrium relationships among the various species are given by:

$$\frac{[CO_2(g)]}{[H_2CO_3^*]} = K_H = 38\,atm/mol\,(35^oC)$$

Requirements of pH and alkalinity

$$H_2CO_3^* = CO_2(aq) + H_2CO_3$$

$$\frac{\left[H^+\right]\left[HCO_3^-\right]}{\left[H_2CO_3^*\right]} = K_{a,1} = 5 \cdot 10^{-7} (35^o C)$$

$$\frac{\left[H^+\right]\left[CO_3^{2-}\right]}{\left[HCO_3^-\right]} = K_{a,2} = 6 \cdot 10^{-11} (35^o C)$$

$$\left[H^+\right]\left[OH^-\right] = K_w = 2 \cdot 10^{-14} (35^o C)$$

At the normal pH of anaerobic treatment, carbonate (CO_3^{2-}) is not important.

$$pH = pK_{a,1} + \log \frac{\left[HCO_3^-\right]}{\left[H_2CO_3^*\right]}$$

Requirements of pH and alkalinity

Alkalinity is defined as the acid-neutralizing capacity of water. When the carbonic-acid system dominates the buffering (as it does in most anaerobic treatment processes), alkalinity can be quantified from a proton condition on the species of interest:

$$\left[H^+\right]+\left[Alkalinity\right]=\left[HCO_3^-\right]+2\left[CO_3^{2-}\right]+\left[OH^-\right]$$

in which all species are in mol/l. With respect to the usual pH and conditions of anaerobic treatment, the concentrations of $[H^+]$, $[CO_3^{2-}]$, and $[OH^-]$ are quite small compared with $[HCO_3^-]$. Also, alkalinity can be expressed in the conventional units of mg/l as $CaCO_3$:

$$\frac{Alkalinity\,(bicarb)}{50,000}=\left[HCO_3^-\right]$$

$$pH = pK_{a,1}+\log\frac{\dfrac{Alkalinity\,(bicarb)}{50,000}}{\dfrac{[CO_2(g)]}{K_H}}$$

The pH is controlled by the concentrations of alkalinity in the reactor liquid and carbon dioxide in the reactor gas phase, assuming that $C0_2$ equilibrium exists between the gas phase and the reactor liquid phase.

Requirements of pH and alkalinity

It is apparent that at the normal percentages of carbon dioxide in digester gas, 25 to 45%, a bicarbonate alkalinity of at least 500 to 900 mg/l as $CaC0_3$ is required to keep the pH above 6.5. A higher carbon dioxide partial pressure makes the alkalinity requirement larger. There are two other important and generalizable trends: **(1)** a quite high alkalinity of 5,000 mg/l with normal carbon dioxide content does not lead to an excessively high pH for anaerobic treatment, and **(2)** the pH is not sensitive to increases in alkalinity once the pH and alkalinity are about 7.4 and 5,000 mg/l as $CaC0_3$, respectively. In practical terms, increasing the alkalinity above about 5,000 mg/l gives little benefit and incurs little risk.

Requirements of nutrients

As with all biological treatment systems, **trace nutrients** must be present to satisfy the growth requirements of the microorganisms involved. With municipal wastewater and treatment plant sludges, essentially all nutrients required for growth are present.

Among the **inorganic nutrients** required for growth are the major ones, **nitrogen** and **phosphorus**. Methanogens also have a requirement for **sulfur** of about the same order of magnitude as that for phosphorus, or perhaps even a little more. An additional requirement in anaerobic systems is for **trace metals**, which are needed for activation of key enzymes for methanogenesis.

Lack of sufficient trace nutrients may be a cause of failure of anaerobic treatment for many industrial wastewaters. The required concentration of each differs considerably.

References

The images where their origin is not mentioned are derived from the book:

Environmental Biotechnology : Principles and Applications,

Bruce E. Rittmann and Perry L. McCarty,

McGraw-Hill Series in Water Resources and Environmental Engineering

Τέλος Ενότητας

Χρηματοδότηση

- Το παρόν εκπαιδευτικό υλικό έχει αναπτυχθεί στο πλαίσιο του εκπαιδευτικού έργου του διδάσκοντα.
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Σημειώματα

Σημείωμα Ιστορικού Εκδόσεων Έργου

Το παρόν έργο αποτελεί την έκδοση 1.0.0.

Σημείωμα Αναφοράς

Σημείωμα Αδειοδότησης