Lecture 3. Anaerobic Wastewater Treatment Technologies

By
Husam Al-Najar
Popularity of anaerobic processes

Energy crisis in 70 and 80’s - a renewed interest in anaerobic process

![Bar chart showing the number of anaerobic treatment plants for industrial applications from 1978 to 1999.](Source: Franklin, 2001)
Types of Biological Process for Wastewater Treatment

The principal biological processes used for Wastewater Treatment can be divided into two main categories:

• Suspended growth processes
• Attached growth processes (fixed film process)
Best industrial wastewaters for anaerobic treatment

- Alcohol production
- Brewery and Winery
- Sugar processing
- Starch (barley, corn, potato, wheat, tapioca) and desizing waste from textile industry.
- Food processing
- Bakery plant
- Pulp and paper
- Dairy
- Slaughterhouse
- Petrochemical waste
### Types of anaerobic reactors

<table>
<thead>
<tr>
<th>Low-rate anaerobic reactors</th>
<th>High-rate anaerobic reactors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry type bioreactor, temperature, mixing, SRT or other environmental conditions are not regulated. Loading of 1-2 kg COD/m³-day</td>
<td>Able to retain very high concentration of active biomass in the reactor. Thus extremely high SRT could be maintained irrespective of HRT. Load 5-20 kg COD/m³-d. COD removal efficiency : 80-90%</td>
</tr>
<tr>
<td>Anaerobic pond</td>
<td>Anaerobic contact process</td>
</tr>
<tr>
<td>Septic tank</td>
<td>Anaerobic filter (AF)</td>
</tr>
<tr>
<td>Imhoff tank</td>
<td>Upflow anaerobic sludge blanket (UASB)</td>
</tr>
<tr>
<td>Standard rate anaerobic digester</td>
<td>Fluidized bed reactor</td>
</tr>
<tr>
<td></td>
<td>Hybrid reactor: UASB/AF</td>
</tr>
<tr>
<td></td>
<td>Anaerobic sequencing batch reactor (ASBR)</td>
</tr>
</tbody>
</table>
1. Anaerobic contact process (ACP)

- Anaerobic contact process is essentially an anaerobic activated sludge process.
- It consists of a completely mixed reactor followed by a settling tank.
- The settled biomass is recycled back to the reactor.
- Hence ACP is able to maintain high concentration of biomass in the reactor and thus high SRT irrespective of HRT.
- Degasifier allows the removal of biogas bubbles (CO$_2$, CH$_4$) attached to sludge which may otherwise float to the surface.
• ACP was initially developed for the treatment of dilute wastewater such as meat packing plant which had tendency to form a settleable flocs.
• ACP is suitable for the treatment of wastewater containing suspended solids which render the microorganisms to attach and form settleable flocs.
• The biomass concentration in the reactor ranges from 4-6 g/L with maximum concentration as high as 25-30 g/L depending on settleability of sludge.
• The loading rate ranges from 0.5 – 10 kg COD/m$^3$-day.
• The required SRT could be maintained by controlling the recycle rate similar to activated sludge process.
2. Anaerobic filter

- Developed by Young and McCarty in the late 1960s to treat dilute soluble organic wastes
- The filter was filled with rocks similar to the trickling filter
- Wastewater distributed across the bottom and the flow was in the upward direction through a bed of rocks
- Whole filter submerged completely
- Anaerobic microorganisms accumulate within voids of media (rocks or other plastic media)
- The media retain or hold the active biomass within the filter
- The non-attached biomass within the interstices forms bigger flocs of granular shape due to rising gas bubble/liquid
- Non-attached biomass contributes significantly to waste treatment
- Attached biomass not be a major portion of total biomass
- 64% attached and 36% non-attached
Upflow Anaerobic Filter

- Feeding tank at 4°C
- Biogas
- Perforated Al plate
- Media
- Water bath
- sampling port
- Constant temperature recirculation line
- Sludge wastage
- Effluent
- Peristaltic pump
- Heaters
- Peristaltic pump
- Water bath
• Originally, rocks were employed as packing medium in anaerobic filter.
• But due to very low void volume (40-50%), serious clogging problems were witnessed. Now, many synthetic packing media are made up of plastics; ceramic tiles of different configuration have been used in anaerobic filters.
• The void volume in these media ranges from 85-95%.
• Moreover, these media provide high specific surface area, typically 100 m²/m³, or above, which enhances biofilm growth.
3. Upflow Anaerobic Sludge Blanket (UASB)

- UASB was developed in 1970s by Lettinga in the Netherlands.
- UASB is essentially a suspended growth system in which proper hydraulic and organic loading rate is maintained in order to facilitate the dense biomass aggregation known as granulation.
- The size of granules is about 1-3 mm diameter.
- Since granules are bigger in size and heavier, they will settle down and be retained within the reactor.
- The concentration of biomass in the reactor may become as high as 50 g/L.
- Thus a very high SRT can be achieved even at a very low HRT of 4 hours.
- The granules consist of hydrolytic bacteria, acidogen/acetogens and methanogens.
- Carbohydrate degrading granules show layered structure with a surface layer of hydrolytic/fermentative acidogens.
- A mid-layer comprising of syntrophic colonies and an interior with acetogenic methanogens.
UASB Reactor

Influent → biogas

Effluent
4. Expanded bed reactor (EBR)

- Expanded bed reactor is an attached growth system with some suspended biomass.
- The biomass gets attached on bio-carriers such as sandman, pulverized polyvinyl chloride, shredded tire beads.
- The bio-carriers are expanded by the upflow velocity of influent wastewater and recirculated effluent. In the expanded bed reactor, sufficient upflow velocity is maintained to expand the bed by 15-30%.
- The expanded bed reactor has less clogging problems and better substrate diffusion within the biofilm.
- The biocarriers are partly supported by fluid flow and partly by contact with adjacent biocarriers, which retain the same relative position within the bed.
5. Anaerobic baffled reactor

- In anaerobic baffled reactor, the wastewater passes over and under the baffles.
- The biomass accumulates in between the baffles which may in fact form granules with time.
- The baffles present the horizontal movement of biomass in the reactor.
- Hence a high concentration of biomass can be maintained within the reactor.
6. Anaerobic Sequential Bed Reactor
**Anaerobic process design**

**Design based on volumetric organic loading rate (VOLR)**

\[
\text{VOLR} = \frac{S_o \cdot Q}{V}
\]

**VOLR**: Volumetric organic loading rate (kg COD/m\(^3\)-day)

- **\(S_o\)**: Wastewater biodegradable COD (mg/L)
- **\(Q\)**: Wastewater flow rate (m\(^3\)/day)
- **\(V\)**: Bioreactor volume (m\(^3\))

**How do we select VOLR?**

- Conducting a pilot scale studies
- Find out removal efficiency at different VOLRs
- Select VOLR based on desired efficiency
Design based on hydraulic loading rate

Volume = $\theta_a \cdot Q$

$$A = \frac{\theta_a \cdot Q}{H}$$

$H$ : Reactor height (m)

$\theta_a$ : Allowable hydraulic retention time (hr)

$Q$ : Wastewater flow rate (m$^3$/h)

$A$ : Surface area of the reactor (m$^2$)
Volatile solids loading rate

The size of an anaerobic digester can also be estimated based on volatile solids loading rate expressed as kg VS/m$^3$-day.

\[
\frac{\text{Volatile solids loading rate, (kg VS/m}^3\text{- day)}}{\text{Influent VS (kg/day)}} = \frac{\text{Influent VS (kg/day)}}{\text{Reactor volume (m}^3\text{)}}
\]

For a given volatile solids loading rate, the size of reactor can be easily determined since influent VS (kg/day) is known to us.

\[
\text{Digester volume, } V \text{ (m}^3\text{)} = \frac{\text{Influent VS (kg/day)}}{\text{Volatile solids loading rate,(kg VS/m}^3\text{- day)}}
\]
Management of Anaerobic Treatment Systems
Organics Conversion in Anaerobic Systems

- **Hydrolysis**
  - Proteins → Amino Acids, Sugars
  - Carbohydrates → Amino Acids, Sugars
  - Lipids → Fatty Acids, Alcohols

- **Acidogenesis**
  - Amino Acids, Sugars → Intermediary Products
  - Fatty Acids, Alcohols → Intermediary Products

- **Acetogenesis**
  - Intermediary Products → Acetate
  - Acetate → Homoacetogenesis

- **Methanogenesis**
  - Homoacetogenesis → Methane
  - Acetotrophic Methanogenesis → Methane
  - Hydrogenotrophic Methanogenesis → Methane

- **Acetate Metabolism**
  - Acetate → Hydrogen, Carbon dioxide
  - Homacetogenesis → Hydrogen, Carbon dioxide
The anaerobic degradation of complex organic matter is carried out by a series of bacteria and archeae as indicated in the figure (with numbers). There exists a coordinated interaction among these microbes. The process may fail if a certain of these organisms are inhibited.

**Fermentative bacteria (1)**

This group of bacteria is responsible for the first stage of anaerobic digestion - hydrolysis and acidogenesis. These bacteria are either facultative or strict anaerobes.

The anaerobic species belonging to the family of Streptococcaceae and Enterobacteriaceae and to the genera of *Bacteroides, Clostridium, Butyrivibrio, Eubacterium, Bifidobacterium* and *Lactobacillus* are most common.
Hydrogen producing acetogenic bacteria (2)

This group of bacteria metabolizes propionate and other organic acids (>C-2), alcohols and certain aromatic compounds (i.e. benzoate) into acetate and CO₂

\[
\text{CH}_3\text{CH}_2\text{COO}^- \quad \rightarrow \quad \text{CH}_3\text{COO}^- + \text{CO}_2 + \text{H}_2
\]

Syntrophic association of acetogenic organisms with methanogenic H₂-consuming bacteria helps to lower the concentration of H₂ below inhibitory level so that propionate degrading bacteria are not suppressed by excessive H₂ level

H₂ partial pressure \(10^{-2}\) (100 ppm)
Homoacetogenes (3)

Homoacetogenesis has gained much attention in recent years in anaerobic processes due to its final product: acetate, which is the important precursor to methane generation. The bacteria are, H₂ and CO₂ users. *Clostridium aceticum* and *Acetobacterium woodii* are the two homoacetogenic bacteria isolated from the sewage sludge.

Homoacetogenic bacteria have a high thermodynamic efficiency; as a result there is no accumulation H₂ and CO₂ during growth on multi-carbon compounds.

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}
\]
**Methanogens (4 and 5)**

Methanogens are unique domain of microbes classified as Archeae, distinguished from Bacteria by a number of characteristics, including the possession of membrane lipids, absence of the basic cellular characteristics (e. g. peptidoglycan) and distinctive ribosomal RNA. Methanogens are obligate anaerobes and considered as a rate-limiting species in anaerobic treatment of wastewater. Moreover, methanogens co-exist or compete with sulfate-reducing bacteria for the substrates in anaerobic treatment of sulfate-laden wastewater.

Two classes of methanogens that metabolize acetate to methane are:

- **Methanoseta** (old name *Methanothrix*): Rod shape, low $K_s$, high affinity

- **Methanosarcina** (also known as *M. mazei*): Spherical shape, high $K_s$, low affinity
Growth kinetics of Methanosaeta and Methanosarcina
Environmental factors

The successful operation of anaerobic reactor depends on maintaining the environmental factors close to the comfort of the microorganisms involved in the process.

Temperature

- Anaerobic processes like other biological processes operate in certain temperature ranges

- In anaerobic systems: three optimal temperature ranges:
  - Psychrophilic (5 - 15°C)
  - Mesophilic (35 – 40 °C)
  - Thermophilic (50-55 °C)
Effect of temperature on anaerobic activity

Rule of thumb: Rate of a reaction doubles for every 10 °C rise in temperature up to an optimum and then declines rapidly.
There exist two microbial domains in terms of pH optima namely acidogens and methanogens. The best pH range for acidogens is 5.5 – 6.5 and for methanogens is 7.8 – 8.2. The operating pH for combined cultures is 6.8-7.4 with neutral pH being the optimum. Since methano-genesis is considered as a rate limiting step, it is necessary to maintain the reactor pH close to neutral.

Low pH reduces the activity of methanogens causing accumulation of VFA and H₂. At higher partial pressure of H₂, propionic acid degrading bacteria will be severely inhibited thereby causing excessive accumulation of higher molecular weight VFAs such as propionic and butyric acids and the pH drops further. If the situation is left uncorrected, the process may eventually fail. This condition is known as going “SOUR” or STUCK”.

**Remedial measures:** Reduce the loading rates and supplement chemicals to adjust the pH: alkaline chemicals such as NaHCO₃, NaOH, Na₂CO₃, quick lime (CaO), slaked lime [Ca(OH)₂], limestone (or softening sludge) CaCO₃, and NH₃ can be used.
pH dependence of methanogens

Relative activity of methanogens to pH

![Graph showing pH dependence of methanogens]
Natural buffering

An anaerobic treatment system has its own buffering capacity against pH drop because of alkalinity produced during waste treatment: e.g. the degradation of protein present in the waste releases NH₃, which reacts with CO₂ forming ammonium carbonate as alkalinity.

\[
\text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{NH}_4\text{HCO}_3
\]

The degradation of salt of fatty acids may produce some alkalinity.

\[
\text{CH}_3\text{COONa} + \text{H}_2\text{O} \rightarrow \text{CH}_4 + \text{NaHCO}_3
\]

Sulfate and sulfite reduction also generate alkalinity.

\[
\text{CH}_3\text{COO}^- + \text{SO}_4^{2-} \rightarrow \text{HS}^- + \text{HCO}_3^- + 3\text{H}_2\text{O}
\]

When pH starts to drop due to VFA accumulation, the alkalinity present within the system neutralizes the acid and prevents further drop in pH. If the alkalinity is not enough to buffer the system pH, we need external additions.
**Nutrients and trace metals**

All microbial processes including anaerobic require macro (N, P and S) and micro (trace metals) nutrients in sufficient concentration to support biomass synthesis. Anaerobic micro-organisms, especially methanogens, have specific requirements of trace metals such as Ni, Co, Fe, Mo, Se etc. The nutrients and trace metals requirements for anaerobic process are much lower as only 4 - 10% of the COD removed is converted to biomass.

\[
\text{COD:N:P = 350:7:1 (for highly loaded system) 1000:7:1 (lightly loaded system)}
\]

**Inhibition/Toxicity**

The toxicity is caused by substances present in the influent waste or byproducts of metabolic activities. Heavy metals, halogenated compounds, and cyanide are examples of the former type whereas sulfide and VFAs belong to latter. Ammonia from either group
Example: How much methane gas can be generated through complete anaerobic degradation of 1 kg COD at STP?

**Step 1: Calculation of COD equivalence of CH₄**

\[
\begin{align*}
\text{CH}_4 + 2\text{O}_2 & \Rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \\
16 \text{ g} & \quad 64 \text{ g}
\end{align*}
\]

\[\Rightarrow 16 \text{ g CH}_4 \sim 64 \text{ g O}_2 \text{ (COD)}\]

\[\Rightarrow 1 \text{ g CH}_4 \sim 64/16 = 4 \text{ g COD} \quad \text{---------} \quad (1)\]

**Step 2: Conversion of CH₄ mass to equivalent volume**

Based on the ideal gas law, 1 mole of any gas at STP (Standard Temperature and Pressure) occupies a volume of 22.4 L

\[\Rightarrow 1 \text{ Mole CH}_4 \sim 22.4 \text{ L CH}_4\]

\[\Rightarrow 16 \text{ g CH}_4 \sim 22.4 \text{ L CH}_4\]

\[\Rightarrow 1 \text{ g CH}_4 \sim 22.4/16 = 1.4 \text{ L CH}_4 \quad \text{---------} \quad (2)\]
Step 3: CH$_4$ generation rate per unit of COD removed

From eq. (1) and eq. (2), we have,

\[
\begin{align*}
=> & \quad 1 \text{ g CH}_4 \sim 4 \text{ g COD} \sim 1.4 \text{ L CH}_4 \\
=> & \quad 4 \text{ g COD} \sim 1.4 \text{ L CH}_4 \\
=> & \quad 1 \text{ g COD} \sim \frac{1.4}{4} = 0.35 \text{ L CH}_4 \\
\text{or} & \quad 1 \text{ Kg COD} \sim 0.35 \text{ m}^3 \text{ CH}_4 \quad \text{---------} \quad (3)
\end{align*}
\]

Complete anaerobic degradation of 1 kg COD produces 0.35 m$^3$ CH$_4$ at STP
Example 2. A UASB reactor has been employed to treat food processing wastewater at 20°C. The flow rate is 2 m³/day with a mean soluble COD of 7,000 mg/L. Calculate the maximum CH₄ generation rate in m³/day. What would be the biogas generation rate at 85% COD removal efficiency and 10% of the removed COD is utilized for biomass synthesis. The mean CH₄ content of biogas is 80%.

Solution:

Maximum CH₄ generation rate:
The complete degradation of organic matter in the waste could only lead to maximum methane generation and is also regarded as theoretical methane generation rate.

\[
(7000 \times 10^{-6})
\]
Total COD removed = \( \frac{\text{Total COD removed}}{\text{Total flow rate}} \) x (2) kg/d = 14 kg/d

\[
(10^{-3})
\]

From eq. (3) in example 1, we have
1 Kg COD produces 0.35 m³ CH₄ at STP
14 Kg COD produces \( \sim 0.35 \times 14 = 4.9 \text{ m}^3 \text{ CH}_4/\text{d} \) at STP
At 20°C, the CH₄ gas generation = \( 4.9 \times \frac{293}{273} \) = 5.3 m³/d
The maximum CH₄ generation rate = 5.3 m³/d
Biogas generation rate

Not all COD (organic matter) is completely degraded. The fate of COD during anaerobic treatment process can be viewed as

- Residual COD (in effluent)
- COD converted to CH$_4$ gas
- COD diverted to biomass synthesis
- COD utilized for sulfate reduction (if sulfate is present)

\[
\text{Total COD removed} = \frac{(7000 \times 10^{-6})}{(10^{-3})} \times (2) \times 0.85 \text{ kg/d} = 11.9 \text{ kg/d}
\]
As 10% of the removed COD has been utilized for biomass synthesis remaining 90% of the removed COD has thus been converted to CH₄ gas.

COD utilized for CH₄ generation = 11.9 x 0.9 kg/d

= 10.71 kg/d

From eq. (3) in example 1, we have:

1 Kg COD produces 0.35 m³ CH₄ at STP

10.71 Kg COD produces ~ 0.35 x 10.71 = 3.75 m³ CH₄/d at STP

At 20°C, the CH₄ gas generation = 3.75 x (293/273)

= 4.02 m³/d

The bio-gas generation rate is larger as it also contains CO₂ and H₂S = 4.02/0.80 = 5.03 m³/d
Advantage of anaerobic processes

1. Less energy requirement as no aeration is needed

0.5-0.75 kWh energy is needed for every 1 kg of COD removal by aerobic processes

2. Energy generation in the form of methane gas

1.16 kWh energy is produced for every 1 kg of COD fermented in anaerobic process

3. Less biomass (sludge) generation

Anaerobic process produces only 20% of sludge compared with aerobic process

Soluble BOD

\[ 1 \text{ kg} \]

Aerobic process

\[ \text{CO}_2 + \text{H}_2\text{O} \]

\[ 0.5 \text{ kg} \]

New biomass

\[ 0.5 \text{ kg} \]

Biodegradable COD

\[ 1 \text{ kg} \]

Anaerobic process

\[ \text{CH}_4 \text{ gas} \]

\[ > 0.9 \text{ kg} \]

New biomass

\[ < 0.1 \text{ kg} \]
4. Less nutrients (N & P) required

Lower biomass synthesis rate also implies less nutrients requirement: 20% of aerobic

5. Application of higher organic loading rate

Organic loading rates of 5-10 times higher than that of aerobic processes are possible

6. Space saving

Higher loading rates require smaller reactor volumes thereby saving on disposal cost

7. Ability to transform several hazardous solvents

including chloroform, trichloroethylene and trichloroethane to an easily degradable form
Limitations of anaerobic processes

1. Long start-up time

Because of lower biomass synthesis rate, it requires a longer start-up time to attain a biomass concentration

2. Long recovery time

If an anaerobic system is subjected to disturbances either due to biomass wash-out, toxic substances or shock loading, it may take longer time for the system to return to normal operating conditions

3. Specific nutrients/trace metal requirements

Anaerobic microorganisms, especially methanogens, have specific nutrients e.g. Fe, Ni, and Co requirement for optimum growth

4. More susceptible to changes in environmental conditions

Anaerobic microorganisms especially methanogens are prone to changes in conditions such as temperature, pH, redox potential, etc.
5. Treatment of sulfate-rich wastewater

The presence of sulfate not only reduces the methane yield due to substrate competition, but also inhibits the methanogens due to sulfide production.

6. Effluent quality of treated wastewater

The minimum substrate concentration ($S_{\text{min}}$) from which microorganisms are able to generate energy for their growth and maintenance is much higher for anaerobic treatment systems. Anaerobic processes may not be able to degrade organic matter to the level to meet the discharge limits for ultimate disposal.

7. Treatment of high protein & nitrogen containing wastewater

The anaerobic degradation of proteins produces amines which are no longer be degraded anaerobically. Similarly nitrogen remains unchanged during anaerobic treatment. Recently, a process called ANAMMOX (ANaerobic AMMonium OXididation) has been developed to anaerobically oxidize $\text{NH}_4^+$ to $\text{N}_2$ in presence of nitrite.

$$\text{NH}_4^+ + \text{NO}_2^- \implies \text{N}_2 + 2\text{H}_2\text{O}$$

$$\text{NH}_4^+ + 1.32\text{NO}_2^- + 0.066\text{CO}_2 + 0.13\text{H}^+ \implies 1.02\text{N}_2 + 0.26\text{NO}_3^- + 0.066\text{CH}_2\text{O}_{0.5}\text{N}_{0.15}$$
Essential conditions for efficient anaerobic treatment

- Avoid excessive air/O$_2$ exposure
- No toxic/inhibitory compounds present in the influent
- Maintain pH between 6.8 – 7.2
- Sufficient alkalinity present (mainly bicarbonates)
- Low volatile fatty acids (VFAs)
- Temperature around mesophilic range (30-38 °C)
- Enough nutrients (N & P) and trace metals especially, Fe, Co, Ni, etc. COD:N:P = 350:7:1 (for highly loaded system) 1000:7:1 (lightly loaded system)
- SRT/HRT >>1 (use high rate anaerobic reactors)