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Initial studies on the temperature-phased anaerobic biofilter process

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Initial studies on the temperature-phased anaerobic biofilter process

by

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DEDICATION

To Sanford and Andrew. Thank you for allowing me to realize my goals, and for your understanding, help and patience.

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I. INTRODUCTION

In recent years, publically-owned wastewater treatment plants (POTWs) have been faced with increased quantities of organic-containing wastewaters which must undergo treatment. Increasing populations and significant industrial wastewater contributions have lead to the situation where many POTWs have approached, or have exceeded their design capacities. Also, in today's economic climate, federal funds for the expansion of POTWs are rare or nonexistent.

In response to organic overloading and a lack of federal funds for expansion, many POTWs have been forced to increase sewer-use fees to wet industries to act as an incentive for industries to develop ways to reduce their organic discharges.

Aside from process engineering applications, which may focus on waste minimization techniques, there are generally three methods industries use to pretreat their wastewaters including:

1. Physical-chemical treatment
2. Aerobic biological treatment
3. Anaerobic biological treatment

Physical-chemical techniques serve to remove organic matter from industrial wastewaters using a variety of mechanisms. An example is dissolved air flotation in which

organic matter along with a large fraction of water is removed by air injection, flotation, and skimming removal mechanisms. In physical-chemical techniques, the organic matter is not destroyed but is simply removed from the waste stream. Characteristically, physical-chemical methods create large volumes of waste sludge.

Aerobic biological treatment involves using aerobic microorganisms to metabolize organic matter in an industrial effluent. Aerobic treatment has several disadvantages, including large power requirements to provide oxygen transfer, nutrient requirements for bacterial growth, large land areas are necessary, and a relatively large quantity of excess biomass is produced which must be dewatered and ultimately disposed.

Anaerobic biological treatment involves using a consortium of facultative and anaerobic microorganisms to metabolize and degrade organic matter in industrial effluents. No oxygen is necessary, less waste sludge is produced, and methane, a useful fuel by-product, is generated during the process.

Several high-rate anaerobic processes have been developed during the last forty years. These processes have the ability to treat industrial wastewaters high in organic matter at low hydraulic retention times (HRTs).

Preliminary research was conducted at Iowa State University on a new high-rate two-stage, two-temperature anaerobic treatment process (Harris, 1992). This new process is being termed the Temperature-Phased Anaerobic Biofilter Process, or TPAB. The TPAB process involves a thermophilic anaerobic biofilter connected in series to a mesophilic anaerobic

biofilter. In a laboratory demonstration at Iowa State University, the TPAB process in its initial configuration of equal size thermophilic and mesophilic stages proved very promising. COD removals were in excess of 90%. This research attempts to more fully characterize the TPAB process.

II. OBJECTIVES AND SCOPE OF STUDY

A review of the literature uncovered several studies on anaerobic treatment using two-stage processes, but no specific study was located where a two-stage process was described using a first-stage thermophilic anaerobic filter connected in series to a second-stage mesophilic anaerobic filter.

Previous studies involved two-phase processes were found to most often involve the concept of phase optimization. Phase optimization involves the use of kinetic controls with dilution rates to provide an optimum environment for the rapid-growing acidogens in the first stage and slower-growing acetogens and methanogens in the second stage.

The TPAB process was first undertaken at Iowa State University not for phase optimization, but for optimum system performance in terms of organic matter removal. The initial TPAB system involved identical size units for both the thermophilic and mesophilic stages at system HRTs of 24 and 48 hrs.

The purpose of this study was to perform an in-depth characterization of the TPAB process in the laboratory over a range of organic loading rates and HRTs.

Some specific objectives of this research were to:

1. Determine if an optimum reactor size ratio exists between the thermophilic and mesophilic phases in the TPAB system.

2. Collect fundamental data on thermophilic anaerobic biofilter treatment using a complex soluble synthetic waste at HRTs of 3, 4.5, 6, and 9 hrs.

3. Investigate the thermophilic anaerobic biofilter to determine the minimum effective HRT.

4. Measure the effect of operation of the thermophilic biofilters after saturation loading has been achieved.

5. Determine the effect of potentially high concentrations of ammonia on both phases of the TPAB process.

6. Measure individual volatile acids produced during treatment, and determine the effect of high concentrations of volatile acids on the TPAB process.

III. LITERATURE REVIEW

The literature review is divided into five sections: a) fundamentals of anaerobic digestion, b) microbiology of methanogens, c) thermophilic anaerobic treatment, d) fixed-film processes, e) two-phase anaerobic treatment, and f) temperature-phased anaerobic biofilter development. This review attempts to include previous work relevant to this research.

Fundamentals of Anaerobic Digestion

Anaerobic digestion is a biological treatment process that involves the use of a mixed population of microorganisms to convert and stabilize organic matter in wastes. The organic matter is stabilized to carbon dioxide (CO_2) and methane (CH_4) in the absence of oxygen. Anaerobic digestion has been practiced for over half a century, and was first used for the degradation of municipal sewage sludge.

Since the 1950s, anaerobic digestion has been applied not only for sewage sludge, but has gained popularity as a treatment technique for both dilute and high-strength industrial wastewaters.

There are two types of biological treatment, aerobic and anaerobic. In aerobic treatment systems, rapidly-dividing microorganisms degrade organic matter into carbon dioxide and water. The aerobic degradation of organic matter releases a large quantity of energy, which is largely converted into new microbial cells. Because the aerobic microorganisms have a high growth rate, excess biomass must be removed and ultimately disposed as biological waste

sludge. Large quantities of oxygen must be supplied to an aerobic system which requires a significant power input to the system. Aerobic biological treatment systems were often viewed in the past as superior to anaerobic systems when energy for oxygen input was less expensive and the land to dispose of excess biomass was more plentiful.

Anaerobic microorganisms are relatively slow-growing because less energy is released in the reactions involved in the anaerobic stabilization of organic matter (McCarty, 1964b). Because the anaerobic microorganisms are slow-growing, there is a low production of waste biological sludge. Also, because of the lower growth yield, fewer nutrients such as nitrogen and phosphorus are required than are typically needed for aerobic systems. Anaerobic systems do not require oxygen, thus eliminating the power requirement and aerating equipment necessary in aerobic systems. Since oxygen is not required in anaerobic systems, treatment rates are not limited by oxygen transfer. This means that a higher degree of waste stabilization is possible using an anaerobic treatment process. Another important advantage of anaerobic systems is the production of methane gas as a useful by-product that results from the stabilization of organic matter. This methane can be utilized as a valuable energy source at the treatment site.

There are several disadvantages of anaerobic treatment systems (McCarty, 1964a; Obayashi, 1985). Because of the slower growth rate of some of the anaerobic microorganisms, there is often a slow start-up period for an anaerobic system. Another disadvantage is that in practice, mesophilic temperatures are often used for optimal growth of the anaerobic microorganisms. Also, anaerobic systems are inable to achieve low soluble substrate concen-

trations in the final effluent. The disadvantages of anaerobic treatment as compared to aerobic treatment are few.

The primary objective of anaerobic digestion is the stabilization of organic matter. Stabilization is accomplished by the conversion of organics into the final end products, methane and carbon dioxide.

Anaerobic digestion of organic matter can be divided into three steps including: 1) hydrolysis, liquefaction, and fermentation, 2) hydrogen and acetic acid formation, and 3) methane formation, as illustrated in Figure 1 (Parkin and Owen, 1986). Although anaerobic digestion is often described as a three-step process, the metabolism of the microbial groups involved are interdependent. At least five different groups of microorganisms are involved, including the fermentive bacteria, hydrogen-producing and hydrogen-consuming bacteria, acetogenic bacteria, carbon dioxide reducing bacteria, and the aceticlastic methanogens.

The first step in anaerobic digestion is hydrolysis and liquefaction (Parkin and Owen, 1986). Hydrolysis and liquefaction involves the breakdown of particulate and complex insoluble matter into smaller molecules which can pass through microbial cell walls. Extracellular enzymes, which are produced by hydrolytic bacteria, accomplish the hydrolysis and liquefaction steps. No waste stabilization takes place during this first step, rather the organic matter is converted into a form which can be taken up by the microorganisms. Anaerobic digestion may be limited by the hydrolysis and liquefaction step if the waste to be treated contains a large portion of particulate material. Some wastes may contain a significant portion

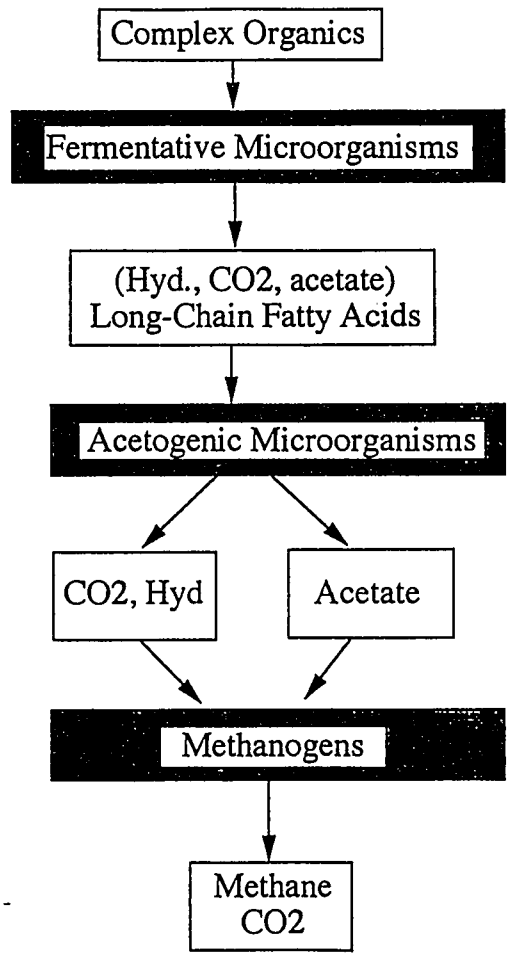


Figure 1. Methane formation in anaerobic digestion

of refractory or nonbiodegradable organic material which is not able to be hydrolyzed by microorganisms.

Once the organic matter has been hydrolyzed into smaller molecules, the smaller molecules are fermented into short-chain fatty acids such as propionic, butyric, and valeric acids. The bacteria which are involved in these fermentative reactions include facultative anaerobes and strict or obligate anaerobes. Acetic acid, hydrogen, and carbon dioxide are also formed during the fermentation step. During the fermentation reactions, organic matter is once again changed in form but is not stabilized.

The long chain fatty acids are next converted into acetate, carbon dioxide, and hydrogen. Some of the fatty acids are converted into propionate, but the majority are converted into acetate by the acetogenic microorganisms (Parkin and Owen, 1986).

Waste stabilization occurs in anaerobic digestion by two main mechanisms, acetate cleavage by aceticlastic methanogens, and carbon dioxide reduction by CO_2-reducing methanogens (McCarty, 1964a; Parkin and Owen, 1986). During acetate cleavage, carbon dioxide is also produced and either escapes as a gas or is converted to bicarbonate alkalinity. From C^{14} tracer studies it was determined that approximately 72% of methane production results from acetate cleavage, and the remaining 28% of methane production results from the reduction of carbon dioxide using hydrogen (Jeris and McCarty, 1962; Parkin and Owen, 1986). Acetate and hydrogen are the major substrates used by methanogens. Other substrates which have been utilized to a lesser extent by a limited number of methanogens include formate, methanol, methylamines, and carbon dioxide (Gottschalk, 1986).

Anaerobic waste treatment kinetics have been evaluated using the kinetic theories of growth and substrate utilization. These theories are based on the continuous steady-state behavior of pure cultures of microorganisms using a single limiting substrate (McCarty, 1966). An understanding of the kinetics of anaerobic digestion is important in understanding the key factors affecting process efficiency and stability (Parkin and Owen, 1986).

The Monod equation describes cellular growth and is often used as a basis to describe bacterial growth kinetics in anaerobic treatment systems:

$$\mu = \frac{\mu_m S}{K_s + S}$$

where μ (1/day) is termed the net specific bacterial growth rate, μ_m (1/day) is the maximum specific growth rate, K_s is the half-saturation or half-velocity constant (mass of substrate/volume), and is equal to the concentration of the rate limiting substrate when $\mu = 1/2\ \mu_m$. S is the limiting substrate concentration (mass/volume) (Shuler and Kargi, 1992).

The Michaelis-Menton equation shown below was first developed for single substrate enzyme catalyzed reactions, and is often used for biological systems to express substrate utilization rates:

$$k = \frac{k_m S}{K_s + S}$$

where k (1/time) is the substrate utilization rate, and k_m is the specific substrate utilization rate (1/time). K_s has been defined as the driving force required to achieve half of the maximum specific substrate utilization rate (Metcalf and Eddy, 1991).

The yield of biomass per unit of substrate utilized is very important, especially for anaerobic systems. The yield can be defined as:

$$Y = \frac{\mu}{k}$$

where k is the substrate utilization rate and μ is the net specific bacterial growth rate.

These fundamental equations have been applied to anaerobic biological treatment systems using the following two equations (Parkin and Owen, 1986):

$$\frac{-dS}{dt} = \frac{k\,S\,X}{K_s + S}$$

and

$$\frac{dX}{dt} = Y\,(dS/dt) - bX$$

where,

$\frac{dS}{dt}$ = Rate of organic matter removal (mass substrate/vol-time)

X = Biomass concentration (mass/volume)

b = Bacterial decay rate (1/day)

The first equation states that the rate of organic matter removal is a function of the substrate concentration (S), the amount of biomass present (X), the substrate utilization rate (k), and the driving force or velocity of the substrate removal by the microorganisms.

The second equation states that the biomass growth rate is a function of the yield, or how quickly microorganisms can grow and utilize the organic matter, less the decrease in biomass as a function of endogenous bacterial decay.

Combining the above two equations results in a third relationship as follows:

$$\mu = \frac{Y\ k\ S}{K_s + S} - b$$

The net specific growth rate of the biomass is a function of the amount of substrate, how quickly the microorganisms utilize the substrate, and the yield of the biomass, less the loss of biomass related to endogenous decay.

The solids retention time is related to the net specific growth rate as follows (Parkin and Owen, 1986):

$$\frac{1}{\theta_c} = \frac{Y\ k\ S}{K_s + S} - b = \mu$$

In this equation, S is the effluent organic matter concentration from a given anaerobic treatment process. This equation states that the net specific growth rate, μ, is equal to the inverse of the biological solids retention time θ_c, also known as the solids retention time, SRT. From the above relationship, it is concluded that bacterial growth rate and process efficiency, in terms of effluent organic concentration S, can be controlled by controlling the SRT or θ_c.

Temperature influences the metabolic rates of microorganisms and the substrate utilization rate. The temperature dependance of biological rate constants is important in assessing the overall removal efficiency of a given biological process (McCarty, 1966). Although temperature influences substrate utilization rates, temperature does not affect growth yields. Although growth yields are not affected by temperature, the net specific growth rate of biomass, μ, is affected, since at higher temperatures the endogenous decay of microorganisms increases. The effect of temperature on the reaction rate of a biological process is expressed as follows:

$$K_T = K_{20}\ \theta^{(T - 20)}$$

where,

K_T = Rate coefficient at any temperature

K_{20} = Rate coefficient at temperature of 20° C

θ = Temperature activity coefficient

T = Temperature, ° C

Successful anaerobic treatment involves many, often interrelated factors. The most important control parameters for anaerobic treatment include (McCarty, 1964b; Dague, 1967; Dague, 1970; Parkin and Owen, 1986):

1. Solids retention time.
2. Maintenance of anaerobic conditions (lack of oxygen).
3. pH of 6.5 to 8.2.
4. Optimum temperatures:

   Mesophilic range - 30 to 38° C

   Thermophilic range - 50 to 60° C
5. Sufficient biological nutrients.
6. Absence of toxic materials.

One of the key factors affecting process stability and efficiency is the solids retention time, or SRT (Dague, 1967; Dague, 1970). SRT is defined at steady-state as the mass of solids contained in a reactor divided by the mass of solids wasted per day.

Dague conducted significant research on solids retention times of anaerobic treatment systems. He stated that since the regeneration rate of methanogenic bacteria is two to ten days at mesophilic temperatures, the minimum SRT for operation in the mesophilic range should be

approximately ten days. Since regeneration rates of microorganisms are higher at higher temperatures, the minimum SRT must be less than ten days at higher temperatures. If high SRTs can be achieved for a given anaerobic treatment process, then the process will have an inherent margin of safety in case of treatment upsets. Parkin recently stated that the SRT is the most important design factor for anaerobic processes (Parkin and Owen, 1986).

Maintenance of anaerobic conditions is imperative in anaerobic treatment processes. Oxygen is toxic to methanogenic microorganisms since they are obligate anaerobes. This is extremely important since the growth of the methanogenic bacteria is considered to be the rate limiting step in anaerobic treatment (McCarty, 1964b).

Maintenance of system pH in the proper range is required for efficient anaerobic treatment. The generally accepted range for good process efficiency is 6.5 to 8.2, with the optimum range being 6.8 to 7.2 (McCarty, 1964b). Deterioration of the anaerobic process has been reported at pH values below 6.5 and greater than 8.2 (Duarte and Anderson, 1983; Seagren, Levine and Dague, 1990). The methanogens are thought to be the most sensitive to pH changes (Parkin and Owen, 1986).

During system imbalance, the volatile acids produced by acetogenic bacteria increase at a faster rate than can be used by the acetoclastic methanogens. Unless the system contains sufficient buffering capacity measured as alkalinity, the pH will decrease. Prevention of pH imbalances may require the addition of buffering materials such as bicarbonates to maintain the pH in the neutral range (McCarty, 1964b). Alkalinities ranging from 2500 to 5000 mg/L (as $CaCO_3$) are desirable in anaerobic treatment systems.

Nutrients must be present in sufficient quantities to ensure efficient anaerobic waste stabilization. Nitrogen and phosphorus are the nutrients which are required in the highest concentration, and are termed macronutrients. The commonly used empirical formula for a bacterial cell is $C_5H_7O_2N$ (McCarty, 1964b). Nitrogen compromises 12% of the bacterial cell mass, and the substrate should contain sufficient nitrogen for microbial growth. The phosphorus requirement is approximately 1/7 to 1/5 of the nitrogen requirement. Nitrogen is used to synthesize structural proteins, enzymes, RNA, and DNA. Phosphorus is required to synthesize energy storage compounds such as ATP, and also in the assembly of RNA and DNA (Gottschalk, 1986; Parkin and Owen, 1986).

Other nutrients are required in lower concentrations than nitrogen and phosphorus, and are commonly termed micronutrients. Micronutrients which are known to be essential for anaerobic growth include iron, nickel, cobalt, sulfur, calcium, and some trace organics (Parkin and Owen, 1986). Although it is known that these micronutrients are required, the complete nutritional requirements for the methanogens has not been fully determined (Takashima and Speece, 1989).

Many industrial wastewaters have been labelled as difficult to treat. Many of these wastewaters are often lacking in essential macro or micronutrients. A detailed analysis of the wastewater is necessary. The addition of supplemental nutrients may reclassify a difficult to treat industrial wastewater into a prime candidate for anaerobic treatment (Takashima and Speece, 1989).

Toxicity in any biological waste treatment process may cause inhibition of microorganisms, leading to system failure. Whether a substance is toxic is a matter of the nature of the substance, concentration, and acclimation. Many substances are stimulatory in low concentrations, and only become inhibitory at higher concentrations. The precise concentration at which a substance may become inhibitory depends on the nature of the substance (McCarty, 1964c; Parkin and Owen, 1986).

It is often mistakenly believed that anaerobic microorganisms, especially methanogens, are more sensitive to toxic substances as compared to aerobic or facultative microorganisms. If a sufficient biological safety factor is provided, in terms of a large SRT, anaerobic and aerobic systems should display similar toxicity responses (Parkin and Owen, 1986).

Industrial wastewaters characteristically can have higher concentrations of potentially toxic substances than are generally found in wastewater sludges. Analysis of the raw wastestream is vitally important in determining the potential for pretreatment of such wastewaters using anaerobic treatment. Higher concentrations of toxic substances may be tolerated if there is proper acclimation of the microorganisms (Parkin and Owen, 1986).

There are a number of different control methods that may be used for toxic substances including (McCarty, 1964c):

1. Remove toxic material from waste.
2. Dilute below the toxic level.

3. Form insoluble complex or precipitate.
4. Antagonize toxicity with another material.

Table 1 summarizes the concentrations of various inorganic substances considered to be inhibitory to anaerobic treatment. Table 2 lists inhibitory concentrations for selected organic substances (Parkin and Owen, 1986).

Ammonia-nitrogen and bicarbonate alkalinity are produced during the degradation of organics containing proteins. Ammonia-nitrogen is thought to be toxic in two ways, depending on pH. As illustrated in the equation below, ammonia-nitrogen may be present in the form of the ammonium ion, NH_4^+, or as dissolved ammonia gas, NH_3 (Albertson, 1961; McCarty and McKinney, 1961):

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

At a higher pH, more ammonia-nitrogen will be present as free ammonia, NH_3-N. At a lower pH, the NH_4^+ ion will predominate. It is generally accepted that ammonia toxicity is associated with the free ammonia, NH_3-N, and concentrations in excess of 100 mg/L potentially may cause severe toxicity (Kugelman, 1971; Kroeker, 1979).

Using the following equations, the concentration of free ammonia can be determined at any given pH (McCarty and McKinney, 1961):

$$\frac{[NH_4^+]\,[OH^-]}{[NH_3]\,[H_2O]} = K_d\ (1.85 \cdot 10^{-5} \text{ at } 35^\circ C)$$

$$\frac{[H^+]\,[OH^-]}{[H_2O]} = K_d\ (2.09 \cdot 10^{-14} \text{ at } 35^\circ C)$$

Combining the above two equations:

$$[NH_3]_{free} = \frac{1.13 \cdot 10^{-9}\,[NH_4^+]}{[H^+]} \quad (\text{at } 35^\circ C)$$

Temperature also has an effect on the relative concentration of free NH_3-N for a system. Higher temperatures result in relatively higher concentrations of free ammonia, and lower temperatures result in lower concentrations of free ammonia (Parkin and Owen, 1986). Total ammonia concentrations exceeding 1,500 mg/L are generally accepted to be inhibitory to any anaerobic treatment system (McCarty, 1964c). With proper microbial acclimation, total ammonia concentrations ranging from 4,500 to 9,000 mg/L have been reported as tolerable in anaerobic treatment (Parkin and Miller, 1982; Koster and Lettinga, 1988).

Table 1. Inhibitory concentrations of inorganics for anaerobic treatment (Parkin and Owen, 1986)

Substance	Moderately Inhibitory mg/L	Strongly Inhibitory mg/L
Na^+	3,500-5,500	8,000
K^+	2,000-4,500	12,000
Mg^{2+}	1,000-1,500	3,000
Ca^{2+}	2,500-4,500	8,000
Ammonia-nitrogen	1,500-3,000	>3,000
Sulfide	200	200
Copper	-	0.5 (soluble) 50-70 (total)
Chromium VI	-	3.0 (soluble) 200-260 (total)
Chromium III	-	180-420 (total)
Nickel	-	2.0 (soluble) 30 (total)
Zinc	-	1.0 (soluble)

Table 2. Inhibitory concentrations of selected organics for anaerobic treatment (Parkin and Owen, 1986)

Organic	Inhibitory Concentration mg/L
Formaldehyde	50-200
Chloroform	0.5
Ethyl Benzene	200-1,000
Ethylene Dichloride	5
Kerosene	500

Volatile acid concentrations increase in anaerobic treatment during system imbalance. It has been reported that acetate is the least toxic of the volatile acids, and that propionate is the most toxic (Mawson et al., 1991). It has also been observed that if the pH is maintained in the proper range, volatile acid concentrations up to 6,000 mg/L can be tolerated with no loss in methane production (McCarty et al., 1964e).

It has been reported that it is the unionized volatile acids which are toxic to methanogens. The concentration of unionized volatile acids is dependent on system pH. Unionized volatile acid levels ranging from 30 to 60 mg/L have been reported to be inhibitory. At a total volatile acid concentration of 5,500 mg/L and a pH of 7.0, the unionized volatile acid level is 30 mg/L. At a system pH of 6.5, a total volatile acid concentration of 1,800 mg/L is required to reach an unionized volatile acid concentration of 30 mg/L. If the pH in the system is maintained at 7.0, a relatively high concentration of total volatile acids can be tolerated (Andrews, 1969; Parkin and Owen, 1986).

High concentrations of organic sulfur compounds are found in many industrial wastewaters, especially pulp and paper mills. Organic sulfur can be degraded by hydrolytic bacteria to form sulfate, and sulfate can be utilized by sulfate-reducing bacteria in anaerobic systems to form hydrogen sulfide (Sarner et al, 1988). There are two problems associated with wastewaters high in sulfate. Firstly, the sulfate-reducing bacteria also utilize hydrogen and acetic acid as energy sources, and outcompete methanogens for these substrates since the sulfur-reducing bacteria are energetically favored. The second problem associated with wastewaters high in sulfate occurs when the sulfate is reduced to sulfide. Soluble hydrogen sulfide concentrations above 200 mg/L are toxic to the methanogenic bacteria, and can cause significant decreases in methane production (Parkin and Owen, 1986). There have been cases where sulfides have been added to a wastestream to precipitate heavy metals, and caution should

be taken so that heavy metal toxicity is not traded for sulfide toxicity. Hydrogen sulfide may be present in a gaseous or liquid form, or as the HS^- ion as shown below (Sarner et al, 1988):

$$H_2S\ (gas) \rightleftarrows H_2S\ (liquid) \rightleftarrows HS^- + H^+$$

At a system pH above 7, the less toxic HS^- will predominate, and at a system pH less than 7, the more toxic free soluble H_2S will predominate. There are several methods for the control of H_2S toxicity including (Sarner et al, 1988):

1. Precipitation of H_2S by the addition of metal ions.
2. Increase of pH by the addition of chemicals to convert H_2S to the less toxic HS^-.
3. Gas washing to remove H_2S from the biogas and the recirculation of the washed biogas to remove more H_2S from the liquid phase.

Heavy metals including chromium (VI), copper, nickel, and zinc are toxic to anaerobic systems. The total concentration of heavy metals in a wastewater may be much higher than the soluble concentration of the free metal ions in solution, due to various chemical reactions. These reactions may reduce the "available" heavy metal concentration by a factor of over 1000. Although the soluble concentrations of free metal ions is usually quite low, it has been reported that extremely low concentrations of these ions have resulted in severe toxicity to anaerobic

systems (Parkin and Owen, 1986). Sulfides have been successfully used to precipitate out heavy metals from various wastewaters (Lawrence and McCarty, 1965).

Successful applications for the treatment of a wide varient of wastes can be possible with a proper understanding of the fundamentals of anaerobic treatment. Better treatment efficiencies and control can be obtained when care is taken to recognize the importance of various control parameters such as proper pH and alkalinity, sufficient nutrients, adequate solids retention time, and an absence or control of toxic materials including ammonia, volatile acids, sulfides, organics, and heavy metals.

Microbiology of Methanogens

In 1776, the Italian physicist Alessando Volta was the first to make the observation of "combustible air" being formed in the sediments of streams, bogs, and lakes (Barker, 1956). This "combustible air" or biogas was later discovered to be a mixture of methane (CH_4) and carbon dioxide (CO_2).

The scientific question as to how this biogas evolved was studied by a number of scientists. In 1868, Bechamp was the first to claim that a microbial process was the cause of biogas formation. Others such as Seyer, Omelianski, and Sohngen substantiated Bechamp's findings (Barker, 1956).

Anaerobic life was first discovered by Pasteur between 1857 and 1876 while he was devoting considerable effort to the study of bacterial fermentations (Dague, 1981). He isolated

Clostridia sp. which under fermentative conditions produced butyric acid from sugars. It was observed by Pasteur that oxygen was lethal to these microorganisms.

During the latter half of the nineteenth century, scientists studied the microbial basis for methane formation using mixed microbial cultures. It was realized that the organisms responsible must be anaerobic, since oxygen was toxic to the mixed cultures. Oxygen toxicity proved to be a major obstacle in attempts to isolate pure cultures of microorganisms responsible for methane production. In 1936, Barker was the first to isolate a pure culture of methane-producing bacteria, which were termed methanogens (Gottschaulk, 1988).

Barker used enrichment cultures to isolate methanogens (Barker, 1936). In his isolation technique, a boiled solution of inorganic salts and tap water served as a source of trace nutrients. Ammonium salts were added as a nitrogen source, and sodium sulfide was added as a reducing agent for the media. Calcium carbon, aspestos fibers, or sterile mud was also added as a sediment material. At the time, it was thought that methanogenic bacteria required sediment for optimal growth. Organic substrates were used, and the enrichment cultures were seeded with one of the following: sewage sludge, black (anaerobic) mud, rumen contents, or animal wastes. Anaerobic conditions were maintained by placing the cultures in glass-stoppered bottles filled to capacity to omit air. The cultures were incubated at 30 to 37° C.

Using his anaerobic enrichment techniques, Barker was able to isolate four distinct groups of methanogenic bacteria. These four groups were classified based on morphological and physiological characteristics (Barker, 1936). The four groups are shown in Table 3.

Table 3. Groups of methanogenic bacteria (Barker, 1936)

Organism	Morphology	Reactions Catalyzed
Methanosarcina methanica	large spherical packets, gram variable, non-sporeforming	Fermentation of acetic and butyric acids to methane.
Methanococcus Mazei n.sp.	small, spherical gram variable, non-spore forming	Fermentation of acetic and butyric acids to methane.
Methanobacterium Sohngenii, n.sp.	rod shaped joined in bundles, gram negative, non-spore forming	Fermentation of acetic and butyric acids to methane.
Methanobacterium Omerlianskii, n.sp.	thin, bent rods, gram negative	Fermentation of ethyl alcohol to acetic acid and butyl alcohol to butyric acid with methane formation.

Hungate and Smith perfected the isolation techniques for methanogens first developed by Barker, which they termed the roll-tube method (Hungate, 1950; Smith and Hungate, 1958). In the roll-tube method, sterile tubes with butyl rubber stoppers were used. The head space of the tubes was replaced with a 80:20 ratio by volume mixture of hydrogen and carbon dioxide, respectively. Innoculating seed fluid was added to molten medium, and the medium was rolled onto the sides of the tubes in an ice-bath until cooled. Small methanogenic colonies were

observed on the surface of the media, which grew larger upon replenishment of the head space gas.

Subsequent applications of the Hungate roll-tube technique, along with a better understanding of the nutritional requirements of methanogens resulted in the isolation of a total of thirteen different species of methanogens (Mah and Smith, 1981).

During the late 1970s and early 1980s, a significant amount of research was conducted on the examination of the 16 S ribosomal RNA (rRNA) oligonucleotide sequences as a classification tool for various microorganisms. During this time, Fox and others determined and compared the 16 S rRNA oligonucleotide sequences for a variety of methanogenic bacteria (Balch et al, 1979). It was discovered that methanogens had distinctly different rRNA sequences than other prokaryotes. The methanogens were reclassified based on the sequence homology of their 16 S rRNA sequences. The reclassification scheme is shown in Table 4, and the characteristics of the different species of methanogens are shown in Table 5.

The methanogens are a morphologically diverse group, consisting of such forms as long or short rods, small or large cocci, and various lancet and spirillum shapes. The majority of methanogens have a temperature optima for growth in the mesophilic range of 30 to 45° C. All methanogens are strict anaerobes and reduce carbon dioxide using molecular hydrogen to

Table 4 . Classification of methanogens (Balch, 1979; Mah and Smith, 1981)

Order	Family	Genus	Species
Methanomicrobiales	Methanomicrobiaceae	Methanogenium	M. cariaci
			M. marisnigri
		Methanospirillum	M. hungatei
Methanobacteriales	Methanobacteriaciae	Methanobacterium	M. formicicum
			M. bryantii
			M. thermoautotrophicum
		Methanobrevibacter	M. rumiantium
			M. arboriphilus
			M. smithii
Methanococcales	Methanococcaceae	Methanococcus	M. vannielii
			M. voltae
	Methanosarcinaceae	Methanomicrobium	M. mobile
		Methanosarcina	M. barkeri

Table 5. Properties of methanogens (Balch, 1979; Mah and Smith, 1981)

Species	Temp. Optima	Substrates	Gram Stain	Morphology
M. formicicum	37-45° C	H_2, formate	+	long rods, filaments
M. bryantii	37-39° C	H_2	+	long rods, filaments
M. thermoautotrophicum	65-70° C	H_2, carbon monoxide	+	long rods, filaments
M. rumiantium	37-39° C	H_2, formate	+	short rods or lancet-shaped cocci
M. arboriphilus	37-39° C	H_2	+	short rods or lancet-shaped cocci
M. smithii	37-39° C	H_2, formate	+	short rods or lancet-shaped cocci
M. vannielii	36-40° C	H_2, formate	-	regular to irregular small cocci
M. voltae	36-40° C	H_2, formate	-	regular to irregular small cocci
M. mobile	40° C	H_2, formate	-	short, curved rods
M. cariaci	20-25° C	H_2, formate	-	small, irregular cocci
M. marisnigri	20-25° C	H_2, formate	-	small, irregular cocci
M. hungatei	30-40° C	H_2, formate	-	long curved rod or spirillum
M. barkeri	35-40° C	H_2, acetate, methanol, methylamines	+	irregular cocci in packets

produce methane. Some methanogens can use other simple substrates to produce methane including: formate, acetate, carbon monoxide, methanol, and methylamines (Mah, Smith, and Baresi, 1978; Mah and Smith, 1981). The genus Methanosarcina is the most diverse in terms of number of growth substrates it can utilize.

Methanogenic bacteria belong to the phylogenetic group of bacteria termed the "archaebacteria". Other archaebacteria include the genera Sulfolobus, Thermoplasma, and the Halobacteria. The archaebacteria lack true murein in their cell walls and contain unusual ether lipids rather than phospholipids in their cell membranes (Gottschalk , 1988).

The methanogens are widely distributed in nature, being most commonly found in anoxic environments where organic matter undergoes anaerobic decomposition (Balch et al, 1979; Mah et al, 1977; Wolfe, 1971). The methanogenic bacteria are found in habitats where redox potential values are - 200 mV or less.

Methanogens have been isolated from aquatic sediments such as ponds, marshes, swamps, lakes, rice fields, and hydrothermal deep-sea vents. Other habitats include the intestinal tract of man and animals (especially the rumen of cattle), sewage digesters, and landfills. Methanogens have been isolated in the hot springs of Yellowstone National Park, where they use geothermally produced hydrogen as a growth substrate (Ziekus, 1977).

Methanogens that reduce carbon dioxide using molecular hydrogen have been discovered in natural environments to often live in close association with rapid-growing hydrogen-producing fermentative microorganisms (Mah and Smith, 1981). In this close association, it

has been postulated that "interspecies hydrogen transfer" occurs between the fermentative microorganisms and the methanogens. This type of living arrangement is thought to be beneficial to both groups of bacteria. The removal of hydrogen by the methanogens allows otherwise thermodynamically unfavorable reactions to take place in the decomposition of organic matter.

Methanogens are limited to simple growth substrates, and do not gain much energy from the metabolism of these compounds. The primary reactions of methane formation with their associated Gibbs free energy values are shown in Table 6 (Gottschalk, 1986; Jones et al, 1987; Thauer, 1990).

It is known that in microbial cells, approximately 50 kJ/mole are required to drive the synthesis of one ATP from ADP and inorganic phosphate (Thauer, 1990). In a comparison of the above reactions, the reduction of carbon dioxide to form methane is more energetically favorable (-131.0 kJ/mole CH_4) than the acetoclastic formation of methane (-36.0 kJ/mole CH_4). This may be one reason why the majority of methanogens can reduce carbon dioxide using hydrogen, and fewer species of methanogens have the ability to derive methane from acetate.

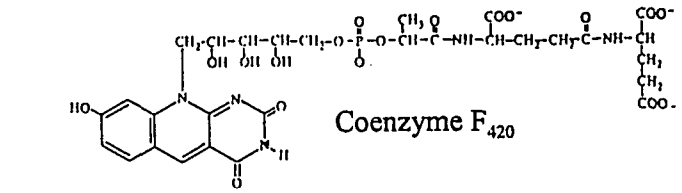
Methanogenic archaebacteria are the only known microorganisms that couple methane synthesis to the generation of energy. Methanogens are known to use novel metabolic pathways for this purpose (Jones et al, 1987).

Table 6. Reactions in methane formation

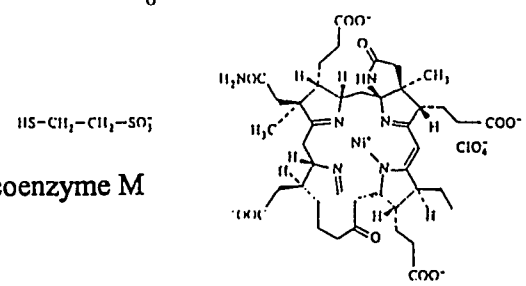
Reaction	$\Delta G^{\circ}{}'$ (kJ/mole CH_4)
$CO_2 + 4H_4 \rightarrow CH_4 + 2H_2O$	-131.0
$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$	-36.0
$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$	-107.0
$4HCOOH \rightarrow CH_4 + 2H_2O + 3CO_2$	-130.1
$4CH_3NH_3^+ + 2H_2O \rightarrow 3CH_4 + CO_2 + 4NH_4^+$	-74.0
$4CO + 2H_2O \rightarrow CH_4 + 3CO_2$	-211.0

In studies of their metabolic pathways, methanogens have been found to possess at least six unique cofactors and coenzymes which are necessary for methane formation during the reduction of carbon dioxide including: coenzyme F_{420}, factor F_{430}, coenzyme M, methanofuran, tetrahydromethanopterin, and factor B (Gottschalk and Blaut, 1988). The structures of these unique cofactors and coenzymes are illustrated in Figure 2.

The first of these unique compounds is coenzyme F_{420}. It was observed that methanogenic bacteria possess a strong autofluoresence due to the presence of conenzyme F_{420} under oxidizing conditions. This autofluoresence has been used as an identification tool for methanogens, and F_{420} has a spectral adsorption maxima at 420 nm (Balch et al, 1979). F_{420} is thought to be involved in the transfer of electrons from hydrogen to intermediates of methane synthesis (DiMarco et al, 1990).

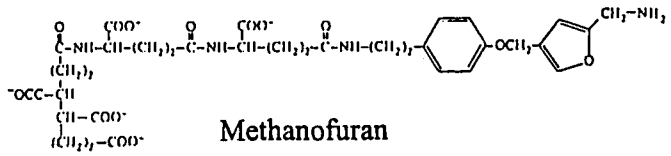


Coenzyme F_{420}

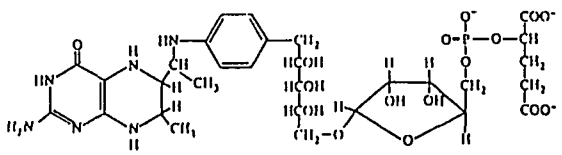


coenzyme M

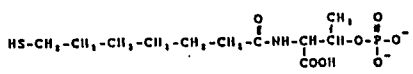
Factor F_{430}



Methanofuran



H_4MPT



Factor B

Figure 2. Unusal methanogenic coenzymes and cofactors

The second of these compounds unique to methanogens is factor F_{430}. F_{430} was first isolated in1977 as a non-fluorescent yellow compound from cell extracts of M. thermoautotrophicum (DiMarco et al, 1990). It was later discovered that this microorganism required nickel for growth, and F_{430} has been found to be the major sink nickel (Jones et al, 1987). Factor F_{430} has a maximum spectral adsorbance at 430 nm, and is involved in the terminal steps of methane formation.

The third unique cofactor of methanogens is methanofuran (MFR). Methanofuran was first discovered in M. thermoautotrophicum by Romesser and Wolfe in 1982 (DiMarco et al, 1990). It was observed that cultures of this organism that were depleted of soluble low molecular weight cofactors were unable to reduce carbon dioxide to methane. Methanofuran was isolated as the cofactor responsible for the initial reduction of carbon dioxide in the synthesis of methane.

The fourth unique cofactor is methanopterin (tetrahydromethanopterin), also known as H_4MPT in the reduced form. H_4MPT was also discovered in M. thermoautotrophicum as a blue fluorescent compound in adsorption studies. H_4MPT was first called factor F_{342} because it has a spectral adsorption maxima at 342 nm. H_4MPT has been found to function in one-carbon transfers in the methane synthesis pathway during the reduction of carbon dioxide (Jones et al, 1987; DiMarco et al, 1990). H_4MPT was studied extensively during the 1980s, and it was found that H_4MPT can be synthesized from acetate by methanogens.

The fifth unique compound is coenzyme M. Coenzyme M was first discovered by McBride and Wolfe in a Methanobacterium strain in 1971 (DiMarco et al, 1990). CoEnzyme M is required for methyl group transfers in the final steps of methanogenisis from the reduction of carbon dioxide. Coenzyme M has been found to be a required growth factor for Methanobrevibacter ruminantium, but most methanogens can independently synthesize coenzyme M (Lovley et al, 1984).

The sixth unique cofactor produced by methanogens is factor B, sometimes termed component B. Factor B was first isolated by Gunsalus and Wolfe from M. thermoautotrophicum in 1980 (DiMarco et al, 1990). Factor B is involved in the final steps of methane formation during the reduction of carbon dioxide.

With the discovery and isolation of these unique cofactors of methanogens, much work proceeded in identifying the metabolic pathways of methane generation. The most studied pathway has been the formation of methane from carbon dioxide using molecular hydrogen.

The pathway of carbon dioxide reduction to methane as it is currently understood is shown in Figure 3. Three coenzymes including methanofuran, tetrahydromethanopterin (H_4MPT), and coenzyme M are involved as one-carbon carriers in the sequential reduction of carbon dioxide to methane. The terminal reduction of the intermediates to methane involves two additional cofactors, component B (factor B), and factor F_{430}.

In the pathway of carbon dioxide reduction to methane, carbon dioxide is first reduced and fixed to methanofuran as a formyl group. In the second step, the formyl group is transferred

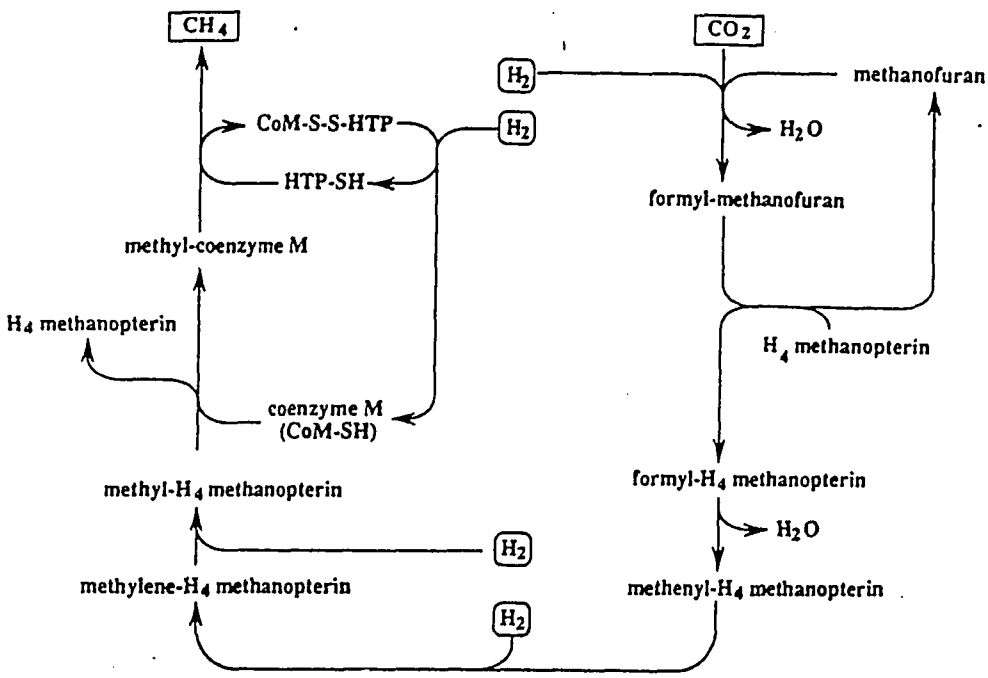


Figure 3. Carbon dioxide reduction pathway in the methane formation

to tetrahydromethanopterin (H_4MPT). The formyl group of the CHO-H_4MPT complex is then converted through a series of reduction steps from methenyl-H_4MPT to methylene-H_4MPT, to methylene-H_4MPT, and lastly to methyl-H_4MPT (DiSpirito, 1993; Gottschalk,1986; DiMarco et al, 1990). Factor F_{420} is thought to play an important role in these reactions as an electron carrier in the transfer of electrons from molecular hydrogen to the metabolic intermediates of methane synthesis.

In the carbon dioxide reduction pathway, methyl-H_4MPT next reacts with coenzyme M to yield methyl-coenzyme M. The termination reaction involves the reduction of the methyl-coenzyme M complex with factor b, also known as HS-HTP or mercaptoheptanoyltheonine. Methane is released in this termination step. The by-product of the termination step is an oxidized coenzyme M-factor b complex, which is reduced with the help of factor F_{430} (DiMarco, 1990).

The second major metabolic pathway for methane production by methanogenic bacteria is the acetate pathway, which is used by acetoclastic methanogens. Approximately two-thirds of all methane production originates from the breakdown of acetate, and about one-third originates from the reduction of carbon dioxide (Ferry,1992).

Several of the acetoclastic methanogens include the Methanosarcina sp. and the Methanothrix sp.. Much less information is known about the acetate pathway as compared to the carbon dioxide reduction pathway for methanogenesis.

In the acetate pathway, the acetate molecule is first activated to acetyl CoA, and then is cleaved by the enzyme carbon monoxide dehydrogenase (CODH). The methyl group is reduced to methane using electrons derived from the oxidation of the carbonyl group acetate to carbon dioxide (Ferry, 1992; Thauer, 1990). Coenzyme M has been identifiedas a carrier of the methyl group from acetate, and a coenzyme M methylreductaase system is thought to be responsible for the reduction of this methyl group to methane.

Very little energy is derived from the cleavage of acetate molecules (-31 kJ/mole methane). If other substrates are available, methanogens may utilize acetate for biosynthesis reactions and form methane using a more energetically favorable pathway (Jones et al, 1987).

The complete metabolic pathways for the formation of methane from methanol, methylamines, carbon monoxide, and formate have not yet been fully understood. It has been determined in microorganisms that utilize methanol and methylamines, one-fourth of the substrate's methyl groups are oxidized to carbon dioxide, and three-fourths of the substrate's methyl groups are reduced to methane. Coenzyme M is thought to be involved as a methyl carrier during the reduction steps in the pathway to methane from methanol and methylamines (Gottschalk, 1986; Jones et al, 1990). The carrier involved in the oxidation of the methyl groups to carbon dioxide is unknown, although in Methanosarcina sp., type b cytochromes may be involved as electron carriers (Jones et al, 1990).

Thermophilic Anaerobic Treatment

Thermophilic bacteria are microorganisms which exhibit optimum growth at elevated temperatures. Thermophilic bacteria have been isolated from hot springs, as well as a variety of other geothermal environments. Thermophilic methanogens include such organisms as Methanobacteria thermoautotrophicum, isolated from the rumen of cattle, and Methanococcus jannaschii, which was isolated from deep-sea hypothermal vents (Clark and Kelly, 1990). Bergy was the first to propose a classification scheme for thermophiles. He defined "true thermophiles" as bacteria which exhibit optimum growth ranging from 60° to 70° C, with a lower limit for growth ranging from 40° to 45° C (Bergy, 1956).

There has been an interest in thermophilic anaerobic digestion since the late 1920s when Rudolfs and Heukelekian conducted bench-scale tests at elevated temperatures on sewage sludge at the New Jersey Agricultural Experimental Station (Rudolfs and Heukelekian, 1930). Since then, numerous experiments have been conducted in the laboratory as well as several plant-scale studies. In the last twenty-years, thermophilic anaerobic processes have been investigated for the treatment of warm or hot industrial wastewaters.

Thermophilic anaerobic digestion offers several potential advantages over conventional mesophilic operations including (Buhr and Andrews, 1977; Shamskhorzani, 1989):

1. Increased reaction rates with respect to the destruction of organic solids.
2. Increased digestion efficiency, with a corresponding decrease in sludge production.

3. Improved solids-liquid separation.

4. Increased destruction of pathogenic microorganisms.

5. Higher rate of digestion and methane production, resulting in shorter residence times and smaller reactor volumes.

Possible disadvantages of the thermophilic anaerobic digestion process over conventional mesophilic systems include:

1. Higher energy requirement for heating.

2. Poorer effluent quality.

3. Greater instability caused by greater sensitivity to potential temperature fluctuations.

4. Production of odors at the higher temperature.

Heukelekian and Rudolfs conducted one of the earliest studies on the comparative performance of thermophilic and mesophilic digestion of sewage solids in 1928 (Rudolfs and Heukelekian, 1930). They conducted studies of the digestion of both fresh solids and solids which were seeded with ripe sludge at temperatures of 37°, 45°, and 55° C. It was observed that seeding was necessary for proper digestion at all temperatures. Digestion was complete within 14 days for the seeded samples at 45° and 55° C, while digestion at 37° C took 26 days. Heukelekian and Rudolfs observed greater production of gas and odors at the higher temperatures.

Further experiments were conducted in the thermophilic digestion of sewage sludge by Heukelekian in 1930 (Heukelekian, 1930). From his earlier experiments, it was known that seeding greatly shortened the time necessary for digestion. Heukelekian believed that the addition of seed sludge had a two-fold function, first, that of regulating the reaction of the digesting mixture, and second, to furnish the proper bacteria for the digestion process.

Heukelekian observed that the optimum temperature for thermophilic digestion ranged from 50° to 60° C, and temperatures of 65° and 70° C greatly increased the time necessary for digestion. Ratios of seed to fresh solids tested ranged from 2:1 to 11.4:1 (fresh solids:seed). It was observed that a 2:1 ratio of solids to seed was necessary for digestion at 50° C. It was also observed that the addition of lime and ammonium salts decreased the time necessary for complete digestion at 50° C from 14 days to 10 days. In a comparison of digestion at 50° C and 22° C, it was observed that gas yields, volatile matter destruction, and decomposition of nitrogenous substances were greater at the thermophilic temperature.

In 1934, Fair and Moore studied the time and rate of sludge digestion with respect to temperature (Fair and Moore, 1934). It was noted that " . . . the range of 35° to 42° C seems to represent a region in which both thermophilic and non-thermophilic organisms work at a disadvantage. " At temperatures below 20° C, the time necessary for digestion was observed to increase dramatically. In this study, Fair and Moore reported four distinct temperature zones for digestion including:

1. Psycrophilic - below 10° C.
2. Temperate Zone - below 28° C.
3. Intermediate Zone - 28° C to 42° C.
4. Thermophilic - above 42° C.

In 1937, Fair and Moore investigated a wide range of temperatures for sludge digestion (Fair and Moore, 1937). They determined that the optimal temperatures for thermophilic treatment ranged from 52° to 54.5° C, and the optimal temperatures for mesophilic treatment ranged from 35° to 40° C. They measured the biogas produced at the experimental temperatures and determined the time of digestion as when the volume of gas produced was equivalent to 90% of the biogas produced at 15° C. They concluded that the optimum mesophilic digestion time to be 22.7 days, and the optimum thermophilic digestion time to be 8.9 days.

In 1948, Heukelekian and Kaplovsky studied the effect of temperature variation during thermophilic digestion. They were interested in characterizing the stability of digestion at thermophilic temperatures to determine the effects of a possible malfunction in heating equipment during the digestion process.

Their experimental procedure involved making pulse changes from a digestion temperature of 50° C down to either 40° or 20° C. Some of the experimental mixtures were maintained at the lower temperatures, while other mixtures were transferred back to 50° C after

2 or 5 days. They observed that digestion was adversely effected by the pulse change decrease in temperature. Temperature declines from 50° to 20° C resulted in a cessation of digestion, while digestion was merely slowed when the temperature was dropped from 50° to 40° C. They concluded that the flora responsible for digestion at 50° C was different from the flora responsible for digestion at 20° C. They also concluded that a short duration of temperature change had no lasting effect on subsequent digestion.

Golueke (1958) studied the effects of temperature on the digestion of primary sludge at temperatures ranging from 30° to 65° C. In his studies, a detention time of 30 days and a volatile solids loading of 1.4 g VS/L/day were applied. He observed no appreciable difference in solids destruction or gas production at temperatures of 35° to 55° C at this long detention time and low volatile solids loading.

Golueke made two important observations during this study. First, he observed that the sludge produced at 50° and 60° C had better dewatering characteristics as compared to the sludge produced at 30° to 45°. Secondly, it was also observed that the levels of volatile acids were considerably higher at the elevated temperatures. Volatile acids ranged from 82 ppm at 35° C to 2210 ppm at 65° C. There was an especially sharp increase in volatile acids from 500 ppm at 50° C to 2200 ppm at 55° C. Golueke postulated that the organisms responsible for the decomposition of volatile acids may not have been functioning efficiently at the higher temperatures.

In 1961, Malina (1961) studied the effects of temperature on the digestion of waste activated sludge at 52.5°, 42.5°, and at 32.5° C. In his experiment, daily feeding and gas recirculation mixing were employed. The volatile solids loading rate was 4.8 g/L/day at a 6 day detention time. Little difference in performance was observed for the three temperatures studied, with volatile matter destruction ranging from 42% at 52.5° C to 39% at 32.5° C. Gas production was observed to be less at 42.5° C than at either 32.5° or 52.5° C. Malina also observed higher production of volatile acids at higher digestion temperatures.

Pohland and Bloodgood (1963) investigated the effect of overloading on anaerobic digestion at temperatures of 36°, 52.5°, and 60° C. In their experiment, they developed an extensive monitoring protocol which included the measurement of total and volatile solids, alkalinity, total and ammonia nitrogen, total volatile acids, pH, gas production, and carbon dioxide content of the biogas. This was one of the first studies which attempted to uncover the metabolic relationships between numerous factors which may affect the efficiency of the digestion process.

Pohland and Bloodgood observed periods of retarded or severely retarded digestion during their experiment when volatile solids loadings were increased. At 60° C, gas production decreased and volatile acids increased at VS loading rates greater than 3.4 g VS/L/day (0.210 # VS/ft^3/day). At 36° C, digester performance was adversely affected at VS loading rates greater than 4.5 g VS/L/day (0.280 # VS/ft^3/day). The best performance was observed at 52.5° C, were

digestion was not adversely affected until VS loading rates exceeded 5.1 g VS/L/day (0.315 # VS/ft^3/day).

Maly and Fadrus (1971) also studied the influence of temperature on anaerobic digestion. In their experiment the reactors retention times ranged from 105 to 186 days at temperatures of 20°, 30°, and 50° C. Because of the long retention times, there was little difference in the degree of decomposition at the end of the digestion process between the three temperatures. Although there was no appreciable difference in the degree of decomposition, there was a difference in the rate of gas production. They observed that gas production was highest at 50° C and lowest at 20° C.

In 1984, Zinder studied the effect on the microbial population of a short-term temperature fluctuation during thermophilic digestion (Zinder et al, 1984). During a digestion experiment, an accidental 24-hr temperature fluctuation occurred in which the temperatures shifted from 58° to 64° C. A large increase in acetate concentration and a sharp decrease in gas production was observed after the accidental temperature increase. Zinder hypothesized that the acetoclastic methanogens were damaged by the upward temperature shift.

Anaerobic thermophilic digestion has been applied to a number of different industrial wastes, using several types of treatment systems.

In 1975, Basu and Leclerc (1975) reported on a comparative study of the treatment of beet molasses distillery waste at thermophilic and mesophilic temperatures. The beet molasses waste contained a high concentration of organic matter, with a COD ranging from 11 to 17 g/L.

The waste also contained a number of potentially toxic substances including the heavy metals copper, zinc, lead, and a high concentration of sulfates.

In their experiment, digestion temperatures of 35° and 55° C were used with COD loading rates ranging from 2 to 3.5 g/L/day, at a 10 day HRT. It was observed that there was little difference in treatment performance between the two temperatures. Mesophilic BOD removals ranged from 95.9 to 96.4% and thermophilic BOD removals ranged from 87.5 to 97.2% at organic loads up to 3.2 g/L/day. A drastic decline in performance was observed at the 3.5 g/L/day loading for both the mesophilic and thermophilic digesters. They attributed the decline in performance to either the heavy metals or high sulfate concentrations in the waste.

Chin and Wong studied the thermophilic digestion of a palm oil mill effluent using completely-mixed reactors (Chin and Wong, 1983). A thermophilic temperature of 55° C was chosen because the raw palm oil mill effluent was a hot industrial waste, with temperatures ranging from 45° to 70° C. Successful thermophilic digestion of this waste was observed. COD reductions of 72% and 90% were achieved at HRTs of 5 and 15 days, respectively.

In 1984, Schraa and Jewell reported on results of studies of an anaerobic attached-film expanded bed process for the treatment of a synthetic sucrose waste at 55° C. In their experiment diatomaceous earth was used as an attachment media, and the reactors were operated at an expansion rate of 10 to 20%. COD loading rates of 6.8 to 154 g/L/day were applied at HRTs of 0.5 to 5.2 hrs. Total COD removals ranged from 90% at the 6.8 g COD/L/day loading to 22%

at the 154 g COD/L/day loading. They observed rapid attachment of a biofilm onto the media at the thermophilic temperature.

In 1985, Wiegant et al reported on the thermophilic treatment of vinesse using both an upflow anaerobic sludge blanket reactor (UASB), and a semi-continuously fed digester. The vinesse used was described as a high-strength industrial wastewater produced in alcohol distilleries. They compared results with that of a mesophilic reactor operated at 30° C with vinesse over the same loading rates.

Wiegant observed that the thermophilic reactors produced an effluent of similar quality as the effluent from the mesophilic reactor. It was observed, however, that propionate was the predominant volatile fatty acid produced in the thermophilic units, which was not observed in the reactor operated at 30° C. It was also observed that the granules in the thermophilic UASB reactor decreased in size from approximately 1-3 mm to 0.5 mm. The authors stated that although the granules decreased in size, overall reactor performance did not decline. The UASB units achieved SCOD reductions of 52 to 65% at COD loading rates of 17.2 to 83.6 g/L/day at HRTs ranging from 2.5 to 49 hrs. In Wiegant's opinion, the UASB reactor outperformed the semi-continuously fed digesters, although a direct numerical performance comparison was not included in the report.

Also in 1985, Rudd et al reported on a comparison study of anaerobic fluidized-bed reactors operated at mesophilic (36° to 39° C) and thermophilic (57° to 60° C) temperatures. A synthetic meat waste supplemented with trace nutrients was used in the experiment. The

synthetic meat waste was formulated to simulate an abattoir wastestream. The mesophilic units were observed to outperform the thermophilic units. At a COD loading rate of 4.6 g/L/day, mesophilic TCOD removals ranged from 72 to 80%, and thermophilic TCOD removals ranged from 45 to 68%, at HRTs ranging from 1.5 to 13 hrs. It was observed that the optimum HRT ranged from 6 to 13 hrs at both temperatures.

In 1988, Puhakka et al reported on the anaerobic treatment of a combined primary and secondary pulp mill sludge in semicontinuous-flow reactors at thermophilic and mesophilic temperatures. They observed no advantages of thermophilic digestion. The thermophilic digestion was observed to produce lower VSS reductions, lower gas production, and a poorer quality effluent. In their experiment, they attempted to acclimate a mesophilic seed to the thermophilic temperatures for a period of one month prior to the experimental testing. Perhaps better results for the thermophilic reactor may have been achieved with a longer acclimation period.

There have been several full-scale studies on anaerobic digestion at thermophilic temperatures.

Fisher and Greene (1945) reported on plant-scale studies of thermophilic and mesophilic anaerobic digestion of primary sludge at Aurora, Illinois in 1931. In this early study, mixing was not employed and the digesters were stratified. Higher solids destruction was observed in the thermophilic digester at a detention time of 12.9 days and an organic loading of

0.45 kg volatile matter/m^3/day (0.028 lb/ft^3/day). It was also observed that the supernatant from the thermophilic digester was of lower quality than that of the mesophilic digester.

Fisher and Greene (1945) also studied thermophilic and mesophilic digestion at Jackson, Michigan from 1942 to 1944. The digesters were fed a mixture of one part primary sludge to three parts of waste activated sludge, and a three-stage digestion process was used. The two parallel, three-tank systems consisted of two primary tanks, heated to 29° and 52° C, respectively, followed by two unheated secondary and tertiary tanks. The digesters were not mixed, and supernatant was withdrawn from the tertiary tanks. The detention time for both systems was 27 days, and the applied organic loading was 0.53 kg volatile matter/m^3/day (0.033 lb/ft^3/day). The thermophilic three-tank system outperformed the mesophilic three-tank system. Higher volatile solids destruction and a higher quality supernatant were observed for the thermophilic system.

The most extensive plant-scale test of thermophilic anaerobic digestion in the United States was conducted at the Los Angeles Hyperion plant from 1953 to 1957 (Garber, 1954,1957). Temperatures of 29°, 38°, and 49° C were studied at detention times of 12 and 24 days at organic loadings of 2.1 and 3.8 kg volatile solids/m^3/day. The digesters were fed a mixture of approximately 70% primary sludge and 30% waste activated sludge. The digesters were heated by direct steam injection, and mixing was employed using draft tubes.

It was observed that the thermophilic digesters achieved approximately 54% volatile solids destruction at both detention times, which was equal to or better than the digesters

performance at the lower temperatures. It was also observed that the volatile acids concentration was higher in the thermophilic digester, with concentrations ranging from 600 to 800 mg/L. Volatile acid concentrations at 29° and 38° C ranged from 100 to 200 mg/L.

In Garber's opinion, the major advantage of the thermophilic process was the production of a sludge with improved dewatering characteristics. Lower coagulant demand and higher filter yields were observed for the thermophilic sludge.

In 1972, Garber et al conducted renewed thermophilic digestion plant-scale tests at the Hyperion plant (Garber et al, 1975). Digestion temperatures of 46° to 51° C were used. They observed sharp increased in volatile acids whenever the digestion temperatures proached 52° C. Similar dewatering characteristics in terms of filtration yields were again observed for the thermophilic sludge. It was also observed that the thermophilic filtrate was of poorer quality than that of the mesophilic filtrate, with higher levels of ether solubles, COD, nitrogen, phosphorus, and heavy metals.

Popova and Bolotina (1964) reported on the use of thermophilic anaerobic digestion in a 260 MGD wastewater treatment plant in what was formerly Moscow, U.S.S.R. They reported that in 1958, the mesophilic digesters were converted to a thermophilic temperature. This process modification permitted a decrease in detention time from 18 to 9 days, and an increase in organic loading from 1.65 up to 3.5 kg volatile matter/m^3/day. After the conversion, organic solids destructions were approximately 50%. Popova and Bolotina considered the primary advantage of the thermophilic process to be the production of a sanitary sludge, free of pathogens.

Anaerobic Fixed-Film Processes

The development of anaerobic fixed-film processes was a major breakthrough which allowed anaerobic treatment to be competitive with aerobic treatment processes. One major disadvantage of anaerobic treatment has been the relative slow growth of the methanogenic bacteria. Anaerobic fixed-film processes involve the use of an attachment media, which allows for a greater retention of the biomass. This provides for long SRTs and the ability to apply shorter HRTs since the biomass is anchored in the reactor. Anaerobic fixed-film processes have been successfully applied for the treatment of a variety of industrial waste streams.

The pioneering work on the anaerobic filter fixed-film process was performed at Stanford University by Young for his doctoral research under McCarty. The results of Young's dissertation work were first presented at the Purdue Industrial Waste Conference (Young and McCarty, 1967).

In this first study two substrates were used, a mixture of proteins and carbohydrates, and also a mixture of acetic and propionic acid. Waste strengths ranged from 1500 to 6000 mg/L at HRTs ranging from 4.5 to 72 hrs, resulting in COD loadings ranging from 0.43 to 3.4 g/L/day. Treatment success was based primarily on COD removals in the system. COD removals ranged from a high of 93.4% at a 72 hr HRT and a COD loading of 0.43 g/L/day, to a low of 36.7% at a 4.5 hr HRT and a COD loading of 3.4 g/L/day.

In a comparison of the anaerobic filter to other anaerobic treatment processes, Young and McCarty stated several observations and advantages including:

1. The anaerobic filter is ideal for the treatment of soluble waste streams.

2. Biological solids accumulate in the anaerobic filter leading to long solids retention times (SRTs), and low effluent total suspended solids (TSS).

3. Because of the long SRTs possible, dilute wastes can be successfully treated at nominal temperatures ($< 37^{\circ}$).

4. One major advantage of the anaerobic filter over other anaerobic systems is the ability of the filter to retain solids without an external clarifier.

In 1977, Schroeder outlined some of the possible disadvantages of anaerobic filters including the following:

1. Anaerobic filters have potential for clogging of the media with waste streams high in suspended solids.

2. The filter must be cleaned or changed after prolonged operation due to channelization of flow caused by heavy biomass growth.

3. Filter cleaning techniques have not been developed, and backwashing is not feasible due to the large size of the units.

Shortly after Young and McCarty's early work on the anaerobic filter, Plummer applied the anaerobic filter treatment process to an actual food processing waste which consisted mainly of carbohydrates (Plummer et al, 1968). Instead of using rock packing media, a plastic ring and saddle media was employed. The plastic media provided for a much higher filter bed porosity (70% porosity vs. 42%) than was the case of Young's quartzite stone media. The higher bed porosity left more physical space in the reactor for the retention of anaerobic biomass.

Plummer's filters were operated mesophilically at COD loading rates ranging from 1.6 to 10.3 g/L/day at HRTs ranging from 13 to 83 hrs. COD removals ranged from 41% to 93.5%. Plummer suggested effluent liquid recycling to avoid the possibility of liquid short-circuiting in the filter.

The anaerobic filter process was applied to a pharmaceutical waste by Jennett and Dennis in 1975. The pharmaceutical waste was low in suspended solids, with an average COD of 16000 mg/L. The reactors were fully-packed with 1.0 to 1.5 inch gravel, and had a 14 L empty-bed volume. HRTs of 12 to 48 hr were studied at 37° C, and applied COD loadings ranged from 0.2 to 3.5 g/L/day. COD removal efficiencies ranged from 94 to 98%. An important observation made by Jennett and Dennis was that bacteria collected on and between the interstitial spaces of the gravel media.

Chain and DeWalle in 1977 utilized an anaerobic filter for the treatment of acidic landfill leachate which had a pH of 5.4 and a COD of 54000 mg/L. They practiced effluent liquid recycle in order to help neutralize the pH of the acidic leachate. They also used plastic media which provided for a high filter bed porosity of 94%.

A high-strength carbohydrate was treated with an anaerobic filter, as reported by Mosey in 1978. A plastic media with a porosity of 90% was used in the reactors. The COD removal efficiency was 89% at a 4 day HRT at a operation temperature of 35° C. Hydraulic retention times of less than 4 days were not applied because of concern for potential wash-out of bacteria from the filter. The high performance of the anaerobic filter was demonstrated in this early study.

The anaerobic filter was used to treat a shellfish processing waste water by Hudson in 1978. Two different types of packing media were used including readily-available oyster shells and stone media, resulting in bed porosities of 82% and 53%, respectively. This was an important study which illustrated the effect of filter bed porosity on treatment performance. The oyster shell media filter provided superior treatment as compared to the stone media, with COD removals 81% and 33%, respectively.

In 1982, Dague reported on the use of the anaerobic filter process for the treatment of a high-strength grain processing waste. Temperatures of 22° and 35° C at applied COD loadings of 2.4 g/L/day were used in the comparative study. COD removal efficiencies were 75% at 22° C, and 90% at 35° C. When the organic loading was increased to 5.6 g COD/L/day for the 35° C filter it was observed that treatment performance declined due to pH fluctuations in the raw waste.

Witt et al reported on the full-scale anaerobic treatment of a guar industrial waste (Witt et al, 1979). The guar wastewater contained soluble gums and propylene glycol. The 36000 ft^3 (1019 m^3) filter was operated at 37° C in the upflow mode with effluent recycle. The raw waste water was pre-heated to 37° C using direct steam injection and heat exchangers which recovered heat from the filter liquid effluent. The filter was operated at a 30 hr HRT with an average COD loading rate of 0.47 $lb/ft^3/day$ (7.4 g/L/day). The system was successfully operated as a pretreatment process with a COD removal rate of 60%.

In 1980, Switzenbaum and Jewell reported on a new type of fixed-film treatment system termed the anaerobic, attached-film expanded bed reactor (AAFEB). The attachment

media used were 500 micron porous aluminum oxide beads. A high biomass concentration was achieved by attachment of microorganisms onto the media which provided for long SRTs. The AAFEB process was demonstrated to be effective in treating low-strength waste waters while operating at low temperatures and short HRTs. The aluminum oxide beads were not recommended for full-scale applications in waste treatment because of its high cost.

In 1981, Jewell and Morris used the AAFEB process to study instantaneous shock effects of changes in treatment temperature and organic loading on the system. They used a synthetic waste water composed mainly of glucose, supplemented with nutrients such as nitrogen and phosphorus, yeast extract, and sodium bicarbonate. Two reactors were operated in parallel at a 5 hr HRT. For both units, treatment temperatures were varied over 42 days in the following sequence: 22.5°,25.3°,19.7°, 28.1°, 16.9°, 32.2°, 12.8°, 35°, 10°, and 22.5° C. In the first reactor, temperature only was varied, and influent substrate concentration was maintained at 500 mg/L. In the second reactor, influent substrate concentration was varied in addition to temperature from 50 mg/L at 10° C to 950 mg/L at 35° C.

Jewell and Morris anticipated that a temperature change from 35° to 10° C would decrease reactor performance in terms of COD removals and suspended solids concentrations in the effluent for the reactors. They observed little difference in reactor performance after the temperature shift. The reactors were allowed to operate for only 80 hr after the shift before the experimental temperature was again changed. Perhaps greater differences in performance would have been observed if the reactors were allowed to operate at one experimental condition for a reasonable length of time to acclimate the microorganisms to the new temperature.

In 1981, Kennedy and van den Berg reported on the effects of overloading on the performance of anaerobic fixed-film reactors at 25° and 35° C. A chemical industry waste water was used in which the organic matter consisted mainly of short chain volatile fatty acids. During the overloading studies, the reactors were operated at COD loading rates of 14 and 17.9 g/L/day and HRTs of 1 and 0.78 days at 25° and 35° C, respectively. The units were shock-loaded for 24 hr, after which time the organic loading rates were returned to 60 to 70% of the steady-state loading of the reactors. At 25° C, shock loadings ranged from 16 to 60 g COD/L/day, and at 35° C, shock loadings ranged from 28 to 90 g COD/L/day. It was observed that the fixed-film reactors could handle the severe shock overloadings, and normal reactor performance was reestablished 12 to 48 hr after overloading was stopped.

In 1982, Dahab investigated the effect of media design on anaerobic filter performance for his dissertation work at Iowa State University. He determined that larger media with larger pore openings but with less specific surface area was superior to smaller media with smaller pore openings with higher specific surface area. Dahab concluded that the larger media was superior since the majority of the treatment was being performed by the microorganisms held in suspension in the interstitial spaces rather than the microorganisms which were attached onto the filter media.

The successful treatment of a low strength domestic waste water using an anaerobic filter was reported by Kobayashi et al in 1983. A tricking filter media was used which had a high specific surface area. Temperatures of 20°, 25°, and 35° C were used at a COD loading of

0.02 lb/ft^3/day. The filter performance was superior at 25° and 35° C, with COD removals of 79%. Performance declined at the lower temperature, with COD removals of 65% at 20° C.

In 1984, Guiot and van den Berg described a modified anaerobic filter, termed the upflow blanket filter (UBF), or hybrid filter. In their design, the bottom two-thirds of the reactor consisted of an open space where a sludge blanket formed. The top one-third of the reactor contained conventional plastic packing media of high porosity. They tested a synthetic waste consisting mainly of sucrose in which applied COD loadings of up to 22 g/L/day resulting in 95% soluble COD removal efficiencies.

The effect of a series of severe shocks to an anaerobic filter was studied by Caine et al in 1990. The anaerobic filter was operated with a dairy effluent substrate under steady state conditions at an HRT of 16 hr and a COD loading of 7.8 g/L/day at 35° C. The experiment then involved exposing the reactor to a series of 8-hr shocks including turning off the heating equipment, terminating caustic addition for pH control, doubling the substrate concentration, and reducing the HRT from 16 to 9 hr.

It was observed that low temperature and low pH shocks resulted in small transient changes in reactor performance, but long-term stability was unaffected. During the low temperature experiment the temperature in the reactor dropped to 25.5° C, and during the low pH shock, the raw waste water pH dropped to 5.3. Organic shock produced a 24% reduction in COD removal, primarily caused by an increased amount of suspended solids in the effluent. After the organic shock experiment, steady-state performance was reestablished 24 hours after the shock period. During the hydraulic shock, it was observed that a large quantity of solids was

washed out of the reactor with the effluent. After the hydraulic shock steady-state was also reestablished. The authors concluded that the anaerobic filter was quite successful in withstanding a variety of different types of short-term shocks that might be experienced in a full-scale operation.

Chiang investigated the effect of reactor configuration on the performance of the anaerobic filter for his doctoral work at Iowa State University under Dague (Chaing and Dague, 1992). They observed no significant difference in the reactor performance based on height to diameter ratio. Based on tracer studies, they also discovered that at high organic loading rates, gas production in the reactor causes significant mixing which allows anaerobic filters to operate like a completely-mixed reactor.

Two-Phase Anaerobic Treatment

A review of the literature revealed no two-stage anaerobic treatment processes in which a thermophilic anaerobic filter was connected in series to a mesophilic anaerobic filter, except the Temperature-Phased Anaerobic Biofilter Process under development at Iowa State University. The majority of the relevant literature described two-stage systems designed for enhanced phase optimization.

In 1930, Buswell reported on a two-stage digestion process for the anaerobic treatment of wastewater sludges. By employing a two-stage process, the detention time in the first stage was shortened, and the second stage completed the digestion process. It was observed that the majority of stabilization occurred in the first stage.

In 1971, Pohland and Ghosh first proposed a two-phase system for the separation of the acidogenic and methanogenic phases of anaerobic treatment.

Their system consisted of two completely-mixed reactors connected in series for waste stabilization. They noted that by separating the acid-forming microorganisms from the methanogenic microorganisms, optimal growth environments could be maintained for each population. By the use of kinetic control using the appropriate dilution rates, they proposed that the rapidly-growing acidogens would predominate in the first stage, forming mainly volatile fatty acids. The slower-growing methanogens would be washed out of the first stage and predominate in the second stage where they could convert volatile acids produced in the first stage to methane. They noted the key to successful treatment was dependant on near-complete phase separation.

In 1973, El-Shafie and Bloodgood reported on a study in which six anaerobic filters were connected in series for the treatment of Metrecal (vanilla flavor) at 30° C.

In their system, the six reactors were filled with 1 to 1.5 inch gravel media and had a working volume of 2.6 L each. The Metrecal wastestream had a COD of 10000 mg/L, and the COD loading on the lead filter was 41 g/L/day. The retention time in each of the six filters was 3 hr, resulting in a system HRT of 18 hr for the combined six filter system. System COD removals averages 76%. El-Shafie and Bloodgood observed an exponential decrease in biological activity from the first to the last filter in the system.

In 1983, a two-phase system treating a food canning wastewater was reported by Nhuan et al. The mesophilic system consisted of an intermittently-mixed first stage and an upflow

anaerobic sludge blanket second stage. The first stage was operated as an acidogenic reactor, with short detention times and short SRTs. The second stage was operated as a methanogenic reactor with a long SRT. They observed in the two-stage system that they system was flexible in terms of methane production. Without adverse long-term effects, the system successfully performed to produce high methane production during normal weekly plant operation, and reduced methane production on the weekends, when methane was routinely flared.

A full-scale two-stage system for the treatment of wastewater sludges at the Rockaway Wastewater Treatment Plant was reported by Torpey et al in 1984. The main objectives of the study were to find an adequate system to reduce quantities of sludge and to destroy pathogens. This study was prompted by a federal mandate to cease ocean dumping of wastewater treatment sludge. The two-stage system included a mesophilic digester operated at 36° C, connected in series to a second stage thermophilic digester operated at 50° C. It was observed that the two-stage system achieved a volatile solids destruction of 60%, with substantial reduction in pathogens.

Hiraoka et al (1984) reported on the thermal pretreatment of waste activated sludge in a pilot-scale wastewater treatment plant. Thermal pretreatment temperatures of 60° to 100° C were applied to thickened waste activated sludge for 2 hr. The waste activated sludge was then combined with thickened primary sludge, and the mixture was digested in a 30 L egg-shaped digester. Two digesters were operated in parallel, one receiving the thermally pretreated sludge mixture, and the other receiving an unaltered primary and waste activated sludge mixture. They observed an increase in gas production in excess of 30% for the system employing thermal

pretreatment. There was no economic analysis reported as to whether the amount of excess gas production would offset the energy costs for thermal pretreatment.

In 1985, Ghosh reported on a comparison study of single-stage and two-stage completely-mixed digesters for the anaerobic treatment of sewage sludge. Two-stage temperature variations of mesophilic to mesophilic, mesophilic to thermophilic, and thermophilic to thermophilic were applied. Single-stage units were operated at both the mesophilic and the thermophilic temperatures. This research did not investigate a two-stage system with a thermophilic first-stage and a mesophilic second stage. HRTs of 15, 7, and 3 days were applied.

Ghosh concluded that the two-stage process was superior to single-stage digestion based on gas yields and production rates, and volatile solids destruction. He also observed enhanced stability of the two-stage system relative to the single-stage system as system loadings and hydraulic dilution rates were increased.

A comparative study of a completely-mixed reactor with a two-stage upflow anaerobic sludge blanket (UASB) at thermophilic temperatures was reported by Wiegant in 1986. It had been previously observed that propionate degradation was often impaired at thermophilic temperatures. Wiegant proposed that the cause of the inhibited degradation of propionate to be high levels of hydrogen gas.

Wiegant designed the two-stage system in order to physically separate the hydrogen-producing microorganisms in the first stage from the hydrogen-consuming methanogens in the second stage. It was observed that significantly better results were obtained with the two-stage system. At COD loadings ranging from 20 to 50 g/L/day, COD removals were 10 to 13% higher

in the two-stage system. Wiegant attributed the better performance in the two-stage system to the removal of biogas (and hydrogen) which evolved in the first stage.

In 1986, Tanaka and Matsuo reported on the anaerobic treatment of a dilute milk wastestream using a two-stage system. The system consisted of a continuously-mixed reactor connected in series to a methanogenic anaerobic filter, both operated at 37° C. At an HRT of 4.4 days, the two-stage system achieved a 92% reduction in COD at a COD loading of 1.5 g/L/day. They observed improved phase separation when the HRT in the CSTR was reduced from 2 days to 1 day. In an analysis of the acidogenic first-stage effluent, it was observed that carbohydrates were more readily degraded than proteins or lipids.

Single and two-stage digestion of cheese whey using rotating biological contact reactors was reported by Lo and Liao in 1986. The two-stage system outperformed the single-stage system based on total methane production. Lo and Liao concluded that the two-stage digestion of cheese whey could be used successfully for rapid waste treatment and energy production.

In 1987, Verrier et al reported on a comparison study of single and two-stage systems for the anaerobic treatment of vegetable solid wastes. The one-stage systems were completely-mixed units operated at both thermophilic and mesophilic temperatures. The two-stage systems consisted of a thermophilic CSTR first-stage connected in series to a mesophilic anaerobic filter, and a mesophilic CSTR first-stage connected in series to a mesophilic anaerobic filter. Phase separation under mesophilic conditions resulted in greater methane production than was obtained in the single-stage mesophilic CSTR. Under thermophilic conditions, there was no observed

advantage of two-stage operation over a single-stage thermophilic CSTR. For the two-stage systems, it was observed that thermophilic liquefaction in the first stage resulted in the production of even-chained volatile fatty acids and ethanol, which were easily converted to methane in the second stage. For the mesophilic two-stage system, mesophilic liquefaction in the first stage resulted in the production of the more difficultly degraded odd-chained fatty acids such as propionate and valerate.

Howerton and Young investigated a unique two-stage cyclic operation of anaerobic filters using a synthetic alcohol stillage waste (Howerton and Young, 1987). The stillage waste consisted mainly of ethanol and sucrose. In their system, two 370 L anaerobic filters were connected in series, with the first reactor termed the lead reactor, and the second reactor termed the follow reactor. As a part of their study, after 136 days of continuous operation of the filters at 30° C, the waste flow was reversed, with the follow reactor becoming the lead reactor. At COD loadings of 4 and 8 g/L/day, using system HRTs of 36 and 18 hrs, COD removals ranged from 98 to 99%..

Chang et al.reported on the anaerobic digestion of wastewater sludge using a two-phase process (Chang et al, 1989). The wastewater sludge was a 55:45 mixture by volume of primary and waste activated sludge. The first stage consisted of a mesophilic CSTR operated at a 2-day HRT, and the second stage consisted of a thermophilic anaerobic filter operated at an 8-day HRT, for an overall system HRT of 10 days. In excess of 40% volatile solids destructions were achieved at volatile solids loadings ranging from 2.7 to 3.5 g/L/day. Chang reported that typical

volatile solids loadings for single-stage systems ranged from 0.7 to 2.5 g/L/day. Total gas production was observed to be slightly higher in the two-stage system as compared to previous studies of single-stage sludge digestion at similar loadings.

In 1990, Hanaki et al compared single-stage and two-stage anaerobic treatment of an oily cafeteria wastewater at 20° C. Similar to previous research, the two-stage system consisted of a CSTR reactor connected in series to an anaerobic filter. The cafeteria wastewater contained approximately 30% lipids, and had a COD ranging from 1300 to 2500 mg/L. Slightly better COD removals were observed in the single-stage filter as compared to the two-stage system.

Aoki and Kawase reported on the use of the two-stage process at a thermophilic temperature for the digestion of sewage sludge in 1990. A thermal conditioning pretreatment step was applied at 90° C for 1 hr using a proteolytic enzyme. The two-stage system consisted of a 70° C CSTR connected in series to a 55° C anaerobic filter. The system achieved a 58% volatile solids destruction at a system HRT of 3.7 days.

McDougal et al reported on a comparative study of single and two-stage anaerobic digestion of a synthetic coffee wastewater in 1993. The single-stage system consisted of an upflow anaerobic filter operated at 37° C. The two-stage system consisted of a first-stage completely-mixed acidification reactor followed by a upflow anaerobic filter operated at 37° C. The first stage was operated at both 37° and 55° C during different phases of the experiment to study the effect of temperature on acidification. Higher levels of volatile fatty acids were produced in the mesophilic acidification unit. It was also observed that the lower levels of

volatile fatty acids produced at the thermophilic temperature in the first-stage did not adversely effect the two-stage treatment performance. At the mesophilic temperature, the two-phase system outperformed the single-stage anaerobic filter. At a COD loading of 3.33 g/L/day, total COD removals were 78% for the two-stage system, as compared to 65% for the single-stage filter.

Temperature-Phased Anaerobic Biofilter Development

At Iowa State University, Harris conducted a comparative study of mesophilic and thermophilic anaerobic filters for his doctoral research under Dague (Harris, 1992; Harris and Dague, 1993).

The four laboratory-scale anaerobic filters had clean-bed volumes of 16.8 liters each, with bed porosities of 0.90. Non-fat dried milk was used as the substrate. The mesophilic and thermophilic filters were operated at 35° C and 55° C, respectively. Harris observed that the thermophilic reactors produced a lower quality effluent than the mesophilic reactors at high organic loadings.

As a result of the poor quality effluent from the thermophilic biofiters, it was decided by Harris and Dague to operate the reactors in series (thermophilic followed by mesophilic) to determine whether such operation would result in increased removals of the high concentrations of volatile acids in the thermophilic effluent.

Overall system HRTs of 24 and 48 hrs were studied at system COD loadings of 4.13 to 24.75 g/L/day. Superior treatment performance was observed in this preliminary study at both HRTs. System total COD removals in excess of 90% were achieved at system loadings up to 20 g COD/L/day. Overall two-stage performance declined at the 24.75 g/L/day loading.

IV. EXPERIMENTAL APPROACH

Reactor Construction

The reactors were obtained from a previous laboratory experiment and were constructed of Plexiglas by the Engineering Research Institute Machine Shop at Iowa State University.

A total of six reactors were constructed, which consisted of 2-ft sections. Three separate TPAB systems were constructed for this work. The various size ratios chosen for the thermophilic and mesophilic stages were guided, in part, to make use of the existing reactor sections. Each of the three TPAB systems consisted of a thermophilic first stage connected in series to a mesophilic second stage.

The three TPAB systems each had a total thermophilic plus mesophilic reactor height of eight feet. Two additional 1-ft reactor sections were constructed with identical cross-sectional dimensions as the existing 2-ft sections. This allowed assembly of the reactor sections to provide for system thermophilic to mesophilic size ratios of 1:7, 1:3, and 1:1 for the three TPAB systems, as illustrated in Figure 4. In the first TPAB system, the thermophilic unit was a 1-ft reactor followed by a 7-ft mesophilic reactor. The second TPAB system consisted of a 2-ft thermophilic unit followed by a 6-ft mesophilic reactor. The third TPAB system consisted of a 4-ft thermophilic unit followed by a 4-ft mesophilic unit. The total clean-bed volumes for the three TPAB systems were nearly identical, ranging from 22.3 to 22.7 L.

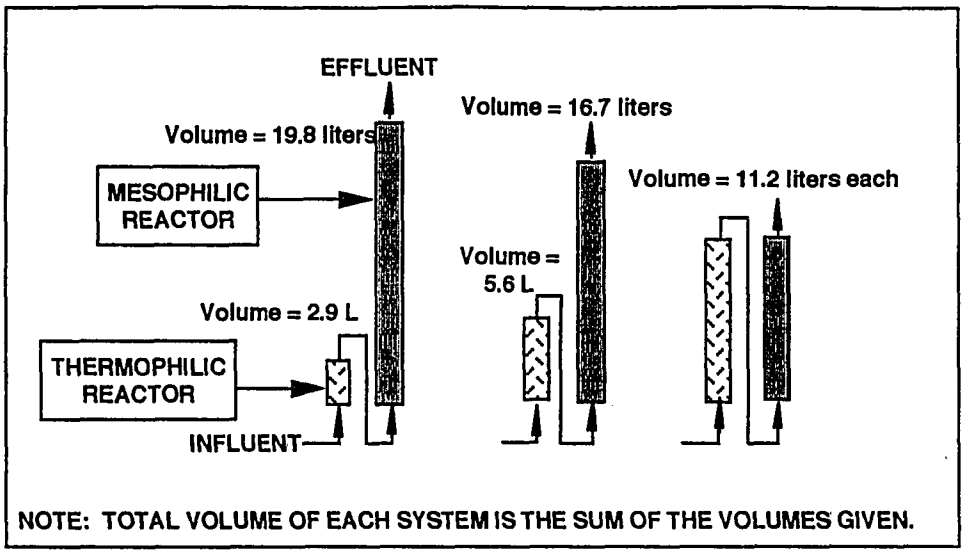


Figure 4. Three experimental TPAB systems

Each of the six Plexiglas reactors included a bottom plate, a top plate, and a bottom feed diffuser plate, as illustrated in Figure 5. Figure 5 shows the six-foot Plexiglas reactor which consisted of three two-foot sections. The top plate is illustrated in Figure 6. The bottom plate is shown in Figure 7. The bottom feed diffuser plate, which was designed to allow for an even upflow distribution of liquid feed, is illustrated in Figure 8.

The 2-ftt and 1-ft reactor sections were identical in cross-sectional dimensions. The cylinders had an outer diameter of 12.7 cm (5 in), an inside diameter of 11.43 cm (4.5 in), and a wall thickness of 0.64 cm (0.25 in). Each cylinder had a top flange (Figure 9) with a 20.32 cm (8 in) outside diameter, and an inside diameter of 12.7 cm (5 in). The flange was equipped with a groove to accept a 0.318 cm (0.125 in) rubber o-ring. The o-ring allowed the reactor sections to be sealed when bolted together.

The bottom of the reactor cylinders consisted of a one-piece flange and deflector, as shown in Figure 10. The outside diameter was 20.32 cm (8 in) with a 8.89 cm (3.5 in) inside opening. The inside opening was beveled at a 45 degree angle to reduce wall effects. The deflector also served as a support for a 0.635 x 0.635 cm (0.25 x 0.25 in) steel mesh screen for media support.

The reactor cylinders were equipped at their midpoint with a 2.54 cm (1 in) solid Plexiglas cylinder mounting which contained a 0.32 cm (0.125 in) boring which allowed

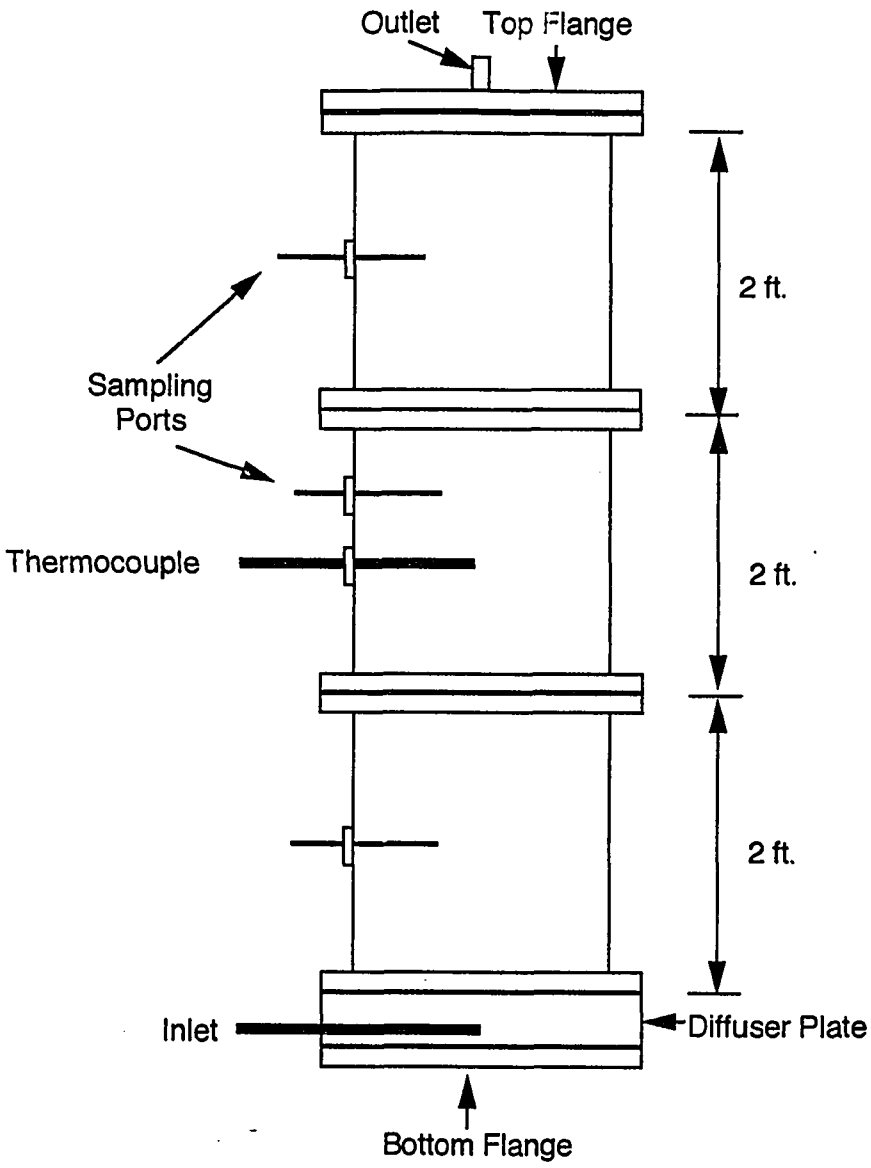


Figure 5. Typical experimental reactor

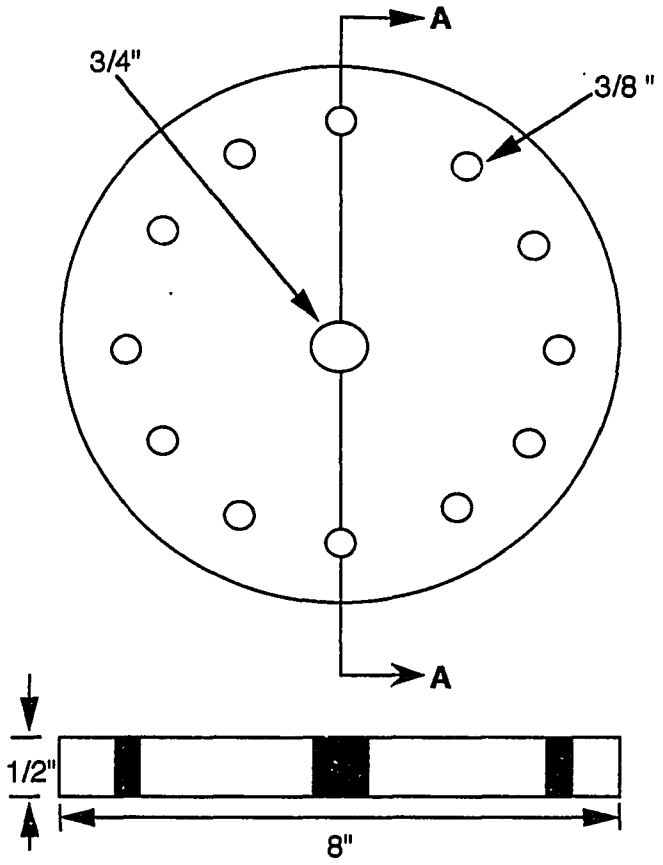


Figure 6. Top plate of reactor

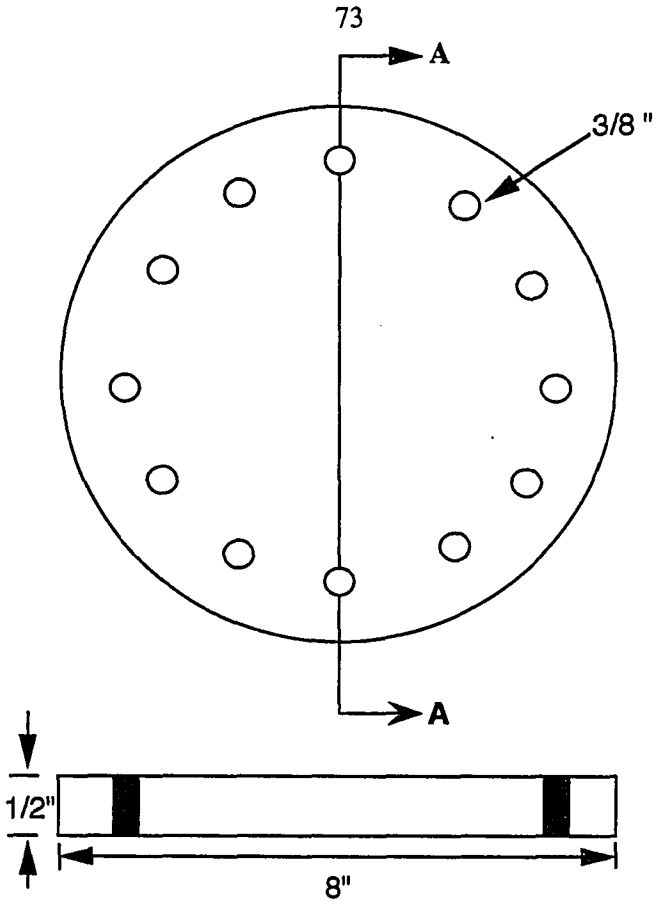


Figure 7. Bottom plate of reactor

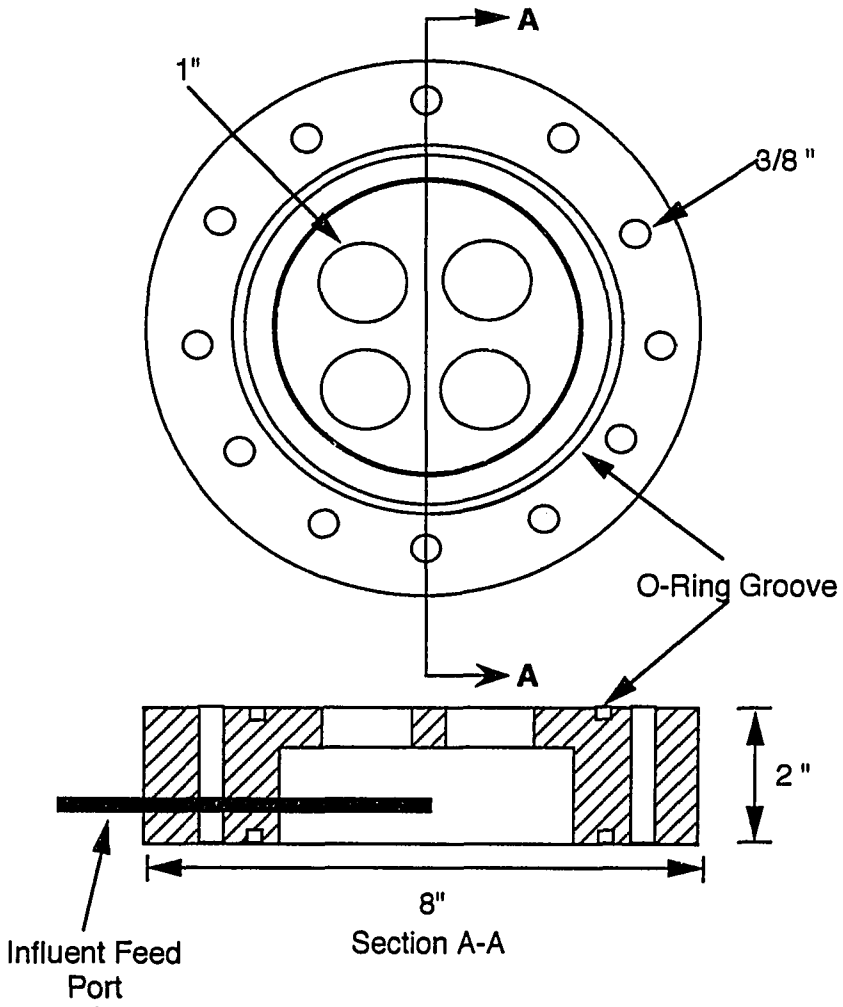


Figure 8. Bottom diffuser plate

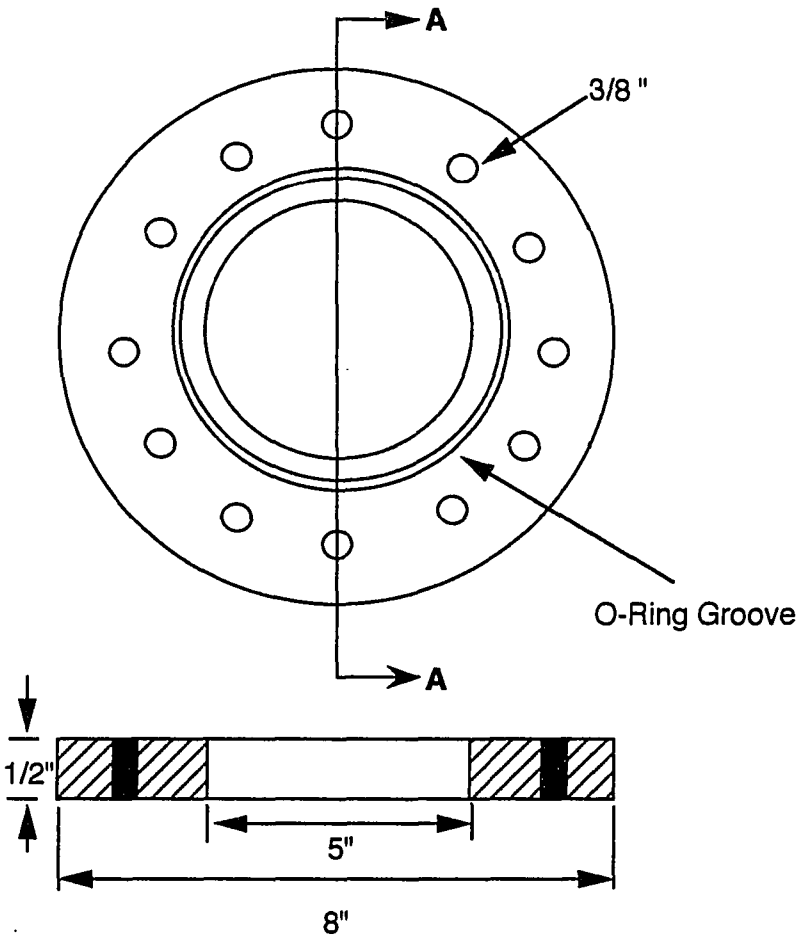


Figure 9. Flange for top of typical reactor cylinder

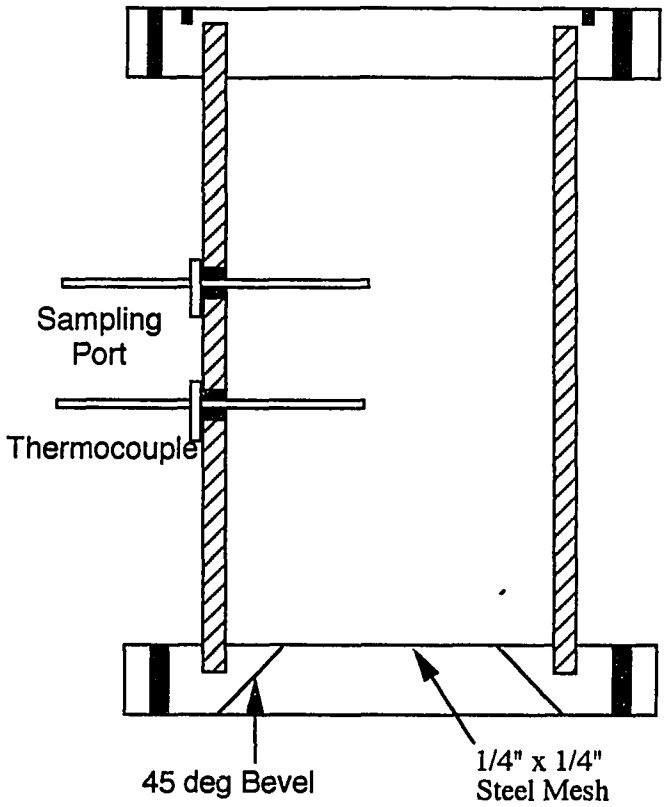


Figure 10. Typical reactor cylinder

for the insertion of a thermocouple and compression fitting. The boreholes were sealed with a brass plug in the mesophilic reactors.

The reactor cylinders were also equipped with sampling ports which were located 7.62 cm (3 in) above the thermocouple ports. The sampling port consisted of a 0.64 cm (3 in) diameter stainless steel tube, 15.24 cm (6 in) in length. The sampling ports were supported by a 2.54 cm (1 in) solid Plexiglas cylinder which was bored to accept the sampling tube.

The top plate design for each of the six reactors is illustrated in Figure 6. The top plate consisted of a 20.32 cm (8 in) diameter Plexiglas plate which was 1.27 cm (0.5 in) thick. A 1.59 cm (0.625 in) hole was drilled in the center of the top flange plate to accept a 0.95 cm (0.375 in) brass pipe adapter. The pipe adapter allowed tygon tubing to be connected to the top of the reactor. The top plate was bolted to the top flange using twelve 0.952 x 5.08 cm (0.375 x 2.0 in) hex-head bolts.

Figure 8 illustrates the bottom feed diffuser plates for the reactors. The feed diffuser plates were 20.32 cm (8 in) in diameter, and 2.54 cm (1 in) thick Plexiglas. The bottom diffuser was designed to ensure the uniform distribution of influent feed across the bottom of the reactor. There were four 2.54 cm (1 in) diameter distribution orifices for even feed distribution. The bottom diffuser plate was equipped with a compression fitting 1.91 cm (0.75 in) from the bottom of the plate to allow for the insertion of a 0.64 cm (0.25 in) diameter stainless steel liquid feed inlet tube, 15.24 cm (6 in) in length. The feed inlet tube was installed such that the influent feed entered into the center of the diffuser plate.

The bottom plate was a 20.32 cm (8 in) diameter and 1.27 cm (0.5 in) thick Plexiglas plate. The plate contained twelve 0.952 cm (0.375 in) boreholes which allowed the bottom plate to be bolted to the bottom diffuser plate. The bottom section required 7.62 cm (3 in) long bolts to secure the bottom plate, the diffuser plate, and the cylinder flange.

Media

The reactors were fully-packed with 1.59 cm (0.625 in) plastic Flexiring media (Koch Engineering Company, Inc. Wichita, Kansas). Reactor bed porosity was 0.89. The media had a specific surface area of 344 m^2/m^3, as reported by the manufacturer. Clean-bed volumes for the three TPAB systems, and for the individual reactors are shown in Table 7. The clean-bed volume is the liquid volume in the reactor packed with clean media. Clean-bed volumes were determined using tap water prior to the start-up of the reactors.

Table 7. Measured clean-bed volumes (CBV) for the TPAB systems

System	Total CBV	Thermo.CBV	Meso.CBV
TPAB 1 (1:7 ratio thermophilic/mesophilic)	22.7 L	2.9 L	19.8 L
TPAB 2 (1:3 ratio thermophilic/mesophilic)	22.3 L	5.6 L	16.7 L
TPAB 3 (1:1 ratio thermophilic/mesophilic)	22.4 L	11.2 L	11.2 L

Temperature Control

The reactors were operated at two temperatures, thermophilic (56° C) in the first stage, and mesophilic (35° C) in the second stage. The mesophilic temperature was maintained by placing the reactors in a 35° C constant temperature room. The temperature was monitored daily with a wet-bulb thermometer.

The thermophilic units were contained within specially constructed insulated boxes which were constructed from Celotex insulation board. Each chamber was heated with a silicon rubber heat tape suspended from the ceiling of the boxes. The thermophilic temperatures were monitored and controlled using thermocouples which were inserted internally into the midsection of each reactor. The thermocouples were connected to Barnett Temperature Controllers which activated the heat tape to provide a constant internal reactor temperature of 56° C.

The insulated thermophilic chambers were also equipped with industrial exhaust fans to maintain a constant air temperature within the chambers. The fans were operated continuously in a downflow mode during the experiment.

Feed System

The feed system for the three TPAB systems is illustrated in Figure 11. The feed substrate was contained in four 22 L carboys housed in a refrigerator that was maintained

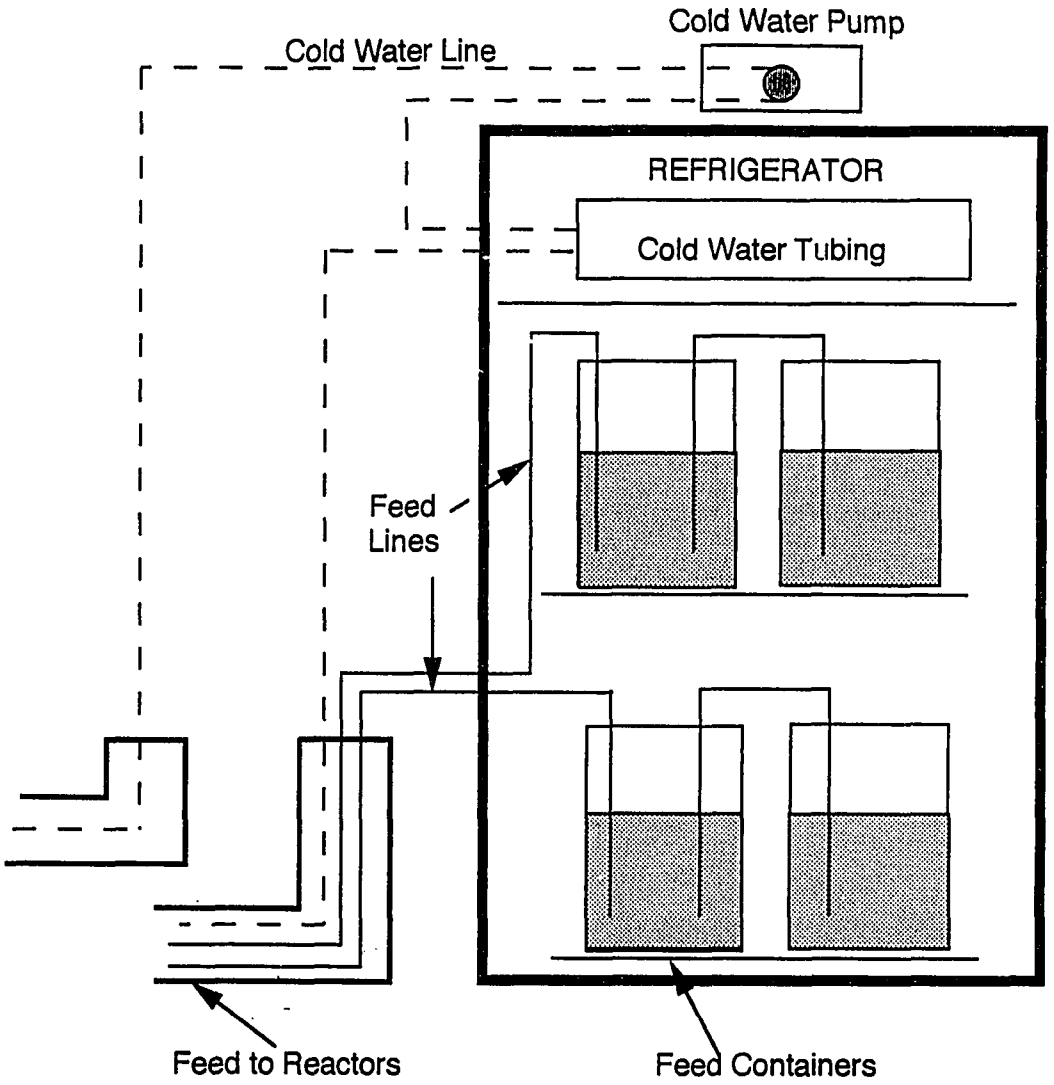


Figure 11. Milk feed system

at 2° to 8° C. The reactors were fed through tygon tubing extended from the refrigerator to the reactors in the constant temperature room. The feed tubing was contained within a 1.91cm (0.75 in) PVC pipe, with cold water circulating through the piping to prevent spoilage of the substrate.

The cold water recirculation system was maintained by coiling approximately 7.6 meters (25 ft) of tygon tubing through the freezer compartment of the refrigerator. The tubing was connected to the 1.91 cm (0.75 in) PVC pipe. The water was recirculated using a Masterflex peristaltic pump with a size 18 pump head operated at a constant speed of 100 rpm.

The feed was delivered to the three first-stage thermophilic reactors using a Masterflex peristaltic pump fitted with three size 16 pump heads. The Masterflex pump operated in the range of 1 to 100 rpm and was equipped with a ten-turn potentiometer speed controller. The ten-turn potentiometer speed controller allowed for precise control of the liquid feed flow rate to the reactors. The feed pump was calibrated weekly, and also when the pump head tubing was replaced during routine system maintenance.

The three mesophilic reactors were fed from three continuously-mixed and sealed 3.5 L holding tanks. The holding tanks collected and stored the liquid effluent from the thermophilic first-stages. The three mesophilic units were fed using a Masterflex peristaltic pump fitted with three size 16 pump heads. The pump was equipped with a ten-turn potentiometer speed controller for accurate flow rate control. The mesophilic feed pump was

calibrated weekly, and also when the pump head tubing was replaced during routine maintenance.

Gas Measurement System

The gas measurement system is illustrated in Figure 12. The gas measurement system included a gas/liquid separation bottle, a backflow trap, and a Rebel Wet Tip gas meter (Rebel Point Wet Tip Gas Meter Co., Nashville, TN). The biogas from each of the six reactors was measured separately. The gas/liquid separation bottles were designed to separate the biogas from the liquid reactor effluent. The gas/liquid stream was introduced into the top of a 4-L aspirator bottle. A liquid level was maintained within the aspirator bottle to prevent biogas from escaping with the liquid effluent. The biogas escaped through a tygon tubing line at the top of the aspirator bottle and entered a water backflow trap. The liquid effluent was discharged through the bottom of the aspirator bottle.

Biogas bubbled through the water backflow trap and into the gas meter. The meters were calibrated to tip once for every 100 ml of gas that entered through an orifice in the bottom of the meter. The meters were equipped with a magnet and digital counting mechanism which advanced one number for every tip of the meter. Biogas measurements were recorded daily.

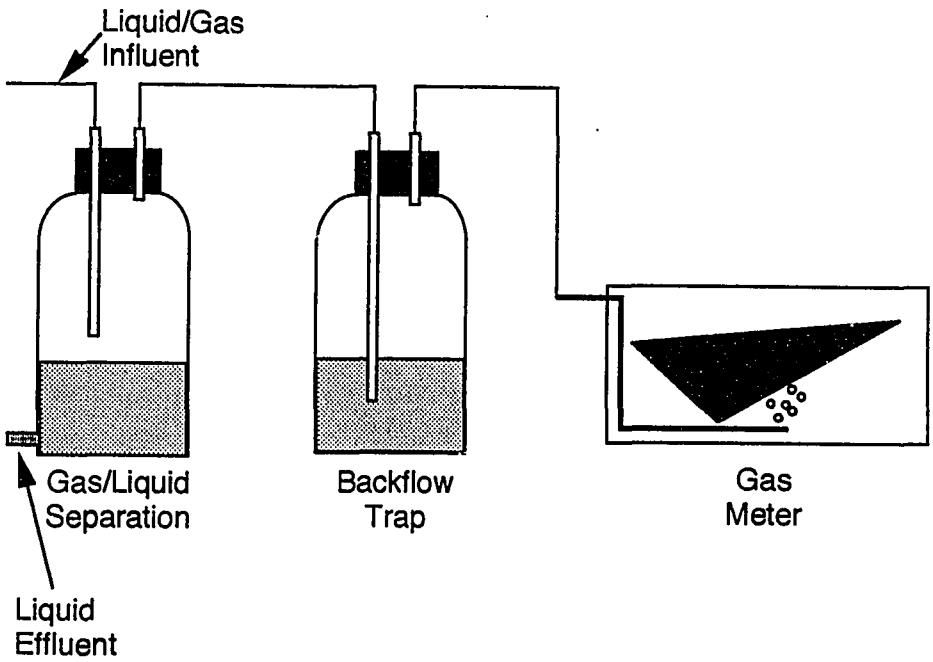


Figure 12. Gas measurement system

Substrate

The substrate used for this study was a soluble synthetic waste, non-fat dry milk (NFDM). The NFDM was supplemented with trace minerals essential for balanced microbial growth. NFDM is a complex material which is high in protein and carbohydrates, and contained sufficient nitrogen for microbial growth. The NFDM used was a stable substrate, with a COD of 1.03 g/ g NFDM, and a five-day biochemical oxygen demand (BOD_5) of 0.49 g BOD/ g NFDM. The properties of the NFDM are shown in Table 8, and follow those reported by Chiang (1988).

To ensure balanced microbial growth, trace minerals were added to the NFDM solution. The trace minerals were added at a rate of 0.1 ml/ g NFDM from a stock solution described in Table 9. The trace mineral solution was previously used by Chiang (1988) and Harris (1992) and was shown to be provide for proper anaerobic microbial growth.

The substrate was prepared daily by the addition of the NFDM to the City of Ames tap water. The desired waste strength was achieved by adding an appropriate amount of weighed NFDM. The NFDM, the trace minerals, and a portion of the tap water was mixed using a kitchen blender (Hamilton Beach, Inc.). The blended material was added to the 22 L carboys. Sodium bicarbonate was added when required to maintain the pH of the reactor effluent between 6.5 and 7.1. Additional tap water was added using a 2 L graduated cylinder. The resulting NFDM feed mixture was stirred to ensure a uniform solution prior to feeding the reactors. The carboys were placed in the refrigerator to prevent spoilage during the feeding cycle.

Table 8. Properties of the non-fat dry milk (NFDM)

Parameter	Value	Units	Reference
COD	1.03	g/g NFDM	Harris
BOD_5	0.49	g/g NFDM	Harris
TOC	0.21	g/g NFDM	Chiang
TKN	5.4	g/100 g NFDM	Chiang
$T\text{-}PO_4$	2.2	g/100 g NFDM	Chaing
Fat	<1.0	g/100 g NFDM	Swiss Valley
Lactose	51.0	g/100 g NFDM	Swiss Valley
Protein	>30.0	g/100 g NFDM	Swiss Valley
Ash	8.2	%	Swiss Valley
Trace Minerals			
Fe	4.6	ppm of NFDM	Chiang
Ni	1.0	ppm of NFDM	Chiang
Co	0.8	ppm of NFDM	Chiang
Mo	3.0	ppm of NFDM	Chiang
Zn	15.0	ppm of NFDM	Chiang

Table 9. Recipe for the trace mineral stock solution

Chemical Compound	Quantity
$FeCl_2 \cdot 4H_20$	35.60 g/L
$ZnCl_2$	2.08 g/L
$NiCl_2 \cdot 6H_20$	4.05 g/L
$CoCl_2 \cdot 6H_20$	4.04 g/L
$MnCl_2 \cdot 4H_20$	3.61 g/L

Experimental Set-up

The experimental set-up consisted of three thermophilic reactors and three mesophilic reactors. A total of three different TPAB systems were used. One TPAB system included one thermophilic unit connected in series to one mesophilic unit.

Figure 13 illustrates a typical TPAB system set-up. The reactors were fully-packed with filter media and were operated in the upflow mode. The thermophilic and mesophilic reactors all had the same components, except for the temperature controls and thermocouples for the thermophilic reactors. The NFDM feed was stored in carboys in a refrigerator outside the constant temperature room.

The feed left the storage carbouy through a 0.95 cm (0.375 in) tygon tube which was inside a 1.91 cm (0.75 in) PVC pipe cold water jacket. The feed was drawn through the tubing using a Masterflex pump decribed previously. The NFDM feed entered the thermophilic units through the stainless steel tube into the bottom of the reactors.

The liquid effluent from the reactors exited from the top of the reactors into tygon tubing. The liquid effluent was split using a t-type polypropylene tubing connector. One-half of the effluent was recycled back to the influent feed line of the reactor using a Masterflex peristaltic pump fitted with size 16 pumpheads. The recycle was maintained at 100% of the influent feed rate resulting in the same liquid pumping rate for the feed and recycle pumps. There were a total of two recycle peristalic pumps, each fitted with three size 16 pumpheads for the six reactors. One of the peristaltic pumps recycled the liquid effluent for the three thermophilic reactors, and the second peristaltic pump recycled

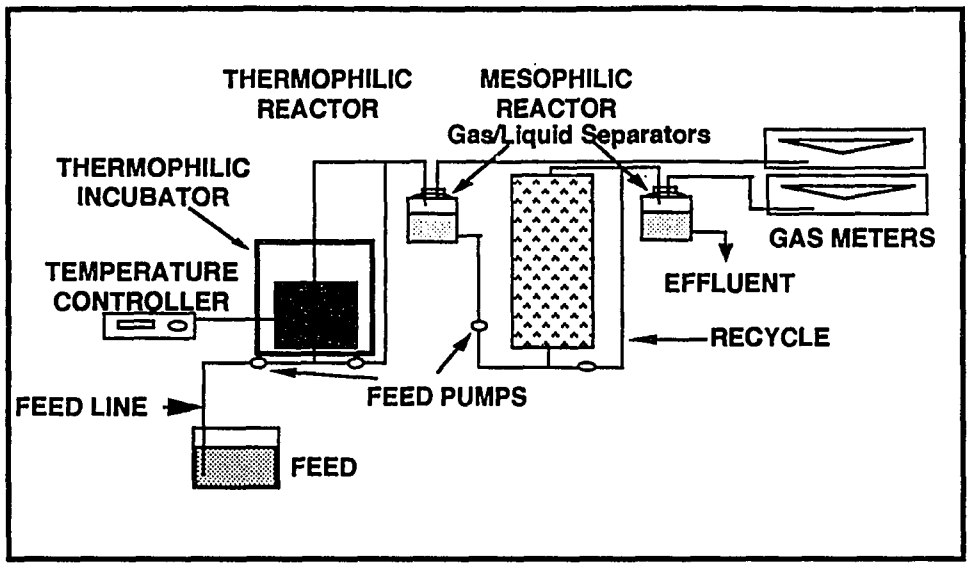


Figure 13. TPAB experimental set-up

liquid effluent for the three mesophilic reactors. The two recycle pumps were calibrated using a graduated cylinder by measuring the liquid flow over a 5- minute time period.

Two existing plywood platforms was used for the experimental set-up in the constant temperature room. The platforms were constructed from 3/4 in plywood and 2 x 4 in lumber. The first platform was 2-ft deep and 5-ft long. This platform was also equipped with a shelf at the 5-ft level with 9 in circular boreholes that encircled the taller reactors to prevent tipping. The second platform was 2-ft deep and 3-ft long. The second platform was equipped with a shelf at the 3-ft level. One in boreholes were placed in the second platform to allow placement of the liquid effluent tygon tubing lines. The 1-ft and 2-ft thermophilic reactors were housed on the second platform. The 4-ft thermophilic reactor, and the three mesophilic reactors were housed on the first platform. Aspirator bottles, gas meters, temperature controllers, and backflow traps were placed on shelves above the two platforms. The feed and recycle pumps were placed near the reactor bases on the platforms. The three, 3.5 L holding tanks were placed on the floor in front of the taller platform.

The reactor cylinders were completely filled with the 5/8 in Flexiring media. The cylinders were then tapped on the ground to allow for maximum compaction of the plastic media. The cylinder sections were then hex-bolted together with the top plate, the bottom plate, and the bottom feed diffuser plate. One thermocouple was placed near the midpoint in each of the three thermophilic reactors in the appropriate ports. The mesophilic and thermophilic sampling ports were fitted with tygon tubing and square screw clamps.

The thermophilic units were placed in the specially constructed insulated housings. The silicon heat tape was secured to suspend from the ceilings of the insulated housings. One air circulating fan was suspended from the ceiling of each of the insulated housings. A 1-in borehole was placed in the top of each of the insulated boxes to allow for a tygon tubing effluent line to extend up from the top of each reactor. The insulated boxes were sealed with duct tape.

Hydraulic Retention Times (HRTs)

There were three separate TPAB systems operated during the experiment. A TPAB system included a thermophilic first stage and a mesophilic second stage. System HRTs of 24, 36, and 48 hrs were evaluated for the three TPAB systems.

Identical liquid pumping rates were used for the thermophilic and mesophilic reactors at each system HRT. The variation in reactor volume resulted in the ability to evaluate a range of HRTs for the thermophilic and mesophilic phases. Thermophilic phase HRTs ranged from 3 to 24 hrs, and mesophilic phase HRTs ranged from 12 to 42 hrs, as shown in Table 10.

Table 10. Hydraulic retention times for the three TPAB systems

System HRT hrs	Thermophilic HRT hrs (volume,L)*	Mesophilic HRT hrs (volume,L)*
24	3 (2.9) 6 (5.6) 12 (11.2)	21 (19.8) 18 (16.7) 12 (11.2)
36	4.5 (2.9) 9 (5.6) 18 (11.2)	31.5 (19.8) 27 (16.7) 18 (11.2)
48	6 (2.9) 12 (5.6) 24 (11.2)	42 (19.8) 36 (16.7) 24 (11.2)

* Reactor volumes shown in parentheses.

Loading Rates

The loading rates were based on total COD. The NFDM had a TCOD of 1.03 g COD/g NFDM. The NFDM feed solution was prepared by adding the appropriate amount of NFDM to the feed stock. As a verification procedure, the COD test was routinely performed on the NFDM feed stock.

System organic loadings are shown in Table 11. System organic loadings of 1 g COD/L/day to 10 g COD/L/day (influent feed concentration 2.0 g/L to 20.0 g/L) were evaluated for the 48 hr and 36 hr system HRTs. System loadings of 10 g COD/L/day to 16 g COD/L/day (influent feed concentration 10.0 g/L to 16.0 g/L) were evaluated for the 24 hr system HRT.

Table 11. COD loadings for the three TPAB systems and for the thermophilic first stages

System Loading g COD/L/day	First-Phase Thermophilic Organic Loadings g COD/L/day		
	No. 1 (2.9L)	No. 2 (5.6L)	No. 3 (11.2L)
1	8	4	2
2	16	8	4
3	24	12	6
4	32	16	8
5	40	20	10
6	48	24	12
7	56	28	14
8	64	32	16
9	72	36	18
10	80	40	20
11	88	44	22
12	96	48	24
13	104	52	26
14	112	56	28
15	120	60	30
16	128	64	32

The thermophili[illegible] different size ratios which enable[illegible] reactors while feeding exactly [illegible] ystem. System loadings on the [illegible] ulted in effective loadings on the [illegible] to 128 g COD/L/da[illegible] also illustrat[illegible]

The thermophili[illegible] C. The mesophilic second phase [illegible] shows that these operating temperatures [illegible] eactors. It was also a research goal [illegible] dy on the TPAB process conduc[illegible]

The performance of [illegible] mples were collected for the analy[illegible] rsion, and alkalinity.

The thermophilic and mesophilic phases for the three TPAB systems were of different size ratios which enabled variation of the COD load on the first stage thermophilic reactors while feeding exactly the same volume and substrate COD concentration to each system. System loadings on the three TPAB systems of 1 g COD/L/day to 16 g COD/L/day resulted in effective loadings on the thermophilic first phases ranging from 2 g COD/L/day to 128 g COD/L/day, also illustrated in Table 11.

Temperature of Operation

The thermophilic first phases of the three TPAB systems were operated at 56° C. The meosphilic second phases of the TPAB systems were operated at 35° C. The literature shows that these operating temperatures are appropriate for both the thermophilic and mesophilic reactors. It was also a research goal to compare the results of this experiment with a preliminary study on the TPAB process conducted at Iowa State University (Harris, 1992).

Sampling and Analysis

The performance of the systems were monitored using several parameters. Samples were collected for the analysis of TCOD, SCOD, VFA, pH, solids, ammonia, gas composition, and alkalinity.

Samples were collected and analyzed at least once a week for each parameter, and more frequently during quasi-steady state periods. As defined by this experiment, quasi-steady state conditions were reached when the measured methane production for the reactors varied less than five percent from the average daily methane production during that period.

pH The pH of the reactor effluents were measured several times a week with a Model 4500 Altex digital pH meter. The pH probe was a standard glass gel-encased membrane probe.

The pH meter was calibrated daily with two standard buffers with a pH 4.0 and 7.0. During sample analysis approximately 20 ml of sample was collected and analyzed immediately to avoid pH changes due to release of carbon dioxide. The pH probe was washed with distilled water after use and stored in pH 4.0 standard buffer.

Chemical Oxygen Demand The chemical oxygen demand (COD) procedure followed was Standard Method 508 B Oxygen Demand (Chemical, closed reflux, titration method). The prinicple of the COD test is to measure the oxygen equivalent of organic matter which can be chemically oxidized using a strong oxidizing agent. Potassium dichromate was used as the oxidizing agent.

In the modified reflux method , the reaction must take place at elevated temperatures in the presence of a strong acid and a catalyst. Silver sulfate was the catalyst. The catalyst is needed to convert organic compounds which are difficult to chemically oxidize.

The digestion vessels were 20 by 150 mm culture tubes which required the following quantities:

Sample	5 ml
Potassium dichromate	3 ml
Sulfuric acid with catalyst	7 ml

The total volume in each tube was 15 ml. The maximum oxygen measuring capacity was 480 mg O_2/L. Most samples required dilution using volumetric flasks. Duplicates of each sample were performed to increase the reliability of the results.

The COD was calculated using the following equation:

$$\text{COD, mg/L} = \frac{(A-B) \times M \times 8000 \times D}{\text{ml of sample}}$$

where,

A = ml of ferrous ammonium sulfate (FAS) used for the blank

B = ml FAS used for the sample

M = molarity of FAS titrant

D = dilution factor of the sample

Total COD (TCOD) and soluble COD (SCOD) were performed on each sample collected. The TCOD was performed on a well-mixed portion of the sample as collected. The SCOD was performed on the filtrate from the samples which passed through a 4.25 cm, 1.2 μm pore size

GF/C glass filter paper. A vacuum apparatus, which included buchner funnels and glass vacuum flasks, was used to aid in filtering samples for the SCOD test.

At each quasi-steady state, a data point was collected for each organic loading on the reactors. During collection of the data point, TCOD and SCOD tests were performed every other day for a total of three COD testing days. The COD data obtained from the runs was averaged and combined into one COD data point.

Solids Analyses Solids were another important parameter monitored. Solids analyses were performed once for each COD loading/HRT data point. The solids tests were performed when the reactors were in quasi-steady state.

Total and volatile suspended solids were performed according to Standard Methods, sections 209 C and 209 D, respectively, with the following modifications:

1. Filter papers were not washed prior to use.
2. A 10 ml sample size was used.
3. Only one series of drying, cooling, desiccating, and weighing was performed for each sample.

For the solids analysis, 9- cm glass fiber filter papers were used. Disposible aluminum weighing dishes were used to hold the filter papers. The solids were run in duplicate on the effluent from each of the reactors for each data point. The following equations were used to determine the total and volatile suspended solids (TSS and VSS):

$$\text{TSS, mg/L} = \frac{(\text{A-B})(1000\ \text{mg/g})(1000\ \text{ml/L})}{\text{sample volume, ml}}$$

where,

A = weight of filter + weighing dish + residue,g,

B = weight of filter + weighing dish,g.

$$\text{VSS, mg/L} = \frac{(\text{A-C})(1000\ \text{mg/g})(1000\ \text{ml/L})}{\text{sample volume, ml}}$$

where,

A = weight of filter + dish + residue before ignition,g,

C = weight of filter + dish + residue after ignition,g.

Gas Analysis Gas analyses on the biogas was performed twice weekly using a Gow-Mac 69-350 Gas Chromatograph (GC). The boigas was analyzed for CH_4, N_2, and CO_2. A standard curve was developed during each sampling period using a calibration gas containing 70% CH_4, 25% CO_2, and 5% N_2. The specifications for the gas chromatograph are shown in Table 12.

The biogas samples were removed from gas sampling ports located in the gas line for each reactor. The samples were obtained using a 1-ml gas-lock syringe fitted with a 22 gauge standard side-port needle. Three samples were used to flush the syringe, and the fourth sample

Table 12. GC operating parameters

Component	Specification
Gas Chromatograph	Gow-Mac 69-350
Column	
packing	Chromosorb P
packing size	80/100 mesh
temperature	65° C
Carrier Gas	helium
flowrate	60 ml/min
Detector	thermal conductivity
temperature	150° C
Injection block temperature	100° C
Sample size	0.90 ml
Data station	Maxima

was taken for analysis. A 0.90 ml sample size was used throughout the experiment. The samples were run in duplicate.

Volatile Fatty Acids The volatile fatty acids were analyzed by the Analytical Services Laboratory in the Department of Civil and Construction Engineering. The analyses were performed on a Hewlett Packard 5730 Gas Chromatograph (GC). The operating parameters for the GC are shown in Table 13.

Effluent samples from each reactor were taken during quasi-steady state at each data point for VFA analysis. The samples were filtered twice through 1.2 μm pore size GF/C glass fiber filter papers using a vacuum apparatus to remove particulate debris prior to analysis. The

Table 13. GC operating parameters for VFA analysis

Component	Specification
Gas Chromatograph	Hewlett Packard 5730A
Column	
packing	GP Carbopack C/0.3% Carbowax 20 M/0.1% H_3PO_4
detection limit	ppm level
temperature	120° C
Carrier gas	helium
flowrate	50 ml/min
Detector	FID
hydrogen:air flowrate	40:240 ml/min
temperature	200° C
Injection port temperature	200° C
Sample size	1 uL
Data station	Maxima

samples were then acidified to a pH of 2.0 using phosphoric acid and frozen for one to six days prior to analysis.

Ammonia Ammonia measurements were performed once for each COD loading/HRT data point for the reactors. Effluent samples were taken from each reactor immediately prior to analysis to prevent ammonia volatilization. Ammonia was determined using an Orion ammonia probe and a Model 4500 Altex digital pH meter operated in the mV mode.

A calibration curve was developed to determine the ammonia concentration of the reactor effluent. Three standard solutions of 10, 100, and 1000 mg/L (as N) of ammonium chloride were used to determine the calibration curve.

For both the standards and the reactor effluents, a 25- ml sample size was used. The 25 ml sample was placed in a 50-ml beaker, and 2 ml of 0.1 N NaOH was added to each sample. The ammonia probe was placed into the beaker, and the sample was continuously stirred. The minimum mV readings were taken from the samples and the standards.

The ammonia values of the samples were determined by plotting the standards on a calibration curve using a regression analysis. For the standards, the mV reading was graphed on the X-axis, and the log of the concentration of the standard was placed on the Y-axis. The equation of a straight line was used to determine the ammonia concentrations of the unknowns as follows:

$$Y = mX + b$$

where,

Y = dependant variable (log of standard concentration)

m = slope of regression line

x = independant variable (mV reading)

b = y intercept

The ammonia concentrations of the samples were determined using the following formula:

$$\text{Ammonia (mg/L as N)} = 10^{(M \times \text{sample mv reading} + b)}$$

Alkalinity The total alkalinity for the reactor effluents were determined once per COD loading/HRT data point using Standard Method 403. A 25-ml sample of the effluent stream was used for all determinations. The samples were titrated with 0.1 N sulfuric acid to the endpoint at a pH of 4.5.

The following equation was used to determine the total alkalinity of the samples:

$$\text{Total alkalinity, mg/L} = \frac{A \times N \times 50{,}000}{\text{sample size, ml}}$$

where,

A = volume of standard acid used, ml,

N = Normality of standard acid.

V. START-UP

Before the experiment was initiated, the reactors were filled with packing media and connected together. The clean-bed volumes were measured for the six reactors using tap water. The three TPAB systems had clean-bed volumes of 22.2 L, 22.3 L, and 22.7 L, and a clean filter bed porosity of 89%.

The systems were assembled together using varying diameters of tygon tubing to connect the reactors to the rest of the experimental set-up, including the feed lines, recycle lines, aspirator bottles, backflow traps, gas sampling ports, and the gas meters.

The reactors were seeded with primary anaerobic digester sludge from the Ames, Iowa, Water Pollution Control Plant. The seed was first screened through a 1 x 1 mm screen, and diluted with the City of Ames tap water in a 3:1 ratio of seed to tap water. The reactors were allowed to sit for 12 hrs before feeding was initiated to allow for the removal of any dissolved oxygen which may have entered the systems.

The temperature in the thermophilic units was increased to 56° C over a 12-hr time period. The thermophilic phases were initially loaded at a rate of 0.6 to 1.2 g COD/L/day at HRTs of 1.15 to 2.5 days for the first 2 weeks. After 2 weeks, organic loadings were increased and HRTs were decreased during the next 45 days.

During the acclimation period for the thermophilic reactors, the mesophilic reactors were fed an interim feed substrate of 50% NFDM, 30% propionic acid, and 20% acetic acid

(as COD) to acclimate the mesophilic reactors. After the 45-day acclimation period for the thermophilic units, the thermophilic effluent was fed into the mesophilic units.

Throughout the start-up phase, the feed was supplemented with alkalinity in the form of sodium bicarbonate to ensure adequate buffer, and to maintain the effluent pH of the reactors between 6.5 and 7.1.

After the thermophilic and mesophilic reactors were connected in series, the three TPAB systems were started at an initial load of 1 g COD/L/day for the system, at a system HRT of 48 hrs.

VI. RESULTS AND DISCUSSION

System Analysis

The three TPAB systems were compared based on both total and soluble COD removals at the three system HRTs of 24, 36, and 48 hrs. Methane production was also monitored and daily methane productions were averaged during pseudoequilibrium at each COD loading data point. Volatile acids and ammonia levels were also measured for each COD loading data point.

COD Removal

The performance data for the three TPAB systems based on both total and soluble COD removals at system HRTs of 48, 36, and 24 hrs are presented in Tables 14 through 22. Throughout the research, the COD removal results were used as a primary indicator of TPAB performance. The total and soluble COD removal results for the three TPAB systems are illustrated graphically in Figures 14 through 40.

Figures 14 through 19 show performance in terms of COD removal for the three different TPAB systems at the 48 hr system (thermophilic plus mesophilic) HRT.

Figures 14 and 15 illustrate the total and soluble COD removal performance for TPAB 1 (1:7 volume ratio thermophilic:mesophilic). The 48-hr system HRT resulted in a thermophilic stage HRT of 6 hrs and a mesophilic stage HRT of 42 hrs. The mesophilic

Table 14. TPAB 1 (1:7 volume ratio) performance at the 48 hr HRT

System Loadings g COD/L/day	TCOD and SCOD Removals Thermophilic Removals,% Total	Soluble	Mesophilic Removals,% Total	Soluble	System Removals,% Total	Soluble
1	67.2	77.7	79.3	80.7	93.2	95.7
2	65.2	83.3	93.7	94.0	97.8	99.0
3	67.9	84.5	95.6	94.8	98.6	99.2
4	58.5	85.0	95.2	95.3	98.0	99.3
5	63.0	85.7	92.7	95.1	97.3	99.3
6	60.2	77.3	92.7	96.9	97.1	99.3
7	50.3	78.0	93.4	97.7	96.7	99.5
8	38.8	76.1	90.5	96.7	94.2	99.2
9	27.0	54.0	95.9	97.8	97.0	99.0
10	19.9	43.0	91.9	97.7	93.5	98.7

Table 15. TPAB 1 (1:7 volume ratio) performance at the 36 hr HRT

System Loadings g COD/L/day	TCOD and SCOD Removals Thermophilic Removals,% Total	Soluble	Mesophilic Removals,% Total	Soluble	System Removals,% Total	Soluble
2	30.1	59.1	92.1	95.4	94.5	98.1
3	32.2	60.0	94.9	96.7	96.6	98.7
5	27.1	56.1	93.0	98.2	94.9	99.2
7	35.6	59.4	96.3	98.0	97.6	99.2
9	38.3	62.0	95.9	97.4	97.5	99.0

Table 16. TPAB 1 (1:7 volume ratio) performance at the 24 hr HRT

System Loadings g COD/L/day	TCOD and SCOD Removals Thermophilic Removals,% Total	Soluble	Mesophilic Removals,% Total	Soluble	System Removals,% Total	Soluble
10	20.7	35.2	87.1	96.6	89.8	97.8
11	28.9	53.6	92.3	96.1	94.5	98.2
12	28.9	52.1	94.4	96.2	96.0	98.2
13	21.3	50.0	92.5	97.8	94.1	98.9
14	20.2	50.9	94.9	97.9	95.9	99.0
15	0.0	38.7	94.8	98.7	94.8	99.2
16	14.3	46.1	95.2	98.3	95.9	99.1

Table 17. TPAB 2 (1:3 volume ratio) performance at the 48 hr HRT

System Loadings g COD/L/day	TCOD and SCOD Removals					
	Thermophilic Removals,%		Mesophilic Removals,%		System Removals,%	
	Total	Soluble	Total	Soluble	Total	Soluble
1	69.2	79.3	70.8	87.0	91.0	97.3
2	83.1	89.8	81.1	86.3	96.8	98.6
3	75.1	84.1	88.8	93.7	97.2	99.0
4	75.8	90.4	93.4	92.7	98.4	99.3
5	78.1	87.8	92.2	94.3	98.3	99.3
6	81.4	91.9	87.6	92.6	97.7	99.4
7	86.0	92.7	83.6	93.2	98.6	99.5
8	71.0	86.6	82.0	95.5	94.9	99.4
9	65.0	86.0	94.3	92.9	98.0	99.0
10	62.3	76.1	94.0	97.5	97.7	99.4

Table 18. TPAB 2 (1:3 volume ratio) performance at the 36 hr HRT

System Loadings g COD/L/day	TCOD and SCOD Removals Thermophilic Removals,% Total	Soluble	Mesophilic Removals,% Total	Soluble	System Removals,% Total	Soluble
2	59.2	72.2	90.0	94.6	95.9	98.5
3	64.3	82.8	90.2	91.9	96.5	98.6
5	67.6	85.9	89.1	93.6	96.5	99.1
7	62.2	77.2	92.3	95.6	97.1	99.0
9	64.2	70.8	89.7	96.2	96.3	98.9

Table 19. TPAB 2 (1:3 volume ratio) performance at the 24 hr HRT

System Loadings g COD/L/day	TCOD and SCOD Removals Thermophilic Removals,% Total	Soluble	Mesophilic Removals,% Total	Soluble	System Removals,% Total	Soluble
10	57.2	73.0	83.4	94.8	92.9	98.6
11	55.0	79.8	86.0	93.1	93.7	98.6
12	48.6	73.7	83.1	92.0	91.3	97.9
13	42.6	69.3	86.6	92.6	92.3	97.5
14	53.7	78.3	89.8	92.6	95.3	98.4
15	53.4	82.0	89.0	92.8	94.9	98.7
16	53.2	77.0	89.7	93.5	95.2	98.5

Table 20. TPAB 3 (1:1 volume ratio) performance at the 48 hr HRT

System Loadings g COD/L/day	TCOD and SCOD Removals					
	Thermophilic Removals,%		Mesophilic Removals,%		System Removals,%	
	Total	Soluble	Total	Soluble	Total	Soluble
1	62.8	83.9	83.6	82.6	93.9	97.2
2	84.9	91.5	79.4	81.2	96.9	98.4
3	77.9	91.8	89.6	85.4	97.7	98.8
4	81.7	93.4	88.5	87.9	97.9	99.2
5	82.1	90.9	88.8	88.9	98.0	99.1
6	85.0	94.1	90.0	88.1	98.5	99.3
7	83.8	90.8	86.4	90.2	97.8	99.1
8	86.2	93.7	81.2	87.3	97.4	99.2
9	86.3	94.7	73.8	83.0	96.6	99.1
10	87.0	92.0	71.5	90.0	96.3	99.2

Table 21. TPAB 3 (1:1 volume ratio) performance at the 36 hr HRT

System Loadings g COD/L/day	TCOD and SCOD Removals Thermophilic Removals,% Total	Soluble	Mesophilic Removals,% Total	Soluble	System Removals,% Total	Soluble
2	53.3	66.5	81.8	92.2	91.5	97.4
3	68.1	81.1	83.7	89.9	94.8	98.1
5	82.8	94.1	71.5	79.7	95.1	98.8
7	80.0	94.0	72.5	83.3	94.5	99.0
9	74.7	89.6	73.1	81.7	93.2	98.1

Table 22. TPAB 3 (1:1 volume ratio) performance at the 24 hr HRT

System Loadings g COD/L/day	TCOD and SCOD Removals Thermophilic Removals,% Total	Soluble	Mesophilic Removals,% Total	Soluble	System Removals,% Total	Soluble
10	69.3	80.8	749.2	91.1	93.6	98.3
11	74.7	86.4	70.8	90.4	92.6	98.7
12	76.5	87.4	67.6	85.7	92.4	98.2
13	77.4	88.8	65.9	81.3	92.3	97.9
14	75.6	87.5	73.4	77.6	93.5	97.2
15	73.0	86.1	80.0	86.3	94.6	98.1
16	77.0	63.3	69.1	92.3	92.9	97.2

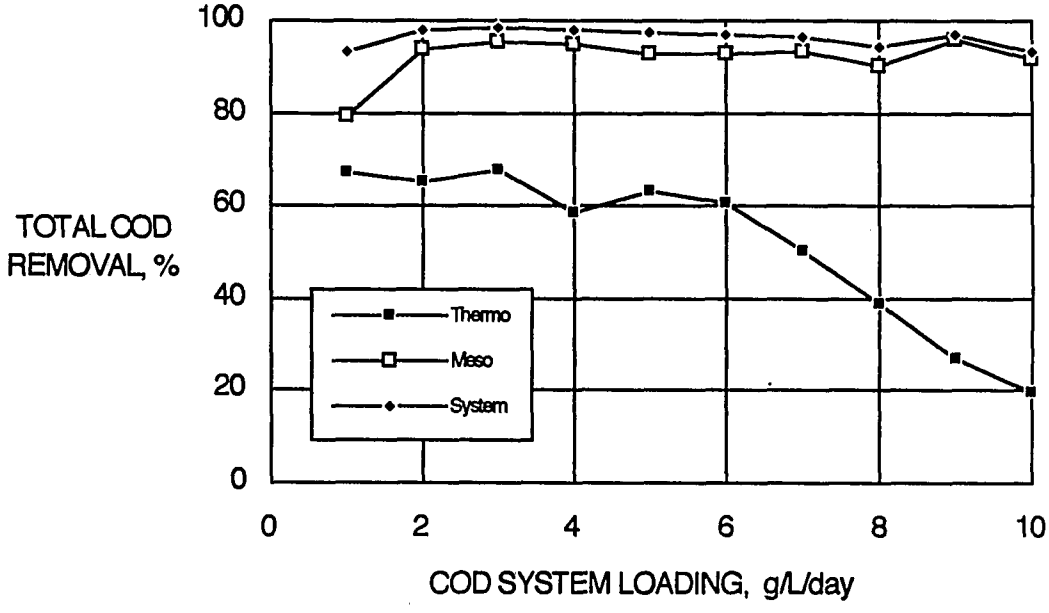


Figure 14. Total COD removals at various COD applied loads for TPAB 1 (1:7) for the 48 hr HRT

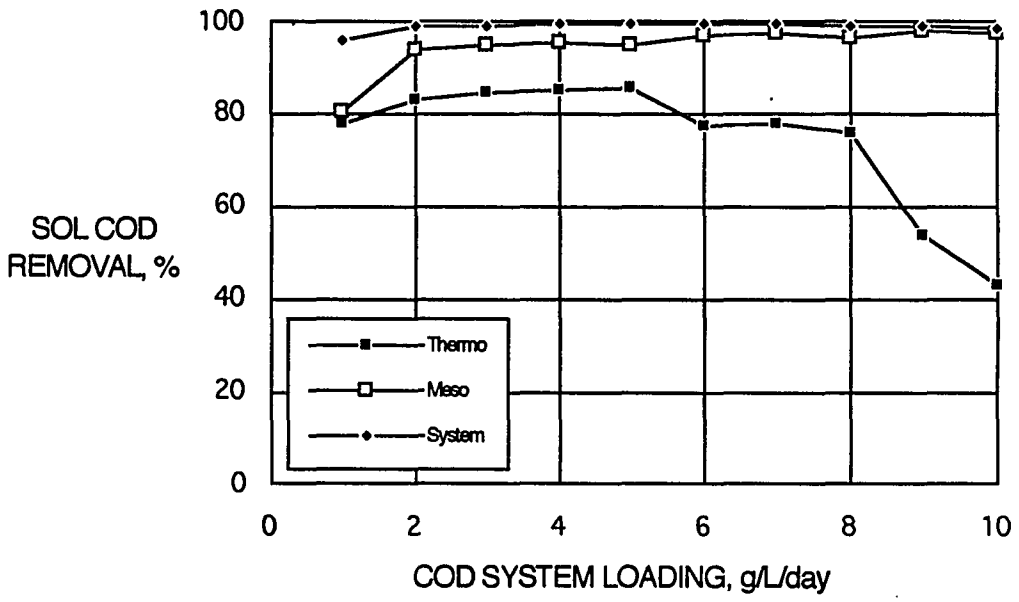


Figure 15. Soluble COD removals at various COD applied loads for TPAB 1 (1:7) for the 48 hr HRT

TCOD and SCOD removals were in excess of 90% at system loads above 2 g COD/L/day. The thermophilic TCOD and SCOD first-stage removals declined above the 6 g COD/L/day system loading. The 6 g COD/L/day system loading corresponded to an effective first-stage COD loading of 48 g/L/day. Although first-stage performance declined above the 6 g COD/L/day loading, the overall two-stage system continued to perform well with TCOD and SCOD removals of 93.2 to 98.6%, and 75.7 to 99.3 %, respectively.

Figures 16 and 17 illustrate the TCOD and SCOD removal performance for TPAB 2 (1:3 volume ratio thermophilic:mesophilic). The 48-hr system HRT resulted in a thermophilic first-stage HRT of 12 hrs, and a mesophilic second-stage HRT of 36 hrs. The mesophilic TCOD and SCOD removals were in excess of 80% at COD system loadings above 2 g/L/day. A slight decline in performance was observed in the thermophilic first-stage above the 7 g COD/L/day system loading. The 7 g/L/day system loading corresponded to an effective first-stage COD loading of 28 g COD/L/day. Performance for the first-stage resulted in TCOD removals which decreased from 86% at the 7 g/L/day system loading to 62.3% TCOD removal at the 10 g/L/day system loading.

TPAB 3 (1:1 volume ratio thermophilic:mesophilic) performance in terms of TCOD and SCOD removals are illustrated in Figures 18 and 19. The 48- hr system HRT resulted in thermophilic and mesophilic stage HRTs of 24 hrs. Thermophilic TCOD removals were in excess of 77.9% at COD system loadings in excess of 1 g/L/day. No decrease in

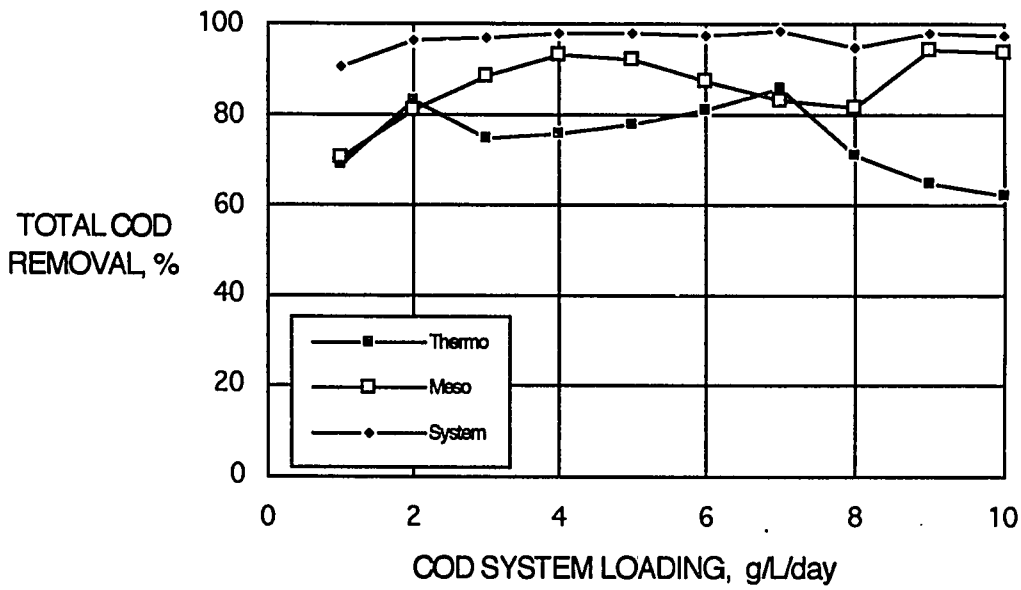


Figure 16. Total COD removals at various COD applied loads for TPAB 2 (1:3) for the 48 hr HRT

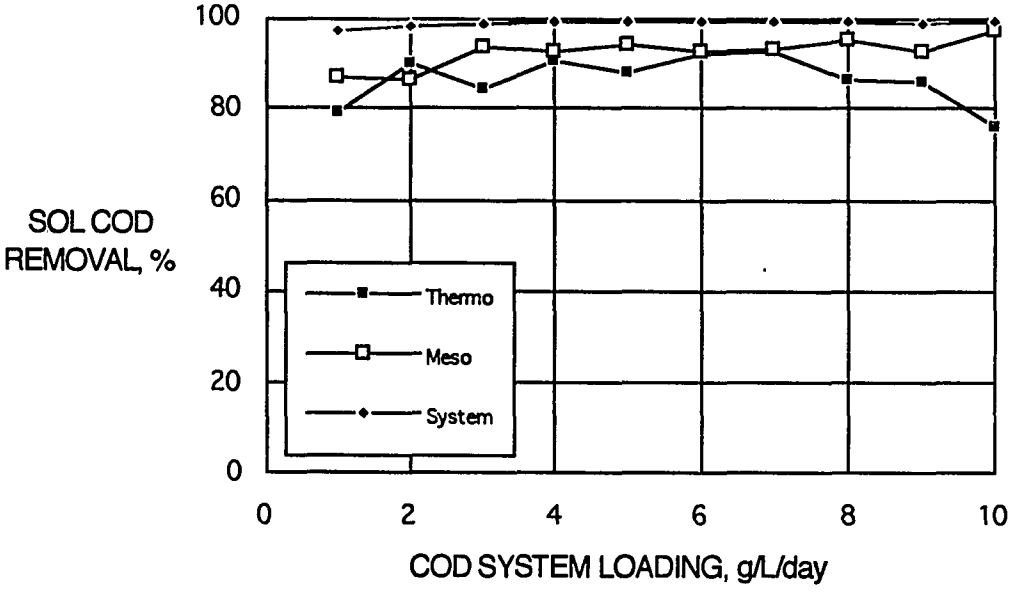


Figure 17. Soluble COD removals at various COD applied loads for TPAB 2 (1:3) for the 48 hr HRT

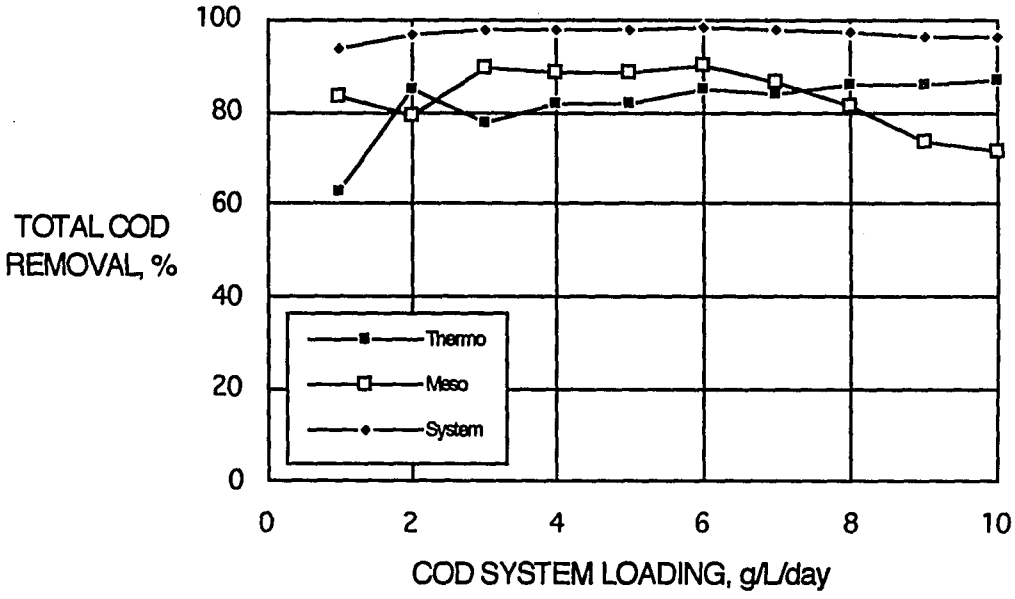


Figure 18. Total COD removals at various COD applied loads for TPAB 3 (1:1) for the 48 hr HRT

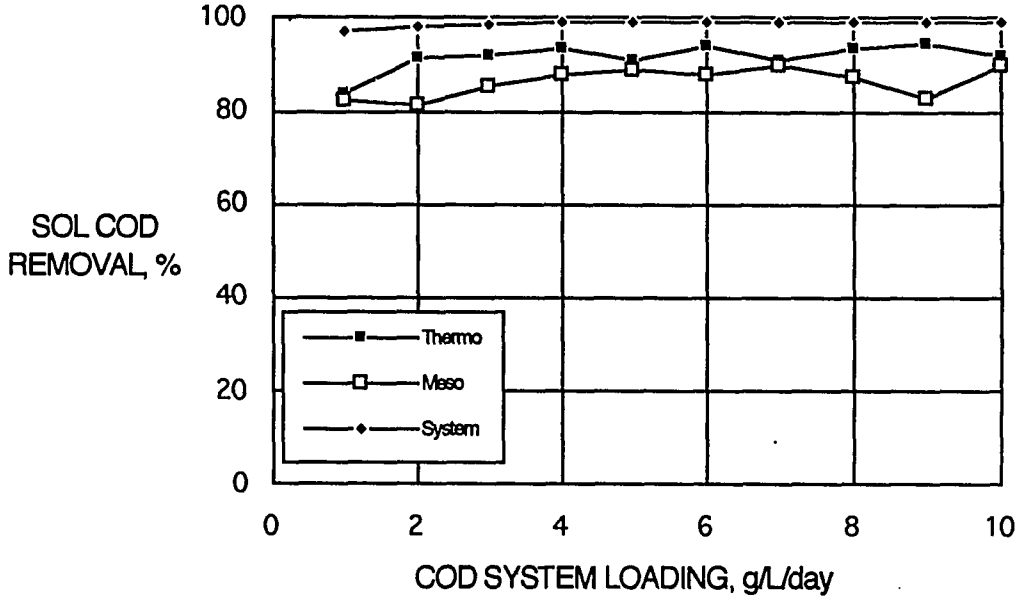


Figure 19. Soluble COD removals at various COD applied loads for TPAB 3 (1:1) for the 48 hr HRT

performance was observed for either phase of TPAB 3 at the applied COD loadings. The effective COD loading on the thermophilic first-stage at the 48- hr system HRT ranged from 2 to 20 g/L/day.

The performance in terms of TCOD removal for the three TPAB thermophilic first stages is illustrated in Figure 20. The 24-hr HRT thermophilic first stage outperformed the 6 and 12 hr HRT units, with TCOD removals in excess of 80% above the 3 g COD/L/day system loading. TCOD removals were higher in the 24- hr HRT thermophilic first-stage unit since the effective COD loadings were much lower than the effective loadings for the 6 or 12 hr HRT thermophilic units. The effective COD loadings for the thermophilic stages for the three TPAB systems at the 24, 12 , and 6 -hr HRTs were 2 to 20 g/L/day, 4 to 40 g/L/day, and 8 to 80 g/L/day, respectively.

Overall two-stage performance in terms of total and soluble COD removals for the TPAB systems at the 48-hr system HRT is illustrated in Figures 21 and 22. There was no significant difference in overall two-stage performance between the three TPAB systems. TCOD removals ranged from 93.5 to 98.6%, and SCOD removals ranged from 98.4 to 99.5%. Total COD removals of 93.5 to 98.6% corresponded to final effluent TCOD ranging from 140 mg/L to 840 mg/L.

Figures 23 through 28 illustrate performance in terms of COD removal for the three TPAB systems at the 36-hr system (thermophilic plus mesophilic) HRT at COD system loadings of 2 to 9 g/L/day.

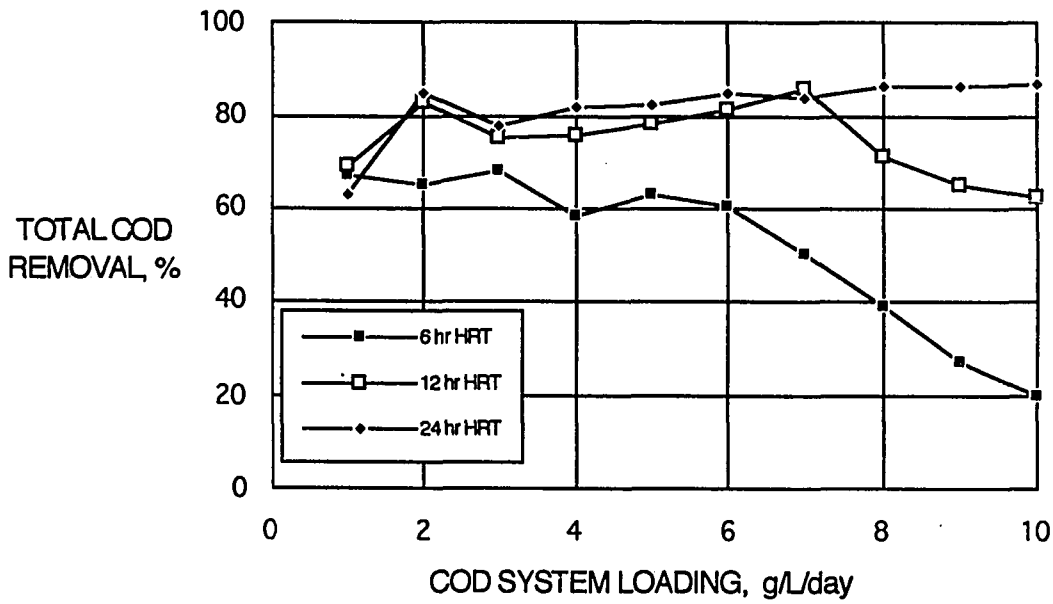


Figure 20. Total COD removals for the three TPAB thermophilic stages for the 48 hr HRT

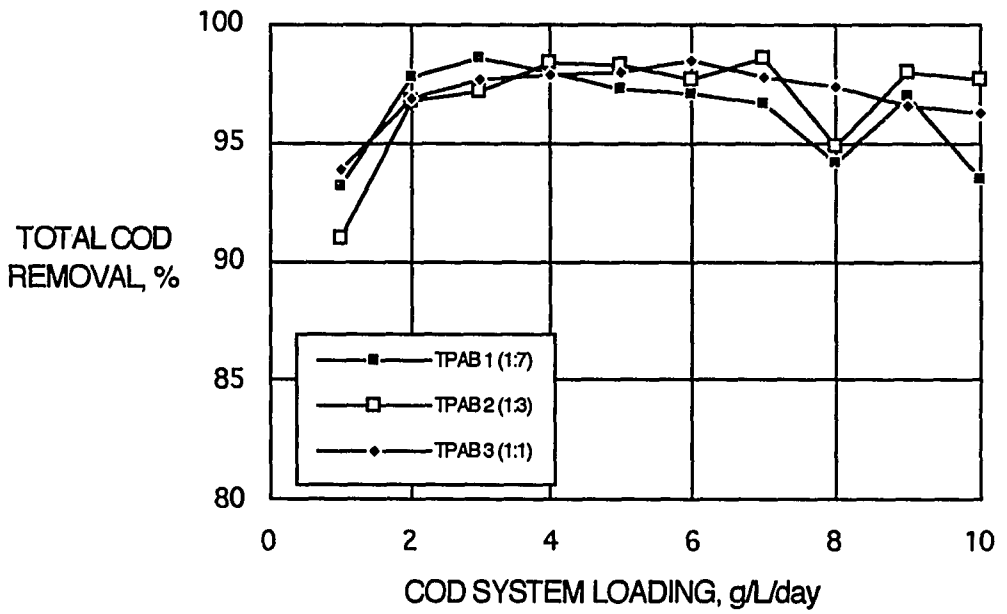


Figure 21. System TCOD removals at various COD applied loads for the three TPAB systems for the 48 hr HRT

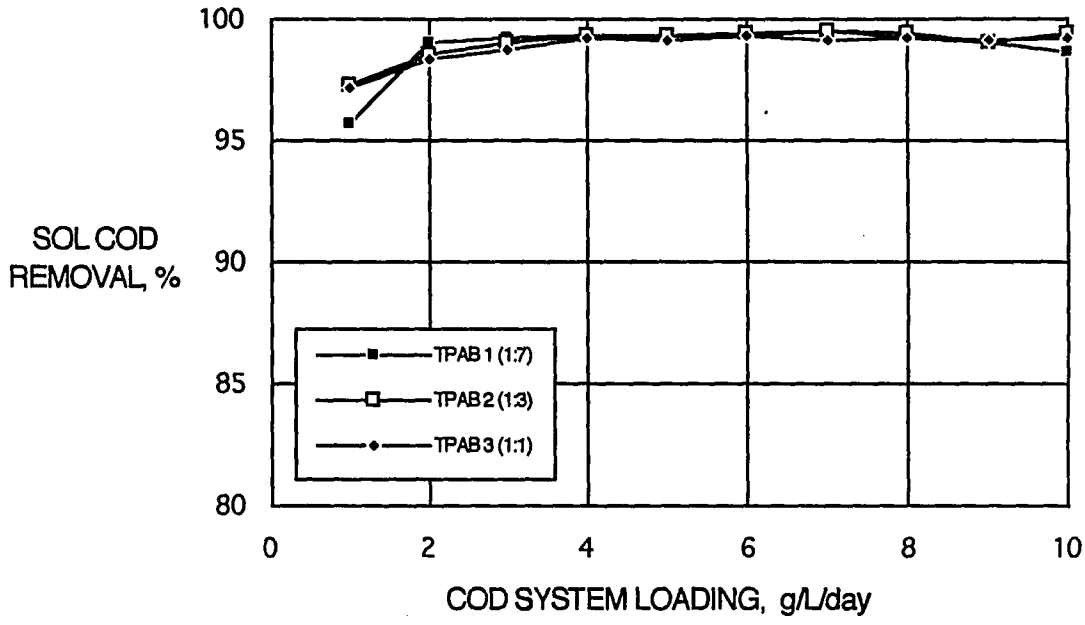


Figure 22. System SCOD removals at various COD applied loads for the three TPAB systems for the 48 hr HRT

Figures 23 and 24 show the performance of TPAB 1 (1:7 volume ratio) in terms of total and soluble COD removals, respectively. For TPAB 1, the 36-hr system HRT resulted in a thermophilic stage HRT of 4.5 hr and a mesophilic stage HRT of 31.5 hr. For the thermophilic first stage, TCOD removals ranged from 21.7 to 38.3%, and SCOD removals ranged from 56.1 to 62%. The performance of the thermophilic first stage at the 4.5- hr HRT was observed to be quite stable in terms of TCOD and SCOD removals, as compared to the decline in performance for TPAB 1 at the 48-hr system HRT. The stability in performance for the thermophilic first stage at the 36- hr HRT may have been caused by a population shift during the course of the experiment, whereby over time a relatively small but stable population of methanogens predominated in this reactor. During the experiment, the three TPAB systems were operated first at the 48- hr system HRT, then at the 24- hr system HRT, and lastly at the 36- hr system HRT. Although thermophilic first-stage TCOD removals were low, the overall two-stage TPAB system performed well, with TCOD removals ranging from 94.5 to 97.5%, and SCOD removals ranging from 98.1 to 99.2%.

Figures 25 and 26 illustrate the performance of TPAB 2 (1:3 volume ratio thermophilic:mesophilic) in terms of total and soluble COD removals, respectively. For TPAB 2, the 36- hr system HRT results in a thermophilic HRT of 9 hrs, and a mesophilic HRT of 27 hrs. For the thermophilic stage, TCOD removals were observed to be nearly constant over the

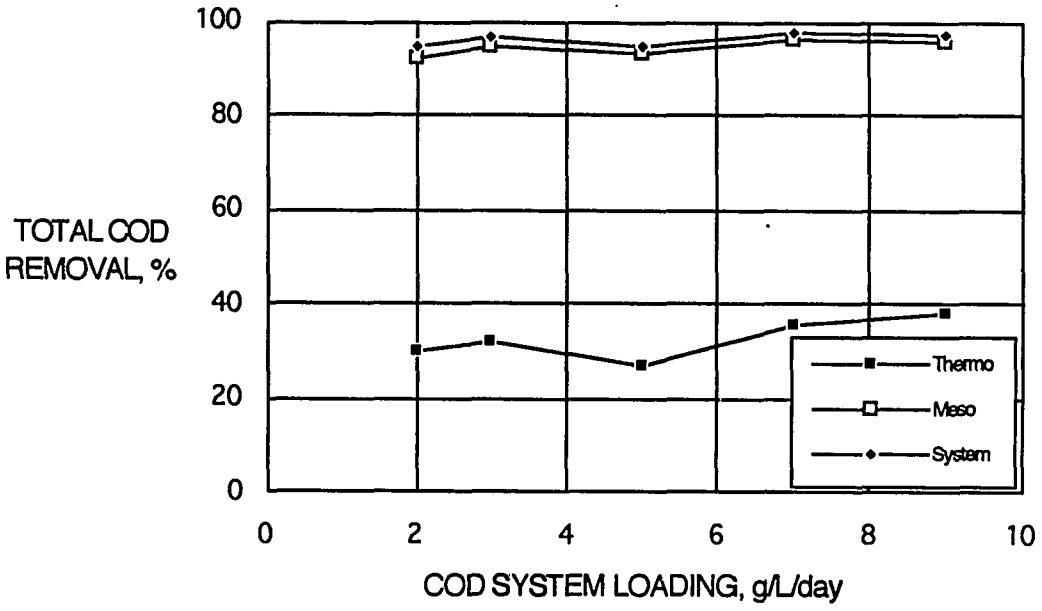


Figure 23. Total COD removals at various COD applied loads for TPAB 1 (1:7) for the 36 hr HRT

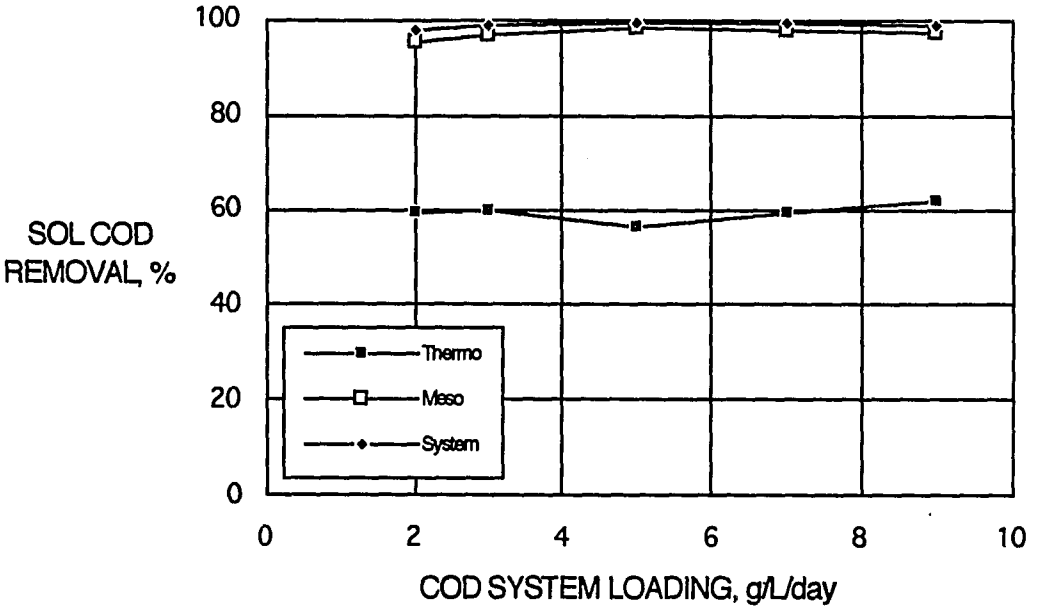


Figure 24. Soluble COD removals at various COD applied loads for TPAB 1 (1:7) for the 36 hr HRT

range of applied COD system loadings of 2 to 9 g/L/day, which correspond to an effective COD load on the first stage of 8 to 36 g/L/day. TCOD removals for the thermophilic stage ranged from 59.2 to 67.6%. This means that at a 9- hr HRT, the thermophilic unit was capable of removing approximately two-thirds of the applied organic loading. SCOD removals were observed to decline slightly above the 5 g COD/L/day system loading. The overall two-phase TPAB 2 system performed well, with TCOD removals ranging from 95.9 to 97.1% and SCOD removals ranging from 98.6 to 99.1%.

Figures 27 and 28 illustrate the performance of TPAB 3 (1:1 volume ratio thermophilic:mesophilic) in terms of total and soluble COD removals, respectively. For TPAB 3, the 36-hr system HRT resulted in an 18-hr HRT for both the thermophilic and mesophilic stages. Higher TCOD and SCOD removals for the thermophilic stage were observed at system COD loadings of 5 to 9 g/L/day. Effective loadings on the thermophilic stage at system COD loadings of 5 to 9 g/L/day ranged from 10 to 18 g COD/L/day. Higher thermophilic removals were observed at effective COD loadings in excess of 10 g/L/day in part because of the somewhat misleading nature of COD removal percentages, in that higher loadings result in higher removal percentages since a higher influent COD is applied. Also, it is believed that thermophilic anaerobic systems operate more efficiently at higher minimum loadings as compared to mesophilic anaerobic systems. The overall two-stage TPAB 3 system performed well with TCOD removals ranging from 91.5 to 95.1% and SCOD removals ranging from 97.4 to 99%.

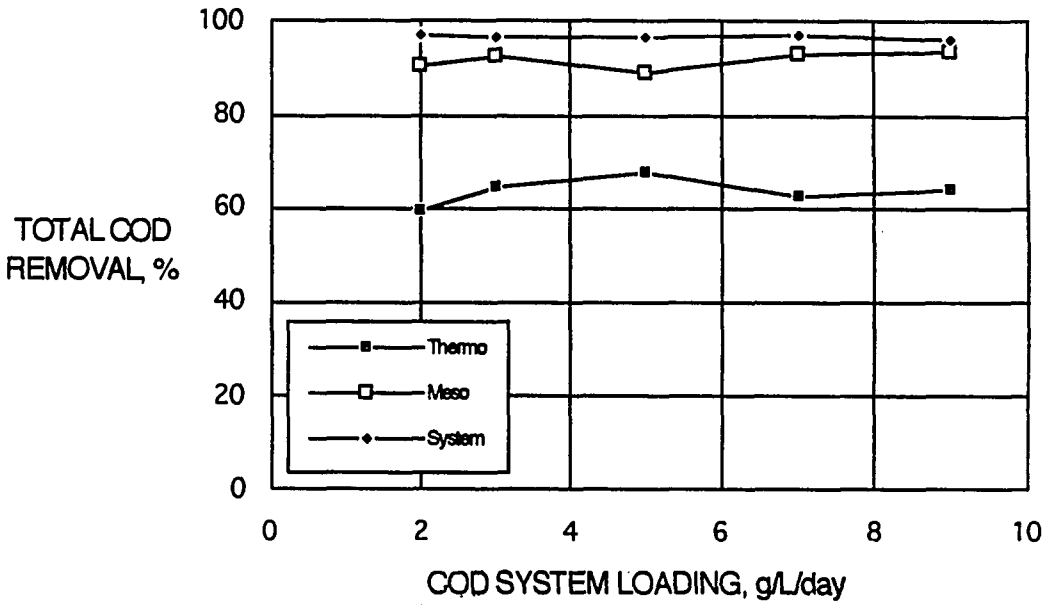


Figure 25. Total COD removals at various COD applied loads for TPAB 2 (1:3) for the 36 hr HRT

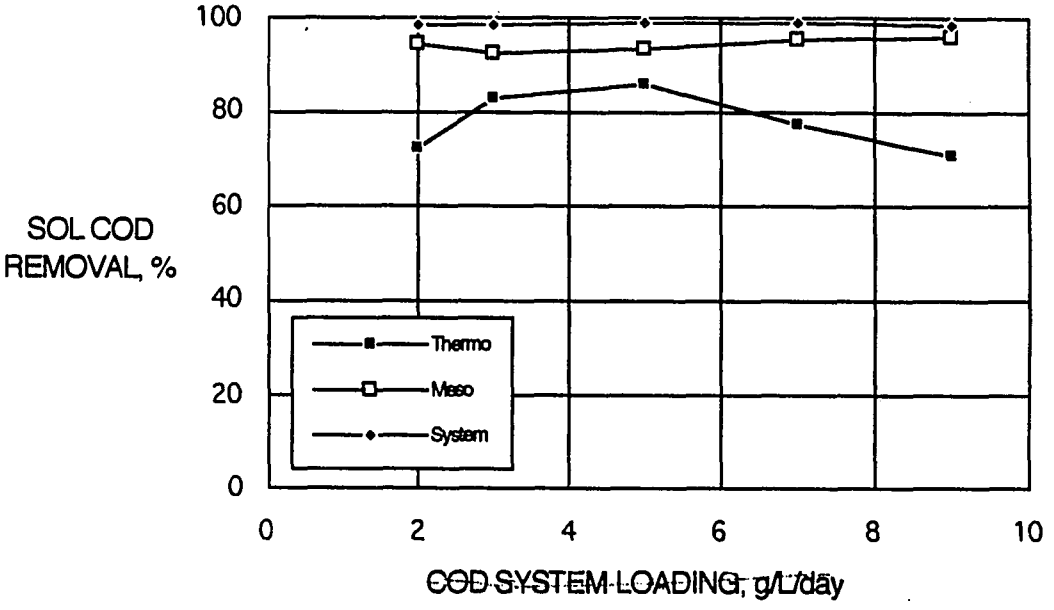


Figure 26. Soluble COD removals at various COD applied loads for TPAB 2 (1:3) for the 36 hr HRT

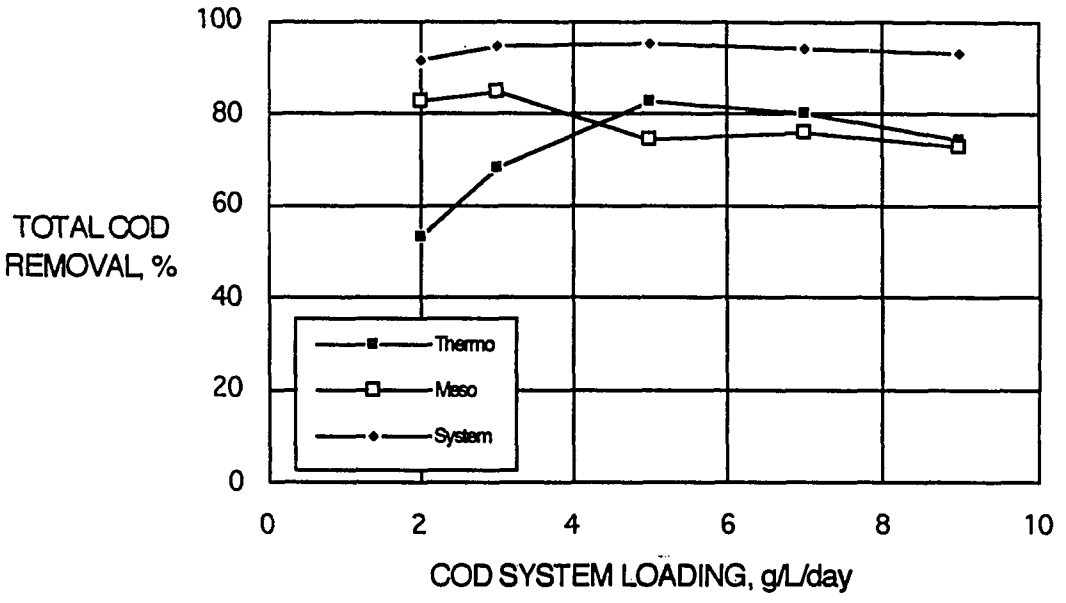


Figure 27. Total COD removals at various COD applied loads for TPAB 3 (1:1) for the 36 hr HRT

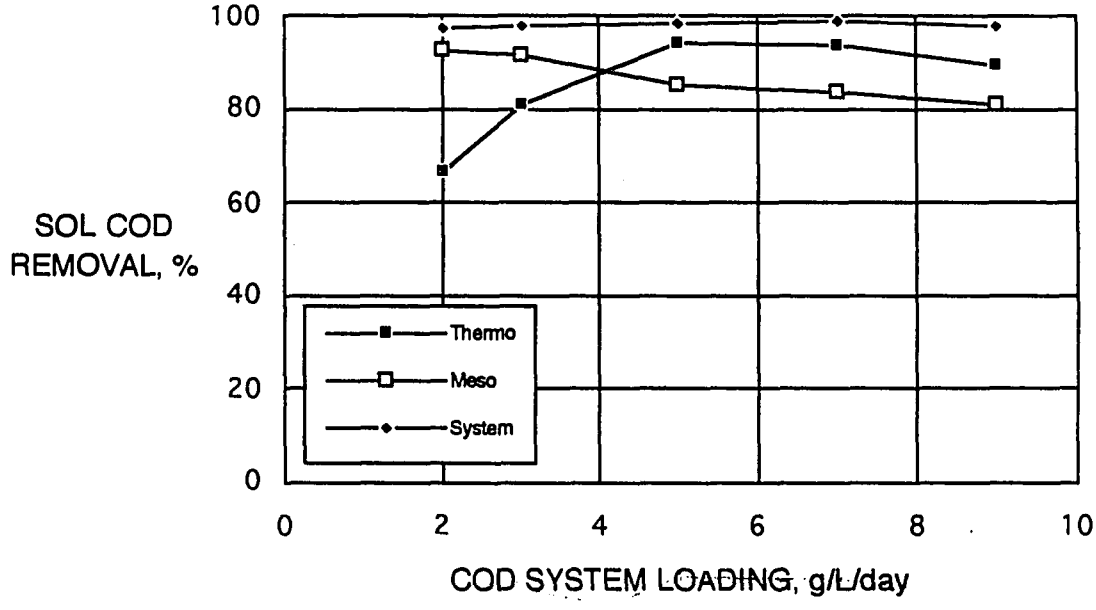


Figure 28. Soluble COD removals at various COD applied loads for TPAB 3 (1:1) for the 36 hr HRT.

Figure 29 illustrates the comparison of the three TPAB thermophilic first stages in terms of TCOD removal at the 36- hr HRT. The 18- hr HRT thermophilic unit outperformed both the 4.5 and 9-hr HRT units at COD system loadings in excess of 3 g/L/day. For the 18- hr HRT unit, TCOD removals ranged from 82.8% at the 5 g COD/L/day system loading, to 74.6% at the 9 g COD/L/day system loading. The 4.5 and 9 -hr HRT thermophilic unit displayed nearly stable TCOD removals at COD system loadings ranging from 2 to 9 g/L/day. TCOD removals for the 4.5- hr HRT unit ranged from 30.1 to 38.3% and TCOD removals for the 9 -hr HRT unit ranged from 59.2 to 67.6%. COD system loadings of 2 to 9 g/L/day resulted in an effective COD load for the thermophilic first stage at the 18- hr HRT of 4 to 18 g/L/day. The effective loadings on the 9 and 4.5- hr HRT thermophilic units were 8 to 36 g/L/day and 16 to 72 g/L/day, respectively. It is believed that a relatively small but stable population of methanogens occupied the 4.5- hr HRT unit because of the stable TCOD removals at applied COD loadings up to the high load of 72 g/L/day.

The TCOD removals at the 2 g/L/day load were slightly higher for the 9-hr HRT unit as compared to the 18- hr HRT unit. This was because the effective load on the18-hr HRT unit was only 4 g/L/day. In the COD test, higher percentages of removal are achieved as applied organic loads are increased.

Performance in terms of total and soluble COD removals for the three TPAB systems at the 36 hr HRT is illustrated in Figures 30 and 31. Similar to the 48- hr system HRT, there was no significant difference in overall two-stage COD removal. TCOD and SCOD removals for the

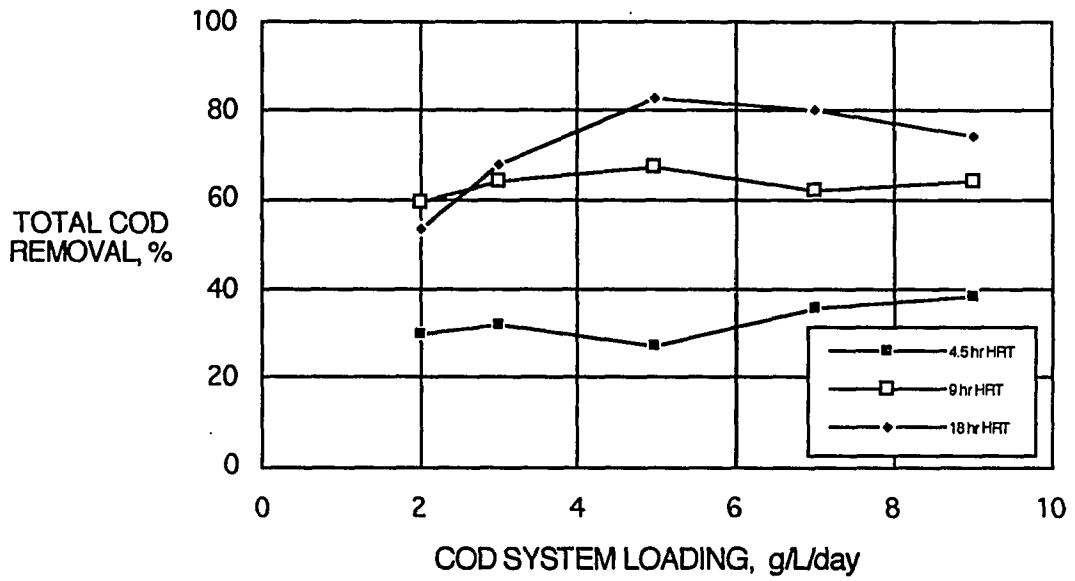


Figure 29. Total COD removals for the three TPAB thermophilic stages for the 36 hr HRT

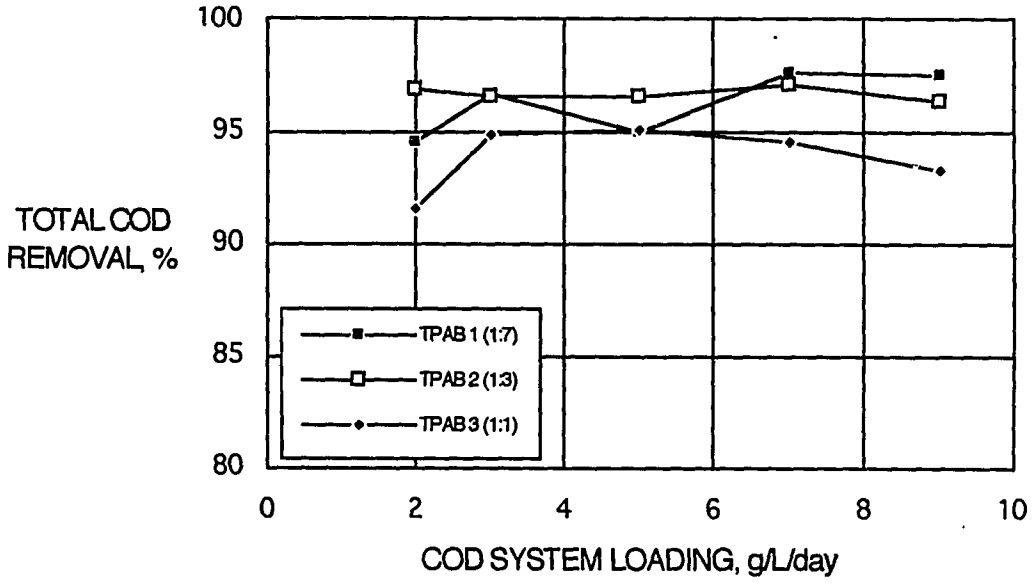


Figure 30. System TCOD removals at various COD applied loads for the three TPAB systems for the 36 hr HRT

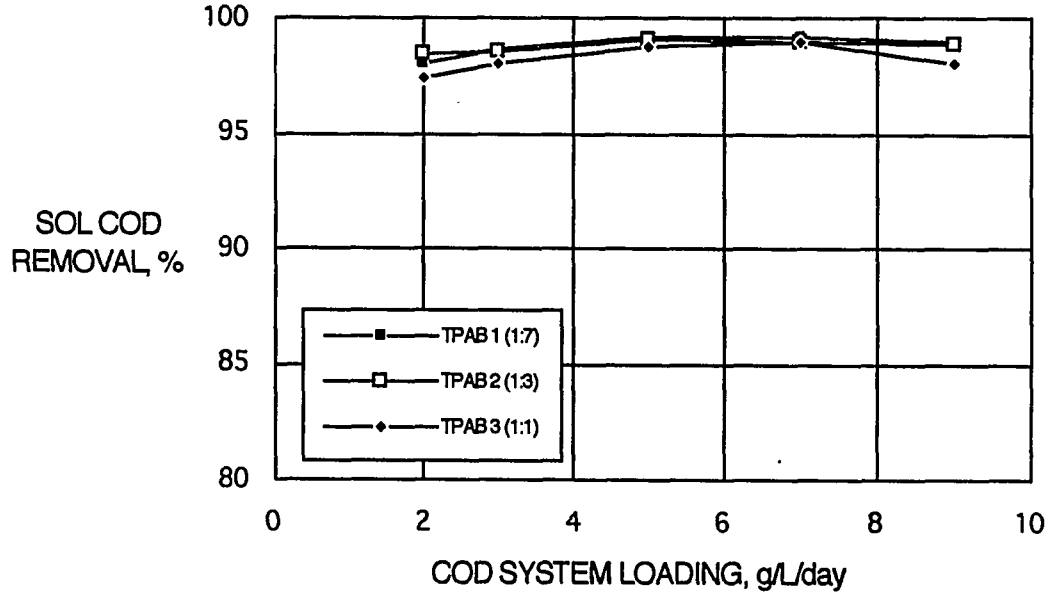


Figure 31. System SCOD removals at various COD applied loads for the three TPAB systems for the 36 hr HRT

three TPAB systems at COD system loadings of 2 to 9 g/L/day ranged from 91.5 to 97.5%, and 97.4 to 99.2%, respectively.

Figures 32 through 37 illustrate performance in terms of COD removal for the three TPAB systems at the 24-hr system HRT at COD system loadings of 10 to 16 g/L/day.

Figures 32 and 33 show the performance of TPAB 1 (1:7 volume ratio) in terms of total and soluble COD removals, respectively. For TPAB 1, the 24-hr system HRT resulted in a thermophilic HRT of 3 hrs, and a mesophilic HRT of 21 hrs. Effective COD loadings on the thermophilic stage ranged from 80 to 128 g/L/day. For the thermophilic stage, SCOD removals were observed to remain relatively stable over the applied COD system loadings, with SCOD removals ranging from 35.2 to 53.6%. TCOD removals for the thermophilic stage declined from 20.2% at the 14 g COD/L/day system loading to 0% at the 15 g COD/L/day system loading. The decline in TCOD removal for the thermophilic stage was caused by a large amount of solids which were produced and released into the effluent at the higher loading rates. The solids released from the first stage were then passed on and retained by the mesophilic second stage. Effluent TSS from the mesophilic second stage were less than 500 mg/L at the 15 g COD/L/day system loading, as shown in Appendix D. Although TCOD removals declined, the overall two-stage TPAB 1 system performed well, with TCOD and SCOD removals ranging from 89.8 to 95.9%, and 97.8 to 99.2%, respectively.

Figures 34 and 35 illustrate the performance of TPAB 2 (1:3 volume ratio) in terms of total and soluble COD removals, respectively. For TPAB 2, the 24-hr system HRT resulted in

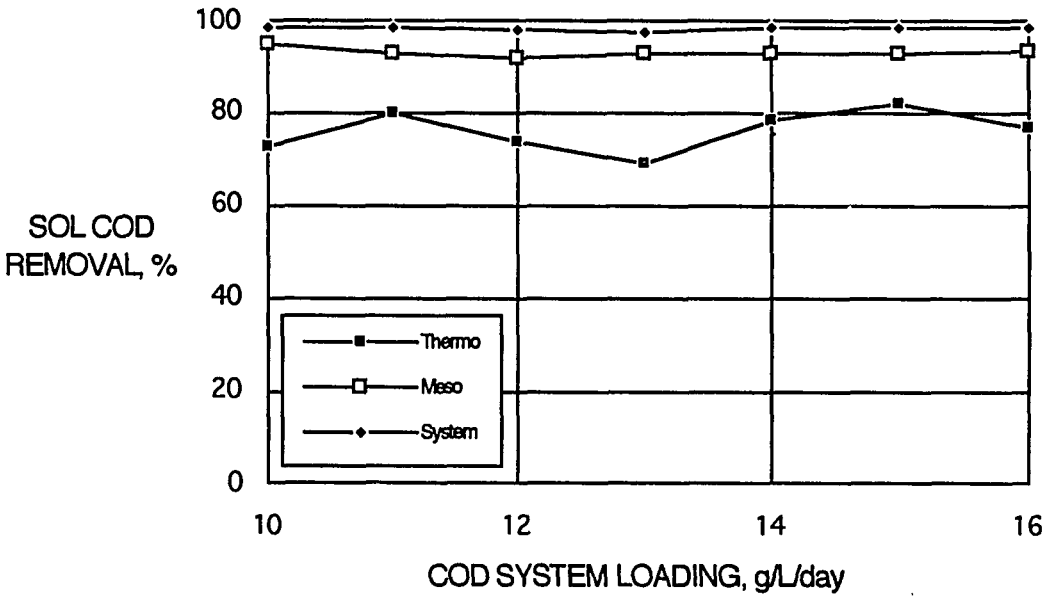


Figure 32. Total COD removals at various COD applied loads for TPAB 1 (1:7) for the 24 hr HRT

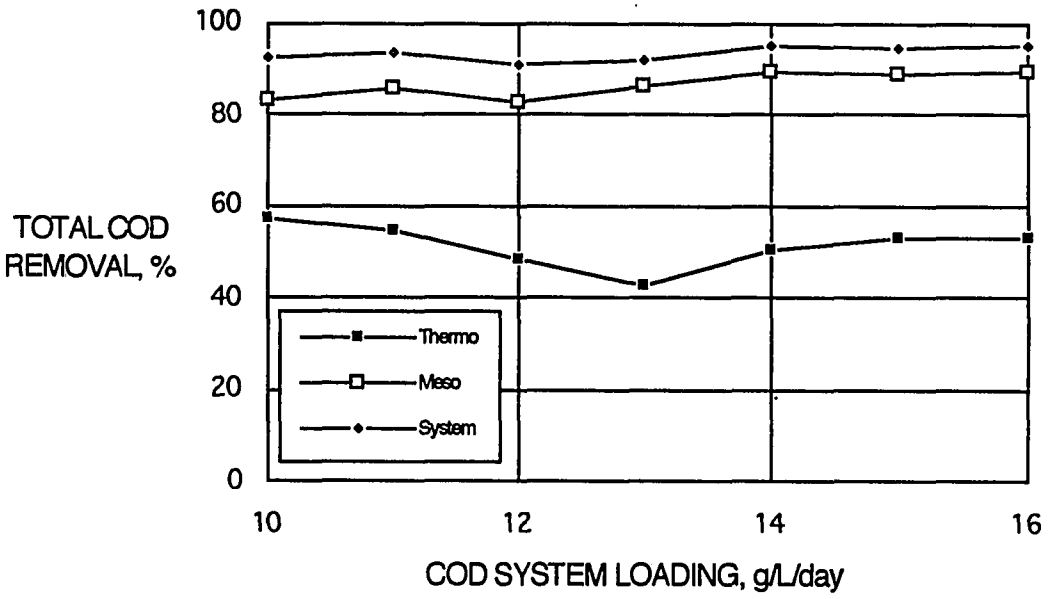


Figure 33. Soluble COD removals at various COD applied loads for TPAB 1 (1:7) for the 24 hr HRT

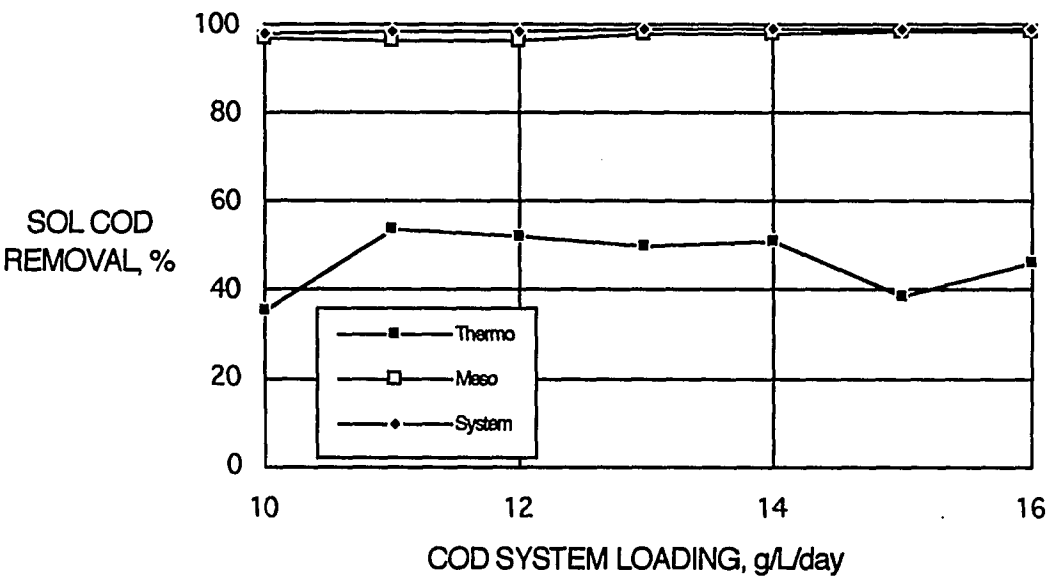


Figure 34. Total COD removals at various COD applied loads for TPAB 2 (1:3) for the 24 hr HRT

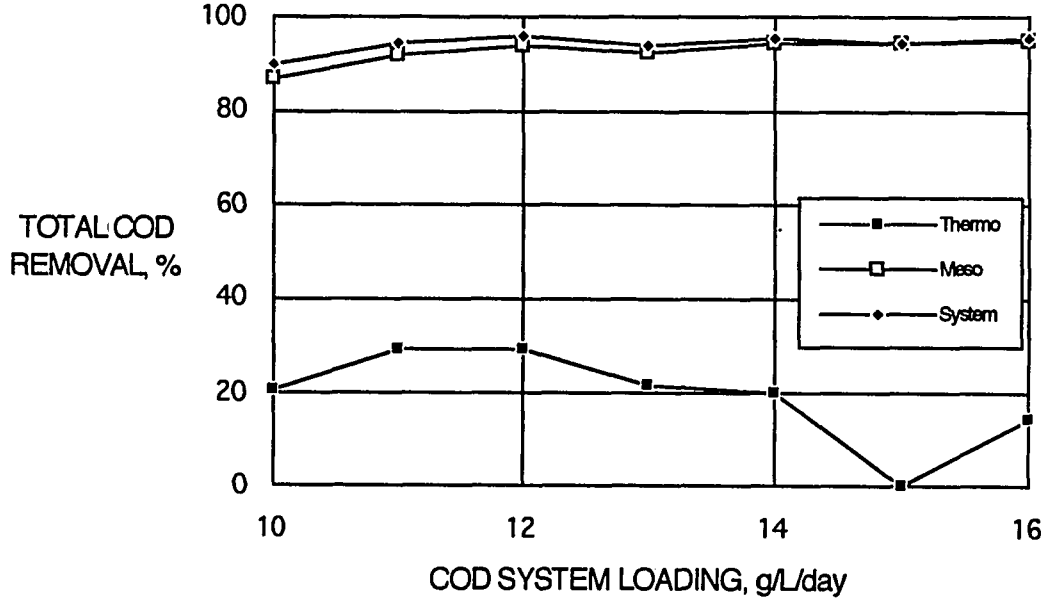


Figure 35. Soluble COD removals at various COD applied loads for TPAB 2 (1:3) for the 24 hr HRT

a thermophilic stage HRT of 6 hrs, and a mesophilic stage HRT of 18 hrs. Effective COD loadings on the 6-hr HRT thermophilic unit ranged from 40 to 64 g/L/day. Both total and soluble COD removals were observed to remain relatively constant for the thermophilic and mesophilic phases over the applied COD system loadings of 10 to 16 g/L/day. TCOD removals for the thermophilic stage ranged from 42.6 to 57.2%, and SCOD removals ranged from 69.3 to 82%. The overall two-stage TPAB 2 system performed well, with TCOD removals ranging from 91.3 to 95.3%, and SCOD removals ranging from 97.5 to 98.7%.

Figures 36 and 37 illustrate the performance of TPAB 3 (1:1 volume ratio) in terms of total and soluble COD removals, respectively. For TPAB 3, the 24-hr system HRT resulted in a 12 hr HRT for both the thermophilic and mesophilic stages. Nearly equal treatment performance was observed for the thermophilic and mesophilic stages, with TCOD removals for both stages ranging from 69.3 to 83.6%. SCOD removals for both stages ranged from 75 to 92.9%. The thermophilic first stage was observed to remove a large portion of the organic matter. This was caused by the relatively long HRT of 12 hrs, and also the low effective COD loadings. First stage effective COD loadings ranged from 20 to 32 g/L/day.

Figure 38 illustrates the comparison of the three TPAB thermophilic first stages in terms of TCOD removal at the 24-hr system HRT. Applied COD loadings of 10 to 16 g/L/day resulted in effective COD loadings on the thermophilic stages for the 3, 6 , and 12- hr HRT units of 80 to 128 g/L/day, 40 to 64 g/L/day, and 20 to 32 g/L/day, respectively. The 12-hr HRT unit outperformed the 6 and 3-hr HRT units, with TCOD removals ranging from 63.3 to 77.4%,

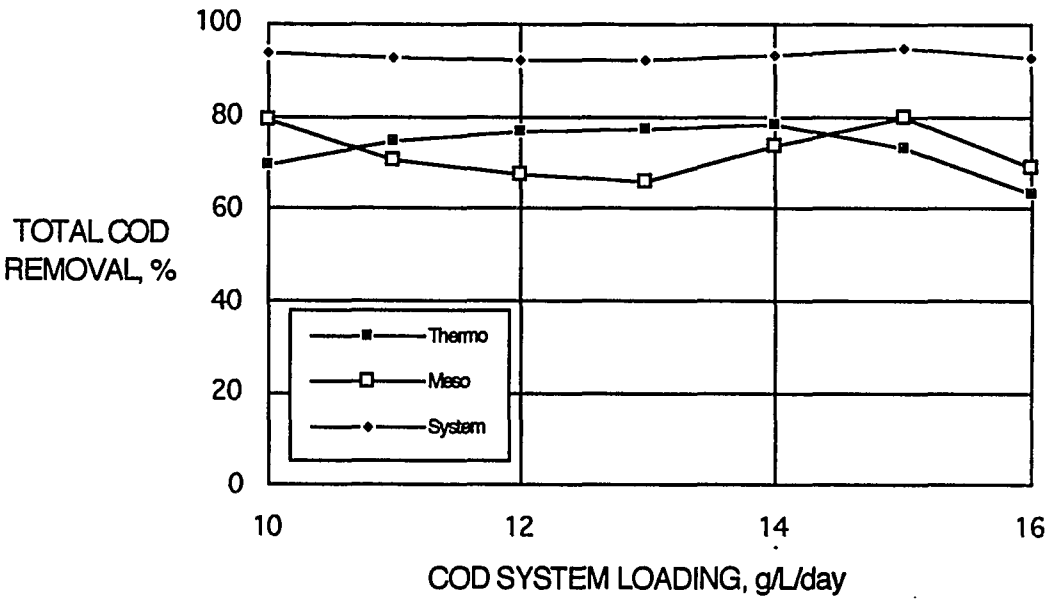


Figure 36. Total COD removals at various COD applied loads for TPAB 3 (1:1) for the 24 hr HRT

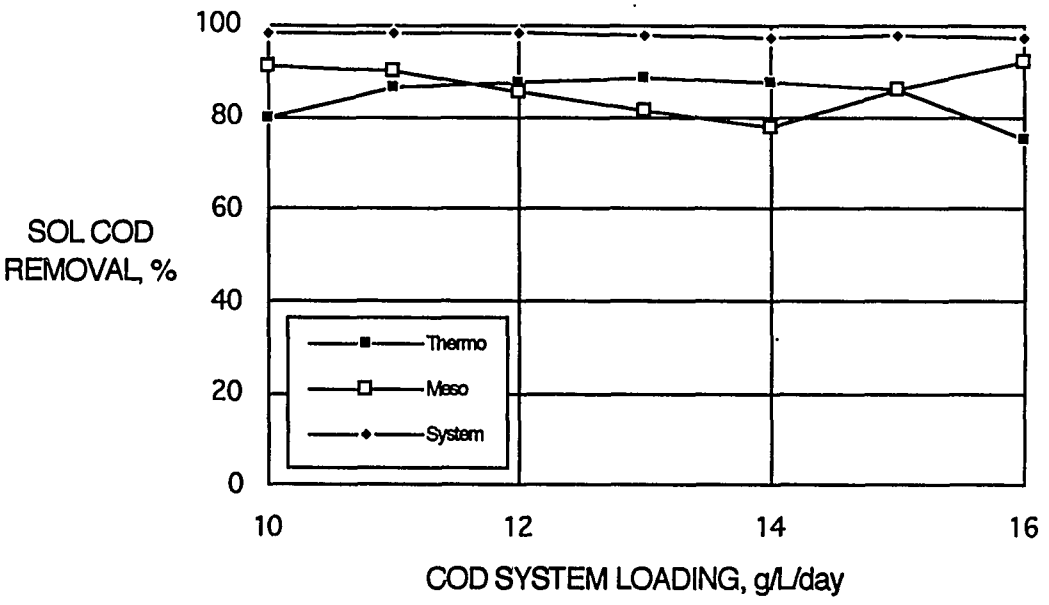


Figure 37. Soluble COD removals at various COD applied loads for TPAB 3 (1:1) for the 24 hr HRT

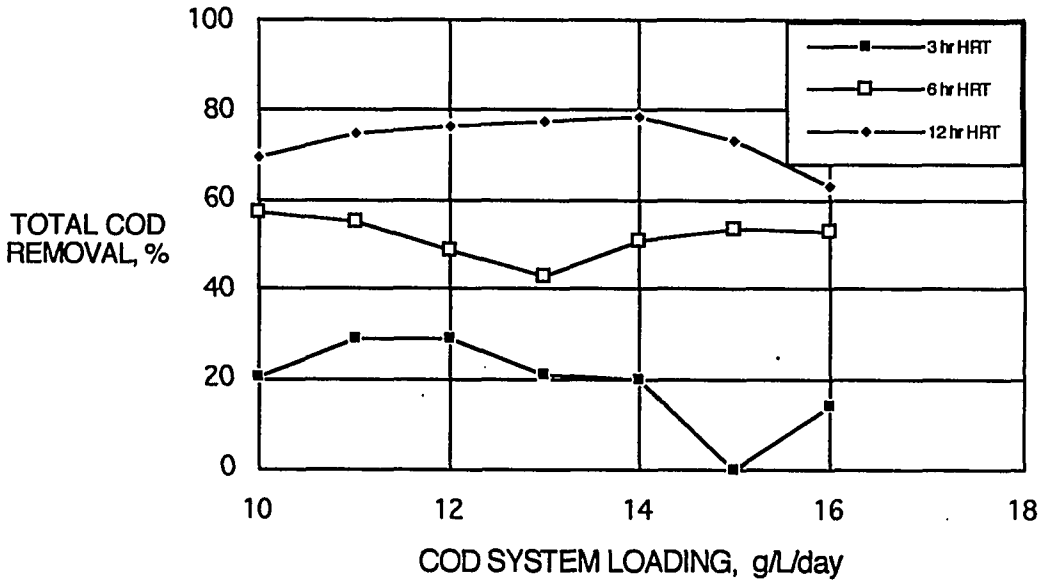


Figure 38. Total COD removals for the three TPAB thermophilic stages for the 24 hr HRT

but the effective loadings for this unit were much lower as compared to the 6 and 3- hr HRT thermophilic units. The 3- hr HRT unit was observed to achieve no TCOD removal at the 15 g COD/L/day system loading. At the 15 g/L/day system loading, the effective COD loading on this unit was 120 g/L/day. The decrease in performance was caused by an increasing production and release of biomass from the 3 -hr HRT unit. The 6- hr HRT unit was observed to provide perhaps the most optimum TCOD removals for the first stage of a two-stage system, with TCOD removals of 42.6 to 57.2%. Performance in terms of total and soluble COD removals for the three TPAB systems at the 24- hr system HRT are illustrated in Figures 39 and 40. There was no significant difference in overall two-stage performance between the three TPAB systems in terms of total and soluble COD removals. TCOD and SCOD removals for the three TPAB systems ranged from 91.3 to 96%, and 97.2 to 99.2%, respectively. Since there was no difference in performance between the three TPAB systems at the 24, 36, or 48-hr HRTs at applied COD system loadings of 1 to 16 g/L/day, the 1:7 volume ratio TPAB system can be used as effectively as the 1:1 or 1:3 volume ratio TPAB systems.

Thermophilic first stage soluble COD removal rates at HRTs ranging from 3 to 6 hrs are shown in Figures 41 through 44. These thermophilic stages for the TPAB systems were operated at very short HRTs and at high COD loadings.

Figure 41 illustrates the 6- hr HRT thermophilic unit performance in terms of SCOD removal rates. The 6- hr HRT unit corresponds to TPAB 1 (1:7) operated at a 48- hr HRT. A near linear relationship between SCOD removal rate and applied load was observed up to the

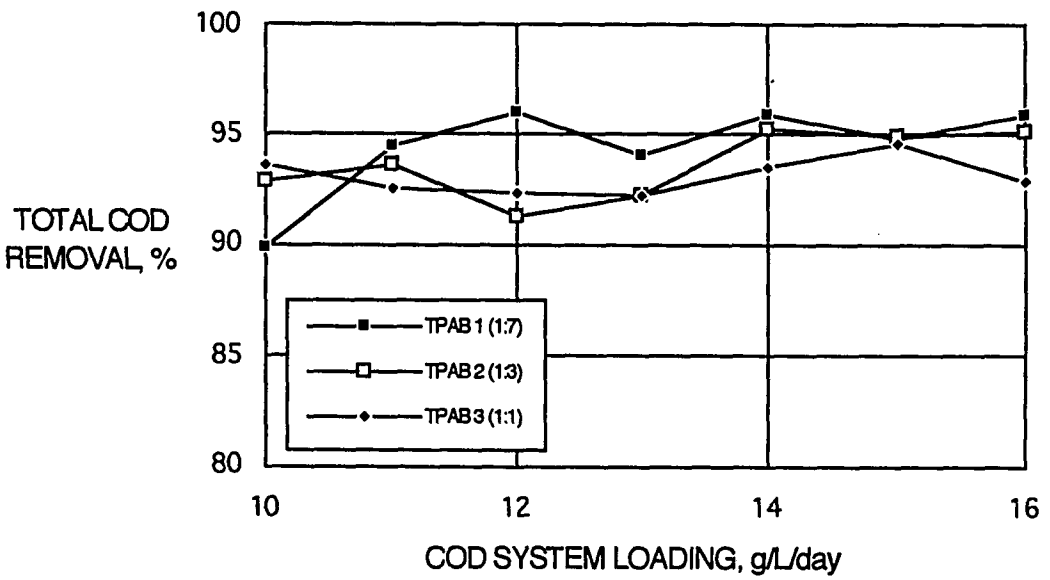


Figure 39. System TCOD removals at various COD applied loads for the three TPAB systems for the 24 hr HRT

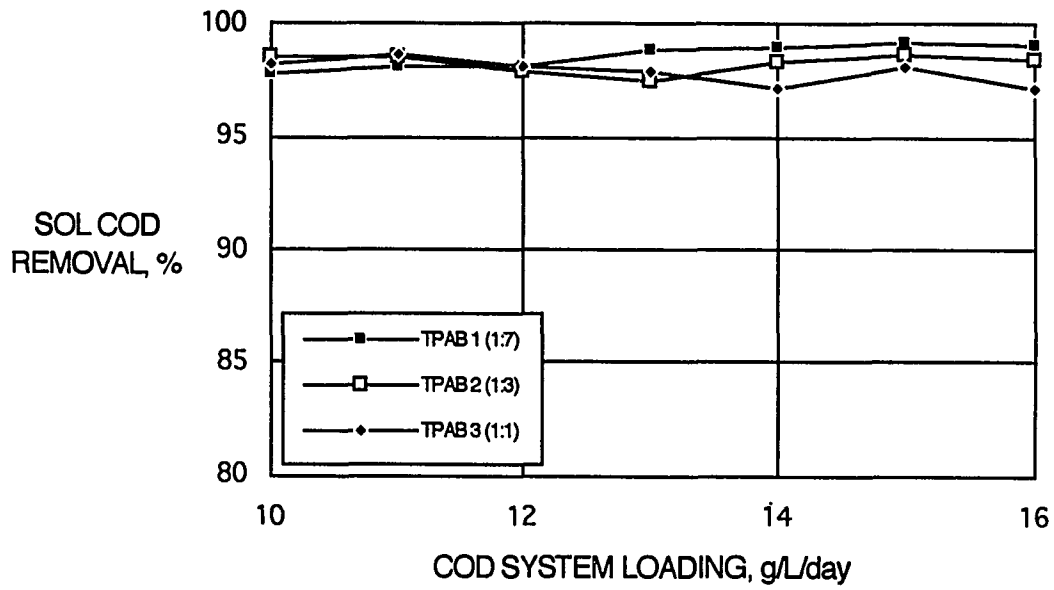


Figure 40. System SCOD removals at various COD applied loads for the three TPAB systems for the 24 hr HRT

64 g/L/day effective COD loading. SCOD % removals averaged 80%. The maximum observed SCOD removal rate was 49 g SCOD/L/day at the 64 g/L/day loading. Above the 64 g/L/day loading, SCOD removal rates declined.

Figure 42 shows the 4.5-hr HRT thermophilic unit performance in terms of SCOD removal rates. The 4.5- hr HRT unit corresponds to TPAB 1 (1:7) operated at a 36- hr system HRT. A linear relationship was observed between SCOD removal rate and effective loading at effective loadings up to the 72 g/L/day loading. SCOD removals averaged 59%. The maximum SCOD removal rate was 47 g SCOD/L/day at the 72 g/L/day load. No decrease in SCOD removal rates were observed. No decrease in SCOD removal rates were observed at the higher loads because it was believed that over time during the experiment, a very stable population of methanogens developed in the reactor. A 4.5 hr- HRT first- stage is sufficient to remove two-thirds of the organic matter up to loads of 72 g/L/day. In the two-stage TPAB system the second stage is able to remove the remaining organic matter.

Figure 43 shows the 6- hr HRT thermophilic unit SCOD removal rates at effective first stage loads of 40 to 64 g COD/L/day. In this case, the 6- hr HRT unit corresponded to TPAB 2 (1:3) operated at the 24-hr system HRT. The maximum SCOD removal rate was 49 g SCOD/L/day at the 64 g/L/day loading. The average SCOD removal percentage was 76% at the applied loads. The results for the 6 -hr HRT unit at the 24 -hr system HRT correlated well with the results in Figure 41 for the 6- hr HRT unit operated at the 48- hr system HRT. There was no observed decline in SCOD removals rates for the 6- hr HRT unit operated at the 24 -hr system

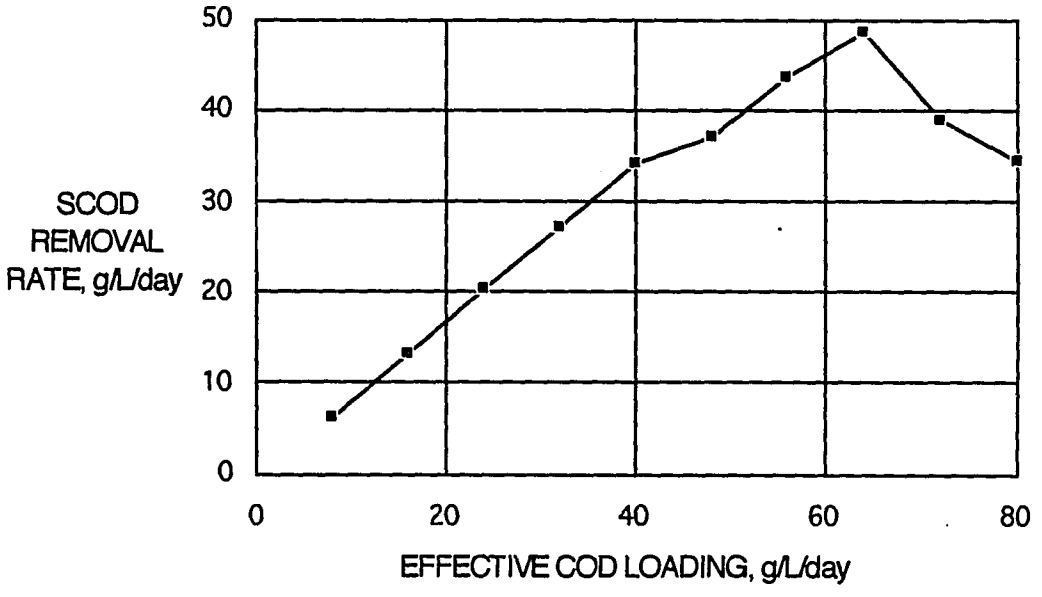


Figure 41. SCOD removal rates at various effective COD loads for the 6 hr HRT thermophilic first stage (System HRT = 48 hrs)

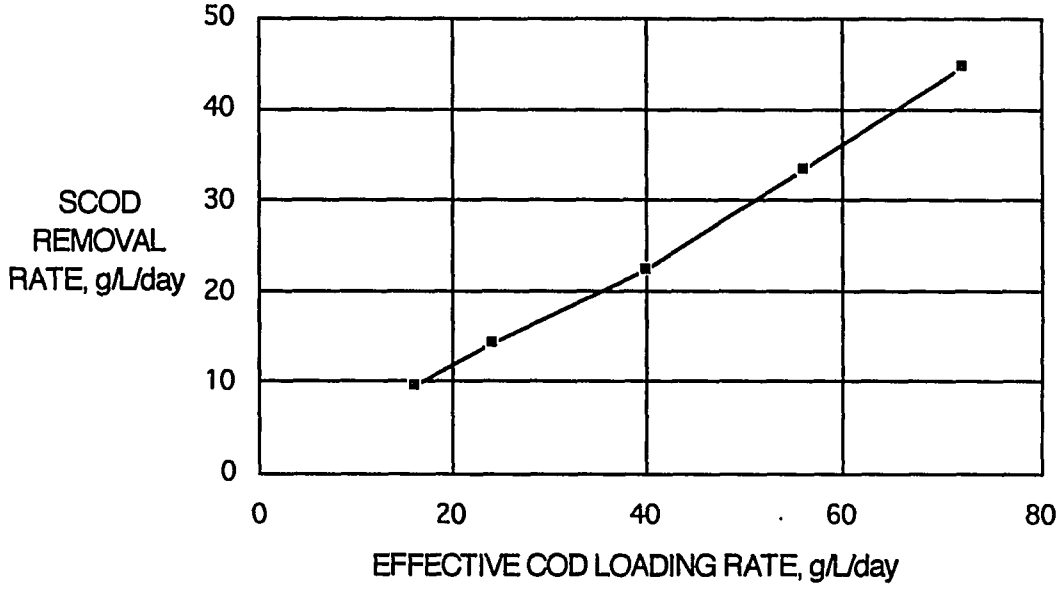


Figure 42. SCOD removal rates at various effective COD loads for the 4.5 hr HRT thermophilic first stage (System HRT = 36 hrs)

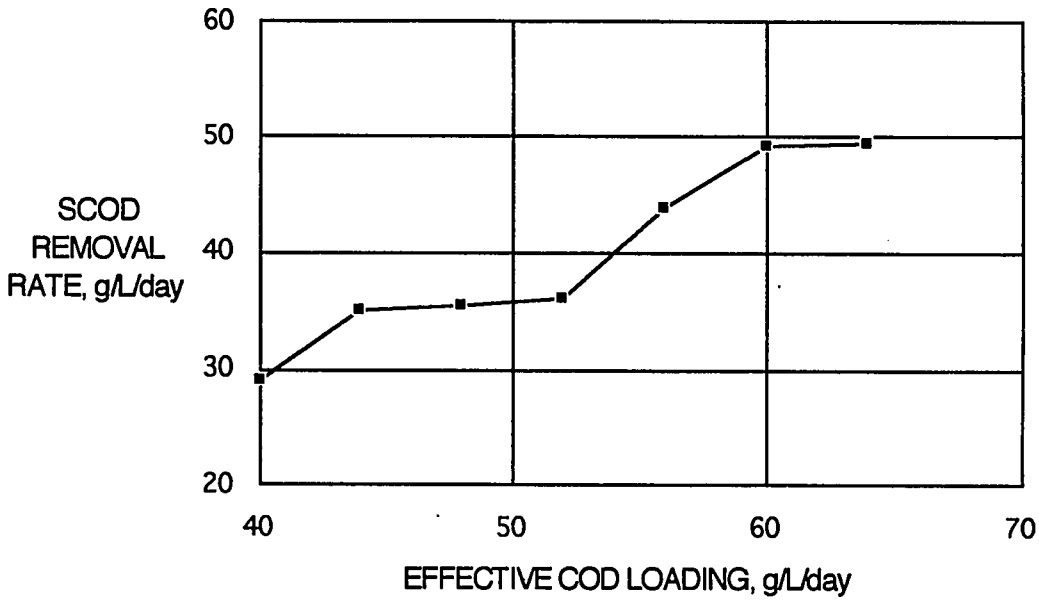


Figure 43. SCOD removal rates at various effective COD loads for the 6 hr HRT thermophilic first stage (System HRT = 24 hrs)

HRT. Although there was no decline in performance, the highest effective COD load applied was 64 g/L/day. Performance for the 6-hr HRT unit in Figure 41 was not observed to decline until effective loadings were in excess of 64 g/L/day.

Figure 44 illustrates the SCOD removal rates for the 3- hr HRT thermophilic unit at effective COD loads ranging from 80 to 128 g/L/day. In this case, the 3-hr HRT unit corresponded to TPAB 1 (1:7) operated at the 24- hr system HRT. SCOD removal rates did not increase linearly with increases in effective loadings. It was observed that SCOD removal rates slowly approached a maximum value of 60 g SCOD/L/day. The average SCOD removal percentage was 47% over the applied effective loadings.

From comparision of Figures 41 and 43, the maximum SCOD removal rates at the 6-hr HRT was 50 g/L/day. The 6- hr HRT thermophilic unit was operated at effective loads up to 80 g COD/L/day. There was an observed leveling off or decline in SCOD removals as higher effective loads were applied.

In Figure 42, the 4.5- hr HRT unit showed no leveling off in SCOD removal rates up to the highest applied load of 72 g COD/L/day. The 4.5- hr HRT data was collected near the end of the 14 month experiment when the most mature and stable population of methanogens had developed.

In Figure 44, much higher effective COD loads ranging from 80 to 128 g/L/day were applied at the 3-hr HRT. In this case, SCOD removal rates approached a maximum of 60 g/L/day, independant of organic loading.

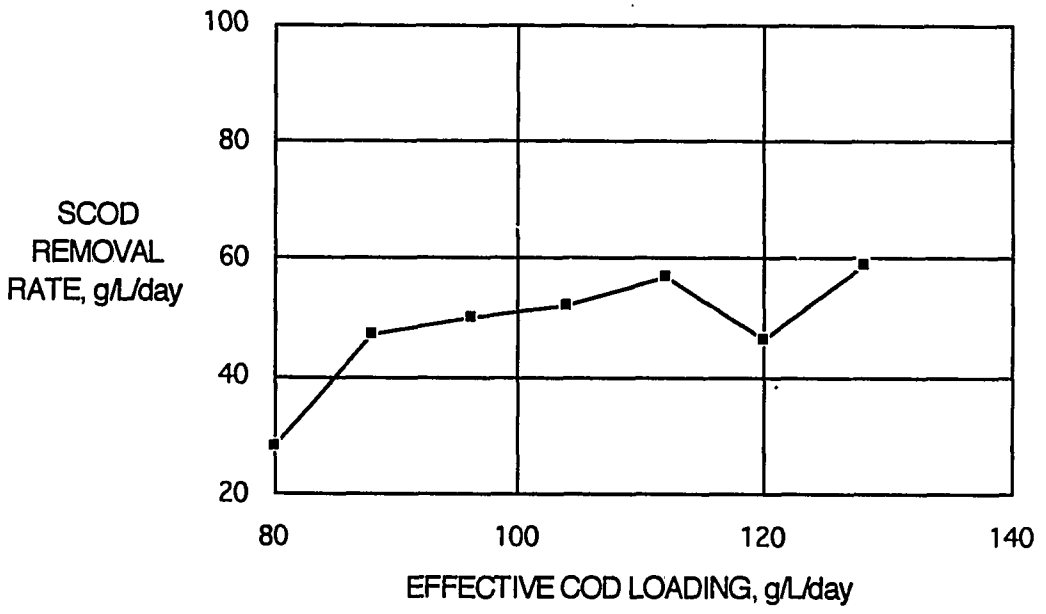


Figure 44. SCOD removal rates at various effective COD loads for the 3 hr HRT thermophilic first stage (System HRT = 24 hrs)

In high applied COD loads at very short HRTs, it is believed that the thermophilicstages were pushed to their limits in terms of how quickly the organic matter could be removed. It is the observation of this research that maximum SCOD removal rates at thermophilic temperatures range from 50 to 60 g/L/day at HRTs ranging from 3 to 6 hrs. A SCOD removal rate of 60 g/Lday corresponds to a 5-day biochemical oxgen demand (BOD_5) removal of 1872 lb/1000 ft^3/day (with a COD/BOD ratio of 0.5). This represents an extremely high rate of organic matter removal for a biological treatment system.

Volatile Acids

An analysis of the volatile acids is necessary to more fully understand some of the mechanisms relating to the two-stage TPAB system performance. In this two-stage system, the first stage converts a portion of the organic matter to methane, and the remainder of the organic matter is incompletely stabilized, and converted to volatile acids. These volatile acids produced in the first stage are further stabilized to methane in the second stage. The quanitity of volatile acids released to the second stage is related to the residence time in the reactor (HRT). Longer HRTs generally result in a higher conversion of volatile acids to methane.

The total volatile acids measured in the effluent from the thermophilic first stages at system HRTs of 48, 36, and 24 hrs are illustrated in Figures 45 through 47, and are recorded in Appendix C.

Figure 45 illustrates the total volatile acid concentrations in the effluent from the thermophilic first stages of the three TPAB systems at the 48- hr system HRT. Total volatile acids increased in both TPAB 1 and TPAB 2 above the 7 g COD/L/day system loading. For TPAB 1, total volatile acids increased from 1129 mg/L at the 7 g COD/L/day system loading to 2152 mg/L at the 8 g COD/L/day system loading. This increase in total volatile acids may have caused the SCOD removal rates to decline in TPAB 1, as shown in Figure 15. TPAB 2 also showed increased total volatile acids at the higher system loadings. The results of the increase in total volatile acids are reflected in Figure 17, with a slight decrease in SCOD removal performance at the higher system loadings. TPAB 3 was observed to display low concentrations of total volatile acids from the thermophilic first stage. The effective COD loads for the 24- hr HRT thermophilic unit ranged from 2 to 20 g/L/day. The longer HRT of 24 hr resulted in a more complete conversion and removal of volatile acids as compared to TPAB 1 or TPAB 2.

Figure 46 illustrates the total volatile acids in the effluent from the thermophilic first stages of the three TPAB systems at the 36- hr system HRT. The thermophilic first stage of TPAB 1 was the only unit that was observed to produce higher levels of total volatile acids with increased loadings. The thermophilic stage of TPAB 1 was observed to produce total volatile acids in excess of 2000 mg/L at the 9 g COD/L/day system loading. Although the total volatile acids increased, SCOD removals remained near 60%, as illustrated in Figure 24. This is another example of the somewhat misleading nature of COD removal values. The volatile acids increased, but COD applied loads also increased, leading to a stable COD removal percentages.

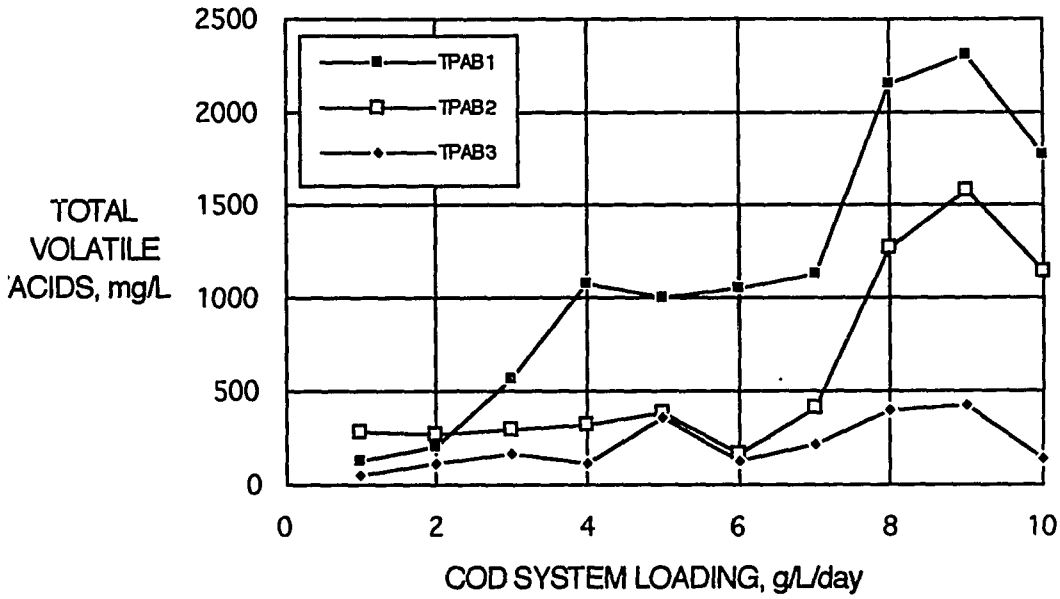


Figure 45. Total first-stage volatile acids at various COD loads for the three TPAB systems for the 48 hr HRT

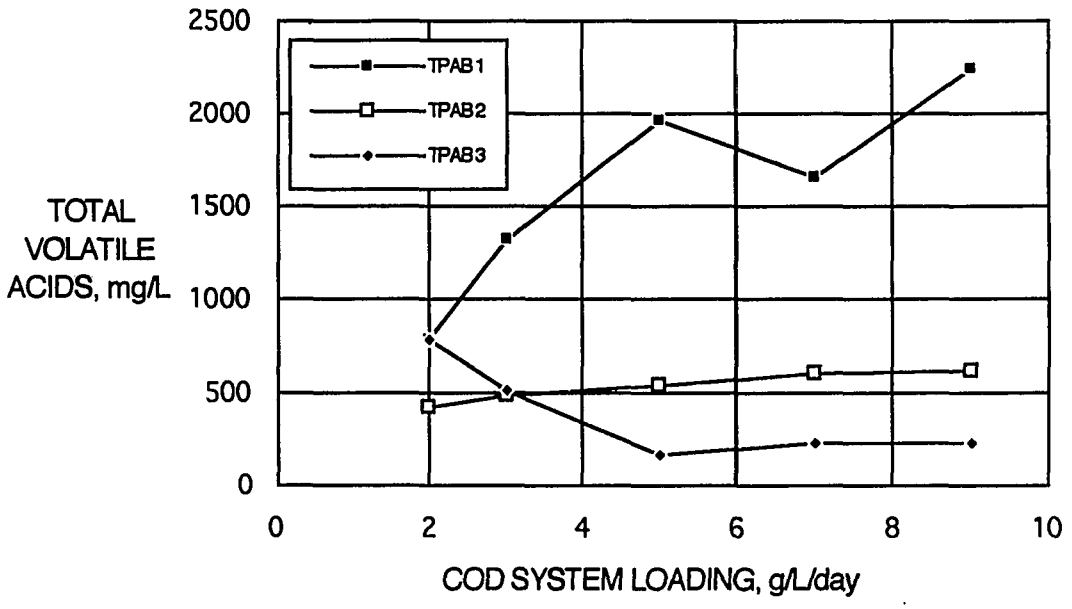


Figure 46. Total first-stage volatile acids at various COD loads for the three TPAB systems for the 36 hr HRT

The thermophilic first stage of TPAB 2 was observed to produce low levels of total volatile acids in the effluent. This was perhaps caused in part by the higher first stage HRT of 9 hr. At the higher HRTs, the organic matter contained in the influent feed may have been held sufficiently long as to provide for more complete breakdown of the volatile acids. The 18- hr HRT thermophilic unit showed a decrease in volatile acids at applied loadings ranging from 2 to 5 g COD/L/day. This was observed since the systems were taken from a 24- hr system HRT with high volatile acids in the effluent to a 36- hr HRT. In retrospect, sufficient time was not allowed to "flush out" the high levels of volatile acids produced at the 24- hr HRT.

Figure 47 illustrates the total volatile acid concentrations in the effluent from the thermophilic first stages of the three TPAB systems at the 24- hr system HRT. Total volatile acid concentrations for the thermophilic stage of TPAB 1 increased from 1422 mg/L at the 11 g COD/L/day system loading to 2679 mg/L at the 16 g COD/L/day system loadings. Although the volatile acids were high at the higher loadings, the SCOD removals for the first stage remained approximately near 50%, as shown in Figure 33. The SCOD removals for TPAB 1 remained constant even as volatile acids increased. Lower SCOD removals for the thermophilic stage of TPAB 1 were not caused by increased volatile acid levels, but by a very short HRT of 3 hrs, coupled with a high effective COD loading rate of 80 to 128 g/L/day.

The total volatile acid concentrations (as acetic) exceeded 2000 mg/L during situations of low HRTs and higher loading rates for the thermophilic units. These high levels of volatile acids were anticipated. It is generally believed that relatively high concentrations of volatile

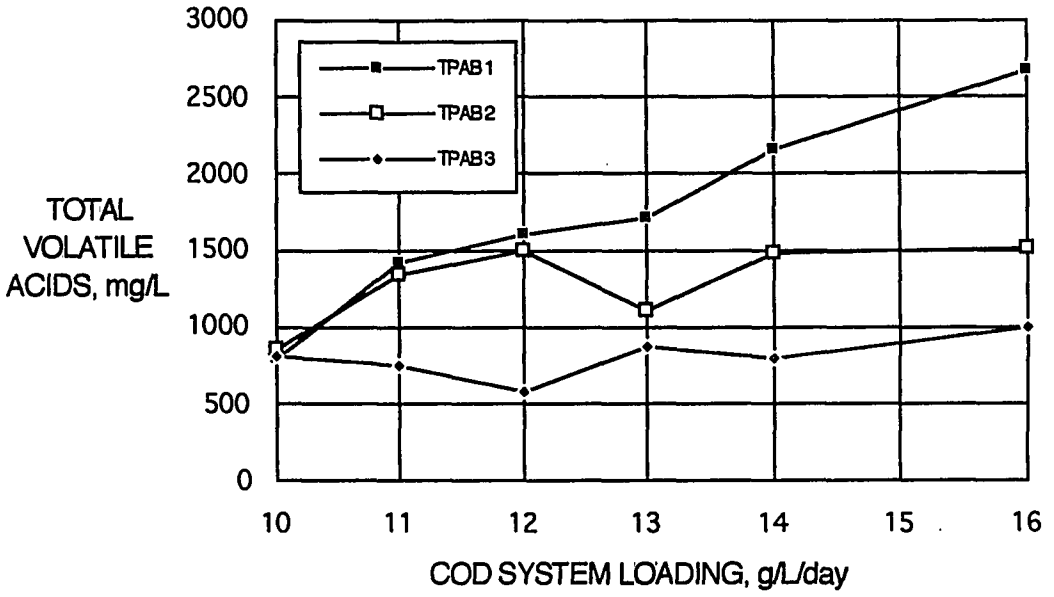


Figure 47. Total first-stage volatile acids at various COD loads for the three TPAB systems for the 24 hr HRT

acids can be tolerated by anaerobic systems provided that sufficient buffering material is present (McCarty and McKinney, 1961).

When total volatile acids increased, the thermophilic units were buffered with sodium bicarbonate to maintain a pH of 6.5 or greater. A concern with supplemental buffering is the potential for salt cation toxicity. The amount of sodium added with the sodium bicarbonate never exceeded approximately 900 mg/L.

In Figure 45, it was observed that at the 48-hr system HRT, the total volatile acids increased sharply at the 8 g/L/day system load for the 6 and 12- hr HRT units. In Figure 47 at the 24- hr system HRT, there was no significant increase in total volatile acids for the 6 and 12-hr HRT units. The highest applied effective COD load on the 6 and12- hr HRT units at the 24-hr system HRT were 64 and 32 g/L/day, respectively. The effective COD loads for the 6 and 12-hr HRT units at the 48- hr system HRT were 64 and 32 g/L/day at the 8 g/L/day system load. The 24- hr system HRT data was collected after the 48- hr system HRT data. It is believed that a more stable population of methanogens developed over time in the thermophilic units. Thus at the 24- hr HRT, the 6- hr and 12- hr HRT units were able to handle equivalent COD loads without a significant increase in volatile acids.

The total volatile acids in the final effluent from the mesophilic second stages of the TPAB systems were generally quite low, as outlined in Appendix C. Total volatile acid concentrations in the mesophilic effluents ranged from 6 to 141 mg/L (as acetic).

The total volatile acids and individual volatile acids for the thermophilic first stages of the three TPAB systems are shown in Figures 48 through 56.

Thermophilic first-stage HRTs for the three TPAB systems ranged from 3 to 24 hrs. In comparing the individual volatile acids for the different applied HRTs, it was observed that longer HRTs of 12, 18, and 24 hrs for the first stages resulted in a larger percentage of propionic acid in the thermophilic effluents, as shown in Figures 48, 49, 51, and 53. Propionic acid is usually the acid reported in the literature which predominates at thermophilic temperatures. At relatively long first stage HRTs, a population shift may occur in which the microorganisms responsible for the breakdown of propionate decline in numbers.

It was observed that at shorter HRTs of 3 and 6 hrs, that the levels of butyric and valeric acids increased, as illustrated in Figure 50. It was also observed that the levels of butyric and valeric acids did not increase proportionately until very high effective loadings were applied to the thermophilic first stages. In Figure 50, the effective COD loadings on the 6- hr HRT thermophilic reactor ranged from 58 to 80 g/L/day. In Figure 56, the 3- hr HRT thermophilic unit showed increases in butyric acid at effective COD loadings ranging from 80 to 128 g/L/day.

Ammonia

Ammonia concentrations were monitored during the experiment, since it is known that total ammonia concentrations higher than approximately 1500 mg/L (as NH_3-N) are potentially

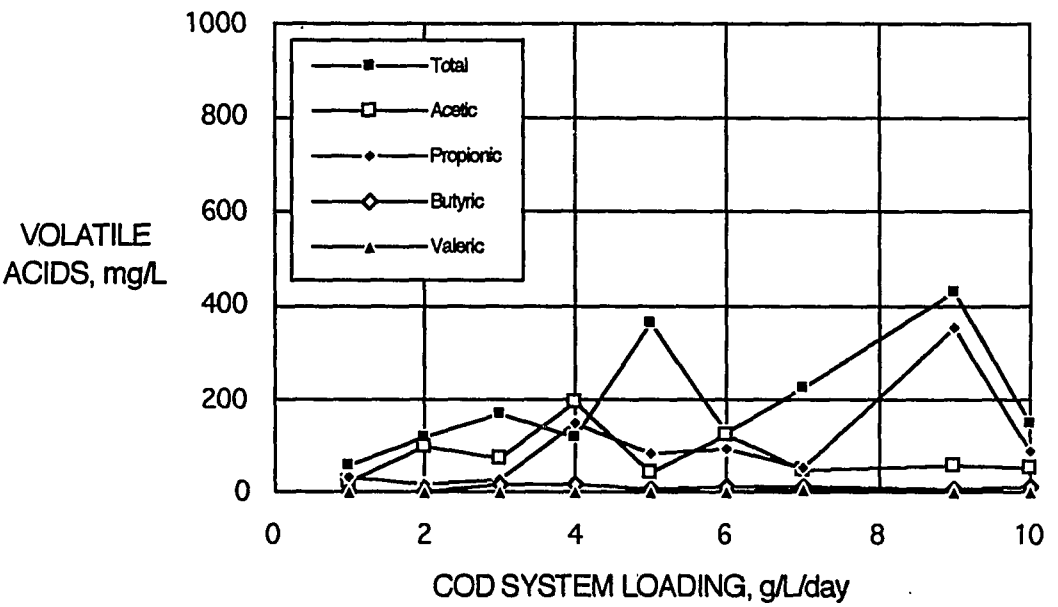


Figure 48. Thermophilic first-stage volatile acids at a 24 hr HRT
(System HRT 48 hrs)

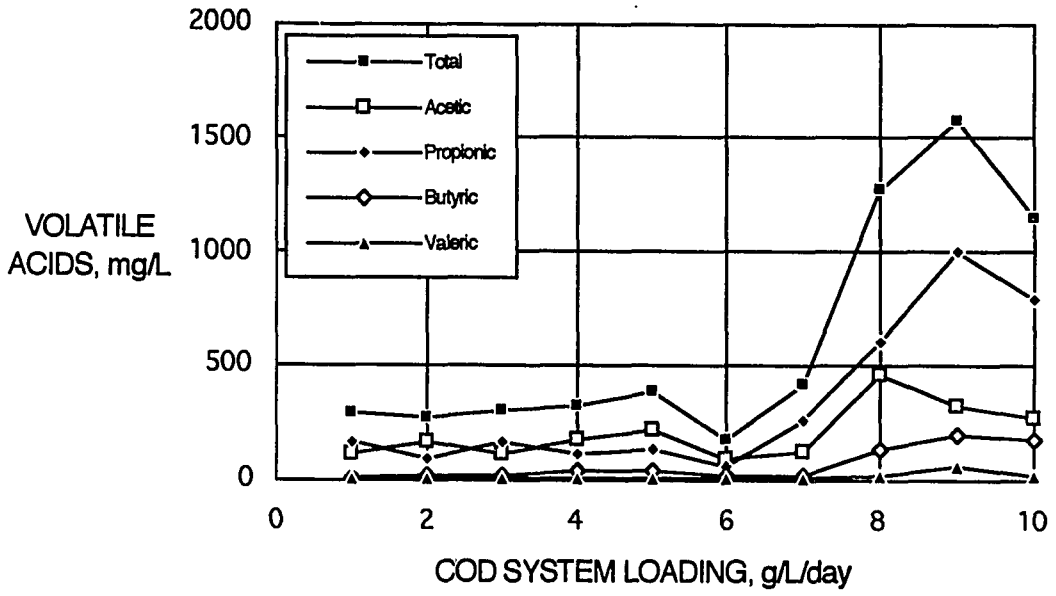


Figure 49. Thermophilic first-stage volatile acids at a 12 hr HRT
(System HRT 48 hrs)

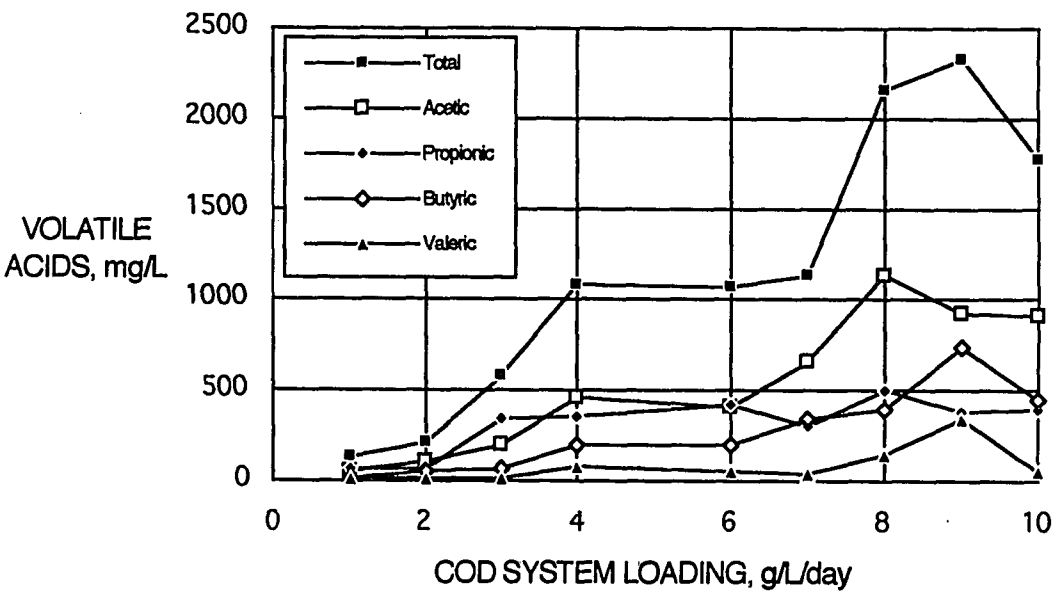


Figure 50. Thermophilic first-stage volatile acids at a 6 hr HRT
(System HRT 48 hrs)

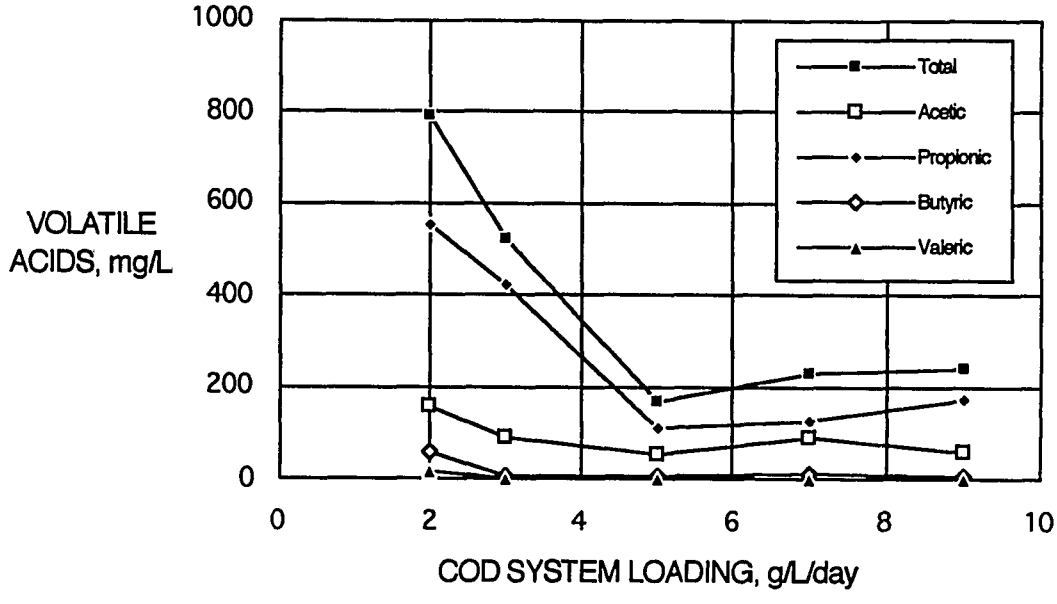


Figure 51. Thermophilic first-stage volatile acids at a 18 hr HRT
(System HRT 36 hrs)

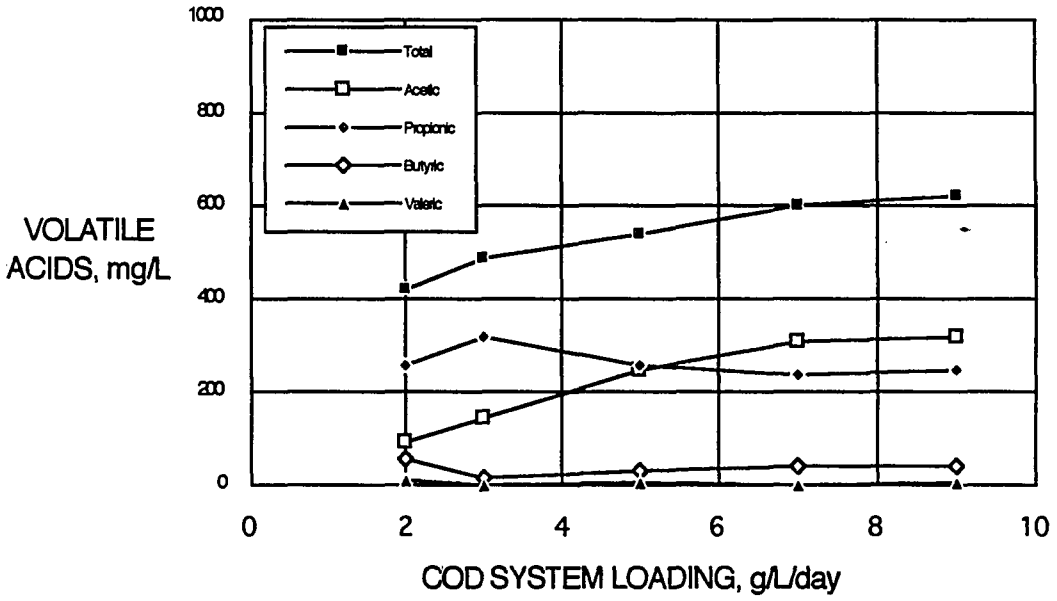


Figure 52. Thermophilic first-stage volatile acids at a 9 hr HRT
(System HRT 36 hrs)

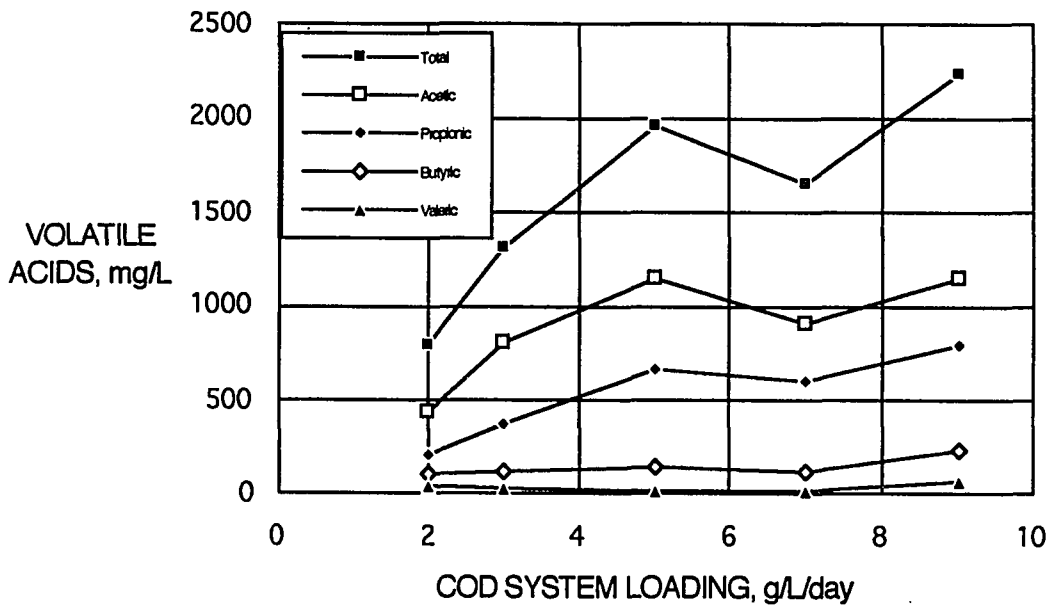


Figure 53. Thermophilic first-stage volatile acids at a 4.5 hr HRT
(System HRT 36 hrs)

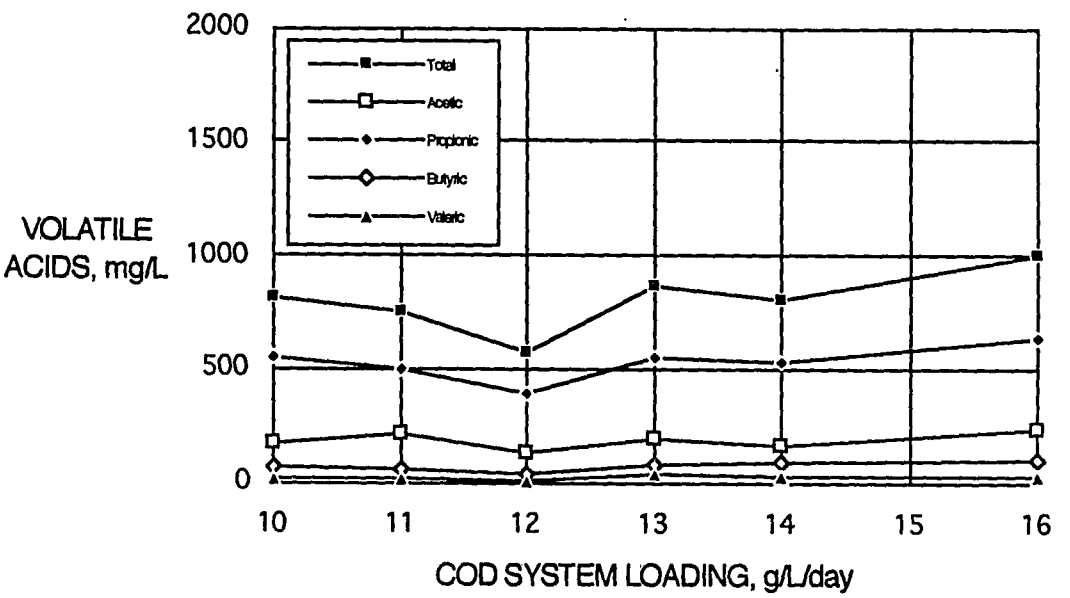


Figure 54. Thermophilic first-stage volatile acids at a 12 hr HRT
(System HRT 24 hrs)

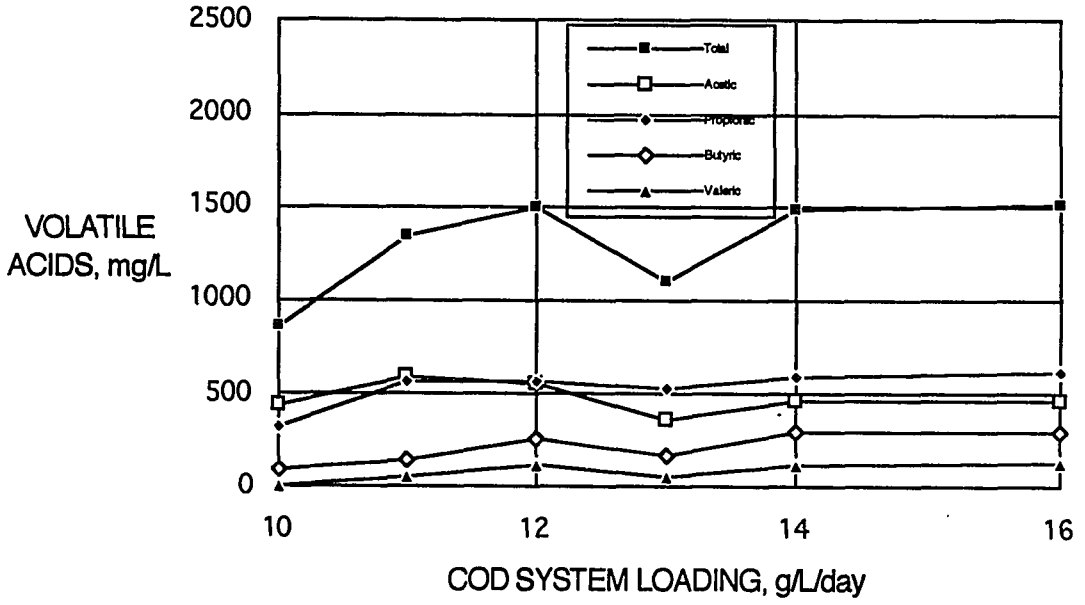


Figure 55. Thermophilic first-stage volatile acids at a 6 hr HRT
(System HRT 24 hrs)

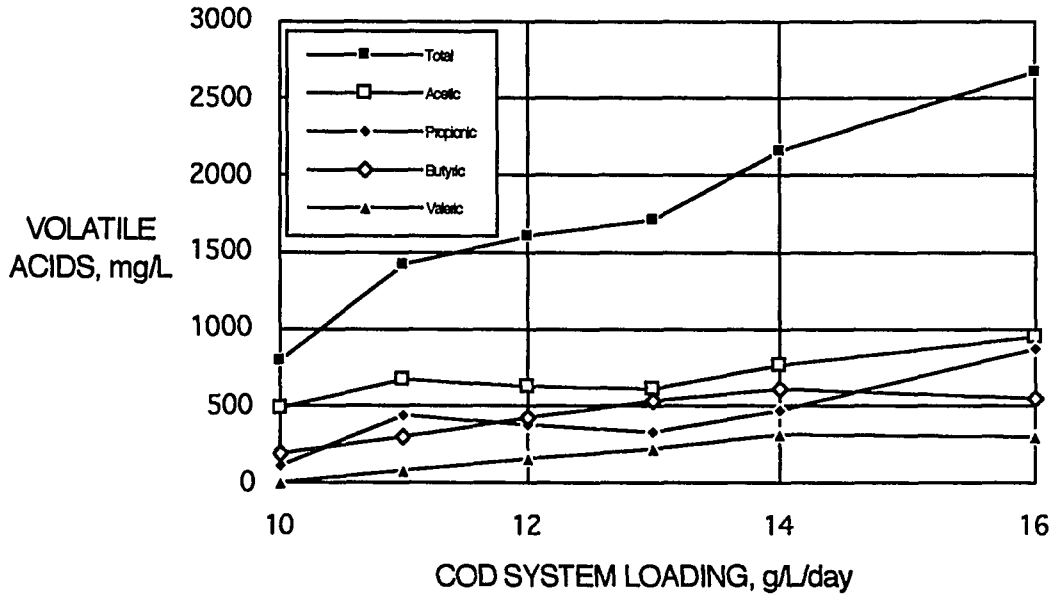


Figure 56. Thermophilic first-stage volatile acids at a 3 hr HRT
(System HRT 24 hrs)

toxic in anaerobic treatment systems. There were concerns that the high effective loadings on the thermophilic first stages of the TPAB systems would result in inhibitory ammonia concentrations.

The total ammonia concentrations for both the thermophilic and mesophilic stages for the three TPAB systems at system HRTs of 48, 36, and 24- hrs are illustrated in Figures 57 through 62. Total ammonia concentrations at the 48- hr system HRT for the thermophilic and mesophilic stages are shown in Figures 57 and 58. Total ammonia concentrations for the thermophilic units increased with increasing loading rates, and never exceeded 1058 mg/L at the highest COD system loading of 10 g/L/day. The 6- hr HRT thermophilic unit was observed to produce lower total ammonia concentrations in the effluent than the 12 or 24- hr HRT thermophilic units above the 6 g COD/L/day system loading. The lower ammonia production in the 6 hr HRT unit corresponded to decreased TCOD and SCOD removal rates for this reactor, as shown in Figures 14 and 15. At the lower HRT of 6 hr, there was a threshold in the amount of protein which could be converted to ammonia. The microorganisms may have been hindered by a lack of sufficient population and sufficient time necessary for organic matter destruction to occur.

The mesophilic ammonia concentrations for the 48- hr HRT are shown in Figure 58. Ammonia was not removed in the mesophilic second stage, but was observed to be removed from the reactor with the mesophilic effluent. Total ammonia concentrations for the mesophilic second stage never exceeded 1198 mg/L.

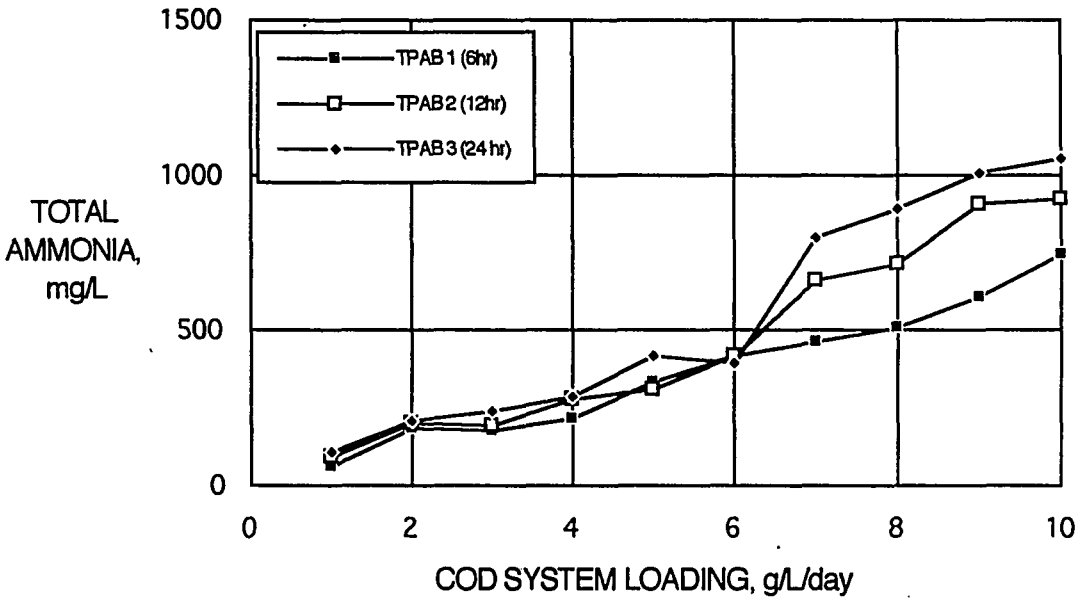


Figure 57. Total ammonia for the thermophilic first-stage effluents at the 48 hr system HRT

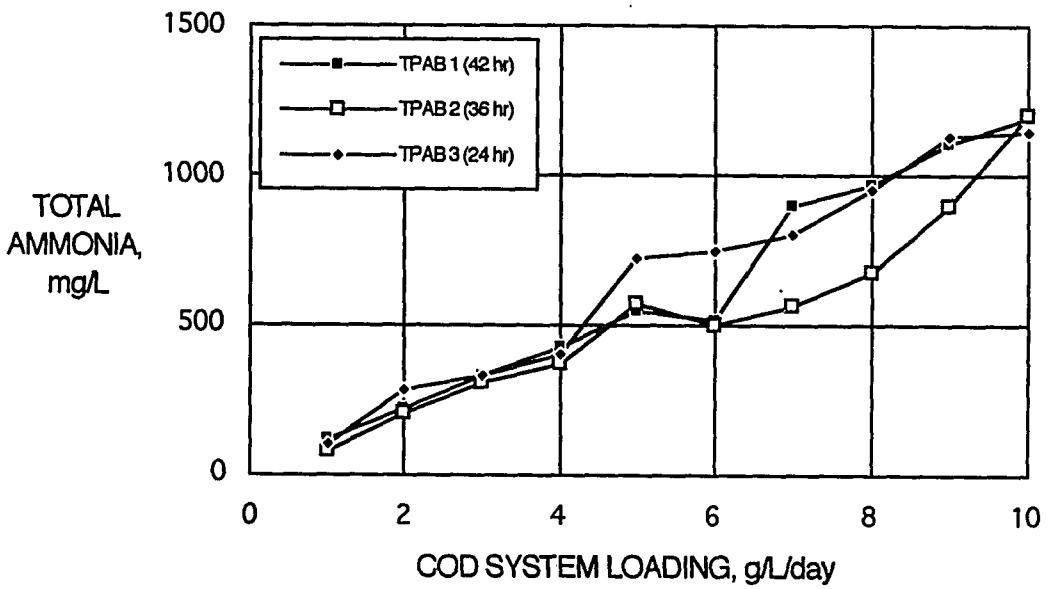


Figure 58. Total ammonia for the mesophilic second-stage effluents at the 48 hr system HRT

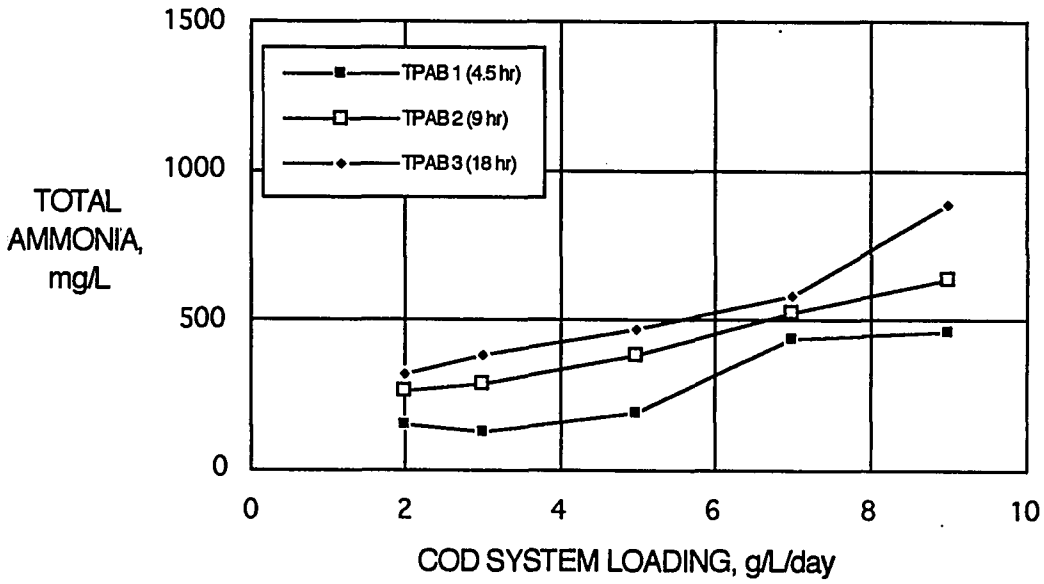


Figure 59. Total ammonia for the thermophilic first-stage effluents at the 36 hr system HRT

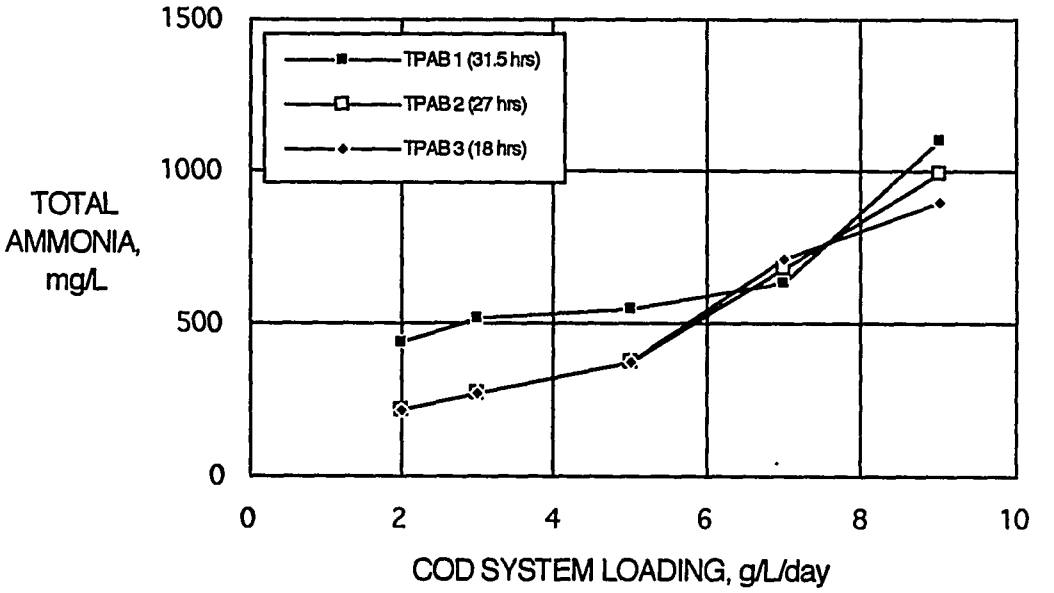


Figure 60. Total ammonia for the mesophilic second-stage effluents at the 36 hr system HRT

Total ammonia concentrations for the 36- hr system HRT for the thermophilic and mesophilic stages for the three TPAB systems are illustrated in Figures 59 and 60. Thermophilic ammonia concentrations never exceeded 888 mg/l, and mesophilic ammonia concentrations remained below 1100 mg/l. For TPAB 1 (1:7 volume ratio), it was observed that lower concentrations of ammonia were produced in the first stage, and higher concentrations were produced in the second stage, as compared to TPAB 2 and TPAB 3. TPAB 1 was operated at a 4.5- hr HRT in the thermophilic stage. This short HRT may have not provided sufficient time for protein breakdown.

The total ammonia concentrations at the 24- hr system HRT for the thermophilic and mesophilic stages for the three TPAB systems are illustrated in Figures 61 and 62. It was anticipated that the high COD system loadings and the high effective loadings on the thermophilic stages would result in increased ammonia concentrations. For TPAB 1 and TPAB 2, the effective COD loadings on the first stages were 80 to 128 g/L/day and 40 to 64 g/L/day, respectively.

The ammonia concentrations for the thermophilic first stages are shown in Figure 61. TPAB 1 and TPAB 2 were observed to have decreased ammonia levels at COD system loads higher than 13 g/L/day. This was thought to be caused by the short HRTs of 3 and 6 hrs in the thermophilic stages of TPAB 1 and TPAB 2. The HRTs were too short to allow for complete protein degradation to ammonia in the first stages.

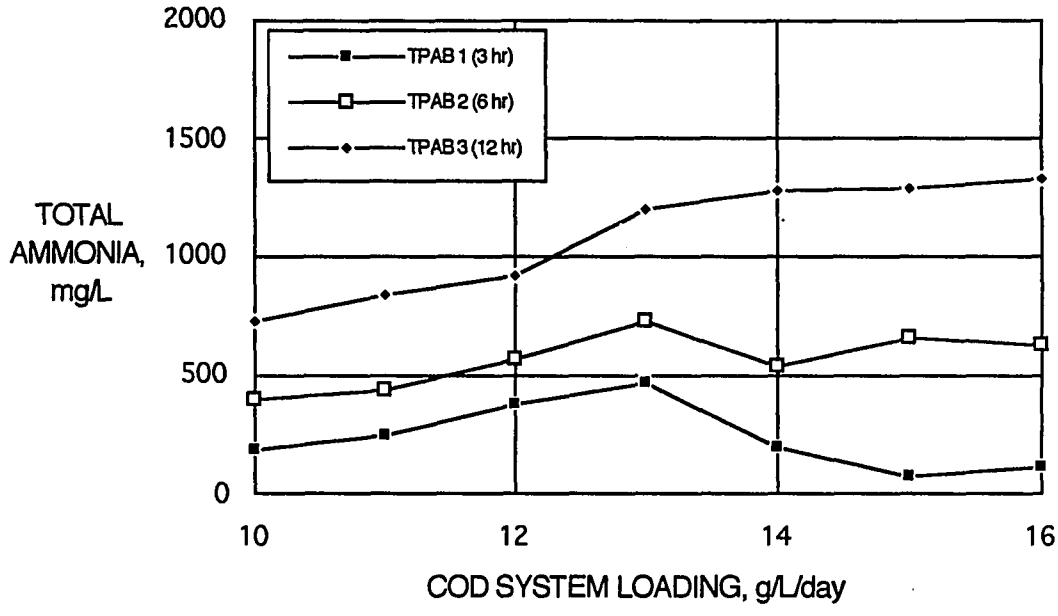


Figure 61. Total ammonia for the thermophilic first-stage effluents at the 24 hr system HRT

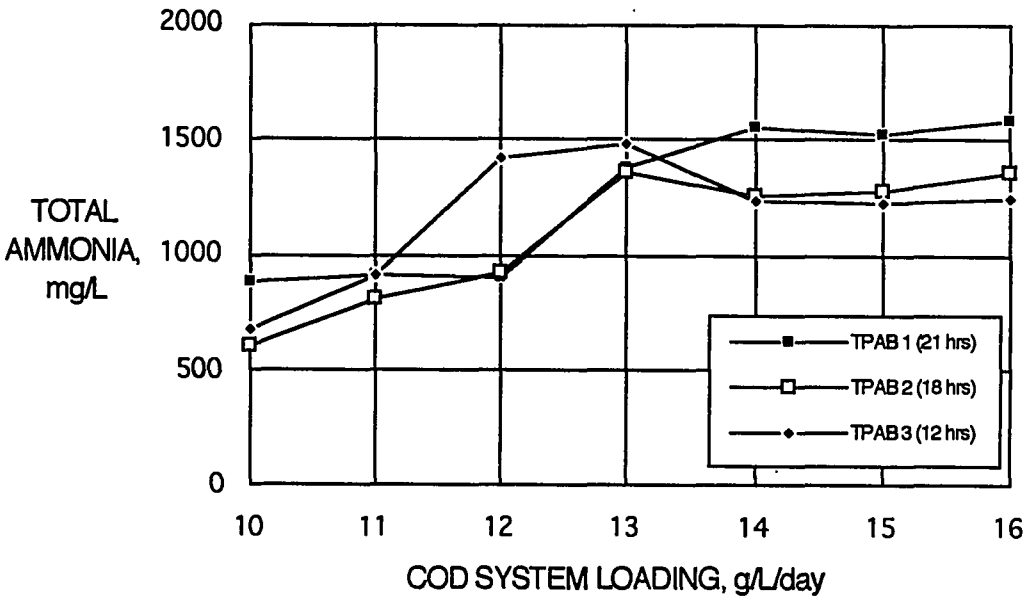


Figure 62. Total ammonia for the mesophilic second-stage effluents at the 24 hr system HRT

The ammonia concentrations for the mesophilic stages at the 24 hr system HRT are shown in Figure 62. Total ammonia concentrations remained below 1591 mg/L at the applied COD loadings, and TCOD and SCOD removals were not adversely affected for any of the three TPAB systems.

Although it was anticipated that there would be potentially inhibitory concentrations of ammonia, ammonia levels never exceeded 1591 mg/L (as NH_3-N), and ammonia levels did not affect TPAB system performance in terms of TCOD or SCOD removals.

In past research (Harris, 1992; Harris and Dague, 1993), thermophilic units capable of high COD loadings eventually produced toxic concentrations of ammonia which affected system performance. With the TPAB system, especially in the 1:7 volume ratio configuration, the thermophilic stage can withstand high applied COD loadings without the development of toxic ammonia concentrations. As higher loadings are applied at low HRTs, the first stage only degrades a portion of the organic protein in the waste to ammonia.

Methane Production

The methane production rates standardized in terms of liters of methane per liter of reactor volume per day for the thermophilic plus mesophilic stages of the three TPAB systems are illustrated in Figures 63 through 65.

Figure 63 illustrates the total methane production for the three TPAB systems at the 48-hr system HRT at COD system loadings of 1 to 9 g/L/day. There was virtually no difference in

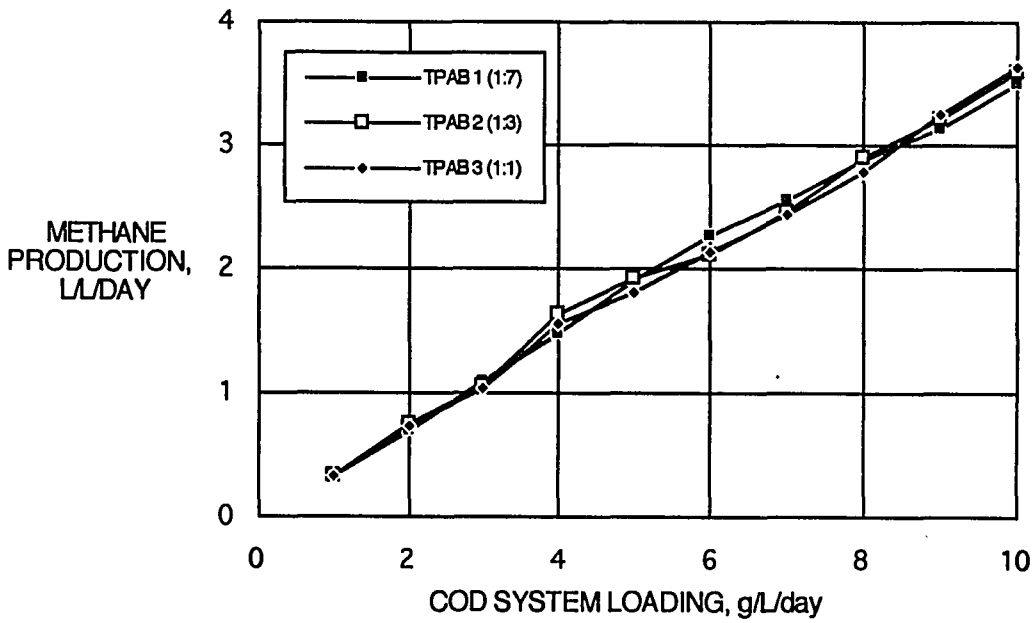


Figure 63. Methane production rates at various COD applied loads for the three TPAB systems at the 48 hr HRT

total system methane production for the three TPAB systems, which corresponded to the similarity in TCOD and SCOD removals for the TPAB systems. This means that any of the volume ratio TPAB systems can operate effectively with equal methane production at the 48-hr system HRT, for the given applied loadings.

Similar results, in terms of equivalent methane production between the three TPAB systems, were observed at the 36- hr and the 24- hr HRT at system COD loadings of 2 to 16 g/L/day, as shown in Figures 64 and 65. The measured methane production for the TPAB systems agreed with the similar TCOD and SCOD removals shown previously.

The methane production for the thermophilic and mesophilic stages for the three TPAB systems at the 48- hr system HRT are illustrated in Figure 66. In TPAB 1, the 6- hr HRT thermophilic unit was connected in series to a 42- hr HRT mesophilic unit. It was observed that at system COD loadings in excess of 7 g/L/day that methane production declined in the thermophilic unit and increased in the corresponding mesophilic unit. These results correlate well with the observed decrease in both TCOD and SCOD removals for TPAB 1 at the 48- hr HRT as shown in Figures 14 and 15. Saturation loading had occurred for the 6- hr HRT thermophilic unit, meaning that with increased applied loadings, there was no increase in COD removal or methane production. The saturation loading occured at effective loadings on the thermophilic first stage in excess of 48 g COD/L/day. Since ammonia levels were not elevated for this unit, as shown in Figure 57, ammonia toxicity was not involved. Total volatile acids became elevated at the 7 g COD/L/day system loading as shown in Figure 45. It is believed that at the high effective loading and low HRT of 6 hr, that the organic matter removal capabilities

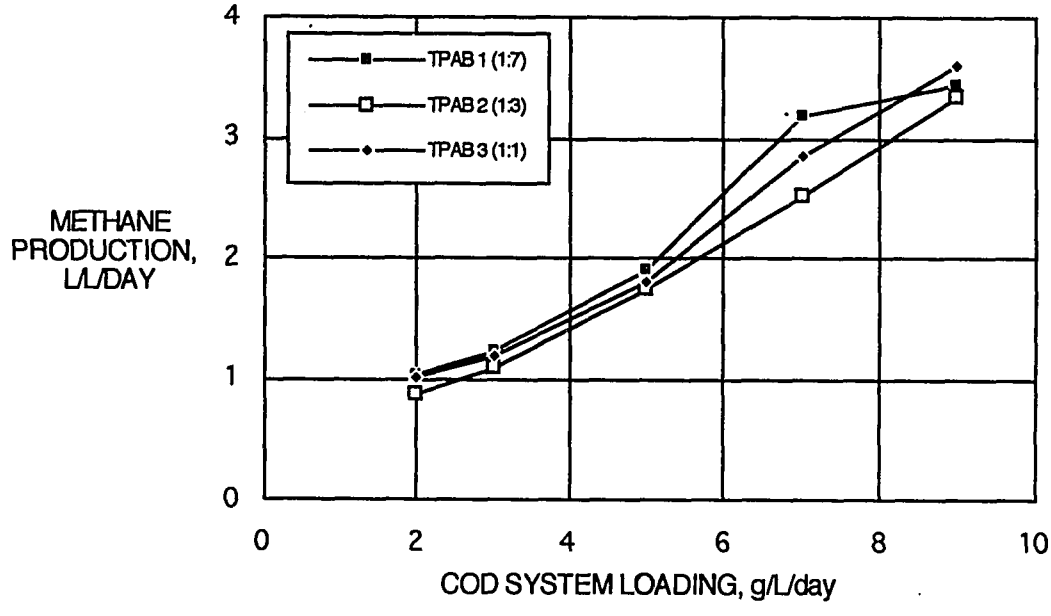


Figure 64. Methane production rates at various COD applied loads for the three TPAB systems at the 36 hr HRT

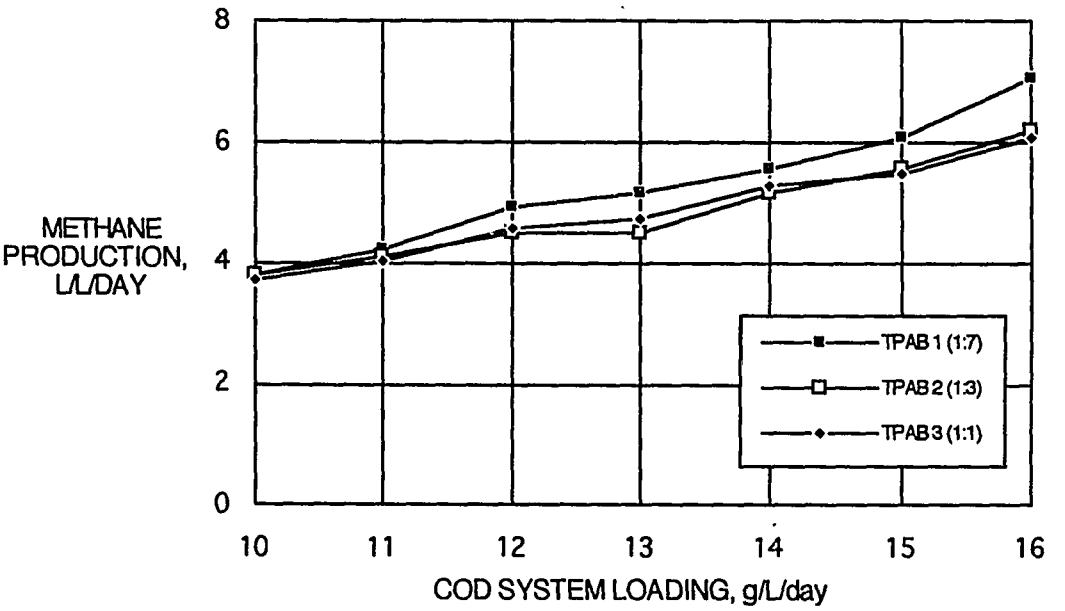


Figure 65. Methane production rates at various COD applied loads for the three TPAB systems at the 24 hr HRT

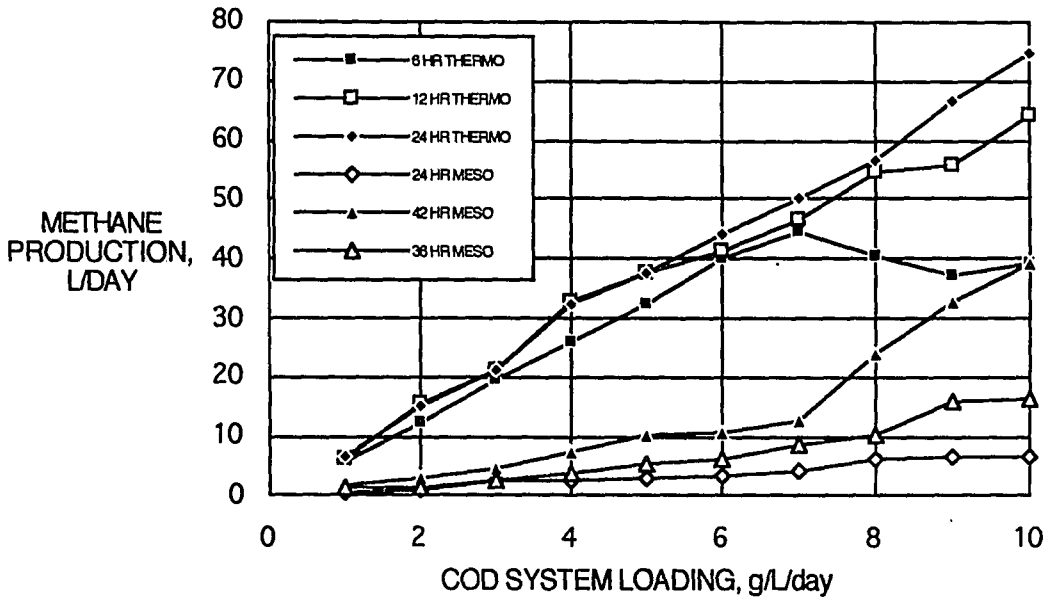


Figure 66. Methane production at various COD applied loads at the 48 hr HRT

for the methanogens in the thermophilic unit had reached their maximum at the 56 g COD/L/day loading. As a result, volatile acids correspondingly increased.

The relative underloading for the mesophilic second stages at the 48- hr system HRT for TPAB 2 and TPAB 3 are also illustrated in Figure 66. The thermophilic units were observed to remove and convert a majority of the organic matter to methane at the applied COD loadings, while methane production for the mesophilic units remained relatively constant over the range of applied loads.

The relative underloading for the mesophilic second stages at the 48- hr system HRT for TPAB 2 and TPAB 3 are also illustrated in Figure 66. The thermophilic units were observed to remove and convert a majority of the organic matter to methane at the applied COD loadings, while methane production for the mesophilic units remained relatively constant over the range of applied loads.

The methane production for the thermophilic and mesophilic stages for the three TPAB systems at the 36 -hr system HRT are illustrated in Figure 67. The relative underloading of the mesophilic unit for TPAB 3 was observed as an steady increase in methane production with increasing loadings for the 18 hr- HRT thermophilic unit, and a relatively constant methane production for the corresponding 18- hr HRT mesophilic unit with increasing loadings. It was observed for TPAB 1 that during the course of the experiment a population shift of microorganisms had occurred, in that the majority of the methane was produced in the 31.5 hr

HRT mesophilic second stage rather than the 4.5- hr HRT thermophilic stage. Previously in the experiment, the 4.5-hr HRT unit was exposed to very high effective loading rates, which may have caused a selection for fewer methanogens and more acidogenic microorganisms. Although the population shift was observed based on methane production for the individual stages for TPAB 1, the overall methane production for the two-stage system parallelled the other two TPAB systems.

The methane production for the thermophilic and mesophilic stages for the three TPAB systems at the 24- hr system HRT are illustrated in Figure 68. Results similar to the 36- hr HRT were observed in terms of methane production. TPAB 1 produced the majority of the total system methane in the mesophilic second stage, and TPAB 3 produced the majority of the total system methane in the thermophilic stage.

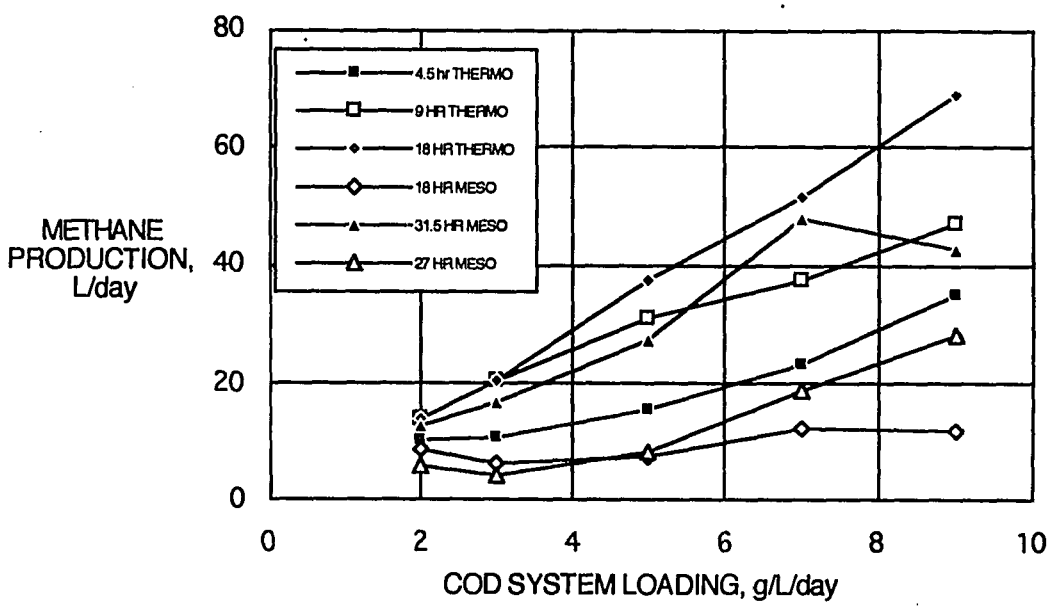


Figure 67. Methane production at various COD applied loads at the 36 hr HRT

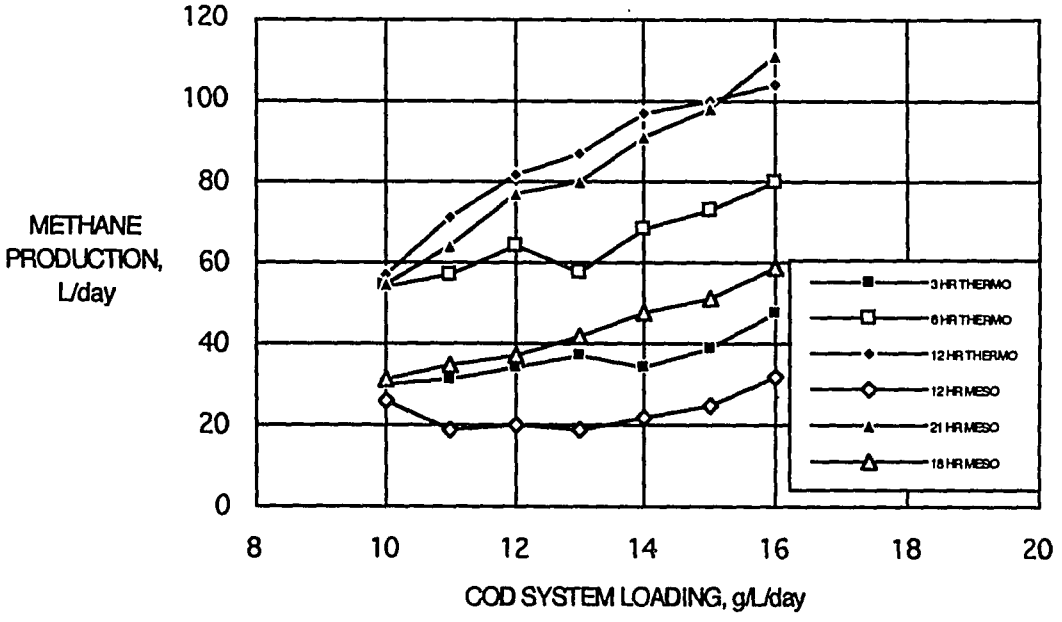


Figure 68. Methane production at various. COD applied loads at the 24 hr HRT

VII. SIGNIFICANCE OF RESULTS

The two-phase TPAB system has been demonstrated to be an effective new anaerobic treatment process. The three TPAB systems displayed excellent treatment performance in terms of COD removals at the 24, 36, and 48 hr system HRTs. Applied loads ranged from 1 to 16 g COD/L/day. Total system COD removals were in excess of 91% at all applied loadings. The overall average TCOD removal was 95.5% for the three TPAB systems at HRTs of 24, 36, and 48 hrs. Soluble system COD removals were in excess of 96% at all applied loadings. The overall average SCOD removal was 98.7% for the three TPAB systems at HRTs of 24, 36, and 48 hrs.

A major factor which allowed the TPAB systems to achieve superior organic matter removals was the unique two-stage, two-temperature operation. The thermophilic first stage is able to provide very high reaction rates to remove and convert a significant portion of the organic material in the waste stream to methane. During periods of extreme overloading on the thermophilic units, the first stage also provided for a significant conversion of organic matter to volatile acids. These volatile acids provide a simple substrate for the mesophilic second stage.

The performance of the thermophilic first stage is dependant on both the HRT and organic loading. At longer HRTs and lower effective loadings, a greater portion of the organic matter is stabilized to methane. At effective loading rates greater than 40 g COD/L/day, greater amounts of volatile acids are produced. Very short HRTs ranging from 3 to 6 hrs in the thermophilic first stage act in a positive manner to dilute the volatile acids.

The mesophilic second stages in the TPAB systems provided for significant "polishing" of the thermophilic effluent. Any residual biodegradable organic matter , along with volatile acids produced in the first stage, were successfully removed in the second stage.

The three TPAB systems were observed to provide very stable treatment. The thermophilic first stages responded quickly to increases in applied COD load. In the past, anaerobic treatment at thermophilic temperatures has been cited as less stable than treatment at mesophilic temperatures. This was not observed for the thermophilic units in this research. The mesophilic second stage responded well to overloaded first- stage conditions. Overall treatment performance was not adversely affected, even when the first stage was operated at extremely high loading rates (up to 128 g COD/L/day). The two stage configuration also has significant stability advantages over comparable single stage systems. The organic loading of industrial wastes can vary significantly over time. The two stage TPAB system provides a built-in safety factor. Transient periods of high organic loads would be tolerated without significantly affecting TPAB system performance.

The thermophilic first- stages were operated at extremely short HRTs of 3, 4.5, and 6 hrs during the experiment. Effective COD loadings up to 128 g COD/L/day were applied. Maximum SCOD removal rates ranged from 50 g SCOD/L/day at the 6 hr HRT, to 60 g SCOD/L/day at the 3 hr HRT. These SCOD removal rates translate to very high 5-day biochemical oxygen demand (BOD_5) removal rates ranging from 1558 to 1872 lb BOD_5/1000 ft^3/day. Table 23 illustrates typical design loadings and HRTs for various aerobic biological treatment processes. As can be seen, the actual BOD_5 removal rates for the thermophilic stages

in the TPAB systems greatly exceed typical design loadings (not removal rates) for any aerobic treatment process. This was accomplished at significantly shorter HRTs in the TPAB systems. The thermophilic first stages of the TPAB systems had an extremely high rate of organic matter removal. Reaction rates generally double for every ten degrees (C) rise in temperature. At 55° C, reaction rates are approximately four times higher than at mesophilic temperatures.

Table 23. Typical design loadings and HRTs for various aerobic treatment processes (Metcalf and Eddy, 1991)

Process	**Typical Design Loading** (# BOD_5/1000 ft^3/day)[1] (# BOD_5/1000 ft^2/day)[2]	**HRT** days
Activated Sludge	20-200[1]	3-15
Aerated Lagoon	< 40[1]	3-6
Trickling Filters		
Low to High Rate	5-100[1]	.02-1.2 gal/ft^2/min
Roughing	100-500[1]	.08-3.2 gal/ft^2/min
Rotating Biological Contact	<12[2]	0.7 to 4

There was no significant difference in treatment performance in terms of total and soluble COD removals between the three TPAB systems. In a full-scale application of the TPAB process, the 1:7 volume ratio TPAB system may be used as effectively as the 1:1 or 1:3 volume ratio TPAB system. In Appendix F, it is shown that the conductive heat losses for the 1:7 volume ratio TPAB system are much less than for the 1:1 or 1:3 volume ratio TPAB systems. This is a significant finding. Since a smaller thermophilic first stage can be used, the overall heating costs will be less in a full-scale application. Also, there was no significant decline in treatment performance for the TPAB systems at a 24 hr HRT, up to the 16 g COD/L/day applied loading. HRTs of even less than 24 hrs may be possible.

In retrospect, greater differences in terms of both COD removals and methane production between the three TPAB systems may have been observed if the systems were redesigned to fully load the mesophilic second stages. In this experiment, the thermophilic phases were often loaded up to their maximum capacity and sometimes beyond. The mesophilic phases were sufficiently large so that saturation loading in the second stage did not occur. In order to achieve greater differences between the TPAB systems in future experiments, it would be wise to either make the thermophilic units larger, or the mesophilic units smaller.

Energy balance calculations are shown in Appendix F for a hypothetical industrial wastestream. A matrix of raw waste influent temperatures of 50 to 110° F (10 to 43° C) were assumed. 5-day biochemical oxygen demand (BOD_5) concentrations ranging from 3.75 to 7.5 g/L were chosen as concentrations which would generally occur for an industrial wastewater.

It was determined that there would be a positive energy balance in terms of excess methane production in all cases. Therefore, raw waste temperatures can be as low as 50° F (10° C) can be treated without addition of supplemental energy. This is a significant finding. Since the majority of industrial wastestreams are 50° F or above, the TPAB process can be applied to any biologically-treatable wastewater. The TPAB process will supply surplus energy via methane formation.

Also in Appendix F are economic calculations for the TPAB process in a full-scale application. An industry with a 95° F wastestream of 2 MGD, at an organic concentration of 3.75 g/L BOD_5 was analyzed. It was determined that for a 3-year payback period, approximately 3.3 million dollars could be initially invested as capital costs. This illustrates that the TPAB process is economically feasible.

Harris and Dague (1993) conducted studies on single-stage anaerobic filters operated at mesophilic and thermophilic temperatures that may be compared to the two-stage TPAB systems used in this study, since identical substrate and similar operating conditions were used. The comparison between the work on single -stage filters, and the two-stage TPAB process results obtained in this experiment are shown in Table 24. At all of the loadings tested, the two-stage TPAB system outperformed both thermophilic and mesophilic single- stage filters. These results clearly illustrate that the TPAB two-stage, two-temperature process has some definite performance advantages over single-stage anaerobic treatment.

Table 24. Comparison of single stage thermophilic and mesophilic filters to the TPAB process

48 hr HRT Results			
TCOD Load g/L/day	Thermo. Single Stage TCOD % Removals	Meso. Single Stage	TPAB
5	87.8	90.3	97.9
8	82.7	83.9	95.5
11	84.5	81	95.8*

24 hr HRT Results			
TCOD Load g/L/day	Thermo. Single Stage TCOD % Removals	Meso. Single Stage	TPAB
11	83.4	67.9	93.6
13	83.1	59.8	92.7
16	81.3	47.5	94.7

* TPAB operated at a 10 g/L/day loading.

A U.S. patent application has been filed through the Iowa State Univerisity Development Office for two-temperature; two-stage treament. This TPAB process experiment provided significant results which demonstrated the treatment advantages of the two- stage process. These results were presented in the patent application.

VIII. CONCLUSIONS

The results from this research support the following conclusions concerning the temperature-phased anaerobic biofilter (TPAB) process:

1. The TPAB process has been demonstrated to be effective in terms of organic matter removal for a soluble, complex waste stream at HRTs of 24, 36, and 48 hrs, at system COD loading rates ranging from 1 to 16 g/L/day.

2. Nearly equal treatment performance was observed using three different reactor size ratios. It feasible to use a proportionately smaller thermophilic first-stage in the TPAB system while obtaining equal treatment performance.

3. At an HRT of 6 hrs in the thermophilic first-stage, it was observed that high levels of volatile acids decreased first-stage performance. At shorter HRTs, performance was not observed to decline at the 3 and 4.5 hr HRTs. This was thought to be caused by a dilution effect in volatile acids at the shorter HRTs.

4. Overloaded conditions and short HRTs in the thermophilic first-stages result in increased levels of butyric and valeric acids at the 3, 4.5, and 6 hr HRT. At longer HRTs of 12, 18 ,

and 24 hrs, propionic acids increased at high effective COD loadings in the thermophilic first-stages. It is believed that there were thermophilic microbial population differences at the longer and shorter HRTs.

5. The TPAB process producted a good quality final effluent. Volatile acids were low in the mesophilic effluent at all times during the experiment. Volatile acids never exceeded 150 mg/L from the mesophilic final effluent.

6. The TPAB process is an energy producer, not an energy consumer. A positive energy balance in terms of no addition of supplemental energy to heat the raw influent wastes is possible at influent temperatures of 50° F (10° C) and above.

7. The TPAB process is economically feasible. Sigificant capital costs can be invested with a short payback period. The TPAB process recovers capital costs through excess methane production and the reduction in sewer-use fees.

8. The TPAB process can achieve higher organic matter removals than is generally possible for single-stage anaerobic filter systems operated at equivalent HRTs and COD loadings.

9. The thermophilic first-stage SCOD removal rates are extremely high, and greatly exceed design loadings for any aerobic biological waste treatment process.

IX. SUGGESTIONS FOR FURTHER RESEARCH

1. Further characterize the TPAB process by application of other reactor configurations, such as a thermophilic hybrid biofilter first-stage, and a mesophilic anaerobic sequencing batch reactor second-stage.

2. Determine methanogenic populations shifts which occur in the thermophilic first-stage as HRTs are decreased and organic loadings are increased.

3. Operate the thermophilic first-stage at HRTs of less than 3 hrs to determine the minimum HRT which can be applied without adversely affecting overall two-stage TPAB performance.

4. Perform further research on the TPAB process at system HRTs of less than 24 hrs, and at higher system loading rates.

5. Operate the TPAB systems in a redesigned configuration, where the mesophilic units are smaller in order to fully load the second stage.

6. Apply the TPAB process to actual industrial waste streams.

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APPENDIX A. METHANE PRODUCTION DATA

DATE	EXP.DAY	METHANE PRODUCTION (L/DAY) RX. 1	RX. 2	RX. 3	RX. 4	RX. 5	RX. 6
04-06-92	1	0.00	0.55	2.74	-	-	-
04-07-92	2	0.00	0.33	1.55	-	-	-
04-08-92	3	0.00	0.22	1.13	-	-	-
04-09-92	4	0.00	0.76	1.61	-	-	-
04-10-92	5	0.00	0.69	1.08	-	-	-
04-11-92	6	0.00	0.00	1.66	-	-	-
04-12-92	7	0.52	0.00	1.31	-	-	-
04-13-92	8	0.63	0.00	1.46	-	-	-
04-14-92	9	0.44	0.29	1.11	-	-	-
04-15-92	10	0.18	0.19	0.80	-	-	-
04-16-92	11	0.08	0.15	0.42	-	-	-
04-17-92	12	0.20	0.23	0.60	-	-	-
04-18-92	13	0.22	0.42	0.66	-	-	-
04-19-92	14	0.30	0.40	0.45	-	-	-
04-20-92	15	0.44	0.36	0.54	-	-	-
04-21-92	16	0.35	0.22	0.41	-	-	-
04-22-92	17	0.35	0.24	0.68	3.64	7.69	6.11
04-23-92	18	0.85	0.31	0.62	3.77	7.50	5.99
04-24-92	19	0.66	0.48	0.73	4.53	8.81	5.88
04-25-92	20	0.38	0.44	0.73	5.97	7.67	7.24
04-26-92	21	0.49	0.44	1.08	5.18	6.66	9.09
04-27-92	22	0.54	0.55	1.42	6.31	5.99	9.52
04-28-92	23	0.52	0.70	2.03	7.13	5.82	11.64
04-29-92	24	0.35	0.52	1.54	5.75	3.24	10.20
04-30-92	25	0.59	0.64	2.45	6.02	4.38	9.05
05-01-92	26	0.70	0.76	4.30	6.41	5.29	6.11
05-02-92	27	0.59	0.76	2.38	6.95	5.90	9.42
05-03-92	28	0.53	0.70	2.63	6.74	6.42	10.07
05-04-92	29	0.65	0.70	2.78	7.49	6.53	9.19
05-05-92	30	0.65	0.82	2.73	8.58	7.45	11.32
05-06-92	31	0.67	0.64	2.68	8.50	6.89	8.30
05-07-92	32	0.66	0.76	3.41	9.05	8.30	8.11
05-08-92	33	0.90	0.75	3.11	10.20	8.56	8.78
05-09-92	34	0.76	1.11	1.91	10.48	8.84	10.55
05-10-92	35	1.27	1.40	4.64	12.69	17.27	13.74
05-11-92	36	1.44	1.67	6.36	11.23	10.20	10.60
05-12-92	37	1.44	1.78	7.51	4.27	7.01	6.72
05-13-92	38	1.21	1.50	4.98	5.54	4.67	5.70
05-14-92	39	1.42	1.62	7.29	5.54	3.82	6.00
05-15-92	40	1.85	2.12	7.33	6.01	4.31	7.60
05-16-92	41	1.80	1.62	6.62	4.79	4.31	5.64
05-17-92	42	1.94	1.91	5.50	5.22	4.14	4.83

DATE	EXP.DAY	METHANE PRODUCTION (L/DAY) RX. 1	RX. 2	RX. 3	RX. 4	RX. 5	RX. 6
05-18-92	43	1.78	2.18	7.80	12.30	9.21	10.50
05-19-92	44	2.00	2.29	7.04	9.41	7.96	8.75
05-20-92	45	2.50	2.79	9.18	6.62	6.94	10.28
05-21-92	46	3.16	3.65	9.68	8.12	7.24	9.84
05-22-92	47	3.79	4.06	12.16	7.13	6.37	9.58
05-23-92	48	3.42	3.93	12.01	6.43	10.47	11.30
05-24-92	49	4.04	4.12	9.24	8.61	7.41	6.41
05-25-92	50	4.67	5.00	9.33	10.87	7.22	9.36
05-26-92	51	4.10	4.62	9.04	7.27	7.61	7.20
05-27-92	52	5.10	5.68	8.90	10.35	7.00	9.86
05-28-92	53	4.79	4.99	6.08	9.13	6.83	9.58
05-29-92	54	4.85	4.80	5.37	9.26	5.85	8.93
05-30-92	55	4.76	4.63	7.38	9.46	7.37	9.82
05-31-92	56	4.83	4.94	10.10	9.63	11.46	9.82
06-01-92	57	5.01	5.06	8.48	8.31	9.18	8.37
06-02-92	58	5.76	6.00	10.60	12.30	7.43	9.60
06-03-92	59	8.01	6.88	8.68	12.64	8.44	9.90
06-04-92	60	7.43	7.72	13.63	10.96	9.94	6.55
06-05-92	61	5.11	5.43	9.23	10.12	8.88	5.91
06-06-92	62	2.20	1.85	5.12	10.88	9.23	8.47
06-07-92	63	6.01	5.32	6.76	9.37	6.25	7.80
06-08-92	64	5.05	6.07	6.95	8.62	5.47	6.91
06-09-92	65	5.76	7.01	8.10	10.04	6.22	6.72
06-10-92	66	5.82	6.89	6.78	8.22	6.37	6.73
06-11-92	67	4.87	8.45	7.68	9.47	9.52	8.40
06-12-92	68	4.99	6.82	9.08	9.32	9.13	7.60
06-13-92	69	5.40	4.95	5.39	9.01	10.70	6.60
06-14-92	70	4.34	6.45	5.45	5.60	7.41	6.97
06-15-92	71	5.94	7.57	6.04	7.75	10.14	8.75
06-16-92	72	4.40	5.45	7.21	9.46	10.30	8.22
06-17-92	73	5.17	4.42	6.84	5.12	6.40	6.92
06-18-92	74	4.92	7.82	6.81	9.64	9.20	8.32
06-19-92	75	3.10	6.57	6.53	1.04	3.00	2.37
06-20-92	76	2.28	6.13	5.83	2.20	1.96	1.37
06-21-92	77	2.62	6.03	7.01	2.40	2.43	0.91
06-22-92	78	3.05	6.36	6.15	1.33	2.49	0.90
06-23-92	79	3.68	6.17	5.95	2.12	2.42	1.83
06-24-92	80	3.04	6.58	6.50	0.62	1.97	1.56
06-25-92	81	4.08	6.51	5.80	0.79	2.11	1.10
06-26-92	82	3.64	6.53	6.77	1.62	1.90	0.73
06-27-92	83	3.30	5.52	6.68	0.60	1.43	0.66
06-28-92	84	3.70	6.11	7.12	1.11	1.35	0.80

METHANE PRODUCTION (L/DAY)

DATE	EXP.DAY	RX. 1	RX. 2	RX. 3	RX. 4	RX. 5	RX. 6
06-29-92	85	3.72	6.88	6.99	1.10	1.31	0.85
06-30-92	86	3.85	6.92	7.05	1.21	1.33	0.92
07-01-92	87	4.13	6.82	4.56	1.54	0.87	0.63
07-02-92	88	4.50	7.25	9.67	0.91	1.51	1.01
07-03-92	89	4.52	8.25	7.05	0.81	2.15	0.92
07-04-92	90	5.52	8.00	6.30	0.71	2.11	0.77
07-05-92	91	5.46	7.13	7.66	1.25	1.55	0.88
07-06-92	92	6.26	7.72	7.42	0.77	2.33	0.95
07-07-92	93	5.98	6.26	7.05	0.66	1.91	0.77
07-08-92	94	6.63	7.44	8.01	1.22	1.87	0.88
07-09-92	95	6.80	7.91	7.79	0.76	1.76	0.99
07-10-92	96	6.30	7.53	7.77	0.79	1.77	1.36
07-11-92	97	5.91	7.52	7.55	0.92	1.97	1.22
07-12-92	98	5.66	7.13	7.92	0.97	1.73	1.25
07-13-92	99	6.52	7.74	6.83	0.70	1.29	1.21
07-14-92	100	6.09	7.19	7.44	1.02	1.27	1.05
07-15-92	101	5.90	6.92	7.09	0.82	1.42	1.11
07-16-92	102	8.04	10.02	10.60	0.99	1.84	1.32
07-17-92	103	10.27	12.08	12.96	1.10	2.83	1.42
07-18-92	104	7.66	9.91	10.67	0.77	1.83	0.99
07-19-92	105	8.01	8.88	12.69	1.15	2.22	1.43
07-20-92	106	8.06	8.99	11.31	1.03	1.75	1.11
07-21-92	107	8.90	9.32	10.44	1.30	2.37	1.22
07-22-92	108	9.37	11.37	12.22	1.33	2.22	1.37
07-23-92	109	10.33	12.61	12.33	2.79	3.01	3.55
07-24-92	110	11.69	13.39	14.06	2.70	3.71	3.31
07-25-92	111	11.20	14.29	15.32	1.61	4.11	3.35
07-26-92	112	12.88	14.77	14.91	2.51	3.75	3.81
07-27-92	113	12.70	15.31	14.77	2.22	3.73	0.82
07-28-92	114	13.22	15.64	11.12	0.77	3.12	0.88
07-29-92	115	11.53	15.33	15.44	1.12	2.36	2.11
07-30-92	116	12.79	13.98	15.66	0.98	2.88	2.12
07-31-92	117	12.03	15.14	15.46	1.05	2.28	1.66
08-01-92	118	12.33	15.55	16.02	1.06	2.89	1.47
08-02-92	119	15.33	17.34	13.22	0.56	3.67	3.12
08-03-92	120	16.32	17.31	15.42	2.03	6.22	3.88
08-04-92	121	15.23	17.56	18.95	1.92	4.47	2.41
08-05-92	122	17.33	19.34	17.11	1.77	4.11	2.69
08-06-92	123	19.91	22.23	20.45	2.11	4.10	3.09
08-07-92	124	20.81	22.13	20.66	2.57	4.12	2.88
08-10-92	127	17.88	17.12	23.92	2.98	4.46	2.52

METHANE PRODUCTION (L/DAY)

DATE	EXP.DAY	RX. 1	RX. 2	RX. 3	RX. 4	RX. 5	RX. 6
08-13-92	130	18.88	21.08	19.22	3.13	4.56	3.99
08-14-92	131	19.87	22.08	19.02	2.66	4.23	3.88
08-16-92	133	20.12	22.35	19.33	2.49	4.12	3.33
08-17-92	134	22.10	23.03	19.14	2.62	4.68	3.77
08-18-92	135	21.62	23.04	20.22	5.20	6.22	3.77
08-20-92	137	21.77	26.78	24.77	2.92	6.80	3.69
08-21-92	138	25.22	28.89	26.22	3.67	7.02	3.32
08-22-92	139	20.77	28.22	27.56	3.11	6.04	3.12
08-23-92	140	21.90	25.40	25.46	3.34	5.12	2.20
08-24-92	141	27.11	30.23	28.03	3.31	5.44	3.44
08-25-92	142	26.02	31.23	30.23	3.99	5.79	2.88
08-26-92	143	24.99	28.77	32.33	3.91	5.88	2.69
08-27-92	144	26.11	28.22	31.98	3.33	6.62	3.14
08-28-92	145	25.89	27.65	30.11	3.12	5.89	3.56
08-29-92	146	28.77	29.12	31.16	3.02	5.28	3.12
08-30-92	147	26.02	28.60	29.22	3.08	6.89	3.98
08-31-92	148	24.88	26.60	28.22	2.97	5.03	3.56
09-01-92	149	26.50	31.22	30.42	3.05	4.89	3.51
09-02-92	150	28.01	33.21	34.76	3.11	7.42	3.81
09-03-92	151	26.81	32.32	30.33	3.30	8.91	4.82
09-04-92	152	25.99	31.01	28.42	2.22	8.13	4.32
09-05-92	153	25.55	32.01	30.66	2.61	8.22	4.25
09-06-92	154	24.88	25.81	29.22	2.44	7.70	4.72
09-07-92	155	25.11	31.11	32.55	3.32	7.99	4.99
09-08-92	156	27.33	33.32	41.55	3.22	8.22	4.98
09-09-92	157	29.41	34.09	36.14	3.19	7.60	5.48
09-10-92	158	28.52	35.63	38.12	3.05	11.29	5.86
09-11-92	159	28.33	34.12	38.01	3.02	8.88	6.78
09-12-92	160	3.22	30.78	36.44	3.34	14.42	5.99
09-13-92	161	4.40	36.88	36.99	4.77	20.55	8.44
09-14-92	162	9.99	37.41	36.88	7.66	9.99	12.01
09-15-92	163	10.01	34.11	43.02	9.23	5.43	8.96
09-16-92	164	11.61	34.68	50.01	8.02	2.12	8.66
09-17-92	165	10.76	35.99	49.56	6.77	5.68	8.65
09-18-92	166	11.99	34.43	41.33	6.43	9.42	7.55
09-19-92	167	12.11	37.92	42.77	5.12	16.42	5.77
09-20-92	168	13.12	37.33	41.55	4.13	16.33	6.51
09-21-92	169	13.97	38.88	41.66	3.67	15.92	4.39
09-22-92	170	15.01	35.33	39.92	3.22	14.01	4.43
09-23-92	171	16.65	39.77	44.62	4.45	11.81	6.44
09-24-92	172	15.55	36.33	39.99	5.55	9.99	4.67
09-25-92	173	16.78	37.67	38.78	5.45	11.12	5.98

DATE	EXP.DAY	METHANE PRODUCTION (l/DAY) RX. 1	RX. 2	RX. 3	RX. 4	RX. 5	RX. 6
09-26-92	174	16.77	40.23	37.23	9.22	12.01	6.23
09-27-92	175	17.12	34.45	38.23	8.33	9.99	6.31
09-28-92	176	18.44	44.23	37.23	9.31	9.51	5.12
09-29-92	177	20.54	44.01	39.23	10.02	6.43	7.62
09-30-92	178	22.77	40.23	39.99	8.77	5.23	7.35
10-01-92	179	21.98	41.12	40.23	10.23	7.01	8.88
10-02-92	180	23.97	40.32	41.02	12.32	11.01	7.78
10-03-92	181	24.45	40.41	41.08	12.23	11.12	7.82
10-04-92	182	24.12	42.12	42.22	10.22	11.23	6.88
10-05-92	183	25.24	44.76	43.22	9.33	11.51	7.93
10-06-92	184	25.23	47.99	44.23	5.88	13.82	8.01
10-07-92	185	25.02	42.23	44.03	4.81	12.92	7.11
10-09-92	187	27.92	39.22	40.12	3.30	13.51	4.64
10-10-92	188	26.88	38.54	39.22	2.72	12.33	2.82
10-11-92	189	27.92	45.01	43.23	2.77	11.20	4.43
10-12-92	190	28.02	42.38	40.12	3.62	11.17	5.79
10-13-92	191	29.22	44.55	42.12	2.83	12.61	7.12
10-14-92	192	30.56	53.22	55.60	2.71	10.01	11.23
10-15-92	193	34.92	50.33	52.23	7.44	12.62	17.81
10-16-92	194	31.43	59.44	59.97	6.72	11.81	12.12
10-17-92	195	35.33	53.22	55.22	6.23	11.23	11.01
10-18-92	196	36.12	49.72	52.77	4.12	11.33	9.54
10-19-92	197	33.12	46.34	55.88	4.63	8.59	7.72
10-20-92	198	34.65	42.23	57.62	6.89	10.69	5.50
10-21-92	199	32.23	38.66	54.77	6.51	9.55	4.76
10-22-92	200	31.13	42.34	55.11	4.49	14.01	4.66
10-23-92	201	34.89	43.23	58.01	4.19	9.97	5.23
10-24-92	202	32.39	53.67	59.07	5.76	10.34	6.78
10-25-92	203	34.23	47.23	62.23	7.66	11.59	7.03
10-26-92	204	33.59	54.65	60.66	6.12	11.77	8.06
10-27-92	205	34.55	54.67	62.01	6.23	9.79	13.90
10-28-92	206	43.12	62.01	69.12	6.23	12.88	13.55
10-29-92	207	40.12	58.12	63.12	5.99	11.02	13.99
10-30-92	208	43.09	64.02	65.02	4.66	11.67	14.53
10-31-92	209	41.98	63.99	67.12	4.98	12.23	16.01
11-01-92	210	40.77	60.12	70.12	3.99	11.44	9.89
11-02-92	211	42.88	59.12	80.12	14.24	8.66	8.88
11-03-92	212	41.12	21.55	72.02	13.88	8.02	6.67
11-05-92	214	40.23	29.26	58.23	9.30	6.66	25.02
11-06-92	215	38.23	35.55	57.02	9.76	12.02	25.78
11-07-92	216	40.23	33.44	58.23	3.23	12.66	17.92
11-08-92	217	39.77	33.23	60.50	7.44	13.23	20.23

METHANE PRODUCTION (L/DAY)

DATE	EXP.DAY	RX. 1	RX. 2	RX. 3	RX. 4	RX. 5	RX. 6
11-09-92	218	42.22	30.23	46.33	5.55	12.76	21.62
11-10-92	219	41.43	33.34	58.42	4.88	14.76	24.12
11-11-92	220	41.45	38.92	59.10	6.24	13.04	25.77
11-12-92	221	40.12	43.56	58.01	7.78	11.76	23.43
11-13-92	222	46.72	41.52	57.44	7.79	7.54	28.12
11-14-92	223	49.48	35.56	46.43	4.02	6.89	22.23
11-15-92	224	47.12	38.12	61.66	6.82	3.53	22.33
11-16-92	225	46.02	49.23	60.92	7.34	8.92	25.23
11-17-92	226	43.23	49.67	60.12	6.92	10.43	19.55
11-18-92	227	44.65	41.88	48.23	7.01	7.66	18.34
11-19-92	228	43.66	52.98	64.56	4.50	10.87	17.45
11-20-92	229	47.23	55.65	68.12	6.24	13.67	22.12
11-21-92	230	45.33	58.71	67.65	6.01	15.66	20.01
11-22-92	231	46.13	59.04	66.54	6.22	11.45	18.23
11-23-92	232	46.77	59.14	66.92	5.92	20.34	16.34
11-24-92	233	47.65	59.79	68.77	6.67	18.23	16.42
11-29-92	237	43.66	57.12	74.67	4.45	29.32	21.72
11-30-92	238	47.89	61.67	78.23	5.12	22.54	16.43
12-01-92	239	43.67	57.89	77.60	5.23	12.23	16.25
12-02-92	240	47.23	55.92	78.23	5.02	14.23	15.34
12-03-92	241	44.23	61.78	80.62	5.34	16.23	15.78
12-04-92	242	42.23	59.56	67.03	5.37	24.12	15.87
12-05-92	243	43.55	58.04	61.89	4.92	16.78	15.52
12-07-92	245	44.45	55.23	59.23	6.23	5.70	18.94
12-08-92	246	46.25	60.45	60.78	5.34	4.12	16.12
12-09-92	247	45.23	68.13	63.23	8.34	19.15	20.83
12-10-93	248	45.12	63.22	71.75	6.62	8.34	17.76
12-12-92	250	46.45	61.12	78.34	12.23	13.43	15.51
12-13-92	251	45.92	66.05	85.45	13.32	20.23	16.78
12-14-92	252	40.76	61.54	75.50	10.23	26.45	13.52
12-15-92	253	46.01	66.60	80.52	9.92	25.52	14.66
12-16-92	254	38.01	60.02	85.23	10.23	27.32	15.56
12-17-92	255	29.54	53.32	76.62	6.77	25.52	15.34
12-18-92	256	41.12	52.23	74.34	5.79	23.23	15.52
12-20-92	258	38.23	56.23	68.12	8.87	29.23	14.76
12-21-92	259	38.44	56.82	76.67	6.87	34.89	16.23
12-30-92	269	41.12	64.23	72.12	8.12	34.56	16.92
12-31-92	270	39.12	64.93	74.23	7.76	36.23	18.12
01-01-93	271	40.12	68.40	74.56	6.89	37.23	16.23
01-02-93	272	42.12	64.23	77.23	7.89	39.23	16.01
01-03-93	273	38.30	64.31	71.78	19.34	33.34	22.12
01-04-92	274	42.92	69.62	60.23	14.72	30.89	23.78

DATE	EXP.DAY	METHANE PRODUCTION (L/DAY) RX. 1	RX. 2	RX. 3	RX. 4	RX. 5	RX. 6
11-09-92	218	42.22	30.23	46.33	5.55	12.76	21.62
01-06-93	276	30.12	53.13	60.12	18.23	49.23	32.23
01-07-93	277	28.33	57.23	63.13	24.23	50.23	32.23
01-08-92	278	33.23	54.23	59.22	24.23	55.23	28.98
01-09-93	279	30.33	56.12	57.23	25.62	54.23	29.24
01-10-92	280	30.01	54.34	59.23	25.62	54.77	30.23
01-11-92	281	32.23	55.27	60.23	23.24	51.23	31.43
01-12-93	282	31.12	53.92	67.23	22.23	58.23	34.33
01-13-92	283	31.41	60.34	72.23	18.23	63.23	32.23
01-14-92	284	29.62	56.93	85.23	13.12	67.26	35.23
01-15-92	285	31.10	63.23	71.12	19.12	61.12	37.66
01-16-92	286	27.11	57.43	76.23	17.23	60.23	36.54
01-17-92	287	30.71	58.23	70.23	19.23	64.55	32.97
01-18-92	288	36.23	59.32	82.23	20.33	69.76	38.12
01-19-93	289	36.34	61.12	79.23	20.92	73.23	38.23
01-20-93	290	33.23	64.46	85.34	17.72	71.03	36.78
01-21-93	291	33.67	62.12	82.23	18.23	77.23	36.67
01-23-93	293	34.23	63.12	80.12	19.23	75.92	40.23
01-24-93	294	35.23	52.10	83.31	22.23	79.23	36.44
01-25-93	295	36.62	54.23	87.34	19.23	80.12	43.12
01-26-93	296	30.90	54.62	95.13	18.77	78.12	41.54
01-27-93	297	36.60	57.72	89.23	18.54	85.23	38.82
01-28-93	298	37.73	56.23	87.23	19.24	79.23	43.12
01-29-93	299	35.44	51.56	79.52	17.23	79.45	42.33
01-30-93	300	31.89	52.34	83.23	15.92	82.34	44.45
01-31-93	301	34.12	57.43	79.52	19.23	85.77	43.64
02-01-93	302	38.32	61.66	96.67	18.87	87.77	43.78
02-02-93	303	33.52	64.76	88.23	21.25	90.74	45.23
02-03-92	304	36.24	69.78	97.23	21.53	89.23	47.27
02-04-92	305	34.12	66.23	96.20	25.54	88.89	46.23
02-05-93	306	33.52	65.17	98.33	20.14	95.23	49.56
02-06-92	307	32.23	68.67	100.23	21.23	92.44	47.23
02-07-93	308	34.77	68.43	97.19	26.23	94.45	47.09
02-08-93	309	27.66	43.81	106.23	24.98	83.12	27.67
02-09-93	310	27.89	41.34	105.23	23.92	80.23	28.53
02-12-93	313	38.72	68.13	100.12	24.23	87.12	46.23
02-13-93	314	42.66	72.15	99.62	25.75	96.12	50.01
02-14-93	315	34.88	69.23	93.14	27.12	95.12	52.56
02-15-92	316	38.77	73.14	97.88	24.92	97.14	49.28
02-16-93	317	43.70	70.12	100.13	32.14	100.41	53.13
02-17-93	318	50.92	73.55	102.13	28.14	104.13	56.34
02-18-93	319	46.23	76.23	99.23	29.23	102.12	57.13

DATE	EXP.DAY	METHANE PRODUCTION (L/DAY) RX. 1	RX. 2	RX. 3	RX. 4	RX. 5	RX. 6
02-19-93	320	43.23	75.44	106.25	28.90	106.43	58.12
02-24-93	326	56.12	79.99	109.28	29.23	108.33	59.12
02-25-92	327	47.12	76.23	103.29	33.73	111.34	57.89
02-27-93	328	45.12	81.12	102.20	32.53	109.00	57.78
02-28-93	329	48.12	80.99	105.66	29.80	111.69	58.47
03-01-93	330	47.21	79.57	103.00	31.89	113.90	59.12
03-10-93	339	9.65	15.01	5.12	26.62	31.32	15.01
03-11-93	340	14.45	16.79	5.78	29.62	17.23	14.59
03-13-93	342	7.98	10.01	6.78	17.98	15.28	9.87
03-14-93	343	6.56	9.67	5.98	15.01	11.23	7.89
03-15-93	344	8.01	10.72	7.68	17.18	16.34	13.45
03-16-93	345	7.80	13.67	8.34	16.01	17.12	9.10
03-17-93	346	7.67	13.23	9.27	13.12	13.94	6.92
03-18-93	347	8.78	11.34	9.67	11.02	15.34	6.90
03-19-93	348	9.78	13.20	11.23	10.01	12.45	5.78
03-20-93	349	8.90	12.97	10.32	10.32	12.89	6.57
03-21-93	350	9.34	12.27	12.47	9.02	13.03	6.97
03-22-93	351	11.00	12.78	12.97	8.57	13.10	6.46
03-23-93	352	9.57	13.67	13.99	8.23	12.65	5.67
03-24-93	353	10.20	13.01	13.85	9.02	13.00	5.61
03-25-93	354	10.01	14.26	14.27	7.44	12.81	5.90
03-26-93	355	10.40	13.87	14.01	8.32	12.73	5.78
03-27-93	356	10.21	14.67	14.29	9.01	13.08	7.01
03-28-93	357	10.47	13.92	14.56	8.10	12.72	5.10
03-29-93	358	9.70	15.78	13.97	8.62	12.67	6.78
03-30-93	359	10.56	18.65	16.78	9.63	14.67	4.78
03-31-93	360	13.20	19.89	17.98	7.02	16.78	4.23
04-01-93	361	7.34	20.02	18.78	7.42	18.03	5.78
04-02-93	362	13.23	19.89	17.90	6.56	16.78	7.40
04-03-93	363	11.44	23.56	19.07	5.78	15.67	6.02
04-04-93	364	11.03	20.08	20.54	3.64	17.40	5.81
04-05-93	365	10.42	18.67	19.55	4.56	14.89	4.56
04-06-93	366	10.80	19.02	19.89	5.69	16.23	4.56
04-07-93	367	10.89	20.02	20.93	5.93	18.34	4.78
04-08-93	368	10.01	20.32	20.90	6.05	18.43	4.90
04-09-93	369	11.05	20.78	21.31	5.98	18.01	4.62
04-10-93	370	10.85	20.48	22.67	6.39	16.10	4.23
04-11-93	371	10.50	20.11	20.46	5.79	16.70	5.43
04-12-93	372	9.90	19.38	19.46	6.02	15.09	4.67
04-13-93	373	14.20	22.67	24.56	6.23	18.03	7.89
04-14-93	374	14.37	32.34	32.89	4.01	33.20	8.42
04-15-93	375	13.72	29.98	31.89	2.56	19.67	7.34

DATE	EXP.DAY	METHANE PRODUCTION (L/DAY) RX. 1	RX. 2	RX. 3	RX. 4	RX. 5	RX. 6
04-16-93	376	15.41	31.13	35.41	3.89	41.34	8.89
04-17-93	377	13.21	27.00	32.29	2.98	31.31	8.98
04-18-93	378	14.89	25.78	32.10	6.67	27.23	8.02
04-19-93	379	15.90	29.98	34.78	6.62	31.23	8.20
04-20-93	380	16.90	32.98	36.79	7.56	27.89	7.21
04-21-93	381	15.61	29.87	36.99	7.02	29.03	7.91
04-22-93	382	15.40	30.91	37.32	7.23	32.12	9.20
04-23-93	383	11.02	32.01	40.78	7.67	27.23	9.34
04-25-93	385	20.21	39.10	45.78	9.23	36.78	9.67
04-26-93	386	16.43	35.34	46.56	10.34	37.89	10.89
04-27-93	387	24.20	38.43	50.78	11.45	43.43	15.82
04-28-93	388	23.43	36.23	51.80	12.46	49.56	19.55
04-29-93	389	22.89	37.40	51.76	12.23	47.80	17.67
04-30-93	390	24.56	38.79	53.34	12.02	48.87	19.00
05-14-93	401	40.77	44.89	70.21	12.10	35.89	26.78
05-15-93	402	40.09	47.01	75.12	11.98	42.67	30.05
05-16-93	403	38.92	47.34	71.02	9.56	48.12	29.80
05-17-93	404	36.80	43.12	61.04	12.10	43.12	26.99
05-18-93	405	35.01	48.12	69.67	13.02	40.43	28.91
05-19-93	406	34.02	47.02	68.02	11.65	42.67	28.90

APPENDIX B. AMMONIA PRODUCTION DATA

System Loading g COD/L/day	48 hr System HRT NH_3, mg/L as N					
	Rx.1	Rx.2	Rx.3	Rx.4	Rx.5	Rx.6
1	66	92	113	113	73	98
2	184	206	209	218	202	280
3	177	198	244	335	304	332
4	215	277	291	429	375	401
5	335	312	422	550	568	725
6	422	419	399	519	502	745
7	462	662	799	899	562	800
8	512	715	898	967	675	952
9	612	914	1011	1102	898	1132
10	752	928	1058	1189	1198	1149

System Loading g COD/L/day	36 hr System HRT NH_3, mg/L as N Rx.1	Rx.2	Rx.3	Rx.4	Rx.5	Rx.6
2	153	260	320	440	223	220
3	126	283	382	520	276	275
5	193	383	467	553	376	380
7	438	523	584	636	680	716
9	464	634	888	1100	996	902

	24 hr System HRT NH_3, mg/L as N Rx.1	Rx.2	Rx.3	Rx.4	Rx.5	Rx.6
10	183	397	728	887	607	678
11	242	434	842	919	812	919
12	379	567	917	906	924	1424
13	463	731	1203	1379	1357	1484
14	190	540	1279	1554	1259	1234
15	71	660	1292	1522	1273	1220
16	109	623	1330	1591	1362	1250

APPENDIX C. VOLATILE ACIDS DATA

System Loading g COD/L/day	48 hr System HRT Total Volatile Acids, mg/L Rx.1	Rx.2	Rx.3	Rx.4	Rx.5	Rx.6
1	128	288	57	25	14	8
2	211	273	117	19	15	6
3	573	296	170	6	6	6
4	1078	325	117	16	15	13
5	999	387	363	44	21	26
6	1057	173	130	21	40	19
7	1129	411	226	23	11	20
8	2152	1273	400	18	38	17
9	2318	1577	431	47	46	56
10	1769	1151	150	10	17	22

System Loading g COD/L/day	36 hr System HRT Total Volatile Acids, mg/L Rx.1	Rx.2	Rx.3	Rx.4	Rx.5	Rx.6
2	793	423	792	113	80	53
3	1319	488	522	37	23	16
5	1964	540	171	23	15	12
7	1660	601	231	34	23	40
9	2245	621	242	39	31	31

System Loading g COD/L/day	24 hr System HRT Total Volatile Acids, mg/L Rx.1	Rx.2	Rx.3	Rx.4	Rx.5	Rx.6
10	805	857	809	80	141	82
11	1422	1343	747	50	76	47
12	1601	1500	575	33	75	98
13	1715	1108	870	85	34	59
14	2168	1482	803	43	38	33
16	2679	1509	1002	66	74	56

TPAB 1 (1:7) Thermophilic First Phase

Loading g COD/L/day	Total	Specific Volatile Acids, mg/L 48 hr HRT Acetic	Propionic	Butyric	Valeric
1	128	41	67	14	6
2	211	103	67	43	12
3	573	193	343	64	12
4	1078	455	353	194	77
6	1057	404	414	187	53
7	1129	650	296	333	37
8	2152	1132	496	386	138
9	2318	918	371	735	339
10	1769	905	386	334	43
		Specific Volatile Acids, mg/L 36 hr HRT			
2	793	433	209	106	45
3	1319	804	372	118	25
5	1964	1153	667	150	14
7	1660	912	606	125	17
9	2245	1153	792	237	63
		Specific Volatile Acids, mg/L 24 hr HRT			
10	805	483	121	193	9
11	1422	675	445	303	84
12	1601	632	374	426	169
13	1715	617	341	536	222
14	2168	760	475	611	324
16	2679	951	876	553	297

TPAB 2 (1:3) Thermophilic First Phase

Loading g COD/L/day	Total	Acetic	Propionic	Butyric	Valeric
		Specific Volatile Acids, mg/L 48 hr HRT			
1	288	113	163	10	2
2	273	167	91	12	3
3	296	108	164	20	3
4	325	171	109	40	6
5	387	211	133	38	5
6	173	93	59	17	4
7	411	122	261	19	9
8	1273	454	606	131	21
9	1577	321	1000	194	62
10	1151	263	792	177	19
		Specific Volatile Acids, mg/L 36 hr HRT			
2	423	96	257	58	12
3	488	148	319	17	4
5	540	246	260	33	6
7	601	311	239	46	5
9	621	320	250	43	8
		Specific Volatile Acids, mg/L 24 hr HRT			
10	857	433	327	90	8
11	1343	587	564	141	51
12	1500	558	560	266	117
13	1108	366	526	165	51
14	1482	466	589	302	125
16	1509	465	612	302	130

TPAB 3 (1:1) Thermophilic First Phase

System Loading g COD/L/day	Specific Volatile Acids, mg/L 48 hr HRT Total	Acetic	Propionic	Butyric	Valeric
1	57	23	30	4	2
2	117	96	16	3	1
4	117	72	27	17	2
5	363	194	147	19	3
6	130	42	82	5	1
7	226	122	92	10	2
9	431	59	351	13	7
10	150	54	90	6	2
	Specific Volatile Acids, mg/L 36 hr HRT				
2	792	161	554	61	16
3	522	89	423	7	3
5	171	57	113	6	1
7	231	89	127	15	2
9	242	58	174	9	1
	Specific Volatile Acids, mg/L 24 hr HRT				
10	809	169	554	66	20
11	747	215	502	55	16
12	575	137	395	33	9
13	870	200	547	84	38
14	803	168	525	85	26
16	1002	232	635	105	30

APPENDIX D. SOLIDS DATA

System Loading g COD/L/day	Total and Suspended Solids (mg/L) 48 hr System HRT Rx.1 TSS	Rx.1 VSS	Rx.2 TSS	Rx.2 VSS	Rx.3 TSS	Rx.3 VSS	Rx.4 TSS	Rx.4 VSS	Rx.5 TSS	Rx.5 VSS	Rx.6 TSS	Rx.6 VSS
1	335	220	330	180	270	180	190	70	180	80	180	100
2	560	480	330	310	385	320	140	130	155	145	160	130
3	925	720	760	670	705	510	240	190	190	170	200	140
4	1320	990	865	720	560	435	215	180	160	145	150	130
5	1250	795	765	520	540	335	200	120	200	130	190	120
6	1480	880	650	490	625	475	220	135	260	140	330	130
7	1560	1240	560	420	1195	880	255	140	295	130	290	90
8	6360	5490	835	760	1010	790	475	420	550	290	320	220
9	5390	4795	1020	870	1000	870	425	330	500	435	355	300
10	11460	9720	1290	1070	1040	965	415	350	615	530	350	320

Total and Volatile Suspended Solids (mg/L)
36 hr System HRT

System Loading g COD/L/day	Rx.1 TSS	Rx.1 VSS	Rx.2 TSS	Rx.2 VSS	Rx.3 TSS	Rx.3 VSS	Rx.4 TSS	Rx.4 VSS	Rx.5 TSS	Rx.5 VSS	Rx.6 TSS	Rx.6 VSS
2	825	720	650	505	570	350	335	250	215	200	165	100
3	970	805	720	610	445	310	210	180	130	115	135	95
5	2990	2420	1260	1010	815	580	330	250	495	320	290	230
7	3000	2210	1420	1105	2160	1760	660	505	435	275	350	235
9	7450	5225	1675	1325	2045	1690	635	515	305	245	415	255

Total and Volatile Suspended Solids (mg/L)
24 hr System HRT

System Loading g COD/L/day	Rx.1 TSS	Rx.1 VSS	Rx.2 TSS	Rx.2 VSS	Rx.3 TSS	Rx.3 VSS	Rx.4 TSS	Rx.4 VSS	Rx.5 TSS	Rx.5 VSS	Rx.6 TSS	Rx.6 VSS
10	1740	1490	1430	1110	895	685	225	165	705	480	375	205
11	3715	3245	4730	4130	1100	1045	490	490	510	420	955	765
12	5545	4565	3605	2980	1205	1130	535	535	925	605	1345	955
13	3925	3560	3980	3505	2005	1710	920	840	995	830	980	900
14	2380	2060	3900	3205	1805	1625	1450	1160	655	425	525	400
15	5685	4690	4430	3750	1370	1310	540	530	540	490	610	440
16	3125	2710	1275	1275	2380	2095	1070	795	700	570	610	340

E. pH DATA

System Loading g COD/L/day	48 hr System HRT pH at COD Loading/Data Points Rx.1	Rx.2	Rx.3	Rx.4	Rx.5	Rx.6
1	7.01	7.24	7.27	7.40	7.51	7.74
2	7.18	7.25	7.13	7.50	7.56	7.37
3	7.07	6.95	7.18	7.33	7.76	7.60
4	7.01	6.90	7.17	7.35	7.66	7.70
5	7.23	6.86	7.10	7.31	7.53	7.63
6	7.35	7.85	7.33	7.46	7.52	7.52
7	6.86	7.10	7.02	7.37	7.53	7.36
8	6.76	7.37	7.40	7.51	7.54	7.47
9	6.62	7.44	7.42	7.47	7.37	7.56
10	6.93	7.56	7.85	7.67	7.61	7.68

System Loading g COD/L/day	36 hr System HRT pH at COD Loading/Data Points Rx.1	Rx.2	Rx.3	Rx.4	Rx.5	Rx.6
2	6.88	7.15	7.24	7.53	8.36	8.35
3	6.90	7.21	7.20	7.67	8.13	8.21
5	6.99	7.32	7.26	7.65	8.31	8.29
7	6.87	6.78	6.78	6.79	7.18	6.92
9	6.73	6.71	7.27	7.56	7.81	7.78

System Loading g COD/L/day	24 hr System HRT pH at COD Loading/Data Points Rx.1	Rx.2	Rx.3	Rx.4	Rx.5	Rx.6
10	7.10	7.34	7.19	7.40	7.42	7.48
11	6.85	7.05	7.30	7.37	7.46	7.51
12	6.46	7.08	7.42	7.47	7.61	7.63
13	6.51	7.12	7.51	7.57	8.02	7.73
14	6.47	7.72	7.86	7.86	8.26	8.00
15	6.48	7.25	7.00	7.28	8.22	7.46
16	6.56	7.03	7.64	7.73	8.12	7.42

APPENDIX F. ENGINEERING APPLICATIONS-ENERGY BALANCE

In a real-world application of the TPAB process, it is necessary to determine the energy balance for the system in terms of energy required to heat incoming wastes and energy produced via methane production. The following example is an energy balance for a hypothetical industrial waste at influent waste temperatures ranging from 50° to 110° F and waste strengths of 7,500 to 15,000 mg/L of COD (3,750 to 7,500 mg/L of BOD). An economic analysis using this example will also be presented including the value of excess methane production and reduction of sewer-use fees.

Energy Balance

1. Assume a daily volume of waste of $\approx$20,000 ft^3/day

   = 564,000 L/day

   = 149,009 gpd

   = 1,242,737 #/day

2. Size the TPAB systems:

   Assume a 24 hr system HRT

   a. System 1 (1:1 volume ratio)

Thermophilic Unit = 10,050 ft^3	Dia=20 ft	Ht=32 ft
Mesophilic Unit = 10,050 ft^3	Dia=20 ft	Ht=32 ft

   b. System 2 (1:3 volume ratio)

Thermophilic Unit = 4,950 ft^3	Dia=15 ft	Ht=28 ft
Mesophilic Unit = 14,725 ft^3	Dia=25 ft	Ht=30 ft

c. System 3 (1:7 volume ratio)

Thermophilic Unit	= 2,650 ft^3	Dia=15 ft	Ht=15 ft
Mesophilic Unit	= 17,180 ft^3	Dia=25 ft	Ht=35 ft

3. Determine the theoretical methane production from the wastestream.

In this example, influent COD conentrations of 7,500 mg/L, 10,000 mg/L, and 15,000 mg/L will be assumed.

Assume TPAB TCOD system removals = 95%
Assume BTU value of methane = 960 BTU/ft^3

a. At influent COD concentration of 7,500 mg/L:

CH_4 BTU/day = (564,000 L/day)(0.35 L CH_4/g COD removed)
(7.5 g COD/L)(1 ft^3/28.3 L)(960 BTU/ft^3 CH_4)(.95)

CH_4 BTU/day = 47,880,000 BTU/day

b. At influent COD concentration of 10,000 mg/L:

CH_4 BTU/day = 63,840,000 BTU/day

c. At influent COD concentration of 15,000 mg/L:

CH_4 BTU/day = 95,760,000 BTU/day

4. Determine the conductive heat losses in the tanks for the three TPAB systems:

$$q = U\ A\ \Delta T$$

where:

q =	Heat loss, BTU/hr
U =	Overall coffficient of heat transfer, (BTU/ft^2-hr-°F)
A =	Area of evaluation
ΔT =	Temperature change, °F

Assume:

Ambient Air Temperature = 23° F
Average Ground Temperature = 50° F

U_{walls} = 0.12 BTU/ft^2-hr-°F
U_{floor} = 0.15 BTU/ft^2-hr-°F
U_{roof} = 0.16 BTU/ft^2-hr-°F

a. System 1 (1:1 volume ratio)

For both stages:

Wall area = (3.14)(20 ft)(32 ft) = 2,010 ft^2
Floor area = (3.14)(20 ft)^2 = 1,260 ft^2
Roof area = (3.14) (20 ft)^2 = 1,260 ft^2

Thermophilic Conductive Losses:

Thermphilic stage operated at 131°F

1. Wall Loss

q = (0.12 BTU/ft^2-hr-°F)(2,010 ft^2)
(131-23°F)(24 hr/day)

q = 625,190 BTU/day

2. Roof Loss

q = (0.16 BTU/ft^2-hr-°F)(1,260 ft^2)
(131-23°F)(24 hr/day)

q = 522,550 BTU/day

3. Floor Loss

q = (0.15 BTU/ft^2-hr-°F)(1,260 ft^2)
(131-50°F)(24 hr/day)

q = 367,400 BTU/day

Total Thermophilic Conductive Losses = 1,515,140 BTU/day

$q_{wall} + q_{roof} + q_{floor}$

Mesophilic Conductive Losses:

1. Wall Loss

$q = (0.12\ BTU/ft^2\text{-}hr\text{-}^\circ F)(2{,}010\ ft^2)(95\text{-}23^\circ F)(24\ hr/day)$

$q = 416{,}800\ BTU/day$

2. Roof Loss

$q = (0.16\ BTU/ft^2\text{-}hr\text{-}^\circ F)(1{,}260\ ft^2)(95\text{-}23^\circ F)(24\ hr/day)$

$q = 348{,}360\ BTU/day$

3. Floor Loss

$q = (0.15\ BTY/ft^2\text{-}hr\text{-}^\circ F)(1{,}260\ ft^2)(95\text{-}50^\circ F)(24\ hr/day)$

$q = 204{,}120\ BTU/day$

Total Mesophilic Conductive Losses = 970,000 BTU/day

$q_{wall} + q_{roof} + q_{floor}$

Total Conductive Losses System 1 (1:1) = 2,485,000 BTU/day
(Thermophilic + Mesophilic)

b. System 2 (1:3 volume ratio)

Same type calculations as illustrated above

Total Conductive Losses = Thermophilic + Mesophilic

Total Conductive Losses = 909,900 BTU/day + 1,277,100 BTU/day

Total Conductive Losses System 2 (1:3) = 2,187,000 BTU/day

c. System 3 (1:7 volume ratio)

Same type calculations as illustrated above

Total Conductive Losses = Thermophilic + Mesophilic

Total Conductive Losses = 719,250 BTU/day + 1,429,750 BTU/day

Total Conductive Losses System 3 (1:7) = 2,149,000 BTU/day

5. Heat Exchanger Analysis for the three TPAB systems:

Assume that the raw waste can be heated to 100° F using a heat exchanger which will remove heat between the first and second stages. Assume heat exchangers will be used to heat raw waste at incoming raw waste temperatures of 50, 65, and 80° F (chosen). Supplemental heat in the form of direct steam injection will add additional heat to increase the temperatures of the the raw waste from 100 to 131° F. At raw waste temperatures of 95 and 110° F, a cooling water heat exchanger will be used to remove excess heat from between the thermophilic and mesophilic stages, and the raw waste will be heated to 131° F using direct steam injection.

a. Mass Flow Rate of Raw Wastes = M

M = (150,000 gal/day)(day/86,400 sec)(8.34#/gal)

M = 14.5 lb/sec

b. Determine heat removed from waste between thermophilic stage (131° F) and mesophilic stage (95° F).

$q = M \times C_p \times \Delta T$

where:

q = heat recovered (BTU/sec)
M = mass flow rate (lb/sec)
C_p = heat capacity (BTU/lb -°F)
ΔT = temperature difference (°F)

q = (14.5 lb/sec) (1.0 BTU/lb -° F) (131-95°F)

q = 522 BTU/sec = 1.88 MBTU/hr = 45.1 MBTU/day

c. Size the heat exchangers, and determine excess energy necessary to heat waste to 131° F.

Example Calculation

Influent raw waste temperature 50° F

Assume raw waste can be heated from 50 to 100° F using heat removed from between the thermophilic and mesophilic stages.

$q = U \times A \times \Delta T_{lm}$

where:

q = heat recovered (BTU/hr)
U = overall heat transfer coefficient (BTU/ft^2-hr-°F)
A = Area heat exchanger (ft^2)

ΔT_{lm}= log mean temperature difference
ΔT_{lm}= $\Delta T_2 - \Delta T_1 / \ln (\Delta T_2/\Delta T_1$
ΔT_1= temperature difference exit heat exchanger
ΔT_2= temperature difference entrance heat exchanger

Note: The log-mean temperature difference should ideally be used when the differences between the entrance and exit heat exchanger temperatures is large.

In this example, the raw waste will be heated from 50 to 100° F, and the thermophilic effluent will decrease in temperature from 131 to 95° F.

$$\Delta T_{lm} = \frac{(95\text{-}50^\circ F) - (131\text{-}100^\circ F)}{\ln \frac{(95\text{-}50^\circ F)}{(131\text{-}100^\circ F)}} = 37.6^\circ F$$

Size the heat exchanger:

Assume U = 210 BTU/ft^2-hr-°F

$A = q / U \Delta T_{lm}$

A = 1.88 MBTU/hr / (210 BTU/ft^2-hr-°F) (37.6° F)

A = 238 ft^2

Assume a 50 (2 in) tube bundle heat exchanger

Area/linear ft. = (2in/12in)(3.14)(50 tubes)(1 ft)

= 26.2 ft^2/linear foot

Total length heat exchanger = 238 ft^2/ 26.2 ft^2/ft

Total length heat exchanger = 9 ft

Excess methane necessary to heat waste from 100 to 131° F.

$q = M \times C_p \times \Delta T$

$q = (14.5 \text{ lb/sec})(1 \text{ BTU/lb-°F})(131\text{-}100°F)$

$q = 450 \text{ BTU/sec} = 26.970 \text{ BTU/min}$

$q = 38.84 \text{ MBTU/day}$

At raw influent waste temperatures of 95 and 110° F, a a heat exchanger will be employed using a cooling water to decrease temperatures from 131 to 95° F. The cooling water temperature will increase from 50 to 80° F. The raw waste will be directly heated using steam injection and will not pass through a heat exchanger.

Table 25. Summary table of heat exchanger areas and excess energy necessary to heat wastes

Inf. Temp. °F	Area Exchanger ft^2	Length Exchanger ft	Excess Methane Needed MBTU/day
50	238	9	38.84
65	293	11	38.84
80	406	16	38.84
95	187	7	45.10
110	187	7	26.31

Energy Balance Calculation:

Positive Energy Balance (BTU/day) =

Methane generated daily - Energy necessary to heat waste - Average conductive heat losses

Example

At an influent waste concentration of 7,500 mg/L and an influent waste temperature of 50° F:

Methane generated daily = +47,880,000 BTU/day

Energy needed to heat wastes = -38,836,800 BTU/day

Average conductive losses = -2,273,700 BTU/day

Excess Energy +6,769,500 BTU/day

The summary table for the energy balances for the three TPAB systems at influent CODs of 7,500 to 15,000 mg/L at influent waste temperatures of 50°, 65°, 80°, 95° and 110° F are shown in the following table.

Table 26. Summary for Total Energy Balance and Methane Production

Inf. COD (g/L)	Waste Temp. (°F)	Energy Balance: Excess Methane Production (MBTU/day)	(MBTU/yr)	Methane Value ($/day)	($/yr)
7.5		6.8	2470.9	27	9880
10.0	50	22.7	8296.3	91	23185
15.0		54.7	19947.1	219	79790
7.5		6.8	2470.9	27	9880
10.0	65	22.7	8296.3	91	23185
15.0		54.7	19947.1	219	79,790
7.5		6.8	2470.9	27	9880
10.0	80	22.7	8296.3	91	23185
15.0		54.7	19947.1	219	79790
7.5		.5	186.2	2	738
10.0	95	16.5	6009.9	66	24040
15.0		48.4	17660.7	194	70642
7.5		19.3	7043.6	77	28175
10.0	110	35.3	12869.0	141	51425
15.0		67.2	24519.8	269	98,080

The summary table illustrates energy balances for the three TPAB systems at wastewater influent COD concentrations ranging from 7,500 to 15,000 mg/l. It can be summarized that there is a positive energy balance in terms of excess methane at any of the influent temperatures. Also, it can be concluded that influent waste concentrations of 10,000 mg/L or higher are necessary to produce excess methane valued in excess of $20,000 per year. At an influent COD concentration of 10,000 mg/L, the major savings for the system will be the reduction in sewer-use fees as shown below.

Reduction in Sewer-Use Fees

In addition to the monitary value of methane production from the TPAB systems, even more sigificant savings would be realized based on reduction of sewer-use fees. Based on the sewer-use fee of $1.79/# BOD/month from the City of Cedar Rapids Wastewater Treatment Plant (July, 1993), the savings on sewer-use fees can be calculated as illustrated below.

1. Assume BOD/COD ratio of the wastewater is 0.50 (this value will vary depending on the wastestream). If the COD of the wastewater is 10,000 mg/L, the BOD of the wastewater will be 5,000 mg/L.

2. Reduction in Sewer-Use Fees - Example Calculation

   Assume BOD reduction = COD reduction = 95% for the TPAB

2. Reduction in Sewer-Use Fees - Example Calculation

Assume BOD reduction = COD reduction = 95% for the TPAB systems.

Q = Wastewater Flow = 564,000 L/day

Influent Wastewater = 10,000 mg/L COD = 5,000 mg/l BOD

Influent Wastewater = 6,211 # BOD/day

Savings($/yr) = (.95)(6,211 #/day)($1.79/# mo)(12 mo/yr)

= $126,740/yr for BOD reduction

Total Savings =COD reduction + Excess Methane Production

At an influent temperature of 80° F, and an influent COD of 10,000 mg/L:

Total Savings = $ 126,740/yr + $ 23,185/yr

Total Savings = $ 149,925/yr

3. Amount of money which can be invested with a 3- year payback period, assuming a total savings of $149,925/yr, at a prime interest rate of 8%:

$$P = \frac{(1+r)^n - 1}{(1+r)^n \cdot r} \cdot A$$

where,

P = Amount invested($), to be paid back in n years

r = Prime interest rate, assume 8%

A = Dollar return per year($149,925/yr)

P = $386,100

Therefore, an initial investment of $386,100 for capital costs can be made, and will have a payback time of 3 years using this example. This is for an industry which would generate only 150,000 gallons/day of wastewater. Initial investment figures would be higher as volumes increased. If known, operating and maintenance costs would normally be included in this calculation.

Example II

Assume a full-scale application of the TPAB process to an industrial wastewater in Cedar Rapids Iowa. Assume a BOD_5 of 3.75 g/L, a waste flow of 2 MGD, and a raw waste temperature of 95° F.

Influent wastewater= (3.75 g/L)(7,570,000 L/day)(1#/454g) = 62,528 # BOD_5/day

Sewer Savings = (.95)(62,528#/day)($1.79/# mo)(12 mo/yr) = $1,275,900/yr

Methane Produced=

(7,570,000L/day)(.35L CH4/g COD)(7.5 g COD/L)(960 BTU/ft3)(1ft3/28.3L)(.95rem)

= 642,644,680 BTU/day

Average Conductive Heat Losses = 30,279,667 BTU/day

Methane to heat wastes

q = M (1 BTU/#-F)(131-95 F)

M = 2 MGD (1 day/86,400 sec)(8.34 #/gal)

M = 193 #/sec

q = (193 #/sec)(1 BTU/# F)(131-95 F)

q = 6950 BTU/sec = 600,480,000 BTU/day

Excess Methane

Methane produced-Methane to heat wastes - Conductive Heat Losses

642,644,680 BTU - 30,279,667 BTU - 600,480,000 BTU

= 11,885,014 BTU/day

= 4338 MBTU/yr

At methane value of $4.00/MBTU

= $17,400/yr

Total Savings:

Sewer Use Fees + Value of Excess Methane

$1,275,900/yr + $17,400/yr

Total Savings = $1,293,300/yr

How much money can be invested at a 3 -year payback period?

P = ?

n = 3 years

r = 8%

A = dollar return/yr = $1,293,300/yr

$$P = \frac{(1 + .08)^3 - 1}{(1 + .08)^3 \cdot .08} \times 1{,}293{,}288$$

P = $ 3,332,800