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Treatment of a wastewater from furfural production in anaerobic filters at mesophilic temperatures

by

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Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
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Signatures have been redacted for privacy

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Iowa State University
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1992

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ALK	Alkalinity (bicarbonate)
BOD	Biochemical oxygen demand
BOD_5	Five day biochemical oxygen demand
BOD_u	Ultimate biochemical oxygen demand
COD	Chemical oxygen demand
°C	Degrees Celsius
d	day
FAS	Ferrous ammonium sulfate
gal	Gallon
GC	Gas chromatography
hr	Hour
HRT	Hydraulic retention time
lb	Pound
mgd	Million gallons per day
mg/L	Milligram per liter
mL	Milliliter
OLR	Organic loading rate
SRT	Solids retention time
SS	Suspended solids
STP	Standard temperature and pressure
VA	Volatile acids
VFA	Volatile fatty acids
VS	Volatile solids
VSS	Volatile suspended solids

I. INTRODUCTION

A. Background

The City of Cedar Rapids, located in east-central Iowa, is highly industrialized with numerous high-strength industrial waste streams directly or indirectly discharged to the city's wastewater treatment plant. To avoid premature overloading of the wastewater treatment plant (before the design life is reached) and to attract future business and industry to the area, the Biotechnology Byproducts Consortium (BBC) was formed. The BBC consists of Iowa State University (Ames, Iowa), the University of Iowa (Iowa City, Iowa), and the City of Cedar Rapids. One of the goals of the BBC is to develop new and alternative methods for treating waste streams, specifically those from industrial sources, before these streams are discharged to the wastewater treatment plant.

The Quaker Oats Company is one of the industries in Cedar Rapids which has a high-strength waste stream and discharges to the wastewater treatment plant. This waste stream, hereafter referred to as furfural wastewater, was selected as the wastewater to be used for this study.

The furfural wastewater is a byproduct of the Quaker Oats Company's furfural manufacturing process, and is currently pumped to the Cedar Rapids water purification plant where it is neutralized with a lime sludge, after which it is discharged to the city's sanitary sewer. An alternative method of disposal for the furfural wastewater was desired to decrease the Quaker Oats Company's sewer fees and to decrease the load on the City's wastewater treatment plant. Pretreatment of the furfural wastewater before discharge to the sanitary sewer was selected as an approach. Anaerobic biological treatment of the wastewater was selected because of the possible fuel production (methane) and because anaerobic treatment can handle high-strength wastes more efficiently than can aerobic treatment. This study reports on a laboratory-scale investigation of the anaerobic pretreatment of the furfural wastewater using anaerobic filters.

B. Wastewater Characteristics

The characteristics of the furfural wastewater are summarized in Table 1. The furfural wastewater is high in strength, contains few nutrients (nitrogen, phosphorous, etc.), and has a high temperature. The wastewater also has a low pH of about 2.6, which will require the addition of buffering chemicals for anaerobic treatment.

The wastewater contains very little suspended matter, and the solids that are present are mainly inorganic and easily-settleable. Because of this, anaerobic filters were chosen as the best pretreatment alternative.

Table 1. Characteristics of furfural wastewater

Characteristic	Values Average	 Range
Flow, mgd	0.143	0.052 - 0.184
Suspended Solids, mg/L	357	89 - 1,046
BOD_5 , mg/L	8,290	6,960 - 10,214
COD, mg/L	13,300	10,800 - 16,000
COD/BOD_5 Ratio	1.60	---------
pH	2.6	2.4 - 2.7
Temperature, °C	98	97 - 99
TKN, mg/L as N	2.24	---------
Total Phosphate, mg/L as PO4	3.90	---------

C. Treatability of Furfural Wastewater

The main concern relative to the treatability of the furfural wastewater was the chemical oxygen demand (COD) removal efficiency that could be achieved by anaerobic pretreatment. [Since a biological treatment system was used, biochemical oxygen demand (BOD) is a better parameter to study; however, since the COD/BOD_5 ratio of the furfural wastewater was about 1.6, and typical ultimate BOD/BOD_5 ratios are near 1.5, COD removal efficiency is a close representation of BOD removal efficiency. The COD test was chosen over the BOD test because of the COD test's simplicity, precision, and accurateness, as compared to the BOD test].

Acetic acid (CH_3COOH) comprised approximately 1.24% of the furfural wastewater, and, therefore, constituted over 90% of the COD in the wastewater. Only traces of furfural (OC_4H_3-CHO), the product of the manufacturing process, are present in the wastewater. McCarty [29] reported that approximately 72% of the methane that is formed in a given anaerobic process is the result of acetic acid cleavage to methane and carbon dioxide. Since acetic acid is the major intermediate before the formation of methane in anaerobic processes, this type of pretreatment appeared to be quite feasible. In effect, the usual three-step anaerobic process is simplified to a one-step process as shown:

3-step process: Complex Organics —> Higher Organic Acids —> Acetic Acid —> Methane and CO_2

1-step process: Acetic Acid —> Methane and Carbon Dioxide

With the elimination of the first two steps in the anaerobic process, the treatment of the furfural wastewater was seen as a relatively stable and simple process.

D. Objectives and Scope of Study

Since this study was undertaken as part of the BBC's efforts to reduce the problems associated with industrial waste in the City of Cedar Rapids, the scope of this study has more of a practical (as opposed to a theoretical) orientation. It has been widely established that anaerobic filters are effective in treating high-strength industrial wastes [3, 4, 11, 13, 15, 16, 17, 23, 26, 39]. Since the main substrate in the furfural wastewater is acetic acid, anaerobic filters should be highly efficient in COD removal.

A major obstacle to applying anaerobic technology in today's industry is a common misconception: that anaerobic processes are slow and easily upset. It was the purpose of this research to show that the furfural wastewater could be treated efficiently with the anaerobic filter; that is, the research was to show a practical application of the anaerobic technology. It is thought that as industry becomes aware of the advantages inherent in anaerobic treatment processes, more industries will accept anaerobic treatment as a sound and economically advantageous alternative to aerobic treatment.

The objectives of the study were as follows:

(1) to compare the performance of partially-packed and fully-packed anaerobic filters;

(2) to achieve as high of an organic loading rate as possible at a given hydraulic loading rate (HRT);

(3) to achieve as low of an HRT as possible;

(4) to feed the furfural wastewater at as low of a pH as possible;

(5) to study the effects of reactor shutdown (no feeding) on re-starting of the reactors;

(6) to determine the amount of biomass within an anaerobic filter and the distribution of this biomass along the height of the reactor.

II. LITERATURE REVIEW

A. Fundamentals of Anaerobic Treatment

1. Microbiology and biochemistry

Anaerobic degradation is the microbial conversion of organic carbon to methane (CH_4) and carbon dioxide (CO_2) in the absence of oxygen or oxygenated compounds (e.g., sulfates and nitrates). This conversion process is carried out by a complex population of microflora that release energy through the reduction of the organic carbon to methane [7]. The bacterial groups responsible for anaerobic degradation are classified according to their catabolism of carbon.

Zeikus [47] classified these bacteria into four trophic groups: (i) *Group 1: hydrolytic/fermentative bacteria* that catabolize polysaccharides, proteins, and other macromolecular components of organic matter to simpler molecules such as volatile fatty acids and sugars. (ii) *Group 2: hydrogen-producing acetogenic bacteria* that catabolize certain fatty acids and neutral end products to acetate and hydrogen. (iii) *Group 3: homoacetogenic bacteria* that catabolize unicarbon compounds (e.g., formate, carbon dioxide) to acetate and hydrolyze multicarbon compounds to acetate. (iv) *Group 4: methanogenic bacteria* that catabolize acetate and unicarbon compounds to methane.

Figure 1 represents the interactions between the four groups of bacteria. The stability of the anaerobic process as a whole is dependent on the stability of each bacterial group, as well as on the smooth interaction between the groups. A brief description of each of the four bacterial groups follows:

a. Group 1: hydrolytic/fermentative bacteria This group of bacteria secrete extracellular enzymes that hydrolyze polysaccharides, (e.g., cellulose) and degrade the products of these to organic acids, alcohols, H_2, and CO_2. These bacteria also ferment proteins and lipids to similar end products [2]. These bacteria include obligate anaerobes such as *Clostridium, Bacteroides,* and *Ruminococcus* species and facultative anaerobes such as *E. coli and Bacillus* spp. [7].

b. Group 2: hydrogen-producing acetogenic bacteria These bacteria utilize the products of the first stage fermentation (i.e., mainly the long-chained fatty acids) and oxidize them to acetate or acetate and CO_2, depending on the compound [2]. The bacteria of this group also oxidize alcohols to the corresponding carboxylic acid, e.g., ethanol to acetate and hydrogen [33]. Members of this group of bacteria include *Syntrophobacter, Syntrophomonas,* and *Desulfovibrio* [7].

c. Group 3: homoacetogenic bacteria This group of bacteria include mixtrophs that catabolize hydrogen and carbon dioxide or multi-carbon compounds (sugars) to acetic acid.

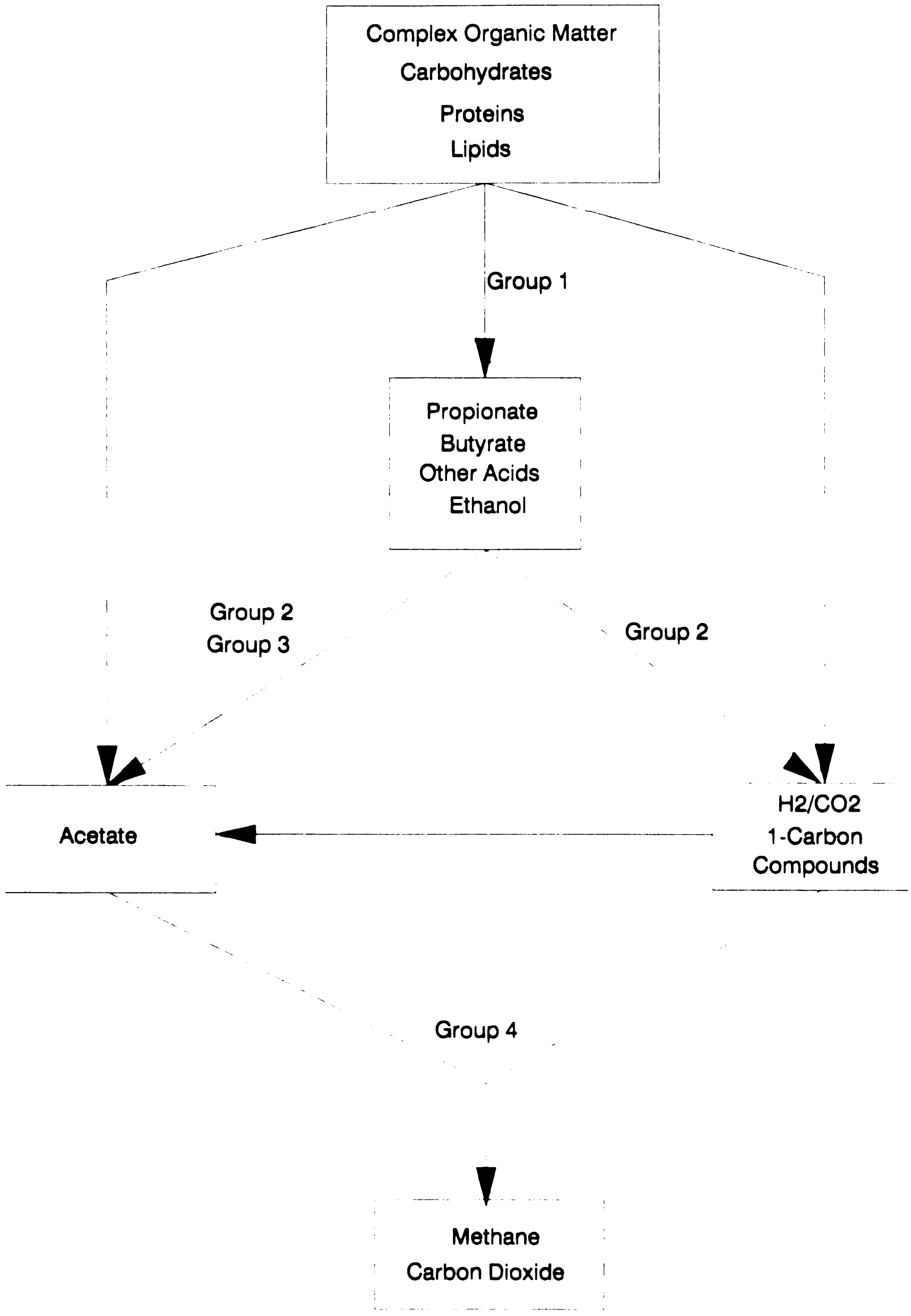

Figure 1. Biochemical pathways of anaerobic digestic

The exact role played by these bacteria is not thoroughly understood; however, it is believed that the metabolism of these bacteria helps maintain a low partial pressure of hydrogen. Homoacetagens include some of the organisms of the genera *Clostridium* and *Acetobacterium* [47].

d. Group 4: methanogenic bacteria The methanogenic bacteria utilize the products of the other stages of fermentation (mainly acetate, H_2, and CO_2) to form the final metabolic end products of methane and CO_2. These organisms are the only anaerobic organisms capable of using electrons in the form of hydrogen and of effectively breaking down acetate in the absence of light or exogenous electron acceptors such as nitrate or sulfate. In their absence, organic matter could not be anaerobically degraded effectively [2]. Bacteria in this group include all methanogens, such as *Methanothrix* and *Methanosarcina* [7].

The substrates that methanogens can use as both an energy and carbon source are limited to H_2/CO_2, formate, methanol, carbon monoxide, methylamine, and acetate. Table 2 shows the chemical reactions by which methanogens utilize these substrates. The final reaction shown in Table 2, the conversion of acetate to methane and carbon dioxide, accounts for about 70% of the methane formed in nature. This reaction also has the least-negative free energy value of all the reactions in Table 2, indicating that this reaction is the least favorable to the bacteria in terms of net energy yield.

Table 2. Energy yielding reactions used by methanogens [34]

Reaction	Free Energy (kJ/reaction)	Free Energy (kJ/CH_4)[a]
$4H_2 + CO_2 \longrightarrow CH_4 + 2H_2O$	-138.8	-138.8
$4HCOOH \longrightarrow 3CO_2 + CH_4 + 2H_2O$	-119.5	-119.5
$4CH_3OH \longrightarrow 3CH_4 + CO_2 + 2H_2O$	-310.5	-103.5
$4CH_3NH_3^+ + 2H_2O \longrightarrow 3CH_4 + CO_2 + 4NH_4^+$	-225.7	-75.2
$4CO + 2H_2O \longrightarrow CH_4 + 3CO_2$	-185.6	-185.6
$CH_3COOH \longrightarrow CH_4 + CO_2$	-27.6	-27.6

[a] Values reported are per mole of CH_4 at standard conditions: pH 7.0, 25°C, and 1 atm of gas.

As a result, the acetate-using methanogens generally grow rather slowly. The replication time for the slower-growing methanogenic bacteria is generally accepted as 10 to 11 days at 35°C. Because of this slow growth, the methanogens are the organisms most susceptible to environmental upset. Failure of the methanogens leads to a rapid increase in volatile acids concentration and a possible decrease in pH. As previously stated, complete degradation of organic matter to final end products in an anaerobic environment is not possible if the methanogens are not performing properly.

2. Important parameters in anaerobic digestion

The parameters affecting anaerobic digestion can be classified as environmental and operational. The following section describes the parameters associated with each.

a. <u>Environmental parameters</u> The main environmental parameters that affect anaerobic digestion are temperature, pH, and toxic materials.

i. <u>Temperature</u> Anaerobic digestion is greatly affected by the temperature at which the process is carried out. As early as the 1930s, Rudolfs [35] and Heukelekian [21] reported on noticeable differences in the rate of digestion at different temperatures (thermophilic and non-thermophilic). Generally, the organisms responsible for digestion at thermophilic temperatures (50 to 70°C) are different from those responsible for digestion at lower temperatures, such as the mesophilic range (28 to 35°C). McCarty [30] also found the presence of two distinct temperature ranges, similar to those given.

Temperature affects the rates at which digestion is carried out, rather than the total degree of digestion that is achieved. Pidaparti and Dague [34] reported similar total COD and volatile solids destruction at temperatures of both 35°C and 25°C.

A general rule of thumb is that microbial metabolism rates (and thus, rates of digestion) approximately double for each 10°C rise in temperature. Therefore, for a given removal efficiency, a smaller reactor will be required as the temperature of the system is increased.

ii. <u>pH</u> Hydrogen ion concentration in an anaerobic reactor has a major effect on the performance of the system. McCarty [30] suggested a range for pH of 6.6 to 7.6 with an optimum between 7.0 to 7.2. Since the methanogens are the most important organisms in an anaerobic system, it is important that the pH be maintained at a level that is not toxic to them, i.e at pH near 7.0. This range of pH has been shown to be the optimum for the anaerobic process as a whole, not just for the methanogenic organisms.

Alkalinity and volatile acid concentrations are associated with the pH of the system. If volatile acids concentrations are high, the pH of the system may decrease. Maintaining a high level of alkalinity will counteract the formation of volatile acids. The use of bicarbonate as the source of alkalinity is ideal since it has a pK_a near 7.0.

iii. Toxic materials Many organic and inorganic materials may be toxic to anaerobic organisms. Often, at low concentrations, these same materials may be stimulatory to the microorganisms, but as the concentration of the material increases, it becomes inhibitory and finally toxic. McCarty [31] reported on the effects of some alkalis on anaerobic digestion. His report stated that below about 200 mg/L, sodium, potassium, calcium, and magnesium were stimulatory to the system. At 3,000 mg/L, magnesium was strongly inhibitory. This level of inhibition was reached at 8,000 mg/L for sodium and calcium and at 12,000 mg/L for potassium. Ammonia and sulfide are other common compounds found in anaerobic systems which are toxic at high concentrations [31].

Parkin *et al.* [33] reported on the effects of industrial toxicants to methane fermentation. The study reported on the toxicity of nickel, ammonium, sulfide, and formaldehyde. In all cases, the inhibition to the methanogenic bacteria appeared to be reversible, and acclimation of the biomass to the toxicant occurred, indicating the inhibition to toxicants can be overcome with time. The study states that a long solids retention time (SRT) is the best safeguard against failures of a treatment system that must handle toxicants.

b. Operational parameters Operational parameters that are important to anaerobic digestion are solids retention time (SRT), organic loading rate (OLR), and hydraulic loading rate (HRT).

i. Solids retention time The SRT of an anaerobic system is a reflection of the average time that a solid particle is retained in the system. If the SRT is less than the microbial regeneration time of the slowest growing organism, failure of the process will result [6].

The required SRT is dependent on the temperature of the system since, as temperature increases, microbial regeneration times decrease. Therefore, at high temperatures, the required SRT is less than that required at relatively low temperatures. Dague *et al.* [6] reported that the required SRT for stable anaerobic treatment at 35°C is approximately 10 days. Because of increased metabolic rates at higher temperatures, the minimum SRT at a temperature of 55°C is only 2 to 3 days.

The SRT has an effect on the degree of stabilization of the organic content of a waste. As the SRT is increased beyond its minimum, removal rates of organic material increase and gradually plateau as the SRT becomes very long [6].

ii. Organic loading rate The organic loading rate (OLR) is the mass flux of organic material into the reactor per time, usually reported as mass of organic material per volume of reactor per time (kg COD/m^3/day). As the OLR is increased, the degree of waste stabilization is normally close to constant, provided that the OLR is below the maximum capacity of the system. As this maximum capacity is approached (termed saturation loading) the system often becomes unstable, with increased concentrations of volatile acids and a lowering of the pH.

It is advantageous for treatment systems to be able to operate at a high OLR for best overall process efficiency. Harris and Dague [16] have demonstrated that temperature has a profound effect on the OLR that may be achieved for a given system. The authors operated anaerobic filters at mesophilic (35°C) and thermophilic (56°C) temperatures and reported that the thermophilic filters were able to attain over twice the OLR than that of the mesophilic filters with similar organic removal rates. Weiland [41] reported exceptionally high OLR (up to 235 kg COD/m^3/day) using fluidized bed anaerobic reactors with porous glass beads as the bed material.

Generally, the OLR will be determined by the type of waste treated and by the type of reactor used to treat the waste.

iii. Hydraulic loading rate The hydraulic retention time (HRT) is the average amount of time that a molecule of water is retained within the reactor. In the case of a completely-mixed reactor, the HRT is equal to the SRT. The HRT is mainly important in that it affects the SRT; that is, as long as the SRT is maintained above the minimum required to prevent washout of the microorganisms, the HRT normally does not have a significant effect on the treatment process. HRT's less than 3 hours have been reported for anaerobic filters treating domestic strength wastewater [10].

B. Development of the Anaerobic Filter

1. Initial studies on the anaerobic filter

Before the 1970s, anaerobic waste treatment was mainly confined to suspended growth treatment processes. Traditionally, the systems were operated as complete-mix anaerobic digesters in which the SRT is maintained the same as the HRT. In the 1950s, the anaerobic contact process was studied and developed [5]. The anaerobic contact process allowed for longer SRT's relative to the HRT by returning sludge to the contact reactor. Long SRT's coupled with short HRT's led to the concept of high-rate anaerobic digestion in which high organic loads could be handled without the excessive dilution or extended digestion period required in the past.

In 1969, Young and McCarty [44] introduced a new anaerobic treatment process which they termed the "anaerobic filter." Their anaerobic reactor included a rock media within the reactor for microbial attachment, similar to the aerobic trickling filters popular for domestic wastewater treatment plants. The anaerobic filter was the first of the so-called second-generation anaerobic treatment processes, which allowed the attainment of very long SRT's without the requirement of returning sludge to the reactor. Rather, the biomass attaches to the media and is caught in the interstitial spaces between the attachment media, and is thus retained in the reactor rather than exiting with the liquid effluent.

In Young and McCarty's paper [44], the authors point out that the anaerobic filter has many advantages over conventional biological treatment processes, including: (1) the anaerobic filter is suited for treatment of soluble wastes, (2) no effluent or solids recycle is required, (3) dilute wastes can be treated efficiently because of the accumulation of high concentrations of biological solids (long solids retention time), and (4) very low volumes of sludge are produced, which reduces sludge disposal costs.

The first anaerobic filters of Young and McCarty were operated at 25°C with the flow introduced at the bottom of the filter and exiting at the top without recycle. The filters consisted of Plexiglas columns filled with smooth quartzite stone (1 to 1.5 inches in diameter); the completed filter had a porosity of 0.42. Two separate synthetic substrates were studied: a protein-carbohydrate mixture and a volatile acid mixture (acetic acid and propionic acid). The filters were operated at relatively low organic loading rates (0.4 to 3.4 kg COD/m^3/day) with COD removals near or above 90 percent except at the higher loadings. The authors obtained the higher organic loadings by decreasing the HRT to as low as 4.5 hours (based on the void volume of the filter). Significant washout of biomass occurred at these low HRT's, resulting in poor COD removal efficiencies.

Since Young and McCarty's initial studies on the anaerobic filter, numerous studies have been undertaken to examine the process with respect to the effects on filter performance of various operating parameters. These parameters include organic loading rate, hydraulic loading rate, substrate type, media type (material, porosity, and surface area), effluent recycle, two-stage operation, and the effects of toxic substances.

In addition, several modifications to the anaerobic filter have been made in an attempt to improve on its initial design. These new reactors include the downflow anaerobic filter, the expanded-bed anaerobic reactor, and the hybrid anaerobic filter (partially-packed with media).

The following is a summary of a few of these studies.

2. Further development of the anaerobic filter

For this report, the anaerobic filter is considered to be any reactor that is operated in an upflow mode and is completely packed with microbial attachment media.

In 1977, Chian and DeWalle [4] studied the treatment of high-strength acidic wastewater with a fully-packed anaerobic filter. The packing media consisted of plastic "Surpac" slabs (Dow Chemical, Midland, MI) with additional plastic strips placed between each sheet of media. The specific surface area of the media was 206 m^2/m^3 of column volume, with a porosity of 94 percent. Chian and DeWalle used a recycle ratio varying from 2.4:1 to 35:1, with the HRT varying from 3 to 74 days. The substrate used in this study was a high-strength leachate (54,000 mg COD/L) with a pH of 5.4. Fatty acids represented 49% of the total COD, with carbohydrates, tannins, and proteins comprising the remaining portion of COD. Because of the high recirculation rates used, and because of gas mixing which occurs in anaerobic filters, the reactors in Chian and DeWalle's study operated close to completely-mixed reactors, which negated the need to add buffer solutions for pH adjustment. The results of this study indicate that greater than 90% removal of COD was obtained when the HRT was more than 7 days; however, below an HRT of 7 days, removal efficiencies decreased dramatically.

Van Den Berg and Lentz [39] studied the effect of surface-to-volume ratios on the performance of upflow anaerobic filters. The filters were operated at 35°C and consisted of a small diameter (1.0 to 7.5 cm) glass column (for simplicity in predicting active surface area-to-volume ratios). The substrate was a bean blanching waste which had a COD of 10,500 mg/L and a total volatile solids content of 8,400 mg/L. The filters were operated at HRT's ranging from 0.55 to 2.6 days and loading rates of 3.2 to 15.3 kg VS/m^3/day. The recirculation ratio was 4:1. The COD and volatile solids (VS) removal efficiencies were 83 to 91% and 77 to 86%, respectively, with the higher removals occurring in the reactors with the higher surface area-to-volume ratio. Van Den Berg and Lentz note that the filters in the study were not true fixed film reactors; that is, much of the microbial activity is the result of suspended biomass, rather than attached biomass. The authors also note that much of the activity is in the lower portion of the reactor, which may lead to channelling or short-circuiting of the substrate and plugging of the media with biomass. The authors point out that a downflow anaerobic reactor would solve these problems, and would also act as a true fixed film reactor. This type of reactor was also studied, and the results are detailed later.

In 1983, Henze and Harremoes [19] undertook an extensive literature review related to anaerobic waste treatment with fixed film reactors. This study summarized numerous articles with respect to start-up of the reactors, substrate type, attached verses suspended biomass, organic loading rates, and hydraulic loading rates, as well as process efficiencies.

Henze and Harremoes summarized their literature review as follows: (1) Fixed film anaerobic treatment is feasible for warm wastes with a high concentration of biodegradable organic matter; colder and more dilute wastes are not yet cost effective to treat, but this may change in the future. (2) Substrate type is very important to process design--acetic acid is removed at much higher rates than more complex organics, such as sucrose. (3) Many anaerobic filters operate with significant amounts of suspended biomass in addition to the attached biomass, which makes design of such reactors more difficult. (4) The question of whether there is diffusional resistance within the biofilm is inconclusive. (5) The existence of a biofilm structure is beneficial with respect to resistance against toxic shocks and acts as a safeguard against biomass washout; the mechanisms responsible for the development of biofilm on support material and in granules is not well understood. And (6) start-up problems associated with anaerobic processes are often the result of a lack of a basic understanding of the microbiology and biochemistry involved, and could be reduced through increased knowledge of biofilm build-up, nutrient and micronutrient requirements, pH, and temperature effects.

Gourdon *et al.* [12] attempted to describe and model the kinetics of volatile acid removal in an anaerobic filter. The filter consisted of seven separate compartments filled with grains of vermiculite and was operated horizontally at a temperature of 35°C. The substrate used was a landfill leachate to which volatile acids were added (acetate, propionate, or *n*-butyrate). The COD of the substrate was approximately 1930 mg/L and the filter was operated at an HRT of 0.5 hours per compartment. The authors concluded from their study that the removal of volatile fatty acids in an anaerobic filter is a very complex process, and that any complete model would be impractical for most treatment applications. They also conclude that simple Michaelis-Menten kinetics (for acetate and butyrate) or first-order kinetics (for propionate) are adequate to describe the apparent removal rates of those volatile fatty acids.

Liu *et al.* [28] also developed a model to simulate the behavior of a packed-bed anaerobic reactor. The basic assumptions of the model are those prescribing steady-state conditions, acetic acid fermentation as the most prevalent reaction, a homogeneous solid phase, a completely-mixed liquid phase, and a negligible concentration of suspended biomass as compared to the attached biomass. The filter media used was Haydite (a light-weight aggregate), and the reactor was operated at 35°C. A recirculation ratio of 20:1 was used to ensure a relatively low influent COD concentration (< 3,000 mg/L) and also to ensure that the liquid phase approached an ideal completely-mixed reactor. The HRT was set at three days and organic loading rates ranged from 3.33 to 19.98 kg COD/m^3/day. The substrate used was a concentrated solution of volatile acids, including acetic, propionic, butyric, valeric, and caporic acids.

The model used in Liu *et al.*'s study [28] was a Monod-type expression which disregarded mass-transport resistances. The model was used to predict the biofilm depth on the support media as a function of the organic loading. From this value, then, the authors claim to be able to compute the total biomass in the reactor, which then leads to a direct calculation of solids retention time (SRT). SRT's as long as 2,700 days were estimated. The model also predicted the organic loading rate at which deterioration of the effluent will occur. The authors suggest a maximum organic loading rate of 13.3 kg COD/m^3/day for the reactor studied. Beyond this value, biofilm depth remains constant and suspended biomass becomes significant, which contributes to increased biomass concentrations in the effluent and shorter SRT's.

In the writer's view, the model developed by Liu *et al.* [28] is overly simplistic, especially with regard to the initial assumption of a negligible concentration of suspended biomass as compared to the attached biomass. In most of anaerobic systems, the majority of the biomass within the system is suspended, not attached.

Harris and Dague [16] studied the effect of temperature on anaerobic filters. The authors operated two reactors at mesophilic temperatures (35°C) and two at thermophilic temperatures (56°C). HRT values of 12, 24, and 48 hours and organic loading rates of 2.75 to 49.5 kg/m^3/day were studied with the intention of determining the effect of these two parameters as independent variables. The authors used a non-fat dry milk as the substrate for all experiments. The non-fat dry milk consisted mainly of lactose (51%) and protein (36%), with smaller amounts of fat (<1%) and ash (8.2%). Each reactor was fully packed with 16 mm Flexirings (Koch Engineering Co., Wichita, KS), and effluent was recycled at a ratio of 1:1.

The results of Harris and Dague's study [16] indicate the following: (1) The effect of decreasing HRT on COD removal efficiency is more significant at mesophilic temperatures than at thermophilic temperatures. (2) Anaerobic filters operated at thermophilic temperatures are capable of higher COD loadings than filters operated at mesophilic temperatures. (3) In the thermophilic filters, as the HRT was decreased, the effect of increasing the COD loading decreased, which may indicate that the thermophilic reactors were inhibited at the longer HRT's. (4) The COD removal efficiency of the mesophilic reactors decreased as a result of both an increase in the COD load and a decrease in HRT. And (5) the filters operated at thermophilic temperatures adapted to changes in the organic load more quickly than the filters operated at mesophilic temperatures.

Weiland [41] reported on the current status of anaerobic filters in Europe. Weiland states that two-phase operation of the filters is usually practiced for flow equalization and for liquefaction of suspended solids and acidification of complex organic compounds. The media used in the filters ranges from plastic rings to lava slag to porous glass rings, and loadings are generally 4 to 10 kg COD/m^3/day, but may be as high as 60 kg COD/m^3/day. The author describes an interesting design in which two different plastic support media are used. In the lower part of the reactor, plastic rings with a relatively small surface area and open ring walls are used to decrease the risk of clogging. In the upper part of the filter, plastic rings with a high specific surface area are used to enhance biofilm attachment in this portion of the filter and to decrease suspended solids concentrations in the effluent. Weiland also reports on newly developed support material which have extremely high specific surface areas. One macroporous glass support (SIRAN, Schott-Glaswerke Company, location not given) has a specific surface area of 30,000 m^2/m^3, with pore diameters between 60 and 300 μm. Extremely high biomass retention capabilities are reported with these support materials, but, due to high production costs, the use of these materials is normally limited to small waste streams with high organic loads.

Young [43] summarized some of the design and operating factors for upflow anaerobic filters. The recommended medium is a cross-flow type with a specific surface area of 95 m^2/m^3 or greater. Reactor height is suggested to be between 3 and 13 meters, and the height to width ratio is not restricted. Sludge withdrawal from the filter should be made possible by incorporating pipe headers along the height of the reactor. Staging is suggested for phase separation and equalization, and cyclic operation of two filters in series can be used to decrease the effects of clogging (the first filter would take the majority of the load while the second filter would undergo a starvation effect and lose biomass through endogenous respiration, and then the process is reversed). Young suggests a hydraulically-controlled system if the ultimate biochemical oxygen demand (BOD_u) is less than about 12,000 mg/L, and an organic loading-controlled system if BOD_u is greater than 12,000 mg/L. HRT's from 9 to 96 hours should be used, with upflow velocities less than 25 m/day at the maximum HRT. Organic loading rate should be less than 16 kg $COD/m^3/day$, depending on the waste strength and HRT, and recycle generally should be used.

Young states that the major parameters to consider in designing an anaerobic filter are hydraulic retention time, media specific surface area, and influent wastewater strength.

3. Development of the downflow anaerobic fixed film reactor

Van Den Berg and Lentz [39] noted several problems associated with the upflow anaerobic filter, most notably channeling of the substrate through the filter because of the large amount of suspended biomass which may clog the filter. They also noted that a downflow mode of operation could actually be operated as a strict attached film reactor, which is not possible with the upflow mode, and that a downflow reactor has fewer limitations with respect to the height of the reactor. Van Den Berg and Lentz were not aware of any previous studies dealing with downflow anaerobic filters; therefore, this article was apparently the first of its kind.

The filters in van den Berg and Lentz's study were operated at 35°C and consisted of a small diameter (1.0 to 7.5 cm) glass column (for simplicity in predicting active surface area-to-volume ratios). The study was conducted simultaneously with identical upflow reactors, the results of which were previously reported. The authors were interested in studying the effect of varying the surface-to-volume ratios on the performance of downflow anaerobic filters. The substrate used was a bean blanching waste which had a COD of 10,500 mg/L and a total volatile solids content of 8,400 mg/L. The filters were operated at HRT's ranging from 0.55 to 2.7 days and loading rates of 3.1 to 15.3 kg VS/m^3/day. The filters were operated in a submerged mode with effluent recirculation. The COD and volatile solids (VS) removal efficiencies were 81 to 90% and 76 to 82%, respectively, with the higher removals occurring in the reactors with the higher surface area-to-volume ratio. These removal values compared closely to the identical filters that were operated in an upflow mode.

In 1985, Kennedy *et al.* [24] studied the stability and performance of the downflow anaerobic filter during organic overloading. The authors reported on the effects of severe, 24-hr organic overloading on the performance of downflow anaerobic filters during treatment of a soluble sucrose waste at 27 and 35°C and an acetic acid wastewater at 27°C. Buffered and unbuffered wastewaters were used in the experiments.

The filter media consisted of needle-punched polyester sewed onto a wire frame. Filters were operated in a submerged mode to protect the biomass and to enhance mixing of the reactor liquid with the incoming substrate. Liquid effluent was recirculated at a rate of 4 times the feed flow, and the HRT of the filters varied between 1 and 2.3 days.

The results of this study indicate that the downflow filters could handle substantial organic overloads with only temporary fluctuations in reactor performance. However, extended recovery periods were required after extreme overloads. The filters treating sucrose at 35°C required up to 7 days to fully recover after a 24-hr overload of 50 kg COD/m^3/day, and a similar time was required for the filters operating at 27°C after an overload of 33.3 kg COD/m^3/day (7 times the normal loading rate). The filters treating acetic acid were even more sensitive, requiring longer periods of recovery at loads of 25 kg COD/m^3/day (5 times the normal loading rate). For unbuffered wastes, lower organic loads could be tolerated, and recovery periods were longer for similar overloadings.

Hamoda and Kennedy [15] studied the effect of hydraulic and organic loading rates on steady-state performance of downflow anaerobic filters, including the effects of biofilm concentration on process efficiency. The filter media consisted of needle-punched polyester sewed onto a wire frame, and, in addition, the authors incorporated removable biofilm supports so that biofilm solids concentration could be determined at each steady-state condition. The filters were operated in a submerged mode, and high recirculation rates were used. Acetic acid was used as the sole carbon source and all experiments were conducted at 35°C. The HRT ranged from 0.4 to 5.7 days and the organic loading rate varied from 0.66 to 17.15 kg COD/m^3/day.

Hamoda and Kennedy's study indicates the following: (1) COD removal efficiency increases with increasing HRT. Generally, an HRT in excess of 1 day was required for stable operation of the filters. (2) COD removal efficiency increases with decreasing organic loading rate. At the longer HRT's, organic loading rates of more than 17 kg COD/m^3/day could be achieved with more than an 80% COD removal efficiency. And (3) the biofilm concentration (and thickness) increased as the organic loading increased and decreased as the HRT increased. The biofilm concentration reached a maximum value of 8.3 kg VSS/m^3 at a loading rate of 17 kg COD/m^3/day.

4. Development of the expanded-bed anaerobic reactor

A brief description regarding the expanded-bed anaerobic reactor is given because of the similarities to the upflow anaerobic filter. The expanded-bed reactor (EBR) was developed in order to overcome the problem of clogging that sometimes occurs in the upflow anaerobic filter. With the use of high upflow velocities, the media (usually sand, glass, or activated carbon) is expanded, or fluidized, creating a high surface area for biomass attachment but preventing clogging. A basic disadvantage of the process is the high effluent recirculation required to expand the media bed.

Wang *et al.* [40] studied the treatment of an acetic acid wastewater using the EBR with granular activated carbon as the media. The reactor was operated at 35°C, and a bed expansion of approximately 25% was maintained by recirculating effluent at about 1000 times the influent feed flow rate. The HRT was maintained constant (value not given), and the acetate concentration in the feed ranged from 800 mg/L to 6,400 mg/L. The results showed that removal of acetic acid and COD exceeded 98 and 97%, respectively, for all concentrations studied (steady-state). The authors also note that the EBR responded positively to sudden increases in the organic load. A doubling of the organic load caused an almost immediate doubling in the gas production rate.

Fox *et al.* [11] compared the performance of EBR's with respect to media types. The media types used were low-density anthracite (0.7 mm average diameter), granular activated carbon (0.7 mm average diameter) and two sizes of sand (0.35 and 0.7 mm average diameters). Temperature was 35°C, bed expansion was 50%, and acetate was used as the sole organic source. The HRT and organic loading rate were maintained at 12 hours and 10.6 kg COD/m^3/day, respectively.

Results from Fox's study show that removal efficiencies for all media were consistently greater than 90%. The granular activated carbon (GAC) accumulated biomass at a faster rate during start-up than the other media studied, and, therefore, required less time to reach maximum efficiency based on COD removal.

5. Development of the upflow anaerobic sludge blanket reactor

A new type of reactor for the treatment of low and medium strength wastes is normally credited to Lettinga of the Netherlands. In their 1980 paper, Lettinga *et al.* [26] introduced this new reactor, termed the upflow anaerobic sludge blanket (UASB) reactor, which had been studied in their laboratories since 1971. The UASB is similar to the upflow anaerobic filter, except that the UASB does not contain media to support the biological growth. Instead, the UASB relies on the formation of a "sludge blanket," which is suspended in the bottom of the reactor. The weight of the sludge blanket is counteracted by the upward velocity of the influent feed.

The authors studied many different substrate types and loading combinations, and found that the UASB could handle organic loading rates in excess of 25 kg COD/m^3/day and hydraulic retention times as low as 3 hours. An important operational characteristic of the UASB is the formation of a sludge of superior quality with respect to settling and specific gravity. The formation of this sludge, known as granular sludge, was thought to be the result of a combination of factors: (1) the sludge was exposed to varying forces of gravity compression; (2) the creation and maintenance of favorable conditions within the reactor, especially the presence of calcium ions and other nutrients, gentle mixing from gas releases, and the absence of a high concentration of poorly flocculating suspended matter in the wastewater; and (3) the finely dispersed fraction of the sludge will naturally be washed out with the effluent, leaving the high quality sludge behind.

In a later paper, Lettinga *et al.* [27] studied the effect of temperature on the UASB reactor performance. The UASB was shown to be efficient in the treatment of several wastes (volatile fatty acids, alcohol, potato processing) at temperatures ranging from 19 to 35°C. The COD loads ranged from 3 to 62 kg/m^3/day, and COD removals (filtered) were consistently greater than 90%. Thermophilic temperatures were cited as future targets of study.

It is generally accepted that the performance of the UASB depends largely on the formation of a granular sludge. The mechanisms responsible for granular sludge formation are not well understood, however. Dolfing *et al.* [9] reported on the chemical and bacteriological composition of a granular sludge which had been cultivated on a waste stream of a liquid sugar plant. The chemical composition of these granules is given below in Table 3.

Table 3. Chemical composition of various granular sludges

Component	Percent of dry weight
Ash	10 - 23
Protein	35 - 60
Carbohydrate	
Total	6 - 7
Extracellular	1 - 2
Total Organic Carbon	41 - 47
Kjeldahl Nitrogen	10 - 15

This study determined that the various groups of bacteria are randomly distributed throughout the granule with no obvious internal organization. The densities of the granules were found to be 1.00-1.05 g/cm^3, which is the same as the densities found for dispersed bacterial cells as reported by

Woldringh *et al.* (1981). This indicates that the settling properties of the granular sludge are mainly due to the aggregation of the microorganisms, rather than a physical property of the granule itself.

Hulshoff Pol and Lettinga [22] presented further insight into the granulation process. Granulation occurs more quickly as waste strength decreases, provided the waste strength is high enough to support bacterial growth. Carbohydrate substrates generally enhance granulation more effectively than mainly VFA-substrates. Another important condition is the presence of high calcium and/or magnesium ion concentrations, which will lead to a granular sludge with a high ash content (inorganic matrix).

6. Development of the hybrid anaerobic filter

The hybrid anaerobic filter, also known as the upflow blanket filter (UBF) combines the standard upflow anaerobic filter with the upflow anaerobic sludge blanket reactor in a single reaction vessel. Normally, the bottom one-third to two-thirds of the reactor are left empty, while the remaining portion is filled with the filter media. A sludge blanket normally forms in the lower, empty portion of the UBF, and further biological mass is retained in the upper portion on and within the filter media. This type of reactor has several advantages over the conventional anaerobic filter. Capital costs are reduced because of the smaller amount of filter media required. Compared with the fully-packed anaerobic filter, the clogging and channeling in the UBF are reduced, since the biomass in the lower portion of the reactor are not held in a fixed position but are actually suspended in the reactor. The UBF also may improve the UASB effluent quality by removing the lighter flocculent particles which escape from the sludge blanket.

Guiot and van den Berg [13] studied a UBF which consisted of an open volume in the bottom two-thirds of the reactor with the top third containing plastic rings as the support media. The authors used a soluble sugar waste as the substrate, and the reactors were operated at 27°C. The COD removal efficiencies were above 95% for loads up to 25 kg COD/m^3/day. Similar removal efficiencies were obtained when the HRT was reduced to as low as 3 hours.

Droste *et al.* [10] used a similar UBF to treat domestic strength wastewater (300-1,000 mg COD/L) at 27°C. Results indicate that 95% soluble COD removal efficiency at HRT's down to 3 hours were possible.

Kennedy *et al.* [23] conducted studies on the UBF to determine the effects of media type and media depth on process efficiency. Results indicate that media type (cross-flow and random-pack) and depth have very little effect on the overall performance of the UBF. Random-pack media and cross-flow media with a low angle of inclination offered slightly better solids retention at short HRT's and high organic loading rates. These media also enhanced granulation of the sludge slightly, but these small differences were not conclusive enough to make an absolute statement regarding the superiority of one media over another.

Chang [3] used a lab-scale UBF to treat landfill leachate at 35°C. The raw leachate had a pH of 5.5 and an alkalinity of 8,500 mg/L, as $CaCO_3$, and VFA's represented 66% of the total COD (58,400 mg/L). Loadings of up to 12.8 kg COD/m^3/day were obtained with soluble COD removals in excess of 92%. At a load of 21.8 kg COD/m^3/day, soluble COD removal was 71%. Chang conducted studies with and without buffer addition and found little difference in process efficiency.

Young and Young [46] documented the performance of two full-scale UBF's operating on a highly variable wastewater which had a fluctuating COD value of 10,000 to 30,000 mg/L at flows of 400 to 1,300 m^3/day (organic load of 2 to 4 kg COD/m^3/day). The treatment system also was exposed to varying levels of methanol, phenols, and solvents. Initially, the UBF's were operated in parallel, and COD removals stabilized at about 80%. After one year of operation, the UBF's were switched to series operation and COD removals increased to approximately 94%. It is interesting to note that the UBF's handled periods of rest quite well, and in some instances the rest periods actually seemed to enhance performance.

III. EXPERIMENTAL SETUP

For the entire length of these experiments, three anaerobic reactors (filters) were used: two of the reactors were fully-packed and one was partially-packed with the bottom third of the reactor void of media. All three of the reactors were identically designed, with the exception that one of the reactors was not fully-packed. Therefore, all descriptions of reactor systems will apply to all three reactors, except where noted. All three reactors were housed in a single incubator (Isotemp Low Temperature Incubator, Fisher Scientific, Pittsburgh, PA), and were maintained at 35°C (+/- 0.5°C).

A. Reactor Dimensions

The filters were comprised of three identical Plexiglas sections, each separated by a 1/4 in. screen to ensure that media in the upper sections did not migrate downward and clog the lower section. The reactor had a total height of 37-7/8 in., with each section of the reactor having a height of 12 in.; a 1-1/2 in. base plate was attached to the bottom of the reactor to distribute the flow to the reactor. Sections were connected to each other with twelve 1/4-in. nuts and bolts, and a rubber gasket was placed between sections to ensure an air-tight connection. The reactor sections had an inside diameter of 4-1/2 in. with 1-in. flanges to allow connection of the sections. The lower flanges had a deflector to reduce wall effects (short circuiting of the substrate along the walls of the reactor), and each section of the reactor had a 3/16-in. sampling port at its midpoint.

The media used in all reactors was 5/8-in. Flexirings (Koch Engineering Company, Witchita, KS), and, as earlier stated, two of the reactors were completely filled with the Flexirings while the third (termed the "hybrid") was filled with Flexirings only in the top two-thirds of the reactor. The empty bed volume of each reactor was 9.5 liters. The media had a void ratio of approximately 90 percent and a specific surface area of 98 m^2/m^3. All reported hydraulic and organic loads are reported based on empty bed reactor volume (9.5 liters).

Figures 2 and 3 illustrate the reactor configuration.

B. Influent/Effluent Liquid Handling System

The influent feed was pumped from 50-liter carboys using Masterflex peristaltic pumps (Cole-Parmer Instrument Co., Chicago, IL). The tubing from the carboy to the pump had an inside diameter of 3/16 in. (5/16-in. O.D.). Size 14 (approximately 1/16-in. I.D.) Masterflex C-Flex tubing was used in the pump, and all other influent lines were 7/16-in. O.D. by 5/16-in. I.D. Masterflex tubing. The influent line

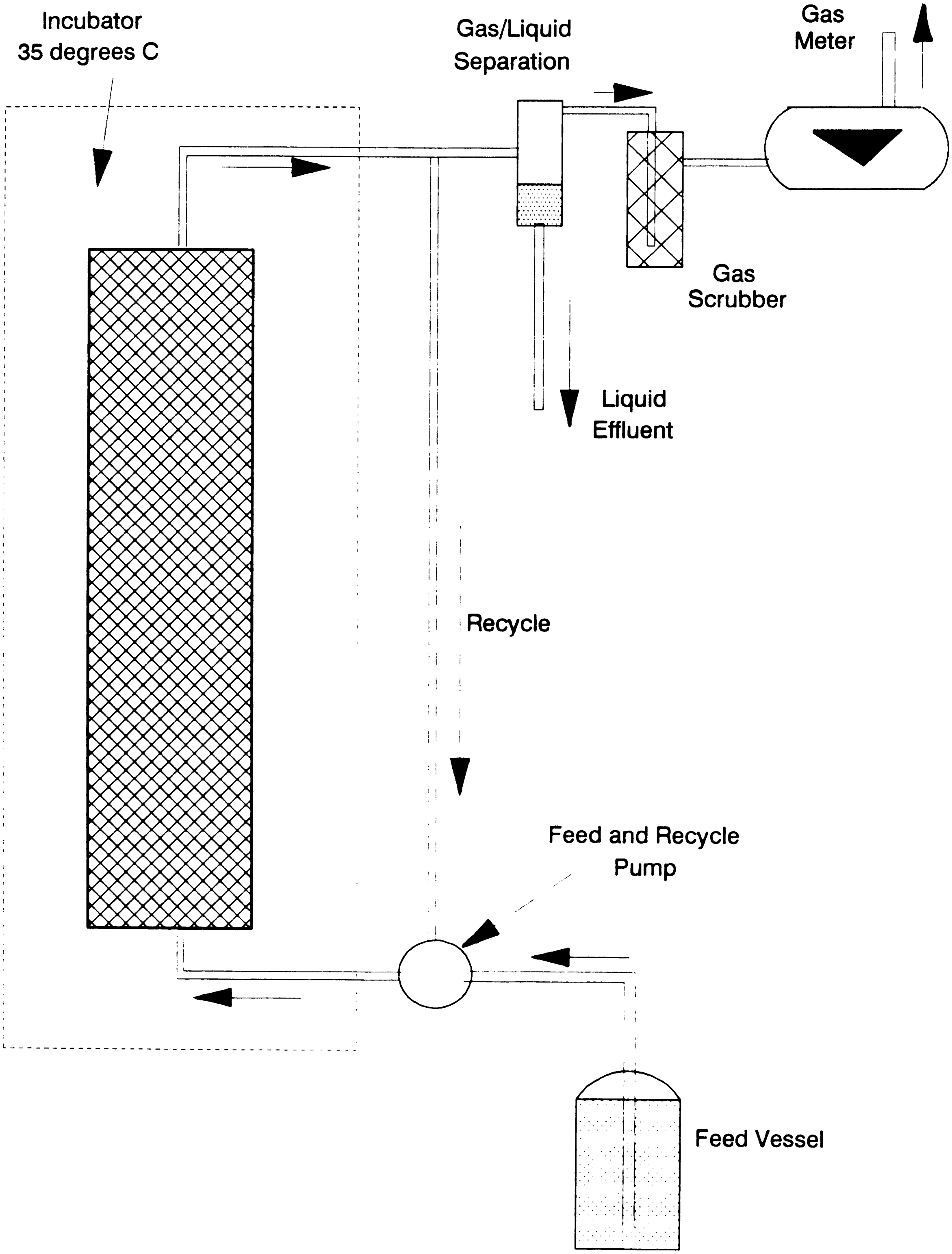

Figure 2. Experimental setup for a typical reactor

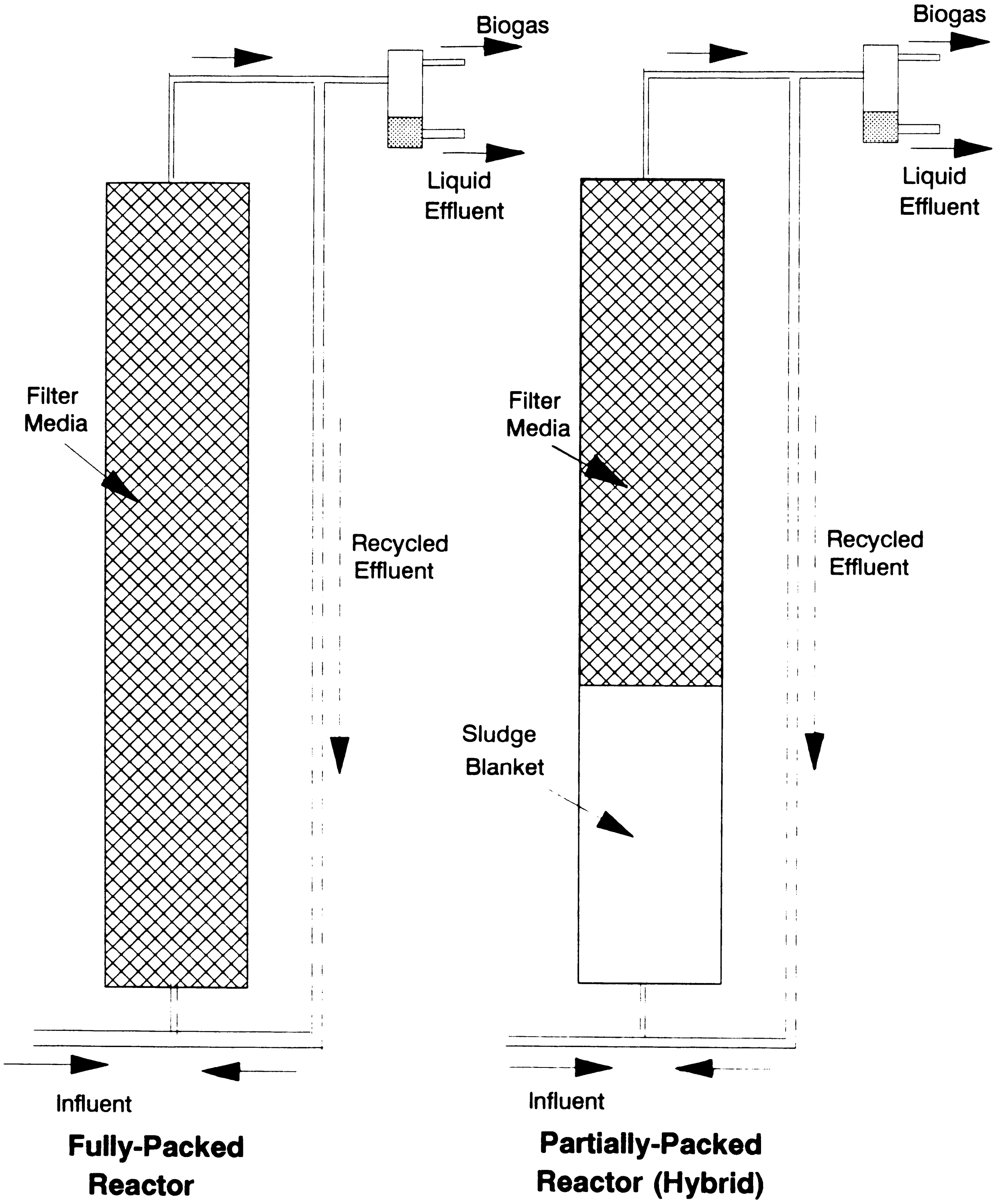

Figure 3. Illustration of the anaerobic filters

entered the anaerobic filter through a single port in the center of the bottom of the reactor.

The liquid effluent exited the top of the reactor through 5/16-in. tubing. The liquid effluent was recycled at a rate of 100% of the influent rate through a T-connection in the effluent line. The recycled effluent was pumped back to the influent line and connected with the raw feed line before entering the reactor. The liquid effluent (which contained biogas) from the system entered a gas-liquid separation bottle (1 liter volume), with the gas exiting the separator bottle at the top and the liquid through a port at the bottom. The liquid effluent was discharged to the sanitary sewer.

C. Gas Handling and Measurement

The gas-liquid separator bottle was capped with a rubber stopper to ensure against loss of gas to the atmosphere. The gas left the separator bottle through 3/16-in. I.D. Masterflex tubing, which led out of the incubator to the gas collection system. The gas entered an observation bottle, which was filled with water to aid in visual observation of gas formation. From there the gas passed through a hydrogen sulfide scrubber (1-liter bottle filled with steel wool) to protect equipment from corrosion. After the scrubber, a gas sampling device was installed in the gas line. The sampling device consisted of a glass bulb with a port in the side. A rubber septum was fitted into this port, enabling a metal syringe needle to be inserted through the septum and into the glass bulb for gas sampling while keeping the system air-tight. From the gas sampling device, the gas line entered Rebel Point Wet Tip gas meters for gas measurement.

IV. EXPERIMENTAL PROCEDURES

A. Reactor Startup

The reactors were initially filled with new 5/16-in. Flexirings and sealed. The reactors were purged with methane to eliminate any oxygen in the system and to test the gas collection system for leaks. The seed sludge was then pumped into the reactors using peristaltic pumps. The seed sludge was obtained from the anaerobic digesters at the Ames water pollution control plant in Ames, Iowa. The sludge was passed through a 1-mm mesh screen, diluted by 50% with tap water, and then pumped into the reactors. The seeded reactors were then allowed to stand for 24 hours without feeding.

After the 24-hr standing period, the reactors were fed (continuously) at an organic loading rate (OLR) of 0.5 kg COD/m^3/day and a hydraulic retention time (HRT) of 48 hr. (Note: The furfural wastewater was used as the substrate during startup and during the normal operation of the filters.) The reactors were operated at this OLR and HRT until all reactors were achieving 90% removal of COD on a steady-state basis. The reactors were then fed at an OLR of approximately 3 kg COD/m^3/day and an HRT of 48 hr for a period of 3 months to develop a relatively mature biomass in the reactors.

B. Feed Preparation

1. Furfural wastewater storage

The furfural wastewater was obtained from the Quaker Oats Company in Cedar Rapids and transported to the Environmental Engineering Laboratory at Iowa State University in Ames, Iowa, as required. The raw wastewater was stored in a 200 gallon fiberglass tank and drawn from this tank for preparation of the feed solution. (Note: The pH of the raw furfural wastewater was approximately 2.6; therefore, little, if any, degradation of the wastewater occurred while it was stored. COD analysis of the stored wastewater over time verified this.) During storage in the fiberglass tank, the solids that were in the furfural wastewater settled out. The solids level in the raw and settled furfural wastewater were approximately 350 and 50 mg/L, respectively. The solids that settled out of the furfural wastewater were emptied from the storage tank as needed and disposed of into the sanitary sewer system. The COD of the furfural wastewater as taken from the storage tank was variable, but normally between 10 and 12 g/L.

2. Chemical additions

The furfural wastewater characteristics were given in the introduction section of this report. As stated, the furfural wastewater is virtually devoid of essential nutrients (N,P,K) and trace metals, and is low in pH; therefore, chemical additions in the form of nutrients, trace metals, and buffering chemicals were required to ensure stable operation of the anaerobic filters.

A stock solution of trace minerals was prepared and added to the feed vessel containing the furfural waste. Table 4 shows the specific recipe of minerals and metals used in the stock solution. This stock solution was added (batch addition) to the influent feed vessel at the rate of 0.6 mL mineral stock solution per gram of COD fed to the reactors.

Table 4. Trace mineral stock solution

Chemical Compound	Amount in Stock Solution	Amount Added (per gram COD)
$FeCl_2 \cdot 4H_2O$	3.560 g/L	2.14 mg
$ZnCl_2$	0.208 g/L	0.12 mg
$NiCl_2 \cdot 6H_2O$	0.405 g/L	0.24 mg
$CoCl_2 \cdot 6H_2O$	0.405 g/L	0.24 mg
$MnCl_2 \cdot 4H_2O$	0.360 g/L	0.22 mg
$Na_2S \cdot 9H_2O$	13.000 g/L	7.80 mg

Nitrogen, potassium, phosphorous, and buffering chemicals were added as shown in Table 5. All chemicals were added in proportion to the COD fed to the reactors. The chemicals were first dissolved in approximately 2 liters of the raw furfural wastewater and then this volume was added to the feed vessel.

3. Influent feed mixing

The feed for the reactors was mixed as follows: (1) the appropriate volume of raw furfural wastewater was taken from

Table 5. Nutrients and buffering chemicals

Chemical Compound	Amount Added (per gram COD)
NH_4OH (29% NH_3)	0.4667 mL
$(NH_4)_2HPO_4$	0.0400 g
KOH	0.1000 g
NaOH	0.1000 g

the fiberglass storage tank and put into a 50-L carboy; (2) the appropriate amounts of nutrients and buffers were dissolved in 2 liters of the raw furfural wastewater and then poured into the remaining volume of wastewater; (3) the trace mineral stock solution was added to the carboy in the appropriate amount; (4) tap water was added to the carboy until the specified volume of influent feed was established (usually 50 L total volume); (5) the carboy was mixed by shaking, and the pH of the feed mixture was measured (the influent was fed at a pH of approximately 4.5); and (6) the influent pump tubing was placed in the carboy, and the reactors were fed directly from the carboy.

C. Daily Maintenance of System

The daily maintenance of the reactor system does not include any of the experimental testing, which will be detailed later in this thesis.

Daily maintenance consisted of (1) recording the gas-measurement reading for all reactors at approximately the same time each day; (2) recording the temperature and pressure in the laboratory (for standardization of gas measurements); (3) feeding the reactors (note: feeding did not always take place daily, depending on the HRT of the reactors); and (4) checking of all equipment for obvious problems, especially for leaks in the gas lines and in the pump lines.

D. Experimental Testing

Several tests were conducted regularly on the operating anaerobic filters. These included (1) influent and effluent total and soluble COD, (2) influent and effluent suspended solids and volatile suspended solids, (3) effluent volatile fatty acids, (4) effluent alkalinity, (5) influent and effluent pH, and (6) biogas composition analysis.

1. Chemical oxygen demand (COD)

The COD test used was the closed reflux method given in Standard Methods [37]. All COD tests were conducted in test tubes and capped with Teflon-lined screw caps. The test consisted of 5 mL liquid samples to which was added 3 mL 0.1 normal $K_2Cr_2O_7$ containing 33.3 mg/L $HgSO_4$, and 7 mL concentrated H_2SO_4 containing 10.0 mg/L $AgSO_4$ (all samples were prepared in duplicate). After the COD samples were prepared, the samples were placed in a 150°C oven for two hr. The samples were then allowed to cool for at least two hr, after which they were titrated to the ferrion endpoint with 0.1 normal ferrous ammonium sulfate (FAS). Two blanks and two standards, which used 5 mL of distilled water in place of the reactor samples, were used to standardize the $K_2Cr_2O_7$ and FAS, respectively. The blanks and standards were treated exactly as the reactor samples, except that the standards were not placed in the oven. The COD of a sample was calculated as

$$\mathrm{COD} = \frac{(A - B)*M*(8{,}000)*(DF)}{V}$$

where: COD = chemical oxygen demand of sample, mg/L
A = volume of FAS required to titrate a blank to the ferrion endpoint, mL
B = volume of FAS required to titrate a sample to the ferrion endpoint, mL
M = molarity of the FAS solution, mol/L
DF = dilution factor of the sample
V = sample volume, mL
8,000 converts mol FAS to mg O_2

Since this version of the COD test has a theoretical measuring capacity of 480 mg O_2/L, dilution of the samples was required in most cases. Both the reactor influent and effluent were tested for total and soluble COD. COD tests to confirm steady-state conditions were conducted after at least 4 HRT's after changing the organic load to the reactors. Steady-state was assumed if three successive COD tests (conducted over a period of not less than 5 days) were within 2% of each other on a percentage removal basis. This criterion was established because of the variable nature of the furfural wastewater; that is, it was difficult to mix a batch of feed that had the identical COD strength on a day-to-day basis. At each COD load, the steady-state removal efficiency of the reactor was determined from the average of the three COD analyses.

2. Suspended solids and volatile suspended solids

The suspended solids (SS) and volatile suspended solids (VSS) tests were conducted mainly to keep records of the solids that escaped from the reactor. Since the furfural wastewater is a very soluble substrate, the effluent from the reactor contained more SS than did the influent. Thus, SS removal efficiency is meaningless for these experiments. As noted earlier, the purpose of the SS and VSS tests were to observe the trends in solids loss as a function of organic loading rate and hydraulic retention time. SS and VSS tests were conducted at the same time and from the same samples as were the COD tests.

The SS and VSS tests were conducted according to standard procedures [37]. The tests were conducted using Whatman GFA filter paper (0.5 µm). Each filter paper was placed in an aluminum weighing dish and heated at 550°C for 20 minutes to burn off any volatile contaminants. After burning, the filters and dishes were placed in a desiccator to cool, after which each was weighed to the nearest tenth of a milligram using an electronic scale. The reactor samples (50 mL) were then passed through the filter paper (with duplicates) using a vacuum, and the aluminum dish and soiled filter paper were dried in a 103°C (+/-0.5°C) oven for one hr. After drying, the dishes with filters were cooled in a desiccator for not less than one hour and then weighed. The suspended solids in the samples were then calculated as

$$SS = (C-D) * 20,000$$

where: SS = suspended solids concentration in sample, mg/L
C = weight of aluminum dish and filter paper after drying, grams
D = weight of aluminum dish and filter paper before filtering, grams
20,000 converts from grams/50 mL to mg/L

To determine VSS, the dishes with filters were placed in a 550°C (+/-15°C) oven for 20 minutes for volatilization of the non-inert material in the samples. After burning, the dishes with filters were cooled for one hour in a desiccator and then weighed again. The VSS were calculated as

$$VSS = (C-E) * 20,000$$

where: VSS = volatile suspended solids concentration in the sample, mg/L
C = weight of aluminum dish and filter paper after drying, grams
E = weight of aluminum dish and filter paper after burning, grams
20,000 converts from grams/50 mL to mg/L

3. Volatile fatty acids

Volatile fatty acids (VFA) testing was conducted on alternate days as were the COD tests and also during the time immediately after a change in COD loading. The VFA tests were conducted using a modified distillation approach [37]. One-hundred mL samples were taken from the reactor effluent and added to 100 mL distilled water and 5 mL concentrated sulfuric acid. This solution was then heated to evaporation on electric burners and passed through the distillation columns. The distillate was collected (150 mL) and titrated to a pH of 8.3 using 0.1 N NaOH. The VFA of the samples was calculated as

$$\text{VFA} = \frac{(V_{NaOH})*(0.1)*(60{,}000)}{(V_{samp})*(0.7)}$$

where: VFA = volatile fatty acid concentration in sample, mg acetic acid/L
V_{NaOH} = volume of 0.1 N NaOH required to titrate the sample to pH 8.3, mL
0.1 = normality of NaOH solution, equiv/L
60,000 = milliequivalent weight of acetic acid, mg/equiv
V_{samp} = Volume of sample taken from reactor, 100 mL
0.7 = assumption that 70% of the VFA's are accounted for by this method

4. Alkalinity

Alkalinity of the reactor effluent was measured on the same days as was VFA to establish the relationship between the two parameters at various loadings. Alkalinity was measured by titrating a known volume of reactor effluent to pH 4.5 with 0.1 normal H_2SO_4. The alkalinity was calculated as

$$\text{Alk} = \frac{(V_s)*(0.1)*(50,000)}{V_{samp}}$$

where: Alk = alkalinity of sample, mg $CaCO_3$/L
V_s = volume of H_2SO_4 required to titrate sample to pH 4.5, mL
0.1 = normality of H_2SO_4, equiv./L
50,000 = milliequivalent weight of $CaCO_3$, mg/equiv.
V_{samp} = volume of sample, mL

5. pH

The reactor pH, influent pH, and effluent pH were all measured on a regular basis. Reactor pH was measured at the bottom, middle, and top of the reactor (via sampling ports) when the reactor appeared to be upset in any way. Influent pH was measured whenever a new batch of feed was prepared, as earlier stated. Effluent pH was measured on a semi-daily basis and also when conducting the alkalinity test. All pH measurements were conducted using an Orion Digital pH meter (Beckman Instruments, Inc., Irvine, CA) which was calibrated before each use using standard pH solutions of 7.00 and 10.00.

6. Biogas composition analysis

The composition of the biogas generated from the reactors was analyzed using gas chromatography (GC) on a daily to weekly basis, depending on the HRT and availability of the testing equipment. Samples were collected using a 1-mL syringe (Hamilton Company, Reno, NV) equipped with Metal Hub Needles (Alltech Associates, Inc., Deerfield, IL). Nine-tenths of a mL of biogas was withdrawn from the gas sampling ports (earlier described) and the gas was then injected into the gas chromatograph. Methane, carbon dioxide, and nitrogen percentages in the biogas were determined. (The nitrogen percentage of the total biogas was generally less than 1%.)

The GC equipment included a Model 69-350 Thermal Conductivity Gas Chromatograph (GOW-MAC Instrument Company, Bridgewater, NJ), equipped with a 6-ft. long by 1/8-in. in diameter GC column with Porapak-Q 80/100 mesh column packing.

The temperatures of the various GC equipment were as follows:

injector port	100°C
detector	150°C
column	ambient
outlet	70°C

The carrier gas was helium, and the gas used for standardization was a custom grade blend comprised of 70% methane, 25% carbon dioxide, and 5% nitrogen. The data from the gas analysis were collected and analyzed using the Baseline 810 Chromatography Workstation software package (Waters Dynamic Solutions, Division of Millipore, Ventura, CA).

E. Experimental Design

1. General background

The experiments in this study were designed to independently determine the effects of COD loading rate and hydraulic retention time (HRT) on the COD removal efficiency of the anaerobic filters. The ultimate goal of the research was to operate the filters at saturation loading, while staying within practical limits since the research was aimed at providing guidelines to the City of Cedar Rapids with respect to treatment of the furfural wastewater.

Steady-state is here defined as a condition of uniform methane production (at STP) for a period of at least 5 days and uniform COD removal efficiencies (± 2%), as earlier described. Testing for steady-state was not conducted until at least 4 HRT's had passed after a change in loading.

It is noted here that one of the fully-packed filters was operated at a higher OLR than were the other fully-packed and the one partially-packed filters. This higher-loaded filter was generally operated at an OLR that was 1.5 to 2 kg COD/m^3/day higher than the other two reactors. This was done (1) to define more operating points for the fully-packed anaerobic filters, and (2) to provide a margin of safety for the reactors as a whole; that is, if the higher-loaded filter failed, the other two filters could avoid failure by maintaining them at a lower OLR.

Throughout the experiments, the two filters that were maintained at lower OLR's were treated identically and were fed out of the same carboy. The third filter had its own feeding vessel, but was treated exactly as the other two filters in all other respects.

2. Reactor operation

The furfural wastewater had a maximum COD value of approximately 13 g/L, but normally the COD was between 10 and 12 g/L. Preliminary studies indicated that efficient treatment of the furfural wastewater at an HRT of 48 hr was very attainable. Therefore, the initial HRT of the anaerobic filters was set at 24 hr (1 day), based on empty bed volumes. To separate the OLR effects from the HRT effects, the HRT was kept constant at 24 hr, while the OLR was stepped up from a low of 3 to 12 kg COD/m^3/day in increments of 3 kg COD/m^3/day. This was accomplished by diluting the raw furfural wastewater with tap water to the desired organic strength. After steady-state was established and all data were collected at that loading, the OLR was increased by 3 kg COD/m^3/day and the process was repeated. After the maximum organic loading rate at the 24-hr HRT was achieved, the HRT was decreased to 12 hr and the OLR was decreased to 3 kg COD/m^3/day. The HRT was then maintained at 12 hr while the OLR was increased by units of 3 to 5 kg COD/m^3/day until maximum organic loading was achieved or process failure occurred. At each OLR, steady-state was achieved and testing was conducted before increasing the OLR to the next level.

V. RESULTS AND DISCUSSION

A. Operation at the 24-Hour Hydraulic Retention Time

1. Organic loading

All three reactors were operated at an HRT of 24 hr for a period of 94 days during which time data were collected. (It should be noted that the reactors were operated at an HRT of 48 hr for a period of approximately 3 months before actual experimentation was begun.) As earlier stated, the HRT was maintained at a constant 24 hr while the organic loading rate was increased after each successive steady-state was achieved.

All three of the reactors were able to handle the furfural wastewater at full strength, that is, without dilution at the 24-hr HRT. Total COD removals consistently exceeded 90%, with soluble COD removals marginally better than the total removals. Interestingly, the total and soluble COD removals actually improved as the organic load was increased (Figures 4 and 5). In the writer's view, the reason for this is two-fold: (1) The biomass in the reactor built up as time progressed, and, therefore, at the higher loadings (and later time periods), there was more biomass in the reactor, and the system operated more efficiently; and (2) the filters appear to have a lower organic loading limit beyond which operation becomes inefficient; that is, even at low organic loads, the effluent from the filters will probably contain a minimum of

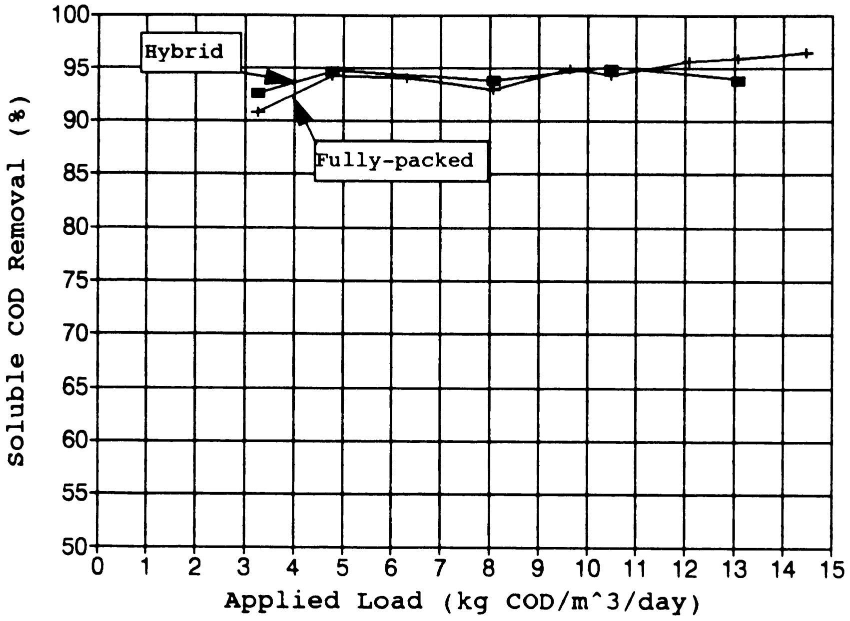

Figure 4. Soluble COD removal at the 24-hr HRT

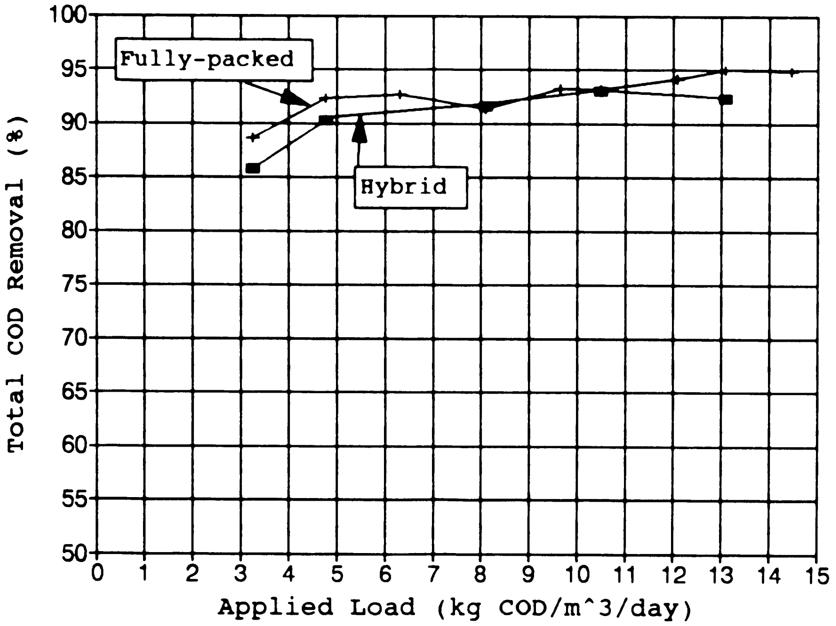

Figure 5. Total COD removals at the 24-hr HRT

150 to 200 mg/L of COD, resulting in poorer removal efficiencies at low loadings. COD removal efficiency is calculated as

$$\% \text{ COD removal} = \frac{C_o - C}{C_o} * 100$$

where, C_o = influent COD concentration, mg/L
C = effluent COD concentration, mg/L

Further evidence of the stability of the systems throughout the operation at an HRT of 24 hr is that the methane production (STP) per volume of the all three reactors were linearly increasing (Figure 6). Instability of the systems would result in a nonlinear curve of volumetric methane production.

To check the methane production with the COD removals efficiencies calculated, the methane produced per day was converted to an equivalent amount of COD removed based on stoichiometry (0.35 liters of CH_4 per gram of COD removed, assuming zero biomass production). COD removal efficiencies were somewhat higher when calculating the parameter using the methane basis, and efficiencies in excess of 100% were calculated at two loadings (Figure 7). The reason for exceeding 100% removal is unclear; however, the gas analyses conducted during these two loadings is a major suspect. GC malfunction or human error may have lead to high reports of

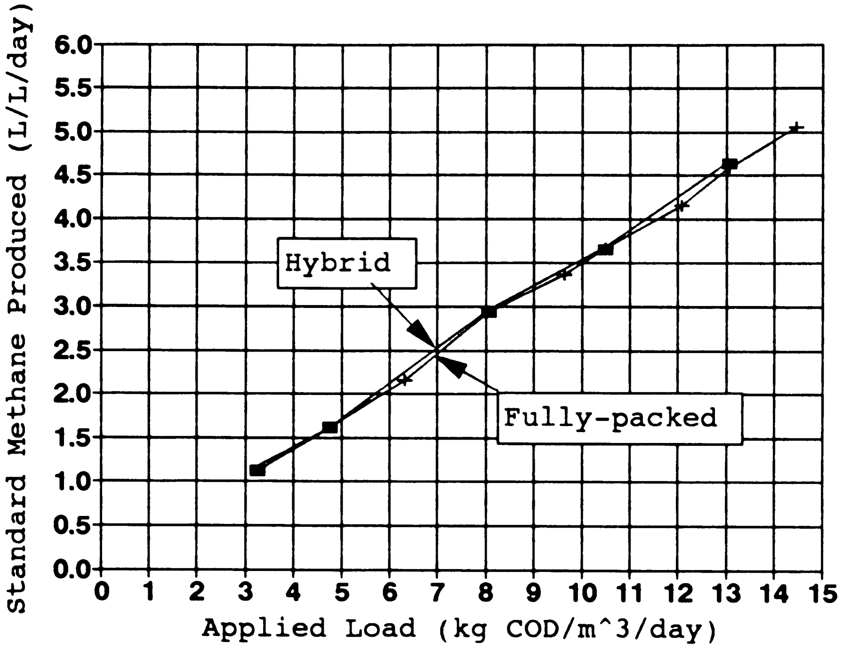

Figure 6. Volumetric methane production at the 24-hr HRT

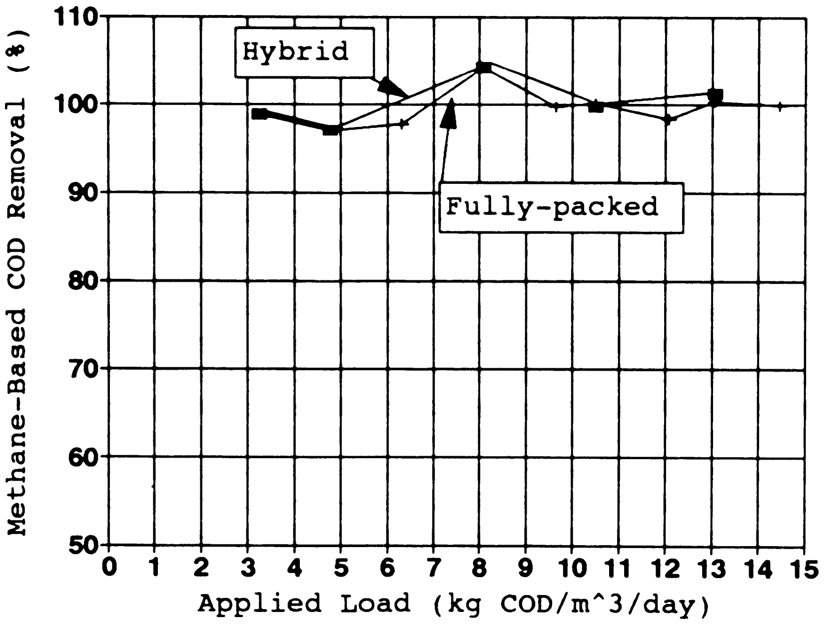

Figure 7. COD removal efficiency based on methane at the 24-hr HRT

methane percentage in the biogas, which then lead to incorrect COD removal efficiencies based on methane. The fact that the methane-based COD removal efficiencies were higher than the efficiencies calculated from the COD tests may be the result of a slight miscalibration of the gas meters, resulting in higher than actual gas measurements. However, since all of the reactors tended to error at the same time, GC error appears to be more probable.

2. Volatile acids and alkalinity

The volatile acids data at an HRT of 24 hr appeared to have little or no correlation with organic loading. Generally, immediately after an increase in organic loading, volatile acids concentrations increased and then after a period of one or two days began to decrease. Figure 8 shows the effluent volatile acids in all three reactors at each loading. A sharp increase in volatile acids concentration at a loading of approximately 7.5 kg COD/m^3/day is observed. This increase in volatile acids coincides with a decrease in the pH of the influent feed, which will be discussed later. It is interesting to note that very little, if any, difference in reactor performance was observed during any part of this phase of the study, regardless of the volatile acids concentration in the reactors. High volatile acids concentrations appeared, at times, to be the result of short

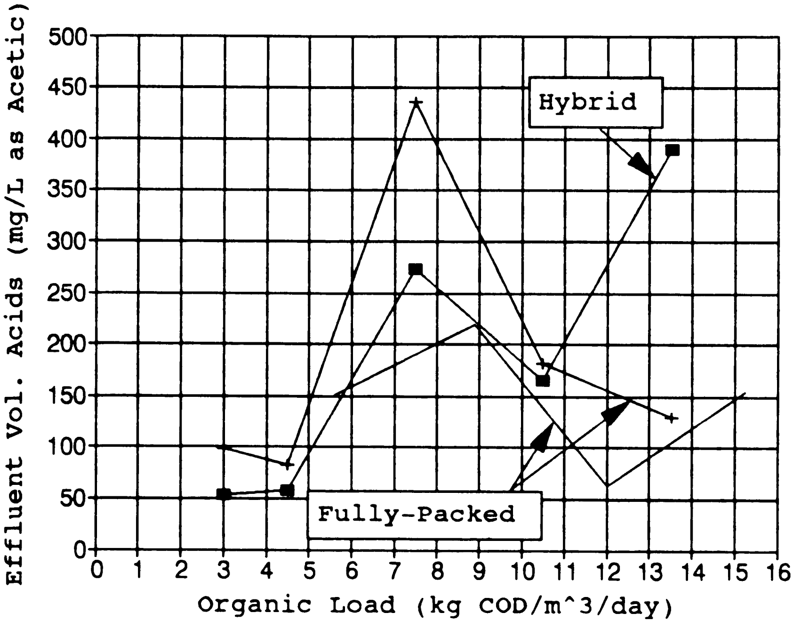

Figure 8. Effluent volatile acids at the 24-hr HRT

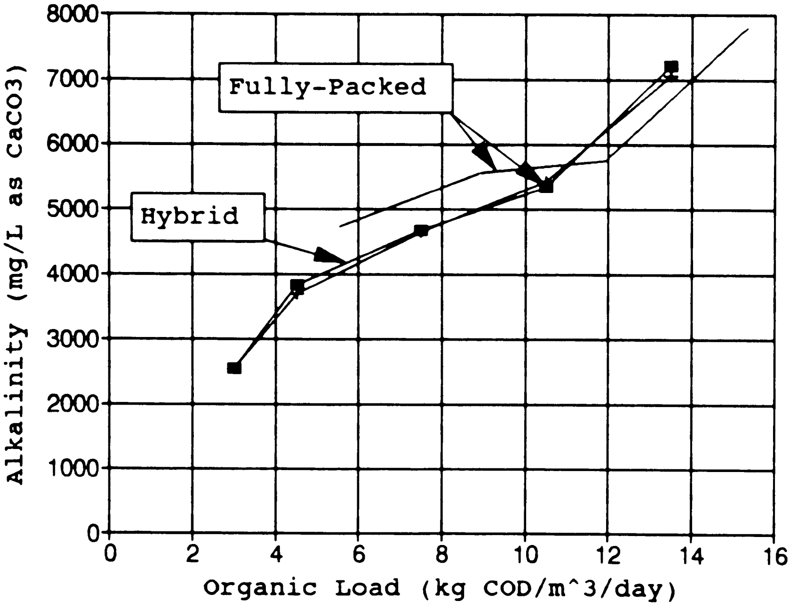

Figure 9. Effluent alkalinity at the 24-hr HRT

circuiting of the influent feed, rather than an inability of the reactor to remove the COD.

The alkalinity in the reactor shows a steady increase (Figure 9) with increasing organic load. This is to be expected since the amount of buffers added to the influent feed was also increased as the organic strength increased. Alkalinity will be discussed later in this report as it relates to influent pH.

3. Suspended solids

The suspended solids (SS) in the effluent of all three reactors appeared to have minimal correlation with the organic loading applied to the reactors. For two of the reactors (one fully-packed and the hybrid), there appears to be an increase in effluent SS as the organic loading rate is increased. For the third reactor, effluent SS does not show a trend. Generally, the effluent SS of all reactors were between 150 and 200 mg/L; however, all three reactors tended to discharge solids at irregular intervals, during which time the SS concentration in the effluent reached 300 to 400 mg/L (Figure 10).

The volatile suspended solids (VSS) percentage of the total SS was approximately 65% for the fully-packed reactors and 68% for the hybrid. This low VSS percentage is probably the result of an inorganic precipitate from the addition of calcium hydroxide as a buffering agent during the startup of

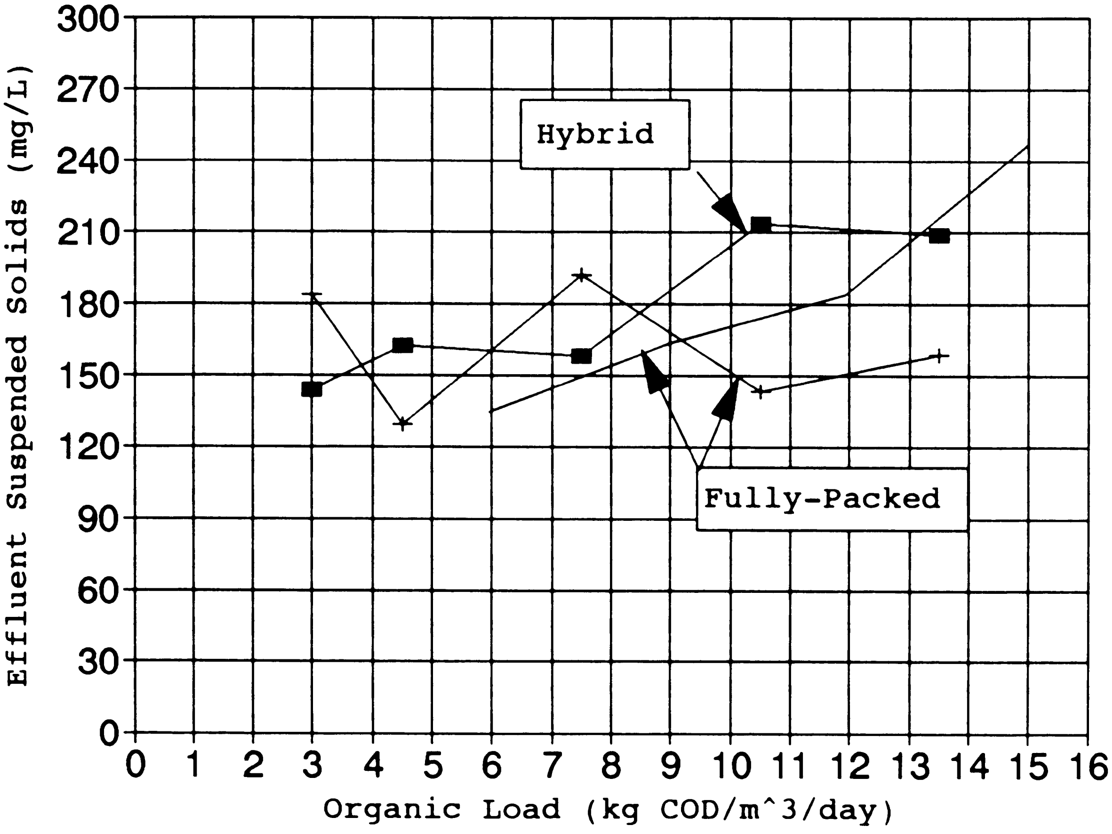

Figure 10. Effluent suspended solids at the 24-hr HRT

the reactors. This was later confirmed when the reactor were opened at the end of the study.

4. Gas production and quality

The daily methane production from the hybrid and the fully-packed reactors is shown in Figure 11. As is evident from this figure, the two reactors produced almost identical amounts of methane per day throughout the study and reactor response to step increases in organic loading was almost immediate. Normally, within 24 hours after an increase in organic loading, the reactors were producing near stoichiometric amounts of methane as calculated from the new organic loading rate.

The period from day 62 to day 72 (Figure 11) reflects large fluctuations in daily methane production. This was the result of a pump malfunction combined with the fact that fresh furfural wastewater (which contained a different strength than the previous batch) was obtained at this point.

The percentage of methane in the biogas was not a constant over the range of organic loadings. The general trend was a decrease in the methane percentage as the organic loading rate increased. At the low load of 3 kg COD/m^3/day, the methane percentage was approximately 85% of the total biogas. At the highest loading of 15 kg COD/m^3/day, the percentage of methane was approximately 70%. There was almost

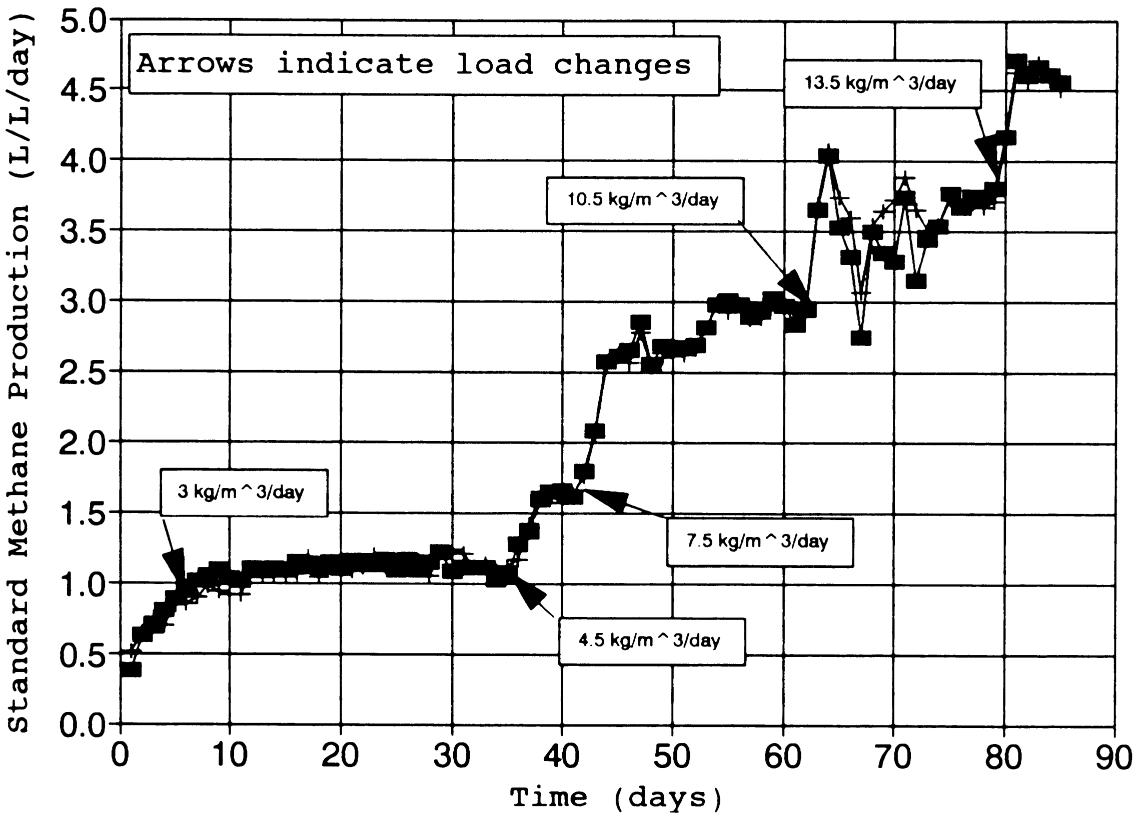

Figure 11. Standard methane production from the hybrid & fully-packed reactors at the 24-hr HRT

no difference in gas quality between the hybrid reactor and the fully-packed reactors.

The decrease in methane percentage as the organic loading rate was increased is presumably the result of alkalinity and pH effects, and not the result of a decrease in reactor performance. The total methane produced was not affected, but the percentage of methane in the total biogas produced decreased. This is explained by considering the bicarbonate/carbon dioxide equilibrium equation:

$$C = \frac{2*(H^+)*(HCO_3^-)*(22{,}000)}{K_1}$$

where: (H^+) = hydrogen ion concentration, equiv./L
(HCO_3^-) = bicarbonate ion concentration, equiv./L
K_1 = equilibrium constant
C = CO_2 concentration in solution, mg/L
22,000 = mg CO_2/equivalent
2 = equivalents of CO_2/mol CO_2
Note: equivalent weight = molecular weight for H^+ and HCO_3^-

Henry's Law is then used to calculate the percentage of carbon dioxide in the biogas:

$$C = a * P$$

where: a = Henry's constant, mg/L-atm
P = partial pressure of CO_2
C = CO_2 concentration in solution, mg/L

From the first equation above, the CO_2 concentration in the reactor liquid increases as the pH and bicarbonate alkalinity increase. This increase results in an increased partial pressure of CO_2. (Note that K_1 and Henry's constant are both fixed at a given temperature.) Therefore, as the alkalinity and pH in the reactor increase (which occurred as the organic load increased), the CO_2 percentage of total biogas increases, resulting in a subsequent decrease in methane percentage.

B. Operation at the 12-Hour Hydraulic Retention Time

1. Organic loading

After all of the data were collected at the 24-hr HRT, the HRT was reduced to 12 hr, and the testing procedures were conducted as they were during the 24-hr HRT experiments. The hybrid reactor and one of the fully-packed reactors were fed at an organic load of 3 kg COD/m^3/day, while the other fully-packed reactor was fed at 4.5 kg COD/m^3/day. After steady-state was achieved and the tests at that load were finished, the organic load was increased as before.

Figures 12 and 13 show the soluble and total COD removals, respectively, for the hybrid and fully-packed filters. Even at the maximum loading of approximately 26 kg COD/m^3/day, all three reactors were removing in excess of 80% of the influent COD. The fully-packed reactors performed marginally better above an organic load of 23 kg COD/m^3/day. Up to loads of 23 kg COD/m^3/day, all three reactors were

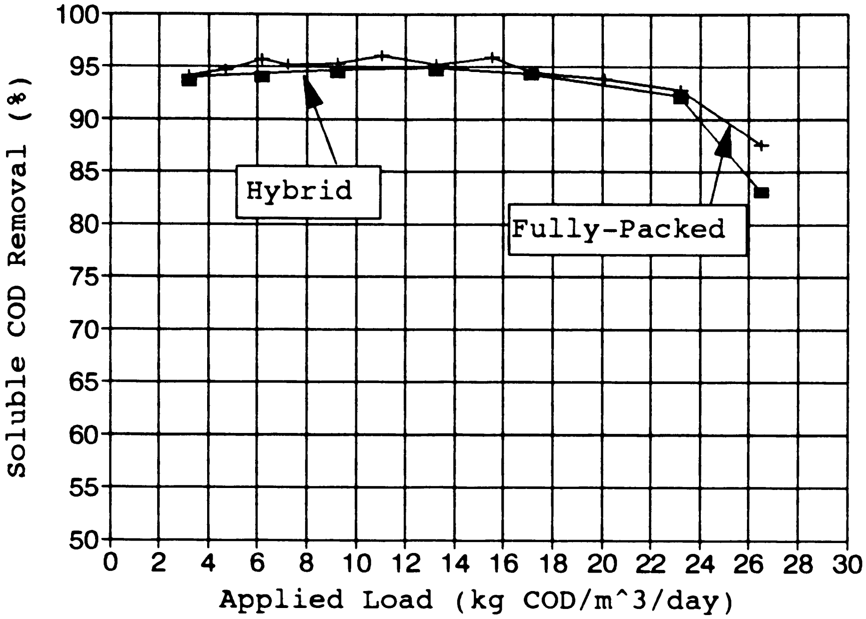

Figure 12. Soluble COD removals at the 12-hr HRT

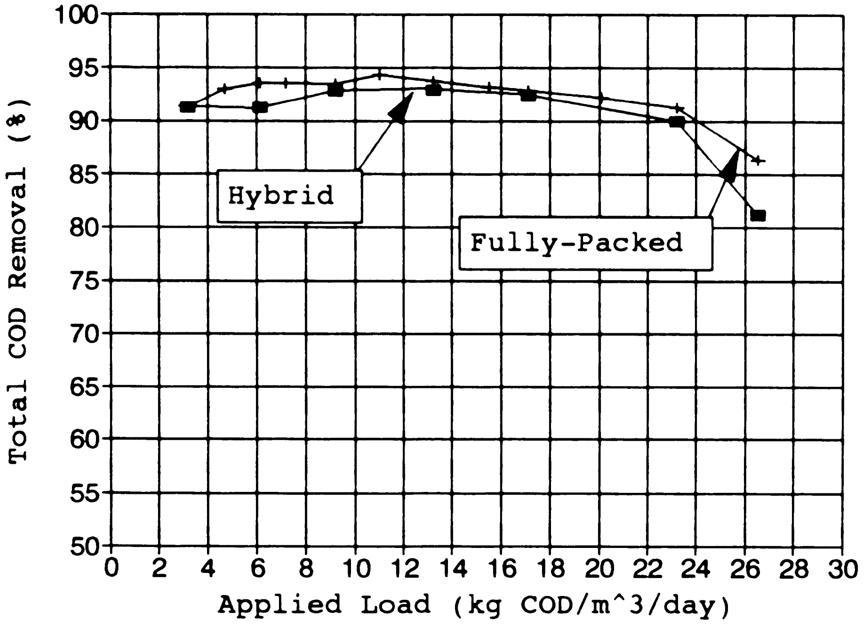

Figure 13. Total COD removals at the 12-hr HRT

removing up to or in excess of 95% of the soluble COD. Total COD removals were normally 92 to 93%. No significant difference was observed between the fully-packed and hybrid reactors throughout the experiments.

When the load was increased to the 26 kg COD/m^3/day load, the efficiency of the fully-packed reactors decreased by about 5% while the efficiency of the hybrid decreased by about 9%. This decrease can be seen in Figures 14 and 15, which show the volumetric methane production (STP) and the methane-based COD removals, respectively. The volumetric methane production remains relatively constant up to loadings of 23 and 26 kg COD/m^3/day, and the methane-based COD removal efficiency decreases when the loadings were increased to 26 kg COD/m^3/day (hockey-stick effect).

It appears that the reactors reached saturation loading at approximately 23 kg COD/m^3/day (at an HRT of 12 hr). It is important to note, however, that the ammonia concentration in all reactors was approximately 1,600 mg/L (as NH_3). This concentration is above the generally accepted inhibitory value of 1500 mg NH_3/L, and may, therefore, be responsible for the decreased performance of the reactors. Since ammonia levels and organic loadings were very similar in all three reactors, and the decrease in performance was nearly identical in each reactor, it is difficult to determine the cause of the decreased reactor efficiency with certainty.

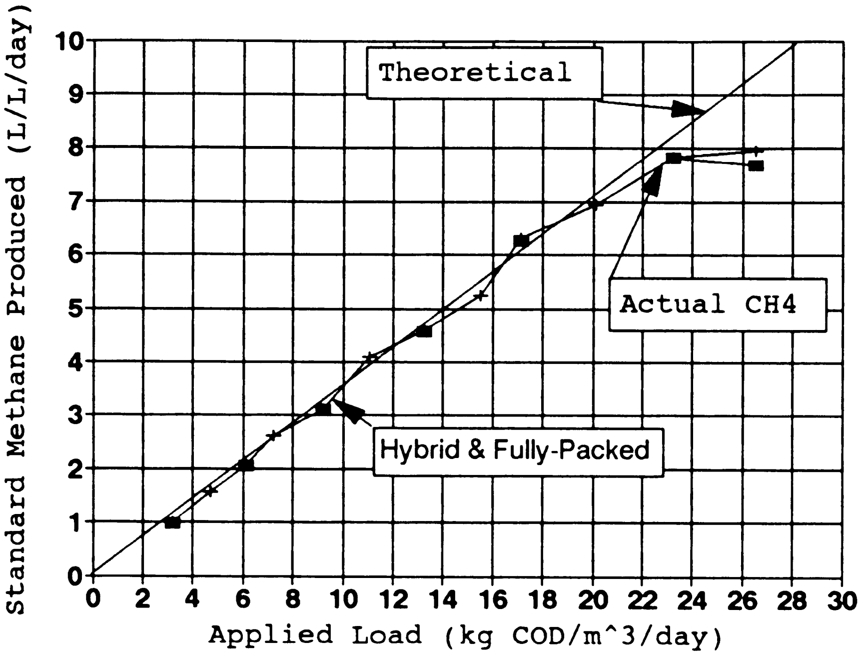

Figure 14. Volumetric methane production at the 12-hr HRT

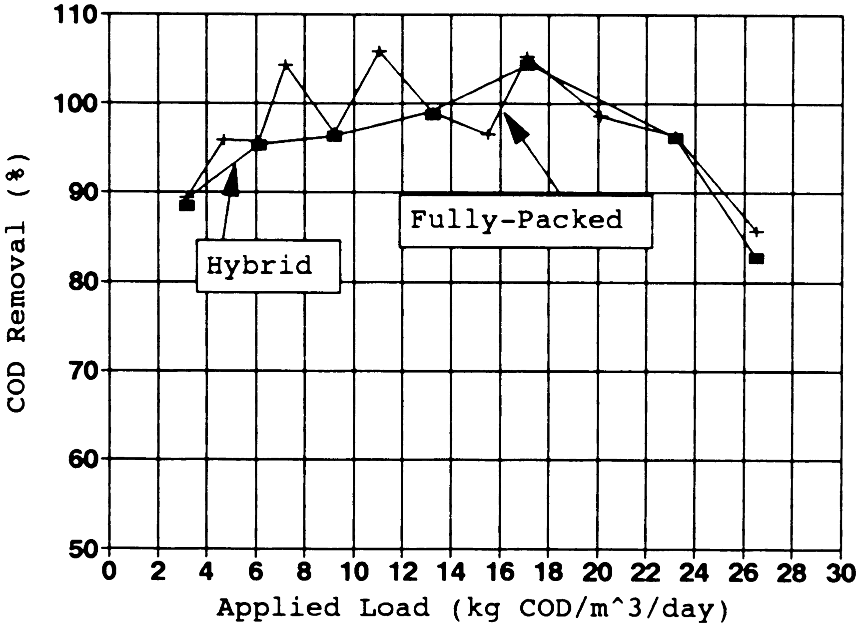

Figure 15. COD removal efficiency based on methane at the 12-hr HRT

2. Volatile acids and alkalinity

The volatile acids data also show the decreased performance of the filters (Figure 16). Volatile acids concentrations for all three reactors (expressed as acetic acid) remained below 200 mg/L at organic loadings up to 18 kg COD/m^3/day. At 23 kg COD/m^3/day volatile acids concentrations jumped up to 350 to 400 mg/L. At maximum loading, the volatile acids concentrations were in excess of 1,000 mg/L. The hybrid had the highest effluent volatile acids concentration at approximately 1,500 mg/L.

Reactor alkalinity was a function of the organic loading rate since the amount of buffer added was proportional to the organic strength. Figure 17 shows the linear increase in alkalinity as the organic loading was increased. Even when the reactor efficiency decreased, the alkalinity of all reactors was approximately 7,500 mg/L, as $CaCO_3$, and the pH of all reactors was between 7.3 and 7.5.

3. Suspended solids

The suspended solids (SS) in the effluent of all three reactors increased in concentration as the organic loading rate was increased (Figure 18). At loadings up to approximately 13 kg COD/m^3/day, the increase in SS was fairly linear for all three reactors. Above 18 kg COD/m^3/day, SS concentrations in the reactor effluents rose sharply but leveled out at 23 kg COD/m^3/day. All three reactors had SS

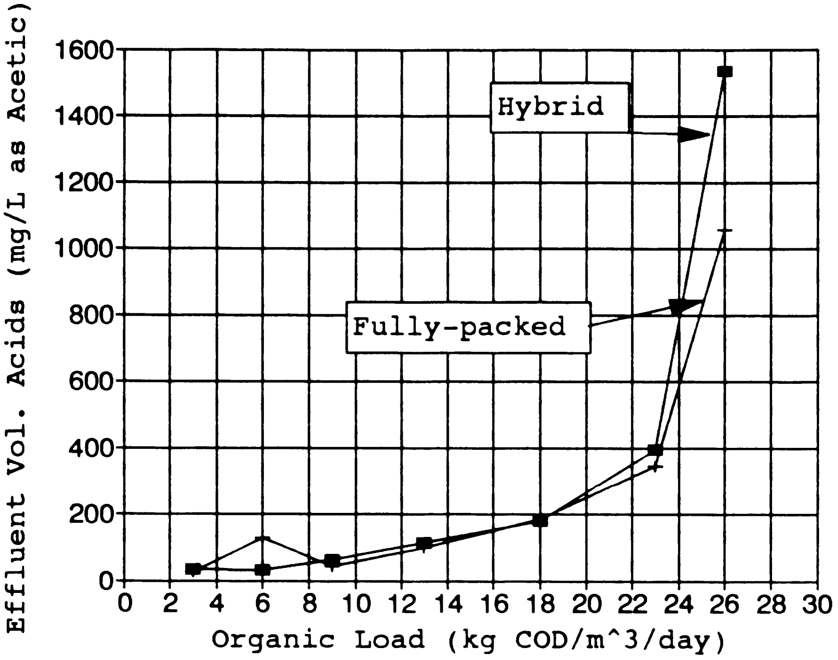

Figure 16. Effluent volatile acids at the 12-hr HRT

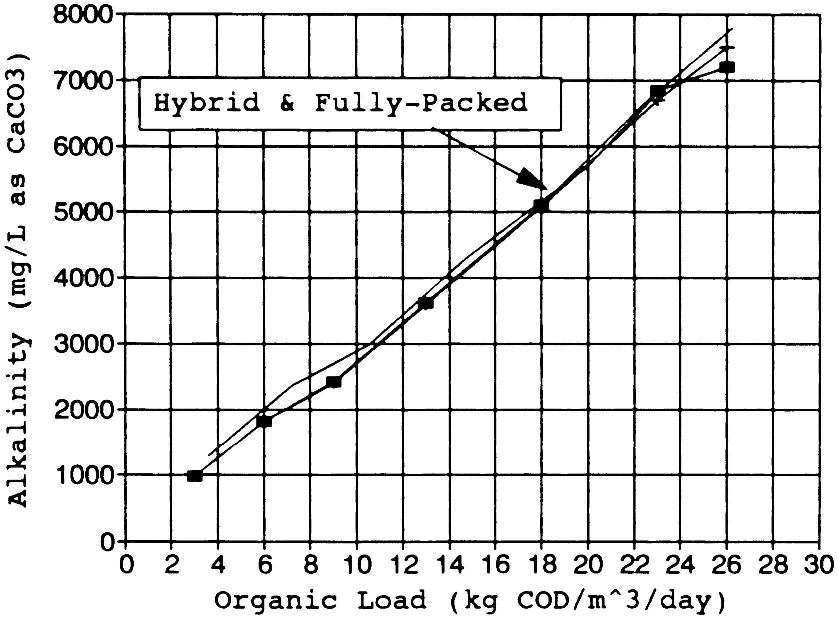

Figure 17. Effluent alkalinity at the 12-hr HRT

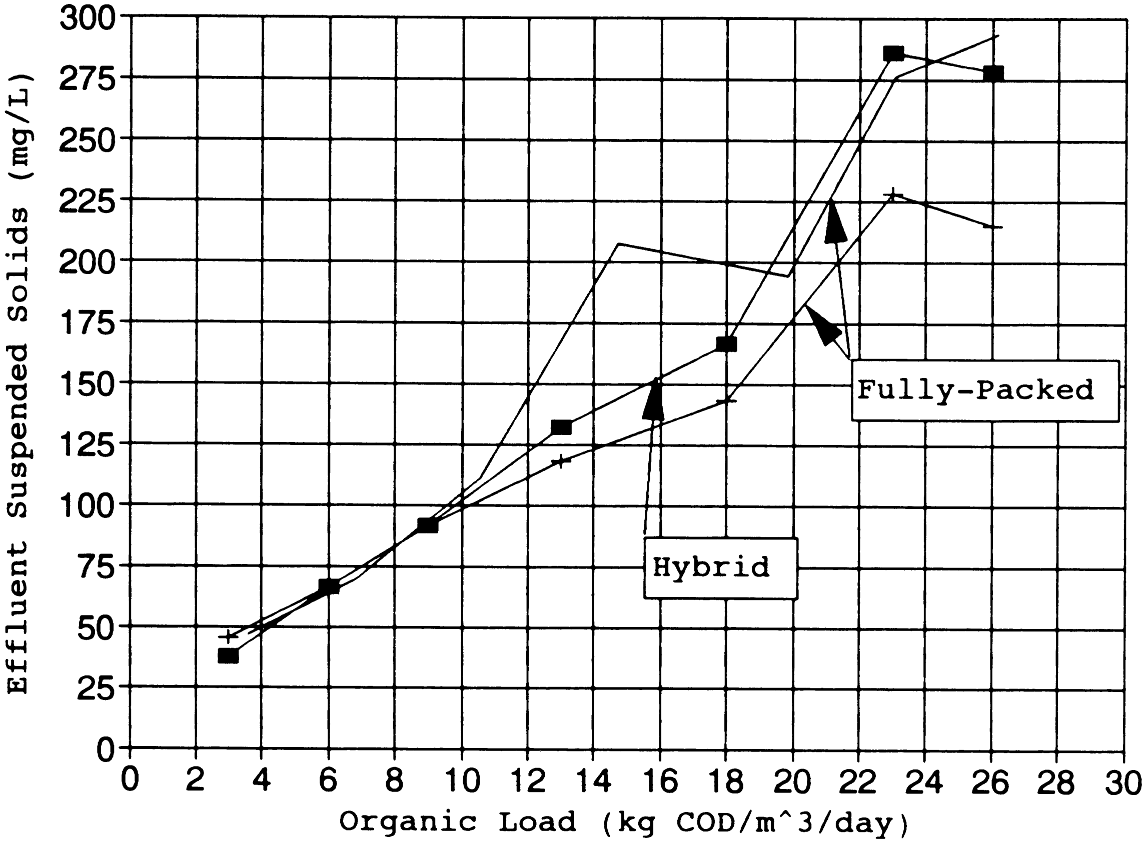

Figure 18. Effluent suspended solids at the 12-hr HRT

concentrations between 200 and 300 mg/L at the maximum loading of 26 kg COD/m^3/day.

The volatile suspended solids (VSS) percentage of the total SS was generally in excess of 70% for all three reactors, but seldom exceeded 77%. The reasons for the low VSS percentage are the same as for the 24-hr HRT study.

4. Gas production and quality

Figure 19 shows the methane production over time for the hybrid reactor and one of the fully-packed reactors. The daily amounts of methane are nearly identical and reactor response to step increases in organic load was almost immediate, as with the 24-hr HRT studies. The reactors appeared to achieve pseudo steady-state within a few hours after the increase in organic load; however, the reactors were allowed to operate at the new load for a period of at least 3 to 4 days (6 to 8 HRT's) before testing commenced.

On day 72 (Figure 19) the organic load was increased to 26 kg COD/m^3/day, but the volumetric methane production remained at approximately 7.8 L CH_4/L/day. This is further indication that saturation loading had been reached at approximately 23 kg COD/m^3/day.

At the beginning of the 12-hr HRT study, the methane percentage in the biogas was approximately 80 to 84% (at organic loadings of 3 and 4.5 kg COD/m^3/day). As the load was increased, the methane percentage decreased as it did in the

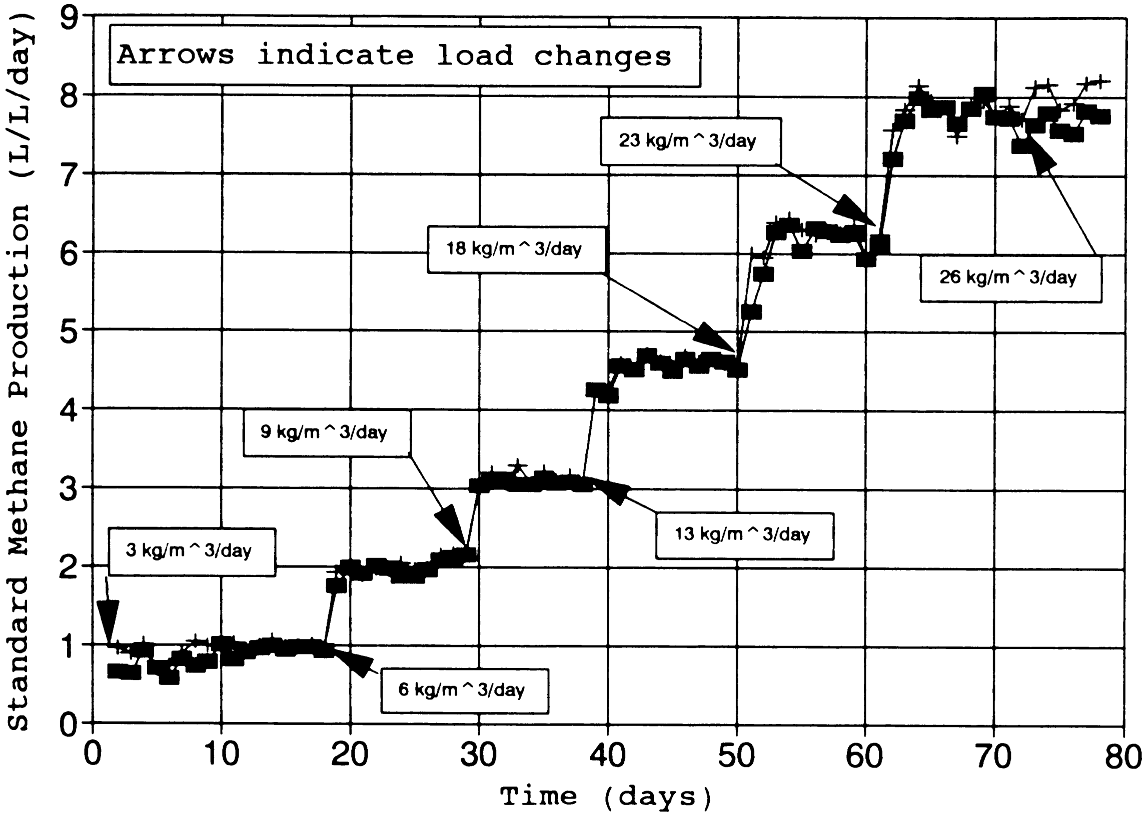

Figure 19. Standard methane production from the hybrid & fully-packed reactors at the 12-hr HRT

24-hr HRT study. At an organic loading rate of 9 kg COD/m^3/day and above, the methane percentage was generally constant up to the maximum organic loading rate of 26 kg COD/m^3/day. The percentage of methane at these loads was approximately 68 to 72%. As observed in the 24-hr HRT study, there was little, if any, difference in gas quality between the hybrid reactor and the fully-packed reactors.

The decrease in methane percentage was explained earlier in Section A, Part 4 of this thesis.

C. Influence of Hydraulic Retention Time

Generally, there was little difference in reactor performance at the two hydraulic retention times studied. The COD removal efficiencies at the two HRT's were nearly identical and were actually marginally better at the shorter HRT of 12 hr, although the difference is small.

The shorter HRT has a diluting effect on all parameters in the operating system; that is, for identical organic loadings (expressed as kg COD/m^3/day), the influent feed for the reactor at the 12-hr HRT will have half of the organic strength as the reactor at the 24-hr HRT, everything else being equal. Because of this, the required buffering chemicals will also be half as much for the reactor at the 12-hr HRT, and toxicant concentrations within the reactor (such as ammonia) will be half as much. Therefore, as long as saturation loading is not reached, a reactor operated at a relatively short HRT is able to handle a larger organic load on a daily basis. This is precisely what occurred in this reactor system. The reactors were able to handle almost twice the organic load at the 12-hr HRT as compared to the 24-hr HRT with a negligible change in reactor efficiency. This is obviously advantageous from an applications point of view because, at a 12-hr HRT as compared to a 24-hr HRT, twice as much waste can be treated and twice as much methane will be produced on a daily basis.

The HRT also has an effect on the solids retention time (SRT) of the reactor. Since effluent suspended solids concentrations were similar at both of the HRT's studied, twice as many suspended solids exited the reactors each day at the shorter HRT, and thus, the SRT was approximately halved at the 12-hr HRT (assuming equivalent total suspended solids in the reactors at the two HRT's studied). Since the SRT at the 12-hr HRT was still in excess of the minimum required at 35°C (see Section F), the system remained stable. However, if the HRT were shortened further, process instability could result.

D. Effect of Influent pH on Reactors

Initially, the influent to the reactors was fed at a pH of approximately 5.5. After 45 days, the influent pH was decreased to approximately 5.0 to 5.1 in an attempt to decrease the reactor pH, which was over 7.5 in all three reactors. At times, the influent pH was as low as 4.4 because of variations in the furfural wastewater; however, no significant adverse effects were noted in any of the reactors.

Immediately after the decrease of the influent pH to 5.0, the volatile acids (VA) concentration in all three reactors increased significantly. For the hybrid reactor, the VA increased from 47 to 408 mg/L. For one of the fully-packed reactors, the VA increased from 55 to 503 mg/L, and in the other fully-packed reactor, the VA increased from 76 to 372 mg/L (all expressed as acetic acid). After several days of operation, the VA concentrations fluctuated over a range from 50 to 300 mg/L. It is important to note that COD removal efficiencies remained essentially constant, even during fluctuations in the effluent VA concentrations.

The pH of the reactors was influenced marginally by the influent pH. After the decrease in the influent pH from 5.5 to 5.0, the pH of all reactors decreased from about 7.6 to 7.3. The pH of the reactors increased as the organic load was increased, but generally remained below 7.6 for the remainder of the study. There was normally a small difference in pH between the top and bottom of the reactor. The pH at the bottom was usually about one to two-tenths of a pH unit less than the pH at the top of the reactor. The reason that the pH at the bottom of the reactor is close to that at the top can be explained by the following: (1) an effluent recycle rate of 100% of the influent was practiced and, therefore, the pH of the influent after mixing with the recycle was actually higher than the 5.0 reported above; and (2) because of gas mixing, anaerobic filters operate closely to complete-mix systems.

E. Reactor Shutdown/Startup Studies

As with any manufacturing process, the Quaker Oats Company's manufacturing process is not in operation 100% of the time. There are instances when the plant is required to shutdown for lengthy time periods for maintenance and repair work. This time period may vary from a few hours to several weeks. Because of these shutdown periods, it was necessary to study the effect of a shutdown on the anaerobic filters. To study the shutdown effects, the reactors were left idle (zero feeding or maintenance) for a period of approximately two weeks. Normal operation of the filters was then commenced at a specified organic load. The reactor startup efficiency was monitored on the basis of COD removal rates and methane production for the few days immediately following the startup of the reactors. Shutdown/startup studies were conducted at both of the HRT's studied and the results are presented below.

1. Shutdown/startup at 24-hr HRT

On day 94 of the study, after all of the data for the 24-hr HRT had been collected, all three reactors were shutdown and maintained at 35°C for the next 15 days without any feeding or maintenance. Previous to the shutdown, the reactors were operating at an organic loading of approximately 13 to 15 kg COD/m^3/day (acetic acid had been added to the influent feed to exceed the furfural wastewater's strength of about 11 kg COD/m^3/day). On day 109, feeding to all three reactors began at an organic load of 11 kg COD/m^3/day and an HRT of 24 hr. Throughout the shutdown period, presumably from the endogenous decay of biomass, minor amounts of gas were produced in each of the reactors, ranging from 0.2 to 1.0 liter of total gas per day (the reactor volume is 9.5 liters).

Within five minutes of reactor startup, noticeable gas production had begun. After 30 minutes, 100 to 200 mL of gas had been produced in all three reactors. After approximately two hours, all three reactors were producing methane (STP) at about the same rate of 8.5 to 9.0 liters of CH_4 per day. As time progressed, however, the hybrid reactor began to lag behind the fully-packed reactors. The pH of the hybrid reactor dropped below 6.5 soon thereafter, and additions of sodium bicarbonate were necessary to raise the pH in the hybrid to a neutral level. The fully-packed reactors responded very well to the startup period and remained stable throughout the experiment. Total COD removals never fell below 87%, and methane production stabilized at normal production rates within 5 hours of startup (with some fluctuations). Figures 20, 21, and 22 show, respectively, the soluble COD removal efficiency, total COD removal efficiency, and standard methane production over time after the startup of all three reactors.

Figures 20 through 22 are somewhat deceiving in that in the first few hours, COD removals are well above 90%. This is the result of the influent not penetrating the entire depth of the filter at that point; therefore, the effluent from the reactor was comprised of the liquid that had been sitting in the reactor for the 15-day shutdown period, and was basically void of COD. From these figures, it is obvious that the fully-packed reactors outperformed the hybrid reactor in the shutdown/startup experiment. The performance of the hybrid reactor gradually decreased and leveled off at a COD removal efficiency of only 40% and methane production rates roughly a third of that of the fully-packed reactors. At the 86th hour after startup, the organic load to the hybrid reactor was reduced to 2.25 kg COD/m^3/day to relieve the stress on the reactor. The hybrid subsequently recovered and the COD removal efficiencies returned to normal.

The reason for the inferior performance of the hybrid reactor is not readily evident. All three reactors were treated identically both during normal operation and during the shutdown period. However, during the shutdown period it

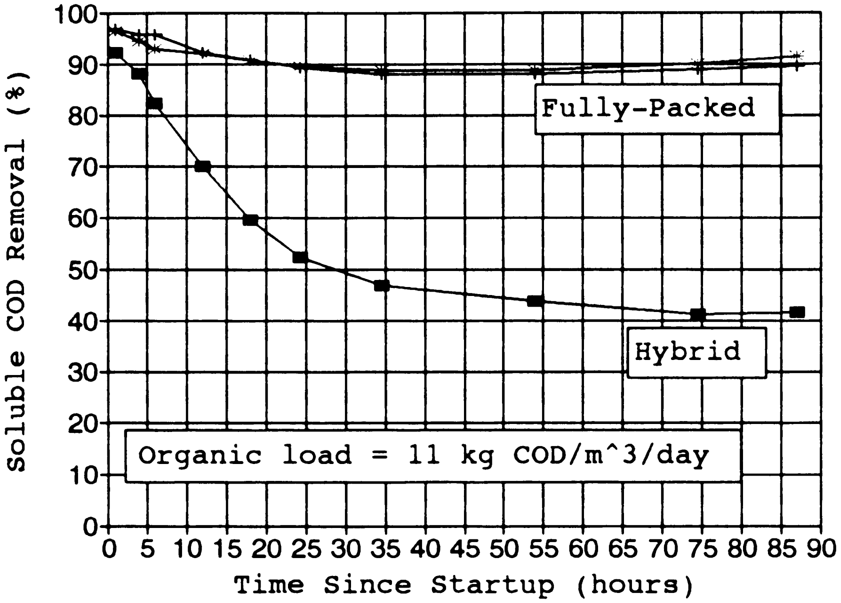

Figure 20. Soluble COD removal after a 15-day shutdown (HRT = 24 hr)

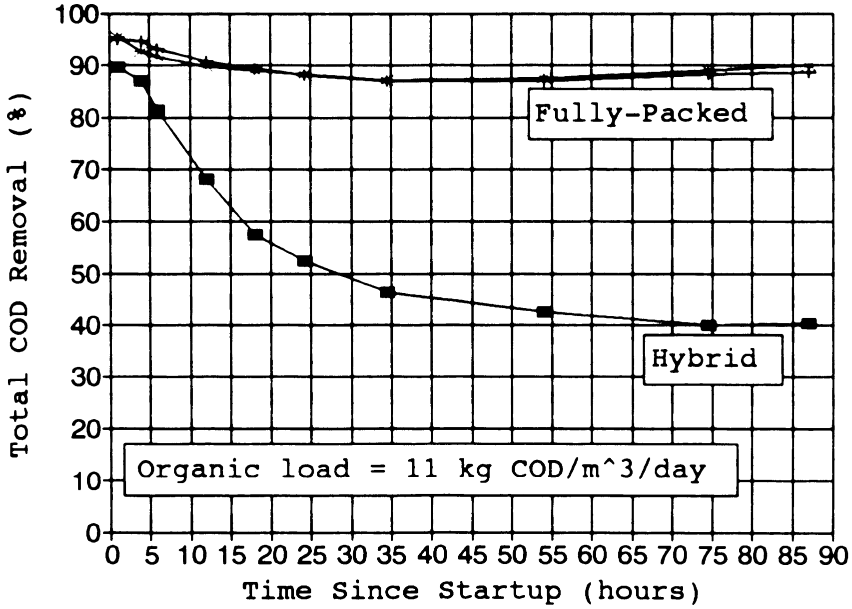

Figure 21. Total COD removal after a 15-day shutdown (HRT = 24 hr)

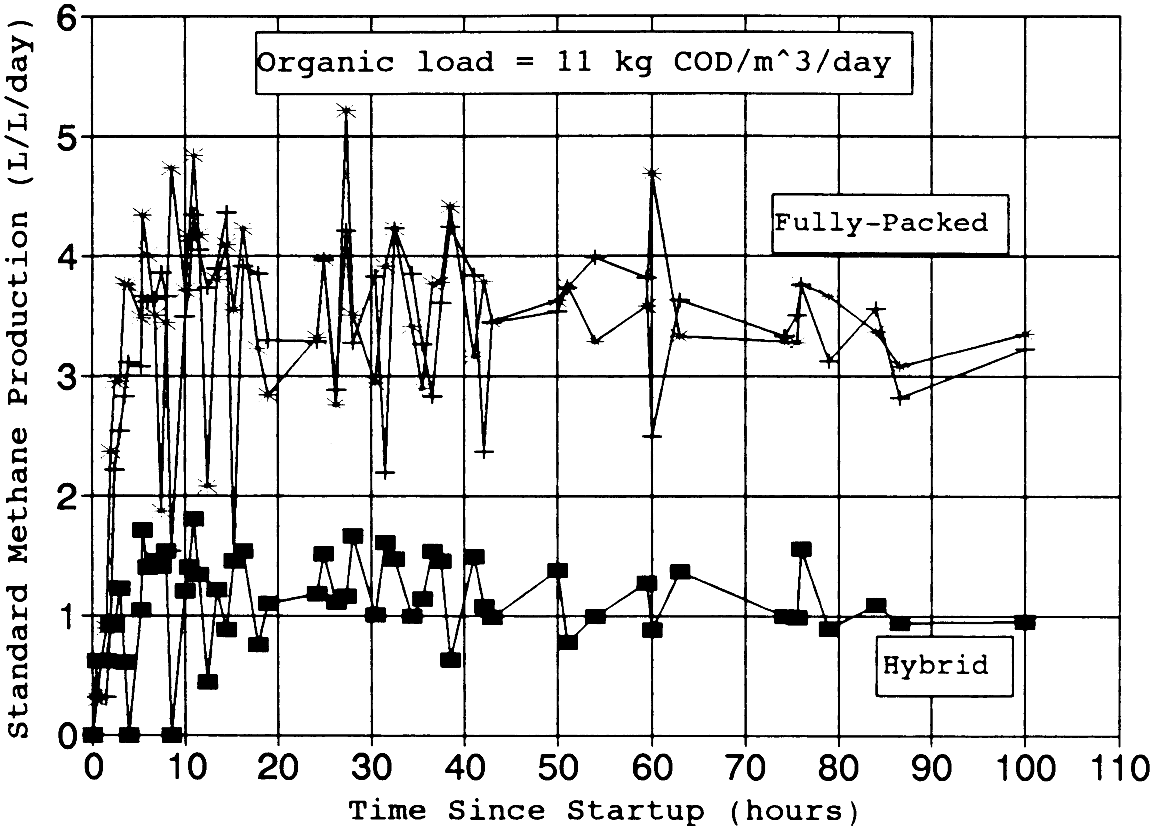

Figure 22. Methane production after a 15-day shutdown (HRT = 24 hr)

was observed that the hybrid reactor was producing gas at approximately twice the rate as the fully-packed reactors. The liquid effluent from the hybrid reactor immediately after startup had a color that was much different than that from both of the fully-packed reactors. The effluent from the fully-packed reactors was fairly clear, almost water-like, while the effluent from the hybrid had a very yellow appearance.

Presumably, the organisms in the hybrid reactor underwent more endogenous decay than did the organisms in the fully-packed reactors. This would explain the higher gas production in the hybrid since after the cells die, they will lyse, making food available to the remaining organisms. It is unclear why the hybrid reactor experienced this phenomenon while the fully-packed reactors did not. Possibly the presence of the media in the lower third of the reactor (the hybrid does not have this media) helps protect the organisms located in this portion of the reactor. The inner layers of organisms attached to the media may be protected against outside influences, and, since the organisms in the lower third of the hybrid reactor were freely floating, no protection was provided to them.

2. Shutdown/startup at 12-hr HRT

On day 86 of the 12-hr HRT study, after maximum loading had been achieved, the reactors were again shut down, this time for a period of 14 days. All three reactor were kept at 35°C for the entire shutdown period with zero maintenance or feeding. Previous to the shutdown, the reactors were operating at an HRT of 12 hr and an organic loading rate of approximately 26 kg COD/m^3/day. After 14 days of shutdown, the reactors were started up at a 12-hr HRT and an organic load of approximately 10 kg COD/m^3/day. The reason that this load was chosen was to compare the 2 HRT's in terms of their startup efficiency at similar organic loadings. Again, during the shutdown period, minor amounts of biogas were produced from all three reactors. The volume of gas ranged from approximately 0.5 to 1.3 liters of gas per day (9.5 liter reactor volume), and all three reactors produced similar amounts of gas during the shutdown period.

Within two minutes of startup of the reactors, gas production was noticeable. Within approximately 5 hours after startup, all reactors were producing methane at a rate equivalent to almost 90% COD removal. Figure 25 shows the methane production from the three reactors as a function of time since startup. Figures 23 and 24 show soluble and total COD removals, respectively, over time. The hybrid reactor performed nearly identically to the fully-packed reactors with respect to COD removal efficiencies and methane production. Total COD removals for all reactors never fell below 85%. After approximately one day, COD removal efficiencies increased to near 90%.

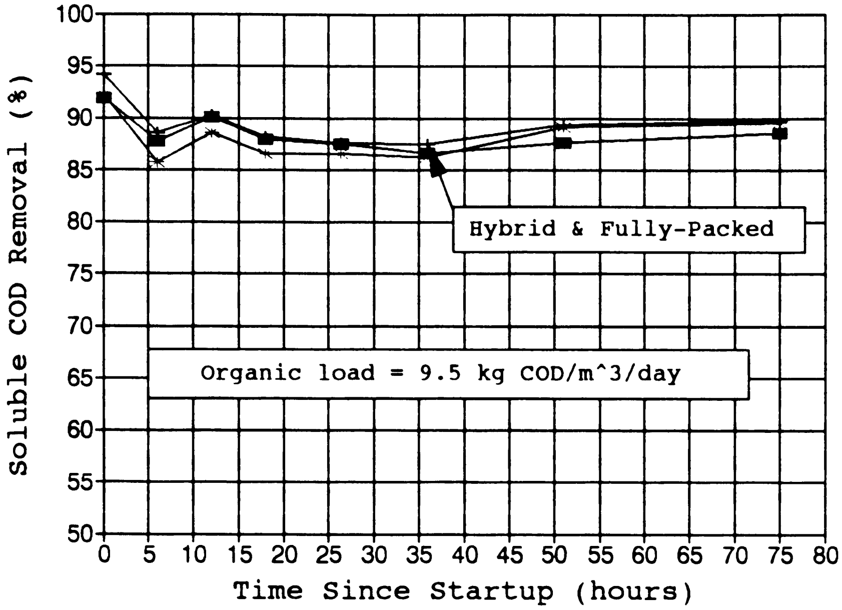

Figure 23. Soluble COD removal after a 14-day shutdown (HRT = 12 hr)

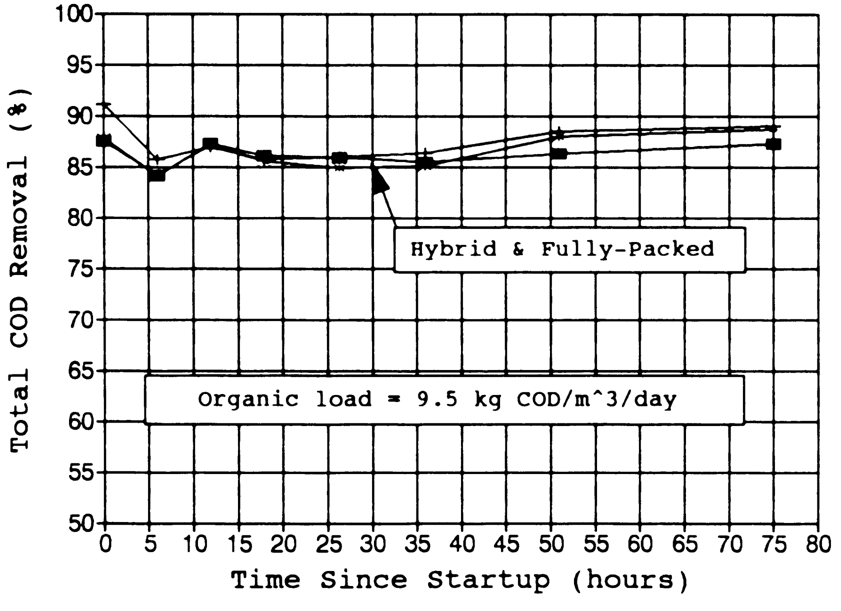

Figure 24. Total COD removal after a 14-day shutdown (HRT = 12 hr)

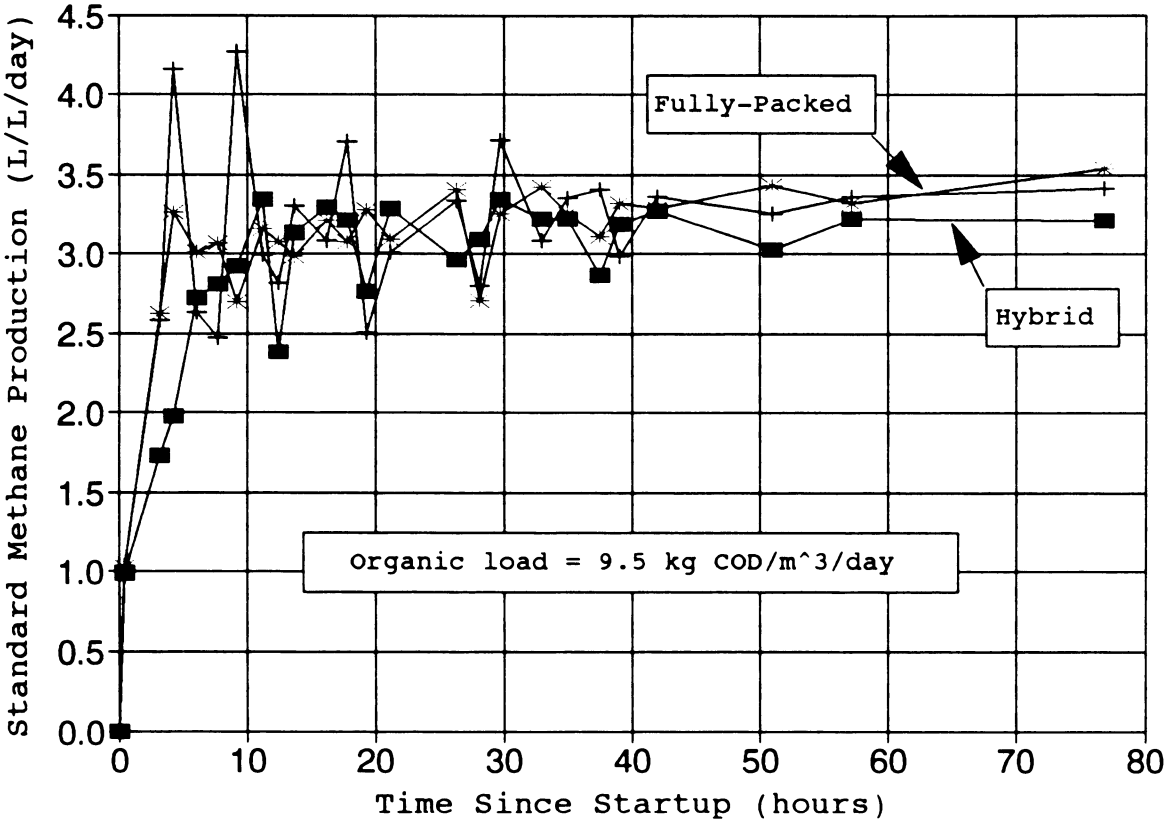

Figure 25. Methane production after a 14-day shutdown (HRT = 12 hr)

As is evident in Figures 20 through 25, the hybrid reactor performed much better during startup at the 12-hr HRT than at the 24-hr HRT. One explanation is that the sludge blanket contained a higher concentration of biomass during the 12-hr HRT than it did during the 24-hr HRT. This is an assumption, however, since the 12-hr HRT startup test was conducted approximately three months after the 24-hr HRT startup test, the assumption should be valid. If, in fact, the biomass concentration was greater, more viable microorganisms were available after the shutdown period, and the reactor was able to handle startup more efficiently.

A second explanation for the increased startup efficiency for the hybrid reactor at the shorter HRT is any adverse conditions in the reactor, which resulted from the reactor sitting dormant for 14 days, would be washed out faster at the shorter HRT. For example, during the shutdown period the reactor's pH generally increases. By feeding at an increased hydraulic rate at a low pH, the high-pH liquid will be washed out, and the environment is then conducive to microbial activity.

F. Reactor Biomass and Solids Retention Time

1. Determination of reactor biomass concentration

After all experiments with the reactors had been completed, one of the fully-packed reactors was dismantled in order to determine the biomass within the reactor. Literature is sparse concerning biomass concentrations within anaerobic filters; therefore, the intent was to get an idea of the total amount of biomass within the reactor as well as to determine the distribution of biomass along the reactor height.

The reactor was taken apart and each compartment was analyzed separately (each compartment was one-third of the total volume of the reactor). The procedure was as follows: (1) the contents of each compartment were emptied into a large wash basin; (2) the inside walls of the reactor compartment were sprayed with a distilled water nozzle into the basin; (3) the media was sprayed with the nozzle one at a time to detached the biomass, which was caught in the basin along with the water; (4) after all of the media had been washed, the contents in the basin were volumetrically emptied into smaller containers which allowed uniform mixing in order to conduct solids tests; (5) total solids and suspended solids tests were conducted on each container in triplicate; (6) total reactor biomass was calculated as the summation of the products of the suspended solids concentration in each container times the volume of that container.

Figures 26 shows the suspended solids concentration in the reactor as a function of the location within the reactor, and Figure 27 shows the cumulative biomass in the reactor as a function of reactor height. The concentration in the lower third of the reactor was almost 40,000 mg of biomass per liter

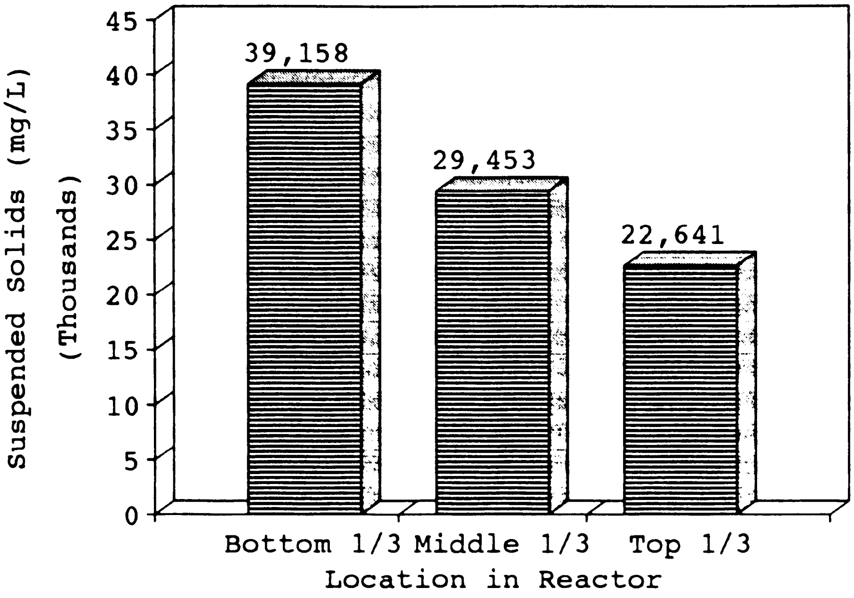

Figure 26. Suspended solids in a fully-packed reactor

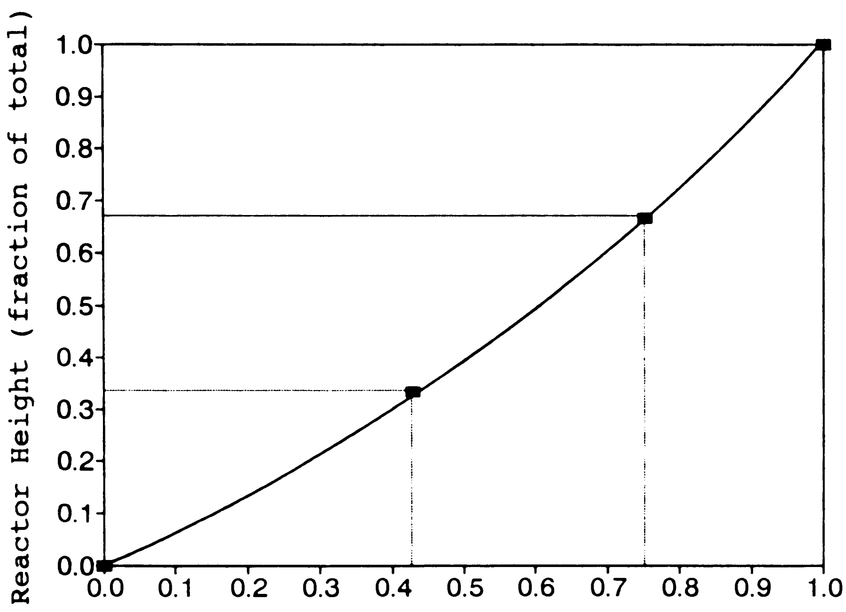

Figure 27. Relative biomass distribution throughout a fully-packed reactor

of reactor. This portion of the reactor was very concentrated with biomass with few, if any, obvious liquid pathways apparent in the media-biomass matrix. Almost all of the media rings were completely filled with biomass and the spaces between the media rings were also filled. The density of this lower portion of the reactor may have lead to short circuiting of the liquid through this compartment and contributed to higher biomass concentrations in the upper two-thirds of the reactor.

The upper third of the reactor contained a fairly high concentration of biomass (22,600 mg/L), but obvious liquid pathways were apparent. Most of the media rings were partially filled with biomass, but few were completely filled. The middle third of the reactor contained approximately 29,500 mg/L of biomass, and media plugging was intermediate between the upper and lower thirds of the reactor.

A total of 289 grams of biomass were in the 9.5 liter reactor, for an average biomass concentration of 30,420 mg/L. Approximately 42% of the total biomass was located within the lower one-third of the reactor; the middle third contained approximately 32% of the total, while the top third of the reactor contained the remaining 26% (Figure 27).

It is pointed out here that values reported for reactor biomass are on the conservative side; that is, actual values were actually greater, but some biomass was lost due to the method of washing the media. Using a spray nozzle to remove the biomass from within the media caused some splashing, and the water that did not land in the catch basin did contain some biomass. It is not clear what the percentage of biomass lost was, but the author is confident that less than 5% of the total biomass was lost due to splashing.

2. Solids retention time

Since the amount of biomass in the anaerobic filter had been determined, an estimate of the solids retention time (SRT) of the fully-packed filter could be made. However, this estimation is only valid during the latter stages of experimentation. (The biomass concentration in the reactors would necessarily increase over time. Since the determination of the amount of biomass in the filter was performed after the completion of all other testing, an SRT estimation is only valid for the period of operation immediately prior to biomass determination.)

The SRT of a system is defined as the average time that a suspended solid (SS) particle remains within the system:

$$\text{SRT} = \frac{\text{SS in system}}{\text{SS removed per time}}$$

The SS in the system was determined above, and the SS removed from the system per time is a function of the effluent SS concentration and the HRT. An example SRT calculation follows:

given: organic loading rate = 26 kg $COD/m^3/day$
HRT = 0.5 days
effluent SS = 215 mg/L (Table 23, reactor #2)
volume of reactor = 9.5 L
SS within the system = 289 g

$$SRT = \frac{(289\ g) * (1{,}000\ mg/g)}{(215\ mg/L) * (9.5\ L)\ /\ (0.5\ days)}$$

$$\underline{\underline{SRT = 71\ days}}$$

The example above shows the calculated SRT for the maximum organic loading rate of 26 kg $COD/m^3/day$. Even at this high loading rate, the SRT was greatly in excess of the minimum SRT required (10 days at 35°C). Although the SRT cannot be calculated for the system at other organic loadings with any degree of accuracy, it is reasonable to assume that the SRT's at the lower organic loadings were also in excess of the minimum of 10 days. At the lower loading rates, the effluent SS concentrations were lower than those at 26 kg $COD/m^3/day$, which results in a longer SRT, everything else being equal.

VI. CONCLUSIONS & RECOMMENDATIONS

From the results of this study, the following conclusions can be made concerning the operation and performance of laboratory scale anaerobic filters (fully- and partially-packed) fed a furfural wastewater with acetic acid as its main carbon and energy source:

(1) Both the hybrid filter and the fully-packed filters were able to remove over 90% of the influent COD (total COD basis) up to an organic loading rate of 23 kg COD/m^3/day. At 26 kg COD/m^3/day, all reactors experienced a decrease in COD removal efficiency; however, ammonia concentrations of about 1,600 mg/L were present in the reactor effluent, indicating possible ammonia inhibition.

(2) The effect of hydraulic retention time on the anaerobic filters was insignificant for the two HRT's studied (12 and 24 hours). COD removals and gas production at similar loadings were nearly identical at the two HRT's for both type of filters studied.

(3) Reactor configuration (partially-packed verses fully-packed) had little, if any, effect on the COD

removal capacity of the reactors. Operational parameters (suspended solids, volatile acids, alkalinity, etc.) in both types of reactors were similar, and methane production over time was nearly identical in the two systems studied.

(4) Startup of the fully-packed reactors after a shutdown period of approximately two weeks at both the 12- and 24-hr HRT's resulted in stable operation almost immediately at an organic loading rate of approximately 10 kg COD/m^3/day.

(5) Startup of the hybrid reactor under the same conditions as in (4) resulted in stable operation at the 12-hr HRT; however, at the 24-hr HRT, the hybrid reactor nearly failed, and a reduced organic loading rate (3 kg COD/m^3/day) was necessary to ensure that complete failure did not occur.

(6) Approximately 42% of the total reactor biomass was located in the bottom one-third of the fully-packed reactors.

(7) The estimated solids retention time for the fully-packed reactors was greatly in excess of the required minimum of 10 days at 35°C.

(8) It is recommended that the hybrid reactor configuration be used in the future since very little difference in performance was observed between the fully-packed reactors and the hybrid reactor. Savings in media cost as well as decreased chance of reactor plugging are the main advantages to the hybrid configuration.

(9) It is recommended that an HRT of 12 hr be used for the furfural wastewater at 35°C, since there was essentially no difference in reactor performance between the 24-hr and 12-hr HRT's.

VII. PRACTICAL APPLICATION/DESIGN

A. Scope

Industrial pretreatment of wastewater can often be an economically advantageous alternative to the traditional means of disposal, namely, discharge to a sanitary sewer. One of the most commonly-used pretreatment systems is the upflow anaerobic filter, especially in foreign countries. The furfural wastewater used in this study is particularly well suited for biological anaerobic pretreatment for several reasons:

(1) The furfural wastewater is a fairly soluble wastewater, and is, therefore, especially well suited for the anaerobic filter (reduced clogging risk).

(2) The organic matter in the furfural wastewater is almost completely biodegradable.

(3) The biological reactions involved in degrading the furfural wastewater are simplified by the fact that the waste is mainly acetic acid.

(4) The waste will not require heating, since it leaves the plant at 98°C. Sufficient time will be required to let the wastewater cool to mesophilic temperatures before treatment.

Anaerobic pretreatment of wastewaters offer two main economic advantages: energy recovery (methane) and reduced sewer-use fees, with the latter yielding the greatest economic returns in the majority of instances.

B. Simplified Design of an Anaerobic Filter

The design herein will only consider sizing of the anaerobic filter, and not a detailed design including inlet and outlet features, pumping requirements, settling tanks, costs, etc.

It is assumed that the filter is of the hybrid configuration, with the lower one-third of the reactor void of media. Design is based on average wastewater flow from the Quaker Oats Company (0.143 MGD), average COD of the wastewater (13,300 mg/L), and HRTs of 12, 18, and 24 hours. A typical design follows, and Table 6 presents alternative filter designs (Note: in the following calculations, the factor 8.34 has units of [lb•L/MGAL•mg]):

HRT = 12 hours = 0.5 days

Required Filter Volume = (0.143 MGD)*(0.5 days)

<u>Required Volume = 71,500 gal. = 9,560 ft^3</u>

**Assume a depth of 25 ft.
**Assume a cylindrical tank

(Design continued on following page)

$$\text{Area} = \frac{9560 \text{ ft}^3}{25 \text{ ft.}} = 382 \text{ ft}^2$$

$$\text{Diameter} = [(382 \text{ ft}^2)*(4/3.14159)]^{1/2} = 22 \text{ ft.}$$

Actual Volume = 9,503 ft^3 = 71,085 gal.

$$\text{COD Load} = \frac{(0.143 \text{ MGD})*(13{,}300 \text{ mg COD/L})*(8.34)*1000}{(9{,}503 \text{ ft}^3)*1000}$$

COD Load = 1,670 lb/1000 ft^3/day = 26.7 kg/m^3/day

$\text{COD/BOD}_5 = 1.60$

$$\text{BOD}_5 \text{ Load} = \frac{1{,}670 \text{ lb COD/1000 ft}^3\text{/day}}{1.6 \text{ lb COD/lb BOD}_5}$$

BOD_5 Load = 1,043 lb/1000 ft^3/day = 16.7 kg/m^3/day

Table 6. Anaerobic filter design parameters

	Hydraulic Retention Time, hours		
Parameter	12	18	24
Filter Depth, ft.	25	25	30
Filter Diameter, ft.	22	26	29
Filter Volume, gal.	71,085	99,284	148,220
COD Load,			
lb/1000 ft^3/day	1,670	1,195	800
kg/m^3/day	27	19	13
BOD_5 Load			
lb/1000 ft^3/day	1,043	747	500
kg/m^3/day	17	12	8

Notes: 1 kg/m^3/day = 62.4 lb/1000 ft^3/day.
1 ft^3 = 7.48 gal.

C. Economic Analysis

The economic returns in terms of methane production and reduced sewer fees are calculated assuming a COD removal efficiency. This study consistently observed COD removals in excess of 90%. However, for conservative estimates, COD removals of 80 and 90% are assumed. Costs for construction and operation of the pretreatment facility are not considered.

1. Methane production and value

Methane production at standard temperature and pressure (0°C and 1 atm, respectively) is calculated using the COD removal efficiency and the theoretical stoichiometric methane production per pound of COD destroyed [29]:

$$CH_4\ (ft^3) = \text{COD destroyed (lb)} * 5.61$$

Therefore, assuming 80% COD destruction:

$$\text{COD destroyed} = (0.8)*(13{,}300\ mg/L)*(0.143\ MGD)*(8.34)$$

$$\underline{\text{COD destroyed} = 12{,}690\ lb/day}$$

The volume of methane produced is then:

$$\text{Volume} = (5.61\ ft^3\ CH_4/lb\ COD)*(12{,}690\ lb/day)$$

$$\underline{\text{Volume} = 71{,}190\ ft^3\ CH_4/day}$$

Assuming that methane has a heating value of 960 BTU/ft^3, and that it is worth \$4/million BTUs, the value of the methane is calculated as:

Value = (71,190 ft^3/day)*(960 BTU/ft^3)*(\$4/10^6 BTU)

<u>Value = \$273/day</u>

Assuming that the Quaker Oats plant is in operation 300 days per year, the annual value of the methane is:

Annual Value = (\$273/day)*(300 day/year)

<u>Annual Value = \$82,000/year</u>

2. <u>Reduced sewer-use fees</u>

A significant economic advantage results from reduced sewer-use fees charged by the wastewater treatment plant. The wastewater treatment plant in Cedar Rapids currently charges customers based on the following rates:

Flow:	\$0.193/1000 gpd
BOD_5:	\$0.054/lb
SS:	\$0.049/lb
TKN:	\$0.264/lb

Assuming that the flow, suspended solids concentration, and TKN concentration will remain similar to their present values, the reduced fees are calculated on the basis of BOD_5 removal efficiency. Since the waste is close to 100% biodegradable, the BOD_5 removal efficiency is approximately equal to COD removal efficiency. Using an average BOD_5 of 8,290 mg/L (Table 1) and assuming an BOD_5 removal efficiency of 80%, the BOD_5 removed (i.e., not discharged to the sanitary sewer) is:

BOD_5 removed = (0.8)*(8,290 mg/L)*(0.143 MGD)*(8.34)

<u>BOD_5 removed = 7,910 lb/day</u>

The money saved from reduced sewer fees is calculated as:

Value = (7,910 lb/day)*($0.054/lb)

<u>Value = $427.14/day</u>

The annual value, assuming that the plant is in operation 300 days per year, is:

Annual Value = ($427.14/day)*(300 days/year)

<u>Annual Value = $128,100</u>

Table 7 summarizes the economic analysis. Methane production and reduced sewer fees account for approximately 39 and 61%, respectively, of the total annual savings/value that could be realized by anaerobic pretreating the furfural wastewater.

Table 7. Economic analysis

Annual Value of	COD/BOD$_5$ Removal Efficiency 80%	90%
Methane	$82,000	$92,200
Reduced Sewer Fees	$128,100	$144,200
Total	$210,100	$236,400

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APPENDIX A. DATA AT THE 24-HOUR HRT

Table 8. Daily methane production at the 24-hr HRT

Date	Day	Nominal COD Load (kg/m^3/day) (#1, #2, #3)a	Standard Methane Production (L/L/day) #1	#2	#3
02/05/91	1	1.0, 1.0, 1.0			
02/06/91	2	2.5, 2.5, 2.5	0.39	0.51	0.58
02/07/91	3	2.5, 2.5, 2.5	0.63	0.65	0.72
02/08/91	4	2.5, 2.5, 2.5	0.69	0.76	0.75
02/09/91	5	3.0, 3.0, 6.0	0.80	0.70	0.84
02/10/91	6	3.0, 3.0, 6.0	0.89	0.85	1.09
02/11/91	7	3.0, 3.0, 6.0	0.97	0.86	1.17
02/12/91	8	3.0, 3.0, 6.0	1.02	0.90	1.25
02/13/91	9	3.0, 3.0, 6.0	1.06	0.98	1.34
02/14/91	10	3.0, 3.0, 6.0	1.09	0.94	1.22
02/15/91	11	3.0, 3.0, 6.0	1.04	0.92	1.19
02/16/91	12	3.0, 3.0, 6.0	1.02	0.92	1.22
02/17/91	13	3.0, 3.0, 6.0	1.11	1.09	1.25
02/18/91	14	3.0, 3.0, 6.0	1.09	1.05	1.25
02/19/91	15	3.0, 3.0, 6.0	1.10	1.05	1.32
02/20/91	16	3.0, 3.0, 6.0	1.09	1.05	1.31
02/21/91	17	3.0, 3.0, 6.0	1.15	1.07	1.38
02/22/91	18	3.0, 3.0, 6.0	1.13	1.19	1.35
02/23/91	19	3.0, 3.0, 6.0	1.11	1.05	1.46
02/24/91	20	3.0, 3.0, 6.0	1.15	1.12	1.40
02/25/91	21	3.0, 3.0, 6.0	1.10	1.14	1.38
02/26/91	22	3.0, 3.0, 6.0	1.16	1.08	1.52
02/27/91	23	3.0, 3.0, 6.0	1.17	1.11	1.60
02/28/91	24	3.0, 3.0, 6.0	1.14	1.20	1.73
03/01/91	25	3.0, 3.0, 6.0	1.17	1.12	1.79
03/02/91	26	3.0, 3.0, 6.0	1.09	1.15	1.83
03/03/91	27	3.0, 3.0, 6.0	1.17	1.11	1.91
03/04/91	28	3.0, 3.0, 6.0	1.10	1.16	1.87
03/05/91	29	3.0, 3.0, 6.0	1.15	1.06	1.62
03/06/91	30	3.0, 3.0, 6.0	1.22	1.22	2.24
03/07/91	31	3.0, 3.0, 6.0	1.09	1.24	2.39
03/08/91	32	3.0, 3.0, 6.0	1.11	1.21	2.06
03/09/91	33	3.0, 3.0, 6.0	1.12	1.12	2.01

a Reactor #1 is the hybrid; #2 & 3 are fully-packed.

Table 8. Daily methane production at the 24-hr HRT(cont.)

Date	Day	Nominal COD Load (kg/m^3/day) (#1, #2, #3)	Standard Methane Production (L/L/day) #1	#2	#3
03/10/91	34	3.0, 3.0, 6.0	1.11	1.14	2.08
03/11/91	35	4.5, 4.5, 6.0	1.03	1.08	2.09
03/12/91	36	4.5, 4.5, 6.0	1.06	1.12	2.06
03/13/91	37	4.5, 4.5, 6.0	1.27	1.17	1.93
03/14/91	38	4.5, 4.5, 6.0	1.36	1.42	2.07
03/15/91	39	4.5, 4.5, 6.0	1.59	1.65	2.17
03/16/91	40	4.5, 4.5, 6.0	1.65	1.62	2.23
03/17/91	41	4.5, 4.5, 6.0	1.66	1.58	2.20
03/18/91	42	4.5, 4.5, 6.0	1.62	1.64	2.16
03/19/91	43	7.5, 7.5, 9.0	1.79	1.75	2.24
03/20/91	44	7.5, 7.5, 9.0	2.09	2.06	2.62
03/21/91	45	7.5, 7.5, 9.0	2.58	2.54	3.00
03/22/91	46	7.5, 7.5, 9.0	2.61	2.63	3.06
03/23/91	47	7.5, 7.5, 9.0	2.65	2.57	3.17
03/24/91	48	7.5, 7.5, 9.0	2.85	2.78	3.06
03/25/91	49	7.5, 7.5, 9.0	2.56	2.54	3.22
03/26/91	50	7.5, 7.5, 9.0	2.68	2.61	3.19
03/27/91	51	7.5, 7.5, 9.0	2.67	2.62	3.21
03/28/91	52	7.5, 7.5, 9.0	2.67	2.63	3.30
03/29/91	53	7.5, 7.5, 9.0	2.69	2.67	3.29
03/30/91	54	7.5, 7.5, 9.0	2.82	2.82	3.48
03/31/91	55	7.5, 7.5, 9.0	2.98	3.00	3.50
04/01/91	56	7.5, 7.5, 9.0	3.01	2.93	3.54
04/02/91	57	7.5, 7.5, 9.0	2.98	2.98	3.38
04/03/91	58	7.5, 7.5, 9.0	2.89	2.88	3.41
04/04/91	59	7.5, 7.5, 9.0	2.96	2.89	3.46
04/05/91	60	7.5, 7.5, 9.0	3.03	3.00	3.61
04/06/91	61	7.5, 7.5, 9.0	2.97	3.01	3.62
04/07/91	62	7.5, 7.5, 9.0	2.83	2.88	3.45
04/08/91	63	10.5,10.5,12.0	2.94	2.98	3.52
04/09/91	64	10.5,10.5,12.0	3.66	3.70	4.26
04/10/91	65	10.5,10.5,12.0	4.04	4.08	4.41
04/11/91	66	10.5,10.5,12.0	3.53	3.74	4.15

Table 8. Daily methane production at the 24-hr HRT(cont.)

Date	Day	Nominal COD Load (kg/m^3/day) (#1, #2, #3)	Standard Methane Production (L/L/day) #1	#2	#3
04/12/91	67	10.5,10.5,12.0	3.32	3.60	4.06
04/13/91	68	10.5,10.5,12.0	2.75	3.07	3.44
04/14/91	69	10.5,10.5,12.0	3.51	3.55	4.08
04/15/91	70	10.5,10.5,12.0	3.35	3.65	4.04
04/16/91	71	10.5,10.5,12.0	3.29	3.72	4.09
04/17/91	72	10.5,10.5,12.0	3.75	3.89	4.11
04/18/91	73	10.5,10.5,12.0	3.16	3.66	3.91
04/19/91	74	10.5,10.5,12.0	3.44	3.51	3.97
04/20/91	75	10.5,10.5,12.0	3.54	3.55	4.01
04/21/91	76	10.5,10.5,12.0	3.77	3.73	4.17
04/22/91	77	10.5,10.5,12.0	3.67	3.69	4.13
04/23/91	78	10.5,10.5,12.0	3.75	3.70	4.26
04/24/91	79	10.5,10.5,12.0	3.75	3.67	4.25
04/25/91	80	13.5,13.5,15.0	3.81	3.71	4.27
04/26/91	81	13.5,13.5,15.0	4.17	4.14	4.65
04/27/91	82	13.5,13.5,15.0	4.72	4.63	5.13
04/28/91	83	13.5,13.5,15.0	4.62	4.56	5.06
04/29/91	84	13.5,13.5,15.0	4.67	4.69	5.15
04/30/91	85	13.5,13.5,15.0	4.61	4.58	5.03
05/01/91	86	13.5,13.5,15.0	4.56	4.50	4.92

Table 9. COD analysis for the hybrid (reactor #1) at the 24-hr HRT

			COD (mg/L)		
		HRT	Influent	Effluent	
Date	Day	(hr)	Total	Total	Soluble
02/12/91	8	24	2,630		
02/15/91	11	24	2,715	630	300
02/17/91	13	24	2,960	552	296
02/20/91	16	24	3,090	565	339
02/25/91	21	24	2,119	538	200
02/28/91	24	24	2,765	388	182
03/04/91	28	24	3,396	479	298
03/07/91	31	24	3,480	412	196
03/13/91	37	24	2,887	471	228
03/15/91	39	24	4,738	499	257
03/17/91	41	24	4,696	451	256
03/19/91	43	24	4,880	439	255
03/21/91	45	24	7,527		
03/24/91	48	24	7,473	883	613
03/27/91	51	24	7,481	795	565
03/29/91	53	24	6,919	651	530
04/01/91	56	24	8,074	717	566
04/06/91	61	24	7,243		
04/08/91	63	24	8,082	638	438
04/10/91	65	24	10,488		
04/12/91	67	24	9,137	635	461
04/15/91	70	24	10,258	785	534
04/17/91	72	24	9,694	718	547
04/20/91	75	24	10,740	940	803
04/22/91	77	24	10,404	809	635
04/24/91	79	24	10,497	656	438
04/29/91	84	24	13,072	1,000	809

Table 10. COD analysis for the fully-packed reactor (#2) at the 24-hr HRT

			COD (mg/L)		
			Influent	Effluent	
Date	Day	HRT (hr)	Total	Total	Soluble
02/12/91	8	24	2,630		
02/15/91	11	24	2,715	420	190
02/17/91	13	24	2,960	576	432
02/20/91	16	24	3,090	508	379
02/25/91	21	24	2,119	345	233
02/28/91	24	24	2,765	333	245
03/04/91	28	24	3,396	502	424
03/07/91	31	24	3,480	272	208
03/13/91	37	24	2,887	337	259
03/15/91	39	24	4,738	370	292
03/17/91	41	24	4,696	331	256
03/19/91	43	24	4,880	395	271
03/21/91	45	24	7,527		
03/24/91	48	24	7,473	954	680
03/27/91	51	24	7,481	943	763
03/29/91	53	24	6,919	844	658
04/01/91	56	24	8,074	801	655
04/06/91	61	24	7,243		
04/08/91	63	24	8,082	598	480
04/10/91	65	24	10,488		
04/12/91	67	24	9,137	793	659
04/15/91	70	24	10,258	795	646
04/17/91	72	24	9,694	685	566
04/20/91	75	24	10,740	834	700
04/22/91	77	24	10,404	719	612
04/24/91	79	24	10,497	712	574
04/29/91	84	24	13,072	662	538

Table 11. COD analysis for the fully-packed reactor (#3) at the 24-hr HRT

			COD (mg/L)		
		HRT	Influent	Effluent	
Date	Day	(hr)	Total	Total	Soluble
02/12/91	8	24	5,250		
02/15/91	11	24	5,370	2,555	2,345
02/17/91	13	24	6,048	3,600	3,456
02/20/91	16	24	5,937	3,373	3,162
02/25/91	21	24	4,109	1,557	1,461
02/28/91	24	24	5,513	1,568	1,536
03/04/91	28	24	6,400	1,883	1,820
03/07/91	31	24	6,560	848	712
03/13/91	37	24	4,440	470	392
03/15/91	39	24	6,296	475	397
03/17/91	41	24	6,262	443	371
03/19/91	43	24	6,347	462	359
03/21/91	45	24	9,031		
03/24/91	48	24	8,560	707	578
03/27/91	51	24	9,191	676	545
03/29/91	53	24	8,591	651	531
04/01/91	56	24	9,675	695	524
04/06/91	61	24	8,546		
04/08/91	63	24	9,600	610	457
04/10/91	65	24	12,046		
04/12/91	67	24	10,641	725	572
04/15/91	70	24	11,669	681	488
04/17/91	72	24	11,023	607	435
04/20/91	75	24	12,214	711	509
04/22/91	77	24	11,902	615	445
04/24/91	79	24	12,100	795	626
04/29/91	84	24	14,457	742	511

Table 12. Alkalinity data at the 24-hr HRT

		Hybrid (#1)		Fully-Packed (#2)		Fully-Packed (#3)	
Date	Day	Load [a] (g/L/day)[b]	Alk., mg/L as CaCO3 [c]	Load (g/L/day)	Alk., mg/L as CaCO3	Load (g/L/day)	Alk., mg/L as CaCO3
03/01/91	25	3.0	2,619	3.0	2,574	6.0	4,474
03/07/91	31	3.0	2,604	3.0	2,574	6.0	4,884
03/11/91	35	3.0	2,424	3.0	2,464	6.0	4,944
03/16/91	40	4.5	3,729	4.5	3,692	6.0	4,839
03/18/91	42	4.5	3,941	4.5	3,690	6.0	4,744
03/23/91	47	7.5	5,624	7.5	5,624	9.0	6,704
03/26/91	50	7.5	4,244	7.5	4,252	9.0	5,244
04/01/91	56	7.5	4,154	7.5	4,054	9.0	4,864
04/14/91	69	10.5	4,744	10.5	5,044	12.0	5,364
04/21/91	76	10.5	5,944	10.5	5,824	12.0	6,354
04/30/91	85	13.5	7,204	13.5	7,044	15.0	7,844

[a] This is the target loading rate and not the actual loading rate.

[b] 1 g/L/day = 1 kg/m^3/day.

[c] Titrated to pH 4.5 with 0.1 N sulfuric acid.

Table 13. Effluent volatile acids (as acetic acid) at the 24-hr HRT

Date	Hybrid (#1)		Fully-Packed (#2)		Fully-Packed (#3)	
	Load [a] (g/L/day)[b]	Vol. Acids (mg/L)[c]	Load (g/L/day)	Vol. Acids (mg/L)	Load (g/L/day)	Vol. Acids (mg/L)
03/04/91	3.0	124	3.0	249	6.0	1407
03/07/91	3.0	21	3.0	21	6.0	296
03/11/91	3.0	17	3.0	26	6.0	183
03/13/91	4.5	70	4.5	139	6.0	138
03/16/91	4.5	58	4.5	55	6.0	98
03/18/91	4.5	47	4.5	55	6.0	76
03/23/91	7.5	408	7.5	503	9.0	372
03/26/91	7.5	235	7.5	493	9.0	184
03/29/91	7.5	177	7.5	313	9.0	135
04/14/91	10.5	195	10.5	206	12.0	100
04/17/91	10.5	54	10.5	165	12.0	51
04/21/91	10.5	246	10.5	176	12.0	73
04/30/91	13.5	391	13.5	129	15.0	161

[a] Target COD load, not actual calculated load.

[b] 1 g/L/day = 1 kg/m^3/day.

[c] Titrated to pH 8.3 with 0.1 N sodium hydroxide.

Table 14. Effluent suspended solids at the 24-hr HRT

	Hybrid (#1)			Fully-Packed (#2)			Fully-Packed (#3)		
Date	Load a (g/L/d)b	SS (mg/L)	% Volatile	Load (g/L/d)	SS (mg/L)	% Volatile	Load (g/L/d)	SS (mg/L)	% Volatile
02/26/91	3.0	144	70.1	3.0	99	65.9	6.0	140	65.8
03/06/91	3.0	138	60.1	3.0	357	61.6	6.0	142	59.8
03/07/91	3.0	150	71.6	3.0	96	60.4	6.0	124	----
03/13/91	4.5	141	58.2	4.5	157	58.6	6.0	117	51.3
03/16/91	4.5	170	63.6	4.5	117	57.3	6.0	105	51.4
03/18/91	4.5	176	64.8	4.5	114	61.4	6.0	105	53.3
03/23/91	7.5	188	64.9	7.5	177	61.6	9.0	154	57.7
03/25/91	7.5	139	67.6	7.5	218	73.0	9.0	171	64.4
03/28/91	7.5	148	69.7	7.5	181	69.1	9.0	166	66.3
04/15/91	10.5	318	73.3	10.5	155	65.2	12.0	196	72.7
04/17/91	10.5	168	70.8	10.5	135	65.2	12.0	174	67.8
04/21/91	10.5	155	64.5	10.5	140	57.3	12.0	181	65.8
04/29/91	13.5	209	70.3	13.5	159	62.2	15.0	245	67.8

a Approximate COD loading rate.

b 1 g/L/day = 1 kg/m^3/day.

Table 15. COD data during startup experiment at the 24-hr HRT

Hours Since Startup	Effluent Soluble COD's (g/L)			Effluent Total COD's (g/L)		
	Hybrid (#1)	Fully Packed (#2)	Fully Packed (#3)	Hybrid (#1)	Fully Packed (#2)	Fully Packed (#3)
0.00	0.000	0.000	0.000	0.000	0.000	0.000
1.00	0.845	0.346	0.384	1.133	0.557	0.480
4.00	1.298	0.453	0.607	1.436	0.568	0.791
6.00	1.928	0.461	0.768	2.027	0.737	0.914
12.00	3.300	0.860	0.884	3.500	1.015	1.111
18.00	4.437	1.003	1.023	4.669	1.150	1.204
24.25	5.230	1.165	1.146	5.230	1.304	1.285
34.50	5.846	1.319	1.227	5.908	1.435	1.396
54.00	6.170	1.306	1.242	6.315	1.422	1.362
74.50	6.459	1.202	1.094	6.587	1.286	1.190
87.00	6.405	1.138	0.946	6.549	1.238	1.086

Notes: Influent COD concentration was 11.0 g/L/day.
Shutdown time was 15 days.

Table 16. Methane production during the startup experiment at the 24-hr HRT

Time Since Startup	Standard Methane Production (L/L/day) Hybrid (#1)	Fully-Packed (#2)	Fully-Packed (#3)
0.00	0.00	0.00	0.00
0.50	0.61	0.32	0.30
1.00	0.61	0.32	0.59
1.50	0.61	0.32	0.89
2.00	0.92	0.95	2.36
2.50	0.92	2.22	2.95
3.00	1.22	2.53	2.95
3.50	0.60	2.82	3.76
4.00	0.00	3.11	3.75
5.25	1.04	3.08	3.48
5.50	1.71	3.66	4.33
6.00	1.40	3.62	4.01
6.75	1.45	3.63	3.50
7.50	1.41	3.85	1.86
8.00	1.54	3.66	3.44
8.50	0.00	1.53	4.73
10.00	1.20	3.49	3.70
10.50	1.40	3.71	4.16
11.00	1.80	4.34	4.83
11.50	1.34	4.04	4.16
12.50	0.45	3.73	2.07
13.50	1.22	3.89	3.80
14.50	0.88	4.37	4.09
15.25	1.45	1.46	3.54
16.25	1.53	3.91	4.23
18.00	0.75	3.85	3.23
19.00	1.10	3.29	2.83
24.25	1.17	3.28	3.32
25.00	1.52	3.96	3.97
26.25	1.11	2.87	2.75

Notes: Influent COD concentration was 11.0 g/L/day.
Shutdown time was 15 days.

Table 16. Methane production during the startup experiment at the 24-hr HRT (cont.)

Time Since Startup	Standard Methane Production (L/L/day) Hybrid (#1)	Fully-Packed (#2)	Fully-Packed (#3)
27.33	1.15	4.20	5.21
28.00	1.66	3.27	3.50
30.50	1.00	3.82	2.94
31.50	1.60	2.19	3.91
32.50	1.47	4.23	4.23
34.25	1.00	3.85	3.40
35.50	1.13	3.26	2.89
36.50	1.53	2.82	3.77
37.50	1.45	3.61	3.77
38.50	0.63	4.23	4.41
41.00	1.49	3.83	3.15
42.00	1.08	2.36	3.79
43.00	0.98	3.44	3.46
50.00	1.38	3.54	3.63
51.00	0.77	3.73	3.75
54.00	1.00	3.99	3.28
59.50	1.27	3.81	3.58
60.00	0.88	2.48	4.68
63.00	1.36	3.62	3.33
74.25	1.00	3.32	3.29
75.50	0.98	3.50	3.27
76.00	1.56	3.75	3.77
79.00	0.89	3.12	3.67
84.00	1.09	3.56	3.36
86.50	0.93	2.81	3.08
100.00	0.95	3.23	3.35

APPENDIX B. DATA AT THE 12-HOUR HRT

Table 17. Daily methane production at the 12-hr HRT

Date	Day	Approximate COD Load a (g/L/day) (#1,#2,#3)	Standard Methane Production (L/L/day) Hybrid (#1)	Fully Packed (#2)	Fully Packed (#3)
05/29/91	1	3.0, 3.0, 4.5			
05/30/91	2	3.0, 3.0, 4.5	0.65	0.95	1.58
05/31/91	3	3.0, 3.0, 4.5	0.63	0.88	1.59
06/01/91	4	3.0, 3.0, 4.5	0.92	1.01	1.54
06/02/91	5	3.0, 3.0, 4.5	0.69	0.68	0.67
06/03/91	6	3.0, 3.0, 4.5	0.57	0.73	1.44
06/04/91	7	3.0, 3.0, 4.5	0.81	0.89	1.48
06/05/91	8	3.0, 3.0, 4.5	0.73	1.04	1.53
06/06/91	9	3.0, 3.0, 4.5	0.78	0.99	1.54
06/07/91	10	3.0, 3.0, 4.5	1.01	0.95	1.56
06/08/91	11	3.0, 3.0, 4.5	0.81	1.02	1.51
06/09/91	12	3.0, 3.0, 4.5	0.91	0.94	1.45
06/10/91	13	3.0, 3.0, 4.5	0.96	0.99	1.51
06/11/91	14	3.0, 3.0, 4.5	0.99	1.05	1.34
06/12/91	15	3.0, 3.0, 4.5	0.95	0.97	1.34
06/13/91	16	3.0, 3.0, 4.5	0.97	1.00	1.28
06/14/91	17	3.0, 3.0, 4.5	0.97	1.00	1.50
06/15/91	18	3.0, 3.0, 4.5	0.93	0.93	1.43
06/16/91	19	6.0, 6.0, 7.5	1.75	1.92	2.36
06/17/91	20	6.0, 6.0, 7.5	1.97	2.06	2.62
06/18/91	21	6.0, 6.0, 7.5	1.90	1.88	2.25
06/19/91	22	6.0, 6.0, 7.5	2.01	1.97	2.56
06/20/91	23	6.0, 6.0, 7.5	1.98	1.96	2.42
06/21/91	24	6.0, 6.0, 7.5	1.86	2.05	2.64
06/22/91	25	6.0, 6.0, 7.5	1.87	1.95	2.59
06/23/91	26	6.0, 6.0, 7.5	1.96	1.98	2.56
06/24/91	27	6.0, 6.0, 7.5	2.08	2.15	2.57
06/25/91	28	6.0, 6.0, 7.5	2.11	2.16	2.56
06/26/91	29	9.0, 9.0, 11.0	2.14	2.16	2.57
06/27/91	30	9.0, 9.0, 11.0	3.02	3.02	3.90
06/28/91	31	9.0, 9.0, 11.0	3.08	3.20	4.01

a Target load, not the actual COD load.

Table 17. Daily methane production at the 12-hr HRT (cont.)

Date	Day	Approximate COD Load a (g/L/day) (#1,#2,#3)	Standard Methane Production (L/L/day) Hybrid (#1)	Fully Packed (#2)	Fully Packed (#3)
06/29/91	32	9.0, 9.0, 11.0	3.11	3.07	4.07
06/30/91	33	9.0, 9.0, 11.0	3.04	3.28	4.11
07/01/91	34	9.0, 9.0, 11.0	3.04	3.05	4.14
07/02/91	35	9.0, 9.0, 11.0	3.10	3.21	4.09
07/03/91	36	9.0, 9.0, 11.0	3.07	3.09	4.18
07/04/91	37	9.0, 9.0, 11.0	3.08	3.16	3.73
07/05/91	38	9.0, 9.0, 11.0	3.03	3.04	3.80
07/06/91	39	13.0, 13.0, 15.0	4.25	4.24	4.90
07/07/91	40	13.0, 13.0, 15.0	4.19	4.27	5.23
07/08/91	41	13.0, 13.0, 15.0	4.56	4.60	5.27
07/09/91	42	13.0, 13.0, 15.0	4.50	4.50	5.27
07/10/91	43	13.0, 13.0, 15.0	4.69	4.71	5.30
07/11/91	44	13.0, 13.0, 15.0	4.60	4.62	5.23
07/12/91	45	13.0, 13.0, 15.0	4.50	4.55	5.38
07/13/91	46	13.0, 13.0, 15.0	4.64	4.68	5.23
07/14/91	47	13.0, 13.0, 15.0	4.55	4.61	5.15
07/15/91	48	13.0, 13.0, 15.0	4.65	4.65	5.08
07/16/91	49	13.0, 13.0, 15.0	4.62	4.59	5.09
07/17/91	50	13.0, 13.0, 15.0	4.50	4.54	4.99
07/18/91	51	17.0, 17.0, 19.0	5.25	6.00	6.00
07/19/91	52	17.0, 17.0, 19.0	5.73	5.94	6.69
07/20/91	53	17.0, 17.0, 19.0	6.28	6.38	6.75
07/21/91	54	18.0, 18.0, 20.0	6.35	6.45	7.01
07/22/91	55	18.0, 18.0, 20.0	6.02	6.30	7.07
07/23/91	56	18.0, 18.0, 20.0	6.31	6.23	6.95
07/24/91	57	18.0, 18.0, 20.0	6.28	6.27	7.00
07/25/91	58	18.0, 18.0, 20.0	6.23	6.25	6.97
07/26/91	59	18.0, 18.0, 20.0	6.26	6.35	7.07
07/27/91	60	18.0, 18.0, 20.0	5.92	5.94	6.86
07/28/91	61	18.0, 18.0, 20.0	6.10	6.23	6.80

Table 17. Daily methane production at the 12-hr HRT (cont.)

Date	Day	Approximate COD Load[a] (g/L/day) (#1,#2,#3)	Standard Methane Production (L/L/day) Hybrid (#1)	Standard Methane Production (L/L/day) Fully Packed (#2)	Standard Methane Production (L/L/day) Fully Packed (#3)
07/29/91	62	23.0, 23.0, 23.0	7.20	7.55	7.53
07/30/91	63	23.0, 23.0, 23.0	7.68	7.82	7.80
07/31/91	64	23.0, 23.0, 23.0	7.98	8.12	8.05
08/01/91	65	23.0, 23.0, 23.0	7.82	7.94	7.98
08/02/91	66	23.0, 23.0, 23.0	7.86	7.86	7.69
08/03/91	67	23.0, 23.0, 23.0	7.65	7.49	7.61
08/04/91	68	23.0, 23.0, 23.0	7.84	7.87	7.73
08/05/91	69	23.0, 23.0, 23.0	8.03	7.94	7.95
08/06/91	70	23.0, 23.0, 23.0	7.73	7.74	7.64
08/07/91	71	23.0, 23.0, 23.0	7.72	7.88	7.77
08/08/91	72	26.0, 26.0, 26.0	7.37	7.71	7.56
08/09/91	73	26.0, 26.0, 26.0	7.63	8.11	7.90
08/10/91	74	26.0, 26.0, 26.0	7.78	8.15	8.00
08/11/91	75	26.0, 26.0, 26.0	7.57	7.81	7.73
08/12/91	76	26.0, 26.0, 26.0	7.53	7.90	7.88
08/13/91	77	26.0, 26.0, 26.0	7.80	8.17	7.76
08/14/91	78	26.0, 26.0, 26.0	7.76	8.20	7.83

Table 18. COD analysis for the hybrid (reactor #1) at the 12-hr HRT

			COD (mg/L)		
		HRT	Influent	Effluent	
Date	Day	(hr)	Total	Total	Soluble
06/04/91	7	12	1,571		
06/05/91	8	12		155	105
06/07/91	10	12	1,577	141	115
06/09/91	12	12	1,611	138	91
06/12/91	15	12	1,512	129	102
06/19/91	22	12	2,930	315	193
06/22/91	25	12	3,205	266	181
06/24/91	27	12	3,098	233	176
06/30/91	33	12	4,591	343	256
07/02/91	35	12	4,564	310	247
07/04/91	37	12	4,658	346	263
07/12/91	45	12	6,705	479	356
07/14/91	47	12	6,543	461	335
07/16/91	49	12	6,622	481	372
07/23/91	56	12	8,971	626	474
07/25/91	58	12	8,761	643	481
07/27/91	60	12	8,924	699	521
08/03/91	67	12	11,358	1,177	949
08/05/91	69	12	11,637	1,112	858
08/07/91	71	12	11,800	1,217	987
08/10/91	74	12	12,878	2,591	2,362
08/12/91	76	12	13,357	2,478	2,236
08/14/91	78	12	13,531	2,439	2,122

Table 19. COD analysis for the fully-packed reactor (#2) at the 12-hr HRT

			COD (mg/L)		
			Influent	Effluent	
Date	Day	HRT (hr)	Total	Total	Soluble
06/04/91	7	12	1,571		
06/05/91	8	12		150	101
06/07/91	10	12	1,577	145	93
06/09/91	12	12	1,611	143	91
06/12/91	15	12	1,512	124	89
06/19/91	22	12	2,930	175	127
06/22/91	25	12	3,205	215	138
06/24/91	27	12	3,098	213	137
06/30/91	33	12	4,591	333	238
07/02/91	35	12	4,564	280	213
07/04/91	37	12	4,658	293	195
07/12/91	45	12	6,705	410	314
07/14/91	47	12	6,543	424	325
07/16/91	49	12	6,622	417	311
07/23/91	56	12	8,971	581	472
07/25/91	58	12	8,761	632	500
07/27/91	60	12	8,924	616	470
08/03/91	67	12	11,358	1,082	879
08/05/91	69	12	11,637	981	823
08/07/91	71	12	11,800	998	798
08/10/91	74	12	12,878	1,821	1,682
08/12/91	76	12	13,357	1,893	1,722
08/14/91	78	12	13,531	1,736	1,559

Table 20. COD analysis for the fully-packed reactor (#3) at the 12-hr HRT

			COD (mg/L)		
		HRT	Influent	Effluent	
Date	Day	(hr)	Total	Total	Soluble
06/04/91	7	12	2,396		
06/05/91	8	12		187	131
06/07/91	10	12	2,357	164	120
06/09/91	12	12	2,324	170	139
06/12/91	15	12	2,149	141	112
06/19/91	22	12	3,522	237	177
06/22/91	25	12	3,677	240	174
06/24/91	27	12	3,616	221	163
06/30/91	33	12	5,448	338	250
07/02/91	35	12	5,619	298	199
07/04/91	37	12	5,508	306	208
07/12/91	45	12	8,067	522	311
07/14/91	47	12	7,358	613	395
07/16/91	49	12	7,841	470	264
07/23/91	56	12	10,057	917	709
07/25/91	58	12	9,922	796	628
07/27/91	60	12	10,177	783	604
08/03/91	67	12	11,358	1,177	985
08/05/91	69	12	11,637	1,018	807
08/07/91	71	12	11,800	1,032	861
08/10/91	74	12	12,878	2,254	2,025
08/12/91	76	12	13,357	2,159	1,886
08/14/91	78	12	13,531	2,253	2,022

Table 21. Alkalinity data at the 12-hr HRT

		Hybrid (#1)		Fully-Packed (#2)		Fully-Packed (#3)	
Date	Day	Load [a] (g/L/day)	Alk., mg/L as CACO3 [b]	Load (g/L/day)	Alk., mg/L as CACO3	Load (g/L/day)	Alk., mg/L as CACO3
06/08/91	11	3.0	1,004	3.0	1,024	4.5	1,574
06/10/91	13	3.0	984	3.0	964	4.5	1,504
06/20/91	23	6.0	1,804	6.0	1,812	7.5	2,766
06/23/91	26	6.0	1,846	6.0	1,842	7.5	2,278
06/29/91	32	9.0	2,392	9.0	2,426	11.0	3,484
07/01/91	34	9.0	2,444	9.0	2,388	11.0	2,944
07/13/91	46	13.0	3,600	13.0	3,586	15.0	4,248
07/15/91	48	13.0	3,666	13.0	3,616	15.0	4,592
07/22/91	55	18.0	5,110	18.0	5,040	20.0	5,612
07/24/91	57	18.0	5,090	18.0	5,118	20.0	5,700
08/03/91	67	23.0	7,000	23.0	6,800	23.0	6,922
08/04/91	68	23.0	6,702	23.0	6,602	23.0	6,516
08/11/91	75	26.0	7,220	26.0	7,440	26.0	7,520
08/13/91	77	26.0	7,198	26.0	7,570	26.0	7,562

[a] Approximate COD loading rate.

[b] Titrated to pH 4.5 with 0.1 N sulfuric acid.

Table 22. Effluent volatile acids (as acetic acid) at the 12-hr HRT

		Hybrid (#1)		Fully-Packed (#2)		Fully-Packed (#3)	
Date	Day	COD Load [a] (g/L/day)	Volatile Acids [b] (mg/L)	COD Load (g/L/day)	Volatile Acids (mg/L)	COD Load (g/L/day)	Volatile Acids (mg/L)
06/08/91	11	3.0	38	3.0	11	4.5	38
06/10/91	13	3.0	29	3.0	42	4.5	43
06/20/91	23	6.0	37	6.0	348	7.5	228
06/23/91	26	6.0	32	6.0	19	7.5	25
06/25/91	28	6.0	22	6.0	20	7.5	23
06/29/91	32	9.0	82	9.0	73	11.0	72
07/01/91	34	9.0	63	9.0	44	11.0	55
07/04/91	37	9.0	46	9.0	15	11.0	21
07/11/91	44	13.0	121	13.0	109	15.0	103
07/13/91	46	13.0	109	13.0	87	15.0	102
07/15/91	48	13.0	110	13.0	100	15.0	120
07/22/91	55	18.0	187	18.0	217	20.0	396
07/24/91	57	18.0	147	18.0	178	20.0	202
07/26/91	59	18.0	207	18.0	162	20.0	243
08/02/91	66	23.0	301	23.0	214	23.0	270
08/04/91	68	23.0	457	23.0	402	23.0	515
08/06/91	70	23.0	432	23.0	417	23.0	473
08/11/91	75	26.0	1,637	26.0	1,146	26.0	772
08/13/91	77	26.0	1,433	26.0	965	26.0	1,508

[a] Approximate COD loading rate.

[b] Titrated to pH 8.3 with 0.1 N sodium hydroxide.

Table 23. Effluent suspended solids data at the 12-hr HRT

Date	Hybrid (#1)			Fully-Packed (#2)			Fully-Packed (#3)		
	Load[a] (g/L/d)	SS (mg/L)	% Volatile	Load (g/L/d)	SS (mg/L)	% Volatile	Load (g/L/d)	SS (mg/L)	% Volatile
06/07/91	3.0	37	62.4	3.0	44	59.1	4.5	50	54.2
06/09/91	3.0	37	51.8	3.0	49	53.0	4.5	48	50.0
06/12/91	3.0	39	61.6	3.0	43	63.0	4.5	61	60.9
06/19/91	6.0	80	67.5	6.0	62	71.0	7.5	98	73.5
06/22/91	6.0	57	70.3	6.0	67	70.3	7.5	66	63.6
06/24/91	6.0	63	61.9	6.0	71	73.3	7.5	68	64.7
06/30/91	9.0	92	76.1	9.0	89	70.8	11.0	101	70.3
07/02/91	9.0	89	64.3	9.0	84	60.8	11.0	131	68.0
07/04/91	9.0	94	62.7	9.0	102	50.0	11.0	114	69.3
07/12/91	13.0	141	71.3	13.0	117	65.8	15.0	217	73.3
07/14/91	13.0	124	73.7	13.0	114	70.2	15.0	219	75.4
07/16/91	13.0	131	70.3	13.0	123	72.4	15.0	192	74.0
07/23/91	18.0	167	70.8	18.0	131	68.7	20.0	249	71.2
07/25/91	18.0	151	70.2	18.0	139	64.7	20.0	142	65.5
07/27/91	18.0	182	76.9	18.0	160	71.9	20.0	188	75.5
08/03/91	23.0	277	72.6	23.0	232	70.7	23.0	250	72.0
08/05/91	23.0	271	76.4	23.0	204	70.6	23.0	263	73.8
08/07/91	23.0	309	79.0	23.0	248	75.5	23.0	310	74.6
08/10/91	26.0	273	76.2	26.0	213	71.9	26.0	283	76.7
08/12/91	26.0	278	75.2	26.0	224	71.9	26.0	294	76.2
08/14/91	26.0	283	77.1	26.0	208	71.6	26.0	283	76.7

[a] Approximate COD loading rate.

Table 24. COD data during startup experiment at the 12-hr HRT

Hours Since Startup	Effluent Soluble COD's (g/L)			Effluent Total COD's (g/L)		
	Hybrid (#1)	Fully Packed (#2)	Fully Packed (#3)	Hybrid (#1)	Fully Packed (#2)	Fully Packed (#3)
0.0	0.386	0.280	0.371	0.598	0.424	0.583
6.0	0.583	0.545	0.681	0.757	0.681	0.757
12.0	0.475	0.464	0.543	0.611	0.623	0.612
18.0	0.577	0.562	0.641	0.664	0.683	0.691
26.3	0.600	0.594	0.643	0.672	0.670	0.722
36.0	0.636	0.598	0.655	0.696	0.651	0.711
51.0	0.589	0.504	0.519	0.656	0.549	0.574
75.0	0.546	0.488	0.497	0.609	0.525	0.544

Notes: Influent COD concentration was 9.5 g/L/day.
Shutdown time was 14 days.

Table 25. Methane production during the startup experiment at the 12-hr HRT

Time Since Startup	Standard Methane Production (L/L/day) Hybrid (#1)	Fully-Packed (#2)	Fully-Pack (#3)
0.00	0.00	0.00	0.00
0.50	0.99	1.04	1.03
3.25	1.74	2.59	2.63
4.25	1.98	4.16	3.26
6.00	2.72	2.63	3.01
7.75	2.81	2.48	3.07
9.17	2.92	4.27	2.70
11.17	3.34	3.00	3.16
12.50	2.38	2.82	3.08
13.75	3.13	3.31	2.98
16.25	3.29	3.09	3.21
17.83	3.21	3.70	3.07
19.25	2.76	2.51	3.28
21.17	3.29	3.01	3.09
26.33	2.97	3.34	3.41
28.17	3.10	2.80	2.71
29.75	3.35	3.71	3.25
33.00	3.22	3.09	3.42
35.00	3.22	3.36	3.26
37.50	2.87	3.41	3.11
39.08	3.18	2.98	3.32
42.00	3.27	3.36	3.29
50.92	3.03	3.25	3.43
57.17	3.22	3.36	3.32
76.75	3.21	3.41	3.54

Notes: Influent COD concentration = 9.5 g/L/day.
Shutdown time was 14 days.