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Treatment of a pharmaceutical waste with the anaerobic filter

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Department:

TREATMENT OF A PHARMACEUTICAL WASTE WITH THE ANAEROBIC FILTER

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ABSTRACT

The anaerobic filter is essentially a plug-flow, packed-bed, column type reactor in which the anaerobic bacteria responsible for the waste stabilization are attached to the filter media. This process is a relatively new concept in waste treatment which has been used only in laboratory studies. The objective of this study was to evaluate anaerobic filter performance when used to treat an actual industrial waste under controlled conditions of flow rate, organic strength and temperature.

Four 0.5 cu ft (14.25 l) laboratory filters were operated for 180 days at 35° C using a pharmaceutical waste as the substrate. By varying influent waste concentrations from 1,000 to 16,000 mg/l COD and varying detention times from 12 to 48 hrs, a range of organic loadings from 13.8 to 220 lb COD/1000 cu ft/day (0.221 to 3.52 kg COD/cu m/day were produced. Filter performance was determined by monitoring selected parameters which included: COD removal, gas production, suspended solids, alkalinity, and volatile acids.

The anaerobic filter was found to be an effective process for the treatment of the pharmaceutical waste studied, COD removals ranged from 80 to 98 percent for the investigated range of loading conditions. The filter also appeared to recover rapidly from shock loading conditions since instantaneous changes in loading conditions did not result in process failure.

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I. INTRODUCTION

The primary purpose for the biological treatment of organic wastes is to change the molecular arrangements of the carbonaceous and nitrogenous compounds present in the waste so that the resulting end products will be in a more stable and unoffensive form. The stabilized end products may be removed from the waste stream in a solid or gaseous form, or in some cases may remain in the waste flow and be discharged to the receiving stream without causing any serious problems.

During the past several decades engineers have been continually seeking new and better methods for the treatment of domestic and industrial wastewaters. The biological processes used for wastewater treatment can be classified as either aerobic or anaerobic depending on whether or not they are carried out in the presence of free oxygen. Originally anaerobic processes were primarily utilized for the treatment of domestic wastewaters, but with advances in technology, these systems gave way to greater employment of aerobic treatment systems which in most cases provided a higher degree of treatment with fewer problems of odor and inefficiency. Today, anaerobic treatment has essentially been restricted to home sewage treatment systems, and the treatment of very high strength organic wastes, such as the sludges obtained from aerobic waste treatment systems.

Anaerobic treatment has a number of definite advantages which would seem to make it a more desirable process for waste treatment than treatment by either chemical or aerobic methods. The prime advantages are that a high degree of waste stabilization can be accomplished with a comparatively low production of biological solids, and as a by-product of the process, methane gas is produced which could be used to supplement fuel requirements. In addition, the nature of the process eliminates the need for costly aeration equipment and reduces the size of sludge disposal equipment which is required with aerobic systems.

Until recently, the potential of anaerobic treatment for low strength soluble organic wastes was not realized. Traditionally, it was felt that anaerobic fermentation was limited in its ability to treat low strength wastes since less energy would be available for cellular synthesis than in aerobic processes, thereby resulting in fewer microorganisms available to treat the waste. However, it should be realized that decreased cellular synthesis can also be an advantage, since the ultimate objective in waste treatment is the removal of organic material, not the production of microorganisms. Recent studies have significantly increased the understanding of the microbiology and bio-chemistry of the anaerobic process enabling engineers to develop and apply new processes to overcome the problems of low cellular synthesis in anaerobic treatment (1).

The development of anaerobic activated sludge and other similar contact processes has been a step in the right direction. According to McCarty (1) the anaerobic activated sludge process has provided reasonably good treatment for both high and low strength wastes due to the fact that a large population can be maintained through sludge recycle. However, this process has proven to be troublesome from the standpoint of solids separation and recycle, particularly in the case of low strength soluble wastes. For these wastes especially, a process with no solids separation, or recycle would seem to be the most attractive.

A recent study in anaerobic treatment using the "anaerobic filter" (2) has indicated that a contact process is available to treat soluble organic wastes efficiently without the need for solids recycle. The anaerobic filter is a plug flow, completely submerged, rock filled, columnar reactor. The anaerobic filter resembles a trickling filter in that it is filled with rock, but unlike the trickling filter the flow in the anaerobic filter is upward so that the rock bed is completely submerged at all times and anaerobic conditions are maintained. The ability of the filter to function well with a short detention time for low and high strength soluble wastes is due to the fact that the wastes come into contact with a large concentration of organisms which have become attached to the rock or entrapped in the void spaces between the rock. This feature produces long solids retention times (SRT) without

long hydraulic detention times (HDT) or solids recycle and is the key to the filter's success.

The anaerobic filter has been applied to various synthetic wastes ranging from acetic acid to protein-carbohydrate substrates. However, it has had limited application to real wastes.

A. PURPOSE

It was the purpose of this investigation to:

1) Apply a pharmacetical waste to an anaerobic filter and determine the treatability of the waste;
2) Evaluate the filter performance for various hydraulic and organic loading conditions in order to determine operational parameters, and;
3) Subject the filter to shock loading conditions in order to determine their effect on its performance.

B. SCOPE

In order to achieve the proposed objectives, a laboratory investigation was carried out using 4 model anaerobic filters to treat the pharmaceutical waste under controlled temperature conditions. The filters were acclimated to the waste and treatment efficiency was measured. During the course of the study the hydraulic and organic loading rates were changed to evaluate their importance as well as the effects of shock.

In order to evaluate the filter performance, parameters including, chemical oxygen demand (COD), volatile acids, pH, alkalinity, gas production and composition, and suspended solids were monitored on a prescribed schedule.

II. REVIEW OF LITERATURE

The objective of this literature review was to study work undertaken in previous investigations pertaining to the use of the anaerobic filter for wastewater treatment. Few references were available which dealt directly with the treatment of waste waters by the anaerobic filter; however, references were available, concerning other anaerobic processes, which could be used as a basis for discussion of the anaerobic filter.

The literature presented herein is divided into three areas: 1) fundamental concepts of anaerobic treatment; 2) evolution of anaerobic processes; and 3) characteristics of the anaerobic filter.

A. FUNDAMENTAL CONCEPTS OF ANAEROBIC TREATMENT

The stabilization of organic material by anaerobic microbial action is basically a three-stage mechanism (3). This process may best be described by Figure 1 (1). While this figure is an over simplification and the percentage relationships may not be representative for various mixed wastes, it does represent the basic relationships that must exist in anaerobic treatment. A waste consisting of proteins fats and carbohydrates may be considered to be a mixed substrate. These constituents are biologically converted to less complex soluble organic compounds by enzymatic hydrolysis. The hydrolysis products then undergo acid fermentation which converts approximately 35 percent of the waste to shortchain

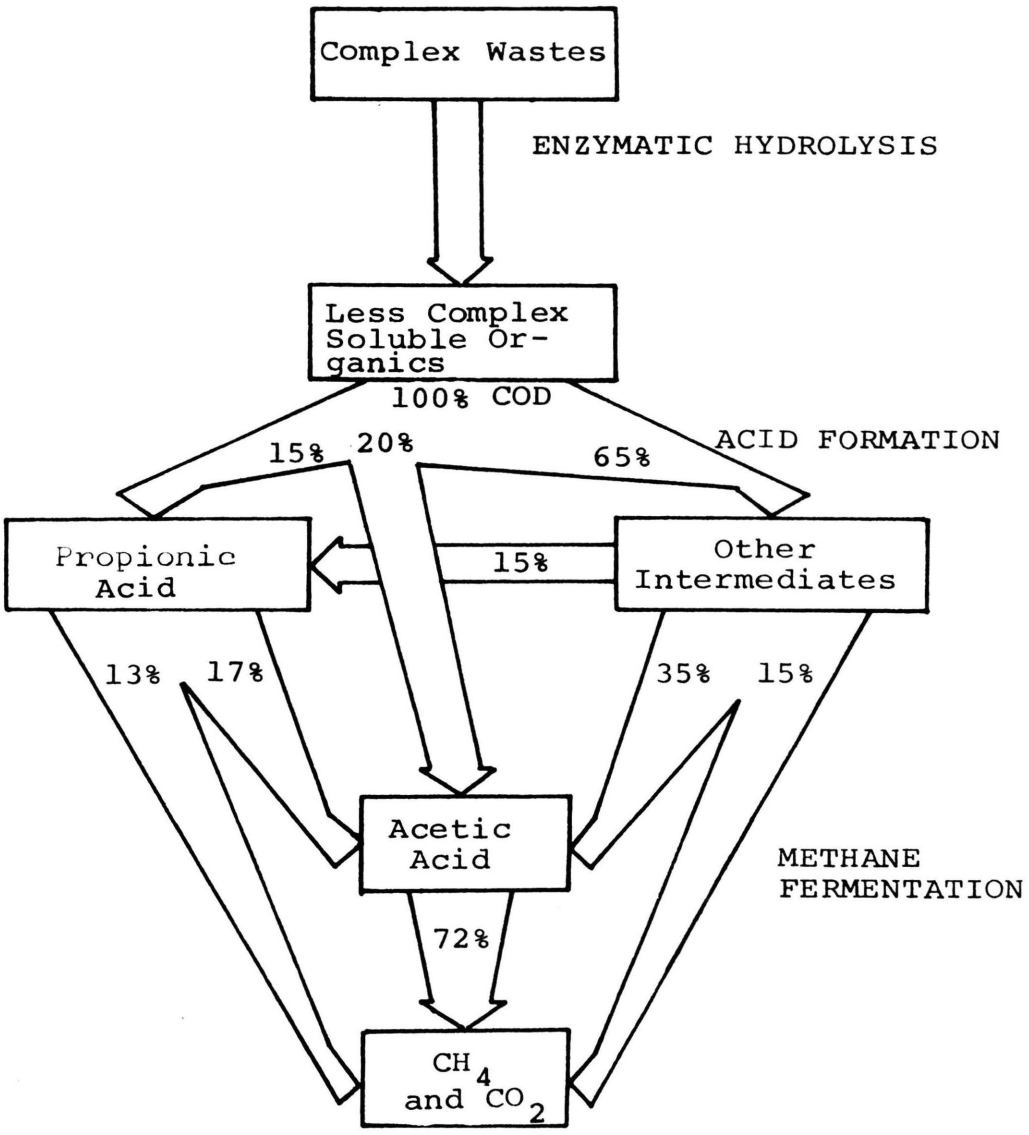

Figure 1. "Methane Fermentation of a Complex Organic Waste," After McCarty (1)

organic acids, and approximately 65 percent to intermediate products such as alcohols, aldehydes and longchain fatty acids.

The enzymatic hydrolysis and acid fermentation stages are carried out by facultative and anaerobic bacteria which are collectively termed "acid formers." In these two stages there is very little stabilization of organic material; the principle event occurring is a chemical rearrangement of the organic molecules. These two stages are therefore often collectively called the "constant-BOD phase."

In the third stage the acid fermentation products are further fermented to methane and carbon dioxide by a group of substrate specific, obligate anaerobic, bacteria called the "methane formers." Thus, organic waste materials are converted to bacterial protoplasm and gaseous end products which are water insoluble and therefore are not in the final digester waste stream. The oxygen equivalent of methane is given by the following equation: (4)

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad [1]$$

According to the equation, each 16 g of methane produced and lost from the process to the atmosphere corresponds to the removal of an equivalent amount of organic material that would require 65 g of oxygen to become fully oxidized. Eckenfelder and O'Connor (5) report that a gas yield of 16 to 18 cu ft/lb (1.02-1.14 cu m/kg) of volatile matter destroyed with a methane content of 65-70 percent can be expected from digesting sewage sludge.

Few studies have been conducted to determine the biological characteristics of the predominant acid forming bacteria associated with the anaerobic fermentation process. According to McCarty (6) the acid formers range from facultative organisms which can anaerobically ferment simple carbohydrates, to strict anaerobes capable of converting complex proteins and carbohydrates to organic acids. Jeris and McCarty (7) and Barker et al. (8) (9), report that the end products from the fermentation of carbohydrates and proteins vary greatly with different organisms. For example, with glucose fermentation, one acid forming organism may produce significant quantities of ethyl alcohol, another lactic acid, while still other species may produce diverse combinations of end products such as acetic acid, lactic acid, and ethyl alcohol. It can be expected that, under natural conditions, changes in the predominant species of acid-forming organisms can result in the formation of various organic acids at different times. The varying end products from the acid formation stage result in inconsistent substrates which could cause acclimation problems for the methane bacteria.

The methane producing bacteria are comprised of several different species of obligate anaerobic organisms. The organisms are similar in the fact that they all produce methane from the fermentation of simple organic compounds under anaerobic conditions. However, each species has been found to have specific requirements and can ferment

only a relatively restricted group of simple organic compounds (8) (9) (10). Table I summarizes a classification of methane bacteria by Andrews, et al. (10), based on the type of substrate which each can ferment. The limited number of substrates which each specie can ferment indicates that several would be required for complete methane fermentation of mixed substrates.

Since the reduction of oxidizable material in the waste stream occurs from the formation of methane, it would be desirable to know how methane is formed from various substrates. Barker (11) has condensed the existing knowledge of methane formation into a series of chemical equations. Barker's equations for the fermentation of those compounds shown in Table I along with the microorganisms responsible for their fermentation are given below.

Hydrogen: M. omelianski, M. vanneilii, M. formicium, M. barkerii

$$4H_2 + CO_2 \longrightarrow CH_4 + 2H_2O \qquad [2]$$

Methanol: M. barkerii

$$4CH_3OH \longrightarrow 3CH_4 + CO_2 + 2H_2O \qquad [3]$$

Ethanol: M. omelianskii

$$2CH_3CH_2OH \longrightarrow 2CH_3COOH + CH_4 \qquad [4]$$

Formic acid: M. formicium, M. vanneilii

$$4HCOOH \longrightarrow CH_4 + 3CO_2 + 2H_2O \qquad [5]$$

Acetic acid: M. sohngenii, M. methanica, M. mazei, M. barkerii

Table I. Compounds Fermented by Methane Bacteria, After Andrews (10)

Microorganism	Compounds fermented
Methanobacterium omelianskii	H_2, ethanol, primary and secondary alcohols
Methanobacterium suboxydans	Butyrate, valerate, caproate
Methanobacterium sohngenii	Acetate, Butyrate
Methanobacterium propionicum	Propionate
Methanobacterium formicium	H_2, CO_2, formate
Methanococcus mazei	Acetate, Butyrate
Methonococcus vanneilii	Formate, H_2
Methanosarcini barkerii	H_2, CO, methanol, acetate
Methanosarcina methanica	Acetate, Butyrate

$$CH_3COOH \longrightarrow CH_4 + CO_2 \quad [6]$$

Propionic acid: M. propionicum

$$4CH_3CH_2COOH + 2H_2O \longrightarrow 4CH_3COOH + CO_2 + 3CH_4 \quad [7]$$

Butyric acid: M. sohngenii, M. methanica, M. suboxydans

$$2CH_3(CH_2)_2COOH + 2H_2O + CO_2 \longrightarrow 4CH_3COOH + CH_4 \quad [8]$$

Valeric acid: M. suboxydans

$$2CH_3(CH_2)_3COOH + 2H_2O + CO_2 \longrightarrow 2CH_3COOH + 2CH_3(CH_2)_2COOH + CH_4 \quad [9]$$

Caproic acid: M. suboxydans

$$2CH_3(CH_2)_4COOH + 2H_2O + CO_2 \longrightarrow 2CH_3COOH + 2CH_3(CH_2)_2COOH \quad [10]$$

Jeris and McCarty (7) have shown that methane can be produced by beta oxidation of long-chain fatty acids. This is a three phase process which occurs simultaneously as shown for stearic acid in equations [11], [12], and [13].

Beta oxidation:

$$CH_3(CH_2)_{16}COOH + 16H_2O \longrightarrow 9CH_3COOH + 32H_2 \quad [11]$$

CO_2 reduction

$$4CO_2 + 32H_2 \longrightarrow 4CH_4 + 8H_2O \quad [12]$$

Acetic acid fermentation:

$$9CH_3COOH \longrightarrow 9CH_4 + 9CO_2 \quad [13]$$

By starting at the carboxyl end of the stearic acid molecule the organism enzymatically oxidizes the beta carbon by removing a hydrogen and adding a water molecule. This reaction splits the stearic acid molecule into 2-carbon acetic acid fragments. The excess hydrogen is disposed of

by the reduction of carbon dioxide to methane. The resulting acetic acid is fermented directly to methane and carbon dioxide.

As can be seen from equations [2] through [13], the major sources of methane are acetic acid, carbon dioxide and methanol. Since methanol is not normally found in domestic wastes and is not a frequent intermediate product it is considered to be only a minor source of methane.

Methane bacteria are limited in the quantity of energy available for cellular synthesis because the rate of substrate utilization per unit of organism is relatively low and the majority of the substrate energy is lost in the methane produced (6). Low energy yields coupled with long cell generation times, on the order of several days (2), make the response time to shock conditions resulting from increases in organic loading or changes in organic substrates very long for methane bacteria. By the time the number of methane bacteria have increased substantially to cope with shock conditions the accumulation of acidic products may have reduced the pH to toxic levels. The accumulation of acidic metabolic end products stems from the activity of the acid forming bacteria which have shorter generation times, are less sensitive to changes in pH, and consequently respond more rapidly to shock conditions than the methane bacteria. Therefore, the important key in anaerobic digestion is to maintain a proper balance between these two groups of bacteria by providing optimum environmental conditions (4).

Optimum methane fermentation has been reported to occur in the pH range of 6.7 to 7.4 (6) (12). Values of pH below 6 or above 8 have been reported to be associated with reduced methane production, and to some extent, toxic to the methane bacteria.

Two optimum temperature ranges for methane production have been noted (5) (13) (14); one in the mesophilic range of 32° to 37° C, and the other in the thermophilic range of 50° to 55° C. Speece (15) has reported that gas production from a sludge acclimated to 35° C could be maintained in the digestor until the sludge temperature fell below 20° C, when no gas production was observed. Speece (15) also reported that an increase in temperature from 35° to 45° C resulted in higher gas production and was a possible solution to balance restoration in digestors suffering from increasing volatile acid formation. This was felt to occur because the increase in acid production was more than compensated by the increase in the acid utilization rate by the methane bacteria at the higher temperature. The fact that Golueke (16) has reported similar results as Speece (15) would seem to indicate that an increase in temperature from 35° to 45° C would allow higher digester loadings without an increase in the volatile acids concentration.

Inorganic salts have also been found to have a significant effect on methane fermentation (17). Optimum fermentation occurs only under a limited range of salt

concentrations. McCarty and McKinney (17) (18) utilized sludge which had been acclimated to acetic acid to investigate the effects of cation concentration on fermentation. Acetic acid salts were fed to the units in high concentrations (2,000-14,000 mg/l). They found that sodium, potassium and ammonium ions exerted a toxic effect while calcium and magnesium were only slightly toxic. Subsequent investigations by McCarty and Kugelman (19) indicated that certain combinations of the above cations had antagonistic effects on digestion. For example, the toxic effects of 0.45 M/l of sodium were offset by the addition of 0.01 M/l of potassium and 0.05 M/l of magnesium.

The nutrient requirements for methane fermentation are relatively small. McKinney (6) reported successful digester operation with the following substrates as the sole source of carbon; glucose, starch, nutrient broth, leucine, oleic acid, palmetic acid, octanic acid, buteric acid, proprionic acid and acetic acid. Work done by Sanders and Bloodgood (20) indicated that, along with other trace substances, uninhibited anaerobic treatment required a nitrogen to carbon ratio of 1:20. This work was in agreement with that of Schoepfer and Zeimke (21) who also reported that a phosphorus to nitrogen to carbon ratio of 1:5:100 was required for successful treatment of wood fiber wastes.

One environmental factor which has been the subject of controversy is the allowable volatile acid concentration

in anaerobic treatment. The limiting concentration of volatile acids usually accepted has been 2000 mg/l (10). However, McKinney (13) stated that it is possible to obtain good gas production with volatile acid concentrations as high as 20,000 mg/l, provided the pH is maintained at or above 6.5. It is reported in the Water Pollution Control Federation Manual of Practice No. 16 (22) that the pH in a digester will not fall below 6.5 until the volatile acid to alkalinity ratio increases above 0.8. This would seem to indicate that successful digestion can proceed with high concentrations of volatile acids, i.e. greater than 2000 mg/l, as long as sufficient alkalinity is present to neutralize their effect on pH.

B. EVOLUTION OF ANAEROBIC TREATMENT PROCESSES

1. Conventional Processes

The conventional anaerobic process used for treating high strength domestic and industrial wastes is basically a holding tank, into which the wastes are passed either intermittently or continuously. Initially, these tanks were designed to hold the sludge solids for several months while microorganisms slowly brought about digestion (13). The simplest version of this process is the unheated and unmixed anaerobic digester which has been widely used in the past to treat domestic waste solids because it was simple though the reaction was extremely slow and inefficient (2).

As centralized treatment of domestic wastes became more widespread and the volume of waste solids increased, there was a demand for a more rapid sludge treatment process. The addition of heating and mixing to the process made it possible to accomplish in days what had previously taken months (13). Today, the conventional digestion process has evolved into a system which uses heated, single and two-stage digestion units and employs some form of mixing.

With single stage digesters, i.e. only one digester, the mixing is usually confined to the upper portion of the digester. Quiescent conditions are maintained in the lower portion to allow sedimentation of the denser digested sludge. In two-stage digestion complete mixing is employed in the first digester with quiescent conditions existing in the second unit. With both processes mixing is accomplished by either mechanical or gaseous mixing. According to McKinney (13), some researchers have reported gaseous mixing to have a catalytic effect on methane production, however there is no firm scientific basis to support this.

The conventional digester is a throw-back to antiquity as far as science is concerned primarily because engineers have yet to translate the basic fundamentals of anaerobic treatment into practical operating systems (23). The major objective in conventional anaerobic treatment has been to stabilize large quantities of high strength organic wastes with little regard for effluent quality, and consequently few studies have considered modifying the digesters

to allow for the economical treatment of low strength wastes.

2. Anaerobic Activated Sludge

Recent studies on the kinetics of anaerobic processes (24) (25), have developed the concept of biological solids recycle for anaerobic systems. This concept has led to the development of the "anaerobic activated sludge process" which is considered to be an anaerobic contact process (1). This system was developed primarily in an attempt to treat wastes with strengths in the range of 800-10,000 mg/l COD, since these wastes are too strong to be treated by most aerobic processes yet too weak to be economically treated by conventional anaerobic processes (26). With this system, the waste is passed through a contact unit containing a high concentration of active biological solids, which are maintained by sedimentation and recycle of the solids to the contact unit. See Figure 2. The biological solids are retained in the system independent of the waste flow, thus permitting the long solids retention times (SRT) necessary for satisfactory anaerobic treatment of low strength wastes. With good separation of the biological solids, anaerobic contact processes have been operated successfully at a detention time of as short as 2.3 hr (21).

Although not in widespread use the anaerobic activated sludge process has been used on a case-by-case basis in both pilot and full-scale plant studies for selected wastes ranging from 1000 mg/l to 6000 mg/l COD. In one of

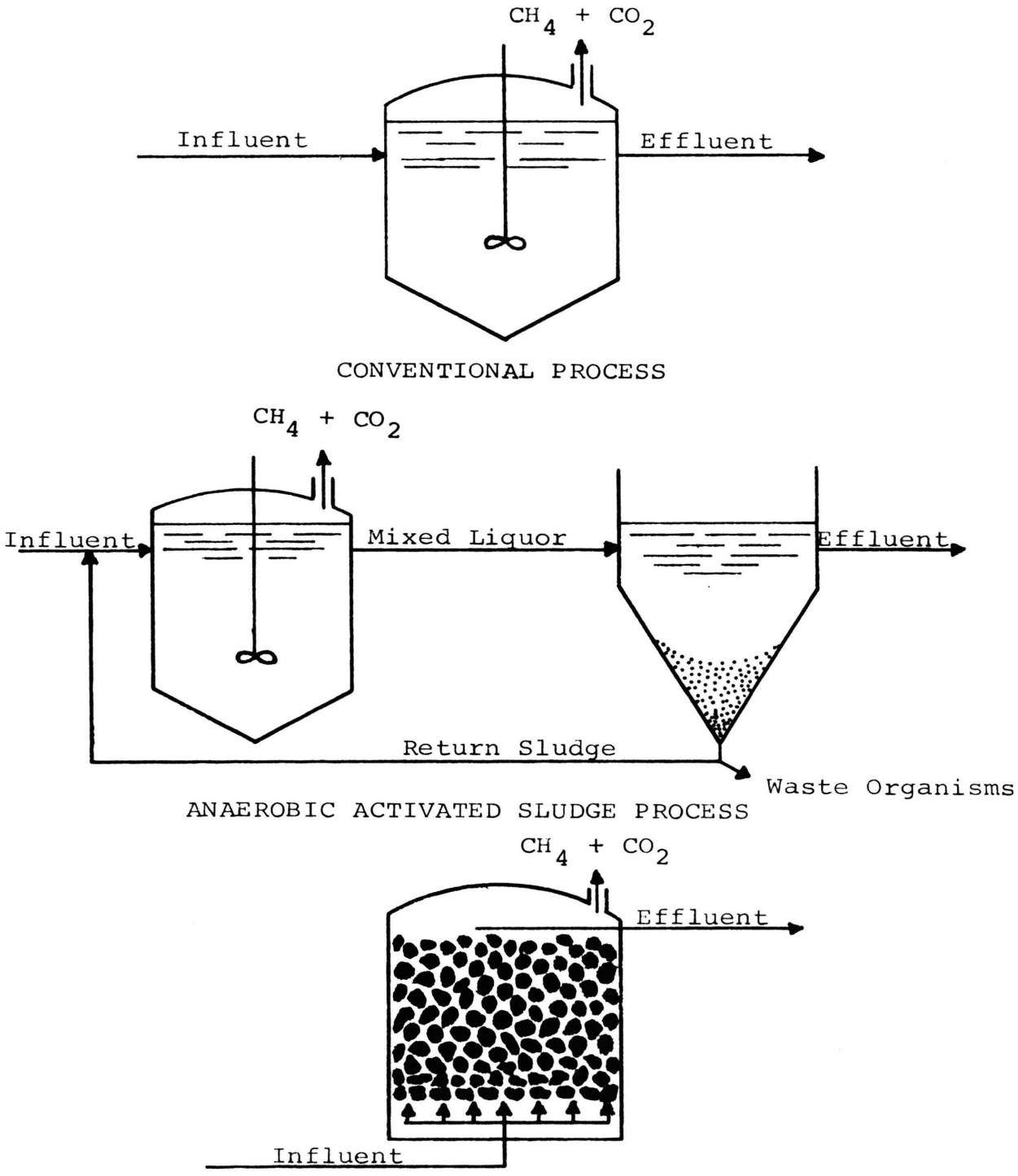

Figure 2. Schematic Diagram of Three Anaerobic Waste Treatment Processes, After Young (2)

the earliest studies, Canham and Bloodgood (27) employed a mechanical flocculator as a reactor to study the treatability of wastewaters from a tomato cannery. Sludge recycle was employed on an intermittent basis. Due to the poor settling characteristics of the sludge, large amounts of solids, i.e. up to 600 mg/l, were lost in the clarifier effluent. With continuous feeding, a detention time of 2.9 days resulted in a BOD reduction of 20 percent.

Using a large-scale laboratory pilot plant, McNary et al. (28) studied the treatment of citrus fruit processing wastewater. BOD removals ranged from 64 to 95 percent, but effluent BOD concentrations ranged from 130 to 1,093 mg/l BOD. The major operational problem involved difficulties with effective solids separation.

Schroepfer and Zeimke (21) (24), conducted an extensive study of the anaerobic contact process. The laboratory studies and pilot-work done by these investigators resulted in the construction and operation of a full-scale facility (29). During the investigation, it was determined that vacuum degasification preceeding gravity sedimentation was the most suitable method for obtaining sufficient solids concentrations to permit continuous solids recycle. Detention times as low as 2.3 hr and loadings ranging from 0.037 to 0.334 lb BOD/day/cu ft (0.6 to 5.4 kg/day/cu m) were used successfully. BOD reductions ranged from 70 to 97 percent for the several wastewaters studied.

Subsequent investigations (3) (4) (23) (26) have been aimed at the development and evaluation of a rational kinetic model for the anaerobic activated sludge process. The basic model presented by these researchers (4) (23) (26) follows very closely that presented by Lawrence and McCarty (3). With their model the net growth rate of microorganisms in a continuous flow, completely mixed, anaerobic system is as follows:

$$\frac{dM}{dt} = a\left(\frac{dF}{dt}\right) - bM \qquad [14]$$

where: dM/dt = microorganisms net growth rate per unit volume of digester, mass/volume - time

$\frac{dF}{dt}$ = rate of waste utilization per unit volume of digester, mass/volume - time

M = microorganism concentration, mass/volume - time

a = growth yield coefficient

b = microorganism decay coefficient time $^{-1}$.

The volumetric rate of waste assimilation (dF/dt) is related to the concentration of waste in the digester. The relationship between biological growth rate and the concentration of the limiting nutrient is described as follows:

$$\frac{dF}{dt} = \frac{kMs}{k_s + s} \qquad [15]$$

where: s = waste concentration in the reactor, mass/volume

k = maximum rate of waste utilization per unit weight of microorganisms occuring at high waste concentration, time $^{-1}$

k_s = half velocity coefficient equal to the waste concentration when dF/dt is equal to one-half the maximum rate, k, mass/volume

combining equations 14 and 15 leads to the following expression:

$$\frac{(dM/dt)}{M} = \frac{aks}{k_s+s} - b \qquad [16]$$

The quantity (dM/dt/M) is equal to the net growth per unit weight of microorganisms per unit time and is designated as the net specific growth rate, μ.

When a continuous flow system is operated under steady state conditions, the mass of microorganisms in the total system will remain constant. This requires that the rate at which microorganisms are wasted from the system must equal the net microbial growth rate, dM/dt. Expressing time in days, the daily net specific growth rate, dM/dt/M, is the reciprocal of the biological solids retention time, SRT:

$$SRT = \frac{Mt}{(\Delta M/\Delta T)_t} \qquad [17]$$

where: M_t = total weight of active microbial solids in the system, mass

$(\Delta M/\Delta T)_t$ = total quantity of active microbial solids withdrawn daily, mass/time

Thus, SRT is the average retention time of microorganisms in the system and is analogous to sludge age in aerobic activated sludge. The efficiency of waste utilization is defined as follows:

$$E = (\frac{S-s}{S})100 \qquad [18]$$

where: E = efficiency of waste treatment, percent

S = influent waste concentration, mass/volume

s = effluent waste concentration, mass/volume

Failure of the anaerobic contact process due to kinetic stress will occur when the SRT is reduced to a value at which the microorganisms are diluted from the system at a rate greater than their maximum specific growth rate. At this point treatment efficiency drops to zero. When the influent waste concentration is large enough to be non-growth-limiting (i.e. $s \simeq k_s + S$), the value of SRT at which the process failure occurs is a characteristic parameter of the waste assimilating microbial population. In such a non-limiting situation, Equation [16] can be reduced to the following form in order to calculate the minimum SRT (SRT_M), for a given microbial process.

$$\frac{1}{SRT_M} = ak-b \qquad [19]$$

Most of the recent work done in anaerobic activated sludge systems has been related to assigning values to the

emperical coefficients a, b, k, and k_s, of the kinetic model (3), (4), (23), (26).

Although these anaerobic contact processes have proven successful for treating low-strength wastes, they appear to be most effective for treating wastes with significant quantities of suspended solids. With such wastes, the biological growth becomes attached to the solid particles so that it settles and is more readily separated from the waste stream. With soluble wastes, the biological solids often remain dispersed or only lightly flocculated and a significant portion may be lost in the effluent. Rates of recycle from the solids separation unit as high as four times the normal waste flow rate are often required to maintain a satisfactory treatment efficiency (21) (29).

In general, anaerobic contact processes have not proven totally satisfactory for waste concentrations less than about 2000 mg/l COD at temperatures below 30° C (1). Although heating greatly improves the waste stabilization rate in anaerobic contact processes, a waste concentration of approximately 6000 mg/l COD is required to produce a sufficient quantity of methane to raise the waste temperature by 10° C (2).

3. Characteristics of the Anaerobic Filter

The success of both the conventional and anaerobic contact processes is dependent upon their ability to bring the waste into contact with an anaerobic microbial mass

for a sufficient length of time to convert the waste to stable compounds (1). This objective is achieved in the conventional process through a long holding time, and in the anaerobic contact process by solids recycle.

An important operating parameter in these systems is the SRT. At long SRTs, sufficient microbial mass can be established for efficient treatment. With the anaerobic contact process, very good solids separation is required to provide an adequate SRT for effective treatment.

If high concentrations of biological solids can be retained in an anaerobic system for a long period of time, i.e. (a high SRT), low-strength wastes could be treated anaerobically at nominal temperatures (2). Pfeffer, (4), has shown, from the treatment of raw sewage sludge by an anaerobic contact process, that increasing the SRT by approximately six days produced the same increase in treatment efficiency as raising the temperature from 25° to 35° C. An ideal process would then be one which was able to retain biological solids independent of the waste flow, and simultaneously maintain these solids for long periods of time.

McCarty's exploratory study (30) with the anaerobic filter suggested the possibility of such a process. With this process, the waste would be passed upward through a bed of stone. See Figure 2. The biological solids would then become attached to the surfaces or trapped within the void spaces of the stones and would not be carried

out in the effluent stream. Good results were obtained by McCarty (30) with a 3-l laboratory filter containing 1 to 2 inch (2.54 to 3.08 cm) quartzite stone. The filter was operated for 307 days while receiving methanol, acetate, and proprionate, as pure or mixed substrates at concentrations of about 2000 mg/l COD. Removals of COD for 12 hr. detention times averaged 81 percent, with the effluent suspended solids usually below 20 mg/l. The average SRT in this filter was estimated to be over 100 days.

McCarty (30), compared the anaerobic filter to other existing biological processes and pointed out a number of distinct advantages:

1. The anaerobic filter is ideally suited for the treatment of soluble wastes.
2. No effluent or solids recycle is required with the anaerobic filter. The biological solids remain in the filter and are not lost with the effluent.
3. The accumulation of high concentrations of active solids in the filter permits the treatment of dilute wastes at nominal temperatures.
4. Very low volumes of sludge are produced by the anaerobic filter. The effluent is essentially free of suspended solids and, sludge wasting, in some cases, is almost non-existent.

The concept of biological growth retention on a support medium or packing material is not new to the

field of waste treatment. The aerobic trickling filter uses the fixed bed principle as a basis for its operation. Its importance is reflected in the many trickling filters in use (31) and the considerable research which has been conducted toward the process improvement and the definition of its mode of operation (31) (32). However, this approach had not been previously used in anaerobic systems primarily because anaerobic processes were generally used for the treatment of sludges, where a physical support matrix would hinder waste transport and mixing.

Young (2) conducted the first in-depth investigation of the anaerobic filter. In this study, eight 1 cu ft (28.5 l) laboratory filters were subjected to a varied range of organic and hydraulic loadings while employing acetic acid and nutrient broth as the substrates. COD loadings from 375 to 12,000 mg/l and detention times from 4.5 to 72 hr, produced COD removal efficiencies from 60 to 90 percent. As one phase of the study, Young developed a mathematical kinetic model to predict the performance of the filter under various loading conditions. The results of the investigation were used to evaluate the emperical constants of the kinetic model. By using this model, Young had some success in accurately predicting the performance of the filter.

A subsequent investigation by Plummer (33) applied the anaerobic filter to an actual food processing waste. Organic loadings of 101 to 638 lb COD/1000 cu ft/day (1.62

to 10.22 kg COD/cu m/day) at HDTs ranging from 83 down to 13 hr, resulted in treatment efficiencies ranging from 30 to 85 percent. However, the BOD of the effluent streams ranged from 546 to 3,890 mg/l, and suspended solids varied from 455 to 1,855 mg/l. In this case, while giving good percentage removals, the effluent quality of the filter would not be considered acceptable.

The anaerobic filter has also had success in applications as a treatment process for reasons other than organic removal. In studies by Tamblyn (34) and Seidel (35), the anaerobic filter was used as a reactor for the biological denitrification of highly nitrified subsurface drainage waters and aerobic activated sludge effluents. By using methanol as a carbon source, nitrate removals exceeding 90 percent were achieved with detention times which ranged from 0.5 to 2 hr.

The anaerobic filter appears to have potential for waste treatment if properly used. If the filter media can trap and retain the biological solids in high concentrations, the SRTs that are required for the treatment of low-strength wastes could be achieved. Sedimentation and recycle of solids from the effluent would not be required in order to maintain a high treatment efficiency, and with the need for solids separation eliminated, the filter would appear to be highly suitable for soluble wastes.

III. EXPERIMENTAL PROCEDURES

Four laboratory scale anaerobic filters were constructed for use in this experimental study. The program of experimentation was designed to evaluate the performance of the filters when treating a complex industrial waste, in this case a pharmaceutical waste. Generally, waste strengths of less than one percent COD were selected, since such waste strengths cannot normally be treated efficiently by conventional anaerobic processes (2). The range of organic loadings studied in this investigation were those commonly applied to more conventional biological systems.

This chapter describes the design of the laboratory filters and feed system, the pharmaceutical waste, and the analytical procedures employed during the course of the investigation.

A. LABORATORY FILTERS

Laboratory filters (Figure 3) were constructed of Plexiglas* columns, 6 in. (0.1525 m) in outside diameter (OD), 3 ft (0.915 m) high, with an inside diameter (ID) of 5.5 in. (0.14 m). The total volume of the empty cylinder was 0.5 cu ft (14.25 l). The base of the column was constructed so that the waste flow would be dispersed uniformly across the bottom of the filter. This was accomplished by drilling eight 1/4-in. (0.635 cm) diameter holes evenly spaced around a 4 in. (0.102 m) diameter circle in

*A product of Cope Plastics, St. Louis, Mo.

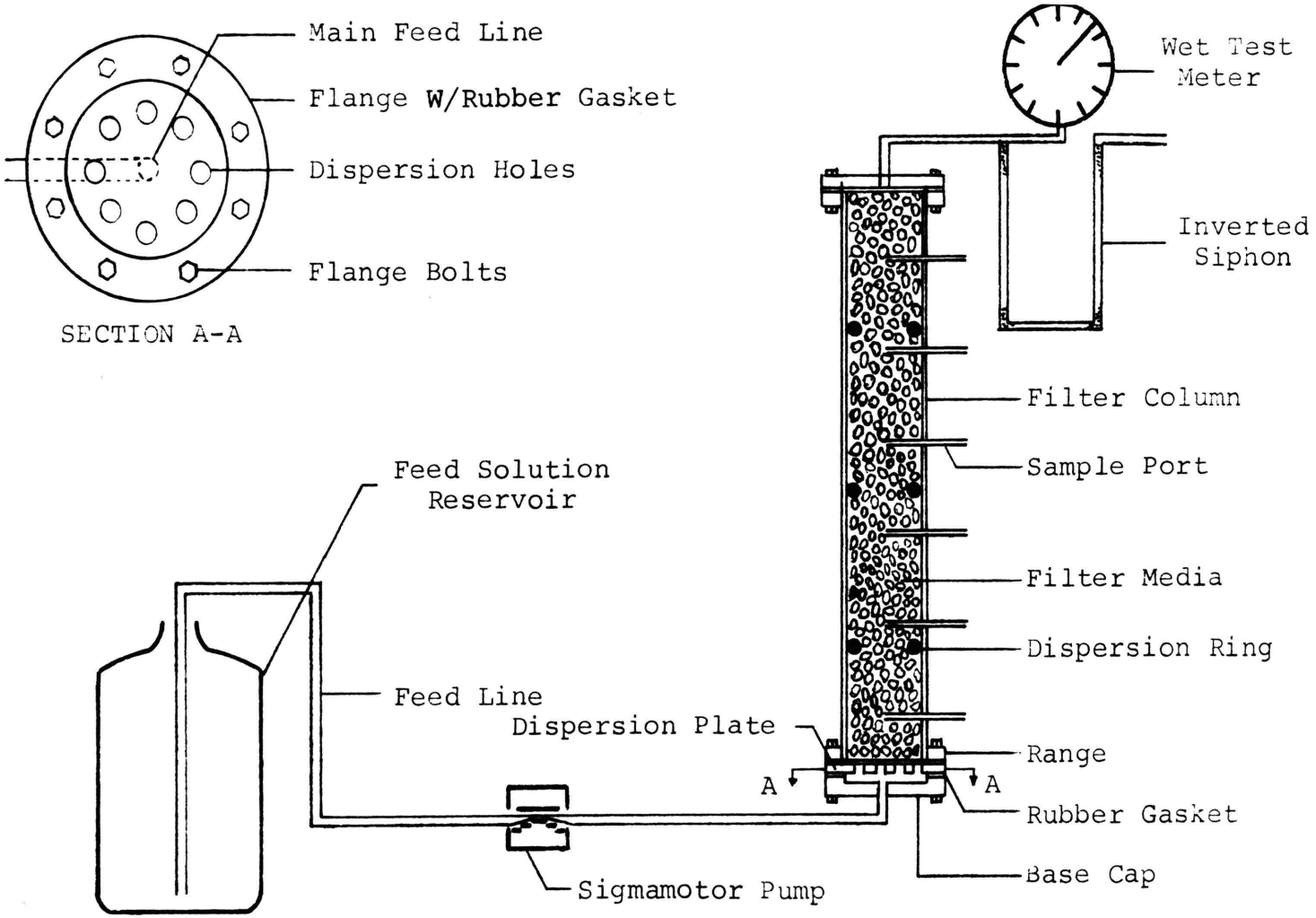

Figure 3. Schematic Diagram of Anaerobic Filter and Feed System

a dispersion plate which capped the end of the column. This plate rested immediately above an open space 4 in. (0.102 m) in diameter and 1/8-in. (0.317 cm) deep in the base of the column. See Figure 3. With this configuration the raw waste entered at the center of this open circular space and flowed upward through the holes in the dispersion plate.

Sample ports were placed at 6 in. (0.1525 m) intervals throughout the column height with additional ports 3 in. (0.0765 m) from the top and base of the filter. These sample ports extended to the center of the column so that a more representative sample of the filter contents could be obtained. The sample ports were made of 1/8-in. (0.318 cm) ID Plexiglas tubing and were sealed into the wall of the column with rubber grommets to give a water-tight yet slightly flexible joint. The base and top caps of the filter were bolted to flanges which were cemented firmly and flush to the top and bottom of the column.

Each column was filled with smooth quartzite stone, 1 to 1.5 in. (2.54 - 3.82 cm) in diameter. The filter stone was hand graded to insure a uniform porosity between filters by removing any broken and extremely large or small stones. Dispersion rings, made of 5/8-in. (1.59 cm) OD vinyl plastic tubing were placed at 1-ft (0.306 m) intervals to prevent short circuiting of the waste through the large void spaces formed at the rock-column boundry. Each completed filter had a porosity of 0.47 and a liquid volume of 0.22 cu ft (6.25 l).

The filter effluents passed through a "T"-fitting and an inverted siphon (See Figure 3) to separate the gas produced from the liquid effluent. Because of the continual loss of solids from the filters and the relatively low flow, these siphons required periodic cleaning to prevent plugging.

B. FEED SYSTEM

Feed solutions for the anaerobic filters were made as required, by dilution of an appropriate volume of the normal strength pharmaceutical waste to 20 l with tap water. Four 25 l, plastic carboys placed one foot above the filters were used as reservoirs for the prepared feed solutions. The feed solutions were drawn from the bottom of the carboys through feed lines made of Tygon tubing by a low speed Sigmamotor Model T8*, peristaltic pump.

By use of tubing with different inside diameters and pump speeds a variety of flows could be achieved. The sections of the feed lines that were subjected to the mechanical finger action of the pump were changed weekly to avoid the possibility of a variable feed rate as a result of worn tubing. A single pump with a four position head was used to pump the waste to all four filters.

The filters as well as the feed system (Figure 4) were housed in a walk-in environmental chamber,** which was maintained at 37° C. To retard any effects of premature

*A product of Sigmamotor, Inc., Middleport, New York.
**Environ-Room, Cat. No. 751AX, manufactured by Lab-Line, Inc., Melrose Park, Illinois.

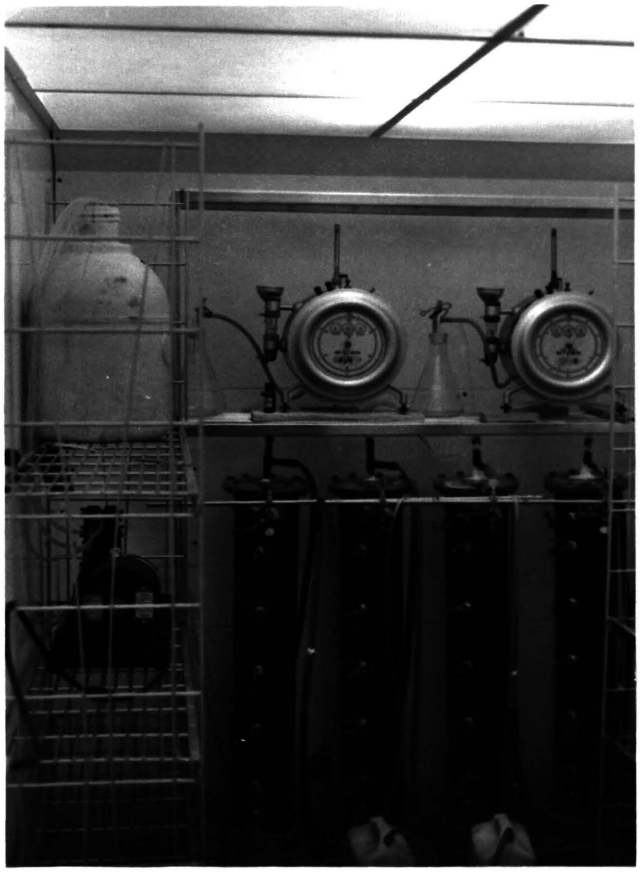

Figure 4. Anearobic Filters and Feed System, Housed in an Environmental Chamber

biological breakdown of the feed solutions at this elevated temperature, the reservoirs were rinsed with hot 1+1 hydrochloric acid prior to each addition of new feed.

C. PHARMACEUTICAL WASTE

A pharmaceutical waste was selected primarily on the basis that it satisfied the prerequisites for treatment with the anaerobic filter by having a relatively high COD and low suspended solids. The waste was obtained from Hoffman Taft, Inc., Springfield, Missouri. At the time of this study Hoffman Taft was discharging approximately 260,000 gpd (1205 cu m) to the city sewers. This flow was only about two percent of the total flow reaching the municipal treatment plant. However, this two percent flow represented almost 50 percent of the organic load reaching the treatment plant, based on COD (36).

At the time of the study the only treatment the waste received prior to discharge to the sewers was equalization and neutralization. Equalization was accomplished by channeling all of the plant waste streams into a holding basin (Figure 5) with a surface area of approximately 5000 sq ft (467 sq m). In this basin much of the oil and floatable organic matter in the waste streams was skimmed off with a floating baffle. The combined waste was then pumped to the neutralization basin (Figure 6) where the pH was raised from approximately 4 to 7.5 by the addition of caustic soda (NaOH). Mixing was employed in the basin to bring the neutralization reaction to equilibrium and to keep any

Figure 5. Equalization Basin With Floating Baffle at Hoffman Taft Inc., Springfield, Mo.

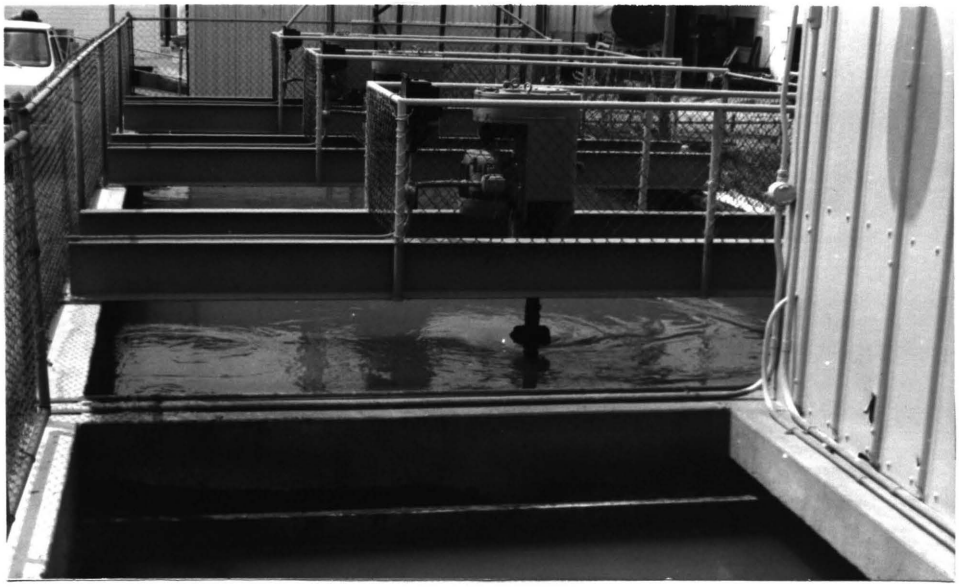

Figure 6. Neutralization Basin at Hoffman Taft Inc., Springfield, Mo.

solid material in suspension prior to discharging the waste to the city sewer.

The waste used in this study was collected from the neutralization basin in 55-gal epoxy lined drums by grab sampling. Once collected the samples were immediately shipped a distance of 120 miles back to the laboratory. Upon arrival at the laboratory the drums were stored in a walk-in cooler which was maintained at 5^{o} C to inhibit any biological activity.

D. TREATMENT SCHEME

1. Waste Characterization

As a first step in this investigation a laboratory analysis was performed on the waste to obtain information regarding the general character of the waste and to establish a required pretreatment scheme. The analysis indicated that the waste was nitrogen and phosphorus limiting.

In order to provide sufficient nutrients for anaerobic growth, nitrogen and phosphorus were added to the feed solutions as they were prepared. Nitrogen in the form of ammonium chloride and phosphorus in the form of dibasic potassium phosphate were added so that the phosphorus: nitrogen:carbon ratio was 1:5.9:100. The nutrient to carbon ratios used were the minimum values reported in the literature (20) which would support unhindered anaerobic growth.

2. Organic Loading

One of the objectives of this study was the determination of filter performance over a range of organic

loading conditions. A review of the literature indicated that the maximum potential for this process could be demonstrated by selecting waste concentrations of less than one percent, since the treatment of industrial wastes with similar strengths is not normally feasible with conventional anaerobic processes. For this reason waste concentrations below 10,000 mg/l COD were normally chosen. However, since the original pharmaceutical waste concentration was approximately 16,000 mg/l COD (Table III), it was considered necessary to use this loading to prove the practical application of the process to this waste. The hydraulic and organic loadings, in terms of several commonly used loading parameters are shown in Table II. The loadings reported in Table II are approximately the maximum range normally used with other biological processes such as the aerobic activated sludge (37), trickling filter (14) (31), and anaerobic contact processes (1).

E. ANALYTICAL PROCEDURES

During the course of this investigation analyses were performed to determine the chemical and physical characteristics of both the pharmaceutical waste and effluents from the anaerobic filters. The anlaysis of the stored pharmaceutical waste was conducted on a periodic basis to insure that the waste character was remaining stable. Throughout the experiment weekly determinations were performed on the effluents of the anaerobic filters in order to evaluate their treatment efficiency. The following is a description

Table II. Organic Loadings Corresponding to Various Combinations of Hydraulic Flow Rates and Waste Strengths Used in the Experimental Study

Hydraulic Flow Rate				Organic Load lb COD/1000 ft^3/Day***			
Detention* Time	Liters/ Filter/Day	Liters/ft^2/ Day**	Gallons/ ft^2/Day	Waste Strength, mg/l			
				1250	4000	8000	16000
48	3.125	19	5.05	13.8	---	---	220
36	4.16	25.3	6.7	22.9	73.21	---	---
24	6.25	38	10.1	34.75	110	220	---
18	9.375	57	15.1	---	146.3	---	---
12	12.5	76	20.2	---	220	---	---

*Based on 0.22 cu ft (6.25 l) liquid reactor volume.

**To convert liters/ft^2/day to liters/m^2/day, multiply by 0.0925.

***Based on total reactor volume of 0.5 cu ft (14.25l), to convert lb COD/1000 cu ft/day to kg/cu m/day multiply by 0.0160.

of the analytical methods utilized.

1. Sampling

Samples were withdrawn by gravity flow through the sample ports provided in the filter. The order of liquid withdrawal was from top to bottom of the filters. In this manner, an undisturbed sample could be obtained at each level of filter height. Normally an 80 ml aliquot was collected to obtain a representative sample on which to perform analysis.

With the exception of pH, all analyses were made on the filtrate of the suspended solids test to avoid interferences which might be caused by suspended material. Generally all analytical determinations were made within 12 hours. However, if any delay in analysis occurred the samples were stored in a cooler which was maintained at 5^{o} C.

2. pH

The pH of each sample was measured within ten minutes of its withdrawal in order to minimize pH changes caused by loss of dissolved carbon dioxide. A Fisher "Accumet" Model 210 pH meter* equipped with glass electrode was used to make this determination.

3. Alkalinity

Total alkalinity was measured on the original waste and effluents from the anaerobic filters by procedures outlined in Standard Methods (38, p.52). Determinations

*A product of Fisher Scientific Co., Pittsburgh, Pa.

were made on 25 ml samples which were titrated with 0.02N sulfuric acid to the methyl orange end point.

4. Suspended and Volatile Solids

With few exceptions solids content of both the waste and filter effluents was determined by gravimetric analysis following procedures outlined in Standard Methods (38, p.537). When large amounts of solids were present in the sample it was centrifuged at 1500 rpm on an International Universal Model UV centrifuge*. This speed resulted in a relative centrifigal force of 250 gravities. By using this procedure the supernatant could be poured through the filter then the remaining solids could be flushed from the centrifuge tube onto the filter with distilled water. Gooch crucibles with grade 934AH Reeve Angel** glass fiber filter pads were used for the determination. Weights of the solids were measured with a Mettler Model H10w Analytical Balance***.

On an irregular basis, determinations of volatile suspended solids were made by igniting the residue from the total suspended solids test at 550° C for 60 minutes. Normally, however, the weight of the solids on the filter pads was so small that the blank correction often exceeded the weight of the ashed residue. Therefore, an accurate determination of volatile suspended solids could not be made.

*Manufactured by International Equipment Co., Needham, Mass.
**A product of Reeve Angel, Clifton, N.J.
***A product of Mettler Instrument Corp., Princeton, N.J.

5. Chemical Oxygen Demand (COD)

The COD test was employed to determine both the strength of the original waste and of the effluent from the anaerobic filters. COD was also monitored as the waste proceeded through the filters in order to determine the rate of organic reduction.

The dichromate reflux method as outlined in Standard Methods (38, p.495) was used for this determination. A 20 ml sample or an appropriate volume diluted to 20 ml was used so that a COD not exceeding about 700 mg/l was obtained.

6. Volatile Acids

Volatile acid determinations were performed on the filter effluents by the column-partition chromatographic method as described in Standard Methods (38, p.577). In this method silicic acid was used as the absorbant column, an acidified aqueous sample as the stationary phase, and n-butanol in chloroform as the mobile phase. All of the short 1- to 6- carbon organic or volatile acids were eluded with the solvent system used in this method and were collectively reported as total organic acids.

7. Nitrogen

The ammonia and organic nitrogen concentrations were measured in the pharmaceutical waste to ascertain whether or not the waste had sufficient nitrogen for anaerobic growth. These tests were run on 100 ml samples using procedures described in Standard Methods (38, p.222,244) for ammonia and total organic nitrogen.

8. Phosphorus

Both total and orthophosphate determinations were measured by the procedure introduced by Jankovic, Mitchell, and Buzzel, Jr. (39). These procedures were employed to measure the concentration of phosphorus present in the pharmaceutical waste in order to determine to what extent, if any, phosphorus would have to be added to the waste to produce an uninhibited anaerobic growth.

For the orthophosphate test, 42 ml of sample plus 8 ml of mixed reagent were placed in a 50 ml Nessler tube. The mixed reagent consisted of mixing thoroughly 125 ml of 5N H_2SO_4, 37.5 ml of ascorbic acid solution and 12.5 ml of potassium amtimonyl tartrate solution. The mixed reagent was freshly prepared for each day's determinations. After placing the sample and mixed reagent in the Nessler tubes and shaking the contents, the tubes were allowed to stand for a minimum of 10 min. to allow color development. After color development the samples were observed using a Perkin-Elmer Model 139 UV-VIS Spectrophotometer* at 710 mμ in 1 cm glass sample cells. Phosphorus concentrations were determined by comparing the light absorption of the sample against a calibration curve prepared using standard phosphate solutions.

Total phosphorus determinations followed the same procedure as those for orthophosphate except that the

*A product of Hitachi, Ltd., Tokyo, Japan.

determinations were preceeded by the following steps: Ten ml of sample, 2 ml of 5N H_2SO_4 and 1.0 g of potassium persulfate were added to a 125 ml Erlenmeyer flask. The solution was then diluted with 30 ml of distilled water and refluxed for 15 min. It was then cooled and diluted to 500 ml with distilled water and the steps for the orthophosphate test were repeated.

9. Gas Measurement and Composition

Total gas production from the filters was measured continuously with Precision Scientific wet test meters* which were read daily.

Periodically determinations for methane and carbon dioxide content were made using a Fisher Hamilton Model 29 gas partitioner** with two chromatographic columns. The first being a 6 ft (1.83 m) by 1/4 in. (0.635 cm) aluminum column packed with 30 percent DEHS on 60-80 mesh Chromosorb P***, and the second a 6.5 ft (1.98 m) by 3/16 in. (0.478 cm) aluminum column packed with 40-60 mesh Molecular Sieve 13X***.

Gas samples were withdrawn from one liter water condensate traps placed between the filters and wet test meters, and analyzed according to instructions given in the instrument instruction manual (40). The samples were collected in 10 cc syringes which had first been purged with

*A product of Precision Scientific, Chicago, Ill.
**Manufactured by Fisher Scientific, Pittsburgh, Pa.
***Distributed by Fisher Scientific, Pittsburgh, Pa.

the sample gas. Immediately upon withdrawal from the condensate traps the syringes were sealed with a rubber cap. The sample, so collected, was then injected into the gas partitioner and captured in a 0.5 ml stainless steel sample "loop". The use of the sample "loop" provided a convenient and highly reproducible system for sampling gas streams.

The concentration of components in the unknown gas sample were determined by comparing the peak heights of the sample gas components to those of standard samples with known component concentrations using the following equation.

$$C_s = \frac{H_s}{H_{std}} (C_{std}) \qquad [20]$$

When: C_s = Concentration of sample component, percent

C_{std} = Concentration of standard component, percent

H_s = Peak height of sample component

H_{std} = Peak height of standard component

10. Heavy Metals

A heavy metal analysis of the pharmaceutical waste was conducted by the University of Missouri, Environmental Trace Substances Center, Columbia, Missouri. The instrument used in this determination was a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer*. Samples were prepared for analysis by adding 2 ml of concentrated nitric acid to a 250 ml sample and storing it in a polyethylene bottle for shipment by car to Columbia.

*A product of Perkin-Elmer Corp., Norwalk, Conn.

F. STARTING THE FILTER

To further evaluate the starting procedures described by Young (2), two methods of biological seeding were studied. Young studied several methods of seeding; one involved a light seed distributed evenly throughout the filter, another employed a heavy seed, 30 g, in the lower one-third of the filter, while still another procedure involved two separate additions of seed organisms, the first addition was made when the filter was started and the second after 20 days of operation. Young found that the most effective way of starting the filter was with the heavy seed in the lower one-third of the filter.

In this study, filters number 1 and 3 were started by injection of 30 g of seed sludge into the lower one-third of a filter which contained a simulated substrate of glucose and trace nutrients. While filters number 2 and 4 were started by distribution of the 30 g of seed sludge evenly throughout the filter height. The seed sludge used in all four filters was obtained from a well operating sewage sludge digester and the dose used per unit of volume was equal to twice that used by Young. The filters were maintained initially during the starting period on the simulated substrate of 1000 mg/l glucose and trace nutrients at a theoretical detention time of 48 hr. During the course of the starting period the filters were acclimated to the pharmaceutical waste by gradually replacing a portion of the glucose organic load with pharmaceutical

waste. The pharmaceutical waste percentage was increased 20 percent after each successive detention time so that by the end of the starting period the organic load received by the filters was comprised totally of pharmaceutical waste diluted to 1000 mg/l COD.

IV. EXPERIMENTAL RESULTS

In order to achieve the stated objectives of this investigation the laboratory filters were operated in pairs under different combinations of substrate concentration and organic loading with the pharmaceutical waste. When the performance characteristics of the filters at a particular loading were adequately determined, the loading was changed, and the resultant filter performance was observed.

The results of this experimental study are reported in this chapter in terms of filter performance during an initial period and subsequent periods of steady-state operation.

A. PHARMACEUTICAL WASTE ANALYSIS

A summary of the physical and chemical characteristics of the pharmaceutical waste is presented in Table III. A description of the plant operation and waste streams by Wallace (36), the plant manager, at the time of this study indicated that the waste contained approximately one percent methanol; this value was arrived at by a mass balance determination for all operations in the plant. Based on this figure almost 95 percent of the waste's COD would theoretically be comprised of methanol. The waste also contained a small fraction of toluene which imparted a distinct odor to the waste.

The waste analysis indicated that the waste was nutrient limited by phosphorus and nitrogen; for unhindered anaerobic treatment of the waste, at full strength, at

Table III. Physical and Chemical Characteristics of the Pharmaceutical Waste

Parameter	Sample 1 Mar. 24, 1972	Sample 2 Aug. 22, 1972
pH	10.1	7.5
COD - mg/l	15,950	16,130
Nitrogen - mg/l		
Ammonia	0	11.8
Organic	33.3	34.2
Phosphorus - mg/l		
Ortho-	0.5	0.4
Total	0.9	0.95
Suspended Solids - mg/l	32	28
Total Solids - mg/l	565	432
Alkalinity - mg/l as $CaCO_3$	540	412
Heavy Metals - mg/l		
Lead	0.007	0.005
Copper	0.140	0.140
Zinc	0.018	0.11
Manganese	0.020	0.22
Iron	0.05	0.56
Cadmium	0.020	0.010
Calcium	9.7	58.7
Magnesium	7.5	14.7

least 800 mg/l of nitrogen and 160 mg/l of phosphorus would need to be present (20). In order to maintain unhindered anaerobic growth, nitrogen, in the form of ammonium chloride, and phosphorus, in the form of dibasic potassium phosphate, were added to the feed solutions in sufficient quantities to maintain a phosphorus to nitrogen to carbon ratio of 1:5.9:100 (20) (21). The addition of the potassium phosphate served two purposes, not only did it provide the required phosphorus, but it increased the buffer capacity of the system to a limited extent. During periods of decreased alkalinity the amount of potassium phosphate added to the feed was increased to provide additional buffer capacity.

B. RESPONSE TO STARTING PROCEDURES

The response to starting procedures as indicated in Figure 7 was rapid. The reactors, operating on a substrate consisting of 1000 mg/l of glucose with the addition of trace nutrients and at a feed rate of 3.125 l/day, produced stable gas production, COD removal and effluent volatile acid levels by approximately the fourteenth day. At this time the conversion from glucose to pharmaceutical waste was started and by day 25 the filters were receiving only pharmaceutical waste diluted to 1250 mg/l COD plus appropriate amounts of nitrogen and phosphorus. The drop in gas production and the increase in effluent volatile acid and effluent COD concentrations corresponds approximately to the period of conversion.

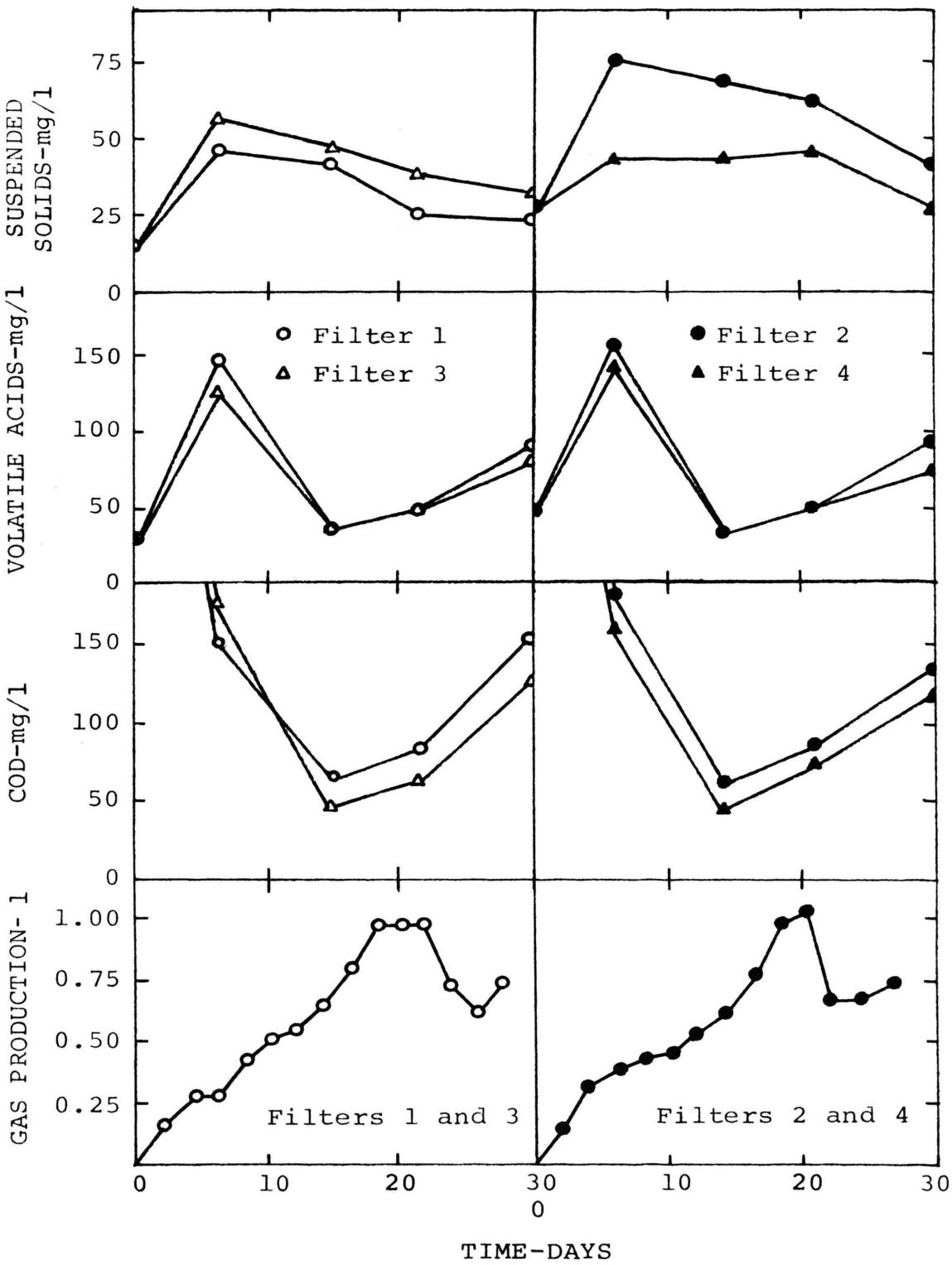

Figure 7. Effluent Characteristics and Average Gas Production for Filters 1 Through 4 During the Start-up Period

The only appreciable variation in the performance of the filters during the starting period, which could be attributed to the different starting procedures, was the concentration of effluent suspended solids. The solids lost from filters 1 and 3 were consistently lower than those lost from filters 2 and 4. See Figure 7.

C. STEADY-STATE FILTER PERFORMANCE

The starting period was considered complete at day 14 and at this point the conversion of pharmaceutical waste was started. Acclimation to the pharmaceutical waste was assumed to be complete when, at 40 days, constant gas production and a high COD removal efficiency were attained for the loading rate of 22.91 lb COD/1000 cu ft/day (0.367 kg COD/cu m/day). At this time the filters were treating a substrate composed solely of pharmaceutical waste plus nitrogen and phosphorus and were assumed to be operating under steady-state conditions.

1. Response to Loading Changes

Figures 8 through 14 give a graphical representation of filter performance throughout the period of study to include the starting period. The organic loads expressed in the upper portions of the graphs were produced by varying the influent COD concentration or the hydraulic detention time as described in Table II. During the first 130 days of operation all filters were operated under the same loading conditions to determine the reproducibility of filter performance. Examination of the figures will

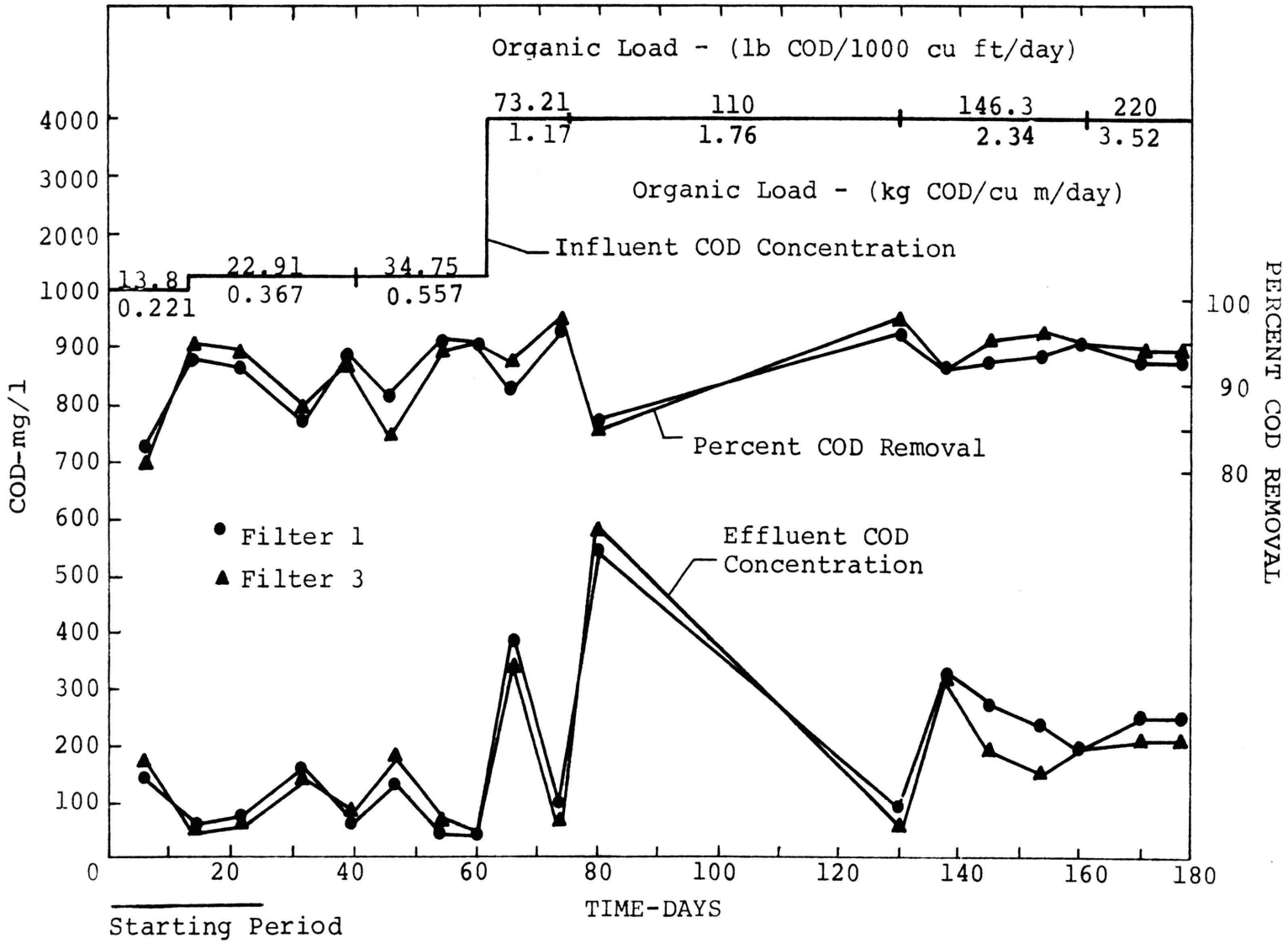

Figure 8. Influent and Effluent COD Concentrations With Percent COD Removal for Filters 1 and 3

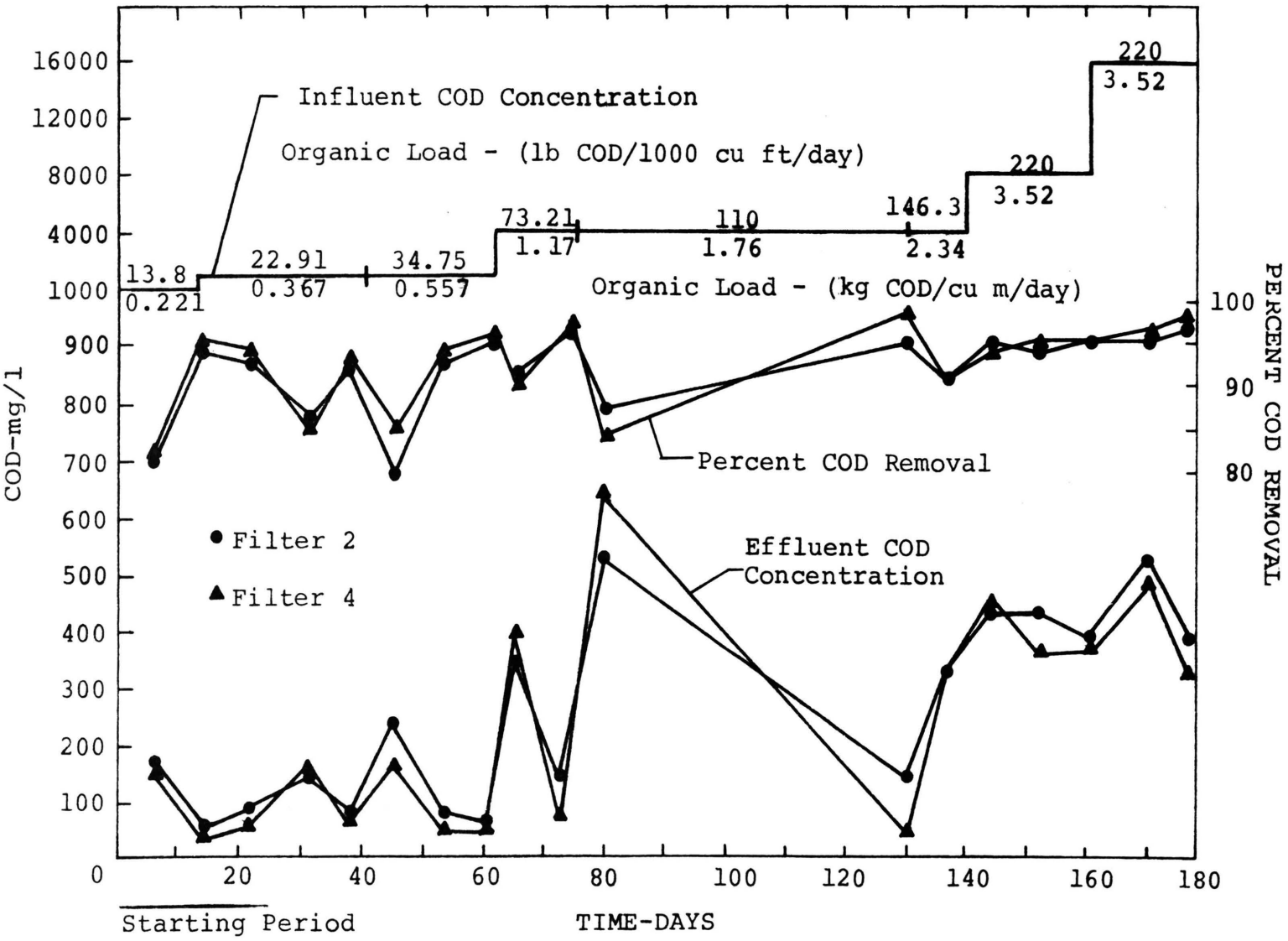

Figure 9. Influent and Effluent COD Concentrations With Percent COD Removals for Filters 2 and 4

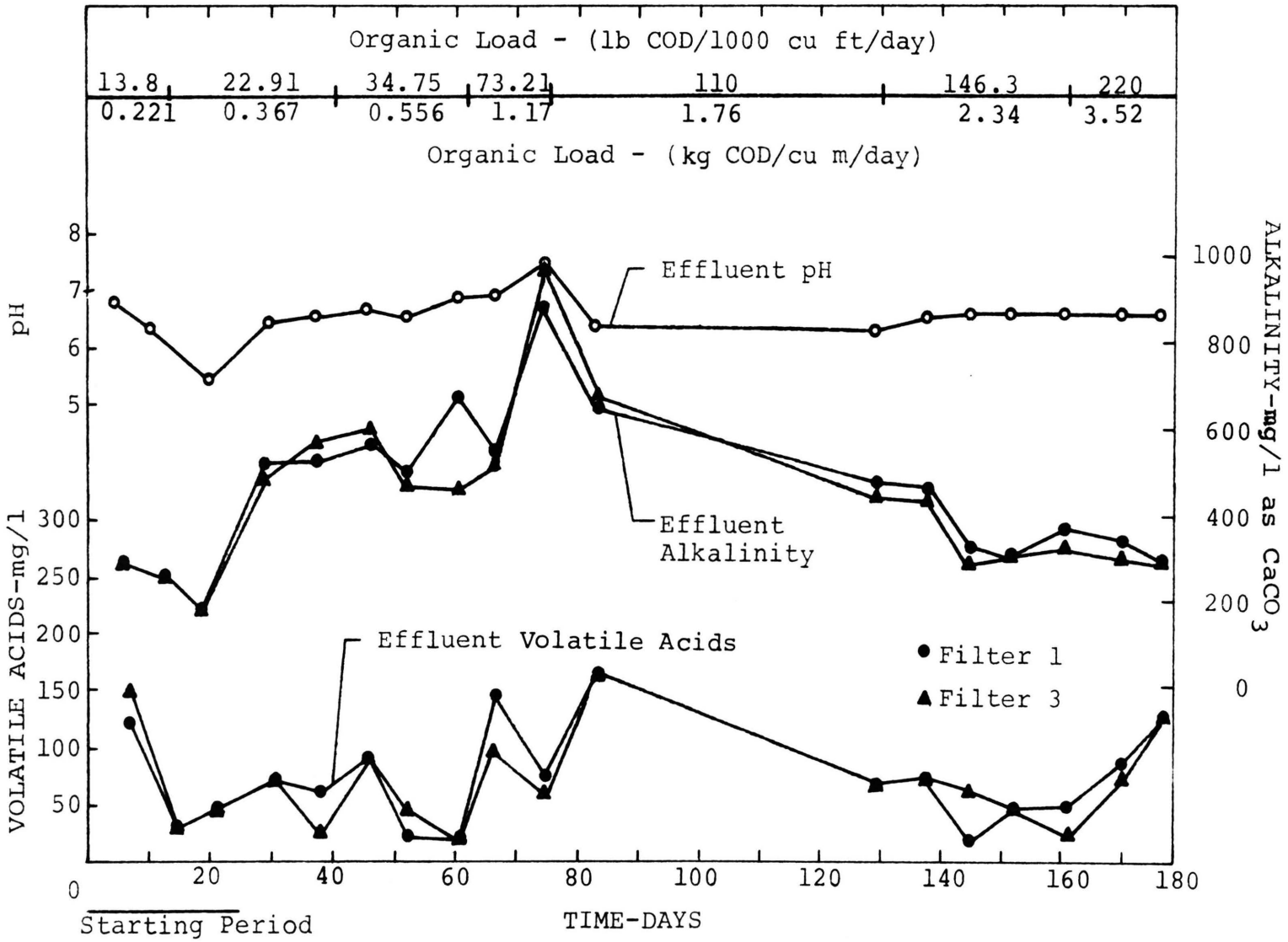

Figure 10. Effluent Volatile Acid and Alkalinity Concentrations for Filters 1 and 3 Along With Average Effluent pH

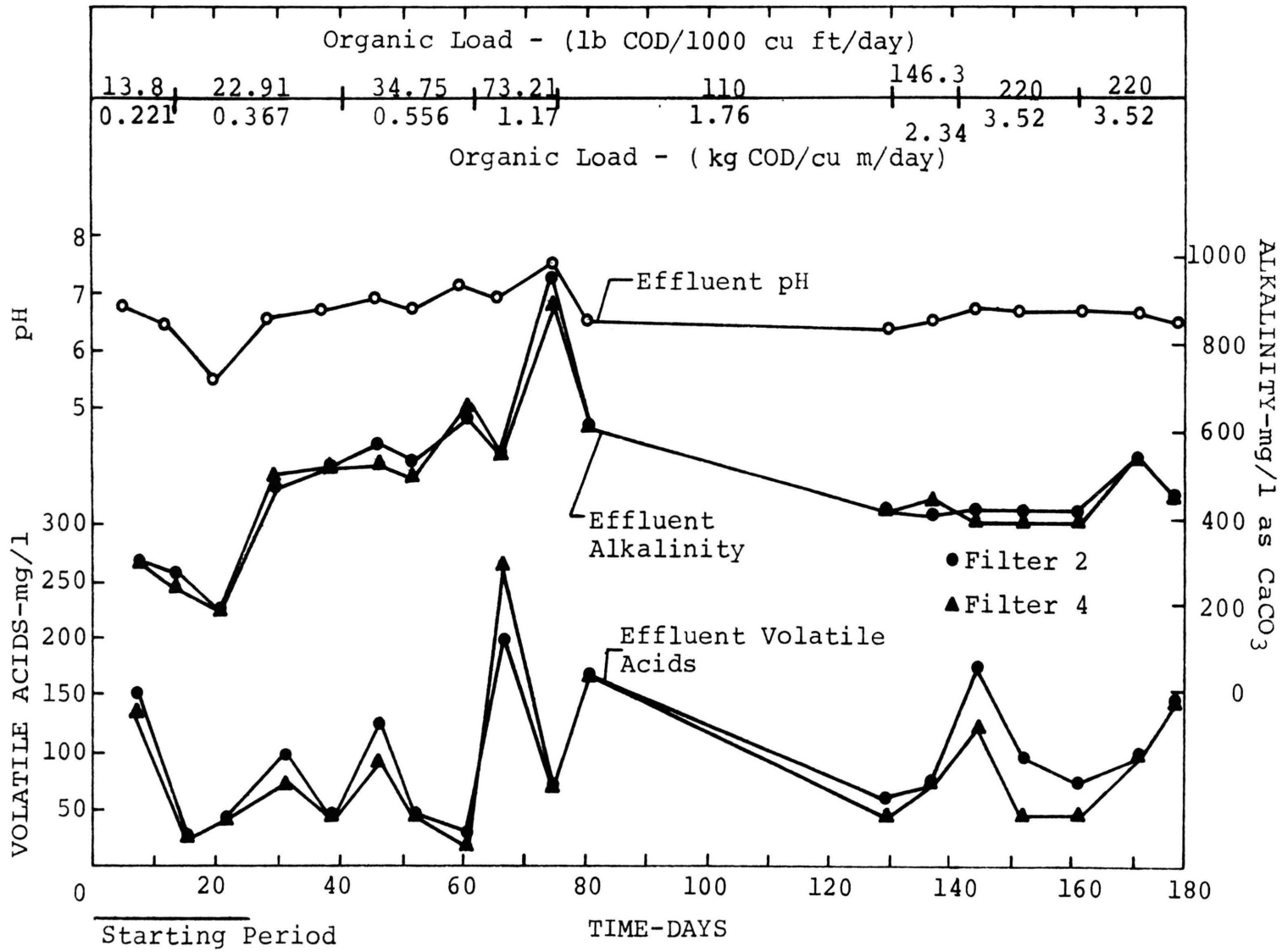

Figure 11. Effluent Volatile Acid and Alkalinity Concentrations for Filters 2 and 4 Along with Average Effluent pH

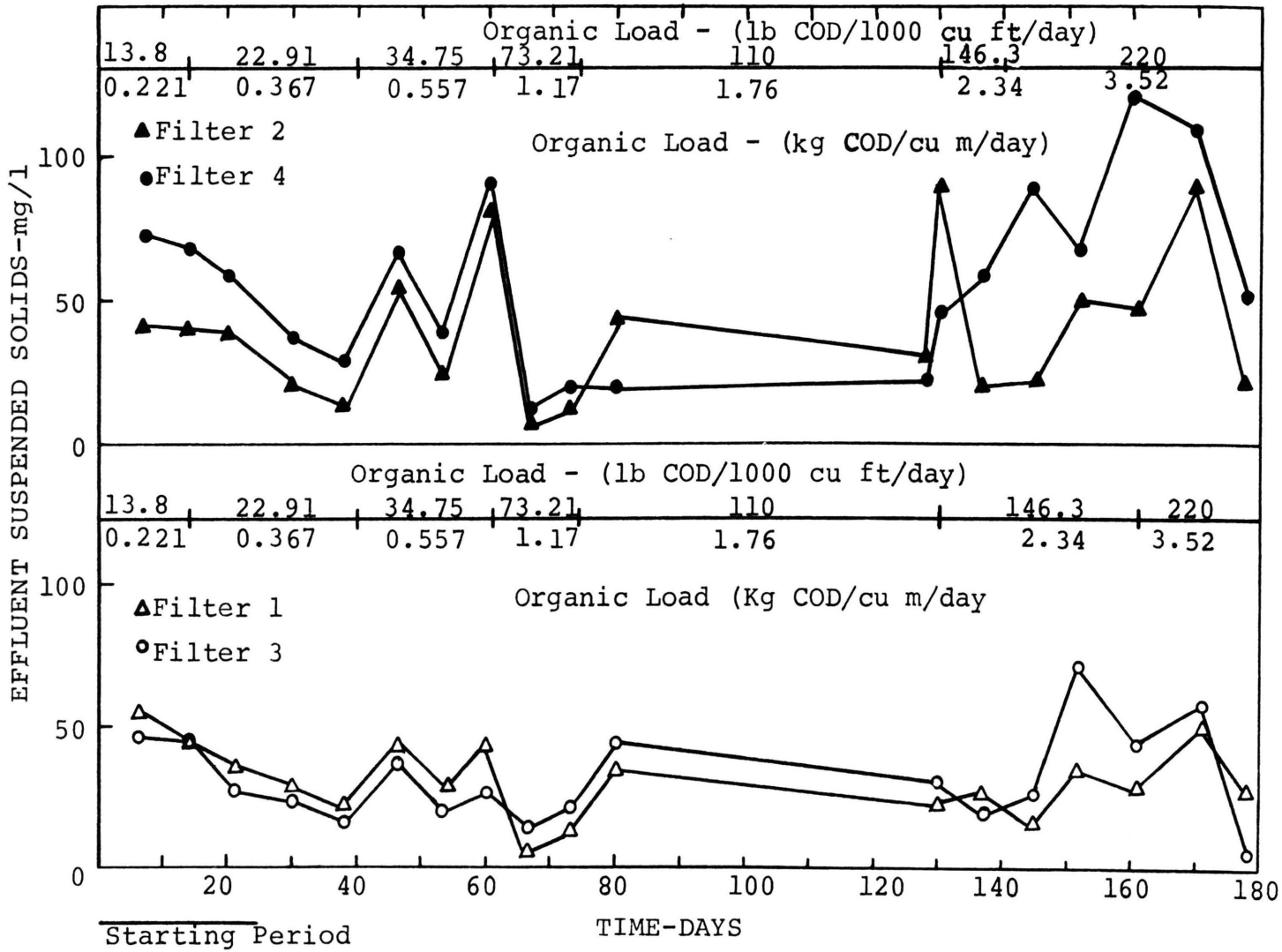

Figure 12. Effect of Hydraulic and Organic Load Variations on Effluent Suspended Solids

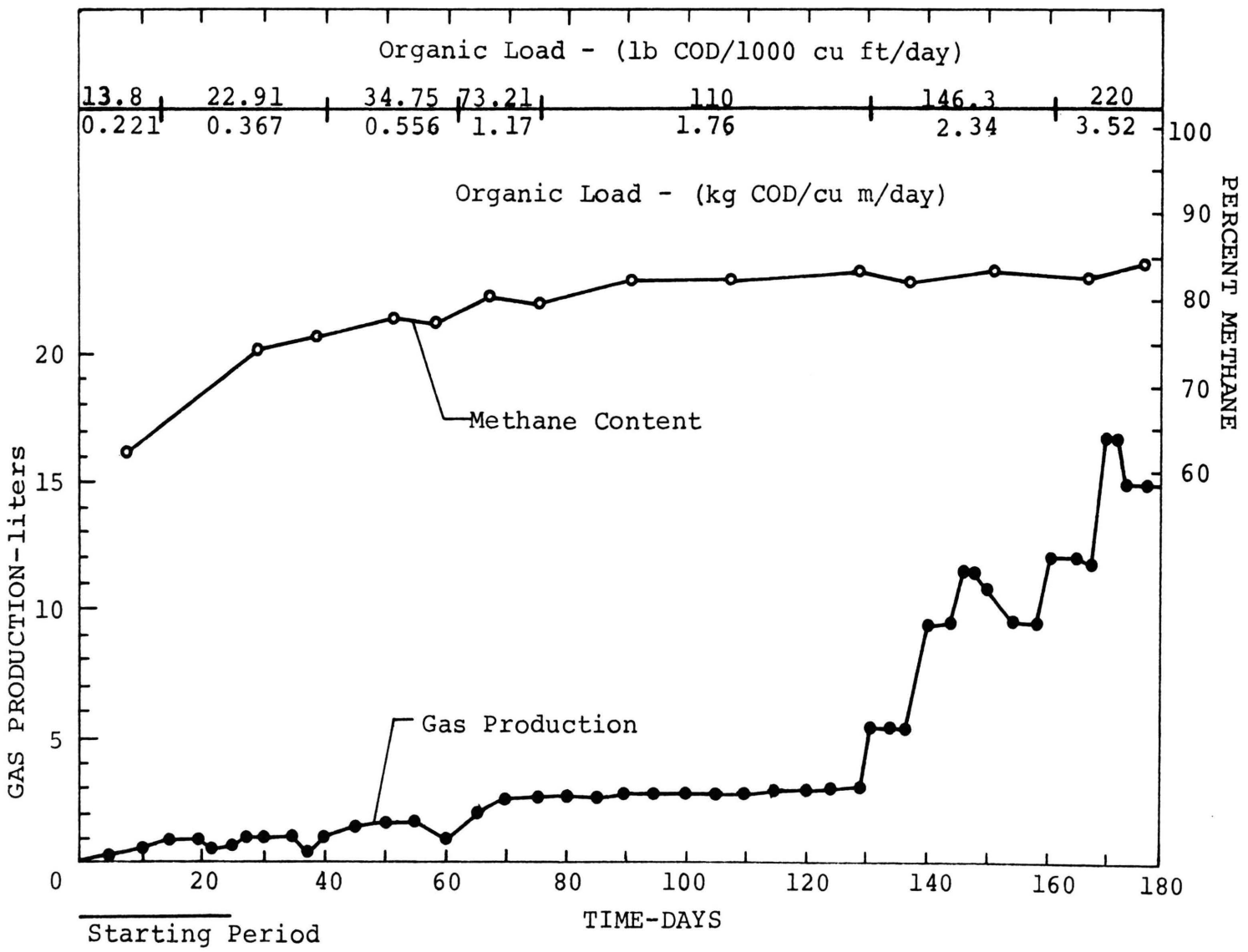

Figure 13. Average Gas Production and Methane Content for Filters 1 and 3 While Receiving a Series of Organic Loads

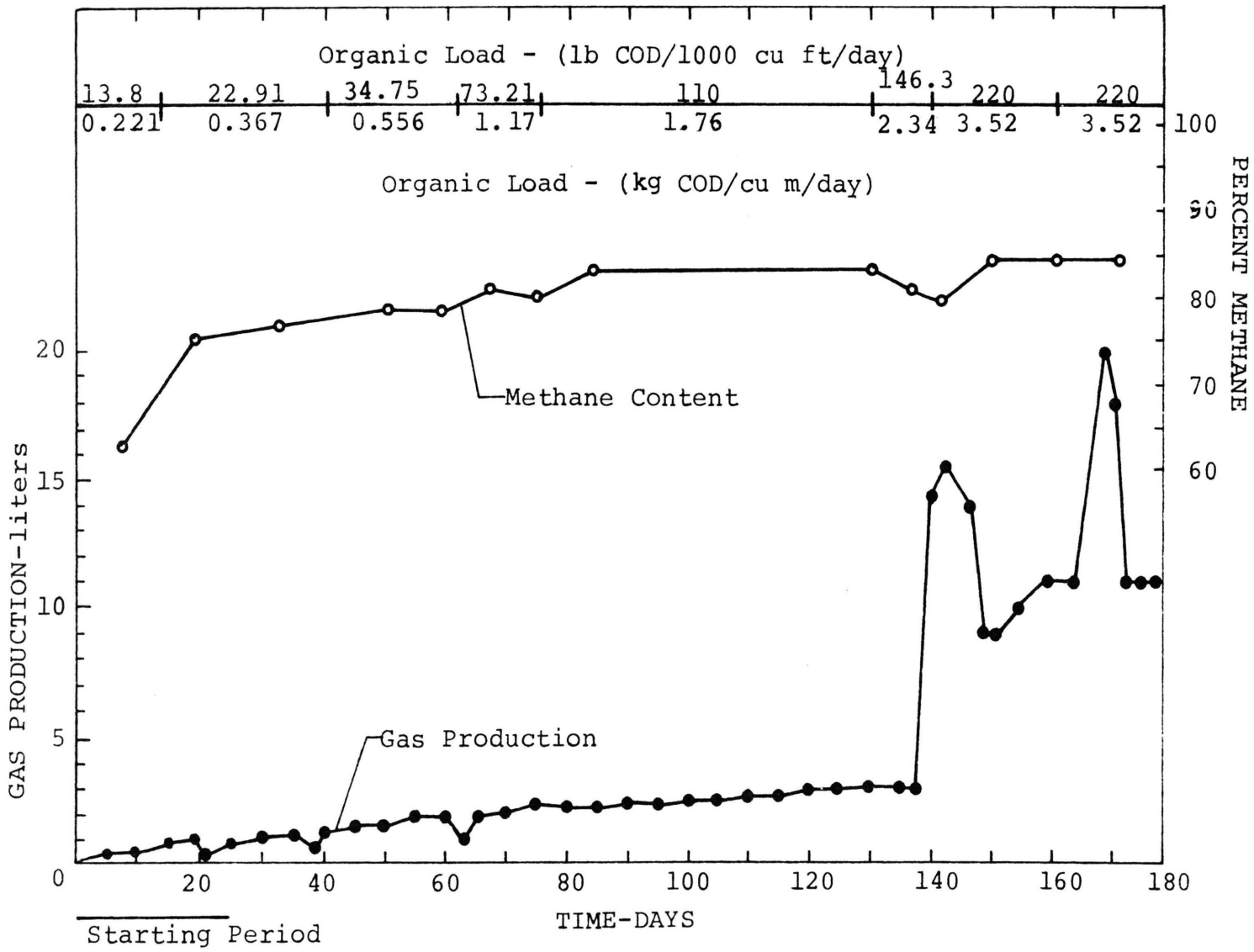

Figure 14. Average Gas Production and Methane Content for Filters 2 and 4 While Receiving a Series of Organic Loads

reveal that a definite trend was established by all filters in their response to loading changes.

The effluent COD concentrations, illustrated in Figures 8 and 9, indicate that immediately following a loading change, effluent COD concentrations increased for a period of time then decreased to steady-state levels. The increases in effluent COD concentrations appeared to be affected more by changes in the influent COD concentration than by decreases in the detention time.

The fluctuations in effluent volatile acid concentrations shown in Figures 10 and 11 followed very closely the pattern of the effluent COD concentrations with sharp increases coming immediately after the loading changes and, once again, the magnitude of the increase appeared to be greater when loading changes were due to changes in influent COD concentrations rather than due to decreases in detention times. Effluent alkalinity is plotted on the same graph to show the volatile acid-alkalinity relationship. At no time did the volatile acid to alkalinity ratio exceed 0.8 so volatile acid toxicity should not have posed a problem in the filters (22).

Effluent suspended solids for all filters were generally below 50 mg/l as shown in Figure 12. The major factor which affected solids loss appeared to be hydraulic loading since the major fluctuations occurred following decreases in detention times rather than after changes in influent waste concentration. Filters 1 and 3, which were

seeded in the lower one-third of the filter height had lower effluent suspended solids concentrations for all loading conditions and did not appear to have been affected as severely by hydraulic changes as filters 2 and 4 which were seeded throughout the filter height.

The filter response to loading changes indicated by gas production is illustrated in Figures 13 and 14. Gas production measurements were taken daily and the data points plotted in Figures 13 and 14 represent an average of the daily readings. For all organic loadings below 146.3 lb COD/1000 cu ft/day (2.34 kg COD/cu m/day) changes were characterized by a slight drop in gas production lasting from 2 to 7 days followed by a gradual increase to a stable level. At loadings of 146.3 lb COD/1000 cu ft/day (2.34 kg COD/cu m/day) and greater, responses to loading changes were characterized by sharp increases in gas production followed by a lag period at which time the production levels reached a temporary plateau. After the lag period, the gas production again increased sharply to a relatively stable level.

The conversion efficiency of COD removed to methane was determined for periods of steady-state operation as shown in Table IV. Any losses in total methane production due to the solubility of the gas in the effluent was considered to be negligible. Theoretically for every gram of COD removed 0.351 liters of methane should be produced (2).

Table IV. COD to Methane Conversion Efficiency for Filters Operating at Steady-State Conditions

Loading Rate lb COD/1000 cu ft/Day*	COD Conc. mg/l		Percent Removal	COD Removed Per Day, g	Gas Production Per Day, l	Percent Methane	Methane Produced Per Day, l	Conversion Efficiency COD to Methane, %
	Inf.	Eff.						
22.91	1250	80	94	4.8	1.1	77.5	.852	50.5
34.375	1250	50	96	7.8	1.8	78	1.375	50.5
73.21	4000	103	97.5	16.2	2.4	82	1.97	34.5
110.0	4000	92	97.7	24.4	2.9	84	2.42	28.5
146.3	4000	197	95.1	31.7	11	83.5	9.2	82.75
220	4000	235	94	47	15.5	85	13.2	80.25
220	8000	390	95.1	47.5	12.5	84.5	10.6	63.7
220	16000	495	97	48.5	18	85	15.3	90

*To convert lb COD/1000 cu ft/day to kg COD/cu m/day, multiply by 0.0160.

2. Effluent Quality

The effluent characteristics for the treatment of the pharmaceutical waste are summarized in Figures 8 through 12 for the range of influent COD concentrations and hydraulic detention times considered. The effluent was normally a rather clear or pale amber colored liquid, except at times of high solids washout when it appeared to be greenish to gray in color. The amber color originated in the untreated waste and was not removed through treatment, at times it was intensified by the apparent color imparted to it by the suspended solids present in the waste. The effluent maintained the telltale odor of toluene at all times, indicating that the toluene passed through the filters receiving little or no treatment. Under heavy loading and low pH conditions a putrid odor was produced which was attributed to the reduction of sulfates present in the waste or dilution water.

COD removal efficiencies normally were above 90 percent. However, for all loadings above 110 lb COD/1000 cu ft/day (1.76 kg COD/cu m/day) the effluent quality would be considered poor since the COD concentration was usually greater than 200 mg/l.

3. Effect of Filter Height

During the periods of steady-state operation for the different loading conditions, samples were withdrawn from the filters at various heights. The resulting profiles for COD and volatile acid concentrations in the filters are shown in Figure 15 for various hydraulic loads at influent

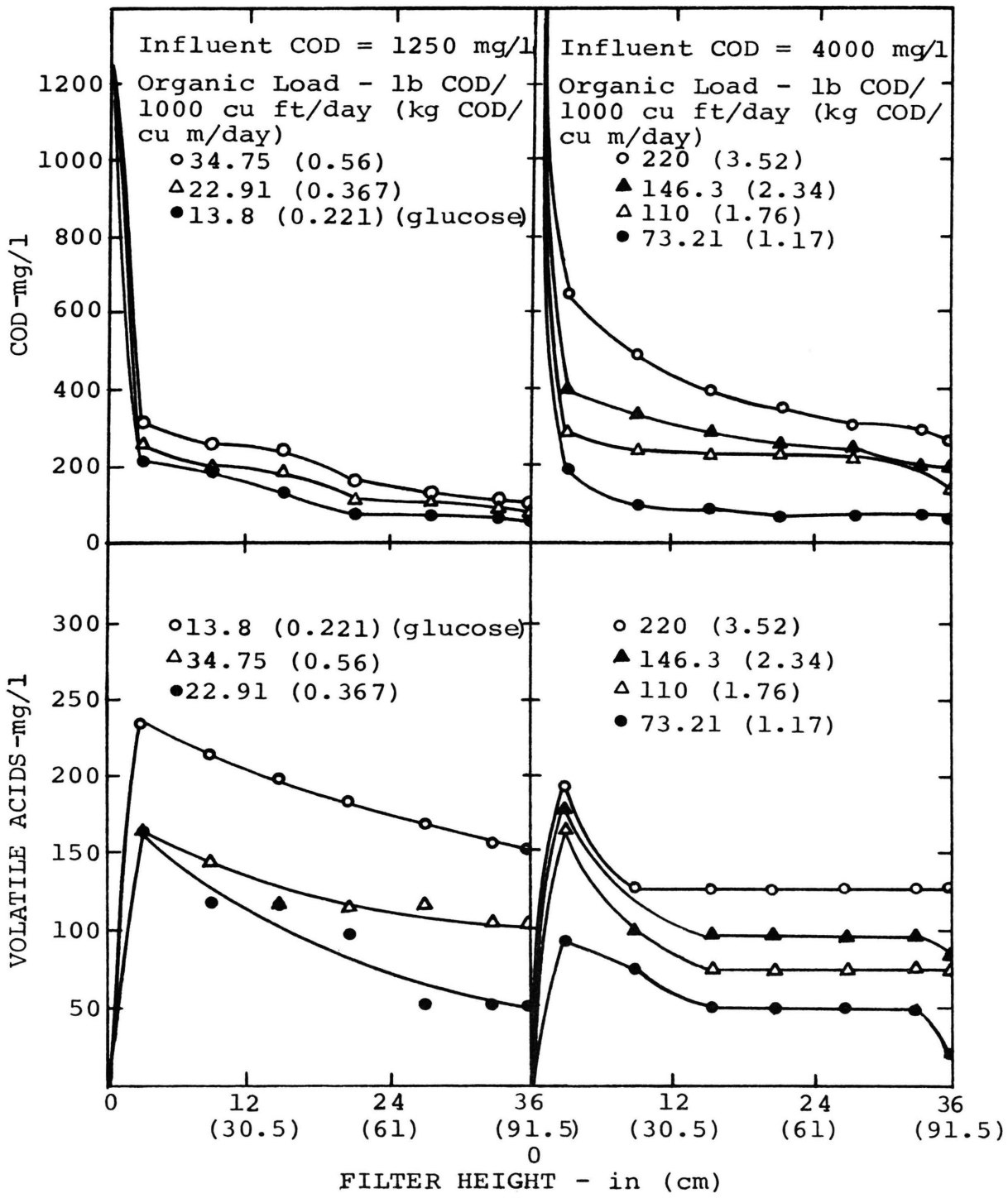

Figure 15. Comparison of Volatile Acid and COD Profiles for Filters Operating Under a Variety of Organic Loads at Influent COD Concentrations of 1250 and 4000 mg/l

COD concentrations of 1250 and 4000 mg/l. These curves indicate that a high rate of waste conversion to volatile acids and direct methane fermentation proceeded concurrently resulting in high COD removals in the lower levels of the filters. Normally, only a few hundred mg/l of additional COD were removed in the upper levels of the filter.

Typical filter responses to loading changes are shown in Figure 16. Shortly after a loading change, volatile acid concentrations were increased throughout the filter and the rate of COD removal was reduced in the lower levels of the filter. With increasing time, however, the methane forming bacteria began to acclimate to the new conditions which was indicated by lower volatile acid concentrations and higher rates of COD removal in the lower levels of the filter. The ability of the filter to operate successfully under shock loading conditions is seen in this figure. While the COD removal rates were reduced greatly in the lower levels of the filter, the overall treatment efficiency was reduced by less than 10 percent.

4. Biological Solids

An observation of the physical characteristics of the solids within the filters indicated that they did not become solidly attached to the surfaces of the filter stone, but lay loosely in the void spaces. The solids appeared to be densely flocculated and were not easily disturbed by rising substrate or gas bubbles. Table V describes the solids profiles of the filters for the various loading

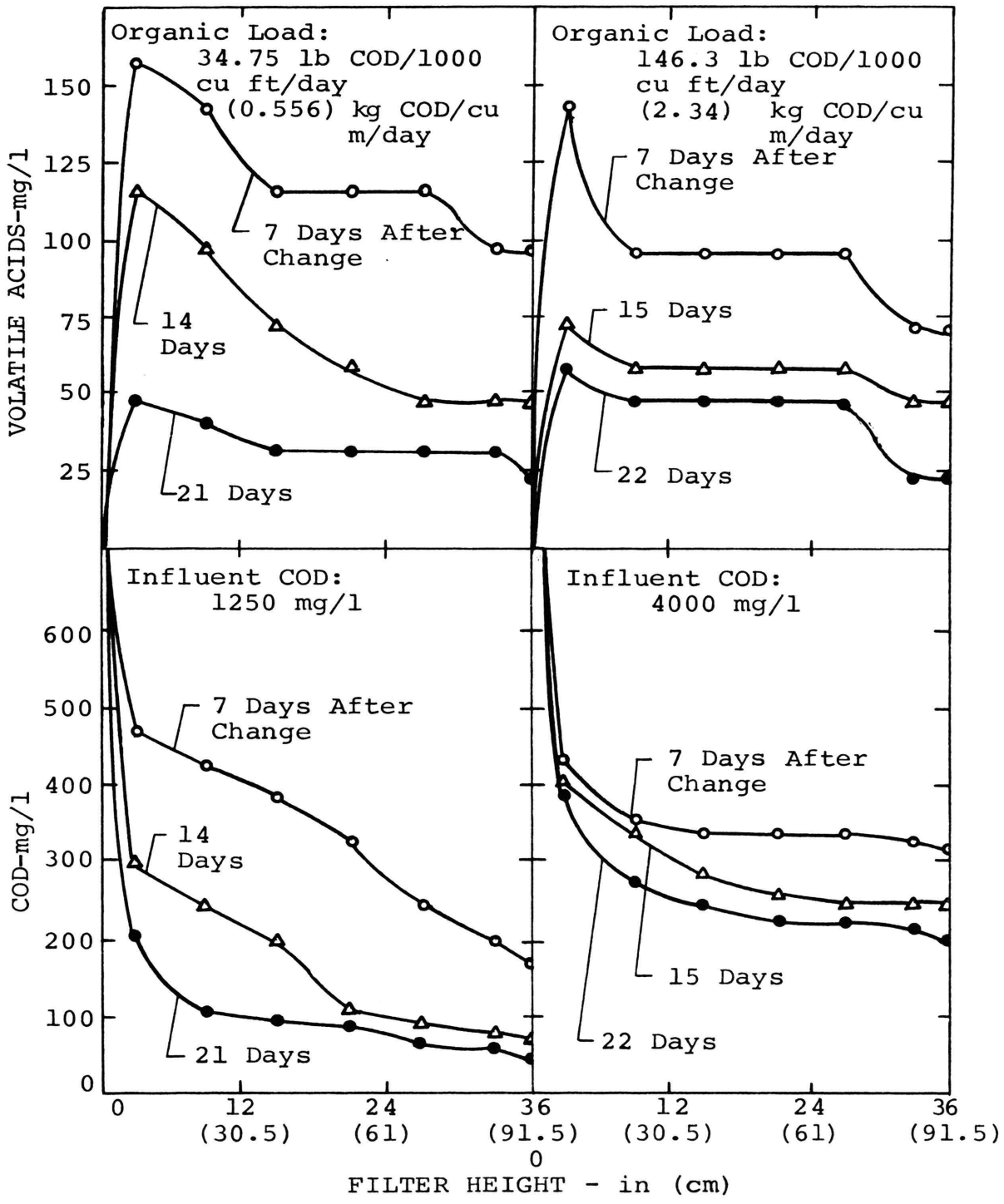

Figure 16. Comparison of COD and Volatile Acid Profiles After Loading Changes From 22.91 to 34.75 lb COD/1000 cu ft/day (0.367 to 0.556 kg COD/cu m/day) and 110 to 146.3 lb COD/1000 cu ft/day (1.76 to 2.34 kg COD/cu m/day)

Table V. Suspended Solids Verses Filter Height for Filters Operating at Steady-State Conditions for a Series of Organic Loads

Filter Height in.*	Suspended Solids mg/l								
	Organic Load - lb COD/1000 cu ft/Day**								
	13.8	22.91	34.375	73.21	110	146.3	220	220	220
	Influent COD Concentration - mg/l								
	1250	1250	1250	4000	4000	4000	4000	8000	16000
3	9206	9542	11512	9473	18644	18430	12512	10560	4080
9	2560	1612	668	376	848	1232	3072	2488	1368
15	655	384	160	44	368	678	616	638	356
21	113	106	128	28	164	454	500	154	120
27	62	56	76	31	28	98	84	96	64
33	47	32	60	17	28	68	56	72	52
36	42	18	44	15	24	32	32	48	24

*To convert inches to centimeters, multiply by 2.54.

**To convert lb COD/1000 cu ft/day to kg COD/cu m/day, multiply by 0.01602.

conditions. The distribution of the solids in the filters corresponds closely to the COD removal and volatile acid conversion rates described earlier. In general the concentration of suspended solids reported in Table V represents those loosely held solids which could be easily removed from the filter for further disposal if required. The remaining solids would provide a good seed to maintain the process at a high efficiency.

A settleability test using an Imhoff cone of solids from the lower one foot of a filter, degasified by stirring, indicated that maximum settling would occur within 12 minutes. The sludge volume index (SVI) averaged 44.2 for 2 samples which contained an average of 9,850 mg/l of suspended solids. Only 58 mg/l of suspended solids remained in the supernatant liquor after 30 minutes of settling. The solids in these samples contained 93 percent volatile matter and averaged 1.45 mg COD/mg volatile suspended solids (VSS).

At the conclusion of the study filter number one was dismantled and the biological solids which had accumulated in the filter were recovered. In order to determine the activity of these biological solids, the COD removal for the filter was calculated in terms of COD removed per gram of volatile suspended solids. These results are reported in Table VI. The total mass of biological solids produced during the period of operation was obtained by adding the accumulated mass of solids less the initial seed and the

Table VI. Total Biological Solids Synthesis for Filter 1, Accumulated During the Course of This Study

Item	Unit	Value
Time of Operation	Days	180
Average Waste Flow	Liters/day	6.58
Weighted Average Effluent Suspended Solids	mg/l mg/day	32 211
Total Suspended Solids Washout	mg	37900
Total Solids Accumulation in Filter	mg	66456
Initial Feed Solids	mg	30000
Total Solids Produced	mg	74356
Total Volatile Solids ss x .93 = VSS	mg VSS	69060
Ave. Solids Retention Time	Days	313
COD Removed	Grams	3693
Net Synthesis:		
COD Basis	gm solids COD/ gm COD removed	0.0272
Solid Basis	gm VSS/gm COD removed	0.0270
Net Accumulation	gm VSS/gm COD removed	0.019

mass of suspended solids lost in the effluent (shown in Figure 12). The total removal of COD during the period of operation was obtained by integrating the area under the curve shown in Figure 8 for filter number one. Using the above calculations the net synthesis rate for the biological solids could be obtained. For filter one approximately three percent of the COD removed was synthesized into biological solids, giving a net rate of biological solids production of 0.027 gm VSS/gm COD removed.

V. DISCUSSION

The primary objective of this study was to show that the anaerobic filter process could be used to efficiently treat an industrial waste containing soluble organic material. In order to accomplish this aim the experimental results obtained had to be interpreted relative to the adequacy of the filter design, and the performance parameters monitored.

A. EXPERIMENTAL DESIGN

The selection of the 1 to 1.5 inch stone and 6 inch diameter column was based on the results of a previous filter study (2). The basic consideration of the filter design was to provide a combination of stone size and column diameter that would minimize geometric distortion of the filter performance. The combination chosen seemed to fulfill this objective. Although treatment efficiency would probably not vary significantly over a range of stone sizes, much smaller stone might interfere with effective solids transport within the filter, resulting in serious plugging of the void spaces. The use of larger stones might result in severe channeling of the waste through the larger void spaces, resulting in lower effective retention times and lower filter efficiency. Additional research would be required to determine the optimum stone size.

The design of the feed system appeared to be adequate. The use of acid to clean the feed reservoirs prevented any

significant permature biological breakdown of the substrate. The dispersion plate in the base of the filters, (see Figure 3), provided an effective means for distributing the waste across the bottom of the filters. By using several holes in the dispersion plate complete plugging of the feed system was prevented. The dispersion rings placed at one-foot (30.5 cm) intervals appeared to be effective in preventing excessive solids transfer and gas channelization through the large void spaces at the stone-column boundary. Possibly the weakest point in the filter design was the inverted siphons, which were used to provide a sealed system for gas collection purposes. Due to the low flow, effluent suspended solids eventually built up and plugged the siphons so that the filter effluent started to back up into the moisture traps. A possible solution to this problem would be to employ a common siphon to all filters so that the flow would be large enough to keep the solids flushed from the system.

Although biological growth eventually became attached to the inside walls of the filters, this effect was not considered to affect the filter performance, since the area of wall growth was small relative to the surface area of the media. However, in practice, the build up of biological solids on the filter walls and in the media void spaces might seriously decrease the design porosity of the filter, resulting in reduced treatment efficiency. This

problem could be overcome by periodically flushing the excess solids from the system.

The expression of organic loadings in lb COD/1000 cu ft/day (kg COD/cu m/day) of total filter volume was selected primarily because of its widespread use in other treatment systems. Loadings per unit of horizontal area might have been used with equal meaning, but would be hard to adapt to filters with unusual geometric configurations, and anaerobic filter designs would have the advantage of no geometric constraints. Loadings based on applied COD per unit of biological mass were considered meaningless, since this system is not uniformly mixed, nor could the mass be conveniently determined.

B. ANALYTICAL MEASUREMENTS

The exact chemical composition of many of the organic constituents in the pharmaceutical waste was not determined because it was considered beyond the scope of this project. The actual concentration of toluene was one such component that was not investigated since it was present only in small quantities. However, it could become significant if present in large quantities since it apparently represented an untreatable portion of the waste by the anaerobic process.

Throughout the study the biochemical conversion of the waste was considered to be complete with the formation of either stable biological solids or methane gas. Consequently, the soluble COD remaining in the effluent was

used as a measure of filter performance. In a practical sense, however, the biological solids present in the effluent must be considered as an additional load to the system receiving the filter effluent unless they were removed by final sedimentation. At times during this study the COD of these effluent solids approached or surpassed the soluble COD of the effluent when the filters approached steady-state conditions.

Volatile acids recovery was assumed to be accurate within $\pm$ 24 mg/l of their actual concentration, since the accuracy of the test is limited for concentrations below 200 mg/l (38). The results of the volatile acid determinations were used only to show trends in methane conversion during different periods of operation, and were not intended to indicate any form of treatment efficiency. Possibly, a more accurate and meaningful method for volatile acid recovery would be liquid-gas chromotography since the concentrations of the individual acids could be determined and conclusions could be drawn from their predominance during various stages of treatment.

C. STEADY-STATE OPERATION

Theoretically steady-state conditions would imply that for a constant influent waste strength and loading, the effluent COD as well as the concentration of any individual operational parameters at any point in the filter would remain constant for an indefinite period of time. Young (2) investigated the possibility that this condition might

actually exist in the anaerobic filter and found that while constant gas production and COD removal was attained, the individual COD producing components in the system were in a continual state of fluctuation. Steady-state conditions in the strictest sense of the word are therefore probably never attained in the anaerobic filter. For this study steady-state conditions were assumed to exist when a stable gas production rate was attained and high, relatively stable COD removal efficiencies were reached. Along with these two parameters, consistently low concentrations of effluent suspended solids and volatile acids in the filter effluents also indicated steady-state conditions but these parameters were considered to be less reliable since they were dependent upon more variables.

The period of time required to reach steady operation appeared to be dependent on the magnitude of the loading change with larger loading changes requiring more time. With the exception of the loading of 110 lb COD/1000 cu ft/day (1.762 kg COD/cu m/day) stable conditions based on effluent COD and volatile acids were established within 20 days for all loadings. It is possible that the 110 lb COD/1000 cu ft/day (1.762 kg COD/cu m/day) loading stabilized within this period, but insufficient data was available to prove this fact. It is questionable whether the higher loadings of 220 lb COD/1000 cu ft/day (3.52 kg COD/cu m/day) ever reached steady-state conditions based on the

fluctuations in gas production, however, percent COD removals varied by less than one percent.

Comparison of Figures 8 and 9 and Figures 10 and 11 show that during periods of steady-state operation over 50 percent of the effluent COD was due to volatile acids. This indicates that at no time during steady-state operation did more than 0.5 percent of the waste pass through the filter without being converted to at least some intermediate product.

Due to the solids retention characteristics of the anaerobic filters, there appeared to be no correlation between effluent suspended solids levels and treatment efficiency based on soluble COD levels. High solids concentrations in the effluent were caused by sudden changes in the hydraulic loading rate, but might also be caused by sloughing of excess biological filter solids. Conditions requiring solids wasting were approached in filters 2 and 4 for a period of time near the end of the study. See Figure 12.

The COD to methane balance conducted during the study indicated that methane conversion efficiencies for certain periods of operation were extremely low. While there is no concrete explanation for this, several possibilities exist: 1) due to some undetected malfunction in the collection system all of the gas produced was not recovered, 2) higher than normal rates of cellular synthesis could consume COD that would not be recorded as methane, 3) in an anaerobic

environment, sulfates can be reduced by microorganisms which utilize sulfur as a hydrogen ion acceptor. COD is oxidized through this reaction and methane is not a product, if abnormally high sulfates were present in the dilution water this difference could be significant. The presence of nitrites and nitrates in the waste would produce similar results.

D. SUMMARY OF FILTER PERFORMANCE

Starting the filters with 30 gm of biological solids gave satisfactory results when compared to the results obtained in previous studies (2). Since the effluent solids concentration in filters 1 and 3 were continually lower than those in filters 2 and 4, addition of the seed sludge to only the lower one-third of the filter would seem to be the preferred method. The problem of high effluent suspended solids might be minimized by a smaller addition of seed material, however, the starting efficiency may be compromised. The slow growth of the methane forming bacteria resulted in an initial build up of volatile acids in the filters. Normally this low concentration of volatile acids would not cause serious problems with operation, but because of the limited buffer capacity present, the pH of the system fell, which undoubtedly increased the time required for the filters to reach maximum efficiency. The problem of limited buffer capacity which persisted in the filters can be partially attributed to the lack of excess nitrogen in the form of ammonia. Excess ammonia contributes to the natural buffer capacity of the system.

After the starting period, the filters responded rapidly to instantaneous increases in organic load (Figures 8 through 14). At each loading between 22.91 and 220 lb COD/1000 cu ft/day (0.367 and 3.52 kg COD/cu m/day) the filters eventually reached some steady-state COD removal efficiency. As indicated by the steady-state profiles of COD concentration throughout the filter, Figure 15, the major fraction of the COD removal took place in the lower levels where both substrate and biological solids existed in high concentrations.

The generally low volatile acid concentrations can be attributed to the fact that the primary constituent of the waste was methanol, which can be fermented directly to methane without intermediate conversion to volatile acids (11). The volatile acid profiles shown in Figure 15 indicate that large variations in influent COD concentrations produced little effect on volatile acid levels in the filters. The volatile acid concentration within the filters is primarily dependent upon hydraulic flow rate which can be seen from the similarity of the profiles.

Responses to loading changes were characterized by an initial increase in the COD concentrations of the upper levels of the filter followed by a steady decrease of these concentrations until the filter was operating at steady-state conditions. During period of steady-state operation the anaerobic filter is analogous to a series of digesters one on top of another with high rate treatment occurring

in the first unit and polishing and solids separation occurring in the following units.

A summary of the effluent quality for the filters, operating at steady-state conditions, for all loadings, is presented in Table VII. From filter performance based percent COD removal was excellent; all COD removals exceeded 93 percent but no definite pattern was established concerning variations in organic loading and its effect on treatment efficiency. Filter performance based on effluent COD concentrations appeared to be affected primarily by influent waste concentration. A generalized statement could not be made about treatment efficiency based on percent COD removal or effluent COD concentration as a function of organic load and influent waste concentration since sufficient experimental data was not available for duplicate organic loading conditions with varying waste strengths.

In summary the anaerobic filter compares favorably to other waste treatment processes with respect to loads which may be applied and the removals which can be attained. For the organic loading range of 13.8 to 220 lb COD/1000 cu ft/day (0.221 to 3.52 kg COD/cu m/day) at waste strengths greater than 1000 mg/l steady-state COD removals ranged from 93.7 to 97.8 percent. However, possibly the most significant factor when comparing the anaerobic filter to other processes is the fact that low cellular synthesis rates and long solids retention times enable it to treat

Table VII. Summary of Steady-State Filter Performance Under Varied Organic Loadings

lb/1000 ft^3 /Day Organic Load (kg/cu m/ day)	Influent COD Conc. mg/l	Det Time Hr.	Soluble Effluent COD Conc. mg/l	Percent COD Removal	Effluent pH	Effluent Suspended Solids mg/l	Effluent Volatile Acids mg/l	Effluent Alkalinity mg/l
13.8 (0.221)	1000	48	45	95.5	6.5	45	36	270
22.91 (0.367)	1250	36	74	93.7	6.8	16	60	538
34.75 (0.556)	1250	24	56.3	95.3	7.2	28	32	672
73.21 (1.17)	4000	36	88	97.8	7.4	13	72	896
110 (1.76)	4000	24	99	97.5	6.4	32	68	463
146.3 (2.34)	4000	18	197	95.1	6.7	44	48	372
220 (3.52)	4000	12	254	93.7	6.7	32	132	332
220 (3.52)	8000	24	381	95.3	6.7	48	102	416
220 (3.52)	16000	48	390	97.6	6.7	52	156	448

wastes efficiently without the need for solids recycle or solids wasting.

VI. CONCLUSIONS

The following conclusions are drawn for the performance of the anaerobic filter, as determined by this laboratory study:

1) The anaerobic filter successfully treated the pharmaceutical waste at COD concentrations which range from 1000 to 16,000 mg/l when operated at 35° C with steady-state removal efficiencies of 93.7 to 97.8 percent.

2) High treatment efficiencies were maintained without solids recycle when operated over an organic loading range of 13.8 to 220 lb COD/1000 cu ft/day (0.221 to 3.52 kg COD/cu m/day).

3) The anaerobic filter was able to operate over a period of six months without the need for solids disposal.

4) Shock increases in organic loadings did not result in a failure of the capability of the filter to treat the waste.

VII. RESEARCH NEEDS FOR THE ANAEROBIC FILTER

Based on the findings of this study the following topics are suggested for future investigations of the anaerobic filter process.

1) An investigation of the various geometric parameters which might affect the performance of the anaerobic filter, to include column diameter and height, filter porosity, stone size, and the possibility of utilization of synthetic filter media.

2) A study of filter performance at temperatures other than 35° C.

3) A thorough investigation of the effects of intermittent operation and shock loading on the filter.

4) A more thorough investigation of the synthesis rates of the biological solids in the anaerobic filter to allow more accurate evaluation of kinetic model parameters.

5) Application of the filter to a variety of real wastes to develop a wider range of parameters to be used in anaerobic filter design.

BIBLIOGRAPHY

1. McCarty, P. L., "Anaerobic Waste Treatment Fundamentals - Part One, Chemistry and Microbiology," Public Works, 95, 107, (1964).

2. Young, J. C., "The Anaerobic Filter for Waste Treatment," A doctoral dissertation presented to the Department of Civil Engineering at Stanford University, (April 1968).

3. Lawrence, A. W. and McCarty, P. L., "Kinetics of Methane Fermentation in Anaerobic Treatment," Jour. Water Poll. Cont. Fed., Research Supplement - Part 2, 41, 2, R2, (1969).

4. Pfeffer, J. T., Leiter, M., and Worlund, J. R., "Population Dynamics in Anaerobic Digestion," Jour. Water Poll. Cont. Fed., 39, 8, 1305 (Aug. 1967).

5. Eckenfelder, W. W. and O'Connor, D. J., Biological Waste Treatment, Pergamon Press, New York, p.251, (1961).

6. McCarty, P. L., "The Methane Fermentation," Principles and Applications in Aquatic Microbiology, John Wiley & Sons, New York, p.314, (1964).

7. Jeris, J. S. and McCarty, P. L., "The Biochemistry of Methane Fermentation Using C^{14} Tracers," Jour. Water Poll. Cont. Fed., 37, 2, 178, (1965).

8. Pine, M. J. and Barker, H. A., Studies on Methane Fermentation, XII, "The Pathways of Hydrogen Acetate Fermentation," Jour. Bacteriology, 71, 644, (1956).

9. Stadtman, T. C. and Barker, H. A., Studies on Methane Fermentation, IX, "The Origin of Methane in Acetate and Methanol Fermentation," Jour. Bacteriology, 61, 81, (1951).

10. Andrews, J. F., Cole, R. D., and Pearson, E. A., "Kinetics and Characteristics of Multistage Methane Fermentations," SERL Rept. No. 64-11, San. Eng. Res. Lab., University of California, Berkeley, (1964).

11. Barker, H. A., Bacterial Fermentations, John Wiley & Sons, New York, (1956).

12. Sawyer, C. N. and McCarty, P. L., Chemistry for Sanitary Engineers, McGraw Hill, St. Louis, (1967).

13. McKinney, R. E., Microbiology for Sanitary Engineers, New York, (1962).

14. Fair, G. M., Geyer, J. C., and Okon, D. A., Water and Wastewater Engineering, Vol. 2, "Water Purification and Wastewater Treatment and Disposal," John Wiley & Sons, New York, (1968).

15. Speece, R. E. and Kem, J. A., "The Effect of Short-Term Temperature Variations on Methane Production," Jour. Water Poll. Cont. Fed., 42, 11, 1990, (1970).

16. Golueke, C. G., "Treatment Effects on Anaerobic Digestion of Raw Sewage Sludge," Sew. and Ind. Waste, 30, 1225, (1953).

17. McCarty, P. L. and McKinney, R. E., "Volatile Acid Toxicity in Anaerobic Digestion," Jour. Water Poll. Cont. Fed., 33, 3, 223, (1961)

18. McCarty, P. L. and McKinney, R. E., "Salt Toxicity in Anaerobic Digestion," Jour. Water Poll. Cont. Fed., 33, 4, 399, (1961).

19. Kugelman, I. J. and McCarty, P. L., "Cation Toxicity and Stimulation in Anaerobic Waste Treatment," Jour. Water Poll. Cont. Fed., 37, 1, 97, (1965).

20. Sanders, F. A. and Bloodgood, D. E., "The Effects of Nitrogen-to-Carbon Ratio on Anaerobic Decomposition," Jour. Water Poll. Cont. Fed., 37, 12, 1741, (1965).

21. Schoepfer, G. J. and Zeimke, N. R., Development of the Anaerobic Contact Process, I, Pilot Plant Investigation and Economics," Sew. and Ind. Wastes, 31, 2, 164, (1959).

22. ----------, "Anaerobic Sludge Digestion, Water Poll. Cont. Fed., Manual of Practice No. 16, (1968).

23. Dagve, R. R., McKinney, R. E., and Pfeffer, J. T., "Anaerobic Activated Sludge," Jour. Water Poll. Cont. Fed., 38, 2, 220, (1966).

24. Schoepfer, G. J., et al., "The Anaerobic Contact Process as Applied to Packinghouse Wastes," Sew. and Ind. Wastes, 27, 4, 460, (1955).

25. Stewart, M. J., "Reaction Kinetics and Operational Parameters of Continuous-Flow Anaerobic-Fermentation Processes," SERL Rept. No. 4, I.E.R. Series 90, University of California, Berkeley, (1958).

26. Gates, W. E., Smith, J. H., Shun-Dar Lin, and Ris, C. H., "A Rational Model for the Anaerobic Contact Process," Jour. Water Poll. Cont. Fed., 39, 12, 1951, (1967).

27. Canhan, R. A. and Bloodgood, D. E., "Anaerobic Digestion of Tomato and Pumpkin Wastes," Proc. 4th Ind. Waste Conf., Purdue Univ., Ext. Ser. 68, 150, (1948).

28. McNary, R. R., Wolford, R. W., and Dougherty, M. H., "Experimental Treatment of Citrus Waste Water," Proc. 8th Ind. Waste Conf., Purdue Univ. Ext. Ser. 83, 256, (1953).

29. Steffan, A. J. and Bedker, M., "Operation of a Full-Scale Anaerobic Contact Treatment Plant for Meat Packing Wastes," Proc. 16th Ind. Waste Conf., Purdue Univ., Ext. Ser., 109, 423, (1961)

30. Young, J. C. and McCarty, P. L., "The Anaerobic Filter for Waste Treatment," Proc. 23rd Ind. Waste Conf., Purdue Univ., Ext. Ser., 134, (1968).

31. Galler, W. S., Gotaas, H. B., "Analysis of Biological Filter Variables," Jour. San. Eng. Div., ASCE, 90, SA6, 59, (1964).

32. Velz, C. J., "A Basic Law for the Performance of Biological Filters," Sew. Works Jour., 20, 4, 607, (1967).

33. Plummer, A. H., Malina, J. F., and Eckenfelder, W. W., "Stabilization of a Low Solids Carbohydrate Waste by an Anaerobic Submerged Filter," Proc. 24th Inc. Waste Conf., Purdue Univ., Ext. Ser., 135, 462, (1969).

34. Tamblyn, T. A. and Sword, B. R., "The Anaerobic Filter for Denitrification of Agricultural Subsurface Drainage," Proc. 25th Ind. Waste Conf., Purdue Univ., Ext. Ser., 136, 1135, (1970).

35. Seidel, D. F. and Crites, R. W., Evaluation of Anaerobic Denitrification Processes," Jour. San. Eng. Div., ASCE, 96, SA2, 267, (1970).

36. Wallace, G., Plant Manager, Hoffman Taft Inc., Springfield, Mo., Personal Communication, 1972.

37. Baver, J. L. and Corrigan, T. E., "Advantages of Packed Tower Reactors," Chemical Engineering, 74, 7, 111, (1967).

38. Standard Methods for the Examination of Water and Wastewater, 13th Edition, American Public Health Association, Inc., (1970).

39. Jankovic, S. G., Mitchell, D. T., and Buzzel, J. C., Jr., "Measurement of Phosphorus in Wastewater," Water and Sewage Wroks, 114, 471, (1967).

40. Instrument Manual, Fisher/Hamilton Gas Partitioner Model 29, Catalogue No. 11-12742, Published by Instrument Division, Fisher Scientific Corp., Pittsburg, Pennsylvania.

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