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Anaerobic Filters: An Energy Plus for Wastewater Treatment

Proceedings of the Seminar/Workshop

January 9-10, 1980
Howey-In-The-Hills, Florida

ARGONNE NATIONAL LABORATORY
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ANAEROBIC FILTERS: AN ENERGY PLUS FOR WASTEWATER TREATMENT

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FOREWORD

The Submerged Media Anaerobic Reactor (SMAR) is the generic term for a new wastewater treatment process. The various design configurations that have been studied in the last 20 years include the static bed, fluid bed, anaerobic rotating biological contactor, vertical tube reactor, and anaerobic sludge blanket. While much work has been performed at the bench-scale level, comparatively few full-scale operations exist. Given SMAR's timely advantages of energy efficiency, low sludge production, and resistance to toxicants, there should be a greater use of this process.

The Anaerobic Filter for Wastewater Treatment Workshop, sponsored by the U.S. Department of Energy and hosted by Argonne National Laboratory, was held at the Mission Inn, Howey-in-the Hills, Florida, January 9-10, 1980. The major objectives of this workshop were:

1. to review the latest results from ongoing projects in the field of anaerobic wastewater treatment, specifically on SMAR designs

2. to summarize the present state-of-the-art of SMARs

3. to encourage interaction and an information exchange among those interested in this process

4. to identify the existing problems related to ongoing research and barriers to acceptance and commercial implementation of the technology

5. to explore opportunities for future research and development.

The workshop attendees included researchers and consultants, as well as representatives from industry and government. The presentations provided an update on the state-of-the-art of the process. All of the participants provided invaluable input on their particular points of view. This publication documents the results of the meeting.

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EFFECTS OF FILM AREA-TO-VOLUME RATIO, FILM SUPPORT, HEIGHT AND DIRECTION OF FLOW ON PERFORMANCE OF METHANOGENIC FIXED FILM REACTORS*

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ABSTRACT

Methanogenic fixed film reactors were capable of producing up to 5 m^3 methane (STP) per m^3 reactor volume per day with chemical oxygen demand removals of 85-94%. Chemical oxygen demand loading rates were 0.07-0.13 kg per m^2 film area per day for reactors with film area-to-volume ratios between 50 and 250 m^2/m^3. Loading rates were slightly greater for reactors 0.55 and 1.1 m high than for reactors 2.2 m high in preliminary tests. A clay support was superior to a plastic or glass support, in that the film developed faster (1-3 months as compared to 7 months or longer) and was less subject to failures. Upflow reactors operated differently from downflow reactors in that performance of upflow reactors depended on suspended microbial growth as well as on the fixed film.

INTRODUCTION

The anaerobic fixed film reactor is a recent addition to a group of new types of anaerobic reactors or processes that have been and are being developed to improve the anaerobic digestion process. These new types have in common a retention of the microbial biomass, particularly the micro-organisms that have mass doubling times of several days or weeks (8). Included in these types (besides the fixed film reactor) are the anaerobic contact process (10-14), the upflow anaerobic filter (1,4,7,16), the upflow anaerobic sludge blanket reactor (2,6,15) and the fluidized-bed type reactor (5). The performance of the new types of reactors, both in terms of methane production and of treatment efficiencies, is very much dependent on the extent the biomass is retained in the reactor.

*NRCC No. 17998.

The biomass retention in turn is affected markedly by the type of waste treated.

This paper discusses results obtained with fixed film reactors* treating a mainly soluble food processing waste, bean blanching waste. The test reactors were designed to have a known and fixed film area-to-volume ratio and to eliminate plugging and bypassing. Factors studied were film area/volume ratios between 50 and 400 m^2/m^3 (effective tube diameters between 0.01 and 0.075 m), height (0.55 to 2.2 m), film support (baked clay, poly vinyl chloride (PVC) plastic, and glass) and direction of flow (up and down). Performance was rated in terms of loading rates, removal of chemical oxygen demand (COD) and rates of methane production. Observations on film characteristics are also discussed.

EXPERIMENTAL

A detailed description of the reactors and their operation (Figure 1) has been published previously (9). Briefly, in downflow reactors, feed (bean blanching waste, 1% total solids, Table 1) was pumped in at the top of the reactor together with liquid recirculated from the bottom of the reactor. Effluent was removed from the bottom of the reactor through a level control device. Gas was removed at the top. In upflow reactors feed was pumped in at the bottom, effluent and gas were removed together at the top of the reactor and then separated. The amount of liquid recirculated was four times the amount of feed pumped in. Pumps were run 5% of the time on a 20-minute cycle to obtain high enough pumping rates to avoid blockages in feed and recirculation tubing. Feed rates were adjusted to maintain volatile acid levels at 400-600 g/m^3 (most of this was acetic acid). The fermenter room was operated at 35°C.

The effect of film area/volume ratio and of liquid flow direction (up and down) were studied using pyrex glass tubes. For comparison with the glass tubes, clay pipes and tubes shaped from PVC plastic of the type used in water

*U.S. patent applied for.

purification filters, were used with downflow. The effect of height was studied with clay pipes, also using downflow.

To determine the distribution of activity between the fixed film and the bulk of the liquid in both up and downflow reactors, 10 ml samples of the liquid were removed at different heights in the column using a syringe attached to a long narrow tube inserted from the top of the column. Samples were taken anaerobically and placed in serum cap vials. Acetic acid was added to a concentration of about 1000 mg acetic acid/l and vials were incubated at 35°C for 2-4 hours, after which time the methane content of the head space was determined (prelininary tests showed that the amount of methane produced with acetate added at the beginning of the test was essentially the same as when bean waste was added frequently during the test; the former was more convenient).

RESULTS

Film loading rates were maximum for the 0.038 m diameter reactors (area/volume 105 m^2/m^3) (Table 2). The decrease of loading rates with increased area/volume ratio may be attributable to an effect of film thickness on effective diameter and hence effective area. At the lower area/volume ratio (0.075 m diameter) differences in diffusion and flow pattern (surface turbulence) may account for the lower film loading rate. The higher suspended solids, and hence lower treatment efficiency of the large column, also points in this direction. Volumetric loading rates increased markedly with area/volume ratio to almost 19 kg $COD/m^3/day$, except for the narrow diameter tube, presumably for the reason already given.

Film support material had a marked effect on reactor performance (Table 3), particularly on the time required to reach maximum performance. Reactors made from baked clay reached maximum performance in 1-3 months as compared to 7 months for PVC plastic and 10-14 months for glass. Visual observations indicated a more uniform film formed on clay than on glass (some glass areas were not covered for a long time). Also the film on clay did not slough off as easily as on glass, leading to greater

process stability. The improved performance of clay over glass and plastic may be related to surface roughness, porosity and physical-chemical characteristics. Presumably the faster a film forms, the more completely it covers the available surface and this may explain the greater surface loading possible with clay.

Treatment efficiencies (percent of COD in feed removed) were high (85-92%) and about the same for clay and glass. The efficiency of the plastic reactor was somewhat higher (94%), because of a lower suspended COD content. The reason for the latter was not apparent, but may reflect a film characteristic.

Limited tests with clay reactors of 0.55, 1.1 and 2.2 m height have indicated that film area loadings are relatively little affected by height. The lower heights tend to be slightly more effective than the 2.2 m reactor but further steady state performance is required before the difference, if any, can be quantified. Because the amount of gas escaping at the reactor top per unit cross sectional area increases with height of reactor, the tendency to foam increases with height.

Upflow reactors differed markedly from downflow reactors in that a substantial part of the total activity resided in the liquid (Table 4, Figure 2). The activity of the film on the narrower reactors was similar for up and downflow, but in addition a substantial activity was present in the liquid in the bottom half of the upflow reactor. In the wide reactor most of the activity was in the liquid rather than in the film. Upflow reactors tended therefore to be a combination of fixed film and upflow anaerobic sludge blanket reactors (16).

Analysis of the film in some of the reactors used showed that the non-soluble volatile solids in the film amounted to about 0.03 to 0.05 kg per m^2 at COD loading rates of 0.025 to 0.06 kg/m^2/day. The specific activity of the non-soluble suspended solids in the film (presumably mostly microorganisms) therefore was 0.8-1.2 kg COD/kg/day. This activity is about

twice that of the volatile suspended solids in the anaerobic contact process and about the same as that of the volatile suspended solids in the upflow reactors in our tests and in the upflow anaerobic sludge blanket reactor (6).

DISCUSSION

Fixed film reactors have several potential advantages over suspended growth reactors:

1. The possibility of washout of the active microbial flora (for example by accidental drainage of the reactor or sudden increase in hydraulic load) is eliminated.

2. Accumulation of suspended material (excess bacterial growth released from the film, indigestible suspended matter in the feed, clay or sand) can be eliminated from the reactor without affecting its performance.

3. Relatively concentrated wastes and wastes with high suspended solids contents can be treated.

4. By using a channel rather than a random packing design, problems of plugging and channelling can be greatly diminished if not completely eliminated.

5. No space or design features are required for gas separation or settling of suspended material.

6. The channel-type packing induces vigorous agitation because of the gas-lift pump action of the gas formed.

7. Fixed film reactors have high COD removal efficiencies, partly because of a low suspended solids content in the effluent.

A disadvantage of the fixed film reactor compared with a suspended growth reactor is the limitation on the loading rate by practical limitations on the film area/volume ratio.

Many questions about fixed film reactors are being studied for the first time or in further detail than reported here. These include:

1. Effect of reactor height.

2. Effect of horizontal scale (multiple channel reactors).

3. Effect of waste strength.

4. Effect of kind of waste.
5. Effect of recirculation rate.
6. Effects occurring during longer term operation.
7. Effect of temperature.
8. Effect of packing material.
9. Effect of packing design.

CONCLUSIONS

1. Volumetric loading rates of fixed film reactors were as high as 19 kg COD/m^3/day, with methane production rates over 5 m^3 (STP)/m^3/day, depending on film area/volume ratio and film support material.

2. Area loading rates were up to 20% higher with baked clay than with glass or PVC plastic as film support material.

3. Active films formed faster on clay than on glass or plastic (1-3 and 7-14 months respectively to reach maximum loading rates).

4. Clay support provided for greater process stability than glass or plastic.

5. Height affected performance of fixed film reactors relatively little in preliminary tests.

6. COD-removal efficiencies were high (85-95%) and increased with the film area/volume ratio.

7. Comparison between upflow and downflow reactors showed that only downflow reactors were true fixed film reactors with practically all activity located in the film. Upflow reactors were combinations of fixed film and sludge blanket reactors.

ACKNOWLEDGMENT

The authors wish to thank K.A. Lamb, E.A. Rooke, D. Wall and M. Muzar for expert assistance in the manufacture and operation of the reactors.

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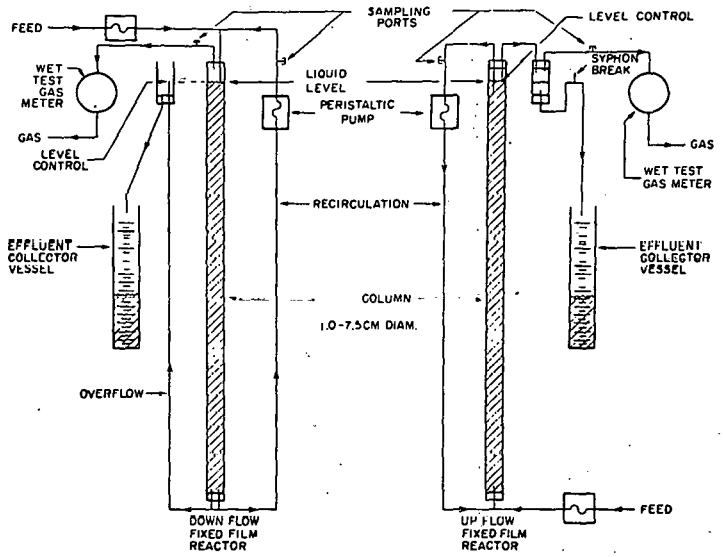

Fig. 1. Sketch of upflow and downflow reactors used in study.

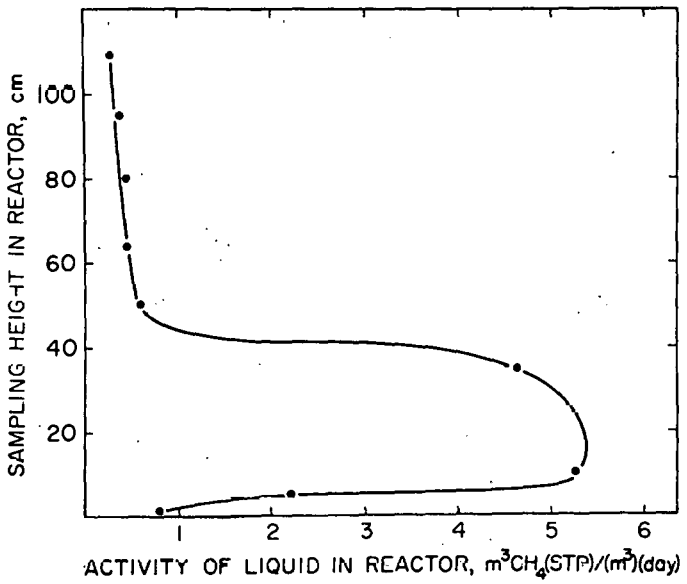

Fig. 2. Effect of height in the 3.8 cm diameter upflow reactor on suspended growth activity.

Table 1. Composition of bean blanching waste used (contents in mg/l).

Total solids	9800
Total volatile solids	8400
Suspended solids	200
Volatile suspended solids	200
Chemical Oxygen Demand	10500
Kjeldahl nitrogen	370
Phosphate (as P)	100
Sodium	7
Potassium	700
Iron[a]	60

[a] Iron was added (1 mM $FeCl_2$) to prevent a possible soluble iron deficiency (3).

Table 2. Effect of film area-to-volume ratio on performance of fixed film reactors (110 cm tall glass tubes, downflow operation).

	Film area/volume, m^2/m^3			
	53	105	250	397
Diameter of tube, m	0.075	0.038	0.016	0.010
Maximum loading rate,				
a) kg COD/m^2/day	0.073	0.106	0.076	0.040
b) kg COD/m^3/day	3.9	11.1	19.0	15.9
COD in effluent, g/m^3				
a) total	2000	1600	1050	1050
b) soluble	500	600	400	400
c) suspended	1500	1000	650	650
COD removal efficiency, %	81	85	90	90
Methane production rates				
a) m^3(STP)/m^2/day	0.019	0.027	0.021	0.011
b) m^3(STP)/m^3/day	1.0	2.8	5.3	4.4

Table 3. Effect of film support on performance of tubular fixed film reactors (110 cm tall, downflow operation)

	Film support		
	Baked clay	Glass	PVC Plastic
Diameter of tube, m	0.028	0.016-0.075	0.025
Surface area-to-volume ratio m^2/m^3	140	105-250	160
Time to reach maximum loading rate, days	30-90	300-400	200
Maximum loading rate, kg COD/m^2/day	0.086-0.129	0.076-0.106	0.072
COD in effluent, g/m^3			
a) total	800-1200	1050-1600	650
b) soluble	300-400	400-600	250
c) suspended	500-800	650-1000	400
COD removal efficiency, %	88-92	85-90	94
Methane production			
a) m^3(STP)/m^2/day	0.028-0.031	0.021-0.027	0.021
b) m^3(STP)/m^3/day	3.9-4.3	2.8-5.3	3.4

Table 4. Distribution of activity between film and suspended growth in downflow and upflow reactors (glass tubes, 110 cm tall)

Film area/volume ratio, m^2/m^3	Activity of film in terms of total activity, %	
	Downflow	Upflow
53	70	72
105	93	62
250	93	25

Note: Measurements were made at loading rates equal to 1/2 to 3/4 of the maximum loading rates. At higher loading rates, the film activity would increase as part of the total for downflow reactors, while the suspended activity would increase as part of the total for upflow reactors.

METHANE FERMENTATION TOXICITY RESPONSE: CONTACT MODE

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ABSTRACT

It is generally assumed that the anaerobic digestion process is unable to cope with waste streams containing toxicants and is therefore unsuitable for treatment of many classes of industrial wastewaters. Toxicants do alter the kinetic parameters of methanogens and thus increase their minimum generation time and decrease pollutant removal efficiency, but proper attention to solids retention time can offset these adverse effects. Also proper acclimation procedures can significantly increase the threshhold concentration of toxicant which causes inhibition. A diverse group of toxicants were administered as slug and continuous doses in the feed to anaerobic filters. Gas production and effluent COD were monitored to establish the recovery pattern. With proper acclimation efficient COD removal could be achieved in the presence of toxicant concentration which were 20 to 50 times greater than toxicant concentrations which exhibited 50% inhibition to unacclimated methanogens.

INTRODUCTION

Methane fermentation is an anaerobic, microbiological process which converts organic material to methane gas. The inherent advantages of methane fermentation over aerobic waste treatment processes are:

1. No energy consumption for oxygen transfer.
2. Energy is produced in the form of methane.
3. Excess sludge production is much reduced over aerobic processes.

The net energy differential in destruction of organic pollution is about 20×10^6 BTU per ton of COD in favor of methane fermentation over aerobic treatment. In some cases, less than one-tenth as much excess sludge is produced by methane fermentation as compared to aerobic processes. The operating cost differential is about $90 per ton of COD in favor of methane fermentation over aerobic treatment. Generally, if an organic waste can be metabolized aerobically, it can also be metabolized anaerobically.

In view of these significant advantages, the question arises as to why methane fermentation has been so little exploited in the treatment of industrial wastewaters. There are a number of factors which are responsible for this situation.

A. Low cell yield. One of the major advantages of methane fermentation - low cell yield of excess sludge - becomes a major disadvantage by prolonging start-up of the process or recovery from a toxic dose which has killed a major fraction of the biomass. The role of solids retention time (SRT), therefore, requires considerably more attention than with aerobic processes. This has not been adequately appreciated by design and operational personnel.

B. Temperature Sensitivity. Cell yield and specific utilization rate mainly determine the minimum generation time, θ_c^{min},

of microbial systems.

$$\Theta_c^{min} = \frac{1}{Yk-b}$$

Since the cell yield, Y, is already relatively low, the specific utilization rate, k, must be relatively high to prevent intolerably long minimum generation times. The specific utilization rate, k, is sensitive to temperature. Below 20°C, the minimum generation time may exceed 30 days as compared approximately 0.5 days for an aerobic process. Therefore, with a safety factor of 5 for plant design, the SRT required would be 150 days. Cold, dilute wastes, therefore, require provision for maintenance of extended SRT and produce insufficient methane to heat the wastewater without supplementary fuel. This restriction does not apply with cold, concentrated wastewaters or warm, dilute wastewaters.

C. Concepts of Environmental Engineers. There is a vague, pervading concept among environmental engineers that methane fermentation requires very long hydraulic retention times (HRT) of 10 to 30 days and is incapable of treating many industrial wastes efficiently. Nemerow (1976) expresses the commonly held concept of environmental engineers that "generally anaerobic processes are less effective than aerobic processes and that anaerobic processes are slow and require low daily loading rates and/or long detention times. Anaerobic digestion only has a definite advantage over aerobic processes where liquid waste volumes are small, contain no toxic matter and have high fractions of readily oxidized dissolved organic matter."

D. Toxicity. The general concept of environmental engineers that methane fermentation is a sensitive process with limited potential for the treatment of dilute industrial wastewaters containing sporadic or chronic levels of toxicity is not without some support in the

literature. Indeed, there are many cases which demonstrate that methane production ceased due to the presence of a toxicant. The evidence of inhibition of methane production is valid, but the conclusion that methanogens are more sensitive to toxicity than aerobic processes is not necessarily valid. With similar biological safety factors, methanogens may be able to withstand toxicant concentrations equal to aerobic systems. However, due to the lack of attention to adequate SRT in design and operation of methane fermentation systems, the biological safety factor has been inadequate and the inhibition due to toxicity has been more pronounced.

Kugelman and Chin (1971) report that:

> "Although this process (methane fermentation) has significant advantages over other methods of waste treatment, its use has been retarded because of a lack of understanding of toxicity phenomena.
>
> The magnitude of the toxic effect generated by a substance can often be reduced significantly if the concentration is increased slowly. This is the phenomenon of acclimation which represents an adjustment of the biological population to the adverse effects of the toxin. In a waste treatment system, this does not usually represent either a mutation or a selection of the fittest because rarely is all of the toxic effect eliminated. Rather acclimation represents a rearrangement of the metabolic resources of the organism to overcome the metabolic block produced by the toxic substance.
>
> In most toxicity studies, the concentration of the toxic substance is raised in one step to the level to be studied, leaving little chance for acclimation to take place. This experimental situation is not adequate for toxicity studies in waste treatment systems because

in most of these systems, acclimation will probably occur. Adequate delineation of toxicity in waste treatment requires an allowance for acclimation.

Although there are good reasons why much of the data on toxicity in anaerobic systems are suspect, such data have not and cannot be interpreted properly. At best, most of these studies are useless: at worst, they are misleading.

It is significant that many of these early studies reported the divalent cations magnesium and calcium were less toxic or equal in toxicity on a molar basis to the monovalent cations sodium, potassium. This is at variance with all previous experience in toxicity studies in pure biology.....Much of the deviation in previous studies was possibly caused by antagonism and synergism."

In view of the exceptional adaptation and acclimation characteristics of microorganisms as demonstrated by the extreme environmental conditions under which they propagate, it is apparent that "ideal" conditions are not required to achieve effective biological treatment as evidenced by the fact that aerobic and anaerobic processes have been treating municipal wastes satisfactorily for years and it is recognized that a host of toxicants is present in municipal wastes at various concentrations and for various periods. In fact, an underlying principle of biological wastewater treatment is that a correlation exists between SRT and toxicity levels, e. g., maintenance of higher SRT levels compensates for less ideal environmental conditions of wastewater treatment temperature, pH, toxicity, etc.

Environmental engineers should consider all published aerobic and anaerobic toxicity data (including that subsequently presented in this report) as being relative to the test conditions under which it was obtained. Too frequently, the published toxicity data are considered absolute and anaerobic digestion has been eliminated as a viable wastewater treatment option without consideration of the ability of the methanogenic bacteria to propagate under much higher concentrations of toxicants with proper acclimation procedures. As will be shown later, methanogenic bacteria can acclimate to toxicant concentrations which are, in some cases, 100 times greater than the

concentrations which exhibit inhibition to unacclimated cultures.

Likewise environmental engineers have prematurely concluded that methanogenic bacteria were "dead" when methane production ceased. Methane production has been observed to abruptly resume at a rate much in excess of that which would be associated with bacterial regrowth. The effect of wastewater flow configuration on toxicity response has not been adequately addressed. A continuously stirred tank reactor (CSTR) exhibits a different toxicity response pattern from a "plug flow" anaerobic filter. This is related to the reversible or irreversible nature of the toxicity and the exposure time effect.

OBJECTIVE

The objective of this study was to evaluate the methane fermentation toxicity response pattern for a number of toxicants under four different contacting modes:

1. Batch CSTR toxicity assay with unacclimated methanogens.
2. Slug addition of toxicant to CSTR being fed and wasted daily.
3. Continuous addition of toxicant at increasing concentrations to filter.
4. Slug additions of toxicant at increasing concentrations.

Methane production served to indicate the toxicity response pattern.

TOXICANTS ASSAYED

Toxicants representative of those found in industrial wastewaters were chosen from the following toxicity categories:

Heavy Metal - Nickel
Cation - Ammonium
Anion - Sulfide
Aldehyde - Formaldehyde
Double Bond - Acrylic Acid

Aldehyde and Double Bond - Acrolein

EXPERIMENTAL PROCEDURES

Innoculum Source

Methanogenic cultures enriched on acetate as the sole organic carbon source (exclusive of 10 mg/l of cysteine) were used in each phase of this study. An innoculum digester was maintained as the source of all methanogenic cultures. Originally, digested sludge from a municipal wastewater treatment plant was used to seed the innoculum digester. Prior to commencement of this study, the innoculum digester had been maintained for 3 years and over 20 detention times with acetate as the organic carbon source. The innoculum digester was a CSTR maintained at a 50 day hydraulic retention time and fed 1 gm/l-day of acetic acid. Gas production from this innoculum digester was quite stable. The background nutrient salt solution fed to the innoculum digester and all related systems is shown on Table II.

Table II

NUTRIENT SALT SOLUTION

1. Nutrient I Constituents	Conc. (mg/l)
NH_4Cl	400
KCI	400
$MgSO_4 \cdot 7H_2O$	400
$FeCl_2 \cdot 6H_2O$	40
$CoCl_2$	4
$(NH_4)_2HPO_4$	80
2. Nutrient II Constituents	
Cysteine	10
KI	10
Na Hexametaphosphate	10

$MnCl_2 \cdot 4H_2O$	0.5
NH_4VO_3	0.5
Nickel	0.5
$ZnCl_2$	0.5
$Na_2MoO_4 \cdot 2H_2O$	0.5
H_3BO_3	0.5
$CuCl_2 \cdot 2H_2O$	0.5
$NaHCO_3$	6000

1. Batch CSTR Toxicity Assay with Unacclimated Methanogens. Owens, et al. (1979) have proposed an anaerobic toxicity assay (ATA) to determine the toxicity of substances to unacclimated methane bacteria using a modification of the Hungate serum bottle technique. In this study, a modification of Owens, et al. ATA was utilized. Fifty ml of an innoculum from the methane culture grown on acetate as the carbon source and described above was anaerobically transferred to a 125 ml serum bottle which had been purged with a gas mixture of 75% N_2 and 25% CO_2. Initially, 100 µl of glacial acetic acid was injected with a microliter syringe to yield an initial acetate concentration of 2000 mg/l. This resulted in the immediate production of about 40 ml of CO_2 due to the neutralization of the glacial acetic acid. Since methanogenic activity is related only to the production of methane gas, only gas production in excess of the 40 ml of CO_2 produced was considered to be indicative of metabolism. In some of the plots total gas production is shown while in other graphs only methane production is plotted.

The desire to increase the acetate concentration without overcoming the buffer capacity led to the addition of calcium acetate at concentrations of 8,000 and 16,000 mg/l as acetate. In this case, only methane gas is evolved because the calcium acetate salt is neutral. The calcium precipitates out as calcium bicarbonate and does not result in any ion toxicity to the methanogens. The pH is maintained between 6.5 and 7.7.

2. Slug Addition of Toxicant to CSTR Being Fed and Wasted Daily. Serum bottles were anaerobically innoculated with methanogens from the innoculum source. Gas production was recorded daily. Glacial acetic acid was then injected with a microliter syringe to stoichiometrically compensate for the methane produced. The mixed contents were then wasted to achieve the

desired SRT, e. g. 12.5, 25 or 50 days. A solution of nutrient salts shown in Table II was then added to replace the volume wasted.

After innoculation, the serum bottles were operated for a period of time to establish steady state gas production. Then a slug dose of a toxicant was added. The serum bottles were then operated for a period of time until gas production returned to the steady state level.

3. Continuous Addition of Toxicant at Increasing Concentrations to Filter. Anaerobic filters were constructed of 5 cm I. D. transparent plexiglas tubes one meter high and packed with 1 cm nominal diameter gravel. The void volume was 1 liter. The filters were fed 1 liter per day of the feed solution shown in Table II to yield a one day nominal hydraulic detention time. The toxicants were added at the desired concentration in the daily feed. Gas production from the filters was measured by liquid displacement and the effluent was collected to determine COD reduction in the filter. The daily feed was administered by positive displacement pumps on automatic timers which injected approximately 20 ml each 30 minutes to approximate continuous feeding. The concentration of acetate in the daily feed was 2000 mg/l (133 lbs/1000 ft^3-day) for part of the study. In the remainder of the study, the acetate concentration in the feed was 3300 mg/l (200 lbs/ 1000 ft^3-day).

4. Slug Additions of Toxicant at Increasing Concentrations to Filter. In this phase of the study, the filters received a background nutrient salt solution containing 2000 or 3300 mg/l of acetic acid. A one day slug addition of a given toxicant was added to this feed solution. The filter received only unadulterated nutrient feed solution on subsequent days and the gas production and effluent COD were recorded until they recovered to their normal level. Then a one day slug addition that was twice the previous concentration was added and the response pattern noted. This continued until a quasi-lethal dose was reached and the filter would not recover adequately.

RESULTS AND DISCUSSION

Nickel

Batch unacclimated methanogens were progressively inhibited by nickel concentrations in the range of 50 to 500 mg/l. Figure 1 indicates that even at 500 mg/l, methane production continued at a low rate. In a CSTR fed daily and slugged once with 70 to 100 mg/l of nickel (as nickel chloride) there was no inhibition of methane production with 70 mg/l as shown in Figure 2. There was inhibition of gas production at 80, 90 and 100 mg/l but the inhibition lagged four days after the nickel injections. Full recovery of gas production was noted within 10 days and gas production exceeded the control rate at the end of recovery.

Continuous additions of nickel chloride to the feed of a filter over protracted periods indicated that 200 mg/l could be tolerated with no adverse effect on gas production. An increase from 200 to 400 mg/l abruptly decreased gas production as shown in Figure 3. However, gas production abruptly resumed when nickel addition ceased, but was followed by a secondary relapse with eventual resumption to full rate. At this point, 300 mg/l of nickel was added continuously with a rapid deterioration in gas production.

One day slug additions of nickel were added to the filter in increasing concentrations as shown in Figure 4.* At slug nickel concentrations up to 500 mg/l, there was only about 25% decrease in gas production with full recovery in a day or two. However, at 1000 mg/l of nickel in the feed the gas production abruptly dropped and did not recover significantly after 5 days.

Ammonium Ion

The pH in these studies was below 7.5. Therefore, less than 1% of the ammonium ion was in the un-ionized form. In the batch CSTR unacclimated methanogens were not inhibited at ammonium ion concentrations up to 6000 mg/l (as N). However, in the daily fed CSTR, there was progressive inhibition in the range of 4000 to 14000 mg/l. Figure 5. At 10,000 mg/l, methane production was

*Figs. 4, 5, 11, 12, 17, 18, 19, 20, 29, 30, and 31 are not available.

nil for 10 days but recovery was rapid. Acclimation of a filter to continuous additions of ammonium ion at step increases in concentration showed no decrease in gas production up to 6000 mg/l. Figure 6. (The increase in effluent COD is due to the excessive chlorides.) At 7000 mg/l of ammonium ion, progressive failure was noted.

One day slug additions of ammonium ion to an unacclimated filter showed a sharp decrease at 4000 mg/l, but it recovered to about normal in one day. Figure 7. A one day slug of 8000 mg/l resulted in an abrupt decrease in gas production without rapid recovery.

Sulfide

With unacclimated cultures, there was no inhibition of gas production up to 100 mg/l of sulfide. However, at 250 mg/l, there was no methane production for the first 9 days, only the carbon dioxide evolved from neutralization of the glacial acetic acid feed. Gradually methane production resumed. Figure 8. The lag in methane production was longer and the rate of resumption of methane production was slower at sulfide concentrations of 500 and 1000 mg/l. It is to be noted, however, that even at 1000 mg/l of sulfide, eventual acclimation and methane production resulted.

In the daily fed CSTR slugged with 100 to 500 mg/l of $S^{=}$ there was an abrupt decrease in gas production followed by an abrupt recovery. Decreased sulfide concentrations due to gas stripping and acclimation coupled to rapidly restore gas production to normal. Figure 9.

Continuous addition of sulfide at step increases in concentration were fed to a filter. Figures 10 and 11. With acclimation, it is noted that no adverse effect on gas production resulted at concentrations up to about 600 mg/l, even though this concentration was strongly inhibitory to unacclimated methanogens. At 800 mg/l of sulfide there was about a 30% decrease in gas production over

the 40 consecutive days of sulfide addition with a slight upward trend indicating acclimation. Addition of 1000 mg/l for 30 consecutive days resulted in about a 40% decrease in gas production with the gas rate being somewhat erratic. After sulfide addition ceased the gas production quickly resumed at the normal rate. Subsequently, 2000 mg/l of sulfide was added continuously for 5 days and gas production almost ceased.

One day slug additions of sulfide were administered in the daily feed to an unacclimated filter. No effect was noted at 500 mg/l. Figure 12. At 1000 mg/l there was an unexplainable increase in gas production. At 2000 mg/l gas production plummeted but quickly returned to normal. A 4000 mg/l slug of sulfide caused gas production to almost cease and recovery to normal was slow.

Sodium Ion

The nutrient salt solution in which the unacclimated methanogens were grown contained approximately 2200 mg/l of sodium which was added as sodium bicarbonate to provide alkalinity. To assay sodium ion toxicity, additional amounts of sodium ion in the form of sodium chloride were added to the system as shown in Figure 13. An additional 2500 mg/l (4700 mg/l total) showed no inhibition. An additional 4000 mg/l (6200 mg/l total) resulted in a lag with subsequent gas production rates comparable to the control. Additions of 7000 and 10,000 mg/l (9200 and 12,200 mg/l total) retarded the gas production rate to about 40 and 30% of the control respectively.

Slight inhibition of gas production was noted in the daily fed CSTR systems slugged with an additional 5000, 7500 and 10,000 mg/l of NaCl (as Na). Figure 14. Full recovery was noted within 13 days. The system receiving 15,000 mg/l of Na^+ ceased gas production for 30 days and very gradually recovered.

Long term acclimation of a filter to increasing levels of continuous sodium additions showed no adverse effect up to additions of 7500 mg/l as Na^+ (9700 mg/l total). Figure 15. Additions of 10,000 mg/l of Na^+ for 35 consecutive days resulted in 30 to 40% decrease in gas production. Figure 16. There was no indication of progressive failure.

One day slug additions of sodium as the chloride salt were added to an unacclimated filter. Figure 17. No significant decrease in gas production was noted at 10,000 mg/l as Na^+ (12,200 mg/l total) but 20,000 mg/l caused a rapid 40% decrease in gas production which recovered to normal in one day. At 40,000 mg/l of the Na^+, gas production ceased abruptly.

Formaldehyde

Formaldehyde is an effective bacteriacide at high concentrations. The aldehyde group is the toxic component. Progressive inhibition of batch gas production assays were noted in the range of 100 to 500 mg/l. Figure 18. Both a lag in onset of gas production and a decrease in rate of gas production were observed as the formaldehyde concentration was increased.

Daily fed CSTR systems slugged with formaldehyde exhibited an abrupt decrease in gas production with rather rapid recovery. Figure 19. The period of minimum gas production was proportioned to the formaldehyde concentration.

Continuous addition of formaldehyde in the feed to an anaerobic filter caused no inhibition of gas production up to 400 mg/l. Figure 20. There was an increase in gas production indicating metabolism of the formaldehyde. However, 600 mg/l resulted in failure of gas production.

A filter was exposed to 500 mg/l of formaldehyde in the feed for progressively longer periods of 1, 2, 4 and 7 days with 5 days rest between each interval. Figure 21. It maintained normal gas production for 4 days continuous feed but failed completely

after 7 days exposure.

Acrylic Acid

The double bond in acrylic acid is the toxic component It demonstrated a very uniform inhibition pattern to unacclimated methanogens as shown in Figure 22. Progressive inhibition of the gas production rate is noted at increasing acrylic acid concentrations as the acetate is utilized. At 500 and 750 mg/1, only 60 and 40% of the control volume of gas was produced after 22 days.

Daily fed CSTR systems slugged with 25 to 100 mg/1 of acrylic acid exhibited inhibition in proportion to the acrylic acid concentration. Recovery to normal gas production was noted in 8 days with 25 mg/1 of acrylic acid. Figure 23. Gas production was nil for about 15 days in the systems receiving 75 and 100 mg/1 of acrylic acid.

Gradual acclimation of a filter to increasing acrylic acid concentrations is shown in Figure 24. After 90 days, 600 mg/1 of acrylic acid in the feed displayed no inhibition of gas production. At 800 mg/1, gas production decreased to about 70% of the background rate as shown in Figure 25. Gas production remained reasonably constant, however. An increase to 1000 mg/1 further depressed gas production to 35% of the background rate. At this point, the acetic acid in the background feed was eliminated to observe the metabolism of acrylic acid. Partial metabolism of acrylic acid was indicated by the gas production and COD reduction in the effluent. Acrylic acid concentrations of 500, 1000 and 1500 mg/1 were assayed with partial metabolism indicated. Figure 26.

Finally, one day slug additions of acrylic acid were made to the feed, followed by a period of unadulterated feeding as shown in Figure 27. A direct inhibition of gas production resulted, followed by a rapid recovery of gas production when the

unadulterated feed was added. Even at 2500 mg/l acrylic acid rapid recovery was noted, but 5000 mg/l caused total inhibition of gas production with relatively slow recovery.

Acrolein

Acrolein has two components which exhibit toxicity to unacclimated methanogens. One is the double bond and the other is the aldehyde group. At 25 mg/l, acrolein exhibited no inhibition to unacclimated methanogens. Figure 28. However, at 50 mg/l, the rate of gas production for Day 1 was only half of the control and total cessation of gas production was noted when only 15% of the acetate was exhausted.

Daily fed CSTR systems slugged with 10 to 50 mg/l of acrolein showed a very uniform pattern of toxicity recovery. Figure 29. A slug of 10 mg/l reduced gas production to 60% of the background with subsequent recovery in one day. A slug of 50 mg/l of acrolein resulted in nil gas production for 20 days with a recovery rate to normal that paralleled the lower doses.

Additions of acrolein to the daily feed to the filters were made over prolonged periods. Acrolein additions were stopped for a number of days. Then continuous additions of acrolein at an increased level were resumed. Figure 30 indicates that 100 mg/l of acrolein could be tolerated in the feed with no decrease in gas production. Subsequent addition of 200 mg/l resulted in total cessation of gas production.

One day slug additions of acrolein to a filter were made at increasing concentrations. Relatively little decrease in gas production resulted with 250 and 500 mg/l of acrolein in the feed. However, a one day slug addition of 1000 mg/l of acrolein markedly decreased gas production which recovered only slowly as shown in Figure 31.

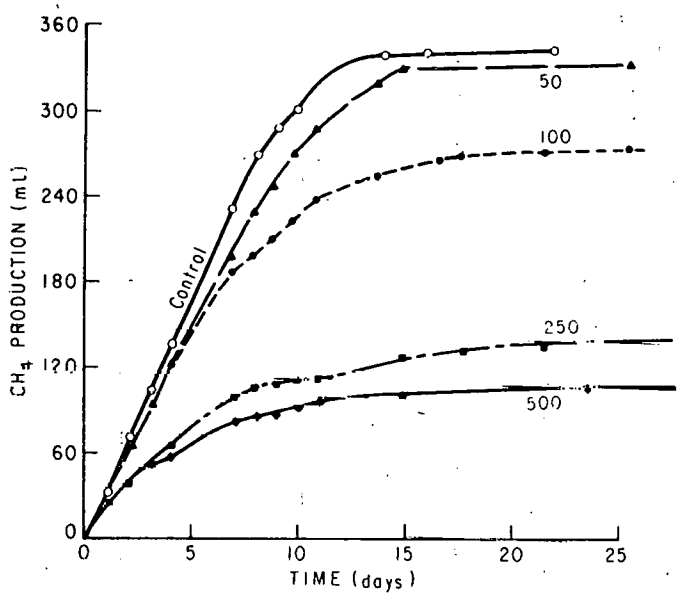

Fig. 1 Response of Unacclimated Methanogens to Ni^{++}

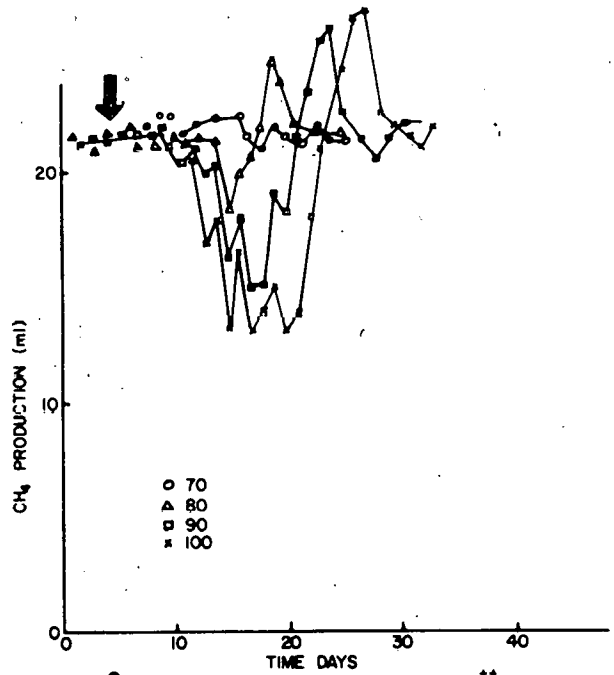

FIG. 2 METHANOGEN RESPONSE TO Ni^{++}

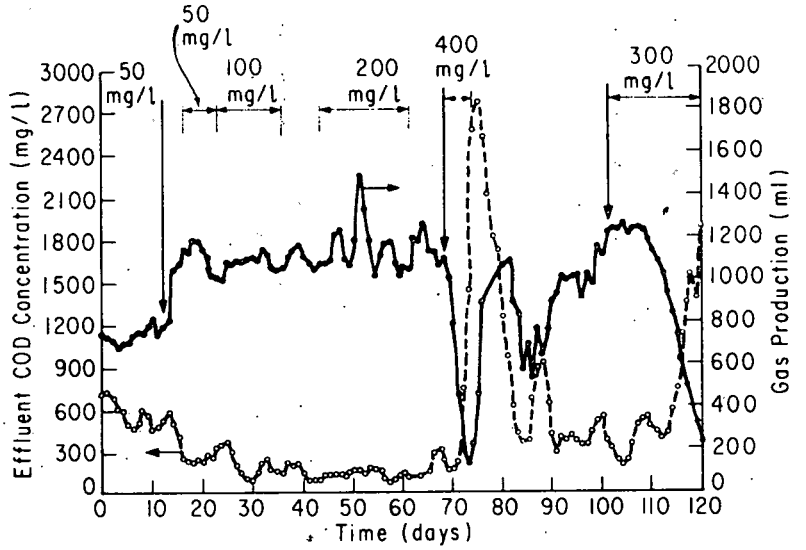

Fig.3 Response of Anaerobic Filter to Toxicant - Ni#

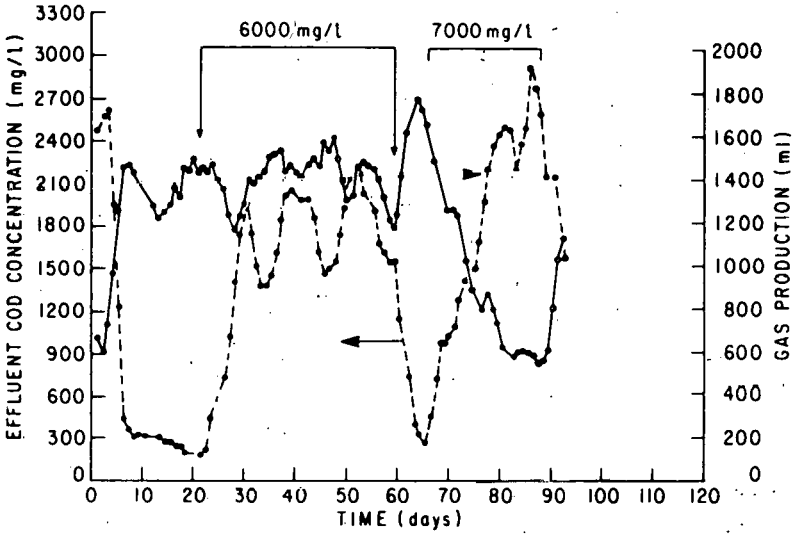

Fig. 6 Response of Anaerobic Filter to Toxicant NH_4 (as N)

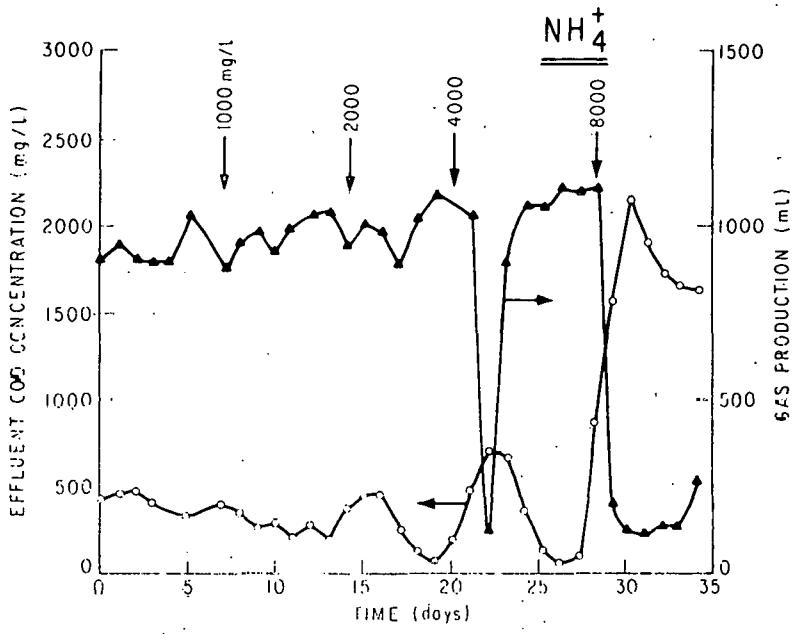

FIG. 7 RESPONSE OF ANAEROBIC FILTER TO TOXICANT

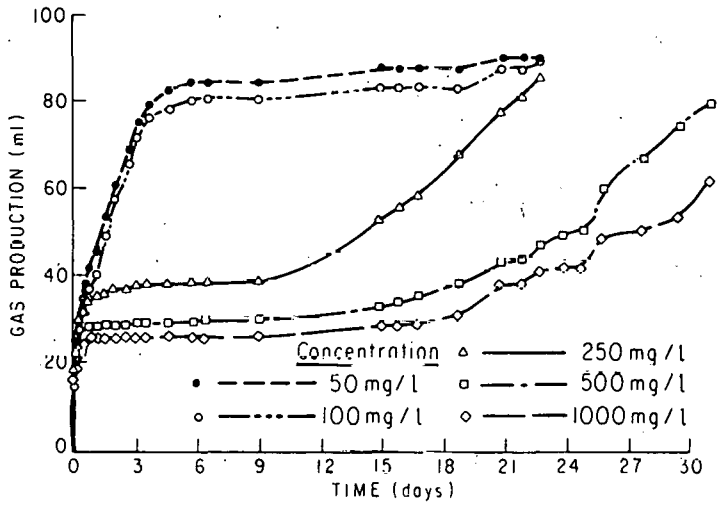

Fig. 8 Batch Kinetics for Toxicant - $S^{=}$

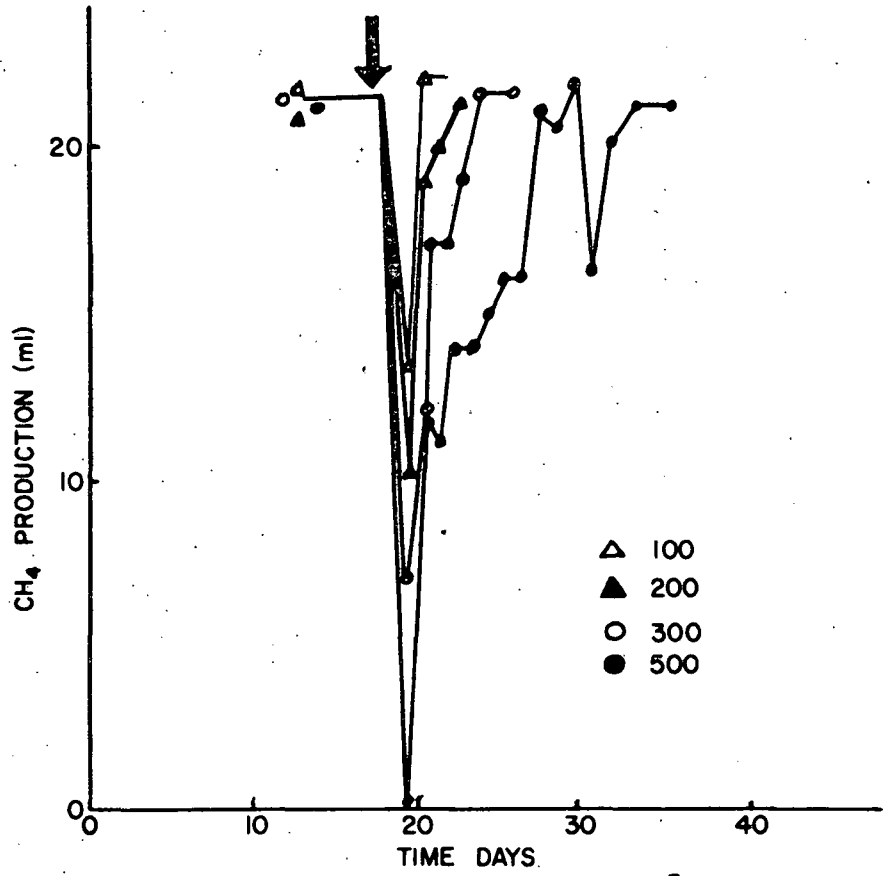

FIG. 9 METHANOGEN RESPONSE TO $S^=$

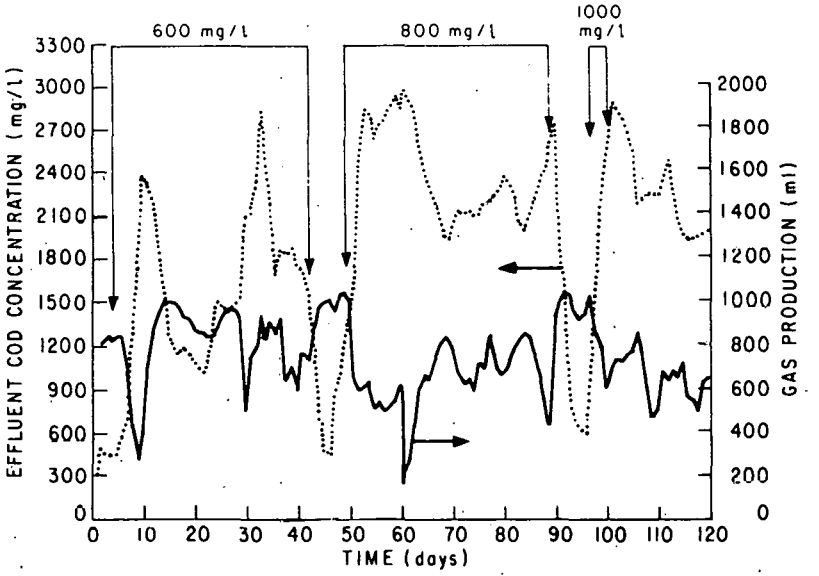

Fig. 10 Response of Anaerobic Filter to Toxicant Sulfide

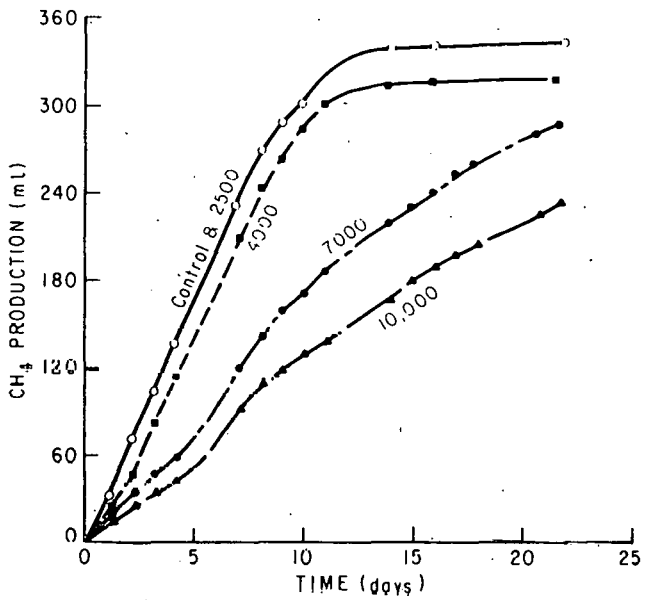

Fig. 13 Response of Unacclimated Methanogens to Na^+

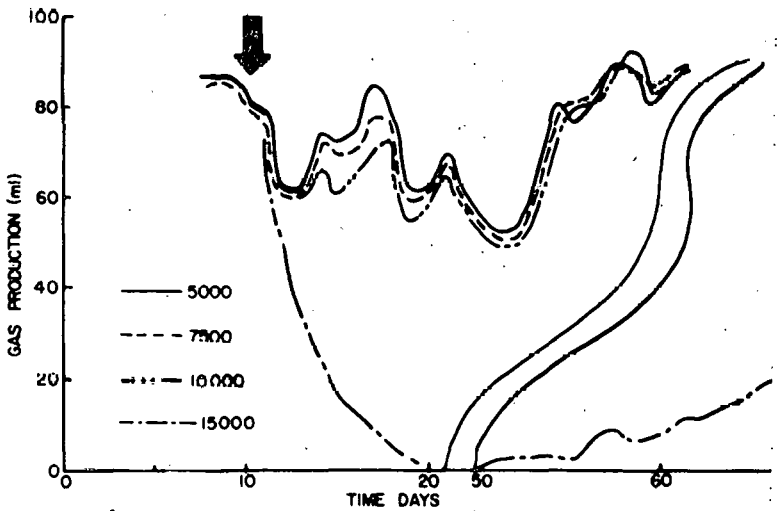

FIG 14 METHANOGEN RESPONSE TO Na^+
35°C 50 DAY SRT

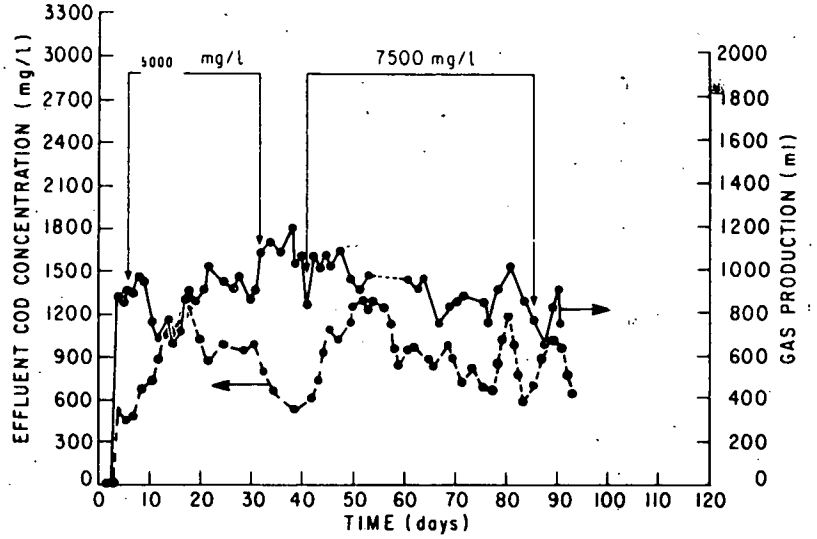

Fig. 15 Response of Anaerobic Filter to Toxicant NaCl (as Na^+)

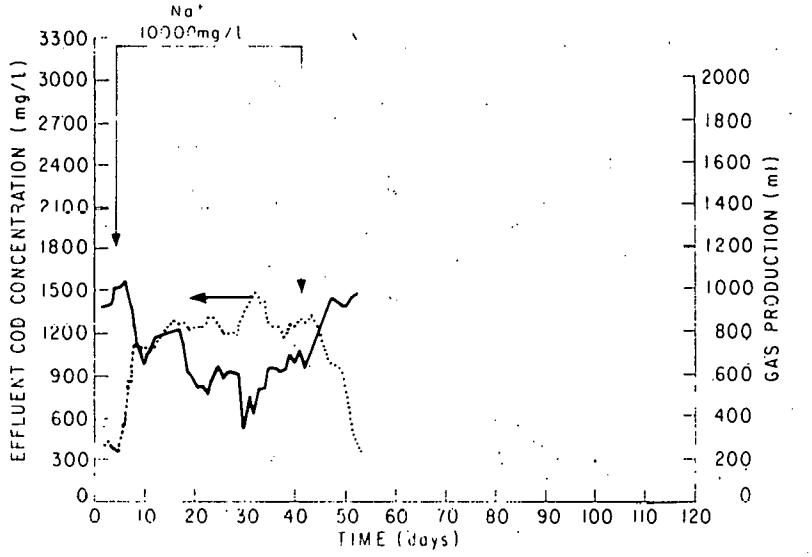

Fig. 16 Response of Anaerobic Filter to Toxicant Na^+

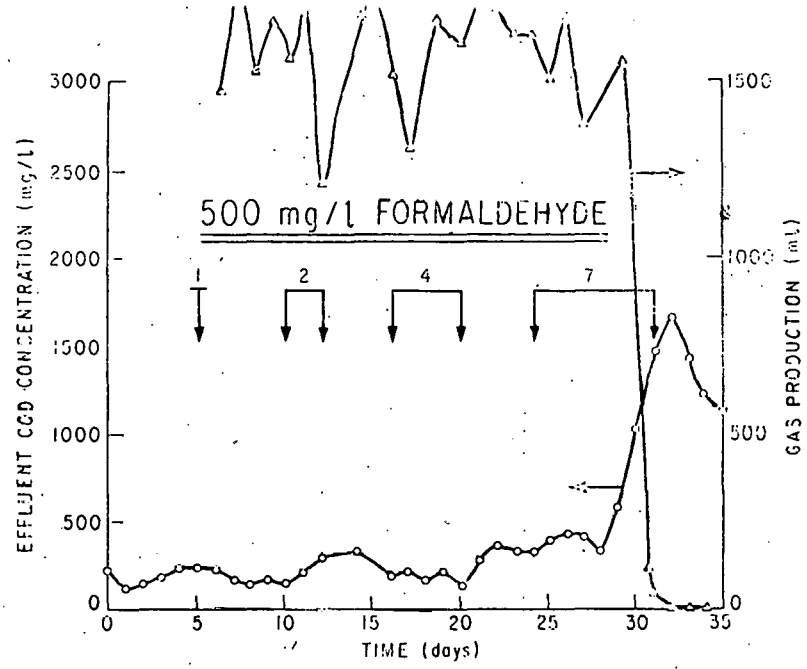

FIG. **21** RESPONSE OF ANAEROBIC FILTER TO TOXICANT

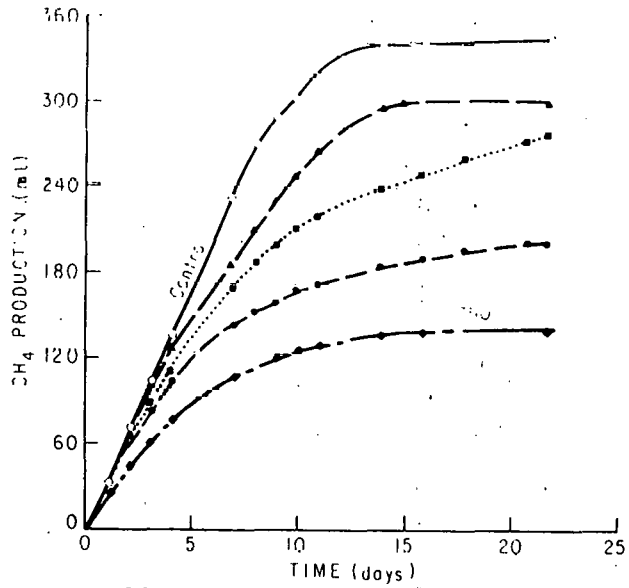

Fig **22** Response of Unacclimated Methanogens to Acrylic Acid

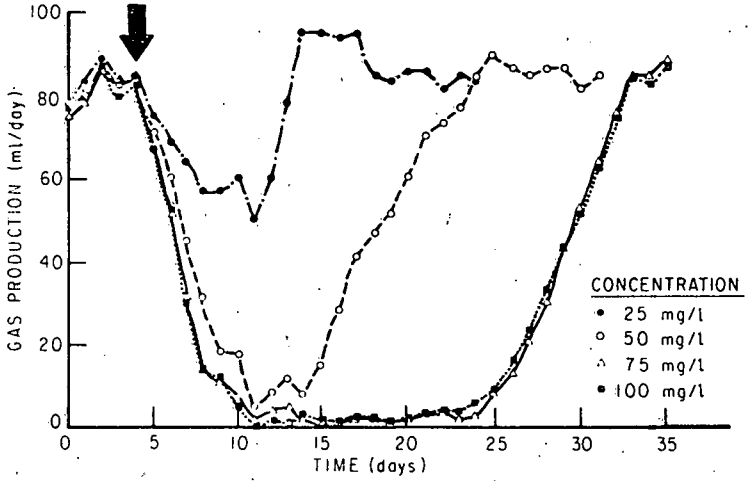

Fig.23 S.R.T. Response to Toxicant - Acrylic Acid
50 days S.R.T., 35°C

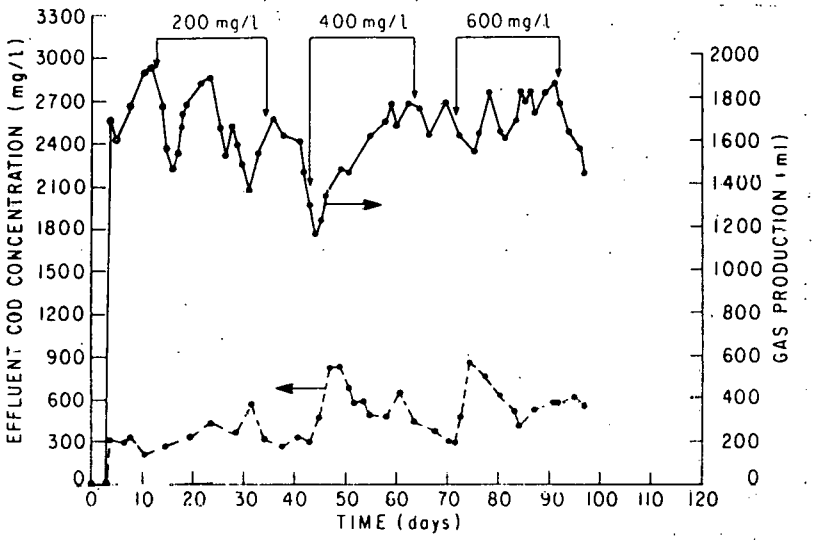

Fig.24 Response of Anaerobic Filter to Toxicant
Acrylic Acid

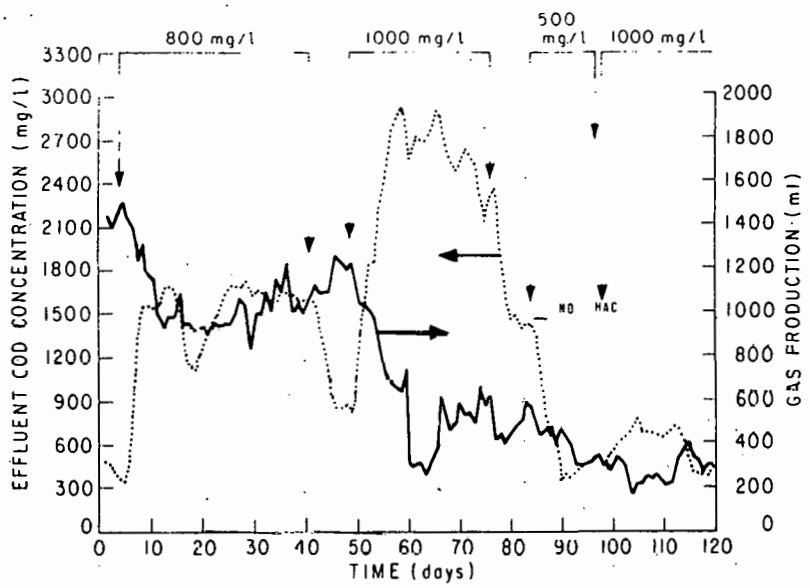

Fig.25 Response of Anaerobic Filter to Toxicant Acrylic Acid

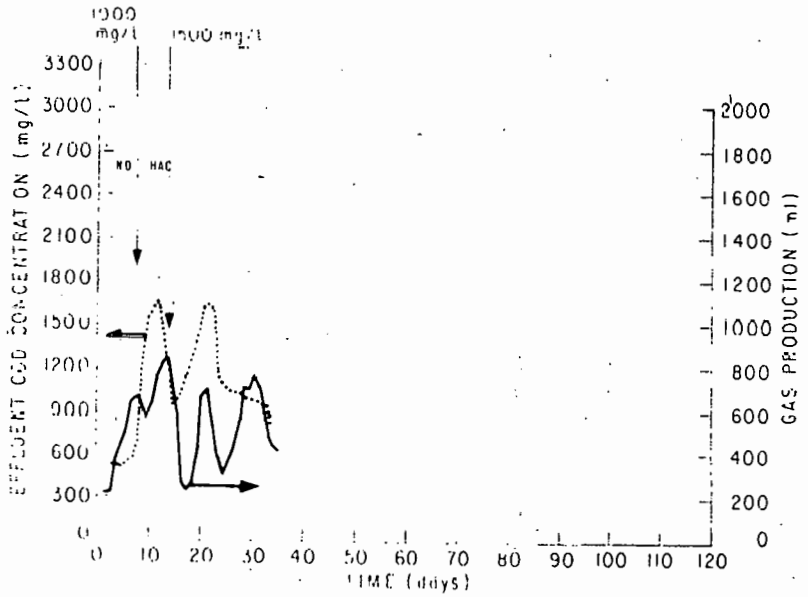

Fig 26 Response of Anaerobic Filter to Toxicant Acrylic Acid

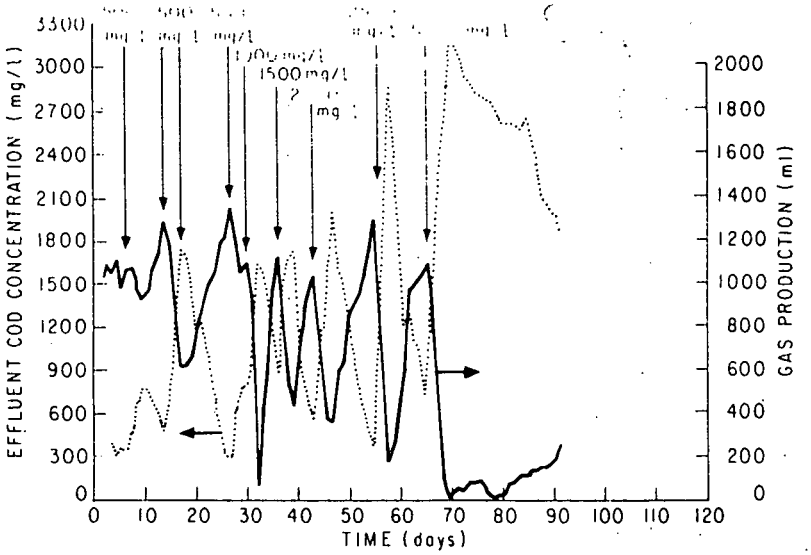

Fig.27 Response of Anaerobic Filter to Toxicant, Acrylic Acid

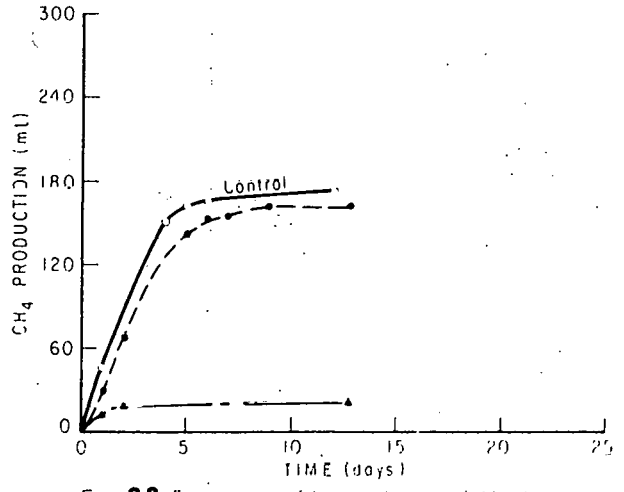

Fig. 28 Response of Unacclimated Methanogens to Acrolein

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A COMPARISON OF THE RESPONSE OF METHANOGENS TO TOXICANTS: ANAEROBIC FILTER VS SUSPENDED GROWTH SYSTEMS

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ABSTRACT

The anaerobic, methane fermentation process offers great potential for treating industrial wastewaters. Application of the process has been limited due to a reputation of process unreliability for wastewaters containing toxicants. Of the two major flow schemes, the anaerobic filter affords two major advantages over complete-mix, suspended growth systems (CSTR) for treating wastewater containing toxic materials: 1) higher inherent solids retention times (SRT) and 2) a plug-flow mode that can pass slug doses of toxicants quickly. High values of SRT are needed to prevent biomass washout during the critical start-up period and to allow methane bacteria to acclimate to the toxic materials. Experimental data indicate that the anaerobic filter, which would pass slug doses of toxicant rapidly (approximately one day for a nominal hydraulic retention time of one day), provides a distinct advantage over the CSTR, which would experience protracted toxicant washout times. Suspended growth systems were exposed to various concentrations of cyanide, chloroform, formaldehyde, ammonia, nickel, copper, and calcium for one to 24 hours, centrifuged and the supernatant replaced with an unadulterated nutrient solution. Depending on the toxicant type and concentration, systems showed no decrease in gas production or recovered to full gas production in much less time than systems that were not centrifuged.

INTRODUCTION

Use of the anaerobic, methane fermentation process for treating industrial wastewaters offers the dual advantages of energy savings and pollution abatement. An additional plus is the approximate 90 percent reduction in bacterial sludge production for anaerobic processes when compared with aerobic processes. However, application of the methane fermentation process has been limited due to a reputation of unreliability when treating industrial wastewaters containing toxic materials.

Presently the two major types of reactors used in anaerobic treatment are the complete-mix, suspended growth reactor (CSTR) and the upflow anaerobic filter. The anaerobic filter affords two major advantages over the CSTR when treating wastewaters containing toxicants: 1) higher inherent solids retention times (SRT or θ_c) and 2) a plug-flow mode that can pass slug doses of toxicants quickly. Of course, a disadvantage of the anaerobic filter is that it works well only for soluble organic wastes.

High values of SRT are needed to prevent biomass washout during the critical start-up period and to allow the methane bacteria to acclimate to the toxic substance. Speece et al (1) have discussed the importance of acclimation; methane bacteria can tolerate levels of toxicants 20 to 50 times higher than previously thought possible if adequate acclimation time is allowed. In addition, the solids capture capability of the filter results in low suspended solids concentrations in filter effluents.

The ability of an anaerobic filter to pass slug doses of toxicants is thought to be an advantage if the toxicity is fully or partially reversible.

Anaerobic filters may have nominal hydraulic retention times of one to six days. If the toxicity is reversible, systems should rapidly recover to full gas production since the toxicant load will be passed quickly. The advantage of a CSTR is an initial, rapid dilution of the toxicant, hopefully to a concentration that is not inhibitory to the bacteria. However, toxicant washout times are protracted and if the dilution is not sufficient, the CSTR, in contrast to the anaerobic filter, may experience long recovery periods.

This paper presents partial results from studies conducted to investigate the reversibility of several toxicants and thus provide a relative comparison of the ability of anaerobic filters and CSTR systems to recover from slug additions of toxic substances. Suspended growth systems were exposed to various concentrations of cyanide, chloroform, formaldehyde, ammonia, nickel, and sulfide for one hour, one day, and four days, centrifuged, and the supernatant replaced with an unadulterated nutrient solution. Depending on the toxicant type and concentration, systems showed no decrease in gas production or recovered to full gas production in much less time than systems that were not centrifuged. Data from anaerobic filters receiving slug doses of the same toxicants are also included.

EXPERIMENTAL PROCEDURES

It is generally accepted that the conversion of acetic acid to methane by methane bacteria is the rate-limiting step in the anaerobic fermentation of complex organics and that approximately 70 percent of the methane produced from such wastes results from acetate fermentation (2,3,4). Therefore, it was decided to use acetate enrichment cultures for this study.

Acetate Enrichment Cultures

A stock enrichment culture was developed from an actively digesting sludge seed and is maintained at a 50-day SRT while feeding 1000mg/l of acetic acid per day. The daily feed solution contains the nutrient salts listed in Table 1.

Table 1. Nutrients contained in the Acetate Enrichment Culture

Component	Concentration in Digester (mg/l)
$NaHCO_3$	6000
NH_4Cl	400
KCl	400
$MgSO_4 \cdot 6H_2O$	400
$(NH_4)_2HPO_4$	90
$FeCl_2 \cdot 6H_2O$	40
Cysteine	10
KI	10
Na Hexametaphosphate	10
$CoCl_2$	4
$MnCl_2$	0.5
$NH_4V_2O_3$	0.5
$ZnCl_2$	0.5
$Na_2MoO_4 \cdot 2H_2O$	0.5
H_3BO_3	0.5

Serum Bottle Studies

The serum bottle technique developed by Miller and Wolin (5) was adapted for this study. Oxygen was removed from 125-160 ml serum bottles by submerging them in water and then displacing the water with a 75 percent N_2-25 percent CO_2 gas mixture. Serum caps were placed on the bottles while still submerged. Inoculum from the acetate enrichment cultures was transferred by an anaerobic transfer technique using a hypodermic syringe. Glacial acetic acid was injected into the serum bottles using a microliter syringe. Chloroform, formaldehyde, and stock solutions of KCN, NH_4Cl, $NiCl_2$, and Na_2S were added using microliter syringes also.

The serum bottles were maintained at a given SRT (25 days in most cases) by daily withdrawal of the requisite volume of mixed contents and replacement with the nutrient salt solution (Table 1) using hypodermic syringes. Gas production was measured daily by displacement of an acid-salt solution contained in a reservoir connected to a hypodermic needle for piercing the serum cap. The acetic acid concentration was restored daily to 1000mg/l by

stoichiometrically adding glacial acetic acid with a microliter syringe in proportion to the methane produced the previous day.

Studies of the effect of toxicant exposure time (refers to liquid phase exposure only and not toxicant bound to the cells) were made by injecting the toxicant to give the desired concentration (see Table 2) in the serum bottle. After the desired exposure time (one hour, one day, or four days for most experiments), the serum bottles were placed directly into a centrifuge and centrifuged for 15 minutes at 3000g. The serum bottles were then carefully inverted and the supernatant was completely removed using a syringe. A 75/25 percent mixture of N_2/CO_2 was introduced as the supernatant was withdrawn. Then, unadulterated, centrifuged supernatant from the acetate enrichment culture was injected into the serum bottle to replace the adulterated supernatant withdrawn. Daily feeding and gas measurement were then continued as described above.

Table 2. Concentrations (mg/l in serum bottle) tested in this study

Cyanide:	1,2,6
	1,5,10,100,200 (second study)
Chloroform:	2,4,12
	50,100 (second study)
Ammonia:	4000,8000, 24,000
Nickel:	400,800,2400
Formaldehyde:	300,600,1800
Sulfide:	250,500,1500

Anaerobic Submerged Filters

The filters (stone media) were operated on a one-day hydraulic retention time (based on void volume) and fed 3300 mg/l of acetic acid in the nutrient salt solution described in Table 1.

Gas production and effluent chemical oxygen demand (COD) were measured. The six toxicants were added to the appropriate filters in the daily feed. After the prescribed exposure time, only unadulterated feed (acetic acid plus nutrient salts) was fed to the filter and the gas production recovery pattern was observed.

RESULTS

Cyanide (CN^-)

The effect of various cyanide concentrations and exposure times is

shown in Figures 1 and 2. Cyanide toxicity seems to be fairly reversible. At cyanide concentrations of less than 6-10 mg/l and an exposure time of one hour, little or no decrease in gas production was experienced. When the concentration exceeded 10 mg/l, a noticeable decrease in gas production was observed; however, even a 100 mg/l dose with a one hour exposure did not result in complete cessation of gas production. Exposure to 100 mg/l for one day did result in a five-day period of zero gas production. The control (no centrifugation and removal of supernatant) system of Figure 1 (6 mg/l dose) decreased to zero gas production rapidly and remained there for the duration of the study.

The observation that dramatizes the potential advantage of the anaerobic filter over the CSTR is shown by the one and four day recovery curves of Figure 1. Once the cyanide in the liquid phase was removed, the systems recovered rapidly. The ability of an actual anaerobic filter to withstand various slug doses of cyanide is demonstrated by data presented in Figure 3.

Chloroform

Data presented in Figures 4 and 5 indicate that for exposure to chloroform, there was a residual and accumulative effect, and the effect was partially reversible. The residual effect may be due to chloroform associated with the biomass, since only chloroform present in the centrifugate was discarded. Removal of chloroform from the liquid phase after a one hour exposure resulted in more rapid recovery to full gas production, as evidenced by comparison with control curves (Figure 4). To appreciate the significance of the periods of zero gas production of 7, 16, and 20 days for the systems of Figure 5, a 40 mg/l control (not shown) had a 'down time' of 48 days.

Again, the important observation is that the anaerobic filter, which will pass the chloroform out of the system quickly, should exhibit much faster recovery from toxicant exposure than a CSTR. Response of an anaerobic filter to chloroform is shown in Figure 6.

Ammonia (NH_4^+)

The response of methane bacteria to 24,000 mg/l of ammonia was very similar to cyanide response: ammonia toxicity appears to be highly reversible (see Figure 7). Once the ammonia was removed, the bacteria recovered

rapidly. Exposure of an anaerobic filter to ammonia confirmed the ability of the filter to pass the toxicant quickly, showing little decrease in treatment efficiency, or recovering rapidly once the toxicant is passed (see Figure 8).

Nickel (Ni^{++})

Data on nickel toxicity (Figures 9 and 10) indicate that recovery was dependent on concentration and exposure time. Concentrations less than 800 mg/l and exposure times less than one day resulted in little decrease in gas production. However, a concentration of 24,000 mg/l (one hour exposure) and an exposure of four days (800 mg/l) resulted in zero gas production. Thus the reversibility, that is, the potential ability of a filter to pass the toxicant and recover quickly is a function of nickel concentration and duration of exposure. It should be mentioned that 800 mg/l of nickel is about two orders of magnitude above the generally reported level of nickel toxicity. As shown in Figure 11,* the anaerobic filter will pass a slug dose of 500 mg/l with little decrease in process efficiency. The serum bottle centrifuge studies seem to do a good job predicting the levels of toxicants that can be handled by the filter.

Formaldehyde

Results from a one-hour exposure to 300, 600, and 1800 mg/l indicate that formaldehyde toxicity is similar to chloroform toxicity: there is a residual toxicity effect, that is, formaldehyde toxicity is partially reversible (Figure 12). The CSTR alternative (controls), however, exhibited complete cessation of gas production for the entire test period for all concentrations tested. The potential advantage of the anaerobic filter is again clear, and further demonstrated by the actual filter data presented in Figure 13.

Sulfide ($S^{=}$)

Serum bottle experiments with a 1500 mg/l concentration of sulfide showed partially reversible toxicity with eventual complete recovery (Figure 14). Once again the CSTR system (control) resulted in extended periods of zero gas production. The response of an anaerobic filter to sulfide substantiated the claim that the filter may 'handle' slug doses of toxicant better than a CSTR (Figure 15).

*Figs. 11, 13, and 15 are not available.

DISCUSSION

The magnitude of the decrease in gas production and rate of return to full gas production was a function of toxicant type and concentration and duration of exposure to toxicant in the liquid phase. In general, cyanide and ammonia toxicity were fairly reversible while chloroform, formaldehyde, and sulfide exhibited some irreversible toxicity. The case with nickel toxicity was less clear; whether the results were indicative of reversible toxicity was highly dependent on nickel concentration. Regardless, the potential advantage of the anaerobic filter over the CSTR was clear in all cases. It should be noted that for each toxicant there no doubt exists a concentration above which even the anaerobic filter cannot recover.

The evidence presented in this paper should have a strong bearing on selecting the process configuration used to treat industrial wastewaters containing toxic substances. Previously it was thought to be an advantage of a CSTR that toxicants would be rapidly diluted, thus lessening their impact on anaerobic treatment efficiency. However, the toxicant slug would also be diluted from the system relatively slowly, resulting in protracted recovery periods as shown by the control systems used in this study.

The submerged anaerobic filter operates predominantly in a plug-flow mode, resulting in no initial dilution of the toxicant slug, but rapid elution of the toxicant from the system. As shown by data presented in this paper, filter recovery times are considerably shorter than those of the CSTR systems. For certain types and concentrations of toxicants, it may be better to elute toxic substances quickly with no dilution (the filter) than to rapidly dilute but elute toxicants slowly (CSTR). Provisions for recycle to the filter shifts the flow mode from plug-flow towards a CSTR. In view of the presented results, such activity may result in decreased process efficiency.

SUMMARY AND CONCLUSIONS

It has been demonstrated that the anaerobic filter has a substantial potential advantage over the more conventional suspended growth, complete-mix system (CSTR) in that the filter can elute toxicant slugs quickly and thus return to full gas production more rapidly. This advantage is magnified when considered in light of the significant acclimation potential of

the anaerobic filter as reported by Speece et al (1).

As previously noted, this paper presented only partial results. The data indicates that the anaerobic filter affords an advantage over a CSTR for some types and concentrations of toxicants. This aspect needs to be studied in detail to better define the advantage of the filter. Future work should also focus on the effect of combinations of the various toxicants and the mechanism of toxicity, although some indirect evidence concerning mechanisms is contained in the data. Toxicant concentrations in effluents should be measured to help in ascertaining mechanisms of toxicity.

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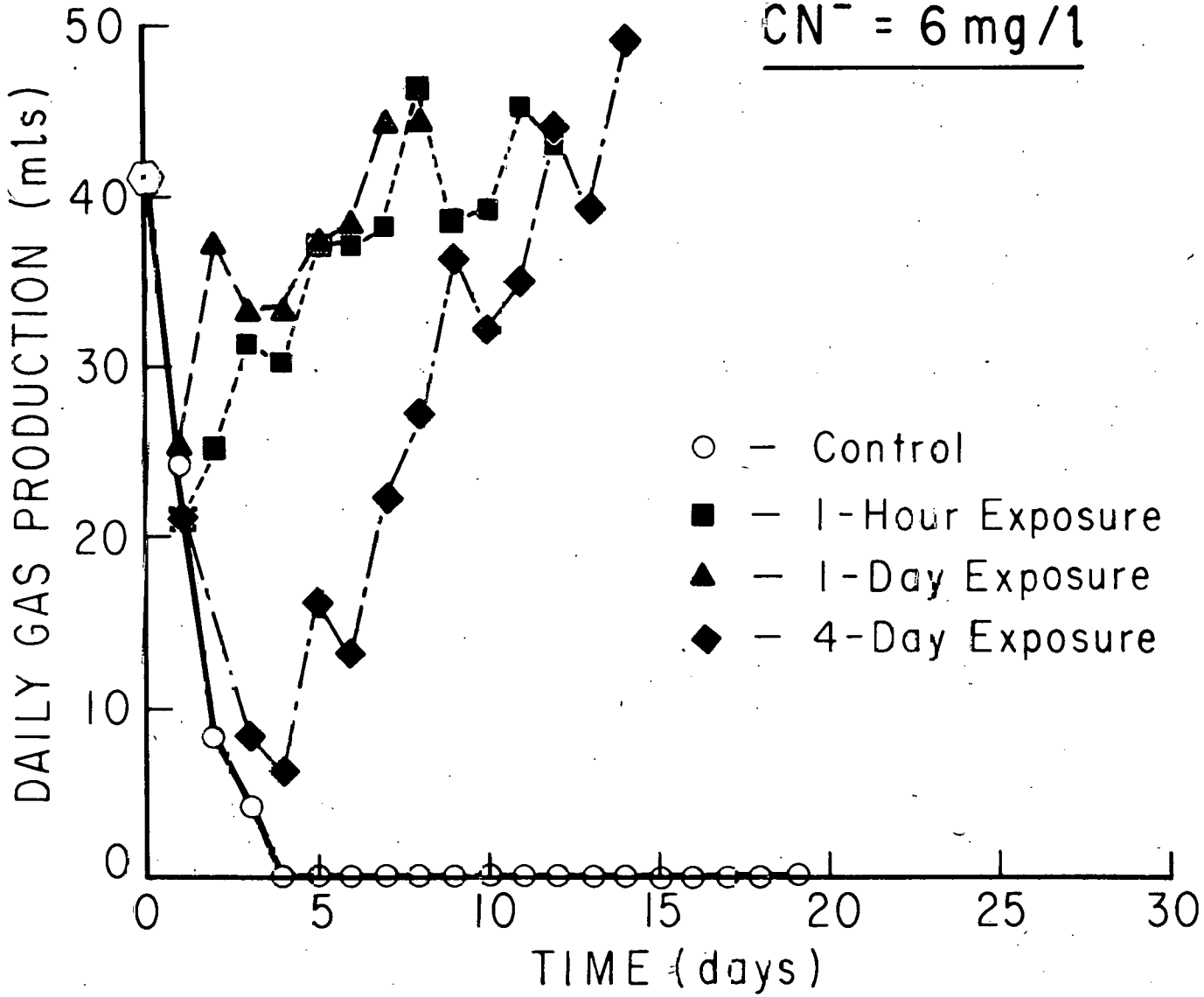

Fig. 1 Effect of Exposure Time on Toxicity Response: CN^-

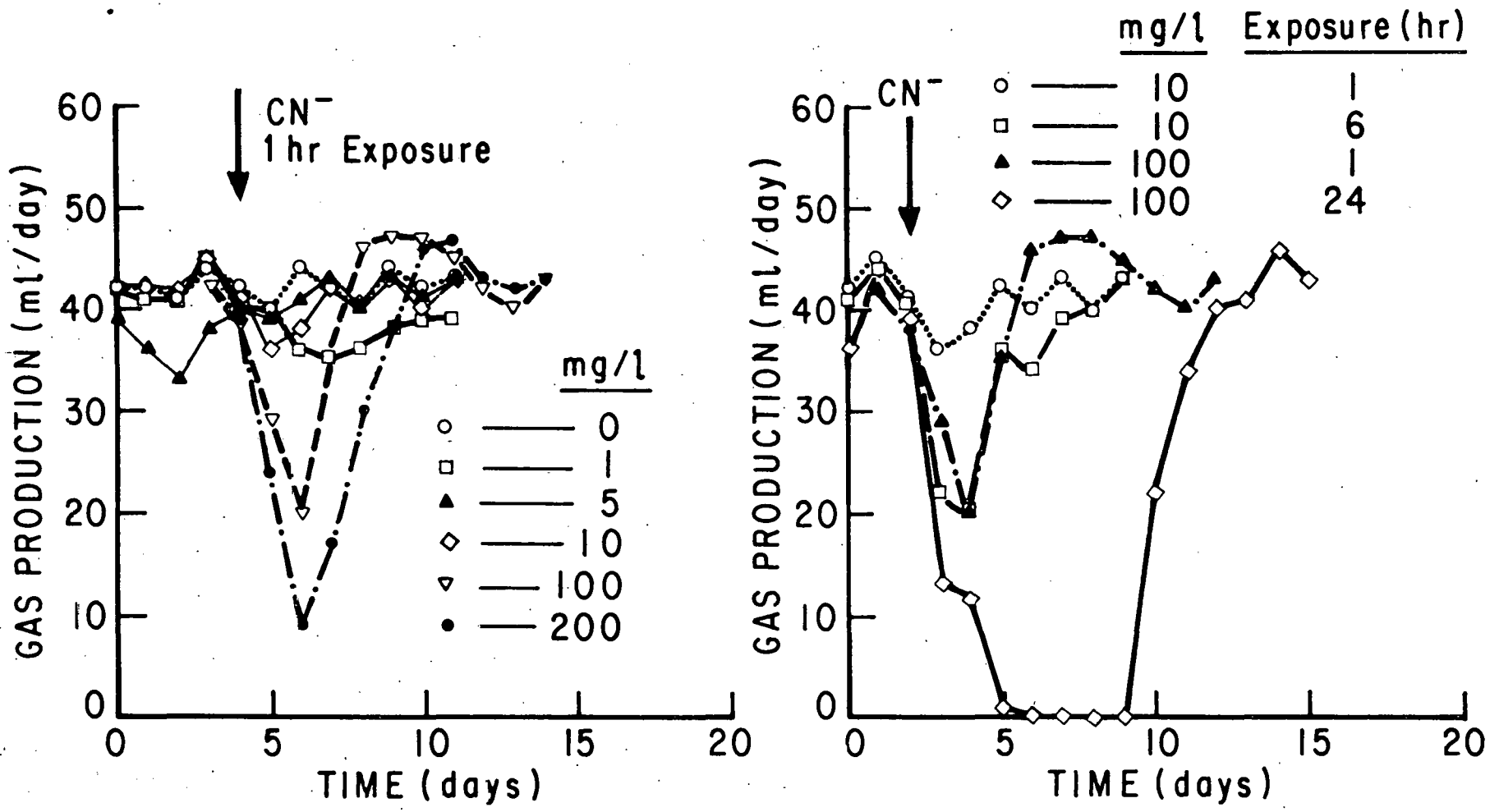

Fig. 2 Effect of Time of Exposure to CN^- on Gas Production

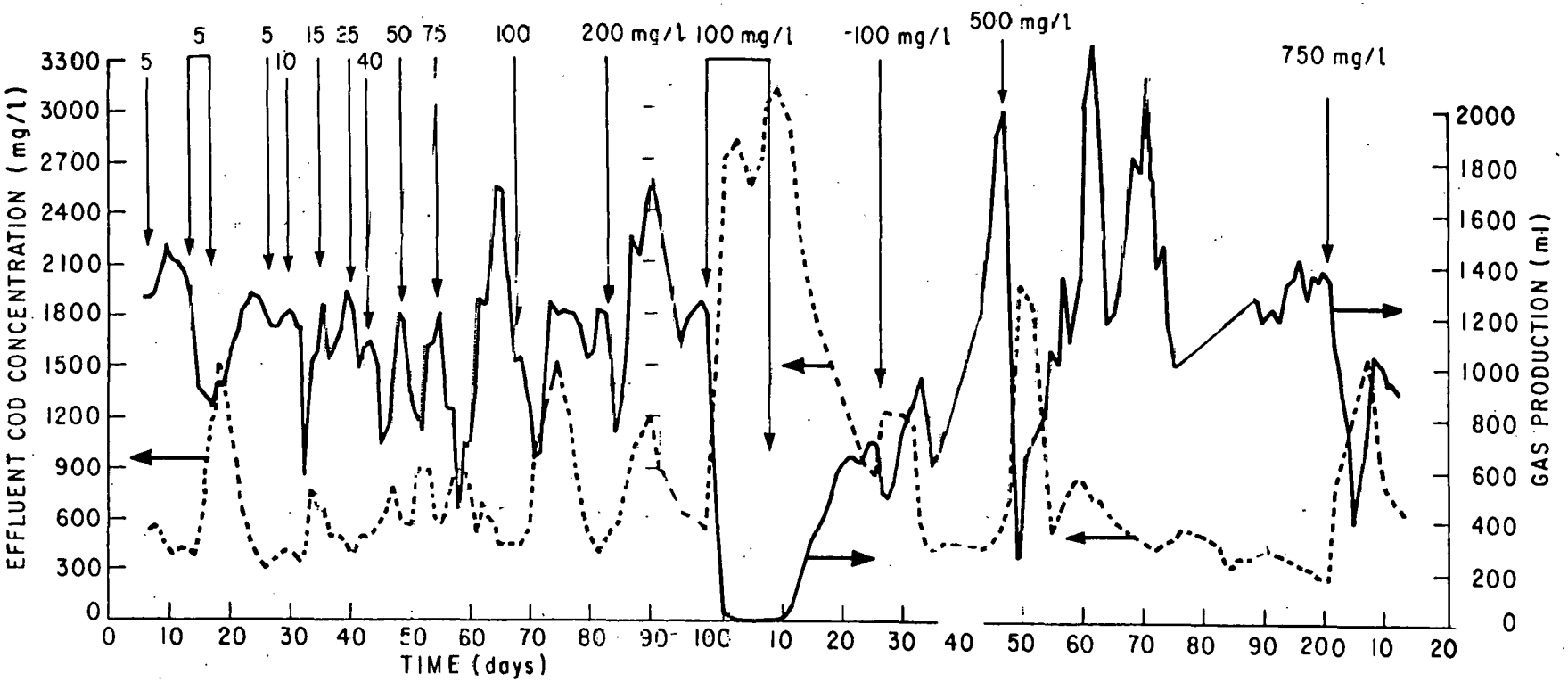

Fig. 3 Response of Anaerobic Filter to Toxicant CN^-

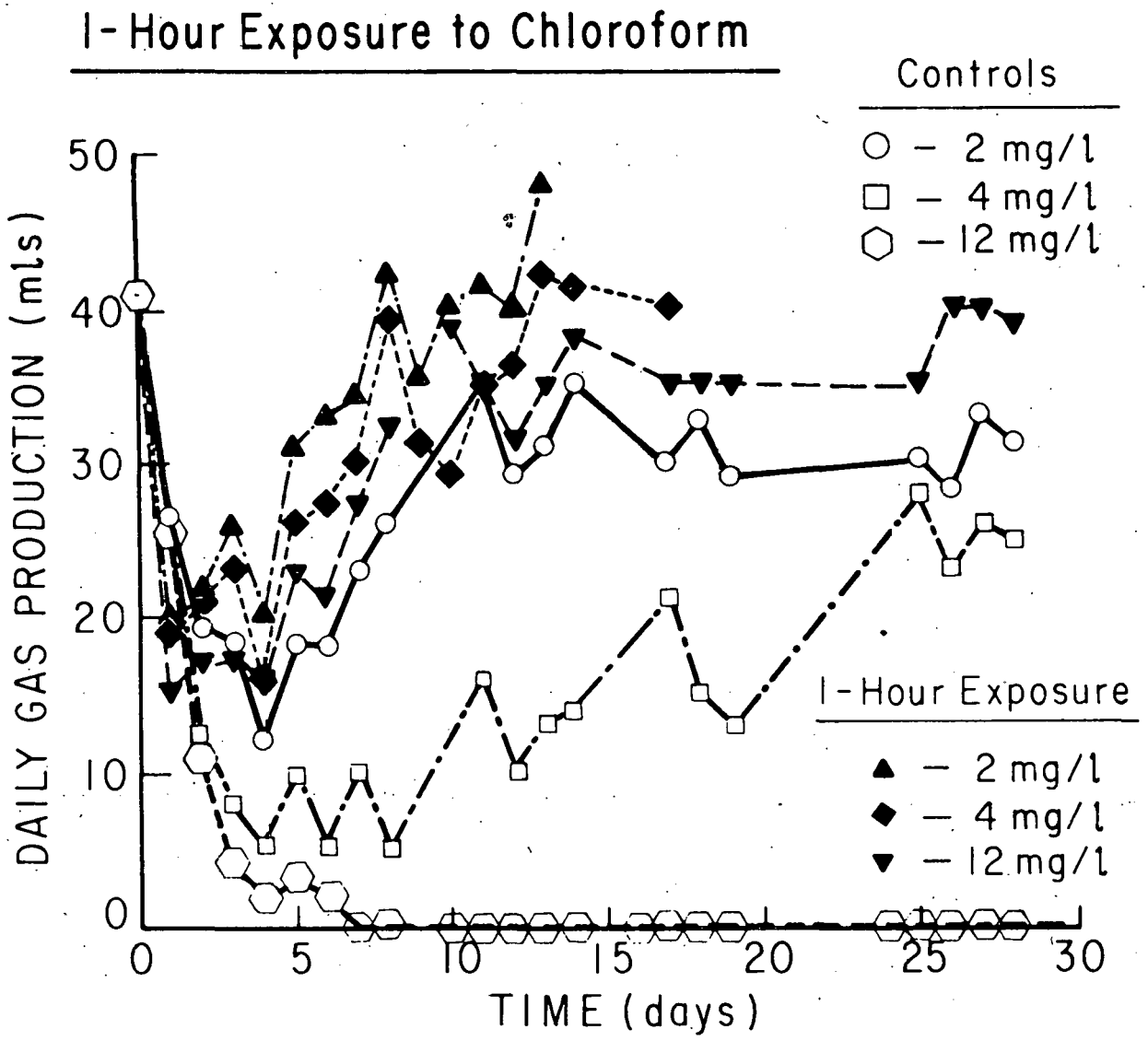

Fig. 4 Effect of Exposure Time on Toxicity Response: Chloroform

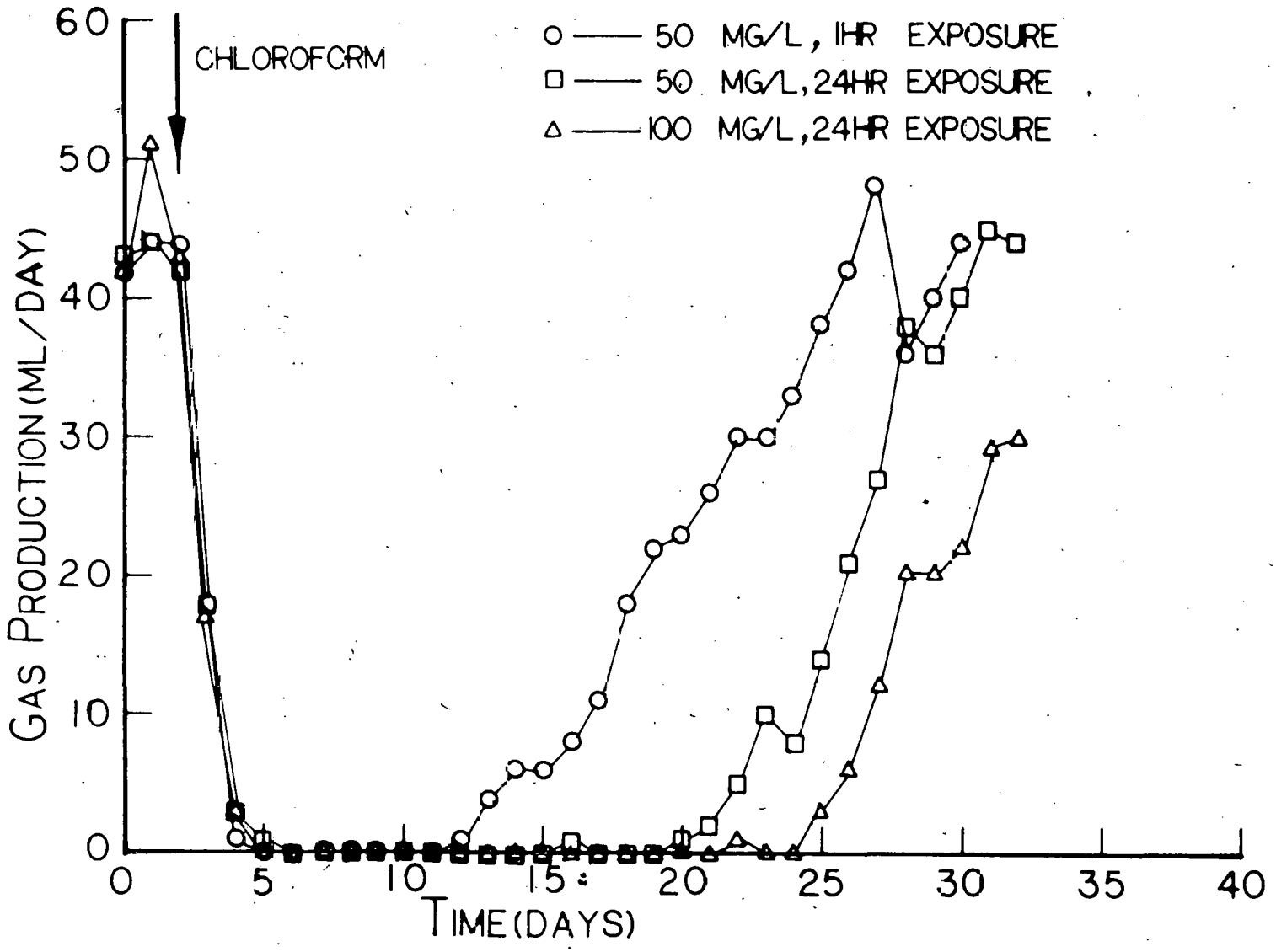

FIG. 5 EFFECT OF TIME OF EXPOSURE TO CHLOROFORM ON GAS PRODUCTION

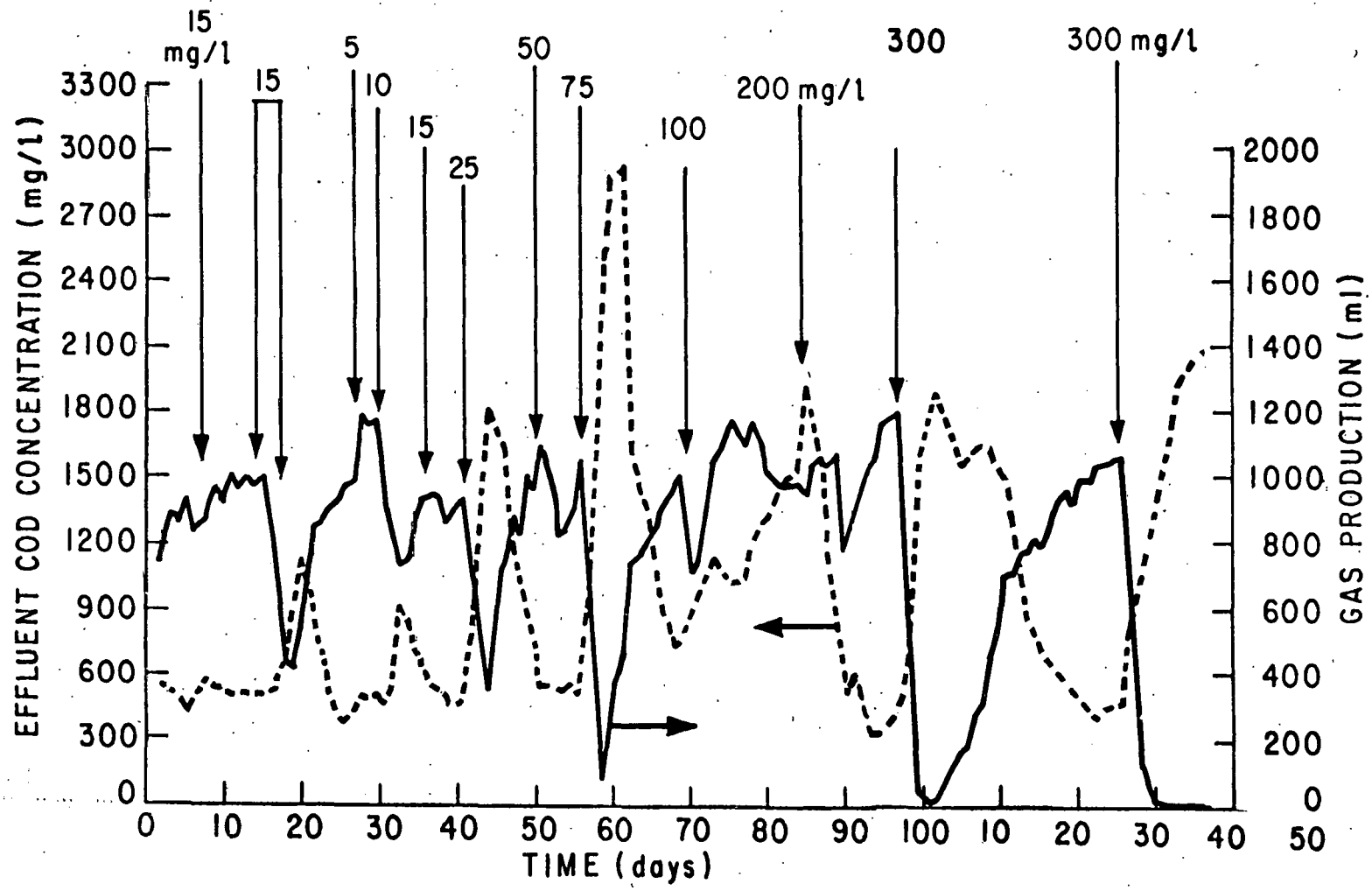

Fig. 6 Response of Anaerobic Filter to Toxicant Chloroform

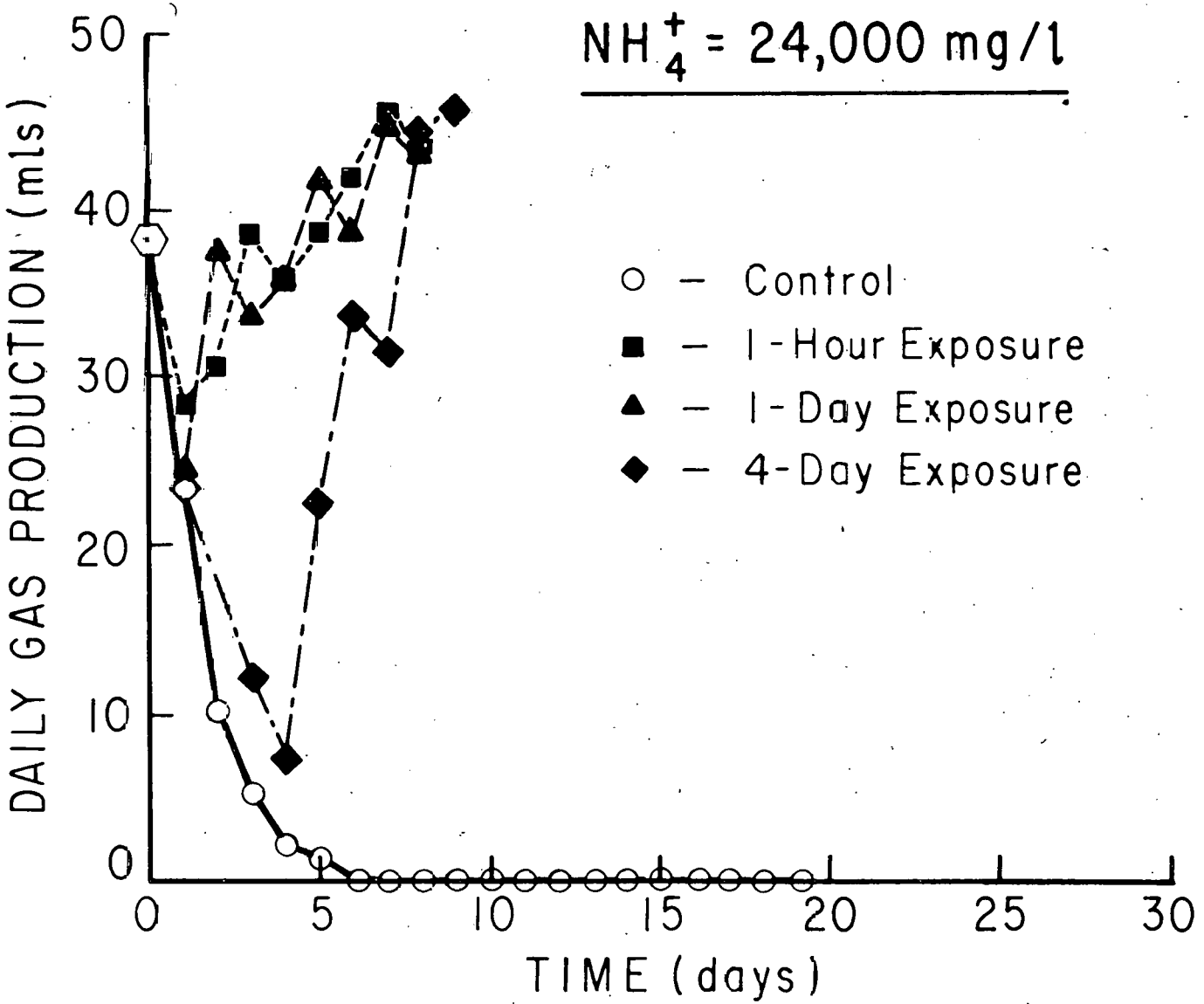

Fig. 7 Effect of Exposure Time on Toxicity Response: NH_4^+

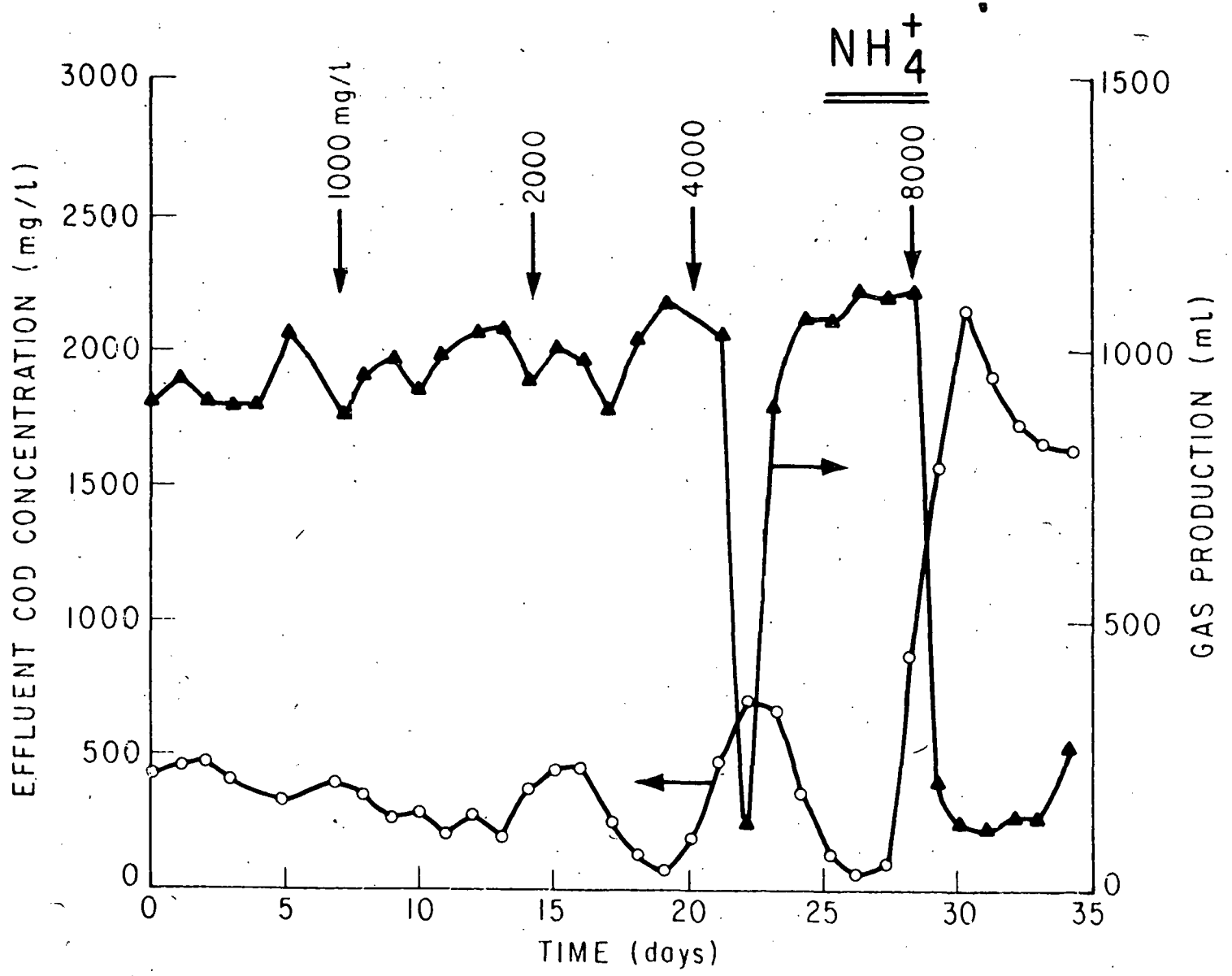

FIG. 8 RESPONSE OF ANAEROBIC FILTER TO TOXICANT

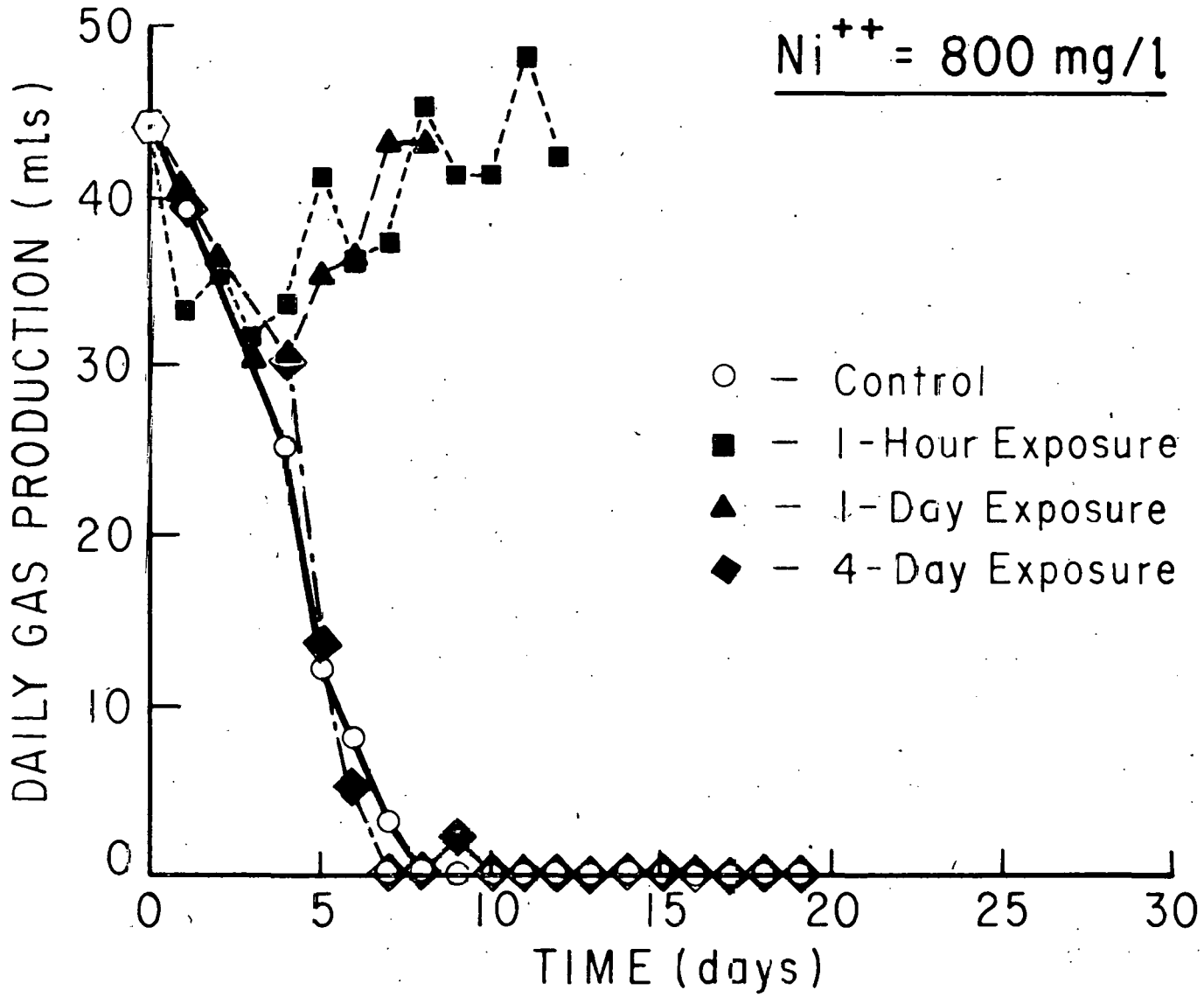

Fig. 9 Effect of Exposure Time on Toxicity Response: Nickel

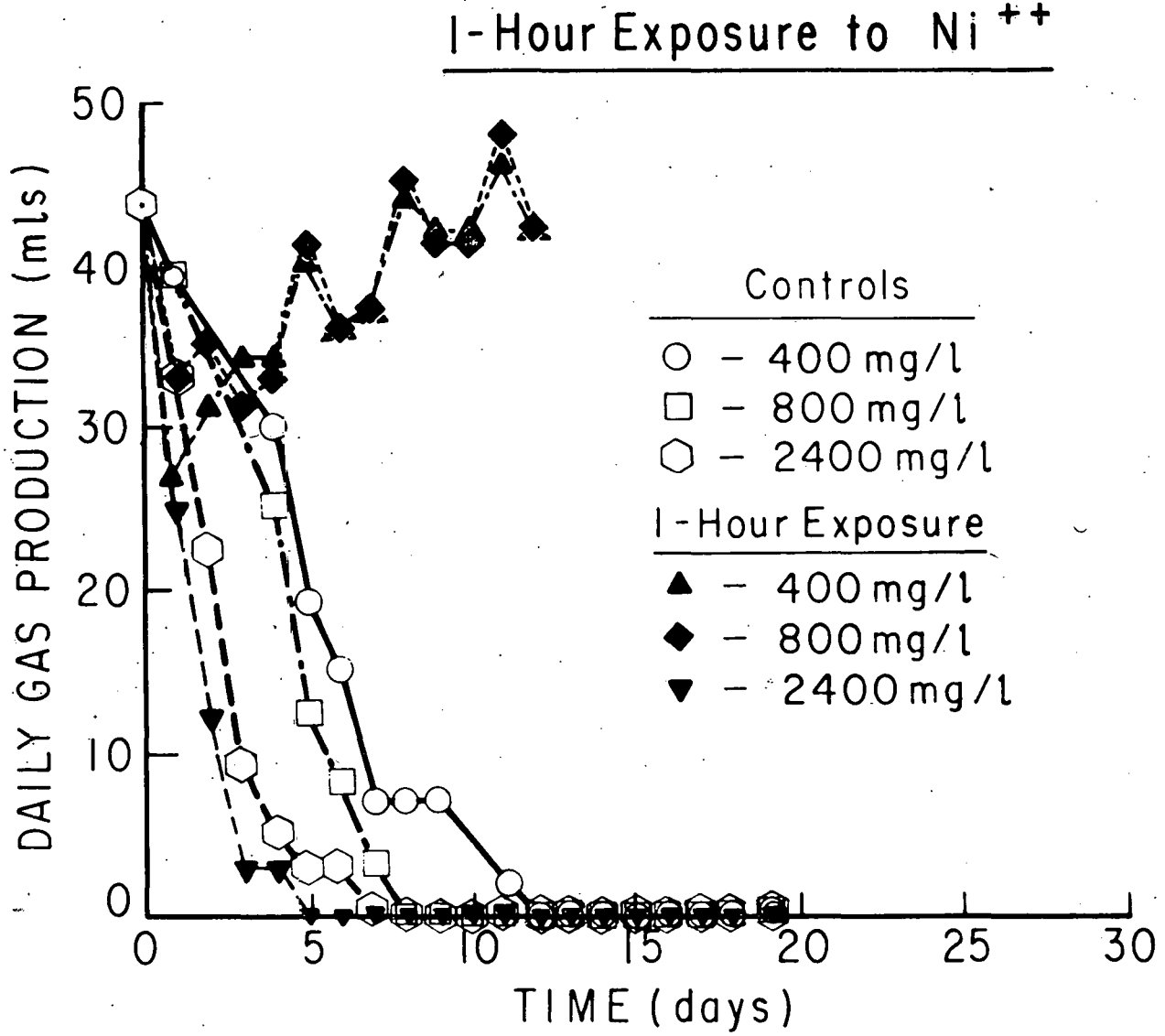

Fig.10 Effect of Exposure Time on Toxicity Response: Nickel

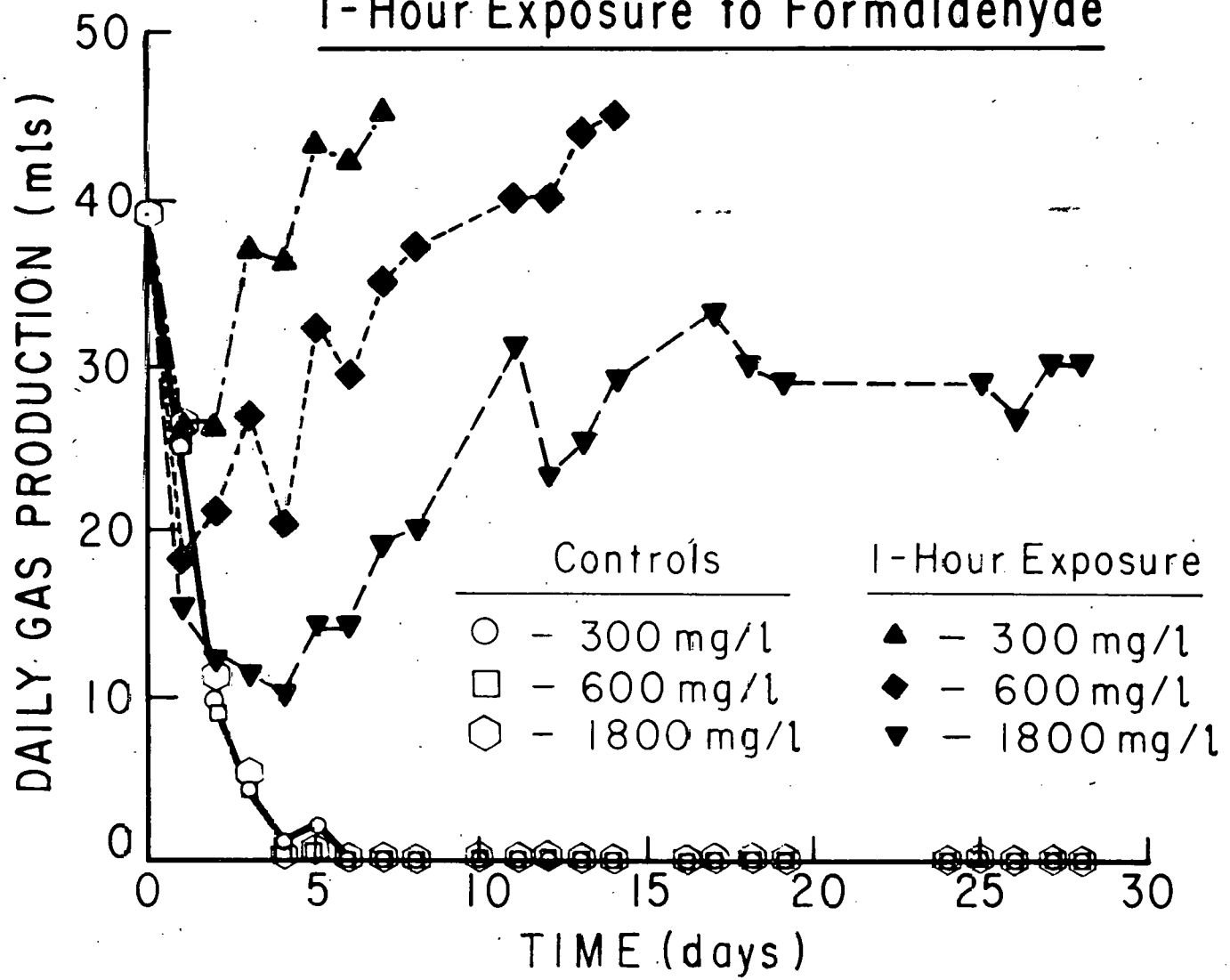

Fig. 12 Effect of Exposure Time on Toxicity Response: Formaldehyde

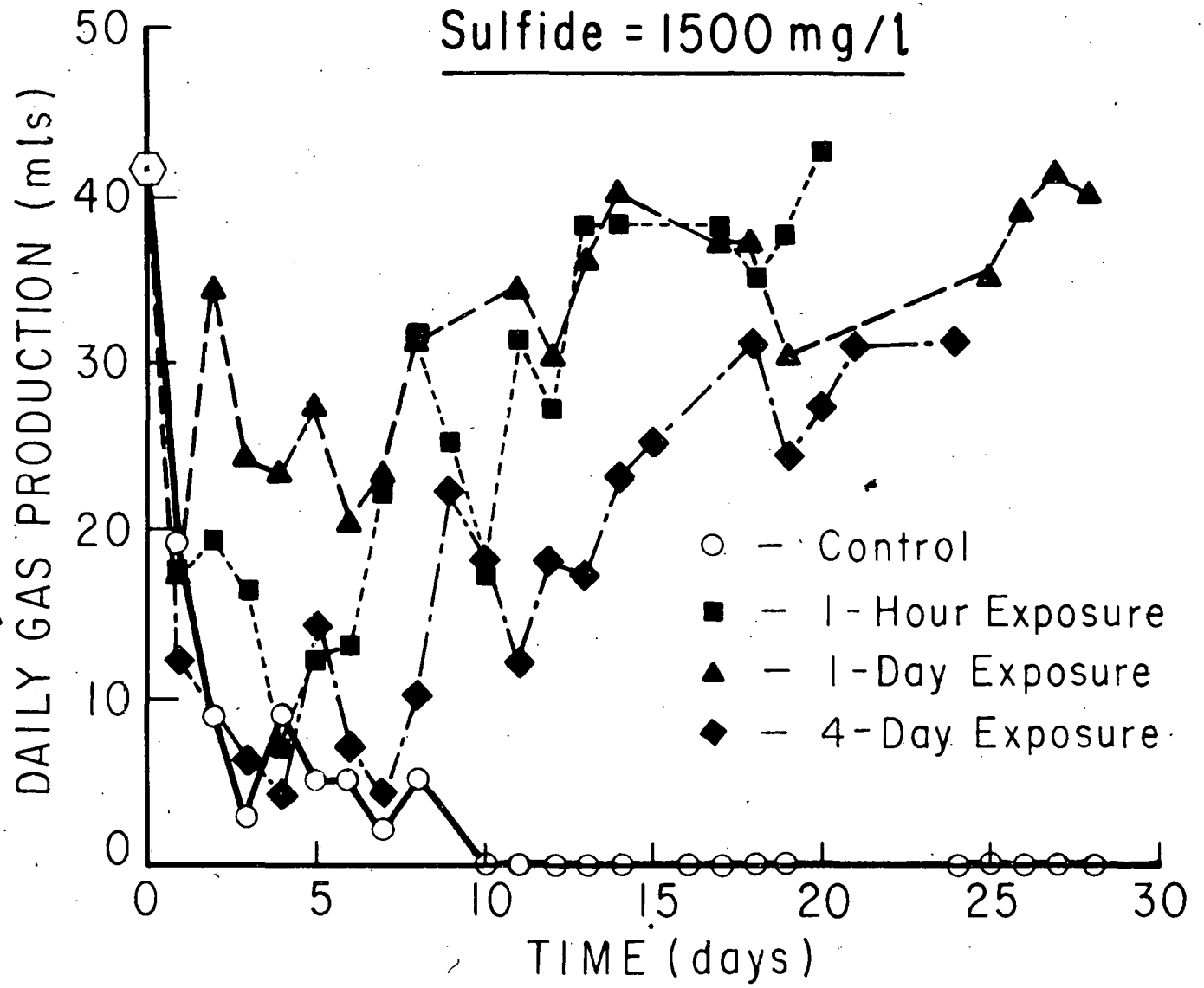

Fig. 14 Effect of Exposure Time on Toxicity Response: Sulfide

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ANAEROBIC ACTIVATED CARBON FILTERS FOR THE TREATMENT OF WASTEWATERS CONTAINING PHENOLS

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ABSTRACT

Phenol and its derivatives present an environmental hazard and are therefore of concern to the coal gasification and coking industry. Traditional treatment processes are energy intensive and frequently exhibit instabilities induced by variations in the chemical characteristics of the influent waste stream.

The treatment system developed in this study consists of an anaerobic filter utilizing granular activated carbon as a contact media. The system combines the attractive features of activated carbon adsorption with the extended service life of the media as provided by the continuous anaerobic bioregeneration of the carbon.

Four experimental reactors were operated continuously for over two years. Influent feed concentrations of phenolic compounds were varied from 200 to 1,000 mg/l. Removal efficiencies in excess of 99 percent were obtained with reactors fed phenol, catechol and a mixture of phenol and glucose. Methane was generated in the quantities expected from the anaerobic degradation of the feed compound. A reactor fed only ortho-cresol exhibited very little microbial activity. Investigation of the adsorption capacity of activated carbon for ortho-cresol indicated removal was due only to surface adsorption.

1. INTRODUCTION

The growth of industry and advancement in technology over the last two decades have resulted in the discharge of extremely complex compounds to the environment. Phenolic compounds, monohydroxy derivatives of benzene, have been and are presently prioritized as a major environmental concern in these wastewaters. Major contributors of phenols bearing wastewaters include coking and coal gasification plants, petroleum refineries, pharmaceutical plants, fertilizer manufacturers solvent and explosive industries, dye manufacturing, steel mills and the paper industry. Phenol bearing wastewaters have traditionally been treated using the extended aeration activated sludge process or other aerobic treatment processes (Juntgen and Klein, 1976). Such processes are very energy intensive because of the employment of excessively long aeration detention times (Ganczarczyk and Elion, 1978 ; Sack and Bokey, 1978), and they often exhibit instabilities induced by variations in the chemical characteristics of the influent waste stream (Sack and Bokey, 1978).

The aerobic biological treatment of coal conversion wastewaters exhibits an additional complicating feature due to the simultaneous presence in these wastes of phenols, ammonia, cyanide, thiocyanate and numerous mono and polycyclic hydrocarbons (Forney et al., 1974; Ho et al., 1976; Singer et al., 1977). These constituents have been shown to exhibit strong co-inhibition characteristics to aerobic degradation (Juntgen and Klein, 1976; Johnson et al., 1977; Valiknac and Neufeld, 1978), and as such the extended aeration activated sludge process has been shown to fail in meeting the treatment requirements of these wastes (Sack and Bokey, 1978; Ganczarczyk and Elion, 1978).

Phenol bearing wastewaters have been treated using a variety of physical and chemical unit operations and processes. Chemical oxidants such as ozone (Eisenhauer, 1968), potassium permanganate (Lanouette, 1977), hydrogen peroxide (Eisenhauer, 1964), and chlorine (Throop, 1975) have been

demonstrated to be very effective in the cleavage of the parent benzene ring of phenol. In the majority of cases, however, a high molar ratio of oxidant to phenol is required to achieve any appreciable reduction in phenols and consequently these methods are only recommended for effluent polishing purposes and not for the treatment of the raw wastewater. Adsorption onto activated carbon has been demonstrated to affect good removal of phenols from wastewater (Juntgen and Klein, 1976; Zogorski and Faust, 1978). However, because of the limited capacity of activated carbon in adsorbing organic matter, thermal regeneration of the spent carbon becomes necessary; thus rendering the process energy intensive and requiring the constant addition of fresh carbon to supplement regeneration losses.

The anaerobic activated carbon biological filter combines the attractive features of adsorption with the extended service life of the adsorbent surface by the continuous anaerobic bioregeneration of the carbon. This treatment process is particularly suited for wastewaters containing mixtures of readily biodegradable organic compounds in addition to more resistant and refractory matter. The less biologically resistant organic compounds are rapidly converted to the poorly adsorbing volatile fatty acids prior to their final conversion to methane and carbon dioxide and, as such, the carbon surface becomes more available for the uptake of the more resistant organic matter which will then be held in intimate contact with the attached microbial culture for acclimation and biodegradation to occur. Other advantages to the use of granular activated carbon as a contact medium include the concentration polarization of organic compounds near the carbon surface where enhanced kinetic rates result in better polishing capabilities of the final effluent. The activated carbon also serves as a buffering reservoir, withholding nutrients during peak influent substrate concentrations and releasing those nutrients back to the biomass when the feed substrate concentration subsides.

2. MATERIALS AND METHODS

Three identical treatment systems were used in this study. Each treatment apparatus consisted of four jacketed columns and three clarifiers connected in series with one clarifier located after each of the first three columns. Figure 1 represents a schematic of one column and one clarifier.

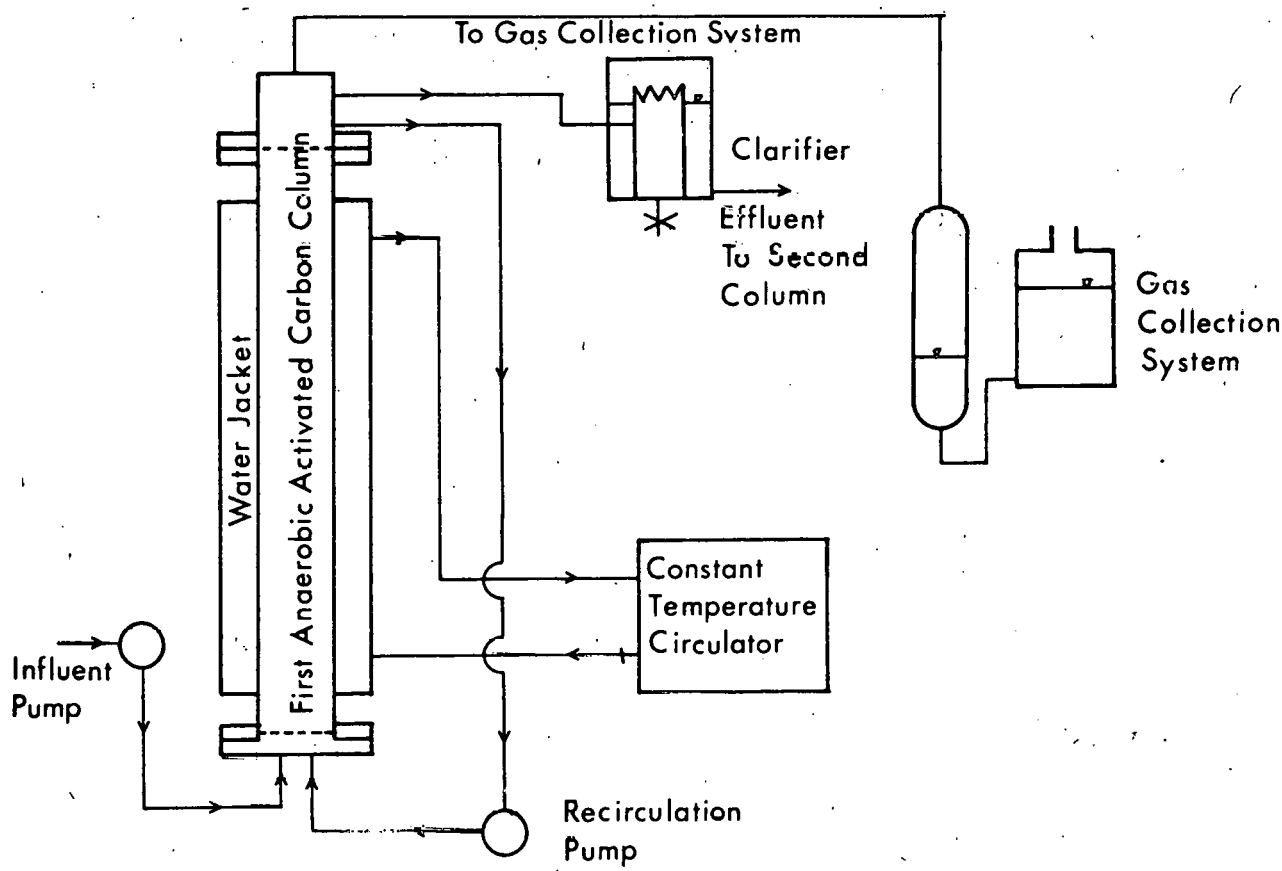

Figure 1. Schematic of First Anaerobic Activated Carbon Filter and Associated Clarifier

Each column was constructed of plexiglas 61 cm long and 5 cm in internal diameter with perforated plates situated on both ends of each column in order to retain the reactor contents and allow for passage of the solution. A short plate section was attached to the lower end of each column in order to allow for the installation of feed and recirculation water fittings, while a 10 cm long plexiglas cylinder was attached to the top of each column to allow for water withdrawal, recirculation and gas collection. Recirculation of the reactor aqueous contents around each individual column was provided through the use of a multiple head tubing pump (Cole-Parmer Model 7567, Chicago, Ill.). The clarifiers were constructed of plexiglas tubes 12.7 cm in length and 7.6 cm in internal diameter. These units served for the removal of excess biomass production and provided a means for the separation between the gaseous phases of the different columns. Water was recirculated from a constant temperature bath through the water jackets of the four columns thus maintaining a system temperature of $35 \pm 0.5^{o}C$.

Each column reactor was charged with 446.6 grams of Filtrasorb 400 granular activated carbon (Calgon Corporation, Pittsburgh, PA). Prior to loading, the carbon was sieved into a number of size fractions and the size distribution of the carbon actually used was 16 percent 18 x 20 U.S. Mesh, 27 percent 16 x 18 U.S. Mesh, and 57 percent 10 x 16 U.S. Mesh.

Synthetic substrates bearing either phenol, catechol or o-cresol along with the necessary trace salts and nitrogen and phosphorus nutrients were used in this study (Suidan et al., 1979 a,b). The synthetic substrates were prepared daily and pumped into the first column of every reactor system at a flow rate of 2 ml/min using positive displacement FMI pumps Model RPG-20 (Fluid Metering, Incorporated, Oyster Bay, NY). At this flow rate, an empty bed contact time of 11.62 h was provided per column resulting in a total empty bed contact time of 46.47 h per reactor system.

In the preparation of the feed substrates, appropriate volumes of a salt solution were mixed with a phosphate buffer solution and accurately weighed quantities of either phenol or catechol or an accurately measured volume of o-cresol. The mixture was then diluted to a volume of four liters with double distilled deionized water and its pH was adjusted to neutral range with a concentrated sodium hydroxide solution. The feed reservoir was then purged with nitrogen gas and placed in a $4^{o}C$ refrigerator for

pumping into the system.

Samples collected from the system were subjected to analysis following the procedure in Standard Methods for the Examination of Water and Waste-Water, 14th Edition, 1975 with the exception of the following analyses: (a) Oxidation Reduction Potential (ORP) was determined following the procedure found in the 1973 Book of ASTM Standards, Water; Atmospheric Analysis, Part 23. Method D 1498; (b) Gas Analyses were performed on a Fisher Model 25V Gas Partitioner using Certified Calibration Standards (Matheson, East Rutherford, NJ); and (c) Phenol, catechol and o-cresol analyses were performed by taking a fixed volume of sample filtered through a 0.45μ membrane filter (Gelman, Type GA-6), adjusting the pH to 12 and diluting to 100 ml with distilled water. The ultraviolet absorption spectra of the samples were obtained using distilled water (pH 12.0) as a reference. The absorbances of phenol, catechol and o-cresol at 286 nm, 268 nm and 235 nm, respectively, were compared to the adsorbance of a series of known concentration solutions (pH 12) of the respective phenolic compounds for the determination of the solute concentration. The minimum detectable concentration of the three phenolic compounds using this method is 0.1 mg/l in distilled water using a 5 cm light path and 1.0 mg/l in the column effluents because of the presence of interfering species, in which case the values determined for the lower concentrations were greater than or equal to the actual phenols concentrations.

3. REACTOR STARTUP AND OPERATION

The three anaerobic activated carbon filter reactor systems employed in this study were operated using phenol, catechol or o-cresol as the respective primary organic carbon source. The experimental units were seeded by adding 100 ml of digester supernatent from a field unit along with a 100 ml of sludge from a glucose fed laboratory digester to each individual column. After seeding, recirculation of the aqueous contents around each individual column was initiated and the systems were fed the appropriate phenolic compound on a batch basis for a period of three weeks, after which continuous pumping of the appropriate substrate was initiated. All systems were continuously fed until steady-state operating conditions were attained, at which time, the influent feed levels of the appropriate phenolic compound

was increased. Steady-state operating conditions were defined as the state of steady gas production and uniform effluent characteristics.

4. PHENOL DEGRADATION STUDIES

The phenol fed anaerobic-activated carbon reactor system was operated continuously for a period of 550 days. During the first phase of this experiment, which extended over a period of 267 days, the feed phenol concentration was maintained at 200 mg/l, while in the second phase of the study, which lasted for 283 days, the phenol concentration in the synthetic feed was raised to 400 mg/l.

Little or no gas production was observed from the reactor system during the first 135 days of continuous operation (see Figure 2), while the phenol content in the effluent from the first column averaged 100 mg/l during the period extending between days 100 and 150 of continuous operation. The data in Figure 3a represent a COD material balance between the feed substrate and the effluent from each of the four columns on day 134 of continuous operation. On that day the substrate COD was reduced from a level of 605 mg/l in the feed to 355, 95, 85, and 84 mg/l in the effluents from columns 1, 2, 3 and 4, respectively. No gas production was observed from the treatment system on that day thus leading to the conclusion that most of the COD removal was due to adsorption onto the activated carbon surface.

After day 135 of continuous feeding, vigorous methane gas production was attained from the treatment system at an average production rate of 622 ml/day at standard temperature and pressure (STP) for the period extending between day 135 and 240. The phenol content in the effluent of the first column decreased to below 5 mg/l during that period. A COD material balance across the experimental system on day 225 which corresponds to the period of vigorous gas production is given in Figure 3b. The COD equivalent of the methane gas liberated from the first column of the experimental reactor on day 225 exceeded the COD of the incoming substrate by 117 mg/l of feed solution. This observation, coupled to a similar result obtained when a carbon material balance was constructed across the system leads to the conclusion that the activated carbon was undergoing biological regeneration during this period of operation. Gas production and COD

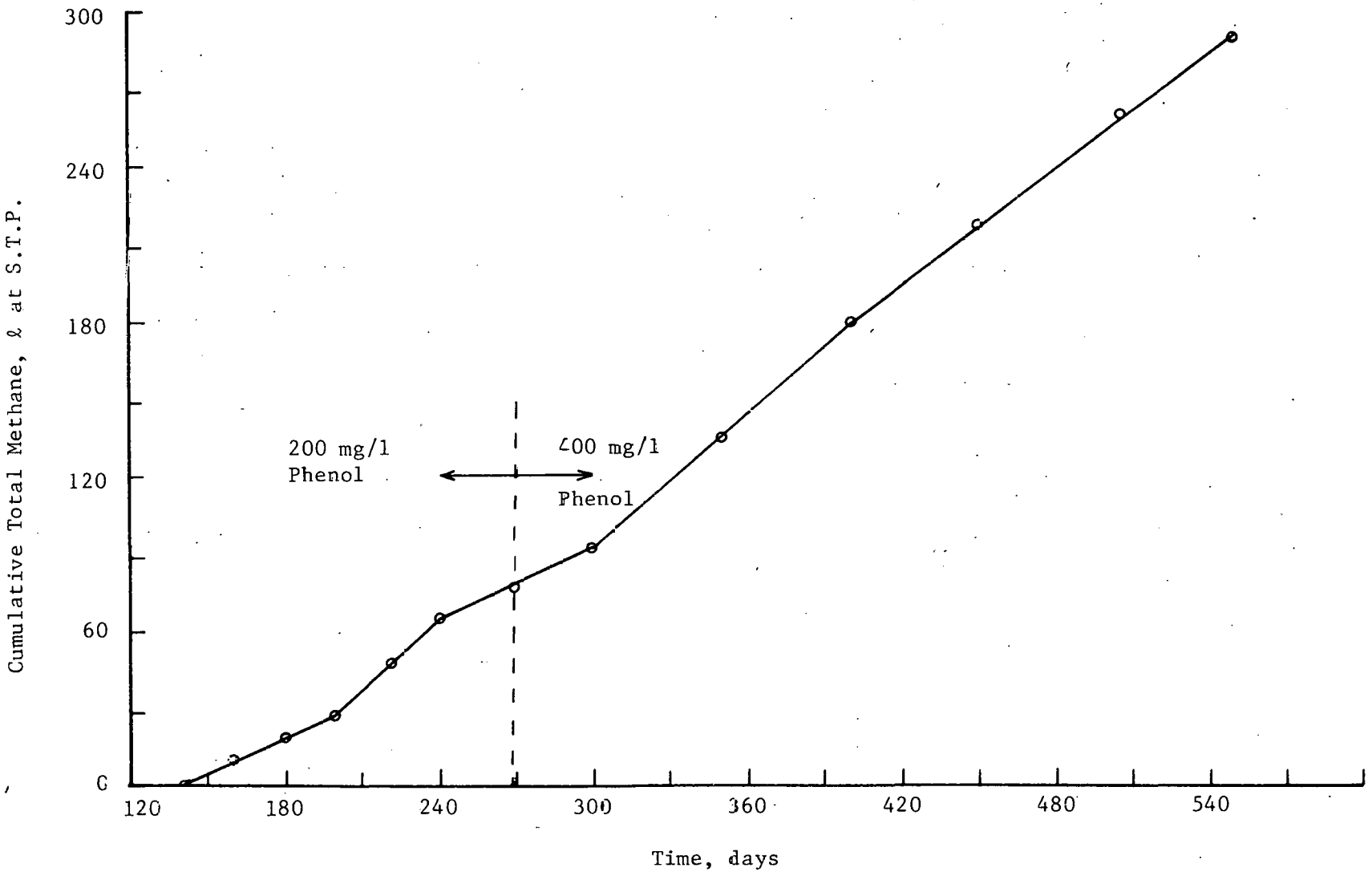

Figure 2. Total Methane Production = Phenol Fed Reactor

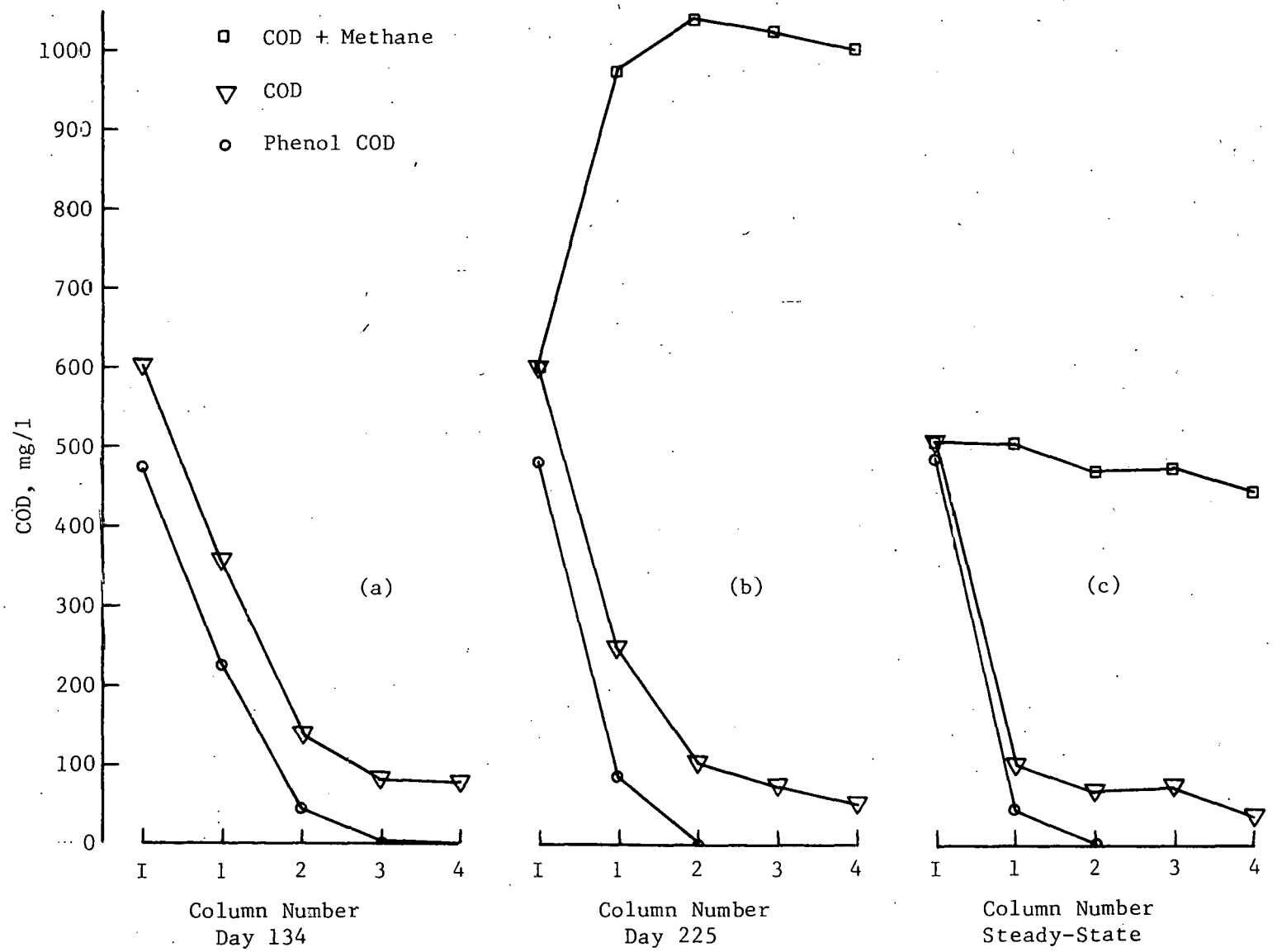

Figure 3. COD Profiles - 200 mg/l Phenol Fed Reactor

reduction were also observed from the second column reactor. The last two columns remained somewhat dormant throughout the study period.

After day 240 and until day 267 of continuous operation, gas production subsided to a methane steady production rate of 420 ml/day of methane gas. A steady state COD material balance across the treatment system (see Figure 3c) reveals that at steady state operating conditions only 78 mg/l of COD was not accounted for in aqueous and gaseous phases of the treatment system. This corresponded to 15 percent of the feed COD and may be attributed to a combination of adsorption desorption and biomass production. At steady-state operating conditions, gas production from the treatment system was virtually limited to the first column although the second column was very active in gas production during the bioregeneration phase which extended from day 135 to day 245 of continuous operation. In addition to being the primary methane producer, the first column was responsible for over 80 percent of the reduction in the feed COD while the whole treatment system accounted for 92 percent reduction in COD.

In order to evaluate the response of the treatment system under conditions of increased phenol concentration, the phenol content of the synthetic feed substrate was increased from 200 to 400 mg/l on day 268 of continuous operation. The initial response of the system was an immediate increase in the rate of gas production over the steady-state production level observed during the first stage (see Figure 2). The effect of an increase in the feed phenol concentration on the treatment system is best illustrated by the COD material balances constructed across the treatment columns for days 344, 395 and when steady-state operating conditions were attained (see Figures 4a, b and c). These three figures illustrate (a) a period of stable operation characterized by adsorption and biodegradation (Figure 4a), (b) a period of active bioregeneration along with efficient biodegradation (see Figure 4b) and (c) a period of steady-state operation with COD removal efficiencies exceeding 93 percent (see Figure 4c). The data in Figure 4c illustrate clearly that at steady-state all removal was accomplished in the first anaerobic filter with very little additional removal attained from the last three columns.

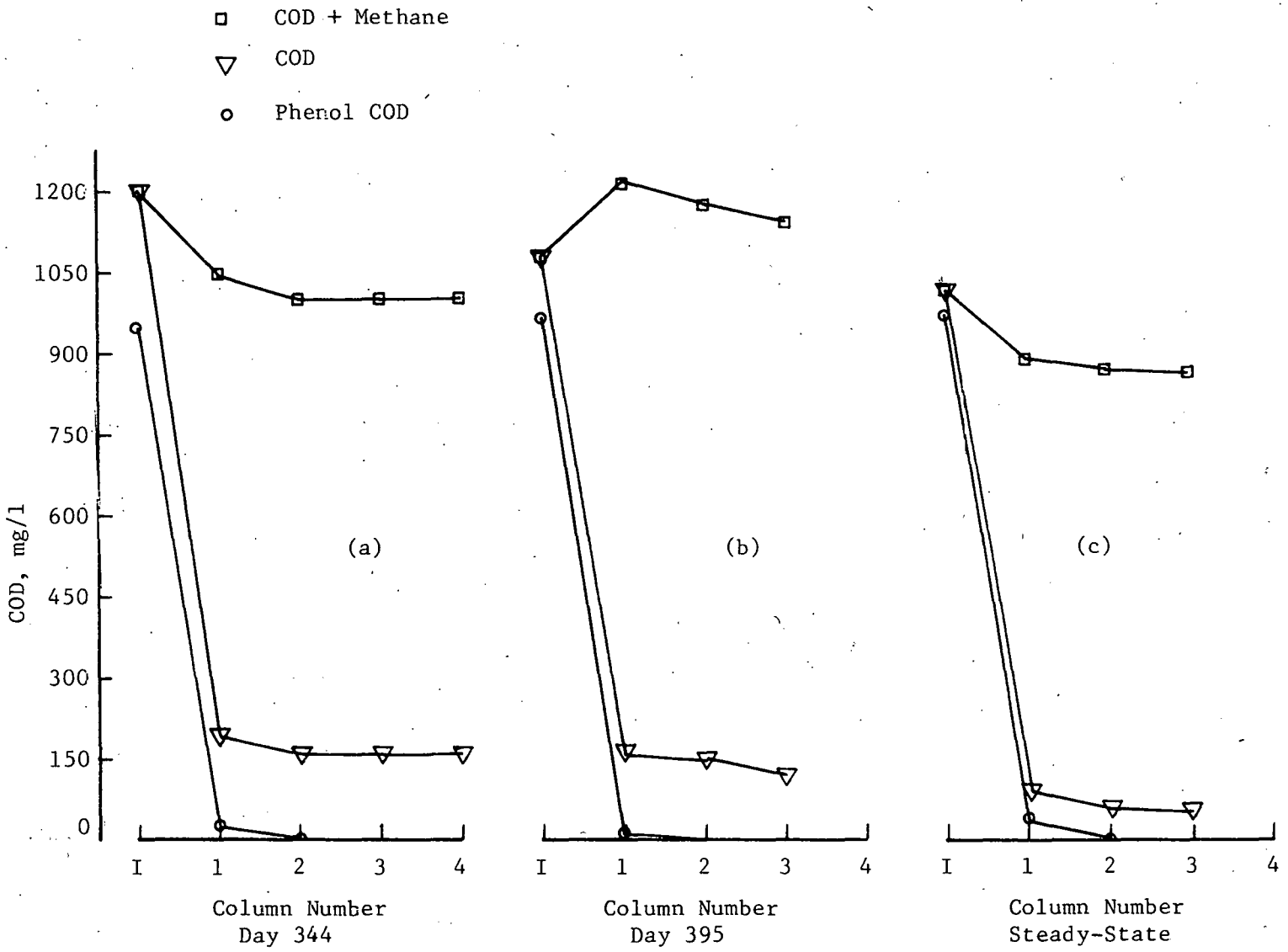

Figure 4. COD Profiles - 400 mg/l Phenol Fed Reactor

5. CATECHOL DEGRADATION STUDIES

The catechol fed anaerobic-activated carbon reactor system was operated continuously for a period of 511 days. During the first phase of this experiment, which extended over a period of 333 days, the feed catechol concentration was maintained at 200 mg/l, while in the second phase of the study, which extended over an additional period of 178 days the catechol concentration in the synthetic feed was increased to 400 mg/l.

The response observed from the catechol fed reactor was similar to the adsorption bioregeneration and steady-state operation obtained from the phenol fed reactor. During the first 120 days of continuous operation, no appreciable gas production was observed from the reactor system (see Figure 5) while, concurrently, no catechol was detected in the effluent. This was due to the adsorption of catechol onto the activated carbon surface thus rendering the substrate unavailable for biodegradation by the microbial culture. Measurable gas production became noticeable on day 120 where for a period of 23 days, a methane production rate of 50 ml/day at STP was recorded (see Figure 6a). Vigorous methane production averaging 582 ml/day was observed from the first two columns during the period extending from day 143 to day 235. During this period bioregeneration of the activated carbon was occurring as evidenced in Figure 6b. After day 235 methane production which became limited to the first column remained relatively constant at a rate of 185 ml/day. A COD material balance across the reactor during that period indicates that steady-state operating conditions have been attained for the 200 mg/l catechol loading phase (see Figure 6c).

The feed catechol concentration was increased to 400 mg/l on day 333 and the corresponding response of the treatment system was an immediate increase in the methane production rate as is obvious from Figure 5. COD material balances across the four anaerobic columns indicate that during this phase of the experiment the treatment system exhibited the same three stages that were observed when the feed phenol content was increased from 200 to 400 mg/l. These phases were (a) adsorption and biodegradation (see Figure 7a), (b) bioregeneration (see Figure 7b) and (c) steady-state performance (see Figure 7c).

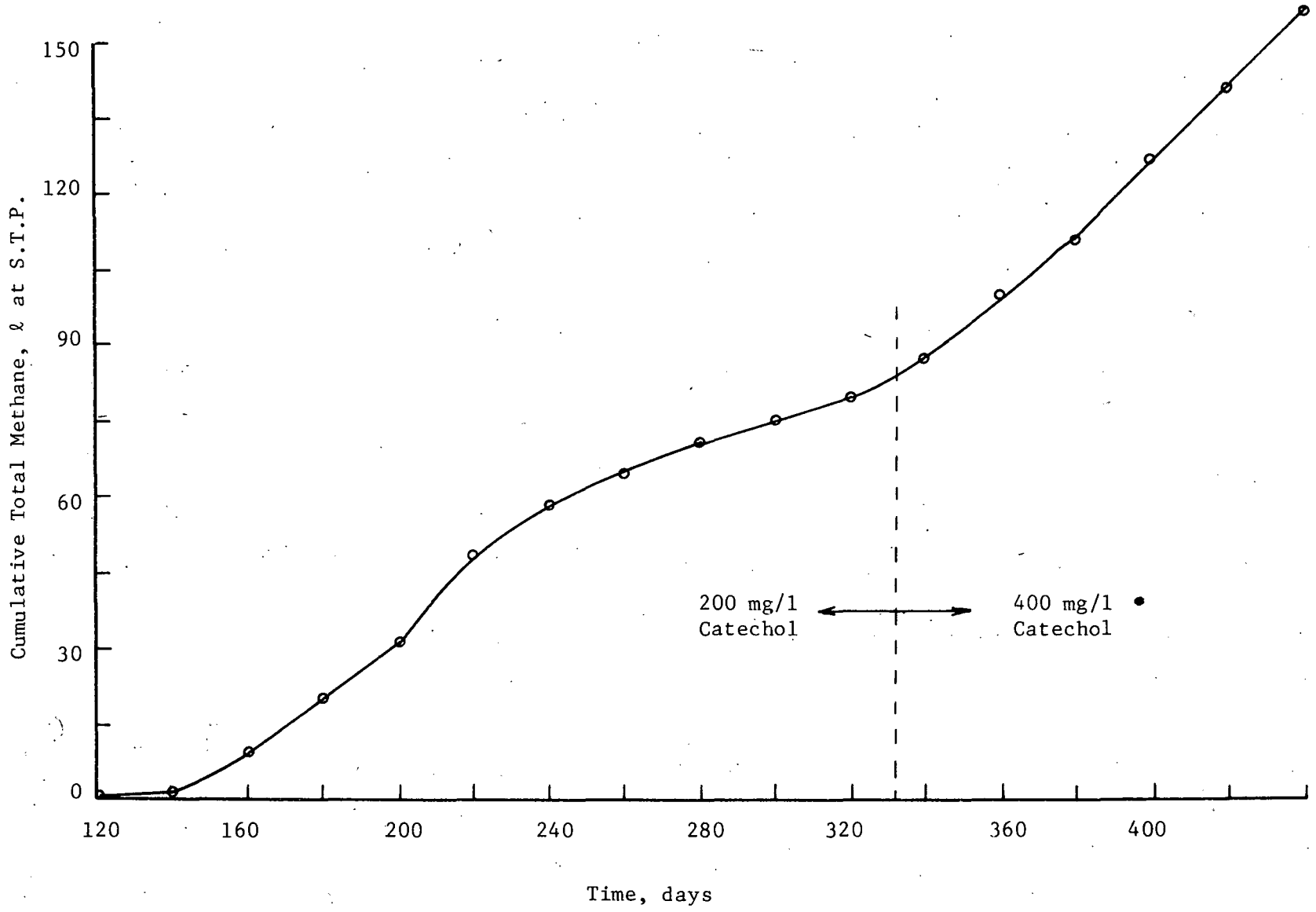

Figure 5. Total Methane Production - Catechol Fed Reactor

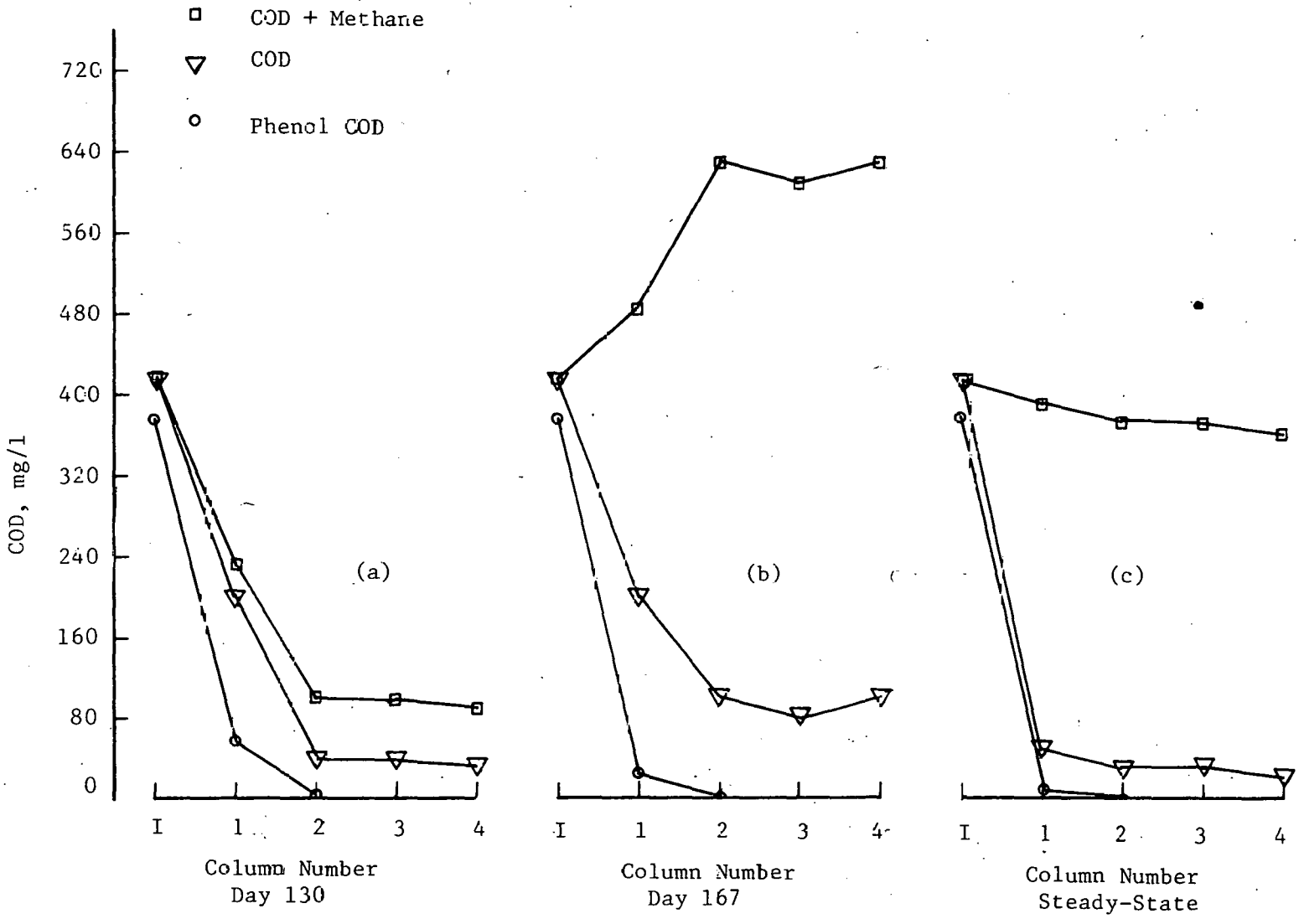

Figure 6. COD Profiles - 200 mg/l Catechol Fed Reactor

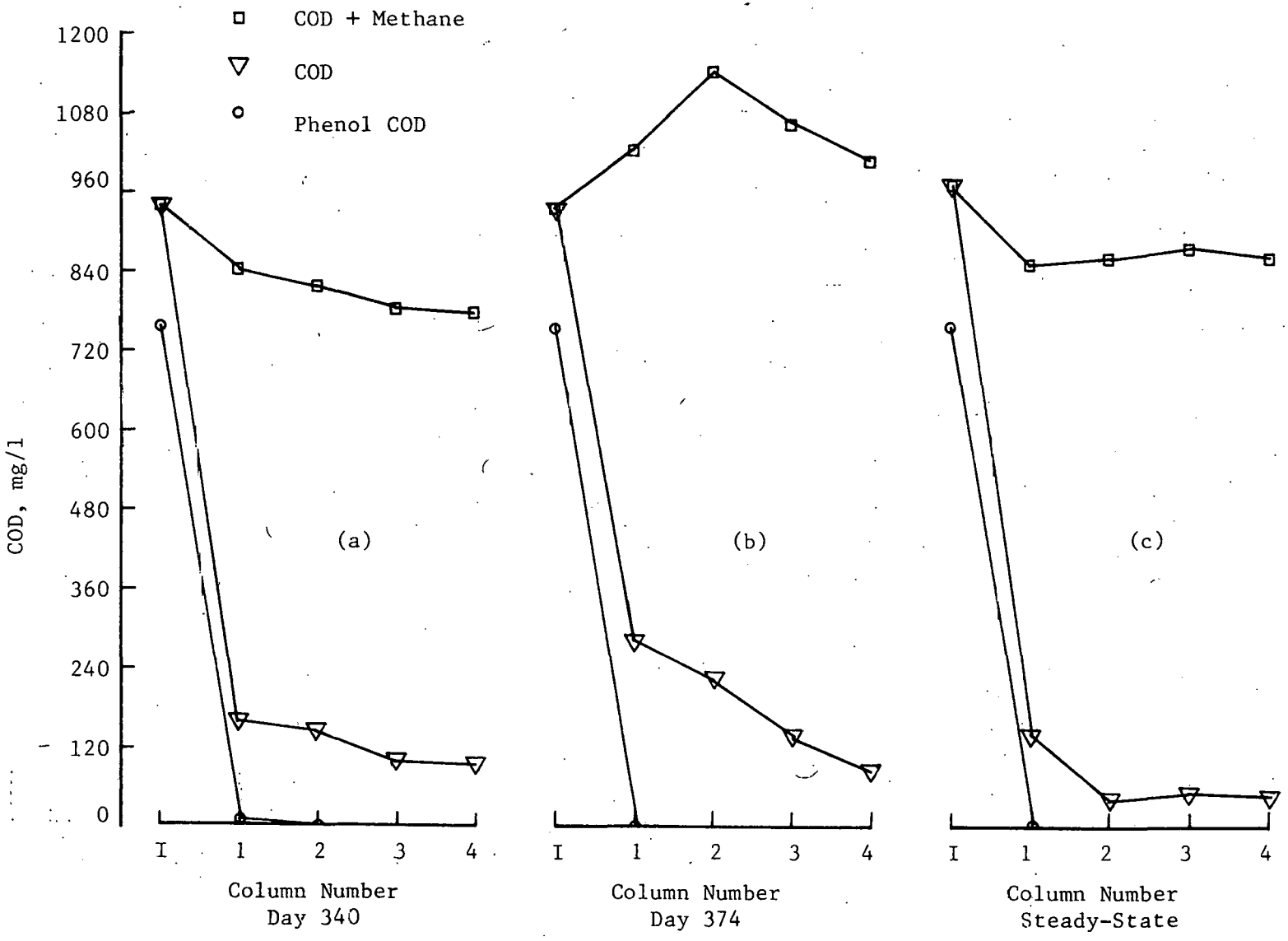

Figure 7. COD Profiles - 400 mg/l Catechol Fed Reactor

6. O-CRESOL DEGRADATION STUDIES

A third series of four anaerobic-activated carbon filters were operated continuously for a period of 420 days with a synthetic feed substrate containing 256 mg/l of o-cresol. Very little gas production was observed from the treatment system throughout the study and the concentration of o-cresol in the effluents from the series of four columns followed a typical adsorption breakthrough curve. After it became obvious that o-cresol was very resistant to this mode of degradation the feed substrate was supplemented with 100 mg/l of glucose in order to serve as a readily biodegradable cosubstrate. Limited data collected todate indicate that methane production from the treatment system has exceeded that anticipated from the complete degradation of glucose and that the treatment system is currently degrading o-cresol.

7. SUMMARY AND CONCLUSIONS

The results of this study demonstrate the potential of the anaerobic-activated carbon filter in the treatment of phenolic compounds. Phenol and catechol were reduced by the process to below detectable levels with corresponding COD removal efficiencies exceeding 90 percent. O-cresol exhibited a stronger resistance to anaerobic biodegradation than the other two phenolic compounds, however, co-acclimation studies with glucose have yielded encouraging results todate.

In conclusion, the anaerobic activated carbon filter developed in this study has the potential of being a treatment effective and energy efficient process for the treatment of various industrial wastewaters.

8. ACKNOWLEDGEMENT

The work upon which this publication is based was supported, in part, by funds provided by the United States Department of Energy Grant No. EF-77-G-01-2756 and by the United States Department of Interior as authorized under the Water Resources Research Act of 1964, Public Law 88-379.

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A COMPARISON OF ANAEROBIC VS. AEROBIC TREATMENT OF PHARMACEUTICAL WASTE

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ABSTRACT

Wastes from pharmaceutical operations are extremely strong, concentrated, difficult to handle, and require some of the most complex and expensive treatment control systems of any industry. This paper reports on investigations of the use of anaerobic filters as a device for treating these wastes. Ideally suited for the removal of soluble organics, the anaerobic filters required no recycle, had virtually no sludge disposal problem and generated more usable energy in the form of methane than it consumed. The experimental system was compared to an existing "exemplary" aerobic treatment system.

The following conclusions were warranted on the basis of our study. Starting an anaerobic system by initially feeding it methanol to develop methane formers and then converting it to a specific waste was found to be very effective and merits further study for future applications in other anaerobic systems. The anaerobic filters successfully treated wastes from the chemical synthesis of pharmaceuticals, with an influent BOD concentration of 2,000 mg/l. Using a 36 hour hydraulic retention time at 35°C, COD removals of 70 to 80% and BOD_5 removals of 94% were constantly realized. In terms of pounds of COD removal per day, the anaerobic treatment system exceeded the efficiency of the existing aerobic treatment system by 33%. The intense color of the raw waste which was unaffected by the existing aerobic treatment system was almost totally removed by the anaerobic system.

INTRODUCTION

The present project was focused on a specific question - the applicability of an anaerobic filter to the treatment of wastewater from the manufacture of certain synthetic pharmaceutical chemicals. In particular, a comparison with the existing aerobic treatment system was made. It is only one of a series of studies being performed at the Civil Engineering Department at Syracuse University in this area, but it does allow direct comparison with an existing plant.

LITERATURE REVIEW:

Historically, anaerobic systems have been particularly effective in treating strong organic wastes. Young and McCarthy (1) described a number of advantages of anaerobic filtration of alternate biological treatment processes: 1) ideal suitability for treatment of soluble organic wastes low in suspended solids; 2) simplistic operation with no solids or effluent recycle; 3) maintenance of high concentrations of active biological solids, permitting treatment of dilute wastewaters even at normal temperature; 4) production of relatively low volume of sludge in contrast to aerobic biological processes; and 5) capability of handling intermittent waste discharges, shock organic and shock hydraulic loading. Their work also concluded that the filter compared favorably with existing biological treatment schemes and efficiently treated soluble organic waste. Since this work, filters have been studied repeatedly on a wide variety of wastes, almost all of them successfully. Probably the most pertinent to this study is the work of Jennett and Dennis (2) in the early 1970's who applied a fermentation pharmaceutical waste to an anaerobic filter and consistently produced between 93.7 and 97.8% COD reductions at loading varying from 0.221 to 3.52 kg COD/day/Cu m. Even though the waste was composed of 95% methanol, an easily degradable substance in the anaerobic environment, the study nevertheless illustrated several features of the filter. They were shown to be capable of producing very high COD reductions and withstanding sharp increases of organic loadings with relative ease.

Few spent solids were lost in the effluent and the presence of stray pharmaceuticals did not harm the system.

EXPERIMENTAL PROCEDURES

Anaerobic Filters - Six laboratory filters (Figure 1) were constructed of clear acrylic tubing: 48 in. (121.9 cm) high, 5.5 in. (14 cm) in inside diameter (ID) and a wall thickness of 0.25 in. (0.635 cm). The total volume of the empty cylinder was 0.667 cu. ft. (18.69 l). The base of the column was constructed so that the waste would be distributed uniformly across the bottom of the filter (Figure 1).

Each filter was filled with stone to produce consistent void ratios from model to model (4). The size of the stone used passed a sieve with 1.5 in. (3.84 cm) openings and was retained on a sieve with 1.0 in. (2.54 cm) openings. The stone was washed and then placed in the column. Large voids were avoided by placing the stone in layers and gently shaking the filter after each layer. The average void volume of the six filters was found to be 0.28 cu. ft. (8.04 l). The average void ratio was computed to be 0.43. Sample ports were placed at 6 in. (15.24 cm) intervals throughout the column height with additional ports 3 in. (7.62 cm) from the top and base of the filter. The sample ports extended to the center of the column so that a more representative sample of the filter contents could be contained. Three dispersion rings made of 0.5 in. (1.27 cm) thick acrylic were evenly spaced through the height of the filter to prevent short circuiting of the waste through the void spaces formed at the stone-column boundary. The filter effluents were passed through "T"-fitting and an inverted siphon to separate the gas from the liquid effluent. They were housed in a walk-in incubator at 35°C. Feed solutions were kept outside the chamber at approximately 19°C to reduce excessive biological growths.

Analytical Measurements - All analytical measurements were done in accordance with the 14th edition of Standard Methods (3), except for the "volatile acids" test (4). Laboratory analyses were conducted on samples withdrawn from the various levels of the filters to determine: COD, pH, total alkalinity, total, volatile, suspended and dissolved solids, volatile acids, sulfates and sulfides. Total gas production was measured daily by reading a volumetrically calibrated bottle containing an acidified salt solution (5).

Volatile acids were determined by the method described by DiLallo and Albertson (4). This method may have caused a problem in determining low

volatile acid concentrations. Effluent volatile acid concentrations were produced in small quantities, as would be expected, when compared to the column influent. The small quantities that did appear in the column may not have been volatile acids at all. These values may represent the quantity of base alkalinity measured by the particular test used. The DiLallo and Albertson method was developed originally for anaerobic digesters treating sewage solids. The authors recognized the interference of the phosphate ion in their test. What appears as the low volatile acids concentrations may actually be mono- and dibasic phosphates used as nutrient supplements in the waste feed makeup. Therefore, in this investigation volatile acid concentrations were used to form a trend and not to define exact amounts.

Waste Description - This organic chemically synthesized pharmaceutical waste was selected primarily because it satisfied the prerequisites for treatment with the anaerobic filter by having a relatively high COD and low suspended solids. The wastewater employed in this study originated from a synthesized organic chemical manufacturing plant and was collected by grab sampling. The samples were immediately taken back to the Syracuse University Environmental Research Laboratory and stored in a walk-in cooler, which was maintained at 4°C to inhibit biological activity.

Prior to any experimentation, a laboratory analysis was performed to determine the general character of the waste and to establish a required pretreatment scheme. The analysis indicated that the waste was either nitrogen or phosphorus limited or both (See Table 1).

To provide sufficient nutrients for unhindered anaerobic growth, nitrogen and phosphorus were added when needed to feed solutions as they were prepared. The C:N:P ratio was used 150:15:1, which was the minimum value reported in the literature (9) that would support unhindered anaerobic growth.

It can be seen (Table 1) that the pH of this waste was low, COD was high, suspended solids were low and dissolved solids were high. Most parameters varied from sample to sample. The BOD_5 values indicated the possibility of toxicity. With increasing dilution, there was increasing BOD_5 (6, 7, 9).

Starting the Filter - As soon as the filters reached a "steady-state" condition (continuous COD reductions within a range of $\pm$10 percent), they were acclimated to the pharmaceutical waste by gradually replacing a portion of the methanol organic load with pharmaceutical waste. By the end of week 30, all filters were receiving a substrate comprised totally of pharmaceutical

waste diluted to 2000 mg/l COD.

RESULTS

Response for Starting Procedures - The response for starting procedures as indicated in Figure 2 was rapid. All six reactors operating initially on 2000 mg/l of methanol as COD with the addition of trace nutrients, at a feed rate of 5.28 l/day, produced stable gas production, COD removal and effluent volatile acid levels by approximately the seventh week. Filter 4 did not recover as fast as the others as shown in Figure 2. To improve gas production, the effluent from filter 6 was introduced into the influent of filter 4. Following this action, gas production improved substantially. The probable reason for the increase in gas production was the reintroduction of active microbial cell mass lost from filter 6. At this time (week 7) the conversion from methanol to pharmaceutical waste was started with appropriate amounts of nitrogen and phosphorus added as needed. The drop in gas production and the increase in effluent volatile acid (Figure 3) and COD concentrations corresponded approximately to the period of conversion for the specific stage in the experiment.

Response to Change in Methanol and Pharmaceutical Waste - Figures 2 through 5 graphically depict performance throughout the period of investigation. The percentages of methanol and waste are shown across the top of each graph. The hydraulic retention time as described in Table 2 was kept constant at 36 hr. During the first 27 weeks of operation, all filters were fed varying amounts of methanol and waste to try to determine the threshold level of toxicity. Examination of the figures reveals a trend to increasing treatment efficiency with increasing percentages of pharmaceutical waste.

The filter response to loading changes as indicated by gas production and effluent COD is illustrated in Figure 2. Gas measurements were recorded in terms of standard temperature and pressure (STP). Measurements were taken daily, and the data plotted represented weekly averages of these daily readings. For the organic loadings at 34.9 lb. COD/1000 cu. ft./day (0.56 kg COD/cu m/day) changes were characterized by slight drops in gas production with corresponding increases in effluent COD concentrations. By the next week, these parameters were back to "steady-state" levels. For the organic loadings at 104.6 lb. COD/1000 cu. ft./day (1.67 kg COD/cu m/day) changes were characterized by drastic decreases in gas production with correspondingly large increases in effluent COD concentration. This organic loading was

monitored until the termination of the investigation, when the filter performance was judged to be impaired.

The effluent COD concentrations in Figure 2 shows that immediately following a waste composition change the effluent COD concentration increased while gas production decreased for a period of time then returned to "steady-state" levels. The increases in effluent COD concentrations appeared to be affected by changes in influent substrate composition in combination with line plugging. Figure 3 indicated that effluent volatile acid fluctuation followed very closely the pattern set by effluent COD concentrations.

Effluent suspended solids for all filters were usually below 50 mg/l as shown in Figure 4. The two major factors that affected solids loss appeared to be abrupt opening of the influent fittings after being clogged, and changes in the percentages of methanol and wastes.

Effluent Quality - The effluent was normally a pale yellow colored liquid except in times of upset and solids washout, when it appeared to be grayish in color. When filters 1 and 2 were fed waste at a concentration of 6000 mg/l COD, the effluent seemed to have a reddish-brown tint. Throughout the project, a disagreeable color was produced which was attributed to the reduction of sulfates present in the waste or dilution water.

As can be seen from Figure 6, the main conversion of sulfates to sulfides took place within the first six in. (2.36 cm) of the filter. Material balance requires that the total sulfur in the column must be constant; that is, the molar concentration of sulfate plus sulfide must be independent of height in the column (except for presumably negligible amounts of other sulfur compounds). In Figure 6, then the graph of $\frac{SO_4^{=}}{3} + S^{=}$ versus column height theoretically should be a horizontal line. To the contrary, it was found that there was a deviation in a downward direction from the horizontal. Therefore, approximately 100 mg/l of sulfur had to be accounted for in the effluent. The effluent was tested for concentrations of sulfites (3). It was found that there were only 15 mg/l as $SO^{=}_3$. The most probable explanations of these phenomena was that sulfides or sulfates or both were precipitated by some component or components of the waste stream, possibly including heavy metal cations, but more likely calcium and magnesium.

COD removal efficiences ranged from 94% during the 100% methanol acclimation period to a constant 70% to 80% reduction when fed 100% waste at

2000 mg/l COD. Once influent waste concentrations in filters 1 and 2 were increased to 6000 mg/l COD, gas production decreased rapidly and only an 18% COD reduction was observed.

Biological Solids - Observations of the physical characteristics of the solids within the filters indicated that these solids are primarily attached to the surfaces of the filter medium, but may also lie loosely in the void spaces. The solids appeared to be densely flocculated and were not easily disturbed by rising substrate or gas bubbles. Solids concentrations were highest in the lower levels of the columns.

"Steady-State" Operation - Theoretically, "steady-state" conditions 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 remain constant for an indefinite period of time. Young's (10) investigation with the anaerobic filter concluded that "steady-state" conditions in the strictest sense of the word are probably never attained because of the continual state of fluctuation within the system. For this study, "steady-state" conditions were assumed to exist when relatively stable COD reductions were produced in a range of $\pm$ 10% of the previous week's values. At 100% methanol COD reductions were averaging 94%. When being acclimated to the pharamaceutical waste, gas production decreased and effluent COD increased until with 100% waste at 2000 mg/l COD, constant COD reduction ranging from 70% to 80% were attained.

As seen in Figure 5, influent and effluent alkalinity pH loads were relatively constant throughout the study. It would appear that the columns had a damping effect on variation in influent pH and variations in it. Two units did not affect operations.

Existing Treatment vs. Anaerobic Treatment - The waste used in this study is currently treated by first putting it into an equalization basin with a retention time that is highly variable, but it essentially serves as a holding basin for the entire waste flow of the plant. From this basin waste goes to an aerated lagoon where it is held for eight days. Influent to this lagoon is approximately 6000 mg/l as COD. This influent concentration is maintained by mixing solution water from the plant with it. From this aeration basin, the effluent goes to a third holding basin for the final several days of sedimentation and release. At this point the effluent contains approximately 1000 mg/l COD. The effluent is a dark "tea" color and is released to

the receiving stream after mixing with a sufficient quantity of water to dilute it to levels acceptable by the State of New York. By computing the value of COD removed, one finds 5,213 lb. COD/mg/day are removed (8.96×10^{-6} kg COD/cu. m/day). The anaerobic filter utilized in this study had a 1.5 day retention time with a COD influent concentration of 2000 mg/l. The effluent from this treatment contains approximately 600 mg/l COD. Correspondingly, the anaerobic filter removed 7,784 lb. COD/mg/day (1.34×10^{-5} kg COD/cu. m/day) and required only 20% of the hydraulic retention time. The anaerobic filter was therefore 33% more efficient than the existing treatment scheme. Furthermore, the anaerobic filter effluent was virtually colorless surpassing existing treatment systems in color removal.

Summary of Filter Performance - In summary, the anaerobic filter would be very useful as a pretreatment device for the treatment of a chemically synthesized pharmaceutical waste. For an organic loading of 34.9 lb COD/1000 cu. ft./day (0.56 kg COD/cu. m./day) at a waste strength of 2000 mg/l "steady-state" COD removals ranged from 70 to 80% and BOD_5 removals 94%. At 104.6 lb. COD/1000 cu. ft./day (1.67 kg COD/cu. m./day) at a waste strength of 6000 mg/l COD removals averaged 18% probably due to the short acclimation period to a very strong, possibly, toxic waste. 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 waste efficiently without the need for solids recycle or solids wasting.

Conclusions - The anaerobic filter successfully treated the pharmaceutical waste at an influent COD concentration of 2000 mg/l when operated at 35°C utilizing a 36 hour hydraulic retention time, while producing constant COD removal efficiencies of 70 to 80% and BOD_5 removals of 94%.

The anaerobic filter exceeded the existing treatment scheme by 33% in terms of lb. COD/MG/day removed, and also greatly reduced the effluent color.

The anaerobic filter could not withstand a three-fold concentration increase as a shock loading as evidenced by 18% COD and 25% BOD_5 reductions, while feeding an influent COD concentration of 6000 mg/l at a 36 hour hydraulic retention time.

Anaerobic systems seem to be good for almost everything. Research repeatedly shows that they are not highly sensitive to either waste strength or the existing physical conditions. Rumors of their sensitivity fly in the

face of the evidence of well-run plants such as the city of Chicago's which has never had an upset digester in 50 years. The system itself is energy sufficient. Once it is started, it can be left out of operation for months at a time and then gotten back on the line in a few weeks. As this study shows, it can beat an aerobic system in a side-by-side comparison. The system appears to be good for almost every practical use.

The question then must be asked - Why are anaerobic systems not used today, except as an interesting laboratory study or an occasional treatment system put up by daring industry?

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Appreciation also goes to Ms. Anna McLean for her help in preparing this manuscript.

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TABLE 1: PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE PHARMACEUTICAL WASTE

PARAMETER	SAMPLE 1	SAMPLE 2
pH	1.5	1.6
COD (mg/l)	70,700	87,800
Total Solids (mg/l)	42,120	28,218
Total Volatile Solids (mg/l)	24,610	15,310
Total Suspended Solids (mg/l)	124	125
Total Dissolved Volatile Solids (mg/l)	24,510	15,240
Alkalinity (mg/l as $CaCO_3$)	0	0
Nitrogen (mg/l)		
Ammonia	996	184
Organic	1,021	440
Phosphorus (mg/l)		
Total	0.2	< 0.1
Sulfates (mg/l)	1,430	3,520
Acidity to pH 8.3 (mg/l as $CaCO_3$)	51,250	53,860
BOD_5 (Neutralized to pH 7) (mg/l)		

*D.F.	Sample 1	Sample 2
300,000	300,000	150,000
100,000	40,000	60,000
30,000	37,000	46,500
10,000	33,000	45,700
6,000	31,000	—

*D.F. = Dilution Factor - $\frac{300}{\text{volume of sample}}$ x 100

TABLE 2: ORGANIC LOADINGS CORRESPONDING TO VARIOUS WASTE STRENGTHS AND HYDRAULIC FLOW RATE USED IN THE EXPERIMENTAL STUDY

HYDRAULIC FLOW RATE				WASTE STRENGTH (mg/l COD)	
Detention Time (hrs)(a)	Liters/ Filter/ Day	Liters/ ft^2/ Day(b)	Gallons/ ft^2/ Day	2000	6000
				ORGANIC LOAD (lb. COD/1000 ft^3/Day) (c)	
36	5.28	32.00	8.45	34.9	104.6

(a) Based on 0.28 cu. ft. (8.04 liters) initial void volume
(b) Based on cross-sectional area of filter 0.165 ft^2 (0.015 m^2)
(c) 0.016 x lb COD/1000 ft^3/Day = kg/cu m/Day

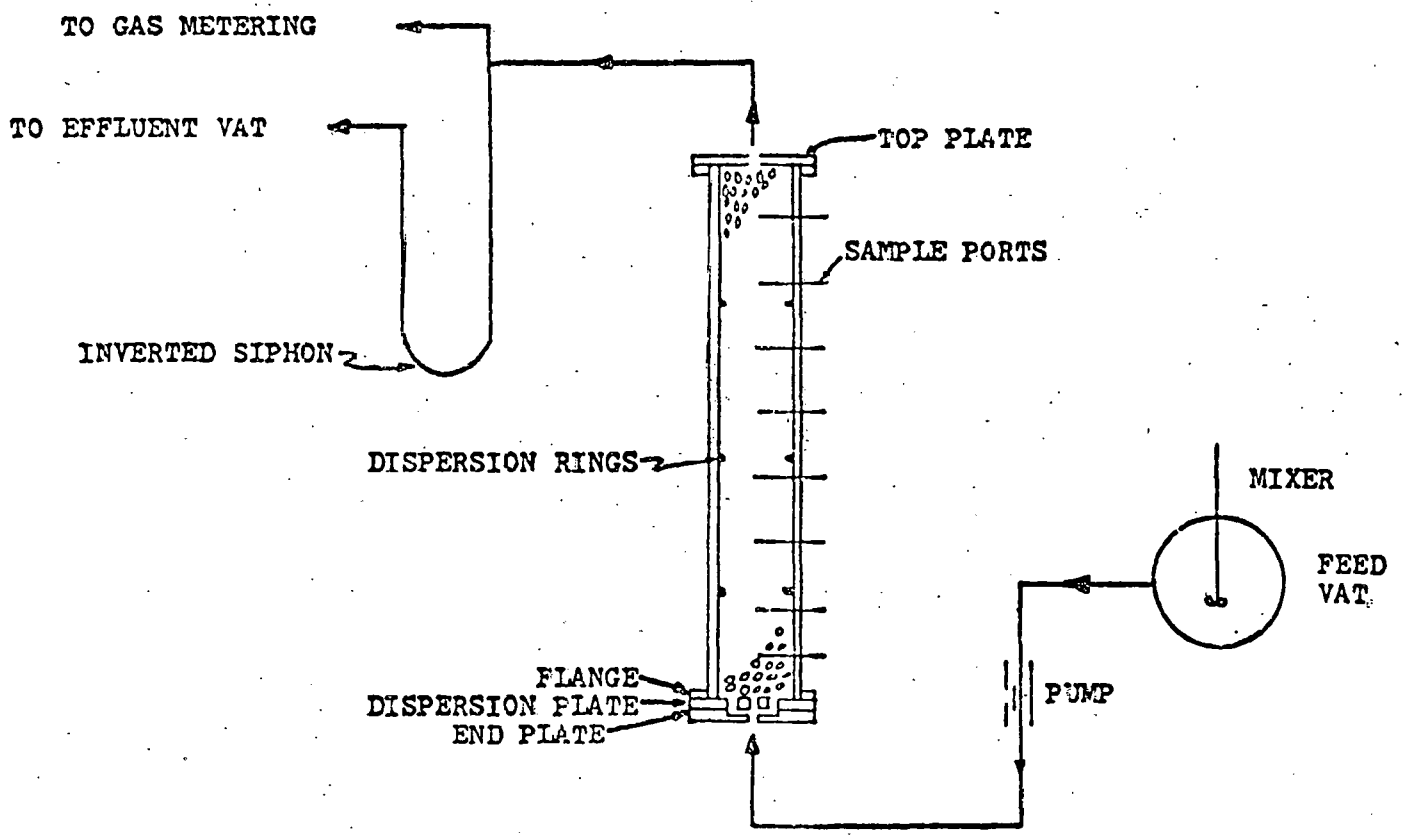


FIGURE 1 - SCHEMATIC DIAGRAM OF ANAEROBIC FILTER AND FEED SYSTEM
(Not To Scale) [After Seeler (6)]

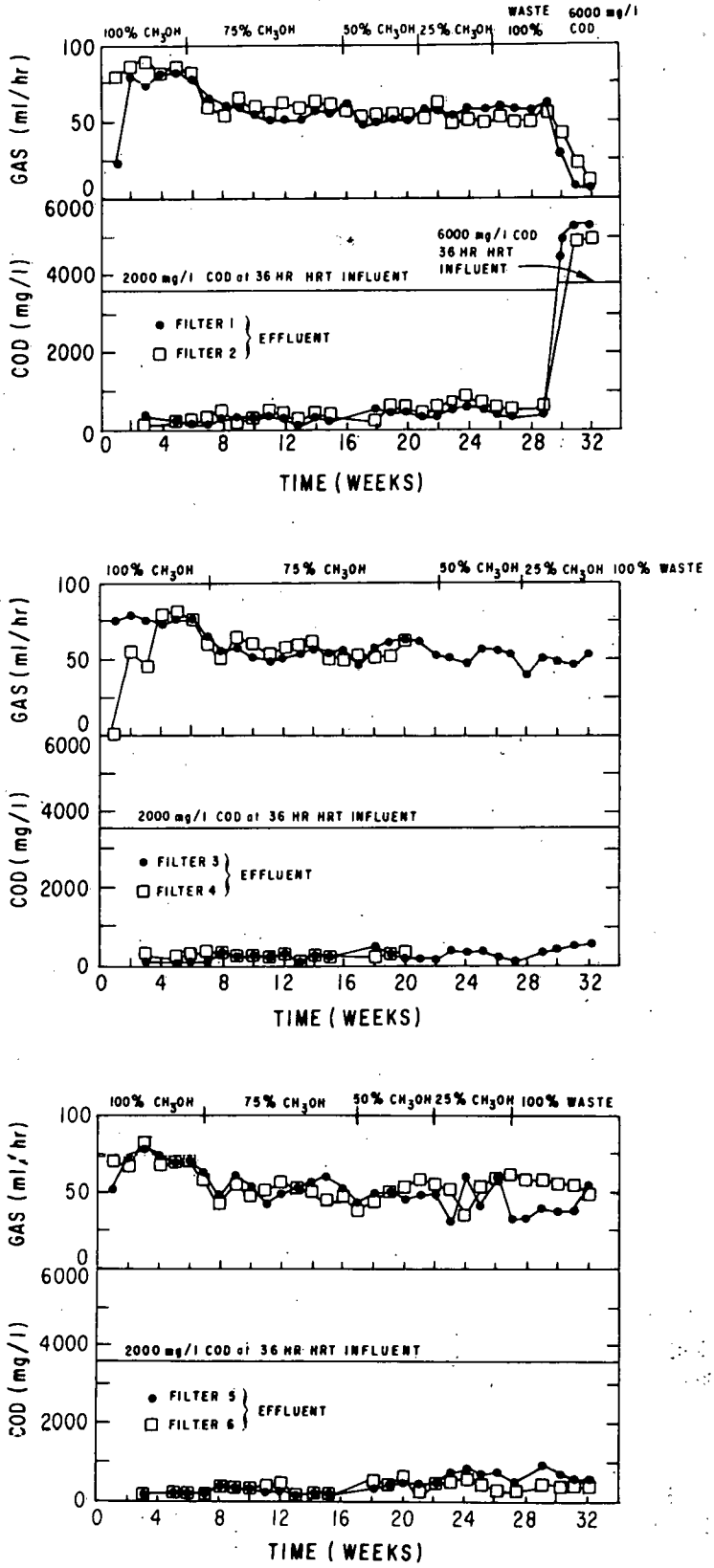


FIGURE 2 - INFLUENT AND EFFLUENT CHEMICAL OXYGEN DEMAND AND GAS PRODUCTION FOR ALL COLUMNS

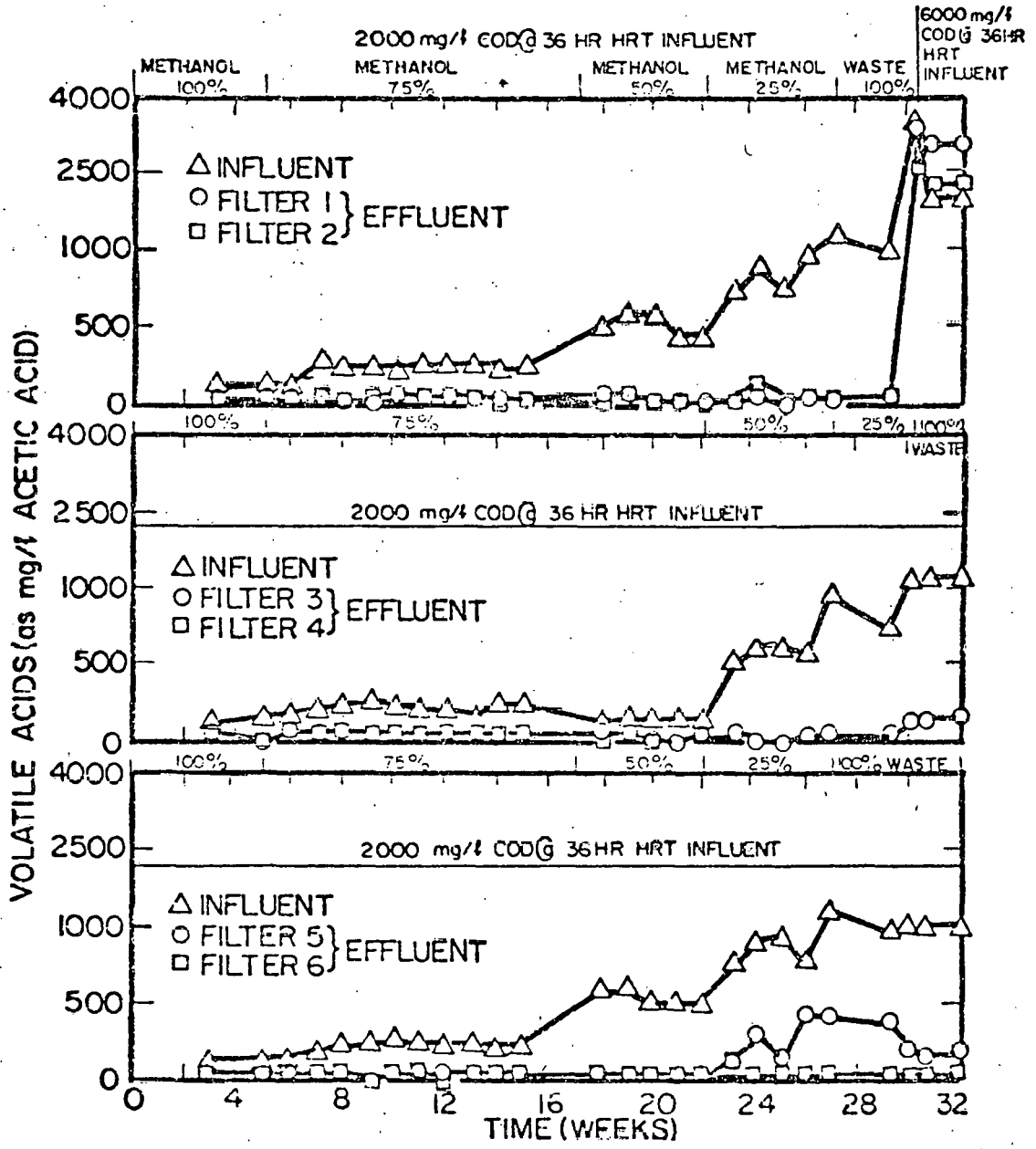


FIGURE 3 - INFLUENT AND EFFLUENT VOLATILE ACIDS

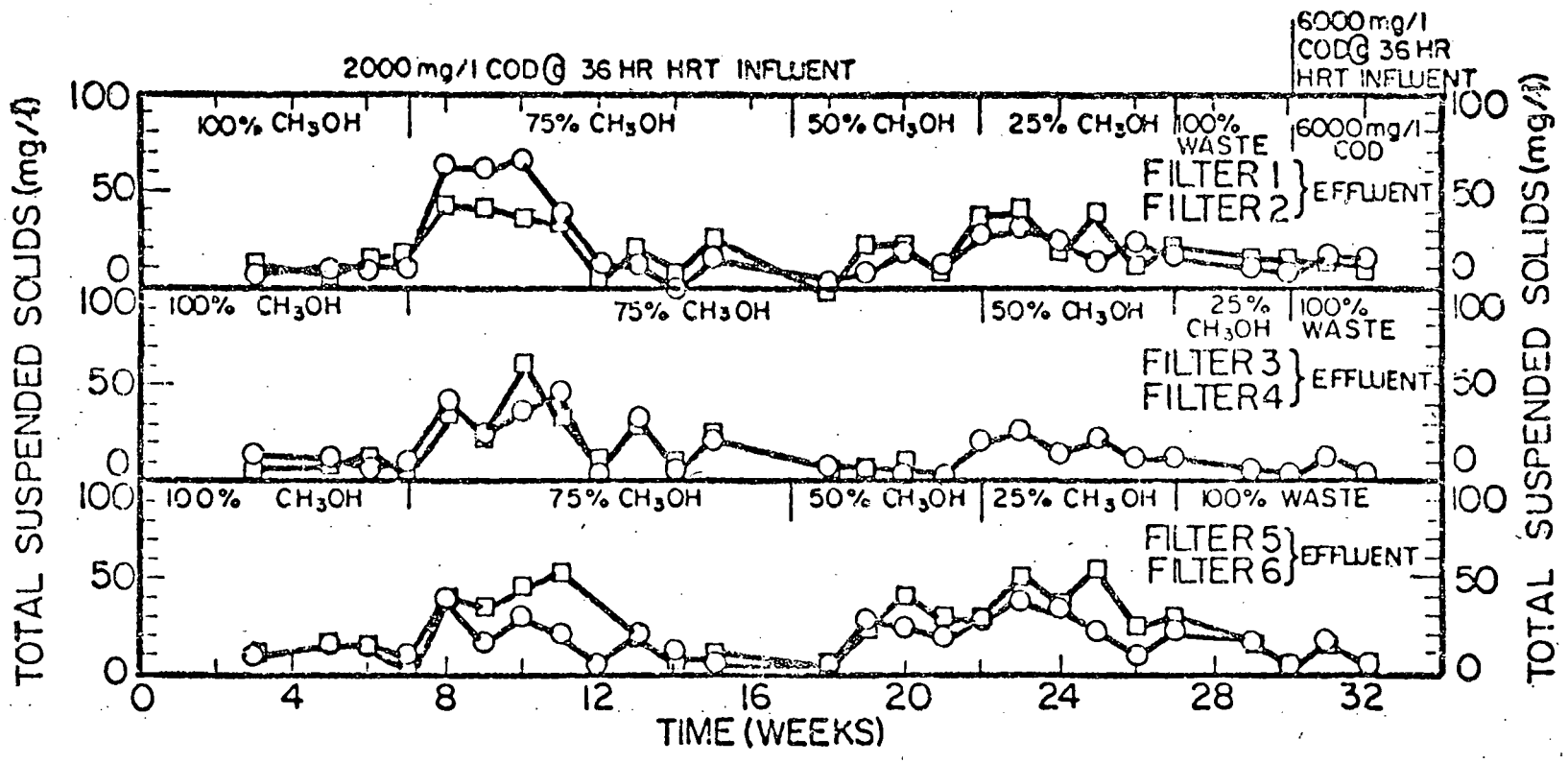
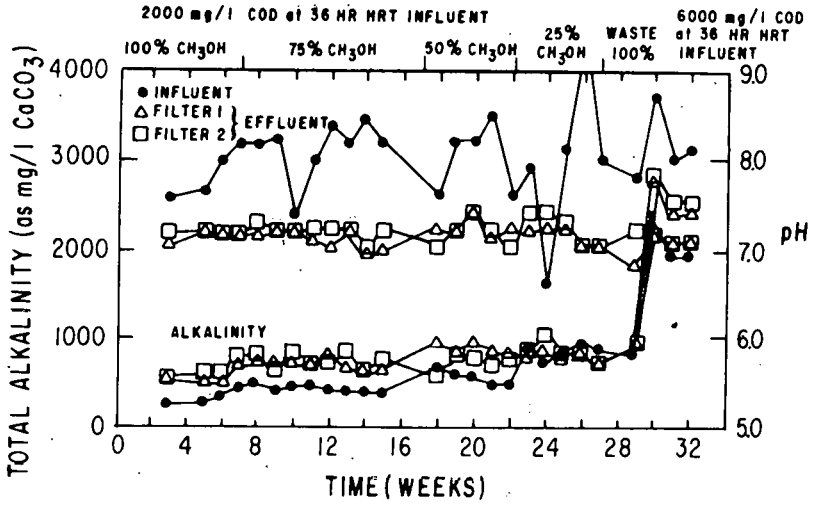
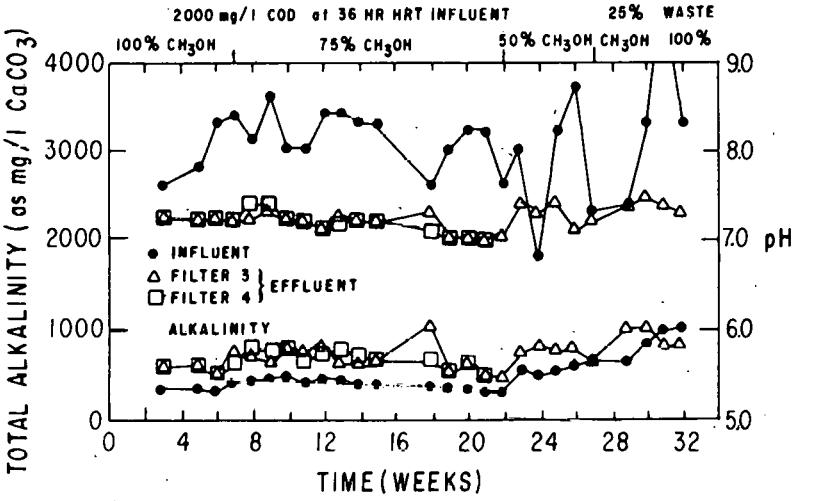


FIGURE 4 - EFFLUENT TOTAL SUSPENDED SOLIDS





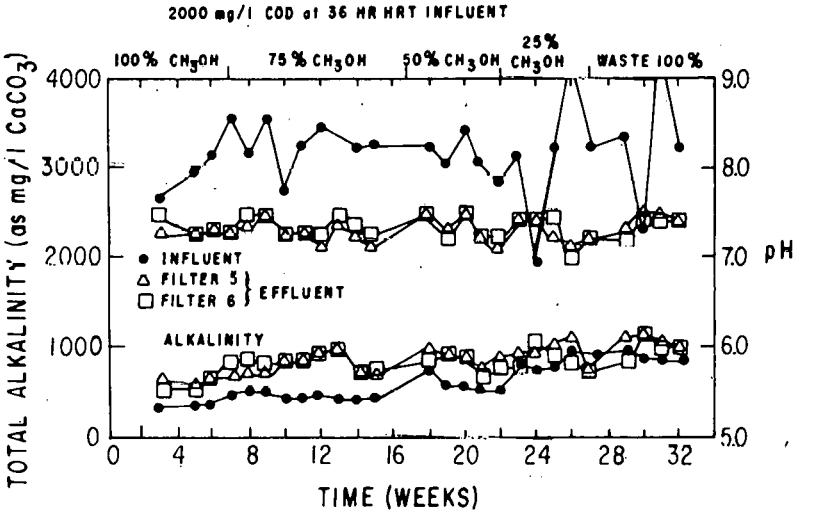


FIGURE 5 - INFLUENT AND EFFLUENT ALKALINITY AND pH FOR ALL COLUMNS

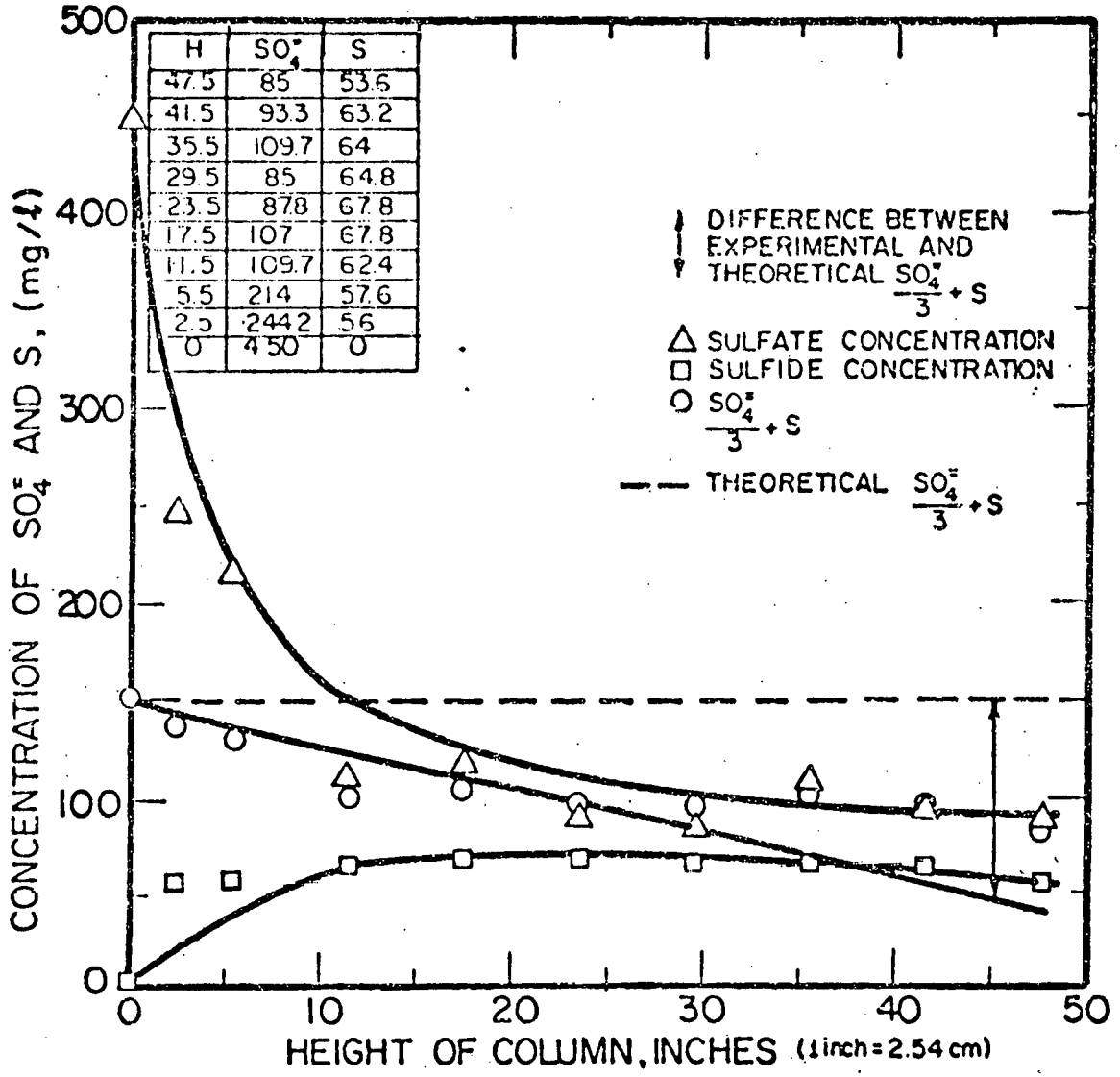


FIGURE 6 - SULFATE TO SULFIDE CONVERSION WITH FILTER HEIGHT

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NEW OBSERVATIONS WITH ANAEROBIC FIXED FILM REACTORS

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ABSTRACT

The treatment of high strength wastewaters by fixed film anaerobic systems is dependent upon a complex series of reactions and interactions. This presentation will describe (1) the anaerobic rotating biological contactor (AnRBC), a new reactor configuration that can be used to conveniently separate some metabolic activities for research purposes and (2) some preliminary and unexpected observations obtained from pilot anaerobic filters treating tannery wastewaters.

AnRBC stage data obtained with high strength carbonaceous wastewaters (2900 to 8100 mg/l COD) under a variety of loading conditions (nominal hydraulic detention times ranging from 2.2 to 17.5 hours) will be presented to indicate how the AnRBC can be used to evaluate phase separation effects on treatment, gas production, gas composition, etc. These studies conclusively show that the majority of the microorganisms in the AnRBC reactor are fixed to rotating surfaces and hence organic removal is clearly a function of available surface area and loading conditions for the treatment of these high strength wastewaters.

On the contrary, preliminary data obtained with anaerobic filters constructed with defined media treating beam house wastewaters from a tannery (COD ≈ 3000 mg/l) indicate maximum COD removals of 40 to 50% for this highly proteinaceous wastewater with a 24 hour contact time regardless of the surface area available. However, deamination and protein degradation routinely exceeded 60 percent. After six months of operation the columns plugged. While systems modification with a strong recycle stream appears to have eliminated the plugging problem, COD removal has not improved. Gas production, COD removal, nitrogen conversion and sulfide data will be presented for several loading conditions. Preliminary findings also indicate that the anaerobic filter effluent is much more amenable to aerobic polishing treatment than the raw beamhouse wastewater.

INTRODUCTION

Anaerobic systems are currently receiving a great deal of attention for the treatment of a wide variety of wastewaters. Freedom from oxygen transfer rate limitations and the potential for energy recovery make anaerobic processes particularly attractive for the treatment of high strength wastewaters as a result of rapidly escalating energy and capital costs. Decades of empirical design and abusive operation of traditional anaerobic sludge treatment processes have resulted in a legacy of myths concerning the difficulties associated with these processes. However, research efforts during the past fifteen years are eradicating these myths at an accelerating rate. The knowledge and understanding obtained from this ongoing research is rapidly being applied to the development of innovative anaerobic processes that show great promise for cost effective wastewater treatment.

Several innovative variations of anaerobic fixed film (AnFF) processes have been and are currently being applied to a wide variety of wastewaters.

Development of high concentrations of fixed biomass in the reactor permits the use of relatively short hydraulic detention times for the treatment of high strength wastewaters. This results both in a reduction of energy loss through reactor walls and in a reduction of reactor capital cost relative to traditional suspended culture systems. Another advantage of AnFF processes appears to be their resistance to short term toxic slugs entering the system. However, much remains to be learned before anaerobic fixed film processes can

enjoy the popularity of conventional energy intensive aerobic processes with wastewater treatment plant designers.

The primary purpose of this paper is to present research results indicating that the potential for anaerobic fixed film wastewater treatment is waste specific. Secondary purposes include the description of several phenomena of importance to the development of predictive design equations and the introduction of the anaerobic rotating biological contactor (AnRBC) as a promising new variation of AnFF reactors.

REACTOR SYSTEMS

Two different types of anaerobic fixed film reactor systems were used with two wastewaters having widely differing characteristics. An easily degradeable carbohydrate wastewater containing ample known required nutrients was used to evaluate the AnRBC process while two anaerobic filters (AF) constructed with carefully defined media were used to treat a highly proteinaceous wastewater. It should be emphasized at this point, that the following data should not, and indeed cannot, be used to compare the merits of the two reactor systems.

AnRBC Reactor System

Conceptually the AnRBC is similar to conventional aerobic rotating biological contactors in that microorganisms become attached to and grow on rotating discs that are partially submerged in the wastewater as shown schematically in Figure 1. Groups of discs, separated into sequential compartments called stages, are partially immersed in the wastewater and rotated continuously both to provide mixing within each stage and to facilitate product gas transfer to the anoxic atmosphere maintained above the water surface. Adjacent stages are separated by baffles to minimize short-circuiting. The flow is passed from stage to stage through holes in the baffles below the waterline.

However, unlike conventional RBC units, the AnRBC is enclosed in an airtight housing with an anoxic atmosphere maintained above the liquid. Also, the depth of disc submergence is substantially greater than in conventional aerobic units. Microorganism attachment to the rotating surfaces provides long mean cell retention times in the reactor, which in turn encourages the development of the slow growing methanogenic bacteria responsible for the con-

version of low molecular weight compounds to methane. Sloughed excess biomass is carried from stage to stage through openings in the baffles and leaves the reactor in the effluent. Conceptually, the AnRBC process couples the advantages of the short hydraulic detention times typical for the fixed film horizontal flow RBC process with the high strength, carbonaceous degradation capabilities of anaerobic systems.

Two identical four stage pilot plants with their 5.0 inch disc diameters about 70 percent submerged in the wastewater were constructed and operated under quasi-steady state conditions. Each unit contained about 10.9 square feet of disc surface area which resulted in a nominal surface to volume ratio of about 41.2 Ft^2/Ft^3 (134.5 m^2/m^3). The wastewater used to evaluate this process contained dissolved sucrose as the only carbon source. Dissolved inorganic ammonium salts served as the sole nitrogen source in order to avoid nitrate reduction reactions in this series of experiments. The AnRBC data presented below resulted from a series of experiments with eight combinations of influent substrate concentration and flow rate. Construction details, reactor start-up, analytical procedures and operational details have been presented elsewhere (1, 2).

AF Reactor System

Two six-inch I.D. anaerobic upflow filters were constructed of clear acrylic plastic as shown in Figure 2. The biomass support media, Norton Company's "Actifil Plastic Bio-ring-25" were randomly packed and separated into six-inch lifts by divider plates. The nominal clean surface to volume ratio was about 56.8 Ft^2/Ft^3 (186 m^2/m^3). Sampling ports and media access hatches were located so that data characterizing each lift could be obtained. It was hoped that operating data obtained as a function of mid-lift elevations could be used to develop a descriptive anaerobic filter model based on areal reaction rates similar to the model proposed by Schroeder (3).

A constant influent feed rate of about 18 l/day provided a nominal clean bed hydraulic detention time of 24 hours. The filters plugged after six months of operation. A recycle system (Q_R/Q_I = 450) was then added, as shown in Figure 2. This high recycle ratio was designed to maintain a bulk upflow velocity of about one foot per minute in order to prevent plugging caused by inorganic precipitates formed in the reactor bed.

Experiments on pretreated tannery beamhouse wastewaters were conducted

with the anaerobic filters. The goals of this ongiong research project are to evaluate the effectiveness both of anaerobic treatment alone and anaerobic treatment followed by aerobic treatment (rotating biological contactors) as possible means for improving upon the existing cost and energy intensive aerobic wastewater treatment systems used by the tanning industry. Pretreatment consisted of neutralization and sedimentation of raw beamhouse wastewater, followed by dilution with tap water to obtain desired influent COD values. The resulting AF influent can be described as a highly proteinaceous poorly degradeable waste having the characteristics shown in Table 1. In addition, this wastewater is saturated with calcium.

RESULTS AND OBSERVATIONS

The AnRBC data presented below were obtained from a recently completed study designed to evaluate the concept and potential of a rotating fixed film anaerobic reactor. By contrast, the AF data and observations presented below represent only preliminary results obtained from a currently ongoing study designed to evaluate the application of anaerobic processes to the treatment of tannery wastewaters.

AnRBC Treatment Of A High Carbohydrate Wastewater

Both AnRBC reactors were operated for a period of 218 days until an O-ring seal failed and reactor fluids began leaking from a bearing. Experimentation was discontinued and both reactors were dismantled for inspection. Microbial solids were observed to coat all disc surfaces and decreased in thickness from the first through the fourth stages, with only a thin film layer present on the fourth stage discs.

Although the data presented in Figures 3-7 have been connected with a series of straight lines for emphasis, it should be noted that each stage is acting as an independent complete-mix reactor and that there are hydraulic and reaction discontinulties between adjacent stages. Total organic carbon (TOC) was the primary parameter used to evaluate the AnRBC process. Tests with this wastewater indicate BOD_5/TOC and COD/TOC ratios of 1.72 and 2.79 respectively.

Figure 3 illustrates the volatile acids alkalinity (VAA) generated in the first stage was accompanied by minor depressions of pH and carbonate alkallnity. About 80% of the TOC removal occured in the first stage. Both TOC and VAA

were further reduced in succeeding stages while the pH and alkalinity increased in the downstream direction. Note that the fourth stage did not contribute to TOC removal for this loading condition and apparently the hydraulic residence time in the reactor could have been reduced from 17.5 to about 13 hours with no loss in soluble TOC removal performance.

The results from Experiment 6, shown in Figure 4, are similar even though the organic loading rate has been increased by a factor of four and the reactor hydraulic detention time reduced to one-half that of Experiment 1 conditions. For this loading situation, the first stage removed about one-half the influent TOC. However, volatile acid production was more significant in the first stage. Note also that the fourth stage TOC and VAA concentrations were significantly higher, and that the overall soluble TOC removal was reduced from the 96% found in Experiment 1 to about 79% in Experiment 6. It is probable that additional stages would have resulted in more complete TOC removal.

Figure 5 illustrates the effects of a high loading rate and short hydraulic detention time on system performance. The organic loading rate in Experiment 4 was increased by a factor of about 8.5 compared to Experiment 1, with the hydraulic detention time being reduced to one-eighth that of the original conditions. The sharp drop in pH and alkalinity along with the high production of VAA suggests that acid fermentation occurred at a rate that overwhelmed the slower growing methanogenic bacteria in the system. Only 46% of the soluble TOC was removed under these loading conditions. The increase in VAA in the fourth stage may suggest that the fermentation process was inhibited by high concentrations of soluble substrate in the first three stages.

When the data from these experiments are arrayed as shown in Figures 5 and 6, the effects of influent feed concentration (C_i) and flow rate (Q) on performance can be observed. Figure 6 shows that increasing the flow rate (reducing the hydraulic detention time (θ)) for constant C_i conditions results in higher TOC concentrations at most points within the reactor. Under relatively low mass loading conditions (Experiments 1 and 2), effluents contained relatively low volatile acid concentrations. At the higher mass loading rates (Experiments 3 and 4), the effluents contained relatively high effluent volatile acid concentrations. Thus, an increase in the influent flow rate has the apparent effect of moving methane fermentation downstream in the reactor. Alternately, these data suggest that there might be a critical reactor hydraulic

detention time required to sustain effective methane fermentation. Based on these data, it appears that this critical time period is between 4.4 and 8.8 hours. Of special interest is the fact that the first stage substrate removal rates shown in Figures 6 and 7 are substantially higher than those reported for conventional aerobic RBC systems.

The data shown in Figure 7 can be used to compare TOC removal as a function of influent substrate concentration for constant flow rate conditions. As expected, it can be seen that the system requires more stages (area) to achieve a specific residual organic effluent concentration with increasing C_i values. Again, the first stage organic removal rates are substantially higher than those reported for conventional RBC treatment.

Mass loading and removal data are shown in Figure 8. Up to a loading of about 22 g TOC per day (21.7 g TOC per m^2-day), soluble TOC removal appears to be independent of either influent concentration or flow rate. Although a smooth curve could be passed through all the data points, a sharp discontinuity in soluble TOC removal exists near this limiting mass loading and it is evident that both additional increments of TOC removal and the overall percent removal are highly dependent on loading conditions.

Due to the small flow rates, gas production was difficult to monitor with the available equipment. However, as shown by the dashed line in Figure 9, a good linear correlation exists between soluble TOC removal and total gas production. When data from Experiments 4 and 8 are omitted because high VAA effluent concentrations indicate incomplete reactions, an even better correlation exists (solid line). Hence, total gas production can be conservatively estimated as 1.76 m^3/kg TOC removed. Methane and carbon dioxide were present in about even quantities for Experiments 1, 2, 5, and 7. The carbon dioxide content increased from 54% in Experiments 3 and 6, to about 60% in Experiments 4 and 8. These, along with the VAA, pH and TOC data, provide evidence that methanogenic activity was unable to proceed to completion under the higher loading conditions.

Models for the prediction of effluent solids production, substrate removal and energy yield have been developed and presented elsewhere (1, 2). The solid lines in Figures 10 and 11 indicate the ability of two empirically developed models to describe the AnRBC performance. The data scatter is surprisingly small considering that relatively simple methods are being used to describe the results of a complex series of anaerobic reactions which were

only partially complete for some of the loading conditions employed. Of course, the empirically determined constants used in these models are only valid for the experimental conditions employed. Additional studies will be required to develop fundamental relationships between these constants and substrate type, disc diameter, disc rotational speed, immersion depth, etc., before the full potential for AnRBC treatment can be evaluated.

AF Treatment of a High Strength Proteinaceous Wastewater: Preliminary Observations

The upflow anaerobic filters (AF) shown schematically in Figure 2 were operated both in recycle and non-recycle modes, with a clean bed hydraulic detention time of about 24 hours. The internal reactor temperatures were maintained at 35± 1°C with the exception indicated below.

Non-Recycle Operation

The filters were initially operated in a non-recycle mode with changes of soluble COD across the reactors and suspended solids concentrations within the reactors serving as the primary monitoring parameters. Start-up consisted of recycling anaerobic seed sludges obtained from another project along with increasing increments of tannery wastewater through the filters for about four weeks until solids attachment to the media was observed. The filters were operated in a non-recycle mode for the next six months. About two months were required to obtain quasi-steady state effluent data. However, since data obtained from several points within each filter indicated a continual increase in suspended solids with depth, operation was continued with hopes of achieving steady state operating conditions with respect to solids within each reactor. Unfortunately, the filters failed due to plugging with accumulated solids near the influent. Table 1 indicates the average influent and effluent parameter values measured during the six month operating period. Soluble COD and soluble BOD_5 removals across the filters averaged 32 and 5 percent respectively. Of special note was the substantial decrease in soluble protein across the column (79%). This rapid degradation of protein is also indicated by the change in reduced nitrogen forms across the filter.

The solids data presented in Table 1 suggest that inorganic solids in the influent represent one source for the solids that eventually led to a plugged filter. It is also possible that calcium precipitates formed in

the reactor and settled to the bottom eventually resulting in the plugging condition. Suspended solids data, obtained at the time of plugging, and shown in Table 2, indicate that solids had primarily accumulated and concentrated in the bottom six-inch lift of the filters. Of special interest is the change in the ratio of organic to inorganic solids as a function of filter height. Apparently, many of the denser inorganic solids could not be transported upward and out of the filter, due to the low bulk velocity through the reactor when operating in the non-recycle mode.

Recycle Operation

Following failure due to plugging, the filters were operated in an upflow recycle mode as shown in Figure 2. A recycle ratio (Q_r/Q_{in}) of 450 was selected to maintain a nominal bulk upflow velocity of about one foot per minute in the hope of being able to transport the heavier suspended solids upward and out of the reactors. Since the media had already been coated with biomass, less than a month was required to achieve quasi-steady state operation, as indicated by gas production, COD stabilization and solids data.

Table 3 presents the average of data obtained over two consecutive days, following a month's operation under quasi-steady state conditions. Total and soluble COD stabilization averaged about 32 and 26 percent respectively, while soluble BOD_5 and soluble BOD_{30} removals averaged about 13 and 39 percent respectively. Solids accumulation and destruction in the reactor appeared to be constant during the month's evaluation period. In addition, average total COD removals and influent solids concentrations were substantially higher than soluble COD removals and effluent solids concentrations. Based on these observations, it is apparent that substantial solids destruction was occurring in the AF. As with the non-recycle mode, substantial protein degradation was occurring, as indicated by both the protein data and the substantial increase in NH_3-N across the filter. The sulfide increase across the reactor is primarily attributable to sulfate reduction, although some sulfides may have been generated as a result of the breakdown of organic compounds and the release of organic sulfur.

At the completion of this portion of the study, the filters were drained and several media rings were carefully removed from different locations and examined. The media were totally coated with solids. Despite the very high recycle ratio employed, the solids coatings decreased in mass with in-

creasing elevation in the filters as shown in Table 4. The volatile suspended solids fraction was surprisingly low and relatively constant throughout both filters.

Soluble COD data taken at different points in the filters suggested only minor changes in soluble COD within the reactors. If future tests substantiate these COD measurements, filters operating at high recycle rates might best be described as completely mixed, fixed film reactors.

Total COD removal for the pretreated tannery wastewater in the AF appears to be a linear function of the mass of COD applied over the loading range investigated to date. As shown in Figure 12, removal averaged about 35 percent for a wide range of loading conditions prior to the system failure described below.

The slow biodegradeability of this wastewater under the aerobic conditions of the BOD test is illustrated by the curves in Figure 13. Each data point represents the average of four replicate measurements. Based on these long term BOD tests, it appears that the biodegradation reactions are not nearing completion at 30 days. However, it appears from this figure that the AF effluent is much more rapidly degraded than the filter influent stream. Obviously BOD_5 is an improper parameter for evaluating this process or the efficiency of its treatment by the AF process.

A comparison between the aerobic treatability of pre-treated beamhouse wastewaters and the AF effluents under nearly equal COD loading conditions in a bench scale rotating biological contactor (RBC) yielded nearly equal soluble COD removal patterns, as shown in Figure 14. The effluent quality did not improve substantially in terms of soluble COD removal when the disc area and hydraulic detention times were doubled for both wastewaters. Despite a 20 hour RBC detention time, this is apparently insufficient to alter the refractory materials contained in either waste stream. This is surprising, since nearly equal treatment was obtained with both wastewaters. Presumably the more biodegradeable organic fraction should have been removed in the columns, leaving difficult to treat refractory materials for the following aerobic process. However, the combination of AF-RBC process removed substantially more COD than could be removed by the RBC process alone. Apparently the anaerobic process resulted in the conversion of some difficult to degrade COD to a morebiodegradeable form within the filters. This suggests that fixed film anaerobic processes have an important role as pretreatment systems for diffi-

cult to treat wastewaters.

OTHER OBSERVATIONS

Several incidents during the course of these experiments indicate the resistance of anaerobic fixed film reactors to presumed toxic or inhibitory conditions. Air was accidentally pumped through both the AnRBC and AF reactors for periods up to eight hours as a result of burst feed lines. Both reactors completely recovered within forty-eight hours. Mechanical failure of the controlled temperature room resulted in a temperature drop to about 20°C for twenty four hours during the AF experiments. Gas production was drastically curtailed, but recovery was complete within the following twenty-four hours. These examples illustrate the ability of anaerobic systems to quickly recover from temporary shocks.

However, we have also recently seen what is thus far an unexplained failure with the AF process. Following the completion of the 3000 mg/l COD loading experiments, the feed concentration to the anaerobic filters was incrementally increased to 6000 mg/l over a two week period. Several monitoring parameters such as pH, COD removal and gas production indicated that the filters could readily accept this increased load without adverse effects. Two weeks of stable operation followed, with nearly constant COD removal rates, pH, alkalinity and gas production. However, during the next two weeks, total COD removal decreased from more than 35 percent to less than 5 percent and total gas production dropped to near zero. The decrease in overall COD removal was accompanied by an accumulation of soluble COD in the reactors. This suggests that methane fermentation activity had been curtailed. However, neither drastic pH or alkalinity changes, the usual warning symptoms of anaerobic process failure, were noted during the two week failure period. The inhibition and/or toxicity effects on column performance could be due to relatively high sulfide or ammonia concentrations in the reactor, a synergystic effect between those two reported toxicants, or the absence of a critical nutrient. A series of batch reactor side experiments that may define the reasons for failure has been initiated. At the present time the filters are being reseeded with newly acclimated microorganisms.

As a final observation, it should be emphasized that attached growth predominated in the AF with recycle reactor as it did in the AnRBC reactor. This implies that predictive equations based on areal removal rates will

probably include a specific area term as a fundamental parameter for design.

CONCLUSIONS

Anaerobic fixed film processes have an important emerging role in the treatment of high strength wastewaters. The AnRBC data suggested that simple high organic strength wastewaters can be effectively treated with short hydraulic detention times. At this time, there appears to be a limiting mass loading rate of about 22 grams TOC/m^2/day that will result in nearly complete organic stabilization for simple substrates. Surprisingly, simple empirical equations have been developed that can serve as predictive models for design until more fundamental relationships are developed.

On the other hand, the full potential for the anaerobic fixed film treatment of complex substrates, such as the tannery derived wastewater described previously, is still to be determined. Based on the preliminary findings reported here, it appears at this time that an anaerobic fixed film process may have the potential to substantially improve the treatment of these complex wastewaters, compared to energy intensive aerobic alternatives currently available. Much additional research and development work needs to be done in order to describe the advantages and disadvantages of AnFF processes before they can be applied to a wide variety of wastewaters.

ACKNOWLEDGEMENTS

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TABLE 1.

ANAEROBIC FILTER TREATMENT OF MODIFIED BEAMHOUSE WASTEWATER - NO RECYCLE

PARAMETER	INFLUENT	EFFLUENT
SOLUBLE COD[1]	2650 MG/L	1790 MG/L
SOLUBLE PROTEIN[2]	2430 MG/L	510 MG/L
SOLUBLE ORGANIC-N[1]	165 MG/L	95 MG/L
SOLUBLE NH_3-N[1]	60 MG/L	170 MG/L
TOTAL SUSPENDED SOLIDS	490 MG/L	60 MG/L
VOLATILE SUSPENDED SOLIDS	270 MG/L	50 MG/L
SOLUBLE BOD_5[1]	610 MG/L	580 MG/L
PH	7.4	7.1

1. Based on separations made with Whatman GF/C Filters
2. Measured by Folin reagent colormetric test

TABLE 2.

AF SUSPENDED SOLIDS PROFILE AT TIME OF PLUGGING, NO RECYCLE

DEPTH FROM BOTTOM (INCHES)	TOTAL SUSPENDED SOLIDS (MG/L)	VOLATILE SUSPENDED SOLIDS (MG/L)	PERCENT VOLATILE (%)
0	610	400	66
2	30,980	13,700	44
11	230	140	61
23	110	90	82
35	80	70	88
44	70	70	95*

* Estimated, VSS Measurement only good to ±10 MG/L
** Both columns plugged simultaneously. Data are average for the two columns.

TABLE 3.

ANAEROBIC FILTER TREATMENT OF MODIFIED BEAMHOUSE WASTEWATER WITH RECYCLE ≈ 450:1

PARAMETER	INFLUENT	EFFLUENT
SOLUBLE COD[1]	2230 MG/L	1660 MG/L
TOTAL COD	2980 MG/L	2020 MG/L
SOLUBLE BOD_5[1]	470 MG/L	410 MG/L
SOLUBLE BOD_{30}[1]	1300 MG/L	795 MG/L
SOLUBLE PROTEIN[1]	2200 MG/L	1440 MG/L
SOLUBLE ORGANIC-N[1]	150 MG/L	70 MG/L
SOLUBLE NH_3-N[1]	50 MG/L	130 MG/L
TOTAL SULFIDES	50 MG/L	200 MG/L
TOTAL SUSPENDED SOLIDS[1]	520 MG/L	340 MG/L
VOLATILE SUSPENDED SOLIDS[1]	430 MG/L	250 MG/L
PH	6.5	6.5

1. Based on separations made with Whatman GF/C Filters.
2. Measured by Folin reagent colormetric test.

TABLE 4.

ATTACHED SOLIDS PROFILE IN AF WITH Q_R/Q_I = 450

DEPTH FROM BOTTOM (INCHES)	TOTAL SUSPENDED SOLIDS (MG/FT^2)	VOLATILE SUSPENDED SOLIDS (MG/FT^2)	PERCENT VOLATILE (%)
4	18,480	4940	27
21	11,610	2800	24
39	9,030	2580	29

Values are averages from both columns.

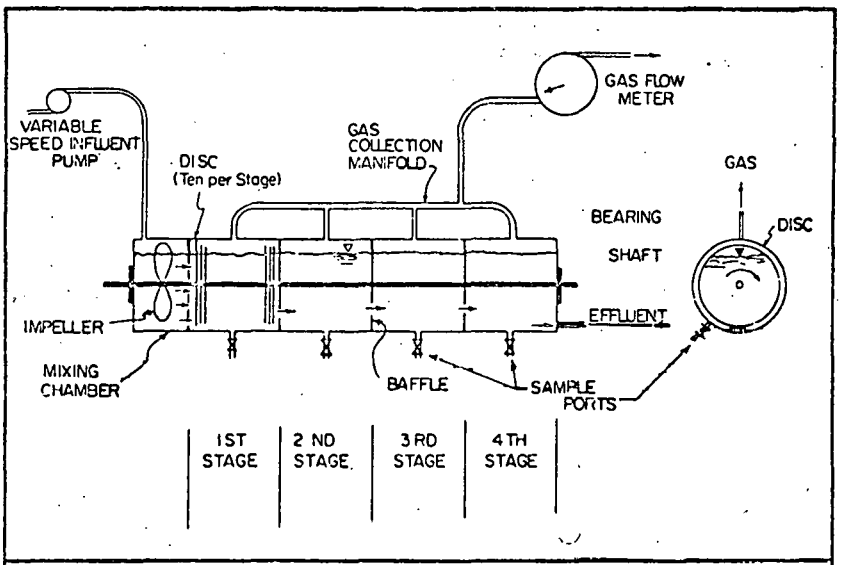

FIGURE 1 ANAEROBIC ROTATING BIOLOGICAL CONTACTOR

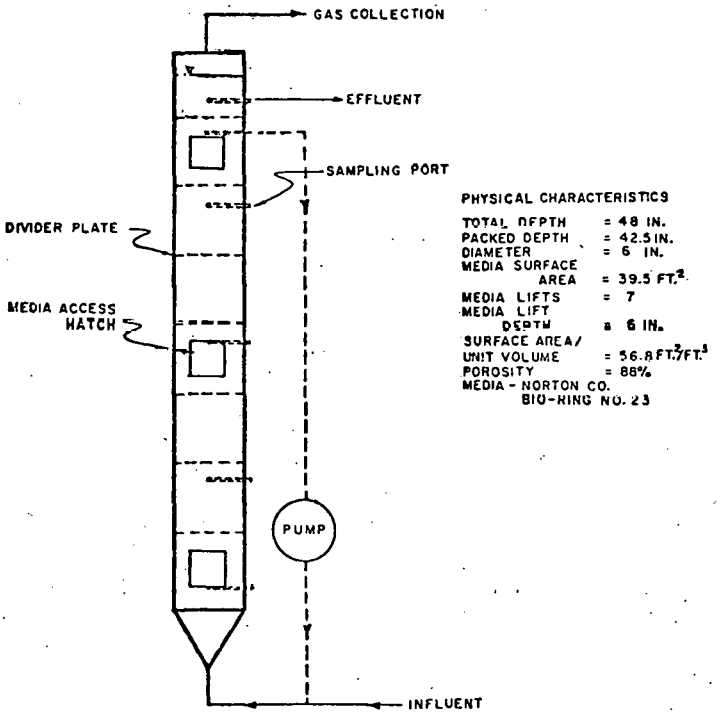

FIGURE 2. ANAEROBIC FILTER SCHEMATIC

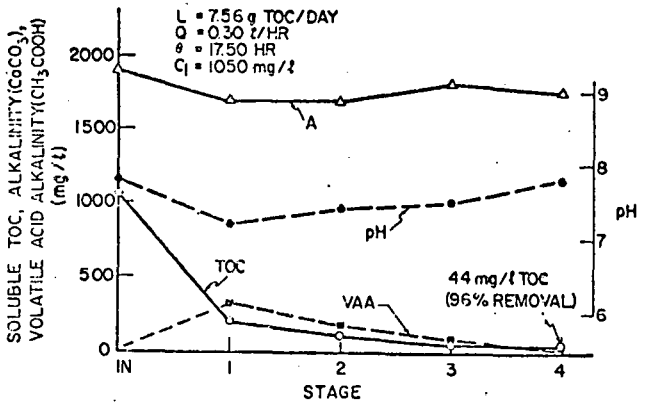

FIGURE 3 EXPERIMENT 3, IF-1H

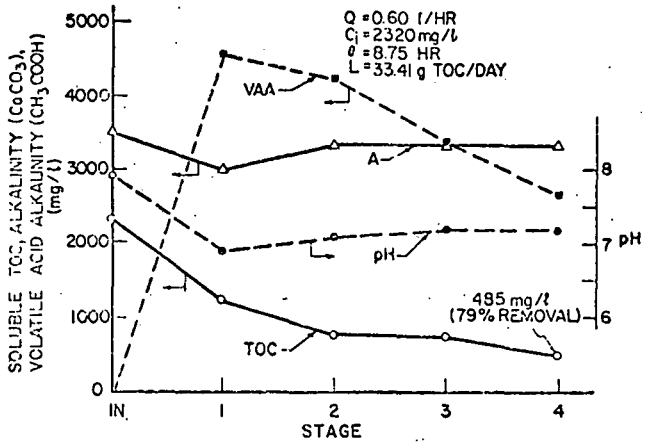

FIGURE 4 EXPERIMENT 6, 2F-2H

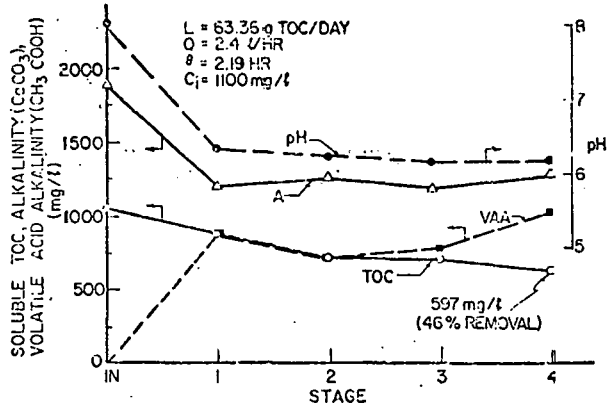

FIGURE 5 EXPERIMENT 4, IF-8H

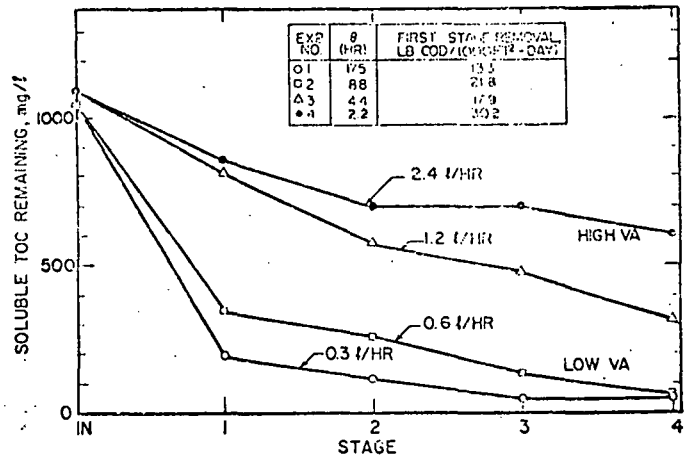

FIGURE 6 EFFECT OF FLOW RATE ON An RBC TREATMENT

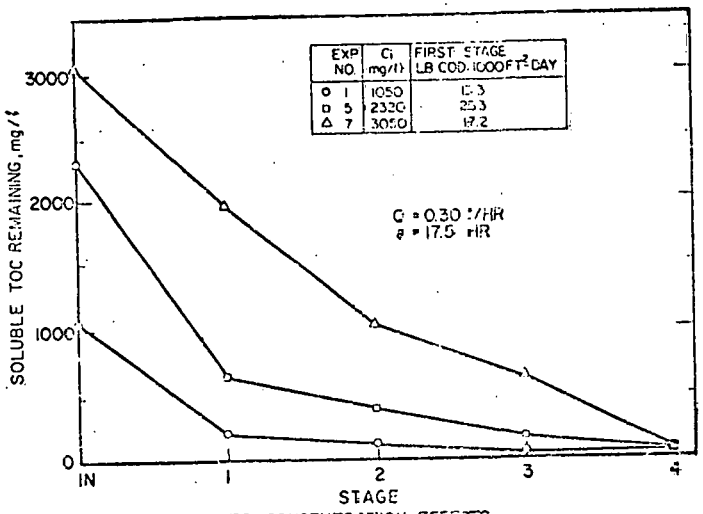

FIGURE 7. SUBSTRATE CONCENTRATION EFFECTS

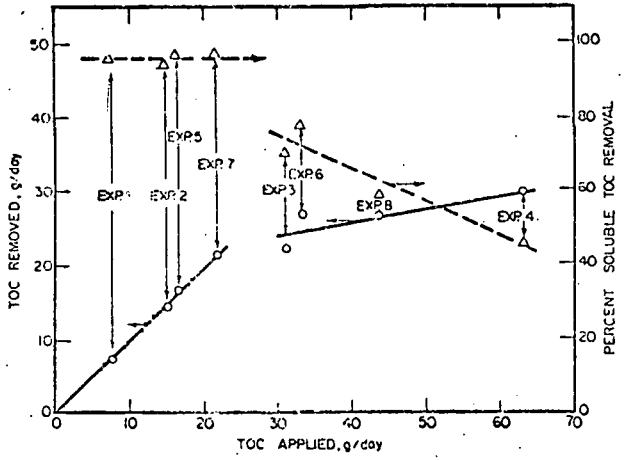

FIGURE 8. SOLUBLE TOC REMOVAL

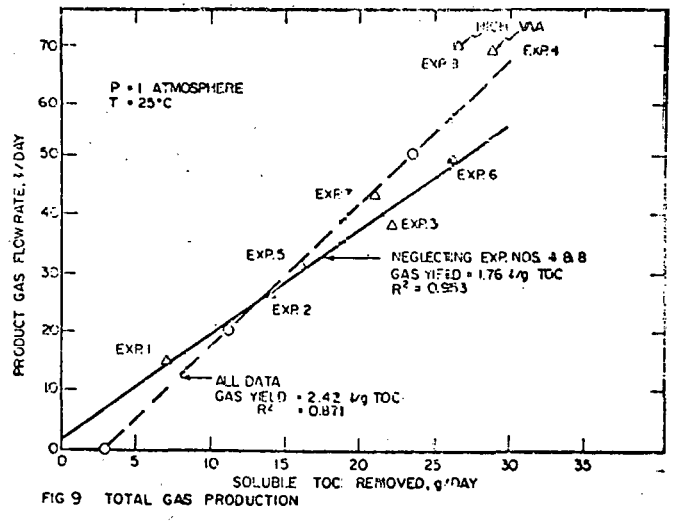

FIG 9 TOTAL GAS PRODUCTION

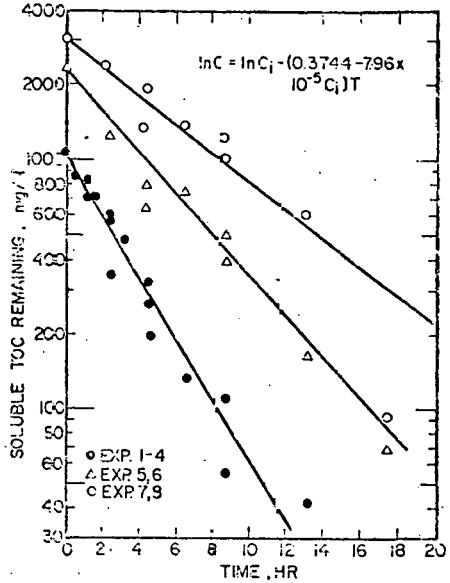

FIGURE 10 PREDICTED TOC VALUES

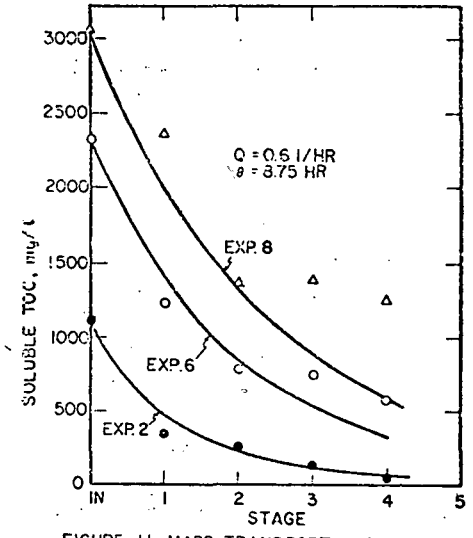

FIGURE 11 MASS TRANSPORT MODEL, EXPERIMENTS 2,6,8

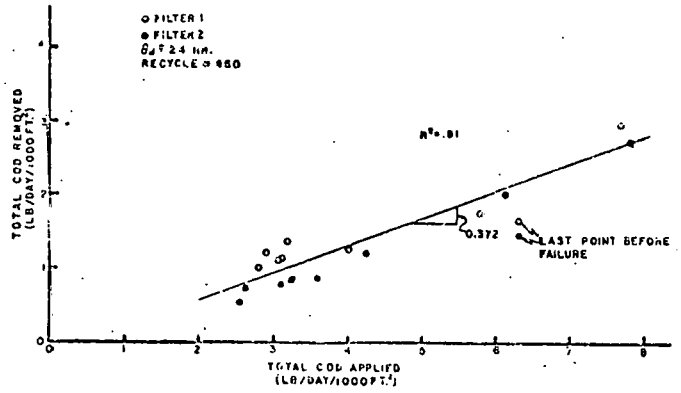

FIGURE 12. TOTAL COD REMOVAL IN ANAEROBIC FILTERS WITH RECYCLE

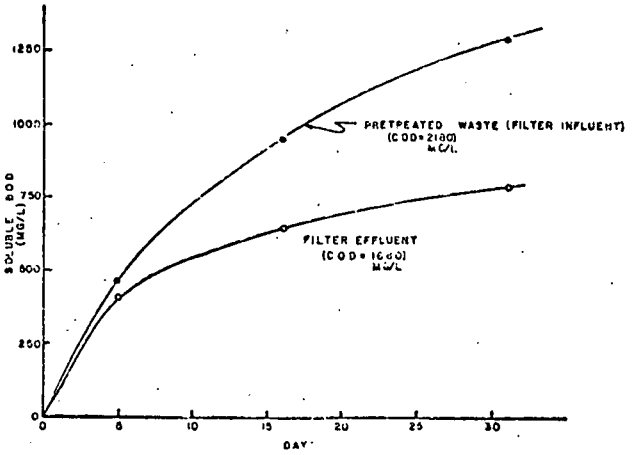

FIGURE 13. BIODEGRADEABILITY OF THE SOLUBLE CONSTITUENTS FOR THE TANNERY WASTEWATERS

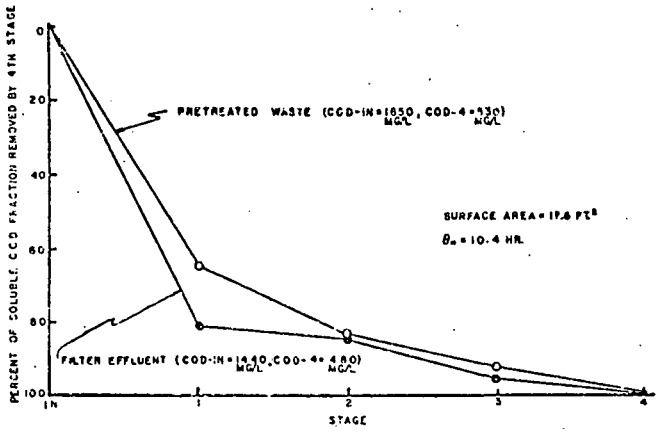

FIGURE 14. ROTATING BIOLOGICAL CONTACTOR TREATMENT OF TANNERY DERIVED WASTEWATERS

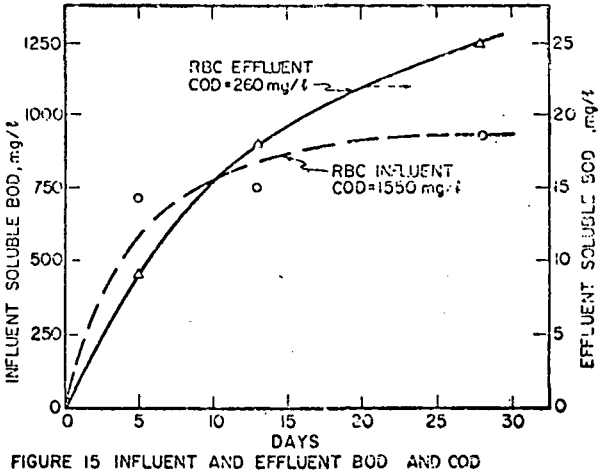

FIGURE 15 INFLUENT AND EFFLUENT BOD AND COD COMPARISONS

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ANAEROBIC EXPANDED BED TREATMENT OF WASTEWATER

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ABSTRACT

A wastewater treatment process capable of treating both dilute wastewaters such as domestic sewage, and more concentrated industrial wastes, such as whey, at ambient temperatures with the production of methane has been shown to be feasible with the anaerobic attached film expanded bed process. The process consists of inert sand sized particles packed in a cylindrical column which expand slightly with the upward flow of waste through the column. The inert particles act as a support surface for the growth of large amounts of attached microorganisms without developing clogging problems. The process permits the maintainance of high solids retention times values with low hydraulic retention time values.

This paper reports on several laboratory investigations of the process involving the treatment of low strength wastes and one high strength waste. The low strength studies involve 1) primary settled domestic sewage which was used as the substrate for a kinetic feasibility study and 2) a synthetic substrate which was used to define the impact of variation of temperature, flow rate, and organic loading rate on the process. The high strength study involves whey which was used to test the feasibility of the process for treating more concentrated wastes. An additional study was conducted to examine the effect of shock loadings (temperature and organic loading conditions) on the process and it was found resistant.

The process has been found to overcome several of the problems commonly associated with anaerobic treatment, these include: 1) treatment of low strength wastewaters; 2) operation of low temperatures; and 3) resistant to shock loadings. In addition the process has been found to be able to operate at high organic loading rates and at low retention times.

INTRODUCTION

In the past, broad scale application of the anaerobic fermentation process has been largely with the treatment of municipal sewage sludge to achieve waste stabilization and solids destruction. However, the anaerobic fermentation can be used for the treatment of soluble wastes. Over the more recent past new process configurations have evolved for application to both municipal and industrial wastewaters. The process has been limited in its application because of the slow bacterial growth rates, the extreme sensitivity of organisms to toxics and environmental fluctuations, and a temperature requirement of 35°C for efficient operation.

Numerous studies have attempted to apply some variation of the anaerobic fermentation process to sewage and other wastewater, but none has been successful in modifying the process so that it could be considered an economic alternative to conventional aerobic processes. So, while the advantages of anaerobic treatment are well known (high degree of stabilization achieved, lower sludge production, oxygen not needed, and methane produced) no approach has successfully developed a modification that can efficiently remove organics from dilute wastewaters at low temperatures.

The anaerobic attached film expanded bed process (AAFEB) represents a breakthrough in the anaerobic treatment of wastewater. It has been shown to be effective for the treatment of domestic sewage (1) and a synthetic dilute waste (2) anaerobically at retention times on the order of several hours, at high organic loading rates (up to 8 kg COD/m^3/day) and at reduced temperatures. In addition, the process was found to be able to acclimate well to changes in temperature and/or organic loading rates (1). A preliminary evaluation of the AAFEB treating a more concentrated waste, whey, was also conducted, and it was found that the process successfully treated the whey at low retention times, at ambient temperatures and at high organic loading rates. These above mentioned studies will be discussed in this paper.

The AAFEB process consists of inert sand-sized particles packed in a cylindrical column which expand slightly with the upward flow of waste through the column (see Figure 1). The inert particles act as a support surface for the growth of large amounts of attached microorganisms. In order to avoid the high flow rates required to maintain particles in a fluidized state, the upflow velocities in the AAFEB are limited to those required to achieve approximately 20% bed expansion. Thus, lower flow-through velocities and smaller bed volume expansions are used with the expanded bed as opposed to fluidized beds.

EXPANDED BED REACTOR DEVELOPMENT

Jewell and Mackenzie (3) showed that under aerobic conditions, static attached films had twice the organic removal capacity of a suspended microbial

system under comparable conditions. In a subsequent study, Jewell (4) proposed the use of an attached film expanded bed process. This application of the attached film concept was based on the assumption that the concept could be most practically applied in an upflow filter composed of small light weight sand-sized particles. Large biomass concentrations, Jewell (4) proposed, could be achieved on a large surface area which would minimize diffusion limitations, and the process in an expanded bed mode would be non-clogging.

This simple design led to adoption of a unit similar to fluidized bed reactors used in other applications (5). Cooper and Wheeldon (6) have summarized the use of fluidized and expanded bed reactors for wastewater treatment. Jeris et al. (7)(8)(9) have used the fluidized bed concept with sand as the attachment medium to obtain high rates of denitrification and BOD removal. Cooper and Wheeldon (6) listed others who have reported on anoxic dentrifying fluidized bed systems (10)(11)(12) and aerobic fluidized beds systems (13)(14)(15).

Beginning in 1974, attention was placed on anaerobic fermentation with expanded bed reactors. Although no literature sources suggested that dilute and cool substrates could be treated with anaerobic processes, it was felt that the large surface area combined with exceptionally high concentrations of biomass were substantial changes over any process examined previously. Leuschner (16) then demonstrated that an expanded bed type of process, using an anaerobic, attached film, was capable of treating dilute wastes at relatively short detention times, at ambient temperatures. An additional study was conducted on carbon conversion to methane with the expanded bed using dilute cow manure (17). These initial studies were followed by four studies which will be summarized in the remainder of this paper.

SEWAGE TREATMENT STUDY

A preliminary study was undertaken in the laboratory to examine the efficiency of the AAFEB in removing low strength organics from municipal wastewaters at an ambient temperature. This initial study (and subsequent studies) was designed to challenge the major weak points thought to limit the application of anaerobic treatment with the AAFEB - i.e., inability to efficiently treat low strength wastes and inability to operate efficiently at low temperatures.

The prototype AAFEB consisted of a one liter reactor portion (empty volume) and a tube clarifier. The reactor was packed with a 500 ml mixture of spent ion exchange resins and PVC particles. During operation the particles were expanded by a closed loop recycle pump. The feed to the AAFEB was primary settled sewage from the Ithaca Sewage Treatment Plant, and was pumped into the recycle line by a separate pump. All loadings and retention times are calculated on an empty volume basis that is occupied by the expanded media. Although this approach does not reflect the actual retention time, it allows estimates of reactor volumes and comparisons to be made to other processes that do not contain inert media. The entire experiment took place at a constant temperature of 20°C.

The reactor was started by innoculation with active biomass from an anaerobic sewage sludge digester and from a poultry manure oxidation ditch.

After 50 days of start-up, the process was monitored over a 200 day test period, for effluent COD and suspended solids. The process was tested at progressively shorter hydraulic retention periods with a constantly flowing unit. A summary of the organic removal efficiency and effluent concentration obtained for each HRT is shown in Figure 2. The graphs indicate that maximum efficiency for the AAFEB treating sewage occurred at retention times of one hour and greater in terms of organic removal efficiency and effluent quality.

It is also observed that even at quite low detention times, the unit was still removing a significant amount of COD. At a detention time of 5 minutes, the system failed as effluent concentration approached influent values, but the system was not destroyed as washout does not occur rapidly in an attached film reactor. This is in agreement with a hypothesis originally posed by Atkinson (18).

The experimental approach used and the results obtained for this preliminary study are described in greater detail elsewhere (1). The data obtained were highly encouraging, representing an exceptionally high efficiency for an anaerobic system treating a dilute low temperature wastewater. The results encouraged further development of the AAFEB.

COMPREHENSIVE DILUTE WASTE STUDY

Following the preliminary sewage study, a synthetic substrate was used to define the impact of variation of temperature, flow rate and organic loading rate on the process. Details of this study have been reported elsewhere (2).

A summary of the scope of this study is shown in Table 1, in terms of variables tested.

Table 1. Scope of Study-Variables Tested

Hydraulic retention time	6 to 0.33 hours
Influent substrate concentration	50 to 600 mg/l COD
Organic loading rate	0.8 to 43.2 kg COD/m^3/day
Temperature	10° to 30°C

The AAFEB used for this study differed slightly from the model used in the preliminary study in that no tube settler was used, as it was shown to be unnecessary. In addition aluminum oxide particles, 500 microns in apparent diameter, were used as biosupport particles. Initially the bed was expanded to a volume of 500 ml. All loadings and retention time values are based on this empty bed volume basis occupied by the expanded bed.

This comprehensive dilute waste study again demonstrated that the AAFEB was effective for the treatment of low strength organic substrates. Temperature was found to be an important variable affecting process efficiency, but the process was shown to compensate well for changes in temperature. The kinetic parameters characterizing the process did not follow the approximate rule of van't Hoff, but increased with increasing temperatures at a lesser rate. This was believed due to the fact that a very large biomass was present in the system and larger biomass concentrations are less

susceptible to temperature changes than small concentrations. Also, it was observed that larger biomass concentrations occurred at lower temperatures. This too is important for temperature compensation.

Modifications of the Monod and specific substrate utilization equations were found to describe the efficiency of the system for low influent substrate concentrations (COD = 200 to 600 mg/1) and for a temperature range of 10° to 30°C and these equations showed the importance of the influent substrate concentration on process efficiency. These equations related the process efficiency to two widely used operational parameters, the net specific growth rate and the specific substrate utilization rate, which are based on fundamental microbial concepts and are controllable paramters.

In conclusion, the AAFEB was shown to be a highly efficient process capable of achieving high organic removal percentages at low temperatures (10°, 20°) treating low strength wastes (COD $\leq$ 600 mg/1) at short hydraulic retention times (several hours) and at high organic loading rates (up to 8 kg COD/m^3/day). The high effectiveness was believed due to the large surface area to volume ratio created by the inert support media which enable a large active mass of attached microorganisms to remain in the reactor at high liquid flow rates.

SHOCK LOADING STUDY

During the comprehensive series of experiments described previously (2), it was observed that the operating conditions of the expanded bed could be drastically changed with little adverse effect. Since anaerobic processes are known to be sensitive to major operating variables, an extended series of instantaneous changes were tested to observe the effect on process efficiencies (1).

Three AAFEB reactors used in the previous study (2) were used for this shock loading study. The units were fed an influent soluble substrate composed of glucose and yeast extract over a wide range of temperatures (10-30°C) and loading rates (0.3 to 24.0 kg COD/m^3/day). Gradually increasing temperature differential, changes in hydraulic retention time and substrate concentration were imposed on these three units with one unit only experiencing temperature and flow rate changes. The differential magnitude was increased until the extreme shocks had been imposed on the reactor. In general, the shock changes had relatively little influence on the process. A summary of the magnitude of instantaneous changes that had little or no effect on the COD removal efficiency is given in Table 2.

The most severe impact of shock loadings is shown in Figure 3. After nearly 30 days of continuous operation at varying operational conditions, the reactor was achieving maximum COD removal efficiencies when the maximum range of variables was tested — the temperature was decreased from 35° to 10°C, the loading rate increased from 1.3 to 24 kg COD/m^3/day and the hydraulic retention time was decreased from 9.5 to 0.5 hours. This caused the COD removal efficiency to decrease to 45%, and a significant amount of the attached film was lost. The total fraction of biomass lost under these extremes was a small fraction of the total. After return to 20°C, however, the process efficiency returned to its maximum value in about 6 days.

Table 2. Summary of Influence of Reactor Variables That Resulted in Little Influence on AAFEB Process Efficiency

	Parameter Change			
Reactor Number	Temp. °C	Loading Rate, Kg/m^3-d	HRT, hours	S_o, COD mg/ℓ
1	13 to 35 35 to 10	Constant at 2.4	Constant at 5	Constant at 500
2	28 to 17 to 33	1.7 to 4 to 1.4	7 to 3 to 8.5	500
3	30 to 12 to 35	4.1 to 4.6	Constant at 5	850 to 150 to 950

PRELIMINARY WHEY TREATMENT STUDY

The AAFEB had been shown to be effective for the removal of domestic sewage (1) and a synthetic dilute waste (2) anaerobically at retention times on the order of several hours; at high organic loading rates (up to 8 kg/m^3/day) and at reduced temperatures. In addition, the process was found to be able to acclimate well to changes in temperature and/or organic loading rates (1). The good performance at low temperatures and the stability exhibited by the process are two important advantages in that these are usually considered major problems with anaerobic treatment. These would also be beneficial in treating more concentrated industrial wastewaters.

The AAFEB had been developed for the treatment of dilute wastes, rather than for more concentrated industrial wastes. Therefore, a preliminary feasibility evaluation of whey treatment was conducted (19). A prototype AAFEB reactor, used in the previous study (2), was used for this preliminary concentrated waste study. The expanded bed occupied a total volume of 500 ml, and again, all subsequent loading values will be based on this 500 ml volume.

The substrate used for this study consisted of sweet whey powder, ammonium phosphate as a supplemental nutrient source and sodium bicarbonate as a buffer. The exact components of the feed are shown in Table 3.

Table 3. Components of Feed Solution

10 grams sweet whey powder
10 ml 1M $(NH_4)_2HPO_4$
5 grams $NaHCO_3$
Tap water
Total volume = 1 liter

The feed was kept in a refrigerator to prevent excessive degradation and pumped into the expanded bed.

The experimental conditions of this preliminary study are summarized in Table 4.

Table 4. Experimental Conditions

Influent substrate concentration:	TCOD = 10,000 mg/l
	SCOD = 8263 mg/l
Hydraulic retention time:	24 hours - 4 hours
Organic volumetric loading rate;	10-60 kg COD/m^3/day
Temperature	25-31°C

The organic strength of the waste was kept constant throughout the study, and the temperature was the ambient room temperature usually around 26°C. However, it did vary throughout the study. The only variable was the hydraulic retention time and subsequent organic loading rate. Six different retention times were investigated ranging from 24 hours to 4 hours.

The AAFEB has been used for the previous studies, and thus had already developed a sufficient biomass when this study commenced at an initial HRT of 24 hours. After 30 days of operation, data were taken on three successive days for the 24 hour retention time. The retention time was then decreased to 18 hours. For all subsequent changes in loading, 20 HRT's were allowed to pass before the next set of three day consecutive data were taken. The following parameters were measured: total and soluble chemical oxygen demand (TCOD, SCOD); suspended and volatile suspended solids (SS, VSS); pH; and organic acids.

Effluent data for TCOD and SCOD are shown in Figure 4. Each point in this and subsequent figures are means of the three data points collected at each loading condition. The performance of the process can be evaluated in terms of removal of soluble COD. Figures 5 and 6 show organic removal efficiency as a function of the hydraulic loading and organic loading respectively.

In examination of the data several promising trends can be noted. The process was able to achieve high organic removal efficiencies (87% and greater) at relatively low retention times (12 hours and greater) and at high organic loading rates (up to 20 Kg COD/m^3/day = 1248 lbs COD/1000 ft^3/day). In addition to high removal efficiencies, large quantities of methane can be generated (5-6 volumes of gas per volume of reactor, based on 500 ml reactor volume).

It should be also noted that although high organic removal efficiencies were achieved, the effluent was still high in COD because of the high influent concentration, and thus might require further treatment. Also, despite the addition of 5 grams of $NaHCO_3$ to the whey feed, the pH of the reactor did decrease at the higher loading conditions, and thus better pH control might be necessary for operation at these conditions.

It was concluded from this preliminary feasibility study that the AAFEB shows significant potential for the treatment of whey. High removal efficiencies can be achieved at low retention times operating at an ambient temperature range. This high rate performance can be more clearly recognized by comparing the results of this study to one conducted with an

anaerobic filter treating whey (20). With an anaerobic filter, Hakannson (20) was able to achieve a high organic removal efficiency (97% COD removal) with an influent COD concentration of 8100 mg/l but at a much lower organic loading rate (1.9 Kg COD/m^3/day, as compared to 20 Kg COD/m^3/day in this study).

It must be pointed out, however, that while these results are encouraging, they are highly preliminary in nature and only demonstrate that the process is potentially feasible for methane generation from whey. More work will be needed to further define the efficiency and the effect of environmental conditions on the process. At the present time, further work is being conducted in laboratory of the author.

SUMMARY

This paper reports on several laboratory investigations of the AAFEB processinvolving the treatment of low strength wastes and one high strength waste. The low strength studies involve 1) primary settled domestic sewage which was used as the substrate for a kinetic feasibility study and 2) a synthetic substrate which was used to define the impact of variation of temperature, flow rate, and organic loading rate on the process. The high strength study involves whey which was used to test the feasibility of the process for treating more concentrated wastes. An additional study was conducted to examine the effect of shock loadings (temperature and organic loading conditions) on the process and it was found resistant.

The process has been found to overcome several of the problems commonly associated with anaerobic treatment. These include: 1) treatment of low strength wastewaters; 2) operation at low temperatures; and 3) resistance to shock loadings. In addition the process has been found to be able to operate at high organic loading rates and at low detention times. The effectiveness of the process is believed due to the large surface to volume ratio created by the inert support media which enable a large active mass of attached microorganisms to remain in the reactor at high liquid flow rates.

In summary, the AAFEB has been found to be able to realize many of the benefits of anaerobic treatment while overcoming several of the problems associated with it. It offers the dual advantage of energy production and pollution control.

ACKNOWLEDGMENTS

Student stipend support in the form of research assistantships were provided by the U.S. Department of Energy Contract EY-S-02-2981 for the work involving the comprehensive dilute waste study and the variability testing. Mr. James W. Morris conducted the variability testing. The whey study was partially supported by the Division of Research of Clarkson College of Technology in the form of a teaching assistantship for Mr. Scott C. Danskin who conducted that study.

Finally, the author wishes to acknowledge the role of Dr. William J. Jewell who originated the anaerobic expanded bed concept and under whose excellent guidance the preliminary sewage, comprehensive dilute waste, and variability testing studies were conducted.

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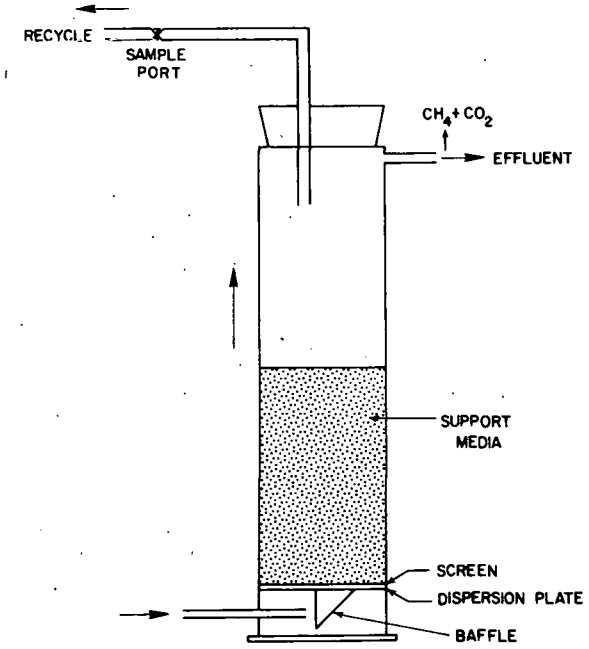

Fig. 1. The Anaerobic Attached Film Expanded Bed Reactor

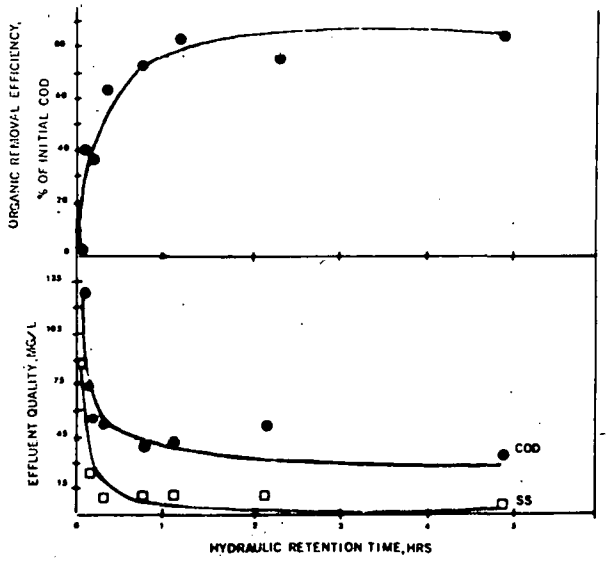

Fig. 2. Summary of the Influence of Decreasing Hydraulic Retention Periods on the COD and SS Removal Capability of the AAFEB Treating Primary Settled Domestic Sewage at 20°C

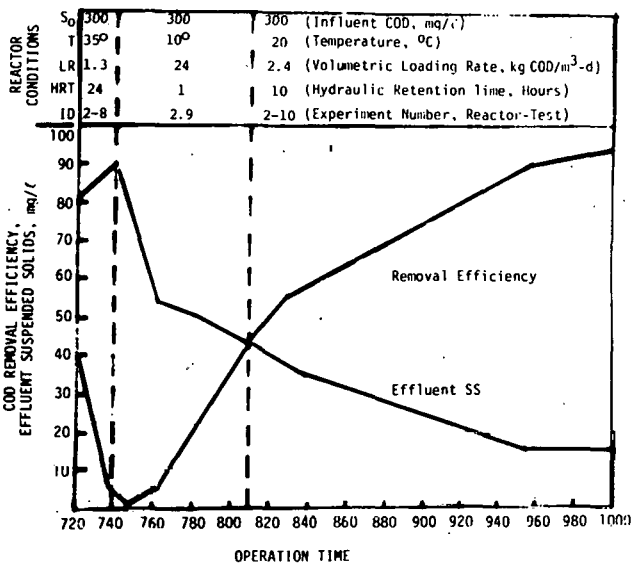

Fig. 3. Influence of Shock Loadings on the COD Removal Efficiency and Effluent SS with the AAFEB

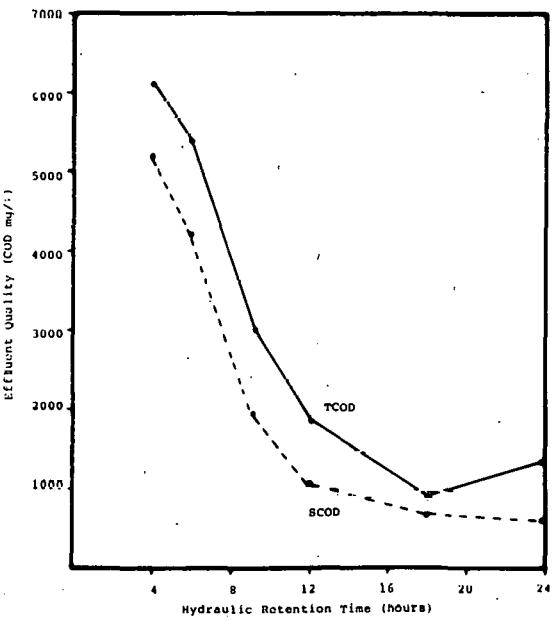

Fig. 4. Influence of Hydraulic Retention Time on Effluent Quality as Chemical Oxygen Demand

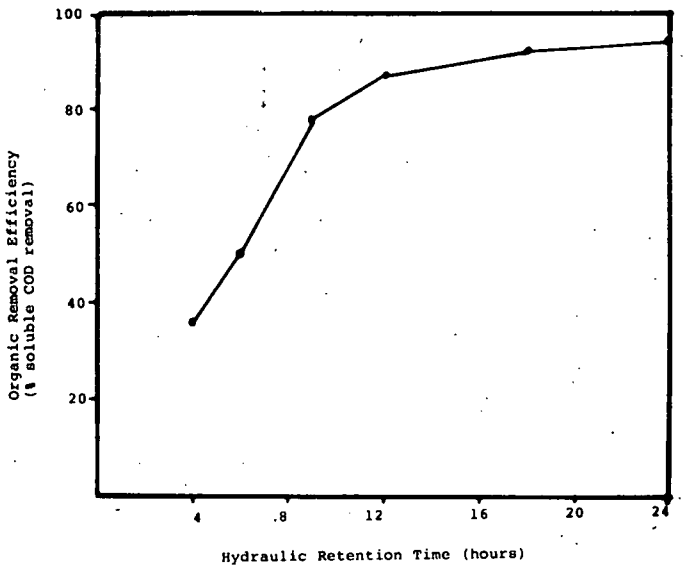

Fig. 5. Influence of Hydraulic Retention Time on the Organic Removal Efficiency of the AAFEB Treating Whey

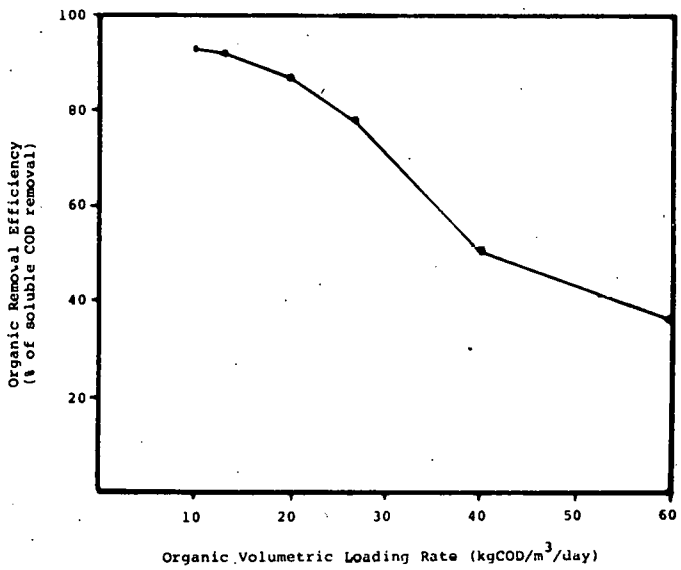

Fig. 6. Influence of Organic Volumetric Loading Rate on the Organic Removal Efficiency of the AAFEB Treating Whey

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CELANESE EXPERIENCE WITH ANAEROBIC FILTERS

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ABSTRACT

Celanese Chemical Company, Inc., has been evaluating applicability of biological treatment for high strength effluents from its chemical plants since the early seventies. This work has led to extensive investigation of anaerobic systems in both laboratory and pilot units and to development of an effective treatment system, particularly for high strength wastes.

To date, one commercial unit, designed for 65% removal of a 36,000 lb/day COD load has been in operation at a Celanese Plant since mid-1977. Two other units, one designed for 75 M lb/Day COD loading and one for 117 M lb/day COD loading are currently under construction in other Celanese plants.

This paper will review briefly the operating history of the existing commercial unit and discuss economic and technical considerations leading to the commitment to install additional units.

Celanese Chemical Company, Inc. has been investigating various types of biological processes for treatment of wastes from its Texas chemical plants since the late forties. During the early seventies work was directed to anaerobic systems as possibly offering significant advantages for treatment of high strength wastes. Among the expected advantages were:

1) greatly reduced net energy requirements;
2) lower sensitivity toward heavy metals;
3) greatly reduced nutrient requirements;
4) greatly reduced sludge production;
5) fewer constraints on food/biomass ratio.

This work culminated in development of a modified anaerobic filter which has been very successful in laboratory and pilot plant treatment of a wide variety of high strengh chemicals and natural wastes.

The anaerobic system comprises a packed filter in which wastewater is circulated upflow through the packing. The overflow is split into two streams, one of which goes forward to such downstream processing (clarifier or second stage) as may be required to meet discharge limitations. The other stream is

mixed with incoming feed to dilute and buffer it and recirculated to the bottom of the filter. Methane gas from the top of the filter is recovered for fuel. Compression and cleanup of the gas may be required depending on its intended use. The system is described in more detail in Belgian Patent 860-261 to Celanese Corporation.

Table I shows laboratory and/or pilot plant performance data on several different chemical wastes. It should be noted that with the very high strength raw waste, a COD removal of typically 80-90% will, in many circumstances, not meet effluent requirements. In these cases an additional treatment step--perhaps an aerobic polishing unit--is required. Also, as with any biological system, an upstream waste equalization may be required to reduce load swings and protect the system against toxic spike loadings.

The first commercial application of the system was an installation at the Celanese Polymer Specialty Company guar processing plant in Vernon, Texas which came on line in mid-1977. The plant, as described by Witt, Humphrey and Roberts (1) was designed for 36,000 lb/day COD feed and a removal efficiency of 65%.

During the first 1-1/2 years of operation the plant operated at COD loading rates from 0.16 lb/ft^3-day to 0.69 lb/ft^3-day, averaging 0.47 lb/ft^3-day. COD removal efficiency averaged 60%--below the 65% design--as a result of changes in plant product mix, waste composition and volume. The 60% COD removal being obtained is low compared to the typical 80-90% COD removal shown in Table I. This results from presence of a substantially nonbiodegradable fraction in the waste. The total treatment plant is being expanded and waste loadings of 1.5 lb COD/ft^3-day and removal efficiency of 60% are expected upon completion of the expansion.

It has been demonstrated that the unit can be shut down for 1-3 days for maintenance without loss of activity on restart. Upsets have occurred during operation, most of which, in retrospect, were preventable. These upsets emphasize the necessity for very careful planning of waste equilization systems ahead of the filter, good control and alarm instrumentation, good analytical support, and careful operator training.

The success of this original installation has led to multimillion dollar commitments by Celanese Chemical Company, Inc. for installation of anaerobic units at two other plants.

One of these units is designed to handle a feed of 12,000 ppm COD waste at a throughput of 75 M lb COD/day. The waste is a complex mixture of effluents from production of a wide variety of oxygenated organic chemicals including formaldehyde, methanol, butanol, polyols and polyacetal copolymer resins.

The anaerobic unit will be added to an existing aerobic waste treatment plant as a first stage to give expanded treatment capacity. Choice of the anaerobic filter in this case was dictated by two factors:

Economics -- Total cost of the treatment system--capital and operating cost--on a net present value basis considering the total stream of cash flows over the life of the project was significantly lower than for the alternatives.

Capability -- Certain streams in the waste are refractory to aerobic treatment alone but can be readily treated in a combination anaerobic-aerobic system, thus reducing the volume of refractory effluent to be dealt with by nonbiological means.

The other unit is designed to treat a feed of 117 M lb/day COD with a feed concentration of about 11,500 ppm COD. Again this waste arises from production of various oxygenated organic chemicals primarily by hydrocarbon oxidation. The unit will be the first stage of a combination anaerobic/facultative pond system. Again, economics dictated the choice of process.

While the anaerobic process was selected by Celanese for these two installations over competitive systems on the basis of overall economics, the economics were strongly affected in each case by site-specific factors. It may be helpful in obtaining a more quantitative perspective on the relative merits of aerobic and anaerobic systems to assume a hypothetical case and look in detail at some of the major cost factors expected to differ between the two systems. For this example, let us assume a unit to remove 50 M lb/day COD from a waste stream containing no nitrogen or phosphorus and consider relative costs for anaerobic and aerobic systems with respect to the following factors:

Nutrients -- A COD/N/P ratio of 1000/2.5/0.5 for an anaerobic system vs 100/2.5/0.5 for an aerobic system. Nitrogen (NH_3) cost of \$0.065/lb and phosphoric acid cost of \$0.22/lb.

Sludge Production -- 0.03 lb/lb COD for the anaerobic system vs 0.2 lb/lb for an aerobic system. Sludge thickened to 20% solids for disposal at \$10/wet ton.

Electricity -- 0.125 KWH/lb COD for the anaerobic system vs 0.5 KWH/lb COD for the aerobic system at a power cost of $0.035/KWH.

Fuel Gas Production -- 5.9 SCF/lb COD for the anaerobic system sold at $3.00/MCF.

Table II, a cost comparison of the two systems in terms of annual operating cost for the above factors, shows an advantage of about $730 M/year for the anaerobic system.

Most project investment decisions are made utilizing some type of discounted cash flow analysis which considers expected cash flow over the project life. Let's make the additional assumptions that project life is ten years and costs inflate at 6%/year and consider the net present value of the sum of the stream of cash flows over the ten-year project life at a discount rate of 15%. Table III shows the result of this calculation as well as the same calculation without inflation. The anaerobic system present value cost advantage for the five factors is $4.8 MM with inflation or $3.7 MM without inflation.

Economics of any installation are, of course, a unique function of site-specific factors. However, it seems reasonable to conclude that the electricity consumption difference, the

methane credit, and the sludge disposal cost difference will exist at any site while the nutrient cost difference would not exist for a waste containing sufficient nitrogen or phosphorus. Thus, it seems likely that the anaerobic unit will always be favored on an economic basis and indeed will be the favored process even if its capital cost is significantly higher than alternative processes.

To summarize, our experience to date suggests that:

a) The anaerobic filter can be used successfully to treat high strength industrial waste containing a wide variety of compounds.

b) It is likely that the anaerobic filter will be the preferred choice on economic grounds in most cases. This will probably be true regardless of whether the anaerobic system is part of a larger mixed anaerobic-aerobic system or a stand-alone unit.

In closing, since energy conservation is currently a matter of national concern, it may be of interest to put two items from our hypothetical plant, methane credit and electricity savings in the larger context of the national energy balance. First, the methane production is 108 MM CF/yr, which presumably will displace 18 M bbls/yr of imported oil. Second, the reduced electricity consumption is about 6.8 MM KWH/yr.

At the national average heat rate of 10,400 Btu/KWH this is equivalent to a utility fuel savings of 11.9 M bbls/yr for a total of 30 M bbls/yr or roughly $750 M/year reduced oil import costs.

REFERENCES

(1) Witt, E. R.; Humphrey, W. J.; and Roberts, T. E.; "Full Scale Anaerobic Filter Treats High Strength Wastes"; Proceedings of the Purdue University Industrial Waste Conference; Lafayette, IN, May 8-10, 1979.

(2) Belgian Patent Patent No. 860-261; April 28 1978 to Celanese Corporation.

TABLE I (a)

ANAEROBIC FILTER PERFORMANCE DATA FOR VARIOUS EFFLUENTS

Feed Description (Main Components)		Feed COD Range (mg/l)	Loading Range	% COD Removal	Misc. Remarks
Acetic Acid Formic Acid 2-Butanone	Live Feed	5,000 - 10,000	0.25 - 0.38	87 - 90	Outfall COD = 90-660 mg/l.
Acetic Acid Acetaldehyde Glycol Vinyl Acetate	Live Feed	7,000 - 10,000	0.38 - 0.50	86 - 94	BOD Removal = 86-97%.
Formic Acid Acetic Acid Methanol Formaldehyde	Live Feed	17,000 - 24,000 (1700-5700 mg/l HCHO)	0.69 - 0.91	72 - 92	BOD Removal = 80-90%. HCHO Removal = 98-99+%.
Acrylic Acid Acrylate Esters	Live Feed	79,000 - 85,000	0.5 - 0.6	94 - 97	-----
Formic Acid Acetic Acid Formaldehyde Methanol	Syn. Feed	25,000	0.520 ± 0.013 0.790 ± 0.010 0.997 ± 0.14	94.1 ± 1.1 93.2 ± 0.7 91.8 ± 0.2	----- ----- -----
Dairy Waste (Evap. Milk)	Sim. Feed	24,000	0.45 - 0.55	80 - 90	-----

(a) Witt, E. R; Humphrey, W. J.; and Roberts, T. E.; "Full Scale Anaerobic Filter Treats High Strength Wastes"; Proceedings of the Purdue University Industrial Waste Conference; Lafeyette, IN; May 8-10, 1979.

TABLE II

COMPARISON OF SELECTED ANNUAL OPERATING COSTS
FOR AEROBIC AND ANEROBIC SYSTEMS

Basis: 50 M Lb/Day COD Removal.

Cost Component	Annual Cost, $M/Yr		
	Aerobic	Anaerobic	Δ
Phosphorus	63.5	6.4	57.1
Nitrogen	36.0	3.6	32.4
Sludge Disposal	91.3	13.7	77.6
Electricity	319.4	79.8	239.6
Methane Credit	0	(323.0)	232.0
ANNUAL TOTAL	510.2	(219.5)	729.7

TABLE III

NET PRESENT VALUE OF CASH FLOWS, $M
TEN YEAR LIFE -- 15% DISCOUNT RATE
6%/YR INFLATION

Cost Component	Aerobic	Anaerobic	Δ
Phosphorus	417.2	42.1	375.1
Nitrogen	236.5	23.6	212.9
Sludge Disposal	599.8	90.0	509.8
Electricity	2098.5	524.3	1574.2
Methane (Credit)	0	(2122.1)	2122.1
TOTAL	3352.0	(1442.1)	4794.1 (a)

(a) $3673 if calculation made in constant dollars.

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TREATMENT OF DOMESTIC SEWAGE WITH THE ANAEROBIC FILTER

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ABSTRACT

The present study conducted a statistical evaluation of performance data of laboratory scale anaerobic filters treating domestic sewage using septic tanks as control treatment units. The R^2 of the regression equation:

$$\%\text{BOD Removal} = b_o + b_1(\ln \text{BOD}_{in}) + b_2(\ln \text{SS}_{in}) + b_3(\text{time}^{-1})$$

indicated that the model accounted for more than 90% of the variability for 4 of the 5 filters studied and for 6 of the 10 septic tanks. A similar equation for the suspended solids removal could not account for any of the variability. The coefficient b_1 ranging from 4 to 19 was significant at the 5% level for 4 of the 5 filters, while b_2 was not significant and b_3 significant for 2 of the 5 filters indicating that the influent BOD is the primary factor determining the removal efficiency and that the actual effluent concentration is independant of the influent concentration.

INTRODUCTION

Although approximately 70% of the homes in the U.S. are served by centralized sewer systems, on-site sewage treatment is becoming more prevalent due to its lower cost in housing areas with a density below 16 persons per acre (Goldstein, 1973). A conventional on-site system generally consists of an anaerobic septic tank and a soil absorption system. A major limitation to the widespread use of such a system is the unsuitable soil conditions in over 70% of the total land area (Otis and Boyle, 1976). It has been suggested that a reduction of the pollution load discharged from the septic tank may retard the clogging of the drain field or may reduce the amount of land required for the disposal of the sewage (Laak, 1974).

Several studies at the University of Washington have evaluated the effectiveness of the upflow anaerobic filter as a domestic sewage treatment method and as a possible replacement of the septic tank to produce a better effluent quality. The present study conducted a statistical evaluation of the main parameters affecting the performance of anaerobic filters and compared the effluent quality of filters in terms of Biochemical Oxygen Demand (BOD) and Suspended Solids (SS), with that of conventional septic tanks.

SELECTION OF ANAEROBIC FILTER

The anaerobic filter basically consists of a reactor filled with a submerged solid support medium in which anaerobic bacteria, treating incoming wastewater, are retained and protected from outwashing. Coulter et al (1957) and Witherow et al (1958) employed an anaerobic rock filter following an anaerobic sludge contacter. The combined processes experienced a 65% BOD reduction and an 84% SS reduction with most of it occurring in the first unit. Pretorius (1971) noted an 85% Chemical Oxygen Demand (COD) removal in an anaerobic digester, followed by a multimedia biofilter with most of the gas production originating from the filter. Winneberger et al (1961) employed an anaerobic filter following a septic tank and noted a 60% BOD removal and a 70% SS removal at a 5 day detention time. Young and McCarty (1969) employed the upflow anaerobic filter as a separate unit process treating high strength synthetic feed.

Four studies at the University of Washington have evaluated the applicability of the anaerobic filter to treat domestic sewage. Caudill (1968) treated settled domestic sewage with a COD of 226 mg/l, using an anaerobic filter having a 1.1 day detention time and a loading of 0.1 kg COD/m^3.d. (5.8 lb. COD/1000 cu. ft. d.), and noted a 60% COD removal for the filter or a 76% COD removal for the settling and anaerobic filter treatment combined. Using a similar waste, Thaulow (1974) noted a 75% COD removal and a 90% SS removal at a maximum loading rate of 0.18 kg. COD/m^3.d. (11.5 lb. COD/1000 cu. ft. d.) and 0.8 day detention time. Roats (1975) observed a 60% COD removal and a 28% SS removal in an anaerobic downflow sandfilter treating septic tank effluent. In

a full scale 2.5 m^3 (650 gallons) anaerobic filter installed following a septic tank and receiving 0.19 kg. COD/m^3.d. (11.8 lb. COD/1000 cu. ft. d.), Hamilton (1975) observed a 28% COD removal and a 39% SS removal.

STATISTICAL ANALYSIS OF THE DATA

The present study used existing data on anaerobic filters (Table 1) and septic tanks (Table 2) treating residential wastewater and determined statistically the effect of major design and operating variables on filter performance. The influent concentration, hydraulic detention time, temperature, sludge seeding, waste type and reactor type, the predictor variables for which data were available, were related to performance response variables for both BOD and suspended solids. Stepwise multiple regressions were applied to the predictor variables to determine the most significant variables and to determine the amount of variability accounted for by the set of identified variables. The results of this testing indicated that, due to confounding among the dummy variables used to represent waste type, temperature, seeding, and reactor type, the influence of the variables could not be determined by this method.

It was therefore necessary to switch to a simplified regression model using only those predictor variables that were shown in previous studies to be of importance. Multiple regressions were used to analyze the effect of each predictor variable on reactor performance, while adjusting for the influence of the other predictors. Since the aggregation of individual reactors into larger sets depends on the similarity of the regression coefficients, the model was applied in a three-step hierarchy. Initially, regressions were made of each individual reactor. If different reactors operated under similar conditions had similar coefficients, a single equation can be used for all reactors within a single study. If the coefficients for each study showed similarity according to reactor types, regressions can be made to predict performance of each type and to establish differences between each type.

RESULTS

Summary statistics of the treatment efficiency of each type of reactor are shown in Table 3. They are based on results from different studies and from separate operating time periods in individual studies for septic tanks (10 periods), anaerobic filters (14 periods), and combined systems (2 periods), i.e. those systems where data were only available for the septic tank filter combination instead of each process separately. In general, percent removals were greater for SS than for BOD. As the detention time for half of the filters was less than one day, this provided enough time for sedimentation but may provide insufficient time for extensive biological degradation. Anaerobic filters showed the highest mean BOD and SS removal, followed by septic tanks and combined systems. As the summary statistics are based on observations of diverse design and operating conditions, these variables, singly or in combination, may be more important than the reactor type differences.

The cumulative data frequency distributions of each reactor showed a normal distribution for percent BOD removal and percent SS removal and a logarithmic normal distribution for effluent BOD (Figure 1) and SS (Figure 2), which is in accordance with results observed for other sewage treatment processes (Garret, 1976). The reactors having the lowest effluent BOD concentrations were exclusively anaerobic filters, and their performance appears more stable than the septic tanks or combined systems as evidenced by a lower slope of the logarithm-concentration/frequency distribution curve. The lower SS concentrations were also noted for the filters, although the differences with

Table 1 Anaerobic Filters Evaluated in the Present Study

Study	Reactor Type	Reactor Volume (gallon)	Porosity	Waste-water Received	Mean BOD_{in} (mg/l)	Mean SS_{in} (mg/l)	Temperature	Detention Time (Days)
Caudill (1968)	AF[1](L)[2]	1.92	0.45	PE[5]	90	---	37° C	1.1
Witherow et al., (1958); Coulter et al. (1957)	AF (P)[3]	419	0.31	CE[6]	116	72	30° C	0.67
Hamilton (1975)	AF (P)	650	0.5	STE[7]	120	72	11.3° C	0.8
Magdoff et al. (1974)	AF (L)	0.013	0.4	STE	120	---	25° C	3.57
Raman & Chakladar (1972)	AF (P)	119	0.5	STE	189	275	20°-25°C (wntr) 26°-33° (other)	10
Thaulow (1974)	AF (L)	2.31	0.5	PE	124	114	21° C 7° C - 14° C 7° C - 14° C 7° C - 14° C	0.83 0.83 1.7 2.5
Thaulow (1974)	AF (L)	2.31	0.5	STE	191	---	21° C 7° C 7° C 7° C	0.83 0.83 1.67 2.5
Winneberger et al. (1961)	AF (P)	261	0.50	MS[8]	153	253	7° C	3.2
Winneberger et al. (1965)	ST[4] AF (P)	ST-9.5 AF-2.5	0.5	MS	128	144	14° C	1.7
	ST-AF (P)	ST-9.5 AF-2.5	0.5	MS	165	205	17° C	0.9
	ST-AF (P)	ST-9.5 AF-2.5	0.5	MS	---	161	17° C	0.7

1) AF=anaerobic filter 2) L=laboratory 3) P=pilot scale 4) ST=septic tank 5) PE=primary effluent
6) CE=effluent of anaerobic upflow chamber 7) STE=septic tank effluent 8) MS=municipal sewage

Table 2 Septic Tanks Evaluated in the Present Study

Study	Reactor Type	Reactor Volume (gallon)	Wastewater Received	Mean BOD_{in} (mg/l)	Mean SS_{in} (mg/l)	Temperature	Detention Time (Days)
U.S. Public Health Service Weibel et al. (1954)	rectangular joint committee type	2060	municipal sewage	396	414	4^{o}-10^{o}C winter	8.2
	round ends	513				20^{o}-28^{o}C summer	2.0
	2-compartment, vert. cylinder	553			398		2.2
	4-compartment, vert. cylinder	673			414		2.7
	oval	525					2.1
	single vert. cylinder	455					1.8
	rectangular joint committee type	539					2.2
	horizontal cylinder	492					2.4
Nottingham & Ludwig (1950)	septic tank-- elongated	5250	municipal sewage	---	246	exposed to Mich. summer	0.50
	septic tank-- standard	800					
National Sanition Foundation (1975)	septic tank-- sanitary elbow	1000	municipal sewage	---	239	exposed to Mich. summer	1.67
	septic tank-- SSR device	1000					1.67
Seabloom & Engeset (1978)	septic tank-- household use	1000	household wastewater	---	---	12^{o} C, buried	4
Hutzler et al. (1974)	single compartment	610	simulated household wastewater	243	280	indoor lab	3.6
	3-compartment	260					0.6

Table 3 Removal Efficiencies of Different Reactors Treating Residential Wastewater

Performance Indicator	Reactor Type	Individual Medians		Group Mean	Standard Error
		Min	Max		
Percent BOD Removal					
	Septic Tank	40	75	50	43
	Anaerobic Filter	10	92	61	63
	Combined System	18	41	22	19
Percent SS Removal					
	Septic Tank	32	93	58	59
	Anaerobic Filter	23	96	64	65
	Combined System	37	73	52	44

septic tanks were less obvious in terms of both concentration and slopes of the frequency distribution curves.

The simplified regression model used influent BOD, influent SS, and hydraulic detention time as predictor variables, as these are the only variables for which sufficient observations are available. The three predictor variables were incorporated into the model in the form of their linear relationship to percentage removal as shown below:

$$\% \text{ BOD} = b_o + b_1 (\ln \text{BOD}_{in}) + b_2 (\ln \text{SS}_{in}) + b_3 (\text{Time}^{-1}) \quad (1)$$

$$\% \text{ SS} = a_o + a_1 (\ln \text{BOD}_{in}) + a_2 (\ln \text{SS}_{in}) + a_3 (\text{Time}^{-1}) \quad (2)$$

where BOD and SS are in mg/l, time is in days, and ln represents the natural logarithm. The dimensionless intercept constants b_o and a_o, representing sewage containing no SS and BOD, were expected bo be equal to zero, while b_1, a_1, b_2, and a_2 were assumed to be positive, and b_3 and a_3 were assumed to be negative.

The general accuracy of the regression model is reflected by the overall R^2 statistic, i.e. the amount of the data variation explained by the variables included in the regression model. The overall R^2 indicated that the BOD removal model accounted for at least 90% of the variability for 4 out of 5 filters, and 6 out of 10 septic tanks, as shown in Table 4. The overall R^2 for the SS model indicated that it did not account for any of the filter variability and 3 out of 10 septic tanks, indicating that the BOD removal is better accounted for than the suspended solids removal.

The overall F statistic tests the hypothesis that all coefficients of the regression equation do not significantly differ from zero. An F value having significance less than or equal to 0.05 indicates that all coefficients differ from zero 95 times out of a hundred, and that the equations model treatment efficiency significantly. At the 0.05 level, the BOD removal model was significant for 4 anaerobic filters and almost significant for one septic tank. The SS removal model was significant for only one out of 10 septic tanks.

The individual coefficients most often significant at the 0.05 level to explain BOD removal were those for $\ln \text{BOD}_{in}$ as compared to the SS or Time coefficients (Table 4). The coefficient b_1 was significant 4 out of 5 times for anaerobic filters and 6 out of 10 times for septic tanks. The coefficients b_2, b_3, a_1, a_2, and a_3 were not significant in most of the filter and

Figure 1 **Frequency distribution of effluent BOD_5 data**

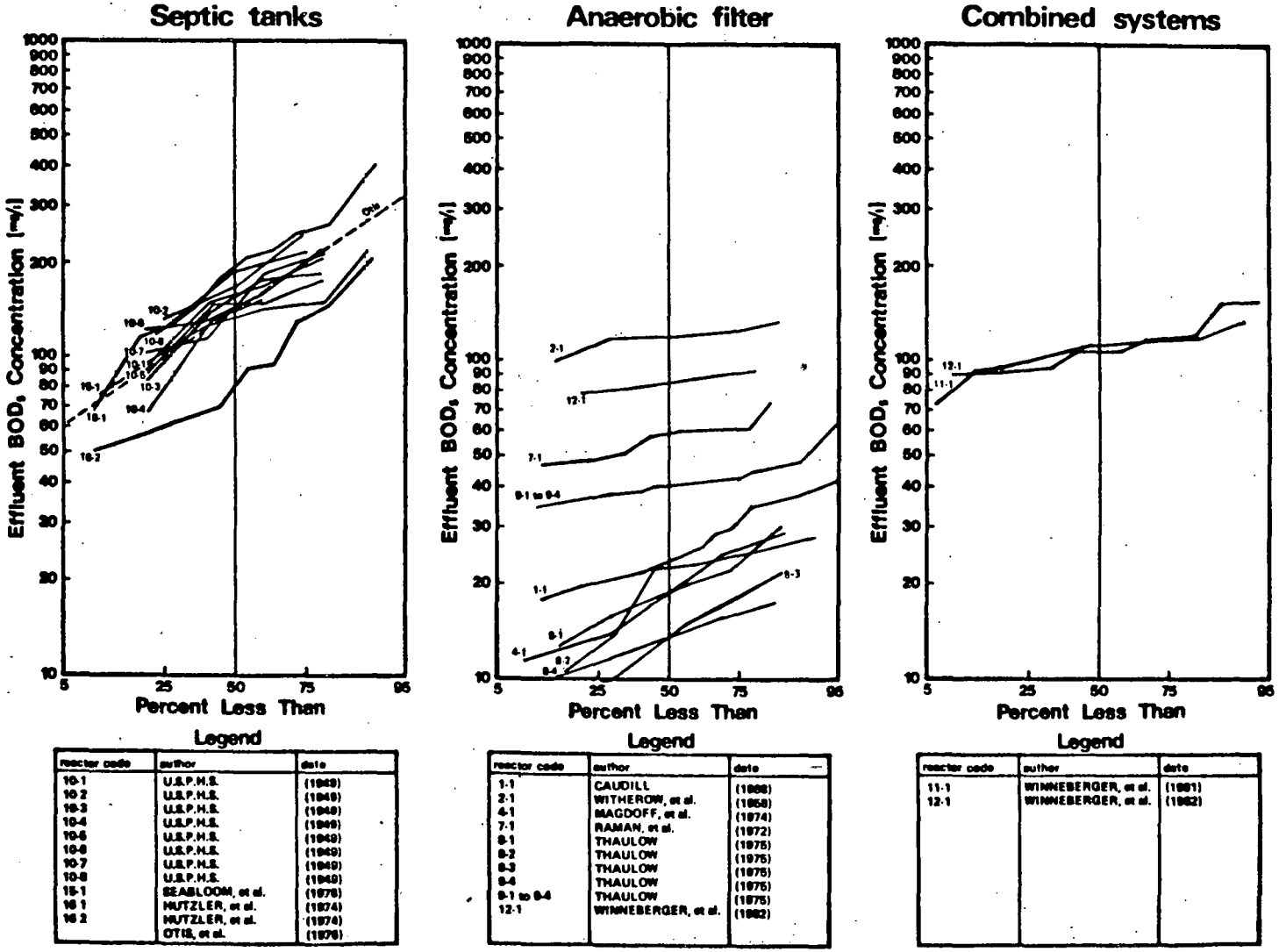
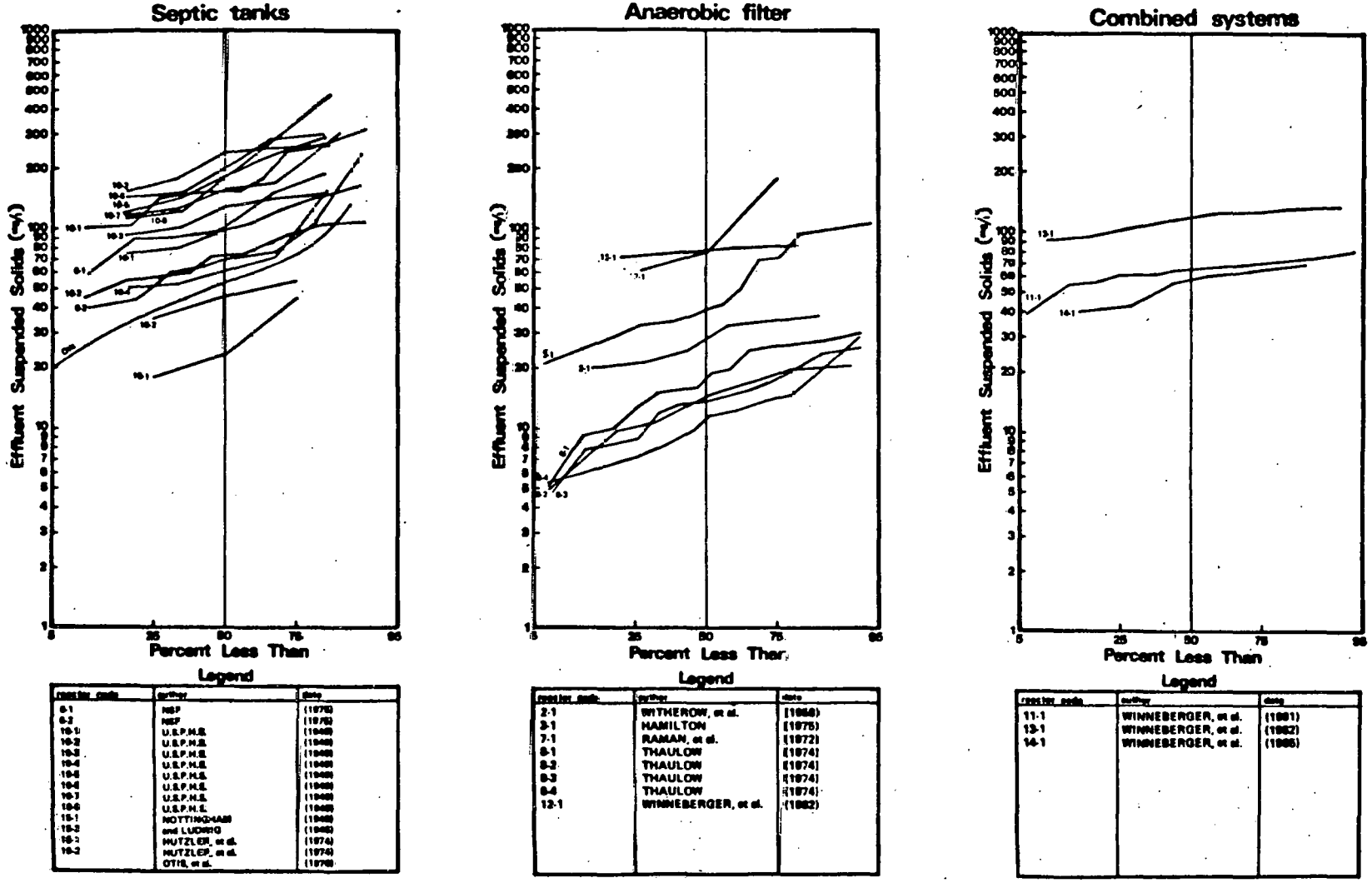


Figure 2 **Frequency distribution of effluent suspended solids data**



septic tank studies, as further detailed by Kennedy (1979). These results indicate that influent BOD was significant in determining the percentage BOD removal for 80% of the filters and for 60% of the septic tanks. The influent SS and time did not significantly affect BOD and SS removal efficiency.

Table 4 Results of Statistical Testing of BOD and SS Model

	Parameter	Anaerobic Filters	Septic Tanks
BOD Removal Model	Coefficient b_1	significant 4/5 neg. 0, pos. 5	significant 6/10 neg. 0, pos. 5
	Coefficient b_2	significant 0/5 neg. 1, pos. 5	significant 1*/10 neg. 3, pos. 7
	Coefficient b_3	significant 0/5 neg. 4, pos. 1	significant 0/10 neg. 10, pos. 0
	--Overall R^2 accounted for $\geq$ 90% variability	4/5	6/10
	--Overall F statistic significant $\leq$ 0.05	4/5	1*/10
SS Removal Model	Coefficient a_1	significant 1*/5 neg. 5, pos. 1	significant 1/10 neg. 2, pos. 8
	Coefficient a_2	significant 0/5 neg. 2, pos. 4	significant 0/10 neg. 1, pos. 9
	Coefficient a_3	significant 0/5 neg. 4, pos. 1	significant 2/10 neg. 7, pos. 3
	--Overall R^2 accounted for $\geq$ 90% variability	0/5	3/10
	--Overall F statistic significant < 0.05	0/5	1/10

*almost significant at 0.05 level

The values for the coefficient b_1 were all positive, indicating that the BOD removal percentages increase with increasing influent BOD value. The value for b_2 was positive in most instances, possibly indicating that with increasing influent SS values, a larger portion of the settleable solids are biodegradable. The values for b_3 are generally negative, reflecting an increasing removal at greater detention times. The values for a_2 and a_3 indicate a larger SS removal with increasing SS influent concentrations and a longer detention time.

The values for the regression coefficients of the BOD removal model showed a substantial degree of variability. For anaerobic filters, b_1 varied between 4 and 19 with an average of the significant values of 18.5, while for septic tanks b_1 varied from 8 to 136 with an average of the significant values of 12.2. At an influent BOD of 169 mg/l, i.e. the median value for all evaluated systems, the coefficients predict a 95% average BOD removal for 4 out of 5 anaerobic filters and a 63% average BOD removal for 6 out of 10 septic tanks. The average b_1 coefficient for both units is 15.4. When this average value is inserted in the model, and the influent BOD concentration is increased from 100 to 150 mg/l, the percentage BOD removal increases from 77% to 82%, corresponding to an effluent BOD of 34 and 37 mg/l, respectively. Thus when the influent concentration increases 50%, the effluent concentration increases only 9%,

indicating that the systems are able to treat the increased organic loading.

DISCUSSION

The above results indicate that the BOD removal is better predicted than the SS, using the multiple regression model. The influent BOD concentration was found to be the most important predictor variable in the percentage BOD removal, and it was generally noted that removal percentage increased with increasing influent concentration. The other predictor variables were not significant in most instances. The equations (1) and (2) are somewhat similar to those developed by Laak and Crates (1978) for septic tanks:

$$BOD_{out} = 4 \times BOD_{in}^{2/3} \quad (3)$$

$$SS_{out} = 2.5 \times SS_{in}^{2/3} \quad (4)$$

as these equations show an increasing removal percentage at increasing influent concentration. When the influent BOD, for example, increases from 100 to 150 mg/l, the removal percentage increases from 14% to 25%. These removal percentages, however, are substantially lower than noted in the present evaluation. Baumann et al (1978) also reported higher BOD removal percentages ranging from 65% to 80%, and SS removal percentages ranging from 60% to 50%. Both models differ from the empirical model developed for anaerobic filters by Young and McCarty (1968), who stated that hydraulic detention time (days) was the most significant operating parameter:

$$\% \text{ BOD} = 100 - 7.5/\text{time} \quad (5)$$

with higher removals observed at greater detention time. Their model, however, was developed for higher strength waste water.

Other researchers have also noted that an increasing influent concentration at a constant organic loading resulted in an increasing percentage removal. Jennett and Dennis (1975) noted an increasing removal percentage when influent concentration increased from 4,000 to 16,000 mg/l at a constant organic loading. Similar findings were reported by Chian and DeWalle (1977) and by Mosey (1978). Young and McCarty (1968) noted a constant percentage removal with increasing influent concentration, at a constant organic loading. The increasing removal percentage at increasing influent concentration is reflected in the effluent BOD values which tend to reach a plateau as shown in Figure 3.

Full scale anaerobic filters have operated successfully for substantial time periods. The 119 gallon filter studied by Raman and Chakladar (1972) consistently achieved BOD removals between 65% and 75% and SS removals between 65% and 70% for 18 months before sludge wasting became necessary. The 650 gallon filter by Hamilton (1975) operated almost four years without clogging.

The data discussed in the present study indicate that the anaerobic filter can biologically treat settled domestic sewage and need not follow a septic tank. Removal of solids by sedimentation can occur in a preceding sedimentation unit/grease trap but can also be incorporated in the filter using a design shown in Figure 4 in which the bottom section of the unit functions as a settling basin where excess solids can be removed by pumping. The bottom section contains a dense anaerobic sludge blanket providing for initial degradation. Additional substrate removal occurs in the plug flow channels of the filter containing attached anaerobic bacteria. The sloped channels also function as tube settlers to achieve additional solids removal. No plugging has been observed in 3 years of continuous operation of a 55 liter laboratory anaerobic filter fed with leachate using such media, as most of the biomass was able to settle freely through the channels and reach the sedimentation section (DeWalle

Figure 3 Relationship Between BOD_5 in the Influent and Effluent (mean values)

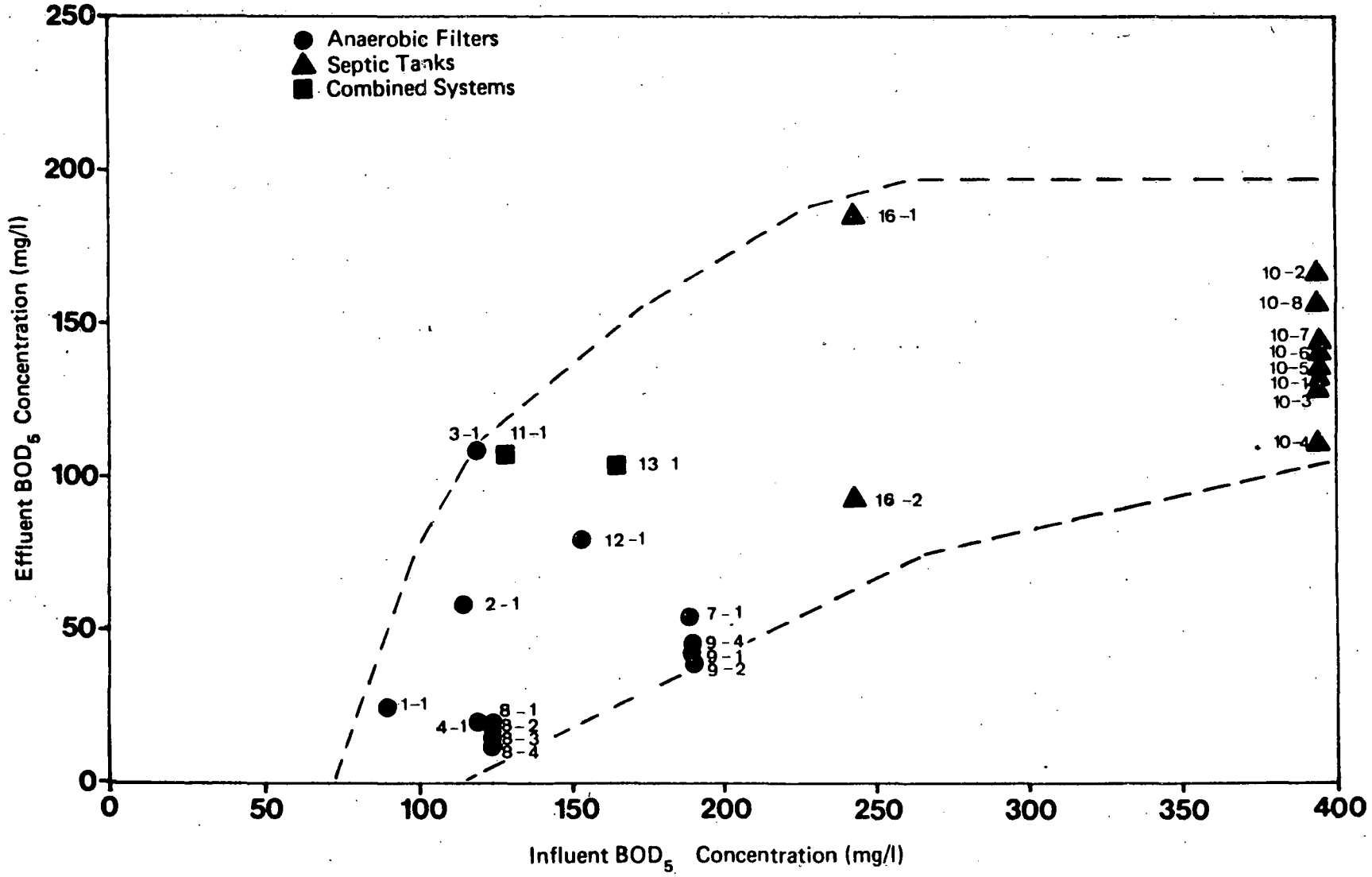
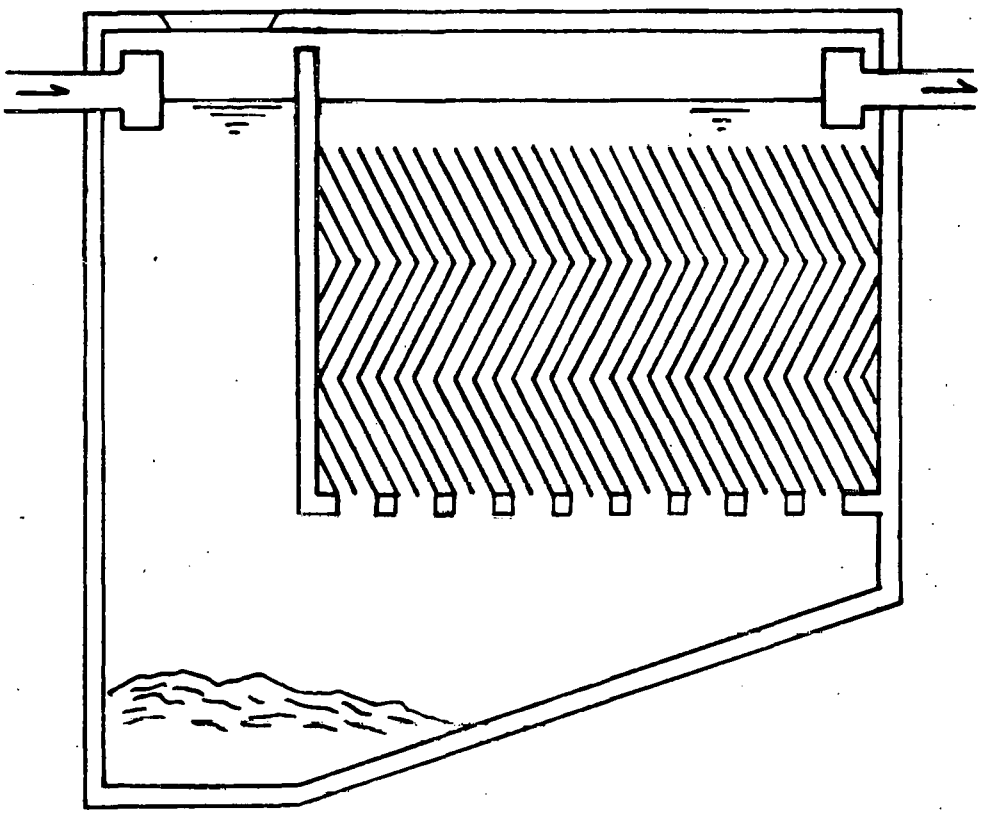


Figure 4. Anaerobic filter design for treating domestic sewage.



and Chian, 1976). In addition, large heavy metal removals were observed (DeWalle et al, 1979). If constriction of the sludge were to cause channeling, the biomass can be fluidized by using an inflow or effluent syphon to provide for surges through the unit. The possible higher sewage treatment provided by an anaerobic filter as compared to a septic tank may reduce the land area required for the drain field. Based on studies with columns of sand, sandy loam, and loam, Laak (1974) formulated the land area reduction as:

$$\text{Adjusted Area} = \text{Standard Area} \times \sqrt[3]{(SS + BOD)/250} \qquad (6)$$

while Bernhart (1973) formulated the empirical equation:

$$\text{Seepage Area} = \text{Flow} \times (BOD + SS)/120 \times \text{Seepage Rate} \qquad (7)$$

When the effluent BOD is 150 and 30 mg/1, values commonly observed for septic tanks and filters, respectively (Figure 1), and effluent SS is 100 and 25 mg/1, respectively (Figure 2), equation (6) predicts that the drainfield for the filter is 0.60 times that of a standard drain area for septic tanks, while equation (7) predicts a filter drainfield 0.22 times that of a septic tank drainfield. Using the conservative estimate (6), one may typically save $500-$3,000 for a drainfield area for a single home in a typical urban setting. This estimate is based on a drainfield of about 550 square feet for permeable soil and 2,300 square feet for less permeable soil, a land price of $1.50 per square foot, and a reduction of both the drainfield area and the set aside area for a reserve drainfield. These savings are partially offset by the higher cost of the anaerobic filter construction. Most states, however, currently do not allow reduction in drainfield area on the basis of effluent quality. The above area equations are based on a limited amount of data obtained over a restricted range of conditions and should therefore be used with caution.

The evaluation of the literature data shows the lack of comprehensive studies in which the anaerobic filter is compared with the septic tank both treating the same sewage over a range of organic loadings. As the anaerobic filter data may promise a higher effluent quality as compared to the septic tank, further research in this area is urgently needed.

CONCLUSION

The present study formulated a simplified regression model predicting BOD and suspended solids removal of anaerobic filters and septic tanks treating domestic sewage. The evaluation showed that the BOD removal is most significantly predicted by influent BOD and increases with increasing concentrations. Effluent BOD values do not show large variations over a range of influent concentrations, possibly due to the low organic loading of the units. The model predicted higher BOD removals for 4 out of 5 anaerobic filters than for 6 out of 10 septic tanks. For those units, the model explained more than 90% of the removal variability. Existing equations predict a 40% reduction in size of drainfield using anaerobic filter effluent quality data as compared to septic tank data.

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PERFORMANCE OF ANAEROBIC FILTERS UNDER TRANSIENT LOADING AND OPERATING CONDITIONS

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ABSTRACT

Anaerobic filters have been shown in numerous situations to be capable of receiving high-strength soluble wastes and of producing high treatment efficiencies when operated at organic loadings well in excess of the loading capabilities of conventional aerobic and anaerobic systems. Less-well known is the fact that anaerobic filters are capable of operating under various transient loading and operating conditions without permanent loss of treatment efficiency. For example, such extreme actions as passing air through the unit or permitting the pH to drop as low as 5.5 or letting the unit stand for weeks to months without feed do not cause the filter to lose the ability for rapid recovery of its former steady-state efficiency.

This paper will explore the ability of anaerobic filters to operate under extreme variations in loading and discuss some of the factors affecting the performance of filters when subjected to adverse operating conditions.

INTRODUCTION

Recent investigations have suggested the possibility of using an "anaerobic filter" for the treatment of low-strength soluble wastes (1-25). In this process, wastes are passed upward through a bed of rocks or similar porous media (Figure 1). Biological solids become attached to the surfaces of the filter media or are trapped in the void spaces in high concentrations so that the long solids retention times necessary for satisfactory anaerobic treatment of organic wastes at nominal temperatures can be attained. Also with long solids retention times, low-strength wastes containing less than one percent biologically degradable material can be treated. Settling and recycle of the effluent solids is not required to maintain a high treatment efficiency, and the need for solids separation is reduced or eliminated. Net solids synthesis is low, nutrient requirements are reduced and solids disposal problems are minimized. The anaerobic filter then potentially approaches the "ideal" waste treatment process for low-strength soluble wastes.

The anaerobic filter is a "fixed-film" anaerobic process in which the stabilization of waste takes place at the surface of a layer of biological solids attached to or held by the filter media. Since flow through the filter approaches plug-flow conditions, a high degree of biological efficiency is approached in this process. A high rate of removal occurs in the lower levels where both substrate and biological solids exist in high concentrations. As the waste flows through successive layers of the filter, organic material is removed continually by the active biological solids in that layer. Biological solids produced in the first regions of contact are worked upward through the filter where they become available for further waste removal. As the solids are moved into the top, or effluent end of the filter, the waste concentration becomes low and the net rate of growth is negative. That is, biological decay of the accumulated microorganisms exceeds the rate of solids synthesis. The effluent liquid is then highly purified and the effluent suspended solids consist largely of dead cells which are highly stable and subject to essentially no further decay.

The mode of operation of the anaerobic filter is analogous to that of a number of reactors in series with a high rate of treatment in the first unit and polishing and solids separation in the subsequent units. The major advantages of such multi-stage anaerobic processes are 1) that an effluent can be produced having much lower concentrations of un-utilized substrate than is possible in single-stage systems, and 2) environmental conditions in each stage may favor the development of a particular group of microorganisms and thereby increase the rate of consumption of a particular component of a waste.

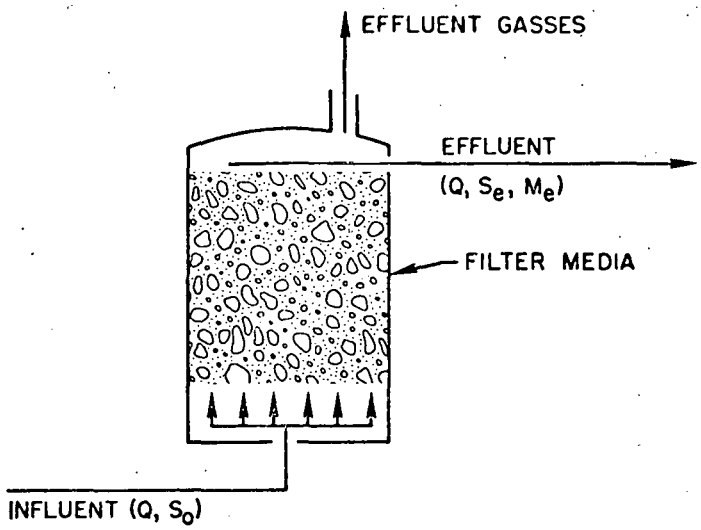

Figure 1. Schematic diagram of the anaerobic filter process

A number of tests have been conducted in which anaerobic filters of various designs were used to treat a variety of wastes when operating under a number of loading and operating conditions (1-25). The results of these studies provide an indication of the response of anaerobic filters to variations in loading and operating conditions. The purpose of this paper is to summarize these responses and to point out how anaerobic filters might be designed and operated to minimize adverse effects of transient loading and operating conditions.

STAGES OF ANAEROBIC FILTER OPERATION

The operation of anaerobic filters can be divided into two stages--start-up and steady-state-- which are affected differently by variations in loading and operating conditions.

Starting the Process

Start-up of an anaerobic filter probably is the most difficult period of operation. Start-up times in experimental and full-scale units has ranged from 10 to 180 days with the shorter times corresponding to the use of large amounts of active seed while the longer times were associated with the use of light seeding.

Detailed analysis of the action of the process during start-up has indicated three factors of importance. First, the slow growth of anaerobic microorganisms, especially at low waste concentrations and at temperatures below 30°C, does not permit rapid build-up of biological solids. Consequently a large seed mass is needed for rapid start-up.

Secondly, decreases in the buffer capacity of the waste so that the pH drops below about 6.5 at any point within the filter for even short periods of time increases the starting time significantly.

A third factor affecting start-up time is related to the physical characteristics of the biological suspended solids within the filter. During the early stages of operation, a significant fraction of the biological solids remain finely dispersed throughout the liquid phase and a significant fraction washes out with the filter effluent. At some time after initial seeding, flocculation of the biological solids occurs in the filter and the solids washout rate decreases, thereby increasing both the rate of active biological solids accumulation and the rate of waste treatment.

The optimum method of seeding a filter is not known. Large seed volumes help to start the filter more rapidly by providing a large viable microbial population, and the large amounts of suspended solids help to promote the surface adhesion and flocculation which seem to be essential to good operation. However, using large seed volumes may also contribute significant amounts of inert volatile and non-volatile solids which only tend to plug the filter and reduce its effectiveness for treating wastes.

"Steady-State" Operation

After a constant gas production rate is achieved, the soluble COD concentration at each filter height may remain essentially constant, but the relative concentration of the individual volatile acids may continue to change slightly. Thus a true biological steady-state condition may never exist in the anaerobic filter. However, the effect of the relative changes in individual volatile acids on total COD removal is sufficiently small so that for all practical waste treatment applications the period of constant gas production may be referred to as "steady-state" operation. In plant-scale operation, these minor fluctuations would be negligible compared to the influence of normal variations in influent waste strength and composition.

A constant COD removal efficiency or gas production rate also does not necessarily indicate that there is a steady-state concentration of biological solids in the filter. The solids retention characteristics of the filter are such that biological solids may accumulate continually until the filter becomes filled and a break-through of biological solids occurs in the effluent. Once "steady-state" is attained, most of the additional solids accumulating in the filter contribute little to additional COD removal.

Anaerobic filters are most resistant to changes in loading or operating environment such as pH changes or temperature fluctuations during "steady-state" operation.

"Steady-State" Treatment Efficiency

Hydraulic detention time appears to be a more significant operating paramenter, than either waste strength or organic loading (Figure 2). BOD_L removal efficiencies are shown to be quite high at the lower hydraulic detention times but decrease as hydraulic detention time decreases. This relationship is the same when treating wastes containing a mixture of volatile acids (V.A.) or a complex mixture of proteins and carbohydrates (P.C.). The data shown in Figure 2 essentially all fall on a line described by the following equation

$$E = 100 \left(1 - \frac{\Phi}{T}\right) \qquad (1)$$

where:

$E = BOD_L$ removal efficiency, present

Φ = A proportionality constant, hours

T = Theoretical hydraulic detention time, hours.

Although Equation 1 is only an empirical description of waste removal in the filter, its applicablity over a wide range of organic loadings and waste strengths for both volatile acids and protein-carbohydrate wastes, suggests that the relationship is fairly general. The efficiency can be predicted by Equation 1 to within about 5 percent for the range of loading conditions represented. However, the coefficient, Φ, would be expected to apply only to the experimental filters from which the data were obtained and should not be used for making performance predictions for

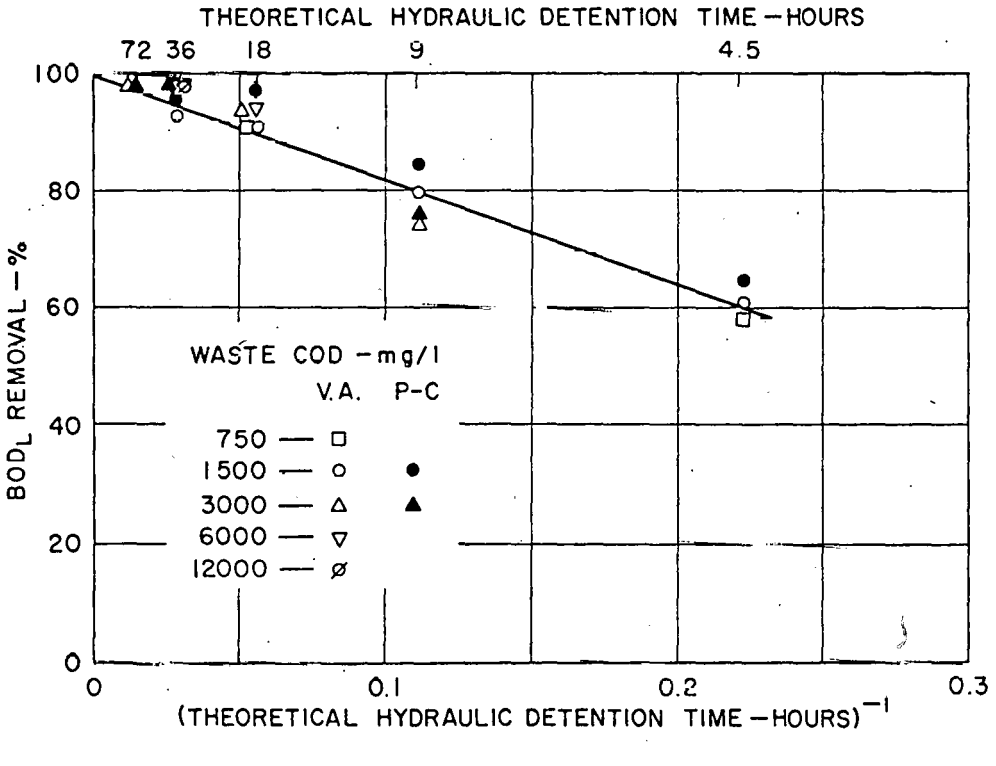

Figure 2. BOD$_L$ removal performance of anaerobic filters as related to the theoretical hydraulic detention time

other filters without verification.

Since

$$E = 100\ (S_o - S_e)/\ S_o$$

and

$$T = \varepsilon V/Q$$

where

S_o = influent BOD_L concentration

S_e = effluent BOD_L concentration

ε = porosity of filter media

V = Volume of reactor tank

Q = flow rate

Equation (1) can be rearranged to give the following expression:

$$S_e = \frac{\Phi\ S_o\ Q}{\varepsilon V} = \Phi'\ L \qquad (2)$$

where L is the organic loading to the filter in mass of BOD_L per day per unit total volume.

It also must be recognized that these data represent soluble BOD only, and the contribution of effluent suspended solids to the effluent quality must be considered. With six-foot (1.83 m) tall laboratory filters this was a relatively minor contribution, while for shallow filters the effluent suspended solids may significantly decrease the effluent quality. High effluent suspended solids concentrations were reported by Plummer et al. (3), but it was not clear whether this was caused by the use of shallow filters or by the treatment of high-solids-producing carbohydrate waste at high hydraulic and organic loadings.

TRANSIENT LOADING AND OPERATION

There are three major types of transient loading or operating conditions that can affect filter performance: 1) variations in loading as a result of changes in flow rate or waste strength, 2) intermittent operation, and 3) changes in pH, temperature and waste composition. Other factors such as the influx of organic toxins or heavy metals also will affect performance but will not be discussed in this paper.

Variations in Waste Loading

Tests by a number of investigators (2, 12, 14, 16) have shown that anaerobic filters can readily accept variations in load--caused by changing either or both the flow rate or the waste strength--without being upset permanently. Equation 2 suggests that changing the flow rate and waste strength simultaneously so that the organic load remains constant will not cause the effluent BOD_L to change. However, this says, and is verified by

Equation 1, that for equal loading conditions, the BOD_L removal efficiency will increase as the waste strength increases. Read another way, Equations 1 and 2 suggest that the "steady-state" effluent BOD_L concentration will vary directly with changes in influent BOD_L if flow rate is held constant or in proportion to the flow rate if waste strength does not change. Data from a number of investigations support this conclusion(2, 10, 14, 16).

Short-term loading increases having a duration of one or two hydraulic detention times can be expected to produce only slight, short-term changes in effluent quality or gas production. Long-term changes, however, will cause the COD and volatile acid profiles, and no doubt the population dynamics and solids concentrations, to shift until a new "steady state" level of performance is reached. Four-fold instantaneous increases in loading have caused no permanent adverse effects on filter performance. This response is illustrated in Figure 3 where the loading was increased by changing the flow rate and maintaining the influent COD at 3000 mg/l. Gas production doubled within two days after the loading increase and increased gradually for twenty additional days of operation. A slight decrease in the methane content of the gas and a corresponding short-term deterioration of effluent quality paralleled this short adjustment until a new "steady-state" level of performance was achieved.

Analysis of COD profiles throughout the height of a filter during a loading change have shown that during the early stages of adjustment there is a rapid decrease in the total COD until a equilibrium treatment level is reached. However, the relative concentrations of propionic and acetic acid continue to shift for a longer period of time (2).

The slow rate of growth of methane formers at COD concentrations below about 1000 mg/l BOD_L may limit the usefulness of anaerobic filters for treating low-strength wastes. Relatively efficient treatment of wastes having a BOD_L of 375 to 750 mg/l has been accomplished when decreasing the influent concentration to a filter that had previously been operating satisfactorily at higher waste concentration. Thus the microorganism mass would not have been the same as would have developed naturally if the filter were started using the 375 mg/l concentration. Heating the water to 30 to 35°C can possibly overcome some of these limitations, but heating normally would not be economically feasible. Design changes and improvements such as the use of smaller media or different reactor configurations also can possibly provide improved treatment of such low-strength wastes.

Intermittent Operation

Rapid response capability to increased loadings suggested the possibility of operating anaerobic filters intermittently. This possibility has been tested by several investigators (2, 7, 14). The effect of stopping all flow and load to filters for several days is illustrated in Figure 4. After 3 days of down-time-- as might be used in practice for weekend operation--there was essentially no loss in COD removal capability or gas production efficiency upon restarting at full load. After fourteen days of down-time without feed, the COD removal efficiency decreased to a greater extent, but full COD removal capacity and gas production were achieved after only three to four days of operation.

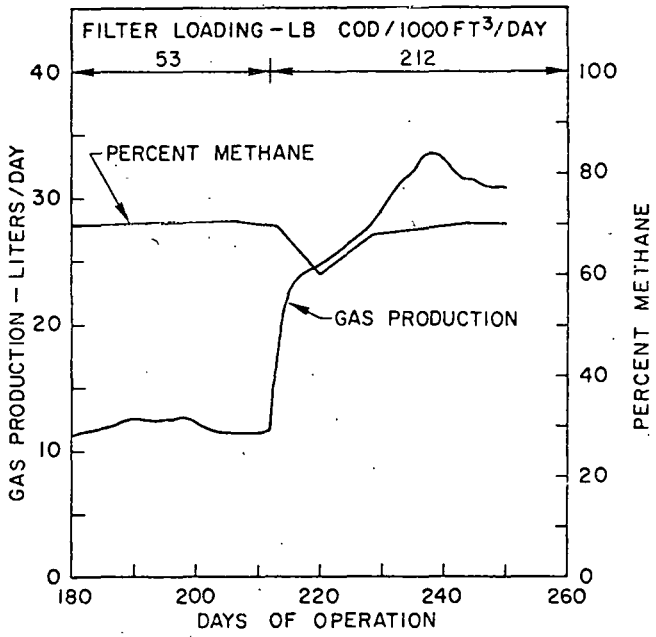

Figure 3. Changes in gas production and composition in response to a four-fold increase in organic load

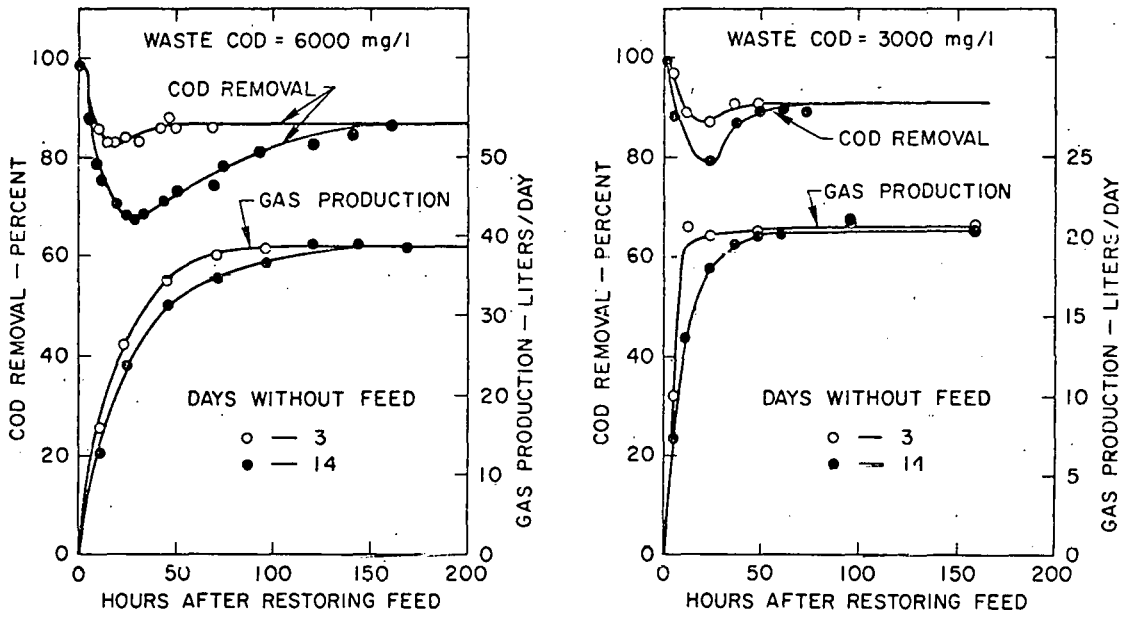

Figure 4. Response of anaerobic filters under intermittent loading conditions as measured by gas production rate and COD removal.

Longer periods without feed might be expected to produce a low quality effluent for quite a long period of time after restoring waste load. However, after standing idle for six months, one laboratory-scale filter reached an immediate 50 percent BOD_L removal when fed a 2740 mg/l BOD_L milk-base waste at a loading of 48 lb BOD_L/1000 ft^3/day (0.77 kg/cu m/day)$_L$(22). A BOD_L removal efficiency of 90 percent was reached within 16 days, and 95 percent efficiency was achieved in 24 days. Rapid start-up after 1 to 4 months of inoperation has been reported when treating potato processing wastes (4, 12). Wastes from industries operating only a few days each week could then possibly be treated with an anaerobic filter on an intermittent cycle and no special restarting procedures would be required. This method of operation is not possible with either conventional digestors or anaerobic activated sludge, which, in fact, require a somewhat continuous feed rate to be operated satisfactorily.

pH, Temperature and Waste Composition

pH

Anaerobic filters are most sensitive to pH changes during start-up. At this stage, a decrease in pH to 6.5 or lower can increase the time of start-up significantly (1, 2). Once "steady-state" operation is achieved, filters become quite resistant to pH changes. Rapid recovery has been observed in filters exposed for a 12-hour period to pH levels as low as 5.4 (8). Exposure to pH levels of 9.3 for as long as 4 days has caused only temporary loss of treatment efficiency. While COD removal and gas production were impaired at these extreme pH values, the filters recovered completely within one to two days after restoring pH to normal levels. This assumes of course that the pH drop is caused by changes in waste characteristics and not by upset of the methane forming microorganisms by toxic materials.

Temperature

Although it normally is not economical to heat low-strength wastes, a number of situations exist in which heating might be desirable. For example, limited heating could be used to maintain the temperature of the filter contents during cold weather. For some wastes, sufficient methane may be produced to heat the waste significantly. Some wastes are naturally warm and heating would not be required.

In general, anaerobic filters are expected to perform best at temperatures greater than 25°C. Filters have been used successfully to treat potato processing wastes at temperatures as low as 19°C (7), but too little information is available from which to draw significant conclusions about the effect of lower temperatures on filter performance. Too little data also are available to indicate filter response to rapid changes in temperature.

Waste Composition

Variations in waste composition are expected to produce little adverse response in anaerobic filters unless there is an associated influx of toxic materials.

With high-protein wastes, a large part of the needed alkalinity may be provided by the ammonium carbonate formed during first-stage anaerobic decomposition. However, the concentration of protein waste is limited to about 10,000 mg/l BOD_L before this ammonia can become toxic to the methane forming microorganisms.

The composition of the waste significantly affects the solids produced in the system. Since synthesis of biological solids is greatest with carbohydrates, biological solids would accumulate much faster when treating carbohydrate wastes; and at high loadings severe problems of plugging or solids washout might be encountered. In studies to date no situation has been reported in which a filter used for organic carbon removal has become plugged beyond use. However, high effluent solids concentrations have been measured when treating carbohydrate wastes (2, 3). Periodic wasting of biological solids from the process would be advisable to prevent the filter from being filled with solids. With fat, fatty acid, and protein wastes solids synthesis is so low that the accumulation of biological solids is almost negligible.

SUMMARY AND CONCLUSIONS

Anaerobic filters have been shown to provide efficient treatment of low-strength soluble organic wastes at nominal temperatures and without the need for solids separation and recycle. Once start-up is accomplished, anaerobic filters are much more resistant to variations in waste load and environmental factors such as pH and temperature than are conventional completely mixed anaerobic digesters. Laboratory-scale filters have shown rapid adjustment to four-fold surges in influent load.

Anaerobic filters can be operated intermittently. Both laboratory and full-scale units have shown rapid recovery of waste conversion and gas production after down-times ranging from 3 days to more than 6 months.

This ability to accept wide variations in load, waste characteristics and operating conditions and the ability to recover rapidly after periods without feed, makes anaerobic filters an attractive alternative for treating low-strength soluble organic wastes as might be required for pretreatment of industrial wastes prior to their discharge to a domestic sewerage system.

ACKNOWLEDGEMENT

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ANAEROBIC FLUIDIZED BED TREATMENT OF THERMAL SLUDGE CONDITIONING DECANT LIQUOR

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ABSTRACT

A pilot scale study of the fluidized bed anaerobic treatment of decant liquors from Thermal Conditioning of a combined municipal/brewery waste sludge was carried out in Jacksonville, Florida. The return of these high strength decant liquors to the activated sludge plant for treatment has caused process upsets and has resulted in high energy costs for the aerobic treatment of the liquors. The study was performed to assess the applicability of fluidized bed anaerobic treatment to decant liquors and to provide data on the cost and energy production which may be expected from a full scale system.

The pilot study was carried out over a several month period in 1978. Feed to the pilot fluidized bed reactor was decant liquor from the full scale thermal sludge conditioning system. Various loadings and recycle rates were investigated along with intermittant feeding studies to simulate full scale system conditions. Parameters measured included total and soluble BOD, total and soluble COD, pH, Volatile Acids, Alkalinity, TSS, Temperature, Gas Production rate and gas composition.

Results of the study indicated that after acclimation the anerobic fluidized bed treatment system was capable of consistantly acheiving over 70% COD reduction and good gas production while exhibiting extremely stable operation even under shock loading conditions. Data from the pilot study are presented along with cost estimates and energy balances for the full scale system.

During the summer and fall of 1978, a pilot investigation was carried out of anaerobic fluidized bed treatment of decant liquor from the full scale thermal conditioning system. The reactor utilized is shown as figure 1.

Decant liquor is pumped from the feed tank through the reactor. The recycle pump provides the flow necessary to maintain the fluidized bed and to control loadings in the desired range. An alkalinity control system, pH probe, and heating probe control system pH and temperature. A gas meter measures the gas production above the top of the reactor. A sand pump is present which functions to prevent the loss of the sand media as well as sludge separation. Early in the acclimation phase of operation, decant tank effluent was used as the source of feed. The feed source was later changed to the decant supernatant from the heat treatment unit effluent before reuse water is added. Finally, the feed to the anaerobic fluidized bed reactor was heat treatment unit effluent which was diluted with tap water to result in a ACOD in the range from 4000 to 5000 mg/1. The feed in the waste feed tank was changed and refilled every few days to insure a "fresh" source of feed with reasonably constant characteristics. Analyses performed included TCOD, SCOD, total alkalinity, bicarbonate alkalinity, volatile acids, total suspended solids, volatile suspended solids, and pH determinations. BOD's and the analysis of the gas produced by the reactor were performed intermittently.

Results

The fluidized bed system took approximately six weeks to acclimate before gas production was evidenced. The amount of sand which was added to the column filled it to about one-half of its height when fluidized. As a result, the wasting of sludge and recycling of sand media in the column was not a concern. The height of the sand varied little, except when the recycle flow rate (flux rate) was changed. Representative flows during this six-week acclimation period were a recycle flow of 16.5

liters/minute and feed flow of 20 milliliters/minute, giving an approximate recycle-to-feed ratio of 825.

Table 1 summarizes the operational parameters and results for the periods of operation in which the operational parameters were held constant, the methane in the off-gas indicative of anaerobic digestion, and the effluent characteristics were steady. In all time periods listed in Table 1 the feed was daily, except the fourth time period in which the feed was intermittent. Recycle was continuous and the feed rate was controlled by a timer on a feed pump which allowed 15-minute increments of pumping.

The operation of the column was observed to be stable. During the various periods of stable operation, the temperature of the liquid in the system had an overall range from 31° C to 38° C. The pH of the system was stable. pH adjustment was not required during the study, as the system maintained a tolerable pH. The pH ranged from 7.10 to 7.75, with a pH of 7.35 being most representative of the values observed. During the stable periods of operation included in Table 1, no alkalinity adjustment was necessary. During these periods, total alkalinity ranged from 1500 to 3400 mg/l as $CaCO_3$, with 1800 mg/l being a representative single value. Bicarbonate alkalinity ranged from 1400 to 2500 mg/l as $CaCO_3$, with 1750 mg/l being representative over the cited periods of time.

Total and volatile suspended solids concentrations were determined intermittently for both the effluent and feed. Total suspended solids in the effluent were approximately 160 mg/l, while volatile suspended solids were about 75 percent of the total suspended solids. Total suspended solids concentration in the feed were approximately half those of the effluent, with the volatile suspended solids concentrations approximately 75 percent of the total suspended solids.

Five-day biochemical oxygen demand (BOD_5) determinations were made intermittently on the effluent and feed. During the second time period as listed in Table 1, a BOD_5 determination on the soluble effluent (SCOD $\cong$ 2300 mg/l) resulted in a COD-to-BOD_5 ratio of approximately 2.3. Determinations on effluents with SCOD concentrations of approximately 1150 mg/l resulted in COD-to-BOD_5 ratios of approximately 5.2 during the

intermittent feed phase. Determinations on effluents with SCOD concentrations of approximately 1170 mg/1, taken during the last period of operation as listed in Table 6-5, resulted in COD-to-BOD_5 ratios of approximately 8.9. Intermittent BOC_5 determinations on the soluble portion of feed samples, resulted in a representative COD-to-BOD_5 ratio of approximately 2.0.

Analysis of the gas produced by the anaerobic fluidized bed column was done on a weekly basis by means of gas chromatography. The percentage of methane and carbon dioxide in the gas produced is approximately 72 and 28 percent, respectively. The percentage of methane in the off-gas for each period of steady operation is presented in Table 1. Gas production rates are presented in Table 1 for each of the operational time periods of interest.

SCOD's were determined for the effluent from the anaerobic fluidized bed reactor on a daily basis for the feed to the unit whenever a change or addition to the feed tank was made. These SCOD concentrations have been averaged for each individual period of steady operation and are presented in Table 1 along with a removal percentage calculated.

The operation of the system during the entire study may be described as stable. No pH, or alkalinity adjustment was required. Given the feed, the system literally "ran itself".

Preliminary Design

The following preliminary design has been prepared using a COD loading rate of 440 lbs/1000 cf/day. This is a conservative design and that even higher loading rates are possible once the process is further optimized.

Description Anaerobic Fluidized Bed Design

Anaerobic treatment of the heat treat effluent is carried out in enclosed reactors. The reactors are arranged into four completely isolated modules, each module consists of three reactors in series. The arrangement ensures that if any one reactor is being serviced the plant will operate at least 75% capacity. The series arrangement of the reactors within each module gives greater overall removal efficiency because of the greater flexibility of this system. The reactors are covered by a concrete slab, which also isolates the gas phases between

the modules. The gas is maintained at a pressure of 6"-9" and all gas safety and disposal equipment is located on the roof of each module. Four independent pumps feed the effluent from the thickening tank to the first reactors of each module. Suitable precautions exist to ensure that there is no mixing of air with the sewage gas above the reactor. The effluent from the first reactor is gravity fed through a weir to the second reactor in series. The effluent of the second reactor is gravity fed to the third reactor and the final effluent from all four modules is combined for further disposal. Since recycle is part of the system's operation, a main recycle pump (one for each reactor) draws liquid from near the top of the reactor and pumps it through the distributor in the bottom, thus fluidizing the sand. Series operation of three reactors allows for individual adjustment of the recycle ratio to achieve optimum removal rates. Pressure regulators release the sewage gas from each module to the proper storage location for futher use. Excess growth is removed by a system that consists of a suspended tube sludge separator, located in the middle of each reactor, a small pump and associated piping.

A preliminary cost estimate was performed for the system described above. The installed cost, first quarter 1970 was estimated to be $3,436,000.

Summary

The anaerobic fluidized bed treatment of decant liquor has been shown to be feasible. The operation was stable and easy to control even under intermittent loading. Biodegradable organic removal was high. Energy balances are favorable.

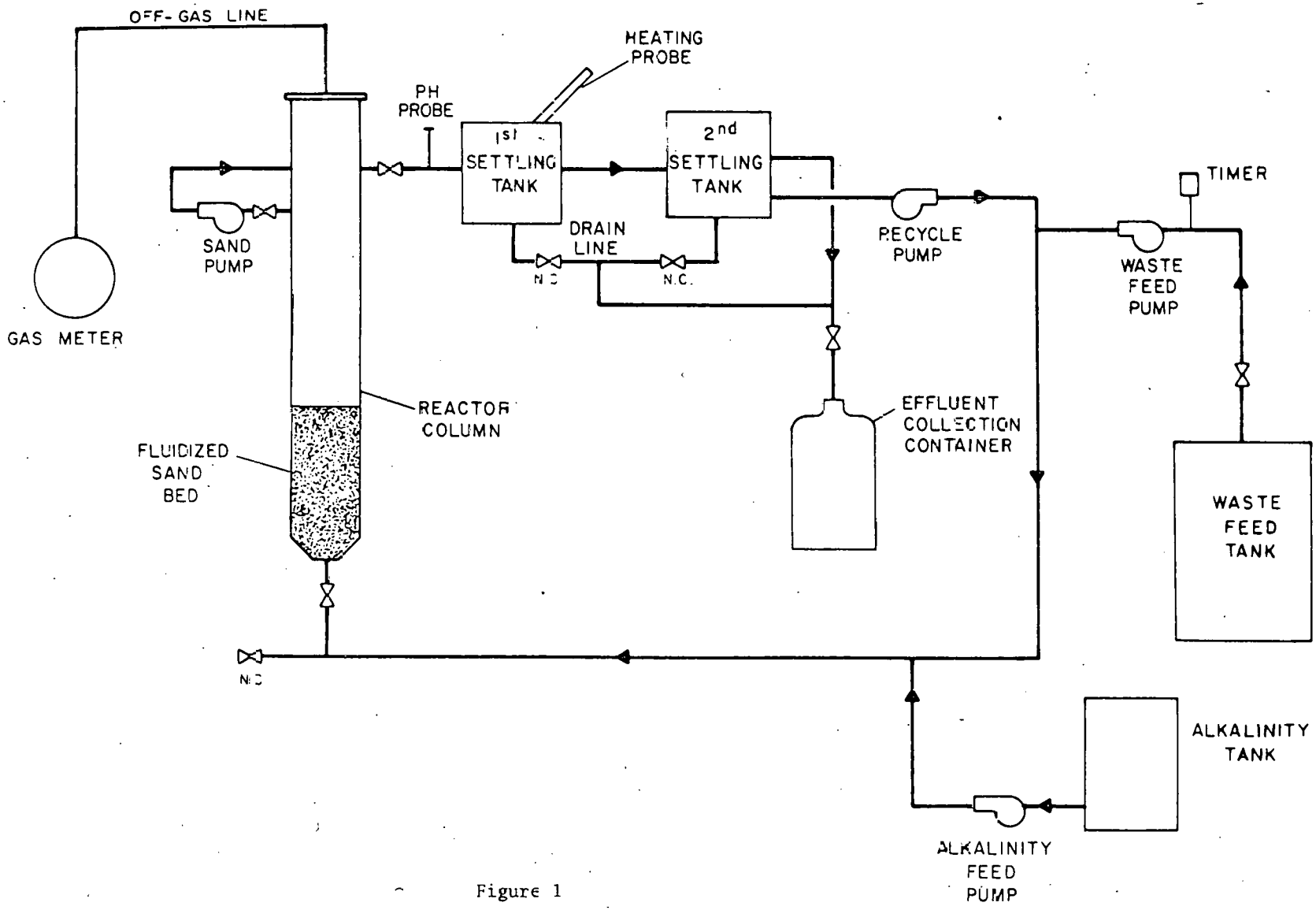

Figure 1

SCHEMATIC OF THE ANAEROBIC FLUIDIZED BED

PILOT PLANT UNIT

Table 1

SUMMARY OF OPERATIONAL PARAMETERS AND RESULTS

FOR PERIODS OF STEADY STATE OPERATION

IN THE ANAEROBIC FLUIDIZED BED REACTOR

Time Period (days)	Type of Feed	Feed Flow Rate (ml/min)	Recycle Flow Rate (l/min)	Recycle Feed Ratio	Flux ($gpm/ft.^2$)	Average Feed SCOD (mg/l)	Average Effluent SCOD (mg/l)	SCOD Removed (%)	Loading Rate lb. SCOD/day/1000 $ft.^3$ fluidized media	Average Gas Production (l/day)	Gas Produced/Destroyed ($ft.^3$/lb.COD Destroyed)	Methane in Off-Gas (%)
11	Heat Treatment Effluent without Reuse Water	20.0	8.7	435	10.6	9386	4825	48.6	1195	45.2	5.52	71
8	Heat Treatment Effluent Diluted with Tap Water	50.0	9.2	184	11.2	5001	2507	49.9	1664	54.8	4.89	70
13	Heat Treatment Effluent Diluted with Tap Water	16.7	9.2	551	11.2	4115	1288	68.7	479	18.8	4.42	71
					SHOCKING PHASE (2 days feed - 2 days no feed)							
14	Heat Treatment Effluent Diluted with Tap Water	16.7*	9.2	551	11.2	4498	1130	74.9	262	9.4†	3.58	74
15	Heat Treatment Effluent Diluted with Tap Water	8.3	9.2	1104	11.2	4408	1129	74.4	268	9.4	3.83	70

* Flow rate on days feeding system only

† Based on total number of days

Table 2: Full Scale Preliminary Design

	Hy-Flo
Loading Rate lbs COD/1000 ft^3-day	440
Hydraulic Detention Time, days	0.7
Sludge Detention Time (SRT), days	60
Reactor Volume, ft^3	145,000
Surface Area, ft^2	5,000
Methane Gas Produced, ft 3/day	284,000
Energy Produced	284×10^6 BTU/d
Horsepower required	200

TREATMENT OF HIGH STRENGTH WASTES BY AN ANAEROBIC FILTER

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ABSTRACT

Laboratory studies using small plexiglass columns and one inch pallrings have been used to develop an understanding of the anaerobic filter process and to determine treatability of several types of high strength wastewaters. The chemistry involved and removal rates have been defined. Organic removals accomplished at various loadings were developed for these columns. Pilot scale anaerobic filters, utilizing full size 3 1/2" pallrings were operated on a heat treatment liquor for approximately 12 months to develop design parameters for anaerobic filter pretreatment of the liquor, prior to return to the aeration basis. Results of these studies and an analysis of the data are presented in this paper. Included are a discussion of experience in starting up the pilot anaerobic filter and the chemistry involved in maintaining optimum pH levels.

INTRODUCTION

Hydroscience has conducted research on the application of the anaerobic filter to high strength wastes since 1973. Initial work involved the development of a model which incorporated a two stage reaction sequence for organic carbon and organic nitrogen degradation to ammonia. The chemistry interactions occurring in the filter among nitrogen, volatile acids, alkalinity, carbon dioxide, and pH, were incorporated. Laboratory anaerobic filters were operated on a synthetic high protein carbohydrate waste to obtain data on the anaerobic filter performance, and to verify the model. This work was presented by Mueller and Mancini (1). Their experimental work was conducted using laboratory filter columns 4 feet deep with 1.6 cm pall ring media. They found that a first order kinetic reaction rate described COD reduction in the filters. Rate coefficients from 0.50 to 0.70/g/l-d (volatile suspended solids) were determined at several loading rates. COD removals of 90%, and greater, were achieved at loadings up to 6.4 kg COD/m^3 filter volume. At 27 kg COD/m^3 loading, removal fell off to 50%. Most of the biological solids growth accumulated in the lower foot of media, however, as loadings were increased, solids levels increased in the upper layers of media. Based on reduction in void volume in the filter, a maximum removal of about 18 kg COD/m^3/day was projected for the waste studied.

Since these studies were conducted, laboratory screening studies have been conducted on anaerobic filter treatment of several wastes including a pharmaceutical spent fermentation liquor, a brewery waste and the heat treatment liquor from a municipal sludge dewatering heat treatment system. Large pilot scale studies were conducted on the heat treatment liquor to develop parameters for an anaerobic filter treatment system, to compare costs with alternative aerobic treatment. The main purpose of this paper is to present the results of the anaerobic filter heat treatment studies, with a comparison of lab and pilot unit performance. The potential application and cost benefit of applying an anaerobic filter to heat treatment liquor is also discussed.

Environmental Factors

The anaerobic filter provides a high sludge age and can be designed for operation at a selected temperature. Depending on the waste volume and organic concentration, as well as its temperature, an analyses of the benefit, with respect to efficiency and capital and operating costs, to maintain an optimum temperature of 35°C can be made. The methane produced by treatment may supply all or part of the energy required to maintain temperature.

The optimum pH for growth of methane forming bacteria is between 6.8 and 7.2, however, a range of 6.0 to 8.0 is generally satisfactory. The evolution of carbon dioxide and formation of volatile acids reduce bicarbonate alkalinity. In wastes containing significant organic nitrogen concentrations, alkalinity production from organic nitrogen hydrolysis will provide additional system buffer capacity. If the alkalinity, or organic nitrogen in the raw waste is not sufficient, supplemental alkalinity must be added. During startup, when volatile acid concentration is high, prior to development of methane formers, greater supplemental alkalinity may be required to maintain pH in the optimum range.

High pH values in the range of 7.5 to 8 may be significant with respect to ammonia toxicity. Various studies have indicated that non-ionized ammonia concentrations greater than 30 mg/l can be inhibitory, with complete inhibition occurring at concentrations greater than 230 mg/l. Control of pH in the range of 7.0 to 7.2, should insure no inhibition due to non-ionized ammonia at total ammonia nitrogen levels of 1500 to 2000 mg/l.

For high strength wastewaters, high inorganic dissolved solids may exist and inhibit methane formers. Certain organics at high concentrations can also be toxic to the methane formers. Acclimation may minimize toxicity. Dilution may be required to successfully anaerobically treat some wastes, and in some cases a waste may just not be amenable to anaerobic treatment. Lab and pilot studies can be conducted to determine treatability and to develop design parameters.

Heat Treatment Liquor (HTL)

Heat treatment of municipal primary and secondary sludge is practiced at over 100 plants. The liquor from dewatering the treated sludge contains a significantly high concentration of organics, solubilized in the process. This load can contribute up to 30% of the raw waste load of the plant, and requires therefore, either pretreatment or significant additional capacity in the treatment plant.

The anaerobic filter was proposed for cost effective, pretreatment of this waste. To develop design parameters, and a cost comparison with alternative aerobic treatment, anaerobic filter laboratory and full scale pilot plants were operated on a typical municipal heat treatment liquor from the Columbus Ohio Sewage Treatment Plant. The characteristics of HTL are shown in Table 1.

TABLE 1

CHARACTERISTICS OF HTL
COLUMBUS OHIO SEWAGE TREATMENT PLANT

Constituent	Range	Average
pH unit	4.9-5.8	5.2
Alkalinity, mg/l	600-1560	1075
Total Solids, mg/l	7390-8460	7735
Volatile Solids %	55-83	71
COD, mg/l	10160-11540	10750
BOD, mg/l	3830-6100	4965
TKN, mg/l	840-990	920
NH_3-N, mg/l	270-390	295
Volatile Acids mg/l	1970-2230	2085

PILOT PLANT STUDIES

Figure 1 is a schematic of the laboratory column used. The filter is 5 cm in diameter and contained 1.25 m of 1.6 cm plastic pall rings media, porosity 85%. The pilot columns, shown in Figure 2 were 60 cm square by 3.5 meters high, and contained 1.85 m of 9 cm (full size) plastic pall rings, porosity 95%. Temperature was maintained at about 35 ^{o}C for these studies.

Startup

The laboratory column had been utilized for screening studies on heat treatment liquor for several months prior to these studies, at a loading of 4 kg COD/m^3/day, and was seeded with volatile acid and methane forming organisms. Heat treatment liquor was introduced directly into the lab filter with no additional alkalinity. The loading rate was about 7 kg COD/m^3/day with a detention of 0.7 days. (Note: All loadings are based on empty filter volume). A chronological plot of influent and effluent characteristics is shown in Figure 3.

The two full scale filters were seeded with 350 liters of digesting sludge. The filter effluent was recycled for about 10 days to bring the units to an uniform temperature. Loading rates were set at approximately 2.5 and 5.0 kg COD/m^3/day, with respective detention times of approximately 3.5 and 1.8 days. A chronological plot of influent and effluent characteristics is presented in Figure 4.

The pH and alkalinity of the influent HTL feed were 4.9 and 600 mg/l as $CaCO_3$, respectively. Sodium bicarbonate was added to the raw waste to increase alkalinity to about 1800 mg/l, and effluent pH to 6.5-6.7. During the second month, effluent COD and volatile acids gradually decreased, and it was not necessary to add additional buffering chemicals to the HTL feed. To increase acclimation rate of the pilot filters additional digesting sludge was added to the filters about 3 months after startup.

Loading Conditions

Column 1 was operated at a constant load throughout the study, while the loadings to Column 2 and the lab column were increased in several increments during the study. Tables 2, 3, and 4 present summarized operational data, after an initial acclimation period, for the pilot units. Figure 5 illustrates the removal of BOD and COD with time through the study for the pilot units.

The gradual increase in BOD and COD removal illustrate the slow build up and retention, within the media in the pilot columns, of methanogenic organisms. Column 1 appeared to achieve full acclimation after about 100 to 110 days of operation. Removals in Column 2 were still gradually increasing at the end of the study. The lab column exhibited a high level of removal throughout the study period, and rapidly accepted increased loadings with an increase in removal efficiency.

The primary gases produced in anaerobic treatment are carbon dioxide and methane. During the study, the methane and carbon dioxide content of gas samples were measured, versus soluble COD removal. The following relationships were developed:

m^3 Total Gas Produced = 0.50/kg COD_R 100%

m^3 Methane produced = 0.34/kg COD_R 68%

m^3 CO_2 Produced = 0.15/kg COD_R 29%

The average value of 0.5 m^3 gas/kg soluble COD removed is consistent with typical gas production, COD correlations found in the literature and in previous studies.

Summarizing the results, Column 1 at 3.7 days detention achieved 80 to 85% BOD removal and 65 to 70% COD removal; Column 2 at one day detention acheived 65 to 75% BOD removal and 55 to 60% COD removal; and the Lab Column at 0.6 days detention achieved 80 to 95% BOD removal and 70 to 80% COD removal. The COD removals reflect the non-biodegradable COD fraction which was in the range of 10 to 20% of the HTL COD.

Loading Removal Relationships

Volumetric

Figure 6 illustrates the relationship found in this study between COD removal and loading rate to the anaerobic filters. The lab column, which was loaded at 2 to 3 times that of the pilot columns, exhibited relatively uniform and high removals over the range of loadings studied. Data from another lab anaerobic filter study on a highly biodegradable brewery waste is shown, and also illustrates uniform removal over a wide range of loadings. The pilot columns, in contrast, with the much larger media, indicate somewhat of a decline in removal with increasing loading. The actual percent removals at lower loadings are also lower than achieved by the lab column. Part of the decline in removal, with increased loading, may be due to the much slower

TABLE 2

LABORATORY ANAEROBIC FILTER
OPERATION SUMMARY

Date Day #	Flow l/d	Deten. Time Days	Loading Rate kg COD/m^3/d	Gas Prod. l/d	Gas[1] m^3/kg COD_R	COD[1] Removed %	BOD[1] Removed %
29-33	2.7	.8	6.7	5.31	.53	71	85
49-55	3.4	.6	7.1	6.43	.61	70	92
57-60	3.0	.7	6.3	4.10	.46	68	92
71-75	2.9	.7	11.6	6.92	.40	70	87
92-96	3.6	.6	12.3	10.28	.58	68	88
113-120	3.5	.6	14.4	16.70	.75	74	93
120-131	4.3	.5	20.1	19.60	.57	81	95
141-147	3.7	.6	14.0	12.80	.55	79	96

TABLE 3

COLUMN #1
10 DAY AVERAGE OPERATION

Date Day #	Flow l/d	Deten. Time Days	Loading Rate kg COD/m^3/d	Gas Prod. m^3/d	Gas[1] m^3/kg COD_R	COD[1] Removed %	BOD[1] Removed %
42-51	174	3.90	2.59	.179	.48	21	
52-61	165	4.12	2.23	.312	.62	33	
62-71	107	6.36	1.56	.252	.48	49	60
72-81	124	5.48	1.84	*		53	66
82-91	184	3.70	3.07	.527	.49	52	
92-102	179	3.80	2.76	.543	.49	59	67
103-112	178	3.82	2.37	.337	.33	63	83
113-122	180	3.78	2.68	.613	.52	65	77
123-133	190	3.58	2.58	.568	.49	66	80
134-143	203	3.35	2.13	.382	.41	64	86
144-148	180	3.78	1.69	.175	.22	68	85

TABLE 4

COLUMN #2
10 DAY AVERAGE OPERATION

Date Day #	Flow l/d	Deten. Time Days	Loading Rate kg COD/m^3/d	Gas Prod. m^3/d	Gas[1] m^3/kg COD_R	COD[1] Removed %	BOD[1] Removed %
42-51	350	1.94	5.21	.187	.31	17	-
52-61	284	2.39	3.85	.241	.24	39	
62-71	210	3.24	3.06	.402	.51	38	45
72-81	170	4.00	2.53	.314	.42	43	57
82-91	268	2.54	4.47	.592	.41	47	-
92-102	263	2.59	4.06	.729	.46	58	56
103-112	245	2.78	3.25	.451	.39	52	74
113-122	272	2.50	4.05	.735	.57	47	74
125-139	717	0.95	8.75	1.230	.40	52	66
140-148	988	0.69	9.39	1.360	.39	55	78

* Meter not operating

(1) Based on influent total and effluent filtered

buildup of organisms in the pilot columns, and increased removals might be expected given a longer period of operation at the higher loadings.

Mass

At the conclusion of the studies, the filter media was removed and a determination of the solids, both attached and suspended was made. The following table presents these results.

A high percentage of the solids in Column 1 were suspended in the bottom 60 cm. Column 2 had a fairly uniform distribution of both attached and suspended solids throughout the column. The lab column had significantly more attached growth in the bottom section of the filter. On an average mass per unit volume basis, the lab column had about 3 to 3.5 times as much attached growth as did either of the two pilot columns.

Dye studies conducted on the two pilot columns showed a high degree of mixing. This was attributed to the turbulence generated by gas production and thermal currents in the filter. Volatile acid measurements at various depths during the study, as shown in Figure 7, indicated a fairly uniform distribution throughout the filter, particularly in Column 2. Undoubtedly, there is a somewhat higher rate of removal in the first foot, however, the uniform distribution of volatile acids, the mixing indicated by dye studies, and solids accumulation, tend to indicate that the total filter volume is contributing to COD removal.

Thus, for purposes of developing a removal rate as a function of solids content (a first order kinetic relationship), it was assumed that the filters acted as completely mixed reactors. Based on the solids measured and removals being achieved at the very end of the study, Figure 8 was developed.

The average non-biodegradable COD of 1200 mg/l was used as the origin. Column 1 removal rate was quite low, however, the lab column and Column 2 data show fair agreement. The reaction rate of 0.0004/mg/l-d (total suspended solids), 0.00056 volatile solids basis, was similar to that found by Mueller and Mancini in their evaluation of plug flow anaerobic filter data. The low rate in Column 1 is indicative of the high solids concentration in the lower foot being essentially inert solids which were not "washed out" of the filter as apparently was the case with Column 2 at the higher flow rate.

The difference in removal between the two pilot columns, and with higher rates reported elsewhere, can be related to the mass of methanogenic organisms retained in the filter, after the period of operation.

ANAEROBIC FILTER DESIGN

General Considerations

The development and retention of methane forming organisms is the apparent factor relating to the differences in removals seen between the lab unit and the pilot columns. The greater solids concentration retained by the small media in the lab column resulted in the greater removals per unit of volume. The practical consideration of media cost and solids plugging, tend

to favor the use of the larger media for a full scale plant, accepting somewhat lower removals and lower volumetric loadings than with the smaller lab type media.

Sizing and Estimating Removal Efficiency

Table 6 presents a summary of the pilot study results and selected design parameters.

Based on the overall results of these studies, and based on a HTL waste COD concentration of 10,000 mg/l, a volumetric loading of 6.5 kg COD/m^3/d was selected. This loading would result in 1.5 days detention. Assuming a solids concentration of 10 kg/m^3, the loading on a solids basis would be 0.65 kg COD/kg Solids/day.

COD removal in the range of 55 to 65% COD, and 75 to 85% BOD were projected for a full scale installation. Figure 9 shows the proposed flow schematic of the anaerobic filter. Elements included in the anaerobic filter include the digestor, filter media, liquor heating and cooling system, pump station, and gas collection and burning equipment. The heat treatment liquor at about 60°C would require cooling in summer, while under severe winter conditions auxiliary fuel may be required to maintain 35°C temperature in the filter.

Cost Comparison

A preliminary cost evaluation was made. The cost of the anaerobic filter system is compared with the incremental cost to increase the treatment plant's aeration system, and with a separate aerobic system for the HTL.

Table 7 presents the preliminary cost estimates. The incremental cost for an aerobic treatment plant were developed based on capacity designed into a 15 MGD plant. Costs are for the additional basin and aeration, capacity required for aerobic treatment, and the additional sludge handling capacity in the heat treatment reactor, sludge holding tank and vacuum filter, required to handle the additional sludge load of about 640 kg per day. Operation and maintenance costs include costs for power, maintenance, labor, and sludge handling.

An estimated cost for a separate aerobic pretreatment system consisting of aeration basin, aeration equipment, clarification, and sludge return pumping, with the sludge handling incorporated into enlarged treatment plant facilities was developed. The cost of a separate system is considerably greater than incorporating additional capacity into a plant design.

TABLE 5

SOLIDS IN PILOT COLUMNS kg/m^3
(Attached Plus Suspended)

Depth cm	Column 1	Column 2	Lab Column
183	(7.2) Est.	(10.4) Est.	-
152	7.2	10.4	-
122	6.6	10.4	20.8
91	7.5	10.0	-
60	15.8	6.5	30.6
30	51.8	7.5	35.6
Empty Bed Avg. Conc.	16.2 kg/m^3	9.20 kg/m^3	31.0 kg/m^3
Bed with Media Avg. Conc.	15.2 kg/m^3	8.7 kg/m^3	26.4 kg/m^3
% Suspended Solids	49	6	3
% Attached Solids	51	94	97

TABLE 6

SUMMARY OF RESULTS

	Pilot Column 1	Pilot Column 2	Lab Column	Design Selected
Detention Time Days	3.5-4.0	0.7-2.5	0.6	1.5
Loading				
Volumetric kg $COD/m^3/d$	2.5	4 to 9	12 to 20	6.5
Mass kg COD/kg/d	<0.1	0.4-0.7	0.2-0.3	0.65
Solids Concentration kg/m^3	15.2	8.7	26.4	10
% BOD_{T-F} Removal	85	65-75	80-95	70 to 80
% COD_{T-F} Removal	60-70	50-60	70-80	55 to 70
Gas Production $m^3/kg\ COD_R$	0.46	0.44	0.55	0.5
Gas - % Methane	0.67	62	-	65

TABLE 7

COST ESTIMATE COMPARISON
HEAT TREATMENT LIQUOR - 340 cm/d; 10,000 mg/l COD
1978 COSTS

		Capital Cost	Operating Cost
ANAEROBIC FILTER			
A.	No Credit for Methane	$ 470,000	$ 28,400
B.	Credit for Methane	$ 470,000	-17,000
AEROBIC TREATMENT			
A.	Incremental Plant Cost	$ 541,000	$ 53,200
B.	Separate Pretreatment	$1,036,000	$ 68,000

SUMMARY

Pilot plant and laboratory studies show that significant removal of soluble organics from a high strength sludge heat treatment liquor can be achieved at relatively low hydraulic retention times of 0.5 to 2 days. A comparison between results using a laboratory filter containing relatively small media and capable of retaining a much higher solids concentration of attached growth, with a full scale pilot plant utilizing typical larger media has been presented.

The identification of a possibly more suitable cost effective media to result in maximizing solids retention is an area which requires further study. The economics for anaerobic treatment of sludge heat treatment liquor compared to aerobic treatment appear quite favorable.

The application of the anaerobic filter to other high strength soluble organic wastes continues to appear quite promising in light of these pilot plant results as well as other anaerobic filter studies. A preliminary evaluation of potential economic benefits and treatability studies with lab and pilot scale units would be recommended for sizing an anaerobic filter system for a particular application.

ACKNOWLEDGEMENT

The pilot plant work on heat treatment liquor was conducted at the Muddy Creek plant of the Metropolitan Sewer District of Greater Cincinnati. The pilot plant studies were funded pursuant to Contract 68-03-2484 with the United States Environmental Protection Agency Municipal Environmental Research Laboratory.

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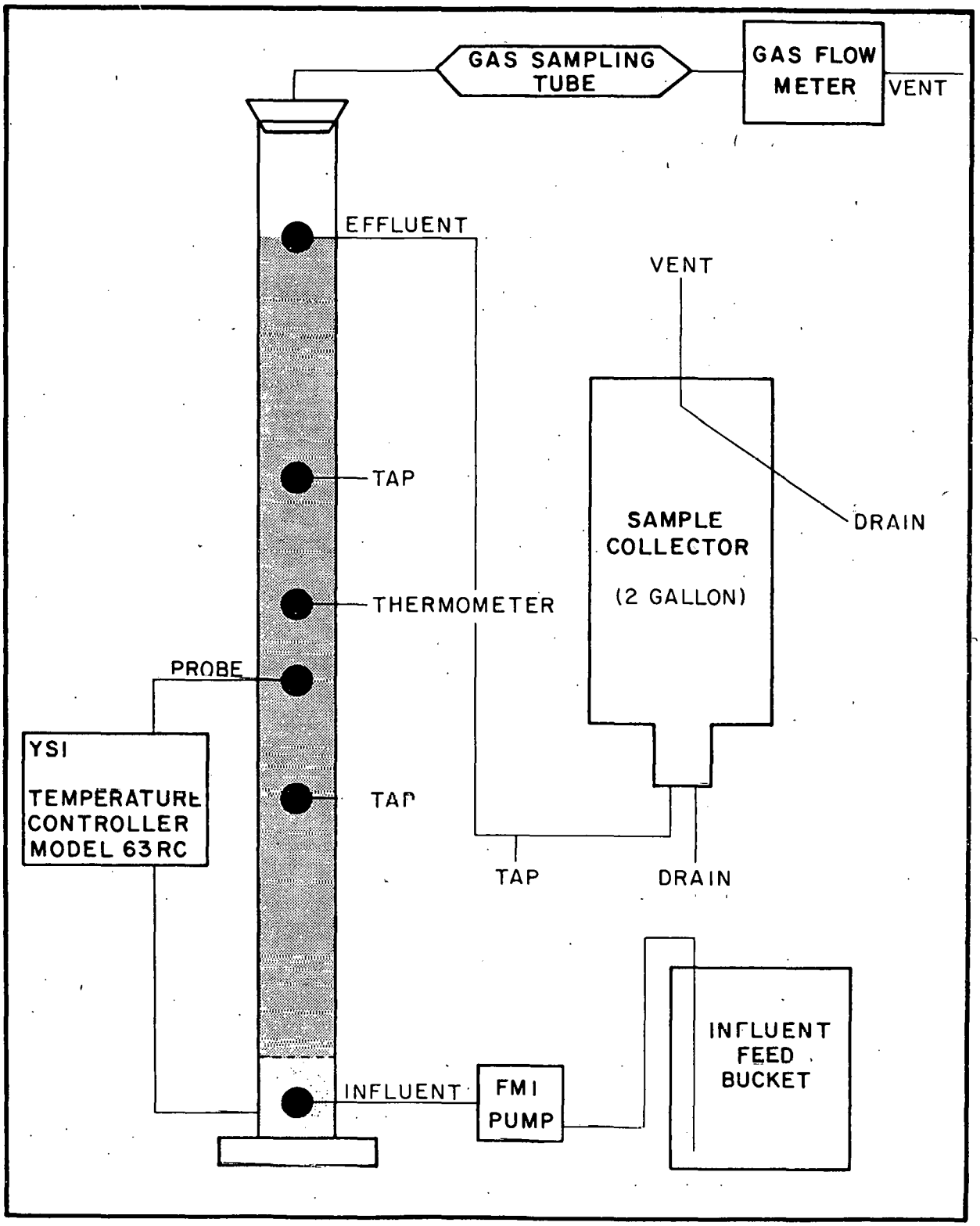

FIGURE 1

SCHEMATIC OF LAB UNIT

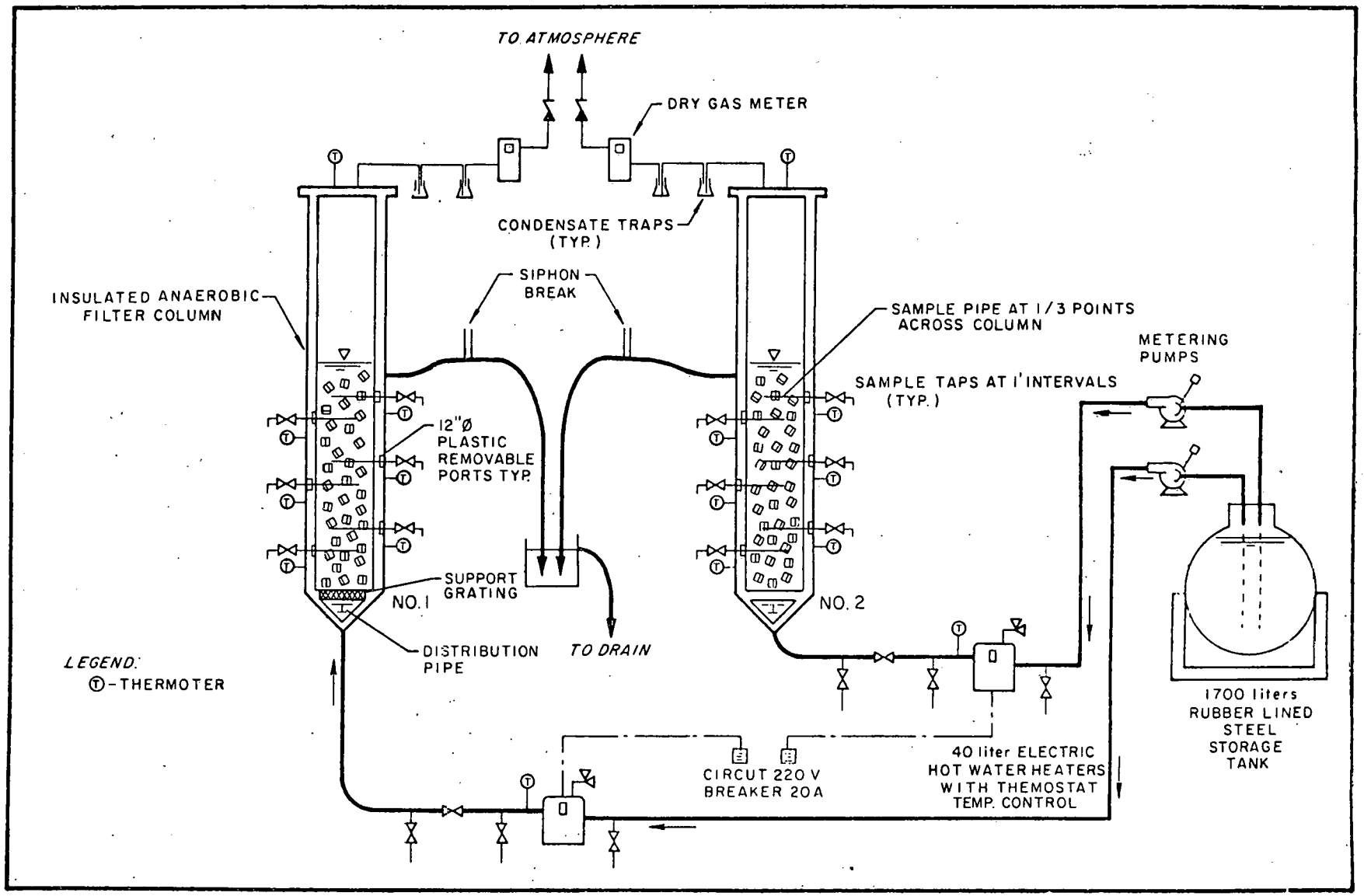

FIGURE 2

ANAEROBIC FILTER PILOT UNITS

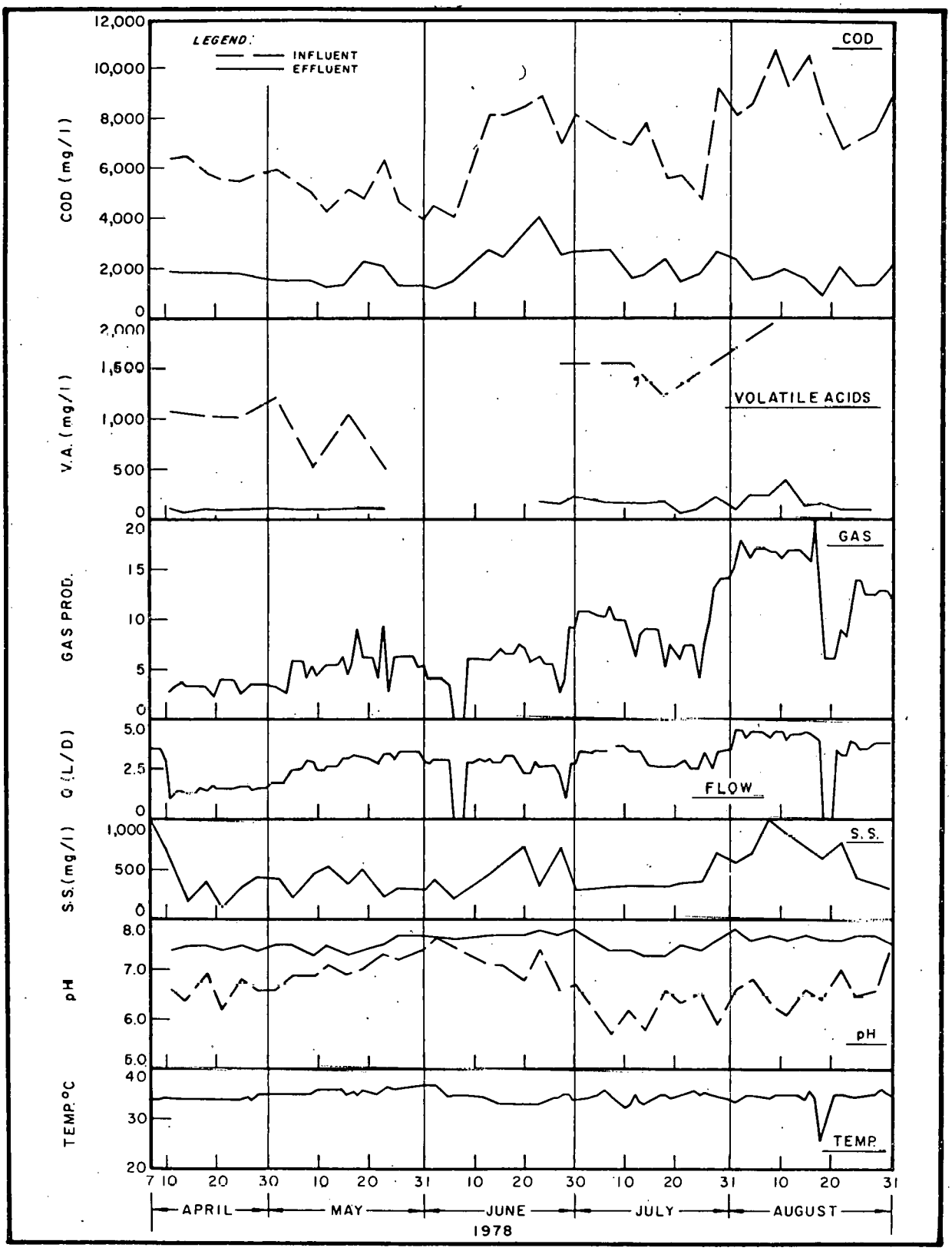

FIGURE 3
ANAEROBIC FILTER LABORATORY UNIT
CHRONOLOGICAL PLOT

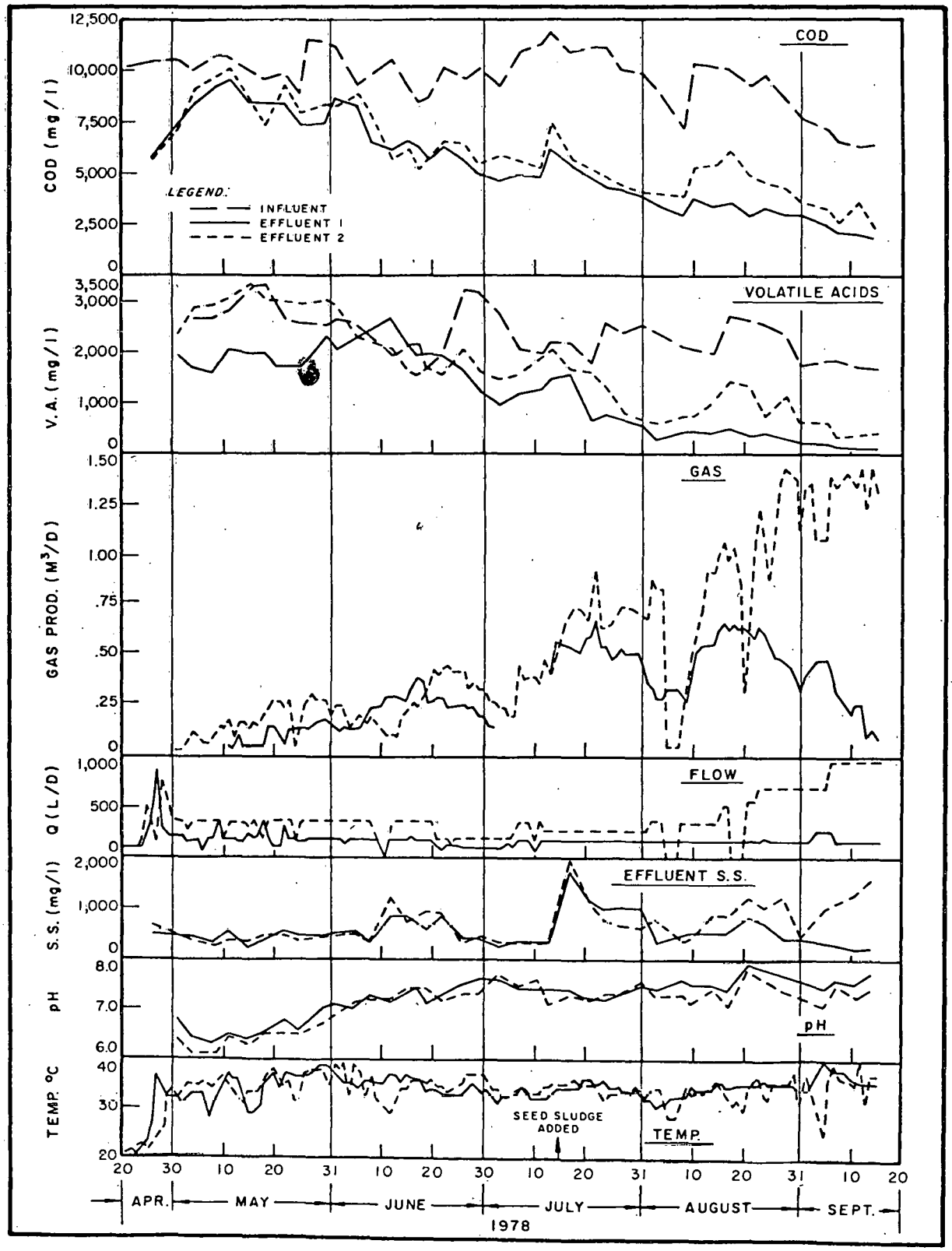

FIGURE 4
ANAEROBIC FILTER PILOT STUDY
CHRONOLOGICAL PLOT

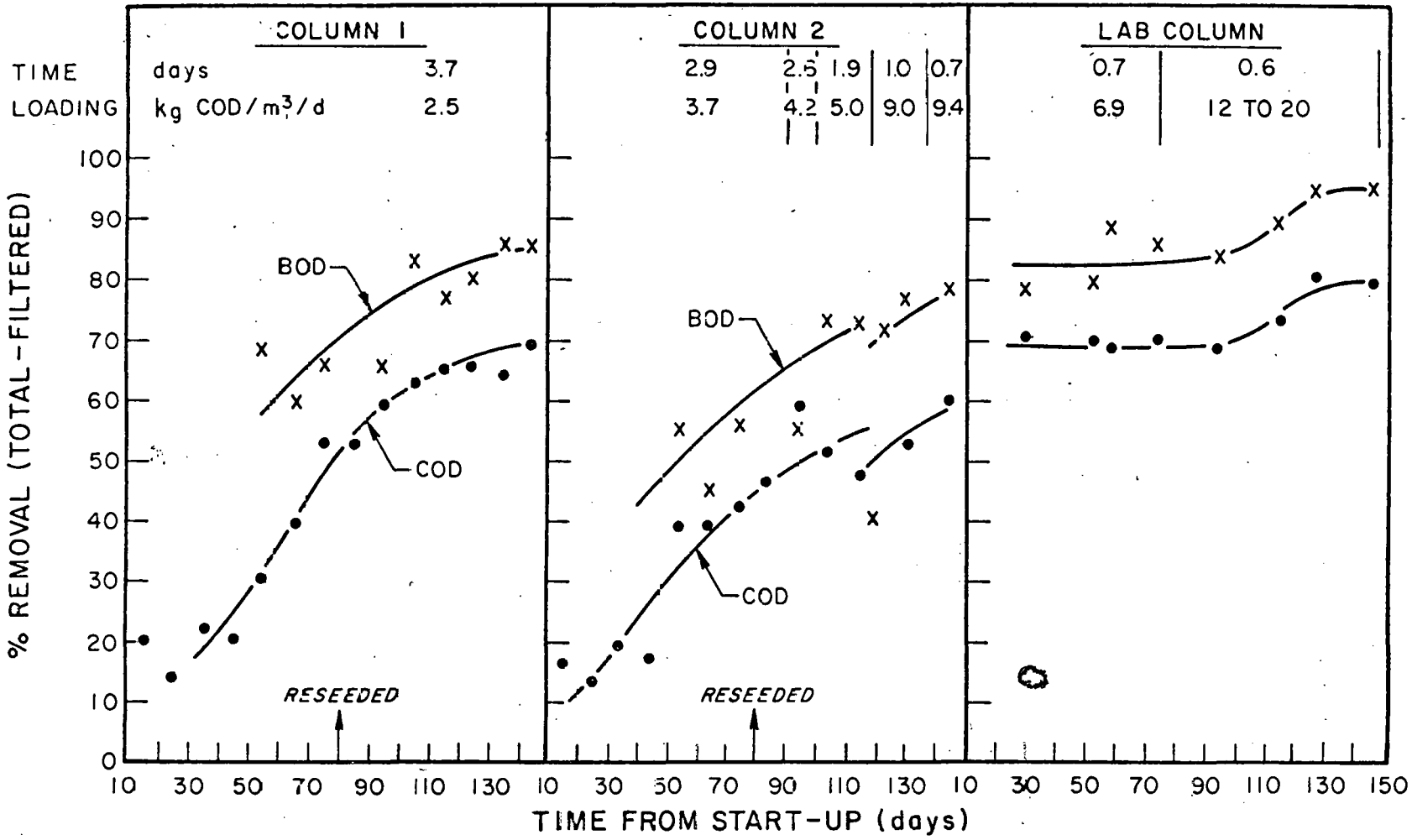

FIGURE 5

ANAEROBIC FILTER STUDY–HEAT TREATMENT LIQUOR T 35°C
BOD AND COD REMOVAL

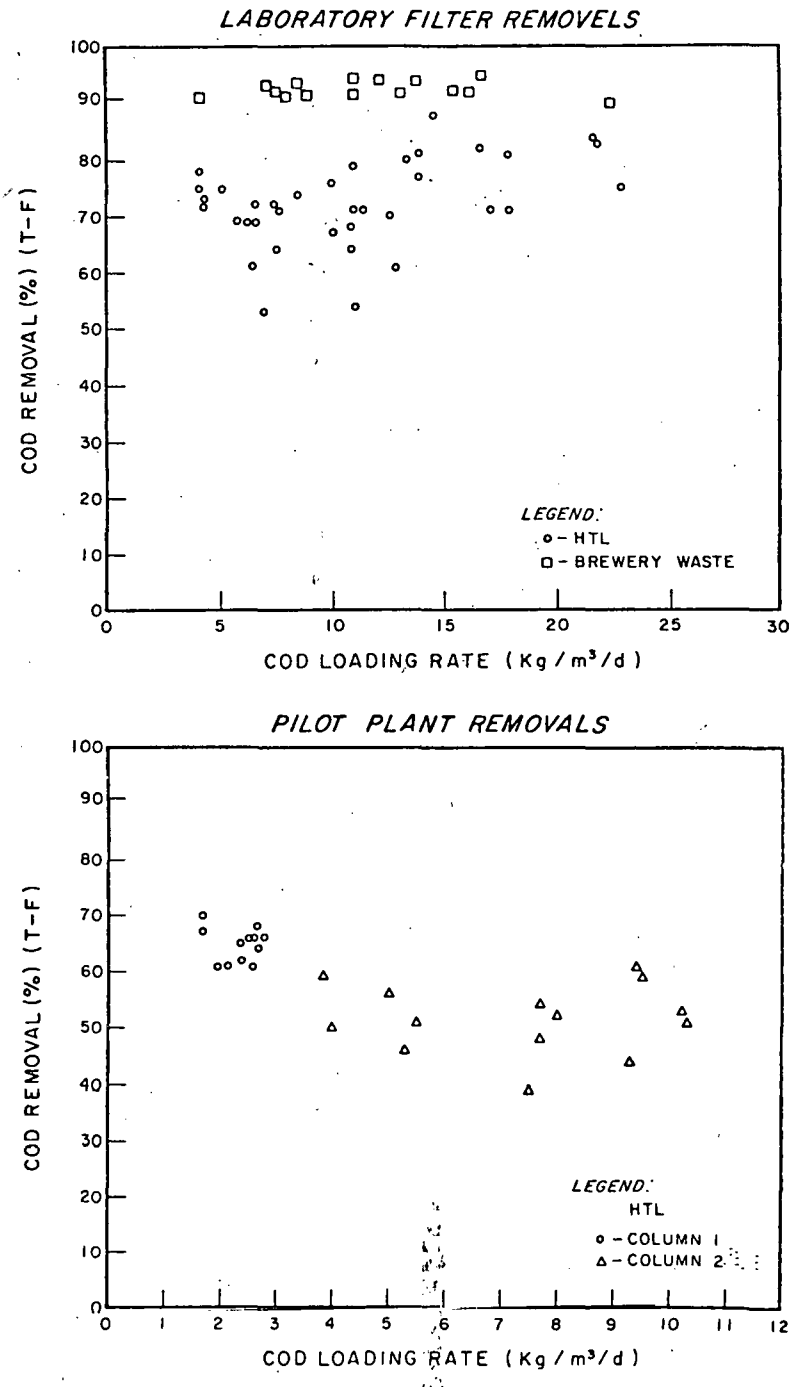

FIGURE 6

COD REMOVAL VERSUS LOADING RATE

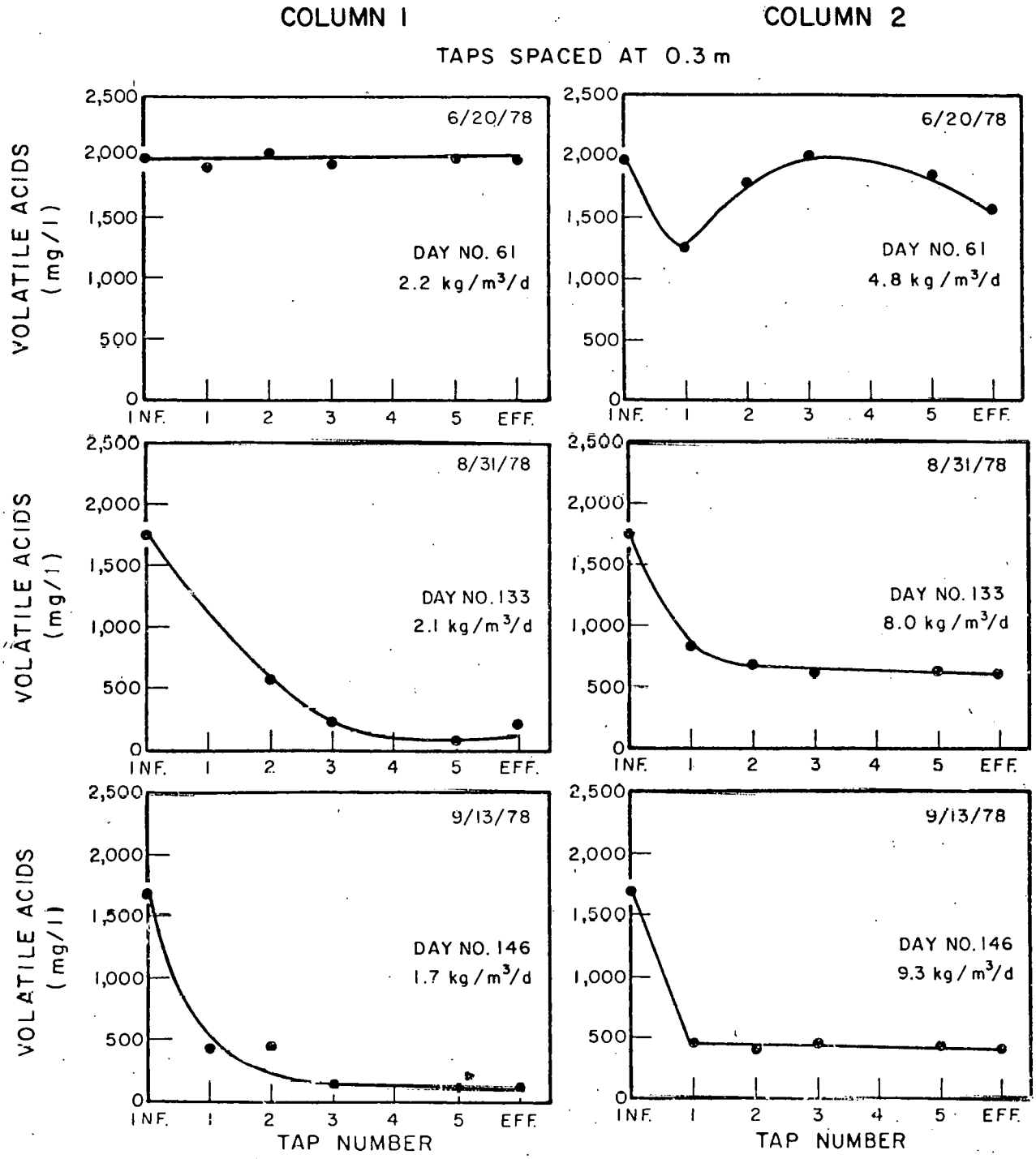

FIGURE 7

VOLATILE ACID CONCENTRATION VERSUS DEPTH

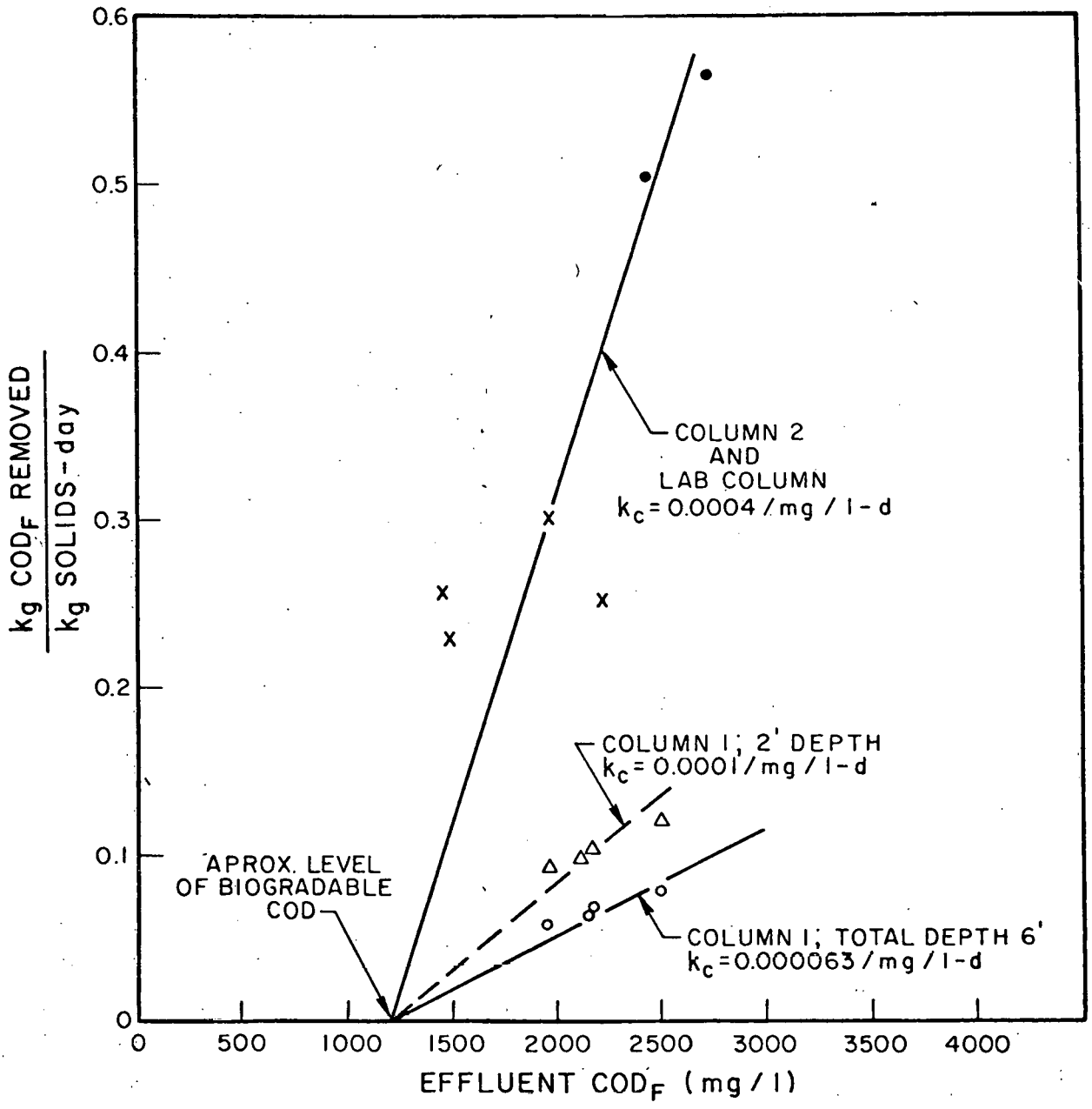

FIGURE 8

COD REMOVAL RATE

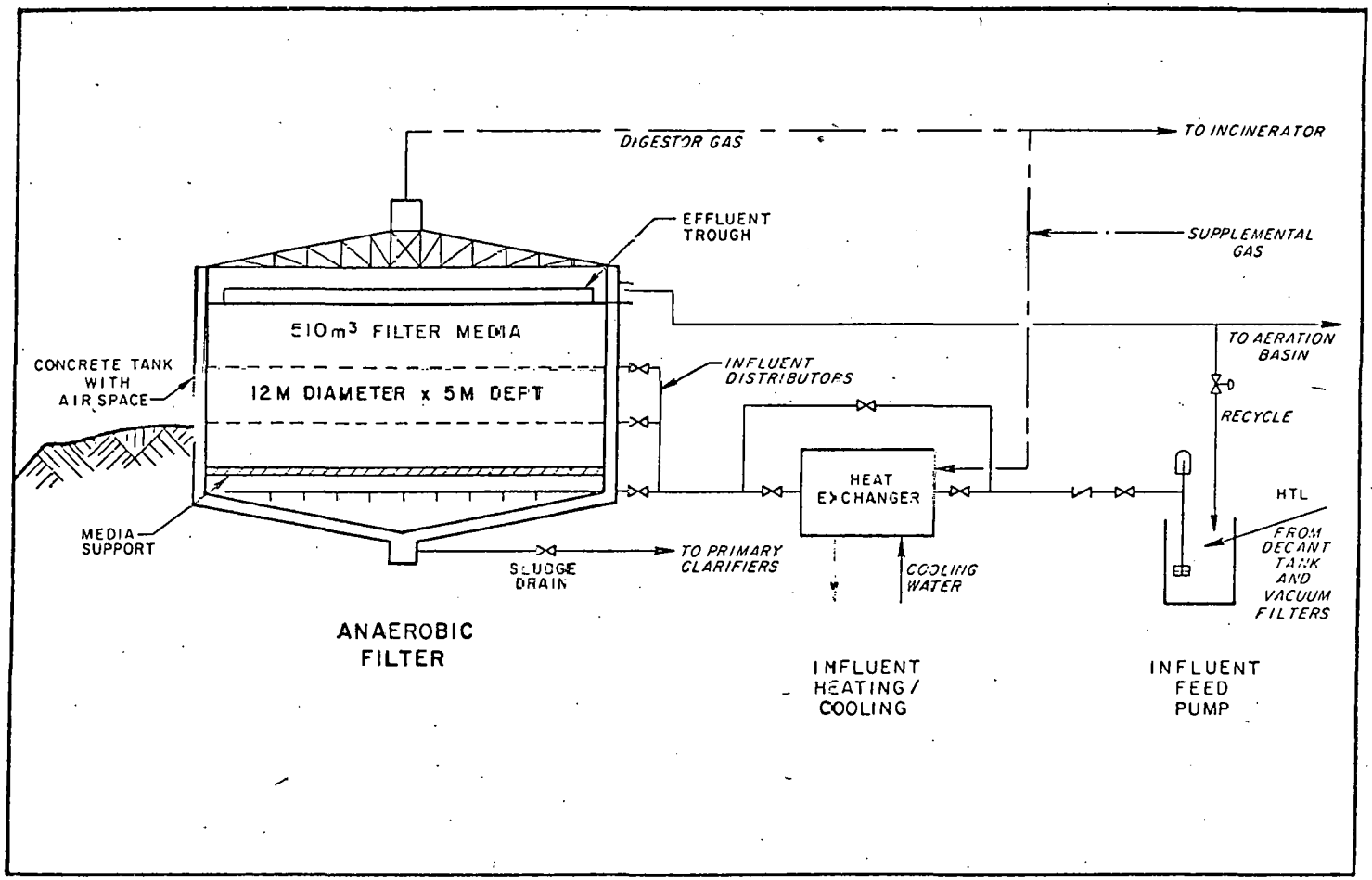

FIGURE 9

SCHEMATIC ANAEROBIC FILTER SYSTEM

Dup

DEVELOPMENT OF A WASTEWATER TREATMENT SYSTEM BASED ON A FIXED-FILM, ANAEROBIC BIOREACTOR*

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ABSTRACT

Oak Ridge National Laboratory is developing an energy conserving wastewater treatment system based on a fixed film anaerobic bioreactor. The treatment process is based on passing wastewaters upward through the bioreactor for continuous treatment by gravitational settling, biophysical filtration and biological decomposition. A two-year pilot plant project using a bioreactor designed to treat 5,000 gallons per day has been conducted using raw wastewater on a municipal site in Oak Ridge, Tennessee. Data obtained for the performance of the bioreactor have been analyzed by ORNL and Associated Water and Air Resources Engineers (AWARE), Inc. of Nashville, Tennessee. From these analyses it was estimated that hydraulic loading of 0.2 gpm/ft^2 and hydraulic residence time of ten hours could be used in designing such bioreactors for the secondary treatment of municipal wastewater. Conceptual designs for total treatment systems processing up to one million gallons of wastewater per day were developed based on the performance of the pilot plant bioreactor. These systems were found to consume as little as 30% of the energy required by activated sludge systems. The economic advantages of the process result from the elimination of aeration and with significant decreases in sludge handling costs. Methane produced during the treatment process represented a significant and recoverable energy production term.

To support its goal of commercializing the process, ORNL is presently engaged in developing a 50,000 gpd wastewater treatment system based on the conceptual design developed by ORNL and AWARE. This project will be conducted jointly with the City of Knoxville, Tennessee both for demonstration purposes and for continuing research and development with the process.

*Research sponsored by the Division of Buildings and Community Systems, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

INTRODUCTION

The Oak Ridge National Laboratory (ORNL) is developing a wastewater treatment system based on an anaerobic, fixed-film bioreactor. The ANFLOW process (an acronym derived from the anaerobic, upflow mode in which the bioreactor operates) has been evaluated during a two-year pilot testing program at a municipal site in Oak Ridge, Tennessee using a bioreactor designed to treat 5000 gpd of municipal wastewater. ORNL was assisted in evaluating the engineering applicability of the process by Associated Water and Air Resources Engineers, Inc. (AWARE). AWARE also developed conceptual process designs for total treatment systems based upon the performance of the pilot-scale bioreactor. These designs were prepared for flows of 0.05 and 1 mgd for typical domestic wastewaters to meet secondary treatment criteria. These designs were used as a basis for estimating capital and operating costs for the system; these costs were compared to the costs for treatment using activated sludge, a conventional treatment system.

To support its goal of commercializing the process, ORNL is presently engaged in developing a 50,000 gpd wastewater treatment system based on the conceptual designs developed by ORNL and AWARE. The project will be conducted jointly with the city of Knoxville, Tennessee, both for demonstration purposes and for continuing research and development with the process.

BACKGROUND

The 5000 gpd pilot-plant wastewater treatment system was designed during the summer of 1976 as a joint venture between ORNL and the Norton Company (Akron, Ohio). It was installed with the cooperation of the city of Oak Ridge in the late fall of 1976, and operated by ORNL for 2 years. The primary motivation for this joint effort was the development of a new technology which could reduce the increases in costs and energy consumption required by the passage in 1972 of Public Law 92-500 (and by PL 92-500 as amended by the Clean Water Act of 1977). Other background for this development and early performance data for the process have been previously reported (1-5).

DESCRIPTION OF PILOT PLANT

The pilot plant was based on the flowsheet shown in Fig. 1. The bioreactor, a cylindrical tank constructed of fiberglass, was 5 ft in diameter and 18.3 ft high; it contained 10 ft of packing (200 ft^3), which consisted of 1-in. ceramic Raschig rings. Both the bioreactor and the packing were supplied by the Norton Company. The bottom of the column was a 45° cone with a flanged outlet; a 4-in. gate valve was installed on the cone flange. Nozzles for feed inlet and gas outlet extended through the tank wall. The column was surrounded by 4 in. of insulation; all external piping was insulated with electrical traces. There were thermocouple taps near the top and bottom of the packed section, and a U-tube manometer tap at the top. An overflow weir and a collection trough in the top of the column were designed to remove effluent from the center of the tank.

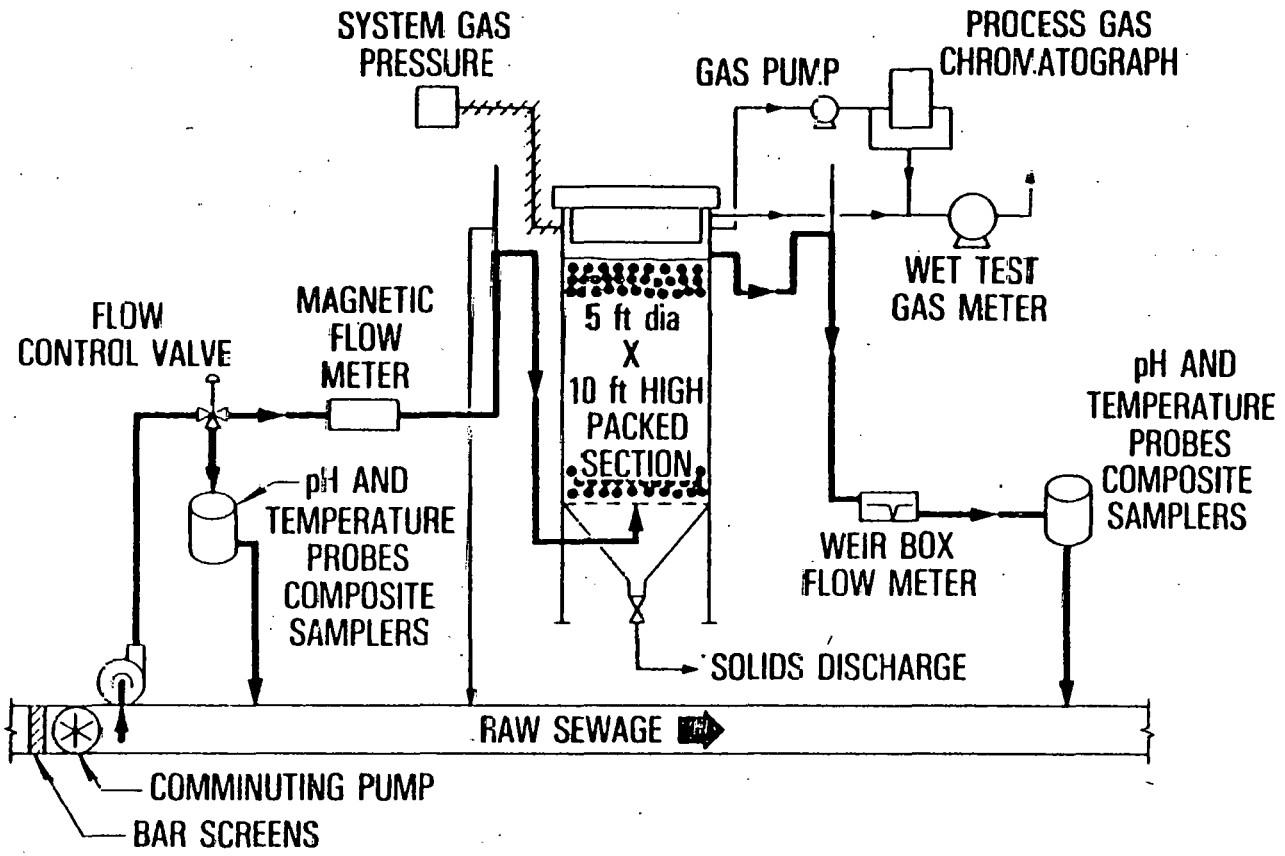


Fig. 1. ANFLOW pilot-plant flowsheet.

Feed Flow Rates

The pilot plant was designed to treat a nominal flow rate of 5000 gpd; as shown in Fig. 2, feed flow rates ranging from 1000 to 7000 gpd were actually used to investigate the bioreactor's response to a range of hydraulic loading rates (HLRs). Notably, the HLR corresponding to a feed flow rate of 7000 gpd at the pilot plant is approximately 0.25 gpm/ft^2. Feed flow rates were maintained at constant levels for extended periods to evaluate bioreactor performance under steady-state conditions. Effects of diurnal variations in flow rates were briefly examined with no noticeable effect on bioreactor performance observed. These investigations will be continued in future work.

Temperature, pH, and Gas Production

The temperature and pH levels of the wastewater fed to the bioreactor are summarized using monthly averages in histograms in Figs. 3 and 4. Temperature variations followed seasonal cycles and ranged from 10 to 25°C. Column effluent temperatures closely followed the temperatures of the raw sewage except for the period of January through April 1977, during which a contingency preheater was used to prevent feed from freezing in external pipelines. This practice was discontinued after early problems with clogging of the flow-control valve were eliminated.

Neither feed nor effluent pH levels differed significantly from the value of 7 during the project. As would be expected, the production of volatile acids by the anaerobic digestion processes in the bioreactor caused effluent pH values to be measurably lower than feed values. In colder months, these acids were not efficiently converted to methane and tended to be discharged with the effluent, thus causing greater pH

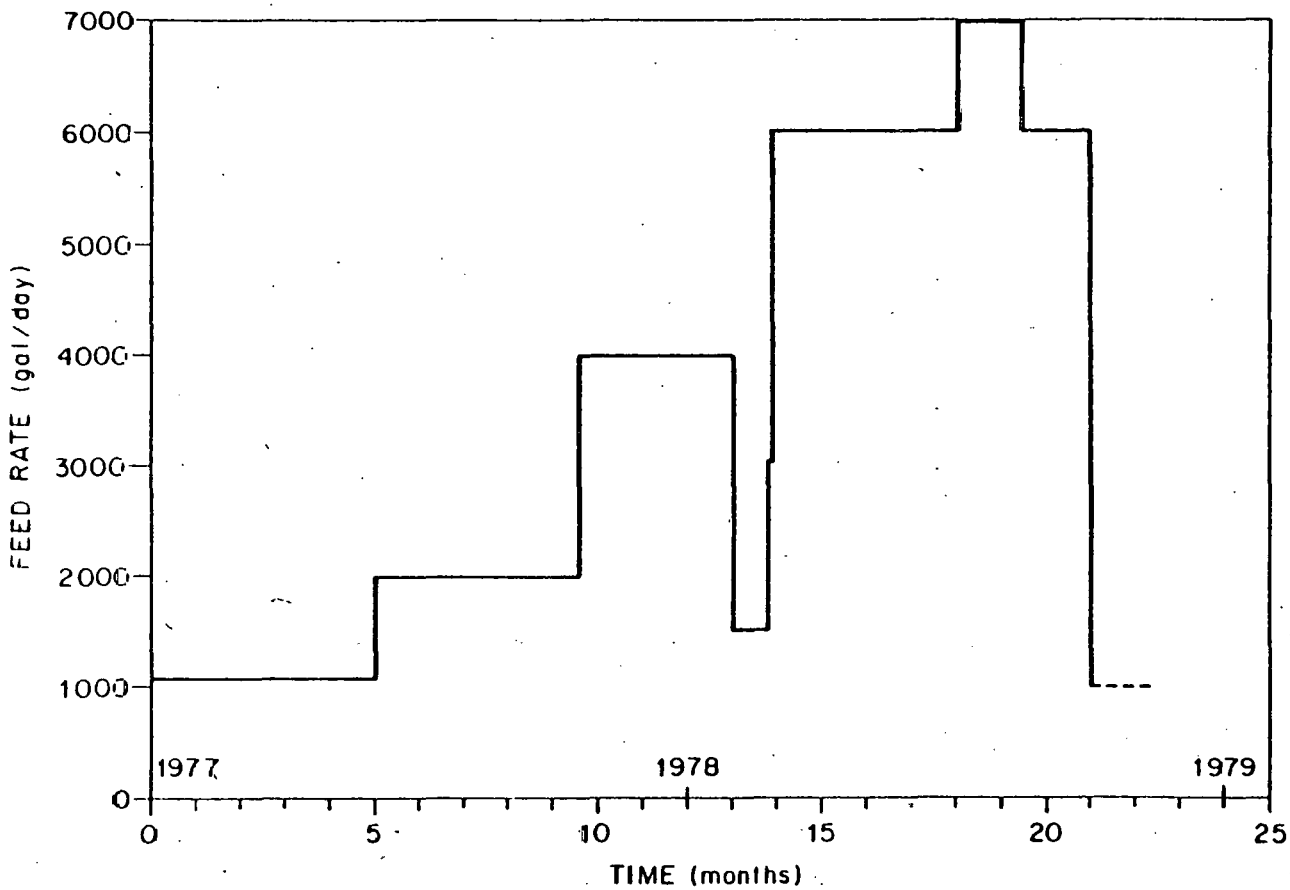


Fig. 2. Feed rate histogram for ANFLOW bioreactor.

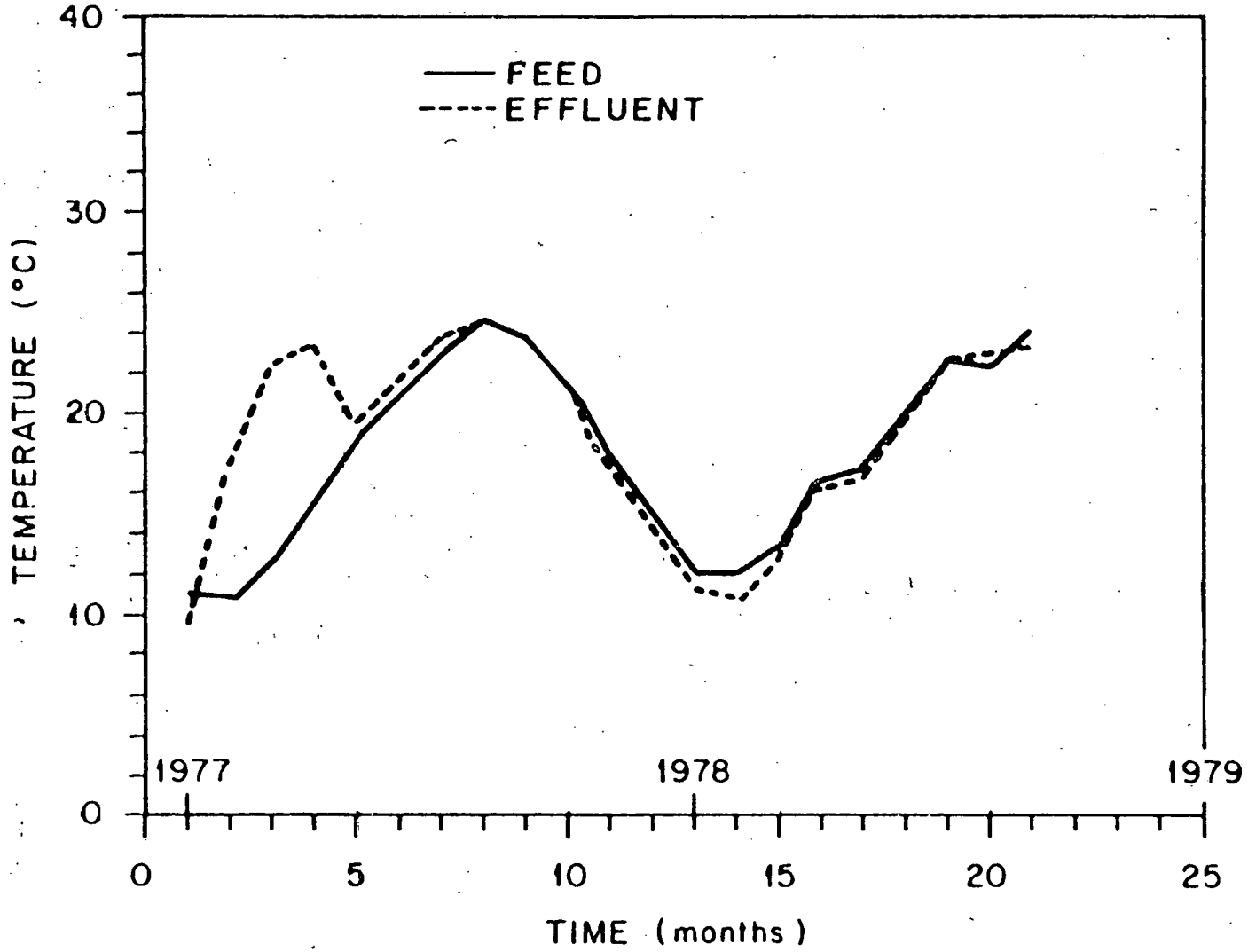


Fig. 3. Temperature histogram for ANFLOW bioreactor.

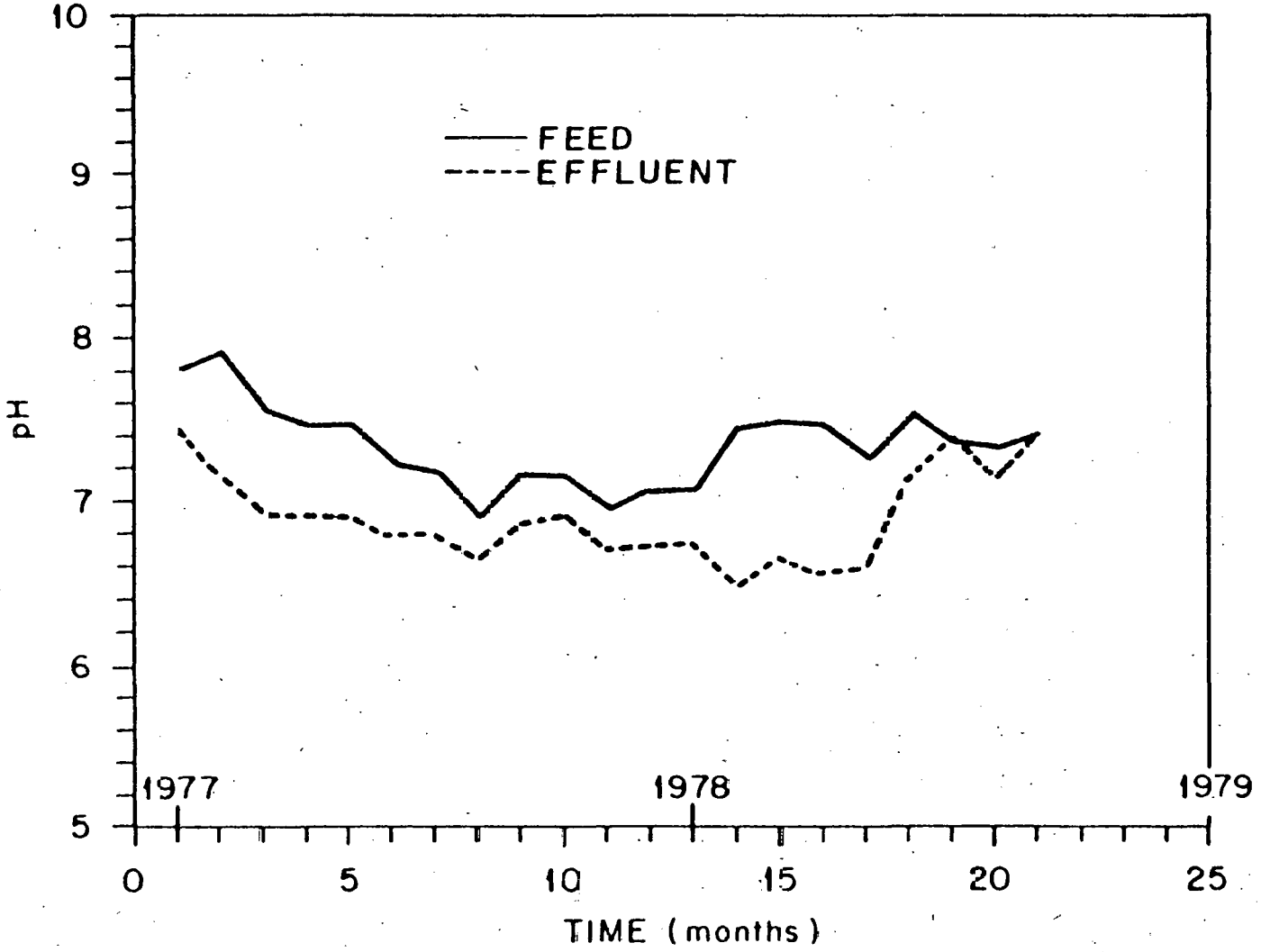


Fig. 4. pH histogram for ANFLOW bioreactor.

differences between feed and effluent during these months than in warmer months.

On several occasions, there were pH disturbances (probably associated with discharges of upstream metal-plating industries) in the feed lasting as long as 8 hr during which pH levels reached lows of 3 and highs of 10; these disturbances were dampened by the column and were observed to alter effluent levels by less than 0.5 pH units. One hypothesis proposed to partially explain the bioreactors resistance to these disturbances is that outer layers of the films attached to the packing absorbed the pH insults, possibly sloughing off as sludge for future removal and leaving protected film layers behind as a regeneration mechanism for the bioreactor.

Gas production rates measured during the project are summarized in Fig. 5; these rates reached monthly averages exceeding 100 liters/day. Methane concentrations in the bioreactor off-gas reached highs of 80%, as shown in Fig. 6. The remainder of the off-gas consisted of carbon dioxide and nitrogen. The methane produced was approximately 33% of that which could theoretically have been produced as calculated from measurements of the organic carbon removed from the wastewater by processes in the bioreactor. This efficiency was difficult to estimate, however, since carbon was removed by many mechanisms, some involving solubilization phenomena, for instance, which occurred over undefined periods.

Production rates followed the seasonal variations described for temperature, increasing as expected in the warmer months. The methane concentrations also increased in warmer months, thus following a pattern

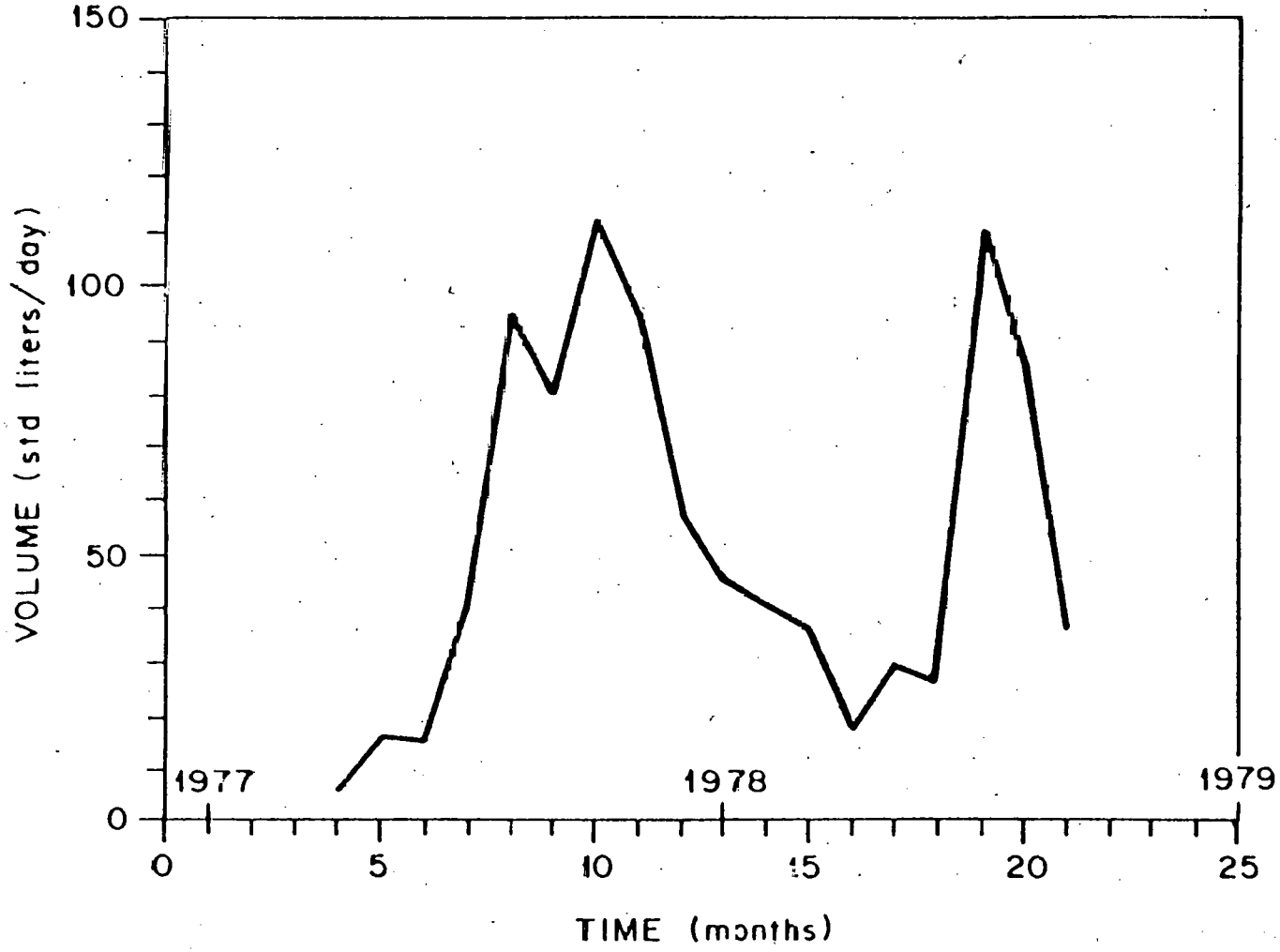


Fig. 5. Gas productior by ANFLOW bioreactor.

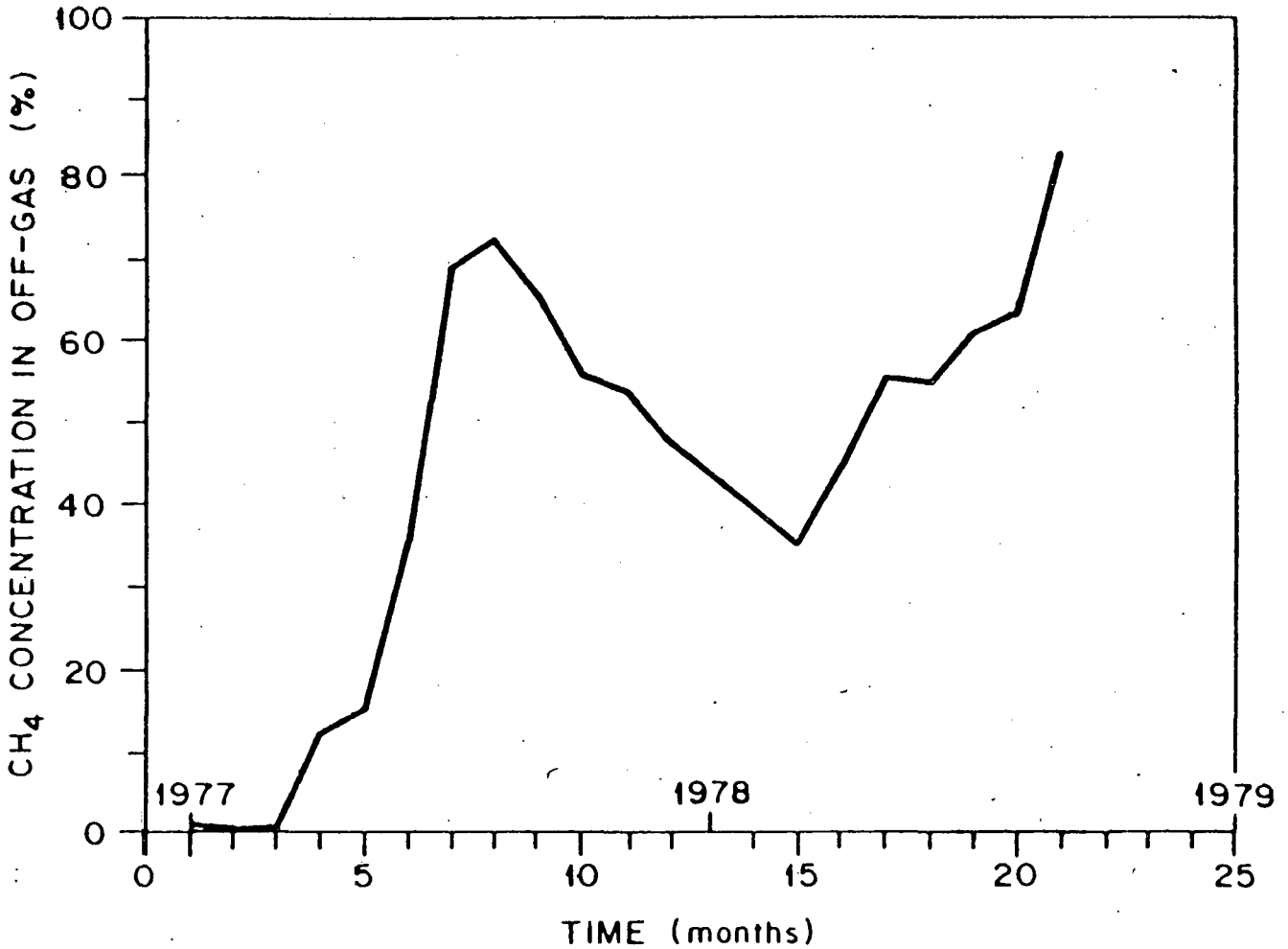


Fig. 6. Methane content of gas produced by ANFLOW bioreactor.

predicted by the decrease in volatile acids accumulation discussed earlier for these months.

Removal of Suspended Solids

The levels of total suspended solids (TSS) in the feed varied significantly, reaching a maximum monthly average of 250 ppm as seen in Fig. 7. TSS levels in the effluent were generally below 30 ppm until the later months of the project. During this period, TSS levels in the feed reached the maximum observed and feed flow rates 20 to 40% above the 5000-gpd design flow rate were used. More importantly, the system had been operated for 15 months without removing nondigesting or slowly digesting solids from the bioreactor. In an optimized operation, the bioreactor would be periodically backwashed to remove such solids and to prevent or minimize their discharge in the effluent.

Figure 8 summarizes the effects of feed flow rate and TSS loading rate on the TSS removal rate obtained with the pilot-plant bioreactor. At design flow rates or less, an average TSS removal rate of 75% of TSS loading was obtained for loading rates as high as 55 lb TSS/day/1000 ft^3 of reactor, as can be seen. However, the bioreactor could not effectively remove TSS at loading rates as low as 25 lb TSS/day/1000 ft^3 of reactor when flow rates approached 7000 gpd. From these results it was postulated that a "sludge blanket" was formed in the bioreactor as solids accumulated, and that this sludge blanket could only be retained in the column by gradually reducing the HLR. It was apparent that periodic removal of solids from the bioreactor would be required if the bioreactor was to be operated continuously at a high HLR, and that the requirement for solids removal would be indicated by the usable HLR decreasing below an allowable limit. The operating cycle would thus be determined by the rate of solids accumulation in the bioreactor under given operating conditions.

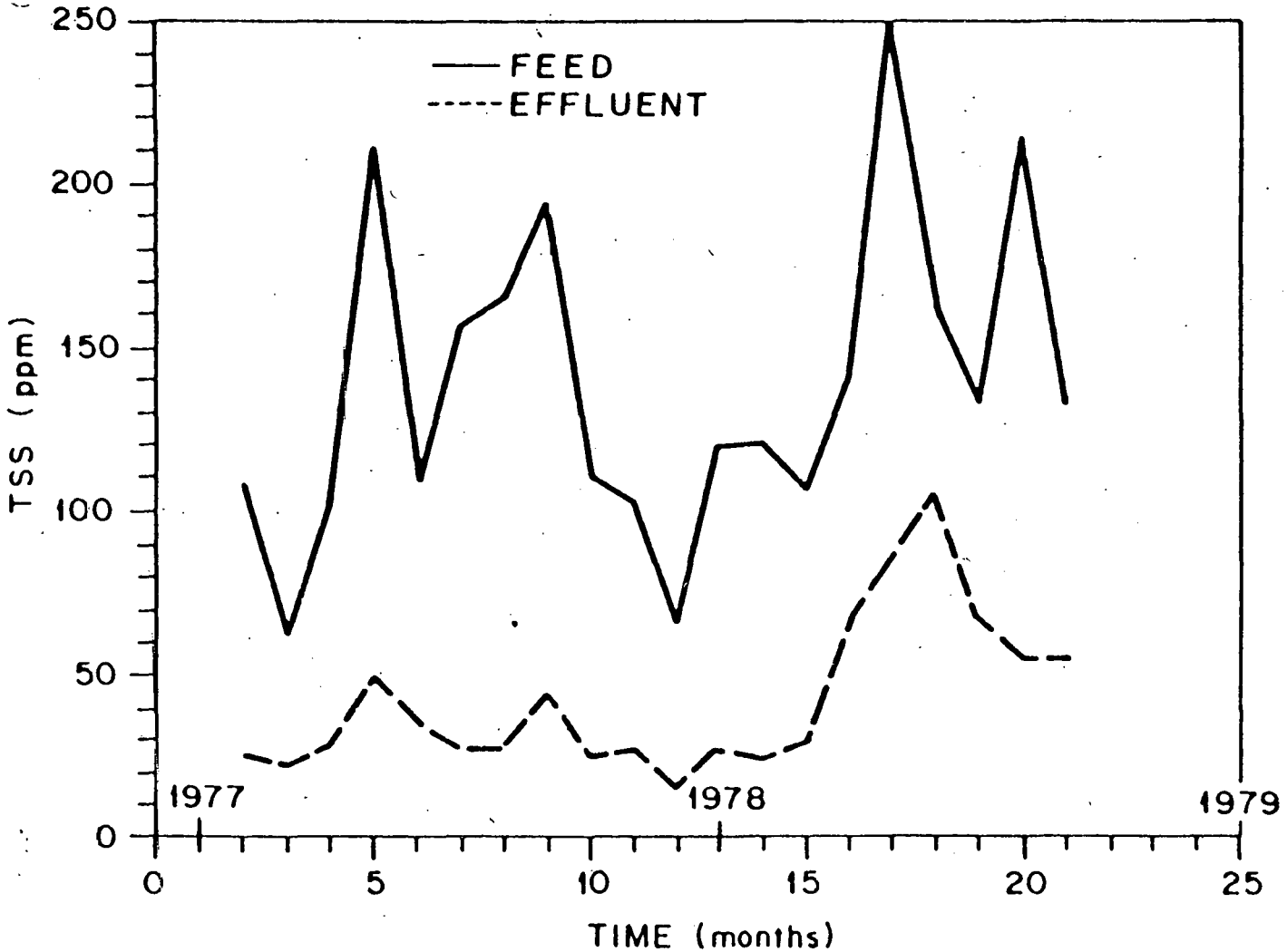


Fig. 7. Solids removal by ANFLOW bioreactor.

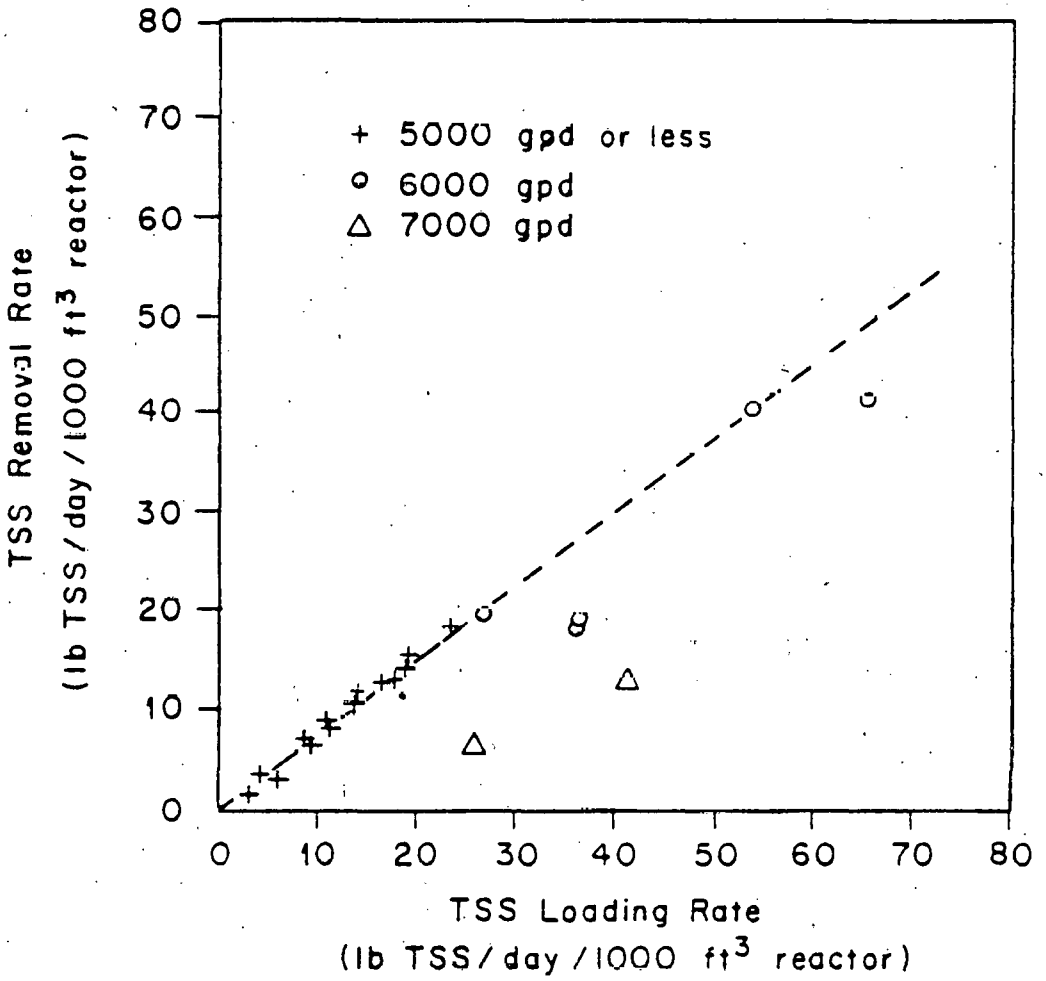


Fig. 8. Solids removal in ANFLOW bioreactor.

The bioreactor was drained by gravity-flow and washed with wastewater fed at 8000 gpd for 24 hr in order to test the feasibility of periodically removing solids. TSS removal rates were then re-evaluated at flow rates of 1000, 5000, and 7000 gpd.

Results are presented in Fig. 9 which shows that after solids removal, flow rates as high as 7000 gpd could be used while obtaining 75% removal of TSS. As shown in Fig. 8, this level of performance was previously limited to flow rates of 5000 gpd or less. Since the draining and washing did not remove films which were firmly attached to the packing, there was no problem in re-starting the bioreactor.

Removal of Biological Oxygen Demand (BOD)

Levels of 5-day biological oxygen demand (BOD) measured in the feed and effluent streams are summarized in Fig. 10 as monthly averages. Levels of BOD in the feed reached monthly averages as high as 220 ppm. Effluent BOD levels followed trends in the feed and ranged from 30 to 90 ppm. Since much of the BOD in the effluent was associated with TSS, increased efficiency in TSS removal, as discussed in the preceding section, would result in significant improvement in BOD removal.

As seen in Fig. 11, BOD removal rates could be correlated with BOD loading rates. These data show an average BOD removal of 55% in the column as operated during the pilot-plant project. During March 1978, the feed rate to the column was increased to 6000 gpd, 20% above the design value. As seen in Fig. 11, the column required an acclimation period but returned to the 55% removal rate in the following months. It is currently postulated that during the acclimation period, the column reached a new steady state with respect to the solids it could retain in the sludge blanket described earlier.

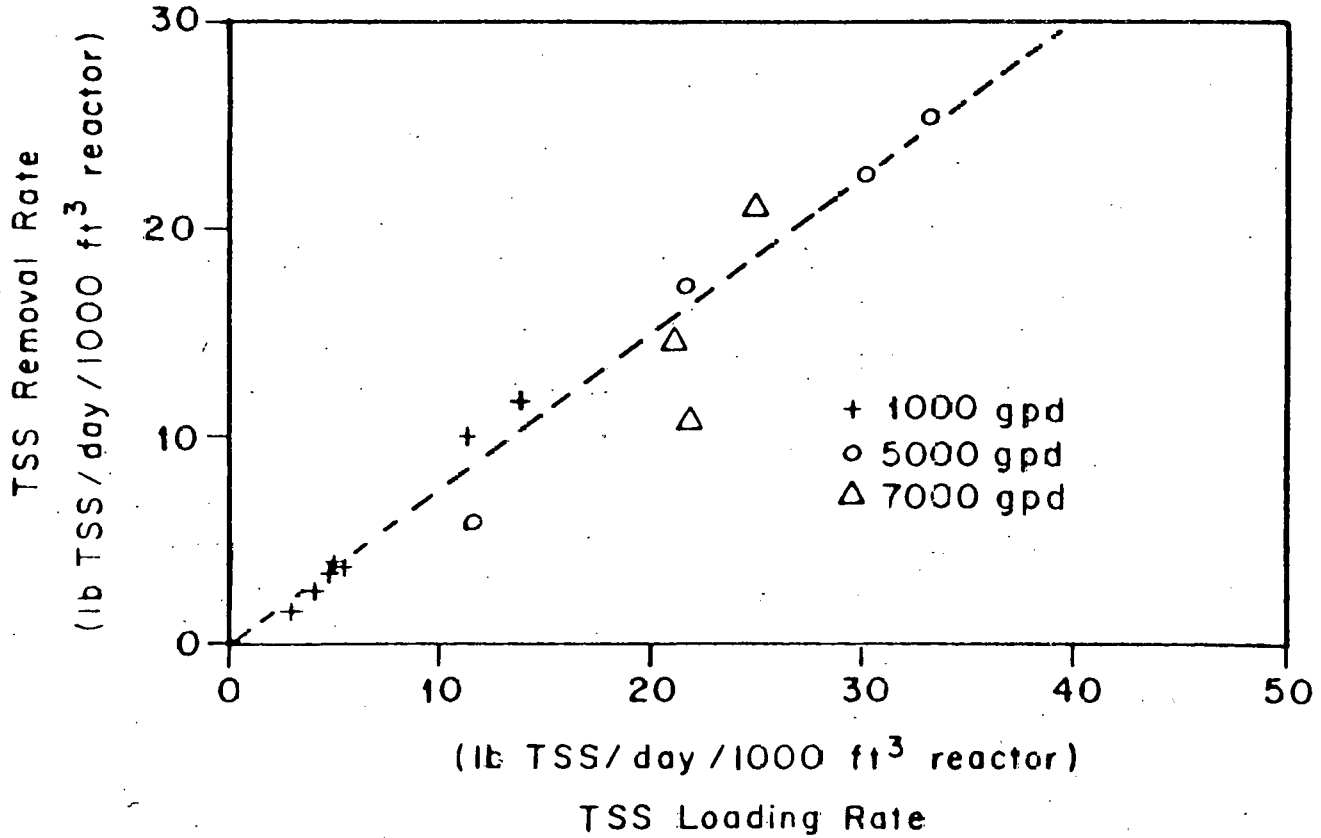


Fig. 9. TSS removal by ANFLOW column after draining and start-up.

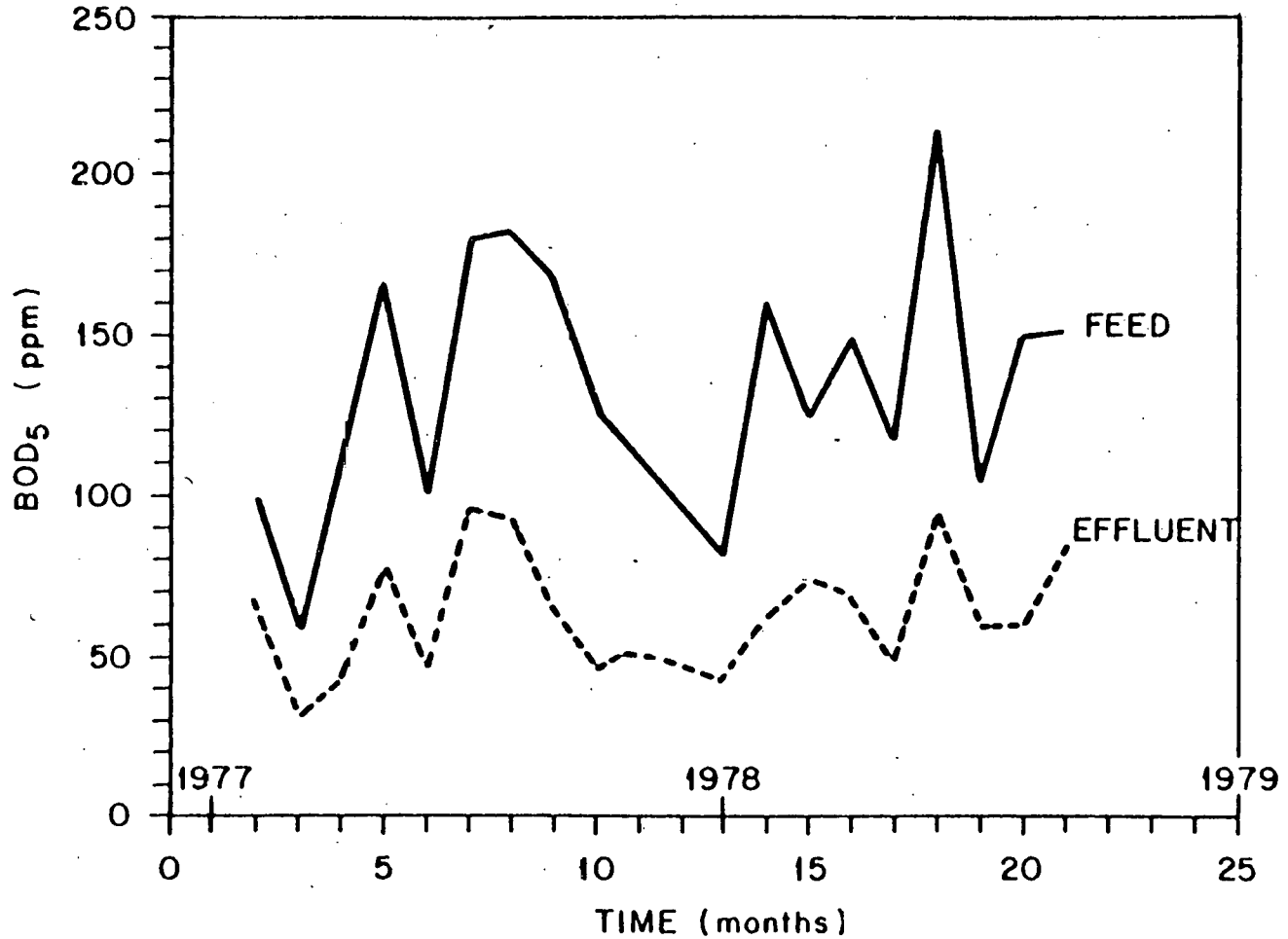


Fig. 10. Biological oxygen demand histogram for ANFLOW bioreactor.

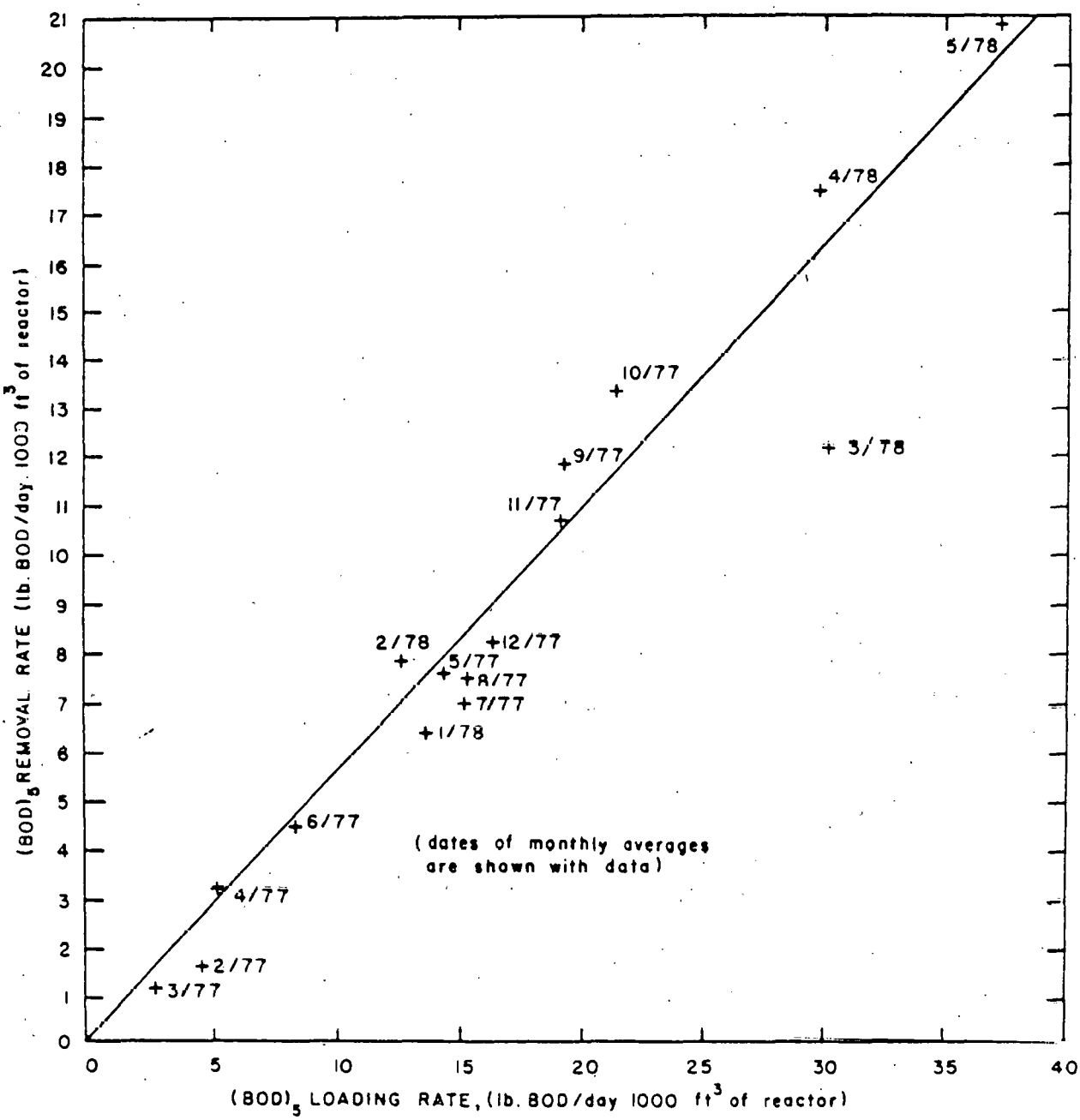


Fig. 11. BOD_5 removal rates at the ANFLOW pilot plant.

The midrange loading data shown in Fig. 11 were used to obtain a correlation of the averaged removal rates with the averaged operating temperatures during the corresponding months. As seen in Fig. 12, temperature changes in the range of 10-25°C did not affect the removal rates for relatively constant loading rates. This suggests that physical processes were very significant and perhaps controlling in the overall removal processes occurring during the pilot-plant project.

Effluent Polishing

To test effluent polishing characteristics, batch samples of ANFLOW column effluent were conditioned with alum and lime (50 and 60 ppm, respectively) and settled. The resultant supernatant suspended solids values ranged from 10 to 15 ppm. Batch samples of column effluent were also poured downflow through 22 in. of 0.25- to 0.50-mm sand. The suspended solids were reduced from approximately 48 to less than 15 mg/liter by sand filtration.

For on-line tests, a granular media filter was added to the pilot-plant facilities and used to treat a sidestream of the column effluent for 3 weeks. The filter bed was dual media with the following characteristics:

Sand layer - 12 in. deep, 0.45-mm grain

Coal layer - 18 in. deep, 1.00-mm grain

The filter was operated in a downflow mode at a hydraulic loading rate of 3.2 gpm/ft^2. Under the test conditions, the removal of insoluble matter was approximately 70%. The average effluent TSS was 18 ppm, while the average effluent BOD was 33 ppm. Operational difficulties with the small-scale filter system were experienced during these tests. It

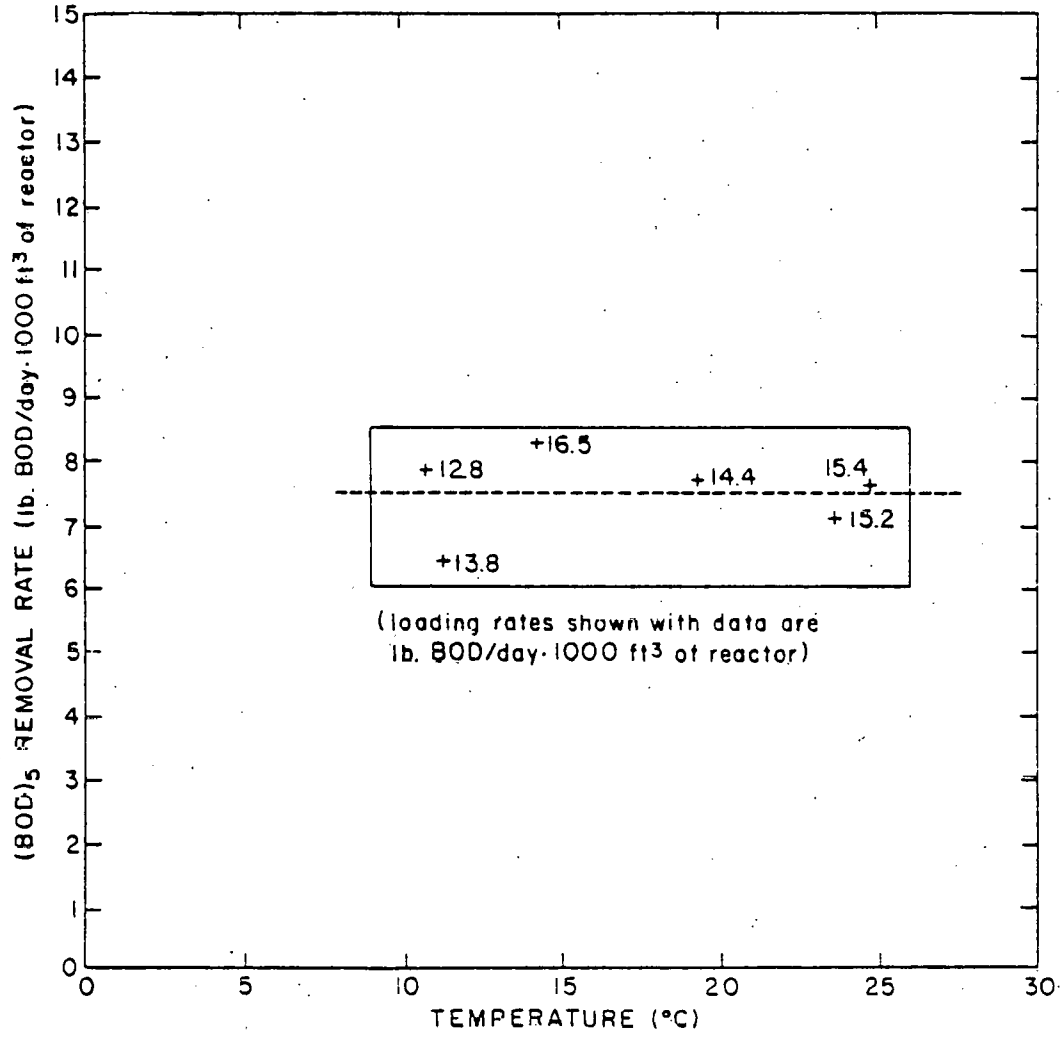


Fig. 12. Effect of temperature on BOD removal rates under constant loading at the ANFLOW pilot plant.

was predicted that better performance would be achieved by optimizing the backwash frequency and by employing chemical conditioning prior to filtration.

Flow Distribution

The hydraulic residence time for wastewater being treated by the ANFLOW column was investigated by residence time distribution (RTD) tests performed at different feed rates. For each test, a dye pulse (19 liters of 10 ppm fluorescein) was introduced into the column through the feed-line standpipe. The column effluent was sampled continuously and combined with a reagent development stream (0.5 M NaOH, 0.005 M EDTA) before being monitored by a fluorometer. The reagent development stream produced a basic pH that enhanced the fluorescence of the dye; the EDTA complexed dissolved-metal ions to prevent precipitation in the flow cell at the basic pH. Results of the RTDs, compared with theoretical plug-flow residence times, are shown in Fig. 13. Two theoretical curves are shown, the first calculated for the actual void volume measured in the packed section of the column and the second calculated for the combined volumes of the packed section and the bottom cone on the column. Since flow was introduced immediately below the packed section (see Fig. 1), it can be assumed that there was little circulation of wastewater in the bottom cone. Therefore, the theoretical curve calculated for the packed section can be used as a model for plug-flow behavior in the column. As seen by the experimental results in Fig. 13, the flow in the ANFLOW column could be approximately described by plug-flow models for feed rates ranging from 1000 to 7000 gpd. No significant channeling problems were indicated for flow in the ANFLOW column.

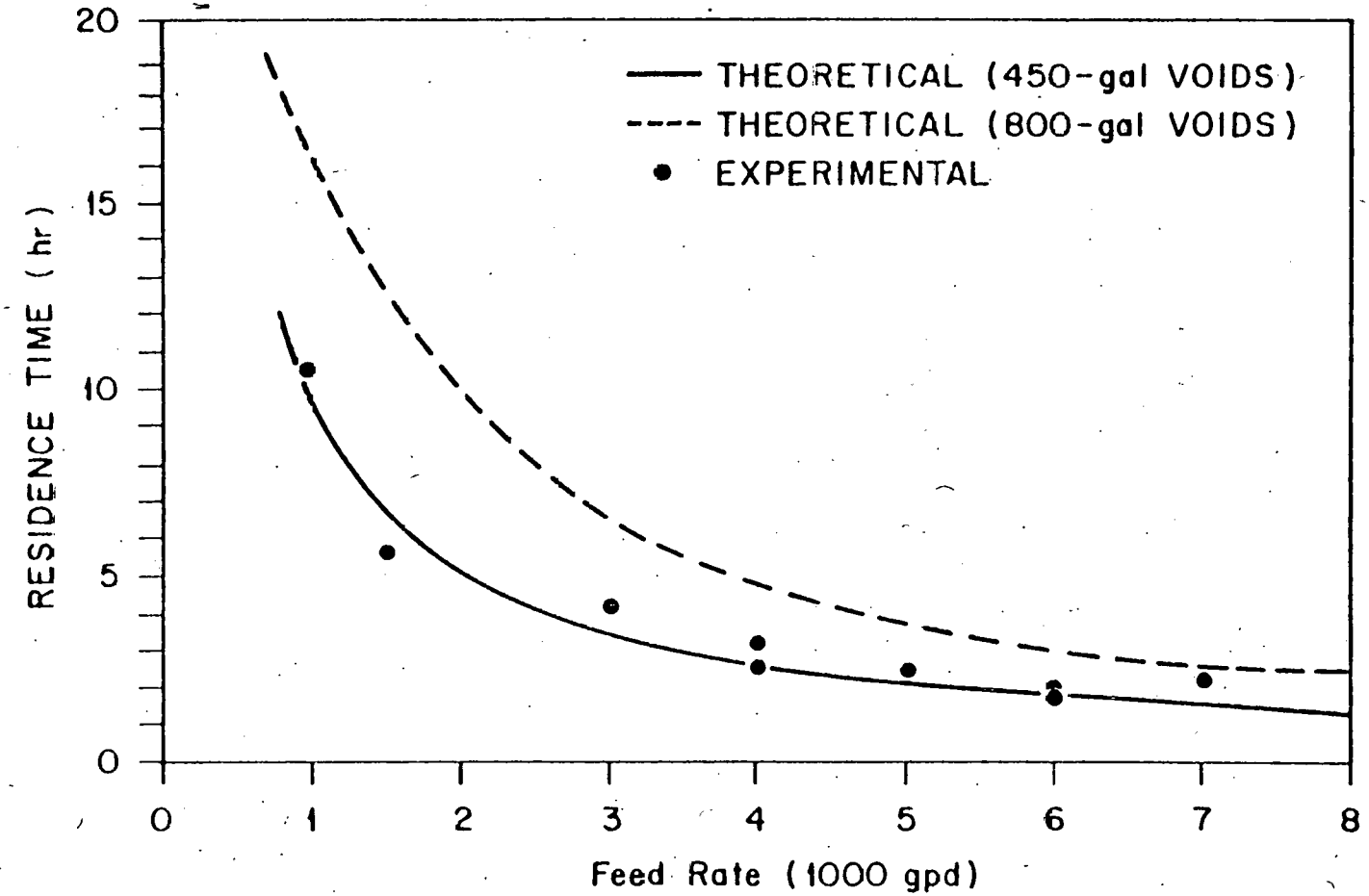


Fig. 13. Hydraulic residence times in ANFLOW bioreactor.

DISMANTLING THE ANFLOW COLUMN

At the conclusion of the pilot-plant operation, the ANFLOW column was drained and the top was opened to allow removal of packing material and accumulated solids. An initial volume increment of 150 gal was collected from the bottom cone; this slurry was 60 vol % solids, produced little odor, and had the qualitative appearance of primary digestor effluent. An additional 650 gal were drained; this mixture was 1.7 wt % solids, and 60% of these solids were volatile. From these measurements it was estimated that 600 gal (or 5000 lb or 80 ft^3) of fixed material (material not removed by draining the column) accumulated in the column during the 2 years of operation. Therefore, approximately 43% of the initial void volume in the packed section remained open to flow after this period.

Of the material remaining as films on the packing surface or in the cores of the packing, approximately 50% was volatile. All film material could be easily removed with a cold-water spray. However, it was obvious that a more open-structured packing material would allow greater efficiency in solids removal during a column draining operation.

The packing was removed from the column in layers starting at the top. There were no radial profiles observed in film thickness at any height above the feed point, and the column did not appear to be plugged at any point. Film thicknesses were observed to be greater in the lower regions of the column where material also accumulated in the cores of the packing material.

ANFLOW SYSTEM CONCEPTUAL DESIGNS

Influent and Effluent Characteristics

ANFLOW system designs were developed for average waste flows of 0.05 and 1.0 mgd and for peak hourly flows of 180 and 2,400 gpm, respectively. The wastewater characteristics used for these designs are summarized in Table 1. Although design examples were developed for "weak" and "strong" wastewater strengths during this investigation, only the designs for the more concentrated wastewater are presented in this paper.

Treatment objectives were based on EPA secondary treatment standards which require 30-day average BOD and TSS concentrations of 30 mg/l and maximum 7-day average values for these constituents of 45 mg/l each. In addition, a minimum removal of 85 percent is required for both constituents based on a consecutive 30-day average. Since nitrogen limitations are not included in the current guidelines, neither oxidation or removal of nitrogen was included in these designs. If nitrogen removal is required for a specific application, the design approach would require modification accordingly.

Design Basis

Data from the pilot investigation were used as the basis for developing anaerobic filter process designs. AWARE experience with other systems was used to supplement the pilot plant data base in developing the designs. This initial design evaluation served to indicate areas of concentration for further pilot and demonstration-scale work should this evaluation indicate a favorable feasibility for the ANFLOW process.

TABLE 1

WASTEWATER CHARACTERISTICS FOR DESIGN EXAMPLES

Quality Characteristics	Value
BOD, mg/l	300
TOC, mg/l	300
COD, mg/l	1,000
TSS, mg/l	350
VSS, mg/l	275
Settleable Solids, ml/l	20
TKN, mg/l	85
NH_3-N, mg/l	50
Temperature[a], Summer, °C	20
Winter, °C	15

[a]Influent sewage temperature.

In addition to developing a basis of design for the ANFLOW system, it was necessary to select attendant processes required for a complete treatment system employing the anaerobic filter and to construct process designs for these processes in addition to developing the design for the filter itself. A summary of process design parameters used as the basis of these designs is presented in Table 2. A flow diagram of the ANFLOW system is presented in Figure 14. A process design summary is presented in Table 3.

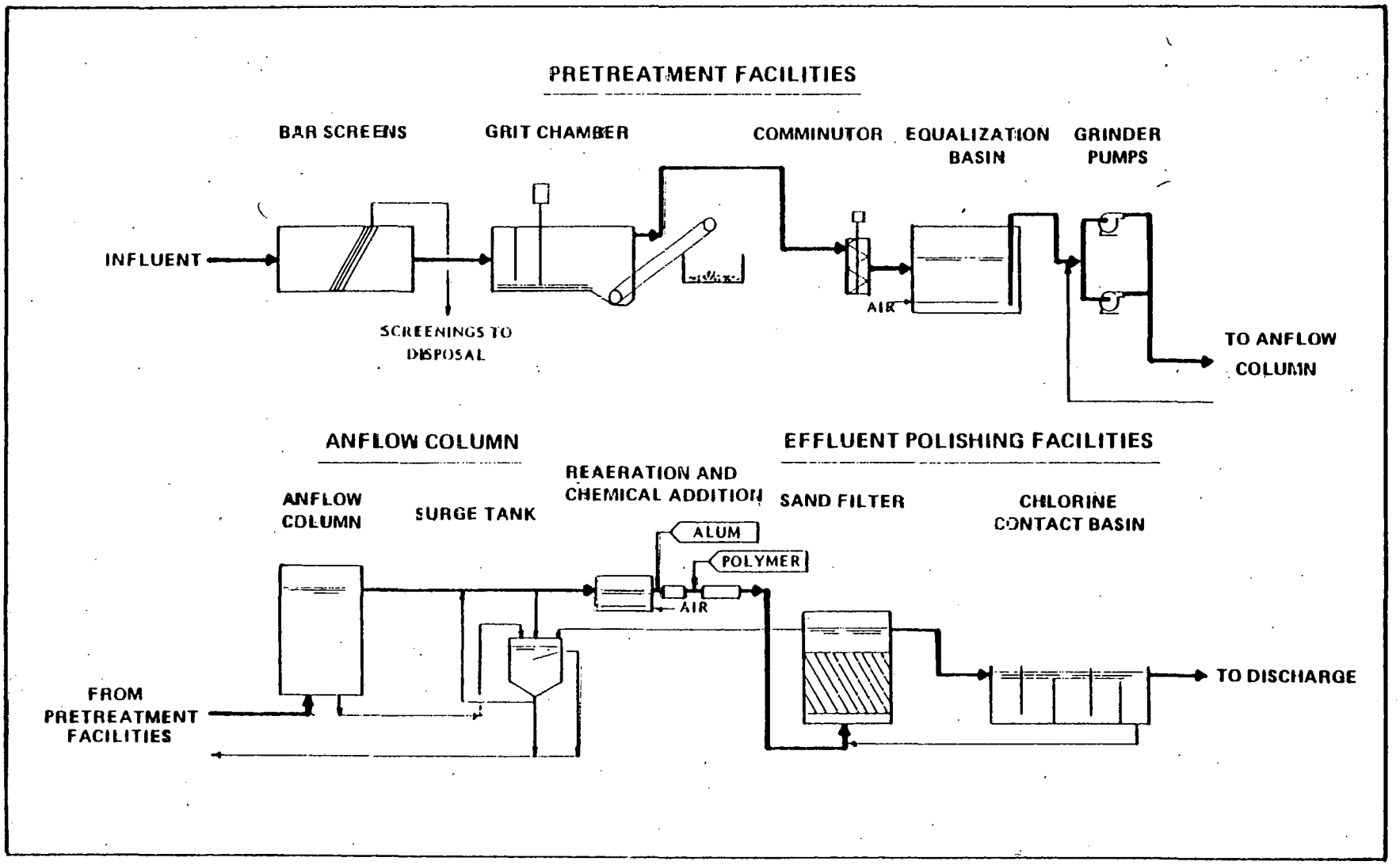
Pretreatment. Pretreatment facilities included in the design were bar screening, grit removal, comminution of solids, equalization, and solids grinding. Requirements for the bar screening and grit chambers were typical of those used in conventional treatment systems. It was felt that both comminution and grinding of influent suspended solids would be required to ensure that the anaerobic filter did not prematurely clog due to the presence of unacceptably large suspended solids. The system was designed to provide influent suspended solids of 0.5 mm or less downstream of the grinder pumps. Equalization was included in order to provide conditions most suitable for biological treatment and to minimize the size requirements for downstream operations based on peak flow sizing requirements. Aeration was included in the equalization basin design for mixing and to prevent uncontrolled septicity of the waste. Primary clarification was not included because of the relatively small size of the example systems and because of the advantage associated with degrading primary solids in the anaerobic filter.

Anaerobic Filter. The ANFLOW system design was based on a substrate reaction rate constant, K, of 5.0 $days^{-1}$ and a hydraulic loading rate of 0.15 gpm/sq ft (4). Design at this hydraulic loading rate would, based

TABLE 2

SUMMARY OF DESIGN CRITERIA AND PARAMETERS

Parameter	Value
Pretreatment Facilities	
Bar Screen	
Volume of Screenings, cu ft/mil gal	3.5
Moisture Content of Screenings, percent	80
Method of Cleanings, Small Plant	Manual
Large Plant	Mechanical
Comminutor	
Largest Size of Particle to be Passed, in.	0.25
Minimum Number of Units	2
Grit Chamber (Large Plant Only)	
Maximum Overflow Rate, gpm/sq ft	30
Minimum Size of Sand Particles to be Removed, mm	0.2
Volume of Grit, cu ft/mil gal	4.0
Moisture Content of Grit, percent	60
Equalization Tank	
Volume, Percent of Average Daily Flow, Small Plant	25
Large Plant	20
Air Supply, cfm/1,000 sq ft	1.5
Power Consumption Rate, hp/100 cfm	4.0
ANFLOW System	
Packing Media	1-in. Raschig Rings
Reaction Rate Constant @ 20°C, day^{-1}	5.0
Average Hydraulic Loading Rate, gpm/sq ft	0.10
Maximum Hydraulic Loading Rate, gpm/sq ft	0.15
Solids Yield Coefficient, g TSS/g BOD Removed	0.2
Non-Degradable Fraction of VSS	0.3
Effluent TSS, mg/l	35
Effluent Insoluble BOD/VSS Ratio	0.76
Effluent Polishing Facilities	
Aeration and Degasification	
Rate of Air Supply cfm/1,000 cu ft	16
Depth of Aeration Basin, ft	10
Power Consumption Rate, hp/100 cfm	4.0
Upflow Sand Filter	
Maximum Head Loss, ft	6.0
Depth of Bed, ft	5.0
Media Effective Size, mm	1.0
Media Uniformity Coefficient	1.2
Average Hydraulic Loading Rate, gpm/sq ft	3.0
Specific Deposit, lb SS/sq ft-ft head loss	0.05
Effluent SS, mg/l	15
Backwash Rise Rate, gpm/sq ft	35
Backwash Duration, min	10
Chlorination	
Cl_2 Dosage, lb/mil gal	50
Mixing Time, sec	10-30
Minimum Contact Time, min	30
Sludge Handling	
Sludge Surge Tank	
Volume, Fraction of ANFLOW Bed Volume	0.7
or, Number of Backwash Volumes	1.5
SS in ANFLOW Drainage Slurry, percent	2
Settling Time for ANFLOW Drainage Slurry, hr	6
Underflow Concentration, percent SS	3
Sludge Drying Beds	
Solids Loading lb/sq ft-yr	25
SS in Applied Sludge, Percent	3
SS in Dried Sludge, Percent	35



Fic. 14. ANFLOW system process flow diagram

TABLE 3

ANFLOW SYSTEM PROCESS DESIGN SUMMARY

Process Unit	Parameter	Plant Size 0.05 mgd	Plant Size 1.0 mgd
Bar Screen			
	Channel Width, ft	0.5	2
	Screenings Volume, cu ft/day	0.18	3.5
	SS in Screenings, lb/day	3.3	64
Comminutor			
	No. of Units	2	2
Grit Chamber			
	Width, ft	1	4
	Length, ft	5.5	20
	Grit Volume, cu ft/day	0.2	4
	SS in Grit, lb/day	12.4	248
Equalization Basin			
	Volume, mil gal	0.0125	0.20
	Power Required, hp	1	12
Grinder Pump			
	No. of Units	2	2
Anaerobic Filter			
	Detention Time, hr	18	18
	Voids Volume, mil gal	0.037	0.74
	Total Volume, 1000 cu ft	7.06	141.2
	Surface Area, 1000 sq ft	0.706	14.12
	Number of Columns	4	4
	On-side Length of Column, ft	13	60
	COD Loading Rate, lb/1000 cu ft-day	59.0	59.0
Aeration System			
	Detention Time, hr	3.2	3.2
	Basin Volume, mil gal	0.0067	0.13
	Air Required[a], cfm	18	362
	Power Required, hp	0.75	15
Upflow Sand Filter			
	Surface Area, sq ft	12.5	242
	Number of Cells	2	2
	Backwash Volume, 1000 gal	2.2	42.9
Chlorination Facilities			
	Chlorine Dosage, lb/day	2.5	50
	Maximum Chlorine Dosage, lb/day	7	105
	Rapid Mix Section Volume, gal	60	800
	Contact Basin Volume, 1000 gal	5.4	72
Surge Tank			
	Volume, gal	3,300	65,000
	Solids Accumulation, lb/day	82	1,650
	Column Drainage Volume, gpd	490	10,000
Sand Drying Beds			
	Area, acres	0.03	0.55

[a]An additional 25 percent included for handling the wastewater immediate and chemical oxygen demands.

on the initial pilot plant experience, reduce the possibility of high effluent suspended solids concentrations. The filter columns were designed to be operated in an upflow mode. No problems with clogging of the filter media were observed during pilot-scale testing in a similar flow configuration.

The pilot investigation was conducted using a 10-ft bed depth packed with 1.0-in. Raschig rings. No data were gathered concerning BOD and suspended solids removal along the depth of the column. Available bench-scale data from preliminary testing indicated that a 6-ft column performed as effectively as a 10-ft column when both were loaded at similar rates. Reports in the literature also indicate that extra benefits derived from extending the bed depth beyond 6 ft are marginal (6). However, some examples exist in which greater than 20-ft bed depths were used (7). For this design a 10-ft column depth was selected since this was the height of the pilot column. A more thorough evaluation of the effect of column depth on treatment performance was left for future investigations.

Very limited data were available on the performance of the ANFLOW system using different packing materials. The amount of active biomass attached to the rings relative to that in the void volume had not been determined at the time this evaluation was performed. Therefore, the significance of the specific surface of the packing could not be determined during this investigation. Furthermore, since Raschig rings appeared to have geometrical characteristics (specific surface, void volume, physical strength, etc.) which were favorable for this application and since these rings were used in the pilot investigations, they were also employed in this design. Despite this selection, it was felt that other packings could

be used. The principal requirements are that the packing provide for suspended solids retention in the filter and having an adequate surface area for biomass attachment. Substitution of an alternative packing manufactured from plastic or stone could result in a significant cost savings for the anaerobic system.

The column was sized to provide an effluent BOD of 30 mg/l from the entire treatment system. This corresponded to an effluent soluble BOD from the ANFLOW system of 25 mg/l. The column off-gas will contain methane, carbon dioxide, nitrogen, and small amounts of other gases. This gas represents a source of energy for power generation. Energy available from the gas generation assumed for these designs is illustrated in Table 4.

Effluent Polishing Facilities. To reduce the effluent suspended solids and BOD for discharge, the pilot results indicated that additional treatment using aeration and filtration should be considered. Aeration of the anaerobic filter effluent would provide for methane stripping and aeration.

An upflow sand filter was included in the design to control suspended solids and insoluble BOD in the anaerobic filter effluent. Based on initial pilot plant results using granular media filtration, some difficulty may occur in achieving low filtrate suspended solids concentrations. Therefore, chemical conditioning using alum and polymer was included in this design. The upflow sand filter would function as an aerobic biological reactor. It was assumed that at least 5 mg/l of soluble BOD removal would be achieved in this system designed at a loading rate of 3 gpm/sq ft employing a 5-ft sand depth. Backwash water would be recycled to the filter from the chlorine contact basin located downstream of the filter.

TABLE 4

ANTICIPATED ANFLOW SYSTEM GAS PRODUCTION
AND ENERGY PRODUCTION

Parameter	Plant Size	
	0.05 mgd	1 mgd
Off-Gas, cu ft/day	1,780	35,820
Power Recovery,[a] hp	11	225

[a]Calculated using the relationship: $P = 0.98Q\ \Delta TOC$

where:

P = power, hp
Q = treated waste flow, mgd
ΔTOC = TOC removed, mg/l

Either chlorination or ozonation facilities would be required to achieve adequate control over fecal coliforms. A conventional plug-flow chlorine contact basin and chlorination system were included in this design.

Sludge Handling Facilities. Intermittently, sludge must be discharged from the ANFLOW system. Since the quantity of solids generated from the anaerobic treatment system would be relatively small, sand drying beds were included in the design for sludge dewatering. It was assumed that underflow from sand drying beds would be recycled to the head end of the treatment system.

COMPARATIVE COST ANALYSIS

In order to determine the economic attractiveness of the ANFLOW process, comparative cost estimates were developed for complete municipal domestic wastewater treatment and sludge handling systems utilizing the ANFLOW process and the activated sludge process. The activated sludge process was selected for comparative purposes because of its predominance in municipal wastewater treatment. The basis for cost development is presented in subsequent sections. Costs were developed from readily available cost curves and were supplemented with vendor quotes and other engineering estimates where appropriate or necessary. The costs presented herein are comparative costs and are considered accurate to ± 50 percent. Installed capital costs were developed on a unit process basis for each alternate treatment system. Total system capital costs were obtained by summation of unit process costs and addition of appropriate non-process related and contingency costs. All capital costs are battery limit costs and do not include costs for sewers, wastewater pumping other than as specified within the treatment plant, outfall construction, and engineering above normal design work. O&M costs include operation and maintenance

labor, laboratory work, electrical, chemical, and other material costs. All costs were adjusted to an ENR Construction Cost Index of 2,860 in August, 1978. All labor costs were based on a rate of $10/hr and all power costs were based on electrical costs of $0.03/kwh. Capital costs were annualized based on a 7 percent interest rate for 30 years. The resulting capital recovery factor was 0.08.

ANFLOW System Cost Basis

ANFLOW media costs were based on the use of 1-in. ceramic Raschig rings at $10/cu ft installed costs. In addition, costs were also prepared using 3-in. polypropylene plastic Raschig rings at $3.50/cu ft installed costs to indicate the sensitivity of ANFLOW costs to the selected tower, packing material. The same column volume was used for both designs although a somewhat smaller volume might be adequate with the larger packing. ANFLOW column costs were developed utilizing concrete as the material of construction with a packing medium depth of 10 ft. Provisions were made for covering both the equalization basin and the ANFLOW reaeration tank for off-gas containment. A granular media filtration system was provided for all ANFLOW design cases. It was assumed that no additional wastewater pumping would be required for the granular filtration system.

ANFLOW system O&M costs were developed on readily available information for conventional unit processes and on engineering estimates for the ANFLOW process itself. The equivalent cost of the recovered energy from the ANFLOW process was computed based on a 40 percent conversion efficiency and an electric cost of $0.03/kwh. This recovered cost was used to offset unit process power costs for the 1.0 mgd flow rate cases. The gas quantity generated at the 0.05 mgd flow rates was judged insufficient to warrant recovery. Even for the 1.0 mgd design flow cases, the off-gas

quantities are quite marginal for recovery by boiler-turbine generation equipment. However, recent work by several investigators utilizing methane gas to power internal combustion engine-generator systems indicates on-site power generation as the prime electrical source is feasible (8).

Cost Basis

The unit process flow scheme for the activated sludge process is presented in Figure 15. A primary clarifier was provided for the 1.0 mgd flow case. Aeration basin sizing was based on a design F/M loading rate of 0.2 lb BOD/day-lb MLVSS. Aeration basins were considered to be steel tanks on concrete pads for the 0.05 mgd case and concrete tanks in the ground for the 1.0 mgd cases. Aeration was by diffused aeration systems. Aerobic sludge digestion was provided for all cases. Gravity sludge thickening and sand drying beds were provided for all cases.

Activated sludge system O&M costs were developed from readily available information for individual unit processes. As with the ANFLOW systems, O&M labor requirements were judged to be commensurate with effluent discharge criteria.

System Comparisons

Comparative capital cost estimates for 0.05 and 1.0 mgd treatment systems are presented in Tables 5, and 6, respectively. ANFLOW system costs are shown for use of 3-in. plastic Raschig ring packing and 1-in. ceramic Raschig ring packing. Results indicate a significant cost reduction using the 3-in. plastic rings. Although no experimental data were available at the time this evaluation was completed to indicate comparative performance of the plastic rings, it is felt the performance of the

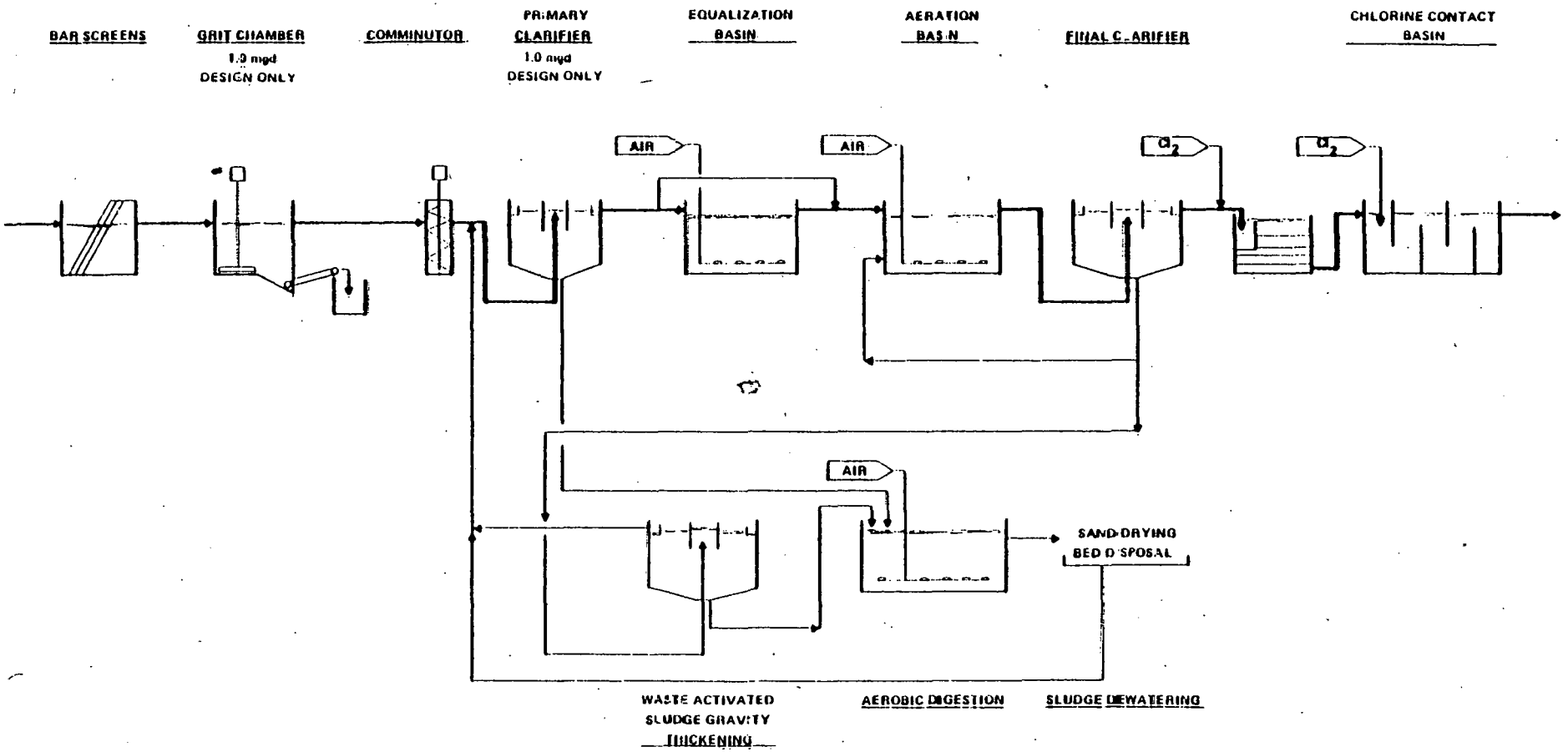


Fig. 15. Activated sludge process flow diagram

TABLE 5

COMPARATIVE CAPITAL COSTS
FOR 0.05 mgd TREATMENT SYSTEMS

Process Area	ANFLOW		Activated Sludge
	3-in. Plastic Ring Packing	1-in. Ceramic Ring Packing	
Preliminary Treatment	$ 81,000	$ 81,000	$ 78,750
Biological Treatment	138,450	204,300	180,000
Effluent Polishing	78,750	78,750	33,750
Sludge Handling	37,500	37,500	116,259
TOTAL COSTS[a]	$335,700	$401,550	$408,750

[a]ENR Construction Cost Index of 2,860 (August, 1978).

TABLE 6

COMPARATIVE CAPITAL COSTS
FOR 1.0 mgd TREATMENT SYSTEMS

Process Area	ANFLOW		Activated Sludge
	3-in. Plastic Ring Packing	1-in. Ceramic Ring Packing	
Preliminary Treatment	$ 296,250	$ 296,250	$ 476,250
Biological Treatment	1,577,250	2,981,250	772,500
Effluent Polishing	412,500	412,500	112,500
Sludge Handling	165,000	165,500	532,500
TOTAL COSTS[a]	$2,451,000	$3,855,000	$1,893,750

[a]ENR Construction Cost Index of 2,860 (August, 1978).

system would not be impaired using the plastic rings. Using costs for use of the 3-in. plastic ring packing for comparison, it can be seen that the ANFLOW system had an 18 percent cost advantage for the 0.05 mgd design flow, while the activated sludge process had a 30 percent cost advantage for the 1.0 mgd design flow on the capital cost basis.

In addition to developing a design for the anaerobic filter, it was necessary to select and determine a design basis for attendant processes required to provide a secondary level of treatment. Pretreatment processes selected for use ahead of the anaerobic filter included bar screening, grit removal, comminution of solids, equalization, and solids grinding. Downstream of the anaerobic filter, facilities were included for aeration, upflow filtration through a granular medium and chlorination. The upflow granular media filter was designed to function as a aerobic biological reactor to remove at least 5 mg/l of soluble BOD in addition to its function in removing suspended solids from the ANFLOW column effluent. Because of the relatively small sizes of the systems selected for analysis, sludge dewatering by application to sand drying beds was selected.

The results of this comparison are summarized as follows:

1. The ANFLOW system exhibited an 18 percent cost advantage over conventional activated sludge treatment for the 0.05 mgd design case, while the activated sludge process had an approximate 30 percent capital cost advantage for the 1.0 mgd design case.

2. Definite cost advantages were indicated for the ANFLOW system using a 3-in. plastic Raschig ring for the column fill material instead of the 1-in. ceramic Raschig ring used in the initial pilot investigations. While it is felt that the larger packing would perform at least as well as the smaller, confirmation of this hypothesis must be the subject of further investigations.
3. A comparison of total annual treatment costs (amortization and operational costs) indicated that the ANFLOW system would afford an approximate 20 percent reduction in annual costs compared to activated sludge treatment for a flow of 0.05 mgd, while treatment costs would be virtually identical for the 1.0 mgd design case.
4. A comparison of energy usage indicated that the ANFLOW system would use approximately 45 percent of the energy required by an activated sludge system for a design flow of 0.05 mgd, while the ANFLOW system use approximately 30 percent of the energy required by a 1.0 mgd activated sludge system.

Based on this evaluation, the ANFLOW process appears to be economically competitive with conventional secondary treatment technology. This evaluation also indicated that the ANFLOW process requires significantly less energy than conventional secondary treatment systems. Initial pilot testing results indicate that the process is technically feasible. Additional aspects of system performance and confirmation of treatment levels achievable using the ANFLOW system will be investigated in a demonstration-scale plant (50,000 gpd) which is currently being designed and will be located adjacent to a trickling filter treatment plant in Knoxville, Tennessee.

Annualized costs for both systems, including amortized capital costs and estimated operation and maintenance costs are presented in Table 7. These estimates indicate that the ANFLOW system would afford an approximate 20 percent reduction in total annual costs compared to total activated sludge treatment for a design flow of 0.05 mgd, while treatment costs would be virtually identical for the 1.0 mgd design case. More recent work at ORNL has indicated that the kinetic basis for design of the anaerobic filter might be too conservative in these designs. While additional data are needed prior to making a firm conclusion regarding system kinetics, such a result would increase the advantage of the ANFLOW system relative to activated sludge treatment.

A comparison between labor requirements for ANFLOW and activated sludge systems for the two design flows are presented in Table 8. This information indicates that labor requirements for the two systems agree to within approximately 5 to 10 percent. However, electrical requirements compared in Table 9 indicate that the ANFLOW system will use approximately 45 percent of the energy required by a 0.05 mgd activated sludge system and approximately 30 percent of the energy required for a 1.0 mgd activated sludge system.

SUMMARY

Initial pilot-scale testing results of the ANFLOW process were used as the basis for developing conceptual system designs. Process designs were developed for domestic wastewaters using flows of 0.05 and 1 mgd. Comparisons were made between the ANFLOW system technology and an activated sludge system (selected as being representative of conventional and more energy-intensive secondary treatment technology).

TABLE 7

TOTAL ANNUAL TREATMENT COST COMPARISON[a]

System	Annual Cost, $ x 10^6/hr	
	0.05 mgd Design Flow	1.0 mgd Design Flow
ANFLOW[b]	0.051	0.30
Activated Sludge	0.061	0.31

[a]Costs based on construction cost index = 2,860 (August, 1978).

[b]Based on use of 3-in., plastic Raschig rings.

TABLE 8

COMPARATIVE LABOR REQUIREMENTS
FOR ANFLOW AND ACTIVATED SLUDGE

Process Area	Labor Requirement			
	0.5 mgd		1.0 mgd	
	ANFLOW	Activated Sludge	ANFLOW	Activated Sludge
Preliminary Treatment	525	500	2,100	2,500
Biological Treatment	450	275	2,000	2,750
Effluent Polishing	243	110	1,310	310
Sludge Handling	360	605	1,080	1,405
TOTAL PROCESS	1,578	1,490	6,490	6,965

TABLE 9

COMPARATIVE POWER REQUIREMENTS
FOR ANFLOW AND ACTIVATED SLUDGE

Process Area	Power Requirement (kw)			
	0.5 mgd		1.0 mgd	
	ANFLOW	Activated Sludge	ANFLOW	Activated Sludge
Preliminary Treatment	3.12	3.04	31.10	30.28
Biological Treatment	0.95	3.81	3.80	57.08
Effluent Polishing	1.14	0.38	6.66	0.95
Sludge Handling	0.0	4.19	0.0	57.45
TOTAL PROCESS	5.21[a]	11.42	41.56[b]	145.76

[a]No power recovery included.

[b]This amount will not be required since power recovery is included for this case.

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GENE F. PARKIN and R.E. SPEECE

A program to encourage implementation of the anaerobic filter needs to resolve a number of questions. The role of packing needs to be defined. It would appear that for concentrated wastewaters having low throughput rates and long solids retention times, there is little or no need for packing. What remains to be resolved is the situation involving dilute wastewaters with associated high throughput rates. Likewise, the situation with high loading rates with relatively low SRT and biological safety factor which may produce a sludge with poor settling characteristics and the role of packing in such a case needs to be defined.

It is essential that the filters be brought on-stream in the shortest possible time both initially and following any upsets, to establish their credibility and reliability. Therefore, optimum procedures and conditions for start-up must be clearly defined.

The lower temperature at which the filter can be expected to operate reliably needs to be established. This would be an operating graph of temperature vs SRT for the rate limiting step, which would normally be volatile acids conversion to methane at the higher loading rates.

One of the major reasons practicing engineers are reluctant to advocate use of the anaerobic filter is lack of a "design and operation strategy" for wastewaters containing toxicants. Information presently available demonstrates that the anaerobic filter can pass slug doses of toxicants and recover rapidly, has tremendous potential for acclimating to chronic toxicant loads, and can degrade compounds previously thought to be toxic. Future fundamental research should be aimed at quantifying (i.e., modeling) and cataloguing the ability of the filter to acclimate to toxicants so that engineers can develop proper "design acclimation strategies." Also, system recovery from toxicant exposure should be modeled in order to predict system downtimes. As a corollary, remedial measures should be studied to handle situations where down-times are protracted and thus intolerable. Such research would help develop an "operation and control strategy" that would enable engineers to better insure continuous, efficient operation. In addition, the applicability of recycle must be investigated in light of recent evidence that indicates that recycle may not be advisable in certain situations. A "recycle strategy" could thus be developed to increase the versatility of the process. All the above suggestions could also be applied to anaerobic expanded bed systems and the anaerobic sludge blanket process.

J. CHARLES JENNETT

A number of outstanding things were accomplished, I believe at this conference. First of all, systems were found which seemed to reliably and rapidly start anaerobic reactors. In particular, the technique presented by Jennett and Rand using methanol to start the methane formers and then following this with the waste to develop the other acid-forming organisms seems to have been found acceptable by many of the researchers.

There seems to be general agreement on the part of researchers that anaerobic filters are extremely effective in industrial waste treatment devices. In the area of municipal waste treatment, it would appear that there is considerable promise in this area for two reasons. The first is the obvious - the production of energy, rather than the consumption of it. The second is a little more subtle, but equally important. These systems produce little sludge, so that one does not have to expend large amounts of energy to dispose of it, nor waste large amounts of land trying to bury it.

The anaerobic systems seem to have other numerous advantages. They can be down for several weeks at a time, allowing you to use them for intermittent municipal systems of industrial systems. They appear to be extremely resistant to the treatment of toxicants. They also seem to break down toxicants and this may have an enormous advantage in municipal treatment for the anaerobic system would be used as pre-treatment and followed by aerobic treatment to remove these substances.

The other thing we found is that there is a great deal that needs to be done particularly in the area of municipal uses of the anaerobic system. We need to have scale-up studies; we need to find out how accurate our laboratory models are; and we need to do work into such new devices as those of Dr. Friedman the anaerobic rotating biological contactors. These systems seem to be able to handle high suspended solids, which will be particularly important in municipal treatment. We also need to have more prototype full-size models being built and tested.

I think this was probably one of the better workshops that this author has attended in many years.

A. A. FRIEDMAN

The Argonne National Laboratory is to be complimented for organizing this timely specialty conference. The sessions brought practitioners, potential users and researchers together to assess the state of the art of AFF reactor technology. Both potential energy recovery and low cost wastewater treatment will undoubtedly serve to increase the importance of this emerging technology in the future.

The majority of the available data and information is derived from bench scale studies with industrial wastewaters. Insufficient data are available at the present to develop a unified design approach based on conventional parameters such as COD or BOD and may never be available for many industrial wastewaters. At present, design guidelines are waste, media and hydraulic regime specific. Despite these limitations, the potential benefits of AFF processes encourage the continued development of highly empirical, highly conservative designs. The publication of complete sets of daily operating data from a large variety of designs would permit the development of a general purpose descriptive model. It is likely that more fundamental models would follow.

Unfortunately, only very limited data are available concerning the application of AFF processes to "typical" municipal wastewater treatment. The upper limits of wastewater stabilization and the lower limits of effluent quality are yet to be reported in the literature. Much additional work is required before AFF processes can be recommended for application to raw municipal wastewaters. Several specialized forms of AFF processes may prove useful for the degradation of waste sludges derived from conventional wastewater treatment systems. However, due to probable plugging problems with anaerobic filters, this potential approach to sludge management is still to be explored. This lack of information is unfortunate, since the organics in waste sludges represent both a source of concentrated substrate that may be converted to methane and a major societal disposal problem.

In summary, this workshop served to disseminate knowledge from diverse sources. This shared information should serve as a stimulus for new research and application directions for anaerobic fixed film processes.

MICHAEL S. SWITZENBAUM

It is obvious that the concept of anaerobic treatment of wastewaters is an idea whose time has arrived. Due to the increasing scarcity of energy resources, the role of anaerobic treatment must and will become more widely used. Yet, at the present time even with an uncertain fuel situation, anaerobic treatment is seldom used for the treatment of soluble wastes.

The reason for this apparent anomalous situation rests with several misconceptions held by the environmental engineering profession. These include such ideas as 1) the process is not as efficient as aerobic treatment, 2) it is slow, 3) it will not work, 4) it can't handle toxic wastes and 5) long hydraulic retention times are needed. There are two reasons for these misconceptions. The first is that recent advances in anaerobic treatment technology are not well known by practicing engineers (i.e., lack of technology transfer). The second, and more important reason is that despite its usage, the fundamental microbiology and biochemistry concerning anaerobic methane fermentation is only at the present time materializing.

In order to increase the usage of anaerobic processes such as anaerobic filters, expanded or fluidized beds, it will be necessary to implement simultaneously a three phase program. The first phase should involve several large scale demonstration projects based on the best currently available technology. The second phase should involve fundamental research concerning the basic microbiology and biochemistry of the anerobic methane fermentation and more studies of a more direct application concerning anaerobic reactors (such as geometric configurations, influence and/or necessity of packing media, toxic handling ability, etc.). Finally, a concerted effort should be made involving technology transfer. This might include design manuals and specialty conferences.

The workshop held at the Mission Inn was a valuable experience for all involved. It was very well organized and contained an excellent scope of papers summarizing the current state of anaerobic wastewater treatment processes. The participants were eager to share their knowledge and learn from others. The views I have expressed above are my personal opinions, but I believe are in general agreement with most of the participants at the workshop.

JAMES C. YOUNG

The Workshop on Anaerobic Fixed-Film Bioreactors served as an important forum for persons conducting research on various aspects of these processes. One important observation of a technical nature was that all researchers seemed to find significant improvement of fixed-film processes over conventional mixed digestors: they are more resistant to shock loads, toxins and changes in environmental conditions and can accept much higher organic loads.

There seemed to be no concensus among workshop participants as to a single most important research and development need. Most participants agreed that more research is needed and that research should be conducted simultaneously in all areas of concern: basic research, development, and demonstration. Specific research to develop design parameters and to evaluate process response using various types and sizes of media seemed to be a common need among the three major types of fixed-film processes -- fixed-bed, expanded or fluidized-bed and rotating contractors.

One important revelation was that a number of fixed-film anaerobic reactors have been placed in operation or are under design for treating high-strength industrial wastes. Suggestions were made that the performance of these reactors be followed closely to verify their success and to refine design parameters for use in designing future installations.

A need was expressed for improved technology transfer. Suggestions ranged from having additional conferences on anaerobic fixed-film processes to wide-spread circulation of research reports. No best method was developed.

In summary, the most important aspect of the workshop seemed to be the communication developed among researchers and Department of Energy and Environmental Protection Agency personnel. Research needs were identified and progress of on-going research was documented. The challenge seems to be to convince prospective users to consider anaerobic fixed-film processes when analyzing cost and energy effectiveness of various treatment alternatives.

JOHN JERIS

The main value of the conference was the transfer of technical information in the anaerobic methane fermentation topical area. The exchange had great value as it allowed the various researchers, developers, and designers of these processes and other interested people to learn the strengths and weaknesses of the process. It helped set the weak areas in focus for continuing work.

The turnout of industrial people and consultants was good. This will help get anaerobic processes into the field more quickly. The education of a number of people who were not at all well versed in this technology is also very worthwhile.

The need for marketing is essential if the process is going to be used in the field quickly. You can look at Union Carbide's entry into the field as an example.

A forum for getting this information into the consultant, public, and industrial sectors would require design- and operation-oriented presentations rather than the research papers which we typically heard. We often posed more questions than solutions.

EUGENE J. DONOVAN, JR.

As was quite evident from the information presented at this meeting, the state-of-the-art of Submerged Media Anaerobic Reactors, which seemingly have a high potential for economical, energy efficient treatment of wastewater, is still in its infancy. Significant movement of these type systems into the field for suitable applications will require a two prong approach. First, continuing fundamental basic research to achieve better understanding of the process is needed. The proposed type of systems (fixed bed, fluidized bed, rotating discs) and specific media for various applications all need further definition. Second, full scale or large scale investigations with plant operation on actual waste discharges, to demonstrate performance and reliability, and to optimize design is needed.

The model developed by Mueller and Mancini of Hydroscience provides an understanding of the chemistry of an anaerobic filter and could provide the basis for further development of a model to fully describe the process for design. Various factors which would be of interest include organism distribution and growth, hydraulic considerations in the filter, solids capture, mass transfer kinetics, and a non-steady state mode to predict startup, response to changing loadings, and the effect and recovery of inhibitory slug loads. The model would provide a means for determining limits of operation for high strength wastes in terms of loadings and detention times.

A major consideration appears to be the relative merits of the fixed "anaerobic filter" the moving media "fluidized bed", and possibly the sludge blanket approaches. There appears to be certain advantages to each, however, there is a need to define and optimize their applications to actual wastes. Field studies, preferably on large scale or full scale systems with concurrent experimental scale (lab units) studies would provide many of the answers with respect to scale up factors, seeding time; operational stability under actual conditions, sizing, and economics. Temperature effect on sizing, economics and performance would also appear to be a significant variable requiring further evaluation.

RICHARD K. GENUNG

A Review of the Technical Content

The discussion initiated under the title "Anaerobic Filters," a well-known term coined by Young and McCarty, actually encompassed many reactor configurations operated under anoxic or anaerobic conditions. These reactors are necessarily three-phase (gas-liquid-solid) systems, with the solid phase including both biomass and various inert materials confined within the bioreactor. The use at this workshop of the acronym "SMAR" (submerged media anaerobic reactors) was recognition that these systems use continuous-liquid-phase, discontinuous-gas-phase arrangements, as contrasted to the more usual continuous-gas-phase arrangement in other fixed-film systems (i.e., trickling filter). Inert materials are confined within reactors in both static configurations (i.e., packed-beds) and dynamic configurations (i.e., fluidized-beds). Packed-bed reactors are generally operated under plug-flow conditions, while fluidized-beds reactors are operated under conditions ranging from the low-mixed states of incipient fluidization to completely mixed states comparable to those achieved in stirred-tank systems. Both mixing and long retention times are achieved with recycle. In both packed-bed and fluidized-bed systems, inert materials serve as support surfaces for microbial attachment; in the packed-bed systems, use of these materials also creates interstitial spaces in which active biomass accumulates. In either case, the use of packing is intended to confine active biomass in the reactor while creating large surface areas for substrate conversions. The use of packing for the above purposes is not required if the physical properties (e.g., settling velocities) of the microbial species involved in a specific conversion do not result in "wash-out" under the operating conditions and in the reactor design used. In fluidized systems, the problem of wash-out has been approached by both replacement of support media and by partial cleaning (to control film thickness and therefore settling velocity) of support media combined with recycle. In packed-bed systems, the problem of "plugging" has been approached by draining or backwashing reactors. The success of the above approaches will depend on the nature of accumulated solids (e.g., film or interstitial), on the rate of solids accumulation (e.g., as dependent upon substrates and microbial populations), and on the choice of packing used (e.g., effect of surface-to-volume ratio on total activity in the reactor and the change in activity associated with backwashing).

The widely recognized advantages associated with developing anaerobic processes using any of the above reactor configurations include the economic advantages of minimizing the energy inputs (such as for aeration and sludge handling) and maximizing the energy recovery potential (i.e., methane). Process advantages include such systems' abilities to handle intermittent flows, to acclimate to various inhibitors, and to survive exposure to toxicants (possibly by sorbing toxicants in outer film layers, leaving lower levels viable for regeneration). The limited industrial work reported to date indicates that the development of process monitoring and control systems can increase process stability and result in increased economic returns through process optimization. Apparently, savings in operating costs for anaerobic systems would compensate for significant increases in capital investment requirements over aerobic systems.

Summary and Recommendations

Various anaerobic reactor configurations have shown sufficient technical and economic viability to justify process development and demonstration efforts in municipal and industrial situations. There is a widespread market for such developments if user-related risks can be minimized. As a result of EPA regulations, the needs of these markets must be met in the near term. Technology transfer will require demonstrations; technology development must include support for more basic studies of topics such as coupled mass-transfer and kinetic phenomena, film formation and growth, effects of support material properties, alternative reactor configurations and control systems, and the applied microbiology of anaerobic systems.

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Salient points gleaned from the anaerobic filter conference are as follows:

1. Startup times for anaerobic filters, both downflow and upflow, are typically six months to one year; however, the following steps may serve to reduce startup to one to three months:

a) Seed heavily, perhaps fill filter, with sludge from a very highly-loaded anaerobic digester to get a very active sludge.

b) Start filter by feeding methanol.

c) Clay media develops biological growth faster than plastic or glass media.

2. Recycle appears to offer no advantages from a biological treatment standpoint, in fact, recycle may reduce treatment efficiency; however, recycle does offer certain physical or mechanical advantages as follows:

a) It may dilute toxic substances below their toxic level; however, if the toxic is not diluted sufficiently by recycle, recycling will maintain the toxic substance in the filter longer.

b) Recycling may prevent plugging of the first stages of a heavily loaded filter and more effectively use the entire volume of the filter. Similarly it may allow construction of deep filters, minimizing surface area requirements rather than shallow filters with large surface area requirements.

3. Operation of an anaerobic filter in a downflow mode may serve to minimize plugging.

4. Solids can deliberately be wasted from the filter by feeding cold water, also an air-water backwash can be used to remove solids from a filter.

5. A fluidized bed of activated carbon may be advantageous for weak wastes because it concentrates the waste on the carbon for subsequent biological treatment. Another advantage of activated carbon is that it would, in effect, start treating the waste almost immediately, in that, waste material would be physically adsorbed immediately and treated biologically later.

6. Rather than completely destroying the bacterial growth in a filter, "toxic" substances frequently inhibit treatment for approximately 20 days after a slug dose. Consequently, if toxic spills are reasonably possible, a storage reservoir with a minimum capacity of 20 days may be advisable following the filter.

7. Many substances typically considered toxic or inhibitory are amenable to treatment in an anaerobic filter.

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Definitions

This topic was not adequately discussed in the sessions such that a consensus could be reached. It was clear that several factors may be active in these systems, especially the process referred to as an anaerobic filter. This process appears to be a combination of a biological reactor as well as a physical sedimentation system. Biological activity exists on the film and in the suspended solids that are retained in the reactor. It may, therefore, be appropriate to identify a family of treatment processes under this general class, consisting of the following sub-classes:

1. Dispersed growth systems, i.e., the Lettinga upflow anaerobic sludge blanket (UASB)
2. Attached biofilm systems
    a. Fluidized bed
    b. Packed bed
3. Anaerobic filter

It will be necessary to make these distinctions if there is any attempt to model these processes with any sophisticated modeling techniques. For a general class of processes, one could accept Dr. Jeris' title of SMAR. I would extend this to Submerged Anaerobic Reactor Treatment System (SMARTS). The only identifying factor common to these systems that might not be apparent from this definition would be the fact that external sludge recycle is not necessary to maintain a solids residence time (SRT) greater than the hydraulic residence time (HRT). When external solids recycle is practiced, the system has been commonly termed the anaerobic contact process.

One should recognize that the anaerobic contact process is a potential competitor for SMARTS. One current limitation is the difficulty of achieving a high efficiency of solids separation in the clarifier. If this problem is solved, it is highly likely that this process will be much more efficient for treatment of moderate strength wastes, especially those wastes that have a measurable quantity of nonbiodegradable solids.

Status of the Process

It is clear that SMARTS can be applied to one or more industrial waste streams with present state-of-the-art. Treatability studies for waste specific parameters are necessary, but this is true for any and all industrial waste treatment systems. There are still many unanswered questions regarding the optimization of these processes for treatment of industrial wastes. These questions can be categorized in the following manner.

1. Packing medium. What is the function of this material in the process? Does it serve as a surface on which the organisms grow or does it simply serve as a flow control device which allows for relatively quiescent zones in which the solids can accumulate with a resultant increase in biomass? Experimental work on the role of this medium should be undertaken to determine if it is necessary for the successful operation of the process. This work should evaluate the role of the medium in all of the flow patterns encountered in this type of process.

2. Toxicity. These systems have been shown to be relatively insensitive to the problems associated with inhibitory substances. All microbial systems can be completely inactivated with the proper type and quantity of toxin. However, the short HRT relative to the SRT of these systems and the relatively large mass of organisms present permit a rapid recovery from

most inhibitory substances. Additional work in this area does not appear fruitful except as it relates to treatability studies for specific wastes.

Clearly, the system must exclude substances that are truly toxic since this generally refers to a complete kill of the system. Inhibitory substances will only reduce the efficiency of the process simply by reducing the metabolic activity of all organisms, or exhibiting toxicity to a portion of the biomass. However, the lack of a complete kill of all of the essential microorganisms allows for system recovery, the speed of which is controlled by the degree of inhibition.

The ability of these cultures to acclimate to many inhibitory materials strongly support the use of an equalization basin to reduce the concentration of inhibitor and extend the exposure period to assist the organisms in acclimation. Research on the acclimation of these cultures to the "nonbiodegradable toxic" materials may be fruitful. Work at Stanford under Dr. Perry McCarty's direction is showing that it is possible to adapt the microbe to many compounds that have been considered nonbiodegradable.

3. Reactor geometry/flow regimes. One issue raised in the sessions that could not be answered was the relative merits of the different types of reactors, i.e., packed bed, fluidized bed, or the anaerobic filter. One can argue the merits of the various flow patterns, but unless side-by-side evaluations are made, this question cannot be resolved. This evaluation could be conducted on industrial wastewater, but in light of the objectives of this meeting, it would be better to evaluate the use of a packed bed, fluidized bed, or the anaerobic filter as applied to municipal wastewater. This study could be used in conjunction with a mechanistic study of the process.

4. Large scale demonstration projects. One of the most effective techniques for technology transfer is the installation of operating systems. Existing installations are few and the application of this process to industrial waste treatment would be greatly accelerated by a few demonstration systems. However, the objective of this program is municipally oriented, not industrial. Data presented to date do not support the application of this system to municipal wastewater. Controlled tests have not been conducted that can be used to justify application of the anaerobic filter, or any other anaerobic processes, to secondary treatment of municipal wastewater.

Theoretical Considerations

Before attempting to apply these processes to the treatment of any wastewater, an analysis of the fundamentals of these systems should be undertaken. I would assume such an analysis has been made for the industrial waste systems. However, I have not seen such an analysis, and I seriously doubt if one has been done for the treatment of municipal wastewater by anaerobic filters. I would divide this discussion into three distinct areas:

1. Aerobic vs. Anaerobic Metabolism

The importance of this analysis relates in part to the kinetics of the process. A more important consideration though is the energy required to maintain an active culture of microorganism. In aerobic systems, this is relatively easy since the energy yield from the metabolism of organic material is high. For example, glucose oxidation to carbon dioxide and water as per the following equation yields 668.7 k-cal per mole or 3487 cal per g COD oxidized.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O - 668.7 \text{ k-cal} \quad (1)$$

However, under anaerobic fermentation conditions, the energy yield from glucose fermentation to methane and carbon dioxide is only 102.1 k-cal per mole or 532 cal per g COD. This is further complicated by the fact

$$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4 - 102.1 \text{ k-cal} \quad (2)$$

that much of the energy yield is from the fermentation of glucose to acetate. The microorganisms obtain very limited energy from acetate fermentation to methane and carbon dioxide as shown by Equation 3. Acetate fermentation yields only 106 cal per g COD. Therefore, approximately four times as much energy is released from glucose fermentation to acetate than from acetate to methane.

$$CH_3COO^- + H_2O \rightarrow HCO_3 + CH_4 - 7.4 \text{ k-cal} \quad (3)$$

Consequently, the growth of the methanogens is severely restricted by this low energy yield.

The following reaction yields somewhat more energy than the above reactions.

$$4H_2 + HCO_3 + H^+ \rightarrow CH_4 + 3H_2O - 32.7 \text{ k-cal} \quad (4)$$

It may be possible to initially stimulate the growth of methanogens by the addition of hydrogen gas during start-up. However, one must remember that the hydrogen gas will block the formation of acids through product inhibition of the acetogenic reactions. Clearly this must be used with care.

Because of the relatively dilute concentration of organics in municipal waste and the low energy yields listed above, another phenomenon is introduced. This is discussed in detail in the enclosed paper by Rittmann.* It appears that this can be a major factor in the treatment of dilute wastes by the anaerobic filter system, or any other anaerobic biological system.

2. SRT Requirements

The Monod model has been widely used to evaluate the kinetics of waste treatment processes. Application of this model to fixed film systems may be debatable. It can be used to illustrate some key requirements in any biological system. The two key equations are the following:

$$S = \frac{K_s[1 + k_d\theta_c]}{\theta_c[Yk - k_d] - 1} \tag{5}$$

$$X = \frac{\theta_c Y[S_o - S]}{\theta[1 + k_d\theta_c]} \tag{6}$$

where S = substrate level in the complete mix effluent - mg/l

S_o = influent substrate level - mg/l

K_s = half velocity coefficient - mg/l

k = maximum specific substrate utilization rate - $time^{-1}$

k_d = organism decay rate - $time^{-1}$

X = organism mass concentration - mg/l

θ = hydraulic retention time

θ_c = mean cell residence time (solids retention time)

Y = yield coefficient

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*The paper by Rittmann is not available.

Equation 5 can be used to calculate the required θ_c for a specified effluent BOD. If one considers the conversion of acetate to methane as the rate limiting step, then the following values for the appropriate constants can be used for a temperature of 30 and 25°C. These constants were determined by Lawrence and McCarty (J. Water Poll. Cont. Fed., Vol. 41, No. 2, Part 2, Feb. 1969, pp. R1-R17). These constants are based on acetic acid, rather than COD. Similar evaluations were conducted at 20°C by O'Rourke ("Kinetics of Anaerobic Treatment at Reduced Temperatures," Ph.D. Thesis, Stanford University, 1968). These constants are listed in the following table:

KINETIC CONSTANTS

	30°C	25°C	20°C
k - day^{-1}	4.8	4.7	3.6
k_d - day^{-1}	0.037	0.011	0.015
K_s - mg/l	333	869	2130
Y	0.058	0.054	0.040

The most important constant to consider is the K_s value. This number is highly temperature sensitive and will dominate the kinetics in relationship to effluent substrate. For example, the calculation of the θ_c (Equation 5) for an effluent level of 20 mg/l COD or acetic acid show that θ_c calculates to be a negative 73 days. In all cases where values of S are assumed to be low, i.e., 20 mg/l, the model fails. This suggests that it is not possible to achieve COD levels in this low range with the methane fermentation process. Even with a mean cell residence time approaching

infinity, one cannot achieve the desired level of effluent substrate as a result of biological processing. If one substitutes 10,000 for θ_c in Equation 5, the value of S at 20°C will be 250 mg/l. This model shows that with a CSRT operating at a mean cell residence time of 10,000 days (27.4 years) the concentration of acetate in the effluent will be 250 mg/l.

One must recognize that you cannot apply the mathematical model for a CSRT to a fixed film reactor. However, it should also be recognized that performance of packed bed reactors and CSRT are not greatly different. Consequently, if the model for a CSRT shows that the required effluent levels are theoretically impossible with the methane fermentation process, one can assume that a fixed film reactor also will not achieve the required effluent as a result of methane fermentation. This is especially true with the wide discrepancy between the predicted level and the required level of effluent COD.

If one does produce low levels of COD with these anaerobic filters, it is not as a result of methane fermentation. Therefore, a definition of the mechanism is necessary before any large scale system is constructed. In fact, it may be desirable to inhibit the anaerobic fermentation of the organic solids. Suspended material is generally easier to remove from wastewater than soluble material. Inhibition of the hydrolysis reactions would retain most of the solids in the suspended form and enhance their removal.

3. Microbial Nutrition and Environmental Factors

There is very little information available on the nutritional requirements of this mixed culture of anaerobic microorganisms. There have been many reports in the literature about the stimulatory effects of certain

compounds. There has never been a coordinated study of the nutrients required to optimize these mixed cultures.

The control of pH and oxidation-reduction potential (ORP) become a key consideration when one applies the anaerobic process to municipal wastewaters. It is generally reported that values of ORP less than -500 mv (E_c) are associated with good methanogenic activity. With a dilute waste, it may not be possible to reduce the ORP to this level, especially when a short HRT is used in the system. The biofilm may be in a highly reduced state, but the bulk liquid is not. If all of the methanogenic activity is relegated to the interior of the biofilms, the mass transfer constraints become a more important issue.

Limited buffer capacity associated with a dilute wastewater may give rise to pH control problems. When the carbon dioxide content of the gas is in the 10 to 20 percent range, a significant buffer capacity is required to keep the pH in the optimum range. When treating dilute municipal wastewater, the pH may be depressed. Of course, when the sample is removed from the anaerobic filter, the pH will increase significantly due to the loss of carbon dioxide when the sample is exposed to the atmosphere. Care must be exercised in making pH determinations.

Summary

The application of the anaerobic filter to treatment of municipal wastewater is premature. The mechanisms active in the filter have not been elucidated and existing microbial kinetic data suggest that the removal of organic material that does occur is not biochemical. The effluent standards for BOD are too low for this system to function as other than a pretreatment system for concentrated wastes.

A substantial amount of research on the fundamental mechanisms of the process is essential before any large scale pilot testing is undertaken.

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