ANAEROBIC TREATMENT OF A HIGH NITROGEN, HIGH TDS INDUSTRIAL WASTE

A Thesis Presented To

The Faculty of Graduate Studies

The University of Manitoba

In Partial Fulfillment

of the Requirements for the Degree of

Master of Science

in Civil Engineering

by

SHAHAB SHAFAI

MAY, 1987

ISBN 0-315-37232-X

ANAEROBIC TREATMENT OF A HIGH NITROGEN, HIGH TDS INDUSTRIAL WASTE

BY

SHAHAB SHAFAI

A thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

MASTER OF SCIENCE

ANAEROBIC TREATMENT OF A HIGH NITROGEN, HIGH TDS INDUSTRIAL WASTE

ABSTRACT

The anaerobic ammonification of wastewater from an estrogen extracting pharmaceutical plant was investigated. The wastewater was high in total dissolved solids, (TDS), nitrogen, (TKN), and organic carbon, (TOC). Laboratory analyses showed that the raw wastewater had the following characteristics: pH = 10.2, COD = 62 g/L, TOC = 24.3 g/L, TDS = 114 g/L, TKN = 9.7 g/L, and NH_3-N = 3 g/L.

Both flow-through and batch anaerobic reactors were used in this study. Three parallel continuously-fed upflow reactors, and three series of batch reactors were operated under quasi-steady state conditions. In the flow-through studies, two upflow anaerobic sludge blanket, (UASB), reactors and an anhybrid reactor, (a combination anaerobic-hybrid reactor comprising of a sludge bed and a media zone), were used. In the batch studies, each of the three series had a constant initial F/M load and was comprised of ten batch reactors. The wastewater was found to be anaerobically biodegradable in general. However, TDS concentrations - over 17 g/L in the flow-through reactors, and in excess of 10 g/L in the batch reactors - were concluded to be inhibitory to both ammonification and methanogenesis.

ACKNOWLEDGEMENTS

The author is sincerely thankful to Dr. Jan Oleszkiewicz of the University of Manitoba for his invaluable guidance and advice during the research, data analysis, and writing of this Master of Science thesis. The author feels fortunate to have worked under the direction of Dr. Oleszkiewicz and is deeply indebted for having had access to his immense knowledge and experience.

Special thanks go to Dr. Arthur B. Sparling and Dr. G. Blank of the University of Manitoba for their valuable advice and for serving on the Examining Committee. Dr. Sparling's advice and help during the preparation of this thesis is specially appreciated.

This study was sponsored in part by the MacLaren Engineers Inc., Winnipeg, Manitoba. The financial support provided by the MacLaren Engineers Inc. is gratefully acknowledged. The author is sincerely grateful to Mr. G. D. Hooper of UMA Engineering Ltd., Winnipeg, (previously with the MacLaren Engineers Inc.), for his involvement and valuable assistance throughout this project.

The author is specially thankful to Judith Tingley for her time and continuous assistance throughout the research and data collection of this study. A special note of thanks to Barry

Hilton for his help in the initial stages of this project and continual assistance in using computer software packages which were essential for the preparation of this thesis.

Special thanks are also due Maryam Jahangard, Masoud Nakhayee and Ilse Frank for typing this thesis. Special thanks is extended to Mr. C. Neil Longmuir of Agricultural Economics, University of Manitoba, for his time and help with the Word Processing package "WordPerfect" in a very critical final stage of this thesis.

The author is also grateful for the support and input of many individuals and fellow graduate students during the preparation of this Master of Science thesis. Here is a list of but a few of those whose help is gratefully appreciated: Ahmad Kazemi, Mehrdad Aidun, Vijay Thadani, Daryl McCartney, Jim Stibbard, David Woytowich, Lynn Arner, Hamid Moheb, Peter Trainor, and the McLachlan research group.

Last but not least, the author is sincerely grateful to his sisters Afsaneh and Fattaneh for their patience and support throughout his studies and to his parents Dr. & Mrs. Z. Shafai to whom this thesis is dedicated.

TABLE OF CONTENTS

Chapter Page

Chapter Page

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

In this study, effluent wastewater from an estrogen-extraction pharmaceutical plant was treated anaerobically. The raw wastewater under investigation contained a significant quantity of spent pregnant mares' urine, (PMU). The extraction plant operates during winter months only, (from October to March for about 27 - 29 weeks). The raw PMU is provided by local farmers who deliver urine from a total of 19,000 mares. Two equalization-storage tanks, with a total volume of 227 m^3, provide approximately 3 days retention for a flow of 77 m^3/d. The total annual volume of PMU processed in this plant exceeds 8,500 m^3. The plant operates 4 days/week from 8 am - 2 pm.

The raw PMU goes through a succession of chemical processes of extraction and evaporation. Sodium carbonate, sodium hydroxide, and hexanol are the main chemicals used during the manufacturing process. Currently, when in operation, the wastewater from this plant is discharged into the city sewer during the night, (8 pm - 8 am), on weekdays, and 24 hr/d on weekends. The wastewater, along with other industrial wastewaters and domestic sewage from the city, is treated in a combination of

an extended-aeration activated sludge plant and a lagoon system. This municipal wastewater treatment plant, (MWTP), is organically overloaded at the present time.

As part of an expansion of the sewage treatment facilities, in this study an attempt was made to determine the feasibility of a separate, on site, pretreatment of the spent PMU, which is very high in organic carbon, (TOC), and nitrogen, (TKN). The pretreatment step was to achieve ammonification and some organics removal by anaerobic means, prior to the discharge of the waste into the city sewer, thereby facilitating nitrification in the MWTP by lowering the presently high organic loadings.

1.2 OBJECTIVES

The specific objectives of this study were to:

a) determine the minimum dilution required to achieve ammonification;

b) examine the potential for the removal of organic matter under anaerobic conditions;

c) determine the extent of COD removal;

d) evaluate the possibility of maintaining loads in excess of 10 kg COD/m^3.d;

e) and, determine the possibility of inhibition, and/or toxicity due to total dissolved solids, (TDS), and/or free-ammonia.

1.3 SCOPE

Preliminary laboratory analyses, including raw wastewater characterization and pH titration of the spent PMU, preceded a series of batch anaerobic bioassays. These bioassay tests, (40 days duration), were performed to evaluate the potential of the wastewater and of pure hexanol to inhibit a methanogenic biomass. This study also included: separate biomethanation potential, (BMP), tests, (40 days duration); batch anaerobic tests, (60 days duration); and flow-through anaerobic studies, (80 days duration).

CHAPTER 2

LITERATURE REVIEW

2.1 BACKGROUND TO ANAEROBIC TREATMENT AND METHANOGENESIS

Although the mechanism of anaerobic digestion is quite complex, the organic degradation follows an orderly and controlled path. Unlike aerobic treatment systems, in anaerobic degradation of organics, the molecular oxygen does not act as the hydrogen acceptor, and the microbial population consists of facultative and anaerobic bacteria that use the chemically bound oxygen in the form of carbon dioxide, nitrates, sulfates, or organic compounds as the final hydrogen acceptor. The existence of facultative organisms is beneficial to the anaerobic process as they use up the small amount, if any, of free dissolved oxygen that may be introduced via feed to the digester (1,2). The energy yield of anaerobic metabolism is low in comparison to the aerobic oxidation of organics to CO_2 and water. This energy is not available to the bacteria, and is contained in the CH_4 gas. Therefore, the biological growth during anaerobic digestion is low; only 10% of proteins and fatty acids are converted to cell mass under anaerobic conditions (1).

Organic matter in anaerobic treatment is transformed into methane through a succession of various bacteriological processes. There are four metabolic groups of bacteria involved

in the anaerobic stabilization: hydrolytic bacteria, fermentative bacteria, acetogenic bacteria, and methanogenic bacteria (3). The hydrolytic bacteria break down-long chain organics, (polymers), like proteins and carbohydrates, into their respective monomers. The fermentative bacteria, in turn, ferment these monomers to organic, (fatty), acids, alcohols, carbon dioxide, hydrogen, and ammonia. The acetogenic bacteria utilize the higher VFA and convert them into acetic acid and hydrogen. Finally the methanogenic bacteria convert acetate, and/or hydrogen, methanol, and carbon dioxide into methane gas (1,3).

To process organic matter and derive energy directly for growth and metabolism, bacteria require dissolved substances. Particulate organic material cannot pass through the bacterial cell wall and membrane, and need to be converted to simpler dissolved compounds - mainly organic acids. Hydrolysis is accomplished by saprophytic bacteria, which attach themselves to the particulate matter and secrete extracellular enzymes. These enzymes remain at the bacterial site and do not diffuse into the medium, resulting in a more rapid organics breakdown. During the acid formation stage, there is virtually no reduction in the organic content of the waste, the pH drops, and the concentration of organic acids increases. Organic volatile acids are the main products of the acid production stage. The main volatile acids produced in this stage are: acetic, propionic, butyric, formic, valeric, isovaleric and caproic acids. As mentioned earlier,

during acid fermentation there is no change in the amount of organic matter content in the system, since no stabilization of organic material takes place. There is merely a redistribution among the different types of simpler organic compounds, and a slight loss of carbon and hydrogen, which are released as carbon dioxide, and hydrogen gas or hydrogen sulfide, respectively (2). The acid formers are generally facultative, although some may be strict anaerobes. They are much more tolerant to changes in pH and temperature, and grow at a much more rapid rate than the methanogens (2).

In the methanogenesis phase, the methane forming bacteria are extremely sensitive to changes in temperature and pH (2). During the methane production stage, the methanogens utilize the organic acids produced in the acid fermentation stage, and convert them to methane and carbon dioxide. The amount of organic material in the system is reduced considerably, and the rate of stabilization is directly proportional to the amount of methane produced. A number of species of methanogens are required for the anaerobic digestion of the organics, because each species of methane forming bacteria can degrade only a restricted group of organics to methane (2). All volatile acids can be utilized by specific methanogenic bacteria to produce methane. However, the primary organic compounds that are degraded, and result in the generation of methane, are acetic and propionic acids. Roughly 70% of methane results from acetate fermentation, and approxi-

mately 15% is generated from the fermentation of propionic acid. The remainder of methane is produced from formic acid, long-chain fatty acids, and from the reduction of carbon dioxide by hydrogen. The three major pathways to methane are, therefore, the biological decomposition of acetic and propionic acids to methane and carbon dioxide, and the microbial reduction of carbon dioxide to methane (2):

$$CH_3COOH \longrightarrow CH_4 + CO_2 \qquad (2.1)$$

$$CH_3CH_2COOH \longrightarrow CH_4 + CO_2 \qquad (2.2)$$

$$CO_2 + 8H^- \longrightarrow CH_4 + 2H_2O \qquad (2.3)$$

It must be noted, however, that although the mechanism of anaerobic digestion is sequential in nature, hydrolysis, fermentation, and gasification take place simultaneously and synchronously in a well-buffered system (2).

Due to the low growth rate of the methanogens, their high substrate specificity, and relatively high susceptibility to environmental stress, the methanogenesis phase is recognized to be the rate-limiting step in the anaerobic treatment process. Therefore, prior to the completion of this, (methanogenesis), step, anaerobic treatment process is far from efficient (3). Because of the importance of the methanogens in anaerobic digestion, the identification and a sufficient knowledge of the toxic or inhibitory materials and their effect on the performance

of the methanogenic bacteria is of utmost importance (3).

2.2 TOXICITY AND INHIBITION IN ANAEROBIC TREATMENT

In addition to organic matter, the majority of wastewaters also contain inorganics. The presence of these inorganic substances, in addition to some of the organics themselves, may be inhibitory to the methanogens and other microbial populations (3). Therefore, in applying the anaerobic process for the treatment of industrial wastewaters, a knowledge of the effect of these inhibitory substances on the methanogens is of vital importance (1).

In studying the toxicity effects in anaerobic digestion, it must be noted that a substance must be soluble to be toxic (4). The effect of any soluble metabolite - organic or inorganic - on the bacterial metabolism is concentration dependant. At low concentrations, these substances often stimulate metabolism. However, at high concentrations, they are normally inhibitory to the organism (5). In other words, changes in the concentration of a substance can change its classification from toxic to biodegradable, or vice versa (6). This phenomenon can be explained more clearly using Fig. 2.1.

McCarty (7) and Kugelman and Chin (5) used a graph similar to

Fig. 2.1 to illustrate the stimulatory, inhibitory, and toxic effects of a compound. In Fig. 2.1, the abscissa is the rate of biological reaction; the ordinate is the concentration of the test compound. The prevalent biological reaction rate under normal operating conditions, and the reaction rate prior to the addition of the test compound is represented by point A. As shown in Fig. 2.1, the metabolic rate increases initially with the increased metabolite concentration. The reaction rate may continue to increase with further increases in concentration of the test compound, (stimulation-region B), to an optimum rate, as represented by point C.

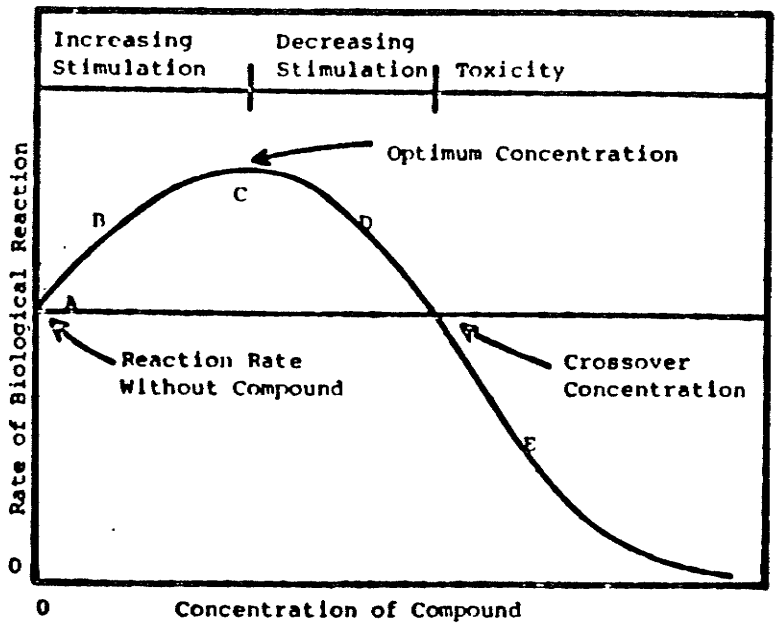

Fig. 2.1 - Effect of a Toxin on the Biological Reaction Rate (1)

Point C is the optimum concentration corresponding to the maximum biological activity, or peak stimulation. Any concentration higher than the optimum concentration will result in a decrease in the biological reaction rate. This region as, denoted by D, represents the inhibitory concentration zone. The biological activity will continue to decrease, with additional concentration of the compound, until the biological reaction rate will actually be less than the rate when the compound was absent from the system. Concentration of the test compound at this point is called the cross-over concentration. Region E represents the concentrations at which the compound is toxic to bacterial population. In this region, with further increases in the concentration of the toxic compound, a point will be reached in which the biological activity will stop completely (1).

In summary, toxicity effects depend largely on the concentration and type of material present in the system. In other words, whether a substance is classified as a food or an inhibitor depends on its relative concentration with respect to the peak stimulation concentration. More toxic materials will inhibit the microbial population at much lower concentrations than the less toxic compounds. In addition, when a system is fed a given concentration of a compound, its stimulation, inhibition, or intoxication may be indicated by the concentration of the compound that is maintained in the system (1,4,5).

The manner in which a given concentration of a toxin is added into a system - gradual or slug dose - also has a bearing on the magnitude of its toxic effects to the biological system. Solids residence time, (SRT), acclimation, and reversibility phenomena are, therefore, important factors that must be considered in studying the toxicity effects in anaerobic biomethanation systems.

2.2.1 Acclimation to toxicity

In anaerobic methanogenesis, the methanogenic bacteria are considered to be the most sensitive to toxicity of all other micro-organisms involved in the process. However, anaerobic bacteria, including the methanogens, can adapt to and tolerate a large number of toxicants, and even biodegrade some of them. In most studies, acclimation to toxicity and reversibility of toxicity is commonly noted (6).

Kroeker et al. (8) stated that many of the laboratory and pilot-scale studies, reporting failure of the anaerobic process, had allowed very short acclimation periods of one month or less when switching to new substrates. Kotze and co-workers (9), monitoring the enzymatic activity of anaerobic digesters, concluded that the adaptation of micro-organisms to new substrates takes more than five weeks. Kugelman and Chin (5)

noted that the magnitude of toxicity could be reduced significantly, if the increase in concentration of the toxin was gradual. They (5) defined acclimation as the adjustment of the biological population to the adverse effects caused by the inhibitory compound. They (5) explained that acclimation represents a rearrangement of the metabolic pathways of the micro-organisms to overcome the metabolic block generated by the toxic substance, rather than the mutation or out-competition by one specific group of bacteria.

Parkin et al. (10), Yang et al. (11), and Parkin and Kocher (12,13), conducted toxicity studies using batch, semi-continuous, and continuous-flow reactors. In all of the above studies (10,11,12,13), the amount of gas produced was used as a measure of metabolic activity, and was compared to a control unit to determine the degree of inhibition. It was concluded (10,11,12,13) that acclimated bacteria could tolerate from 2.4 to 12 times the levels that caused inhibition to the unacclimated systems. This indicated that gradual introduction of the test compound had allowed the methanogens to acclimate to the new substrate.

The means by which a toxicant is added to a system determines the ability of the microbial population to acclimate to that substrate (1). A toxic material may be introduced into a system by either slug or gradual doses. McCarty and McKinney (14), and

Kugelman and McCarty (15), studying salt toxicity in anaerobic treatment, concluded that cations such as calcium, sodium, potassium, and magnesium - when injected on a slug basis - are from 2 to 3 times more toxic than when they are added gradually. Acclimation of the methanogens to ammonia nitrogen, (NH_3-N), is also noted in the literature. Van Velsen (16), studying the NH_3-N toxicity, concluded that the methane bacteria can acclimate to ammonia-N concentrations as high as 5000 mg/L, although considerable acclimation time is required.

In addition to acclimation, reversibility of toxicity is another phenomenon in anaerobic digestion that also depends on substrate concentration and exposure time. Speece and Parkin (17) observed full gas production recovery within 24 to 48 hours after immobilized cultures of methanogens were temporarily exposed to high concentrations of toxic substances. These toxic concentrations were on the order of 100 times the level that would normally be sufficient to stop methane production completely. This recovery occurred after the adulterated supernatant was replaced. Parkin and co-workers (10) conducted studies on reversing inhibition and toxicity effects in anaerobic fermentation systems. They (10) concluded that the time required for such recovery depended on the concentration of the toxicant and its respective exposure time.

The role that solids retention time, (SRT), plays in the

successful acclimation and the reversibility must also be emphasized (1,12,13). Parkin et al. (13) stressed the importance of an adequate SRT in the biological systems recovering from toxicant exposure. They (13) pointed out that a period of zero gas production, in excess of three times the SRT, will lead to the complete, (more than 95 percent), washout of the methanogens prior to acclimation, and will result in total system failure. Providing an adequate SRT furnishes the system with a biological safety factor that guards against process failure from toxicant exposure.

Introduction of toxic materials into an anaerobic system may lead to unbalanced digestion conditions, and may potentially result in a drop in the performance and efficiency of the system. In studying the possible reasons for digester imbalance, possible toxicities due to heavy metals, sulfides, pH, volatile acids, TDS, and NH_3-N must be investigated. In reviewing toxicity problems in digesters, a knowledge of the role of alkalinity, in buffering the system until the source of imbalance is found, is also of prime importance.

2.2.2 Heavy Metal Toxicity

Heavy metals, at very low concentrations, are toxic to the anaerobic digestion, and are frequently thought to be responsible for the poor performance of anaerobic waste treatment systems

(4,5). McKinney (18) described the mechanism of heavy metal toxicity as follows:

> Heavy metals are toxic to micro-organisms because of their ability to tie up the proteins in the key enzyme systems. The heavy metallic salts prevent the proteins from reacting normally. They cause repelling reactions, instead of attracting reactions, by changing the protein's charge from negative to positive. If the concentration of the heavy metal is increased to a certain limit that the outer surface of the cell becomes coated, materials from the exterior of the cell will be prevented from entering the cell. Precipitation of the cellular protein may even occur.

Several studies have shown that low concentrations of heavy metals in soluble, (free-ionic), form will cause a total shut down of gas production (5,19,20). These studies (5,19,20,21,22) have also shown that if divalent sulfide ions, (soluble sulfides), are present in the system for precipitation, high concentrations of heavy metals could be tolerated. Soluble sulfides react with soluble heavy metal ions to form a metal sulfide, which is relatively insoluble and, therefore, non-toxic since, as mentioned before, substances must be soluble to be toxic (2,14,19,21,22). It is suggested that ferrous sulfate, as a source of sulfides (S^{2-}), be added to digesters with heavy metal toxicity problem.

Heavy metal toxicity problem can, therefore, be effectively eliminated by precipitation with sulfides. Approximately 1.8 to 2.0 mg/L of heavy metals are precipitated as metal sulfides by

1.0 mg/L of sulfide (1). This chemical reaction may reduce the available heavy metal concentration by a factor of 1000 or more (4,5). However, in control of heavy metal toxicity, it must be noted that soluble sulfides per se, in high concentrations, could be toxic to the anaerobic bacteria. This will happen if sufficient heavy metal ions do not exist to enter the chemical reaction with the soluble sulfides, and eventually be precipitated.

Lawrence and McCarty (21), studying the effect of heavy metals in anaerobic digestion, found that at toxic concentrations of heavy metals, there was a considerable decrease in the volatile acid concentration prior to the expected drop in gas production. This observation indicated the equal toxicity of heavy metals to both the acid formers and the methanogens (5).

There is considerable variation among the reported concentrations at which heavy metal toxicity occurs in anaerobic treatment. This variability is mainly due to the ease with which heavy metals take part in complex-type reactions with other constituents of wastewater. Precipitation by sulfides, sequestering by ammonia, and by the reactive portion of organic materials, are prime examples of such reactions. Table 2.1 lists the reported toxic concentrations for different heavy metals:

Table 2.1 - Toxic concentrations (to the methanogenic bacteria) of heavy metals.

Metal	Inhibitory Concentration (mg/L)		References
	Total	Soluble	
Copper	50 - 70	0.5	Total
Chromium VI	200 - 260	3.0	(23 , 24)
Chromium III	180 - 420	-	
Nickel	30	2.0	Soluble
Zinc	-	1.0	(20,25,26)

2.2.3 Sulfide Toxicity

Sulfides can be toxic to anaerobic bacteria in concentrations above 200 mg/L at neutral pH values (2,27), but can be tolerated with little or no acclimation at concentrations between 50 and 100 mg/L (2). Therefore, if sulfide precipitation is used to control heavy metal toxicity problem in digesters (21,22), caution must be exercised to avoid possible toxicity due to sulfides themselves.

Wastewaters with high concentrations of sulfates may lead to the potential sulfide toxicity problem in anaerobic digestion systems that contain a mixed culture of micro-organisms,

(including sulfate-reducing bacteria). These bacteria reduce sulfates, and convert them to their more toxic form, namely sulfides (4).

2.2.4 pH Toxicity and Alkalinity

There is a slight variation in the values reported for the optimum range of pH for anaerobic treatment. McCarty (7) has reported pH values of 6.6 - 7.6 as the optimum range for methane fermentation. Other reported optimum pH values are: 6.5 -7.6, Parkin and Owen (4); 6.4 - 7.5, Kugelman and Chin (5); and 6.8-7.4, Malina (2). Beyond these pH limits, digestion can proceed, but with much less efficiency. For example, at pH values below 6.2, the efficiency drops off so rapidly that the acidic conditions produced in the acid fermentation stage can become inhibitory to the methane bacteria. Therefore, a pH drop below 6.2 must not be permitted for a significant period of time (1).

Under balanced digestion conditions, the pH is maintained automatically in the proper range by biochemical reactions. Production of volatile acids during decomposition of complex organics results in a drop in pH. This is counteracted by the volatile acids destruction and the reformation of bicarbonate buffer during methane fermentation. pH drops in systems where an imbalance develops, and the acid formers outpace the methane formers. This leads to a build up of volatile acids in the

system. pH drops even further if these unbalanced digestion conditions are allowed to continue. The low pH values, while affecting the activity of the acetogenic bacteria only slightly, stop methane production completely. Restoration to balanced conditions normally takes a long period of time because of the low growth rate of methanogenic bacteria (5).

For proper pH control, sufficient alkalinity is required to provide a buffer for the system. Alkalinity in the digester is derived from the organics breakdown, and is mainly present in the form of bicarbonate ions. The equilibrium between the bicarbonate ions and carbon dioxide in the generated gas, is the main chemical system governing and controlling the pH levels in the anaerobic system (1,2). The relationship between alkalinity and CO_2 is pH-related, and may be illustrated as follows (2,7):

$$CO_2 + H_2O \quad \text{----->} \quad H_2CO_3 \qquad (2.4)$$

$$H_2CO_3 \quad \text{----->} \quad H^+ + HCO_3^- \qquad (2.5)$$

$$[H^+] = K_1 \frac{[\ H_2CO_3\ ]}{[\ HCO_3^-\ ]} \qquad (2.6)$$

Where K_1 = ionization constant for carbonic acid

$[H_2CO_3]$ = carbonic acid concentration (depends on % of CO_2 in gas)

$[HCO_3^-]$ = bicarbonate ion concentration (bicarbonate alkalinity)

To provide a buffering capacity to offset volatile acids increase, with only a minimal decrease in pH, a bicarbonate alkalinity value of 2500 to 5000 mg/L may have to be maintained in the system (1).

The total alkalinity in an anaerobic system is the sum of bicarbonate alkalinity and volatile acid alkalinity, (which is, like CO_2, a product of the reaction of volatile acids and bicarbonate ions). For most wastes, especially at low volatile acids concentrations, the bicarbonate alkalinity is approximately equivalent to total alkalinity. However, with increased volatile acids concentration, the bicarbonate alkalinity becomes lower than the total alkalinity. It is reported that, not all but only, approximately 83.3 percent of the volatile acids concentration contributes to the volatile acid alkalinity (1,2).

If alkalinity drops drastically due to an increase in volatile acids concentration which, in turn, results in a serious drop in pH, supplemental bicarbonate alkalinity will have to be

provided. Lime is frequently used for this purpose:

$$Ca(OH)_2 + CO_2 \longrightarrow Ca(HCO_3)_2 \qquad (2.7)$$

Any further addition of lime results in increased levels of bicarbonate alkalinity to a point where insoluble calcium carbonate precipitates:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \qquad (2.8)$$

Therefore, when controlling pH with lime, the inter-relationship between the added lime, pH, bicarbonate alkalinity, dissolved CO_2, and volatile acids concentration must be kept in mind. Other chemicals, such as sodium hydroxide and sodium bicarbonate, may also be used for pH control, and as a source of supplemental bicarbonate alkalinity (1,2).

In pH control of anaerobic digesters, however, it must be realized that using alkaline chemicals for maintaining CH_4 production during unbalanced biochemical conditions should not be regarded as a permanent solution to the cause of the imbalance. This method is only valid until the cause of the imbalance is discovered (2,4,5).

2.2.5 Volatile Acids Toxicity

As mentioned earlier, in an anaerobic digester the acid fermentation and methane formation occur simultaneously. The stability of the anaerobic process depends on the maintenance of a balance between the fast-growing acid formers and the slower-growing methane formers. When an anaerobic system is in balance, the methanogenic bacteria use the volatile acids formed in the acid fermentation stage as soon as they are produced, and convert them into gaseous end-products. Introduction of toxic substances into the system upsets this balance by causing a breakdown in the gasification phase.

In optimal operating conditions, the volatile acids are produced at a rate that maintains a suitable environment for the methanogens. Under unfavorable operating conditions, such as those caused by the introduction of toxic materials, the methanogens are unable to utilize the volatile acids as rapidly as they are produced. This leads to a volatile acids accumulation in the system. A sudden increase in the volatile acids concentration is, therefore, an indication of an imbalance between the methane formers and the acid formers (2,4,5). Therefore, in dealing with the volatile acids problem, it must be kept in mind that a high concentration of volatile acids is caused by other unfavorable conditions, and is not the cause but a result of this unbalance.

A controversy exists in literature over extent of the toxic effects of volatile acids on performance of methane forming bacteria. Buswell (28) and Schlenz (29), in their studies, reported that at concentrations above 2000 mg/L, volatile acids are toxic to the methane bacteria. However, McCarty and Mckinney (14) have concluded that a sudden increase in the concentration of volatile acids is the result of unbalanced treatment, and not the direct cause of it. In a follow up study, McCarty et al. (30) concluded that total volatile acids, (TVA), concentrations of up to 6000 mg/L would have no effect on the CH_4-production, provided that pH is maintained at the optimal range. This study (30) was conducted in response to the conclusion to a previous study by Buswell and Morgan (31) who had reported that propionic, and not acetic acid, was the inhibitory substance in the methane fermentation process. McCarty et al. (30) concluded that propionic acid at 6000 mg/L concentrations, under controlled pH, was inhibitory to the acetogens and not to the methanogens. In other studies, Andrews (32) and Brune (33) suggested that the toxicity was due to the unionized volatile acids, (UVA), portion of the volatile acids. A later study by Kroeker et al. (8) concluded that the process toxicity occurred at 30 - 60 mg/L UVA, (as acetic acid).

The following equilibrium, using acetate as an example, shows that at low pH values, (high hydrogen ion concentrations),

volatile acids exist mainly in the unionized form, which is thought to be the real source of the toxicity problem:

$$CH_3COOH \quad \text{----->} \quad CH_3COO^- + H^+ \qquad (2.9)$$

Heyes and Hall (34), on the other hand, have postulated that hydrogen, (H_2), produced during the acetogenic phase is the real reason for the toxicity. In either case, it is widely accepted that whether it is the UVA or pH that is the cause of toxicity, if the pH is kept within the optimal range for anaerobic digestion, volatile acids pose little or no problem to the anaerobic biomethanation process (4,5).

2.2.6 Total Dissolved Solids Toxicity

In the previous sections discussing imbalance in anaerobic digestion, pH control, and alkalinity, it was pointed out that care must be exercised so that the cation of the alkaline material does not produce toxic effects itself. Many industrial wastes themselves may contain high concentrations of light metal cations. High concentrations of total dissolved solids may have adverse effects in the operation of anaerobic treatment systems.

Total dissolved solids, (TDS), by definition, is that part of the total solids that remains in solution after filtration. If the filtered water containing TDS is evaporated, the remaining

solid residue is referred to as TDS (35). Dissolved substances may be organic or inorganic in nature. However, when dealing with industrial wastewaters containing high concentrations of TDS, the bulk of TDS exists in the form of light metal cations. Therefore, TDS may be taken to approximately equal salinity, which is defined as the remainder of dissolved solids after all dissolved organics have been oxidized (36).

As mentioned earlier, one of the most common problems in the operation of anaerobic digesters is the unbalanced digestion conditions which leads to a drastic drop in microbial activity, which is signaled by a large increase in volatile acids concentration. This is an indication that the methanogens are not keeping pace with the volatile acids production. McCarty and McKinney (14), studying the nature of salt toxicity in anaerobic treatment, suggested that the toxicity associated with a large increase in volatile acids concentration was not related to the concentration of volatile acids, but was rather dependent on the concentration and type of the metallic cations contained in the alkaline compound used for neutralization. Thus, a volatile acid build-up would be of no concern if alkaline materials containing non-toxic cations were used for volatile acids neutralization. For example, lime and magnesium hydroxide would be ideal for volatile acids neutralization up to concentrations of 10,000 mg/L. On the other hand for volatile acids concentrations above 2,000 mg/L, sodium hydroxide, potassium hydroxide, and ammonium

hydroxide would not be recommended (14). Therefore, in avoiding the development of toxic conditions, the choice of the alkaline material for pH control in anaerobic reactors would obviously depend on the toxic nature of its cation.

In anaerobic digesters, unbalanced digestion conditions may occur at the initial start-up before a viable methanogenic population has been developed. Unbalanced conditions may also occur later due to changes in temperature or sudden organic load increases, or they may alternatively arise from the addition of foreign toxic materials. All these unbalanced conditions, except the addition of toxic materials, are temporary in nature and can be corrected easily. These conditions may be controlled by lime addition until the slow-growing methanogens reach a sufficient population level, by adjusting the temperature, and/or by decreasing the organic loading. In the case of toxic materials added to the system, neutralization does not offer a permanent solution and dilution may be the only answer to the problem of imbalanced conditions.

The adverse effect of TDS on the biological degradation systems, aerobic or anaerobic, has been widely documented. Tokuz and Eckenfelder (37), and Petros and Davis (38) observed the inhibitory effect of TDS on activated sludge performance. Davis et al. (39) and Kincannon and Gaudy (40,41) found that salinity may inhibit microbial activity, and that reduced salinities may

stimulate metabolic reactions. There is a considerable number of studies in the literature (5,7,14,15,39,42) documenting the inhibitory effect of TDS on biomethanation in anaerobic systems.

De Baere et al. (42), studying the influence of salt levels on methanogenic associations, noted that high salt concentrations influenced the activity of methane producing bacteria. In addition, high TDS levels were shown to cause bacterial dehydration, arising from the osmotic pressure effect, and result in the subsequent destruction of the bacterial cells. Davis et al. (39) found that TDS was inhibitory to the methanogens, and showed that when the toxic level of TDS was reached, methane production was severely affected while only a small decrease in bacterial population was recorded. Kugelman and Chin (5) noted the adverse effects of light metal cations, contained in industrial wastes, on the anaerobic methanogenesis. They (5) found that concentrations causing inhibition to unacclimated systems were approximately 0.25 M for Na^{+}, approximately 0.1 M for K^{+} and Ca^{2+}, and near 0.05 M for Mg^{2+}. Kugelman and Chin (5), in agreement with Davis et al. (39), indicated that methane producers were much more sensitive to toxic effects of light metal cations than the acid formers. Davis et al. (39) concluded that at a salt level of 1.3%, (13 g/L), methane production was severely affected, 13 g/L being the threshold of toxic inhibition. De Baere et al. (42), studying the effect of salt toxicity, found that initial inhibition occurred at shock loads

of 30 g/L for NaCl and NH_4Cl. Other reported inhibitory concentrations of light metal cations are summarized in Table 2.2:

Table 2.2 - Reported inhibitory concentrations (to methanogenesis) of light metal cations in anaerobic digestion.

Cation	Concentration (mg/L)		Reference
	Moderately Inhibitory	Strongly Inhibitory	
Na^+	3500 - 5500	8000	(5,7)
K^+	2500 - 4500	12000	(5,7)
Ca^{2+}	2500 - 4000	8000	(5,7)
Mg^{2+}	1000 - 1500	3000	(5,7)

Compared to other metal cations, Kugelman and McCarty (15) concluded that the sodium ion was the strongest inhibitor. Sodium showed a moderate inhibition at 3.5 - 5.5 g/L, and a strong inhibition at 8 g/L. McCarty and McKinney (14) noted that, prior to their work, divalent cations such as calcium and magnesium were thought to be more toxic, on a molar concentration basis, than monovalent cations such as sodium and potassium. McCarty and McKinney (14) studied the chloride and acetate salts of calcium,

magnesium, sodium, and potassium, and based on equivalent concentrations listed these cations in the order of increasing toxicity as: (1) calcium, (2) magnesium, (3) sodium, and (4) potassium. Kugelman and McCarty (15) regarded this discrepancy in reported conclusions to be a result of antagonism and synergism effects. Studying dual cation systems, they (15) attempted to clear up this controversy. The results of their study are listed in Table 2.3.

These investigators (15) found that the addition of antagonistic cations can reduce, and in some instances even eliminate, the high metal concentration toxicity. Furthermore, in some cases, units with added antagonistic cations were able to achieve metabolic rates higher than the control unit, indicating that antagonism of toxicity was complete. They (15) concluded

Table 2.3 - Antagonistic cations to the given toxic light metal cation (5).

Toxic Metal	Antagonistic Cation
Na^+	K^+
K^+	$Na^+, Ca^{2+}, Mg^{2+}, NH_4^+$
Ca^{2+}	Na^+, K^+
Mg^{2+}	Na^+, K^+

that, regardless of the concentration of the toxic cation, the concentration of the antagonist, that produced peak antagonism, remained the same. These findings showed that antagonism was a direct result of the stimulatory effect of the antagonist, and not a result of the neutralization of the toxin by the antagonist. These researchers (15) observed that maintaining the light metal cation concentration at levels that produce peak antagonism, (0.01 M for monovalent cations, and 0.005 M for divalent cations), even when no toxic material was present, would result in optimum metabolic activity and optimum digester performance.

In addition to the inhibitory effects of TDS, acclimation of anaerobic bacteria to high TDS levels is equally well documented in the literature. De Baere et al. (42) concluded that adaptation affects tolerance of methanogens to TDS. Abram and Nedwell (43) suggested that methanogenesis was possible at high TDS levels- after a period of acclimation - and noted that methane production in marine or salt marsh sediments was documented at 35 g/L NaCl. Paterek and Smith (44) also noted the occurrence of methanogenesis in hypersaline ecosystems, while Mathrani and Boone (45) reported the presence of moderately, and even extremely, halophilic methanogens in natural sediments.

McCarty and McKinney (14), and Kugelman and McCarty (15), studying salt toxicity in anaerobic treatment, injected bench-

scale anaerobic reactors with cations such as calcium, sodium, potassium, and magnesium on a shock loading basis. They concluded that these cations are 2 to 3 times more toxic in a slug-fed basis than when they are introduced gradually. McCarty and McKinney (14) observed the ability of the anaerobic digestion to proceed, without a drastic drop in metabolic activity, at relatively high cation concentrations, when added gradually over a period of time. They concluded that these cations were much more toxic when added on a slug basis.

De Baere et al. (42), while acclimating two anaerobic reactors to increasing levels of NaCl and NH_4Cl, subjected two other anaerobic reactors to shock loadings of these two salts. Initial inhibition, (when first signs of a drop in gas production, (G.P.), and TOC removal efficiency were noticed), and 50% inhibition, (when G.P. and TOC removal efficiency dropped to a half), for both salts occurred at much higher concentrations for the acclimated reactors than for the reactors that received shock treatment of the salts. Initial inhibition for both NaCl and NH_4Cl occurred at 30 g/L shock loading. While occurring, respectively, at 65 and 95 g/L for the system adapting to NaCl, initial and 50% inhibition occurred respectively at 30 and 45 g/L for the reactors adapting to NH_4Cl. In addition, comparing the reversibility of toxicity, these researchers (42) found that the reactor receiving NaCl shock-concentration required a longer period of time to recover than the reactor receiving NH_4Cl.

It may be reiterated that TDS, at high concentrations, is toxic to the methanogenic bacteria. However, if TDS is introduced into a system slowly, and its concentration increased in a gradual fashion, the anaerobic system is able to acclimate to the inhibitory effects of TDS. In this manner, the bacteria are able to adapt to, and tolerate higher concentrations of total dissolved solids than if TDS is introduced on a slug-concentration basis (15,46,47).

2.2.7 Ammonia Toxicity

Ammonia nitrogen and bicarbonate alkalinity are produced during anaerobic digestion of nitrogenous organics. These organics are mainly made up of protein, and their digestion under anaerobic conditions produces ammonium bicarbonate which acts as a natural buffer against the drop in pH due to volatile acids accumulation (4,14). Ammonia toxicity is a common problem associated with the wastes that contain high concentrations of nitrogen, (predominantly urea and protein). Breakdown, (anaerobic ammonification), of urea in such wastes results in high concentrations of ammonia (48). Ammonia nitrogen concentrations of up to 50 to 200 mg/L are beneficial to the anaerobic bacteria, because it is an essential nutrient (2,7). However, at high concentrations, ammonia-N could be toxic to biological systems.

Koster and Lettinga (3), studying the effects of ammonia toxicity, have reported nitrogen concentrations as mg/L of "ammonium ion", (NH_4^+-N). Assuming this to mean "total ammonia", (NH_3-N), and taking their reported values to be total ammonia concentrations, Koster and Lettinga (3) found that there was a discontinuous linear negative correlation between NH_3-N concentration and CH_4-production rate. The threshold level, above which methane production was possible only after a prolonged period of acclimation, was estimated at 1700 mg/L NH_3-N. These researchers (3) also concluded that an acetate build-up, above the ammonia-N threshold level, indicated that NH_3-N had relatively more effect on the metabolism of the acetate-consuming methanogens than the hydrogen consuming methanogenic bacteria.

Van Velsen (16) found that 1700 mg/L of NH_3-N was the threshold toxicity level for CH_4-production. Other researchers (49,50,51,52,53) have reported stable digester operations at ammonia concentrations in excess of 2000 mg/L. Kroeker et al. (8), for example, indicated that although progressive inhibition occurred as NH_3-N concentrations increased beyond 2000 mg/L, toxicity did not occur even at ammonia concentrations as high as 7000 mg/L. Hashimoto (54), on the other hand, found that the ammonia inhibition threshold started at about 2500 mg/L in unacclimated digesters. Malina (2) listed the effect of different concentrations of ammonia as shown in Table 2.4.

Table 2.4 - Effect of different concentrations of NH_3-N in anaerobic digestion (2).

Observed Effect	NH_3-N Concentration (mg/L)
Beneficial	50 - 200
No adverse effect	200 - 1000
Inhibitory at high pH's	1500 - 3000
Toxic	> 3000

McCarty (7) concluded that ammonia-N concentrations of 1500-3000 mg/L are "inhibitory" at high pH values, (above 7.4 - 7.6). He also stated that, at higher than 3000 mg/L NH_3-N concentrations, ammonium ion itself becomes "toxic" at all pH values. In a later study, Hobson and Shaw (55) confirmed these guidelines. Webb and Hawkes (56) noted that ammonia toxicity problems limit the maximum concentration of a waste that can be treated. One suggested solution to this problem is to dilute the waste. Another, technically more viable option, would be to lower the toxicity effects by pH-control.

Sathananthan (57) observed that the inhibition of total ammonia nitrogen, (NH_3-N), was related primarily to the concentration of free ammonia, (free-NH_3). In anaerobic

digestion, total ammonia-N exists in two forms - NH_4^+-ion and free-NH_3 - according to the following equation:

$$NH_4^+ \longrightarrow NH_3 + H^+ \qquad (2.10)$$

Fig. 2.2 shows the effects of pH and temperature on the ionization of total ammonia. At a constant temperature, an increase in pH will cause an increase in free-NH_3 concentration, or a shift to the right in the above equation. Keeping the pH constant, and increasing the temperature, will also increase the free-NH_3 concentration. Thus, the lower the pH, the higher will be the concentration of required ammonium ion to produce a given free-NH_3 concentration. The percentage of total ammonia in the form of free-NH_3, (dissolved ammonia gas),can be calculated using the following equation:

$$f = \frac{1}{10^{(pKa - pH)} + 1} \times 100 \qquad (2.11)$$

where:

f = % of total ammonia in the un-ionized state

pKa = dissociation constant for ammonia

$$= 0.0901821 + \frac{2729.92}{T}$$

T = temperature (^{o}K)

Kroeker et al. (8) reported that process inhibition was related to free-ammonia, rather than NH_4^+-ion. McCarty and McKinney (14), and Kroiss and Wabnegg (58) reported that free-NH_3 was the actual toxic agent in ammonia toxicity. Van Velsen (16), and Stevens and Schulte (52) observed a lower gas production (G.P.) at 55°C fermentation than at 35°C. Both of these research papers attributed the lower G.P. to free-NH_3 inhibition. Zeeman et al. (48) also suggested that toxicity was due to free-NH_3, and not the ammonium ion.

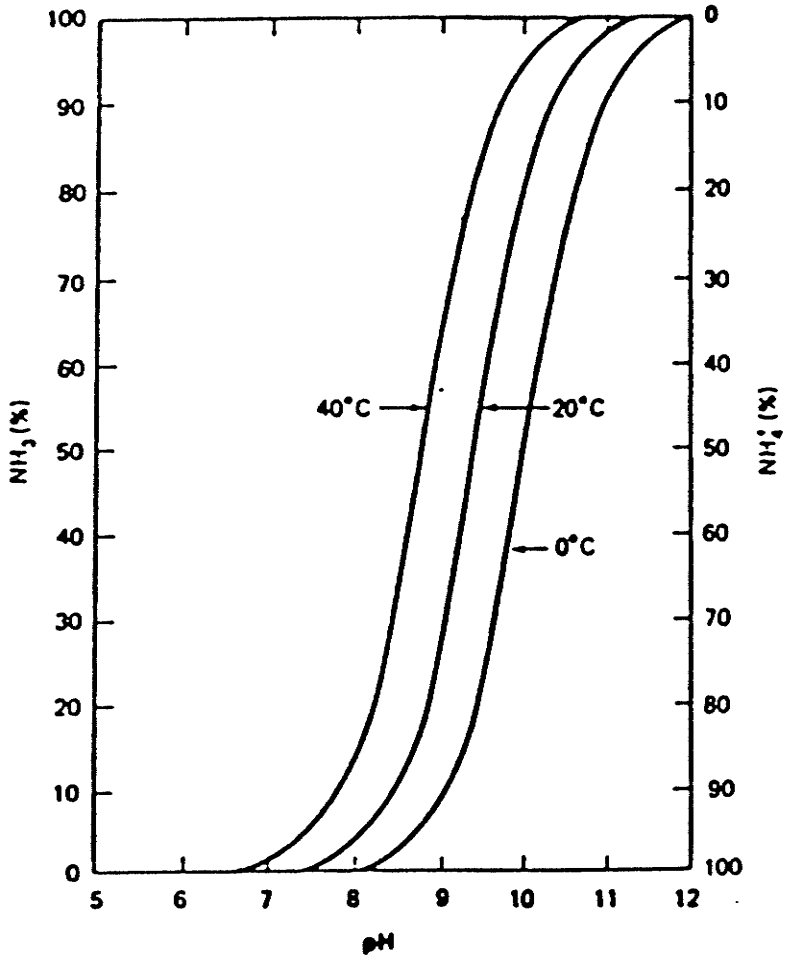

Fig. 2.2 - Effects of pH and Temperature on the Ionization of Total Ammonia

McCarty and McKinney (14) found that, when free ammonia concentrations exceeded 150 mg/L, severe toxicity resulted, and the biological process stopped completely. However, Ripley et al. (59) stated that there was no absolute methanogenic toxicity threshold evident in the 150 - 300 mg/L range. Webb and Hawkes (56) concluded that the threshold for free-NH_3 inhibition was above 138 mg/L, and below 225 mg/L. De Baere et al. (42) suggested that free-NH_3 should be kept below 80 - 100 mg/L for optimal performance. McCarty and McKinney (14), on the other hand, concluded that ammonia appeared to be toxic in two ways : at low pH values, (approximately 7.0), ammonium ion produced toxic effects similar in nature to toxicity due to other cations in solution, (that is, it resulted in a decrease in the acetate utilization rate); and with increased pH values, free-ammonia, (free-NH_3), concentration increased and resulted in the complete stoppage of the methanogenic activity.

The most recent hypothesis on the nature of ammonia toxicity has been extended by Sprott (Nurski,60), who postulated that ammonium ion, (NH_4^+), may also act as an inhibitory factor. Ammonium ion may interfere with methane production in two ways. In one reaction, NH_4^+-ion displaces Mg^{2+}-ion at the plasma membrane surrounding methanogens. The membrane protein, that activates methane production from CO_2 inside the cell, is adversely affected by this Mg^{2+}-ion removal. In a different way, toxic amounts of ammonium ion also affect the cell's internal

balance by diminishing the charge difference that exists between the negative charge on the inside of the cell and the positive charge outside. This change in electrical potential across the membrane affects the methane production.

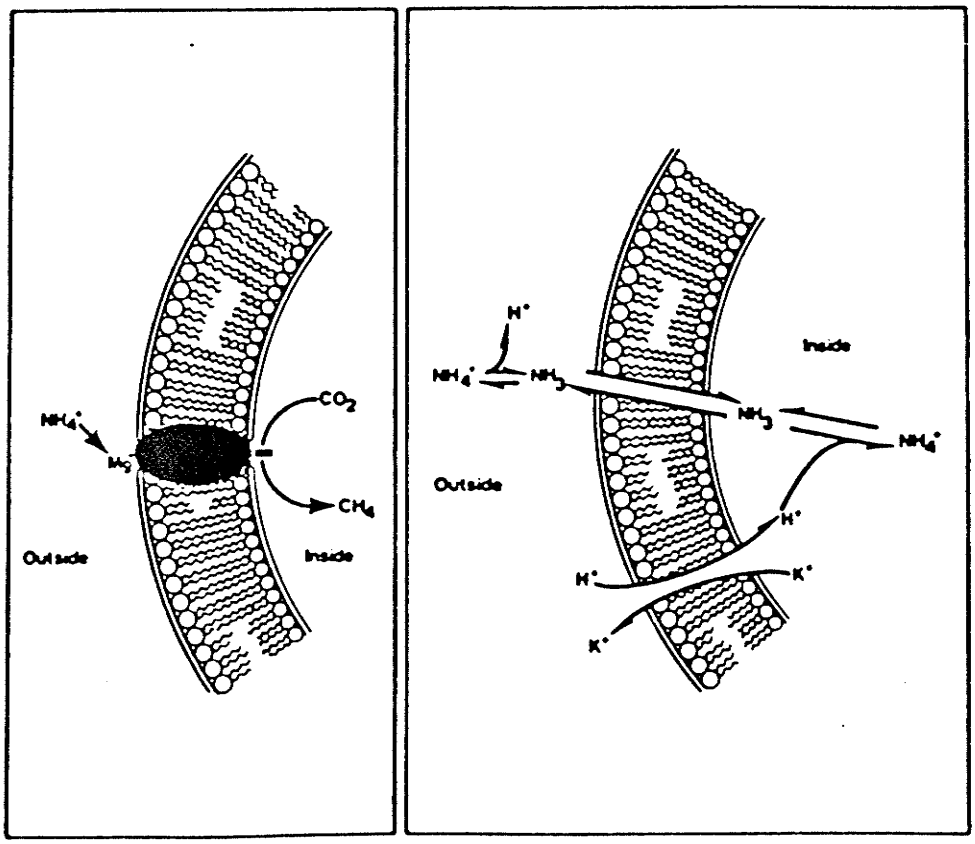

Fig. 2.3 - Mechanism of NH_4^+-ion Toxicity (60)

On the other hand, free-NH_3, which is in a state of chemical equilibrium with NH_4^+-ions on the outside of the cell, may diffuse through the cell membrane, and draw off the cells protons, (H^+), to create the same type of an equilibrium condition with ammonium inside the cell, as it exists on the outside, (Fig. 2.3). This upsets the acidic nature of the inner cell. The cell counteracts by drawing in protons from the outside to maintain its internal pH balance, thereby building up positive charge inside the cell. In maintaining this internal balance, the cell releases potassium ion, (K^+) and, in the process, it dies.

Acclimation to ammonia toxicity is also observed in the literature. Van Velsen (61) reported that methane-producing bacteria can acclimate to NH_3-N concentrations as high as 5000 mg/L, if considerable acclimation time is provided. He found that methanogens, acclimated to 1700 mg/L ammonia-N, had no trouble acclimating to NH_3 concentrations up to 2700 mg/L. Parkin and Miller (62) stated that with acclimation 8000 - 9000 mg/L concentration of NH_3-N could be tolerated, with little drop in performance.

Koster and Lettinga (3) noted that methane-bacteria can prepare for ammonia-N concentrations exceeding the threshold level while maintained at sub-threshold concentrations. Kroeker et al. (8) stated that excessive ammonia-N may even contribute to

process stability. In addition it was suggested that, if adequate acclimation time is allowed for the micro-organisms to adapt to NH_3-N, the anaerobic fermentation of high nitrogen organics will be more stable than if the digestion process is carried out within the limits of normal anaerobic treatment (8).

2.3 ANAEROBIC REACTORS

2.3.1 Flow-Through Reactors *

(i) Upflow Anaerobic Sludge Blanket Process

Upflow anaerobic sludge blanket,(UASB), is a suspended growth anaerobic digestion process for the stabilization of organic matter in the wastewater. It was developed by Lettinga (63,64) in Holland in early 1970's as an upflow modification of an Imhoff tank or clarigester. This process utilizes the superior flocculation and settling characteristics that the anaerobic sludge exhibits under favorable physical and chemical conditions. This means that, using UASB reactors, high SRT's can be maintained at even very high loading rates (1).

The reactor consists of two zones: the sludge bed and the sludge blanket zone, (Fig. 2.4). The waste is fed at the bottom of the reactor, and moves upwards in the reactor. The flow must

* Flow-through reactors are also referred to as continuous flow reactors. In this report, both these terms will be used interchangeably.

be distributed uniformly across the cross-sectional area to avoid short-circuiting, and to ensure efficient substrate utilization by the anaerobic bacteria. Moving upwards, the waste first encounters the sludge bed zone, which is formed by the settled and thickened sludge. It is at this zone that waste stabilization

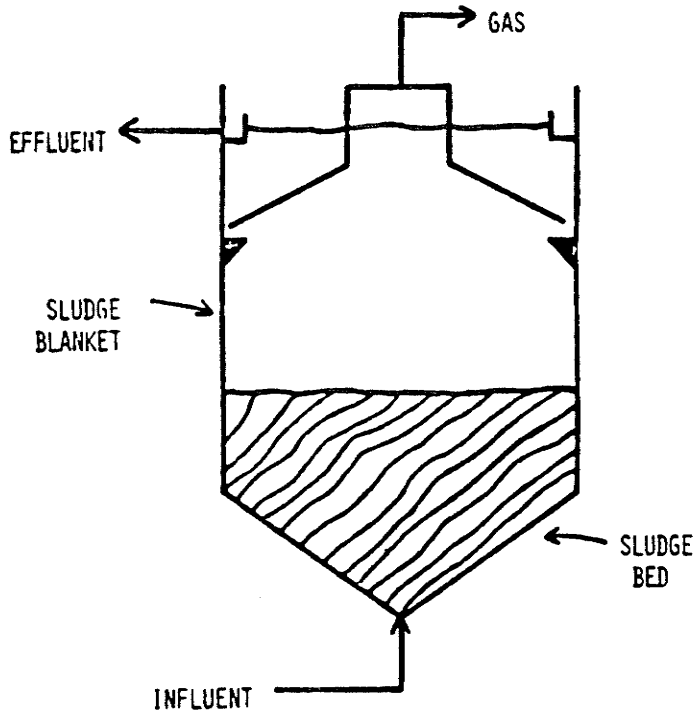

Fig. 2.4 - The Upflow Anaerobic Sludge Blanket Reactor (1)

takes place. The sludge bed zone is characterized by a highly developed granular sludge with superior settling properties (1,65). Mechanical mixing is kept to a minimum in this zone to prevent any erosion of this granular sludge. The granular sludge at the sludge bed zone is highly concentrated, and could amount to as high concentrations as 100 - 150 g/L (1).

The sludge bed zone is a continuously mixed region. The mixing occurs as a result of gas production by the microbial population, i.e. by the free rising gas bubbles generated during the anaerobic process. The sludge bed zone accounts for 80 - 90% of the waste stabilization in the reactor, while occupying only 30% of the total reactor volume (1). The upper section of the UASB reactor is the sludge blanket zone, which is ideally mixed by the slow, free-rising, gas bubbles generated at the lower, (sludge bed), zone. Even though the sludge in this region is also highly flocculated, the solids concentration is considerably lower than that in the sludge bed zone. The biological solids tend to rise through the sludge bed and the sludge blanket zones by the rising gas. In order to protect the biomass from loss to the effluent, and to retain long SRT's, these biological particles must be separated from the overflow and returned to the reactor. A settler/gas collector device is, therefore, necessary to accomplish this objective (1).

There are a considerable number of studies in the literature

documenting the suitability of UASB reactors for anaerobic degradation of various, high-strength, industrial wastewaters. These studies were carried out at laboratory bench-scale, pilot plant, and full-scale operations. Wastes such as skimmed milk (64), potato (66), methanolic (67), liquid sugar (68), and fatty acids (68) were treated successfully using UASB's.

(ii) Anaerobic Attached Growth Process (Upflow Anaerobic Filter)

Young and McCarty (69) developed the anaerobic filter process while studying the possibility of increasing organic loading, by maintaining long SRT's independent of waste flow. The system, that was eventually adapted, consisted of an upflow reactor containing solid support medium, (or packing material), that retained the microbial population on its surface.

In an upflow anaerobic filter, (Fig. 2.5), the wastewater flows upwards through the filter media. The biological growth develops on the media surfaces, or becomes trapped in the voids between the support medium. The packed filter media not only retains microbial population, but also provides a mechanism for separating the biological solids and the gas generated during the digestion process. By trapping the sludge solids, and thus maintaining a high concentration of micro-organisms, long SRT's can be obtained in an anaerobic filter. The upflow anaerobic filter process may, therefore, be used for the treatment of low strength wastes at large waste flows (1).

Many studies have been cited in the literature documenting the appropriateness of the upflow anaerobic filter for laboratory and pilot plant studies, and the success record of the attached growth process in full-scale operation. Young and McCarty (69), using an upflow filter to treat a volatile acid and a protein-

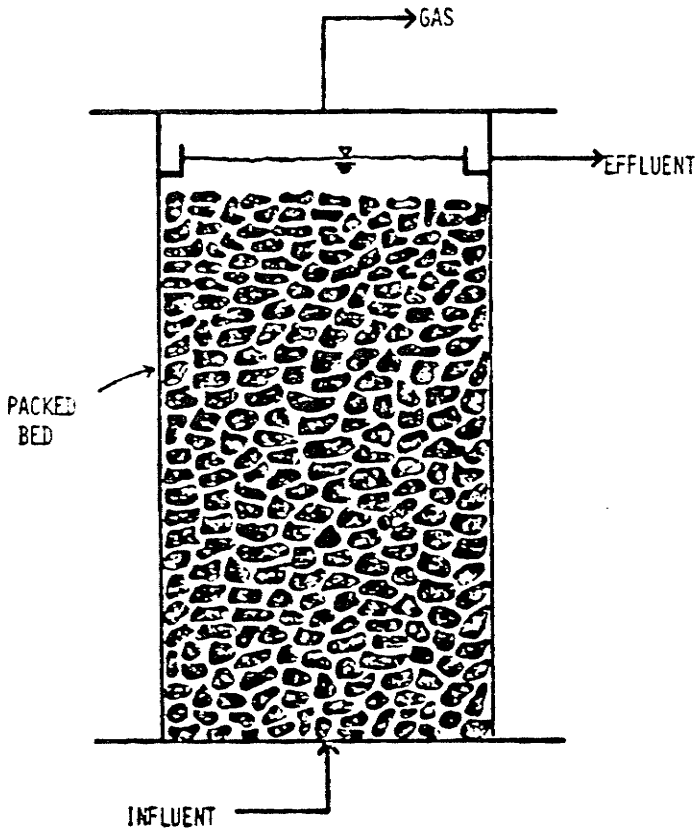

Fig. 2.5 - The Upflow Anaerobic Filter (1)

carbohydrate waste, and using 0.42 - 3.4 kg COD/m^3.d loading rates, achieved COD reductions of up to 60 - 98 percent. Jennet and Dennis (70), using a pharmaceutical waste containing 95 percent methanol, (on a COD basis), and a small fraction of toluene, achieved 95 percent COD reduction, at 3.5 kg/m^3.d COD loadings. Sachs et al. (71) studied the feasibility of treating organic-chemical pharmaceutical wastes, and achieved 80 percent COD reductions, at 0.56 kg/m^3.d COD-loadings and 36-hour HRT's. Obayashi and Roshanravan (72) were successful in treating rendering plant wastes, at pilot-plant scale, using the anaerobic filter. This plant, at 2 kg COD/m^3.d loadings and 36-hour HRT, achieved a COD reduction of 70 percent.

A full-scale anaerobic filter to treat guar bean waste was installed by the Celanese Company, located in Corpus Christi, Texas. It achieved 65 percent COD removal, at 16 kg COD/m^3.d loading and 1-day HRT (73).

(iii) Anaerobic-Hybrid (Anhybrid) Process

The anhybrid concept was originally introduced by DLA (74). The anhybrid process is a cross between the UASB and the upflow anaerobic filter processes. The reactor is a combination anaerobic-hybrid reactor comprising of a sludge bed and a media zone. As evident from its name, an anhybrid reactor contains both suspended and attached biological growths (46). Many combinations, in relative size and arrangement of the two

biological growth zones, may be experimented. For example, the lower part of the anhybrid reactor may contain flocculating sludge, while the upper portion may be filled with support media to trap and maintain the biological solids, and to induce a stable plug flow regime in the reactor (75). In this case, the sludge bed acts as the main treatment zone, while the media acts as a gas-solids separator. Like UASB and anaerobic filter reactors, the anhybrid reactor can provide very long SRT values without requiring excessively large volumes (10).

2.3.2 Batch Anaerobic Reactors

Batch anaerobic reactors are used to evaluate biodegradability and toxicity. They provide useful information for sorting out variables that can be used in design and full-scale operation of continuous flow reactors. Therefore, in dealing with a new, or potentially hard to degrade substance, batch reactors can be useful in 2 ways: (1) in determining if the compound is biodegradable, and (2) in evaluating whether, and at what concentrations, the compound is toxic to anaerobic bacteria.

Owen et al. (76) have devised techniques for measuring biodegradability, (biochemical methane potential - BMP), and toxicity, (anaerobic toxicity assay - ATA), of a given test compound under anaerobic conditions. In a BMP test, cumulative methane production is monitored in a chemically defined medium in

order to measure the biodegradability of the unknown compound. In this test, the substrate being tested is the only carbon source available for the methanogens. If the bacteria are able to utilize and degrade the test substrate, then it is biodegradable. The ATA, on the other hand, is a measure of the adverse effect of a compound on the total gas, or methane, production rate from an easily biodegradable methanogenic substrate, (i.e. a carbon source other than the test compound).

Jeris and McCarty (77) defined anaerobic toxicity as the adverse effect of a compound on the predominant methanogens, (the acetate utilizing methanogens). They (77) pointed out that anaerobic toxicity may be studied, and its extent determined by comparing the performance of the test units against that of a control unit. Parkin et al. (10), like Jeris and McCarty (77), devised a slightly different test, and used a fixed volume of acetate in stoppered serum bottles as the only source of carbon, (ATA technique uses both propionate and acetate). These researchers (77) referred to their technique as the "Batch Toxicity Assay". Batch toxicity assay may be modified to use syringes in place of serum bottles. Use of syringes, instead of serum bottles, makes the gas measurement, and the liquid and gas sampling much simpler (1).

Useful as they may be, batch anaerobic tests can successfully evaluate only the influence of shock loadings on the

anaerobic system, and tend to produce a conservative measure of the toxicity threshold concentration. Even though these tests do not simulate full-scale continuous flow anaerobic operations, in comparison to flow-through toxicity techniques, they are quick, relatively inexpensive, and highly reproducible (78). Being much less costly in terms of equipment, time, and personnel, the batch anaerobic tests are ideal techniques for toxicity studies, and give the researcher much more flexibility, since a large number of samples and a wide variation of concentrations can be handled in a relatively short period of time (76).

CHAPTER 3

EQUIPMENT AND METHODS

3.1 START-UP PROCEDURE

3.1.1 Bioassay Tests

The following steps were involved in the preparation and set-up of the bioassay tests:

1) An erlenmeyer flask was fitted with a rubber stopper, which contained two open ports. The air in the flask was purged with nitrogen gas; a volume of sludge was transferred into the flask by the negative pressure created by an Air-Cadet compressor, (Cole-Parmer); and the flask, containing the anaerobic sludge, was further purged with nitrogen for an additional period of time. Nitrogen entered the flask through one of the two open ports and, being heavier, pushed the air out through the other port;

2) The nitrogen was shut off, one port was clamped, and a rubber septum was placed on the other port;

3) The rubber septum was pierced with a syringe, (the syringe was used to withdraw the required volume of sludge);

4) In a similar manner, appropriate volumes of nutrients and micro elements were transferred into the syringe;

5) pH was adjusted to the optimum range by adding hydrochloric acid;

6) Steps 3, 4, and 5 were repeated for preparing other syringes with varying combinations of substrates;

7) The syringe ends were sealed with rubber stoppers;

8) Finally, the syringes were placed in a water bath incubator, which was kept at 35°C.

3.1.2 Flow-through Reactors *

1) On day 1, all tygon tubing lines into and from each reactor were clamped off - except for two: one at the reactor top, and one at the reactor bottom;

2) Nitrogen was forced into the reactor through the open port at the bottom. Almost all the air was purged out through the other port at the top by the heavier nitrogen gas;

* For a schematic of the flow-through reactors, refer to Fig.3.1

3) While the reactors were being purged with N_2 gas, volumes of sieved-flocculant sludge were drawn into each reactor from a storage-breeder tank, (which itself was being continuously purged with N_2 gas). The sludge was introduced into each reactor by opening a side port in the reactor. This process was facilitated by the vacuum created inside the reactors by the Cole-Parmer Air-Cadet compressors, which were connected to the ports at the top of each reactor;

4) After the desired volumes of sludge were transferred into the reactors, the lines, (tygon tubing), to the sludge storage tank and the Air-Cadets were disconnected, and the appropriate connections to the split box and the recycle pumps were made;

5) The flow-through study commenced when the feed and recycle pumps were switched on and the reactors started to operate.

3.1.3 Batch Reactors *

A similar technique used for the start-up of the flow-through reactors was used to start the batch reactors:

* For a schematic of the batch reactors, refer to Fig. 3.2

1) Each reactor was sealed with a rubber stopper that contained two open ports;

2) Nitrogen gas was forced into the batch reactors through one port, which caused the "lighter" air to be forced out through the other port;

3) Desired volumes of anaerobic sludge were transferred into each reactor by the vacuum created by the Air-Cadet compressors, (Cole-Parmer);

4) In a similar manner, corresponding volumes of nutrients and micro elements, and any required additional TDS, were transferred into each batch reactor;

5) pH was adjusted to the optimum range by adding hydrochloric acid;

6) Finally, the batch reactors were placed in a water bath incubator, which was kept at 35°C.

3.2 LABORATORY SET-UP

3.2.1 Bioassay Tests

Bioassay tests were performed in 60 mL plastic syringes,

incubated under water, at 35°C. Several series were run, all at an initial food to micro-organisms ratio, (F/M), of 0.1 gTOC/gVS. During the 40 day incubation period, samples of gas were collected for analysis of CH_4, CO_2, and N_2. The test was run on duplicate syringes, which contained the following combinations of substrates: raw wastewater, (W), only; acetate, (A), only; hexanol, (H), only; W+H; W+A; A+H; and W+H+A.

3.2.2 Continuous Flow Studies

Three parallel upflow anaerobic reactors, made of plexiglass, were used. Reactors 1, (R_1), and 2, (R_2), were upflow anaerobic sludge blanket, (UASB), reactors with conical bottoms, while reactor 3, (R_3), was an anhybrid reactor of cylindrical shape with a flat bottom and its upper 75% of volume filled with 1 inch plastic rings. The design of this reactor was based on the original concept introduced earlier by DLA (74). Fig. 3.1 is a schematic of reactor R_3. Except for the reactor shape, the set-up, shown in Fig. 3.1, was identical for the other two flow-through reactors, (R_1 and R_2).

Each reactor was equipped with variable speed feed and recycle pumps, (Masterflex), and was connected to a split box to equalize pressure between its recycle line and the reactor top. The recycle line allowed blending of the raw and recycled wastewater just before the influent end of the reactor. The

recycle pumps were adjusted to maintain a recycle/raw wastewater flow ratio of 10:1 at all times. The reactors were placed in a walk-in environmental chamber, maintained at 35° C. An adjacent environmental chamber, maintained at 5° C, housed the feed and effluent storage tanks. The excess gas was evacuated through positive displacement gas meters. Tygon tubing was used for all gas and liquid lines.

All reactors were charged on day 1 with, sieved-flocculant, anaerobic sludge from a local municipal sludge digester. On day 39, R_1, (total volume 2.46 L), was emptied and was filled with imported, anaerobic-granular, sludge from a functioning pulp mill wastewater treatment plant, marketed by Paques, Lavalin. On day 39, R_2, (2.50 L), and R_3, (2.80 L), were supplied with only 30% and 25%, (volume basis), of imported granular sludge per total sludge volume, respectively. Hydraulic residence time, (HRT), over the 80 day study period, ranged between 15 and 20 h.

3.2.3 Batch Experiments

Two separate batch experiments were conducted. A biomethanation potential, (BMP), study (79) was performed using the dilution technique to determine the existence, and the magnitude of toxicity of the raw wastewater. The method used was based on that of Owen *et al*. (76). In this study, 80 mL serum bottles and an unacclimated municipal digester sludge were used

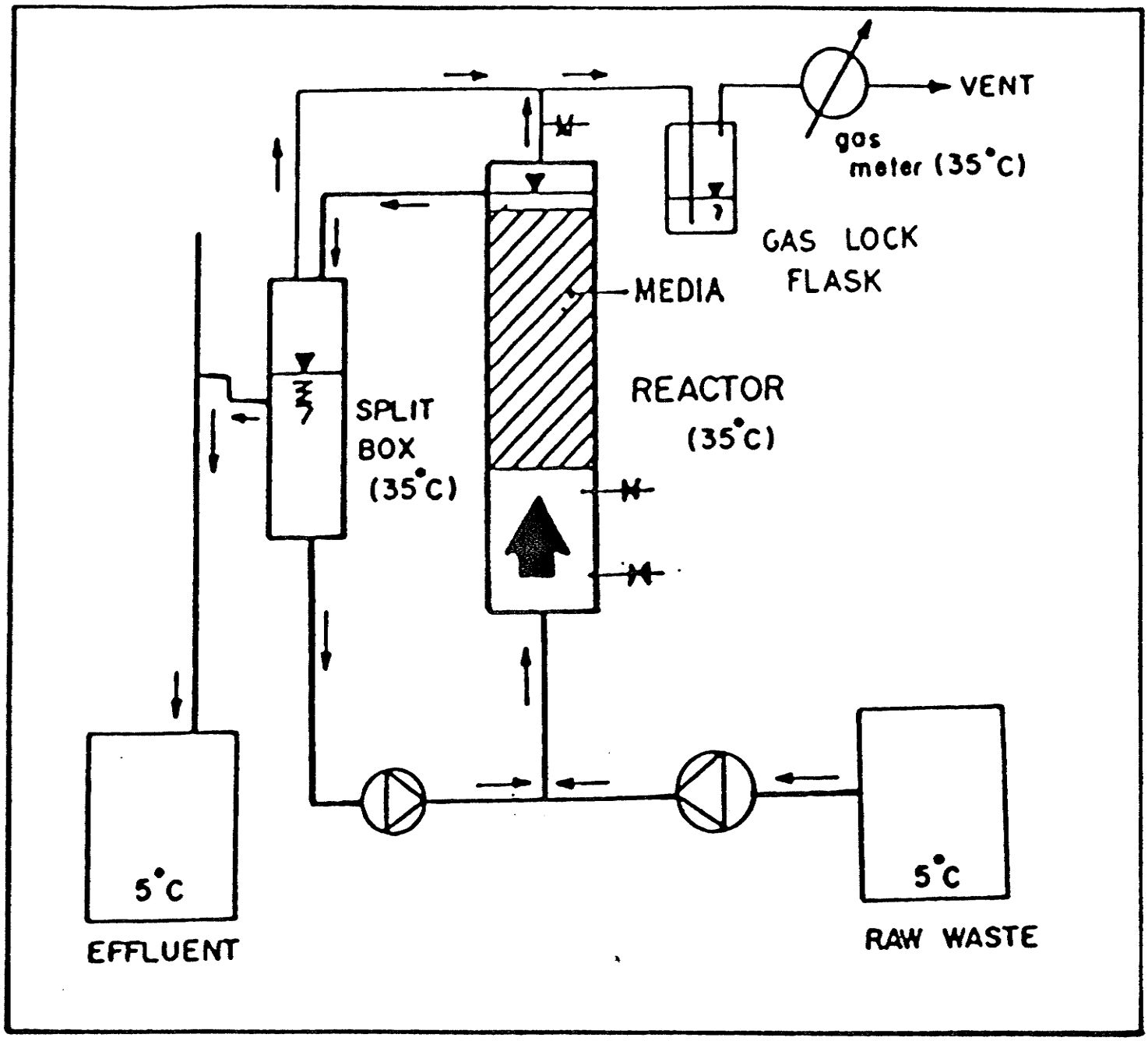

Fig. 3.1 Schematic of the flow-through reactor R_3 (anhybrid reactor)

for a 40 day study period.

A parallel study comprised of three series of batch anaerobic reactors, (Fig. 3.2), was run for a 60 day period. Each series was comprised of ten, 450 mL in volume, reactors and had a constant initial F/M load of 0.25, (series 1), 0.50, (series 2), and 0.80 gCOD/gVS, (series 3). The concentration of TDS within each series varied from 5 to 35 g/L. The reactors in the lower F/M ratio series could not be subjected to higher TDS concentrations from undiluted wastewater. The TDS levels above 20 g/L in series 1 were obtained by adding NaCl. NaCl was chosen for this purpose because sodium carbonate and sodium hydroxide are the main inorganics present in the raw wastewater, and hydrochloric acid is the main candidate for the neutralization of the raw wastewater before any anaerobic treatment.

The biomass used consisted of a mixture of flocculant, and 30% by weight, granular sludge. The sludges were from the same source used in the continuous flow studies. All reactors were equipped with gas volume measurement, gas sampling, and pH measurement ports, and were placed in a water bath incubator, maintained at 35°C.

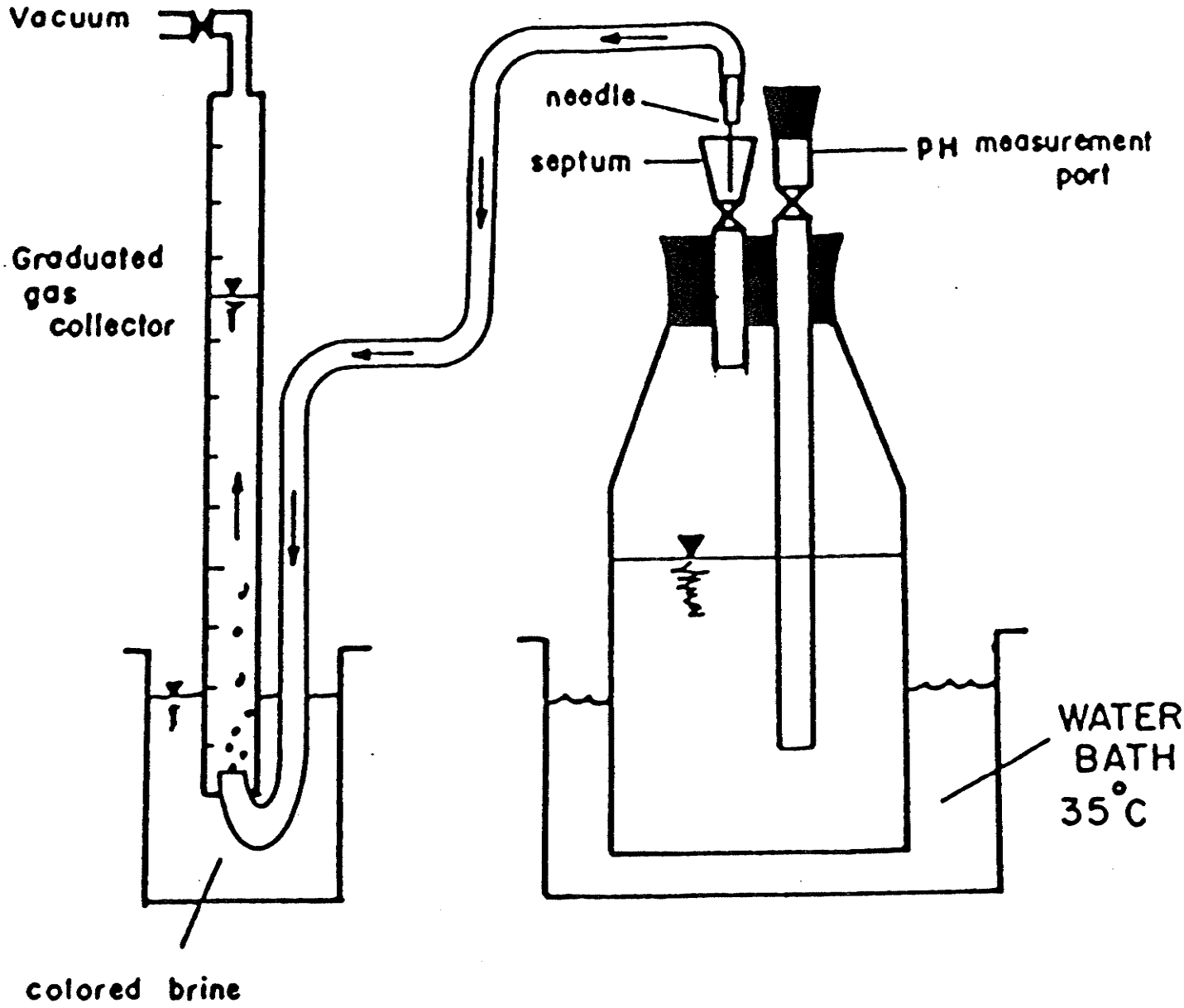

Fig. 3.2 Schematic of the batch anaerobic reactors

3.3 FEED PREPARATION

Feed for the flow-through reactors was prepared using raw wastewater, (spent PMU), diluted with tap water. Nutrients and micro-elements were added in the form of K_2HPO_4, KH_2PO_4, $FeCl_3$, $MgSO_4$, $NiCl_2.6H_2O$, $CoCl_2.6H_2O$, $ZnCl_2$, $CuSO_4$, and yeast extract.

Table 3.1 is a list of the chemicals and their corresponding concentrations used in preparing feed in this study. The feed was prepared, depending on the flow rate, 1 to 2 times a week. It was stored in 20 liter storage tanks in an environmental chamber, which was maintained at 5°C.

Hydrochloric acid was used to adjust and maintain the reactor pH in the optimum range of 6.8 - 7.4, (chapter 2). It was added to the diluted wastewater, and its amount was determined using the titration curves, (figures 4.1 and 4.2), developed in this study. The applied organic loading, controlled by varying the flow rates and the influent concentration, was incrementally increased from 1.5 to 11.8 kg COD/m_3.d. The dilutions used were from 1:22 to 1:5, which corresponded to the influent COD concentrations of 2.8 to 11.5 g/L, and the influent TDS concentrations of 5.2 to 21 g/L.

Table 3.1 - Nutrients and micro-elements used in the feed (Flow-through Study).

Chemical	Concentration
K_2HPO_4	0.10 g/L
KH_2PO_4	0.10 g/L
$FeCl_3$	0.02 g/L
$MgSO_4$	0.06 g/L
$NiCl_2.6H_2O$	0.40 mg/L
$CoCl_2.6H_2O$	0.40 mg/L
$ZnCl_2$	1.00 mg/L
$CuSO_4.5H_2O$	2.00 mg/L
Yeast Extract	0.20 g/L

For the batch anaerobic reactors, the initial feed included the same nutrients and micro-elements combination used in the continuous study. The initial F/M load ranged from 0.25 gCOD/gVS for series 1, to 0.50 and 0.80 for series 2 and series 3, respectively. The TDS concentrations within each series varied from 5 to 35 g/L.

3.4 TESTING AND ANALYSIS

All scheduled tests were performed according to APHA (36). Gas analyses were performed on a Gow-Mac gas chromatograph, (Poropak Q column), equipped with a thermal conductivity detector. Volatile fatty acids, (VFA), were analyzed on a Gow-Mac gas chromatograph, (Chromosorb 101), equipped with a flame ionization detector. TOC was determined using a Dohrman DC-80 total organic carbon analyzer. TKN and NH_3-N were measured using a Tecator Kjeltec distillation system. COD was measured colorimetrically, using a Bausch and Lomb Spectronic 20, spectrophotometer. For additional, interim, volatile acids monitoring; a faster titration method was occasionally used. This method was originally introduced by Dilallo and Albertson (80).

3.5 TESTING AND MEASUREMENT SCHEDULE

Table 3.2 contains a list of tests and measurement procedures used in the flow-through studies. This table also shows the frequency of these tests and measurements on a weekly basis.

In the batch studies and the bioassay tests, the contents of the reactors and the syringes were mixed manually twice a day, and the gas volume was measured once a day. Gas composition was analyzed once every 2 days initially, and whenever gas production was observed at later stages of the study. The reactor pH was

measured on a weekly basis in the batch studies. In the bioassay tests, it was measured twice: once at the start, and once at the end of the study.

Table 3.2 - Tests and measurements and their respective frequency.

test/measurement	No. of times/week
Gas Volume Measurement	7
Effluent Volume Measurement	7
pH Measurement	7
pH Adjustment	7
Influent COD /or TOC	1-2
Effluent COD /or TOC	1-2
Alkalinity	1
Volatile Acids	1
NH_3-N	1
TKN	1
Gas Analysis	1

CHAPTER 4

RESULTS AND DISCUSSION

4.1 PRELIMINARY LABORATORY ANALYSES

4.1.1 Raw Wastewater Characteristics

A batch of spent PMU from the pharmaceutical plant was collected for this study. It was maintained at 5° C, in unadulterated form, in an environmental chamber. The raw wastewater was tested for BOD_5; TOC; COD; TKN; NH_3-N; total solids, (TS); total volatile solids, (TVS); total dissolved solids, (TDS); total suspended solids, (TSS); volatile suspended solids, (VSS); pH; and alkalinity. Table 4.1 lists the results from these analyses. Also included in this table are the values obtained by other laboratories that have analyzed this wastewater in the past, at various times prior to this study.

4.1.2 pH Titration

The pH of the spent PMU was measured to be 10.2, (Table 4.1). High pH of the raw wastewater is due to the addition of soda-ash and sodium hydroxide in the extraction process. Figures 4.1 and 4.2 show the titration curves for undiluted and diluted PMU samples, respectively. In both titration tests, 1N hydrochloric

Table 4.1 - Raw Wastewater, (Spent PMU), Characteristics.

(*) Parameter	University of Waterloo (1968)	Ayerst (1983)	Simplot (1984)	MacLaren (1985)	University of Manitoba (1985)
BOD_5	38,400	45,240	-	41,000	43,500
TOC	-	21,000	-	10,800	24,300
$COD_{(unfilt)}$	69,000	68,300	-	59,500	62,000
$COD_{(filt)}$	68,000	-	-	52,000	-
TKN	8,500	14,200	14,400	11,600	9,700
NH_3-N	1,600	4,440	-	3,400	3,000
PO_4	5	3	-	4	-
TS	115,000	131,100	-	105,000	114,000
TVS	41,000	-	-	-	36,000
TDS	-	115,000	115,000	-	113,760
TSS	2,800	-	-	500	241
VSS	1,000	-	-	245	121
pH	9.9	10.0	10.1	10.3	10.2
Alkalinity (as $CaCO_3$)	-	73,000	-	56,500	60,400

(*) All parameters are in mg/L, except pH

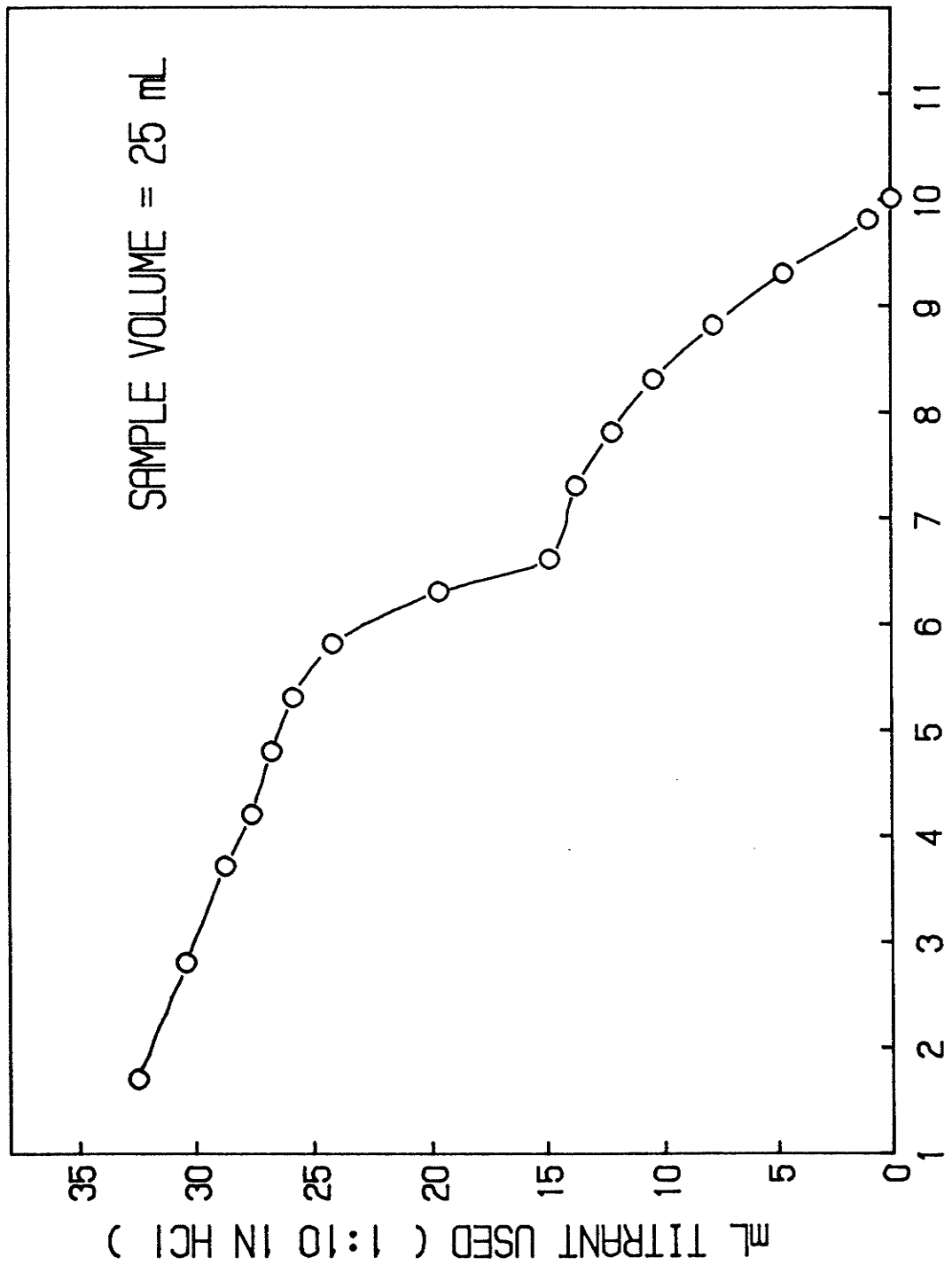

Fig. 4.1 Titration curve (raw wastewater)

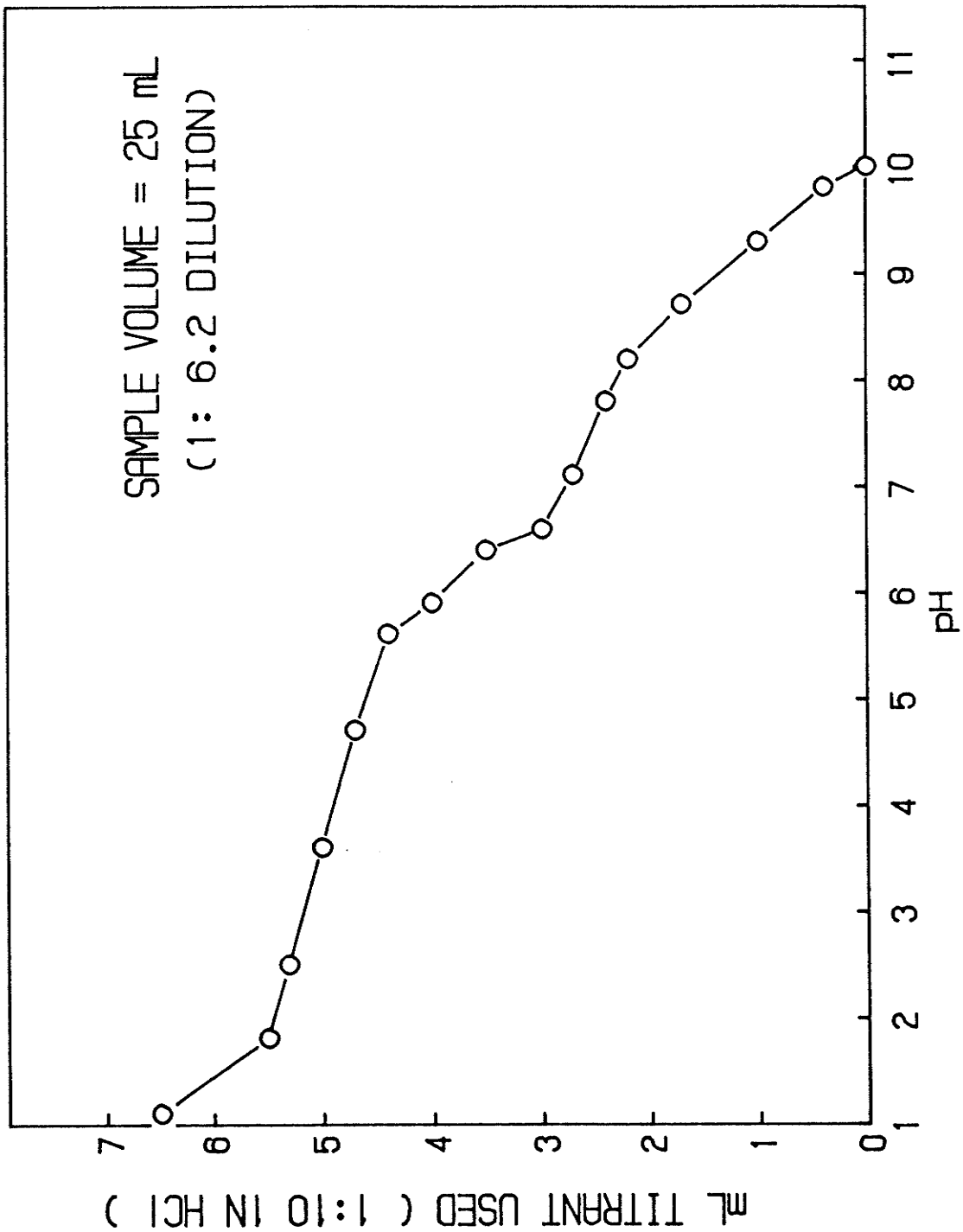

Fig. 4.2 Titration curve (diluted wastewater, 1: 6.2 dilution)

acid diluted to 1:10, was added to 25 mL volumes of the sample. As shown in Fig. 4.2, a 1:6.2 dilution of the raw wastewater was used which corresponded to the equivalent COD concentration of 10,000 mg/l.

4.1.3 Bioassay Tests

Bioassay tests were performed on spent PMU to evaluate the inhibitory potential of the wastewater and pure hexanol under batch anaerobic conditions, (hexanol is used during the estrogen extraction process). These tests were run on duplicate syringes. The following combinations of substrates were used: wastewater, (W), only; acetate, (A), only; hexanol, (H), only; A+H; W+H; W+A; and W+H+A. The performance, (CH_4 Production), of each combination was compared to the total volume of methane generated by the acetate only, (A), and the sludge only, (blank), syringes.

The bioassay tests showed that both the wastewater and hexanol were biodegradable under anaerobic conditions. However, the A+H and A+W combinations produced approximately 15% less methane than the control syringes containing only acetate, (A). Based on the results from these bioassay tests, it was assumed that, if sufficiently diluted, the raw wastewater would be amenable to anaerobic methanogenesis.

4.2 ANAEROBIC TESTS

4.2.1 Continuous Flow Studies *

Fig.4.3 illustrates the performance of the UASB reactor, R_1. On day 39, reactor R_1 was completely emptied of the flocculant sludge and was filled with a granular sludge. Performance, (as indicated by gas production and COD removal efficiency), improved immediately, while an initial drop in the ammonification rate, (defined as the ratio of NH_3-N to TKN), was observed. The NH_3-N/TKN ratio gradually returned to almost the 100% level under a relatively constant COD loading of 5.0 kg/m^3.d.

The COD removal efficiency increased from 12%, on day 37, (prior to the addition of the granular sludge), to a maximum of 60%, on day 52, (after the granular sludge was added). An increase in COD loading to 11.8 kg/m^3·d, on day 52, resulted in a drop in the percentage of COD removal. The COD removal efficiency, even with a step-wise decrease in loading, continued to drop to as low as 9%, on day 72, under a COD load of 9.2 kg COD/m^3.d. A subsequent decrease in COD loading to 6.1, on day 75, resulted in an increase in the percentage of COD removal to 21%.

* Like in the literature review, continuous flow reactors are also referred to as flow-through reactors. In this report, both these terms are used interchangeably.

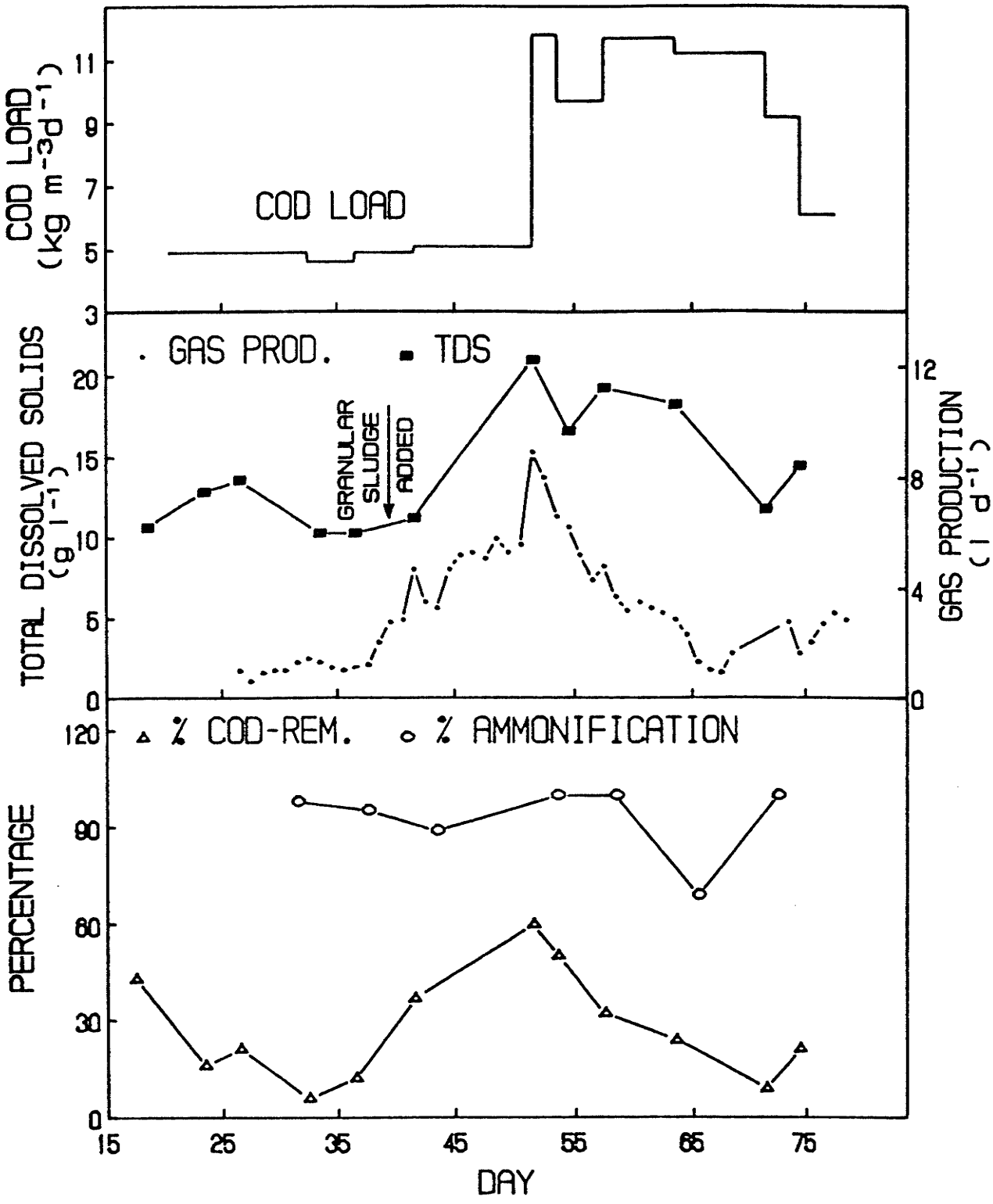

Fig. 4.3 Performance of the flow-through reactor R_1 (UASB)

The ammonification ratio for R_1 remained relatively constant over the period of this study, and averaged at about 97%. Nevertheless, after a prolonged period of exposure to these excessively high loading conditions, the ammonification ratio dropped to a low of 69%, on day 66. However, the NH_3-N/TKN ratio returned to the 100% level, on day 73, when the load was decreased to 9.2 kg COD/m^3.d.

Fig.4.3 also shows the effects of the influent TDS on gas production. An increase in TDS concentration beyond a certain threshold level, (21 g/L), corresponding to a dilution of 1:5.4, resulted in a drop in gas production. The maximum removal of COD attained for R_1 was 5.5 kg/m^3.d at a COD load of 11.8 kg/m^3.d and the corresponding TDS concentration of 21 g/l. The ammonification rate for R_1 was at 100% during the peak performance. After this peak, the performance deteriorated sharply.

The drop in the reactor performance can be explained by the possible inhibitory effects of TDS, and/or may be due to the poor performance of the granular sludge, which was developed using a totally different substrate. A definite change in physical and biological nature, and appearance of the granular sludge was evident, as the originally gritty sludge granules had become more fluffy at the end of this experiment.

Fig.4.4 shows the performance of reactor R_2, (UASB). At an initial COD load of 5.0 kg/m^3.d, starting from day 18, the COD removal increased initially from 55% to 64%, on day 24. A further increase in COD load to 6.6 kg/m^3.d, on day 27, lead to a decrease in COD removal to 24%. The COD removal continued to drop to a minimum value of 18% on day 33, at which time the load was decreased to 4.0 kg COD/m^3.d.

A decrease in COD loading resulted in an increase in the COD removal efficiency. COD removal increased, even with a step-wise increase in loading, to as high as 72% until day 54. COD removal dropped when COD loading was increased to 6.6 kg/m^3.d, on day 58. Further increases in loading, from day 58 on, resulted in subsequent decreases in COD removal efficiency.

Conversion of org-N to NH_3-N, (deamination or ammonification), for R_2 is also shown in Fig.4.4. The ammonification rate, (ratio of NH_3-N to TKN), followed a similar pattern to COD removal efficiency with respect to changes in COD loading; increasing ammonification was noticed at low loads, and decreasing performance was evident at high loads.

TDS concentrations in R_2, over the study period, is also illustrated in Fig.4.4 . The effect of high TDS levels in the performance of R_2 is similar to the adverse effects experienced

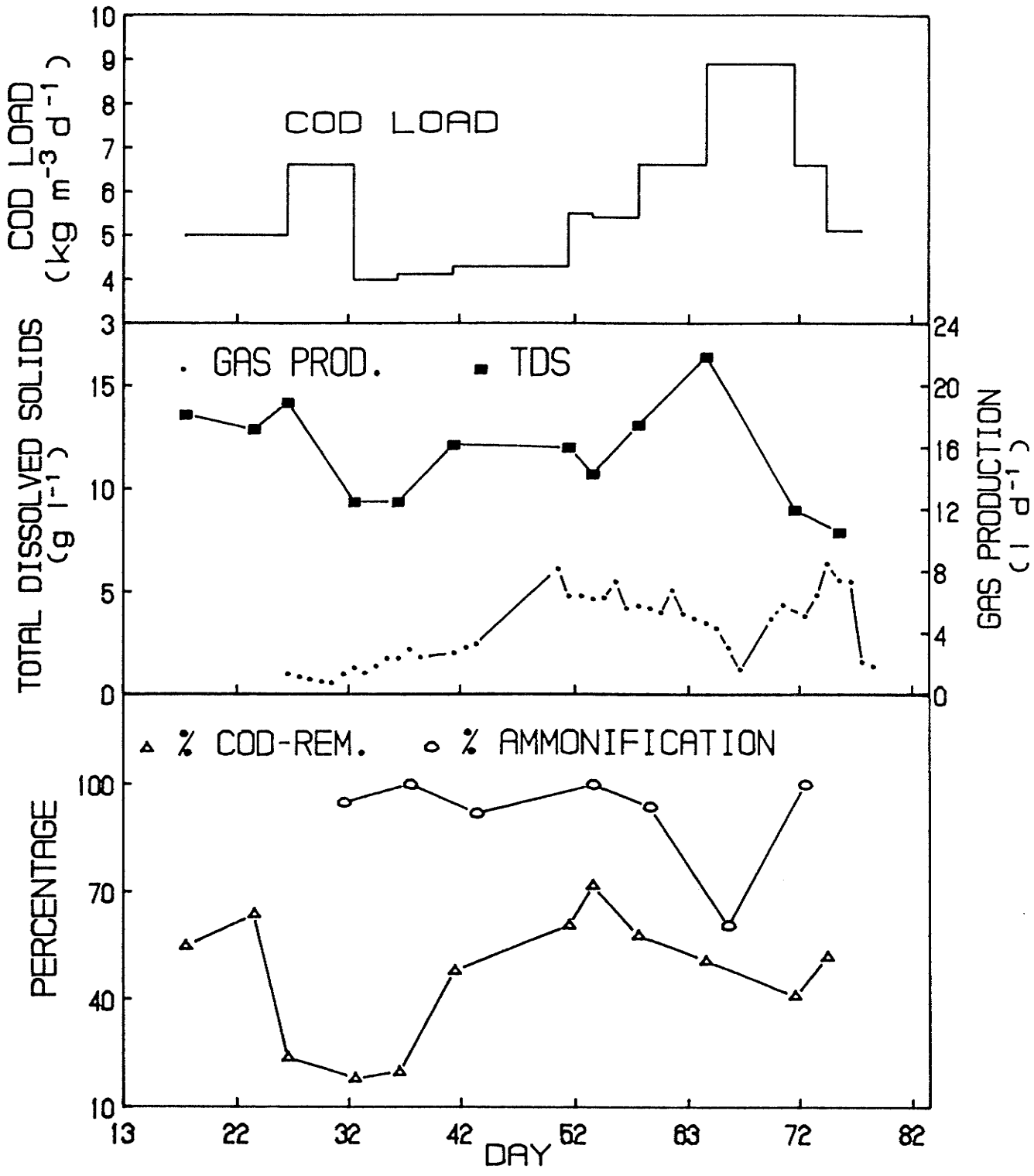

Fig. 4.4 Performance of the flow-through reactor R_2 (UASB)

in reactor R_1 under high TDS concentrations. Gas production in R_2 dropped drastically when a 16.4 g/L TDS concentration, corresponding to a dilution of 1:7, was reached.

Fig.4.5 depicts performance of the anhybrid reactor, R_3. In reactor R_3, as in R_1 and R_2, increases in COD loading and TDS levels resulted in decreases in gas production, (G.P.), COD removal efficiency, and ammonification rate. A considerable drop in G.P. was observed in this reactor at a TDS concentration of 18.8 g/L, corresponding to a dilution of 1:6.1 .

In all three flow-through reactors, therefore, the COD removal efficiency, the gas production, and the ammonification rate improved gradually until the COD load was increased over 10.0 $kg/m^3.d$, and the TDS concentration averaged over 17 g/l. Above these COD loading conditions and TDS concentrations, performance of the flow-through reactors deteriorated sharply.

The first sign of inhibition was given by an immediate drop in G.P., followed by a decrease in COD removal, and a drop in ammonification ratio. A reverse trend in performance was first shown by the ammonification ratio, and started as soon as the TDS concentration and the COD load increased above 17 g/L and 10.0 $kg/m^3.d$, respectively.

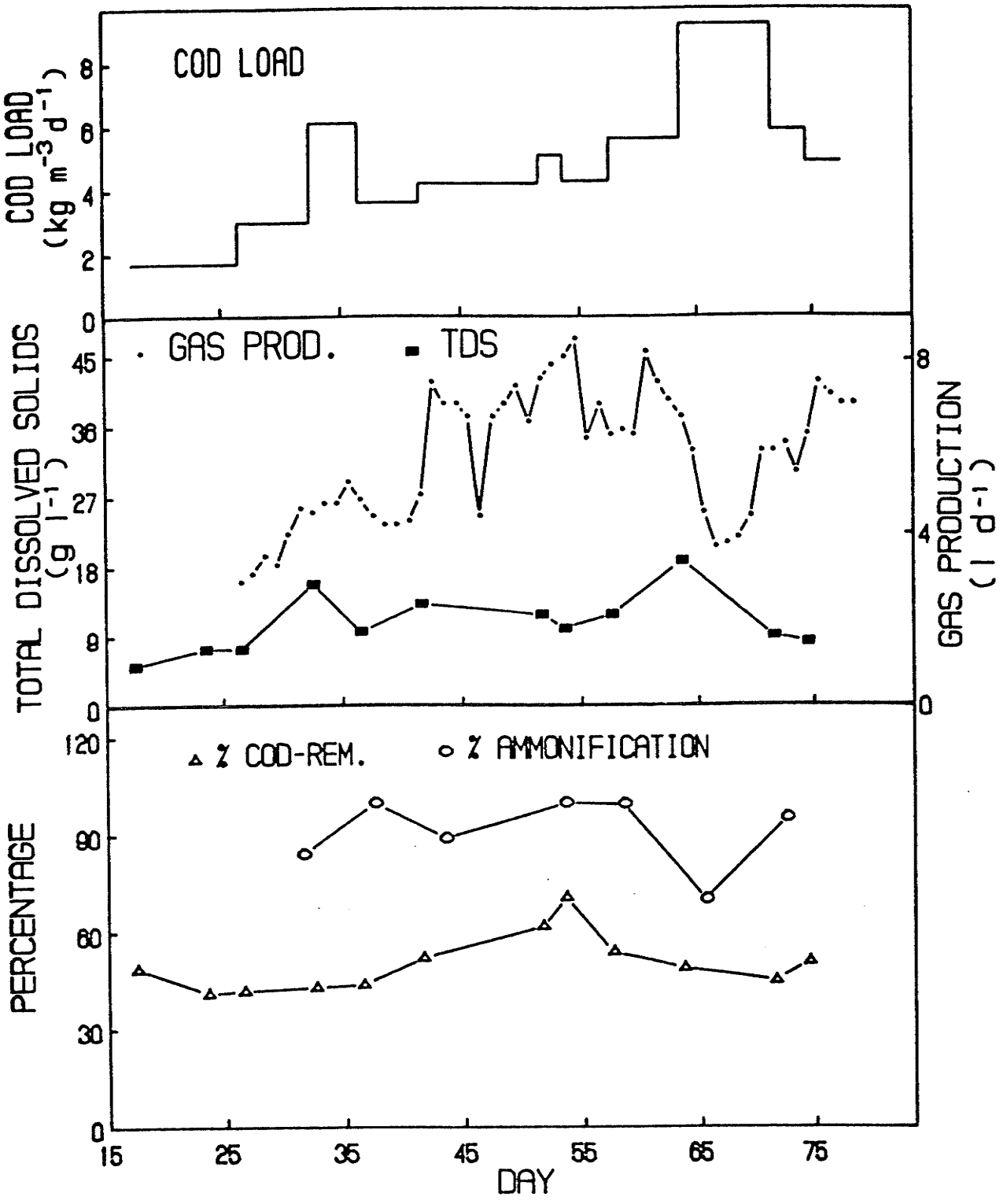

Fig. 4.5 Performance of the flow-through reactor R_3 (anhybrid)

Increased performance in all three reactors was noted at COD loads below 5.0 - 6.0 kg/m^3.d. At these loads, COD removal efficiency was found to exceed 60 - 70 %, and ammonification was noted to be virtually complete. Additionally, comparing COD mass removals and COD removal efficiencies, it was observed that an increase in the COD load removal per unit volume of either reactor usually coincided with a slight deterioration of the COD removal efficiency. A sharp deterioration in the reactor performance at high COD loads was noted for all three reactors. However, signs of a progressive increase in the tolerance to higher loads were evident on days 75-78, at which time the experiment was terminated.

The anhybrid reactor, (R_3), partially packed with plastic rings, showed increased retention of the biological solids as compared to reactor R_2, (UASB). The volatile solids concentration in this reactor, (R_3), increased from 58%, on day 46, to 67%, on day 78. In comparison, a progressive increase in the mineral content of the biomass in R_2, (from 40%, on day 46, to 48%, on day 78), pointed to the gradual loss of active biological solids in this, (UASB), reactor. This phenomenon was previously discussed in Chapter 2, (literature review).

Performance of the three reactors may be compared using Table 4.2 . The best performance of the three reactors is summarized in

this table. It must be emphasized that, the data listed in Table 4.2 was selected from the whole run and does not represent a steady state performance. It is merely an illustration of the peak performance, (in terms of kg $COD_{rem}/m^3.d$), accomplished by

Table 4.2 - Best performance of the flow-through reactors in terms of the mass of COD removed, (non-steady state conditions).

Parameter	Reactor R_1	Reactor R_2	Reactor R_3
Day	52	66	64
COD Load ($kg/m^3.d$)	11.8	8.9	8.0
COD removed ($kg/m^3.d$)	5.5	4.2	4.2
COD removed per mass TS ($kg/kg.d$)	0.08	0.08	0.08
Ammonification ratio (%)	100+	61*	70*
NH_3-N (mg/L)	1620+	1260*	1600*
Free-NH_3 (mg/L)	28	17	28
TDS (g/L)	21.0	16.4	18.8

+ tested on day 54

* tested on day 66

the three reactors. In fact a progressive deterioration in all parameters was observed when the applied loads remained as high as those shown in Table 4.2 .

The COD loads removed per mass of total solids in the reactors were calculated and are presented in Table 4.2. At peak performance, the COD removals were found to approximately equal 0.08 kg/kg TS.d in all three reactors. However, based on this non-steady state comparison and considering the COD mass removals and the ammonification rates in the three flow-through reactors, reactor R_1, (UASB), containing 100% granular sludge, showed a better performance at higher loads than R_2, (UASB), and R_3, (anhybrid), which contained sludge samples with only 30% and 25% of the granular solids, respectively.

There was a threshold in performance evident above certain COD loadings in all three reactors. This indicated the existence of some inhibition. TDS was suspected to be the inhibitory component of the raw wastewater. This was based on the fact that the raw waste was found to be non-toxic with some not easily degradable components, and the COD loads used in this flow-through study were not excessive enough to cause metabolite inhibition.

4.2.2 Batch Studies

To further study the effects of TDS and to determine the level of its toxicity, three series of anaerobic batch reactors- with three different initial F/M ratios - were set up. Each series was comprised of ten batch reactors. Fig. 4.6 is a typical cumulative CH_4 production curve obtained in this study. The results from these batch anaerobic tests are directly applicable to the explanation of TDS and free-NH_3 toxicities and are, therefore, presented in the following sections which deal with toxicities due to TDS and free-NH_3.

4.3 TOXICITY AND INHIBITION

Toxicities due to heavy metals, sulfides, pH, volatile acids, total dissolved solids, and ammonia were discussed previously in detail in the literature review, (Chapter 2), and, therefore, will not be repeated in this section. However, in the following discussion, whenever warranted, references to the reviewed literature will be made.

Possible toxicities due to heavy metals, sulfides, and nitrates were investigated. It was concluded that these compounds posed no danger to the anaerobic digestion process stability in this study. Concentration of heavy metals and the sulfate concen-

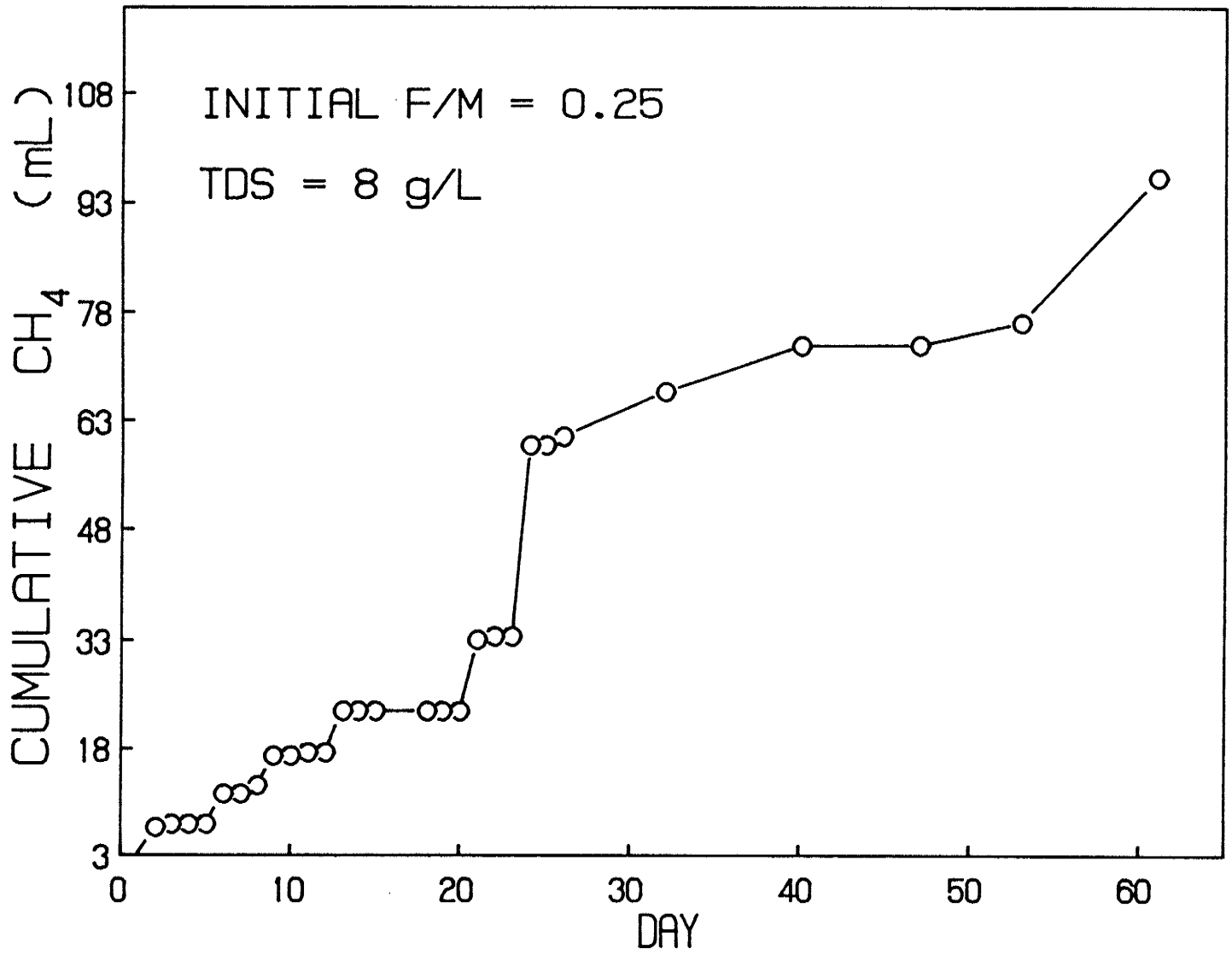

Fig. 4.6 **Typical cumulative methane production curve (batch studies)**

tration in a sample of diluted waste were found to be well below the toxic levels reported in the literature. The concentration of NO_3-N in the raw wastewater, (spent PMU), was measured to be virtually nil. Kugelman and Chin (5) have reported that NO_3-N is toxic above 50 mg/L concentrations.

To avoid the pH toxicity problem, the pH of the flow-through reactors were maintained in the optimum range of 6.8 - 7.4. This was accomplished by the daily measurement of the reactor pH, and if necessary, by the subsequent adjustment of the feed pH. For this purpose hydrochloric acid and the titration curves, (figures 4.1 and 4.2), developed in the preliminary investigation of the wastewater characteristics, were used.

To control the volatile acids toxicity, the VFA/ALK, (volatile fatty acids to alkalinity), ratio was kept below 0.5. This ratio gives an advance warning before trouble starts in the digester. When the ratio is below 0.5, loading and seed retention of the digester are under control. However, when the VFA/ALK ratio increases and becomes greater than 0.5, the digester is out of control and will eventually become "stuck" (81).

It may, therefore, be summarized that, initially in this study, the possible toxic effects of heavy metals, sulfides, nitrates, pH, and volatile acids were considered. The possibility

of toxicity due to heavy metals, sulfides, and nitrates was ultimately ruled out due to their low concentrations. In addition, the possibility of pH and volatile acids toxicity was eliminated by the frequent monitoring and a close control of the reactor pH and the volatile acids concentration, which were part of a scheduled operation and maintenance program. At this juncture, the possibility of toxicity due to total dissolved solids and ammonia-N had to be investigated in more detail. The analysis of the TDS and the NH_3-N data from both the flow-through and the batch anaerobic reactors are presented below.

4.3.1 Total Dissolved Solids Toxicity

A review of the literature dealing with total dissolved solids toxicity is contained in Chapter 2. The major finding of these studies (37,38,39,40,41) was that the TDS were, in general, inhibitory to microbial activity. In more specific terms, the results of a number of studies were presented in these papers (5,14,15,39,42) documenting the inhibitory effects of TDS in anaerobic biosystems.

In section 4.2.1, the effect of TDS on anaerobic treatment performance was discussed. As it was noted before, data from the flow-through studies clearly showed a drop in microbial activity, (G.P.), as the TDS levels rose, suggesting an inhibition due to TDS, (figures 4.3, 4.4, and 4.5). This observation was confirmed

by the data obtained from the subsequent batch studies, which were set up to further study the toxic effects of TDS, and to determine the level of its toxicity.

Fig. 4.7 shows the effects of TDS on methane production in the batch studies. Each point in this curve represents the L CH_4 $_{prod}$/g COD_{infl} obtained from the three series of anaerobic batch reactors, (each series with a different initial F/M loading). The most representative results for each TDS concentration from the three series of different initial loadings were selected. Inhibition starts almost immediately at 5 g/L of TDS. G.P. drops drastically until 8 g/L, gradually dropping from 8 to 13 g/L, before it levels off completely.

In section 4.2.1, (continuous flow studies), it was pointed out that TDS at concentrations above 17 g/L were inhibitory to the methanogenic bacteria. It is evident, from the difference in the toxicity threshold concentrations for the two types of anaerobic reactors, obtained in this study and detailed above, that inhibition occurs at higher TDS levels in the flow-through type reactors than in the batch type anaerobic reactors. According to Obayashi and Gorgan (1), continuous flow studies permit the evaluation of reduced toxicity that may result from acclimation to the inhibitory substances. In comparison, anaero-

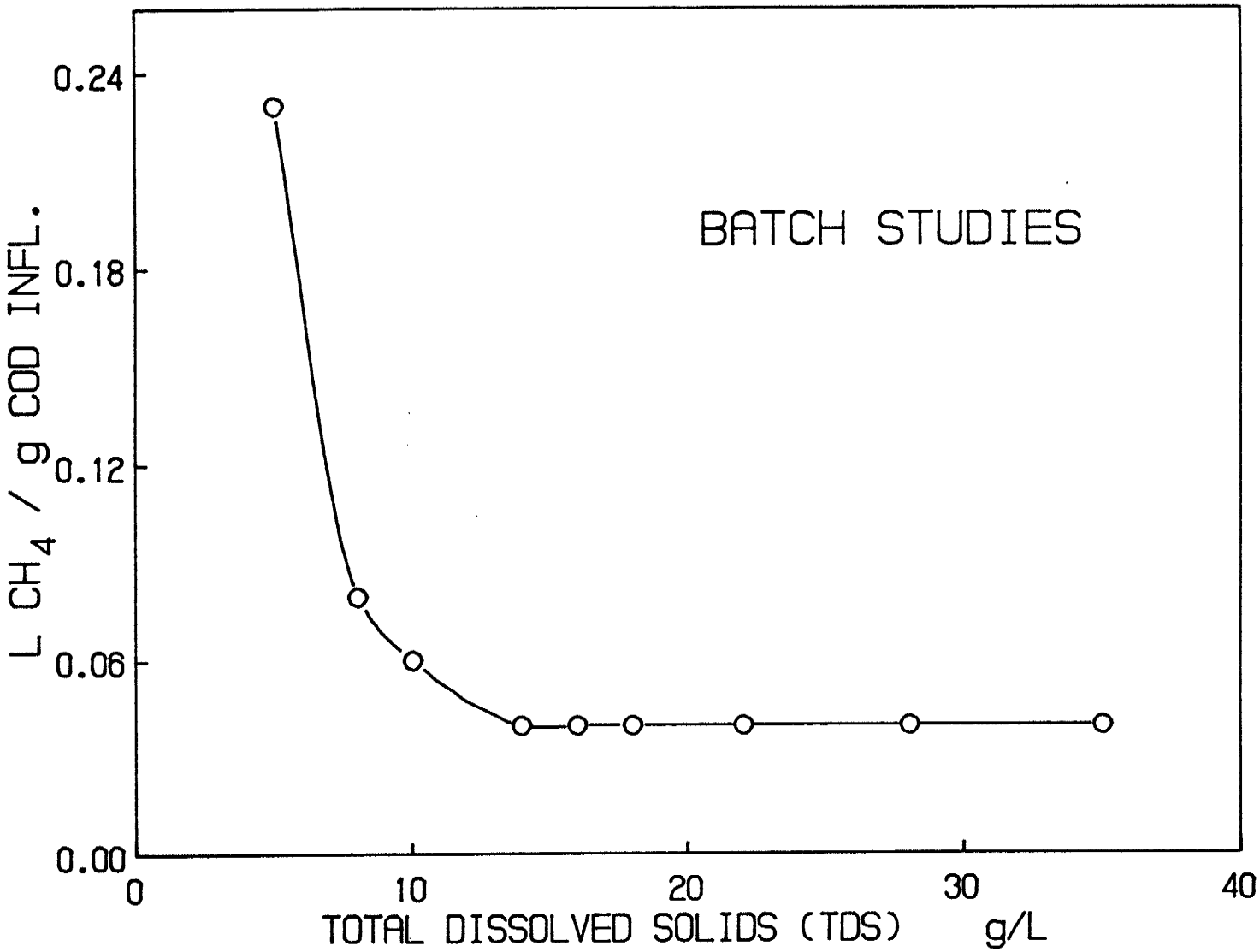

Fig. 4.7 Effect of TDS on methane production (batch studies)

bic batch studies produce a more conservative value of the toxicity threshold concentration. The reason for the occurrence of TDS toxicity at higher levels in the flow-through reactors may, therefore, be due to the acclimation of methanogens to the higher TDS levels in this type of reactors.

The results from this study are comparable to the inhibitory TDS concentrations reported in the literature. For example, as mentioned in Chapter 2, Davis et al. (39) reported a TDS concentration of 13 g/L as being severely toxic to the anaerobic methanogenesis. Fig. 4.8 is a plot of TDS and G.P. data from both the batch and the continuous flow reactors. Fig. 4.8 shows a negative correlation between the methane production, expressed in terms of L CH_4/g COD_{infl}, and TDS concentration in the reactors. As shown in this graph, the CH_4 production drops with the increased TDS concentrations, and an inhibition threshold is evident above 10 g/L of TDS.

Chapter 2, (literature review), included a list of studies (14,15,42,43,44,45,46,47) that have documented evidences of microbial acclimation to high TDS levels. Fig. 4.8 above does not, however, show the effects of a prolonged contact with TDS on the increased tolerance of methanogens to total dissolved solids, (i.e. the acclimation effect), under anaerobic conditions. Results from the batch BMP study (79), conducted in parallel to this study, are plotted in Fig. 4.9 and illustrate the effects of

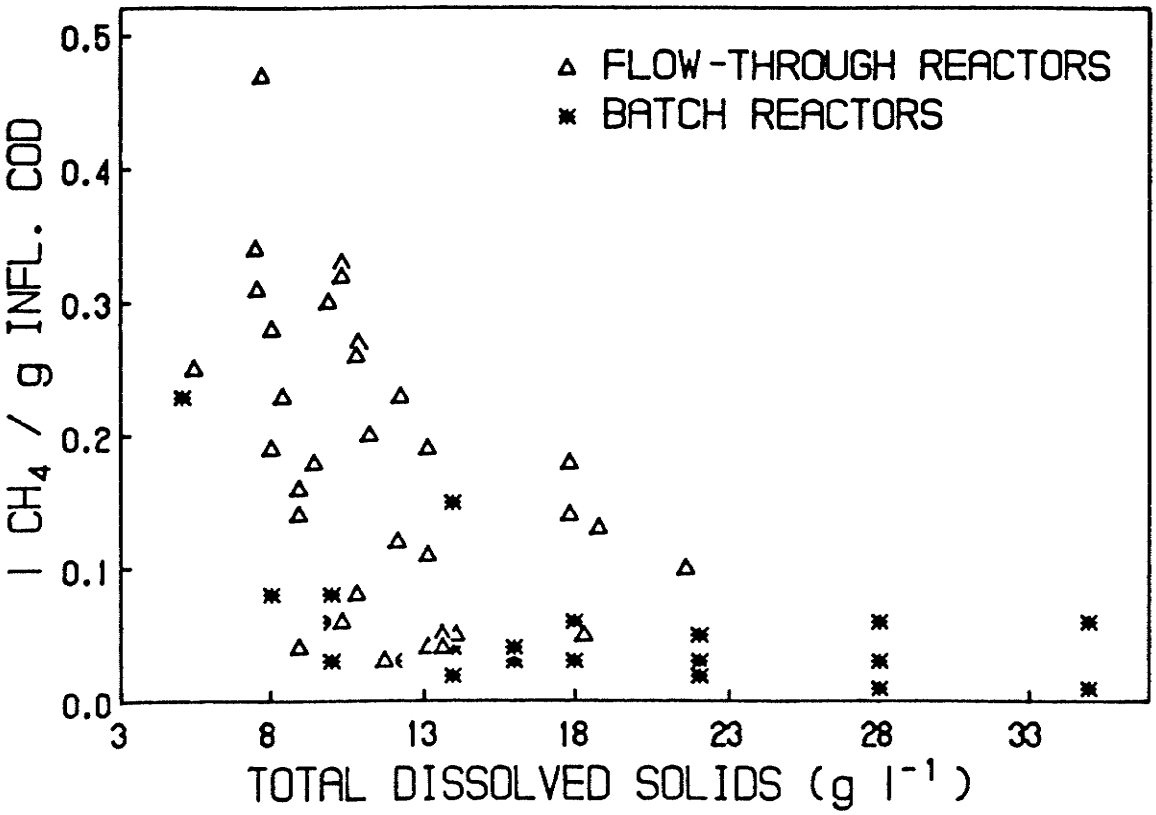

Fig. 4.8 Effect of TDS on methane production per mass of incoming COD (flow-through and batch studies)

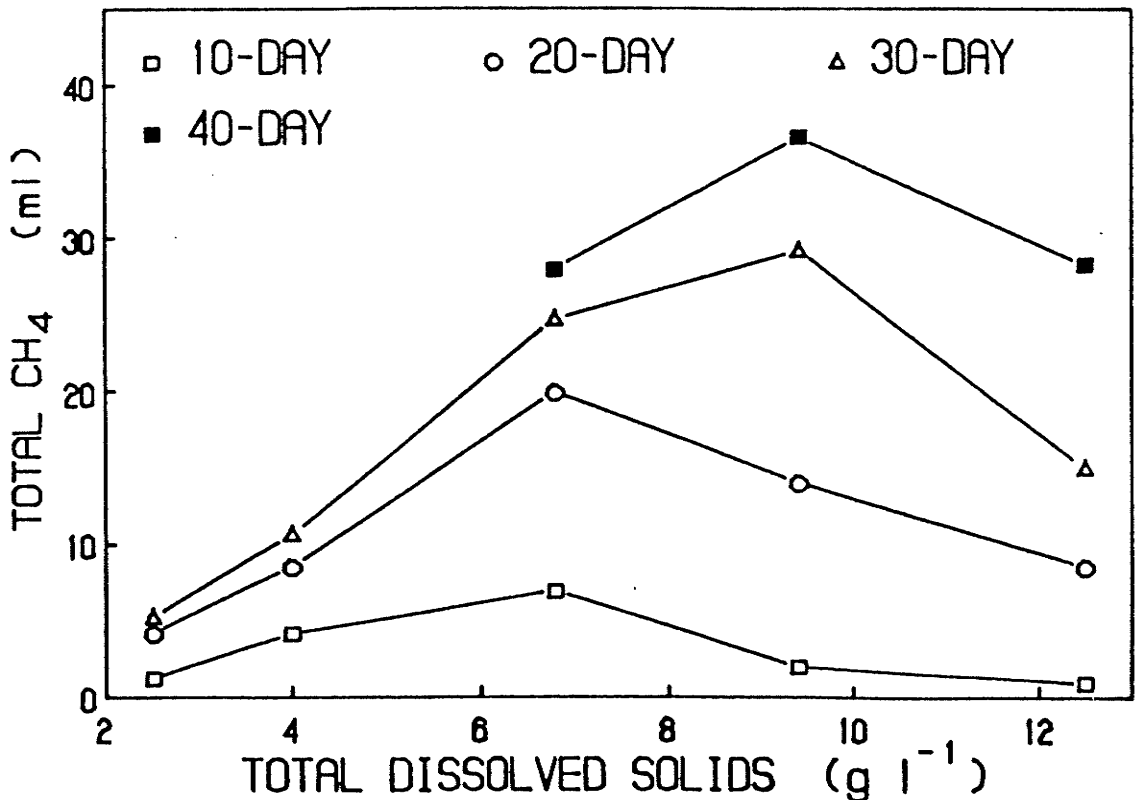

Fig. 4.9 Cumulative methane production versus TDS concentration

TDS and incubation time on methane production from the raw wastewater.

In the above study (79), samples with varying amounts of wastewater, and the corresponding TDS concentrations, were incubated for a 40 day period. Methane production was monitored on day 10, 20, 30, and 40. Each concentration was tested in triplicate. Fig. 4.9 shows the arithmetically averaged results. This graph shows an increase in TDS level at the peak of methane generation as the incubation progresses.

In this study (79) the inhibition threshold increased from 7 g/L at 10, and 20 days to approximately 10 g/L after 40 days incubation. This indicates a progressive acclimation to TDS, in proportion to the contact time, of the static bioassay environment. The data in Table 4.1, (flow-through reactors), shows the feasibility of methanogenesis at twice these TDS concentrations.

The raw wastewater was tested for calcium and magnesium ion concentrations. Concentrations of these two ions in spent PMU were found to be 3.64 mg/L and 165.8 mg/L, respectively. These concentrations are well below the toxic levels reported in the literature, (Table 2.2). In this study, TDS in the wastewater was mainly due to the sodium ion, which was thought to be the main inhibitory component of TDS. This ion is contributed by sodium

hydroxide and sodium carbonate, which are added to wastewater in the manufacturing process.

4.3.2 Free-Ammonia Toxicity

Toxicity due to ammonia nitrogen, (NH_3-N), was discussed in Chapter 2. Results of many studies in the literature (3,7,8,14,16,42), (48,49,50,51,52,53), and (55,56,57,58,59,60), discussing the ammonia toxicity, together with their reported toxic NH_3-N levels, were also presented in Chapter 2.

As ammonification was found to be virtually complete in all three flow-through reactors, it was deemed necessary to investigate the possibility of NH_3-N toxicity. Koster and Lettinga (3), studying the effects of ammonia toxicity, have reported nitrogen concentrations as mg/L of "ammonium ion". In this report, this is assumed to mean "total ammonia nitrogen", as defined in APHA (36). Van Velsen (16), and Koster and Lettinga (3) found that 1700 mg/L of NH_3-N was the threshold toxicity level for CH_4 production. In this study, however, methane production was achieved at NH_3-N concentrations above 1700 mg/L in R_1, above 1200 mg/L in R_2, at 1600 mg/L in R_3, and at 808 mg/L in the batch reactors.

Importance of pH in NH_3 toxicity was emphasized in Chapter 2, (literature review). Inhibition due to free-NH_3 is widely docu-

mented (7,8,14,16,48,52,56,57,59) in the literature. To illustrate the effect of free-NH_3 on CH_4 production, using a pH of 7.75, a temperature of 30° C, and equation 2.11, the ammonia concentrations reported by Koster and Lettinga (3) were converted to the corresponding free-ammonia concentrations. These results are shown in Fig. 4.10. A negative correlation was obtained between CH_4 production and free-NH_3 concentration, with CH_4 generation decreasing rapidly from 130 mL/h, at 30 mg/L of free-NH_3, to less than 20 mL/h, at free-NH_3 concentrations above 70 mg/L.

In this study, free-NH_3 levels in both the flow-through and the batch reactors, were well below the toxic levels cited above. The maximum free-NH_3 concentration was 30 mg/L for the flow-through reactors, and 66 mg/L for the batch reactors. However, a plot of the average volume of methane produced per reactor versus the free-NH_3 concentration for the batch reactors, (Fig. 4.11), showed a similar type of a curve as in Fig. 4.10. Methane production per reactor dropped from almost 48 ml, at a free-NH_3 concentration of 21 mg/L, down to 42 ml, at a free-NH_3 concentration of 67 mg/L.

For the flow-through reactors, at a pH of 7.2 and a temperature of 35°C, the maximum total NH_3-N concentration of

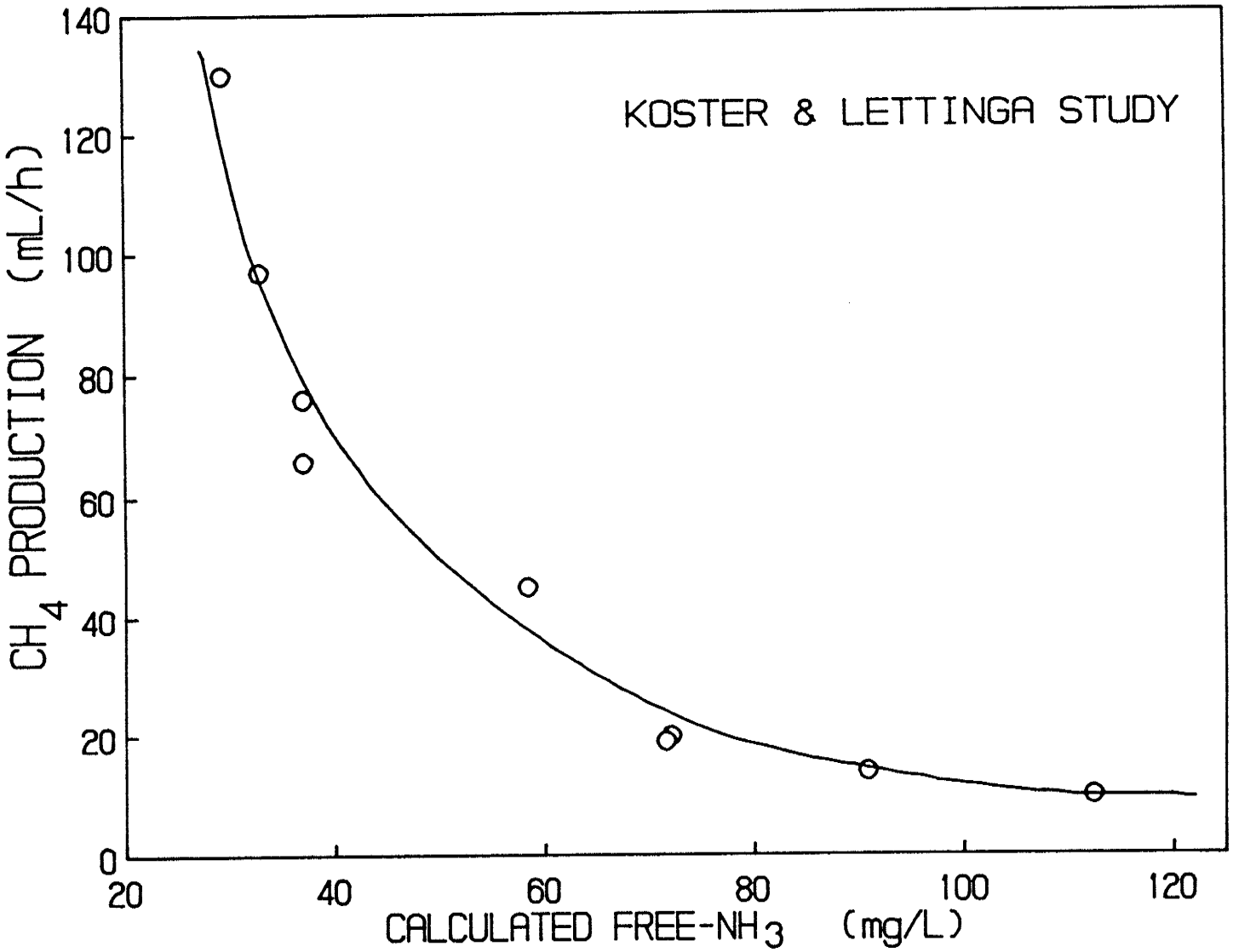

Fig. 4.10 Effect of free-ammonia on methane production (Koster and Lettinga (3) study)

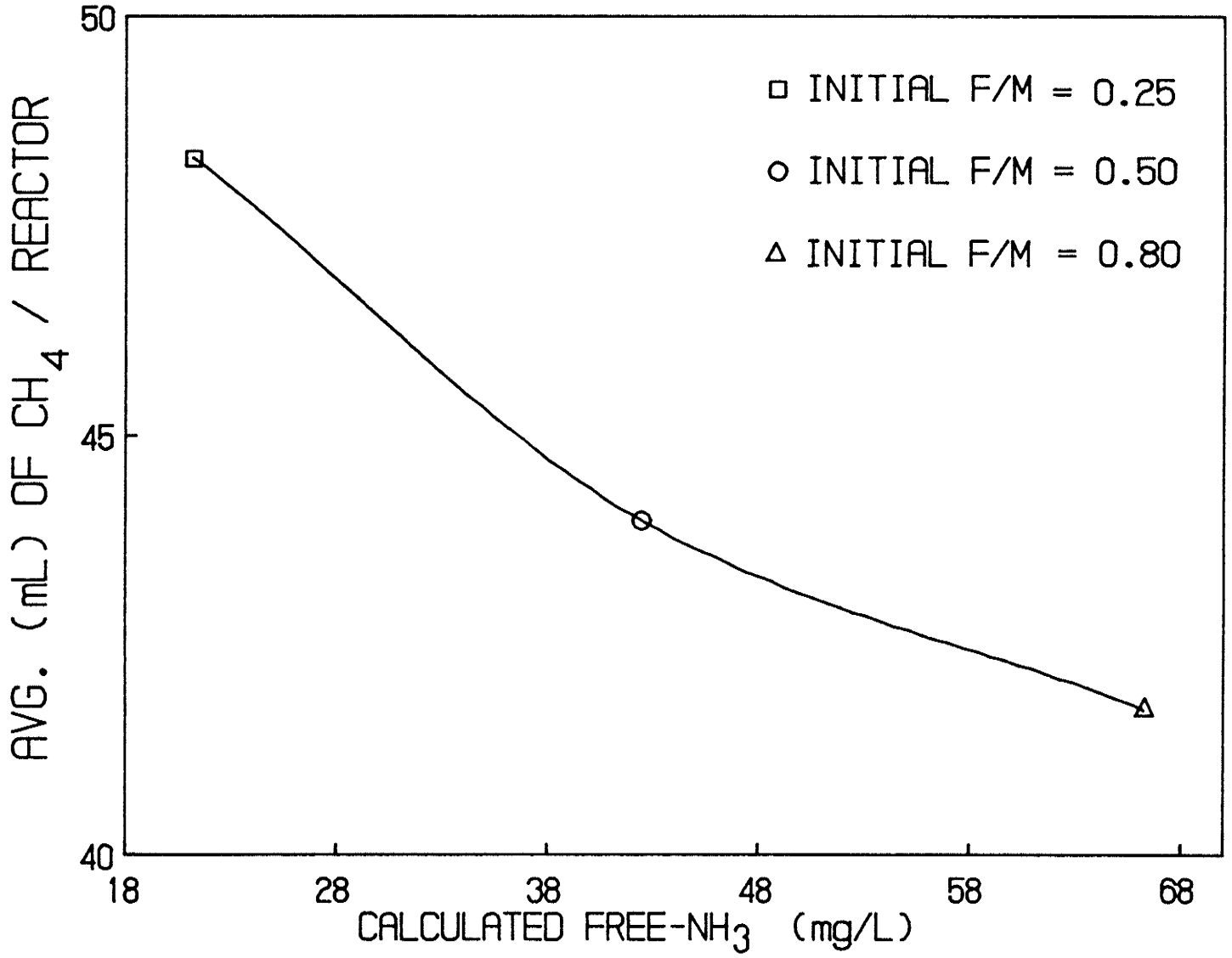

Fig. 4.11 **Effect of free-ammonia on methane production (batch study)**

1740 mg/L, (a toxic concentration), corresponds to a maximum free-NH_3 concentration of 30 mg/L, (well below the toxic levels). This explains the reason for the continued generation of methane at total NH_3 concentrations in excess of 1700 mg/L, and illustrates the importance of pH in ammonia toxicity.

CHAPTER 5

SUMMARY AND CONCLUSIONS

An engineering study was conducted on anaerobic ammonification of a pharmaceutical industry effluent containing high concentrations of TDS, TOC, and TKN. The study included preliminary bioassay tests, separate biomethanation potential tests, batch reactor experiments, and flow-through anaerobic reactors, (two upflow sludge bed reactors and a combination hybrid reactor comprising of a sludge bed and a media zone). The study duration did not allow for development of steady state conditions in the flow-through reactors, as the continuously increased COD load created transient conditions. Several conclusions can be drawn from this study:

1. Conversion of organic nitrogen to ammonia nitrogen, (ammonification), for both flow-through and batch reactors was accomplished at a wide range of loads;

2. The ammonification process could be monitored by methane production, as a drop in ammonification coincided with the decreased generation of methane;

3. Process upsets affected both the COD removal and the ammonification efficiencies;

4. Accommodation of target COD loads in excess of 10 $kg/m^3.d$ could not be accomplished in the course of this study. Satisfactory performance in terms of COD removal ratio and ammonification rates were attained by R_1 at 5.1 $kg/m^3.d$ COD loading, (50% $COD_{rem.}$, 89% NH_3-conv.); by R_2 at 6.6 $kg/m^3.d$ COD loading, (60% $COD_{rem.}$, 100% NH_3-conv.); and by R_3 at 4.3 $kg/m^3.d$ COD loading, (60% $COD_{rem.}$, 95% NH_3-conv.);

5. Best performance data showed that reactor R_1, (a UASB type reactor containing 100% granular sludge), was the best performer. R_1 achieved higher COD mass removals and ammonification rates at higher COD loads than the other two reactors, R_2 and R_3;

6. Possibility of toxicity due to heavy metals, sulfides, and nitrates was ruled out due to their low concentrations. Possibility of pH and volatile acids toxicity was eliminated by the frequent monitoring and a close control of the reactor pH and the volatile acids concentration;

7. Performance, in terms of methane generation and COD removal, appeared to be primarily affected by the total dissolved solids, (TDS), levels. TDS was inhibitory to methanogenesis and ammonification at concentrations over 17 g/L in the flow-through reactors and at concentrations in excess of 10 g/L in the batch reactors;

8. The above inhibition thresholds translate to the minimum recommended dilution of 1:6.7 for the anaerobic treatment of this wastewater;

9. Acclimation time increased the tolerance to the total dissolved solids content. Prolonged acclimation may, therefore, allow lower dilutions;

10. Due to the maintenance of pH near neutral conditions, the free-ammonia inhibition was found to be insignificant in this study;

11. A separate anaerobic pretreatment, prior to the discharge of this waste into the city sewer, was found to be feasible;

12. TDS and free-ammonia toxicities dictate significant operational constraints for the anaerobic stabilization of this industrial waste. The possibility of TDS and free-ammonia toxicity must be considered in any successful treatment of this wastewater. It is, therefore, recommended that the above conclusions regarding acclimation, pH control, the minimum dilution, the COD loading limits, and the TDS threshold concentrations be considered in the future design and operation of any full-scale anaerobic digesters, treating this pharmaceutical wastewater.

REFERENCES

(1) Obayashi, A.W., Gorgan, J.M., Management of Industrial Pollutants by Anaerobic Processes, US EPA, (1985).

(2) Malina, J.F., Manual of Wastewater Treatment, The Texas Water Utilities Association, 335-363, (1983).

(3) Koster, I.W., Lettinga, G., "The Influence of Ammonium-Nitrogen on the Specific Activity of Pelletized Methanogenic Sludge", Agric. Wastes, Vol.9 , 205-216, (1984).

(4) Parkin, G.F., Owen, W.F., "Fundamentals of Anaerobic Digestion of Wastewater Sludges", J. Env'l Eng. Div., ASCE, Vol.112, No.5, 867-920, Oct., (1986).

(5) Kugelman, I.J., Chin, K.K., "Toxicity, Synergism, and Antagonism in Anaerobic Waste Treatment Processes", Anaerobic Biological Treatment Processes, Advances in Chemistry Series, Vol.105, American Chemical Society, (1971).

(6) Speece, R.E., "Anaerobic Biotechnology for Industrial Wastewater Treatment", Env'l Sci. & Tech., Vol.17, No.9, 416A-427A, (1983).

(7) McCarty, P.L., "Anaerobic Waste Treatment Fundamentals: I. Chemistry and Microbiology; II. Environmental Requirements and Control; III. Toxic Materials and their Control; IV. Process Design", Public Works, No.9-12, Sept.-Dec., (1964).

(8) Kroeker, E.J., Schulte, D., Sparling, A.B., Lapp, H.M., "Anaerobic Treatment Process Stability", J. Wat. Poll. Con. Fed., Vol.51, No.4, 718-727, Apr., (1979).

(9) Kotze, J.P., et al., "A Biological and Chemical Study of Several Anaerobic Digesters", Wat. Res., Vol.2, p.195, (1968).

(10) Parkin, G.F., Speece, R.E., Yang, J., Kocher, M., "Response of Methane Fermentation to Industrial Toxicants", 53rd Annual WPCF Conference, Las vegas, Nevada, Sept., (1980).

(11) Yang, J., Speece, R.E., Parkin, G.F., Gossett, J., Kocher, W., "The Response of Methane Fermentation to Cyanide and Chloroform", Prog. Wat. Tech., Vol.12, 977-989, (1980).

(12) Parkin, G.F., Kocher, W.M., "Microbial Methane Fermentation Kinetics for Toxicant Exposure", Nat. Sci. Found. Wat. Res., Urban and Environmental Engineering Program, Pennsylvania, Jul., (1980).

(13) Parkin, G.F., Kocher, W.M., "Microbial Fermentation Kinetics for Toxicant Exposure", The Air Force Office of Scientific Research, Pennsylvania, Sept., (1980).

(14) McCarty, P.L., McKinney, R.E., "Salt Toxicity in Anaerobic Digestion", J. Wat. Poll. Con. Fed., Vol.33, 399-415, (1961).

(15) Kugelman, I.J., McCarty, P.L., "Cation Toxicity and Simulation in Anaerobic Waste Treatment", J. Wat. Poll. Con. Fed., Vol.37, 97-116, (1965).

(16) Van Velsen, A.F.M., "Adaptation of Methanogenic Sludge to High Ammonia Concentrations", Wat. Res., Vol.13, p.995, (1979).

(17) Speece, R.E., Parkin, G.F., "The Response of Methane Bacteria to Toxicity", 3rd International Symposium on Anaerobic Digestion, Boston, (1983).

(18) McKinney, R.E., Microbiology for Sanitary Engineers, McGraw-Hill Book Co. Inc., U.S.A., (1962).

(19) Ghosh, S., "Anaerobic Processes", J. Wat. Poll. Con. Fed., Vol.44, 948-959, (1972).

(20) Mosey, F.E., "Assessment of the Maximum Concentration of Heavy Metals of Crude Sludge which will not Inhibit the Anaerobic Digestion of Sludge", Wat. Poll. Con., Vol.75, p.10, (1976).

(21) Lawrence, A.W., McCarty, P.L., "The Role Of Sulfide in Preventing Heavy Metal Toxicity in Anaerobic Treatment", J. Wat. Poll. Con. Fed., Vol.37, p.392, (1965).

(22) Masselli, J.W., Masselli, N.W., Burford, M.G., "Sulfide Saturation for Better Digester Performance", J. Wat. Poll. Con. Fed., Vol.39, p.1369, (1967).

(23) Culp/Wesner/Culp, "The Submerged Media Anaerobic Reactor in Municipal Wastewater Treatment", U.S. Dept. of Energy, Argonne National Laboratory, (1981).

(24) Hayes, T.D., Theis, T.L., "Digestion of Heavy Metals in Anaerobic Digestion", J. Wat. Poll. Con. Fed., Vol.50, p.61, (1978).

(25) DeWalle, F.B., Chain, E.S.K., Brush, J., "Heavy Metal Removal with a Completely Mixed Anaerobic Filter", J. Wat. Poll. Con. Fed., Vol.51, p.22, (1979).

(26) Process Design Manual for Sludge Treatment and Disposal, US EPA, Office of Technology Transfer, (1979).

(27) Lawrence, A.W., McCarty, P.L., Guerin, F.J.A., "The Effects of Sulfides on Anaerobic Treatment", Proceedings of the 19th Purdue Industrial Waste Conference, West Lafayette, Ind., p.343, (1964).

(28) Buswell, A.M., "Important Considerations in Sludge Digestion II-Microbiology and Theory of Anaerobic Digestion", Sew. Works J., Vol.19, p.28, (1947).

(29) Schlenz, H.E., "Important Considerations in Sludge Digestion I-Practical Aspects" Sew. Works J., Vol.19. p.19, (1947).

(30) McCarty, P.L., Kugelman, I.J., Lawrence, A.W., "Ion Effects in Anaerobic Digestion", Tech. Rept. No.33, Dept. of Civil Eng., Stanford University, (1964).

(31) Buswell, A.M., Morgan, B.G., "Paper Chromatographic Methods for Volatile Acids", Proceedings of the 17th Purdue Industrial Waste Conference, West Lafayette, Ind., p.377, (1962).

(32) Andrews, J.F., "Dynamics Model of the Anaerobic Digestion Process", J. San. Eng. Div., ASCE, (SA1), 95, (1969).

(33) Brune, D.E., "C:N Ratio and Anaerobic Digestion" M.S. Thesis, University of Missouri, (1975).

(34) Heyes, R.W., Hall, R.J., "Anaerobic Digestion Modelling-The Role of H_2", Biotech. Letters, Vol.3, P.431, (1981).

(35) Peavy, H.S., Rowe, D.R., Tchobanoglous, G., Environmental Engineering, McGraw Hill Book Co. Inc., U.S.A. (1985).

(36) APHA/AWWA/WPCF, Standard Methods for the Examination of Water and Wastewater, APHA, N.Y., (1980).

(37) Tokuz, R.Y., Eckenfelder, W.W., "The Effect of F:M Ratio on an Activated Sludge System Treating High Salinity Wastewater", Proceedings of the 33rd Purdue Industrial Waste Conference, West Lafayette, Ind., 200-203, (1978).

(38) Petros, J.k., Davis, E.M., "Organic Degradation by Biological Treatment of Hypersaline Wastewaters", Proceedings of the 31st Purdue Industrial Waste Conference, West Lafayette, Ind., 132-138, (1976).

(39) Davis, E.M., Bishop, J.R., Guthrie, R.K., "Microbial Behavior in Hypersaline Wastes: Effects on BOD and Degradablity", Proceedings of the 33rd Purdue Industrial Waste Conference, West Lafayette, Ind., 457-463, (1978).

(40) Kincannon, D.F., Gaudy, A.F., "Sequential Substrate Removal After Change in Salt Concentration", Biotech. & Eng., Vol.8, p.371, (1966).

(41) Kincannon, D.F., Gaudy, A.F., "Some Effects of High Salt Concentrations on Activated Sludge", J. Wat. Poll. Con Fed. 38(7), 1148-1159, (1966).

(42) De Baere, L.A., Devocht, M., Van Assche, P., and Verstraete, W., "Influence of High NaCl and NH_4Cl Salt Levels on Methanogenic Associations", Water Res., Vol.18, No.5, 543-548, (1984).

(43) Abram, J.W., Nedwell, D.B., "Inhibition of Methanogenesis by Sulfate-reducing Bacteria Competing for Transferred Hydrogen", Arch. Microbio., Vol.117, 89-92, (1978).

(44) Paterek, J.R., Smith, P.H., "Isolation and Characterization of a Halophilic Methanogen from Great Salt Lake", Appl. & Env'l Micr., Vol.50, No.4, 877-881, (1985).

(45) Mathrani, I.M., Boone, D.R., "Isolation and Characterization of a Moderately Halophilic Methanogen from a Solar Saltern", Appl. & Env'l Micr., Vol.50, No.1, 140-143, (1985).

(46) Shafai, S., Oleszkiewicz, J.A., Hooper, G.D., "Anaerobic Treatment of High Nitrogen, High TDS Industrial Wastes", Proceedings of the 41st Purdue Industrial Waste Conference, West Lafayette, Ind., (1986).

(47) Gamal-El-Din, "Biogas from Organic Waste Diluted with Seawater", International Conference on the State of The Art on Biogas Technology, Transfer and Diffusion, Cairo, Egypt, 417-423, NOv., (1984).

(48) Zeeman, G., Wiegant, W.M., Koster-Treffers, M.E., Lettinga, G., "The Influence of the Total Ammonia Concentration on the Thermophilic Digestion of Cow Manure", Agric. Wastes, Vol.14, 19-35, (1985).

(49) Gramms, L.C., Polkowski, L.F., Witzel, S.A., "Anaerobic Digestion of Farm Animal Wastes", Trans. of the ASAE, Vol.14, 7-13, (1971).

(50) Lapp, H.M., Schulte, D.D., Kroeker, E.J., Sparling, A.B., Topnic, B.H., "Start-up of Pilot Scale Swine Manure Digesters for Methane Production", Managing Livestock Wastes, ASAE, St. Joseph, MI, 243, 234-237, (1975).

(51) Fischer, J.R., Sievers, D.M., Fulhage, C.D., "Design Criteria and Operational Guidelines for a Pilot-scale Anaerobic Digester", Resource Recovery and Conservation, Vol.4, 1-11, (1979).

(52) Stevens, M.A., Schulte, D.D., "Low Temperature Anaerobic Digestion of Swine Manure", J. Env'l Eng. Div., ASCE, Vol.105, 33-42, (1979).

(53) Converse, J.C., Evans, G.W., Robinson, K.L., Gibbons, W., Gibbons, M., "Methane Production from a Large-size On-farm Digester for Poultry Manure", Livestock waste: A Renewable Resource, ASAE, St. Joseph, MI, 122-125, (1981).

(54) Hashimoto, A.G., "Ammonia Inhibition of Methanogenesis from Cattle Wastes", Agric. Wastes, Vol.17, 241-261, (1986).

(55) Hobson, P.N., Shaw, B.G., "Inhibition of Methane Production in Methanobacterium Formicicum", Wat. Res., Vol.10, p.849, (1976).

(56) Webb, A.R., Hawkes, F.R., "The Anaerobic Digestion of Poultry Manure: Variation of Gas Yield with Influent Concentration and Ammonia-nitrogen Levels", Agric. Wastes, Vol.14, 135-156, (1985).

(57) Sathananthan, s., "Ammonia Toxicity in Anaerobic Digesters", M.S. Dissertation, University of Newcastle-Upon-Tyne, (1981).

(58) Kroiss, H., Wabnegg, F., "Testing Method to Characterize Anaerobic Sludge and Anaerobic Removal of Substrate", Technical University of Vienna, Austria, (1983).

(59) Ripley, L.E., Kmet, N.M., Boyle, C., Converse, J.C., "The Effects of Ammonia Nitrogen on the Anaerobic Digestion of Poultry Manure", Proceedings of the 39th Purdue Industrial Waste Conference, West Lafayette, Ind., 73-80, (1984).

(60) Nurski, J., "The Third Kingdom", Science Dimension, 17-23, May, (1985).

(61) Van Velsen, A.F.M., "Anaerobic Digestion of Piggery Waste", 2. Start-up Procedure, Neth. J. Agric. Sci., 27, 142-152, (1979).

(62) Parkin, G.F., Miller, S.W., "Response of Methane Fermentation to Continuous Addition of Selected Industrial Toxicants", Proceedings of the 37th Purdue Industrial Waste Conference, West Lafayette, Ind., (1982).

(63) Lettinga, G., "Direct Anaerobic Treatment Handles Waste Effectively", Ind. Wastes, Vol.53, 18-24, (1979).

(64) Lettinga, G., Van Velsen, A.F., Hobma, S.W., de Zeeuw, w., Klapwijk, A., "Use of the Upflow Sludge Blanket (UASB) Reactor Concept for Biological Wastewater Treatment", Biotech. Bioeng., Vol.22, 699-734, (1980).

(65) Fernandes, X.A., Cantwell, A.D., Mosey, F.E., "Anaerobic Biological Treatment of Sewage", Wat. Poll. Con., 99-110, (1985).

(66) Lettinga, G., Vinken, J.N., "Feasibility of the Upflow Anaerobic Sludge Blanket (UASB) Process for the Treatment of Low Strength Wastes", Proceedings of the 35th Purdue Industrial Waste Conference, West Lafayette, Ind., (1980).

(67) Lettinga, G., Van Velsen, A.F., de Zeeuw, W., Hobma, S.W., "Feasibility of the Upflow Anaerobic Sludge Blanket (UASB) Process", Env'l Eng., 35-45, (1979).

(68) Heertjes, P.M., van der Meer, R.R., "Dynamics of Liquid Flow in an Upflow Reactor Used for the Anaerobic Treatment of Wastewater", Biotech. Bioeng., Vol.20, 1577-1594, (1978).

(69) Young, J.C., McCarty, P.L., "The Anaerobic Filter for Waste Treatment", Dept. of Civil Eng., Stanford University, Technical Report No.87, (1968).

(70) Jennet, J.C., Dennis, N.D., "Anaerobic Filter Treatment of Pharmaceutical Waste", J. Wat. Poll. Con. Fed., Vol.47, 104-121, (1975).

(71) Sachs, E.F., Jennet, J.C., Rand, M.C., "Anaerobic Treatment of Synthesized Organic Chemical Pharmaceutical Wastes", Proceedings of the 33rd Purdue Industrial Waste Conference, West Lafayette, Ind., (1978).

(72) Obayashi, A.W., Roshanravan, M., Illinois Institute of Technology, Chicago, Ill., (1980).

(73) Witt, E.R., Humphrey, W.J., Roberts, T.F., "Full-Scale Anaerobic Filter Treats High Strength Wastes", Proceedings of the 34th Purdue Industrial Waste Conference, West Lafayette, Ind., (1979).

(74) Duncan, Langanese & Associates, (DLA), Anaerobic Treatment and Energy Recovery, International Seminar, DLA Inc., Pittsburgh, Phil., Nov., (1981).

(75) Shafai, S., Oleszkiewicz, J.A., "Anaerobic Pretreatment of Concentrated Pharmaceutical Wastes", Env'l Tech. Letters, (1987).

(76) Owen, W.F., Stuckey, D.C., Healy, J.B., Young L.Y., McCarty P.L., "Bioassay for monitoring Biochemical Methane Potential and Anaerobic Toxicity", Wat. Res., Vol.13, 485-492, (1979).

(77) Jeris, J.S., McCarty, P.L., "The Biochemistry of Methane Fermentation Using C14 Tracers", J. Wat. Poll. Con. Fed., Vol.37, 178-186, (1965).

(78) Stuckey, D.C., Owen, W.F., Parkin, G.F., McCarty, P.L., "Anaerobic Toxicity Evaluation and Semi-continuous Assays", J. Wat. Poll. Con. Fed., Vol.52, 720-729, (1980).

(79) MacLaren Engineers Inc., The Sewage Collection and Treatment Facilities in the City of Brandon, Manitoba, Appendices, Report to MWSB, Brandon, Man., June, (1986).

(80) DeLallo, R., Albertson, O.E., "Volatile Acids by Direct Titration", J. WAT. POLL. CON. FED., Vol.33, No.4, 356-365, Apr., (1961).

(81) Kerri, K.D., Operation of Wastewater Treatment Plants, 2nd Ed., Vol.II, CSU, Sacramento, US EPA, (1980).

APPENDIX A

pH TITRATION

TABLE A.1 pH TITRATION, RAW WASTEWATER

pH	mL TITRANT(1:10 1N HCl)
10.2	0.0
10.0	1.3
9.5	5.0
9.0	7.5
8.5	10.5
8.0	12.5
7.5	14.0
6.8	15.0
6.5	19.5
6.0	24.0
5.5	26.0
5.0	27.0
4.5	28.0
4.0	29.0
3.0	30.0
2.0	32.5

TABLE A.2 pH TITRATION, DILUTED WASTEWATER (1:6.2)

pH	mL TITRANT(1:10 1N HCl)
10.2	0.0
10.0	0.4
9.5	1.0
8.9	1.7
8.4	2.2
8.0	2.4
7.3	2.7
6.8	3.0
6.6	3.5
6.1	4.0
5.8	4.4
4.9	4.7
3.8	5.0
2.7	5.3
2.0	5.5
1.3	6.5

APPENDIX B

LABORATORY TESTING AND ANALYSIS RESULTS

(FLOW-THROUGH REACTORS)

TABLE B.1(a) LABORATORY TESTING AND ANALYSIS RESULTS, R_1

DAY	G.P. (L/d)	FLOW (mL/d)	pH In-Out		ALK-VFA (mg/L)		VFA/ALK	GAS COMP CH_4-CO_2-N_2
1			10.2	9.1				
2								
3		905						
4		1021			4520	1335	0.30	
5		1656						
6		1440			5080	1425	0.28	
7		1920		8.1				
8		2249		8.2				
9		2021			5650	1935	0.34	
10		1218		8.2				
11		1244		8.3	5590	1740	0.31	
12		1231		8.2				
13				8.1	5320	1485	0.28	
14		1416	7.5	8.2				
15								
16								
17								
18		3555		7.6				
19				8.3				62 8 30
20		1062						
21		1632		7.8				
22		1165	5.7	7.8				80 15 5
23		633						
24								
25								
26		400		7.7				
27	1.0	1646		7.5				
28	0.6	1572		7.5				
29	0.9	2000		7.5	3860	945	0.24	60 30 10
30	1.0	1840	6.0	7.2				
31	1.0	1715		7.6				
32	1.3	1959	6.0	7.0				
33	1.4	2031		7.5				
34	1.3	1879		7.2				
35	1.1	1920		7.1				
36	1.0	1975		7.7				
37		2117		7.1	2800	500	0.27	60 25 10
38	1.2	1996	6.5	7.2				
39	2.0	2030		7.1				
40	2.8	3840		7.8				
41	2.9	2123		7.3				
42	4.7	2070		7.2				
43	3.5	1675	6.0	7.3	3360	200	0.09	65 25 5
44	3.3	1606		7.3				
45	4.7	1990		7.2				

TABLE B.1(a) (Continued)

DAY	G.P. (L/d)	FLOW (mL/d)	pH In-Out		ALK-VFA (mg/L)		VFA/ALK	GAS COMP CH_4-CO_2-N_2
46	5.2	2850		7.2				
47	5.3	2133	6.0	7.7				
48	5.1	2655		7.7				
49	5.8	2523		7.2				
50	5.3	2445	5.5	7.6				
51	5.6	2700		7.2				
52	8.9	2550		7.3				
53	8.0	2850		7.4				60 30 0
54	6.6	2618		7.2				
55	6.2	2770		7.4	5400	870	0.16	
56	5.2	2817	5.5	7.3				
57	4.3	2487		7.1	5200	1170	0.23	65 30 0
58	4.8	2742		7.0				
59	3.7	2734	5.5	7.2				
60	3.2	2585		7.2				
61	3.5	2590		7.1				
62	3.3	2410		7.0				
63	3.1	2837		7.0				
64	2.9	2784		7.0				45 25 0
65	2.3	2816		7.0				
66	1.3	1960		7.2				
67	1.0	1900		7.3	4200	1770	0.42	
68	0.9	2810	5.5	7.3				
69	1.6	3333		7.0				
70		3190		6.8				
71		3550		6.6				40 50 5
72		3460		6.9				
73		3640	5.5	6.8				
74	2.8	3550		6.8				
75	1.6	3200		7.1				
76	2.0	3580		7.1				
77	2.7	3620		7.2				
78	3.1	3480		7.3				
79	2.9		5.5	7.5				

NOTE : gas composition expressed in (%)

TABLE B.1(b) LABORATORY TESTING AND ANALYSIS RESULTS, R_1

DAY	LOAD ($kgCOD/m^3.d$)	TOC (mg/L)	TOC-REM (mg/L)	%COD-REM	TDS (g/L)	TKN (mg/L)	NH_3 (mg/L)	NH_3/TKN (%)
1								
2								
3								
4								
16								
17								
18	8.4	2274	978	43	10.7			
19								
20								
21								
22								
23								
24		2750	450	16				
25								
26								
27	4.9	2900	600	21	13.6			
28								
29								
30								
31								
32						1040	1020	98
33	4.6	2200	120	6	10.3			
34								
35								
36								
37	4.9	2200	250	12	10.3			
38						840	800	95
39								
40								
41								
42	5.1	2375	880	37	11.2			
43								
44						970	860	89
45								
46								
47								

TABLE B.1(b) (Continued)

DAY	LOAD ($kgCOD/m^3.d$)	TOC (mg/L)	TOC-REM (mg/L)	%COD-REM	TDS (g/L)	TKN (mg/L)	NH_3 (mg/L)	NH_3/TKN (%)
48								
49								
50								
51								
52	11.8	4470	2670	60	21.0			
53								
54	9.7	3526	1768	50	16.6	1380	1620	100
55								
56								
57								
58	11.7	4120	1311	32	19.3			
59						1680	1740	100
60								
61								
62								
63								
64	11.2	3944	937	24	18.3			
65								
66						2180	1500	69
67								
68								
69								
70								
71								
72	9.2	2520	220	9	11.8			
73						840	860	100
74								
75	6.1	1864	395	21	14.4			
76								
77								
78								
79								

NOTE : TOC value = Influent TOC
TKN & NH_3 values = Effluent TKN & NH_3

TABLE B.2(a) LABORATORY TESTING AND ANALYSIS RESULTS, R_2

DAY	G.P. (L/d)	FLOW (mL/d)	pH In	pH Out	ALK-VFA (mg/L)		VFA/ALK	GAS COMP CH_4-CO_2-N_2
1			10.2	8.8				
2								
3		1666						
4		1531			4010	1350	0.34	
5		2256						
6		546			4210	1455	0.35	
7								
8		2550		8.3				
9		1339			4260	1965	0.46	
10		1830		8.1				
11		1831		8.2	4920	1635	0.33	
12		1523		8.2				
13				8.1	5380	1695	0.32	
14		1776		8.1				
15								
16								
17								
18		1706		7.6				
19				8.3				65 5 30
20		1600						
21		2016		7.8				
22		582	5.8	7.8				65 5 15
23		2300		7.8				
24								
25								
26		2000		7.6				
27	1.3	2135		7.6				
28	1.1	1899		7.7				
29	0.9	1846		7.8	3540	152	0.04	80 20 0
30	0.8	2000	6.0	7.5				
31	0.7	1829		7.5				
32	1.3	1959	6.5	7.5				
33	1.7	1939		7.5				
34	1.4	1879		7.3				
35	1.9	1960		7.4				
36	2.4	2151		7.4				
37	2.4	2048		7.5	3700	130	0.04	70 20 5
38	3.0	1808	6.9	7.4				
39	2.5	1846		7.7				
40				7.5				
41		1255		7.4				
42	2.7	1656		7.4				
43	3.1	2545	6.2	7.4	4320	185	0.06	65 25 5
44	3.3	2351		7.3				
45		2692		7.3				

TABLE B.2(a) (Continued)

DAY	G.P. (L/d)	FLOW (mL/d)	pH In-Out	ALK-VFA (mg/L)		VFA/ALK	GAS COMP CH_4-CO_2-N_2
46		2820	7.3				
47		1600	6.2 7.4				
48		2700	7.6				
49		1920	7.3				
50		2354	5.5 7.4				
51	8.2	2504	7.2				
52	6.4	2057	7.2				
53	6.4	2265	7.4				55 30 5
54	6.2	2284	7.1				
55	6.3	2123	7.4	4000	405	0.10	
56	7.3	2191	5.5 7.1				
57	5.6	2181	7.1	3980	539	0.14	55 25 15
58	5.8	2361	7.1				
59	5.6	2240	5.5 7.1				
60	5.4	2215	7.1				
61	6.8	2090	7.1				
62	5.3	2000	7.0				
63	4.9	2435	7.1				
64	4.7	2457	7.0				55 20 10
65	4.3	2240	7.1				
66	3.1	2260	7.1				
67	1.6	2100	7.3	3800	1335	0.35	
68		2100	5.5 7.1				
69		2933	7.0				
70	4.9	3350	6.9				
71	5.9	3950	6.7				50 30 25
72		3400	7.0				
73	5.1	3500	5.5 7.1				
74	6.5	3318	7.0				
75	8.5	2902	7.3				
76	7.4	3050	7.2				
77	7.3	3260	7.2				
78	2.1	3413	7.2				
79	1.9		5.5 7.4				

NOTE : gas composition expressed in (%)

TABLE B.2(b) LABORATORY TESTING AND ANALYSIS RESULTS, R_2

DAY	LOAD ($kgCOD/m^3.d$)	TOC (mg/L)	TOC-REM (mg/L)	%COD-REM	TDS (g/L)	TKN (mg/L)	NH_3 (mg/L)	NH_3/TKN (%)
1								
2								
3								
16								
17								
18	5.0	2888	1578	55	13.6			
19								
20								
21								
22								
23								
24		2750	1750	64	12.9			
25								
26								
27	6.6	3000	700	24	14.2			
28								
29								
30								
31								
32						780	740	95
33	4.0	2000	360	18	9.4			
34								
35								
36								
37	4.1	2000	400	20	9.4			
38						860	860	100
39								
40								
41								
42	4.3	2570	1235	48	12.1			
43								
44						1000	920	92
45								
46								
47								

TABLE B.2(b) (Continued)

DAY	LOAD ($kgCOD/m^3.d$)	TOC (mg/L)	TOC-REM (mg/L)	%COD-REM	TDS (g/L)	TKN (mg/L)	NH_3 (mg/L)	NH_3/TKN (%)
48								
49								
50								
51								
52	5.5	2530	1550	61	12.0			
53								
54	5.4	2260	1633	72	10.7	1000	1040	100
55								
56								
57								
58	6.6	2799	1629	58	13.1			
59						1150	1080	94
60								
61								
62								
63								
64	8.9	3476	1765	51	16.4			
65								
66						2080	1260	61
67								
68								
69								
70								
71								
72	6.6	1941	794	41	9.0			
73						880	920	100
74								
75	5.1	1710	891	52	7.9			
76								
77								
78								
79								

NOTE : TOC value = Influent TOC
TKN & NH_3 values = Effluent TKN & NH_3

TABLE B.3(a) LABORATORY TESTING AND ANALYSIS RESULTS, R_3

DAY	G.P. (L/d)	FLOW (mL/d)	pH In	pH Out	ALK (mg/L)	VFA (mg/L)	VFA/ALK	GAS COMP CH_4	CO_2	N_2
1										
2										
3		1503								
4		1460			2630	675	0.26			
5		2112								
6		2184			2540	720	0.28			
7										
8		2715		8.3						
9		1086			2800	795	0.28			
10		1786		8.2						
11		1777		8.2	2950	645	0.22			
12		1460		8.2						
13				8.1	2840	660	0.23			
14		1674	7.5	8.2						
15										
16										
17										
18		1600		7.6						
19		1554		8.3				50	10	40
20		1680		7.7						
21		617	6.0	7.7						
22		2022		7.7				82	10	5
23										
24										
25										
26		2000		7.8						
27	2.9	2096		7.5						
28	3.1	1787		7.6						
29	3.5	1900		7.7	2600	130	0.05	60	20	20
30	3.3	1800	6.0	7.1						
31	4.0	1943		7.1						
32	4.6	1959	6.1	7.2						
33	4.5	1893		7.2						
34	4.7	2004		7.1						
35	4.7	2040		7.2						
36	5.2	2179		7.2						
37	4.8	1920		7.2	3500	100	0.03	65	25	5
38	4.4	1902	6.4	7.3						
39	4.2	1716		7.4						
40	4.2			7.4						
41	4.3	1292		7.5						
42	4.9	1619		7.5						
43	7.5	2512	6.5	7.6	5340	300	0.06	60	25	10
44	7.0	2155		7.4						
45	7.0	2575		7.4						

TABLE B.3(a) (Continued)

DAY	G.P. (L/d)	FLOW (mL/d)	pH In-Out		ALK-VFA (mg/L)		VFA/ALK	GAS COMP CH_4-CO_2-N_2
46	6.7	3000		7.4				
47	4.4	1155	6.0	7.5				
48	6.7	2685		7.6				
49	7.0	2250		7.2				
50	7.4	2390	5.5	7.3				
51	6.6	2400		7.2				
52	7.6	2194		7.2				
53	7.9	2295		7.3				50 30 15
54	8.1	2124		7.1				
55	8.5	2124		7.3	3900	300	0.08	
56	6.2	2504	5.5	7.2				
57	7.0	2181		7.1	3760	290	0.12	55 25 15
58	6.3	2438		7.1				
59	6.4	2211	5.5	7.1				
60	6.3	2068		7.1				
61	8.2	2150		7.1				
62	7.5	2130		7.1				
63	7.1	2197		7.2				
64	6.7	2496		7.2				
65	5.9	2090		7.2				
66	4.5	2320		7.2				
67	3.7	2000		7.4	4800	1275	0.27	
68	3.8	2182	5.5	7.3				
69	3.9	3200		7.0				
70	4.4	3380		6.9				
71	5.9	4080		6.8				40 30 25
72	5.9	3380		7.1				
73	6.1	3600	5.5	7.2				
74	5.4	3005		7.1				
75	6.3	3100		7.2				
76	7.5	3180		7.2				
77	7.2	3300		7.1				
78	7.0	3510		7.3				
79	7.0		5.5	7.5				

NOTE : gas composition expressed in (%)

TABLE B.3(b) LABORATORY TESTING AND ANALYSIS RESULTS, R_3

DAY	LOAD ($kgCOD/m^3.d$)	TOC (mg/L)	TOC-REM (mg/L)	%COD-REM	TDS (g/L)	TKN (mg/L)	NH_3 (mg/L)	NH_3/TKN (%)
1								
2								
3								
16								
17								
18	1.7	1147	564	49	5.3			
19								
20								
21								
22								
23								
24		1575	650	41	7.4			
25								
26								
27	3.0	1550	650	42	7.3			
28								
29								
30								
31								
32						740	620	84
33	6.1	3360	1440	43	15.8			
34								
35								
36								
37	3.6	2050	900	44	9.6			
38						860	860	100
39								
40								
41								
42	4.2	2815	1480	52	13.2			
43								
44						1120	1000	89
45								
46								
47								

TABLE B.3(b) (Continued)

DAY	LOAD ($kgCOD/m^3,d$)	TOC (mg/L)	TOC-REM (mg/L)	%COD-REM	TDS (g/L)	TKN (mg/L)	NH_3 (mg/L)	NH_3/TKN (%)
48								
49								
50								
51								
52	5.1	2550	1570	62	12.0			
53								
54	4.3	2170	1532	71	10.1	920	1120	100
55								
56								
57								
58	5.6	2552	1375	54	12.0			
59						1025	1020	99.5
60								
61								
62								
63								
64	9.2	4038	1990	49	18.8			
65								
66						2300	1600	70
67								
68								
69								
70								
71								
72	5.9	1928	862	45	9.0			
73						880	840	95
74								
75	4.9	1748	896	51	8.2			
76								
77								
78								
79								

NOTE : TOC value = Influent TOC
TKN & NH_3 values = Effluent TKN & NH_3

APPENDIX C

LABORATORY TESTING AND ANALYSIS RESULTS

(BATCH ANAEROBIC REACTORS)

TABLE C.1(a) GAS ANALYSIS RESULTS, (% OF CH_4), IN BATCH STUDIES, F/M = 0.25 SERIES

DAY	TDS (g/L)									
	5	8	10	12	14	16	18	22	28	35
2										
3										
4										
5										
6	60	44	47	40	50	50	36	33	55	50
7										
8										
9	60	48	47	56	50	59	47	69	53	50
10										
11										
12										
13	50	47	52	44	50	50	71	47	42	44
14										
15										
18										
19										
20										
21	60	47	53	63	69	50	65	55	47	50
22										
23										
24	50	65	53	30	40	25	31	31	21	20
25										
26										
32		70								
40	59	69	55	65	67	47	0	0	0	0
47	0	0	0	0	71	0	0	0	0	0
53	70	70	60	0	76	60	0	0	0	33
61	76	72	65	77	86	64	50	49	64	33

TABLE C.1(b) GAS VOLUME MEASUREMENT RESULTS, (mL of CH_4), F/M = 0.25 SERIES

DAY	TDS (g/L)									
	5	8	10	12	14	16	18	22	28	35
2	6.6	7.0	2.6	0	0	0	4.0	0.7	3.3	5.0
3	0	0.4	2.6	0.8	2.0	0.5	1.4	0.7	2.8	1.0
4	0	0	0	0	0	0	0	0	0	1.0
5	0.6	0	0	0	1.0	1.0	1.1	0.3	0	0
6	7.8	4.4	0.5	2.8	3.5	3.5	1.8	1.7	2.8	2.0
7	0	0	0.5	0	0	1.0	0	0	0	0
8	5.4	1.0	0	0.6	3.0	0.6	3.3	0	0	0.5
9	19.8	4.3	0.5	2.2	2.5	2.4	3.3	3.5	3.7	2.5
10	8.4	0	0	0	0	0	0	0	0	0
11	6.6	0.5	0	0	0	0	0	0	0	0
12	1.0	0	1.6	0	0.5	0.5	0	0.5	0.8	0
13	5.0	5.6	2.6	0.9	5.0	1.0	3.6	4.7	3.8	1.3
14	0	0	0	0	0	0	0	0	0	0
15	0.5	0	0	0	0.5	0	0	0.9	0	0
18	0.6	0	0	0	0	0	0	0	0	0
19	0	0	0	0	0	0	0	0	0	0
20	1.2	0	2.4	0	0.7	1.0	0	0	0.5	0
21	9.0	9.9	4.2	1.9	9.0	2.0	6.5	5.5	5.2	2.5
22	0	0.5	0	0	0	0	0	0.6	0	0
23	3.5	0	0.5	0	2.0	0	0.3	0.9	0.2	0.4
24	8.5	26.0	5.2	0	6.4	0.8	2.5	5.3	3.2	2.2
25	0	0	0	0	0.4	0	0	0.6	0	0
26	1.5	1.3	0	0.3	1.2	0.3	0.3	0	0.2	0.4
32	0	6.0	0	0	0	0	0	0	0	0
40	3.5	6.4	6.1	3.9	4.7	0.5	0	0	0	0
47	0	0	0	0	2.0	0	0	0	0	0
53	4.0	3.0	1.0	0	9.0	2.0	0	0	0	4.0
61	22.5	20.0	11.5	3.1	24.5	8.0	0.3	1.0	7.0	9.0
TOTAL	116	96	41	16	76	21	28	26	32	31

TABLE C.2(a) GAS ANALYSIS RESULTS, (% OF CH_4), IN BATCH STUDIES, F/M = 0.50 SERIES

DAY	TDS (g/L)								BLANK
	8	10	12	14	16	18	22	28	(*)
2									
3									
4									
5									
6	55	43	50	75	43	56	40	60	60
7									
8									
9	50	57	58	50	71	58	53	52	67
10									
11									
12									
13	50	57	47	67	48	47	53	44	50
14									
15									
18									
19									
20									
21	58	67	41	50	63	64	38	56	50
22									
23									
24	50	38	42	44	48	15	9	13	62
25									
26									
32	70								
40	85	40	40	40	27	29	38	14	60
47	85	40	0	0	0	0	0	25	0
53	0	40	0	0	0	0	0	0	73
61	86	40	40	50	41	44	54	50	71

* Sludge only blank

TABLE C.2(b) GAS VOLUME MEASUREMENT RESULTS, (mL of CH_4), F/M = 0.50 SERIES

DAY	TDS (g/L)								BLANK
	8	10	12	14	16	18	22	28	(*)
2	3.3	3.4	6.5	0.8	3.4	6.2	4.0	5.4	5.4
3									
4	2.2	1.3	2.0	1.5	0.4	0	0	0	2.4
5	0	0	1.0	2.3	0	1.1	0	0	0.6
6	5.5	3.0	3.5	4.5	2.2	3.9	2.4	3.0	4.8
7	0.6	0	0	0	0	0.6	0	0	0
8	0.5	0	0	2.5	1.4	0.6	0	1.6	1.3
9	3.5	0.6	8.7	4.0	8.5	5.2	6.4	5.2	5.4
10	0	0	0	0	0	0	0	0	0
11	0	0	0	0	0	0	0	0	0
12	0	0.6	0	2.7	1.0	0	0.5	0	0.5
13	2.5	5.1	4.7	8.0	4.8	2.4	1.1	3.5	3.5
14	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0.5	0	0	0	0
18	0	0	0	0	0	0	0	0	0
19	0	0	0	0	0.6	0	0	0	0
20	1.7	0.7	0	0	0.6	0.6	0.4	0	0
21	5.2	1.3	0.8	5.5	7.6	6.4	2.7	6.7	5.5
22	0.6	0	0	0.5	0	0	0	0	0
23	0	0.4	0	0	0	0.2	0	0	1.2
24	8.5	4.2	4.6	10.1	8.6	2.1	0.5	2.1	6.2
25	0.5	0.4	0	0	0.5	0	0.2	0	0
26	0.5	0.4	0.8	1.3	0.5	0	0	0.1	1.2
32	14.0	0	0	0	0	0	0	0	0
40	24.0	1.2	0.8	0.2	0.1	0.1	0.2	0.1	0.3
47	1.0	1.0	0	0	0	0	0	1.0	0
53	0	1.0	0	0	0	0	0	0	1.0
61	7.0	3.0	0.4	0.3	0.4	0.2	1.6	4.5	6.0
TOTAL	82	28	32	44	42	30	19	31	38

* Sludge only blank

TABLE C.3(a) GAS ANALYSIS RESULTS, (% OF CH_4), IN BATCH STUDIES, F/M = 0.80 SERIES

DAY	TDS (g/L)							
	10	12	14	16	18	22	28	35
2								
3								
4								
5								
6	55	33	44	78	40	78	44	56
7								
8								
9	52	63	67	52	53	47	56	44
10								
11								
12								
13	52	47	60	55	47	46	44	56
14								
15								
18								
19								
20								
21	64	50	57	40	39	63	67	41
22								
23								
24	50	36	32	19	28	13	4	17
25								
26								
32								
40	67	36	25	40	33	10	0	0
47	71	0	0	0	36	0	0	0
53	83	0	0	0	0	40	0	0
61	93	63	43	52	46	67	0	0

TABLE C.3(b) GAS VOLUME MEASUREMENT RESULTS, (mL of CH_4), F/M = 0.80 SERIES

DAY	TDS (g/L)							
	10	12	14	16	18	22	28	35
2	3.9	1.3	0.4	10.9	4.8	8.6	5.7	0
3								
4	0	0	0	0	0.4	0	0.4	0
5	0	0	0	0.8	0.8	0.8	0	0
6	3.9	2.3	1.3	1.6	3.2	3.1	0.4	0.6
7	0.6	0	0	0	0	0	0	0
8	0.5	1.3	0	0	0.5	0.9	1.7	0
9	4.7	13.0	3.4	6.8	7.4	8.0	1.7	0.4
10	0	0	0	0.3	0	0	0	0
11	0	0.6	0	0	0	0.5	0	0
12	0	2.4	0	3.9	0.5	1.4	0	0
13	5.2	7.1	6.0	6.6	4.2	4.1	2.2	1.1
14	0	0	0	0	0	0	0	0
15	0	0.5	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0
19	0.6	0	0	0	0	0	0	0
20	0.6	0	0	0.8	0	0.6	0	0.4
21	9.6	7.0	1.7	7.2	4.3	5.7	4.7	5.3
22	0	0	8.0	0	0	0	0	0
23	0	0.7	0	0	0	0	0	0
24	10.5	7.2	0.3	3.4	2.8	1.3	0.4	3.4
25	0	0	4.5	0	0.3	0	0	0
26	0.5	0	0	0.2	0.3	0.3	0	0
32	0	0	0	0	0	0	0	0
40	16.1	0.2	0.1	0.2	0.3	0.1	0	0
47	10.0	0	0	0	1.0	0	0	0
53	12.0	0	0	0	0	1.0	0	0
61	30.0	2.5	0.2	0.3	2.3	12.4	0	0
TOTAL	100	46	26	40	52	49	11	10

APPENDIX D

TOTAL DISSOLVED SOLIDS DATA

TABLE D.1(a) EFFECT OF TDS ON G.P., FLOW-THROUGH STUDY

DAY	L $CH_4/gCOD_{INFL.}$			TDS (g/L)		
	R_1	R_2	R_3	R_1	R_2	R_3
19	0.08	0.05	0.25	10.8	13.6	5.4
23	0.11	0.04	0.34	13.1	13.1	7.5
29	0.04	0.05	0.31	13.6	14.1	7.5
37	0.06	0.18	0.30	10.3	9.4	9.9
43	0.20	0.12	0.47	11.2	12.1	7.7
53	0.18	0.26	0.32	17.8	10.8	10.3
55	0.14	0.27	0.33	17.8	10.8	10.3
58	0.10	0.19	0.23	21.6	13.1	12.2
64	0.05	0.23	0.13	18.3	8.4	18.8
71	0.03	0.16	0.14	11.7	8.9	8.9
75	0.04	0.28	0.19	8.9	8.0	8.0

TABLE D.1(b) EFFECT OF TDS ON G.P., BATCH REACTORS

TDS (g/L)	L $CH_4/gCOD_{INFL.}$ F/M=0.25	F/M=0.50	F/M=0.80
5	0.23		
8	0.19	0.08	
10	0.08	0.03	0.06
12	0.03	0.03	0.03
14	0.15	0.04	0.02
16	0.04	0.04	0.03
18	0.06	0.03	0.03
22	0.05	0.02	0.03
28	0.06	0.03	0.01
35	0.06		0.01

TABLE D.2 ACCLIMATION TO TDS, BATCH BMP STUDY (79)

TDS (g/L)	CUMULATIVE CH_4 (mL) 10-DAY	20-DAY	30-DAY	40-DAY
2.5	1.3	4.2	5.3	
4.0	4.2	8.6	10.7	
6.8	7.0	20.0	24.7	28.0
9.5	2.0	14.0	29.3	36.7
12.5	1.0	8.6	15.0	28.3

APPENDIX E

FREE-AMMONIA DATA

TABLE E.1 EFFECT OF FREE-AMMONIA ON CH_4 PRODUCTION, KOSTER & LETTINGA STUDY (3)

TOTAL AMMONIA (mg/L)	CALCULATED FREE-AMMONIA (mg/L)	CH_4 (mL/h)
680	130	29.4
759	97	32.8
853	76	36.9
853	66	36.9
1351	45	58.4
1653	19	71.5
1666	20	72.0
2101	14	90.8
2601	10	112.4

TABLE E.2 EFFECT OF FREE-AMMONIA ON CH_4 PRODUCTION, BATCH STUDY

	AVG. (mL) OF CH_4 / REACTOR
F/M = 0.25	48.30
F/M = 0.50	44.00
F/M = 0.80	41.75