ANAEROBIC DIGESTION OF HIGH-STRENGTH OR TOXIC ORGANIC EFFLUENTS

A Survey of Anaerobic Digesters in the KwaZulu-Natal Region to Assess their Availability for the Treatment of High-Strength or Toxic Organic Effluents

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Abstract

The objective of this investigation was to assess the potential for the treatment of high-strength or toxic organic effluents in available anaerobic digester capacity, in the KwaZulu-Natal province. A strategy was developed for the simultaneous assessment of available digester capacity and effluent degradability evaluation prior to loading into a full-scale digester.

A number of under-utilised and under-performing anaerobic digesters were identified. Collation of physical and operating data facilitated the evaluation of the performance efficiency of each digester. Available capacity was assessed in terms of hydraulic load and organic load. Suggestions for remedial action were made. Industries producing high-strength or toxic organic effluents were identified and the effluent compositions detailed.

A laboratory-scale (serum bottle) test protocol was developed for the evaluation of the anaerobic degradability and potential toxicity of a substrate. The batch tests provided information on the volumes and concentrations of an effluent that could be treated effectively, thereby preventing digester failure due to overloading or the loading of an inhibitory substrate. Material and energy balances provided an indication of the efficiency of the digestion process within the serum bottles. This method was illustrated by the degradation of a known substrate, glucose.

A detailed evaluation of the anaerobic digesters at the Umbilo Sewage Purification Works verified the availability of digestion capacity. The hydraulic load to the entire works was 15 % (v/v) below its design capacity and the flowrates to the anaerobic digesters were low which indicated available hydraulic capacity. The organic load to the anaerobic digesters was low. The digesters were well mixed and heated to 36 ± 1 °C, therefore they had the ability to accept an organic load of ca. 3 kg VS/m^3.d The digesters were only fed an average of 1.12 kg VS/m^3.d ; there was available organic capacity. The operation of the digesters was *healthy* and they could accept a greater load in the form of industrial effluents. The average HRT was calculated at ca. 17.29 d. The residence time distribution test showed that there was no dead volume and that the mixing was efficient as the digester was found to be comparable to an ideal completely stirred tank reactor (CSTR).

The serum bottle screening test was applied to assess the anaerobic degradability of a textile size effluent. Investigation of the individual components of the size solution identified those that were potentially inhibitory, and the concentrations at which they would inhibit the anaerobic biomass. These included: PVA, which became inhibitory at concentrations > 30 g/l; Plystran, at concentrations > 10 g/l; acrylic, at concentrations > 4 g/l; and biocide which became inhibitory at concentrations > 0.5 mg/l and toxic at a concentration of 50 mg/l. Investigation of the synthetic size solution showed that it was degraded by the anaerobic digester biomass although the tests suggested that the system could become overloaded at high size concentrations. This verified the importance of the screening tests prior to loading into a digester to prevent digester failure. The results were applied for the prediction of treatment in a full-scale digester. The ability of anaerobic microorganisms to acclimate to inhibitory substrates was demonstrated by the enrichment tests. The biomass was acclimated to the inhibitory components of the size solution. The acclimated biomass was able to degrade the substrate at a concentration that had previously been inhibitory, the lag period was reduced and the degradation rate increased. This investigation identified and verified the potential for treatment of high-strength or toxic organic effluents in available anaerobic digester capacity in the KwaZulu-Natal region.

Preface

I, Joanne Sacks, declare that unless indicated, this dissertation is my own work and that it has not been submitted, in whole or in part, for a degree at another University or Institution.

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Glossary

Acclimation The adaptation of a microbial community to degrade a previously **recalcitrant** compound through prior exposure to that compound.

Adaptation A change in the microbial community that increases the rate of transformation of a test compound as a result of prior exposure to that test compound.

Agro-industry Industry based on the processing of agricultural products.

Anaerobe A microorganism capable of growing or metabolising in the absence of free oxygen. These microorganisms may be facultative or obligate; the latter will perish in the presence of free oxygen.

Anaerobic digestion/ biodegradation The microbial degradation of an organic compound in the absence of oxygen. It is effected by anaerobic bacteria which degrade the compound in a step-wise process yielding organic acids, carbon dioxide and hydrogen and, ultimately, methane and carbon dioxide.

Anoxic An environment where oxygen is present in the form of chemical compounds such as nitrate or sulphate.

Archaebacteria An evolutionary distinct group of prokaryotes, including the methanogenic, extremely halophilic and sulphur-dependent bacteria.

Batch culture A closed culture environment in which conditions are continuously changing according to the metabolic state of the microbial culture.

Biodegradable A property which allows the microbial decomposition of an organic compound to inorganic molecules.

Biorefractory A property which renders a compound resistant to biological degradation.

Biogas	The gas produced, principally methane and carbon dioxide, by the action of anaerobic microorganisms on organic compounds.
Catabolism	The degradation of complex organic molecules into simpler compounds with the release of energy.
Chemical oxygen demand (COD)	A measure of the total amount of organic material in a waste stream.
Co-disposal	The calculated and monitored treatment of industrial and commercial liquid and solid wastes by interaction with biodegradable wastes in a controlled landfill.
Degrade	Break down into simpler substances by bacterial action.
Dewatering	The removal of water from a sludge.
Eco-efficiency	The delivery of competitively priced goods and services that satisfy human needs and quality of life, while progressively reducing ecological impacts and resources intensity throughout the life cycle to a level in line with the Earth's carrying capacity.
Effluent	A stream flowing from a sewage tank or industrial process.
Facultative anaerobe	An organism capable of either aerobic or anaerobic growth.
Feed schedule	Pre-determined schedule which sets out the digester feed programme.
Grit	Heavy mineral matter associated with wastewater e.g.. sand.
Hazardous waste	An inorganic or organic element or compound that, because of its toxicological, physical or chemical properties, may cause detrimental impacts on human health and the environment.
Headspace	The volume in a sealed vessel not occupied by the liquid phase.

Immobilisation	A mechanism of bacterial agglomeration and bacterial attachment to support material.
Inhibition	An impairment of bacterial function.
Kinetics	The explanation of the observed characteristics of chemical reactions.
Labile	Readily degradable.
Lithotroph	An organism that can obtain its energy from oxidation of inorganic compounds.
Loading rate	Measure of the organic content of the feed in relation to the digester volume.
Methanogens	Bacteria which utilise volatile organic acids as substrates and produce methane and carbon dioxide.
Mineralisation	Microbial decomposition of an organic compound to inorganic constituents such as carbon dioxide, methane and water.
Pollution	An adverse alteration of the environment.
Primary anaerobic digester	Digester, at a sewage works, in which the substrate is anaerobically digested by the microorganisms in the sludge; it is usually heated and mixed.
Recalcitrant	Resistant to microbial degradation.
Retention time	Average period of time that the incoming sludge is retained in the digester for completion of the biological reactions - calculated by dividing the digester volume by the incoming flow.
Screen	Device for the removal of large solids from the waste water.
Scum	Layers of fats and oils which float on a liquid surface.
Secondary anaerobic digester	Digester, at a sewage works, in which the separation of the sludge from the supernatant takes place; usually unheated and unmixed.

Seeding	The use of an actively digesting sludge to aid the start-up of a digester by supplying a quantity of the preferred types of organisms. This usually reduces the time taken for a digester to become active.
Size	A coating applied to **warp** yarn to improve its weaving efficiency.
Sludge	The general term applied to the accumulated solids separated from waste water. A large portion of the sludge material in a digester consists of bacteria which are responsible for its decomposition.
Suspended solids	Undissolved non-settleable solids present in wastewater.
Syntrophy	A nutritional situation in which two or more organisms combine their metabolic capabilities to catabolise a substance not capable of being catabolised by either one alone.
Total solids	The sum of dissolved and suspended constituents in wastewaters or sludges.
Toxicity	An adverse effect (not necessarily lethal) on bacterial metabolism.
Treatability	The ability of a given digestion system to stabilis effluent.
Volatile fatty acids	Short-chain organic acids produced by the anaerobic digestion process.
Volatile solids	Organic solids which are lost on ignition at 600 °C.
Warp	The longitudinal threads in a length of fabric.
Waste water	General term to denote a combination or mixture of domestic sewage and industrial effluents.
Working volume	The portion of the total volume that is actively involved in the digestion process.
Xenobiotics	Synthetic organic chemicals or natural chemicals present in unnatural concentrations.

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List of Abbreviations

ADWF	Average dry weather flow
ATA	Anaerobic toxicity assay
ATP	Adenosine triphosphate
BMP	Biochemical methane potential
BOD	Biochemical oxygen demand
CMC	Carboxymethyl cellulose
COD	Chemical oxygen demand
CSTR	Completely stirred tank reactor
DAF	Dissolved air flotation
IC	Inorganic carbon
MRR	Maximum rate ratio
NADH	Nicotinamide-adenine-dinucleotide (oxidised form)
OA	Oxygen absorbed
OFN	Oxygen-free nitrogen
OMS	Oxidised modified starch
PCB	Polychlorinated biphenyl
PVA	Polyvinyl alcohol
PST	Primary settling tank
SRB	Sulphate-reducing bacteria
SRT	Sludge residence time
STP	Standard temperature and pressure
TC	Total carbon

TCA	Tricarboxylic acid
TOC	Total organic carbon
TS	Total solids
US EPA	United States Environmental Protection Agency
USPW	Umbilo Sewage Purification Works
VFA	Volatile fatty acid
VS	Volatile solids
VSS	Volatile suspended solids
WWTW	Wastewater treatment works

Nomenclature

b	Death constant (1/d)
D	Dilution rate (1/d)
k	Maximum rate utilisation coefficient
K_s	Saturation constant (mg/l)
Q	Flow rate (l/h)
S_o	Inlet substrate concentration (mg/l)
S	Substrate concentration (mg/l)
U	Mass of COD destroyed per unit mass of biomass
μ	Specific cell growth rate (1/d)
μ_{max}	Maximum specific cell growth rate (1/d)
V	Volume (m^3)
X_o	Inlet biomass concentration (mg/l)
X	Biomass concentration (mg/l)
Y	Yield (mg COD/ mg COD)

Chapter 1

Introduction

Water is essential to life, to social development and to economic progress

(Department of Water Affairs, 1986).

According to the new constitution of the Republic of South Africa (Constitutional Assembly, 1996), *everyone has the right to an environment that is not harmful to their health or well-being and to have the environment protected, for the benefit of present and future generations, through responsible legislative and other measures that prevent pollution and ecological degradation, promote conservation, and secure ecologically sustainable development and use of natural resources while promoting justifiable economic and social development. Everyone has the right to have access to water.*

1.1 WATER QUALITY IN SOUTH AFRICA

In South Africa, the increasing demand for water arising from the growth of the population and the economy has to be met from limited resources (Department of Water Affairs, 1986). **Sustainable development** is development that meets the needs of the present generation without compromising the ability of future generations to satisfy their own needs. Water is a public commodity and the actions of users and polluters generally affect others. The country lies in a semi-arid region in which rainfall waterbodies are unevenly distributed. The average annual rainfall of South Africa, compared to the world average of 860 mm, is low at 497 mm (Department of Water Affairs, 1986). An expanding demand due to rapid population increase and demographic changes will result in water becoming increasingly scarce in many parts of South Africa. Greater pollution loads and reduced flows in the country's rivers, due to the expanding demand, will in future place additional pressure on the already limited water resources (Department of Water Affairs and Forestry, 1993). Another measure of water availability is the amount of water resources already being used. In South Africa more than half the total available water is used, while arid countries such as Namibia and Botswana use only 5 to 10 % of their available water (Department of Water Affairs and Forestry, 1997).

South Africa is poorly served with natural lakes, therefore rivers are the most important source of water (Department of Water Affairs, 1986). The river water quality has been impacted by the multiple uses of the water. Although industry accounts for approximately 16 % of South Africa's direct water use, its impact is much higher because effluents often contain toxic pollutants (Stander, 1997). The monitoring and management of water quality in rivers is thus vital for the adequate long-term protection of South Africa's water resources.

The use of land has a major impact on water resources. Similarly, air pollution can gravely affect water quality (Department of Water Affairs and Forestry, 1997). Abuse of rivers has an effect on estuaries and oceans. Human activities are beginning to have a noticeable impact on the climate which could affect the amount and distribution of rainfall and rates of evaporation. In light of the steady deterioration of water quality in rivers, the Department of Water Affairs and Forestry adopted a pollution prevention approach to control hazardous pollutants and a receiving water quality approach to control non-hazardous pollutants. In coastal areas, the biggest problem with industrial water users is the amount of fresh water lost via effluent pipelines to sea; the

water should be treated and returned to the rivers for reuse. The strict effluent discharge regulations promulgated in terms of the Water Act of 1956 have resulted in the construction of wastewater purification plants which discharge highly treated effluent (Department of Water Affairs, 1986). Technically, it is possible to purify effluent to any desired quality. The reuse of effluent as a source of water will assume increasing importance in many areas of the country, particularly in areas of urban and industrial growth (Department of Water Affairs, 1986). For this additional source to be used to its best advantage requires the purposeful management of effluent and not merely its incidental return to a river.

1.1.1 Water regulations

Before the advent of the Water Act of 1956, there was no statutory provision for State control over the purification and disposal of effluent, except that the discharge of sewage into public streams was prohibited (Department of Water Affairs, 1986). The Water Act, in anticipation of water shortages, made provision for the compulsory purification of effluent by the user to specified standards and its subsequent disposal in a manner that would make it available for reuse. The Act provided for control over the use of water for industrial purposes as well as for control over and the prevention of water pollution.

An intensive review of the 1956 Water Law was conducted in 1997 by the Department of Water Affairs and Forestry. The review was motivated by the need for preparation for new legislation that would reflect democratic principles and equitable access to the resource by all; symbolised by the slogan *some for all, forever* (Department of Water Affairs and Forestry, 1997). While management's goal is to ensure all water users will benefit from access to the water resource, ecological integrity provides a good indication of sustainability in the use of the resource. The proposed policy (Department of Water Affairs and Forestry, 1997) integrated resource-directed measures for protection, such as resource quality objectives, with source-directed measures, such as effluent standards. This policy included :

1. Setting water resource-based objectives which clearly defined acceptable values for water resources for each of the components (chemical, physical, biological) of ecological integrity;

2. Use of source-directed standards which clearly defined acceptable values for waste discharge or impact generation and encouraged movement towards minimisation of waste disposal and impacts; and

3. Where source-directed standards could not be met in the short term, a temporary exemption from the standards could be considered if an impact assessment indicated the water resource-based objectives could still be met.

The source-directed measures included the use of discharge or impact standards. These standards should be stringent enough to protect the specific water resource affected. The development of new standards, which should be more flexible and may be more strict than existing standards, was proposed. Waste discharge or impacts which can meet these national standards would not require an impact assessment, thus minimising the human and financial resources needed for administration (Harris, van Vliet and MacKay, 1997). Specific criteria will probably be developed to provide guidelines for impact assessment studies to determine allowable exemptions. Development of a successful source-based classification system for emission standards requires that stakeholders, who are interested and affected by waste discharge, participate in the development of the standards. With the adoption of the White Paper (Department of Water Affairs and Forestry, 1997), a new process of consultation will begin in support of the development of a new National Water Bill and regulations for implementation of the policy. Participation will include communities, water users, academic institutions, scientific councils, and Government at national, provincial, and local levels. The Water Bill will provide the

basis from which to ensure that all South Africans are able to satsify their basic needs for water supply and sanitation with dignity and equity. *Unless measures are taken to cherish and maintain the scarce water resources on which these services depend, these efforts will come to nothing* (Department of Water Affairs and Forestry, 1997).

1.2 INDUSTRIAL EFFLUENT TREATMENT

The KwaZulu-Natal region has the potential to attract a significant amount of industry in the near future. Due to the abundance of water relative to the rest of the country, it is probable that some of these industries will be from the agro-industrial sector. One of the characteristics of this class of industries is the high concentration of organic compounds in the effluents. A second class of industry that could be attracted is that which produces high-strength or toxic organic effluents. Industries of this type already exist in the region and, due to the nature of the effluents that they produce, encounter difficulties in the safe disposal of the effluents, with co-disposal into municipal landfill sites or marine discharge being the common solutions. Researchers (Meric, Kabdash, Tunay and Orhan, 1997) have identified the problem of disposal of high-strength organic effluents and have investigated treatment options such as oxidation, coagulation, flotation and biological treatment.

Cleaner production is the continuous application of an integrated preventative environmental strategy, applied to processes, products and services to increase eco-efficiency and to reduce risks for humans and the environment. Implementation of cleaner production and waste minimisation practices, at the effluent source, will lead to the production of more concentrated effluents. Anaerobic digestion has the potential to treat these concentrated wastewaters.

Investigations have indicated that there a the need for anaerobic digestion facilities that can accept high-strength organic effluents. Tracer tests on a number of anaerobic digesters in the KwaZulu-Natal region have indicated that the average mixing volume is 50 % of the actual volume (Barnett, 1995; Barclay, 1996). These results confirmed studies undertaken previously, on digesters in the United States of America, by the United States Environmental Protection Agency. Other research projects, undertaken in the Department of Chemical Engineering of the University of Natal, Durban, have shown that there are a number of sewage works, in KwaZulu-Natal, with under-utilised anaerobic digestion facilities (Barnett, 1995; Barclay, 1996).

The KwaZulu-Natal region has a great need for the provision of sanitation. The increasing urban and peri-urban population will require the extension of sewage reticulation and an increase in sewage treatment capacity. The increased use (and income) from existing but under-utilised capacity will assist in financing the additional infrastructure in areas where it is needed. The Durban Metropolitan Council is currently taking over control of 30 wastewater treatment works. This provides the opportunity for the utilisation of the under-utilised capacity which would facilitate relief at plants operating at, or over, design capacity. This would delay the need for capital expenditure and increase the income from capital already expended. The net result should be the lowering of costs associated with the provision of sanitation services.

This project is part of a larger overall plan in which the existing anaerobic digestion capacity in South Africa can be extended and used more intensively. The main objectives of this research were to:

1. Establish a protocol or mechanism which could be applied for the safe disposal of high-strength or toxic organic effluents;

2. Identify under-performing digesters with a view to recommending courses of remedial action and thus facilitate the optimal utilisation of effluent treatment facilities in the region;

3. Identify industries in the region that produce high-strength or toxic liquid effluents to allow rational decisions to be taken for their safe disposal; and

4. Provide information that would allow the rational location in KwaZulu-Natal of new industries which produce high-strength or toxic organic liquid effluents.

1.3 PROJECT OUTLINE

The principal objective of this investigation was to assess the potential to treat high-strength or toxic organic effluents in the under-utilised anaerobic digester capacity in the region. The following approach was adopted.

A review of the literature was undertaken to gain familiarity with the fundamentals of anaerobic digestion such that the required techniques for anaerobic test work could be understood and mastered. A literature review was also undertaken to investigate the kinetics and modelling of anaerobic systems.

The literature gave an indication of the parameters affecting the efficient functioning of an anaerobic digester. A survey questionnaire was compiled. The local authorities were interviewed and the digesters were visited. Physical and operating data for each of the digesters were obtained and used to calculate the performance efficiencies. This allowed for the identification of under-performing digesters and digesters available for the treatment of high-strength or toxic industrial effluents.

Selected industries were contacted to obtain data on their effluents and the local authorities provided information on the proposed development of new industries. From these data, a matrix was compiled which identified potential anaerobic digesters for treatment of effluents produced in the vicinity.

Anaerobic digestion has the potential to stabilise the degradable fraction of high-strength or toxic organic effluents either entirely or such that they can be further degraded aerobically. To achieve the research objective, a strategy was followed (**Figure 1.1**). The strategy, which can be applied to different effluents, was developed during the course of this research project.

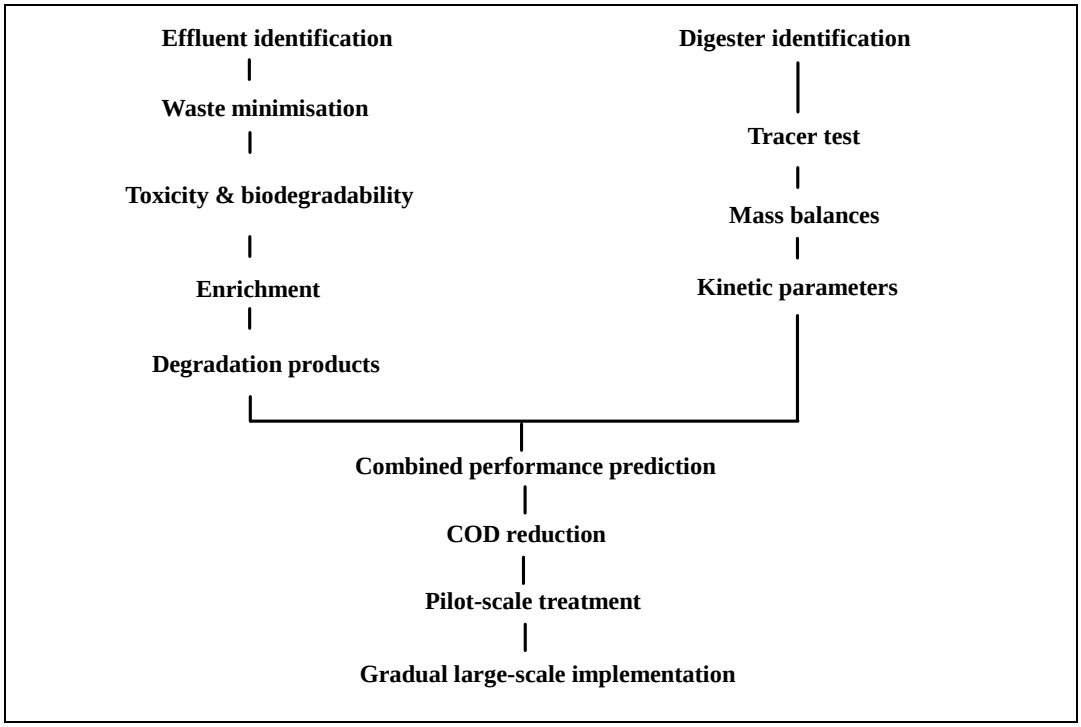


FIGURE 1.1: Strategy for the anaerobic treatment of organic effluents.

The overall strategy follows two concurrent pathways; one investigates the effluent and the other the digester.

Effluent: the first step is to identify an appropriate effluent. Effluents of interest are those with very high chemical oxygen demand (COD) values which would overload conventional treatment processes; those that are co-disposed on municipal landfill sites; and those that are discharged to sea. Options for waste minimisation are examined with the aim to concentrate the high-strength waste. The principal objective is for the industries to concentrate the high-strength waste on site rather than to dilute and discharge. The waste could then be tankered to the nearest wastewater treatment works for treatment in the available digester capacity. It is critical to determine the anaerobic degradability and potential toxicity of an effluent prior to its loading into a digester, to prevent digester failure. A laboratory-scale batch test protocol was developed to screen the effluents. Anaerobic biomass may have to undergo a period of enrichment to acclimatise it to a particular effluent if, during the laboratory-scale tests, it is found to be toxic or inhibitory. The biomass is exposed to small, but increasing, concentrations of the molecule over a period of time. The culture could then be used to seed digesters thus preventing digester failure and reducing the lag period. In the event of inhibition, degradation products should be identified since anaerobic digestion is a multi-phase process and intermediates formed during the degradation of a specific effluent may be inhibitory to the microorganisms performing the later stages of the digestion process. The batch tests allow for the determination of the degradation rate and the ultimate degradability of an effluent.

Digester: a locally available anaerobic digester is identified. A tracer test should be done on the digester to assess the mixing efficiency. Other important considerations include mass balances and kinetic parameters.

The two pathways then merge. Knowledge of the digester efficiency and the effluent degradation kinetics should facilitate the prediction of whether an effluent can be treated anaerobically, on a large scale. The reduction in COD is important as it gives an indication of the extent of organic degradation. The batch tests provide information of the volumes and concentrations of an effluent that can be treated effectively. This

information can then be applied, initially at pilot-scale and ultimately for full-scale implementation, in an existing digester.

The described strategy was applied to determine the feasibility of the anaerobic digestion of a textile size effluent. The effluent was chosen due to its high organic strength (ca. 140 000 mg/l) and because the mill producing it was located within 10 km of the Umbilo Sewage Purification Works which had available anaerobic digestion capacity.

1.4 THESIS OUTLINE

The thesis begins with a review of literature on the subject of anaerobic digestion of industrial effluents which is presented in **Chapter 2**. **Chapter 3** is a discursive literature review of current knowledge of the kinetics and modelling of anaerobic systems. An inventory of the anaerobic digesters, in KwaZulu-Natal, and an assessment of their performance efficiencies is given in **Chapter 4**. **Chapter 5** describes the laboratory-scale protocol which was developed to determine the anaerobic degradability of an effluent. Details are given for the assessment of an effluent, in terms of anaerobic biodegradability, and the results of the industry survey are presented.

The case study, investigated in this project, aimed to assess the feasibility of treating a textile size effluent in available digester capacity at a nearby municipal treatment works. **Chapter 6** describes the investigation of these digesters and the evaluation of their potential to treat the high-strength textile effluent. Results of the investigation of the treatment of the textile size effluent are presented in **Chapter 7** with a discussion of the application of these results for full-scale treatment.

The thesis is concluded with **Chapter 8**. A summary of the experimental work is presented and recommendations for future research are made.

Chapter 2

Anaerobic Digestion ~ An Overview

Anaerobic digestion has gained popularity, in recent years, as an efficient, cost-effective treatment method. This literature review describes the mechanism and the microbiology of anaerobic digestion (**Section 2.1**) and details the numerous digester configurations that have been developed to treat wastewaters of various compositions (**Section 2.2**). **Section 2.3** describes the anaerobic degradation process in detail with emphasis on conventional anaerobic sewage treatment. A brief overview is given of research that has been done to investigate the utilisation of anaerobic digestion as a treatment method for industrial effluents. The description (**Section 2.4**) of the current fates of high-strength organic effluents, in the KwaZulu-Natal region, provides an insight of the motivation for this research project.

2.1 ANAEROBIC DIGESTION

Anaerobic digestion is a process by which a wide variety of organic molecules can be converted into a gas rich in methane. In view of the current problems, both in the protection of the environment and the search for sources of renewable energy, anaerobic digestion appears to be a favourable biotechnological process to treat an organic waste through bioconversion into energy.

The increasing presence of organic compounds in the country's water resources is cause for major concern. In future years, the removal of organic materials will be of higher priority than water quantity or mineralisation aspects. There are a range of techniques (advanced oxidation, activated carbon and membranes) for the removal of organic molecules from drinking water. These processes are, however, expensive and treat the symptoms not the cause. Anaerobic digestion has the potential to break down complex biorefractory organic compounds so that they may be further degraded aerobically or to mineralise biorefractory compounds.

Anaerobic digestion is a biological process in which organic matter is catabolised to methane and carbon dioxide. The process involves a complex bacterial population with complex nutritional requirements and specialised ecological roles (Tracey, Spangenberg and Britz, 1989). In aerobic respiration, molecular oxygen serves as an external electron acceptor, accepting electrons from electron carriers such as NADH by way of an electron transport chain (Brock and Madigan, 1991). In the absence of oxygen, a number of other electron acceptors can be used in which case the process is called anaerobic respiration. Anaerobic microorganisms are ubiquitous and occur in many natural ecosystems as well as in process simulations used for waste management (Pohland, 1992).

Anaerobic treatment of complex organic materials is a multi-phase process (**Figure 2.1**).

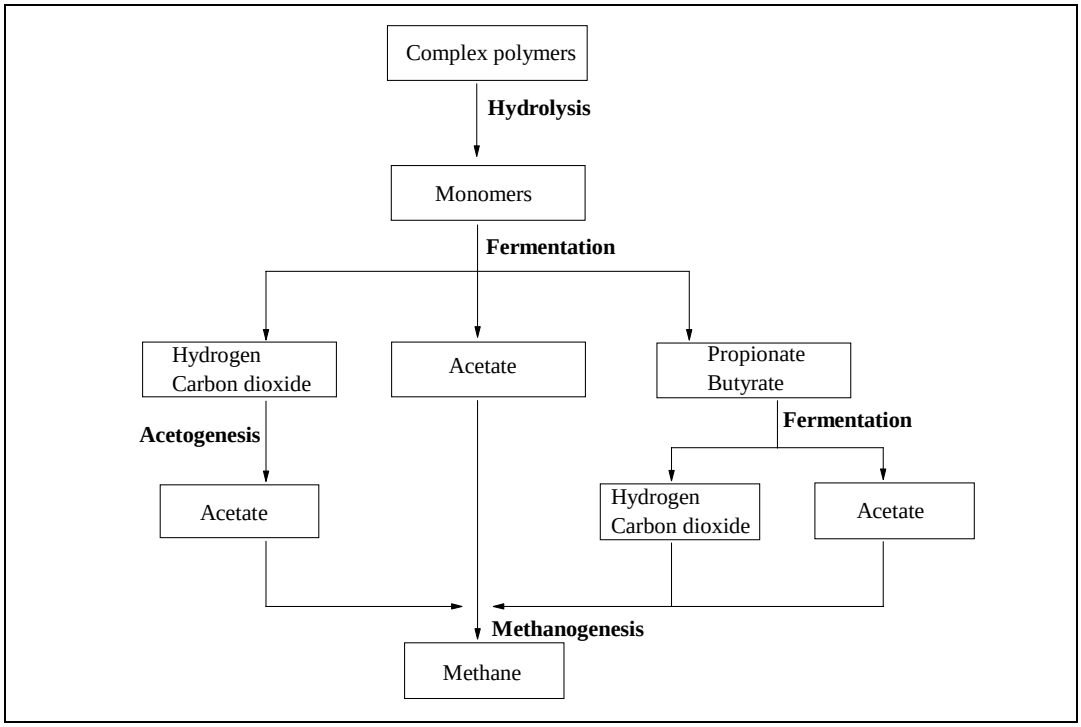


FIGURE 2.1 : Overall process of anaerobic decomposition (After: Brock and Madigan, 1991).

Currently, most soluble effluents, which are treated at wastewater treatment works, are treated by the activated sludge process and not by anaerobic digestion. The anaerobic degradation process has several advantages over aerobic processes for treatment of high-strength organic effluents. Although the microbiology and biochemistry of the process are complex, it normally operates effectively with minimal control (McCarty, 1964). The anaerobic bacteria are ubiquitous and proliferate with suitable conditions.

In aerobic treatment, the microorganisms use the organic waste as substrate and use the oxygen in the air to metabolise a portion of this to carbon dioxide and water. Since these organisms obtain energy from this oxidation, their growth is rapid and a large portion of the organic waste is converted to new cells (Speece, 1996). The portion converted to biomass is not actually stabilised but is simply biotransformed. Although these cells can be removed from the waste stream, the biological sludge they produce still presents a significant disposal problem. Unlike aerobic oxidation, the anaerobic conversion to methane gas provides relatively little energy to the microorganisms. Thus, their rate of growth is slow and only a small portion of the waste is converted to new biomass with the major portion converted to methane gas. Conversion to methane represents waste stabilisation since methane is poorly soluble and escapes from the waste stream where it can be collected. As much as 80 to 90 % of the degradable organic portion of a waste can be stabilised in anaerobic treatment, even in highly loaded systems. This is in contrast to aerobic systems where only about 50 % of the waste is actually stabilised, even with conventional loadings (McCarty, 1964).

Another advantage of anaerobic digestion is, since only a small portion of the waste is converted to cells, the problem of disposal of excess sludge is greatly minimised. The absolute quantity as mass of organic matter is low and the dewatering capacity is high (Jewell, 1987; Lettinga, de Man, van der Last, Wiegant, van Knippenberg, Frijns and van Buuren, 1993; Etheridge and Leroff, 1994).

Since anaerobic treatment does not require oxygen, the treatment rates are not limited by oxygen transfer and the non-requirement for oxygen also reduces the power requirements. In contrast, the methane gas produced is a

good source of fuel energy (McCarty, 1964). A disadvantage of anaerobic digestion, however, is the global warming potential of the methane gas, which is approximately 11 times greater than that of carbon dioxide. Some 250 x 10^6 tonnes/year of methane are released world-wide into the atmosphere from uncontrolled methanogenic fermentation of organic wastes and residues. A 20 % reduction in global warming may be achieved by utilisation of organic wastes and residues for the production of biofuels and chemicals, both by preventing methane emission and replacing fossil fuels (Ghosh, 1997).

2.2 ANAEROBIC MICROBIOLOGY

During **hydrolysis** (**Figure 2.1**) complex long-chain macromolecules (carbohydrates, lipids and proteins) are hydrolysed extracellularly, via the Embden-Meyerhof pathway (EMP), to short-chain compounds (sugars, fatty acids and glycerol, and amino acids, respectively). Hydrolysis can be a slow process and can be the rate-limiting step in fermentation particularly if the influent contains particulate or large complex molecules in significant quantities. The resulting monomers are **fermented** to various intermediates, primarily acetate, propionate and butyrate, with the production of carbon dioxide and hydrogen. The biochemical pathways and end products for this phase depend upon the substrate and the hydrogen partial pressure (**Figure 2.2**). At a low hydrogen partial pressure, glucose is catabolised to acetate, carbon dioxide and hydrogen. At both low and high hydrogen partial pressures, glucose can be degraded to butyrate, carbon dioxide and hydrogen (McCarty and Smith, 1986; Sam-Soon, Wentzel, Dold, Loewenthal and Marais, 1991). When the hydrogen partial pressure is high, acetate, propionate, carbon dioxide and hydrogen will be formed from glucose. The propionate and butyrate produced in this phase cannot be used directly for methanogenesis and they are converted to acetic acid, carbon dioxide and hydrogen in a second fermentation phase. This conversion can only occur under conditions of low hydrogen partial pressures. Additional acetate is produced by a second group of microorganisms termed acetogenic bacteria (Pfeffer, 1979; Sam-Soon et al., 1991). The acetic acid becomes the substrate for a group of strictly anaerobic methanogenic bacteria. These bacteria ferment acetic acid to methane and carbon dioxide. This methane, together with the methane formed by bacteria which reduce carbon dioxide utilising hydrogen gas or formate produced by other species, accounts for the methane produced in this process (Pfeffer, 1979). The methane formed in this last stage, being poorly soluble in water, is lost to the gas phase. It can be collected and used for its energy value. The carbon dioxide that is evolved partially escapes to the gas phase (Pfeffer, 1979; Fang and Lau, 1996). Thus, two main substrate sources are used for methanogenesis, namely, hydrogen and acetate. The methanogens are classified into three groups according to their energy source: hydrogenotrophs, which use hydrogen as the only energy source, acetoclastic methanogens, which use acetate as their sole energy source, and hydrogen/acetate utilisers, which can utilise both hydrogen and acetate.

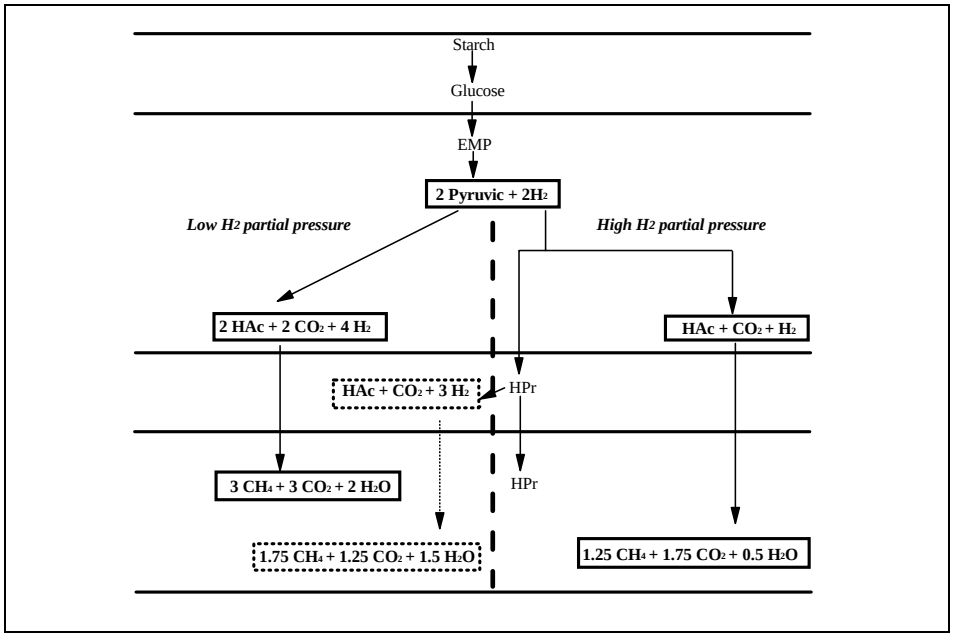


FIGURE 2.2 : Methane fermentation under high and low hydrogen partial pressure conditions (After : Sam-Soon, Loewenthal, Wentzel and Marais, 1989).

The methanogens (e.g. *Methanosaeta, Methanosarcina* and *Methanospirillum*) belong to a special group of bacteria (the Archaebacteria). They differ from other bacteria in their type of metabolism and in the composition of cell constituents (Zehnder, 1988; Schlegel, 1992). Methanogens are obligate anaerobes with strict requirements for low redox potentials and the absence of dissolved oxygen. They normally grow in close association with other non-methanogenic bacteria to form a symbiotic community of microorganisms with a self-regulating fermentation which automatically controls its own pH value, redox potential and oxygen tension.

Many anaerobic bacteria can perform electron-transport phosphorylation (regeneration of ATP) under anaerobic conditions, by transferring electrons derived from a substrate via a short electron-transport chain to an external electron acceptor supplied in the nutrient medium or an internal electron acceptor derived from substrate degradation (Senior, 1991; Schlegel, 1992). In most cases, the energy sources used by organisms carrying out anaerobic respiration are organic compounds but several lithotrophic organisms are also able to carry out this process (Brock and Madigan, 1991). Nitrate, sulphate, carbonate and fumarate ions, as well as sulphur and carbon dioxide can function as electron acceptors (Schlegel, 1992). The presence of alternative electron acceptors may inhibit methanogenesis since sulphate-reducing bacteria (SRB) and nitrate-reducing bacteria can outcompete methanogens for available substrates (Pohland, 1992).

Therefore, for the conversion of a typical polysaccharide, such as cellulose, as many as five major physiological groups of bacteria may be involved in the overall process (Brock and Madigan, 1991) and the microorganisms involved at each stage are metabolically dependent on each other for survival. Anaerobic digestion, therefore, has the potential to degrade complex organic molecules with the production of an energy-rich biogas.

2.3 ANAEROBIC DIGESTERS

When a digester is commissioned for industrial purposes the emphasis must be placed on the efficiency of bioconversion, on both thermodynamic and kinetic grounds (Nyns and Naveau, 1979). The design of an anaerobic digester and the engineering associated with it depends upon the type and volume of the waste it is required to process (Horton, 1979).

Anaerobic digestion tanks can vary in shape but are usually either cylindrical or egg-shaped (Pohland, 1992). The bottoms of the tanks usually slope towards the centre, to form a cone in which the digested solids can collect. A number of design configurations have been used in anaerobic treatment (**Figure 2.3**).

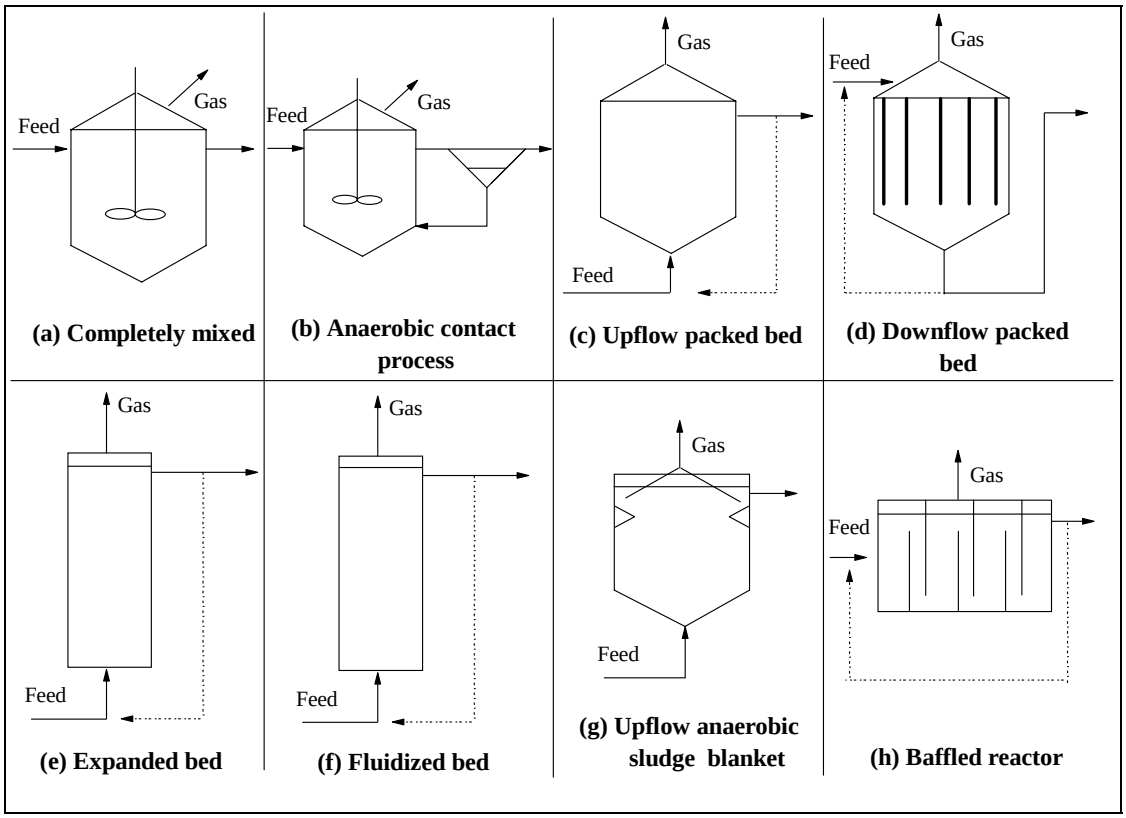


FIGURE 2.3 : Schematic diagrams of various anaerobic digester configurations (After: McCarty and Mosey, 1991; Speece, 1996).

The conventional **completely stirred tank reactor** (CSTR) (**Figure 2.3 (a)**) contains a mechanical agitation system consisting of a vertical shaft with a number of impellers and a number of baffles around the vessel perimeter. The impeller and baffle system provide an effective agitation system for the dispersion of the effluent. Mixing in anaerobic digesters is advantageous as it eliminates scum and thermal stratification. It also provides good contact between the active biomass and the sludge (Pohland, 1992). The major disadvantage of complete mixing in digesters, in addition to the cost of mixing, is the need for a facility that will enhance the separation of the digested solids from the liquid phase.

In the **anaerobic contact process** (**Figure 2.3 (b)**) the wastewater is treated in a continuously stirred tank reactor with an active population of flocculating bacteria degrading the organic material into methane and carbon dioxide. The effluent passes through a sludge settler where the bacteria settle before being returned to

the reaction tank. The biomass separation system retains both active microorganisms and undigested influent suspended solids thus promoting more extensive biodegradation of wastewater particulates (Pohland, 1992). This process requires effective mixing, settleable biomass and efficient clarification and degassing. The process has a limited tolerance to hydraulic loading and biomass retention.

Stationary biofilm reactors use a fixed film for the development of the high biomass concentrations required for the efficient anaerobic treatment of wastewater (Pohland, 1992; van Haandel and Lettinga, 1994). An inert medium or biomass carrier is added to the treatment vessel and the process is operated to favour the growth of the microorganism biofilm on the medium surface. This prevents biomass wash out, allowing the reactors to operate with liquid flow velocities which would wash out non-attached biomass. The fixed film anaerobic reactor designs include upflow fixed bed reactors, downflow fixed bed reactors and expanded and fluidised bed reactors. In general, fixed bed processes provide a stable and easily operable form of anaerobic treatment technology.

Upflow fixed / packed bed reactors (**Figure 2.3 (c)**). The wastewater is passed upwards through the medium particles resulting in a large proportion of the retained biomass not being attached to the packing medium. This non-attached material is retained in the interstices between the medium particles partly by settling and partly through the influence of physical contact with the medium (Pohland, 1992). Since the non-attached biomass contributes significantly to the treatment activity in an upflow fixed bed system, relatively low upflow velocities are usually maintained to prevent washout of the material. New synthetic packings are large open structures with high void volumes. The large voidage maximises the available reaction volume and provides space for the accumulation of non-attached biomass (Pohland, 1992). A disadvantage of this system is blockage due to excess biomass accumulation which ultimately leads to decreased retention capacity of the bed.

For wastewaters with high concentrations of suspended solids, **downflow fixed bed reactors** (**Figure 2.3 (d)**) may be preferable to operation in the upflow mode. They utilise ordered, modular packing which provides a surface for the development of the biofilm (Pohland, 1992). By operating the reactor in a downflow mode, suspended solids and sloughed biofilm solids will be carried down with the liquid flow and out of the reactor. This efficient removal of the suspended solids results in a process which retains only the attached microorganisms. These systems are able to withstand severe hydraulic overloading conditions with only a slight reduction in treatment efficiency. Mixing in the downflow system is provided by a combination of both effluent recycle and the action of rising gas bubbles (Pohland, 1992).

With the expanded and fluidised bed processes, attempts have been made to improve anaerobic reactor mass transfer characteristics by the utilisation of small or medium particles with very high surface-to-volume ratios. By applying high liquid upflow velocities, the medium can be expanded to produce a substantial increase in bed porosity (Pohland, 1992; van Haandel and Lettinga, 1994). The differences between expanded and fluidised beds are the upflow velocity used and the degree of medium expansion maintained. In **expanded bed** systems (**Figure 2.3 (e)**), sufficient flow is applied to increase the settled bed volume by 15 to 30 %. At this point, individual particles are supported partly by the fluid flow and partly by contact with adjacent particles. **Fluidised beds** (**Figure 2.3 (f)**) utilise higher upflow velocities to produce 25 to 300 % bed expansion. In the fluidised state, the medium particles are supported entirely by the flowing liquid and are, therefore, able to move freely in the bed (Pohland, 1992). In both processes an anaerobic biofilm is developed on the surface of the medium particles by the process of immobilisation (Lettinga, 1995). The large upflow velocities applied in these systems provide turbulence at the biofilm liquid interface, thus producing good mass transfer into and out of the biofilm. The high upflow velocities allow the reactors to be designed with relatively large height to diameter ratios and, thus, smaller land area requirements (Pohland, 1992). The major disadvantages of these

systems include the energy cost required for effluent recycle and the combination of thin biofilms and high turbulence prevents the capture and retention of influent suspended solids within the reactor. Sloughed biofilm solids are also rapidly washed out of the reactor.

Upflow anaerobic sludge blanket (UASB) (**Figure 2.3 (g)**) digesters are designed to treat low- and medium-strength wastewaters at high volumetric loading rates and, therefore, at short hydraulic retention times. The most characteristic device of the UASB reactor is the phase separator. It is situated at the top of the reactor and divides it into the lower digestion zone and the upper settling zone (van Haandel and Lettinga, 1994). No support medium is added to the reactor since the process is based on the immobilisation of the biomass in the form of sludge granules. Thus, the success of the reactor depends on the formation of these highly flocculated granules. The granules allow the active biomass to be retained in the reactor, independent of the flow rate, thus maintaining a good conversion efficiency. The wastewater enters at the bottom of the digester and flows up through the bed of anaerobic granular sludge. The biomass of the sludge blanket converts the organic compounds to biogas. At the top of the reactor, the mixture of wastewater, sludge and biogas is separated into its components by the phase separator. The anaerobic granular sludge is retained in the reactor and an effluent, essentially free of suspended solids, is discharged (van Haandel and Lettinga, 1994). Baffles, placed beneath the apertures of the gas collector units, operate as gas deflectors and prevent biogas bubbles from entering the settling zone where they would create turbulence and, consequently, hinder the settling of sludge particles (van Haandel and Lettinga, 1994). Periodically, excess granular sludge can be removed and stored for use in other anaerobic treatment plants. The UASB system relies on the agitation brought about by biogas production since there is no mechanical mixing (Lettinga, 1995). The UASB is a simple process to operate.

The **anaerobic baffled reactor** (**Figure 2.3 (h)**) is a simple rectangular tank which is divided into a number of equal volume compartments by means of partitions from the roof and bottom of the tank (Gunnerson and Stuckey, 1986). The liquid flow is alternately upward and downward between the partitions and on its upward passage the waste flows through an anaerobic sludge blanket (Gunnerson and Stuckey, 1986). Hence, the waste is in contact with the active biomass but, because of the design, most of the biomass is retained in the reactor. Due to its physical configuration, this type of reactor should be able to treat wastes with high solids contents (Gunnerson and Stuckey, 1986). In principle, all phases of the anaerobic degradation process can proceed simultaneously (Lettinga, 1995). The sludge in each compartment will differ depending on the specific environmental conditions prevailing there and the remaining compounds or intermediates to be degraded. A staged reactor can provide a higher treatment efficiency because more biorefractory intermediates, such as propionate, will be in an optimal environment for degradation (Lettinga, 1995). The process stability is a distinct advantage.

2.4 ANAEROBIC DEGRADATION PROCESS

The applicability of anaerobic processes for treatment of industrial wastewaters and domestic sludges has been recognised for many years. However, there has been some scepticism due to the lack of quantitative information on the capability of such processes to handle potentially toxic or high-strength wastes (Haghighi-Podeh and Bhattacharya, 1996).

The main aims of anaerobic treatment are the purification of the wastewater so that it can be discharged into watercourses (Baader, 1981) and the transformation of sludges to innocuous and easily dewatered substances (Pohland, 1992). Thus, there is a marked reduction in the amount of organic material, measured as COD. The final product is a stable, innocuous sludge which can be used as a soil conditioner or which can be co-disposed (Pohland, 1992). The anaerobic digestion system applied should offer the highest possible organic matter

removal efficiency and the shortest possible hydraulic retention time, i.e. the volume of the system should be as small as possible (van Haandel and Lettinga, 1994) .

2.4.1. Conventional anaerobic sewage treatment

Ross et al. (1992) provided a comprehensive overview of the anaerobic digestion process in the form of an operating guide. A brief description of the process is given below. Initially the larger, heavier solids in the effluents are removed by screens. Screening is essential since the raw wastewater contains solids which, if not removed, will accumulate in the digester thus reducing its volume (Ross, Novella, Pitt, Lund, Thomson, King and Fawcett, 1992). Grit is also removed to prevent reduction of the digester volume. The wastewater then passes into primary sedimentation tanks where the settleable suspended material settles out. This sludge is withdrawn and used in the secondary treatment. The volume of primary sludge removed represents about 2 % of the influent wastewater volume being treated but around 40 % of the organic load received, expressed as the COD, or around 60 % of the influent loading expressed as suspended solids. Primary sedimentation is the process by which the velocity of the wastewater is reduced below the point at which it can transport the settleable and a major part of the suspended solids (Ross et al., 1992). It is essential that the primary sedimentation tanks are operated correctly as this is the first stage of water and solids separation in a treatment works. If this separation is not carried out correctly then the processes downstream will be adversely affected. The solids content of the sludge being withdrawn from the tanks should be maintained between 2 % to 5 % total solids. The longer the desludging period, the less concentrated the sludge will become resulting in a very thin sludge being passed to the digester. As the cost of sludge handling and treatment may exceed 50 % of the operating costs of the works, the efficient operation of the sludge processing stream offers the potential for significant savings in treatment costs.

The primary sludge comprises ca. 70 % organic and 30 % inorganic solids. The organic solids are problematic and have to be reduced or stabilised. It is this fraction which is mostly used as the substrate for the anaerobic bacteria (Ross et al., 1992). The inorganic fraction is not generally considered such a problem since the larger inorganic materials should have been removed in the screening stage.

The sludge may be thickened in a process which increases the concentration of suspended solids by the separation and removal of some of the liquid phase. This increase in solids concentration is important to promote effective digestion (prevent dilution of the bacterial substrate) and to maximise the use of the available digester capacity, i.e., excess water uses up digester capacity and reduces retention time. Thickening also reduces the amount of heat required in a heated digester and prevents the washout of solids and organisms from a hydraulically overloaded digester (Ross et al., 1992).

Environmental factors, such as pH, temperature, ionic strength or salinity, nutrients and toxic or inhibitory substances, affect the rates of methanogenesis in anaerobic microbial conversion processes (Pohland, 1992). Most anaerobic conversion processes operate best at a near neutral pH and methanogenesis only proceeds at a high rate when the pH is maintained in the neutral range (Ross et al., 1992). At pH values lower than 6.8 or higher than 7.8 the rate of methanogenesis decreases (van Haandel and Lettinga, 1994). The eventual pH obtained in a specific anaerobic digester will be determined, to a large extent, by the substrate supplied to the digester (Kotze, Thiel and Hattingh, 1969). Two factors closely associated with pH are the concentration of volatile fatty acids and the alkalinity of the system. The alkalinity of an anaerobic digester is a measure of the buffering capacity of the contents of the digester. Alkalinity is important to counteract sudden increases in the fatty acid content (Kotze et al., 1969). Digesters usually have a good buffering capacity due to the presence of nitrogen in urine which forms ammonium bicarbonate (NH_4HCO_3).

Temperature is a key variable in biological processes (Zinder, Anguish and Cardwell, 1984) and since methanogenesis is a microbially-mediated process it is strongly temperature-dependent. There are two temperature ranges generally used for anaerobic digestion: mesophilic (30 to 40 ^{o}C) and thermophilic (50 to 60 ^{o}C) (Zinder et al., 1984). Most digesters are heated and operated in the mesophilic temperature range of 32 to 38 ^{o}C. The optimum temperature is approximately 35 to 37 ^{o}C and results in effective digestion in some 20 d. Anaerobic digesters are heated for two principal reasons: to increase the activity of the methane-producing bacteria thus reducing the digestion time; and to liquefy fats and greases to hasten their decomposition (Ross et al., 1992). The methane-producing bacteria are sensitive to temperature changes and their activity can be severely affected by sudden changes. Controlling the temperature is largely determined by the degree of mixing in the digester. An important advantage of thermophilic digestion is a greater destruction of pathogenic organisms although these processes are not always cost effective (Pfeffer, 1979; Pohland, 1992). Thermophilic processes are less stable than mesophilic processes.

High salinities (> 0.2 M NaCl) have an inhibitory effect on mixed methanogenic populations (Dolfing and Bloemen, 1985). The total ionic strength also affects chemical activity and, therefore, the possible effects of other chemical species in terms of inhibition (Pohland, 1992).

In addition to the fundamental requirements for macronutrients such as carbon and nitrogen, the inability of many anaerobes to synthesise some essential vitamin or amino acid often necessitates supplementation (Pohland, 1992; Lettinga, 1995). Four elements, iron, cobalt, nickel and sulphur, have been found to be obligatory nutrient requirements for methanogens to convert acetate to methane (Speece, 1983).

Toxicity or inhibition of methanogenic processes can be caused by a variety of conditions such as the generation of inhibitory intermediates. The effects of these compounds can depend on the particular culture and the system configuration and operation. Heavy metals, present in concentrations greater than those required for enzyme viability, can be potentially toxic and inhibitory (Pohland, 1992; van Haandel and Lettinga, 1994). Compounds in low concentrations may provide stimulation while in high concentrations they may be toxic (**Table 2.1**). Adaptation to inhibitory substances is possible.

TABLE 2.1 : Total concentration of individual ions required to inhibit anaerobic digestion (After: Water Pollution Control Federation, 1987).

Molecule	Maximum concentration (g/l)
Sodium	2.2
Ammonia	1.1
Potassium	1.71
Calcium	1.4
Magnesium	0.6
Sulphide	0.2
Copper	0.0005
Zinc	0.001
Nickel	0.002

There are various other factors which affect the rate and efficiency of the anaerobic digestion process. The composition of the sludge is one such factor and is determined by properties of the sludge such as the nutrient content, solids content and toxicity. The method of sludge addition to the digester is important. The concepts of feeding and loading a digester are interrelated but do differ. Feeding concerns the physical transfer of sludge to the digester only, while loading considers the feeding in relation to the contents and volume of the digester (Ross et al., 1992). The *specific hydraulic load* can be defined as the ratio of the influent flow rate to the working volume of the bioreactor. Therefore, the specific hydraulic load is numerically equal to the inverse of the hydraulic retention time (van Haandel and Lettinga, 1994). The *organic load* of a system is defined as the mass of influent organic material per unit time and the *specific organic load* is the mass of influent organic material per unit time and per unit of reactor volume (van Haandel and Lettinga, 1994). The best influent feed schedule is a continuous feed at a low rate as it eliminates any abrupt flow rate or organic loading changes that could result in shock loading. Shock loading can result in fluctuations in gas production, pH, alkalinity, organism growth rate, volatile acids concentration, etc. (Ross et al., 1992).

Digestion cannot occur without actual contact of the bacteria with the substrate (Osborn, 1992). Contact occurs most efficiently by mixing. Good mixing has numerous other benefits which include: an even distribution of contents throughout the digester; reduction of grit settlement and scum formation so that there is less reduction in effective digester volume; reduction of the effects of toxic substances by promoting rapid dispersion and dilution; provision an even temperature profile throughout the digester; and enabling chemicals added for pH control to be evenly distributed throughout the digester (Kotze et al., 1969; Pohland, 1992; Ross et al., 1992; Lettinga, 1995). Mixing may be brought about by gas recirculation, sludge recirculation or mechanically turned impeller blades (Kotze et al., 1969).

If the solids retention time in the digester is too short, the slow-growing methane-producing bacteria will be washed out. For high rate digestion, retention times of 25 to 30 d may be used. For cold digestion, retention times in excess of 50 d are required (Ross et al., 1992).

The main constituents of the gas produced in a digester are carbon dioxide (25 to 40 %) and methane (65 to 75 %). Small volumes (1 to 5 %) of nitrogen, hydrogen sulphide and hydrogen are also produced (Ross et al.,

1992; Etheridge and Leroff, 1994). The composition of the digester gas depends mainly on the mean oxidation state of the carbon in the organic matter (**Figure 2.4**). For monitoring anaerobic digestion, the $CH_4 : CO_2$ ratio represents a rapid and sensitive parameter (Kotze et al., 1969). Any sudden marked change in this ratio is indicative of unbalanced conditions. The volume of biogas produced per unit mass of volatile solids destroyed is an important and sensitive process control indicator to assess the activity of the microorganisms and the progress of digestion (Ross et al., 1992). The earliest definition of the stoichiometry of anaerobic digestion was that of Tarvin and Buswell (1934). This still provides a good approximation of the biogas composition from a waste of known chemical composition (Tarvin and Buswell, 1934):

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right)H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CO_2 + \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)CH_4 \qquad [2.1]$$

This equation reflects algebraically what is shown in **Figure 2.4**, i.e., that the higher the oxidation state of the carbon in the organic substrate, the lower will be the proportion of methane in the biogas.

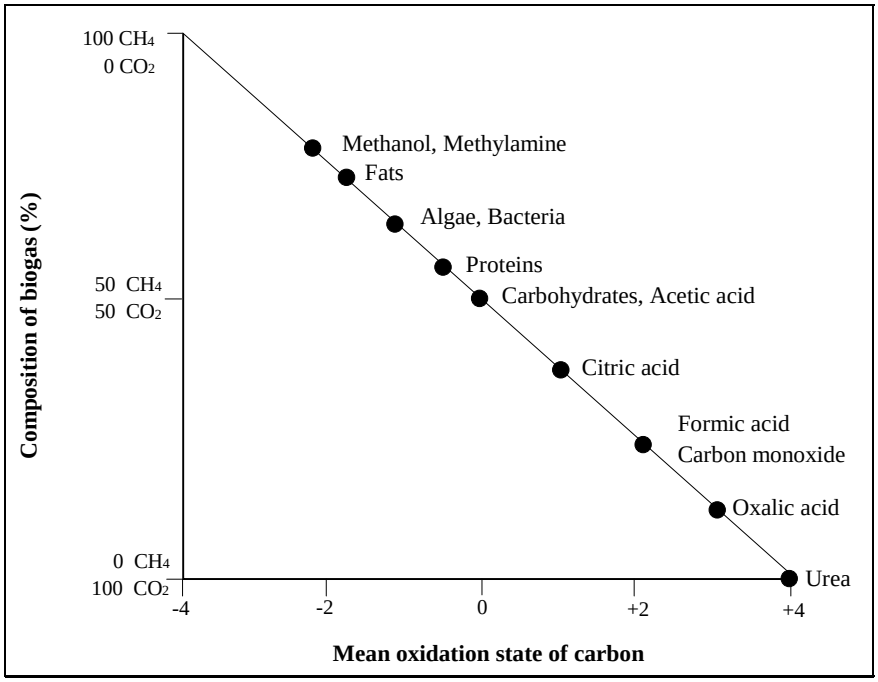


FIGURE 2.4 : Composition of the biogas depending on the mean oxidation state of the carbon in the substrate (After: Gujer and Zehnder, 1983).

The methane produced in the process is usually partly used and partly flared. The energy in the digester gas can be used to heat the sludge and to maintain the digester at the desired temperature. The digester is covered to contain odours, maintain temperature, keep air out and to collect the gas. There is a space between the cover and the liquid surface of the digester contents for gas collection. Many anaerobic digestion plants have a means of storing excess gas, such as a separate gas holder. If a constant flow and load are applied and organic matter does not accumulate in the treatment system (steady-state conditions), the daily mass of influent COD should be equal to the sum of the daily mass of COD leaving the system as methane and in the excess sludge produced, in the effluent (van Haandel and Lettinga, 1994).

Anaerobic sludge digestion can be divided into two phases (primary and secondary). The main role of the primary phase is to stabilise the sludge while the secondary phase is to allow for solid liquid separation (Ross et al., 1992; van Haandel and Lettinga, 1994). There is no mixing in the secondary phase and the sludge can,

therefore, settle to the bottom of the digester. This creates a layered structure of the contents inside the secondary digester. A scum layer is often formed on the surface while the middle zone of supernatant is relatively solids free. It is important that the supernatant and sludge are drawn off correctly from the digester as incorrect procedures can upset the sludge stabilisation process. The supernatant, or final effluent, produced by anaerobic treatment contains solubilised organic matter which is amenable to quick aerobic treatment or can be recycled as the primary sedimentation tank influent (Gray, 1989). Efficiency of anaerobic digestion may be measured from a knowledge of the COD or carbon content of the substrate supplied and the COD or carbon content of the final effluent, i.e., by doing a mass balance on the substrate (Kotze et al., 1969):

in - out - cell growth - product formation - maintenance = accumulation

The withdrawn sludges are discharged to a dewatering process such as sludge drying beds or mechanical dewatering systems (Ross et al., 1992). Drying beds are the most common method of dewatering sludges at wastewater treatment plants. The primary objective in the drying bed operation is to reduce the moisture content of the sludge cake to a level consistent with the mode of sludge removal and final dry cake utilisation (Ross et al., 1992). There are various other dewatering methods available including centrifugation, belt filter press, vacuum filter, filter press and tubular filter press.

A very large percentage of the solids loading received at the wastewater treatment works is present as, or is converted into, sludge. Although the anaerobic digestion process reduces the mass of sludge produced, the remaining sludge mass requires disposal. It is necessary to ensure that secondary pollution does not occur as a result of unsuitable disposal practices. In addition to macro-nutrients, such as nitrogen and phosphorus, the sludge also contains minor nutrients such as calcium, magnesium, iron and sulphur. Depending on the source of the wastewater, the sludge may also contain heavy metals (Ross et al., 1992). The organic content, nutrients and trace metals present in the sludge may be advantageously utilised if the sludge is incorporated into agricultural land as a soil conditioner. However, due to the presence of certain contaminants, such as heavy metals, viable pathogens and complex organic compounds, consideration must be given to its potentially dangerous and hazardous properties when disposing of sludge.

The Department of National Health and Population Development produced a set of guidelines indicating permissible utilisation and disposal routes for waste water sludge (Department of National Health and Population Development, 1991). Sludge is classified into three types, A, B and C, in decreasing order of its potential to cause odour nuisances, fly breeding and to transmit pathogenic organisms to man and his environment (Department of National Health and Population Development, 1991; Ross et al., 1992; Department of Water Affairs and Forestry, 1994). When the sludge cannot be disposed of as a soil conditioner, it could be co-disposed in admixture with refuse in a sanitary landfill.

Control of anaerobic digestion is complicated since the different parameters that characterise the environment within the digester tank are all interrelated and one variable may directly or indirectly affect the others (Pohland, 1992).

2.4.2. Anaerobic degradation of industrial wastewaters

Anaerobic processes have been used for the treatment of concentrated municipal and industrial wastewaters for well over a century (McCarty and Smith, 1986). Concentrated organic industrial wastes such as distillery effluents and wastes from the manufacture of various foodstuffs generally create serious treatment or disposal problems for the industry or the local authority concerned because of their high organic load. These wastes have

high chemical oxygen demand (COD) concentrations compared with domestic sewage (Ross, 1989). A COD measurement gives an indication of the amount of organic material in the wastewater, which could be oxidised by microorganisms. The efficiency of a treatment process can, therefore, be expressed in terms of the decrease of the initial COD (Boyd, 1988). Effluents with a low fraction of readily degradable COD are reluctantly accepted into communal sewers by the controlling authority and the manufacturer is faced with heavy trade-effluent charges. Research has shown that aerobic methods are seldom efficient in treating these effluent types (Ross, 1989).

The surge of interest in the anaerobic digestion process, supported by advances in process engineering, has been translated into numerous treatability studies of various industrial wastewaters (Speece, 1983). The fruition of this activity has been manifested in the commissioning of a number of full-scale industrial wastewater anaerobic treatment installations. Initially, the anaerobic digestion process was applied primarily to complex feedstocks, such a municipal wastewater sludges, which contained a wide range of nutrients and alkalinity sources (Speece, 1983). Other candidate feedstocks considered for anaerobic treatment were food processing wastewaters such as the effluent from meat-packing plants (Steffen and Bedker, 1961) and sugar beet operations (Speece, 1983). It was found that these wastewaters contained readily degradable organic molecules and that the solutions had normal complements of inorganic ions such as those commonly found in surface or ground waters. Other feedstocks which have been investigated include those from pulp and paper mills, coal conversion processes and deionised industrial process wastewaters. Anaerobic digestion of inorganic wastewaters has also been investigated with acclimation of bacteria to inhibitory concentrations of heavy metals. The basic question is no longer whether an industrial effluent can be anaerobically biodegraded to methane, since most organic molecules are amenable to anaerobic treatment, but rather at what rate is it degradable and to what degree is it degradable (Speece, 1983).

2.5 CURRENT FATES OF HIGH-STRENGTH INDUSTRIAL EFFLUENTS

High strength, or toxic, organic effluents are difficult to dispose of. Current disposal options, in the KwaZulu-Natal region, include marine outfall or co-disposal into municipal landfills.

2.5.1. Marine outfall

Marine disposal of wastewater, via submarine pipeline, relies on the powerful dispersing capability of the sea, its ability to biodegrade many organic wastes and the binding ability of sea sediments. Marine disposal has proved to be an inexpensive disposal option and has been widely used in South Africa (Department of Water Affairs and Forestry, 1994).

In 1983, a need for seawater quality guidelines in South Africa became apparent to make decisions regarding pipeline discharges of effluents to sea (Department of Water Affairs and Forestry, 1992). The South African National Scientific Programme Report No. 94 was published and now forms the basis for the planning of sea outfalls and also for environmental assessments of areas subjected to pollution loads (Department of Water Affairs and Forestry, 1992). Maximum allowable concentrations were stipulated for the discharge of effluents to the sea. An important consideration was to involve a broad spectrum of the community concerned with the management of the marine water quality in South Africa (Department of Water Affairs and Forestry, 1992). The main purpose of these guidelines was to maintain South Africa's marine water resources in a state fit for use. Fitness for use is related to the specific characteristics of the coastal zone and its physical ability to assimilate external inputs such as discharges from land (Department of Water Affairs and Forestry, 1992).

A number of industries are situated in the KwaZulu-Natal region, especially along the south coast of Natal and in the Durban area and at Richards Bay. Situated along the upper south coast are three large companies which discharge industrial effluent into the sea via pipelines subject to the conditions of a permit granted by the Department of Water Affairs and Forestry. The east coast is also one of the most popular tourist and recreation areas in South Africa (Department of Water Affairs and Forestry, 1992; Scott, 1997). Marine pollution can be defined as the introduction by man, directly or indirectly, of substances or energy into the marine environment resulting in such deleterious effects as harm to living resources, hazards to human health, impairment of quality for use of seawater and reduction of amenities (Department of Water Affairs and Forestry, 1992). Aquatic systems do have a limited capacity to assimilate or disperse some substances or energy without unacceptable effects. The water quality guidelines define the level of acceptability and thereby the water quality management objectives or goals to be achieved by controlling or limiting waste discharges or other man-induced impacts on the marine environment (Department of Water Affairs and Forestry, 1992). Standards are set by the Department of Water Affairs and Forestry for the discharge of water into the marine environment. Stricter standards are set for discharge into rivers due to potential contamination to humans. Discharge into rivers is the preferred option as it results in the recycling of water whereas discharge to sea results in the loss of freshwater.

2.5.2. Co-disposal in municipal landfill sites

The objectives of co-disposal are to absorb, dilute and neutralise any liquids or sludges, and to provide a source of biodegradable materials in order to encourage microbial activity that will assist in the degradation of hazardous compounds (Department of Water Affairs and Forestry, 1994). The major problem with the co-disposal of wastewater is the generation of excess leachate (Ross et al., 1992).

In a sustainable world, little or no industrial and hazardous waste would be generated by society and those which were produced would be treated and re-used in other processes. However, in the real world, considerable quantities of industrial wastes are generated and must be treated and disposed of in an environmentally acceptable manner (Forster, 1994). Efficient wastewater treatments are, therefore, critical and anaerobic digestion has potential as an efficient, cost-effective treatment process.

Chapter 3

Anaerobic Kinetics & Modelling

This literature review presents a discussion of the principles guiding the experimental elucidation of microbial growth and substrate utilisation kinetics, and the development of mathematical models for anaerobic wastewater treatment systems. Mechanisms for bacterial growth are described (**Section 3.2**) as well as the associated bioenergetics (**Section 3.3**). **Section 3.4** briefly introduces microbial kinetics and the Monod equation which is the basis of the kinetics and modelling of anaerobic cultures (**Section 3.5**). Lastly, **Section 3.6** provides a brief overview of population dynamics and the effect of prevailing conditions on determining the predominant species in a population.

3.1 INTRODUCTION

Anaerobic treatment is a multi-disciplinary field. Whilst numerous studies have significantly increased the understanding of the microbiology and biochemistry of anaerobic treatment, knowledge of process kinetics is needed to establish a rational basis for system design and analysis. The efficiency of a wastewater treatment process is influenced by the microbiology and the associated biochemistry and, when located in a reactor, biochemical reactions are also affected by flow dynamics and associated mass transfer considerations (Harper and Suidan, 1991). Much of the kinetic data available in the literature were derived in laboratories where the methods used may not clearly represent microbial behaviour in pilot- or full-scale wastewater treatment reactors. However, these data are useful in describing critical associations. This review concentrates on the concepts behind the equations for the determination of kinetic parameters associated with the complex microbial conversion of wastewater substrates, and the ways in which the equations can be linked together to build a mathematical model.

3.2 BACTERIAL GROWTH

When a bacterium is inoculated into a new culture medium, it exhibits a characteristic growth curve composed of four phases: the lag phase; the log or exponential growth phase; the stationary phase; and the death phase. (**Figure 3.1**).

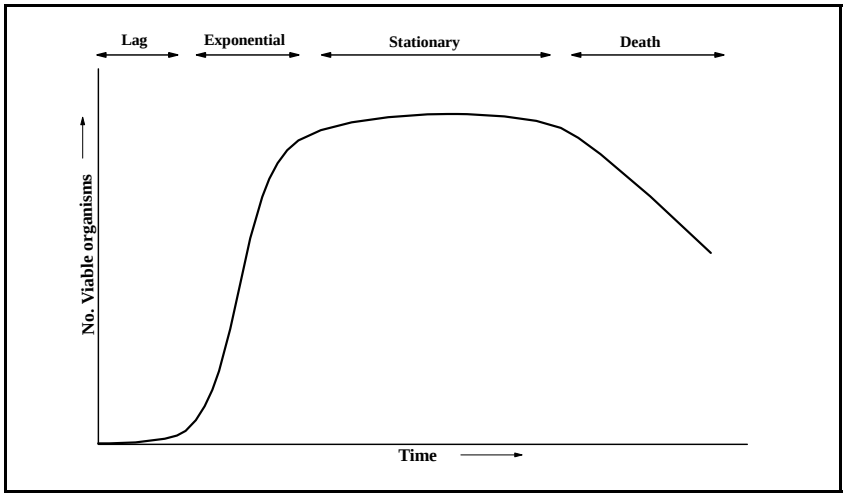


FIGURE 3.1 : Bacterial growth curve (After: Atlas, 1988).

During the lag phase there is no increase in cell numbers but the bacteria are preparing for reproduction and synthesising DNA and various inducible enzymes required for cell division. They may increase in size during this stage. During the exponential phase of growth, bacterial reproduction occurs at a maximal rate for the specific growth conditions (Atlas, 1988). If a bacterial culture, in the exponential phase, is inoculated into an identical fresh medium, the lag phase is usually bypassed and exponential growth continues. This occurs because bacteria are already actively carrying out the metabolism necessary for continued growth. If, however, the inoculum is not transferred to a new medium and no fresh nutrients are added, the stationary growth phase is reached where there is no further net increase in bacterial cell numbers. During the stationary phase, the growth rate is exactly equal to the death rate. A bacterial population may reach stationary growth when a required nutrient is exhausted, when inhibitory end products accumulate, or due to the physical conditions. In all of these cases, there is a feedback mechanism that regulates the bacterial enzymes involved in key metabolic steps. The duration of the stationary phase varies. The death phase is the result of the inability of the bacteria to carry out further reproduction.

The described bacterial growth curve is characteristic of bacteria in batch culture. In a continuous system, nutrients are continuously supplied and end products removed.

3.2.1 Batch culture

In batch culture growth nutrients are expended and metabolic products accumulate in the closed environment. Cell growth can be defined as:

$$\frac{dX}{dt} = \mu X \qquad [3.1]$$

The rate of cell growth is written as μX, where X is the cell mass per unit culture volume and μ, which has the units of reciprocal time, is the specific growth rate of the cells (Bailey and Ollis, 1986). In a batch system the biomass concentration is still low when the growth rate attains its maximum value. In a later stage, when the limiting substrate (S) nears exhaustion, growth approaches zero in the stationary phase while the biomass concentration is at its maximum (Mitchell, 1972). The microorganisms present will continue to metabolise thus exhausting the growth-limiting substrate. This will eventually lead to changes in species predominance. Thus, the mass balance on the limiting substrate is coupled to the cell mass balance since μ depends on S.

3.2.2 Continuous culture

In batch tests the production and time sequence are determined by a given fermentation tank. The **continuous-flow** cultivation method is characterised by the continuous supply of an amount of nutrients to the microorganisms at optimum flow, corresponding to the most advantageous multiplication dynamics (Malek and Fencl, 1966). The objective of these systems is to approach the conditions at the initial part of the exponential phase of the bacterial growth curve. The application of this method requires exact knowledge of the optimum conditions for growth; provision of these conditions to the continuously cultivated cells with maximum uniformity and in proportion to their growth; and maintenance of optimum conditions not only to the culture as a whole but to each individual cell. This is generally effected by intensive stirring of the culture to secure uniform distribution of the influent medium in the total cultivation volume (Malek and Fencl, 1966). Thus, the general features of a continuous-flow culture in practice are the nutrient medium flows continuously and uniformly at a predetermined rate from the storage tank into the cultivation vessel, where it is rapidly mixed with the microorganisms which are cultivated in this medium. The volume of the culture is chosen in such a way as to allow optimum co-ordination of growth rate and nutrient inflow while the effluent contains the grown microorganisms and is equal to the inflowing volume of substrate (Malek and Fencl, 1966). If the inflow rate surpasses the limit given by the growth capacity of the microorganisms these begin to be washed out.

In a completely mixed reactor (**Figure 3.2**), with volume V containing a concentration of organisms X, and substrate, S, the flow rate through the system is Q and the influent contains a constant concentration of substrate S_o.

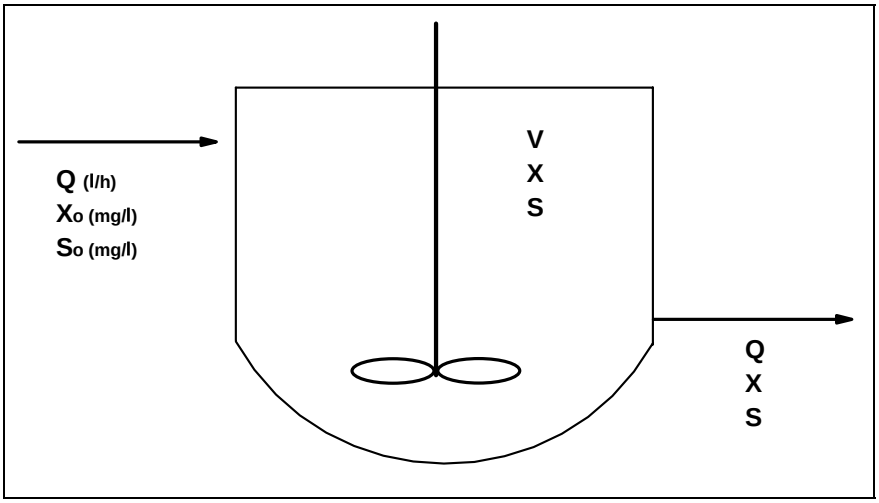


FIGURE 3.2 : Diagram of a continuous reactor (After: Bailey & Ollis, 1986).

When a cell mass balance is performed over the reactor in **Figure 3.2**:

$$in - out + growth - death = accumulation$$

$$\frac{QX_o}{V} - \frac{QX}{V} + \mu X - bX = \frac{dX}{dt} \qquad [3.2]$$

where b = death constant

For a sterile feed, $X_o = 0$, and if the death rate is low, i.e., $b << \mu$, then:

$$\frac{dX}{dt} = -\frac{Q}{V}X + \mu X \qquad [3.3]$$

At steady state $dX/dt = 0$, hence the growth rate of the microorganisms in the system (μXV) must equal the loss if microorganisms from the system (XQ) and the dilution rate (D) is equal to the specific growth rate.

$$D = \frac{Q}{V} = \mu \qquad [3.4]$$

Within limits, the growth rate of the bacteria is governed by the concentration of substrate available. S is the concentration of substrate that will keep the bacteria growing at a rate μ. When a material balance is performed on the limiting substrate:

$$\frac{Q}{V}S_o - \frac{Q}{V}S - \frac{\mu X}{Y} = \frac{dS}{dt} \qquad [3.5]$$

where Y is the yield coefficient. Yield is defined as:

$$\frac{dX}{dt} = Y \cdot \frac{dS}{dt} \qquad [3.6]$$

i.e. the rate at which the microbial population is growing is directly proportional to the rate at which the substrate is consumed (McCarty and Mosey, 1991). At steady state, $dS/dt = 0$, therefore:

$$D(S_o - S) = \frac{\mu X}{Y}$$

or
$$Y(S_o - S) = X \qquad [3.7]$$

From this derivation, S increases with increases in the growth rate imposed by the dilution rate, D (Bailey and Ollis, 1986; Hobson, 1983).

3.3 MICROBIAL BIOENERGETICS

Bacterial growth occurs at the expense of energy released by the flow of electrons from donors to acceptors (Mitchell, 1972) although only a portion of the free energy released can be captured for useful work and the remainder escapes as heat. The extent to which bacterial growth occurs is a function of the energy released by the electron transfer and the efficiency of energy utilisation by the organism mediating the transfer (Mitchell, 1972). A cell also requires a certain amount of energy per unit time for its maintenance. The material and energy balance restrictions and thermodynamic principles applicable for the analysis of chemical process systems apply equally well to biological systems (Bailey and Ollis, 1986). Although they do not determine the rates of enzymatic reactions, the laws of thermodynamics govern the chemical reactions that occur in a cell and prescribe the flow of energy through the microorganism.

According to the first law of thermodynamics, energy is conserved. The enthalpy (ΔH) of a chemical reaction is a measure of the heat of the reaction. Entropy is defined as the degree of randomness of a system (Mathews and van Holde, 1990). Since living systems are open to exchange energy with their surroundings, both energy and entropy changes are important in determining the direction of thermodynamically favourable processes. The change in free energy, termed Gibbs free energy (ΔG), combines an enthalpy term, which measures the energy change at constant pressure, and an entropy term. According to the second law of thermodynamics, all

processes proceed in the direction that increases the total entropy of the system and the surroundings, that is, in the direction of maximum randomness or disorder. A reaction can occur spontaneously only if ΔG is negative (exergonic). A system is at equilibrium when ΔG = 0 and if ΔG is positive (endergonic) an input of free energy is necessary to drive the reaction.

Many of the metabolic pathways of microorganisms are involved in coupling thermodynamically favourable reactions with the endergonic conversion of ADP and inorganic phosphate to ATP. Others use ATP and generate ADP as a product. The cycling of ADP and ATP within the cell is fundamental to the bioenergetics of microorganisms and the cell must continuously form and consume ATP (Atlas, 1988). Free energy is released when ATP is converted to ADP. The amount of ATP used for biosynthesis depends on the routes of carbon fixation and on the cellular composition.

3.4 MICROBIAL KINETICS

The tools of the mathematical modeller's trade are the kinetic equations, rate constants, mass balances and conversion coefficients that are used to describe the process (McCarty and Mosey, 1991).

3.4.1 Monod growth kinetics

Microorganisms, inoculated into a suitable growth medium, will grow at a rate which is the maximum possible under the given conditions. During their growth the environment will change but if the conditions remain favourable growth will continue until one of the essential substrates is depleted. If all other nutrients are available in excess this substrate is called the growth-limiting substrate. The growth rate of a given species of bacterium growing on a single limiting nutrient can be estimated from the empirical equation presented by Monod (Mitchell, 1972). This equation relates the rate of uptake of that substrate to its concentration in the growth medium. It assumes that all other substrates and nutrients are present in excess and it further assumes that the products of the reaction do not accumulate sufficiently to inhibit the fermentation (McCarty and Mosey, 1991). The Monod equation describes the relationship between the specific growth rate μ and the concentration of an essential substrate *S*:

$$\mu = \frac{\mu_m S}{K_s + S} \qquad [3.8]$$

where: μ = specific cell growth rate (1/d).

μ_m = maximum specific growth rate which the population can achieve in the absence of any nutrient limitations (1/d).

K_s = saturation constant (mg/l).

S = substrate concentration (mg/l).

The maximum specific growth rate (μ_m) is the maximum growth rate achievable when the mass concentration of a limiting substrate, *S*, is much greater than K_s and the concentrations of all other essential nutrients are unchanged. K_s is that value of the limiting nutrient concentration at which the specific growth rate is half its maximum value (**Figure 3.3**) (Bailey and Ollis, 1986). K_s marks the division between the lower concentration range, where μ is strongly (linearly) dependent on *S*, and the higher range, where μ becomes independent of *S*.

K_s represents the affinity of the bacterium for the substrate; the smaller K_s, the greater the affinity. When the value of K_s is small, i.e., $S >> K_s$, then the term $S/(K_s + S)$ can be regarded as an adequate description for calculating the deviation of μ from μ_m. Since a high treatment efficiency is required in practice, it is best to maintain the substrate concentration of the reactor contents at a very low level. The loading potentials, therefore, theoretically depend on the value of K_s. The waste treatment significance of a small value of K_s is that the system can be operated at short solid retention times and correspondingly high rates of specific utilisation without sacrificing effluent quality and treatment efficiency (Lawrence and McCarty, 1969). At high concentrations the substrate may become inhibitory, depending on the type of substrate (Lettinga, 1995). The relation also suggests that the specific growth rate is finite for any finite concentration of the rate-limiting component.

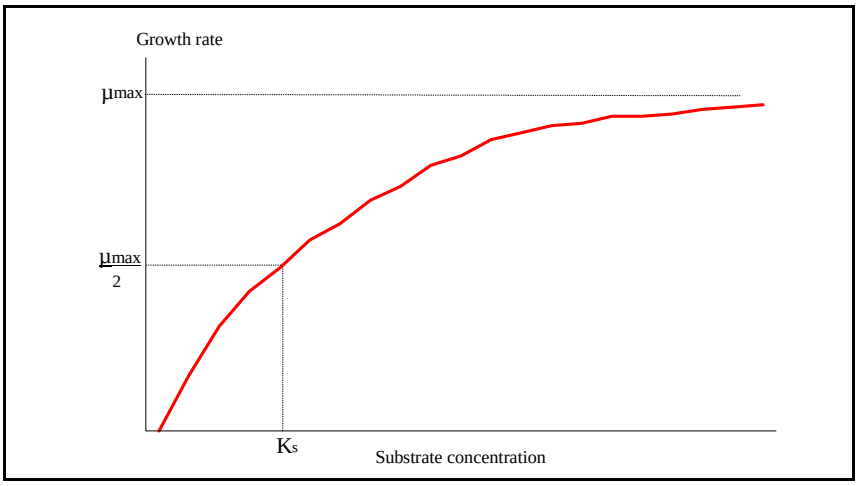


FIGURE 3.3 : Graphical representation of the Monod equation (After: Bailey & Ollis, 1986).

So, for a continuous system, at steady state, with dilution rate D, Eq. 3.7 can be related to the Monod equation (Eq. 3.8) to give:

$$D = \frac{\mu_m S}{K_s + S} \qquad [3.9]$$

$$S = \frac{DK_s}{\mu_m - D} \qquad [3.10]$$

Substituting Eq. 3.7 into Eq. 3.10:

$$X = Y\left(S_o - \frac{DK_s}{\mu_m - D}\right) \qquad [3.11]$$

The specific growth rate, m, can be approximated by the reciprocal of the sludge retention time (t) since it is equal to the specific removal rate of the cells from the system. This is based on the fact that a constant viable cell mass will develop in a reactor at steady state (Wukasch, Leslie Grady and Kirsch, 1980). However, this approximation ignores the effect of viable cell decay. Viable cells are lost from the reactordue to cell lysis and must be replaced. Thus, decay acts to make the specific growth rate higher than estimated by the reciprocal of the retention time:

$$\mu = \left(\frac{1}{\tau}\right) + b$$

$$\cong \left(\frac{\mu_m}{K_s}\right)S \qquad [3.12]$$

Rearranging Eq. 3.12 gives:

$$S = \left(\frac{K_s}{\mu_m}\right)\left(\frac{1}{\tau}\right) + \frac{K_s\, b}{\mu_m} \qquad [3.13]$$

Thus, for a situation where the substrate concentration can be measured, a plot of S versus $1/\tau$ should give a straight line with a slope equal to K_s/μ_m and an ordinate intercept of $K_s\, b/\mu_m$ (Wukasch et al., 1980).

Due to the immense complexity of a bacterial cell, it is apparent that the Monod equation is probably a great oversimplification. As in other areas of engineering, however, this is a case where a relatively simple equation reasonably expresses interrelationships.

3.5 ANAEROBIC CULTURES

Anaerobic treatment is an extremely complex process involving the parallel and consecutive reactions of many interrelated populations whose biochemical behaviour can be dynamic or transient. Metabolic rates are coupled with physicochemical reactions effected by two physical transport phases (liquid and gas). Therefore, substrate conversion reactions are sometimes mass transfer limited, sometimes nutrient limited ($S << K_s$) and sometimes metabolically limited ($S >> K_s$). In a complex multi-step process such as anaerobic treatment, the kinetics of the slowest step will govern the overall kinetics of waste utilisation (Lawrence and McCarty, 1969). In anaerobic digestion, the rate-limiting step is thought to be methane fermentation since the bacteria that ferment acetate to biogas grow notoriously slowly (McCarty and Mosey, 1991).

3.5.1 Kinetics

In anaerobic methane fermentation, K_s tends to be much larger and Y much smaller than for aerobic oxidation (Mitchell, 1972) and the cellular yield coefficient in anaerobic systems is only 0.02 to 0.06 g cells/g COD (Gujer and Zehnder, 1983). Acetic and propionic acids are the precursors of approximately 85 % (Lawrence and McCarty, 1969) of the methane formed from the complete treatment of a complex waste. Thus, a knowledge of the kinetics of methane fermentation of these acids is a key element in the development of a rational approach to the analysis and design of anaerobic treatment systems.

The net growth rate of microorganisms in a continuous-flow completely-mixed anaerobic treatment system can be described as:

$$\frac{dX}{dt} = Y\left(\frac{dS}{dt}\right) - bX \qquad [3.14]$$

The volumetric rate of waste assimilation (dS/dt) is related to the concentration of waste in the digester. This relationship is described by an expression which is similar to the Monod equation:

$$\frac{dS}{dt} = \frac{k\,SX}{K_s + S} = -\frac{dS}{dt} \qquad [3.15]$$

Using Eqs. 3.14 and 3.15, a model to describe the rate of waste utilisation in a reactor can be developed. In a completely-mixed reactor, the biodegradable portion of the waste that flows into the reactor is catabolised by the microorganisms. The concentrations of waste and microorganisms in the effluent are equal to the concentrations in the reactor itself since it is fully mixed. The effluent concentration of organic material consists of the remaining refractory and biodegradable portions of the original waste and the organic portion of the microorganisms. These relationships can be explained by the determination of mass balances around the reactor (Jeyaseelan, 1997).

Combining the above two equations gives the following expression:

$$\mu = \frac{dX/dt}{X} = \frac{Y\,k\,S}{K_s + S} - b \qquad [3.16]$$

The quantity (d*X*/d*t)*/X is equal to the net growth per unit weight of microorganisms per unit time and may be designated as net specific growth rate, μ. This equation is applicable to both the CSTR reactor and the anaerobic contact process (Lawrence and McCarty, 1969). The maximum specific growth rate is a function of temperature since it increases with increasing temperature. The significance of this is that more stable and faster fermentation occurs at higher temperatures (Terzis, 1994).

To evaluate the coefficients of the kinetic model (Eq. 3.16), it is necessary to calculate the specific utilisation, *U* which is defined as the weight of substrate converted per unit weight of microorganisms per unit time (Lawrence and McCarty, 1969). Calculation of substrate-specific fractions of the microbial mass are based on thermodynamic considerations which show that microbial growth is related to the free energy made available as a result of biochemical transformations of the substrate. Methane production can be used to determine relative growth of substrate-specific microbial populations. Since 2 moles of oxygen are required to oxidise one mole of methane gas, the COD equivalent of methane is 64 g/mole. From this relationship, the grams of substrate COD converted to methane gas can be determined. The reduction of 1 g of COD (at 0 °C and 1 atm) is equivalent to the production of 0.35 l of methane (Speece, 1996).

Identification of the kinetic coefficients of the Monod kinetic rate equation for each component of the solids in the wastewater allows for the improved prediction of the anaerobic digestion process (Jeyaseelan, 1997; McCarty, 1974). Separate kinetic coefficients for acid formation and methane formation should be identified from the literature or determined through laboratory analysis (Jeyaseelan, 1997). **Table 3.1** presents several kinetic constants as reported in the literature.

TABLE 3.1 : Kinetic and stoichiometric constants reported in the literature.

	μ_{max} (1/d)	*Ks* (mg COD/l)	*b* (1/d)	*Y* (mg cells/mg COD)
Acidogens				
Denac et al., 1988	1.2	140	0.04	0.03
Zoetemeyer et al., 1982	7.2	22	-	0.1
Acetogens				
Lawrence and McCarty, 1969	0.31	48	0.01	0.042
Gujer and Zehnder, 1983	0.15	246	-	0.036
Acetoclastic methanogens				
Denac et al., 1988	0.34	237	0.015	0.03
Lawrence and McCarty, 1969	0.24	356	0.037	0.038
Smith and Mah, 1966	0.6	320	-	0.04
Gujer and Zehnder, 1983	0.34	165	0.015	0.04
Kuba et al., 1990	0.26	20	-	-
Jeyaseelan, 1997	-	400	0.037	0.03
H_2 utilising methanogens				
Denac et al., 1988	1.40	0.6	0.09	0.029
Gujer and Zehnder, 1983	1.4	0.6	-	0.04

b = death rate
K_s = half saturation constant
Y = yield
μ_{max} = maximum specific growth rate

The variation in parameters arises from the fact that no two mixed cultures will have the same population of bacteria, even when grown on the same substrate, since the populations of the inocula will vary (Grobicki, 1989).

A continuous flow system can eventually reach a steady state in which the mass of microorganisms in the total system will remain constant, i.e. the rate at which microorganisms are wasted from the system equals the net microbial growth rate (dX/d*t*). Expressing time in days, the daily net specific growth rate is the reciprocal of the biological solids retention time (SRT). Since the conventional process is completely mixed, the microorganism concentration is the same in the digester and in the effluent. The quantity of solids wasted daily is equal to Q/V times the total mass of microorganisms in the system, where Q and V are the daily flow rate and volume of the digester, respectively. Since Q/V is the reciprocal of the hydraulic retention time (HRT), the equation reduces to SRT = HRT for the CSTR process. Process failure due to kinetic stress will occur when the SRT is reduced to a value at which the microorganisms are washed out from the system at a rate greater than their maximum net specific growth rate. Under these conditions waste treatment efficiency decreases and the effluent waste concentration, S, approaches the influent waste concentration, S_o. When the influent substrate concentration is

large enough to be non growth-limiting, the value of SRT at which process failure occurs is a characteristic parameter of the waste assimilating microbial population (Terzis, 1994).

To identify the optimum conditions for anaerobic digestion of an effluent the kinetic parameters of the Monod rate model, namely maximum growth rate (μ_m), yield (Y), saturation constant (K_s) and endogenous decay rate (b) must be determined (Terzis, 1994).

3.5.2 Modelling of the anaerobic degradation process

A model can be defined simply as a purposeful representation or description of a system (Cloete and Muyima, 1997). The correct design of an anaerobic process requires a reliable model (Valentini, Garuti, Rozzi and Tilche, 1997). Several mathematical models have been developed to characterise the anaerobic digestion process (Jeyaseelan, 1997). Different types of models are useful for different purposes: design; operation; enhancing fundamental learning; and predicting short- and long-term responses to changes in substrates, their concentrations, and various operational parameters (Hobson, 1983). All models invoke selected simplifying assumptions. The best models are those which make assumptions carefully and fully explain or justify the assumptions made. Models should be flexible enough to accommodate new findings in biochemical mechanisms, pathways and microbial ecology. Engineers use models of biological processes to aid design, as a tool for process optimisation and as a method of reducing extensive and complex experimental data to simple, manageable formulae (McCarty and Mosey, 1991). A mathematical model incorporates a number of kinetic and stoichiometric expressions which represent the biological interactions. These expressions are based on hypotheses which are proposed for the biological processes occurring within the system (Billing and Dold, 1988). To test these hypotheses, specific experiments are designed and data on the system response are collected. These experimental data can then be compared with the predictions obtained from the model. Models of biological processes tend to be empirical models based upon observed correlations between the performance of the plant and its main design and operating variables. Given the desire to minimise the number of simplifying assumptions which must be made, and the large number of interrelated variables associated with anaerobic treatment, some of the models which have been developed are so complex that they become operationally cumbersome and difficult to apply effectively (Harper and Suidan, 1991). On the other hand, too many simplifying assumptions (black box model) may lead to gross technical inaccuracies.

Two extremes in mathematical models can be identified, empirical and mechanistic (Sam-Soon et al., 1991). An empirical model is based on recognition of the parameters that appear to be essential to describe the behavioural pattern of interest, and linking these by empirical relationships established by observation when the mechanisms and/or processes operating in the system are not known or are ignored. In contrast, a mechanistic model is based on some conceptualisation of the biological/physical mechanisms operating in the system (Sam-Soon et al., 1991). From the conceptual model, the process rates and their stoichiometric interactions with the compounds are formulated mathematically to develop the mechanistic model.

The various uses of mathematical models in wastewater treatment can be summarised as follows: A model

1. Gives mathematical expression to conceptual ideas and allows evaluation of hypotheses;

2. Provides information not apparent from laboratory-scale tests;

3. Provides guidance for the selection of feasible solutions for testing;

4. Assists in identifying the parameters that significantly influence the system response and thereby gives guidance for the establishment of design criteria; and

5. Assists in identifying possible causes for system malfunction or failure, and in devising remedial measures (Sam-Soon et al., 1991).

In developing a model, the processes and compounds should be set out in a compound-process matrix which facilitates clear and unambiguous presentation of the interactions (Sam-Soon et al., 1991). For all models, various kinetic constants are needed for the equations assumed to govern the reactions.

Many models have been developed to describe different aspects of the anaerobic degradation process: formate transfer (Harper and Suidan, 1991); biofilm formation (Harper and Suidan, 1991); pelletised sludge bed (Sam-Soon et al., 1991); modelling over a wide pH range (McCarty and Mosey, 1991); the anaerobic digestion of farm wastes (Hobson, 1983); abattoir effluent (Batstone, Keller, Newell and Newland, 1997); olive mill wastewater (Borja, Martin, Alonso, Garcia and Banks, 1995); glucose (Graef and Andrews, 1973); and molasses wastewater (Denac, Miguel and Dunn, 1988). The Monod model has been the most popularly used empirical model to investigate the applicability of the anaerobic digestion of an organic effluent (Jeyaseelan, 1997). The estimation of the kinetic parameters of the Monod model provides a quantitative description of the anaerobic degradation of the organic molecules and also offers useful design information for such a process (Terzis, 1994). The Monod model has been widely accepted and readily used in biological treatment because of its mathematical simplicity and the relative ease that the kinetic parameters can be estimated. First order rate equations are commonly used for the initial hydrolysis of complex organic molecules and Monod kinetics are used to describe methanogenesis from acetate (McCarty and Mosey, 1991). Thermodynamic calculations provide a valuable tool for modelling intermediate metabolism (McCarty and Mosey, 1991). This model can be used to set operating parameters such as organic loading, retention time and temperature that will produce desired efficiency in the systems within practical limits (Jeyaseelan, 1997); (Lawrence and McCarty, 1969).

The first step is to evaluate the kinetic coefficients Y, b, k and K_s of the kinetic model (Eq. 3.16) for a particular experimental situation. The following linearised form of Eq. 3.14 is used to determine values of the growth coefficients, Y and b:

$$\frac{1}{\tau} = YU - b \qquad [3.17]$$

Eq. 3.15 transformed into the following linearised form facilitates the evaluation of k and K_s:

$$\frac{1}{U} = \frac{K_s}{k}\left(\frac{1}{S}\right) + \frac{1}{k} \qquad [3.18]$$

From these calculated kinetic coefficients, the kinetic model (Eq. 3.16) can be used to compute the values of effluent waste concentration and waste removal efficiency. These relationships are then compared with the experimental values of S and the closeness of the fit of the data to the calculated curves indicates whether the model provides a satisfactory description of methane fermentation. The kinetic coefficients together with the proposed model can be used to predict the performance of a digester treating soluble wastes.

With complex substrates, acetate fermentation is not always the rate-limiting step. The usual practice is to undertake long-term incubation tests to determine the overall biodegradability or gas yield and then attempt to model the hydrolysis or fermentation of the biodegradable fraction (McCarty and Mosey, 1991). The problem

here is that a single equation is used to simulate the overall rate of microbial hydrolysis of a multitude of unspecified organic compounds.

3.6 POPULATION DYNAMICS

In addition to the numerous metabolic pathways for the biodegradation of organic compounds exhibited by diverse species of microorganisms, there are also many interactions in microbial populations that influence the fates of compounds in the environment and within the bioreactors of waste treatment facilities. Microorganisms rarely exist in isolation; rather, numerous microbial populations of different types coexist (Cloete and Muyima, 1997). Often there is an interactive association between microorganisms, called a consortium, that results in combined metabolic activities. These microbial populations interact within a community. A variety of positive and negative population interactions lead to a stable functional community. The microbial community is structured so that each population contributes to its maintenance. Some microbial populations within the community adversely influence others and can even lead to their exclusion from the community. Other populations interactions are beneficial so that multiple microbial populations can live together in a particular niche.

One common type of population interaction, called a **commensal** relationship, occurs when one population benefits and the other remains unaffected. Co-metabolism, in which an organism growing in a particular substrate gratuitously oxidises a second substrate that it is unable to utilise as a nutrient and energy source, is the basis for various commensal relationships. The second substrate is not assimilated by the primary organism but the intermediates are available for use by other microbial populations that do not possess the enzymes needed to utilise the complex organic molecules (Cloete and Muyima, 1997). In some cases a competitive relationship can develop for the available simpler substrates. Another basis for commensalism between populations is the production of growth factors that can be utilised by other microbial populations. Commensalism often results when the unaffected population, in the course of its normal growth and metabolism, modifies the habitat in such a way that another population benefits because the modified habitat is more suitable to its needs. For example, when a population of facultative anaerobes utilises oxygen and lowers the oxygen tension, it creates a habitat suitable for the growth of obligate anaerobes (Cloete and Muyima, 1997).

Synergism occurs when two populations co-operate so that each population benefits. Sometimes a consortium of two or more populations co-operate in this manner and supply each other's nutritional needs. Population 1 is able to metabolise compound A, forming compound B, but cannot go beyond this point without the co-operation of another population because it lacks the enzymes to bring about the next transformation in the pathway. Population 2 is unable to utilise compound A but it can utilise compound B, forming compound C. Both populations 1 and 2 are able to perform the metabolic steps subsequent to the formation of compound C, producing needed energy and end products that neither population can produce alone. The fully chlorinated but unsaturated tetrachloroethylene, for example, can be dechlorinated by a consortium under anaerobic conditions in a step-wise fashion with partial conversion to carbon dioxide. More complex examples of synergism are based on the simultaneous removal of toxic factors and the production of usable substrates.

Often different microorganisms within complex communities attack different compounds but also, quite commonly, diverse microorganisms within those communities compete for the same substrates. **Competition** for available substrates is a main driving force that determines community structure and the diversity of biological populations that can coexist (Cloete and Muyima, 1997). In theory, competitive exclusion will eliminate all but one of the populations competing for an identical substrate. In some cases, however,

microorganisms that utilise the same substrate coexist because of spatial separation within microhabitats or because of differing affinities for substrate at various concentrations. Some of the microorganisms involved in the decomposition of organic compounds within communities are themselves the substrates (prey) for other organisms.

Anaerobic digestion is a multi-phase process carried out by a spectrum of facultative and obligate anaerobes. Determination of the kinetic constants for different species could facilitate the modelling of population shifts during the degradation process and provide an indication of species predominance under specific conditions.

For example, *Methanothrix* species and *Methanosarcina* species both ferment acetic acid to carbon dioxide and methane but they have very different morphologies and growth kinetics (McCarty and Mosey, 1991). *Methanothrix* species are sheathed rods which sometimes grow as long filaments. They grow slowly with minimum doubling times around 4 d at 35 °C. They survive because they have a high affinity for acetate (K_s = 30 mg/l). *Methanosarcina* species are coccoid bacteria that grow together in discrete clumps. They grow faster with minimum generation times of ca. 1,5 d (McCarty and Mosey, 1991) but they are less efficient scavengers (K_s = 400 mg/l). Competition between these two genera provides opportunities for modelling population drift as the basis for acclimatisation to a new substrate.

The determination of kinetic coefficients facilitate the quantification of a biological process. Models provide a mathematical basis for the reactions and allow for the prediction of a process under various conditions. Models are, however, only tools and cannot be seen as absolute.

Chapter 4

Digester Performance Evaluation

This chapter presents the investigation of the anaerobic digesters in KwaZulu-Natal in terms of physical and operating data and ultimate performance efficiencies. The purpose of this investigation was to identify under-utilised digesters, for the proposed treatment of high-strength or toxic organic industrial effluents, and to identify under-performing digesters with an aim of effecting remedial action to assist in the optimal utilisation of effluent treatment facilities in the region. The results of the anaerobic digester survey are presented in **Section 4.2**, in the form of an inventory, highlighting under-utilised digester volume. **Section 4.3** outlines the operating parameters which promote an effective digestion process. An evaluation of the performance of each of the digesters is given. A batch test was made (**Section 4.4**) to determine the activity of a digester sludge. These data could play a major role in the prevention of digester failure. **Section 4.5** discusses possible options for the improvement of the anaerobic degradation process and **Section 4.6** highlights factors which should be taken into account when determining the feasibility of treating an industrial effluent in available anaerobic digesters.

4.1 INTRODUCTION

Several of the wastewater treatment plants, in the KwaZulu-Natal region, have anaerobic digestion facilities which are under utilised. Tracer tests on a number of these digesters (Barnett, 1995; Barclay, 1996) have indicated that the average mixing volume is 50 % of the actual volume. In 1997 the Durban Metropolitan Council took control of approximately 30 treatment plants in the region. This provided the opportunity to utilise the under-utilised capacity of some of the plants and to relieve the bottleneck at the plants operating at or over design capacity. The ultimate result is a delay in the need for capital expenditure and an increase in the income from capital already expended. Other wastewater treatment works in the region are either controlled by regional municipalities or independent organisations such as Umgeni Water.

Despite the widespread use of anaerobic treatment, optimum process performance is seldom achieved due to the high degree of empiricism which prevails in the design and operation (Lawrence and McCarty, 1969). The aim of this chapter is to present the operating data for each anaerobic digester and to assess the performance efficiency.

The concept of *available digester capacity* needs to be clearly defined. A digester with available **hydraulic capacity** is one which is receiving a smaller volumetric load than its design specifications. The hydraulic load is measured in the units of m^3/d. **Loading capacity** is the ability of a digester to accept a greater organic load (kg $VS/m^3.d$) without experiencing an overload or shock loading.

4.2 ANAEROBIC DIGESTER SURVEY

The regional authorities were approached for information regarding digesters in their areas. The individual digesters were visited and physical details and operating data were obtained (**Appendix A**). An inventory of the anaerobic digesters in the KwaZulu-Natal region is given in **Table 4.1**.

TABLE 4.1 : Inventory of the anaerobic digesters in KwaZulu-Natal.

Treatment works	Primary digesters				Secondary digesters		
	No.	Design vol. per digester (m^3)	Design volume not used (m^3)	HRT (d)	No.	Design vol. per digester (m^3)	Design volume not used (m^3)
Amanzimtoti	6	2 012 (x3) 2 068 (x1) 3 640 (x2)	6 036 0 0	0 26 46	3	587	0
Cato Ridge Abattoir	2	2 866	N/D	5	0	-	-
Darvill	2	4 500	0	20	2	1 000	0
Estcourt	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Kwa Makutha	1	1 650	0	18	1	540	0
Kwa Mashu	2	1 750	0	27	1	2 310	462
Kwa Ndengezi	1	1 550	0	53	0	-	-
Mpophomeni	2	683 (x1) 683 (x1)	0 683	15 0	1	330	0
Mpumalanga	4	1 052	0	94	2	300	0
Newcastle	3	850 (x1) 850 (x2)	0 1 700	N/D 0	0	-	-
New Germany	2	1 000	0	200	1	450	0
Noodsburg	1	11 700	0	15	0	-	-
Northern	3	2 350 (x2) 2 350 (x1)	0 0	36 24	1	4 420	0
Phoenix	2	2 600 (x1) 2 600 (x1)	0 2 600	31 0	1	1 794	0
Scottburgh	1	1 130	0	108	1	565	0
South African Breweries	1	1 700	0	0.5	2	N/D	N/D
Southern	2	4 620 (x1) 4 620 (x1)	4 620 4 620	0 0	1	3 830	3 830
Sundumbili	4	1 387	0	14	4	1 387	0
Tongaat southern	2	2 000	0	100	0	-	-
Umbilo	4	1 340	0	22	4	1 340	0
Umbogintwini	1	103	0	26	0	-	-
Umlazi / Isipingo	6	964 (x5) 964 (x1)	0 964	16 0	6	704	0
Umzinto	1	705	0	200	0	-	-
Treatment works	**Primary digesters**				**Secondary digesters**		

	No.	Design vol. per digester (m³)	Design volume not used (m³)	HRT (d)	No.	Design vol. per digester (m³)	Design volume not used (m³)
Verulam	3	4 120 (x1) 8 200 (x2)	0 0	120 240	1	3 600	0
TOTAL			**21 223**				**4 292**

N/D : Not determined

Photographs of the digesters are presented in **Appendix A**. The data obtained in the survey facilitated the calculation of the performance efficiency of each digester. They also identified idle digesters (those not being used at all) and digesters with low hydraulic loads.

The theoretical hydraulic retention times (d) were calculated based on the volume of the digester and the flow to the digester. Most of the digesters which were investigated were completely mixed, thus the hydraulic retention time (HRT) was equal to the solids retention time (SRT). The nominal HRT is in the range of 20 to 30 d. The available volume of a digester could be increased by a reduction in the HRT. This would, however, result in a reduction in the quality of the final sludge. Acclimation of the anaerobic biomass can result in increased digester capacity since, if the biomass is adapted to the substrate, degradation rates increase with a subsequent decrease in the HRT.

The survey revealed that, although the utilised digester volume was maintained at a maximum, to prevent explosion by the accumulation of biogas, the retention time was often much greater than the nominal 20 to 30 d (Ross et al., 1992). The reason for this is that the hydraulic load to the digesters was below the design capacity. These digesters could, therefore, receive a greater hydraulic load. The stability of an anaerobic digester, however, is dependent on the organic load and digesters are designed to treat a specific loading. High rate digesters, which are those that treat labile substrates, have a higher loading rate than conventional digesters treating municipal sewage sludge. An exceedence of this load may result in shock loading and ultimate digester failure. Options for waste minimisation at the effluent source should, therefore, be examined to reduce the volumes of high-strength effluent being produced. These lower volumes of industrial effluent could then be loaded into the available digesters without a marked increase in the hydraulic load. With lower volumes, the retention time would still be greater which would provide the necessary time for the degradation of the high concentration of organic molecules in the effluents.

The volumes of screenings and grit removed, at the head of the works, were important as the presence of screenings and grit in a digester can significantly reduce the working volume. Ideally, digesters should only be fed with sludge from the primary sedimentation tanks (PST) (Ross et al., 1992); and not with waste activated sludge, dissolved air flotation (DAF) sludge or grit as these occupy digester volume and are not as effectively degraded.

Hydraulic overloading occurs when a digester residence time is reduced to the point where organisms are washed out or diluted faster than they are formed (Graef and Andrews, 1973). Increased digester flow rates and decreases in effective digester volume caused by grit and scum accumulations can both lead to hydraulic overloading (Graef and Andrews, 1973). Organic overloading is caused by an increase in the rate of organic mass loading to the reactor. The organic substrate concentration in the reactor increases and inhibits the microbial conversion of volatile acids to methane and carbon dioxide. Thus, organic substrate accumulates in the digester causing it to fail or *sour*.

As stated, the survey facilitated the identification of idle and under-performing digesters. The Amanzimtoti Wastewater Treatment Works had a total of 6 anaerobic digesters although only three of these were operational (**Table 4.1)**. The three off-line digesters could, therefore, be utilised for the treatment of industrial effluents produced in the vicinity. The Amanzimtoti Works is located near to the Prospecton industrial area thus this potential digester capacity could be well utilised.

The two primary anaerobic digesters and the one secondary digester, at the Southern Wastewater Treatment Works, in Durban, are no longer operational. They have been off-line since 1985. The influent to the works is screened and degritted prior to marine discharge via a 5 km pipeline. This works serves the industries in the Durban Mobeni, Jacobs and Prospecton areas. The digesters could, therefore, be used to treat either effluents which do not meet the General Standards for marine discharge or the low volumes of high-strength effluents which are currently diluted to meet discharge standards with excessive wastage of potable water.

One of the anaerobic digesters at the Mpophomeni Works was idle, as was a primary anaerobic digester at the Umlazi Works. This digester could be used to treat effluent from the surrounding Jacobs, Prospecton and Island View industrial areas. Two of the 3 anaerobic digesters at the Newcastle Works are no longer used for active digestion. The one digester is used for the pre-treatment of blood waste from the local abattoir to prevent organic overloading of the works.

Only one of the 2 primary anaerobic digesters at the Phoenix Wastewater Treatment Works was operational due to the works operating at only 44 % (v/v) of its design load. The Phoenix area is zoned for industrial development within the next 5 to 10 years. The idle digester should, therefore, be seen as available capacity for the treatment of industrial effluents and should be considered during the decision-making for the rational location of new industries that produce high-strength or toxic organic effluents

The digesters at the Cato Ridge abattoir operate entirely for the treatment of the abattoir waste. According to the works operators, the digesters are not run at their full volumetric capacity although the actual working volume was undetermined. The UASB reactor at the South African Breweries plant, in Prospecton, treats the brewery effluent. The organic load to this reactor was high and, consequently, the hydraulic retention time (HRT) was low.

Table 4.1 is an inventory of the anaerobic digesters in the province. The table summarises the design volume of each digester and the digester volume which is not utilised. The un-utilised digester volume was totalled at 21 223 m^3.

Several of the digesters were operated at extended hydraulic retention times (HRT) because they were running below design capacity. These included the digesters at Amanzimtoti (46 d retention time), Kwa Ndengezi (53 d), Mpumalanga (94 d), New Germany (200 d), Scottburgh (108 d), Tongaat southern (100 d) and Verulam (120 and 240 d). These digesters could receive a higher hydraulic load and operate at lower retention times.

The function of the secondary digesters is merely phase separation. They could, therefore, be seen as available digestion capacity since the closed settling tanks could be operated as primary digesters. This would, however, require an increase in the HRT of each digester to provide a period, without mixing, for the settlement of the sludge.

4.3 DIGESTER PERFORMANCE CALCULATIONS

Collation of data from the digester survey facilitated the determination of whether the operation of a digester was *healthy*, i.e., an evaluation of the efficiency of the anaerobic digestion process. Identification of unhealthy digesters provided information for the suggestion of remedial action. Available capacity should only be utilised in healthy digesters to prevent failure of the digester. The health of a digester can be assessed by the investigation of the following parameters:

1. Organic load (kg VS/m^3.d);
2. Gas production per kg volatile solids destroyed (m^3/kg) ;
3. pH, alkalinity and volatile fatty acid concentrations in the sludge;
4. Reduction of volatile solids;
5. Sludge temperature;
6. Biogas composition;
7. Digester mixing; and
8. Hydraulic retention time.

The organic load to a digester has a significant effect on the process efficiency since if the organic content of the substrate is too high it may result in a shock load to the digester, with a concomitant reduction in degradation efficiency or even complete digester failure. The ideal organic load, for a high-rate reactor, is in the region of 1.5 to 3.0 kg VS/m^3.d (Ross et al., 1992). Continuous feed to a digester is optimal as it prevents shock loading and promotes biomass stability. It is more favourable to feed small volumes frequently than to feed large volumes infrequently.

The efficiency of the degradation process can be assessed in terms of biogas production with an ideal system producing 1 m^3 biogas per kg of volatile solids destroyed. The gas composition is also an important indicator of the state of the process. The ratio of carbon dioxide to methane should be in the region of 35 % to 65 %. A change in this ratio is indicative of stress in the system.

The volatile solids represent the organic portion of the feed, thus the reduction in volatile solids gives an indication of the degradability of the organic molecules in the substrate. The volatile solids in the influent are normally in the region of 70 % (m/v) of the total solids. A volatile solids concentration lower than this suggests the presence of grit in the feed sludge. A reduction of 50 to 70 % of the volatile solids is expected in a properly functioning system. The volume of total solids in the feed sludge should be in the region of 5 to 6 % (m/v). The thinner the feed sludge, the greater the digester volume occupied by water and the greater the amount of energy required to heat the sludge. A rise in temperature results in a concurrent increase in metabolic activity to a certain point, therefore, heating of a digester can result in a shorter hydraulic retention time and potentially increase the active or working volume. A decrease in temperature of the sludge can result in an organic overload as the drop in temperature would result in a decrease in the metabolic activity.

Control of the pH value and the VFA and alkalinity concentrations of the sludge is important. If these are not properly controlled, the biomass will not metabolise effectively and degradation rates will decrease with a concomitant increase in the necessary HRT. The VFA : alkalinity ratio (Ripley ratio) is important and, ideally, should be in the range of 0.1 to 0.35. An increase in this value suggests digester failure i.e., the lower the Ripley ratio, the healthier the digester (Ross et al., 1992).

The mixing efficiency of a digester can be assessed by the temperature and total solids profiles throughout the digester. Efficient mixing is represented by no stratification and a uniform distribution of temperature and solids. The efficiency of the mixing can be assessed in terms of power requirements and the number of volume displacements per unit time. This provides an indication of the turnover rate of the digester since digester contents should be displaced at least once in 24 h.

The anaerobic digestion process may be regarded as being umbalanced or *upset* when the process control indicators show deviations from normal (Ross et al., 1992). The main changes indicating an upset digester are:

1. Increased percentage carbon dioxide in the gas produced;
2. Decreased gas production;
3. Increased volatile acid : alkalinity ratio of the sludge;
4. Production of malodorous sludge;
5. Decreased pH;
6. Increased solids in the supernatant;
7. Decreased volatile solids reduction; and
8. Increased foaming.

Process trouble-shooting is the identification of the causes of the process upset and determination of the best remedial action.

From the data collected in the digester survey, performance and operating efficiencies, for the individual digesters, were calculated (**Appendix B**) and the results for each are described below. A summary of these results is given in **Table 4.2**.

Available digester capacity was identified at the **Amanzimtoti** Works, both in the form of the 3 idle digesters and the potential capacity in the operating digesters by improvement of the operating conditions. The feed sludge was thin with a total solids content of ca. 3.8 % (m/v). A batch feeding schedule was followed and the organic load was low (0.25 kg VS/m^3.d) which suggested available organic capacity. The biogas was wasted to the atmosphere as the on-site gas holder was not operational. Biogas production was, therefore, not monitored. The digester sludge pH, VFA and alkalinity concentrations suggested healthy operation, with measured averages of 7.4, 566 mg/l and 3 343 mg/l, respectively. These gave a Ripley ratio of 0.17. Volatile solids reduction was efficient at 60 %. The digesters were unheated and operated at ambient temperature. It is believed, however, that the temperature within the digesters increases due to the heat released during

metabolism and the air-tight environment. It is, therefore, assumed that the unheated digesters operate at ca. 30 °C. The works was operating at 77 % (v/v) of its design capacity and the low hydraulic load to the anaerobic digesters resulted in the extended HRT (46 d). The process efficiency could be improved by heating the digesters (decreased HRT), increasing the organic load and, according to the works operator, more efficient mixing. Approximately 50 % of the volumetric load to the works is composed of industrial effluent.

The effluent treatment plant at the **Cato Ridge** abattoir was operating at only 14.3 % (v/v) of its design capacity and, therefore, had the potential to treat a greater hydraulic load. It was estimated, by the operator, that the digesters only operated at 17 % of their total design volume. The organic load to the digesters was high (4.1 kg $VS/m^3.d$) due to process and washwater effluent from the abattoir. Feeding to the digesters was continuous. This high organic load could result in a shock load and digester failure but, due to the acclimation of the biomass to the effluent, the process was effective. The retention time was low at ca. 5 d. The sludge alkalinity was low and resulted in a high VFA/alkalinity ratio (0.24), which indicated the need for buffering capacity in the digester. Volatile solids reduction was very efficient at 72 %. There was no mechanical mixing of the digesters. The biogas was vented directly to the atmosphere, thus gas production was not measured. Digester performance could be improved by mixing, thickening of the feed sludge from 3 % to 5 % (m/v), heating and providing buffering capacity. These digesters showed that high-strength organic effluents can be successfully treated by anaerobic digestion.

The **Darvill** Wastewater Treatment Works, in Pietermaritzburg, was operating at 91.7 % (v/v) of its design capacity. The anaerobic digesters were run at a retention time of 20 d with a high organic load (2.03 kg $VS/m^3.d$). The two egg-shaped digesters were fed in alternating sequence, i.e., 3.5 d to the first then 3.5 d to the second. Thus, the digesters could accept a greater load, in the form of high-strength industrial effluents, as both digesters could be loaded simultaneously. The digesters were heated to 35 °C which is optimal for mesophilic digestion. Gas production was measured at ca. 10 000 m^3/d with a 60 % (v/v) methane content thus 6 000 $m^3\,CH_4$ were produced per day. With a volatile solids reduction of 64.6 %, this was reduced to a volume of 1.01 $m^3\,CH_4$/kg VS destroyed. The reported parameters indicated the efficient performance of these digesters. There was significant reduction in COD (95 %) over the entire works. The sludge parameters were ideal (**Appendix A**) and the mixing was efficient. Only 10 % (v/v) of the influent to the works was industrial effluent.

The data for the **Escourt** digesters were not made available by the local authority.

Kwa Makutha is located just west of Amanzimtoti, on the Natal south coast. It is a small works (3.0 Ml/d), treating purely domestic sewage. The works was operating at 117 % of its design capacity. This overloading resulted in a relatively high organic load to the digesters (2.1 $kgVS/m^3.d$) and a short HRT of 18 d. The volatile solids reduction averaged ca. 56 %. Biogas production was not measured. The sludge characteristics indicated that the process was healthy with an average pH of 7.0 and the ratio of VFA to alkalinity at 0.02. The digesters were not heated thus process efficiency could be improved by heating as degradation rates would increase. Mixing was achieved by a draft tube.

The **Kwa Mashu** Wastewater Treatment Plant is a large plant treating ca. 65 Ml/d. It is situated between Kwa Mashu and Phoenix, in Durban. The works treated mainly domestic sewage from these two areas with only ca. 10 to 15 % of the inflow volume being industrial wastewaters. The operation of the anaerobic digesters was stable and measured parameters indicated healthy conditions. The organic load to the digesters was 1.09 kg $VS/m^3.d$. The volatile solids reduction was ca. 59 % and the process efficiency was calculated at 0.76 $m^3\,CH_4$/kg VS destroyed. Operation could, therefore, be slightly improved but, overall, the digesters were

healthy. The pH of the digester sludge averaged at ca. 7.2 and the ratio of VFA to alkalinity was 0.033. The digesters were heated to 37 °C and mixing was achieved by recirculation of the digester sludge. The average HRT was calculated at 27 d. The works was operating at 86 % of its design volume. Acceptance of a higher hydraulic load would reduce the HRT in the digesters which may not be optimal if the additional load was high-strength organic effluent. A reduced HRT may thus negate mineralisation of the high concentrations of organic molecules.

Kwa Ndengezi is a small works (2.9 Ml/d), recently taken under control by the Durban Metropolitan Council. The works treats purely domestic sewage from the surrounding area and is operated over (121 % (v/v)) its design volumetric capacity. The volumetric load to the anaerobic digester was, however, low; ca. 29 m^3/d with a low organic load (0.5 kg VS/m^3.d) resulting in an extended HRT of 53 d. Operation was not healthy with a volatile solids reduction of only 26 %. The digester sludge had an average pH of 7.1 and the ratio of VFA to alkalinity was 0.038. Biogas was not collected but vented to the atmosphere. Mixing was achieved by recirculation of the digester sludge. The efficiency of the degradation process could be improved by increasing the organic load and heating the digester. If the digester was operated at a retention time of 30 d, it would be able to accept a volumetric load of 52 m^3/d, compared to the current 29 m^3/d, thus verifying the availability of hydraulic capacity. The digester also had available loading capacity since the organic load to the digester was low.

Mpophomeni is a small works operated by Umgeni Water and serving the nearby rural areas. The works, which treats only domestic sewage, was overloaded relative to its design specifications (130 %). One of the digesters was idle which put an increased load on the operating digester (3.2 kg VS/m^3.d). Due to the overloading, the digester was operated at a low retention time (15 d) resulting in insufficient volatile solids reduction, ca. 33 %. The feed sludge was very thick (7.0 % total solids) and the percentage of total solids was not reduced during the treatment process. The pH of the sludge was stable at 7.0 and the VFA to alkalinity ratio was 0.04. Biogas production was not measured but vented to the atmosphere. Efficiency could be improved by operating both digesters and heating the digesters. If both digesters were operated, the additional volume could be used to treat high-strength or toxic organic effluents produced in the region.

The **Mpumalanga** Wastewater Treatment Works has also recently been taken over by the Durban Metropolitan Council. It was previously controlled by Umgeni Water. The works, which treats only domestic sewage, is operating at 49 % (v/v) of its design capacity. The hydraulic load could be increased in the form of high-strength or toxic organic effluents. The Mpumalanga Works is located 4 km from Hammarsdale, which is an industrial area with mostly textile industries (producing high-strength organic size and scour effluents), and a chicken abattoir, producing a very high-strength organic effluent.

The organic load to the Mpumalanga digesters was relatively low (0.34 kg VS/m^3.d) and the anaerobic digesters were operated at an extended retention time of 94 d. The digester sludge was healthy, with average values calculated as follows: pH 7.1 and VFA/ alkalinity ratio of 0.03. The reduction in volatile solids was low (34.5 %). The reason for this was unclear as the extended retention time should have facilitated mineralisation of the organic molecules. The hydraulic load to the digesters was 45 m^3/d. This could be increased to 140 m^3/d if the digesters were operated at a HRT of 30 d. A draft tube facilitated agitation of the digester contents. Biogas production was not measured and the gas was vented to the atmosphere. The anaerobic degradation process efficiency could be improved by heating the digesters and thickening the feed sludge since, according to the operator, the sludge thickener did not operate efficiently. These digesters were sensitive due to the dosing of alum ($Al_2(SO_4)_3$), for pH control. A buffering method, more conducive to digester stability, should be employed. This works should be targeted for the treatment of industrial effluents.

There are 3 anaerobic digesters at the **Newcastle** Wastewater Treatment Works which are not used for active digestion. New pond reactors have been built with an anaerobic pit followed by aerobic treatment in the pond. One anaerobic digester is used to store and pre-treat blood waste from the local abattoir. The operators do not monitor any parameters on the digesters thus the performance calculations could not be assessed. The COD reduction over the entire works was ca. 90 %. The idle digesters could be used to treat industrial effluents produced in the region.

New Germany is located near to Pinetown, thus this wastewater treatment works could receive industrial effluent from the Pinetown, Westmead and New Germany industrial areas. The works currently treats only ca. 30 % (v/v) industrial effluent, with the majority of the inflow being domestic sewage from the nearby Claremont township. The anaerobic digesters at this works were greatly neglected and the operators knew very little of the operating parameters. The majority of the influent to the works was treated in the activated sludge plant while only an estimated 10 m^3/d was fed to the digesters. With such a low feed, the resulting HRT was 200 d. The organic load to the digesters was very low (0.08 kg VS/m^3.d). The volume of methane produced per kg VS destroyed could not be determined since biogas production was not measured. The digester sludge was unhealthy with an average pH of 6.6 and the VFA to alkalinity ratio at 0.1 due to the high concentrations of volatile fatty acids. The volatile solids reduction was low at 24 % indicating unhealthy operation. The digesters were heated to 37 °C. Mixing was facilitated by recirculation of the digester sludge. The efficiency of the digestion process could be improved by buffering the digester to reduce the concentration of volatile acids. Once the digester sludge was stable, the volumetric and organic loads should be increased. Under the conditions the digester contents were almost stagnant. The plant was operating at only half of its design capacity and, therefore, could receive a greater hydraulic load, in the form of industrial effluents. The hydraulic load to the digesters could be increased from 10 m^3/d to 67 m^3/d to give a HRT of 30 d. These digesters should be targeted as available capacity due to the abundance of industry in the vicinity.

The effluent treatment plant at Illovo Sugar, in **Noodsberg,** has an anaerobic lagoon committed entirely to the treatment of the mill effluent. The lagoon is large and very few operating parameters were monitored since the final effluent meets the required discharge standards (Department of Water Affairs and Forestry, 1994).

The **Northern** Wastewater Treatment Works, located in Springfield Park, is a large works, treating 43 Ml/d. It was, however, only operating at 61 % of its design hydraulic capacity. There were 3 anaerobic digesters on site, one was fed an extra 35 m^3/d, resulting in a lower HRT (24 d) than the other 2 digesters (36 d). These extended HRTs indicated the availability of hydraulic capacity which could be utilised for the treatment of effluents from the many industries in the Springfield Industrial Park. The performance efficiency of these digesters was good, with an average organic load of 1.6 kg VS/m^3.d, volatile solids reduction of 62 % and methane production of 0.3 m^3 CH_4 /kg VS destroyed. Biogas production was measured at ca. 3 550 m^3/d, with a CH_4 content of 64.7 % (v/v). A portion of the methane was used to heat the digesters to 37 °C. Mixing was achieved by recirculation of the digester sludge. The digester sludge was healthy with a pH of 7.4 and a Ripley ratio of 0.05.

Phoenix is currently a residential area although the region has been targeted for industrial development in the next 5 to 10 years. There are 2 anaerobic digesters at the Phoenix Wastewater Treatment Works of which only one was operational. These digesters were designed for thermophilic operation but are successfully operated under mesophilic conditions. The evaluation of the performance efficiency of the operating digester indicated a healthy digestion process. The organic load of 1.06 kg VS/m^3.d could be increased by feeding thicker sludge (5 to 6 % (m/v) TS instead of 3.9 % (m/v) TS). The reduction of volatile solids was efficient (66 %) with a residence time of 31 d. This works was operating at 44 % (v/v) of its design capacity, therefore operation of the idle digester would facilitate the treatment of industrial effluents. Biogas production averaged ca. 1 500 m^3/d

with a 65 % (v/v) CH_4 content. This resulted in CH_4 production of 0.55 m^3/kg VS destroyed. This could be improved by increasing the organic load to the digester. The digester sludge was healthy and the Ripley ratio averaged ca. 0.04. The pH was relatively low at 6.8 but was still within the range for efficient degradation. The digester sludge was recirculated to facilitate mixing.

Scottburgh, on the Natal south coast, has a small Wastewater Treatment Works treating only domestic sewage. The flow to the works is seasonal due to the tourism associated with the area. Out of season, the works operated at only 49 % (v/v) of its design capacity. During holiday season, however, it operates near to the design specifications. The operating data for this Wastewater Treatment Works, as presented in **Appendix A**, were collected during an off-season period thus reflecting the high retention time (108 d) and the low loading rate (0.14 kg VS/m^3.d). Biogas was not collected but was vented to the atmosphere. Volatile solids reduction was relatively low at 50.3 %. This could be improved by heating the digester and increasing the organic load. The VFA concentration in the digester sludge was high resulting in a high VFA to alkalinity ratio (0.6) which indicated the need for buffering capacity. It is not suggested that this works should accept industrial effluent as the seasonal variations in its load could result in overloading.

The volumetric load the UASB reactor at the **South African Breweries** effluent treatment plant was great (3 303 m^3/d) and the organic load was high (3.3 kg VS/m^3.d). The phase separator, in the digester, separated the sludge from the effluent, resulting in a low HRT (0.51 d). This was necessary due to the large volumes of effluent produced by the brewery. The efficient functioning of this digester is proof that high-strength organic effluents can be efficiently treated by anaerobic digestion. A volatile solids reduction of ca. 66 % was achieved and biogas was produced at a rate of 4 900 m^3/d. The CH_4 content of the biogas was ca. 73 % (v/v) resulting in the production of 1.3 m^3 CH_4 /kg VS destroyed. The pH of the pelletised sludge was relatively low (6.5) resulting in a high VFA to alkalinity ratio (1.1). The temperature of the reactor was maintained at 37 °C and mixing was achieved with gas spargers. These parameters indicated that the digester was operating effectively and remedial action need not be taken except, perhaps, the suggestion to reduce the digester loading and implement better control of the pH.

The anaerobic digesters at the **Southern** Wastewater Treatment Works, in Jacobs, have been off-line since 1985. The operating data presented in **Appendix A** and the performance calculations (**Appendix B)** were from recorded data from the time when the digesters were operational. The omission of data was due to the unavailability of old records. During their operation, these digesters were efficient and are, therefore, a very ready source for the treatment of industrial effluents produced in the vicinity.

Sundumbili is located on the Natal north coast, just north of the Tugela River. This works is managed by the Water and Sanitation Services of South Africa (Pty) Ltd. There are 4 small anaerobic digesters on the plant which was operating close to its design capacity (99 % (v/v)). The feeding schedule to the anaerobic digesters was such that all 4 digesters are used alternately as primary and secondary digesters. A digester was fed for 3 d, with continuous mixing, whereafter the digester was taken off-line for 4 d to settle the sludge. The performance efficiency of these digesters was relatively good although the high volumetric loading resulted in a short HRT (14 d) which could be the cause of the low reduction in volatile solids (36 %). The loading to the digesters was in the region of 1.01 kg VS/m^3.d. Performance efficiency could be improved by thickening the feed sludge, at present it is only ca. 2 % (m/v), and heating the digesters. Biogas production was not monitored. Mixing was achieved by recirculation of the digester sludge. Approximately 50 % (v/v) of the inflow to the works was industrial effluent, mostly from the Esithebe region. The industrial effluents contained heavy metals, oils and vegetable oils.

Tongaat Wastewater Treatment Works is managed by Aquafund (Pty) Ltd. The works was operating at its design capacity (3 Ml/d) and treating only domestic sewage. The load to the digesters was relatively low (0.28 kg VS/m^3.d) resulting in an extended HRT (ca. 100 d). The reduction in volatile solids averaged around 45 %. This could be improved by heating the digester and thickening the feed sludge. Biogas was vented to the atmosphere without measurement. A pH of 7.1 and a VFA/alkalinity ratio of 0.05 suggested relatively healthy digestion. The digester throughput could be increased resulting in a shorter HRT. Reduction of the HRT to 30 d would facilitate an increase in the digester feed from 40 m^3/d to 133 m^3/d.

The **Umbilo** Wastewater Treatment Works is located in Pinetown, on the banks of the Umbilo river. The works treats ca. 75 % of its design volumetric load, at 17 Ml/d. There are 8 anaerobic digesters on site, 4 of which have been converted to secondary digesters, without mixing, for phase separation. The design volume of each digester was 1 340 m^3. The digesters were built into the ground. Each of the 4 primary digesters was fed ca. 60 m^3/d with an organic load of 1.12 kg VS/m^3.d. The operation of the digesters was efficient with a 72 % reduction in volatile solids and methane production of ca. 0.63 m^3/kg VS, at a retention time of 22.3 d. The pH of the digester sludge was high at 7.5. These values are annual averages calculated from the monthly data reports. The VFA to alkalinity ratio of the digester sludge was 0.008. These performance calculations indicated that more of the digester capacity was being utilised than that estimated by the operators. The retention time was not protracted. Degradation was efficient and additional loading could be accepted in terms of both hydraulic and organic loads. However, investigations should be done to prevent an organic overload. Biogas production was estimated at ca. 1 200 m^3/d, with a CH_4 content of 65 % (v/v). A portion of the CH_4 was used to heat the digesters to 36 °C. Mixing was achieved by a draft tube. The operation of these digesters was efficient. Detailed performance calculations are presented in **Chapter 6**.

The control of the **Umbogintwini** sewage disposal plant falls under AECI Operations Services (Pty) Ltd. Operational parameters were not monitored as the effluent met the General Standard for Wastewater (Department of Water Affairs and Forestry, 1994). This works treated only domestic sewage. The flow to the works was low and the digester was only fed ca. 4 m^3/d. Parameters such as total solids and volatile solids were not monitored, therefore, the performance efficiency calculations could not be determined. The HRT of the digester was 27 d. This digester could receive a greater load but it is not recommended until the operational parameters of the digester are thoroughly assessed.

The **Umlazi** Wastewater Treatment Works has recently been renamed the Isipingo Wastewater Treatment Works, due to the take over by the Durban Metropolitan Council. This works treated purely domestic sewage, except for ca. 100 m^3 /d of landfill site leachate. There were 6 small anaerobic digesters on this plant, 1 of which was idle. The works was operating at 64 % (v/v) of its design capacity. The organic load to the digesters was 1.7 kg VS/m^3.d with a resultant 62.5 % reduction in volatile solids. The HRT was relatively low at 16.1 d, although an efficient reduction of volatile solids was achieved. The digester sludge was healthy with a pH of 7.3 and VFA/alkalinity ratio of 0.04. The digesters were unheated; heating could improve performance efficiency. Biogas production was not measured.

Umzinto is located on the Natal south coast. The works is monitored by the Umzinto Local Council and operated at ca 40 % (v/v) of its design capacity, with ca. 20 % (v/v) of the inflow being industrial effluent. There are several textile industries in the region. The operating parameters of the anaerobic digester were not monitored thus it was impossible to evaluate the performance efficiency of the digester. The digester was, however, operated at an extended retention time (ca. 200 d). There is the potential for the anaerobic digestion of high-strength or toxic organic effluents produced in the region. To ensure efficient degradation, the sludge

would have to be stabilised, the digester should be heated and mixed to optimise degradation efficiency and digestion parameters should be monitored to evaluate the performance efficiency.

Verulam Wastewater Treatment Works is managed by Aquafund (Pty) Ltd. Almost 79 to 80 % (v/v) of the inflow to the works was industrial effluent, however, the works was still operating at half of its design capacity. A result of this was a low organic load to the anaerobic digesters (0.14 kg VS/m^3.d) and an extended HRT of ca. 120 d. for the smaller digester and 240 d for the 2 larger digesters. Volatile solids reduction was efficient (57 %) due to the extended HRT. This could be improved by increasing the temperature of the digester sludge and reducing the HRT. The digester sludge had an average pH of 7.2 and a VFA/alkalinity ratio of 0.04. These digesters have available capacity both on a hydraulic and organic scale.

A summary of these results is given below.

TABLE 4.2 : Digester performance details.

Treatment works	Fraction of design flow to works (%)	Fraction of total design digester vol. (%)	VS redn. in digester (%)	Vol. CH_4 / mass VS destroyed (m^3/kg)	COD red. in works (%)	Retention time (d)	Fraction ind. efflnt to works (% v/v)
Amanzimtoti	78	61	45	N/D	90	46	50
Cato Ridge Abattoir	14	17	72	N/D	95	5	100
Darvill	92	100	65	1.01	95	20	10
Estcourt	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Kwa Makutha	117	100	56	N/D	86	18	0
Kwa Mashu	87	100	59	0.76	70	27	10
Kwa Ndengezi	121	100	26	N/D	93	53	0
Mpophomeni	130	50	33	N/D	94	15	0
Mpumalanga	51	100	35	N/D	94	94	0
Newcastle	N/D	33	N/D	N/D	90	N/D	10
New Germany	50	100	24	N/D	95	200	30
Noodsburg	9	100	N/D	N/D	25	15	100
Northern	61	100	62	0.3	72	36	4
Phoenix	44	50	66	0.55	76	31	0
Scottburgh	49	100	50	N/D	92	108	0
S.A. Breweries	110	100	66	1.3	96	0.5	100
Southern	N/D	0	55	1.2	N/D	0	40
Sundumbili	99	100	36	N/D	94	14	50
Tongaat southern	100	100	45	N/D	93	100	0
Umbilo	75	100	72	0.63	71	22	20
Umbogintwini	55	100	N/D	N/D	75	26	0
Umlazi	64	83	63	N/D	90	16	2
Umzinto	40	100	N/D	N/D	87	200	20
Verulam	50	100	57	N/D	80	240	80

No correlation could be drawn between the reduction in volatile solids and the industrial effluent content of the feed sludge. The degree of reduction of the substrate is dependent on the degree of acclimation of the biomass to the particular substrate.

4.3.1. Assessment of available digestion capacity

In summary, the following parameters should be considered when assessing the extent of available capacity in an anaerobic digester:

1. Composition of the feed sludge;
2. Concentration and organic content of the feed sludge;
3. Organic loading rate (kg VS/m^3.d);
4. Grit and scum contents of the digester;
5. Sludge temperature;
6. Mixing efficiency;
7. Hydraulic retention time;
8. Sludge pH, VFA and alkalinity concentrations;
9. Biomass activity; and
10. Acclimation of the biomass.

4.4 SLUDGE ACTIVITY TESTS

Simple batch tests were made to assess the microbial activity of several anaerobic digester sludges. The rate of gas production is indicative of the activity of the digester sludge. Sludge activity should be assessed before a high-strength or toxic organic effluent is fed to a digester. If the sludge is not metabolising efficiently, then addition of a high-strength organic load may cause digester failure.

4.4.1. Materials and methods

Samples of primary digester feed and primary digester sludge were collected from 5 municipal wastewater treatment works. A 40 ml sample of the digester sludge was decanted and added to a 125 ml serum bottle. Feed sludge (60 ml) was added to give a working volume of 100 ml in each of the serum bottles. The serum bottles were sealed with butyl rubber septa and aluminium caps. The bottles were incubated in a constant temperature room at 37 °C. Gas production was measured by the syringe method (**Appendix C**)

4.4.2. Results and discussion

The objective of these tests was to give an indication of microbial activity in each sludge. This was assessed by measurement of the volumes of gas produced due to the degradation of the feed sludge by the bacteria present in the digester sludge. Gas production was monitored over 60 d (**Figure 4.1**).

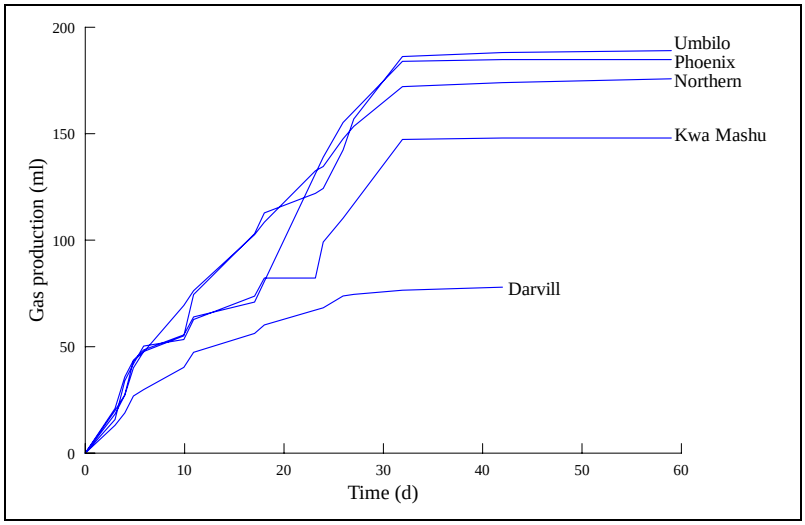


FIGURE 4.1 : Biogas production for the five investigated anaerobic digester sludges.

The volumes of gas produced indicated the relative activities of the different sludges. Biogas production stabilised after ca. 30 d due to the exhaustion of substrate in the serum bottles. The initial rate of gas production for each digester sludge was calculated (**Table 4.3**).

TABLE 4.3 : Gas production rates of several anaerobic digesters.

WWTW	**Gas production rate (ml/d)**
Darvill	2.4
Kwa Mashu	5.4
Northern	5.4
Umbilo	5.8
Phoenix	6.8

The tests were made to provide an indication of the activity of the digester sludge. These tests were performed under batch conditions and, therefore, may not be representative of activity levels in the full-scale anaerobic digesters which are operated under continuous or semi-continuous conditions.

The batch test did, however, give an approximation of the sludge activity. From the results presented in **Table 4.3**, the sludge from the Phoenix digesters was the most active and that from Darvill was the least active. No correlation could be drawn between the activity of the sludge and the volume of industrial effluent fed to each plant.

This simple test can be made in any laboratory and could play a role in the prevention of digester failure.

4.5 IMPROVING DIGESTER PERFORMANCE

A wastewater treatment works can provide all of the necessary nutrients and biomass required for the treatment of an industrial effluent. The nutrients are present in the raw sewage feed so this eliminates the costly need for supplementation. Another advantage of treatment of an industrial effluent at a sewage purification works is that the digesters are usually stable and should facilitate quick treatment of the effluent. However, optimum process performance is seldom achieved due to poor operating conditions.

One way to improve the performance of a treatment works is to improve the flow through the processes. If the flow is poor, for example, it does not use the entire volume of the process, or it bypasses part of the process, the performance will then be impaired. The flow patterns determine the length of time spent in the reactor by each element of the fluid and are also important to determine the heat and mass transfer (Rabbitts, 1982). The flow must, therefore, be understood and assessed. For this, it is necessary to model the process flow (Barnett, 1995). A model of flow patterns, or a flow model, facilitates possible improvements for more efficient operation and process intensification to be postulated. The effect of improvements may also be predicted. A flow model can, in addition, be used as a diagnostic tool in process failure as condition changes will be indicated by flow pattern changes.

The performance of large-scale reactors is affected primarily by the retention time of the substrate in the reactor and the degree of contact between the incoming substrate and the viable bacterial population. These parameters are, primarily, a function of the hydraulic regime in the reactor (Smith, Elliot and James, 1996).

Other operating problems which may be encountered include pH control and a reduction in concentration (thickness) of the feed which could cause alkalinity wash-out and necessitate better temperature control. If the digester is found to be unhealthy, the organic load should be reduced.

4.6 TREATMENT OF HIGH-STRENGTH OR TOXIC ORGANIC EFFLUENTS IN AVAILABLE ANAEROBIC DIGESTER CAPACITY

The anaerobic digester survey identified the availability of either hydraulic or organic capacity, or both, in several of the municipal anaerobic digesters in KwaZulu-Natal (**Table 4.1**). It was proposed that this available capacity could be utilised for the treatment of high-strength or toxic organic effluents, produced by industries in the vicinity, which are currently either disposed of onto municipal landfill sites or via marine discharge. The feasibility of this proposal must be questioned in terms of the ability of sewage works to accept effluent tankers.

In terms of the "Cradle to Grave" concept, a waste generator must assume full responsibility for its waste, including its safe disposal. The generator must be able to define the composition of the waste, as a guide to the presence of toxic, biorefractory or inhibitory components. A gross sample analysis, or screening test, can be performed to assess the feasibility of treating a particular effluent in an anaerobic digester, i.e., to assess the biodegradability and potential toxicity of the effluent and its individual components (**Chapter 5**).

The principle objective is to concentrate high-strength wastes at the source. Implementation of waste minimisation practices, such as recycling, should reduce the volumes of high-strength waste being produced. The concentrated waste could be collected on site and then tankered to a nearby Wastewater Treatment Works for treatment in the available anaerobic digester capacity. The waste generator would bear the costs of tankering

and the tariffs imposed by the sewage works. Tariffs are calculated based on COD and suspended solids contents of an effluent. These tariffs may be increased, with increased usage of tankers, for road maintenance. In terms of estimation of cost, a quote was obtained for a municipal tanker (10 m^3), of R35/km (1997).

On-site pre-treatment is an alternative although the waste generator would have to assess the overall capital and maintenance costs of an on-site treatment plant in comparison to the tankering and tariff costs.

Chapter 5

Effluent Evaluation

Assessment of the anaerobic degradability of an effluent, prior to its loading into a digester, is critical to prevent digester failure. This chapter focuses on organic industrial effluents and mechanisms for screening and assessing the feasibility of anaerobic treatment. **Section 5.2** briefly describes various organic molecules found in industrial effluents. Laboratory-scale screening tests for the evaluation of the anaerobic biodegradability and identification of inherent toxicity are presented in **Section 5.3** . Analysis of these results is described in terms of material and energy balances (**Section 5.4**). The results of the industrial effluent survey are presented in **Section 5.5** with a summary of the results in the form of a matrix.

5.1 INTRODUCTION

Industrial water usage results in large volumes of liquid wastes rich in organic pollutants (Terzis, 1994). In the future, industry will use less water due to the implementation of cleaner production and waste minimisation practices. Increased water charges will lead to more precise control and integrated processes will reduce wastage. The lower volumes of more concentrated waste could be treated by anaerobic digestion in available digester capacity.

Effluents of interest are those with very high chemical oxygen demand values which would overload conventional treatment processes, those that are co-disposed in municipal landfill sites and those that are discharged to sea.

5.2 EFFLUENT COMPOSITIONS

Wastewaters contain a mixture of organic and inorganic solids which are suspended and/or dissolved in water (Ross et al., 1992). Some of these substances could be toxic and, in high concentrations, these compounds may kill the microorganisms and, in sub-lethal concentrations, significantly reduce the microbial activity (Gray, 1989; Lettinga, 1995). Substantial volumes of organic effluents are discharged to rivers and the sea where they can have adverse effects on the aquatic environment (Department of Water Affairs and Forestry, 1992). The presence of organic materials depletes the dissolved oxygen content of the water courses and can create unpleasant tastes and odours (Walters, 1981).

Organic matter comprises of carbon, hydrogen and oxygen with nitrogen frequently present (Gray, 1989). The majority of the organic carbon can be attributed to the major organic groups, namely, the carbohydrates, fats, proteins, amino acids and volatile fatty acids. Synthetic organic materials which may be present in industrial effluents include pesticides, polychlorinated biphenyls and ethane derivatives (Boyd, 1988). Many of the synthetic organic molecules are recalcitrant whereas others are only decomposed at very slow rates (Gray, 1989). Below are descriptions of organic molecules commonly found in industrial effluents.

Hydrocarbons : hydrocarbons contain only carbon and hydrogen and the majority are poorly soluble in water (Brock and Madigan, 1991). Low molecular weight hydrocarbons are gases, whereas those of higher molecular

weight are liquids or solids at room temperature. Relatively few microorganisms can utilise hydrocarbons for growth (Brock and Madigan, 1991). In aliphatic hydrocarbons, the carbon atoms are joined in open chains (Brock and Madigan, 1991). Utilisation of saturated aliphatic hydrocarbons is strictly an aerobic process although unsaturated aliphatic hydrocarbons containing a terminal double bond can be oxidised by certain sulphate-reducing and other anaerobic bacteria (Brock and Madigan, 1991). Aromatic hydrocarbons can be degraded anaerobically (Brock and Madigan, 1991).

Fats and phospholipids : fats are the major organic constituents in the suspended solids fractions of wastewaters since they are only sparingly soluble in water (Gray, 1989). Fats is a general term to describe the whole range of fats, oils and waxes that are discharged. Fats are esters of glycerol and fatty acids and are among the more stable organic compounds. They are not easily degraded biologically (Gray, 1989). Microorganisms utilise fats only after hydrolysis of the ester bond, and extracellular enzymes (lipases) are responsible for the reaction (Brock and Madigan, 1991). The end result is the formation of glycerol and free fatty acids. Fatty acids are oxidised by the process of ß-oxidation, in which two carbons of the fatty acid are cleaved off at a time, with the subsequent release of acetyl-CoA molecules (Brock and Madigan, 1991). Acetyl-CoA is then oxidised by the tricarboxylic acid cycle (TCA) cycle or is converted into hexose and other cell constituents via the glyoxylate cycle (Brock and Madigan, 1991).

Proteins : proteins are a comparatively important source of carbon in wastewater although they are less important than soluble carbohydrates or fats (Gray, 1989). Protein is the principal constituent of all animal and, to a lesser extent, plant tissue thus waste from food preparation and excreta is rich in protein. Apart from containing carbon, hydrogen and oxygen, proteins also contain high proportions of nitrogen (Gray, 1989). Proteins are made up of long chains of amino acids connected by peptide bonds and are readily broken down by bacterial action to form free amino acids, fatty acids, nitrogenous compounds, phosphates and sulphides (Gray, 1989). Ammonia toxicity is often a problem in feedstocks with a high protein content since ammonia is rapidly formed in a digester by deamination of protein constituents (Gunnerson and Stuckey, 1986).

Nitrosamines and nitrophenols : are used as intermediates in the synthesis of rocket fuel, as solvents in fibre and plastics industries, antioxidants in fuels and additions to fertilisers, insect repellents, insecticides, fungicides, bactericides and lubricating oils (Department of Water Affairs and Forestry, 1992; Haghighi-Podeh and Bhattacharya, 1996). These compounds are relatively persistent in the natural environment as they are not readily degraded.

Polychlorinated biphenyls (PCB's) : are a class of aromatic compounds which have found widespread applications because of their general stability and excellent dielectric properties (Oellerman and Pearce, 1995). The persistence of PCB's in the environment has invoked concern because of their tendency to be bioaccumulated and because of their possible adverse health effects (Oellerman and Pearce, 1995).

Phthalate esters : represent a large group of chemicals which are widely used as plasticisers in polyvinyl chloride (PVC) resins, adhesives and cellulose coatings (Department of Water Affairs and Forestry, 1992). A number of organisms have been found to be capable of metabolising phthalate esters under different environmental conditions.

Resin acids : are contained in compounds used in the manufacture of tar, pitch, turpentine and rubber (Department of Water Affairs and Forestry, 1992). They are normally insoluble in water and recalcitrant.

Surfactants : are organic chemicals which reduce surface tension in water and other liquids and are, therefore, used in soaps, laundry detergents and shampoos. They are compounds with both hydrophobic and hydrophilic groups. Because of these properties, surfactants tend to concentrate at the interfaces of aqueous mixtures. The anaerobic digestion of surfactant wastewaters is advantageous since severe foaming problems are often encountered with aerobic treatment.

Volatile fatty acids : the toxic effect of high concentrations of volatile fatty acids (VFA's) on methanogenic bacteria is important because VFA's are intermediates in the anaerobic digestion process (Zeikus, 1979). Their toxic effects in high concentrations are attributed either to the toxicity of the VFA's themselves or the reduction in alkalinity which they cause (Zeikus, 1979). Long-chain fatty acids such as palmitic, stearic and oleic acids can exert a toxic effect in anaerobic digestion if they are present in solution (Kugelman and Chin, 1971; Gunnerson and Stuckey, 1986).

Not all compounds are degradable. Many **xenobiotic** compounds, which are chemicals synthesised by humans that have no close natural counterparts, have molecular structures and chemical bond sequences that are not recognised by existing digestive enzymes (Cloete and Muyima, 1997). These compounds, e.g. pesticides, plastics and other synthetics, resist biodegradation or are metabolised incompletely with the result that some xenobiotic compounds accumulate in the environment (Cloete and Muyima, 1997). Xenobiotic organic compounds might be recalcitrant to biodegradation due to unusual substitutions, unusual bonds or bond sequences or excessive molecular size. In some cases, one portion of a molecule is susceptible to degradation while the other is recalcitrant. Thus, a diverse array of chemical modifications to a xenobiotic compound can occur as a result of microbial metabolism.

Thus, there are numerous industrial wastewaters which may be toxic to the anaerobic biomass due to the presence of xenobiotics or recalcitrant molecules. Fortunately, **acclimation** of the biomass facilitates the anaerobic biodegradation of many organic toxicants. It is well established that acclimated cultures can be induced to biodegrade highly toxic, or recalcitrant, compounds which had previously impaired metabolism (Speece, 1996). The time required for acclimation is dependent on the substrate structure, the inoculum source and the environmental conditions. Research has shown that the acclimated biomass does not require a constant presence of the toxicant since the *microbial memory* facilitates degradation of the toxicant when it is present (Speece, 1996). In an acclimated biomass there is no reduction in metabolic activity at concentrations of the toxicant that would normally be inhibitory.

The composition of the effluent is important in the identification of effluents which could be treated anaerobically. Concentration of an organic compound may be a significant factor affecting its susceptibility to microbial attack (Boethling and Alexander, 1979). The ultimate fate of the effluent is also important since treatment in available anaerobic digester volume may be more attractive, not only financially but also with regard to the protection of the environment.

5.3 LABORATORY-SCALE TEST PROTOCOL

It is important that the anaerobic degradability and inherent toxicity of an effluent are evaluated prior to loading into a full-scale digester, in order to prevent digester failure. A batch test protocol has been developed for simple effluent evaluation in the laboratory. The incubation time is short and the test functions as a screening mechanism to assess the anaerobic degradability and potential toxicity of an effluent and its constituents.

5.3.1 Batch culture

Although experimental models greatly simplify the interactions between microbial populations and between the microbial community and the environment, the extent to which a model simulates the real ecosystem must be critically appraised. Laboratory-scale models attempt to simulate the conditions prevailing in the whole or part of the natural environment under study (Atlas and Bartha, 1993). In a batch culture, or model closed system, enrichment initially takes place under defined conditions, with no further input of growth substances or removal of metabolic end products (Parkes, 1982). Biological components and a supportive nutrient medium are added to the closed system. It is a self-sustaining system. As the biological process under the conditions of batch cultivation proceeds dynamically, but in the spatially closed and constant volume of the cultivation medium, it gradually changes with time (**Section 3.2**). With gradual exhaustion of the nutrients and accumulation of metabolites in the living system a point is reached where exchange of free energy no longer occurs.

Anaerobic treatment has not always been an efficient and reliable treatment method since some potential residues for bioconversion are relatively recalcitrant and may contain materials which are toxic to methanogenic microorganisms (Owen, Stuckey, Healy, Young and McCarty, 1979). Bioassay techniques for measuring the degradability, as well as the presence of inhibitory substances, could resolve anaerobic treatment problems. Batch bioassay techniques facilitate the evaluation of a wide range of variables (Owen et al., 1979).

5.3.2 Biodegradability and toxicity assays

A number of experiments were made to determine the optimum assay conditions for laboratory-scale batch assessment of organic effluent biodegradability and toxicity to the biomass. The most effective technique is described.

Owen et al. (1979) described techniques for measuring the biodegradability (biochemical methane potential, BMP) and toxicity (anaerobic toxicity assay, ATA) of material subjected to anaerobic treatment. The bioassays were relatively simple and could be conducted without the need for sophisticated equipment. Biochemical methane potential is a measure of substrate biodegradability and is determined by monitoring cumulative methane production from a sample which is anaerobically incubated in a chemically defined medium (Owen et al., 1979). The anaerobic toxicity assay measures the adverse effect of a compound on the rate of total gas production from a labile methanogenic substrate (Owen et al., 1979). Both techniques involved anaerobic serum bottles which contained samples, defined medium and seed inoculum which were incubated at the desired temperature and the respective gas productions were monitored volumetrically (Owen et al., 1979). The incubation period was typically 30 d which, in most cases, ensured mineralisation of biodegradable organic molecules (Owen et al., 1979). Some organic molecules, however, may require a longer period for the microorganisms to acclimate. A protracted incubation period should provide more information on the degradation kinetics and allow for the acclimation of the biomass to inhibitory compounds.

The experimental method is described in **Appendix C**. For the BMP assay, controls were prepared, in duplicate, which contained only sludge and the mineral medium. The function of the control was to determine the volume of gas produced due to the microbial degradation of residual organic molecules in the inoculum. The gas volumes measured were corrected by subtracting the volume of gas produced in the controls such that the results represented the gas which was produced as a result of the degradation of the substrate alone. The sludge and medium were mixed together to give a working volume of 100 ml in each serum bottle, with a headspace of 25 ml. Similarly, in the ATA assay, the control contained sludge, medium and sodium acetate-propionate solution.

The defined nutrient medium (**Appendix C**) contained nutrients and vitamins for anaerobic cultures. Resazurin was added to detect oxygen contamination. Sodium sulphide was added to provide a reducing environment.

Sodium bicarbonate ($NaHCO_3$) was added to the nutrient medium to provide buffering. This is important in the control of the alkalinity of the system. The final assay concentrations of nitrogen, phosphorous and alkalinity, respectively, were 122 mg/l as N, 19 mg/l as P and 2 500 mg/l as $CaCO_3$. The C : N ratio was 6 : 1.

The loading rate to each bottle can be calculated in terms of volume, i.e., g COD/ml. The bottles were incubated in a constant temperature room (37 °C). The assay bottles were shaken manually once a day to facilitate contact between the microorganisms and the substrate. The methods for gas volume sampling and removal are described in **Appendix C**. Gas production was measured daily for the first 10 d and periodically thereafter. Gas was vented as necessary to prevent inadvertent gas leakage and gas overpressure effects (Owen et al., 1979). The biogas compositions were determined by gas chromatography (**Appendix C)**.

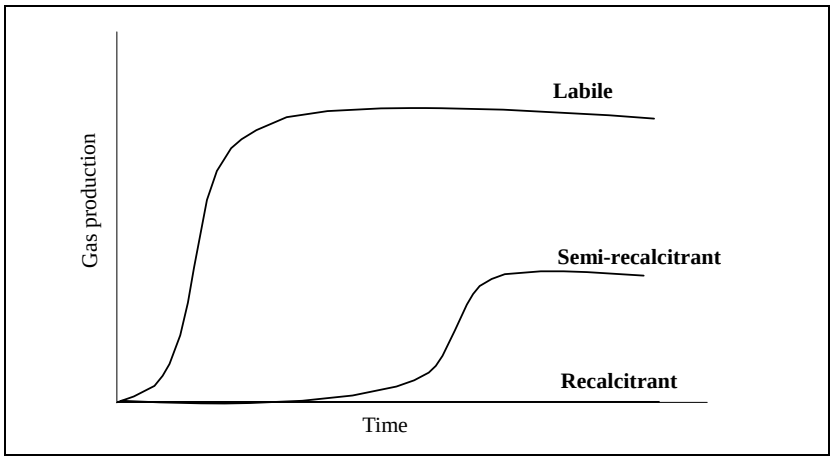


FIGURE 5.1 : Comparison of gas production curves for the degradation of labile, semi-recalcitrant and recalcitrant substrates.

Gas production is indicative of metabolic activity, thus the shape of the gas production curve indicates the degree of degradability of a substrate (**Figure 5.1**). A labile substrate should have a short lag period followed by the exponential growth phase. The gas production rate should be high due to the efficient metabolism of the available substrate. With a semi-recalcitrant substrate, the lag period would be protracted. During this time the biomass would metabolise more readily degradable compounds in the substrate and acclimate to the recalcitrant molecule, i.e., develop the necessary digestive enzymes. There would be not degradation of a recalcitrant substrate.

Appropriate sample size and liquid to headspace volume ratios are important for the precision and accuracy of the results. The estimated degradable COD should be kept to > 2.0 g/l in the assay liquid. This can be adjusted when toxicity and/or low degradability are anticipated. Multiple dilutions can be used when an estimate of degradability is not available. The headspace can be decreased, by increasing the liquid volume, to improve the accuracy of methane determinations when low gas production is expected.

The biochemical methane potential (BMP) assay provided an indication of the ultimate anaerobic degradability of an effluent. It also gave information on degradation rates and volumes and concentrations of an effluent that could be treated effectively. A detailed methane balance should be kept for each sample during the assay and gas volumes monitored periodically. Methane content was determined whenever gas was wasted.

Test precision and accuracy are functions of the standard error of estimate of the methane contribution due to seed inocula and substrate metabolism (Owen et al., 1979). The total methane produced from the seed alone, i.e., the control, should be limited to less than 1.5 ± 0.5 ml over a 30 d incubation period. A typical sample could correspondingly be analysed as 50.0 ± 1.0 ml of methane during the same period resulting in an overall precision of ± 2 %. Biochemical methane potential is referenced either to sample volume ($m^3 CH_4 / m^3$ sample), sample mass ($m^3 CH_4$ /kg sample), or sample organic content ($m^3 CH_4$ / kg COD). The latter method permits direct transfer of results into percent organic matter converted to methane by the theoretical 0.350 $m^3 CH_4$ produced per kilogram COD catabolised (at STP) (McCarty, 1964).

Whilst toxicity is not often a problem in digesters operating on natural substrates, problems can often occur in treating industrial wastes. The anaerobic toxicity assay (ATA) indicates the inherent toxicity of an effluent, which was determined by a decrease in metabolic rate, relative to the control. The acetate-propionate solution was added to these assay bottles as a direct methanogenic precursor; i.e., as a labile source for the methanogens. Substrate was then added. If the substrate or its constituents were inhibitory to the methanogens, the metabolism would decrease and gas production would be lower than in the controls. Thus, anaerobic toxicity was determined as the adverse effect of a substrate on the predominant methanogens (Owen et al., 1979). The ATA is, typically, conducted under quiescent incubation conditions therefore periodic manual agitation is sufficient to facilitate contact. To test a substance, assay concentrations should be selected to provide a range from *non-inhibitory* to *severely toxic* (Owen et al., 1979). The first week of incubation is critical.

Total gas production data were employed for determining relative rates of metabolism of the sodium acetate-propionate solution. The maximum rate of gas production was computed for each sample over the same period and data were normalised by computing ratios between respective rates for samples and the average of the controls. This ratio was designated the maximum rate ratio (MRR) (Owen et al., 1979). Since measurement of gas production was relatively accurate, a MRR of < 0.95 suggested possible inhibition and one < 0.9 suggested significant inhibition.

5.3.3 Bioassay modifications

The laboratory-scale protocol was based on the method described by Owen et al. (1979). A few modifications were imposed to ensure the applicability of the bioassay in the least sophisticated laboratory. The aim was for the protocol to be implemented at the wastewater treatment works as a screening mechanism prior to the acceptance of an industrial effluent for anaerobic treatment.

Owen et al. (1979) used different bottle sizes for the BMP (200 ml) and ATA (125 ml) tests. The adapted protocol used only one bottle size (125 ml) for simplification of the method and to prevent increased expenses. The working volumes were kept constant, at 100 ml , in all the bottles.

The inoculum size was 30 % (v/v) of the total working volume. Owen et al. (1979) used an inoculum size of 20 %. The important factor is that the volume of feed sludge is kept constant, in a particular trial, for comparison between different bottles.

Owen et al. (1979) designed an elaborate apparatus for the anaerobic transfer of the defined medium and substrate into the serum bottles. In the adapted protocol the components were simply measured in measuring cylinders and added to the serum bottles with as little oxygen contamination as possible. Once all of the components were added, the solutions were overgassed (OFN) to expel any oxygen contamination acquired during inoculation.

A gas mixture of 30 % (v/v) CO_2 and 70 % (v/v) N_2 was used by Owen et al. (1979) to overgas the solutions. This gas mixture was not readily available in KwaZulu-Natal resulting in an extended delivery period and the gas being expensive. Oxygen-free nitrogen (Fedgas) was, therefore, used for overgassing. This gas was readily available and inexpensive. The oxygen-free nitrogen could not be used to sparge the solutions since it would strip them of carbon dioxide. This restriction was not applicable with the carbon dioxide/nitrogen gas mixture. The oxygen-free nitrogen was, therefore, only used to overgas the headspace.

The serum bottles were incubated at 37 °C, as compared to 35 °C in the Owen assay. A temperature of 37 °C was chosen since, from the digester survey, it was established that most digesters were heated to this temperature which is optimal for mesophilic digestion. It is unlikely that there would be much difference in results between the two temperatures. What is important is that incubation should occur at the temperature at which the digester of interest is operated. Thus, if the digester is not heated then the bottles should be incubated at ambient temperature or slightly higher due to the exergonic nature of the methanogenic process.

5.3.4 Possible improvements of the protocol

At a wastewater treatment works, the raw sewage, or feed sludge, provides the necessary nutrients for anaerobic digestion and should, therefore, be incorporated into the batch tests to simulate the full-scale digester since the aim of these tests is to provide a screening mechanism for industrial effluents and to give an indication of the effects that a particular substrate may have on the operation of a full-scale digester. Constant volumes of feed sludge should, therefore be included in the serum bottles and realistic feed to industrial effluent ratios calculated. The bioassays without the feed sludge are important as they provide information on the biodegradability of the effluent alone. When mixed with the feed sludge, distinction between metabolism of the feed and the industrial effluent would not be possible. Therefore, it is believed that both tests should be performed. The assay without the feed sludge provides an indication of the substrate degradability and identifies the inhibitory components and the concentrations at which the components may become inhibitory. Based on this information, incorporation of the feed sludge aims to simulate, on a batch-scale, what occurs in the full-scale digester. This facilitates scale-up directly from the batch test to full scale.

A possible improvement for the bioassay would be to have a syringe dedicated to the measurement of gas production in each serum bottle. This would prevent gas loss associated with the re-injection of gas into the bottle and the subsequent removal of the syringe to measure the gas production in another bottle. However, the cost and weight of the glass syringes would necessitate the use of plastic disposable syringes. The plastic syringes could be sealed to the septum with silicon sealant. This is not optimal as it was found that plastic syringes were not as accurate as glass syringes. The reason for this was that the plunger has a rubber seal on the end which tended to stick and a significant gas pressure was required to move the plunger. The glass syringe was, therefore, better for the accurate measurement of gas production.

Mixing the bottle contents could be improved by placing the bottles on a mechanical shaker. Manual shaking of the bottles, on a daily basis, was insufficient to prevent settlement of the contents.

The pH and alkalinity of the solution should be determined at the end of the test to provide an indication of the efficiency of the process.

The method used for COD determinations is described in **Appendix C**. This method was based on the open reflux method presented in Standard Methods (American Public Health Association, 1989). This method is not suggested for samples containing solids. If the method is used, the samples should be homogenised. In these

tests, the biomass contributed to the overall COD and, therefore, had to be incorporated in the calculations. The presence of solids or flocs can greatly affect the COD measurement. In full-scale digesters, the organic fraction of the digester feed and effluent is quantified by the determination of the volatile solids in each stream. This method (**Appendix C**) could be applied in the laboratory tests and a reduction in the volatile solids, over the incubation period, would provide an indication of the substrate reduction. The COD could be determined on the soluble components, prior to inoculation, and the supernatant of the final effluent. This would provide an indication of COD reduction over the incubation period.

5.3.5 2l Batch tests

The serum bottle tests were scaled up to 2 l reaction vessels as it was thought that a higher working volume would be more representative of the full-scale condition. The experimental set-up is illustrated in **Figure 5.2** and the method is described in **Appendix C**.

These reaction vessels had a working volume of 1 600 ml and a headspace of 400 ml. The gas trap was filled with an acidified solution (20 % (m/v) NaCl and 0.5 % (m/v) citric acid) to prevent the dissolution of carbon dioxide. Thus, displacement of the solution was representative of the total volume of biogas produced and not only the methane. Biogas composition was analysed and the method of gas sampling is described in **Appendix C**. The successful operation of the gas trap relied on positive displacement of the acidified solution. The positioning of the gas trap was important. The level of the acidified solution should be the same as that of the reactor contents to prevent the formation of a back-pressure.

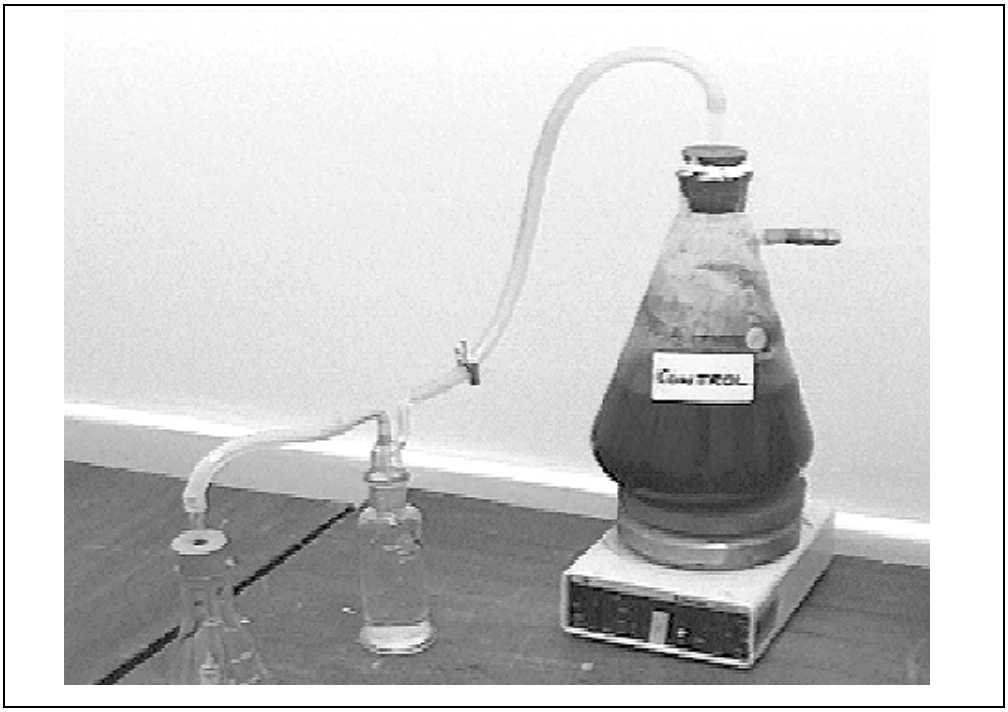


FIGURE 5.2 : Experimental set-up for the 2 l batch tests.

The 2 l tests were cumbersome to set up and monitor compared to the serum bottles. Accurate measurement of gas production was difficult. The results obtained from the 2 l batch tests (**Chapter 7**) were less informative than those from the serum bottles. Serum bottles are small and, therefore, allow for the simultaneous investigation of several variables such as various substrate concentrations. Results from the serum bottle tests

provide an adequate screening mechanism to evaluate the anaerobic degradability and potential toxicity of an effluent. This method is, therefore, suggested for the laboratory-scale test protocol.

The philosophy of screening tests is that they should be simple and cheap and at the same time stringent, meaning that a positive test result indicates ready biodegradability whereas a negative result does not exclude environmental biodegradability but indicates that more investigation is necessary (Nyholm, 1991). These simple laboratory-scale tests could be applied to any effluent to determine its anaerobic degradability and inherent toxicity, prior to loading into a digester. This screening technique is important for measuring the presence or absence of inhibitory substances and, therefore, offers promise for resolving anaerobic treatment problems. The bioassays are relatively rapid and accurate and provide information on the volumes and concentrations of an effluent which can be treated effectively. This information can then be applied in scale-up, initially in pilot-scale and ultimately full-scale implementation in an anaerobic digester. The results can be expressed in useful engineering terms which can be applied for assessing process performance. The procedures are flexible and allow fundamental studies beyond those described. The described technique was used to evaluate a textile size effluent and the results are presented in **Chapter 7**.

5.3.6 Batch vs continuous culture

Batch cultivation methods are not always suitable, especially when it is necessary to work under exactly defined conditions and biological material of constant properties is required (Malek and Fencl, 1966; Parkes, 1982). In batch cultivation, empirical knowledge with only a limited scientific basis is sufficient, whereas the continuous methods require fundamental knowledge of the process as well as its total kinetics. The kinetics of a continuous system are described in **Section 3.2.2**.

A way of circumventing the short-comings of batch cultivation, which approaches the continuous-flow process, is **semi-continuous** cultivation, where a part of the fermented substrate is withdrawn at suitable time intervals and replaced by new substrate. The semi-continuous systems are transient forms between the batch and the continuous systems. If the intervals between the additions of fresh substrate and the removals are shortened, the semi-continuous systems approach fully continuous (Malek and Fencl, 1966).

The advantage of using batch tests to evaluate toxicity and biodegradability is that they can be easily set up, in any laboratory, can evaluate a wide range of variables and can investigate the influence of shock loads. The advantage of continuous screening tests would be the close simulation of full-scale operation although they are costly in terms of facilities, equipment, time and personnel (Owen et al., 1979). Batch tests do not simulate the effects of real systems very well, however, they are still very useful for sorting out important variables and for the development of an efficient continuous-feed assay program.

5.4 MATERIAL AND ENERGY BALANCES

According to the basic laws of thermodynamics, mass and energy are conserved within a system. The form may change but the total quantity remains constant. Material and energy balances can, therefore, be analysed for a system to give an indication of the process operation. This concept was applied to the serum bottle tests, where material and energy balances provided an indication of the efficiency of the process within the bottle. This study investigated the response of a batch anaerobic system with a defined substrate, glucose. Glucose was selected because its biochemical fermentation pathways are well known (Sam-Soon, Loewenthal, Wentzel and Marais, 1990). The results obtained from the assay were used to establish a protocol for the calculation of material balances in an anaerobic batch test (**Appendix E**).

5.4.1 Materials and methods

Standard serum bottle assay conditions were applied (**Appendix C**). The substrate consisted of glucose solutions of various concentrations (5, 10, 20, 50 and 100 g glucose/l).The controls and test assays were prepared in duplicate, for reproducibility. The bottles were incubated (37 °C) in a constant temperature room for 30 d. The contents were mixed daily by manual shaking. Gas production was measured and the composition determined.

Total suspended solids (**Appendix C**) were measured before and after incubation to assess the amount of new biomass formed during the test period. Total carbon, inorganic carbon and COD analyses were made at the start and termination of the test.

5.4.2 Carbon balance

To monitor sample decomposition and process efficiency, it is appropriate to perform a mass balance over the process. A **carbon balance** is particularly useful. A theoretical balance can be calculated from the Tarvin and Buswell equation (**Eq. 2.1**).

If the empirical formula of the substrate is known, then a carbon balance can be determined from the following relation:

Moles of carbon in - moles of carbon in biogas = moles of carbon remaining

The empirical formula of glucose was known ($C_6H_{12}O_6$), as well as the volume and concentration of glucose solution added to each sample. The carbon mass balance for the 5 g/l assay was calculated (**Appendix E**) by determination of the amounts of carbon entering and leaving the system, incorporating the following components:

$$C_{glucose} + C_{biomass} + C_{nutrient\ medium} \rightarrow C_{CO_2} + C_{CH_4} + C_{biomass} + C_{final\ solution} \qquad [5.1]$$

The carbon balance was based on mass since mass is a conserved parameter. The mass of carbon added in the glucose solution was calculated at 80.0 mg/100 ml (**Appendix E**). This calculation was based on the chemical formula of glucose and the concentration of the glucose solution added to each serum bottle.

The total suspended solids of the inoculum sludge were determined by the method described in **Appendix C**. This provided an estimate of the biomass concentration in the seed sludge (6.43 mg/l). For fermentation with live cells, growth and other metabolic activity must be accomodated in the mass balance (Doran, 1995). There are several possible stoichiometric formulations for bacterial protoplasm although the formula most commonly accepted is $C_5H_7O_2N$ (Bailey and Ollis, 1986). The formula is a reflection of the biomass composition. Although microorganisms contain a wide range of elements, 90 to 95 % (m/v) of biomass can be accounted for by carbon, hydrogen, oxygen and nitrogen. The amount of carbon present in the biomass was determined from this empirical formula.

The nutrient medium was made up of trace elements and vitamins necessary for the metabolism of anaerobic cultures. An empirical formula of $C_{12}H_{14}O_3N_2$ was adopted. The nutrient medium contributed to the COD of the assay and was measured as 651 mg/l. From the theoretical COD calculation (**Appendix E**), 1 g of medium had

a COD equivalent to 10 g. The mass of nutrient medium added to the serum bottle was calculated based on the COD. The mass of carbon was then calculated from the chemical formula.

The biogas components containing carbon were carbon dioxide and methane. From the theoretical equation (Eq. 2.1), it was calculated that, under the set conditions, addition of 40 ml of a 5 g/l glucose solution was equivalent to 0.001 moles of glucose. The theoretical volumes of carbon dioxide and methane production were calculated, based on the mineralisation of 0.001 moles of glucose. The theoretical gas production was 0.003 moles for both carbon dioxide and methane. The theoretical mass of each gas was calculated. These were calculated as 132 and 48 mg for carbon dioxide and methane, respectively. The reason for the greater mass of carbon dioxide relative to methane, when anaerobic biogas usually has a composition of ca. 60 % methane to 40 % carbon dioxide, is that the molecular mass of carbon dioxide is much greater than that of methane. From the experimental results, 84.4 mg of carbon dioxide was produced. This was 64 % (m/w) of the theoretical production. Methane production was only 51 % (w/w) of the theoretical, at 24.5 mg. These results suggested that the glucose was not completely degraded. The reason for this could have been that since glucose is a labile substrate, it was readily converted to volatile acids, by the acidogens. It is probable that the acids were not as efficiently converted to methane resulting in a build-up of acids within the serum bottle. This could have caused inhibition of the methanogens. The mass of carbon produced in each biogas component was calculated from the molecular masses.

The carbon contents of the individual components could not be determined upon termination of the assay since they were mixed together in the bottles. A total carbon analysis was thus performed on the final solution. This incorporated the biomass (including new biomass formed during the incubation period), undegraded substrate and un-utilised nutrient medium. The solutions were mixed to obtain representative samples for total carbon and inorganic carbon analyses. The method used is described in **Appendix C**. The residual total organic carbon was determined by subtracting the inorganic carbon from the total carbon. The carbon balance, as calculated in **Appendix E**, is presented in **Table 5.1**.

TABLE 5.1: Carbon balance for the 5 g/l glucose assay.

	Carbon IN (mg)	**Carbon OUT (mg)**
Glucose solution	80.0	-
Biomass	0.1	-
Medium	1.2018	-
Carbon dioxide	-	23.0
Methane	-	18.38
Final solution	-	32.5
TOTAL	**81.3**	**73.88**

These calculations suggested that the carbon mass was not entirely conserved with a recovery of ca. 91 % (m/w). The carbon that was unaccounted for could have been lost in the form of biogas during measurement with the syringe. As stated above, this method is not optimal and may result in gas losses. Although, theoretically, mass is conserved, it is difficult to obtain a 100 % recovery under experimental conditions due to experimental error such as that described.

5.4.3 COD balance

Another means of performing a material balance is by measuring the COD of each assay sample before and after the incubation period. The chemical oxygen demand of a sample is an indication of the amount of organic matter present. Chemical oxygen demand is a conserved parameter in the anaerobic process. Degraded COD is transformed to COD in the form of methane in the biogas, thus recalcitrant COD contributes to the COD of the final solution and not the COD of the biogas.

The COD mass balance for the 5 g/l glucose assay was calculated (**Appendix E**) by determination of the amounts of COD entering and leaving the system, incorporating the following components:

$$COD_{substrate} + COD_{biomass} + COD_{nutrient\ medium} \rightarrow COD_{CH_4} + COD_{final\ solution} \qquad [5.2]$$

The technique for determining the COD of a sample (**Appendix C**) involved the oxidation of organic matter by a boiling mixture of chromic and sulphuric acids. The sample was refluxed in the strongly acidic solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). After digestion the amount of $K_2Cr_2O_7$ consumed was determined and the amount of oxidisable organic matter was calculated in terms of oxygen equivalent. The initial and final COD measurements were taken for each assay sample .

The equation for the oxidation by dichromate shows that for each mole of dichromate, three oxygen atoms are required.

$$Cr_2O_7^{2-} + 8\ H^+ \rightarrow 2\ Cr^{3+} + 4\ H_2O + 3\ O \qquad [5.3]$$

The oxidation of organic material, by dichromate, follows the following reaction pathway (Sawyer, McCarty and Parkin, 1994):

$$C_nH_aO_bN_c + dCr_2O_7^{2-} + (8d+c)H^+ \rightarrow nCO_2 + \frac{a + 8d - 3c}{2} H_2O + cNH_4^+ + 2dCr^{3+} \qquad [5.4]$$

where $d = 2n/3 + a/6 - b/3 - c/2$.

From this equation, the theoretical COD of a compound can be calculated (**Appendix E**) based on the equivalent amount of oxygen required to oxidise it. The theoretical COD calculation was used as a mechanism to assess the accuracy of the COD method by comparing the theoretical COD values with the measured values. Potassium hydrogen phthalate was used as a standard in the COD test. The theoretical COD of this solution was 500 mg/l. This calculation is illustrated in **Appendix E**.

The COD balance for the 5 g/l glucose solution is described. The input COD values (substrate, biomass and nutrient medium) were measured. These values were summed to calculate the total COD entering the system (**Table 5.2**).

The amount of COD in the inoculated 40 ml of glucose solution was calculated from the measured COD. From the theoretical equation (Eq. 5.4) it was calculated that 1 g glucose had an equivalent COD of 1.067 g (**Appendix E**). This calculation has been reported by other researchers (Sam-Soon et al., 1990). A 40 ml sample of the 5g/l solution of glucose contained 0.0011 moles of glucose. From the theoretical equation, this should

have had a COD of 211.2 mg. The measured COD was, however, much higher (443.6 mg) and could have been due to experimental error with the COD method.

The biomass contributed to the COD of the solution within the serum bottle. As stated, the open reflux COD test is not optimal for samples which contain solids and may result in inaccurate measurements. Although very little, the nutrient medium also contributed to the total input COD.

Methane production is directly proportional to COD reduction. Mineralisation of 1 g of COD results in the production of 0.350 l methane (at STP) (McCarty, 1964). The theoretical COD of a produced amount of methane can be calculated from Eq. 5.5. A total volume of 24.5 mg of methane was produced in the 5 g/l serum bottles.

For methane, d = 1.33

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O \qquad [5.5]$$

thus, 1 mole CH_4 requires 2 moles O_2

16 g CH_4 requires 64 g O_2

1 g CH_4 requires 4 g O_2

Therefore, 24.5 mg CH_4 = 98 mg COD

Carbon dioxide has a COD value of 0 (**Appendix E**).

The COD at the end of the incubation period was determined on the mixture of components in the assay solution. This incorporated the biomass, undegraded substrate and un-utilised nutrient medium. The solutions were mixed to obtain representative samples. The COD of the final, unfiltered sample, was determined. The sample could be filtered and the COD of the biomass and the filtrate measured separately. These values would then be added together to determine the total COD of the final solution if the relative volumes or masses were known. The COD balance, as calculated in **Appendix E**, is presented in **Table 5.2**.

TABLE 5.2 : COD balance for the 5 g/l glucose assay.		
	COD IN (mg)	**COD OUT (mg)**
Glucose solution	443.6	-
Biomass	80.3	-
Medium	19.53	-
Methane	-	98
Final solution	-	422.5
TOTAL	**543.4**	**520.5**

The COD reduction in the serum bottles was only 62 %. A greater reduction was expected. This could be attributed to the possible inhibition of the methanogens, as described above. Increased COD reduction would have resulted in a lower COD for the final solution and a greater methane production. From **Table 5.2**, 96 % of the input COD was recovered.

The open reflux COD technique is relatively simple and can be done in most laboratories whereas not all laboratories have access to total carbon analysers. However, the carbon balance is recommended over the COD balance as it is believed to be more accurate and reproducible.

These balances could be transformed into energy balances. The organic matter present in the wastewater is an energy source for the digester biomass. In anaerobic digestion, methane and carbon dioxide are the major constituents of the evolved biogas. The organic matter is only transformed, i.e., the capacity for electron transfer is maintained in the methane which is produced.

5.4.4 Biomass yield

Despite its complexity and the many intracellular reactions involved, cell growth obeys the law of conservation of matter (Doran, 1995). When cell growth occurs, they are a product of the reaction and must be represented in the reaction equation. This requires knowledge of the growth stoichiometry.

Any increase in solids during the incubation time was attributed to cell growth. As cells grow there is, as a general approximation, a linear relationship between the amount of biomass produced and the amount of substrate consumed. The amount of biomass formed during the course of the experiment was determined by the increase in suspended solids.

TABLE 5.3 : Table showing the average biomass and total gas production in the serum bottles fed with different concentrations of glucose substrate.

Glucose concentration (g/l)	Biomass growth (mg)	Total biogas (ml)
Control	4.8	24.6
5	3	88.8
10	2.5	94.5
20	4.1	118.5
50	7	177.8
100	24.0	323.4

The results show an increase in cell growth with an increase in glucose concentration. This was expected, since an increased concentration of substrate should result in an increased rate of metabolism and more energy available for cell growth. Concurrently, with the increase in cell growth there was an increase in biogas production illustrating substrate utilisation.

5.5 INDUSTRIAL EFFLUENTS IN KWAZULU-NATAL

The aim of this section was to identify industries producing high-strength or toxic organic effluents and to identify available digester capacity for potential treatment.

5.5.1 Effluent survey

A survey was conducted to identify industries which produce effluents of this nature. The survey incorporated a range of industries. The Durban Metropolitan Council provided information on those effluents monitored by them. Details of the effluents, for each region, are presented in **Appendix F**. These data include volumes of effluent produced and approximate strength (COD) based on monthly records. All effluents with a COD > 2 000 mg/l were included.

Emphasis was placed on two particular regions due to the concentration of industry and the availability of anaerobic digester capacity. These two areas were Durban South and Pinetown. Effluents in the Durban South area could be treated in the idle digesters at the Southern Wastewater Treatment Works. Effluents produced in the Pinetown region have the potential for treatment at the Umbilo Wastewater Treatment Works. Industries in these regions were visited to gain familiarity with the processes and on-site pre-treatment methods.

5.5.2 Discharge of industrial effluent to sewer

This survey revealed the necessity for the identification of point sources within factories. This would, however, require an extensive survey in which researchers would need to become familiar with each process and to be able to identify sources of high-strength or toxic organic effluents within a factory. These effluent sources could be segregated from the bulk effluent, concentrated on site and then tankered to a nearby wastewater treatment works for treatment in the available anaerobic digester capacity. A study of such depth would facilitate identification of possibilities for pollution prevention and waste minimisation. Segregation of the high-strength or toxic components of an effluent should facilitate compliance of the remainder of the effluent to the standards

for discharge to sewer. The most recent discharge standards, for the acceptance of trade effluent into a sewage disposal system, are presented (**Table 5.4**) (Durban Metropolitan Council, 1997).

TABLE 5.4 : Standards for the discharge of trade effluent into a sewage disposal system.

General Quality Limits	**Large Works (> 25 Ml/d)**	**Small Works (< 25 Ml/d)**	**Units**
Temperature	< 44	<44	°C
pH	6 to 10	6.5 to 10	pH units
Oils, greases, waxes of mineral origin	50	50	mg/l
Vegetable oils, greases, waxes	250	250	mg/l
Total sugar and starch (as glucose)	1 000	500	mg/l
Sulphates in solution (as SO_4^{2-})	250	250	mg/l
Sulphides (as S^{2-})	1	1	mg/l
Chlorides (as Cl^-)	1 000	500	mg/l
Fluoride (as F^-)	5	5	mg/l
Phenols (as phenol)	10	5	mg/l
Cyanides (as CN^-)	20	10	mg/l
Settleable solids	Charge	Charge	ml/l
Suspended solids	2 000	1 000	mg/l
Total dissolved solids	1 000	500	mg/l
Electrical conductivity	-	400	mS/m
Anionic surfactants	-	500	mg/l
COD	Charge	Charge	mg/l
Heavy Metal Limits			
Copper (as Cu)	50	5	mg/l
Nickel (Ni)	50	5	mg/l
Zinc (Zn)	50	5	mg/l
Iron (Fe)	50	5	mg/l
Boron (B)	50	5	mg/l
Selenium (Se)	50	5	mg/l
Manganese (Mn)	50	5	mg/l
Lead (Pb)	20	5	mg/l
Cadmium (Cd)	20	5	mg/l
Mercury (Hg)	1	1	mg/l
Total chrome (Cr)	20	5	mg/l
Arsenic (As)	20	5	mg/l
Titanium (Ti)	20	5	mg/l
Cobalt (Co)	20	5	mg/l
TOTAL METALS	100	20	mg/l

Industrial effluents from the Pietermaritzburg area are discharged to the Darvill Wastewater Treatment Works. Discharge standards are monitored by Umgeni Water. The major problem in this area is the disposal of effluent from the four vegetable oil refineries. The survey did not concentrate on this region since the Darvill Wastewater Treatment Works was operating almost at full capacity therefore additional loading of high-strength industrial effluents could be detrimental to the operation of the digesters.

The Durban Metropolitan Council was approached for information on the proposed establishment of new industry in the province. The main area demarcated for industrial development is Phoenix. High-strength or toxic organic effluents, produced in this region, could be treated in the idle digester at the Phoenix Wastewater Treatment Works. Thus, Phoenix would be a rational location for the development of new industries producing effluents of this nature. No other plans of extensive industrial development were divulged

5.5.3 Source / digester matrix

A source / digester matrix (**Table 5.5**) was compiled with the digesters identified with available capacity and the industrial effluents for potential treatment. Individual factories are named in the two regions covered by the survey. Potential for treatment of a specific effluent in a particular digester is identified by a tick. More detailed data are given in **Appendix F**.

What is evident from the matrix is that many of the industries in these two regions were agro-industrial. These industries often produce high-strength organic effluents which are monitored by the local authorities to ensure compliance to the stipulated discharge standards. To meet the standards, for discharge to sewer, the effluents are often diluted with excessive wastage of potable water. Another option for the disposal of effluents with a COD too high to be accepted at a sewage works, without either dilution or the imposition of high tariffs, is discharge to sea, e.g.. CG Smith. Marine discharge standards are much lower than those for discharge to sewer since it is believed that the rapid turnover of water prevents adversity to marine ecosystems. The end result, with marine discharge, is a loss of water. Industries utilise fresh water from the rivers, however, when this is discharged to sea, the water can not be re-used. Co-disposal in municipal landfill sites is the only option for very high-strength or toxic organic effluents. A potential problem with co-disposal is the generation of excess leachate which, if the landfill is not properly lined, may cause contamination of the groundwater. The co-disposal of liquid effluents has even resulted in landfill subsidence e.g., the BulBul Drive landfill site, in Chatsworth, Durban, where a large mass of compacted waste collapsed on 8th September 1997 (Anon, 1997).

Examples of industries which produce high-strength organic effluents are dairies, bakeries, chemical and pharmaceutical manufacturers and yeast processors. Many of these effluents have been found to be amenable to anaerobic degradation (Van Der Merwe-Botha and Britz, 1997). Pesticide effluent is an example of an effluent which contains toxic organic molecules. Effluents of this nature are usually co-disposed in municipal landfill sites. They could, however, be treated by anaerobic digestion upon acclimation of the biomass. Also, implementation of waste minimisation practices and identification and segregation of point sources, would reduce the volumes of toxic effluent being produced. These lower volumes could then be treated in a digester without causing toxic shock.

TABLE 5.5 : Source / digester matrix illustrating the potential for the treatment of specific effluents in anaerobic digesters with available capacity.

DIGESTERS	Amanzimtoti	Cato Ridge	Mpophomeni	Mpumalanga	New Castle	New Germany	Northern	Phoenix	Southern	Tongaat	Umbilo	Umlazi	Umzinto	Verulam
INDUSTRIES														
Albany Bakery									✓					
Alex Cartage											✓			
Auto Armor											✓			
Associated Biscuits											✓			
Beacon Sweets									✓					
Beier Industries									✓					
Bromor Foods									✓					
Cargo Carriers									✓					
Cato Ridge region		✓												
CFC											✓			
Chemical Specialities									✓					
CHT South Africa						✓								
CG Smith									✓					
Coates Brothers	✓								✓					
Competition Motors									✓					
Dan Perkins											✓			
Distillers Corp.						✓								
Drum Services									✓					
Durban Confectionary									✓					
Durban South region									✓			✓		
Elida Ponds									✓					
Engen Refinery									✓					
Ferrobond											✓			
Fine Foods									✓					
Frametex						✓					✓			
Frame Textiles									✓					
Golden Lay Farms									✓					
Hammarsdale region			✓	✓										
Huletts Refinery									✓					
Huls						✓					✓			
Ind. Oil Processors									✓					
Kohler Carton											✓			
Lever Bros./ Unifoods									✓					
Marachia Laundry									✓					
Mondi Paper									✓					
Nampak											✓			
NCD											✓			
NCP Umgeni							✓							
NCP/Sentrachem									✓					
NCP Yeast									✓					
Nelba											✓			
New Castle region					✓									
New Germany region						✓					✓			
Ninian & Lester											✓			
O.T.H. Beier									✓					
Paperkem									✓					
Pekay Chemicals											✓			
Phoenix region								✓						
Pinetown region						✓					✓			
Plascon Paints									✓					

DIGESTERS	Amanzimtoti	Cato Ridge	Mpophomeni	Mpumalanga	New Castle	New Germany	Northern	Phoenix	Southern	Tongaat	Umbilo	Umlazi	Umzinto	Verulam
INDUSTRIES														
Pure Fresh Foods											✓			
Printpak									✓					
Prostruct											✓			
Qualichem											✓			
R&B Engineering											✓			
Rapidol											✓			
Rentokil											✓			
Republican Press	✓													
Resmed											✓			
Revertex									✓					
Robertsons	✓													
Sapref Refinery									✓					
Sanachem								✓						
S.A. Sugar Terminals									✓					
Springfield Park							✓							
Sorghum Breweries									✓					
South coast region													✓	
Staflex											✓			
Status Chemicals											✓			
Sunningdale							✓	✓						
Sunrise Dairies											✓			
Sybron Chemicals											✓			
Syndachem											✓			
Tanker Services									✓					
Tongaat region										✓				✓
Trek Express											✓			
Triumph Printers											✓			
Unitrans Natal									✓					
Verulam region														✓
Vision Creations									✓					
Waste Services									✓					
Waste Tron											✓			
Westmead						✓					✓			
Whiteheads										✓				

This matrix provides an indication of the potential for treatment of *problematic* effluents in available anaerobic digester capacity. The matrix only includes those digesters which were identified with available capacity, and those industries (in the 2 chosen regions) producing effluents with a COD > 2 000 mg/l. This matrix could be extended to incorporate a wider range of industries and digesters. What can be deduced from this survey and the compilation of the matrix is that there is definitely the potential for the utilisation of available resources to effectively stabilise effluents which otherwise may have an adverse effect on the environment.

Chapter 6

Evaluation of the Umbilo Digesters

The objective of this chapter was to assess the efficiency of the anaerobic digestion process at the Umbilo Sewage Purification Works for the determination of whether the digesters could be used for the treatment of high-strength or toxic organic effluents. The basic design of a biological wastewater treatment works is described in **Section 6.2** with emphasis on the design of anaerobic systems. **Section 6.3** is an overview of the layout and operation of the Umbilo Sewage Purification Works. The performance evaluation is detailed in **Section 6.4** with detailed descriptions of the operating conditions and process characteristics. Background information on tracer tests is provided (**Section 6.5)**. The flow patterns and digester mixing characteristics were investigated in detail in a residence time distribution study (**Section 6.6**).

6.1 INTRODUCTION

Efficient substrate degradation by anaerobic digestion is dependent on favourable digestion conditions. The focus of this chapter is the evaluation of the performance efficiency of the anaerobic digesters at the Umbilo Sewage Purification Works. The detailed evaluation concentrated on this plant because its location in the industrialised Pinetown region. The superficial evaluation (**Chapter 4**) identified the works as having available hydraulic and organic loading capacity.

6.2 DESIGN OF A BIOLOGICAL WASTEWATER TREATMENT WORKS

The design of a new wastewater treatment works is based on the volumetric assessment of the flowrate, which would determine all hydraulic aspects of the works, and sewage strength, which would determine the biological and chemical processes in the works (Cloete and Muyima, 1997). Rainfall records, conditions of sewer systems and enforcement of by-laws should be considered. It is necessary to inspect the functioning of an existing works to establish possible shortcomings in its design and to assess the maximum capacities of the various units. The quality of the final effluent should be aligned with the standard requirements

6.2.1 Assessment of flow

Infiltration of groundwater and ingress of surface stormwater into the sewage system would affect the rate of flow significantly. Hence, flow recording during both wet and dry weather is necessary (Cloete and Muyima, 1997). The domestic sewage component is normally the major contributor to the total flow. In providing for the full design life of a sewage works the upward trend in per capita sewage contribution should be taken into consideration and an annual increase of 1.5 to 2.5 % could be expected (Cloete and Muyima, 1997). The average dry weather flow (ADWF) is the flow used for the design of treatment units and is measured in m^3/d. This flow should, however, include provision for peak dry weather flow, infiltration of groundwater and stormwater and peak wet weather flow.

6.2.2 Assessment of sewage strength

The strength of the sewage fed to a wastewater treatment works varies depending on the domestic living standards of the contributing population. Sewage characteristics can be divided into three main categories: the concentration of oxidisable organic material (substrate), the concentration of nutrients present and the solids concentration (Cloete and Muyima, 1997). Assessment of the organic concentration could be achieved by the COD, BOD or oxygen absorbance (OA) methods.

The design parameters attained from the preceding estimates should be moderated by reference to appropriate expertise and consultation.

6.2.3 Design parameters for anaerobic digesters

The normal design rules for anaerobic digesters are based on an extensive removal of labile matter (Henze, Harremoës, la Cour Jansen and Arvin, 1997). The purpose of the design is to ensure the survival of the methanogens

The basis for the design of these plants is the organic load or the sludge age. The organic load (kg VS/m^3.d) varies with the type of plant as well as the flow and organic strength characteristics. The purpose of design by means of sludge age is to ensure that the methanogens can survive in the plant. Sludge separation is designed on the basis of the hydraulic surface load and the sludge surface load (Henze et al., 1997).

Operational problems can be experienced in anaerobic plants. The slow growth rate of the methanogens can result in an extended start-up period for a new anaerobic digester. Seeding with anaerobic bacteria, for example from another plant, could reduce the start-up period. There should be a step-wise increase in the substrate load, starting with approximately 10 % of the maximum load (Henze et al., 1997). When the volatile fatty acid content of the digester effluent is sufficiently low then the load can be increased. The washout of biomass may occur if the sludge age is reduced. Inhibition of the biomass may occur by means of internally produced inhibition (fatty acids, ammonia, pH) or by means of substances supplied from the external environment (sulphate, ammonia, metals, specific organic materials). External inhibition normally occurs faster than internal inhibition. The type of substance and exposure time determine the inhibitory effects of external substances on the anaerobic wastewater treatment processes.

Several anaerobic digester designs, or configurations, were described in **Chapter 2**. In the conventional anaerobic digester, the entire reactor content is mixed by internal stirring or cyclic external pumping (Zehnder, 1988). Fresh and digested materials are thus kept in close contact but separation of biomass and treated water is difficult. Recycling of biomass overcomes the general drawbacks of anaerobic versus aerobic treatment, namely, the low growth rates and yields of anaerobes. The main drawbacks of anaerobic bacteria (low growth rates and yields) have been overcome by the construction of various types of anaerobic reactors which either retain or recycle the active biomass to maintain substrate conversion rates which are competitive with aerobic processes (Zehnder, 1988).

6.3 UMBILO SEWAGE PURIFICATION WORKS

The Umbilo Sewage Purification Works (USPW) is situated in Pinetown on the banks of the Umbilo River. It is divided into two sections: the old plant, which uses biofilters for primary treatment; and the new activated sludge plant, which was commissioned in 1992.

6.3.1 Biofilter plant

Raw sewage and industrial wastewater flow into 1 of 6 primary settling tanks. The primary sludge which collects at the bottom of the settling tanks is removed every morning and anaerobically digested. The supernatant liquor is treated in biofilters. The effluent then passes into one of 6 secondary clarifiers, the sludge is returned to the primary settling tanks and the supernatant flows onto rapid sand filter beds. The filtrate is chlorinated and discharged to the Umbilo River.

6.3.2 Activated sludge plant

Raw sewage and industrial wastewater flow into one of 2 primary sedimentation tanks. The settled sludge is pumped to the biofilter plant for anaerobic digestion. The supernatant is aerobically treated in an activated sludge reactor. The mixed liquor from the activated sludge reactor is then sent to 2 clarifiers, the sludge is returned to the reactor and the clarified effluent is chlorinated and discharged to the Umbilo River. Waste mixed liquor is concentrated by dissolved air flotation (DAF). The float (sludge) is pumped to the anaerobic digesters and the underflow returned to the activated sludge reactor.

6.3.3 Anaerobic digestion

There are 4 primary anaerobic digesters and 4 secondary digesters on site, each with a volume of 1.34 Ml. They are cylindrical with a coned base. The digesters are built into the ground. The primary digesters are heated to 36 ± 1 °C. The secondary digesters are unheated and have an extended residence time (ca. 100 d).

The raw sludge from the primary settling tanks in the biofilter and activated sludge plants and the waste activated sludge from the DAF unit are distributed equally to the anaerobic digesters approximately 4 times per day. The raw sludge is pumped from the raw sewage sump to a division box where it is evenly split into four streams which flow into each of the primary digesters. The digested sludge is displaced from the primary digesters for between 2 and 3 h per day. There are two overflow points: one at the bottom of the digester; and the other just below the half-way mark. The bottom draw-off lines are prone to blockages. The displaced sludge from the primary digesters is fed to the secondary digesters where the sludge settles and is separated from the supernatant (Carliell, Barclay and Buckley, 1996).

6.4 DIGESTER PERFORMANCE EVALUATION

The parameters for the assessment of digester performance efficiency were outlined in **Chapter 4**. The performance efficiency of the Umbilo anaerobic digesters was evaluated based on these parameters. The relevant information was obtained from the local authority and calculations were based on annual averages which were obtained from the monthly performance figures and technical reports.

6.4.1 Screening and grit removal

Raw wastewater contains solids which, if not removed, accumulate in the digester and reduce the efficiency by reduction of the active volume. The removal of these materials is important to extend the operational periods between digester shutdown for maintenance. Larger particles are removed by screens while grit is removed by the grit removal system. If these materials are not removed they could cause problems such as blockage of pipes and pumps and accumulation in the digesters.

The screen at the Umbilo works consists of a series of bars spaced across the inflow channel at the inlet to the works. The screens are raked periodically and the screenings disposed. The Umbilo works has a second screen positioned between the primary settling tanks and the digester sludge sump, thus the sludge fed to the digesters is screened twice to remove large materials. An average of 4.1 m^3 of screenings is removed per month which is equivalent to ca. 0.14 m^3/d (**Appendix B**).

Grit removal is essential as it can cause mechanical malfunctions and reduce the effective volume of the digesters. Grit removal channels at the inlet to the works allow for settlement of the grit which is manually removed. A monthly average of 8.5 m^3 grit is removed (**Appendix B**), with a daily removal of ca. 0.28 m^3.

6.4.2 Process evaluation

The Umbilo Sewage Purification Works (USPW) was designed (1992) to treat a flow of 23.2 Ml/d (10 Ml in the activated sludge plant and 13.2 Ml in the biofilter plant). Currently, 17.4 Ml is treated per day which is 75 % (v/v) of the design load. The USPW does, therefore, have the capacity to treat a higher hydraulic load. The biofilter plant was operating at 73 % (v/v) of its capacity at 9.67 Ml/d and the activated sludge plant at 77 % (v/v) of its design capacity at 7.71 Ml/d.

At the USPW the primary sludge is fed straight to the digesters. Since there is no thickener, the concentration, or percentage total solids, of the feed sludge is relatively low. The concentration of solids should be as high as possible to promote effective digestion but not too high to adversely affect pumping and mixing of the sludge (Ross et al., 1992). The feed sludge to the Umbilo digesters had an average concentration of 3.6 %.

Continuous or near continuous feeding should eliminate any abrupt flowrate or organic loading change which could result in shock loading. The Umbilo digesters had 2 main feeds per day. One at 08h00 and the second at 16h30. During these feeds the sludge from the primary sedimentation tanks was pumped to the anaerobic digesters. There were, on average, an additional 2 to 3 feeds per day. These consisted of sludge overflow from the activated sludge plant and the DAF unit. This feeding schedule could be improved to have more frequent feeds at lower flowrates. The distribution box ensured that each of the four digesters received an equal volume of feed. The volumes of sludge, pumped to the digesters are presented in **Appendix B**.

According to the design drawings, the feed sludge is added at the top of the draft tube (**Figure 6.1**). The digester sludge is drawn up the draft tube, thus the feed sludge is fed in the opposite direction. The advantage of this is that the feed sludge enters the digester at a point of great turbulence thus ensuring mixing. The feed is drawn into the sludge pathway. The digester level is kept constant and there is positive displacement of sludge, i.e., addition of sludge resulted in a sludge overflow, of an equal volume.

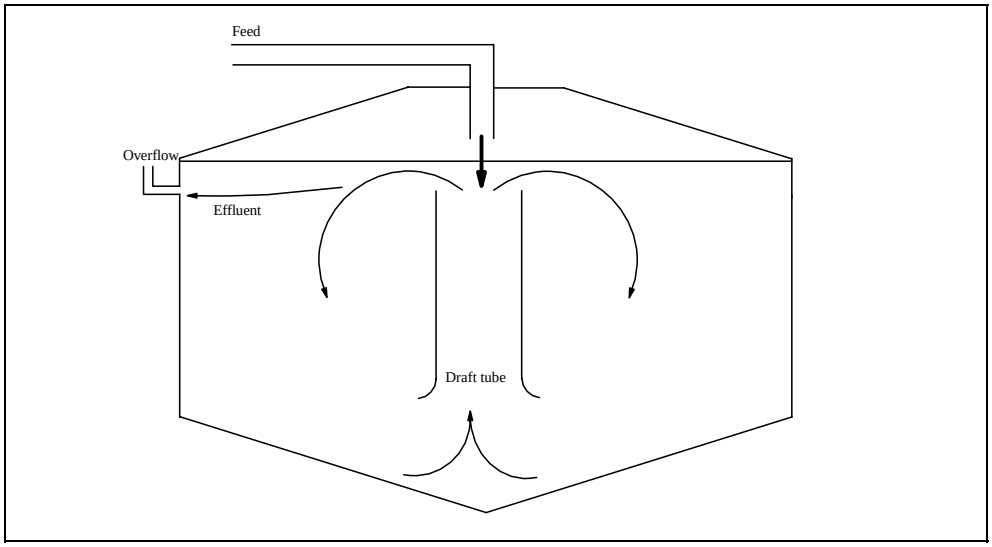


FIGURE 6.1 : Schematic diagram of the Umbilo digester feed and overflow streams.

From the data in **Appendix B**, the average loading to the digesters was calculated at 1.12 kg VS/m^3.d. The recommended loading rate for a high rate digester (with mixing and heating) is between 1.5 and 3.0 kg VS/m^3.d. Thus, the Umbilo digesters were under-loaded.

The USPW has a laboratory on site for analysis of samples taken from the plant. Under balanced conditions, the volatile acid concentration of the digesting sludge is usually in the range of 50 to 300 mg/l, as discussed in **Section 4.3**. The average VFA content of the Umbilo digester sludge was within this range (169 mg/l). The alkalinity (2 026 mg/l) of the Umbilo digester sludge also indicated that it was healthy. These values gave a volatile acids : total alkalinity ratio (Ripley ratio) of 0.08. A ratio < 0.3 indicates an efficient degradation process (Ross et al., 1992). The VFA to alkalinity ratio was plotted over a one year period from May 1996 to May 1997 (**Figure 6.2**). The plot shows that the ratio was relatively constant which suggested that the sludge was stable. The average is indicated by the solid line.

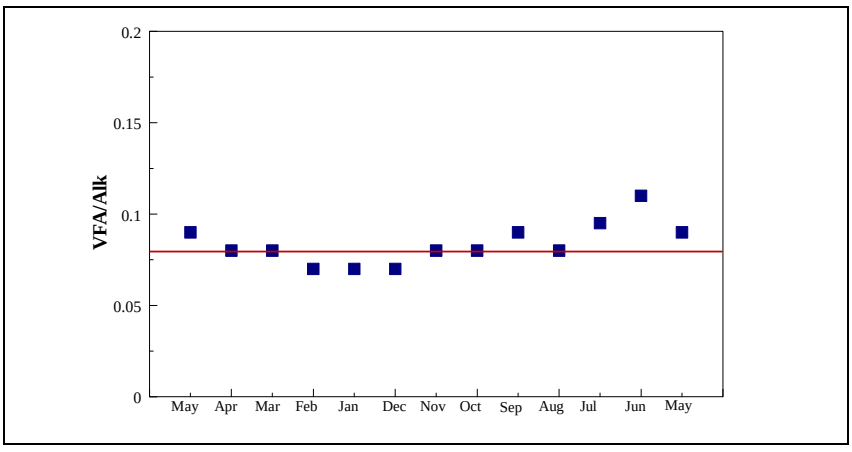


FIGURE 6.2 : Plot of the VFA to alkalinity ratio of the Umbilo Sewage Purification Works anaerobic digester sludge over a one year period.

The average pH of the Umbilo sludge was 7.5 (**Figure 6.3**) which indicated that the buffering capacity of the digesters could be improved. This pH still facilitates digestion. The plot shows that the sludge pH was relatively

constant over the one year period, which verified that the process was stable. The broken line indicates the optimal digestion pH of 7.

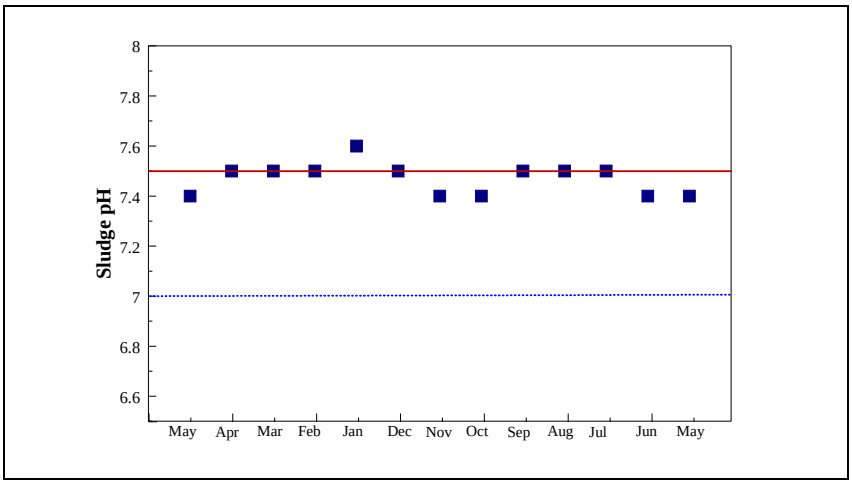


FIGURE 6.3 : Plot of the Umbilo digester sludge pH over a one year period.

The average COD reduction over the works was 71 %. The COD reduction was not calculated for the anaerobic digesters. The reduction in volatile solids within the digesters (72 % or 1 081.5 kg/d) provided an indication of the extent of organic degradation.

Effective anaerobic digestion occurs with the stoichiometric production of biogas. Based on the fact that 1 m^3 biogas is produced per kg volatile solids reduced (**Section 4.3**), the biogas production rate of the USPW anaerobic digesters was calculated to be 1 082 m^3 . The methane content of the biogas was approximately 65 % thus the methane production was 0.65 m^3/kg VS.

A mass balance was calculated for each digester (for the period May 1996 to May 1997) (**Table 6.1**). This provided an indication of the process efficiency.

TABLE 6.1 : Mass balance of the Umbilo anaerobic digesters.

Mass (kg/d)	**Feed sludge**	**Digested sludge**	**Biogas**
Volatile mass	1 505	424	-
Ash mass	450	228	-
Biogas	0	0	1 000
Total	1 955	652	1 000

The mass of biogas produced was calculated from the theoretical density of 1kg/m^3. The total mass in (feed sludge) was c. 15 % (m/m) greater than the total mass out (digested sludge and biogas). This error in the mass balance could be attributed to sampling or analytical inaccuracies as it is unlikely that 222 kg/d of solids built up in the digester. The poor balance could be due to the erratic feed flows to the digesters (**Section 6.6.2**). The periodic high flows could have been due to longer pumping times if the solids concentration of the feed sludge was low. A more accurate balance would be a total carbon balance across the digester, incorporating alkalinity and CO_2.

6.4.3 Mixing

Although mixing is only one factor which affects digester performance, it increases the overall rate of biological activity by promoting contact between the substrate and microorganisms. The degree of mixing of the primary digester is important to prevent dead pockets of sludge.

Mixing efficiency can be measured by a vertical traverse of the temperature or solids concentration in the digester or by tracer techniques (United States Environmental Protection Agency, 1987). A tracer test was performed on one of the Umbilo anaerobic digesters to evaluate the mixing efficiency and to identify any dead volume. These results are presented in **Section 6.6**.

Mixing of the Umbilo digesters is achieved by mechanical mixers. Each mixer is mounted above a draft tube to direct the flow within the digester (**Figure 6.4**). Each impeller is driven by an electric motor. The sludge is drawn into the bottom of the draft tube and discharged at the top. This ensures that the heavier sludge is mixed throughout the digester. If the motor is operated in the opposite direction, the light sludge and scum layer from the top of the digester is forced down the draft tube to the bottom of the digester. It is generally recommended that for adequate mixing the entire contents of the digester should be turned over at least once every 24 h. From the design specifications, the power of the motor running each mixer was 11 kW. The mixer speed was 960 rpm, with a duty of 250 l/s. The pump is operated continuously so there are 16 volumetric displacements of the digester contents per day.

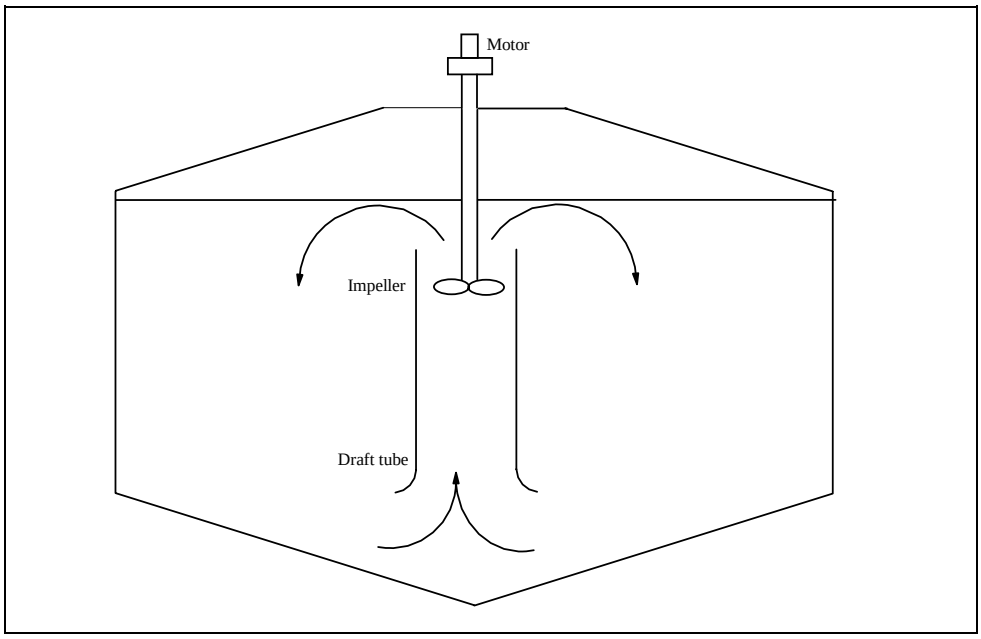


FIGURE 6.4 : Schematic diagram showing the mixing of the anaerobic digester contents at the Umbilo Sewage Purification Works.

Mixing of the Umbilo digesters was efficient as verified by the residence time distribution study (**Section 6.6**). A drawback of this mixing system is that impellers tend to wear from sludge abrasiveness and build-up of dirt and rags on the vanes. A decrease in the current of the motor is an indication that the impeller should be replaced.

6.4.4 Heating

The Umbilo digester sludge temperature is maintained at 36 ± 1 °C by a process of steam injection. A portion of the biogas, from the anaerobic digesters, is used to heat water in a tube boiler. The gas pressure of the boiler is regulated to 1 000 kPa. Steam from the boiler is injected ihrough 15 mm steam lances mounted on top of each digester. Temperature probes in the digesters are set at 36 ± 1 °C and the temperature of the digester sludge is maintained at this temperature by the control of the steam inlet valve on the steam manifold. When this temperature is reached the valve closes and the gas burner shuts down. The boiler pump has a gas firing rate of 89.9 m^3/h. The heating surface of the boiler is 11 148 m^2. The evaporation rate is 626 kg steam/h,a t 100 °C. Water is fed to the boiler from a 2 000 l tank.

A disadvantage of this system is that the steam causes the liquid to rise, resulting in a counter-current with the sludge recirculating through the draft tube (**Figure 6.5**). Injection of the steam may also be detrimental to the biomass in the vicinity of the point of injection. The process does, however, seem to be efficient to maintain a constant digester sludge temperature.

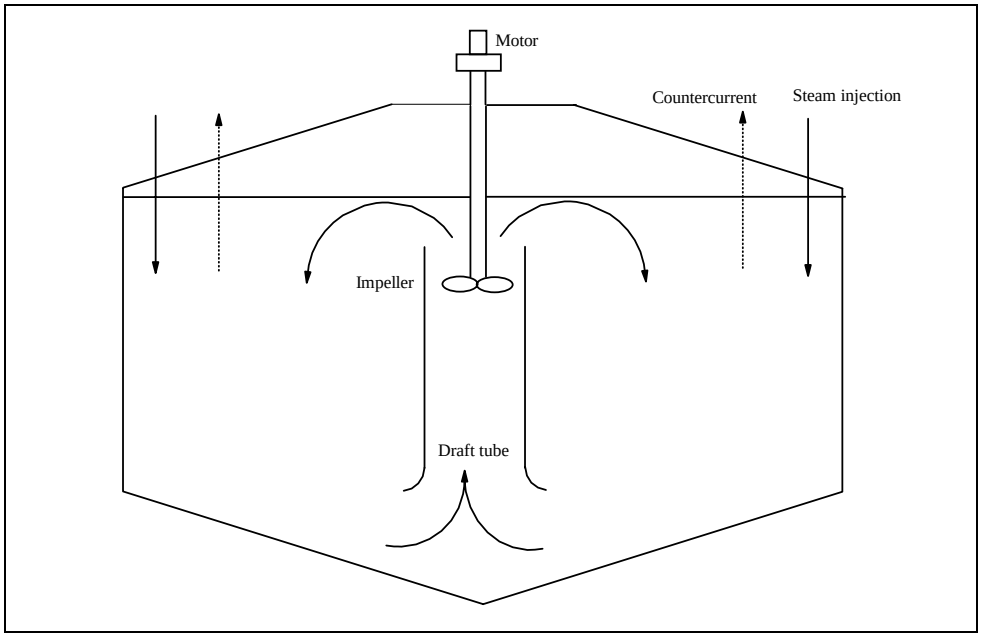


FIGURE 6.5 : Schematic diagram showing the mixing and heating flows in each digester.

6.4.5 Gas system

The digesters have fixed covers with a space for gas collection between the cover and the liquid surface of the digester contents. Each digester has a pressure relief valve mounted on top to relieve excess pressure and prevent damage to the digester cover. The vacuum relief valve functions in the opposite manner and allows air to enter the digester in the event of the sludge being withdrawn too rapidly.

The biogas produced in the digester is collected in the cone above the digester contents and then flows through the gas line. The gas pressure should be constant at all points in the gas system. The gas lines from all four digesters joins onto the main gas line. Gas leaving the digester is almost saturated with water vapour. As the gas cools, the water vapour condenses. The water trap functions to remove the water from the gas system and thereby prevents corrosion in the valves and regulators.

Flame traps are emergency devices which are installed in gas lines to prevent flames travelling back up the gas line and reaching the digester. The flame trap usually consists of a box filled with stone or a metal grid. If a flame develops in the gas line, the temperature of the flame is reduced below the ignition point as it passes through the trap and the flame is extinguished. Non-return valves are installed in the gas line to allow gas flow in one direction only, i.e. out of the digester. Pressure regulators are used when a lower pressure than the system operating pressure is required for a specific device such as the boiler. The gas system at the USPW is illustrated in **Figure 6.6**.

The Umbilo gas holder has a volume of 500 m^3. The upper half of the steel dome moves freely by means of guide rails attached to the concrete structure and rollers attached to the steel dome. The holder is filled with water and the gas is collected in the headspace above the water. This results in a build up of pressure which causes the dome to rise. There is a pressure relief valve on top of the dome for pressure control. Excess gas is flared to the atmosphere at the gas burner.

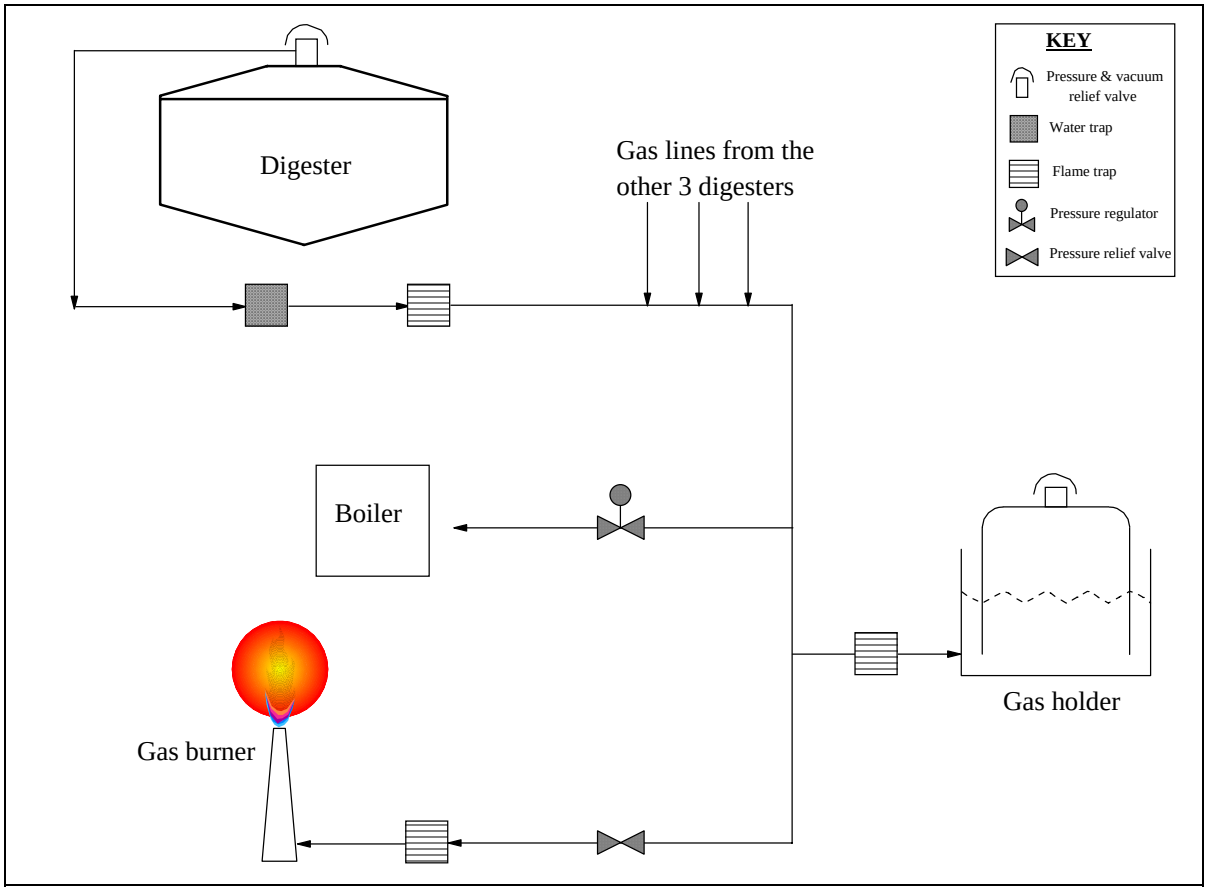


FIGURE 6.6 : Biogas system at the Umbilo Sewage Purification Works.

There is no gas flow meter at the USPW, thus the rate of gas production is not be measured. This should be rectified since the rate of gas production is an important process control indicator.

6.5 RESIDENCE TIME DISTRIBUTION TEST

A technique for determining the flow model of processes is the residence time distribution method. Danckwerts (1953) developed the residence time distribution concept to characterise the overall flow behaviour in a process.

The effluent stream from a continuous flow process is a mixture of fluid elements which have resided in the process for different lengths of time. The distribution of these residence times is an indicator of flow patterns within a process. Analysis of these data allows calculation of the actual hydraulic retention time in the digester, a parameter which is controlled by the extent of mixing (Tenney and Budzin, 1972).

6.5.1 Introduction

The flow patterns found in real processes usually lie between the two extremes of perfect mixing (complete mixing of the fluid) and plug flow (no mixing in the direction of flow). This is due to bypassing, channelling, dead space, dispersion and recycling (Barnett, 1995). In bypassing, some elements of the fluid bypass the entire process whereas in channelling some elements of fluid move through the process significantly faster than others. Dead space refers to a region in the process with no flow. This does not often occur in real processes as there is usually some contact between the dead space and the bulk fluid. As this contact is extremely slow, it is usually assumed that there is no flow. Recycling occurs when fluid is recirculated to the process inlet or to another region of the process (Rabbitts, 1982).

The residence time distribution (RTD) is determined experimentally by injecting an inert chemical, called a tracer, into the reactor at some time $t = 0$ and then measuring the tracer concentration, C, in the effluent stream as a function of time (Nachaiyasit, 1995). Introducing tracer into the inlet stream of a process and measuring the concentration-time relationship of the tracer in the effluent stream provides an indication of the distribution of the residence times of the tracer (Barnett, 1995). If the tracer has the same flow attributes as the fluid, this residence time distribution can be said to approximate to the residence time distribution of the fluid. In general, tracer tests cannot be used to determine the residence time distributions of processes with open boundaries, that is, systems which allow material which has left the system to re-enter.

In an ideal plug-flow reactor, all the material leaving the reactor has been inside it for exactly the same time (Fogler, 1992). Similarly, in an ideal batch reactor, all the material within the reactor has been inside it for an identical length of time. The time the material has spent in the reactor is called the *residence time*. In all other reactor types, the various molecules in the feed spend different times inside the reactor, that is, there is a distribution of residence times of the material within the reactor.

6.5.2 Mixing efficiencies in anaerobic digesters

Biomass growth and retention, together with gas production and turbulence provided by rising gas bubbles or effluent recirculation, strongly affect the residence time distributions in reactors (Harper and Suidan, 1991). The influences of biomass growth and gas production are directly linked to substrate loadings and other operational strategies such as flushing and wasting of accumulated biomass. The importance of mixing in achieving efficient substrate conversion has been noted by several researchers (Monteith and Stephenson, 1981; Smith et al., 1996) although the optimum mixing pattern is a subject of debate. Under plug flow conditions, incoming substrate remains in the reactor for one retention time, allowing maximum time for conversion. However, high substrate concentrations resulting from lack of dispersion may inhibit bacterial activity. An intermediate degree of mixing appears to be optimal for substrate conversion (Smith et al., 1996).

In a digester, the active decomposition of organic material occurs in the volume that is mixed. Conversely, the zones that are not mixed remain stagnant and are, essentially, lost to the digestion process (Tenney and Budzin, 1972). The need for efficient mixing in anaerobic digesters is essential to transfer substrate and heat to the microorganisms, to maintain uniformity and to prevent solids deposition and scum formation (Monteith and Stephenson, 1981). If mixing is inadequate, the efficiency of digestion and the stability of the product sludge

may be adversely affected. If a tracer is introduced into the digester, it will disperse throughout the actively mixing zone and the concentration of the tracer which will be observed, with time, in the effluent, will reflect the hydraulic conditions occurring only in the mixed zones. This analysis will, thus, determine the actual digester volume available for digestion, thus accounting for poor operational performance (Tenney and Budzin, 1972).

6.5.3 Tracers

A tracer is used to label substances or objects to distinguish them and to follow their movement, changes of concentration and distribution between phases. The tracer should allow sensitive detection and should not significantly change the properties of the fluid being traced. The tracer should have approximately the same density and viscosity of the fluid of interest since it is important that it flows with a residence time distribution identical to that of the fluid of interest. The tracer must not chemically react or adsorb on the medium through which it is flowing (Fogler, 1992). The three main types of tracer used are radioactive tracers, dyes and electrolytes.

Wastewater treatment processes are aqueous flow processes in which dissolved or suspended solids are removed. The most common electrolytes for tracing water processes are lithium chloride (LiCl) and sodium chloride (NaCl). Sodium is generally present in higher concentrations in water treatment processes than lithium. The background concentration is often variable (Barnett, 1995). Methanogens have the ability to adapt to high concentrations of NaCl (Jackson-Moss, Duncan and Cooper, 1989). Lithium chloride is relatively inexpensive and lithium is detectable in µg/l concentrations by flame photometric methods. Lithium is stable in solutions and is not lost by deposition.

Anderson, Campos, Chernicharo and Smith (1991) investigated the potential inhibitory effects of the lithium ion on anaerobic sludge. It was found that with Li concentrations > 2.0 g/l, there was a degree of inhibition, with a sharp drop in gas production and methane content, followed by a long period of reactor upset with very poor performance.

The two most used methods of injection are pulse input and step input. In a pulse input, an amount of tracer N_o is suddenly injected into the feed stream in as short a time as possible. A material balance, for a pulse addition of tracer, compares the actual amount of tracer added to the amount that leaves the process:

$$N_o = A \,.\, q \qquad [6.1\ ]$$

where: A = area under the response curve

q = the volumetric flow rate of the effluent stream

The area under the response, A, is found from:

$$A = \int_0^\infty C(t)dt \qquad [6.2\ ]$$

In a step input, a constant rate of tracer addition to the feed is initiated at time $t = 0$. Before this time, no tracer is added to the feed. The concentration of the tracer in the feed is kept at this level until the concentration in the effluent in indistinguishable from that in the feed. The test is then discontinued.

6.5.4 Modelling

For first order reactions, the RTD curve can be used directly to predict conversion in the reactor. For more complex reaction kinetics, it is necessary to first set up a model for the flow patterns in the reactor before an estimate of conversion can be made. The next step is, therefore, to fit simple non-ideal flow models to the RTD curves. Selection of a flow model is based on the physical configuration of the reactor, visual observations of the flow patterns where possible, and the shape of the RTD curve (Rabbitts, 1982). The model is fitted to the RTD curve by comparing the theoretical model with the experimental RTD curve. The parameters of the theoretical flow model are varied until the closest fit between the theoretical and experimental curves is achieved.

The two simplest models which describe deviation from ideal flow are the dispersion model and the tanks-in-series model (Levenspiel, 1961). In the **dispersion model** the dispersion number ($D/\mu L$) is the inverse of the dimensionless Peclet number, Pe:

$$Pe = \frac{vL}{D} \qquad [6.3]$$

where D = longitudinal dispersion coefficient (m^2/s)

v = fluid velocity (m/s)

L = fluid path length (m)

Pe is used to characterise the spread of the concentration-time response around the mean residence time caused by longitudinal mixing. When the dispersion number is small (< 0.002) the flow within the reactor approximates to plug flow (Nachaiyasit, 1995).

The **tanks-in-series model** assumes that the flow system can be characterised by a number, n, of perfectly-mixed tanks in series. Ideal flow occurs when n=1. The greater the number of tanks in series needed to approximate the flow pattern, the closer the system is to plug flow.

A computer program, IMPULSE, was written by Baddock, Barnett, Brouckeart and Buckley (1993) which allows easy modelling of systems using curves obtained from tracer response tests. The user assumes a flow model for the system. The program determines the theoretical response for the model and optimises a chosen set of parameters of the model to fit the experimental curve.

6.6 UMBILO RESIDENCE TIME DISTRIBUTION TEST

Knowledge of the residence time distribution of a reactor is necessary to describe non-ideal conversion patterns and can lead to the diagnosis of common operational problems such as short-circuiting or dead volumes (Battaglia, Fox and Pohland, 1993). To determine the residence time and mixing patterns of the digester of

interest, a tracer test was performed on Digester 2 at the USPW to determine the residence time distribution (RTD). Lithium chloride was chosen as the tracer.

6.6.1 Materials and methods

The 10 kg of LiCl (1.65 kg as Li) were dissolved in tap water by a person not involved in the sampling to avoid contamination of the samples during the test. This quantity should give a concentration of approximately 1.2 mg/l Li in the design digester volume (1.34 Ml). Tests were carried out to determine the background concentration of lithium in the feed sludge and in the digester sludge prior to dosing. Dosing of the tracer to the digester took ca. 10 min.

When raw sludge was pumped into the digester, an equal volume of digested sludge automatically overflowed. This positive displacement of sludge meant that samples could only be taken when there was an overflow, i.e., when the digesters were being fed. A sample was taken 3 min after the tracer addition and every 5 min thereafter for the first hour. The interval between the samples was gradually increased until only one test sample was collected per day. The test ran for a total of 91 d, from 26 May 1997 to 28 August 1997. Samples were filtered (Whatman No. 4) and the filtrate analysed for lithium using an atomic adsorption (AA) spectrophotometer (GBC 906AA). Samples of the feed and digester sludge, prior to dosing, were used as blanks. The AA conditions were set as follows:

Instrument mode : Flame emission

Wavelength : 670.8 nm

Slit width : 0.5 nm

Flame : air-acetylene

The AA was calibrated with standards of Li of 0.1, 1.0 and 10 mg Li/l.

A simulation was performed using the modelling program IMPULSE (Baddock et al., 1992). Details of the concentration of lithium in the overflow at the various feed times were entered. It was assumed that the digester was operating as an ideal CSTR and that all lithium dosed into the digester would be recovered. The volume of the digester and the time during which the LiCl was added were entered as the constant inputs. The initial lithium concentration and the flow rate at the time of addition were entered as regressable parameters. From these data, a curve predicting the lithium output was obtained. The experimental data were entered and the output, or model, curve was then regressed against the reference curve.

6.6.2 Results and discussion

Previous work showed that lithium did not adsorb onto sludge particles and was not assimilated by the microorganisms as a nutrient (Grobicki, 1989). This was verified with the Umbilo digester sludge (Barclay, 1996).

Tenney and Budzin (1972) found that ca. 63 % of the tracer was removed in the period equal to one hydraulic retention time, 86 % in two and 95 % in three. Therefore, an experimental analysis of three times the hydraulic retention time is generally sufficient to accurately determine the actual hydraulic retention time of an anaerobic

digester. The tracer test ran for a period of 91 d, when all of the tracer was recovered, which was approximately three times the nominal retention time of 22 d.

The background levels of lithium, in the digester sludge, were measured and found to be ca. 0.006 mg/l. The raw data were corrected for this and entered into IMPULSE as the experimental data.

The results from the experimental analysis, referred to as the experimental data, are presented in **Figure 6.7**.

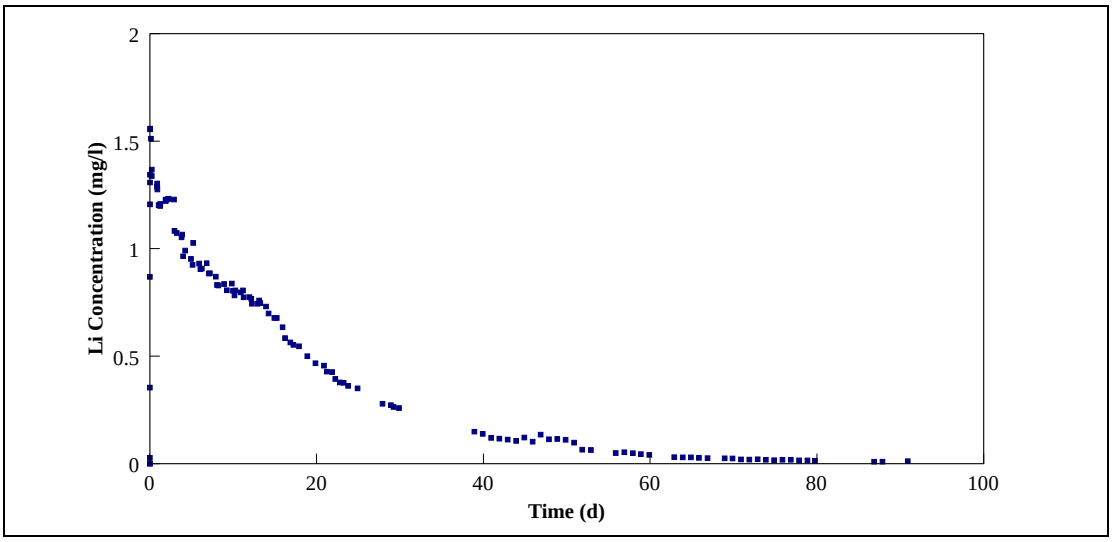


FIGURE 6.7 : Diagram of the experimental data for the residence time distribution study

The data showed an instantaneous lithium concentration peak which indicated perfect mixing conditions. This initial peak (ca. 1.6 mg/l) was greater than the concentration calculated for the design digester volume (1.2 mg/l) (**Section 6.6.1**) which indicated the presence of a sludge bypass. An exponential decay, indicative of a mixed flow reactor (CSTR), then ensued. A second concentration peak was observed after ca. 2d (**Figure 6.8**). This could be associated with the signal fluctuation around the observed trend curve, however, since the peak concentration approximated the calculated concentration for the design digester volume (1.2 mg/l), the peak was associated with the digester volume.

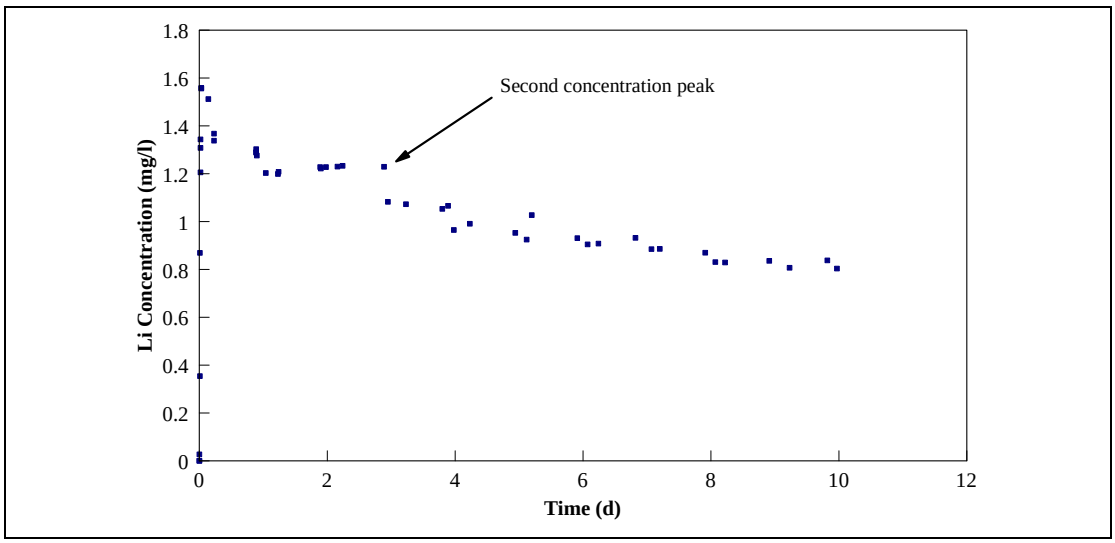


FIGURE 6.8 : Indication of the second lithium peak which was associated with the anaerobic digester volume.

The second lithium concentration peak was ca. 1.2 mg/l which was the concentration calculated from the design digester volume (1 340 m^3) which suggested that the entire design volume was active, i.e. there was negligible dead volume.

Based on this assumption, the design digester volume (1 340 m^3) was entered into IMPULSE as a constant input. The digester was modelled as a tanks-in-series CSTR (**Figure 6.9**), with a variable number of tanks which would account for the apparent sludge bypass. The *input* lithium concentration was calculated such that the area below the spike curve equalled the initial amount of lithium dosed, over one time step (1 d) (**Appendix G**). The initial concentration was inputted as a regressable parameter.

The flowrates (**Appendix G**) were calculated from the hour meter readings on the digester sludge pumps and the pump ratings. The pump rating was determined as the time taken to pump a known volume of sludge from the sump to the distribution box. It was assumed that the feed was equally distributed to all 4 digesters. The flowrates were erratic, thus the accuracy of the measurement was uncertain. The flows were, therefore inputted as regressable parameters.

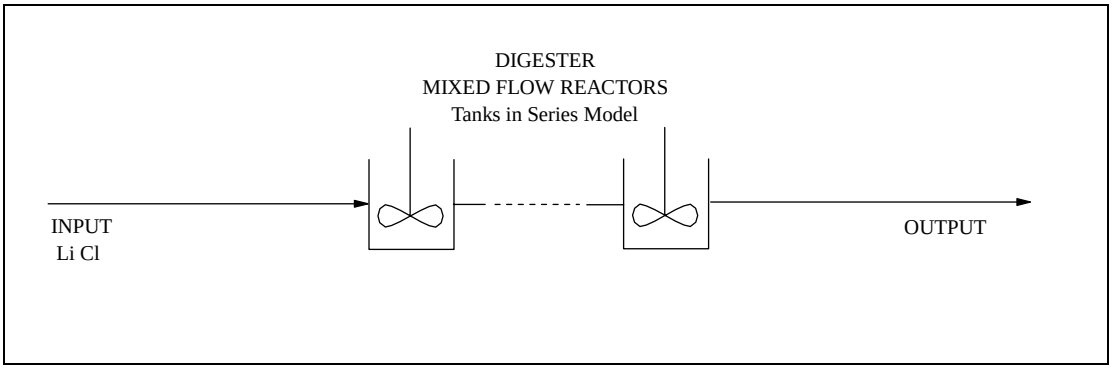


FIGURE 6.9 : Schematic diagram of the IMPULSE model for the initial evaluation of the experimental data.

This initial IMPULSE evaluation provided an estimate of the digestion conditions. Since the digester volume was fixed, the number of tanks in series, flows and salt concentration were varied to fit the experimental data. IMPULSE calculated the number of tanks-in-series as 0.985 which suggested that 0.015 of the of the flow bypassed the digester. From this it was deduced that the sludge bypass was ca. 1.5 % of the digester flow.

The input flow was scaled up by ca. 34 % which suggested that the flows had been under-estimated. The input lithium concentration was not scaled significantly which indicated that the inputted concentration was accurate.

The information obtained from this initial assessment was used to model the experimental data. The model (**Figure 6.10**) assumed that the digester volume was constant (1 340 m^3) and that it was operating as an ideal CSTR since the initial evaluation had calculated $n \approx 1$. The sludge bypass was initially modelled as both a CSTR and a plug flow reactor (PFR) but neither were found to be representative of the experimental results. It was then modelled without any dead time or mixing. The split ratio to the bypass was variable and the resolution time was set at 0.1 d. The input flows were variable.

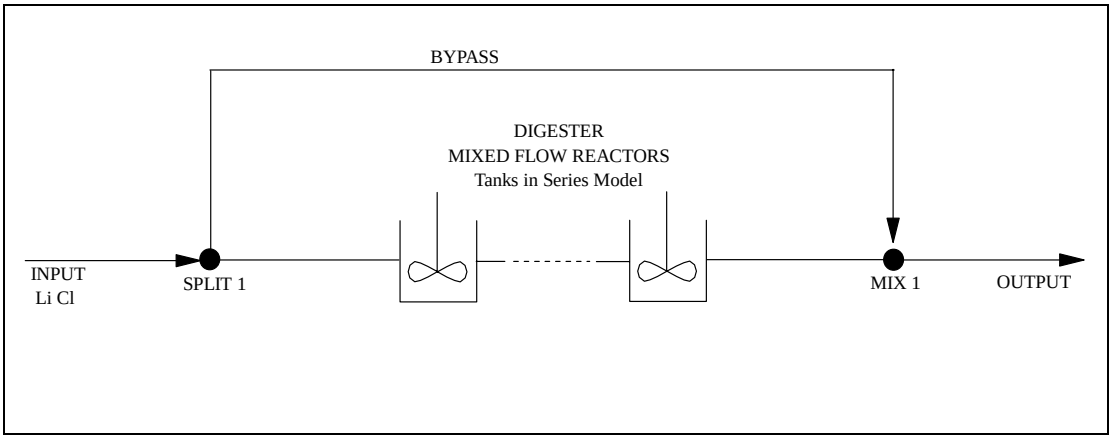


FIGURE 6.10 : Schematic diagram of the IMPULSE model chosen to fit the experimental data.

The average residence time is the calculated residence time of the liquid component in the reactor. The average residence time was calculated from the following equation:

$$\tau = \frac{\sum t_i c_i \Delta t_i}{\sum c_i \Delta t_i} \qquad [6.4]$$

where: t = time (d)

c_i = concentration of Li at time t_i

τ = average residence time

The residence time distribution function C(T) is the normalised distribution function obtained from the average residence time results. The normalised RTD curve (**Figure 6.11**) shows the fraction of input Li present at each time step. That is, the area below the curve between any time t and $t + \Delta t$ is the fraction of the tracer at the outlet stream with age between $t + \Delta t$ (Battaglia et al., 1993). The reduced time is:

$$T_i = \frac{t_i}{\tau} \qquad [6.5]$$

The residence time distribution function was then calculated in reduced time:

$$C(T) = \tau \frac{c_i}{\sum c_j \Delta t_j} \qquad [6.6]$$

The normalised distribution function, C(T) is a dimensionless plot of the residence time distribution. Based on the set parameters, the following results were obtained from the IMPULSE model fit:

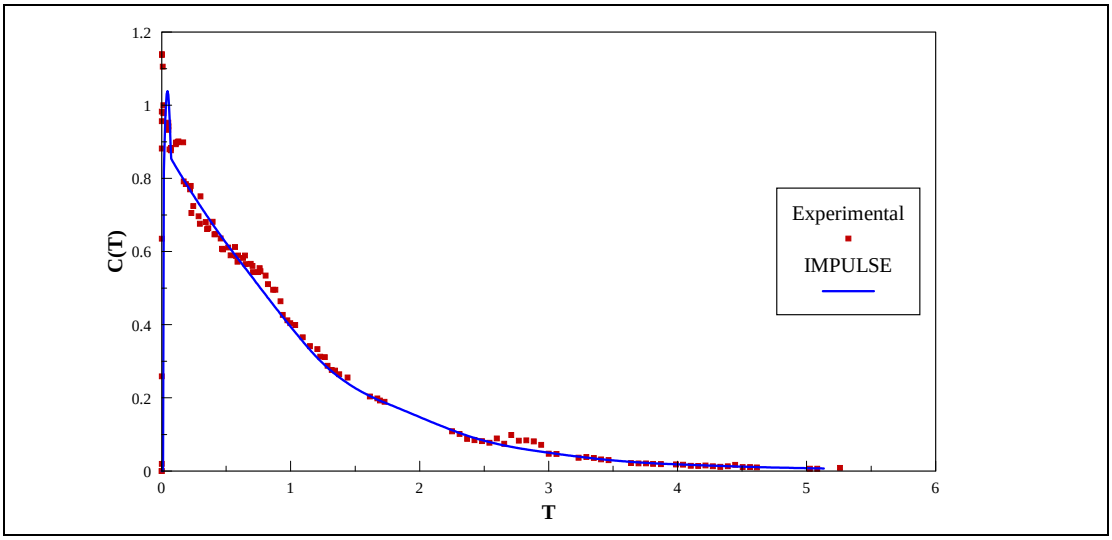


FIGURE 6.11 : Diagram of the normalised residence time distribution curve for the experimental data and the IMPULSE model.

IMPULSE produced a close fit to the experimental data. In the model, the digester volume was fixed which forced the flows and the bypass split ratio to vary, to fit the experimental data. The IMPULSE output (**Appendix G**) indicated that the split to the sludge bypass was ca. 1.94 % of the flow to the digester. This value was close to the initial estimation thus verifying the accuracy of the model.

Assuming steady state in the digester, the split ratio to the bypass is shown:

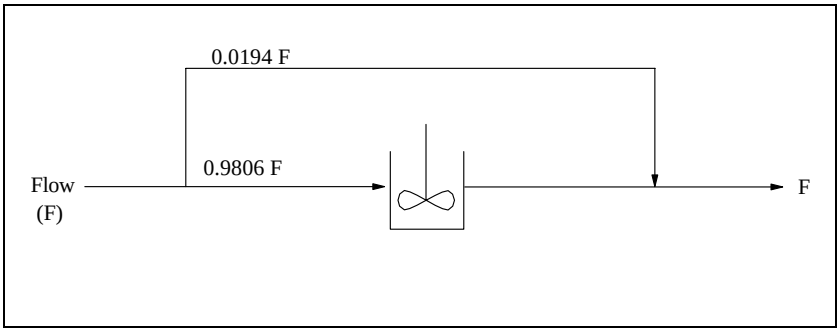


FIGURE 6.12 : Output split ratio to the digester bypass.

Although this volumetric flow rate was small, it was not insignificant and effectively meant that undegraded substrate was leaving the digester. This could be detrimental if high-strength effluents were added to the feed. Based on the digester configuration, the bypass stream is represented in **Figure 6.13**.

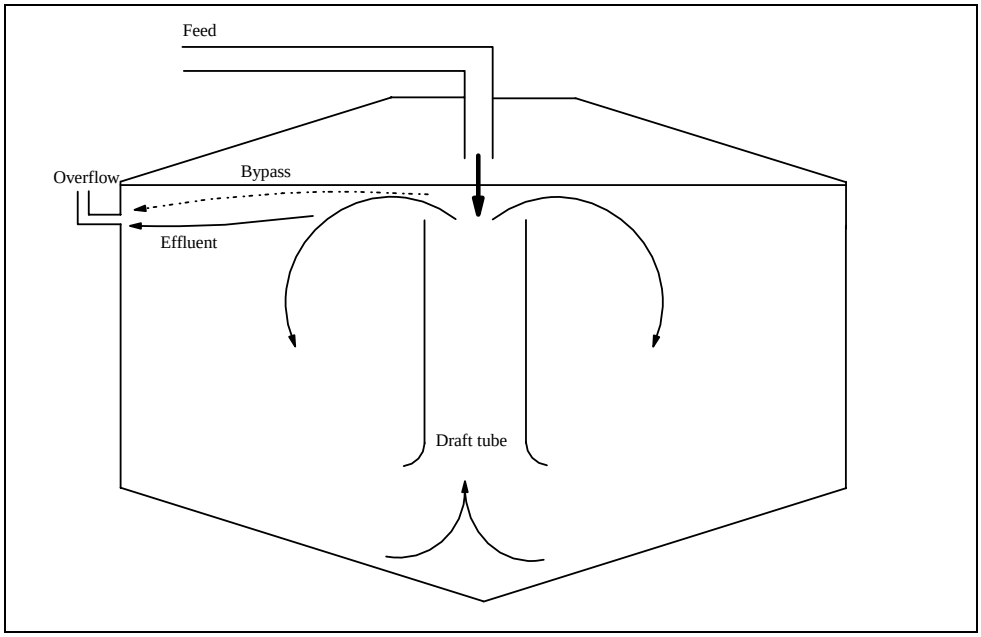


FIGURE 6.13 : Schematic diagram of the Umbilo anaerobic digesters indicating the sludge bypass.

The bypass could be overcome by changing the position of the feed inlet. If the feed was added at the bottom of the digester, it would be drawn into the draft tube and the bypass would be alleviated. Another option would be to uncouple digester sludge withdrawal and raw sludge feed; the feed would be added after sludge withdrawal. The flow through the draft tube could also be reversed.

In the model, the digester volume was fixed based on the assumption that the entire volume was being utilised. If the output lithium concentration had been higher than expected, it would have suggested reduced digester volume since the tracer would have been less diluted. A reduction in volume of the digester would have been indicative of dead volume which is volume where there is no, or little, active mixing. In the active volume, the solids are suspended, by the mixing action, thus facilitating contact between the substrate and the microorganisms. In the dead volume, there is no active movement since these regions are, essentially, stagnant and do not contribute to substrate degradation (Barona and Prengle, 1973). These results indicate that, apart from the initial sludge bypass, the digester mixing, i.e. by draft tube, was efficient and there were no stagnant areas within the digester.

This model assumed that the digester was operating as an ideal CSTR. The real average residence time of the reactor was calculated from the experimental data, by a numerical integration method, as **17.29 d.** The average residence time, as calculated from the IMPULSE model, can be used to assess the accuracy of the model. The average residence time, as calculated from the IMPULSE output, was **17.59 d** which indicated that the model was a close representation of the system. The theoretical residence time of a digester can be estimated by dividing the total digester volume by the total flow rate into the reactor (Spalding, 1958; Tenney and Budzin, 1972; Bell, Barclay, Brouckeart, Buckley and Carliell, 1997). The IMPULSE output indicated that the flows were under estimated by 34.6 %. Thus, correction of the measured flows by this scaling factor, resulted in an estimated residence time of ca. **20 d**. This was within the recommended range of 15 to 25 d for a high-rate reactor (Ross et al., 1992), thus verifying the accuracy of the model and the operation of the reactor.

The flows to the digesters were erratic (**Figure 6.14**) which accounted for the oscillations in the experimental curve. The average flow (54 213 l/d) is indicated by the solid line across the graph. These changes in flowrate would have affected the observed lithium concentrations since a decrease in the flowrate would result in the lithium being less diluted and a concomitant increased output concentration. The oscillating lithium concentrations and low theoretical average residence times were attributed to these erratic flows.

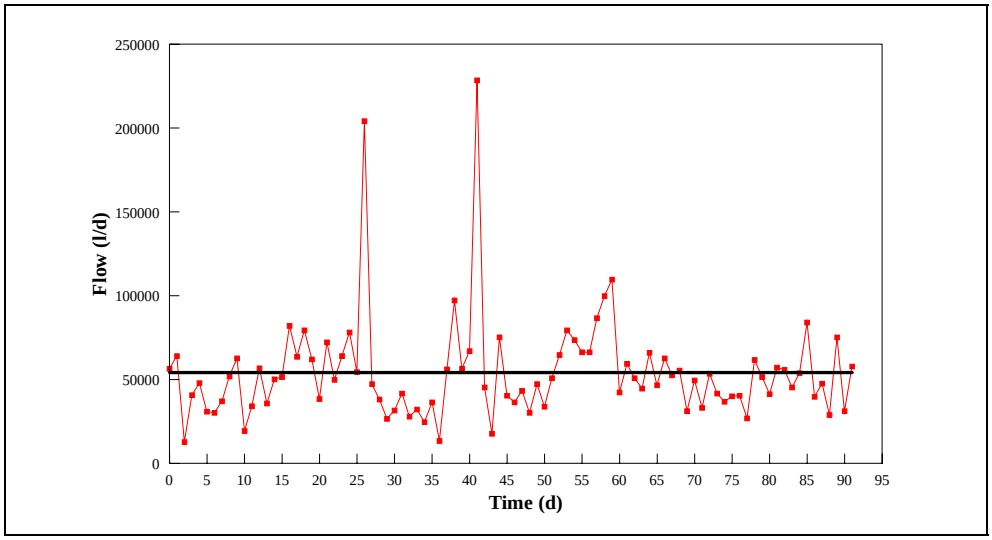


FIGURE 6.14 : Flow to the anaerobic digester distribution box during the RTD test period.

The rainfall data, for the test period, were investigated to assess the impacts of the daily rainfall patterns, at the sewage works, on the flow data (**Appendix G**). This comparison is illustrated in **Figure 6.15**.

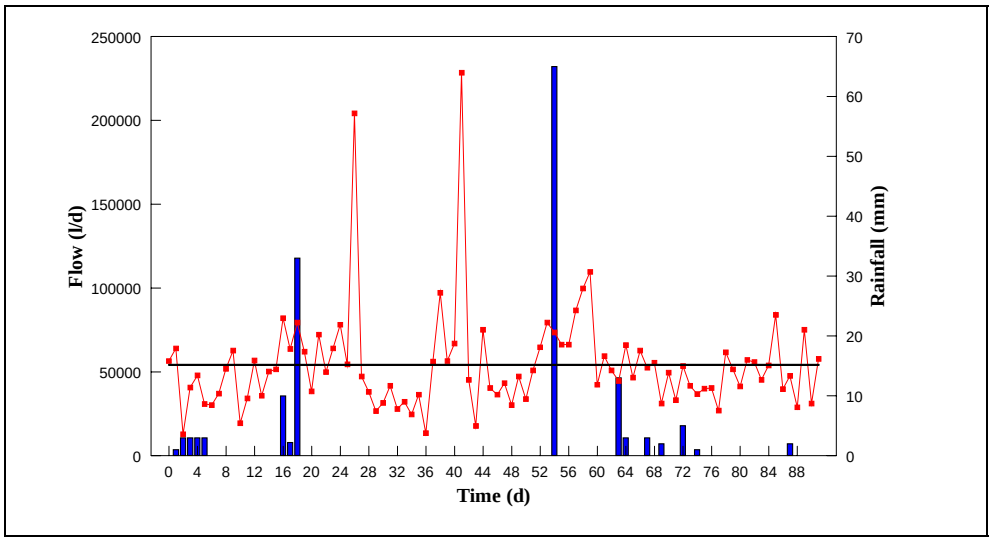


FIGURE 6.15 : Comparison of the digester flowrates and the measured daily rainfall during the RTD test period.

This figure shows that there was no definite correlation between the rainfall and the flowrates. From this, it can be concluded that the flowrates should be controlled for more efficient operation of the digesters and better assessment of the process efficiency.

From a mass balance of lithium (**Appendix G**), the percentage of recovered lithium was determined. For each time step, the area under the curve (**Figure 6.7**) was calculated. These were summed to obtain the total amount of lithium recovered which was **1.5407 kg**, compared to the dosed 1.65 kg. This equated to **93.4 %** recovery of the lithium. The calculation for lithium recovery was based on flowrates and measured concentrations at the outlet. The flowrates were corrected by a factor of 1.34 as calculated from the IMPULSE output, thus the efficient lithium recovery also provided verification of the model.

From these results, if the IMPULSE model was correct and the flows were under-estimated by 34.6 % then the digester was operating at its full capacity, i.e. there was no dead volume and the average residence time was 17.29 d. If, however, the flow data were accurate, then the system would be modelled with constant flows and a variable digester volume. To assess this scenario the model parameters were altered to set the flows constant and the digester volume variable. This model showed that the digester volume would decrease by ca. 27 % to fit the experimental data. This would suggest that the digester had a dead volume of 27 %. The lithium recovery for the uncorrected flows was, however, only 69 % compared to 93 % obtained for the corrected flows. This suggested that the IMPULSE model was correct and that the measured flows were under-estimated.

6.6.3 Conclusions

The residence time distribution test allowed for the following conclusions to be drawn regarding the mixing efficiency and flow patterns within the digester:

1. The entire digester volume was utilised indicating the absence of dead volume. The mixing process was efficient.

2. There was a sludge bypass of 1.94 % of the flow thus a more efficient mixing mechanism should be adopted.

3. The measured flows were under-estimated by 34.6 %.

4. Accurate flow details should be kept.

Chapter 7

Evaluation of a Textile Size Effluent

The focus of this chapter is the assessment of the anaerobic treatment of a textile size effluent, by application of the strategy described in **Chapter 1**. The choice of effluent was justified by its high COD content, its problematic disposal and the location of the mill, which was in the vicinity of available digester capacity. The textile sizing process is described in **Section 7.2** with a description of the composition of the textile size solution. **Section 7.3** reports on the initial screening of the biodegradability of the textile size effluent, in the 2 l batch tests. The tests were repeated in serum bottles (**Section 7.4**) to provide a more accurate assessment of the anaerobic degradability and potential toxicity. These results provided an indication of the concentration of each component that could be treated effectively. **Section 7.5** outlines the effect of toxic compounds on the anaerobic biomass and describes the ability of microorganisms to acclimate to a particular substrate. This was illustrated by enrichments used to acclimate sludge to inhibitory components of the size solution. The acclimated sludge was able to degrade the components more efficiently. The topic of scale-up is discussed in **Section 7.6**.

7.1 INTRODUCTION

Increasingly strict environmental legislation has led to textile finishing industries being labelled as high priority industries with respect to pollution (Carliell, 1993). Size effluents represent the main component (ca. 60 %) of the organic load of the effluents from textile finishing mills (Schluter, 1991). In the sizing operation, the individual yarns are coated with a protective film of size in order to resist the abrasive effects of the weaving loom; the size strengthens the yarn (Water Research Commission, 1983). The quality of the sizing treatment influences not only the efficiency of the weaving process but also the quality of the cloth, both in the loom state and after finishing (Smith, 1964). The traditional sizing agent was starch thus the effluent originating from the size kitchen and size slashers, in the mill, was a high-strength organic effluent. When mixed with the remainder of the mill effluent, it increased the COD of the final trade effluent thereby introducing disposal problems.

The described strategy (**Figure 1.1**) was applied to determine the feasibility of the anaerobic digestion of the textile size effluent produced by a mill in New Germany. The mill was located within 10 km of the Umbilo Sewage Purification Works and produced a total of 110 m^3 of effluent per day; of which 10 m^3 was size effluent. The size effluent was segregated, at the mill. However, for disposal, all of the effluent was mixed and the total effluent was tankered 40 km for marine discharge, at the Southern Wastewater Treatment Works pipeline. The segregation of the size effluent allowed for the investigation of its degradability and would facilitate the concentration of the high-strength effluent on site. Depending on the colour component of the remainder of the effluent, it could then be discharged directly to sewer.

7.2 TEXTILE SIZE

Starch has been the traditional sizing material used in textile manufacturing, however, in recent years the trend has been towards synthetic sizes because of the increased demand for synthetic fibres. To overcome the

deficiencies of single component sizes, size blends are commonly used (Water Research Commission, 1983). Some of the components of size blends are outlined below.

Starch : starches are flours without the glutens (Seydel, 1972; Water Research Commission, 1983). Starch granules consist of α- and β-amylose; the former is insoluble in water. The β-amylose is contained within a membrane of the α-amylose. On heating the water permeates through the outer membrane causing the β-amylose to dissolve and swell. The granules expand and the viscosity increases (Water Research Commission, 1983). The qualities which give starch its usefulness as a sizing agent are its ability to form a pliable film and its ability to adhere and provide a good coating without excess penetration into the yarn (Seydel, 1972). Since the prime function of sizing is to produce weavability in the warp, the essential part of the size formula is the film-forming ingredient. Modified starches are formed by substituting acetyl or hydroxy-ethyl groups for hydrogen or hydroxide groups on the starch molecule (Water Research Commission, 1983). An example is **oxidised modified starch (OMS)**, which is prepared by treating starch in an alkaline, aqueous medium with hypochlorite (Kirk-Othmer, 1982). The oxidising action introduces zig-zag discontinuities into the linear molecules, which decreases the gelling characteristic of starch (Seydel, 1972).

Carboxymethyl cellulose (CMC) : is generally a sodium salt and is formed by treating cellulose with sodium hydroxide and mono-chloroacetic acid (Water Research Commission, 1983). CMC tends to absorb and hold moisture and its value in textiles hinges on its water-binding ability as this reduces the need for high humidity conditions in the weaving shed (Seydel, 1972).

Polyvinyl alcohol (PVA) : is a synthetic polymer resin and is produced by acid or alkaline hydrolysis of polyvinyl acetate (Water Research Commission, 1983). The viscosity and hydrolysis of PVA are controlled in the manufacturing process and are important in determining end-product sizing characteristics (Seydel, 1972). PVA is an excellent textile warp size because of its strength, adhesion, flexibility and film-forming properties (Kirk-Othmer, 1982). PVA can be recovered from wash-waters by ultrafiltration (Groves et al., 1978).

Acrylate : polymeric methyl acrylate is used principally as the soldium salt. It is hydroscopic and cannot be used under high humidity conditions (Sharp, 1990).

Waxes : the term wax includes almost any lubricant of a solid nature. The chemical composition varies widely, but is generally based on a long-chain hydrocarbon molecule or a derivative, such as fatty acid or fatty alcohol (Seydel, 1972).

Plystran : is a commercial blend of a number of size components, made up of ca. 58 % (w/v) modified potato starch, 40 % (w/v) PVA and 2 % (w/v) wax. This component is often difficult to dissolve because of the wax content.

Biocide: the purpose of which is to prevent bacterial or algal growth in the highly organic size solutions. Microbial growth could impair the efficacy of the yarn treatment and could also stain the material. It was expected that the biocide would prove problematic during the microbial treatment of the effluent. The disinfectant added to the investigated size was a water-soluble Dodigen 2451 (Hoechst), which was composed of alkyl dimethylbenzyl ammonium chloride.

For a size formula to approach perfection it should have several basic characteristics which will serve to eliminate warp breaks during weaving (Seydel, 1972). These include the ability to increase the tensile strength

of the yarn, adhere to the fibre structure and protect the warp yarn, and provide flexibility to the yarn as it must withstand repeated and extensive bending during the weaving operation.

The COD of the size effluent, sampled at the New Germany Frametex mill, was measured at 112 000 mg/l.

7.3 2l BATCH TESTS

Laboratory-scale batch tests were made to obtain a quantitative measure of the biodegradability of the textile size solution.

7.3.1 Materials and methods

The experiments were made with anaerobic digester sludge collected from the Umbilo Sewage Purification Works. Characteristics of the sludge are given in **Table 7.1**.

TABLE 7.1 : Properties of the Umbilo primary digester sludge.

Parameter	
pH	7.5
Total solids (%)	3.6
Temperature (^oC)	36
Volatile fatty acids (mg/l)	169
Alkalinity ($CaCO_3$) (mg/l)	2 026

The biodegradability of each component of the textile size solution was investigated. The solution was synthesised in the laboratory, according to the mass of each component utilised by the mill (**Table 7.2**). A synthetic effluent was chosen, over a real effluent, so that components were concentrated and not diluted by wash-waters. It also avoided variability in the composition which facilitated accuracy in the calculations.

Table 7.2 : Composition of the synthetic size effluent.

Component	Formula	Measured COD (mg/l)	Mass added (g/l)	g COD/g	Thoeretical COD/g
Polyvinyl alcohol	$(C_2H_4O)_n$	53 700	30.7	1.70	1.79
Starch	$(C_6H_{10}O_5)_n$	90 526	23.9	3.79	1.19
Plystran	$(C_8H_{14}O_6)_n$	19 200	16.1	1.19	1.32
Carboxymethyl cellulose	$(NaC_7H_{13}O_5)_n$	15 400	13.6	1.13	1.24
Oxidised modified starch	$(C_6H_{11}O_6Cl)_n$	4 900	2.9	1.69	0.86
Acrylic	$(NaC_3H_3O_2)_n$	1 900	0.73	2.60	0.94
Biocide	$C_8H_{12}ONCl$	13 300	0.05	2.66	1.94

The 2 l flasks were set up according to the conditions described in **Appendix C**. There was one control and three experimental flasks. The control contained only anaerobic sludge and nutrient medium. The purpose of the control was to determine the amount of gas produced due to the degradation of residual organic molecules in the sludge. Two of the experimental flasks contained the normal size solution concentration and 1.5 times this concentration, respectively. The third flask contained the 24 g/l starch solution. Each flask had a working volume of 1 600 m/and a headspace of 400 m/. The compositions are outlined below:

Table 7.3 : Sample compositions for the 2 l batch tests on the synthetic size solution.

Sample	Inoculum (ml)	Nutrient medium (ml)	Substrate (ml)	dH_2O (ml)	Organic load (g COD/1 600 ml)
Control	480	1 120	0	0	2.01
Normal	480	480	15	625	3.67
High	480	480	15	625	4.71
Starch	480	480	15	625	2.95

The flasks were overgassed with OFN then incubated in a constant temperature room (37 ^oC). Mixing was achieved with magnetic stirrers. The volumes of gas produced was determined by measurement of the amount of NaCl/citric acid solution that was displaced (**Appendix C**).

7.3.2 Results and discussion

The reaction vessel and the cylinder containing the acidified water were both at atmospheric pressure, therefore, any production of gas would have resulted in displacement of the water. The connective rubber tubing was clamped shut when the displaced solution was measured. The gas in the solution bottle was vented at the same time.

Accurate gas measurements were not obtained in these tests. Reasons for this could have been the development of a back pressure in the gas measurement system. No solution displacement was observed in the control and normal size solution flasks. Gas production was recorded in the high size solution flask at 29.2 ml and 60 ml in the starch flask. This degradation was achieved within ca. 10 d.

These tests were regarded as a screening mechanism and indicated degradability of the size solution. More accurate degradation details were then determined by the serum bottle method.

7.4 SERUM BOTTLE TESTS

7.4.1 Materials and methods

These experiments were made with anaerobic sludge collected from the Umbilo Sewage Purification Works **(Table 7.1**). The synthetic size solution was made as described in **Table 7.2**.

Based on the quantities of each size component utilised by the mill, and an effluent production rate of ca. 10 m^3/d, it was calculated that the size effluent contained 88 g of size per litre. The COD of the synthetic size solution was measured at 138 500 mg/l.

Standard assay conditions were followed as described in **Appendix C**. The controls were prepared in triplicate and each assay sample, in duplicate. Three concentrations were investigated for each compound, namely, the concentration of that compound in the typical size solution, one half of the concentration, and 1.5 times the concentration. The three concentrations are referred to as normal, low and high, respectively. The composition of each serum bottle, in the BMP assay, is shown in **Table 7.4** and for the anaerobic toxicity assay in **Table 7.5.**

TABLE 7.4 : Sample compositions for the biodegradability (BMP) assay with components of the textile size solution.

Component	Sample concentration	Inoculum (ml)	Nutrient medium (ml)	Substrate (ml)	Organic load (g COD/100 ml)
Control		30	70	0	0.13
PVA	High	30	30	40	3.25
	Medium	30	30	40	2.25
	Low	30	30	40	1.17
Starch	Medium	30	30	40	3.77
Plystran	High	30	30	40	1.27
	Medium	30	30	40	0.89
	Low	30	30	40	0.51
CMC	High	30	30	40	1.03
	Medium	30	30	40	0.76
	Low	30	30	40	0.45
OMS	High	30	30	40	0.43
	Medium	30	30	40	0.33
	Low	30	30	40	0.23
Acrylic	High	30	30	40	0.23
	Medium	30	30	40	0.20
	Low	30	30	40	0.17
Size solution	High	30	30	40	3.53
	Medium	30	30	40	2.35
	Low	30	30	40	1.18

The anaerobic toxicity assay was made with the biocide (concentrations of 0.5, 5 and 50 mg/l) and with the synthetic size effluent.

TABLE 7.5 : Sample compositions for the anaerobic toxicity assay (ATA) with components of the textile size solution.

Component	Sample	Inoculum (ml)	Nutrient medium (ml)	Substrate (ml)	Acetate/Prop. (ml)	Organic load (g COD/100 ml)
Control		30	70	0	2	0.15
Biocide	High	30	30	40	2	0.68
	Medium	30	30	40	2	0.20
	Low	30	30	40	2	0.16
Size solution	High	30	30	40	2	3.56
	Medium	30	30	40	2	2.37
	Low	30	30	40	2	1.19

The bottles were incubated in a constant temperature room (37 ºC) for 200 d. They were shaken manually once a day to facilitate contact between the microorganisms and the substrate. Gas production was measured daily for the first 2 weeks and periodically thereafter. Incubation in a constant temperature room ensured that the headspace was at the incubation temperature (37 °C). The gas volumes were corrected to STP. Gas composition was determined whenever biogas was wasted. COD and total suspended solids measurements were taken at the beginning and end of the incubation period. The methods used are described in **Appendix C**.

Mean values were used to determine the results that are reported in the following sections. The inconsistency of units is due to the inability of the graph package to vary the font to italic or subscript.

7.4.2 Polyvinyl alcohol (PVA)

PVA is the most widely used synthetic size and several forms are available commercially. Because of the extensive use of PVA several studies of its biodegradation and removal by biological treatment have been conducted (Porter and Snider, 1976). PVA contains acetate and acrylonitrile substituent groups to decrease rotting and decay. Thus it was reasonable to expect PVA to resist biodegradation. The degradation of PVA is dependent upon the stereochemical arrangement of the substituent groups around the anomeric carbon atom. The number and location of these residual groups may vary causing the degradability to vary considerably. PVA is biodegradable although preliminary adaptation of the biomass is necessary (Schluter, 1991). The discrepancy in the reported results may be attributed to the different forms of PVA that have been marketed in recent years. The biodegradability of three concentrations of the PVA used at the Frametex mill were investigated.

The cumulative gas production curves, over the 200 d incubation period, are illustrated in **Figure 7.1 (a)**. The volumes were corrected against those produced by the controls. The three concentrations are represented such that any concentration effects could be identified.

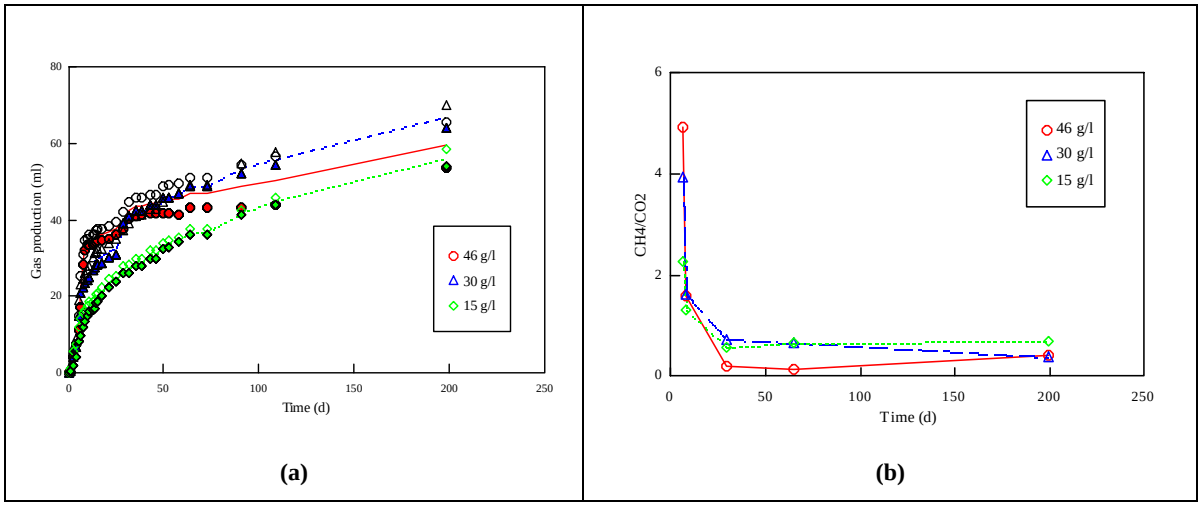


FIGURE 7.1: Plots of the cumulative gas production and the ratio of methane to carbon dioxide in the biogas for the three investigated PVA concentrations.

In the figures the symbols represent the results from each of the duplicate samples and the lines are the means for each set. The data for these tests are presented in **Appendix H**. The average standard deviations were calculated to provide an indication of the similarity of the duplicates. The 46 g/l PVA concentration showed a substantial degree of scatter, with a standard deviation of ± 2.4 ml . Error bars were not drawn onto the graphs for ease of reading. There was improved reproducibility for the 30 g/l solution, with a standard deviation of ± 0.85 ml . The deviation for the 15 g/l concentration was ± 1.16 ml. The lag period was negligible, at ca. 1 d, which suggested that the PVA was labile. From the plot (**Figure 7.1 (a)**) it could be seen that the high PVA concentration was slightly inhibitory as less gas was produced than with the normal concentration (30 g/l). This suggested that the PVA became inhibitory to the biomass at concentrations > 30 g/l. The reaction rates, for each concentration, were calculated from the initial gradient of the cumulative gas production curve:

TABLE 7.6 : Gas production rates for the three PVA concentrations.

PVA concentration (g/l)	Rate (ml/d)	R-squared
46	2.45	0.95
30	3.24	0.96
15	1.83	0.99

The degradation rate of the high concentration (46 g/l) was lower than that for the 30 g/l solution, which verified the inhibitory effect of the high PVA concentration on the anaerobic biomass. The gas production curve is indicative of the metabolic rate. The total gas production of the high PVA concentration was lower than that of the normal concentration (30 g/l) which indicated that the substrate was not readily degraded by the biomass. The continued gas production suggested that the substrate was not exhausted during the incubation period. The continued metabolism of the PVA suggested gradual acclimation of the biomass to the potentially inhibitory substrate. The amount of gas produced was not proportional to the increase in concentration which verified a slight degree of inhibition of the biomass at the higher wastewater concentrations.

The theoretical gas production was calculated from the Buswell equation (Buswell and Mueller, 1952):

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right)H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CO_2 + \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)CH_4 \qquad [7.1]$$

The theoretical volumes of methane and carbon dioxide production were compared with the measured volumes (**Table 7.7**).

TABLE 7.7 : Comparison of theoretical and actual gas production values for the three PVA concentrations.

	Theoretical		Actual		Ratio (Actual/Theoret.)	
Mass of PVA (g)	**CO_2 (g)**	**CH_4 (g)**	**CO_2 (g)**	**CH_4 (g)**	**CO_2**	**CH_4**
1.84	0.92	1.1	0.024	0.016	0.03	0.015
1.20	0.6	0.72	0.018	0.019	0.03	0.026
0.60	0.3	0.36	0.019	0.017	0.06	0.047

From these results, it is evident that the amount of produced was much lower than those expected. The reason for this could have been that the substrate was not completely degraded; this is verified by the continued gas production which suggested that the biomass were still metabolising the substrate. Some of the biogas may also have been lost during measurement by the syringe method. These results verify the inherent recalcitrance of the PVA to the anaerobic biomass. **Figure 7.1 (b)** shows the ratio of methane to carbon dioxide in the evolved biogas, for each PVA concentration. In all 3 concentrations the methane concentration of the biogas decreased after ca. 30 d. It was lowest for the high PVA concentration (46 g/l) which suggested inhibition of the methanogens. The reason for the decrease in methane concentration is not known but it suggests that the methanogens were most active at the commencement of the test. This was verified by the negligible lag period. The gas production was not inhibited after 30 d, however, which suggested an acclimation of the biomass, especially in the lower PVA concentrations where there was a gradual increase in the ratio.

The biochemical methane potential (BMP) was calculated for each PVA substrate, in terms of l methane per g COD destroyed. This provided an indication of the efficiency of the anaerobic process on the basis of the theoretical production of 0.395 l per g COD (at 35 °C) (Speece, 1996). These calculations are shown in **Appendix H**. The calculated Buswell theoretical methane production (**Table 7.7**) was ca. twice that calculated from the Speece theoretical equation, which suggested that the assumed molecular weight for PVA was half of what it should be; there were two PVA structures in the polymer. The BMP of the 46 g/l PVA substrate was calculated at 0.01 l/g COD which was much lower than the theoretical 0.395 l/g COD. This poor methanogenic conversion of the PVA substrate verified its inhibitory effect on the methanogens. The biochemical methane potential was also low for the two lower PVA concentrations : 0.05 l/g COD for the 30 g/l concentration and 0.07 l/g COD for the 15 g/l concentration. These results suggested that the substrate was being utilised by the biomass but the conversion was slow which resulted to the low biogas production (**Table 7.7**).

The COD of each of the PVA concentrations was determined at the end of the 200 d incubation period. Reduction was relatively high (70 %) for the 46 g/l substrate. There was no lag period (**Figure 7.1 (a)**) which suggested that the substrate was labile; thus the majority of the substrate may have been utilised by the methanogens within the first 30 d. This was verified in **Figure 7.1 (b)** where the methane production decreased after ca. 30 d. COD reduction was much lower in the lower PVA concentrations at 24 and 28 % for the 30 and 15 g/l PVA concentrations, respectively. The COD balance for each concentration was calculated (**Table 7.8**).

The initial COD for each bottle was calculated as the sum of the COD of the inoculum sludge, nutrient medium and substrate (**Table 7.4**). The final COD was measured on the entire solution.

TABLE 7.8 : COD balance for each of the three investigated PVA concentrations.

	46 g/l PVA		**30 g/l PVA**		**15 g/l PVA**	
	COD_{in} (g)	**COD_{out} (g)**	**COD_{in} (g)**	**COD_{out} (g)**	**COD_{in} (g)**	**COD_{out} (g)**
Initial solution	3.32	-	2.25	-	1.17	-
Methane	-	0.07	-	0.08	-	0.07
Final solution	-	1.17	-	1.7	-	0.84
TOTAL	**3.32**	**1.24**	**2.25**	**1.78**	**1.17**	**0.91**
% Balance	37		79		78	

COD recovery was very low for the high concentration (37 %). This could have been due to loss of biogas during the incubation period or inaccurate measurement by the described COD method due to the samples not being properly homogenised. A more accurate indication could have been obtained by measurement of the volatile solids and calculation of the reduction in volatile solids over the incubation period. Since COD was a measured parameter, the results of the COD balance provide an accurate assessment of the accuracy of the test. From the balance, it can be expected that the degradation of the 46 g/l PVA solution was not efficient.

Production of new biomass was determined by an increase in total solids over the incubation period. These values were compared to the total amount of biogas produced in each assay concentration. These results are presented in **Table 7.9**.

TABLE 7.9 : Biomass growth and total biogas production for each PVA concentration.

PVA concentration (g/l)	**Biomass growth (mg)**	**Total biogas produced (ml)**	**Vol. biogas/ mass COD destroyed (ml/mg)**
46	9.8	59.74	0.03
30	7.3	66.93	0.12
15	4.9	56.18	0.17

There was an increase in biomass production with increase in substrate concentration. The inhibitory effect of the high PVA concentration was evident in the comparison of total volumes of biogas produced. Less biogas was produced during the metabolism of the 46 g/l concentration than in the 30 g/l concentration. The specific biogas production (ml biogas produced per mg COD destroyed) showed the degradability of the lowest PVA concentration to be most efficient, verifying that as the concentration increased, the PVA became less amenable to degradation by the anaerobic biomass.

The degradability of PVA has been controversial since there are many forms available (Porter and Snider, 1976). These results showed that the PVA used by the Frametex mill was degradable, however, not readily

degradable since the substrate was not completely metabolised. The batch tests indicated potential inhibition of the biomass at PVA concentrations > 30 g/l.

7.4.3 Starch

Starch is a labile substrate and its addition to anaerobic digesters should enhance methane production (Schluter, 1991). This ***readily biodegradable*** classification should presumably apply to most starch derivatives but should not generally be assumed without investigation (Schluter, 1991). Since the starch component of the size solution was expected to be readily degraded, only one concentration (24 g/l) was investigated.

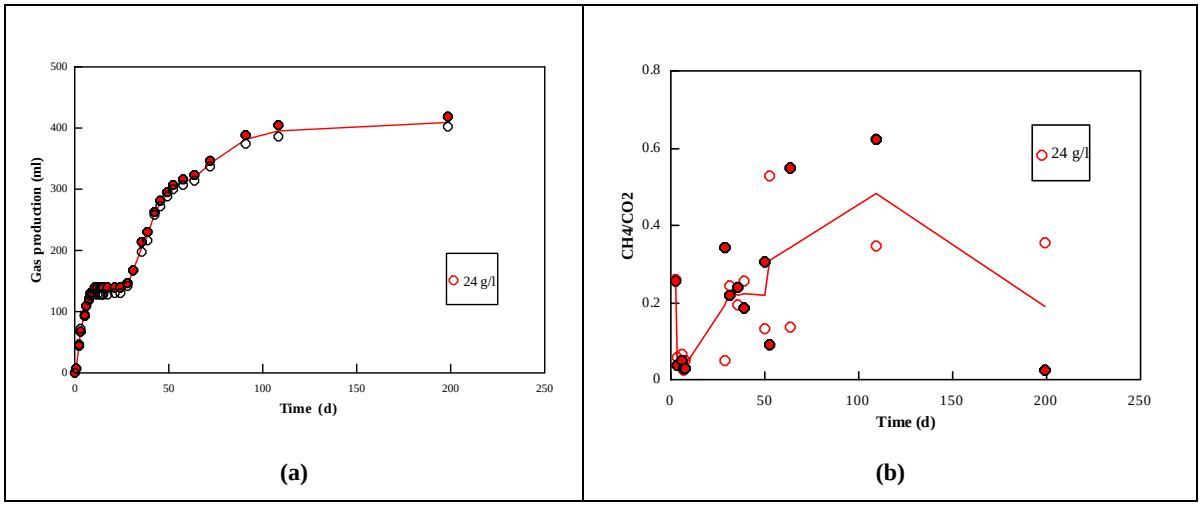


FIGURE 7.2: Plots of the cumulative gas production and the ratio of methane to carbon dioxide in the biogas for the 24 g/l starch concentration.

Large volumes of biogas were produced, with production stabilising at ca. 400 ml after 100 d of incubation. The average standard deviation was calculated at ± 3.64 ml, which, with the production of such large volumes of biogas, suggested similarity between the duplicates. Diphasic, or secondary digestion of a starch intermediate, was observed. This was unexpected since it has been found that the methane fermentation of starch converts the entire grain to carbon dioxide and methane (Buswell and Mueller, 1952). It was thought that the diphasic production was caused by the composition of the starch mixture; it is unlikely that chemically pure starch was used at the mill. It is believed that the mixture was made up of α- and β-amyloses. The β bonds would be more susceptible to degradation and, therefore, degraded first (initial degradation phase). The breakdown of the α bonds was then attributed to the second degradation phase. The initial degradation of the substrate was immediate; there was no lag period. The gas production stabilised after ca. 15 d then increased again from day 40. This secondary gas production stabilised after ca. 100d. The reaction rates, for both the initial and secondary digestion phases, were calculated from the cumulative gas production curve:

TABLE 7.10 : Gas production rates ror the 24 g/l starch concentration.

Digestion phase	Rate (ml/d)	R-squared
Initial	13.7	0.97
Secondary	6.3	0.93

The initial gas production was faster than the secondary phase. These results suggest diauxic digestion where, initially, the starch was degraded into its simple components and the labile glucose intermediate was readily degraded. Thereafter, the remaining intermediates were mineralised. Another possibility for the secondary digestion could have been that oxygen was present at the commencement of the incubation period, due to contamination during inoculation, resulting in initially aerobic degradation, followed by anaerobic digestion once all of the oxygen had been depleted.

Despite the observed diphasic digestion, the starch was readily degraded by the sludge biomass and the available substrate was eventually depleted as illustrated by the stabilisation of the gas production curve after ca. 100 d. In retrospect, varying concentrations of the substrate should have been investigated to assess the extent of the diphasic digestion.

The theoretical gas production volumes were calculated from Eq. 7.1 and compared to the measured volumes of biogas.

TABLE 7.11 : Comparison of theoretical and actual gas production values for the 24 g/l starch concentration.

	Theoretical		Actual		Ratio (Actual/Theoret.)	
Mass of starch (g)	CO_2 (g)	CH_4 (g)	CO_2 (g)	CH_4 (g)	CO_2	CH_4
0.96	0.77	0.29	0.27	0.04	0.35	0.14

The measured values were lower than the theoretical values. The biogas production plot showed substrate exhaustion, therefore, it was assumed that all of the available substrate was degraded. The low gas production could be attributed to loss of biogas during gas measurement. **Figure 7.2 (b)** illustrates the analysed methane to carbon dioxide ratio of the biogas. The methane content in the biogas was very low, ca. 12 % (w/w), which resulted in the low values on the y-axis of the graph. The initial peak suggested that the methanogens were active during the initial degradation stage. The methane content decreased during the first 15 d which suggests that the methanogens were not predominant. As stated, this initial degradation could have been achieved by aerobic bacteria or else the acidogens, which degraded the starch molecules into the intermediate components. Both of these degradation processes would have produced carbon dioxide. The methane content then increased, which suggested that the methanogens became more active during the second digestion phase. Still, more carbon dioxide was produced than methane which suggested that the acidogens were more active than the methanogens; they were the predominant population. The decrease in the ratio after ca. 100 d coincided with the depletion of the substrate and the subsequent decrease in metabolism and gas production.

The degradation of the starch substrate was efficient, with a COD reduction of 85 %, over the incubation period. Due to the low methane production, however, the calculated biochemical methane potential was low at 0.019 l methane/g COD. COD reduction is linked to methane production, thus the large reduction in COD should have resulted in greater volumes of methane being produced. It is believed that this imbalance was due to the loss of biogas during measurement.

TABLE 7.12 : COD balance for the 24 g/l starch concentration.

	24 g/l Starch	
	COD_{in} (g)	**COD_{out} (g)**
Initial solution	3.77	-
Methane	-	0.17
Final solution	-	0.56
TOTAL	**3.77**	**0.73**
% Recovery	19.00	

These results illustrate the need for more accurate analytical procedures. The syringe method for biogas measurement resulted in loss of small but substantial volumes of biogas, when gas was re-injected into the bottles. The final COD should have been measured on homogenised samples to provide more accurate results.

Biomass growth was measured at 5.85 mg over the 200 d incubation period. Total biogas production was 409.87 ml, which resulted in a specific biogas production of 0.13 ml/mg COD.

These results showed that although the starch was labile and readily degraded by the biomass, the methanogenic conversion of the substrate was not efficient. The biomass in an anaerobic digester is a mixed culture, therefore, the starch would be degraded if loaded into the digester. The starch was not inhibitory to the biomass. Starch is a complex pollutant and, therefore, may require relatively long hydrolysis times (Speece, 1996).

7.4.4 Plystran

Plystran, also termed Pre-Mix, is a commercial formulation consisting of ca. 58 % (w/v) modified potato starch, 40 % (w/v) PVA and 2 % (w/v) wax. The Frametex size solution contained 18 % (w/v) Plystran. Due to the expense, Plystran is no longer added to the size solution. To compensate for it, the operators have proportionally increased the concentrations of PVA, starch and wax in the recipe.

At the time of the investigation Plystran was still incorporated in the size solution. It was thought that the inhibitory effect of the PVA could affect the microbial degradation of the Plystran. Three concentrations of the Plystran were investigated, viz. 24, 16 and 8 g/l.

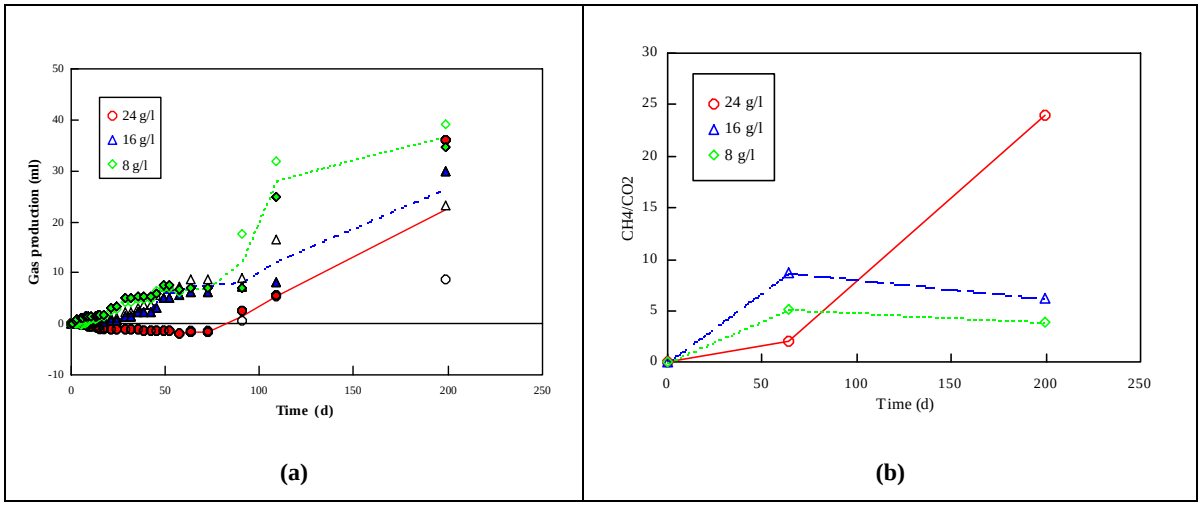


FIGURE 7.3 : Plots of the cumulative gas production and the ratio of methane to carbon dioxide in the biogas for the three investigated Plystran concentrations.

The samples were prepared in duplicate, to assess reproducibility, and the standard deviation was calculated for each set. The deviations were very small showing close reproducibility between samples. They were ± 0.5 ml, ± 0.4 ml and ± 0.14 ml for the 24, 16 and 8 g/l Plystran concentrations, respectively. Very low degradation rates were observed for the first 80 d, with the high Plystran concentration (24 g/l) completely inhibiting the biomass. This was illustrated by the negative gas production which resulted due to more gas being produced in the controls than in the experimental samples. A definite concentration effect was evident as the volume of gas produced decreased with increasing Plystran concentrations. Since the Plystran sample was a commercial formulation, it was impossible to know the exact composition, other than the major components stated. It is likely that a biocide was added to the formulation to prevent microbial growth either during transport to, or storage at, the textile mills. The presence of a biocide would explain the low metabolic rate. The PVA could also have contributed to the inhibitory effect on the biomass. Gas production increased after ca. 100 d of incubation. This suggested acclimation of the biomass to the inhibitory components of the substrate. The prolonged period of zero gas production seemed to indicate that the methanogens were no longer active, however, the rapid gas production recovery suggests that the biomass remained viable; metabolisism was prevented until there was acclimation of the biomass. After acclimation, the concentration effect was still evident, however, with the lowest gas volumes being produced for the highest Plystran concentration. The initial degradation rates were very low. The degradation rates of the acclimated biomass were also calculated, i.e. after ca. 80 d when gas production increased.

TABLE 7.13 : Gas production rates for the three Plystran concentrations.

Plystran concentration (g/l)	Digestion phase	Rate (ml/d)	R-squared
24	Initial	0.021	0.96
	Acclimated	0.18	0.99
16	Initial	0.029	0.86
	Acclimated	0.166	0.99
8	Initial	0.084	0.94
	Acclimated	0.589	0.92

These results show the increase in the gas production rate with time, i.e. with acclimation of the biomass to the Plystran. The degradation of the 16 and 24 g/l concentrations was low indicating inhibition of the biomass at the high concentrations. Gas production was higher in the 8 g/l concentration at 0.59 ml/d. These low gas production values verified the inherent toxicity or inhibitory effect of the Plystran on the anaerobic biomass.

The adopted chemical formula for the Plystran ($C_8H_{14}O_6$) was based on the Plystran being composed of starch, PVA and wax. The formulation may contain additional components and, therefore, the formula may not be correct. This formula was used to calculate the theoretical gas production values, from Eq. 7.1.

TABLE 7.14 : Comparison of theoretical and actual gas production values for the three Plystran concentrations.

	Theoretical		Actual		Ratio (Actual/Theoret.)	
Mass of Plystran (g)	CO_2 (g)	CH_4 (g)	CO_2 (g)	CH_4 (g)	CO_2	CH_4
0.96	0.6	0.29	0.0015	0.015	0.0025	0.052
0.64	0.512	0.192	0.0022	0.013	0.0043	0.068
0.32	0.256	0.096	0.0042	0.015	0.016	0.156

The inhibitory effect of the Plystran resulted in very low gas production. The methane content of the biogas was high with average percentages of 76, 78 and 61 % (w/w) for the 24, 16 and 8 g/l concentrations, respectively. The plot of the methane to carbon dioxide ratio in the biogas (**Figure 7.3 (b)**) showed the methane concentrations to increase steadily for all three concentrations, over the first 80 d when biogas production was low. In the 24 g/l concentration, gas was only produced after ca. 80 d. This resulted in a steep increase in the ratio indicating methanogenic activity. For the two lower concentrations, small volumes of biogas were produced from the commencement of the test. The methane concentration increased linearly during this period. After ca. 80 d when the gas production increased, the methane content of these two samples decreased gradually. This could have been due to the samples turning sour, i.e. the methanogens, which were slightly inhibited by the substrate, did not convert the volatile fatty acids to methane at a rate comparable to the production of the fatty acids. This would have resulted in an accumulation of fatty acids in the assay samples.

The biochemical methane potential of each concentration was low due to the low methane production rates. A volume of 0.033 l methane was produced per g COD destroyed, for the 24 g/l Plystran concentration. An increase in biogas and subsequently, methane production, in the degradation of the 16 g/l concentration resulted in an increase in the biochemical methane potential to 0.046 l CH_4 /g COD. There was a further increase in the metabolism to yield a production of 0.068 l CH_4 /g COD in the 8g/l Plystran concentration. These values were much lower than the theoretical methane production of 0.350 l CH_4 /g COD destroyed verifying the inhibitory effect of the Plystran on the biomass which prevented its degradation.

The COD reduction was greatest in the 8 g/l samples (61 %). Reduction in COD decreased in the higher concentrations due to the inhibition of the biomass. There was a 49 % reduction in the highest concentration and a 44 % reduction in the 16 g/l samples. The COD balance was calculated for each sample.

TABLE 7.15: COD balance for each of the three investigated Plystran concentrations.

	24 g/l Plystran		**16 g/l Plystran**		**8 g/l Plystran**	
	COD_{in} (g)	**COD_{out} (g)**	**COD_{in} (g)**	**COD_{out} (g)**	**COD_{in} (g)**	**COD_{out} (g)**
Initial solution	1.27	-	0.89	-	0.51	-
Methane	-	0.06	-	0.10	-	0.06
Final solution	-	0.65	-	0.50	-	0.20
TOTAL	**1.27**	**0.71**	**0.89**	**0.60**	**0.51**	**0.26**
% Recovery	56		67		51	

Despite the inhibitory concentration effect, the growth of biomass increased with Plystran concentration. **Table 7.16** shows the low volumes of biogas that were produced during the 200 d incubation period. The specific biogas production verified the concentration effect with most efficient degradation being achieved with the lowest Plystran concentration.

TABLE 7.16 : Biomass growth and total biogas production for each Plystran concentration.

Plystran concentration (g/l)	**Biomass growth (mg)**	**Total biogas produced (ml)**	**Vol. biogas/ mass COD destroyed (ml/mg)**
24	9.5	22.38	0.04
16	8.1	26.58	0.07
8	6.9	36.87	0.12

These results showed that the Plystran formulation was inhibitory to the anaerobic biomass. A definite concentration effect was evident with metabolism of the substrate decreasing with increasing concentration. These tests showed the acclimation of the biomass to the inhibitory substrate, with an initial protracted lag period and ultimate adaptation to the substrate and subsequent degradation, albeit slow. Similar trends were obtained as in the PVA assay. This suggests that the PVA in the Plystran contributed to the inhibitory effect of the Plystran on the biomass.

7.4.5 Carboxymethyl cellulose (CMC)

Carboxymethyl cellulose is generally sold as the sodium salt, however, it is a fairly well established trade practice to call the commercial product CMC (Seydel, 1972). By using three chemical variables, namely, degree of substitution, uniformity of substitution, and degree of polymerisation, a wide variety of CMC grades are produced. Physical characteristics such as particle size and shape, and particle density, can also be varied over a considerable range. CMC is relatively insoluble and requires heating. The CMC solution has a high viscosity. CMC is not readily degradable and is unlikely to be completely degraded in a wastewater treatment works (Schluter, 1991).

Three concentrations (20, 14 and 7 g/l) of the CMC grade used by the Frametex mill were investigated for their anaerobic biodegradability. The results of these assays are given below:

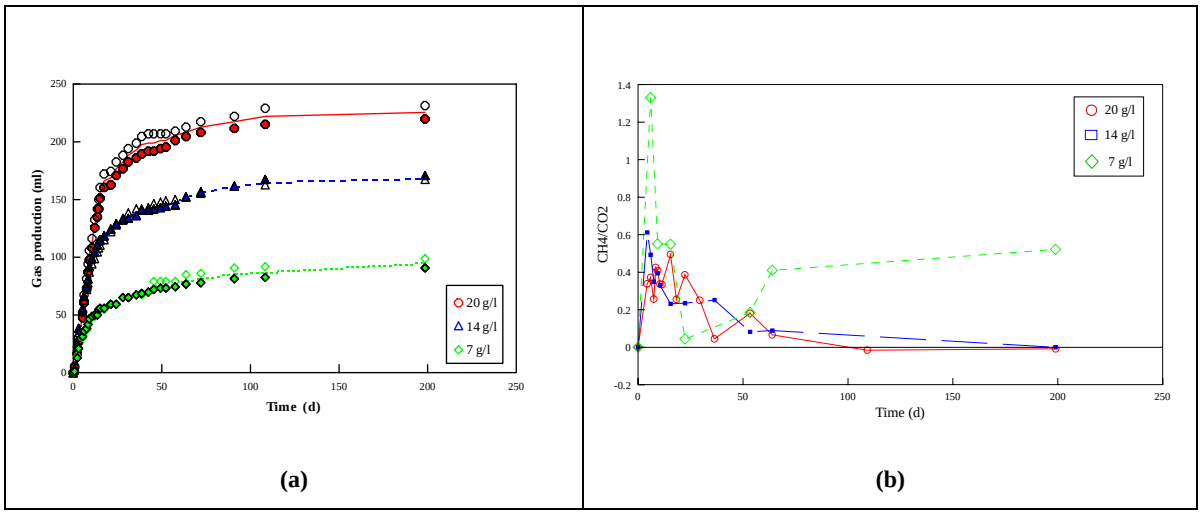


FIGURE 7.4 : Plots of the cumulative gas production and the ratio of methane to carbon dioxide in the biogas for the three investigated carboxymethyl cellulose (CMC) concentrations.

Biogas production (**Figure 7.4 (a)**) showed the CMC to be a labile substrate. This contradicts the findings of other researchers where CMC was found to be non-degradable under anaerobic conditions (Speece, 1996). The standard deviations were calculated for each concentration set: ± 4.8 ml for the 20 g/l solution i.e. there was a degree of scatter in these results. Reproducibility was much better with the lower CMC concentrations, at ± 0.6 ml for the 14 g/l solution and ± 0.9 ml for the low (7 g/l) concentration. A concentration effect was evident in that there was a proportional increase in gas production, with an increase in CMC concentration. This suggested that the CMC was a readily degradable substrate. Gas production stabilised after ca. 40 d due to depletion of the substrate. The biogas production rate was calculated for each concentration (**Table 7.17**). These results verified the degradability of the CMC as the biogas production rate increased with increasing CMC concentration.

TABLE 7.17 : Gas production rates for the three CMC concentrations.

CMC concentration (g/l)	Rate (ml/d)	R-squared
20	10.2	0.99
14	7.04	0.95

7	3.27	0.91

The chemical formula for CMC ($NaC_7H_{13}O_5$) was derived from the sodium cellulose salt with an additional methyl group. This formula was used to calculate the theoretical gas production for the degradation of CMC under anaerobic conditions, according to the Buswell equation (Eq. 7.1). These values were compared to the measured biogas production values:

TABLE 7.18 : Comparison of theoretical and actual gas production values for the three CMC concentrations.

	Theoretical		**Actual**		**Ratio (Actual/Theoret.)**	
Mass of CMC (g)	**CO_2 (g)**	**CH_4 (g)**	**CO_2 (g)**	**CH_4 (g)**	**CO_2**	**CH_4**
0.8	0.624	0.28	0.12	0.0394	0.192	0.141
0.56	0.44	0.2	0.0737	0.026	0.168	0.13
0.28	0.22	0.1	0.0311	0.0197	0.141	0.197

The substrate was thought to be exhausted in each assay bottle, as illustrated by the stabilisation of the gas production curves. However, the gas production values were much lower than the theoretical values. This could have been due to loss of biogas. The plot of the ratio of methane to carbon dioxide in the biogas (**Figure 7.4 (b)**) was erratic for all three concentrations. The methane concentration was low, ca. 21 % (w/w), in the 20 g/l CMC solution. The biogas produced by these samples contained low concentrations of methane until ca. day 60, after which the ratio decreased to zero. This coincided with the depletion of substrate and subsequent drop in biogas production. A similar trend was observed in the 14 g/l CMC solution, with a methane content of ca. 24 % (w/w). The largest concentration of methane was analysed in the low 7 g/l CMC concentration (35 % (w/w)). The ratio for this plot was erratic and the methane content was observed to increase towards the termination of the test even though the gas production had stabilised.

The biochemical methane potential of the 20 g/l CMC solution was relatively close to the theoretical at 0.219 l CH_4 /g COD destroyed. This suggested that the anaerobic conversion of the CMC substrate was relatively efficient. The volume of methane produced, per g of COD destroyed, was much lower (0.084 l/g) in the 14 g/l CMC solution, illustrating the decrease in metabolism with a decrease in the CMC concentration. The biochemical methane potential of the 7 g/l CMC solution was calculated at 0.106 l CH_4/g COD destroyed.

COD reduction was relatively low in the 20 g/l solution, at 24 %. A greater reduction was expected since the biogas production curves depicted complete utilisation of the substrate. The final COD measurement of the assay samples may have been too high since the samples were not properly homogenised prior to digestion. This could also account for the *loss* of COD in the COD balance (**Table 7.19)**. COD reduction was greater in the two lower CMC concentrations, at 55 % and 58 % for the 14 g/l and 7g/l solutions, respectively.

TABLE 7.19 : COD balance for each of the three investigated CMC concentrations.

	20 g/l CMC		**14 g/l CMC**		**7 g/l CMC**	
	COD_{in} (g)	**COD_{out} (g)**	**COD_{in} (g)**	**COD_{out} (g)**	**COD_{in} (g)**	**COD_{out} (g)**

Initial solution	1.03	-	0.76	-	0.45	-
Methane	-	0.16	-	0.10	-	0.08
Final solution	-	0.78	-	0.33	-	0.19
TOTAL	**1.03**	**0.94**	**0.76**	**0.43**	**0.45**	**0.27**
% Recovery	91		57		60	

Biomass growth was observed in all the experimental samples. Biogas production increased with increasing CMC concentration, as did the specific biogas production (**Table 7.20**):

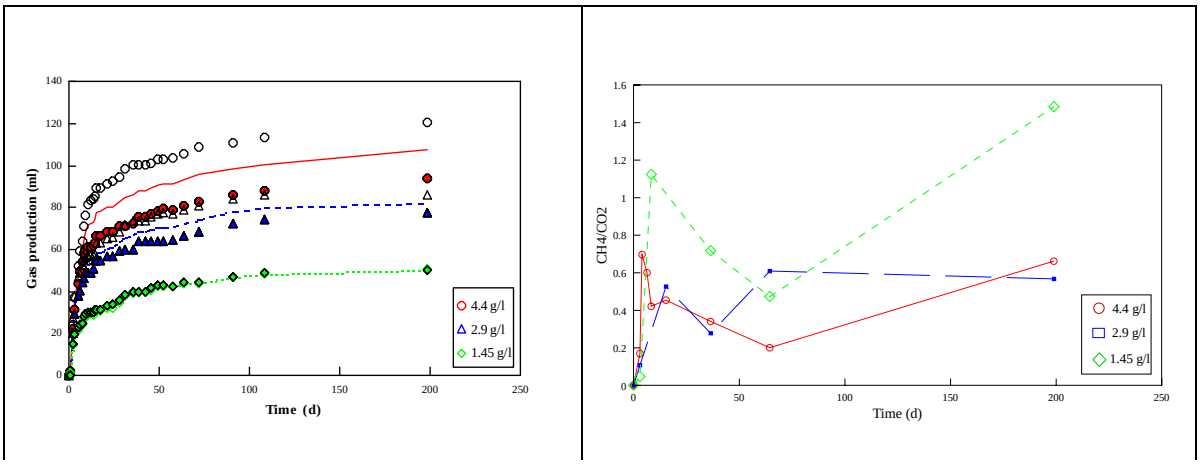
TABLE 7.20 : Biomass growth and total biogas production for each CMC concentration.

CMC concentration (g/l)	Biomass growth (mg)	Total biogas produced (ml)	Vol. biogas/ mass COD destroyed (ml/mg)
20	6.54	225.92	0.9
14	7.02	169.11	0.4
7	6.2	94.88	0.36

Schluter (1991) found that CMC was not completely degraded and deduced that it was unlikely to be completely degraded in sewage treatment works. These tests were, however, only run for 30 d (Schluter, 1991). Speece (1986) also found CMC to be non-degradable. The results from these tests showed the CMC component of the Frametex size solution to be readily degraded by the anaerobic biomass. The metabolic rate increased with increasing CMC concentration and no inhibitory effects were observed.

7.4.6 Oxidised modified starch (OMS)

Oxidised modified starch (OMS) is a derivative of starch. The COD, or organic content, is much lower than that of starch due to it being oxidised. The COD of OMS was measured at ca. 4 900 mg/l, whereas that of normal potato starch was ca. 90 526 mg/l. Lower concentrations of OMS were added to the size solution, at the Frametex mill. The three investigated concentrations were 4.4, 2.9 and 1.45 g/l. Similar trends were observed as in the CMC assays. The biogas production data are illustrated in **Figure 7.5 (a)**.



(a)	(b)

FIGURE 7.5 : Plots of the cumulative gas production and the ratio of methane to carbon dioxide in the biogas for the three investigated oxidised modified starch (OMS) concentrations.

No lag period was observed which suggested that the substrate was readily degraded. There was a substantial degree of scatter between the 4.4 g/l duplicates with a standard deviation of ± 10 ml. An improvement on this method would be to perform the tests in triplicate to provide a more accurate degree of reproducibility. The standard deviation was also relatively high for the 2.9 g/l OMS solution, at ± 4.7 ml. Good reproducibility was attained with the 1.45 g/l solutions, with a standard deviation of ± 0.4 ml. A concentration effect was evident in that biogas production increased with an increase in the OMS concentration. The increase in gas production, between the 2.9 and 4.4 g/l concentrations, was not proportional to the increase in concentration, which suggested that the OMS may become inhibitory to the biomass at concentrations > 3 g/l. These results were verified by the initial biogas production rates (**Table 7.21**).

TABLE 7.21 : Gas production rates for the three OMS concentrations.

OMS concentration (g/l)	Rate (ml/d)	R-squared
4.4	8.59	0.99
2.9	7.18	0.96
1.45	3.79	0.91

The theoretical gas production values were calculated and compared to the measured volumes. The measured values were relatively close to the theoretical values which suggested efficient conversion of the substrate.

TABLE 7.22 : Comparison of theoretical and actual gas production values for the three OMS concentrations.

	Theoretical		Actual		Ratio (Actual/Theoret.)	
Mass of OMS (g)	CO_2 (g)	CH_4 (g)	CO_2 (g)	CH_4 (g)	CO_2	CH_4
0.18	0.108	0.036	0.078	0.03	0.722	0.833
0.12	0.072	0.024	0.043	0.015	0.597	0.625
0.06	0.036	0.012	0.021	0.014	0.583	1.167

The methane content of the biogas was relatively low at 22 % (w/w) for the 4.4 g/l solution, 22 % (w/w) for the 2.9 g/l solution and 35 % (w/w) for the 1.45 g/l solution. The plot of the methane to carbon dioxide ratio of the biogas (**Figure 7.5 (b)**) was quite erratic for all three concentrations. The ratio of the 4.4 g/l solution showed an initial peak, after which the methane concentration decreased gradually. A similar trend was observed in the 2.9 g/l solution, however, the ratio tended to be more stable. The ratio for the 1.45 g/l concentration contained the highest methane concentrations of the three OMS concentrations. In all of the experimental samples, the methane concentration tended to increase towards the termination of the test, even though the gas production curves indicated depletion of the available substrate. This was most pronounced in the 1.45 g/l solution. The

reason for this could be that the methanogens converted volatile acids that had accumulated during the degradation of the substrate.

From these results, the biochemical methane potential was calculated for each sample. The calculated values were relatively close to the theoretical value of 0.395 l methane per g COD destroyed, which suggested efficient methanogenic conversion of the substrate. The biochemical methane potentials were 0.244, 0.1 and 0.213 l CH_4 /g COD for the 4.4, 2.9 and 1.45 g/l OMS solutions, respectively. COD reduction was 40 % in the 4.4 g/l solution, 64 % in the 2.9 g/l solution and 40 % in the 1.45 g/l solution. These reductions were low based on the assumption that the substrate was completely degraded. The COD balance was calculated for each OMS concentration, over the 200 d incubation period.

TABLE 7.23 : COD balance for each of the three investigated OMS concentrations.

	4.4 g/l OMS		**2.9 g/l OMS**		**1.45 g/l OMS**	
	COD_{in} (g)	**COD_{out} (g)**	**COD_{in} (g)**	**COD_{out} (g)**	**COD_{in} (g)**	**COD_{out} (g)**
Initial solution	0.43	-	0.33	-	0.23	-
Methane	-	0.12	-	0.06	-	0.06
Final solution	-	0.26	-	0.12	-	0.14
TOTAL	**0.43**	**0.38**	**0.33**	**0.18**	**0.23**	**0.20**
% Recovery	88		55		87	

Total biogas production increased with increasing OMS concentration (**Table 7.24**).

TABLE 7.24 : Biomass growth and total biogas production for each OMS concentration.

OMS concentration (g/l)	**Biomass growth (mg)**	**Total biogas produced (ml)**	**Vol. biogas/ mass COD destroyed (ml/mg)**
4.4	5.6	107.31	0.63
2.9	5.3	82.34	0.39
1.45	6.4	50.26	0.56

From these tests it was concluded that the OMS was a labile substrate for the anaerobic microorganisms in the anaerobic digester sludge. A correlation was drawn between the increase in OMS concentration and the increase in metabolic activity. Relatively large volumes of biogas were produced for the small quantities of substrate added. This verified the degradability of the substrate.

7.4.7 Acrylic

Acrylic sizes have been developed for the treatment of nylon filament yarns (Seydel, 1972). Polyacrylate sizes have been found to undergo very little, if any, biological degradation (Schluter, 1991). Acrylic acid was found to be inhibitory to a *Methanosarcina* enrichment culture in a batch reactor (Demirer and Speece, 1997). The

acrylic component of the Frametex size solution was very small; only ca. 0.7 g/l were added. Three concentrations were investigated to assess the anaerobic degradability and inherent toxicity. The acrylic concentrations were 1, 0.7 and 0.35 g/l.

Biogas production (**Figure 7.6 (a)**) was relatively low. Good reproducibility was attained between replicates: ± 2.3 ml for the 1 g/l solution, ± 0.9 ml for the 0.7 g/l solution and ± 1.2 ml for the 0.35 g/l solution.

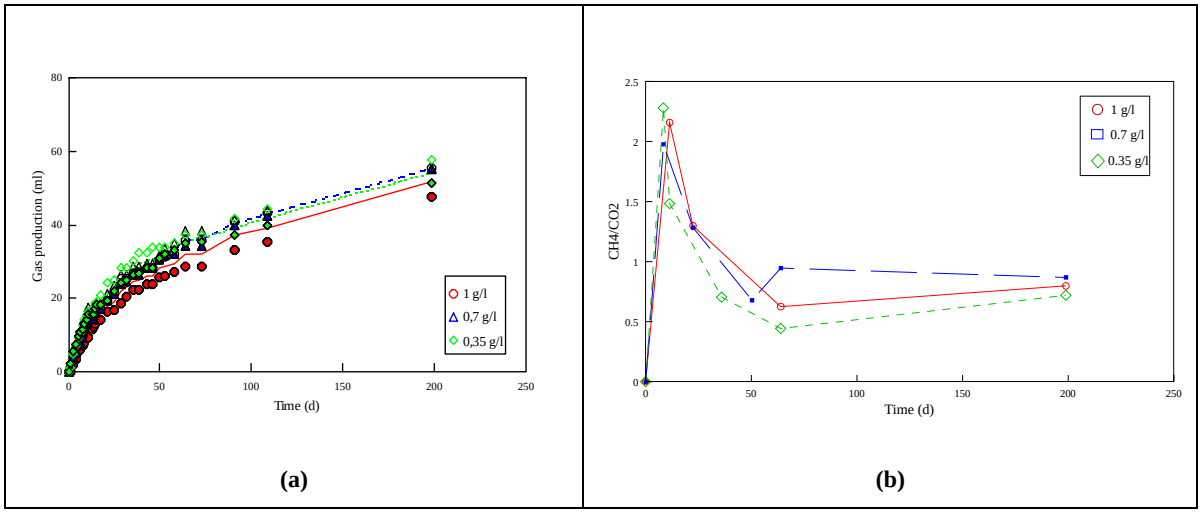


FIGURE 7.6 : Plots of the cumulative gas production and the ratio of methane to carbon dioxide in the biogas for the three investigated acrylic concentrations.

The lag period was negligible which suggested that the acrylic was labile. The volumes of biogas produced were relatively low and similar volumes were produced for all three concentrations which indicated an inhibitory effect of the acrylic at the higher concentrations. The continued gas production indicated that the substrate was not completely utilised. This suggested slow metabolism of the acrylic and gradual acclimation of the biomass to the substrate, over the incubation period. The gas production rate was calculated for each concentration. The rates were very similar which verified the inhibitory effect of the acrylic with increasing concentration. The lowest acrylic concentration (0.35 g/l) had the highest reaction rate.

TABLE 7.25 : Gas production rates for the three acrylic concentrations.

Acrylic concentration (g/l)	Rate (ml/d)	R-squared
1	0.60	0.93
0.7	0.65	0.91
0.35	0.67	0.92

The theoretical gas production values were calculated from Eq. 7.1. The comparison with the measured values is shown in **Table 7.26**:

TABLE 7.26 : Comparison of theoretical and actual gas production values for the three acrylic concentrations.

Mass of acrylic (g)	Theoretical		Actual		Ratio (Actual/Theoret.)	
	CO_2 (g)	CH_4 (g)	CO_2 (g)	CH_4 (g)	CO_2	CH_4
0.04	0.032	0.008	0.0164	0.016	0.513	2
0.03	0.024	0.006	0.0164	0.016	0.683	2.667
0.014	0.011	0.003	0.0172	0.0156	1.564	5.2

The measured gas volumes were similar to the expected volumes, as calculated from the theoretical equation. Larger volumes of methane were produced which suggested efficient methanogenic conversion of the substrate. This was verified by high biochemical methane potentials for each concentration. The calculated values were greater than the theoretical 0.395 l methane/ g COD destroyed. The biochemical methane potential of the 1 g/l acrylic solution was 0.509 l CH_4/g COD. A volume of 0.572 l methane was produced per g of COD catabolised in the 0.7 g/l acrylic assays. The biochemical methane potential was greatest for the low (0.35 g/l) concentration, at 0.732 l CH_4/g COD.

The methane concentration of the biogas was calculated for each acrylic concentration. The biogas produced due to the metabolism of the 1 g/l acrylic substrate had a methane content of 41 % (w/w). The methane content of the biogas from the lower two acrylic concentrations were similar at 40 % (w/w) and 36 % (w/w) for the 0.7 g/l and 0.35 g/l concentrations, respectively. The plot of the ratio of methane to carbon dioxide in the biogas (**Figure 7.6 (b)**) showed similar trends for all three concentrations: the methane concentration increased at the commencement of the test. It then gradually decreased until day 50, when the concentration increased. This pattern could be explained by the negligible lag period which indicated that the acrylic was readily degradable. This would have accounted for the initial methane peak. The subsequent decrease in methane concentration could have been due to the inhibition of the methanogens due to the accumulation of volatile fatty acids, i.e., the methanogens did not convert the acids as efficiently as they were produced. The gradual increase in methane concentration, after 50 d, would be due to the ultimate conversion of the fatty acids into methane and perhaps a degree of acclimation of the methanogens to the substrate.

COD reduction was relatively low at ca. 45 % for each of the concentrations. This was expected as the gas production curve showed the continued metabolism of the substrate; it was not depleted. The COD balance of each acrylic concentration was calculated.

TABLE 7.27 : COD balance for each of the three investigated acrylic concentrations.

	1 g/l acrylic		0.7 g/l acrylic		0.35 g/l acrylic	
	COD_{in} (g)	COD_{out} (g)	COD_{in} (g)	COD_{out} (g)	COD_{in} (g)	COD_{out} (g)
Initial solution	0.23	-	0.20	-	0.17	-
Methane	-	0.06	-	0.07	-	0.06
Final solution	-	0.15	-	0.11	-	0.09
TOTAL	**0.23**	**0.21**	**0.20**	**0.18**	**0.17**	**0.15**
% Recovery	91		90		88	

Biomass growth was greatest in the low (0.35 g/l) concentration, as was the specific biogas production.

TABLE 7.28 : Biomass growth and total biogas production for each acrylic concentration.

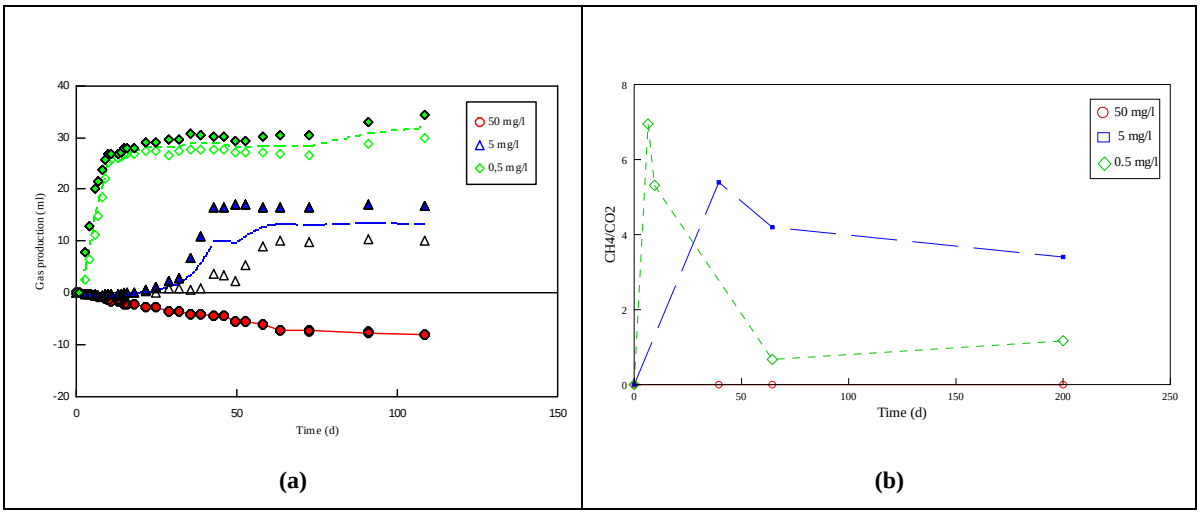
Acrylic concentration (g/l)	Biomass growth (mg)	Total biogas produced (ml)	Vol. biogas/ mass COD destroyed (ml/mg)
1	6.3	51.88	0.62
0.7	6.4	55.33	0.61
0.35	7	54.47	0.68

These results verified that the acrylic component became inhibitory to the biomass at concentrations > ca. 4 g/l. However, even at concentrations below 4 g/l, the biogas production was low although there was efficient methanogenic conversion of the substrate. The acrylic component could be treated anaerobically, at low concentrations, with an acclimated biomass.

7.4.8 Biocide

A biocide was added to the size solution to prevent bacterial or fungal growth. Microbial growth could impair the efficacy of the yarn treatment and could also stain the material. The recipe used by the Frametex mill incorporated 0.5 kg of the biocide, in a total volume of 450 l. This was equivalent to a biocide concentration of 1 g/l. In a worst case scenario, the highest concentration that could be fed to the Umbilo digester, without dilution, would be 500 g. Within the digester volume (1 340 m^3), this would be diluted to a concentration of 0.4 mg/l. The mill produced ca. 10 m^3 of size effluent per day. The highest concentration of the biocide in the effluent would be 500 g. At this concentration, the final concentration of the biocide in the effluent would be 50 mg/l. It is unlikely that the biocide concentration would be this high due to dilution by wash-waters etc.

The anaerobic toxicity assay was made with three biocide concentrations, viz. 50, 5 and 0.5 mg/l. From these results, toxicity of the substrate could be identified by a reduction in the initial rate of gas production, in proportion to the volume of substrate added. The results are illustrated in **Figure 7.7 (a)**.



(a) **(b)**

FIGURE 7.7 : Plots of the cumulative gas production and the ratio of methane to carbon dioxide in the biogas for the three investigated biocide concentrations.

The standard deviation of each concentration set was calculated to give an indication of the reproducibility between the duplicate samples. The reproducibility was good with a standard deviation of ± 0.008 ml for the 50 mg/l concentration, ± 1.9 ml for the 5 mg/l solution and ± 1.5 ml for the low 0.5 mg/l concentration. The 0.5 mg/l concentration of biocide was catabolised. Only ca. 30 ml of gas were produced at a degradation rate of 2.88 ml/d (**Table 7.29**). The lag period was only ca. 2 d which suggested that the substrate was readily degraded at this concentration. The reason for the low gas volume could be the limited availability of substrate due to the low concentration of biocide added (0.5 mg/l).

In the 5 mg/l biocide solution, gas was produced after about 40 d of incubation, indicating acclimation of the biomass to the inhibitory biocide concentration. Gas production was very low and stabilised around 10 ml. The degradation rate of the acclimated biomass was 0.43 ml/d. A biocide concentration of 50 mg/l was toxic to the biomass, as shown by the negative gas production volumes. The negative values were obtained because the control produced greater volumes of gas than the experimental samples. These results showed that the biocide became severely toxic to the biomass at concentrations > 5 mg/l.

TABLE 7.29 : Gas production rates for the three biocide concentrations.

Biocide concentration (mg/l)	Digestion phase	Rate (ml/d)	R-squared
50	Initial	0	0.92
5	Initial	0	0.87
	Secondary	0.43	0.86
0.5	Initial	2.88	0.99

The biocide used at the Frametex mill was a water-soluble Dodigen 2451 (Hoechst), which was composed of alkyl dimethylbenzyl ammonium chloride. The formula derived from this composition ($C_8H_{12}ONCl$) was substituted into the Buswell equation (Eq. 7.1) to determine the theoretical mass of carbon dioxide and methane produced, upon complete degradation of the substrate under anaerobic conditions.

TABLE 7.30 : Comparison of theoretical and actual gas production values for the three biocide concentrations.

Mass of biocide (g)	Theoretical		Actual		Ratio (Actual/Theoret.)	
	CO_2 (g)	CH_4 (g)	CO_2 (g)	CH_4 (g)	CO_2	CH_4
0.002	0.0014	0.001	0.0003	0.0001	0.214	0.1
0.0002	0.00014	0.0001	0.004	0.015	28.6	150
0.00002	0.000014	0.00001	0.008	0.008	571.4	800

Biogas production in the 50 mg/l samples was negligible. Biogas production in the 5 and 0.5 mg/l samples was higher than the theoretical values. This could have been caused by the adopted chemical formula not being correct. The methane content of the biogas reduced due to the metabolism of the experimental samples contained relatively high concentrations of methane: 60 % (w/w) for the 0.5 mg/l concentrations and ca. 80 % (w/w) for the 5 mg/l concentration. The biogas methane to carbon dioxide ratio plot (**Figure 7.7 (b)**) showed the zero ratio of the 50 mg/l due to the inhibition of the biomass. In the degradation of the 5 mg/l biocide sample, the methane content increased between days 10 to 50; it was during this time that the biomass acclimated to the substrate and very small volumes of biogas were produced. The ratio decreased and then stabilised which indicated acclimation of the methanogens and subsequent degradation of the substrate, as verified by the biogas production curve (**Figure 7.7 (a)**). The ratio of the 0.5 mg/l concentration increased immediately indicating the degradability of the low biocide concentration. The ratio then decreased which could have been due to the accumulation of volatile fatty acids within the sample bottles. Stabilisation was indicated by a subsequent increase and stabilisation of the ratio.

To quantify the toxicity of the biocide, in the anaerobic toxicity assay, total gas production data were employed to determine the relative ratios of metabolism of the feed source among the samples. The maximum rate of gas production was computed for each sample over the same time period and the data were normalised by computing ratios between respective rates for samples and the average of the controls. The ratio was designated the maximum rate ratio (MRR). A MRR of less than 0.95 suggested possible inhibition and one less than 0.9 suggested significant inhibition (Owen et al., 1979). The results of the biocide toxicity assay are presented in **Table 7.31**. The 50 mg/l substrate had a biogas production rate of 0 which resulted in an MRR of 0; this indicated total inhibition of the biomass. The unacclimated biomass of the 5 mg/l biocide substrate was also inhibited. Acclimation of the substrate resulted in degradation of the biocide and consequently, the substrate was no longer inhibitory (MRR = 6.14). The 0.5 mg/l concentration was readily degraded, as shown by the high MRR; this low concentration was not inhibitory to the biomass.

TABLE 7.31 : Maximum Rate Ratios (MRR) for the biocide anaerobic toxicity assay.

Biocide concentration (mg/l)	Digestion phase	Rate (ml/d)	MRR
50	Initial	0	0
5	Initial	0	0
	Secondary	0.43	6.14
0.5	Initial	2.88	41.1

Due to the inhibition of the biomass, the COD reduction of the 50 mg/l substrate was very low at ca. 12 %. Reduction was higher in the lower concentrations, as shown in the COD balances:

TABLE 7.32 : COD balance for each of the three investigated biocide concentrations.

	50 mg/l biocide		5 mg/l biocide		0.5 mg/l biocide	
	COD_{in} (g)	COD_{out} (g)	COD_{in} (g)	COD_{out} (g)	COD_{in} (g)	COD_{out} (g)
Initial solution	0.68	-	0.20	-	0.16	-
Methane	-	0.00	-	0.06	-	0.03

Final solution	-	0.60	-	0.12	-	0.11
TOTAL	**0.68**	**0.60**	**0.20**	**0.18**	**0.16**	**0.14**
% Recovery	88		90		88	

The good recovery in these balances suggested that the degradation process was efficient. Biomass growth was greatest in the 0.5 mg/l concentration due to the availability of the substrate for metabolism by the microorganisms. The specific biogas production was also greatest for the this concentration.

TABLE 7.33 : Biomass growth and total biogas production for each biocide concentration.

Biocide concentration (mg/l)	**Biomass growth (mg)**	**Total biogas produced (ml)**	**Vol. biogas/ mass COD destroyed (ml/mg)**
50	2.9	0	0.00
5	4.4	13.5	0.17
0.5	6.3	32.05	0.64

The biocide became severely toxic to the biomass at concentrations greater than 5 mg/l. The biomass required a period of acclimation to the 5 g/l concentration. The low concentration of 0.5 mg/l was readily degraded, however gas production was low. This was thought to be due to the limited availability of substrate due to the low concentration. From these results it can be concluded that a biocide concentration of > 5 g/l, in the size effluent, would have an inhibitory effect on the digester sludge biomass. The highest possible biocide concentration in the Umbilo anaerobic digester would be 1 g/l, therefore, the biocide component of the textile size effluent would not be toxic to the biomass.

7.4.9 Synthetic size solution

The components of the textile size were combined according to the recipe used by the Frametex mill, in New Germany. The ultimate degradability of the solution was determined by the biochemical methane potential assay. The anaerobic toxicity assay was also performed to identify any toxicity effects on the anaerobic digester biomass. Results from both tests are discussed below and comparisons are drawn. Three concentrations were investigated, namely, the normal size solution, 1.5 times this concentration and 0.5 times the concentration. A synthetic solution was chosen over the real effluent such that more accurate analyses could be performed; the composition of each sample was known. The conditions in these tests represent the worst case scenario. The degradability of the undiluted textile size solution was investigated. The concentration would be much lower in the effluent due to dilution by wash-waters etc. The size solution was the only substrate added to the serum bottles; no feed sludge was added. The results thus represented the degradation results of the substrate alone.

The gas production data for the BMP and ATA trials are illustrated in **Figures 7.8 (a)** and **(c)**, respectively.

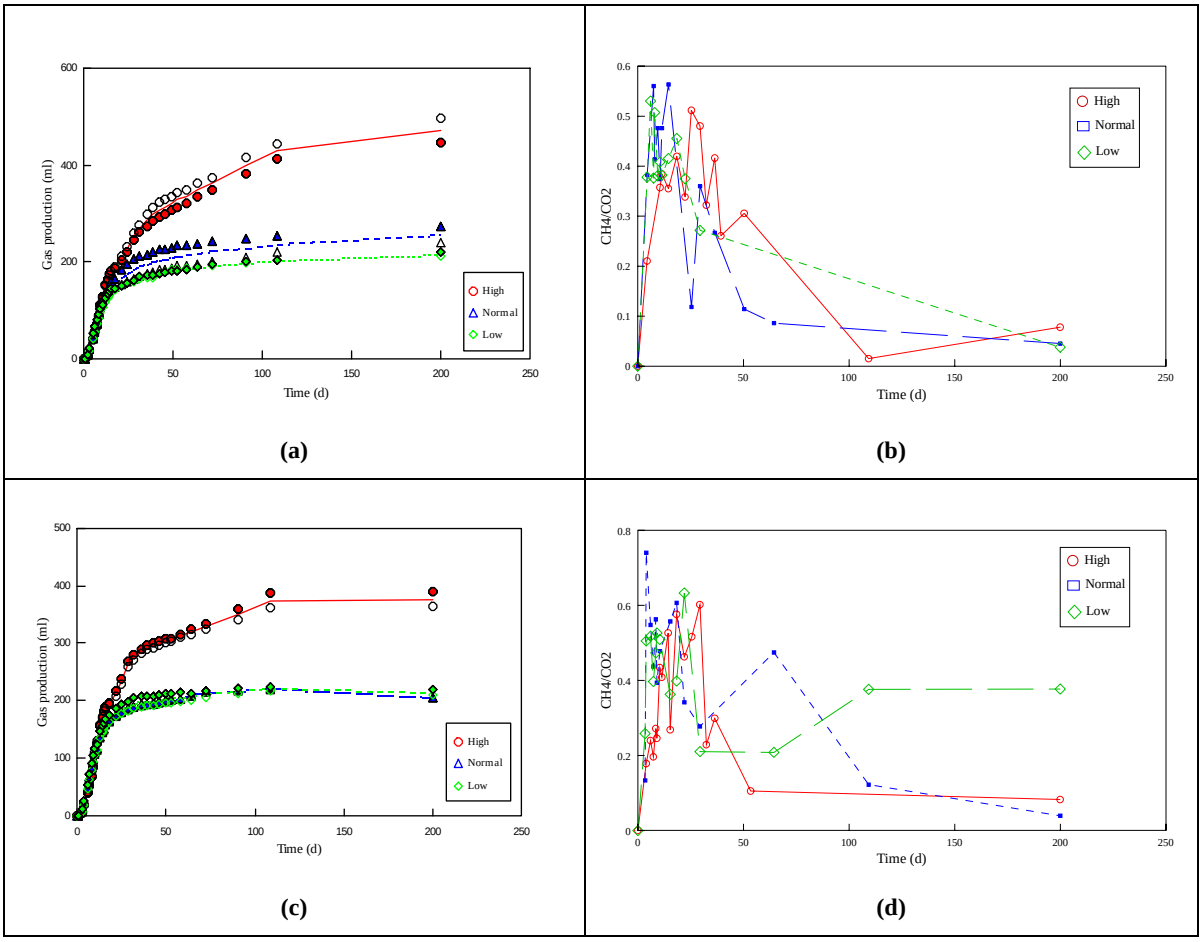


FIGURE 7.8 : Plots of the cumulative gas production and the ratio of methane to carbon dioxide in the biogas for the BMP assay ((a) and (b)) and the ATA ((c) and (d)) for the synthetic size solution..

In the BMP assay, a lag period of ca. 3 d was observed before gas was produced. The standard deviations between duplicates, in each concentration set, were determined to assess the reproducibility. There was a significant degree of scatter. The standard deviation of the high concentration was ± 6.6 ml, 11.0 ml for the normal size concentration and 1.8 ml for the low concentration. The initial lag period could have been attributed to the inhibitory constituents of the size solution or the high organic load. Gas production was high with ca. 400 ml produced upon degradation of the high concentration, at a rate of 8.27 ml/d (**Table 7.34**). Half of this volume was produced for the normal effluent concentration (rate of 9.3 ml/d). Similar biogas production results were obtained for the normal and low concentrations. This suggested that the higher concentrations may have overloaded the system. The substrate was labile but the organic content was high, therefore, causing an organic shock.

Similar results were obtained for the anaerobic toxicity assay. The standard deviations for these sample sets were much smaller, indicating improved reproducibility. The standard deviation for the high concentration was ± 2.6 ml, ± 0.9 ml for the normal size concentration and ± 5.9 ml for the low concentration. The lag period was slightly shorter in these sample bottles, at ca. 1 to 2 d. The observed biogas production trends were the same as those described for the BMP assay. The degradation rates are given :

TABLE 7.34 : Gas production rates for the three synthetic size concentrations, for both the BMP and ATA trials.

Size concentration	Assay	Rate (ml/d)	R-squared
High	BMP	8.27	0.91
	ATA	8.22	0.93
Normal	BMP	9.30	0.92
	ATA	9.75	0.93
Low	BMP	9.26	0.92
	ATA	10.10	0.93

The highest size concentration exhibited the lowest gas production rates which suggested that it was not as readily degraded as the lower concentrations. The substrate was labile and biogas was produced for all concentrations but degradation was most efficient in the samples of the lowest concentration.

Methane production was low with ca. 20 % (w/w) methane in the biogas produced in all sample concentrations. Similar concentrations of carbon dioxide and methane were produced in samples from the BMP and ATA trials (**Table 7.35**).

TABLE 7.35 : Synthetic size biogas compositions.

Size concentration	Assay	CO_2 (g)	CH_4 (g)
High	BMP	0.263	0.0832
	ATA	0.202	0.0745
Normal	BMP	0.156	0.0483
	ATA	0.116	0.0482
Low	BMP	0.104	0.0367
	ATA	0.106	0.0453

Figures 7.8 (b) and **(d)** are the biogas methane to carbon dioxide ratios for the BMP and ATA tests, respectively. In both tests and in all three concentrations, methane was produced from the commencement of the test and the ratio stabilised after ca. 50 d which coincided with stabilisation of the gas production curves i.e., depletion of the substrate. Similar volumes of biogas were produced in the low and normal substrate concentrations.

The biochemical methane potential was calculated for each concentration. These values were relatively low which suggested poor methanogenic conversion of the substrate. This was verified by the small concentrations of methane in the biogas. The biochemical methane potential of the high size concentration was 0.056 l CH_4 /g COD catabolised. Methanogenic conversion was more efficient in the degradation of the normal concentration of size solution with 0.089 l methane produced per g of COD destroyed. These values were much lower than the theoretical 0.395 l CH_4 /g COD. The most efficient methane production was achieved in the lowest size concentration (0.198 l CH_4 /g COD). This also suggested that the low concentration was more readily degraded than the higher concentrations.

The mixed rate ratio (MRR) was calculated for the anaerobic toxicity samples. The controls produced an average of 8.05 ml biogas over the 200 d incubation period, at a rate of 0.07 ml/d. The substrates were degraded as shown by the biogas production curves (**Figure 7.8 (c)**), thus the MRR of each substrate was high. The high ratios indicated that the size solution was not inhibitory to the biomass. The calculated mixed rate ratios were: 117, 139 and 144 for the high, normal and low size concentrations, respectively.

COD reduction was determined over the incubation period. In the biochemical methane potential (BMP) assay, the COD of the high size concentration was reduced by 59 %. The COD reduction in the normal concentration was 32 % and 22 % in the low concentration. These reductions were small; it was expected that the COD reduction would be greater due to the apparent depletion of the substrate. Similar COD reductions were observed in the anaerobic toxicity assay with 53 %, 58 % and 11 % reductions in the high, normal and low concentrations, respectively. COD may have been lost in the form of methane during gas measurement. COD balances were calculated for each sample.

TABLE 7.36 : COD balance for each of the three synthetic size concentrations in the BMP assay.

	High		**Normal**		**Low**	
	COD_{in} (g)	**COD_{out} (g)**	**COD_{in} (g)**	**COD_{out} (g)**	**COD_{in} (g)**	**COD_{out} (g)**
Initial solution	3.53	-	2.35	-	1.18	-
Methane	-	0.33	-	0.19	-	0.15
Final solution	-	1.46	-	1.59	-	0.92
TOTAL	**3.53**	**1.79**	**2.35**	**1.78**	**1.18**	**1.07**
% Recovery	51		76		91	

TABLE 7.37 : COD balance for each of the three synthetic size concentrations in the anaerobic toxicity assay.

	High		**Normal**		**Low**	
	COD_{in} (g)	**COD_{out} (g)**	**COD_{in} (g)**	**COD_{out} (g)**	**COD_{in} (g)**	**COD_{out} (g)**
Initial solution	3.56	-	2.37	-	1.19	-
Methane	-	0.30	-	0.19	-	0.18
Final solution	-	1.68	-	1.00	-	1.06
TOTAL	**3.56**	**1.98**	**2.37**	**1.19**	**1.19**	**1.24**
% Recovery	56		50		104	

Growth of new biomass was observed in all of the sample bottles. The biogas production per mg of COD destroyed was greatest in the lowest size concentration which suggested that the low substrate concentration was the most labile.

TABLE 7.38 : Biomass growth and total biogas production for each synthetic size concentration.

Size concentration	Assay	Biomass growth (mg)	Total biogas produced (ml)	Vol. biogas/ mass COD destroyed (ml/mg)
High	BMP	13.5	472.15	0.23
	ATA	9.5	376.34	0.20
Normal	BMP	10.7	257.48	0.34
	ATA	9.4	205.32	0.15
Low	BMP	10.6	216.35	0.83
	ATA	10.6	214.93	1.65

From these results it can be concluded that the size solution could be degraded by the microorganisms in the anaerobic digester sludge. Caution would have to be taken to prevent overloading of the digester as these results suggested decreased degradation with increasing concentration of the substrate. Methane production was relatively low which suggested that the degradation of the substrate was achieved by the interactions of a consortium of bacteria. It is likely that the substrate was co-metabolised, i.e. different components of the size solution were degraded by different populations and intermediates produced became substrate for other populations. Labile components would have been degraded initially with concurrent acclimation of the biomass to the more recalcitrant molecules. It is due to these interactions and co-metabolic pathways that the degradation of the combined size solution could not be predicted from the results of the individual components. The previous discussion did, however, give an indication of the inhibitory and labile components of the size solution.

7.4.10 Discussion

This screening method measured the potential for anaerobic degradation, i.e., whether organisms with the capacity for mineralisation of the size solution, and its components, were present in the inoculum. Investigation of individual components identified those with an inherent inhibitory effect on the anaerobic biomass and the concentrations at which each component could be effectively degraded. Investigation of the combined size solution indicated that the effluent could be degraded anaerobically.

These tests investigated the anaerobic degradability of each component alone since no other substrate, such as feed sludge, was added to the serum bottles. The tests also investigated undiluted samples; the relative concentrations in the size effluent would be much lower due to dilution by wash-waters etc.

Owen et al. (1979) suggested that < 2 g COD should be placed in each bottle, for the correct C : N ratio. **Table 7.4** and **7.5** show that some bottles contained more than 2 g of COD. This could have resulted in an organic overload, increased biogas production and/or increased biomass growth.

Reproducibility was good in most sample sets with standard deviations generally < 10 %. Discrepancies, due to scatter, could be alleviated by running each sample in triplicate. Due to the small sample sizes and the ease of setting up and monitoring the bottles, several replicates could be run simultaneously. A control test should be run, simultaneously, with a known substrate such as glucose. The glucose assay could serve as a control against which to check biogas prodcution and COD measurements, to assess the accuracy.

Gas production, in the control bottles, was 2.75 ml over 200 d. Owen et al. (1979) estimated a gas production of ca. 1.5 ml, in the control, over 30 d. This gas production was due to the degradation of residual organic molecules in the inoculum sludge. The gas production curves provided an indication of the metabolic activity and the degradability of each component. The ability to consume many substrates simultaneously is clearly an important survival strategy, especially in natural environments where often a mixture of organic compounds occurs. The result is the development of generalist and specialist species, or populations. A generalist microorganism can consume more than one substrate whereas specialist microorganisms develop the necessary digestive enzymes (they acclimate) to a particular substrate. Gas production results of the synthetic size solution did not follow first order kinetics which suggested that the degradation of the multi-component size solution involved a complex microbial community with specific interspecies interactions.

The biochemical methane potential assays provided for the identification of concentrations effects by comparison of the levels of metabolic activity between different compound concentrations. Inhibition of the biomass was illustrated by a negative or negligible gas production.

The tests were run for a protracted incubation period (200 d). The tests would normally only run for ca. 30 to 60 d. The extended period may have caused the often observed decrease in methane production due to the cessation of degradation. Exhaustion of the substrate could have resulted in the bacteria utilising the methane as a carbon source, during the endogenous respiration phase. The extended incubation period did, however, allow for the observation of biomass acclimation to inhibitory substrates.

Schluter (1991) did similar work to determine the biodegradability of different size components and the ultimate ecological impact of the sizes. Schluter concluded that sizes were not ecotoxic and, because they are only water-soluble and not fat-soluble, they tend not to accumulate. In a particular anaerobic environment the potential may not be expressed if the particular degrading organisms are absent or if toxic chemicals or other environmental conditions limit the expression of activity. Methods screening for potential biodegradability are useful in that they provide an inexpensive first-level evaluation of molecule fate.

7.5 TOXICITY

Anaerobic organisms, particularly methanogens, are susceptible to a large variety of compounds. However, even severely inhibitory compounds (e.g.. chloroform) can be degraded by anaerobic consortia once they have become adapted (Lettinga, 1995). The key factor in the application of anaerobic treatment of *toxic* wastewaters is acclimation. The acclimation of an anaerobic sludge to a specific substrate brings significant changes to its microbial population (Gavala and Lyberatos, 1997). The activity of the sludge related to a specific substrate is a critical parameter since the anaerobic degradability of wastewaters depend strongly on it.

The objective of the following tests was to acclimate anaerobic biomass to compounds that were found to be inhibitory, or toxic, during the serum bottle tests. The acclimated sludge could then be used as a seed to reduce the lag period and easily degrade the substrate at concentrations that would previously have been inhibitory.

7.5.1 Plystran enrichment culture

An enrichment culture was set up in a 10 l aspirator bottle. The inoculum was obtained from a primary anaerobic digester at the Umbilo Sewage Purification Works. A 40 % (v/v) inoculum was added. A defined medium of trace elements, minerals and vitamins was prepared according to Owen et al. (1979) (**Appendix C**) and added to the digester with the inoculum. The reactor was overgassed with OFN (Fedgas) for 30 min at a

flow rate of 0.5 l/min and incubated, in the dark, at 37 ºC. Gas was released from the reactor into a gas trap. The trap consisted of an enclosed measuring cylinder containing 1 l of a 20 % (w/v) NaCl and 0.5 % (w/v) citric acid solution. This solution was used to prevent dissolution of the biogas. The gas produced in the digester was channelled into the measuring cylinder, where it displaced the solution.

Once the digester was stable, i.e. there was no gas production (approximately 30 d of incubation), Plystran solution was added to the reactor to give an initial concentration of 5 g/l. The Plystran concentration was periodically increased, over the following 6 months to a final cumulative dose of 50 g/l. Gas production with increasing Plystran concentration indicated that the slow and gradual increase in the concentration had allowed for acclimation of the biomass to the substrate. This culture could be used to seed a reactor known to treat Plystran and thereby prevent inhibition and the usual lag period.

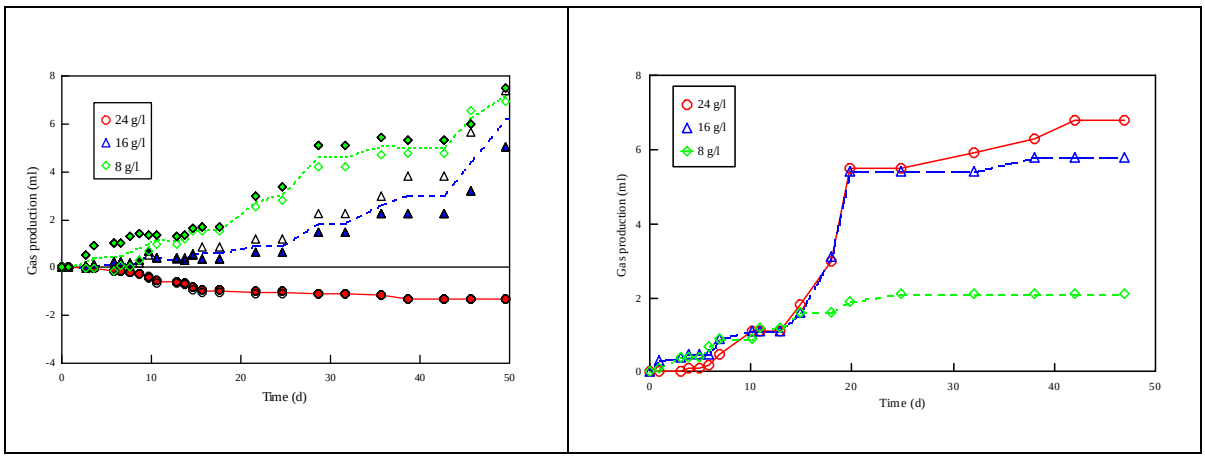
7.5.2 Acclimated sludge

In these tests the acclimated sludge from the serum bottles, previously containing the Plystran and biocide solutions, was used to seed new serum bottles. The objective of the test was to determine whether there was a change in the degradation rate and in the length of the lag period, with the acclimated sludge.

The acclimated sludge was separated by settlement and the supernatant was decanted. A 30 ml sample of the acclimated sludge was added to each bottle, with 30 ml of the defined nutrient medium (**Appendix C**). To the Plystran-acclimated sludge, concentrations of 24, 16 and 8 g/l Plystran were added, respectively. To the biocide-enriched sludge, solutions of 5 mg/l were added. That is, the sludge in each bottle was exposed to the same conditions as in the previous assay.

The bottles were incubated in a constant temperature room (37 ºC). The assay bottles were shaken manually once a day to facilitate contact between the microorganisms and the substrate. Gas production was measured.

The gas production results were compared to those of the unacclimated sludge. For the tests with the acclimated Plystran sludge, the biogas production results were compared to those of unacclimated sludge, over the same time period (**Figure 7.9**). The initial gas production rates were compared to provide an indication of the improved degradation ability of the acclimated sludge. The lag periods were reduced. In the lower Plystran concentrations (16 and 8 g/l) degradation was almost instantaneous, whereas with the unacclimated sludge there was a lag period of ca. 20 to 30 d.. In the 24 g/l concentrations the lag period was reduced from ca. 80 d to ca. 5 d.



(a) **(b)**

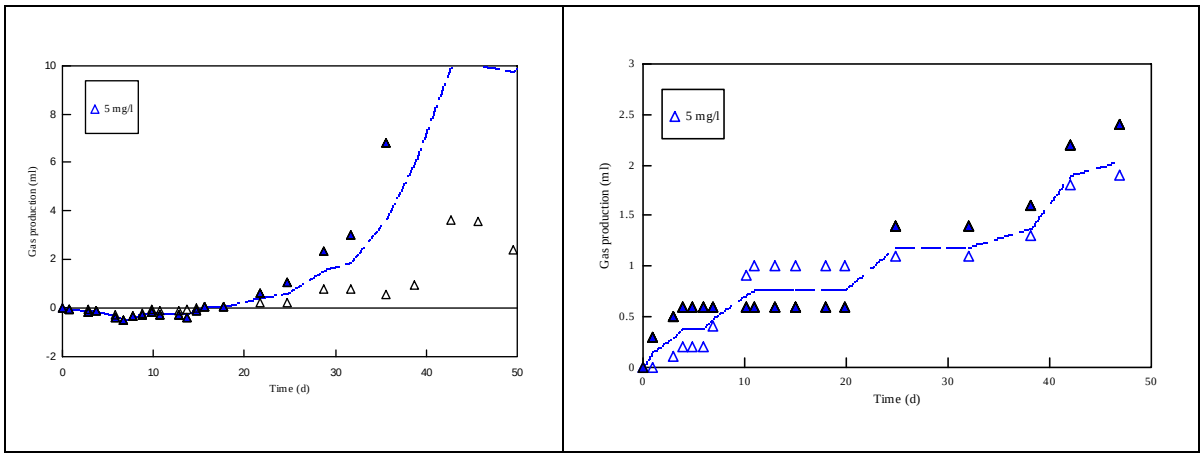
FIGURE 7.9 : Comparison of the biogas production curves for the three Plystran concentrations seeded with the unacclimated (a) and acclimated (b) sludge.

The initial biogas production rates were compared (**Table 7.39**). The results showed higher biogas production rates with the acclimated sludge, i.e. the acclimated sludge was able to degrade the Plystran more readily than the unacclimated sludge. The reaction rates, with the acclimated sludge, all tended towards the rate of the 8 g/l Plystran concnetration.

TABLE 7.39 : Comparison of biogas production rates between the unacclimated and acclimated Plystran sludges.

		Unacclimated	Acclimated
Plystran concentration (g/l)	**Digestion phase**	**Rate (ml/d)**	**Rate (ml/d)**
24	Initial	0.02	0.103
16	Initial	0.03	0.1
8	Initial	0.08	0.098

The same procedure was followed with the biocide-acclimated sludge. The 50 mg/l biocide concentration was not investigated as, from the previous assays, it was deduced that this concentration was completely inhibitory to the biomass. In the previous assay, the 5 g/l biocide concentration was readily degraded thus this concentration was not investigated with the acclimated sludge. In the previous assay, without the acclimated sludge, the lag period of the 5 g/l biocide concentration was ca. 25 d. This was reduced to ca. 5 d with the acclimated sludge which showed that the biocide was more readily degraded, upon acclimation (**Figure 7.10**). The initial reaction rate was calculated at 0.06 ml/d, whereas in the assay with the unacclimated sludge, the biogas production rate was zero until ca. day 25.



(a) **(b)**

FIGURE 7.10 : Comparison of the biogas production curves for the 5 mg/l biocide concentration seeded with the unacclimated (a) and acclimated (b) sludge.

These tests showed that biomass can be acclimated to a potentially toxic, or inhibitory, substrate. Acclimation facilitates degradation of the substrate, at concentrations that were previously inhibitory, with reduced lag periods and increased reaction rates.

7.6 SCALE-UP

The batch tests are a screening mechanism to provide an indication of the anaerobic degradability and potential toxicity of a substrate. These results could be used for prediction of digester operation and process efficiency in the full-scale. Conditions change during scale-up and this should be taken into consideration when predicting operation on the full-scale. To provide a more accurate indication, the serum bottle tests could first be scaled up to a larger semi-continuous or continuous laboratory-scale reactor. This would facilitate prediction of the kinetic parameters in the semi-continuous or continuous feed mode of the full-scale digester.

Problems are associated with scale-up of a process. An example of a scale-up problem in the biotechnological field is that of a reduced yield obtained at large scale compared to the small scale results (Luyben, 1997). As a consequence of scale-up mixing, mass transfer and heat transfer will be more problematic and result in the microorganism *seeing* a different micro-environment. Basically the problem with scale-up is a problem of transfer (mass, momentum or heat) and the lack of knowledge with respect to the interaction of hydrodynamics and other relevant sub-processes in a large scale process. The best approach is to develop an adequate scale-up methodology based on the results obtained at experimental scale (Luyben, 1997).

To achieve this, a 20 l laboratory-scale reactor could be set up. The set-up and operation of the 20 l reactors is described in **Appendix I**.

7.6.1 Full-scale prediction

The laboratory-scale tests should allow for the prediction of the feasibility of the treatment of a particular substrate in a full-scale anaerobic digester, with indication of the volumes and concentrations that could be treated effectively.

At the commencement of the treatment process the volume of effluent in the feed should be low with a gradual increase to allow for acclimation of the biomass. If possible, the effluent should not be mixed with the feed sludge prior to feeding the digesters as the high concentrations could be detrimental to the bacteria present in the feed sludge. The effluent should be fed separately.

A thorough process evaluation and performance efficiency assessment should be carried out prior to the loading of an additional substrate in a digester. High-strength or toxic organic effluents should only be fed to digesters that are operating efficiently. The digetser sludge should be monitored regularly and biogas should be monitored to assess the efficiency of the degradation process.

The serum bottle tests allowed for the identification of inhibitory components of the textile size effluent. Although the synthetic size solution was degraded, the batch tests indicated that high concentrations of the size solution could result in an organic overload on the digesters. The Frametex mill produced ca. 10 m^3s ize effluent per day, with a measured COD of ca. 112 000 mg/l. If all 10 m^3 of the size effluent was loaded into an anaerobic digester at the Umbilo Sewage Purification Works (1 340 m^3), the organic load, from the effluent, would be 0.8 kg COD/m^3.d. This load is relatively high and could cause the microorganisms to go into shock if they are

not introduced to the substrate gradually. Treatment of this load is feasible, however, since in the serum bottle tests, the equivalent load for the normal size solution was 23.7 kg COD/m^3 and 35.6 kg COD/m^3 in the high size solution. Both of these concentrations were degraded by the biomass. Thus, the textile size effluent has the potential for treatment in an anaerobic digester.

Chapter 8

Conclusions and Recommendations

From this investigation of the anaerobic digestion of high-strength or toxic organic effluents in available anaerobic digester capacity, the following can be concluded:

1. The implementation of **cleaner production** and waste minimisation strategies should facilitate the identification of point source emissions. The high-strength or toxic organic components of the effluent could then be segregated from the bulk effluent and concentrated on-site. These concentrated components could be recycled in the process. Upon segregation, the remainder of the trade effluent should meet the General Standards for disposal to sewer. The concentrated wastes could be tankered separately for treatment in available anaerobic digester capacity.

2. A survey of 24 wastewater treatment plants was undertaken which included a total of 56 anaerobic digesters. The survey identified the availability of hydraulic or organic capacity. It was proposed that this available capacity could be utilised for the treatment of high-strength or toxic organic effluents, produced by industries in the vicinity of the wastewater treatment works. Six of the investigated treatment plants had digesters that were not utilised at all with a total available volume of 21 223 m^3. The average residence time of all of the investigated digesters was 61 d which was 36 d longer than the nominal retention time of 25 d. This indicated that the digesters were under-loaded. Using the design criteria of 25 d hydraulic retention time and 3 kg VS/m^3.d organic load, on average the digesters were 32 % hydraulically under-loaded and 58 % organically under-loaded.

3. Industries producing high-strength or toxic organic effluents were identified and selected industries were visited. Disposal of these types of effluent is problematic if the General Standards for disposal into a sewer system are not met. The solution generally involves costly tariffs, dilution of the wastewaters with valuable potable water, marine discharge or co-disposal into municipal landfill sites. Anaerobic digestion has been shown to have the potential to treat effluents of this nature. Microorganisms have the ability to acclimate to xenobiotic or toxic substrates which provides the potential for the anaerobic degradation of most substrates. The survey concentrated on two regions, viz. Durban South and Pinetown, due to the availability of anaerobic digestion capacity at the Southern, and Umbilo and New Germany Works, respectively. Industries producing an effluent with a COD > 2 000 mg/l were included in the survey. A matrix was compiled in which available digestion capacity was matched with potential effluents for treatment. From the investigation of the industries and the composition of effluents it was concluded that there was the potential for the utilisation of available resources to effectively stabilise effluents which otherwise could have an adverse effect on the environment.

4. The laboratory-scale screening test was based on the method of Owen et al. (1979) which was found to be a suitable method for the easy assessment of the anaerobic degradability and potential toxicity of a compound. These assays facilitated the determination of whether the loading of a substrate into an anaerobic digester would be detrimental to its operation and provided information on volumes and

concentrations of an effluent that could be treated effectively. Material and energy balances provided an indication of the efficiency of the digestion process in the serum bottles.

5. The batch tests should run for a period of ca. 30 d. The method is simple to apply and is no more time-consuming than standard analytical procedures e.g. COD determination. No specialised equipment is necessary, apart from a gas chromatograph for gas composition analyses.

6. Detailed evaluation of the anaerobic digesters at the Umbilo Sewage Purification Works (USPW) identified available capacity in terms of both hydraulic and organic load. This was determined by investigation of the flow to the digesters and the properties of the feed sludge. The hydraulic load to the USPW was 75 % of the design capacity (it was designed to treat a flow of 23.2 Ml/d but was only treating 17.38 Ml/d) hence the load the anaerobic digesters was below capacity. The anaerobic digesters were high-rate digesters in that they were heated and mixed. They could, therefore, receive an organic load of between 1.5 and 3 kg VS/m^3.d. The annual average feed to the digetsers was 1.12 kg VS/m^3.d which indicated that the digesters were organically underloaded.

7. The stability of the Umbilo digestion process was assessed by analysis of the characteristics of the digester sludge. Operation of the digesters was efficient. Similar analyses were performed at the other wastewater treatment works to determine the performance efficiency and highlight under-performance. This facilitated the recommendation for remedial action and the ultimate improvement of utilisation of digestion facilities.

8. Tracer tests are useful to assess the mixing and flow patterns within an anaerobic digester as well as the quantification of active volume. A residence time distribution test was performed on an anaerobic digester at the USPW. The tracer test indicated that the entire digester volume was utilised thus indicating the absence of dead volume. The mixing process was efficient with the reactor approximating a perfect completely stirred tank reactor (CSTR). A sludge bypass of 1.94 % of the flow was detected. This should be remedied to prevent the presence of undegraded substrate in the final effluent.

9. The laboratory-scale test protocol was applied to assess the anaerobic degradability of a textile size solution. The size solution was chosen due to its high organic strength (ca. 120 000 mg/l) and because the textile mill producing the effluent was located in the vicinity of the USPW. The effluent was being tankered approximately 40 km for marine discharge. The serum bottle tests showed that the size solution was anaerobically degradable. Interactions between microbial populations together with co-metabolism resulted in the efficient degradation of the substrate even though components of the size solution were found to be inhibitory to the biomass. Acclimation experiments were undertaken with the inhibitory size components since it is known that microorganisms have the ability to acclimate to inhibitory substrates so that they can be degraded at concentrations which were previously inhibitory. These results indicated the potential to treat of the textile size effluent in the available anaerobic digester capacity at the Umbilo Sewage Purification Works.

Based on the above conclusions, the following work is recommended:

1. The anaerobic digester performance evaluation should be extended throughout the country. The utilisation of these available resources would generate income which could be used for social improvement such as the provision of sanitation.

2. A thorough survey of industries with emphasis on the identification of point source emissions within the factories should be undertaken. This would facilitate the segregation and concentration of the high-strength or toxic effluent components on-site. These could then be tankered to a nearby wastewater treatment works for anaerobic treatment in available capacity.

3. Segregation of high-strength or toxic components on-site would promote cleaner production strategies such as recycling. Raw material substitution could also be implemented. This involves the replacement of recalcitrant components with biodegradable substitutes.

4. The information from the effluent survey could contribute to the proposed national database on effluent production and characteristics.

5. Assessment of the cost-effectiveness of the proposed treatment option and logistical considerations, such as road quality and maintenance with increased usage by tankers, should be undertaken.

6. There should be long-term monitoring of effluent degradation by the staff at the wastewater treatment works.

7. Research into the concentration, or thickening, of digester sludge for the efficient utilisation of digester volume should be carried out. Investigation of the computational fluid dynamics of an under-performing digester could also contribute to improved process efficiency.

8. Detailed research in anaerobic modelling systems should be undertaken.

9. The serum bottle test should be scaled up to a 20 l laboratory-scale reactor to provide more accurate information for prediction of operation in a full-scale digester. The set-up and operating procedure for these tests are presented in **Appendix I**.

10. The described protocol should be employed in the laboratories at the respective wastewater treatment works for the assessment of effluents prior to their acceptance for anaerobic digestion.

11. The closure of the Bulbul Road landfill site to co-disposal has necessitated the co-disposal of toxic wastes onto the unlined Bisasar landfill site, in Springfield Park. Approximately 200 m^3 of liquid wastes are being discharged to this site per day. This poses grave environmental problems in terms of contamination of the groundwater and rivers. There is the potential for these effluents to be treated in available anaerobic digester capacity thereby safeguarding the environment. This recommendation was supported by Durban Solid Waste.

12. The implementation of anaerobic digestion of liquid wastes, instead of co-disposal, should promote a reduction in the leachate production problems experienced at the landfill sites.

13. Dedicated or specialised digesters could be developed to treat the toxic effluents on-site. Acclimation of the biomass would facilitate efficient pre-treatment of the effluent, which could then be discharged to sewer. The digesters would be under the control of the local authority who would monitor the effluent quality. This would reduce transportation risks.

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