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Ph.D. THESIS

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MONITORING AND CONTROL OF ANAEROBIC DIGESTERS TREATING
INDUSTRIAL EFFLUENTS

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**Abstract.**

Increasing charges by the private utilities for the treatment of industrial waste water are making on-site effluent treatment more attractive. On-site anaerobic digestion is increasingly being used by food processing factories as a cost effective solution to waste liquid waste disposal. Discharge of treated effluent to sewer or water course requires compliance to a maximum admissible concentration (MAC) value, therefore, there is a need for careful control of on-site waste water treatment. This research investigates the treatment of effluent from instant coffee production. This results in a liquid waste that contains recalcitrant and toxic compounds formed during the roasting process. This waste varies in strength and composition according to the different processes that are performed in the manufacture of instant coffee. Anaerobic filters are particularly attractive for wastes containing recalcitrant or inhibitory compounds requiring a long sludge age. Therefore, this study was aimed at firstly investigating the treatability of coffee waste, using anaerobic filters; and secondly monitoring and control of the digestion process in order to maintain a constant effluent quality.

The study was carried out in four stages. In the first stage pilot plant ($5m^3$) and laboratory scale (10 l) anaerobic filters were used to investigate the treatability of instant coffee processing effluent. The results from this stage showed that the anaerobic digestion of coffee waste was relatively inefficient; at an organic loading rate of 4.2 kgCOD/$m^3$/day only 65% of the COD was removed, in addition there was a low average methane yield of 238 l/kgCOD. These efficiencies are low compared to results from the anaerobic digestion of other food processing wastes.

In the second stage of the study the efficiency of an adaptive control algorithm was investigated. The results show that the control strategy is able to maintain a constant digester effluent quality during fluctuations in feed strength and the increase in concentration of two toxic substances (pyrogallol and furan). The control was, however, unable to prevent the souring of a digester treating coffee waste with an increased concentration of 1 g/l pyrazine. The monitoring of other potential control

parameters identified hydrogen as being able to detect digester stress earlier than the process indicators used in the original control algorithm.

Therefore, in the third stage of the study, hydrogen was incorporated into the control strategy. The performance of the new control strategy was tested by the application of both toxic shock loads (1 g/l pyrazine) and increases in organic strength of the feed. The results confirmed that hydrogen concentration is an important control parameter to rapidly detect digester upset, particularly in the case of toxic inhibition. Hydrogen concentration was shown to be less useful in the case of increased organic loading in which case COD was still the most important parameter. A disadvantage of hydrogen as a control parameter is that it decreases to normal operational levels before the digester has fully recovered. It is therefore most useful when combined with other parameters, such as COD/VFA which do not respond as quickly, but are better indicators of longer term digester instability.

In the final stage of the study the potential of another control strategy based on an artificial intelligence technique was investigated. A neural network control strategy was programmed using data from laboratory scale experiments and tested on data from the pilot plant. The results showed that only small periods of training (30-40 hours) were required to provide a logical control response. The neural network was also shown to be capable of responding to fluctuations in control parameters outside the range of data used during its training. This showed that a neural network trained to work on laboratory digesters can be used to control pilot plant digesters without additional training being required.

## ABBREVIATIONS

| | |
|---|---|
| ABR | Anaerobic baffle reactor |
| AF | Anaerobic filter |
| AI | Artificial intelligence |
| ALK | Alkalinity |
| ANN | Artificial neural network |
| ADP | Adenosine diphosphate |
| ATP | Adenosine triphosphate |
| BOD | Biological oxygen demand |
| Ca. | Circa |
| $CH_4$ | Methane |
| $C^1$ | Compounds containing a single carbon atom |
| CO | Carbon monoxide |
| $C_o$ | Initial concentration of tracer |
| $CO_2$ | Carbon dioxide |
| COD | Chemical oxygen demand |
| $COD_{(I)}$ | Indirect measurement of COD using SS and TDS probes |
| CSTR | Continuous stirred tank reactor |
| $C_t$ | Concentration of tracer at time t |
| $\Delta G$ | Standard free energy change of a reaction |
| d | Day(s) |
| D | Dilution rate |
| $D_{(H)}$ | Dilution rate incorporating hydrogen concentration |
| DNA | Deoxyribosenucleic acid |
| DS | Dried solids |
| EPSRC | Engineering physical science research council |
| g | Gram |
| GC | Gas chromatography |
| h | hour(s) |
| $H_2$ | Hydrogen |

| | |
|---|---|
| $H_2S$ | Hydrogen sulphide |
| FB | Fluidised bed |
| $K_c$ | Waste specific constant for estimated $COD_{(t)}$ calculations |
| kJ | Kilojoule |
| kWh | Kilo watt hour |
| l | Litre |
| ml | Millilitre |
| mV | Millivolt |
| $NAD^+$ | Nicotinamide-adenine-dinucleotide (oxidised form) |
| NADH | Nicotinamide-adenine-dinucleotide (reduced form) |
| $NADP^+$ | Nicotinamide-adenine-dinucleotide-phosphate (oxidised form) |
| NADPH | Nicotinamide-adenine-dinucleotide (reduced form) |
| norm. | normal |
| OLR | Organic loading rate |
| ORP | Oxidation-reduction potential |
| $p$ | Partial pressure |
| PC | Personal computer |
| ppb | Part(s) per (American) billion |
| pH | minus log of the hydrogen ion concentration |
| ppm | Part(s) per million |
| q | Methane production rate |
| SERC | Science and Engineering Research Council |
| SLP | Substrate level phosphorylation |
| SS | Suspended solids |
| t | time (days) |
| $t^*$ | average residence time (days) |
| TDS | Total dissolved solids |
| TOC | Total organic carbon |
| UASB | Upflow anaerobic sludge blanket |
| VSS | Volatile suspended solids |

## ACKNOWLEDGEMENTS

Frankie Mouse:

"Well, I mean, yes idealism, the dignity of pure research, the pursuit of truth in all its forms, but there comes a point I'm afraid when you begin to suspect that if there's any real truth, it's that the entire multi-dimensional infinity of the universe is almost certainly being run by a bunch of maniacs. And if it comes to a choice between spending another 10 million years finding that out and on the other hand just taking the money and running, then I for one could do with the exercise."


Quote from Don't Panic, Neil Gaiman. Cut from The Hitch Hikers Guide to the Galaxy TV series episode 5-6, by D. Adams.

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## 1. INTRODUCTION

Anaerobic digestion is the process of degradation of complex organic matter to end products of methane and carbon dioxide by a consortium of bacteria in the absence of oxygen. Anaerobic digestion was first applied at a large scale in the UK to treat strong sludges at the turn of the century (McCarty, 1982). Since then the anaerobic process has become the most popular method of sewage sludge treatment. More recently anaerobic digestion has become the focus of interest for treating strong industrial effluents and for generating renewable energy. Moreover, increasing charges by the private water companies in Britain for the treatment of industrial waste water has made on-site anaerobic waste treatment more attractive. Waste treatment is a particular problem for food processing factories where water quality requirements restrict the possibility for recycling and conservation. These wastewater producers are therefore turning to on-site anaerobic digestion as a cost effective solution. To date, both common types of bioreactors, biofilms as well as mixed (CSTR) have been used, however, anaerobic filters are particularly attractive for wastes containing recalcitrants requiring a long sludge age. The number and types of full-scale anaerobic reactors treating food processing waste in Europe are shown in Figure 1.1 (Nyns, 1994). This process has several advantages over traditional aerobic methods, such as the production of a useful by-product (biogas), low sludge production and no aeration requirements. However, factors such as fluctuating organic load and potential toxins in industrial waste water are especially problematic for on-site treatment, especially as the anaerobic micro-organisms are slow growing. Food processing produces effluents that often vary in quality and quantity over short time periods and occasionally pose further problems by containing components toxic or inhibitory to the anaerobic micro-organisms. This can lead to instability of the treatment process resulting in inefficient breakdown of pollutants and, in the case of anaerobic digestion, souring of the reactor. For these reasons monitoring and control of anaerobic digesters treating industrial waste waters is desirable (Switzenbaum et al., 1990). Furthermore, it is now common European practice to require a 90-95% discharge compliance to a maximum admissible concentration (MAC) value, which reinforces the need for careful control

of waste water treatment. The control objective would be to regulate final effluent quality at a prescribed level irrespective of fluctuating loads or to keep another parameter within a desired range, for example gas production or quality.
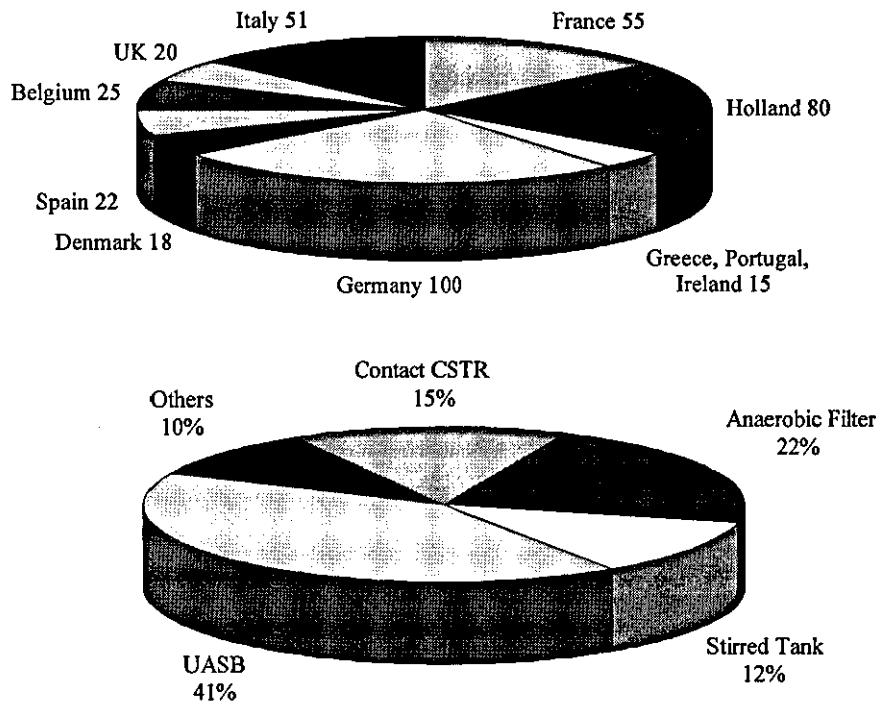


Figure 1.1 Numbers and types of anaerobic digester by country treating industrial effluent.

## 1.1 Review of Anaerobic Reactor Types

The basic CSTR anaerobic digester design has been used for the anaerobic digestion of sewage sludge for nearly 100 years. Since the 1960s industrial effluent has been treated by the anaerobic contact process. The other anaerobic digester designs, shown in Figure 1.2 and Table 1.1, have been more recently developed specifically for the treatment of industrial wastewaters. The anaerobic filter was developed in the 1950's and reintroduced by Young and McCarty in 1969. It is used primarily for industrial wastewater treatment. There are also other designs which are either modifications or combinations of the basic configurations (UASB and fluidised bed).

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Table 1.1 Overview of anaerobic digestion reactor configurations.

| Anaerobic Reactor Type | Advantages | Disadvantages | Application |
|---|---|---|---|
| CSTR | Simple and well tested technology | Slow rate process requires a larger tank and therefore footprint. | Wastewater and sludge digestion (Ross et al., 1992) |
| Anaerobic contact | Reduces HRT required by CSTR by settling and return of biological solids | Susceptible to toxic inhibition because bacteria not attached to any support | Industrial and sewage treatment |
| Anaerobic Filter | Anaerobic bacteria attached to support media are less susceptible to toxic inhibition | Not suitable for high solids wastewaters and high price of many carrier materials increases cost | Industrial waste water treatment (Young and Yang, 1990) |
| UASB | Achieves good contact between the wastewater and sludge without mixing | May not be suitable for wastes containing high concentrations of fat and grease and other solids | Industrial waste water treatment (Souza et al., 1992) and domestic wastewater treatment (Vieira et al., 1994) |
| Fluidised Bed | High rate process capable of 25 kg/m$^3$/d | Pumping costs are high because of necessity of keeping bed of bacteria fluidised. Few examples at full scale exist - may be stability problems | Industrial waste water treatment (Holst et al., 1995) |
| Anaerobic Baffle Reactor | High rate hydraulic throughput possible | Few full scale examples | Short hydraulic retention time makes this suitable for a wide variety of wastes |

page 4 diagrams of reactor types.

## 1.2 Project outline

Anaerobic treatment technology in the UK still lags behind that of several European neighbours (Figure 1.1). In order to raise the profile of anaerobic digestion in the UK and to encourage collaboration between some of the key researchers in the subject the EPSRC (formerly SERC) funded a programme of research based on a central facility of a large pilot plant. The pilot plant consisted of a CSTR, a UASB, an anaerobic filter, and a fluidised bed reactor (these are described in greater detail in the methods chapter). The facility has operated on two industrial sites : at the Birds-Eye Walls factory in Gloucester, treating ice-cream waste, and at the Nestle factory in Hayes, treating instant coffee processing effluent, and is currently treating landfill leachate. For the duration of this study the pilot plant was used for a comparative study of the anaerobic digestion of instant coffee processing waste. Five universities have been involved in research conducted into various aspects of anaerobic digestion at the facility, and a number of papers have been published containing the results of these studies (Table 1.2). The pilot plant was run for approximately three years, manned full-time by two technicians. Laboratory scale studies were performed in parallel to the pilot plant experiments. Based on information from laboratory experiments and relevant literature, the operation of the pilot plant was directed by a project management team from the universities. This thesis is concerned with the monitoring and control of anaerobic digestion for the treatment of instant coffee processing effluent.

The monitoring and control of anaerobic digesion was investigated using both the pilot plant facility and laboratory scale anaerobic digesters. The Loughborough laboratory has extensive previous experience in operating anaerobic filters to investigate the anaerobic digestion of industrial wastes. Moreover, the pilot plant anaerobic filter had given the best performance compared to the other pilot plant digesters in the previous EPSRC study. Therefore, anaerobic filters were chosen for the main focus of this study.

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Table 1.2. Publications resulting from EPSRC anaerobic pilot plant facility.

| University | Area of research | Publications arising from project |
|---|---|---|
| Loughborough | Monitoring and control | Johnson *et al.*, 1995, Johnson et al., 1994, Monroy *et al.*, 1994. |
| Imperial College London | Recalcitrants | Azhar and Stuckey 1994, Azhar and Stuckey 1993. |
| Glamorgan | Waste degradability | Hawkes *et al.*, 1992, Hawkes *et al.*, 1995, Dinsdale *et al.*, 1996. |
| Birmingham | UASB granule formation | Morgan *et al.*, 1990, Daoming and Forster 1993, Daoming and Forster 1994, Ugurlu and Forster 1991, Ugurlu and Forster 1992. |
| Newcastle | Two stage operation (preacidification) | Alexiou *et al.*, 1994, Anderson *et al.*, 1994. |

## 1.3 Thesis Outline

The anaerobic digestion of instant coffee processing waste is known to be problematic. Therefore, it is necessary to understand the microbiology and biochemistry of the anaerobic process in order to develop an adequate approach to digester control which will maintain digester effluent quality. Therefore, in the subsequent chapters the following subjects are discussed and reviewed:

- The microbiology and biochemistry of anaerobic digestion

- Chemical and physical factors affecting anaerobic digestion

- Monitoring of the anaerobic digestion process

- Control of anaerobic digestion

- Anaerobic digestion of toxic and recalcitrant compounds

- Coffee processing effluent

Results are presented and discussed from the following experiments

- Monitoring of the pilot plant

- Monitoring and control of the laboratory scale digesters

- Incorporation of hydrogen as a control parameter

- Neural network training and testing

Finally, conclusions are drawn from the results and further recommendations are made regarding the monitoring and control of anaerobic digestion.

## 2. MONITORING AND CONTROL OF ANAEROBIC DIGESTION

There are two basic control philosophies. One is a empirical black box approach, which utilises previous operational experience. The other is a mechanistic analysis identifying rate limiting pathways using thermodynamics or kinetics. This latter technique requires extensive research to fully understand the processes involved. The choice of control strategy and process control indicators to be used must be based on the characterisation of the anaerobic digestion process. This chapter reviews information relating to the microbiology, process biochemistry and chemical and physical factors affecting anaerobic digestion. Examples describing control strategies for anaerobic digestion are reviewed. Suitable control strategys are identified from these examples. A detailed review of the response of control parameters to fluctuations of feed composition and strength has been collated. Using this knowledge anaerobic digestion is characterised and suitable parameters chosen for control.

### *2.1 The Microbiology and Biochemistry of Anaerobic Digestion*

A wide range of electron transfer shuttles and intermediates are used in the anaerobic degradation of organic matter, resulting in a complicated biochemistry. The anaerobic digestion process can be divided into four basic steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Figure 2.1). Different consortia of micro-organisms perform each stage. At least four physiologically different bacterial populations must be present for the overall conversion of organic matter to methane and carbon dioxide. Many of the intermediate stages are solubilisation and biotransformation steps resulting in little carbon removal.

Anaerobic micro-organisms require an oxygen free environment; they are inhibited and in some cases killed in the presence of oxygen. Thermodynamically, anaerobic oxidation/reduction is less efficient than aerobic respiration. When oxygen is the electron acceptor it releases more energy during electron transfer reactions. Thus, oxygen is inhibitory to anaerobic micro-organisms because its presence automatically favours aerobic micro-organisms with a more efficient biochemistry.

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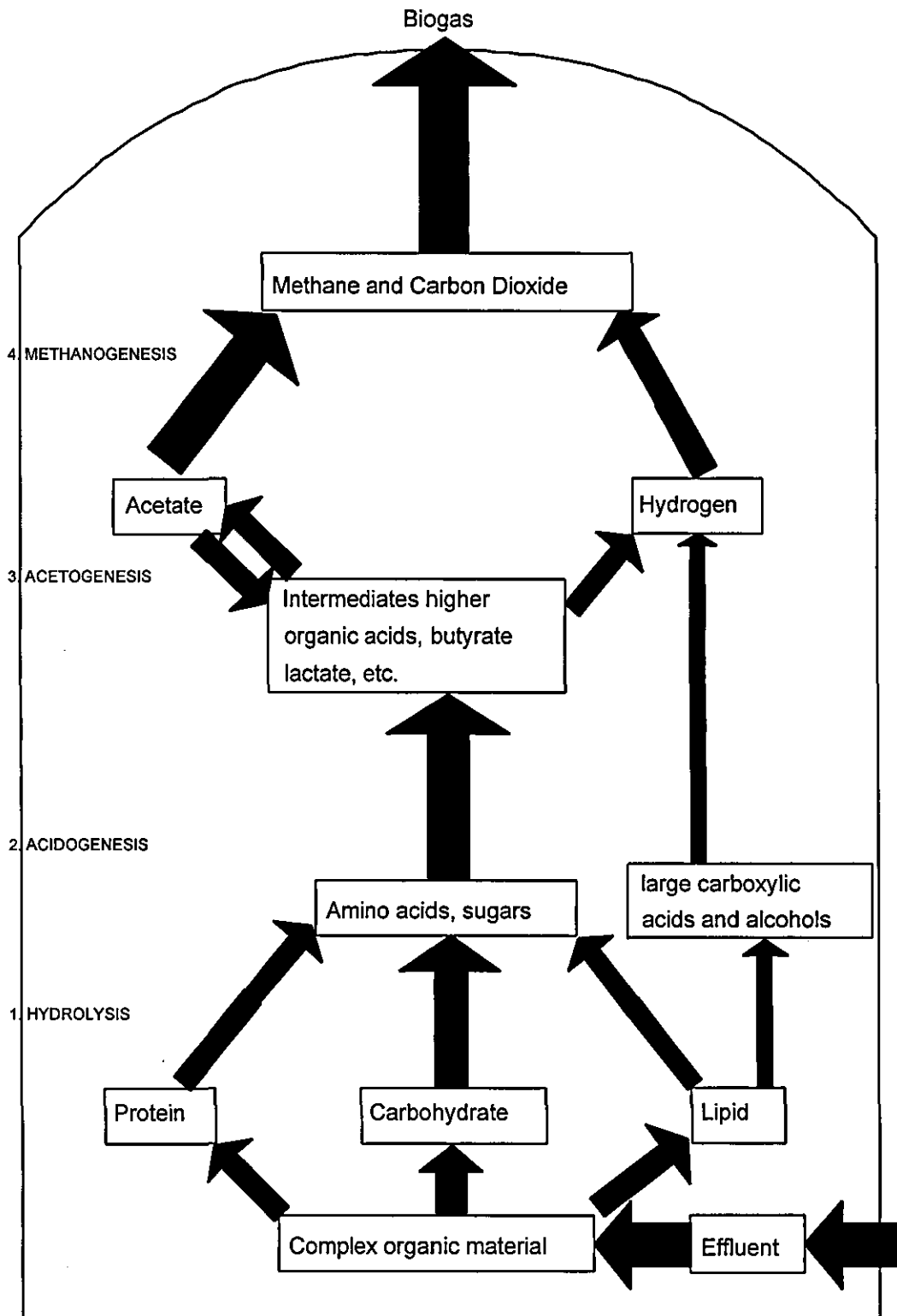
Figure 2.1 Biochemical steps in Anaerobic Digestion.

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### 2.1.1 Hydrolysis

If the wastewater to be treated contains particulate material, initial hydrolysis (liquefaction) is an important reaction (Pohland, 1994). Breakdown begins with bacterial attachment to the suspended solids. Polymers of polysaccharide and cellulose are the most abundant natural solids and polymers. In this first stage of anaerobic digestion a heterogeneous group of micro-organisms, using extracellular enzymes, convert proteins via (poly)peptides to amino acids, carbohydrates are transformed into soluble sugars (mono- and disaccharides) and lipids to long chain fatty acids and glycerine (McCarty *et al.*, 1964). Hydrolysis is, therefore, the rate limiting step in anaerobic digestion of high solids wastes such as sewage sludge.

### 2.1.2 Acidogenesis

The dissolved compounds produced during hydrolysis are rapidly fermented to a variety of simple organic compounds such as volatile fatty acids, alcohols, lactic acid and mineral compounds such as carbon dioxide, hydrogen, ammonia and hydrogen sulphide gas. Acidogenic fermentation involves a diverse group of bacteria, the majority of which are obligate anaerobes. However, some are able to metabolise organic matter via the oxidative pathway (facultative bacteria). The ability to use oxygen by the facultative acidogenic bacteria is important to anaerobic digestion, as dissolved oxygen is removed which might otherwise inhibit obligate anaerobic organisms such as the methanogens.

Holland *et al.* (1987) describes ATP production in anaerobic digestion. The formation of ATP is described as an exergonic process accomplished by the energy release during redox reactions. An electron donor within a cell is oxidised, reducing an intermediate, often NADH, and in turn this reduced coenzyme reduces an acceptor molecule:

$$\text{Donor} \xrightarrow{\quad} \begin{array}{c} \text{NADH} + \text{H}^+ \\ \\ \text{NAD}^+ \end{array} \xrightarrow{\quad} \text{Acceptor}$$
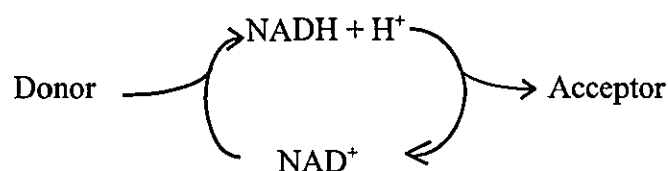
Substrate level phosphorylation (SLP) would be to the left-hand side of the above equation, this is associated with ATP formation via covalently linked energy rich intermediates. The reduced NADH + H$^+$ is oxidised by an organic electron acceptor (see above) and becomes the fermentation end product. In an aerobic organism; oxygen is used as the final electron acceptor. The reduced cofactor NADH + H$^+$ is oxidised; this is coupled to the synthesis of ATP.

$$2 \text{ ADP} + 2\text{P} \qquad 2 \text{ ATP}$$

Glucose (6C)

2 NAD+     2 NADH +    2 pyruvate (3C)

+

2 Lactate (3C)
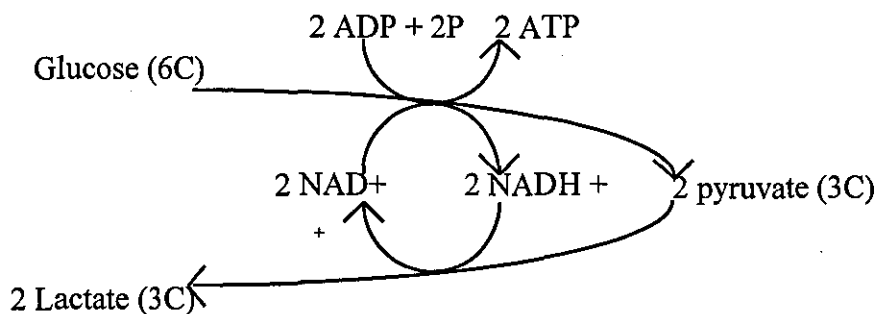
The equation above shows a simplified scheme of substrate level phosphorylation by oxidation of glucose to lactate, lactic acid fermentation (Holland *et al.* 1987).

In the case described above, hydrogen is transferred within one cell. However, during anaerobic digestion hydrogen is also produced by one species and utilised by another; this is called interspecies hydrogen transfer. Holland *et al.* gives the example of the isolate *Methanobacillus omelianskii* as a consortium of two anaerobic species found in sewage digesters.

Although hydrogen is produced in large amounts, it is rapidly consumed, and can be considered as a very convenient vehicle for transport of electrons from one organism to another. The efficiency of such interspecies hydrogen transfer is such that very little hydrogen escapes into the immediate environment (Sparling and Gottschalk 1990).

Wolin (1975) summarised the most significant aspects of hydrogen production and methane formation as: Hydrogen production provides an energy source for the methanogens, which all use hydrogen to reduce carbon dioxide to methane and thereby obtain energy for growth. The rapid use of hydrogen for methanogenesis, by methanogens, maintains a low partial pressure of hydrogen, which is necessary for the

production of this gas from some thermodynamically poor precursors. Although methanogenesis is not obligatory for the metabolism of substrates by some fermentative bacteria, it permits the flow of electrons from NADH away from the formation of electron sink products, e.g. succinate, lactate and ethanol. In general, this causes a shift of flow of pyruvate carbon from these electron sink products to acetate.

Methane producing bacteria use acetate or carbon dioxide and hydrogen as their main substrates (Mosey 1983). They are reliant, therefore, on other bacteria to convert more complex carbon compounds to acetate, hydrogen and carbon dioxide before they can finally produce methane. Fermentation of various compounds leads to the production of these two methanogenic substrates; however, other reactions occur during acidogenesis that produce fatty acids (propionate, butyrate) and/or amino acids (e.g. alanine, leucine).

### 2.1.3  Acetogenesis

Intermediates from hydrolysis and acidogenesis that the methanogenic bacteria are unable to utilise, such as alcohols, fatty acids and aromatics, are further degraded into the final products for methane production: acetate, hydrogen and carbon dioxide by acetogens (obligate hydrogen producing bacteria). The breakdown of these products to hydrogen, carbon dioxide and acetate is endergonic under standard conditions. However, in the anaerobic digestion environment, standard conditions do not apply because hydrogen is constantly removed by the methanogens.  Hydrogen concentration greatly influences $\Delta G$.  At low partial pressures (concentrations) of hydrogen, below $p\mathrm{H}_2$ of $10^{-4}$ atm (10.1 Pa or 10100 ppm), the oxidation of propionate becomes exergonic and the acetogenic bacteria can grow at the expense of the reaction (see Table 2.1). $\Delta G$ goes from +74 under standard conditions to -1 kJ/reaction when the hydrogen is consumed (Zender and Stumm, 1988).  This synergistic interaction between methanogens and acetogens is known as interspecies hydrogen transfer.

As the acetate and hydrogen must be continuously removed by methanogens to make the reactions involved in this breakdown thermodynamically viable, the two groups

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are mutually dependent on each other (syntrophism). Intensive cell contact between the acetogenic and methanogenic bacteria is required to allow interspecies hydrogen transfer. This symbiotic relationship between the two organisms is referred to as an obligate syntrophic nutrient exchange and is necessary as methanogens are unable to use more complex substrates than $C^1$ carbon compounds, acetate, and hydrogen. Only the acetogens and methanogens are strictly anaerobic, but the symbiotic fermentations which occur generate a very low redox potential in the digester which favours the anaerobes.

Thauer *et al.* (1977) reported a second type of acetogenic bacteria named the nomoacetogens. These produce acetic acids and longer chain fatty acids by reducing carbon dioxide with hydrogen via the intermediate acetyl coenzyme.

Table 2.1  Influence of hydrogen partial pressure (concentration) on the free energy of some typical hydrogen producing reactions catalysed by syntrophic microbial associations under methanogenic conditions.

| Reaction description | Reactants | Products | $\Delta G$ (kJ/reaction) std | low $H_2$ |
|---|---|---|---|---|
| Fatty acid oxidation | Propionate + $H_2O$ | $\rightarrow$Acetate + $HCO_3^-$ + $H^+$ + $2H_2$ | +74 | -1 |
| Alcohol oxidation | Ethanol + $H_2O$ | $\rightarrow$Acetate + $H^+$ + $2H_2$ | +2 | -44 |
| Amino acid oxidation | Alanine + $3H_2O$ | $\rightarrow$Acetate + $HCO_3^-$ + $3H^+$ + $NH_4^+$ + $2H_2$ | +8 | -38 |
| Oxidation of aromatics | Benzoate + $7H_2O$ | $\rightarrow$3 Acetate + $HCO_3^-$ + $3H^+$ + $3H_2$ | +53 | -16 |

Mosey's mathematical model of the anaerobic digestion process took into account propionate breakdown inhibition by hydrogen, which was seen by Mosey in previous studies, and reported by Kaspar and Wuhrmann (1978). Kaspar and Wuhrmann found that propionate degradation was inhibited by concentrations of 500-50000 ppm hydrogen in biogas. The model stated that the oxidised form of NAD acts as a rate-limiting substrate causing a 50 per cent decrease in the rate of propionate degradation when the concentration of hydrogen reaches 670 ppm in the gas (Mosey, 1983 and Mosey and Fernandez, 1984).

Wolin and Miller (1982) defined interspecies hydrogen transfer as the coupling or syntrophic relationship between the production of hydrogen by some species (hydrogenogens) and the consumption of hydrogen by other species (hydrogenotrophs). In addition, by utilising hydrogen, hydrogenotrophs can cause hydrogenogens to produce more hydrogen than they would produce in the absence of hydrogenotrophs. Wolin and Miller concluded that hydrogen was not only a product and a substrate in anaerobic fermentations, but also an important regulator. Therefore, the monitoring of the partial pressure of hydrogen was being considered as a sensitive means of early detection of fermentations failure. Detection of very low partial pressures of hydrogen would signal that the fermentation was becoming unbalanced and that syntrophic conversion of butyrate and propionate to methane as well as the interspecies transfer that prevents the formation of these acids was beginning to fail.

Conrad *et al.* (1985) conducted experiments to test a hypothesis that hydrogen produced (by acetogens) was able to equilibrate with a common hydrogen pool before it was utilised by a hydrogen consumer (methanogen). Previously it had not been demonstrated that there was a need for physical contact or juxtapositioning of the syntrophic partners, rather that syntrophism occurred via a common pool of hydrogen. Hydrogen pool size was found to be 205 nM in sewage sludge from an anaerobic digester, the hydrogen turnover rate constant determined as being 103 $h^{-1}$. This observed turnover rate accounted for only 5 - 6% of the expected $H_2$- $CO_2$ derived methane production, whereas the expected contribution was 30%. Therefore, it can be assumed that the rest of the hydrogen was directly transferred between syntrophic associations of hydrogen producers and methanogens that were juxtaposed within a floc or consortium. Given that high partial pressures of hydrogen result in imbalance, the reliance of a juxtaposition of hydrogen consumers would keep a low hydrogen concentration in a microniche. This may enable favourable thermodynamic conditions to persist at a microniche level, despite overall levels of hydrogen. The high bacterial cell densities in UASB granules minimises the distances between bacteria and maximise interspecies transfer of hydrogen. Granular sludge, therefore, gives ideal conditions for syntrophic association of hydrogen producing acetogenic bacteria with methanogens (Schmidt and Ahring, 1993).

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## 2.1.4 Metabolism of methanogenic bacteria

In the final stage (methanogenesis), the acetate, carbon dioxide and hydrogen gases are converted into methane and carbon dioxide by a physiologically unique group of strict obligate anaerobic bacteria termed the methanogenic bacteria. Methanogenic bacteria are widespread in nature and can be found in ordinary garden soil, black mud, the rumen of herbivorous animals (Bryant, 1965), marshes, ponds, lakes and in sewage and sewage treatment processes (McCarty, 1964). Methanogenic bacteria are present in anaerobic digesters in numbers of $10^6$ to $10^8$ per ml. When these numbers are compared with the values of $10^6$ to $10^8$ recorded for obligate anaerobic non-methanogenic bacteria in digesters the numbers of the bacteria of the non-methanogenic phase and those of the methanogenic phase are nearly equal (Toerien *et al.*, 1967).

Methanogenesis is the final step in the production of methane. Methanogens have been shown to use very few substrates; acetate, formate, hydrogen, carbon dioxide, carbon monoxide, methanol and methylamine. Approximately 70-75% of the methane formed comes from acetate (acetoclastic methanogenesis) The remainder comes from hydrogen and carbon dioxide (hydrogenotrophic methanogenesis) (Mosey 1983).

(i) $CH_3COOH \quad CH_4 + CO_2 \quad \Delta Go = 32\,kJ$      Acetoclastic methanogenesis

(ii) $CO_2 + 4H_2 \quad CH_4 + 2H_2O \quad \Delta Go = 139\,kJ$      Hydrogenotrophic methanogenesis
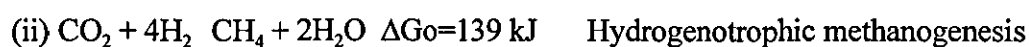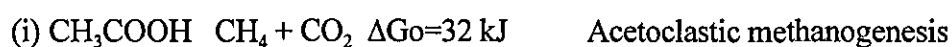
Zeikus (1980) postulated that there may be another group of methanogens which form acetic acid from hydrogen and carbon dioxide which is subsequently converted into methane by acetoclastic methanogens.

Most of the methanogens have been shown to be hydrogenotrophic. This is the preferred pathway since more energy is generated (see above). The methanogens are strict anaerobes and require a very low redox for growth (-330 mV).

Zeikus (1977) reviewed the biology of methanogenic bacteria and concluded that interspecies hydrogen transfer resulted in: (i) increased substrate utilisation, (ii)

different proportions of reduced end products, (iii) more ATP synthesised by non-methanogens, (iv) increased growth of both organisms, and (v) displacement of unfavourable reaction equilibria.

The metabolic feature that unites the rather diverse species of methanogenic bacteria are their capacity to couple hydrogen oxidation with the concomitant reduction of carbon dioxide. Furthermore, the ability of many species to grow autotrophically indicates the diversity of these microbes. Methanogens differ from other autotrophs in that their $CO_2$ metabolism involves both fixation to cell carbon and reduction to methane (Zeikus, 1977).

## 2.2 Chemical and Physical Factors Affecting Anaerobic Digestion

Factors which exert an influence on the digestion process include temperature, presence of oxygen, pH, volatile fatty acid concentration, redox potential, nutritional requirements and inhibitors. Given domestic wastes the anaerobic digestion proceeds with little adjustment or control; with a temperature of 28-35°C and exclusion of air. There are usually sufficient nitrogen and phosphorus, trace minerals and biodegradable carbon for anaerobic digestion. Once active, the pH remains between 6.6 and 7.5 and in the absence of biological inhibitors, the production of methane and the stabilisation of degradable solids continues at a steady state level. The change of one of these factors will result in a significant change in operating characteristics. Many industrial wastes, even those from the food industry, contain compounds that are either recalcitrant and potentially inhibitory. Biocides and caustic soda are commonly used to clean factory equipment and can result in poor efficiency or failure of the treatment plant.

The presence of oxygen in very small quantities will not affect the system if it is removed by the facultative (hydrolytic and acetogenic) bacteria. However, if oxygen or other oxidising agents are present in the reactor at a higher level it will not be completely removed by the facultative bacteria and will have a marked effect on the obligate anaerobic bacteria (methanogens). The pH can be in the range of 2-8 for the hydrolytic and acetogenic bacteria to be active; however the methanogens need a

range of between pH 6.6-7.5 to remain active. The presence of typical industrial reactants, e.g. heavy metals, chlorinated hydrocarbons and anionic detergents, have an inhibitory effect on the reactor population of micro-organisms (Durarte and Anderson, 1982, Rittmann and McCarty, 1980, McAvoy *et al.*, 1993).

## 2.3 Monitoring of the Anaerobic Digestion Process

As with any process operated with a variable feed the anaerobic treatment system must be monitored to ensure successful operation. Instability of the system may be caused by hydraulic and organic overloads, and the presence of inorganic or organic toxic or inhibitory materials. Some of the more commonly used process indicators used to monitor anaerobic digestion include:

- pH,

- volatile acids to alkalinity ratio,

- gas production rates and gas composition (methane and carbon dioxide),

- redox,

- volatile solids,

- COD reductions and

- Temperature.

Usually several of these are monitored together as they supply complementary information. The best operation is achieved by daily monitoring and the charting of trends of these parameters which enables corrective actions to be applied before the process gets out of control. These indicators are effective for detecting gradual changes. They are also useful for detecting process upsets once they are underway. In many instances they may be adequate to avoid process failure for slow-to-develop difficulties. However, shock organic or hydraulic overloads as well as toxic events require prompt corrective response. Rapid techniques are needed to avoid significant process deterioration and failure for these events. This is especially true for the newer high-rate systems which operate at Hydraulic Retention Times (HRTs) as low as 12 h. Instrumentation systems that monitor the process can be categorised into three

groups: in-line, on-line and off-line. In off-line systems discrete samples are removed at pre-set intervals for later analysis. This is usually time consuming and impractical for on-line monitoring and control. On-line systems involve the continuous sampling of a process stream with subsequent analysis. Results are gained fast enough for process control decisions. An example of on-line monitoring is gas analysis. Finally, in-line systems are those which analyse the effluent or process stream giving continuous and rapid results; an example of this is in-line pH and temperature monitoring.

Previous researchers have put effort into developing better indicators for process monitoring (Table 2.2), some of these are off-line and entered manually into a control system. An ideal indicator is easy to measure, available on a real-time and perhaps on-line basis, and has intrinsic meaning as it must reflect the current metabolic status of the system. While much progress has been made in anaerobic treatment of industrial effluent, it is only through the development of better monitoring and control strategies that anaerobic treatment will reach its full potential for waste management.

Table 2.2 Sensors used in control of anaerobic digestion

| Research team | Control strategy | Performance indicators |
|---|---|---|
| Prodruzny and van den Berg. (1984) | adaptive control | gas flow rate |
| Renard et al. (1988) | adaptive control | gas production rate, $CH_4$ in $CO_2$%, pH, temperature and manual COD values |
| Johnson et al. (1995) | adaptive control | gas production rate, SS, TDS, and $CH_4$ in $CO_2$% |
| Alatiqi et al. (1990) | | temperature and total organic carbon of effluent |
| Chynoweth et al. (1994) | expert system | methane yield |
| Slater et al. (1990) | adaptive control | $CH_4$, $CO_2$, $H_2$, CO, VFA $(C_1-C_4)$ temperature, pH, ORP, and gas production rate |
| Wilcox et al. (1995) | neural network | bicarbonate alkalinity |

## 2.3.1 Characterisation of Anaerobic Digestion

The anaerobic digestion process can be pictured as a three-phase process (solid-liquid-gas) (Figure 2.2, as modified from Switzenbaum *et al.*, 1990). Each phase is closely related to the other two, and usually information drawn from one phase can be related to the status of the others. Several parameters have been proposed to characterise the anaerobic digestion process, and they will be discussed below.
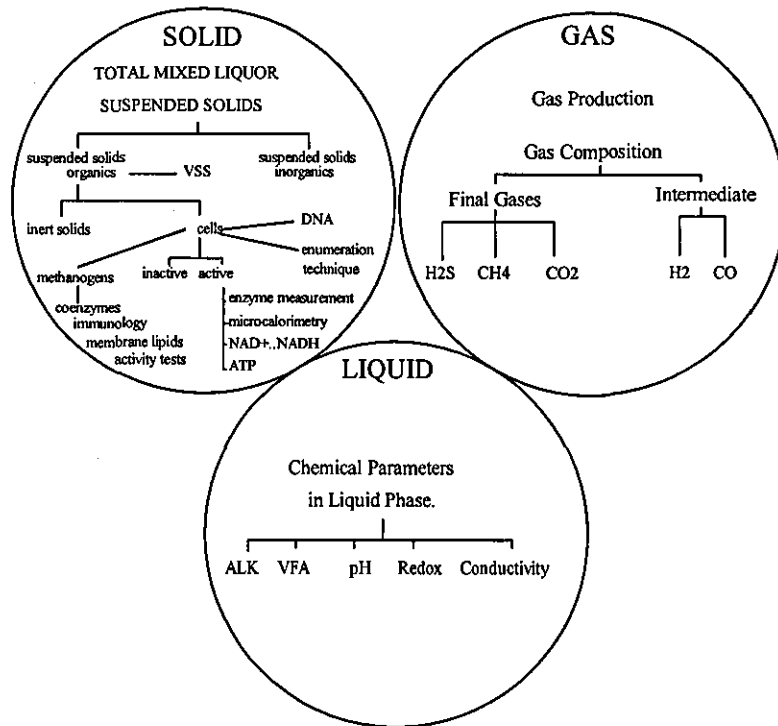


Figure 2.2  The Three Phases of Anaerobic Digestion.

### 2.3.1.1  Solid Phase Characterisation

Solid phase is the combination of non-soluble materials immersed in the liquid phase. This mixture is composed of organic and inorganic solids, the former of which can be divided into inert organic solids and cells (see Figure 2.2). Measurements of the active cells and their current metabolic status are very important parameters in defining the control strategies that can be undertaken. Chemical parameters in the liquid phase provide little, if any, information about the metabolic status of the micro-organisms. Large variations in the microbiological and biochemical characteristics of anaerobic digesters have been found when the liquid phase parameters reflected

steady-state conditions. Possible parameters for the characterisation of microbial status are discussed below.

Table 2.3 Solids phase monitoring parameters.

| Parameter | Reference | Comments |
|-----------|-----------|----------|
| VSS | Hattingh and Siebert, 1967 | VSS were shown to be related to the DNA content of anaerobic sludge, but not suitable for rapid changes in reactor performance. |
| DNA | Delcambe et al., 1983 | Found that determinations of DNA and ATP gave a measurement of biomass which could be related to methane yield. |
| enumeration | Williams and Shih, 1991 | Direct cell enumeration used to investigate population during volatile solids and retention time changes. |
| enzyme measurement | Liwen et al., 1988 | Found good correlation between hydrogenase activity and the methanogenic activity of the sludge tested |
| microcalorimetry | Pauss et al., 1988 | Used a microcalorimeter to find that heat generated decreased as a result of toxic shock loading to a laboratory reactor. |
| ATP/NAD_NADH | Delcambe et al., 1983 | Found that determinations of DNA and ATP gas a measurement of biomass which could be related to methane yield. ATP was more precise and rapid than DNA. |
| coenzymes | Samson et al., 1988 | F-420 probe proved useful in pure bacterial cultures, however, when tested on anaerobic sludge it did not produce satisfactory results due to the dark colour of the sludge. |

- Suspended Solids.

Solids are generally not a good estimation of the active micro-organism population when the feed entering the reactor also contains suspended solids. However, solid measurements are a common control parameter used in domestic sludge digesters (Ross et al., 1992). Volatile suspended solids has been shown to be significantly related to the DNA contained by living cells (Hattingh and Siebert, 1967). However, VSS is not a suitable method for determination of reactor performance during rapid changes in substrate strength or composition due to the slow growth rate of anaerobic bacteria.

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- Cell enumeration.

Direct cell enumeration has been used by researchers to identify microbial groups. Williams and Shih (1991) used direct cell enumeration to investigate the change in populations over time and the effect of different combinations of retention time and volatile solids. The procedures used are elaborate and time-consuming, and are therefore not suitable for regular use. Estimates of cell numbers can be made by more indirect measurements, such as DNA quantification.

- Deoxyribonucleic acid (DNA).

Determination of DNA gives an estimate of the micro-organisms present in the anaerobic sludge. This technique does not distinguish between the different trophic groups in the anaerobic ecosystem, and no information about the metabolic status of the micro-organisms is gained. Correlations have been found between the DNA content of a sludge and suspended solids by Hattingh and Siebert (1967a); but the ease of suspended solids analysis prevented the further exploitation of this technique. Delcambe *et al.* (1983) performed DNA determinations to provide a measurement of biomass which they used to estimate methane yield, but this was only possible when samples were taken from digesters that were perfectly homogenised.

- Protein Content.

This is an indirect way of measuring the microbial biomass. Good correlation was found between the protein content and DNA content of the sludges (Hattingh *et al.*, 1967a and Hattingh *et al.*, 1967b). Protein content yields no information about the metabolic status of the micro-organisms.

- Bacterial lipids.

Certain phospholipids, which are found in cell membranes, can act as indicators of different types of bacteria (Henson *et al.*, 1988). Henson's group have proposed that lipid analysis would provide relevant information about micro-organism numbers, ecosystem composition and nutritional status. The methods are unfortunately destructive, and are not suitable for on-line measurements.

- Adenosine triphosphate (ATP).

ATP has been shown to reflect changes in activity within the digester as well as toxic inhibition by Chung and Neethling (1988). No distinctions can be made, however, between the different populations of bacteria in the digester, and the determination is not suitable to on-line monitoring. ATP was found to be more reliable and precise than DNA to provide a measurement of biomass to estimate methane yield (Delcambe *et al.*, 1983) but had the same drawbacks.

- Enzyme activities.

Activities of enzymes can give an estimate of the substrate flow in the microbial ecosystem. Protease activity was shown to be a good indicator of digester stress during an organic overload by Agardy *et al.*, 1963. Other enzymes were found to show toxic events and organic overload before the accumulation of volatile acids occurred (Ashley and Hurst, 1981), and to provide an estimation of the active biomass in anaerobic digesters (Lenhard, 1968). More recently Liwen *et al.* (1988) found good correlation between hydrogenase activity and the methanogenic activity of the sludge tested. Despite the usefulness of enzyme activity tests to show metabolic status of the biological phase, they are not at the present suitable for on-line monitoring.

- Methanogenic activity measurements.

These tests evaluate the maximum potential utilisation rate of intermediate products in the anaerobic digestion process, which allows an estimation of the size of the different populations in the consortium and provides a diagnosis of the status of the micro-organisms. These assays are not on-line and require hours to be performed.

- Microcalorimetry.

Heat generated by the micro-organisms as they metabolise has been measured using microcalorimeters to evaluate the activity of the anaerobic digestion ecosystem by Pauss *et al.* (1988). A drop in the heat signal is generated by toxic shock to the reactor. Samson *et al.* (1988) found that 95% of the heat from an anaerobic digester was generated by the acidogenic micro-organisms. This process is suitable for on-line monitoring, but its application to full scale is unproved.

- Co-enzymes and Cl-carriers of methanogens

Quantification of F-420 a coenzyme factor has been used to quantify the presence of methanogens. Samson *et al.* (1988) used a miniaturised fluorescence detector to monitor the level of F-420 on-line. Although the probe was useful in pure bacterial cultures, when applied to anaerobic sludge it did not produce satisfactory results due to the dark colour of the sludge.

- Immunology of methanogens

Macario and Conway de Macario *et al.,* (1988) used monoclonal antibodies (over a 14 month period) to identify methanogens in ecosystems resembling anaerobic digestion and later to measure the quantitative and qualitative changes of methanogenic subpopulation in a high rate anaerobic bioreactor. This system may be a useful tool for investigating the ecology of a digester but is unable to allow on-line monitoring.

### 2.3.1.2  Liquid Phase Characterisation

Liquid phase parameters are most commonly used for monitoring anaerobic digestion. On-line monitoring is possible with all liquid phase characteristics, but calibration, maintenance and probe fouling make their long term use problematic. It is desirable to prevent any variation in the liquid phase caused by reactor imbalances.

Table 2.4  Liquid phase monitoring parameters.

| Parameter | Reference | Comments |
|-----------|-----------|----------|
| pH | Moletta *et al.*, 1994 | pH used as one of three monitoring parameters for the control of lab and pilot scale FB reactors. |
| Conductivity | Chang *et al.*, 1983 | Electrical conductivity was used to monitor the salinity level. |
| VFA | De Haas and Adam, 1995 | Titrimetric VFA results were compared with those from colorimetric and chromatographic methods. |
| Alkalinity | Hawkes *et al.*, 1994 | An automatic analyser and controller was used to monitor and control the bicarbonate concentration in laboratory-scale digester. |
| Redox potential | Mathieu, 1989 | The significance of the redox potential and its measurement and application as a control parameter on effluent treatment processes are discussed. |

- pH

Digesters operate optimally in a pH range of 6.6 to 7.6. Below a pH of 6.2 methanogens are severely inhibited (Ross *et al.*, 1992). A low pH is the result of an event that has already occurred, and as such is not useful as an early indicator of imbalance.

- Volatile fatty acids

Several methods exist for the determination of VFA (De Haas and Adam, 1995), including on-line methods Rozzi *et al.* (1985). VFA accumulation is typical of reactor stress situations and can be a cause of subsequent problems if the system lacks enough buffering capacity to avoid a drop in pH. This group of indicators may be adequate for conventional sludge digestion, but not for high rate system treating liquid wastewaters (Switzenbaum *et al.*, 1990).

- Alkalinity

A direct relationship exists between alkalinity variation and VFA accumulation in anaerobic digestion. Rozzi *et al.* (1994) proposed bicarbonate alkalinity measurement by measuring the carbon dioxide evolved as the sample is decomposed with concentrated acid. Wilcox *et al.* (1995) used automatic bicarbonate alkalinity analysers to monitor and control the bicarbonate concentration in laboratory scale digesters. These analysers have been shown to be more sensitive than pH (Rozzi *et al.*, 1994). However, the utility of alkalinity as a control parameter in anaerobic digesters under toxic stress scenarios has not been established (Switzenbaum *et al.*, 1990). On-line bicarbonate alkalinity analysers have recently been marketed, however the price is still high.

- Redox potential

In theory redox would provide a good means of detecting variations in the intermediate product composition in an anaerobic digester. However, redox potential measurement for digester control is not used because an anaerobic digester is a multiredox system that is not in equilibrium. It is not known which reaction are being coupled (Stumm, 1967, cited by Switzenbaum *et al.*, 1990).

### 2.3.1.3 Gas Phase Characterisation

The gas phase monitoring parameters are summarised below in Table 2.5. Biogas is always produced during anaerobic digestion. The quantities of the various components vary dependent on the effluent and digester type. As a guide, methane production rate is 350 $lCH_4kgCOD$. Methane concentration is typically 60-80%, carbon dioxide 20-40%, hydrogen, carbon monoxide and hydrogen sulphide are present in smaller quantities.

Table 2.5. Gas phase monitoring parameters.

| Parameter | Reference | Comments |
|---|---|---|
| Gas production rate | Moletta *et al.*, 1994 | biogas production used as one of three monitoring parameters for the control of lab and pilot scale FB reactors. |
| Methane | Renard *et al.*, 1988 | Used methane production rate as one of 2 control parameters for an adaptive controller for anaerobic digestion. |
| Carbon dioxide | Graef and Andrews, 1974<br><br>Mathiot *et al.*, 1992 | Developed a dynamic model of AD indicating that total VFA, rate of methane production, pH and carbon dioxide concentration can all be used to indicate digestion failure.<br><br>Carbon dioxide was one of eight control parameters used to monitor the effects of shock loadings. All the parameters measured responded to shock within one hour. |
| Hydrogen | Moletta *et al.*, 1994 | Hydrogen was one of three control parameters used in an expert system control for lab and pilot FB reactors. |
| Carbon monoxide | Hickey and Switzenbaum, 1990 | CO concentrations in anaerobic biogas was found to be redox regulated, with levels increasing with either increasing acetate or decreasing methane concentrations. |
| Hydrogen sulphide | McFarland and Jewell, 1989 | $H_2S$ was found to be a function of pH, sulphate loading rate, metal concentration and biogas production rate. |

- Gas production rate

Hickey and Switzenbaum (1991) measured total gas and methane production during organic overload and concluded that it did provide some indication that a potential problem situation was occurring. The responses observed were far less sensitive than those observed for trace gas analysis, and they concluded that it is unlikely that total gas or methane production could provide adequate early warning of an upset, due to

variations in sludge composition, volume and concentration normally encountered at treatment plants.

- Gas composition

a) Methane and carbon dioxide

Both methane and carbon dioxide can be measured by gas chromatography and infra-red detectors. Methane can also be quantified by calorimetry. IR. and calorimetry are relatively inexpensive detection methods which can provide in-line analysis.

Hickey and Switzenbaum (1991) measured methane and carbon dioxide concentrations and compared their use as a control parameter with hydrogen, carbon monoxide and VFA:TA ratio. They concluded that they were less sensitive than carbon monoxide to fluctuations in loading.

b) Trace gas monitoring

Hydrogen sulphide, hydrogen and carbon monoxide gas are all found in the biogas produced during anaerobic digestion. The ease of detection and possible mechanisms of control are discussed below for each of these trace gases.

- Hydrogen sulphide monitoring

Little has been published on hydrogen sulphide monitoring. Sulphide volatilisation is a function of many digester operational parameters including pH, sulphate loading rate, metal concentration and biogas production rate. McFarland and Jewell (1989) investigated the control of hydrogen sulphide emissions during anaerobic digestion of a synthetic effluent at laboratory scale. Sulphide volatilisation was found to be sensitive to the pH variations. As pH levels increased from 6.7 to 8.2 gaseous sulphide concentrations decreased from 2900 to 100 ppm $H_2S$. Control of sulphide concentration through insoluble iron (3+) phosphate addition was shown to work, however, soluble sulphide concentrations do increase which have an inhibitory effect. The incorporation of hydrogen sulphide gas as a parameter into a control strategy may be of use for wastes which contain high concentrations of influent sulphur.

However, addition of iron (3+) phosphate as a control variable could not be used for wastes with influent sulphide concentrations above inhibitory levels.

Sarner *et al.* (1988) used a gas washing system to scrub hydrogen sulphide from biogas produced from a full scale anaerobic digester treating a pulp and paper mill effluent containing high concentrations of sulphurous compounds. Scrubbed biogas was recycled back into the anaerobic digester. This maintained $H_2S$ levels below 100 ppm. The scrubber contained a liquor of sodium sulphide and sodium carbonate. This has demonstrated that in addition to the methods mentioned by McFarland and Jewell the pumping of biogas through a scrubber could be used to control $H_2S$ inhibition due to fluctuations in an effluent.

- Carbon monoxide monitoring

Hickey *et al.* (1989) investigated the inhibition of anaerobic digestion by heavy metals. Increases in carbon monoxide concentrations up to 12000 ppb were observed using gas chromatography. They concluded that carbon monoxide displayed what appeared to be a characteristic response pattern, rising in response to inhibition of methane production. They also concluded that the monitoring of several trace and major gaseous components along with the gas production rate may prove to be an effective way not only to detect upsets, but to also identify what type of conditions (organic overload) or toxicant (organic or inorganic) is responsible for the observed upset. Hickey et al. thought that the monitoring of carbon monoxide and hydrogen may allow detection of heavy metal induced inhibition more quickly than is possible using conventional monitoring strategies.

Hickey and Switzenbaum (1990) found an increase in carbon monoxide in response to increased acetate or organic loading. They used gas chromatography for carbon monoxide and hydrogen determination. Carbon monoxide was found to vary between 300 to 2000 ppb. They noted that the levels of gaseous carbon monoxide in anaerobic digester samples are directly related to the acetate concentrations and inversely related to methane concentration. Hickey and Switzenbaum hypothesised that acetoclastic methane producing activity controlled system carbon monoxide levels, this is supported by their results, however this may not be true in all cases. Carbon

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monoxide can be produced and consumed by a number of bacterial types normally present in anaerobic consortia. They concluded that analysis of hydrogen and carbon monoxide together should give information on the metabolic status of both of the terminal methanogenic steps in the degradation process.

Hickey and Switzenbaum (1991) described in detail a dedicated system consisting of two gas chromatographs for the detection of methane, carbon dioxide, hydrogen and carbon monoxide. This was used to monitor gas composition at 15 minute intervals during organic and hydraulic overloads. During the experiments accumulation of acetate was always mirrored by a proportional increase in carbon monoxide. Carbon monoxide response appeared to provide a convenient surrogate on-line measurement of the VFA level within a system. The hydrogen results are discussed fully in the following section.

The concentration of carbon monoxide in anaerobic digestion biogas is reported as varying between 300-12000 ppb. Dedicated on-line gas chromatography used to measure carbon monoxide is a very expensive technique and therefore relatively little investigation has been conducted into this potentially useful control parameter.

• Hydrogen monitoring

As described in detail in Section 2.12 - 2.14, hydrogen produced during fermentation is rapidly consumed by methanogenesis. Therefore, any accumulation of hydrogen in the biogas is usually an indication of an operational imbalance.

Figure 2.3 (Mosey, 1983) shows that hydrogen is present in many of the stages of anaerobic digestion. Accurate measurement of concentrations of hydrogen in an anaerobic digester has been shown to be difficult, however, within the last decade more reliable and sensitive hydrogen monitors have enabled researchers to investigate hydrogen concentration and to use it as an on-line control parameter (Table 2.6).

The hydrogen shown in Figure 2.3 would be both in the digester biogas and dissolved in solution. Mosey and Fernandes (1989) state that at room temperature and pressure 1400ppm $H_2$ in the gas is equal to 1 $\mu M/l$ $H_2$ in solution. However, there is some disagreement about correlation of gaseous hydrogen and dissolved hydrogen in

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anaerobic systems. Pauss *et al.*, (1990) pointed out that caution should be exercised in using gas phase hydrogen measurements as a direct measure of liquid phase concentrations. Pauss *et al.*, reported that under conditions of short HRT and high OLR, hydrogen was over-concentrated in the liquid phase by as much as 70 times the value at thermodynamic equilibrium (based on Henry's Law, which equals [gas partial pressure. pascals] x [Henry's law constant. Moles/l-pascal]) as a consequence of a low mass transfer coefficient, and hence a high interphase transfer resistance (Robinson and Tiedje, 1982).

Mosey and Fernandes (1988) briefly describes experiments using a laboratory scale completely mixed anaerobic reactor treating synthetic effluent, deficient in trace metals, causing a gradual loss of methanogenic activity. Early indication of impending process failure was obtained by monitoring the transient accumulations of hydrogen during the hourly or daily feed cycle of the digester. The hydrogen level in the biogas increased off scale (greater than 1100 ppm) then slowly decreased over 6 hours when feed was added once a day in a single dose, hourly feeding resulted in hourly 80 ppm increases in hydrogen concentration. Later Mosey and Fernandes (1989) described this and further experiments in greater detail. The addition of trace metals to the feed resulted in a decrease in hydrogen produced on a daily feed regime from greater than 1100 ppm to 125 ppm. Chloroform was added at 1.5 mg/day to investigate the hydrogen response to toxic shock. This produced large peaks of hydrogen in the biogas and severe inhibition of gas production. Interestingly, at each of the four chloroform injections hydrogen is seen to start to increase before the drop in gas production is seen, however this is not discussed in the paper. The fermentation of sugar to acetate, carbon dioxide and hydrogen, avoiding the production and subsequent breakdown of higher acids is discussed. This is used to explain the generally low turnover of propionate in anaerobic digesters. If propionate formation is usually bypassed, then populations of propionate degrading bacteria will be low. In the event of an increase of propionate the population of bacteria able to degrade it will require a considerable length of time to grow due to slow doubling times (see Table 2.7). Mosey concludes that the hydrogen generated from the fast fermentation of sugars acted more like an event marker, producing a clear rapid

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indication of the operation of the feed pump. With industrial waste digesters it might also prove to be of use to detect fluctuations in waste water strength at constant flow rate or as feedback control signal to adjust the speed of the feed pump to suit the strength of the wastewater.

Hydrogen is also likely to be of use as an alarm indicator for detection of intermittent discharges of industrial biocides. Mosey does not include the possibility of helping to detect changing concentrations of toxins found in industrial effluent. The speed of the response of hydrogen to a toxic load is described as likely to be the most valuable feature of its use.

Wolin and Miller (1982) reviewed the production and use of hydrogen in anaerobic digestion and concluded that hydrogen was not only a product and a substrate in anaerobic fermentations, but also an important regulator. Therefore, the monitoring of the partial pressure of hydrogen was being considered as a sensitive means of early detection of fermentations failure. Detection of very low partial pressures of hydrogen would signal that the fermentation was becoming unbalanced and that syntrophic conversion of butyrate and propionate to methane as well as the interspecies transfer that prevents the formation of these acids was beginning to fail. They speculated that this may permit the development of control measures to correct the imbalance before the microbial community is drastically disturbed by the accumulation of large amounts of acids.
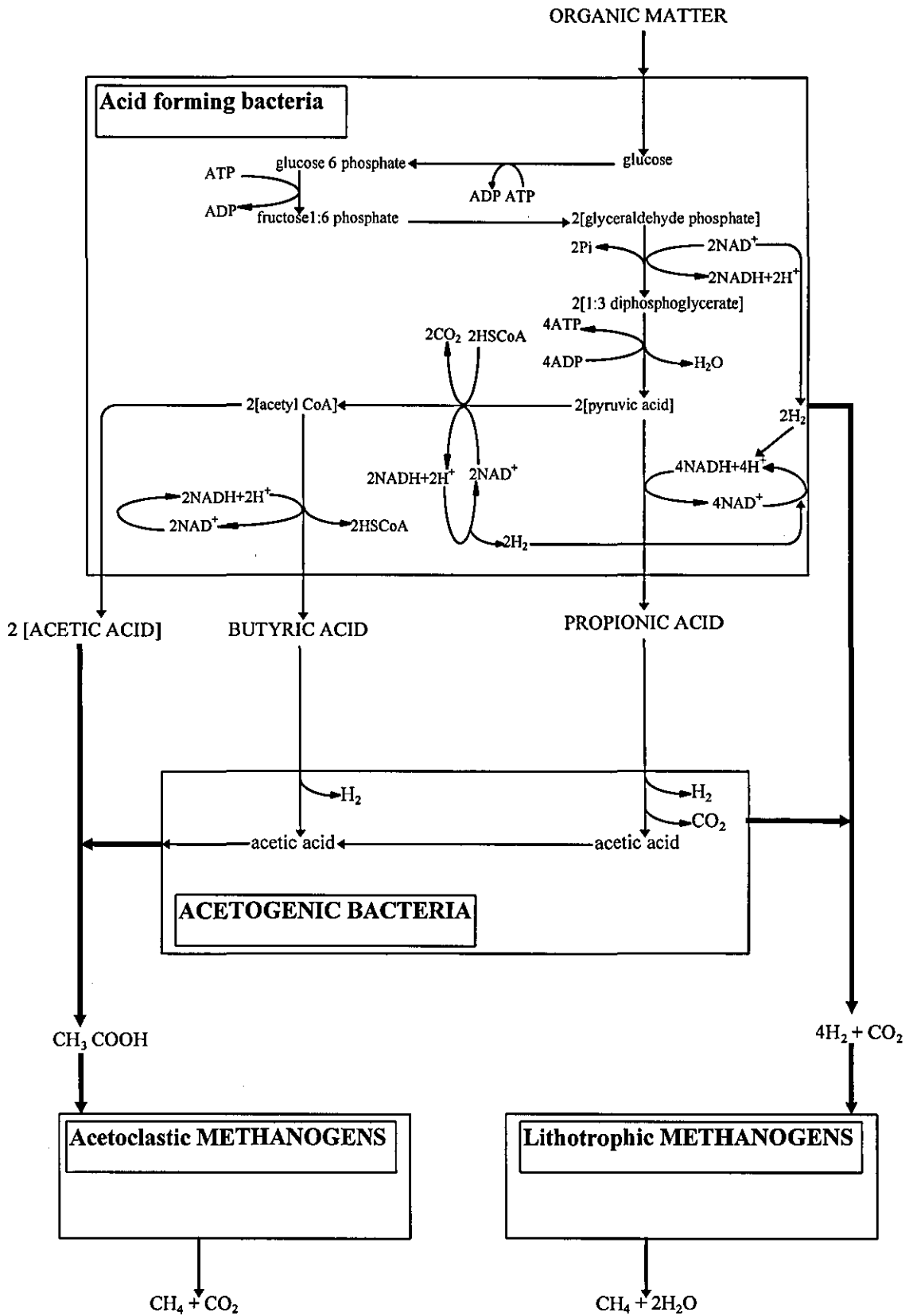
Figure 2.3 Metabolic pathways of anaerobic digestion.

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## Table 2.6 Previous important references on trace gas analysis

| | |
|---|---|
| Archer *et al.*, 1986 | Used the GMI $H_2$ monitor, recorded values in the range 5-15 ppm noted the system had potential for a sensitive and rapid indicator of perturbations within the digester. |
| Hickey *et al.*, 1987 | Using GC measured $H_2$ in the range 20 - 600 ppm compared to VFA and alkalinity concluded that $H_2$ would provide a more rapid indication of process upsets due to toxic shocks. |
| Collins and Paskins, 1987 | Used the GMI $H_2$ monitor and recorded $H_2$ in the range 15 → 199 ppm. Surveyed 20 full scale AD plants recorded reservations about field applications. |
| Mosey and Fernandes, 1984 | A mathematical model was used to simulate $H_2$ production during the digestion of glucose, also a GMI $H_2$ monitor was used to measure $H_2$ concentrations at 12 municipal sludge digesters. Hydrogen was found to be between 40-220 ppm. |
| Mosey and Fernandes, 1988 | Also used GMI $H_2$ monitor and concluded it could give an early indication of impending process failure. They compared the results with gas production and $CH_4$ and $CO_2$ analysis. |
| Mosey and Fernandes, 1989 | GMI $H_2$ monitor with a range of 1-1000 ppm. Concluded '$H_2$ was a very sensitive event marker', tested toxins and noted that a large pulse was caused by chloroform. |
| Slater *et al.*, 1990 | Used GC analysis for $H_2$ + CO. Concluded that $H_2$ concentration was a sensitive indication of small imbalances. They found the response was specific to the type of disturbance affecting the system e.g. organic or toxic overload - this may be useful in process control. |
| Hickey and Switzenbaum, 1990 | Used GC for CO + $H_2$ analysis CO range 300 - 2000 ppb $H_2$ range 14 - 100 ppm. They noted that analysis of $H_2$ + CO together should give information on the metabolic status of both of the terminal methanogenic steps in the degradation process. Useful control system. |
| Kidby and Nedwell, 1991 | GMI $H_2$ monitor range 25-500 ppm concluded the use of $H_2$ as an early warning indicator of full scale sewage sludge digesters was limited. Its full potential may be exploited with reactors treating wastes high in potentially toxic organics. |
| Hickey and Switzenbaum, 1991 | Used GC for $H_2$ + CO. Noted both $H_2$ + CO supply additional information beyond that which current monitoring strategies provide. $H_2$ provided information as to the level of stress being exerted on the $CO_2$ reducing methanogenic population. CO gives insight to the status of the acetate catabolising population. |
| Labib and Ferguson, 1992 | Used GC to give range of gases CO 0.1 - 0.4 ppm $H_2$ 20 - 100 ppm. Also concluded that CO and $H_2$ gave a useful advantage over other methods for the early detection of potentially toxic organics. |
| Moletta *et al.*, 1994 | Hydrogen was one of three control parameters used in an expert system control for lab and pilot FB reactors. |
| Holst *et al.*, 1995 | Hydrogen, biogas production rate and pH were used in an algorithm similar to an expert system to monitor and control a full scale fluidised bed reactor by regulating the feed flow rate. |
| Guwy *et al.*, 1997 | Hydrogen, carbon dioxide, biogas production rate and VFA concentration were monitored during HRT changes and organic overload experiments. $H_2$ varied from 75 − 1450 ppm during reported experiments. |

Hickey *et al.* (1987) conducted batch serum bottle assays to examine the response of hydrogen, methane and VFA in the anaerobic digestion process to inhibition induced by the addition of organic toxicants (chloroform, bromoethanesulfonic acid (BES), trichloroacetic acid (TCAA) and formaldehyde). It was found that severe inhibition of methane production (>70% reduction of methane produced compared to control) resulted in rapid accumulation of hydrogen in the gaseous headspace (above 1000 ppm). When inhibition was less severe, hydrogen accumulated to levels only slightly above controls. Hickey *et al.* stated that BES, TCAA and chloroform appeared to inhibit the acetate and hydrogen utilising methanogens equally. The slow build up of hydrogen in the gas phase at lower levels of inhibition was concurrent with a build-up of reduced VFAs. It was speculated that this build-up of soluble reduced (hydrogen sink) products may tend to interfere with the ability to detect the beginnings of inhibition of the hydrogen utilisers and reduce the sensitivity of hydrogen as an early warning indicator of toxic inhibition. The authors thought that this damping effect may, however, be useful in avoiding false warning of upset that could occur if hydrogen response proved to be too sensitive. They concluded that the potential for hydrogen as an early warning indicator of digester upset was limited, but that monitoring hydrogen in concert with conventional process indicators should improve digester monitoring and may provide more rapid indication of process upsets due to toxic shocks, i.e. hydrogen should be used to augment and enhance existing monitoring strategies rather than replace them. There was, however, concern that before control strategies could be developed, it would be necessary to accurately detect the hydrogen level variation due to normal background variation imposed by changes in loading rate and/or substrate concentration and composition.

Kidby and Nedwell (1991) investigated the suitability of hydrogen concentration within anaerobic digestion biogas as a performance monitor. Laboratory scale CSTRs had their HRT decreased from 20 to 8 days. Digester failure was preceded by a decrease in biogas volume and methane content, increased VFA production and decrease in pH. Hydrogen accumulation was not evident until after failure had occurred, however, high numbers of methanogenic bacteria in faecal material were introduced during daily feeding. It was suggested that this addition of methanogens

was responsible for the continued ability of the hydrogenotrophic methanogens to maintain a low hydrogen concentration. The authors concluded that hydrogen was not of use as an indicator of impending digester failure due to volumetric overloading, but that the reasons for digester failure under conditions of a decreasing HRT could be different from failure under conditions of organic load stress.

Hickey and Switzenbaum (1991) used laboratory scale digesters to investigate the effect of increased organic and hydraulic loading on sludge digesters. A decrease in HRT from 10 to 5 days and an organic overload of 2.65 times, both resulted in the hydrogen concentration quickly rising and stabilising at a new steady state diurnal pattern, which declined after 4-5 days. During a fourfold hydraulic and organic overload, hydrogen concentrations remained low while COD accumulated as "hydrogen sink" products such as propionate and other organic acids. Hydrogen production was sufficiently low for hydrogen consuming bacteria to maintain a low hydrogen concentration. This suggests that the hydrogen concentration reflects the loading or level of stress being imposed on the hydrogen using population, but not stress exerted on the acetate catabolising population. In the discussion of the results it was noted that for the treatment of industrial wastes where periodic upsets due to toxicants are of concern hydrogen monitoring appears to be extremely sensitive and therefore, useful for early indication of an oncoming upset. High rate anaerobic treatment systems are also less likely to be hydrolysis limited, overloading is more likely and will result in a decrease in efficiency. In these instances closer monitoring of trace gases would help. They noted that both hydrogen and carbon monoxide supply additional information beyond that which current monitoring strategies provide. Hydrogen concentration provided information as to the level of stress being exerted on the carbon dioxide reducing methanogenic population. Carbon monoxide gave insight to the status of the acetate catabolising population, but neither is able to be used as stand-alone indicators, however further work is recommended to determine how they could be used as process indicators.

Pauss and Guiot (1993) monitored dissolved hydrogen concentration in four laboratory scale upflow sludge bed reactors using an $H_2$-air fuel cell probe (Syprotech,

Pointe Claire, QC, Can). The upflow velocity differed in each reactor providing different hydraulic regimes. The dissolved hydrogen concentration was found to increase proportionally with the OLR of the reactors to values as high as 20μM, but remained independent to the hydraulic regime. The hydrogen mass-transfer rate showed a reasonable and positive correlation with the OLR values and the gas flow rates, however, no correlation was found for the sursaturation factor values. They concluded that this indicated that dissolved hydrogen concentrations can not be predicted from hydrogen gaseous measurements in these reactors.

Slater *et al.* (1990) used two dedicated gas chromatographs to measure methane, carbon dioxide, hydrogen and carbon monoxide in the biogas from a laboratory scale fluidised bed reactor. Hydrogen was shown to be more sensitive to feed pulses than biogas production rate. In general they found that the biogas hydrogen concentration was very sensitive to small imbalances in the production and consumption of hydrogen, and that the response pattern was specific to the type of disturbance affecting the anaerobic system, e.g. an increase in organic loading or a toxic event. They concluded that hydrogen might be useful as a process control variable because of its role as an important regulator of metabolic activity and its demonstrated fast response and short term sensitivity. Later the same team (Labib *et al.*, 1992) conducted experiments on a laboratory scale fluidised bed reactor, by transient additions of butyrate, hydrogen, acetate and formate. It was found that increases in hydrogen and acetate concentrations above their values at steady state can partially inhibit butyrate degradation. Increases of hydrogen and acetate concentrations that resulted in a positive free energy change stopped butyrate oxidation completely. This suggested that there is a concentration dependent product inhibition in addition to inhibition when the reaction becomes energetically unfavourable. A ten-fold increase in methane production from hydrogen utilising methanogens was seen when formate was added. This indicates that the hydrogen utilisers have a large and under-utilised capacity at steady state.

Ehlinger *et al.* (1994) monitored and controlled a fluidised-bed anaerobic digester treating wine distillery waste water (vinasse). Three parameters were chosen for the

monitoring of the reactor, based on previous work by the same research group (Mathiot *et al.*, 1992): the pH of the liquid phase, the flow rate of the biogas and the concentration of hydrogen in the gas phase. Control of the anaerobic digester was by variation on the dilution rate determined by a control algorithm based on a principle very close to an expert system. The control system was tested during pH variations and organic overloads. During an increase in substrate COD from 20 to 60 g/l the control system decreased dilution rate until gas production rate, pH and hydrogen concentration stabilised. However, VFA, methane and carbon dioxide concentrations indicated that the digester was unstable during the prolonged high organic load. Hydrogen did increase from 80 to 600 ppm when the problem arose, but decreased back close to the initial value despite the persistence of the problem. This set of experiments would support the conclusions of Mosey and Fernandes (1988), Hickey and Switzenbaum (1991), and Kidby and Nedwell (1991) who stated that hydrogen gas concentration is useful as an event marker used in conjunction with other control parameters in a control strategy. Ehlinger *et al.* (1994) conclude that methane and carbon dioxide concentrations were the only parameters able to detect the long term instability of their anaerobic digester. However, their results show that VFA concentrations would also have indicated reactor instability.

More recently the same research team (Holst *et al.*, 1995) used an algorithm similar to an expert system called Méthaveil to monitor and control a full scale Anaflux® (anaerobic fluidised bed) reactor treating corn processing effluent. Méthaveil uses three on-line sensors measuring the biogas production rate, concentration of hydrogen and pH. Every 30 minutes an average reading is used by the control algorithm. The control output is either that the reactor is: stable and can accept a higher feed flow rate; stable but cannot accept a higher feed flow rate; or not stable and the feed flow rate must be reduced. Flow rate changes were + or - 5%. The control system was used in the start-up and operation of the fluidised bed. Although the control strategy is not discussed in detail, it can be seen that as hydrogen increases and pH decreases feed pump speed is slowed until the trend these parameters reversed. The only controlled shock given to the reactor to test the control system was an organic one. The feed rate was deliberately increased by 200% to test the control system.

Hydrogen was seen to increase from a steady base line of 65 ppm to 120 ppm, the control action of slowing feed pump speed resulted in hydrogen decreasing to a new higher steady state of approximately 100 ppm.

Guwy *et al.* (1997) carried out experiments on a laboratory scale fluidised bed anaerobic digester fed with synthetic baker's yeast wastewater. Hydrogen was monitored using a GMI exhaled hydrogen monitor. Other parameters monitored were VFA production and carbon dioxide concentration of the biogas. Hydrogen was found to increase in concentration during step overloads in organic loading, e.g. $H_2$ increased from 290 to 640 ppm within 3 hours after an increase in loading rate from 40 to 63 kg COD m$^3$/day. Biogas flow rate was shown to increase approximately proportionally to each increase of volumetric loading rate applied to the reactor. However, hydrogen concentration of the biogas showed no such linear relationship, but gave very distinct increases just after the changes in feed quantity and quality. It was reported that similar overloads in organic loading did not give rise to the same absolute levels of biogas hydrogen concentration. Hydrogen concentration was also found to increase during a change in feed quality, i.e. a change in the degree of acidification of the feed. Guwy *et al.* (1997) concluded that the use of hydrogen concentration in the biogas as a control parameter would be questionable especially if the pre-acidification of the feed to the digester is variable. However, they did also state that the rapid response and ease of on-line measurement of hydrogen support its use in digester control along with other parameters which can be measured on-line. This conclusion is in agreement with previous research reviewed (Hickey and Switzenbaum, 1991 and Hickey *et al.*, 1987) which also concluded that hydrogen should be used in conjunction with other process indicators for control.

Hydrogen has been shown to be involved in many stages of anaerobic digestion. The measurement of the low concentrations of hydrogen that occur in anaerobic digestion biogas was not common before low cost analysers became available. Hydrogen concentration in the biogas of anaerobic digesters has been shown to be low (usually 5-50 ppm), and the metabolism of glucose is directed almost entirely towards the formation of acetic acid. As the concentration of hydrogen rises, NAD concentration

is reduced which slows down the overall rate of fermentation. An increase in NADH speeds up the production of butyric and propionic acid. Overall an increase in hydrogen concentration in the digester gas:

i) reduces the overall rate of acid formation

ii) changes the mixture of acids produced, decreasing the proportion of glucose converted to acetate and increases the proportion converted to propionic and butyric acids.

Thus, an increased concentration of hydrogen that accompanies a surge of glucose entering an anaerobic digester tends to damp down any violent fluctuations in acetic acid production and protect the pH buffer of the fermentation from acid overload. All the reactions of anaerobic digestion involving hydrogen are affected by the partial pressure of hydrogen. Overloading of the anaerobic system, due to the slow growth rates of the methanogens and acetogens compared to the acidogenic bacteria (see Table 2.7 from Mosey and Fernandes, 1989), causes the hydrogen to increase in the system and production of propionic acid instead of acetic acid (Mosey, 1983).

Table 2.7  Approximate minimum doubling times at 35°C of the major groups of bacteria in anaerobic digestion.

| sugar fermenting, acid forming bacteria | 30 minutes |
| methanogens growing on hydrogen (or formate) | 6 hours |
| acetogenic bacteria fermenting butyrate | 1.4 days |
| acetogenic bacteria fermenting propionate | 2.5 days |
| methanogens growing on acetate | 2.6 days |

**Summary of Gas Phase Characterisation Section**

The use of gas phase indicators have been investigated as they have the advantage of significantly faster response times to stress of the anaerobic micro-organisms than liquid phase indicators (Switzenbaum *et al.*, 1990, Hickey and Switzenbaum, 1991), as well as being less susceptible to probe fouling. Other researchers (Johnson, 1991)

have found probe fouling to be a significant problem when monitoring lipid containing wastes. No single gas phase parameter is found to be sufficient for control. In combination, however, toxic and organic events can be detected. Hydrogen and carbon monoxide monitoring do offer the potential of providing earlier and more sensitive warning of upset by being rapid and on-line parameters. However, economics may not justify the use of trace gas monitoring unless fluctuations in toxicants are likely.

### 2.3.1.4 Conclusions from gas phase characterisation

A significant quantity of research has been conducted to find the control parameter or combination of parameters which can be used to determine the metabolic status of an anaerobic digester. This is difficult to find; partially due to the fact that the microbial ecosystem developed in a particular anaerobic digester is unique to that digester. The premise of any control system must be to take remedial action as fast as possible after an upset to the anaerobic digester. To this end the control parameter should indicate an upset as quickly as possible. Parameters measured in the liquid phase are the most commonly used. However, liquid phase parameters are slow and most determination techniques are not suitable for real time data acquisition, in comparison to those of the gas phase which are faster and can provide real time data (see Table 2.8).

Relative response time of the liquid phase parameters are shown in Table 2.8, with the relaxation time. Relaxation time refers to the behavioural response of a reaction following a shift in an independent variable, described in Switzenbaum *et al.,* (1990).

Gaseous hydrogen has been identified as a possible control parameter by extensive previous work in recent literature. Fluctuations in toxicant concentration is likely during the treatment of instant coffee processing effluent, hydrogen has been shown to be potentially useful to detect the effect of these fluctuations. Additionally, it is non-invasive and has the advantage of not being susceptible to probe fouling. Furthermore, equipment to measure hydrogen in biogas is commercially available and it is also low-cost. For these reasons it was chosen has a control parameter for this research.

Table 2.8 Theoretical relaxation times for different substances and microbial population in anaerobic digestion

| Substance | Relaxation time |
|---|---|
| $H_2$ | 15 seconds |
| Glucose | 3 minutes |
| $CO_2$ | 1 hour |
| Acetate | 2 hours |
| Propionate | 4 hours |
| Methane | 2 days |
| CO | unknown - most likely controlled by $H_2$ relaxation time |
| Microbial Population | |
| Acidogens | 30 minutes |
| Propionate consumers | 5 days |
| Acetoclastic methanogens | 10 days |
| Hydrogenotrophic methanogens | 25 days |

## 2.4 Control of Anaerobic Digestion

The demands for wastewater treatment to cope with variable industrial wastes and to meet higher environmental quality standards with greater consistency whilst reducing treatment costs has led to the desire for better control of the treatment process. This has encouraged the use of various control techniques on water treatment plants. The most common form of feed-back controller is the Proportional Integral Derivative (PID) device. This is based on three actions (proportional, integral and differential) combined to give a correcting signal that is proportional to the error between the controlled variable and a desired set-point and to the integral of this error and to its time derivative. PID controllers do not require a model of the controlled process, instead relying on empirical rules. However, if a model is available a PID can be fine tuned resulting in better performance (Andrews and Kambhu, 1971 and Andrews, 1968). These models were simple, assuming a single group of bacteria. More complex models were proposed considering an acid forming and a methanogenic phase (Hill and Barth, 1977, Kiely *et al.*, 1997), the acetogenic and acetoclastic

bacteria (Rozzi and Labellarte, 1984) and all four microbial groups (Mosey, 1983). However, the microbial groups response to control is non-linear, especially after disturbances to the anaerobic digestion process.

A non-linear adaptive control strategy uses external linearisation, therefore, both the biological process and the controller are non-linear, so the feed back system becomes linear.

More recently artificial intelligence control methods have been investigated as a non-linear control strategy, suitable to be applied to biological processes. These have the advantage of being able to learn from past data from a biological system and apply deduced rules to a control strategy.

### 2.4.1 Control variables

There are three control variables of use to control anaerobic digestion: influent flow rate (assuming a reservoir of influent or diversion of untreated substrate); addition of chemicals; and removal of inhibitory factors.

Table 2.9. Control variables used in the literature.

| Research team | Control strategy | Controlled variable |
|---|---|---|
| Prodruzny and van den Berg (1984) | Adaptive control | Feed pump speed |
| Sarner et al. (1988) | None | Removal of $H_2S$ |
| Renard et al. (1988) | Adaptive control | Feed pump speed (HRT) |
| Johnson et al. (1995) | Adaptive control | Feed pump speed |
| Alatiqi et al. (1990) | None | Heat input and feed pump speed |
| Chynoweth et al. (1994) | Expert system | Feed pump speed |
| Slater et al. (1990) | Adaptive control | Feed pump speed |
| Wilcox et al. (1995) | Neural network | Bicarbonate dosing pump |

## 2.4.2 Adaptive Control

Adaptive control models work on similar principles to a moving average. The variance allowed in the average (i.e. the fluctuations allowed before control action is taken) is determined using previous data. In this way the model is able to differentiate between background variability and significant disturbances likely to damage system performance. This type of self tuning has been applied to wastewater treatment processes to cope with the vagueness in waste characteristics and biological performance (Dochain and Bastin, 1985, Bastin and Dochain, 1988, Johnson *et al.*, 1995, Marsili-Libelli and Lasagni, 1985). In these applications judgements are made as to what excursions in feed strength, effluent quality and gas production are allowable before corrective action is taken, which is usually a reduction in feed rate. A detailed description of the theoretical approach is given by Bastin and Dochain (1988).

## 2.4.3 Artificial Intelligence

Artificial intelligence (AI) is a computer system that has the ability to learn, that is to say that the computer system is able to evaluate the results of its own actions and to modify its own behaviour in order to ensure that incorrect or invalid actions are not repeated. The potential of artificial intelligence was first described in the 1940's, but the computational power required to use this as an on-line control technique was unavailable at this time. Since the 1940's the phenomenal advances in the field of computers has resulted in the ability to utilise AI technology more fully. The early attempts to apply fuzzy control to a waste water treatment plant took place in the 1970's, Tong *et al.* (1980) applied fuzzy control to the activated sludge process. However it was since 1980 that there has been a large increase in the number of publications on the application of AI techniques in a multitude of previously untried fields. AI techniques that have been applied to the control of anaerobic digestion are; expert systems, neural networks and fuzzy logic. Artificial or machine intelligence are useful in bioprocesses because of the potential variability and complex responses possible.

The choice of AI technique best suited to a particular system is based primarily on the level of understanding of the process concerned. Baba *et al.* (1990) described the selection process as a decision tree (Figure 2.4). When unsure of knowledge or there are not enough rules to specify expertise, then the neural network approach is commonly used. However although neural networks provide a way of handling uncertainty, when it comes to explaining their reasoning in arriving at a particular conclusion then expert systems do much better.
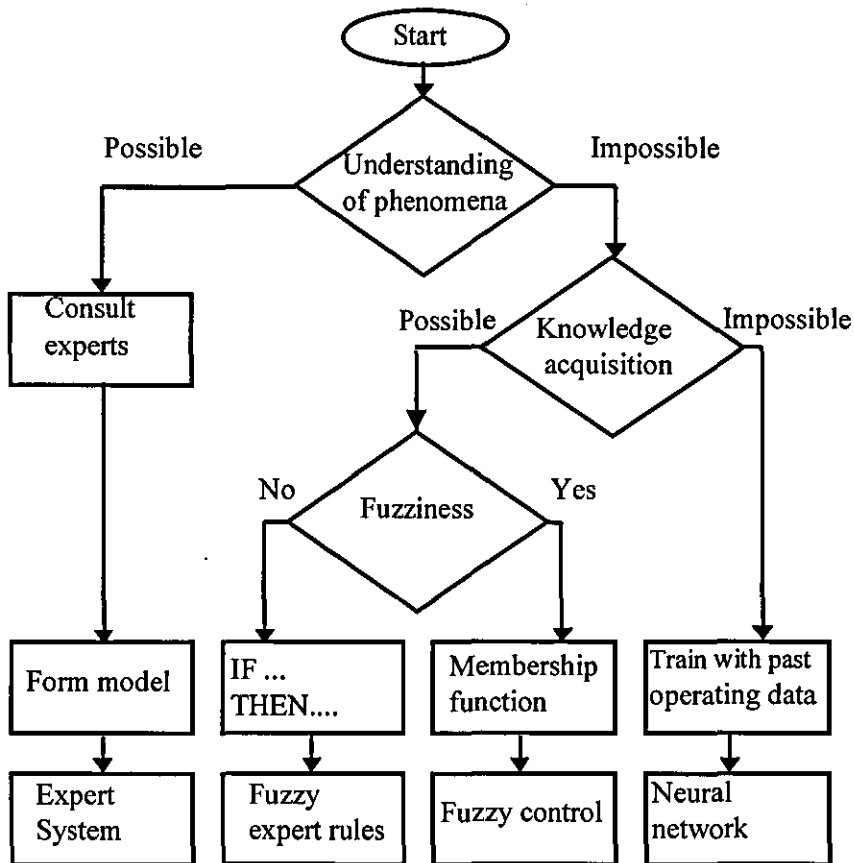
Figure 2.4   Decision tree to assist in AI technique selection

### 2.4.3.1 Expert systems

The expert system approach is the most prevalent in the literature and has been used to both design and operate anaerobic digesters. *An expert system is a means of capturing*

*the knowledge of experts in the form of programs and data where disagreement among the experts are settled by mediation and the results presented in such a way that it can be used by less experienced people within the field. The expert system is a tool and a means of coherent communication of the latest views of the experts to the users (Addis, 1981; cited by Smith, 1989).* An expert system is a means of capturing the knowledge of experts in the form of programs and data, enabling the knowledge to be used by less experienced people within the field. An expert system is based on the process of turning an expert's knowledge into a computer system. Some expert systems take several years to construct because of the lengthy process of extracting and compiling expertise and then finding the desired way to present this to the user. They can be periodically updated to take account of the latest research but extensive prior knowledge of the process is required.

In its most simple form an expert system can be described as a series of IF... THEN rules joined together, for example:

IF methane production is reduced THEN problem is either reduced influent COD or inhibition ask for further details

IF COD is constant THEN inhibition of the methanogens is occurring.

This is an example of a production rule expert system, other types that can be used store the knowledge in a different way (e.g. object-orientated programming, frames and scripts).
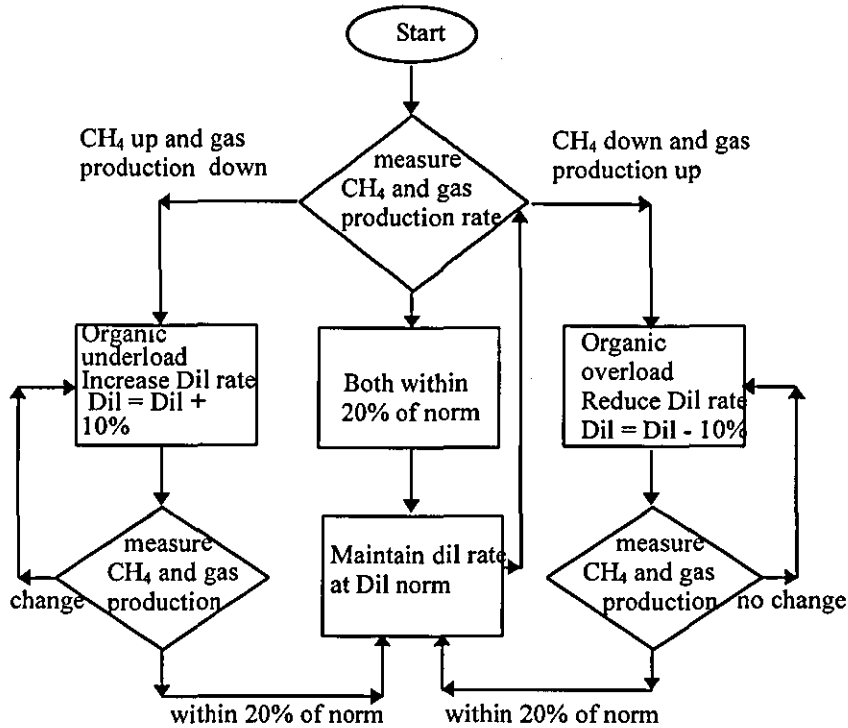
Figure 2.5 Flow chart of a simplified expert system.

Lapointe *et al.* (1989) developed BIOEXPERT, a prototype expert system to instruct plant operators working on anaerobic digestion plants. Data was input manually and the expert system was used to explain the behaviour of the process and to help operators during the diagnosis of faults. Barnett and Andrews (1992) also used an expert system to simulate the control of anaerobic digestion during hydraulic and ammonia upsets. Pullammanappallil *et al.* (1991) and Chynoweth *et al.* (1994) used an expert system to control dilution rate during upsets caused by changes in feed substrate concentration or the presence of inhibitors in the feed. In another example Ehlinger *et al.* (1994) used an expert system based control algorithm to control dilution rate during pH variation an organic shock loads applied to a fluidised-bed anaerobic digester treating vinasse. This expert system based control algorithm is similar to that used by Holst *et al.* (1995) also to treat vinasse.

An example of a simple expert system for the control of the anaerobic digestion process is shown in Figure 2.5. The process of turning an expert's knowledge into a computer system can be a lengthy one. Although expert systems are a good method,

extensive prior knowledge of the process is required therefore other AI techniques such as artificial neural networks or fuzzy logic have been tried.

### 2.4.3.2 Fuzzy logic

Fuzzy logic is often referred to as using common-sense rules that refer to indefinite quantities e.g. warm, rather than hot or cold. Fuzzy systems often glean their rules from experts. When no expert is available to give the rules, adaptive fuzzy systems learn the rules by observing how people regulate real systems (Kosko and Isaka, 1993). The fuzzy logic approach combines two techniques so that actions suggested by the controller are taken on the basis of an emulation of expert reasoning instead of a mathematical representation of the waste treatment reactor behaviour. This can be used for formulating expert rules from historical plant operating data. Enbutsu *et al.* have produced a series of papers on the application of fuzzy logic to raw water treatment (Baba *et al.*, 1990, Enbutsu *et al.*, 1991, Enbutsu *et al.*, 1993). They performed fuzzy rule extraction using a multi-layered neural network which controlled coagulant dosing rate based on the inputs of alkalinity, pH, temperature, flow rate, turbidity and floc characteristics. Tong *et al.* (1980) describes the application of fuzzy logic to control an activated sludge plant. Nine inputs were used, four of which (flow rate, mixed liquor solids, final effluent solids and dissolved oxygen) were measurable on-line. The system was based on the operating expertise of one of the authors. Boscolo *et al.* (1993) used a wider range of input parameters with fuzzy control of an anaerobic digester treating solids waste. Only three of these could be measured on-line (flow rate, methane production and pH). Significant expertise was required to describe the rules for the program and further time was required to validate the rules for their particular application. They concluded that a fuzzy controller for anaerobic digestion was feasible and had advantages for complex waste treatment plants.

### 2.4.3.3 Neural networks

ANNs are the result of an attempt to create a computer model that matches the functionality of the brain in a very fundamental manner. The brain consists of tens of

billions of neurones densely interconnected. The biological neurone consists of the axon (output path) which splits up and connects to dendrites (input paths) of other neurones through a junction referred to as a synapse. When a brain learns, the efficiency of the synaptic connections is strengthened. In an ANN the unit analogous to the biological neurone is called the processing element. As an ANN learns the weights on its input paths are adjusted. An ANN consists of many processing elements joined together, usually into groups called layers. A typical network consist of a sequence of layers with connections between successive layers (see Figure 2.6).
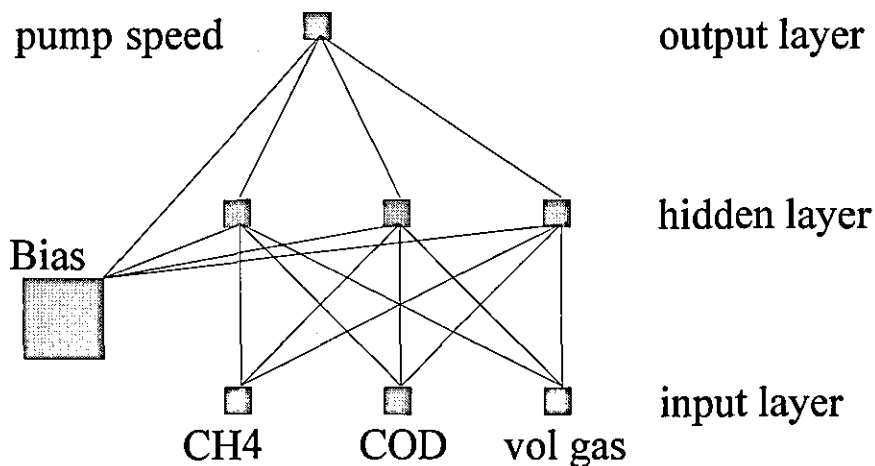


Figure 2.6 An artificial neural network

Artificial neural networks have several advantages over expert control methods. The network generates its own rules based upon learning examples. In supervised learning for each input a desired output signal is presented to the system and the network gradually configures itself to achieve that desired output. Neural networks have what is known as distributed associative memory, in which an item of knowledge is distributed across many of the memory units in the network and is shared with other items of knowledge stored in the network. As an ANN learns, the weights attached to the importance of the input paths are adjusted. Neural networks also therefore, have the ability to learn and build unique structures specific to a particular problem, such as the indications of a specific type of shock to an anaerobic system. The nature of ANN memory leads to a calculated response even when presented with incomplete or previously unseen input. This property is referred to as *generalisation. Intelligent*

responses to ª«)0omplexity. However, many variations on the basic algorithm that improv

performance have been applied (Emmanouilides and Petrou, 1997). Also, anaerobic

digestion is a process with slow dynamics and the computational time required by

neural networks are relatively short. Back propagation neural networks are simple to train and are the most popular training algorithm, therefore, they were chosen to investigate the application of an artificial intelligence technique to data from this research.

## 2.5 Anaerobic digestion of effluents containing toxic and recalcitrant compounds

There has been a considerable amount published on the influence of toxins on anaerobic digestion. The slower growth rate of the methanogens and hydrogenotrophic bacteria means that inhibitory compounds can have a significant long term effect on an anaerobic digester.

Parkin and Speece (1982) defined the threshold dose as *the dose of a toxicant resulting in the onset of reduced gas production.* Parkin and Speece developed three models to describe toxicity phenomena in anaerobic digestion. One describing the recovery pattern from slug addition of toxicants, the other two incorporating the effect of toxicity on the fundamental Monod-type expressions. The primary effect of toxicant addition was said to be to alter process kinetics by temporarily or permanently increasing the bacterial washout time. They concluded that to minimise the severity of both transient and chronic toxicity, a sufficiently large solids retention time was required. Parkin and Speece commented that their experiments demonstrated that methanogenic bacteria have a substantial potential to recover from and acclimate to toxin exposure. Parkin and Speece tested 30 toxins including cations, such as ammonium and sodium; sulphide; detergents; antibiotics; heavy metals, e.g. Ni, Cu, Cr, and Cd; organics, including chloroform, formaldehyde, acrolein, tricholoethylene; and oxygen. The recovery pattern exhibited was similar for all toxicants studied. The importance of biological retention time was demonstrated, Parkin and Speece concluded that a sufficiently large biological retention time will protect against process deterioration due to a chronic toxicant addition and that to minimise the severity of transient toxicity a sufficiently large biological retention time was required. Both transient and chronic toxicity can be handled with no significant decrease in process efficiency by the provision of a large biological retention time; not only does this maximise process stability, it also allows for prolonged operation under

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the temporary washout conditions caused. This gives plant personnel more time to locate and minimise the cause of the toxicity.

Later, Demirer and Speece (1998) demonstrated the ability of an UASB to utilise acrolein, acrylic acid and allyl alcohol as sole substrates. Acrolein, acrylic acid and allyl alcohol were shown to be inhibitory to acetate-enriched *Methanosarcina* cultures starting from the concentrations of 20, 60 and 3000 mg/l respectively. Demirer and Speece stated that the ability to biotransform these compounds was due to proper acclimation through careful control of the operating parameters, such as step-wise increases in the influent concentration. That is, unless a considerable transformation (>80%) and/or a stable level in effluent acrolein, acrylic acid and allyl alcohol was observed, the concentration of the test compound in the influent was not increased any further).

A common potential toxin are the tannins. These are used in the leather processing industry but are also present in food processing industry wastes. Tannins are phenolic compounds which are highly reactive with proteins. Field and Lettinga (1987) listed examples of sources highly concentrated with tannins that may enter an anaerobic digestion process, including; apples, sorghum, grapes, banana, coffee, cacao, beans and bark. Field and Lettinga evaluated the effect of a tannin (gallotannic acid) on the methane production from granular anaerobic sludge. Gallotannic acid was found to be highly toxic to methanogenic activity, 50% inhibition occurred at 700 mg/l. The monomeric derivatives of gallotannic acid, gallic acid (3,4,5-trihydroxybenzoic acid) and pyrogallol (1,2,3-trihydroxybenzene) were much less toxic (50% inhibition occurred at 3000 mg/l) and their toxicities were not persistent. At concentrations of less than 1000 and 2000 mg/l pyrogallol and gallic acid respectively, biogas production was enhanced. They concluded that the lower toxicities of the monomers compared to the gallotannic acid polymer suggests that the mechanism of toxicity was "tanning", since data in the literature indicated that tannin polymers are more effectively adsorbed and precipitated with proteins compared to their monomeric counterparts. Functional proteins (enzymes) located at accessible sites in or on the methane bacteria are most likely disturbed by the tanning action. Field and Lettinga

discuss cross acclimation of anaerobic bacteria, concluding that the mechanism(s) involved in anaerobic galloyl derivative degradation differ from those involved in the decomposition of other simple phenolic and aromatic compounds. From other literature they suggest that the population of organisms responsible for the anaerobic digestion of trihydroxbenzenes are different from the degraders of other simple phenols. This supports their results showing short lag periods required by their granular sludge to initiate the degradation of pyrogallol, gallic acid and gallotanic acid of 2 to 5 days, the same sludge is reported to have needed 31 days to initiate the degradation of phenol and 56 days to initiate the degradation of catechol under the same conditions. Horowitz *et al.* (1983) observed that municipal digester sludge needed one week to degrade 50 mg/l pyrogallol while 2 and 3 weeks were required for the same amount of phenol and catechol, respectively. This large difference in time required is likely to be due to the difference in anaerobic sludges used in the experiments.

Later Field *et al.* (1989) examined the methanogenic toxic products of pyrogallol in detail. In the first stages of the autoxidation of pyrogallol its first autoxidation intermediate, purpurogallin is formed. This is shown to cause a high level of methanogenic toxicity. 45 mg/l of soluble purpurogallin was shown to cause 50% inhibition of the methanogenic activity. The rapid increase of methanogenic toxicity during the initial period of pyrogallol autoxidation is explained by the formation of small levels of purpurogallin. Purpurogallin is more toxic to methanogenic bacteria than would be expected. Since purpurogallin lacks tannin features and is highly toxic, other factors besides the tannin quality are involved in the methanogenic toxicity of autoxidised pyrogallol. VFA analysis revealed that at above 50% inhibition only acetic acid was being consumed. The toxicity of purpurogallin on the metabolism of propionic acid was more severe, very little propionic acid was consumed during the assay. Similar results were reported for the pyrogallol treatments that were autoxidised from within 10 minutes to 1 hour, although the results are not shown in this paper. There was a 3 day delay in the full expression of the toxicity of purpurogallin. It was suggested that the lack of this delay for the pyrogallol

treatments autoxidised from 10 minutes to 1 hour may have been due to interactive effects between pyrogallol and purpurogallin.

Bajwa and Forster (1988) investigated the inhibition of anaerobic processes by vegetable tanning agents. Chestnut is given as an example of a plant extract used for leather tanning, the active components being condensed polyhydric phenols which have the potential for being inhibitory to microbial activity. Pyrogallol and gallic acid were found to be in vegetable tannery effluent at 600 and 10 mg/l respectively. Fresh digested sludge from municipal sludge digesters was used throughout the experiments. Inhibition of acidogenesis and methanogenesis was examined by VFA concentration in the effluent and from gas production, however, only methane production is given for tests with pyrogallol and gallic acid. Pyrogallol and gallic acid were added at the above concentrations and compared to addition of effluent from a tanning plant. Both pyrogallol and gallic acid exhibit a greater degree of inhibition than tannery effluent initially, but after 30 hours gas production increases from 50 to 80% of the control for pyrogallol. These results differ from those reported by Field and Lettinga (1987) who showed that feed supplemented with pyrogallol and gallic acid at concentrations of less than 1000 and 2000 mg/l respectively enhanced biogas production, with only higher concentrations resulting in a reduction of biogas concentration, conversely Bajwa and Forster show inhibition at a much lower concentration. Bajwa and Forster conclude that the granular sludge used by Lettinga has a much higher metabolic activity than their diffuse sludge, suggesting that the variation in results between the two experiments are explained by the differences in sludges used.

Disley *et al.* (1993) investigated inhibition of anaerobic digestion caused by 6 organic compounds. Inhibition was tested for thermophilic anaerobic digestion and compared with previous results at mesophilic operation. They found that thermophilic sludge is far more sensitive to the organic inhibitors than mesophilic sludges. Pyrogallol was found to inhibit 50% of biogas production at a concentration of 1.45 g/l. The sludge used in this experiment was taken from a completely mixed digester operating at 55°C for a number of years in a laboratory.

The widely varying results reported in the literature reflect wide variability of the anaerobic sludges used in the experiments and their solids concentration and retention times. These variables will define the microbial populations which are present in the experiment. This is a factor which will have an effect on the activity on the sludge and its response to the presence of toxic compounds.

Parkin and Speece (1983) performed experiments to compare the response to toxic substances of attached and suspended growth anaerobic reactors. They used a laboratory scale anaerobic filter and CSTR reactors to investigate six toxicants; cyanide, chloroform, formaldehyde, ammonium, nickel and sulphide. Both transient and chronic exposure to toxic substances were investigated. Transient toxicity to CSTR resulted in periods of zero gas production, which was a function of the toxicant concentration. Once recovery started, return to the control gas production level was rapid, too rapid to be explained solely by bacteria regrowth, indicating acclimatisation to the toxin. The anaerobic filter was able to withstand much higher transient concentrations of toxins (10 to 100 times the concentration) to result in a similar decrease in biogas production. Parkin and Speece in their discussion say that "despite the dilution capability of a CSTR, which is considered to an advantage, it is shown that in some cases the rapid elution of a toxic sludge from a plug-flow reactor ensures more rapid recovery than the protracted washout of the toxicant from a CSTR". However, it has been shown by other authors that an anaerobic filter is not really a plug flow reactor (Johnson *et al.*, 1994). This is due to the mixing occurring from the rise of biogas though the filter. It is worth noting, however, that if an anaerobic filter is inhibited to the point of a cessation of biogas production it will revert to being plug flow. Parkin and Speece conclude that their results indicated the importance of an adequate sludge retention time (SRT) in ensuring that systems will recover. The SRT providing a biological safety factor that guards against process failure from transient toxicant exposure. Tests on chronic toxicity showed that comparable maximum tolerable concentrations were obtained from both the anaerobic filter and CSTR. Parkin and Speece refer to two main differences in these reactor types with respect to acclimation.

1. A CSTR allows for a gradual build-up of toxicant concentration.

2. An anaerobic filter does not lose biomass during the acclimation process. It is worth noting that an anaerobic filter with a recycle will experience a more gradual exposure to a toxicant.

Biodegradation and enzymatic pathway alteration may be considered to be true acclimation, Parkin and Speece also mention the possibility of volatilisation, chemical precipitation and complexation or adsorption to solids which may occur, resulting in the removal of toxicants from the liquid phase. Parkin and Speece conclude that in some cases methane bacteria can operate with no loss in efficiency at influent toxicant concentrations 10 to 25 times those causing inhibition to unacclimated systems and that sludge retention time is of importance regardless of the nature of the acclimation.

## 2.6 Coffee processing

Coffee is a tropical tree or shrub; belonging to the Rubiaceae family. It produces fruit approximately 15-20 mm in diameter that grow in bunches. The kernels (coffee beans) are processed into a powder that is used as a drink. The processing of coffee beans for the manufacture of instant coffee occurs in all parts of the world, both in the countries producing coffee beans and countries that consume coffee. The UK alone produces some 50-60 x $10^3$ tonnes of instant coffee each year (Fernandez and Forster, 1994). The primary processing of coffee beans (the separation of coffee beans from coffee berries) gives rise to 36.4% solids wastes, 45.4% liquid wastes and 8.2% clean finished product. In the secondary processing to manufacture instant coffee hot water is used to extract essence from roasted, milled coffee beans (Lane, 1983). The extracted product is only 33% by weight of the raw material (Kostenberg and Marchaim, 1993a). These processes produce a high quantity of both liquid and solid wastes that require disposal.

### 2.6.1 Coffee processing solid waste

Pulp produced during primary processing can be anaerobically digested (Boopathy, 1987), however, its composition (up to 8.5% tannins, 3% caffeine and caffeic acid,

2.6% cholorgenicic acid and 6.5% pectic materials (Bressani and Braham, 1980) makes the digestion process unstable (Lane, 1983). Solids from the secondary processing to produce instant coffee have also been treated by anaerobic digestion (Kida et al., 1992 and Kostenberg and Marchaim, 1993a) and subsequently used as a growth media for ornamental plants (Kostenberg and Marchaim, 1993b). However, in both cases pH was required to be maintained above 7.

Lane (1983) conducted experiments on the anaerobic digestion of spent coffee grounds. Lane found that he was unable to achieve long term stability of the anaerobic digestion process. He investigated the possible reasons for this and ruled out; organic over load, nutrient deficiency, loss of biologically active solids and deficiency of trace metals. He suggested that the feed stock contained toxic organic components. Brown pigments produced during the roasting of coffee beans were thought to be potentially toxic to anaerobic digestion, these were extracted and tested, but they did not cause inhibition in fresh digested sludge. Strong inhibition resulted from the addition of instant coffee powder to fresh sludge, but not from the addition of decaffeinated instant coffee powder or chicory. The inhibition was shown not to be due to the presence of caffeine, but Lane concluded that caffeine may be inhibitory in combination with other components in spent grounds.

### 2.6.2 Coffee processing liquid effluent

The liquid effluent produced during instant coffee processing is strongly coloured. The solids content of the effluent will depend on removal processes employed such as settlement and filtration. The final strength of the effluent will also depend on the practises of the production factory, the type of extraction and drying processes used. The COD of wastewater can vary from about 4 g/l to 60 g/l (Fernandez and Forster (1993).

The liquid waste is mainly carbohydrates which can be degraded anaerobically. However, due to the roasting process a number of complex heterocyclic nitrogen compounds are formed (caramels). These compounds are frequently strongly

coloured and resistant to breakdown during the residence times typically encountered in anaerobic digestion (Azhar and Stuckey, 1994).

Several teams have treated liquid effluent from instant coffee processing:

Lanting *et al.* (1989) used a pilot plant UASB (6m$^3$) and a 10 litre lab-scale reactor to investigate the treatment of instant coffee processing wastewater in the US. Two trials were conducted at both mesophilic and thermophilic conditions. The first mesophilic trial at pilot plant scale ended after 8 weeks when VFA levels rapidly rose. The second mesophilic trial at lab-scale ended after 7 weeks when VFA levels rose again showing reactor instability. Once VFA levels increased the authors operated the reactors in effluent recycle mode which they reported as giving the reactors 'temporary relief' until fresh effluent was added which increased VFA levels again. The first thermophilic trial only lasted 8 weeks due to a factory shut down. Reactor temperature was increased from 33 to 55°C. Instability of VFA was encountered at 50°C, during which effluent was recycled back into the digester. The second thermophilic trial ran for 4.5 months. It experienced two periods of instability which corresponded to two periods in which tap water used in the preparation of feed batches was replaced with effluent from the digester. The authors concluded that either the tap water provided micro nutrients lacking in the wastewater (which consisted of condensates) or that there was product inhibition from the effluent. The latter theory contradicts results from the first two mesophilic trials in which recycled effluent provided reactor stability during instability. Micro-nutrients were added after the second period of effluent recycle due to continued instability. VFA levels are reported as stabilising after this addition and loading rates increased to 10 g COD/l/d. Average COD removal during the second thermophilic trial was 69%. Oil and grease was reported to build up during mesophilic operation which was thought to interfere with the mechanical operation of the reactor, however, under thermophilic operation the increased solubility of oil and grease reduced this problem.

Hajipakkos (1992) presented data from the treatment of instant coffee processing wastewater using a full scale UASB (880m$^3$). This operated with a preacidification tank and a submerged aerated filter for polishing of the effluent prior to discharge to

sewer. Data is presented for a period of 115 days. Biogas production was 0.33 m$^3$ methane/kg COD removed, however COD removal was only 54.6 % and BOD removal of 74.6 % at a volumetric loading rate of 5.24 kg COD/m3/d. - 2.37 kgBOD/m$^3$/d. Flow rate was 1373 m$^3$/d. The low COD removal rate was thought to be due to inhibition of the anaerobic digestion process.

Clarke and Macreae (1985) found that anaerobic digestion of quinic acid (present in the liquid fraction of coffee waste) produced hydroquinone, pyrogallol, phenol and catechol as end-products. Pyrogallol has been shown to be 54% degraded under anaerobic conditions (Azhar and Stuckey, 1994), however, tests were performed using fresh anaerobic sludge from a domestic application.

In comparison to the treatment of other food processing effluents, instant coffee processing effluent has been shown to be problematic to the anaerobic digestion process in that COD removal and organic loading rates are generally low. For example, Ince (1998) reported 90% COD reduction and an OLR of 7kg COD/m$^3$/d during the treatment of dairy wastewater.

The literature has shown some of the effects that toxic compounds have on anaerobic digestion. This is relevant because fluctuations in concentrations of toxins are expected at the coffee plant. This highlights the need for a control system capable of maintaining digester performance during such fluctuations. Pyrogallol, pyrazine and furan were identified as potentially inhibitory compounds present in the instant coffee processing effluent (Azhar, personal communication 1994). Therefore, it was decided to investigate the control of anaerobic digestion during toxic shock containing these compounds.

## 2.7 Aims and Objectives

Several unresolved control issues have been highlighted in the previous sections which have introduced this area of research. The literature review identified more specific gaps in understanding from which the following aim and objectives were chosen.

Aim: To develop a control strategy to improve the consistency of performance of anaerobic digestion of industrial wastes including inhibitory and refractory components. This strategy involved the investigation and application of a gaseous hydrogen sensor to develop a new adaptive control model. The literature review established that the treatment of industrial wastes would require sensors that are sensitive to rapid fluctuation in load and potentially inhibitory compounds. The specific objectives were:

1. To undertake a comprehensive study of the treatability of instant coffee processing waste at laboratory and pilot scale.

2. To undertake a detailed investigation of the pilot plant by monitoring on-line and off-line performance when treating instant coffee processing effluent. This includes the assessment of on-line $COD_{(t)}$ measurement using conductivity and suspended solids probes.

3. To identify appropriate sensors and combination of sensors for the incorporation into an overall control strategy.

4. To incorporate a new sensor as a control parameter into an adaptive control strategy and to subsequently test and compare the new control using organic and toxic shock loads likely to occur to an anaerobic digester treating instant coffee processing effluent.

5. To investigate the potential use of artificial neural networks for the control of an anaerobic digestion process.

# 3. MATERIALS AND METHODS

## 3.1 Materials

### 3.1.1 Pilot plant materials

The pilot plant facility consisted of a CSTR, a UASB, an anaerobic filter and a fluidised bed reactor, operating in parallel (see Figure 3.1). The pilot plant was designed to allow comparison between the four reactor types operating on identical waste. The pilot plant had operated previously on ice-cream waste, at the Birds-Eye factory in Gloucester prior to the coffee factory at Hayes in Middlesex. A comparison of the two food processing effluents is shown in Table 3.1. The design of the pilot plant facility is described in detail in Anderson *et al.* (1988).

Table 3.1. Ice-cream and coffee effluent characteristics.

| Parameter | Ice-cream waste water (2.5 year average) | Coffee waste water (6 month average) |
|---|---|---|
| COD total (mg/l) | 4934 | 10380 |
| COD filtered (mg/l) | 2220 | 9055 |
| total suspended solids (mg/l) | 1150 | 1850 |
| volatile suspended solids (mg/l) | 1120 | 1041 |
| pH | 6.87 | 6.65 |
| alkalinity (mg/l $CaCO_3$) | 3000 | 3000 |
| volatile acid (mg/l) | 630 | 2200 |
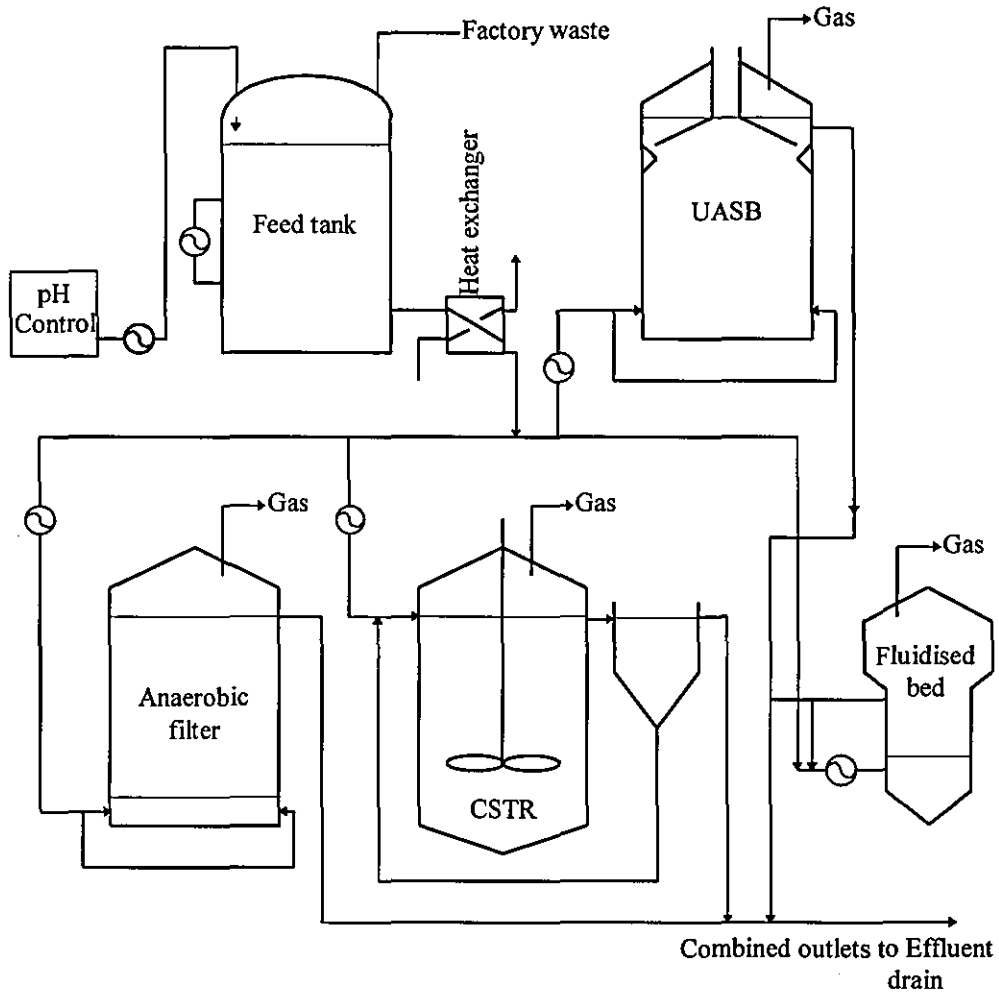
Figure 3.1  EPSRC Pilot plant facility

### 3.1.2  Laboratory scale digester materials

Experiments were carried out using laboratory scale 10 litre biological anaerobic upflow filters containing randomly packed plastic media. The laboratory reactors have previously been described in detail (Johnson *et al.*, 1994). The liquid volume of both reactors was 10 litres and normally set to run with a hydraulic retention time of 24 hours. The reactors were located in a constant temperature room which was maintained at 37 ± 0.5°C. Effluent from instant coffee production was used as the feed (stored at 4 ± 0.5°C). In order to run the laboratory reactors in a similar manor to pilot plant experiments this effluent was pre-acidified and settled within an on-site pilot-scale treatment system before collection for use in laboratory trials. The effluent

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was normally added to the laboratory reactor at a 50% dilution. Higher effluent concentrations were used for organic shock loading tests to be performed.
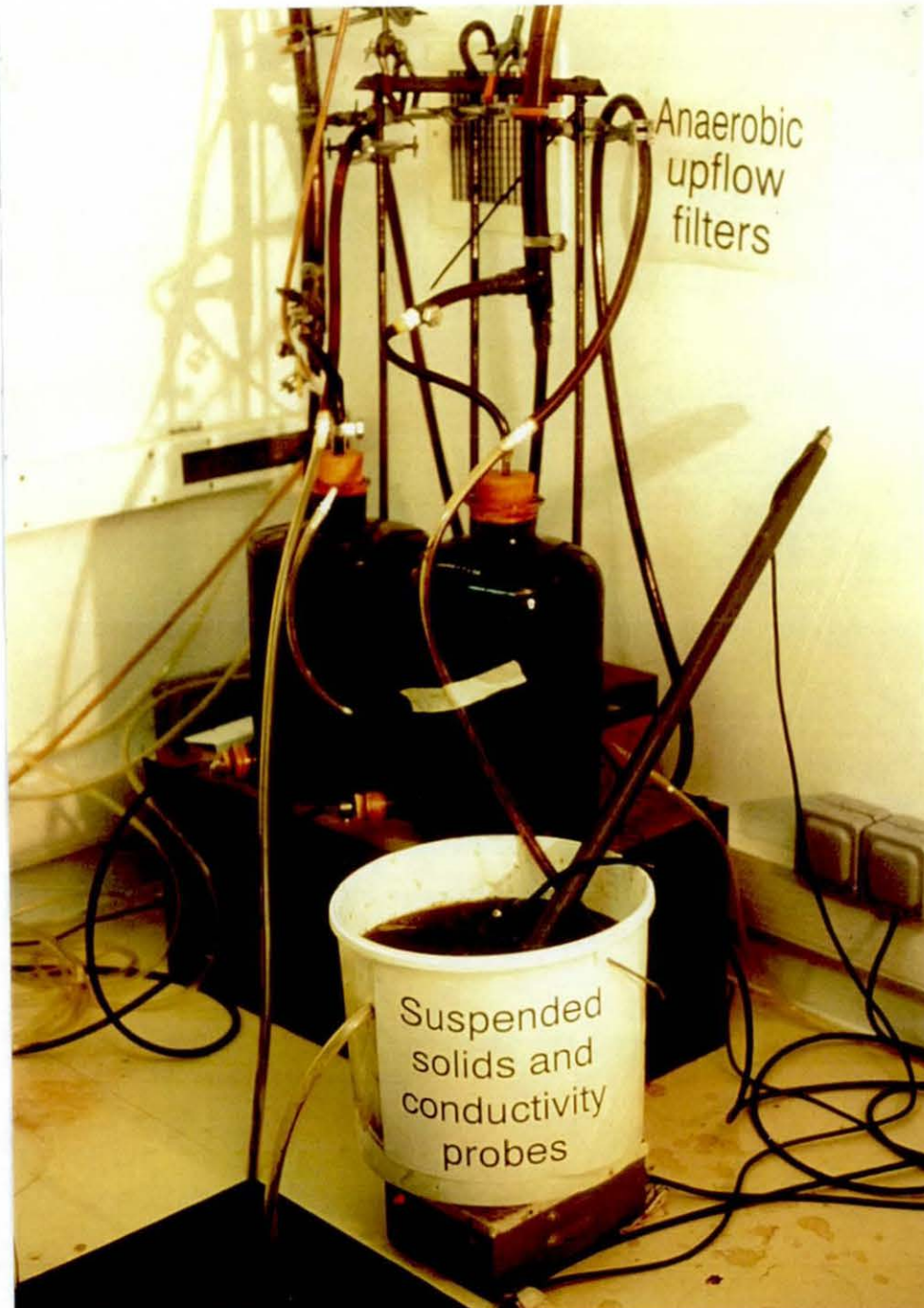
Figure 3.2  The laboratory scale anaerobic filters, suspended solids and conductivity probes
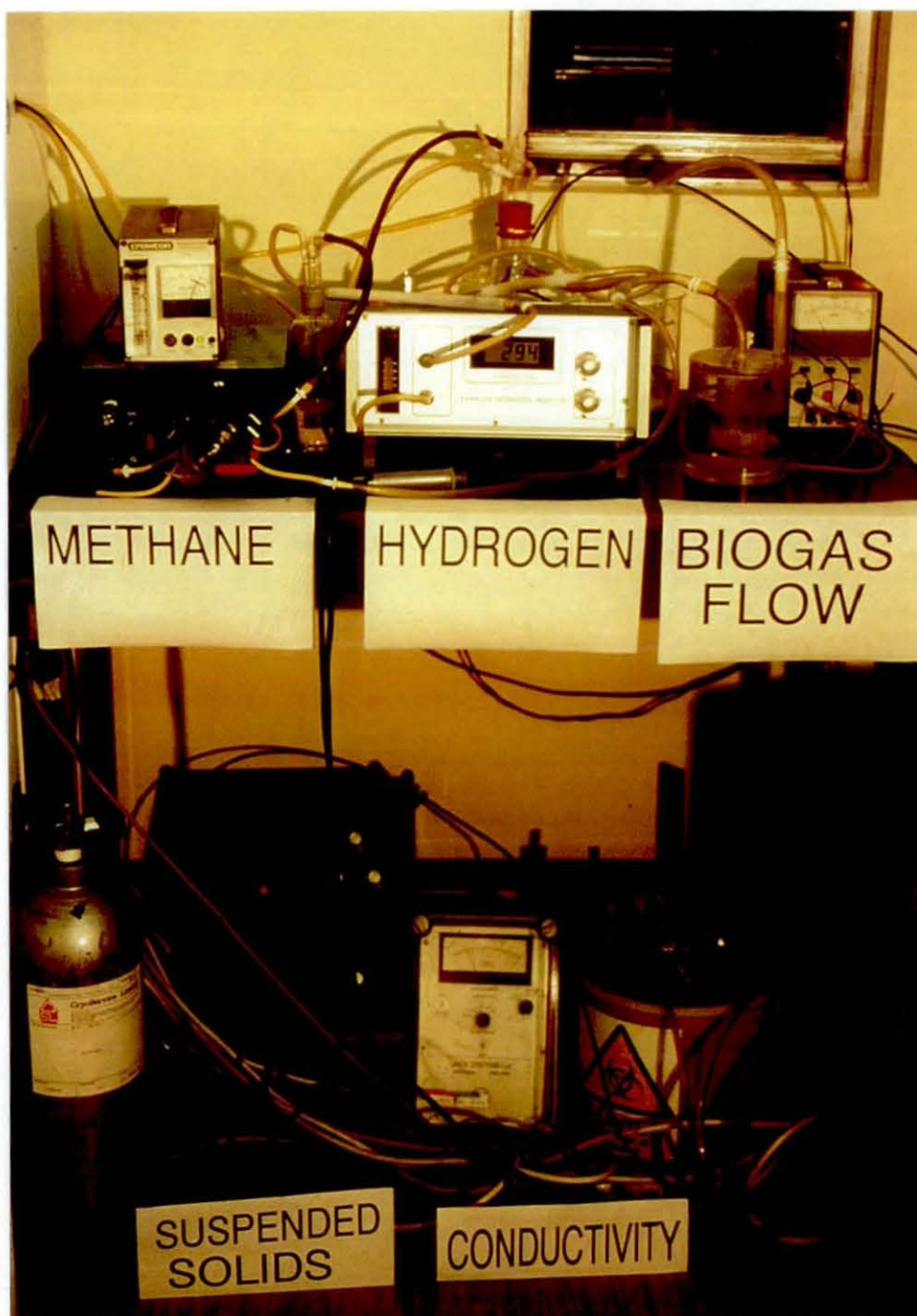
Figure 3.3 The gas phase control parameter measurement equipment and suspended solids and conductivity meters

## 3.2 Methods

### 3.2.1 Digester control system
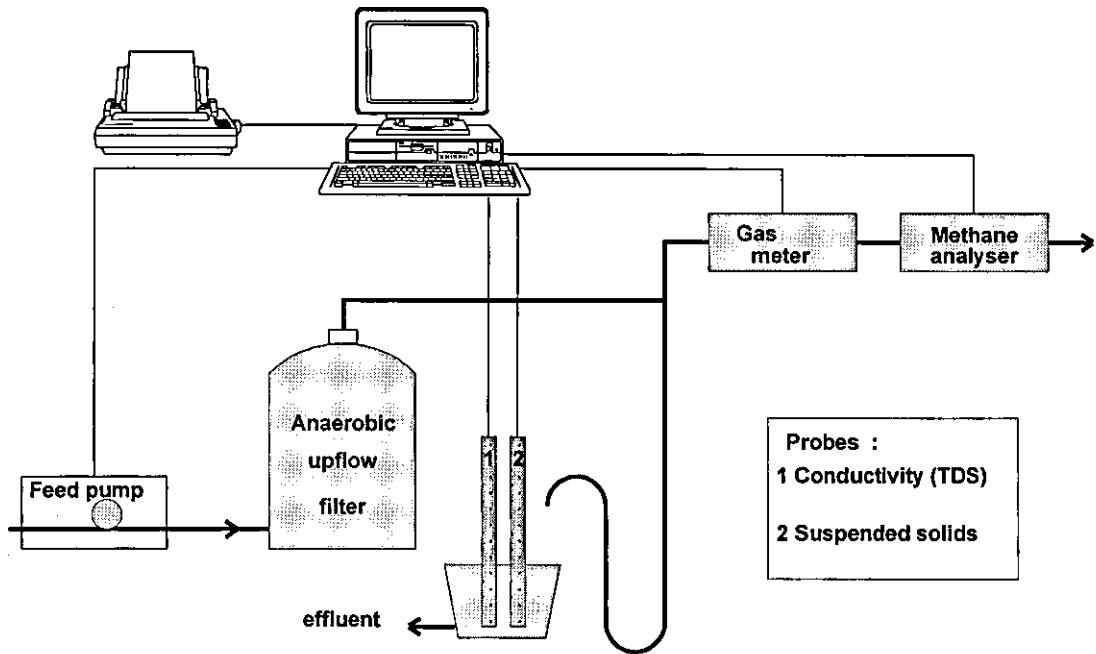


Fig. 3.4. Control equipment

The principal components of the original control system are shown in Figure 3.4. A variable speed pump (Watson Marlow 503U) was used to feed the anaerobic upflow filter. Gas and liquid effluent from the reactor were separated using a T-piece. Gas flow and methane concentration were determined and recorded by the computer prior to being vented to the atmosphere. The treated effluent stream entered a fixed volume analysis tank (3 l) continuously mixed by a magnetic stirrer (Figure 3.2). This allowed analysis of a flow of treated effluent from the anaerobic digester. The suspended solids and conductivity probes were suspended in the analysis tank and connected to the computer, which in turn controls the variable speed feed pump.

The suspended solids probe, conductivity probe and methane-in-carbon-dioxide analyser individually output a 4-20 mA signal which was converted to conventional units by the microcomputer using predetermined calibration factors (details of probes are given in Table 3.2). The rate of gas flow was determined by a work shop gas

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flow meter, that output a signal to the computer for every 40 ml of biogas produced. The methane-in-carbon-dioxide analyser was adversely affected by condensation of water vapour and high concentrations of hydrogen sulphide gas. Therefore, a buchner flask containing desiccant material and a drechsel bottle containing a solution of zinc acetate were located upstream of the gas analyser (Figure 3.3).

Initially, a BBC microcomputer and interface was used to run the control algorithm. This was later replaced by a IBM compatible PC, fitted with an analogue to digital conversion (ADC) and digital to analogue conversion (DAC) card, which allowed more parameters to be monitored. Computer equipment used is listed in Table 3.2.

Table 3.2 Equipment used for the adaptive control system

| Parameter | Equipment |
|---|---|
| data processor | BBC microcomputer / 386 Nimbus PC |
| interface | Harlyn multi application peripheral system / ARCOM DAC and ADC cards |
| suspended solids | Eur-control mex 3, SS meter and RD 120/25 probe |
| total dissolved solids | pHOX series 55 conductivity meter with a D1 conductivity measuring cell |
| gas production | Workshop model based on WRc design |
| biogas quality | Crowcon 76 TC methane in carbon dioxide analyser |

### 3.2.2 Routine analysis methods

During the start up and steady state operation of the laboratory digesters, routine analysis was carried out to investigate their performance. The analytical methods used in this study are listed in Table 3.3.

Table 3.3 Routine analytical methods

| Parameter | Method | Frequency | Reference |
|---|---|---|---|
| COD | Dichromate open reflux | daily | Standard methods (1989) |
| Suspended solids | Gravimetric | weekly | Standard methods (1989) |
| Ripley's ratio | Titration | daily | Ross et al. (1992) |
| Volatile fatty acids | Titration | daily | Standard methods (1989) |
| pH | pH meter | daily | Mettler delta 340 |

### 3.2.2.1 Ripley's Ratio

Ripley's ratio was used to provide simple off-line monitoring of the anaerobic digesters. This method was used to measure the biological stability of the anaerobic digestion process so that any change in alkalinity could be quickly detected (Ripley *et al.*, 1986). The alkalinity provides a buffering capacity to an anaerobic digester to compensate for changes in concentration of volatile acid, which would otherwise result in undesirable changes in pH. The most common way to measure digester alkalinity is outlined in Standard Methods 1989. This involves the settling or centrifugation of a sample, the supernatant is then titrated with standardised $H_2SO_4$ to an endpoint of pH 4.3. However, titration down to pH 4.3 will measure volatile acid buffering in addition to bicarbonate buffering, which is not desirable due to the volatile acids not being a useful part of alkalinity. Ripley *et al.*, (1986) proposed titration from original pH to pH 5.75 (partial alkalinity) to detect alkalinity that corresponds roughly to bicarbonate alkalinity (Jenkins *et al.*, 1991), followed by titration from pH 5.75 to pH 4.3 (intermediate alkalinity) which approximates the volatile acid alkalinity (Ripley *et al.*, 1986). The Ratio of intermediate alkalinity to partial alkalinity is useful because successful digester operation depends on both maintenance of adequate bicarbonate buffering and avoidance of excessive volatile acid concentrations. This method was chosen over other similar methods because it requires only one simple analytical procedure. Also, during a period of instability within an aerobic digester the volatile acids increasing when bicarbonate alkalinity decreases would make total alkalinity measurements less useful. Additionally, the ratio is dimensionless, therefore, any analytical errors from incorrect titrant standardisation or sample volume are avoided. The full Ripley's Ratio method is detailed in Ross *et al.* (1992).

### 3.2.3 Estimation of on-line $COD_{(I)}$

Automatic determination of TOC is available, and can be correlated to COD, but the equipment requires the continual preparation of reagents and is expensive. Therefore, an on-line estimation of $COD_{(I)}$ using a suspended solids and conductivity probe was

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utilised. The strength of a waste as measured by COD is proportional to the dissolved and suspended solids, i.e.

$$COD_{(I)} \propto (SS + TDS)$$

where SS     = Suspended solids (mg/l)

TDS     = total dissolved solids (measured by conductivity) ($\mu$s)

$COD_{(I)} = K_c (SS + TDS)$ where $K_c$ = constant for a particular type of waste

A correlation between SS, TDS and COD was established using the open reflux method for COD analysis (Standard methods, 1989), which enabled the determination of $K_c$.

The value of $K_C$ was checked by comparing the on-line values of SS + TDS with COD obtained conventionally by wet analysis. Using the combination of these two probes and regular cleaning (every 2 or 3 days) the COD could be obtained to within 5% of the wet analysis result (see Figure 3-1 Appendix 3). Problems with this approach would occur if there were changes in the inorganic content of the waste. An increase in inorganic salts would result in a disproportionate increase in the $COD_{(I)}$ than wet test COD and a decrease would cause a lower $COD_{(I)}$ than wet test COD. Similarly, changes in silts would cause distortion of $COD_{(I)}$ result. In order to avoid inaccuracies the ratio between the TDS and SS would have to be continually checked by the model to identify, for example, caustic clean downs. Periodic checks were performed to re-calibrate $COD_{(I)}$ in order to ensure such interferences were not present.

### 3.2.4 Feed-back control algorithm

The control model used in these experiments was based on that reported by Renard *et al.* (1988) who used an adaptive algorithm to control a pilot anaerobic filter. This model was chosen because of previous experience of its use within Loughborough's water research laboratories and availability of equipment to monitor the control parameters. The objective of the control algorithm was to regulate the treated effluent COD concentration (S) to a fixed predetermined level (S*). This was to be achieved

regardless of fluctuations in the influent COD concentration ($S_{in}$) by control of the hydraulic and organic loading rate (dilution rate, D). The dilution rate is flow (l/d) over volume of reactor (l), and is thus quoted with the unit $d^{-1}$. This is the inverse of HRT i.e. volume of reactor (l) over flow (l/d). Thus, a dilution rate of 0.2 $d^{-1}$ is equal to a HRT of 5 days. The algorithm assumed that the reactor was well mixed and that ultimately the methanogenic step controls the removal of COD from the liquid phase. A mass balance of the reactor according to the well known microbial growth equations was used (see Renard *et al.*, 1988, for more detail) to produce the dynamic control equation (1) used as the basis for control.

$$\frac{dS(t)}{dt} = -KQ_{(t)} + D_{(t)} S_{in(t)} - D_{(t)} S_{(t)} \tag{1}$$

where $K = k_1/k_2$

$S_{(t)}$ = substrate biomass concentration in the effluent (g COD.$l^{-1}$)

$S_{in(t)}$ = substrate biomass concentration in the influent (g COD.$l^{-1}$)

$Q_{(t)}$ = methane gas production rate (l.$h^{-1}$)

$D_{(t)}$ = dilution rate (day$^{-1}$)

$k_1$ and $k_2$ = yield coefficients

This equation assumes that the growth rate is positive with a value between 0 and $m_{max}$, the maximum specific growth rate, and also that there was no growth without substrate i.e. $m_{(t)} = 0$ when $S_{(t)} = 0$.

$X_{(t)}$ = methanogenic bacterial (active biomass) concentration

$m_{(t)}$ = specific growth rate (day$^{-1}$)

Equation (1) is a dynamic equation for the substrate concentration $S_{(t)}$, in which the measurable on-line variable $Q_{(t)}$ has replaced the difficult to measure concentration $X_{(t)}$ and specific growth rate $m_{(t)}$ of the methanogenic biomass. K is the yield coefficient for converting biomass substrate, $S_{(t)}$, into methane. The yield coefficient K, was unknown and was replaced by $K_{(t)}$, an on-line estimate of K, which was a function of

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time and continually updated and re-used for automatic control. Based on the adaptive theory of Dochain and Bastin (1985) two discretised control equations were established:-

$$K_{t+1} = K_t + T C_2 Q_{t+1} [S^* - S_t]$$  (2)

and

$$D_{t+1} = \frac{C_{1t+1} [S^* - S_t] + K_{t+1} Q_{t+1}}{S_{int} = S_t}$$  (3)

Where $K_{t+1}$ was the present value of K which had been estimated from $K_t$ the value of K, t hours earlier ($K_t$ at t = 0, the first value was arbitrarily chosen). The value $S_t$ was the on-line estimate of the effluent COD measured every t hour period, $Q_{t+1}$ was the on-line measured methane production rate over this period. $C_1$ and $C_2$ are control or design constants adopted from Renard $et$ $al.$ (1988). These constants were tested empirically in the present experiments and also found to produce realistic results.

The algorithm starts by calculating a value for effluent $COD_{(t)}$ ($S_t$) from measurements of SS and TDS. The biogas production rate and % methane were derived directly from sensors. From these figures $K_{t+1}$ was estimated by the application of equation (2). The dilution rate (D) was then calculated by substituting the $K_{t+1}$ value in equation (3) and used to control the pump speed (and hence dilution rate) via the DAC. The calculations were then continuously repeated to keep updating $K_{(t)}$ to give an adaptive control.

### 3.2.5 Tracer study

Measurement of the flow pattern in the laboratory anaerobic filter was important as the degree of mixing which occurred is relevant to the rate of reactor response to a change in feed concentration or composition. The hydraulic profile was analysed at a HRT of 0.5 days, using lithium as an inert tracer material in a method described by

Levenspiel (1972). Lithium chloride was dissolved in distilled water and injected in a pulse into the base of the anaerobic filter. The quantity of lithium chloride added was enough to give an equivalent fully mixed concentration ($C_o$) of approximately 8.2 mg/l lithium based on reactor working volume. Samples were collected from the reactor outlet at regular intervals. Sampling continued until over 50% of lithium had been recovered. Lithium concentrations in the samples were measured on a flame photometer (Corning 410) and read off a standard calibration curve. The recovery of the tracer can be interpreted to give a dimensionless value for the axial dispersion within the vessel. A low value of dispersion number (0-0.025) indicates negligible mixing; i.e. plug flow, a high value (above 0.2) indicates good mixing and dispersion (Levenspiel, 1972).

Figure 3-2 (Appendix 3) shows the data from the tracer study. The dispersion number was calculated to be 0.31. This indicates that there was a high degree of mixing occurring within the anaerobic filter. Results have been reported that show that the anaerobic filter to be virtually plug flow reactor design prior to inoculation with anaerobic bacteria (Johnson *et al.*, 1994). After inoculation with active anaerobic bacteria however, it was reported that the production of biogas results in a high degree of mixing (Hickson, 1995 and Johnson *et al.*, 1994).

### 3.2.6 Neural network training and testing

For this study a commercially available neural network package (Neuralware's Neural Explorer) was used to train and test a back propagation neural network.

### 3.2.7 Trace gas analysis

A study on the various types of trace gas analysis i.e. $H_2$, $H_2S$ and CO was performed. Four potential on-line analytical techniques were compared experimentally. These are; the Bruel Kjaer acoustic density monitor; a GMI land surveyor and an exhaled hydrogen analyser both based on fuel cells; an ADC and Miran infra-red analyser and a Crowcon hot wire thermal conductivity detector. The most practical instrument in terms of reliable analytical range and expense was found to be the GMI exhaled hydrogen analyser.

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### 3.2.8 Measurement of hydrogen in digester biogas

The instrument used for the measurement of trace concentration of hydrogen is shown Figure 3.3. The GMI exhaled hydrogen monitor was originally developed for a medical application. A polarographic cell is used as the sensing element which also reacts to $H_2S$. Therefore, removal of $H_2S$ before analysis was necessary and was achieved by passing the sample through a zinc or lead acetate filled tube connected to the inlet port of the instrument. A detailed description of the calibration and testing of a GMI $H_2$ monitor is given in Collins and Paskins (1987).

### 3.2.9 Experimental programme

Digester performance was investigated during increases in concentration of digester feed and during the addition of single toxins to a steady state, laboratory scale, upflow anaerobic filter that was monitored and controlled by the adaptive control algorithm. The chemical structure of pyrogallol, pyrazine and Furan, purchased from Sigma Aldrich Ltd, are shown in Figure 3.5. Table 3.4 shows the concentration and method of application of each of these changes in digester feed.
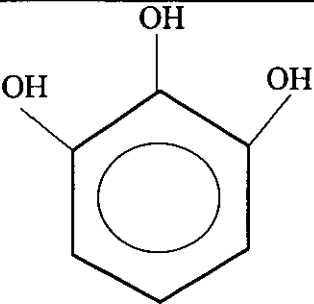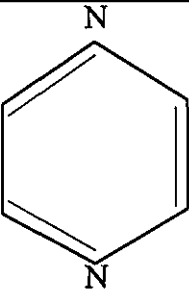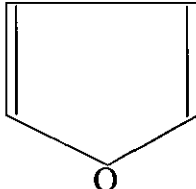
| | | |
|---|---|---|
| OH OH OH | N N | O |
| Pyrogallol (1,2,3 trihydroxybenzene) | Pyrazine (1,4 diazine) | Furan |
| $C_6H_6O_3$ Molecular weight 126.1 | $C_4H_4N_2$ Molecular weight 80.09 | $C_4H_4O$ Molecular weight 68.8 |

Figure 3.5 Chemical structure of pyrogallol, pyrazine and furan.

Table 3.4 Concentration and method of application of change in digester feed

| Addition to digester feed | Method of application | Concentration |
|---|---|---|
| pyrogallol | addition to feed | 0.25 g/l<br>1 g/l<br>3 g/l |
| furan | addition to feed<br>direct injection | 2 g/l<br>1 g/l |
| pyrazine | addition to feed | 1 g/l |
| increased organic load | dilution of high strength effluent | 16000 mg/l<br>33000 mg/l |

## 4. PILOT PLANT ANAEROBIC FILTER MONITORING

### *4.1 Pilot plant monitoring*

As mentioned previously in Chapter 1, in order to raise the profile of anaerobic digestion in the UK and to encourage collaboration between some of the key researchers in the subject the EPSRC (formerly SERC) funded a programme of research based on a central facility of a large pilot plant. The pilot plant consisted of a CSTR, a UASB, an anaerobic filter, and a fluidised bed reactor (these are described previously in greater detail in the Chapter 3). The facility has operated on two industrial sites : at the Birds-Eye Walls factory in Gloucester, treating ice-cream waste, and at the Nestle factory in Hayes, treating instant coffee processing effluent. In order to provide a comparison to research conducted at laboratory scale, results are presented from the EPSRC's pilot plant anaerobic filter treating coffee waste and ice-cream waste over a four year period based on daily on-site analysis. Comparisons are made between the performance of the anaerobic filter treating these two food processing effluents.

Data is also presented from the on-line monitoring of the pilot plant anaerobic filter treating coffee waste during a period of this research. The application of the on-line $COD_{(t)}$ probe is tested at pilot plant scale and its performance discussed.

### 4.1.1 Anaerobic pilot plant filter performance on ice-cream waste

Data is presented in Figure 4.1 and 4.2 from the anaerobic treatment of ice-cream waste by the anaerobic filter. Figure 4.1 shows monthly average percentage COD removal over an 800 day period. Variations occurring in the percentage COD removal coincide with changes in reactor packing and other experiments conducted on the pilot plant during this period of research. The percentage COD removal is seen to rise to greater than 80% during times of stable operation, the average percentage COD removal however is 74%. The performance of the pilot plant gas flow meter is shown to be poor during periods of low gas flow. Once the rate of gas flow decreased below $1m^3/hr$ the gas flow meter registered a flow of zero. This resulted in a zero methane

yield being recorded. Methane yield (Figure 4.2) does not vary to the same extent as percentage COD removal. The average methane yield over the entire experimental programme treating ice-cream was 260 l/kgCOD.
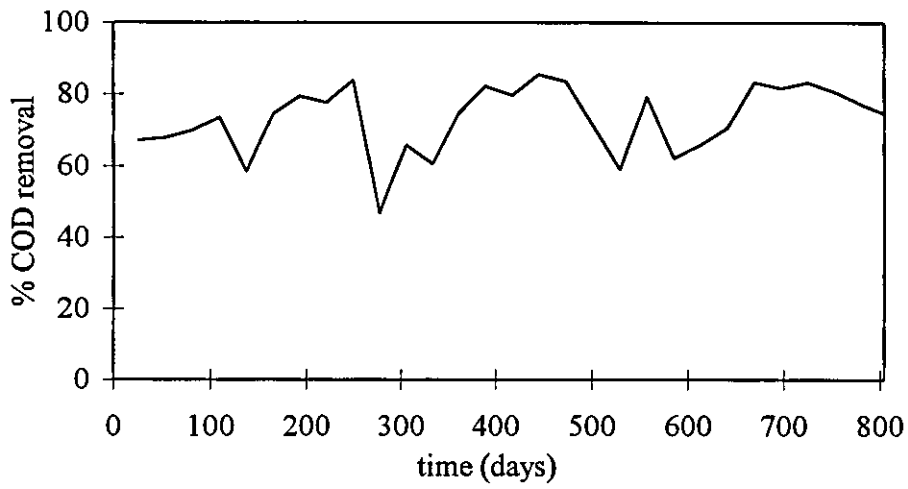
Figure 4.1 Monthly average %COD removal for the anaerobic filter treating ice-cream waste
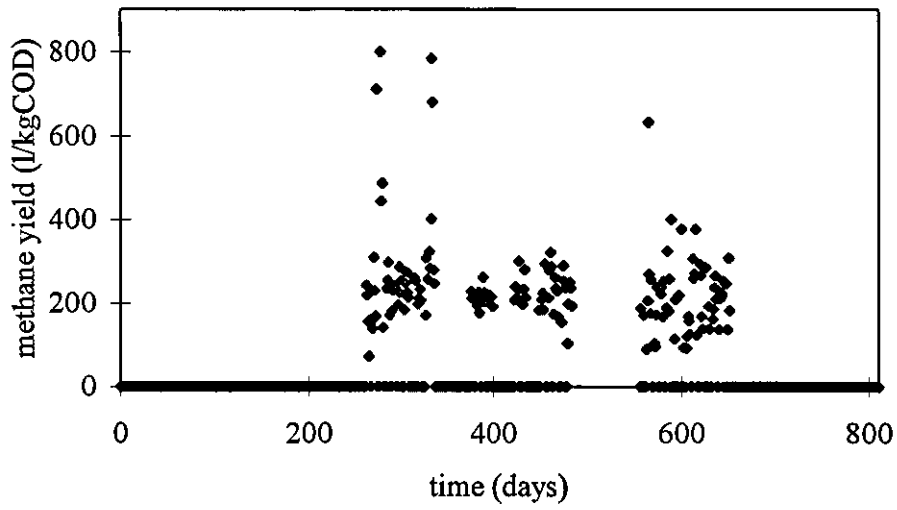


Figure 4.2 Gas yield for the anaerobic filter treating ice-cream waste
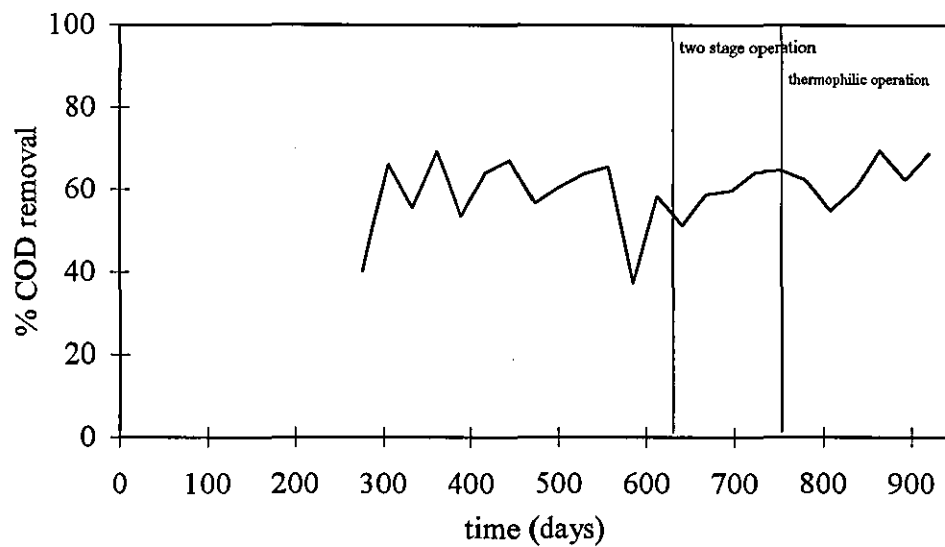
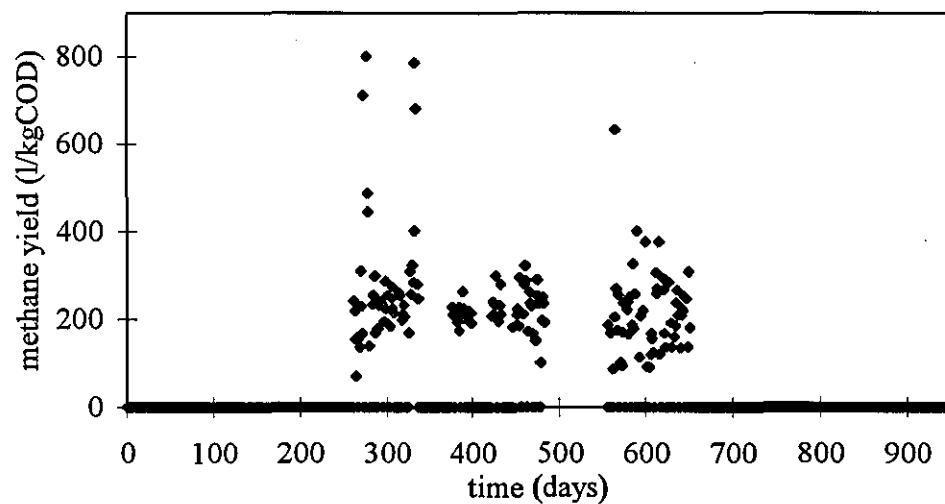Figure 4.3 Monthly average %COD removal for the anaerobic filter treating coffee waste



Figure 4.4 Gas yield for the anaerobic filter treating coffee waste

### 4.1.2 Anaerobic pilot plant filter performance on coffee waste

Data is presented in Figure 4.3 and 4.4 from the anaerobic treatment of coffee waste by the anaerobic filter. Figure 4.3 shows monthly average percentage COD removal over the experimental period. Changes in configuration and running are indicated on this graph. Figure 4.4 shows gas yield for the treatment of coffee effluent. The gas yield does not show any marked change during the experimental programme, however, readings are not available after 650 days due to equipment problems. The average methane yield during the operation of the mesophilic, single stage anaerobic filter is 238 l/kgCOD removed. After 640 days the reactor was operated as a two stage digester. After 760 days the digester was operated at thermophilic temperatures. The average percentage COD removal was 65%. This removal efficiency did not appear to increase during two stage operation. During thermophilic operation the COD removal efficiency initially decreased as expected. However, after a period of acclimatisation to the higher temperature the efficiency of anaerobic digestion as measured by percentage COD removal increased back to the highest level of the two-stage operation of the anaerobic filter.

### 4.1.3 Discussion: comparison of ice-cream and coffee treatment

A summary of the performance of the pilot plant anaerobic filter is shown in Table 4.1. The treatment of ice-cream effluent is relatively good compared to that of instant coffee processing effluent.

Results from the pilot plant experiment treating coffee effluent showed that the methane yield declined when the loading rate was increased above 4 kgCOD/m³/day. Since the average loading rate to the pilot plant anaerobic filter was 4.2 kg/COD/m³/day this would have resulted in a reduction in the activity of the methanogenic bacteria. This reduction in activity implies that the anaerobic bacteria were unable to metabolise the coffee effluent as efficiently as the ice-cream effluent previously tested at pilot scale (see Table 4.1). The resulting average reduction in COD of 65% is a consequence of the properties of the effluent treated. The organic loading rate reported here for coffee effluent compares with a maximum of 5.24

kg/COD/m³/day reported by Hajipakkos (1992) for the treatment of similar instant coffee processing waste water. The coffee effluent contained more recalcitrant and toxic substances (e.g. pyrogallol, Azhar and Stuckey, 1994) then the ice-cream waste, and the concentration of these substances fluctuated with different production processes taking place in the coffee factory. Hence the fluctuations in COD removal were primarily due to changes in the feed. These fluctuations in digester performance are problematic when they result in a breach of discharge consent. This is potentially a more difficult problem than the low COD removal efficiency. The problem of digester effluent quality fluctuations could be addressed by a control system which is able to monitor digester effluent COD and adjust the organic loading rate accordingly in order to maintain a steady effluent quality. Examples of control systems which are capable of this are reviewed in the literature in Chapter 2. In particular, Renard et al. (1988) describe a simple adaptive control system which was able to control a pilot plant scale (60 l) CSTR during a shock load from a fermentation industry waste water. It was decided to evaluate such a system for its ability to maintain digester effluent quality during the treatment of coffee waste.

Table 4.1 Anaerobic filter performance, comparing treatment of ice-cream and coffee effluent.

| Average performance | AF treating ice-cream effluent | AF treating coffee effluent |
|---|---|---|
| COD removal (%) | 74 | 65 |
| Organic loading rate (kgCOD/m³.d) | 6.1 | 4.20 |
| methane yield (l/kgCOD) | 260 | 238 |

The methane yield is low for both ice-cream and coffee effluent treatment, compared to similar anaerobic digesters (350 l/kgCOD). Additionally, COD removal and the OLRs achieved during the EPSRC programme treating both wastes are relatively low compared with typical full-scale experience of similar reactor types treating similar wastewaters. For example, at full-scale Fenton (1991) describes COD removal

efficiencies of up to 80% during the anaerobic digestion of waste from milk processing. Also, at laboratory scale Ince (1998) reports COD removal efficiencies of 90-95% for the treatment of dairy wastewater in a two stage anaerobic digestion system operating at an OLR of up to 7 kg $COD/m^3/day$. There are number of reasons for the relatively poor results from the pilot plant. Inadequate design of some of the reactors due to lack of experience may have played a part. During most of the time, the operation was geared to the observation of the four types of reactors under a set of comparable conditions rather than the optimisation of a particular reactor type for the treatment. Certain operating conditions and reactor set-up were aimed at testing the impact of a specific parameter, and by definition would not always produce the best overall performance. The particular types of waste used in the pilot programme increased the challenge to achieve satisfactory results for some of the reactors types which was not favoured for such application by past experience.

Finally, it should be pointed out that to operate a treatment plant (either on pilot or full scale) to handle an industrial effluent on a real time basis is a difficult experimental task. Start-up and acclimatisation to a new waste may take 6 months to one year to bring a new industrial effluent treatment plant to its optimum performance. For the EPSRC programme, two entirely different waste waters were tested over a four year period during which many changes were made as part of the research programme, the time may not have been sufficient for the operators to gain enough experience to achieve optimisation.

The initial decrease in efficiency during the thermophilic operation of the anaerobic filter treating instant coffee effluent could be influenced by increased sensitivity of thermophilic bacteria to organic inhibitors present in the effluent. This was shown to be the case by Disley *et al.* (1993) who compared the activity of the thermophilic and mesophilic sludges exposed to 6 organic compounds which caused inhibition.

The data presented here is in agreement with that quoted in the literature reviewed in Chapter 2. In particular low treatment efficiencies for the treatment of instant coffee wastewaters are also shown reported by Hajipakkos (1992). Hajipakkos removed 54.6% COD using a two stage $880m^3$ UASB, operating at a loading rate of

5.24kgCOD/m$^3$/day. This shows a lower operating efficiency than that of the EPSRC anaerobic filter (65% COD removal). The lower operating efficiency could be due to the higher loading rate which would result in increased inhibition of the anaerobic bacteria. Alternatively the higher efficiency of the EPSRC anaerobic filter may be due to better retention of the anaerobic bacteria. This would result in a higher quantity of anaerobic bacteria within the reactor and in a longer sludge age, which may result in acclimation of the bacteria to recalcitrant and inhibitory compounds contained by instant coffee processing effluent. Also Lanting *et al.* (1989) reported inhibition which resulted in digester failure during start-up. After successful start-up maximum removal of COD of 69% was reported during laboratory scale (10m$^3$) thermophilic digestion using a UASB. This compares well with results reported by the EPSRC pilot plant anaerobic filter, however we do not know the loading rate applied by Lanting *et al.* (1989).
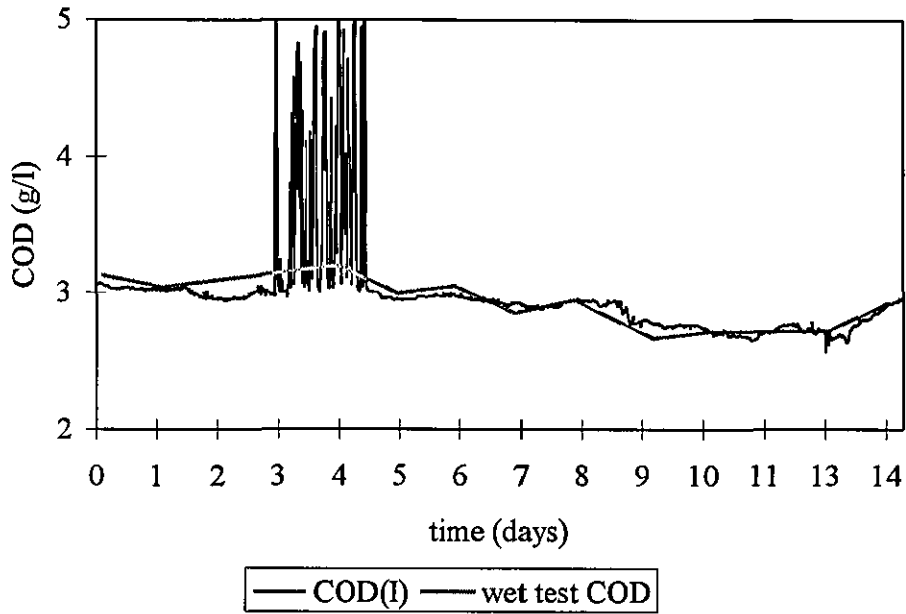
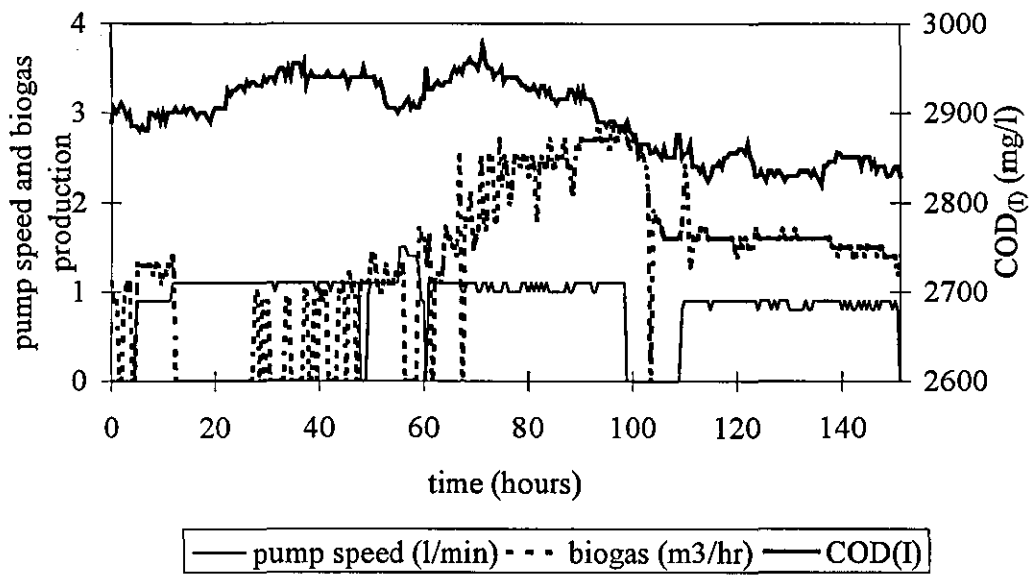Figure 4.5 Monitoring of the pilot plant (coffee waste) using $COD_{(I)}$



Figure 4.6 Monitoring of the pilot plant (coffee waste) using $COD_{(I)}$ and biogas production

## 4.2 On-line results from pilot scale

Equipment from the control system described in Chapter 3 was taken to the pilot plant treating coffee waste for evaluation. Figure 4.5 and Figure 4.6 show data from a 14 day period when the pilot plant anaerobic filter digester effluent COD was measured using the on-line $COD_{(I)}$ probe. Figure 4.5 presents data from wet test COD and on-line $COD_{(I)}$ to allow a comparison of the two methods. It is demonstrated that there is a good correlation between the on-line $COD_{(I)}$ and wet test COD. The probe was able to follow fluctuations in digester effluent $COD_{(I)}$. However, after 3 days large fluctuating increases in probe $COD_{(I)}$ occur, this is due to probe fouling. Regular probe cleaning occurred after 4.5 days the probe fouling does not reoccur. Figure 4.6 displays data from a period of 150 hours. An increase in pump speed after 11 hours correlates to a subsequent increase in digester effluent $COD_{(I)}$ at 17 hours. Biogas production, after a decrease below the limits of the gas flow meter, subsequently increases from 1 to 2.4 $m^3$/hour between 50 and 97 hours. The increase in biogas production is expected as the increased load of $COD_{(I)}$ is metabolised. After the increase in biogas production the digester effluent $COD_{(I)}$ decreases back to its original level at 100 hours. The feed pump is switched off between 97 and 108 hours, at this time the biogas production rate drops from 2.4 to 1.5 $m^3$/hour and the digester effluent $COD_{(I)}$ continues to decrease to 2850 mg/l. When the feed pump is turned on again at 108 hours and remains at a steady state, both the digester effluent $COD_{(I)}$ and biogas production remain constant. This set of data shows that the control computer and $COD_{(I)}$ probe are capable of closely monitoring changes in performance to the pilot plant digester.

## 4.3 Conclusions from pilot scale data

- The pilot plant data provided a characterisation of the coffee effluent, showing it to be difficult to degrade and consistently achieve a target effluent COD quality.

- In order to consistently meet effluent discharge consents during fluctuations in waste characteristics the provision of a control system is required which is capable

of maintaining a steady digester effluent stream quality. A suitable control system has been identified from examples in the current literature (Chapter 2)

- It is possible to monitor the pilot plant digester effluent $COD_{(t)}$ on-line using a combination of suspended solids and conductivity probes.

## 5. MONITORING AND CONTROL OF THE LABORATORY SCALE DIGESTERS

Operational data from the pilot plant discussed in Chapter 4 show that the anaerobic digestion of instant coffee processing waste is less efficient than for other food processing effluents. This conclusion is supported by literature reviewed in Chapter 2. Several potentially recalcitrant and toxic compounds present in instant coffee processing waste are identified in Chapter 2. The strength and composition of this waste is known to vary during the normal operation of the instant coffee factory. It was decided therefore to investigate the application of a control algorithm to maintain anaerobic digester effluent quality during changes in organic loading and additions of known quantities of toxic compounds.

For this research an adaptive control algorithm was used to monitor and control laboratory scale digesters. Results are presented in this chapter from both organic load increase experiments and additions of toxins that arise from instant coffee processing. Firstly data is presented from the start-up of laboratory digesters fed with instant coffee processing effluent (Section 5.1), showing a low percentage removal of COD compared to a synthetic food processing effluent. Data is presented to compare uncontrolled and controlled reactor performance during a 100% increase in feed concentration. In the second section (Section 5.2) data is presented from the addition of three potential toxins to anaerobic digestion. Increasing concentrations of potential toxins are added to digester feed, and the actions of the control system discussed. Data from the steady state operation of a laboratory scale digester is presented and discussed. Finally, strategies for improving digester control are discussed and conclusions are drawn from the data.

### 5.1 Organic shock load results

Data from the first 20 weeks operation of a laboratory scale digester are presented in Figure 5.1. The reactor achieves a relatively steady COD removal after approximately 17 weeks (65%). However, the removal efficiency is low compared to that reported for other food processing effluents discussed in Chapter 2. Figure 5.2 shows data from a control laboratory anaerobic filter fed with a synthetic food processing waste

made with yeast extract. COD removal efficiency in Figure 5.2 is shown to be more steady and higher (80%) compared to start-up shown in Figure 5.1. This data concurs with that reported at pilot plant scale in Chapter 4. We can conclude that the relatively poor performance is due to the instant coffee processing effluent containing compounds which are recalcitrant or inhibitory to anaerobic digestion.

Figure 5.3 presents data from an increase in digester feed COD from 6 g/l to 11 g/l, applied to the digester for 10 hours. The digester was operating at steady state with a hydraulic retention time of 24 hours. The data was derived from using the wet test COD method. The digester effluent COD was seen to rise after 17 hours from steady state at 2.9 to 3.26 g/l at 26 hours. The increase in reactor effluent COD earlier than 24 hours is expected as the digester is known to be operating on a semi-mixed flow basis due to biogas mixing occurring within the digester (as discussed in Chapter 3). However, the results from the tracer test performed in the methods Chapter would suggest that an increase in effluent COD would be seen earlier than 17 hours after increased feed concentration. There are two possible explanations for the delayed increase in digester effluent COD concentration. Firstly there will be a delay as the contents of the digester are increased in concentration, i.e. the high concentration feed will be diluted as it is pumped into the digester. This will result in a gradual increase of COD within the digester. Secondly, this gradual increase of COD within the digester will give the anaerobic bacteria some time to metabolise the increased load. Once the anaerobic bacteria within the digester are metabolising at their maximum rate, the efficiency of treatment is decreased. We can conclude that initially the increased influent COD concentration is metabolised by the digester, therefore a rapid change in effluent COD is not evident. Thereafter, once a threshold loading rate is reached the digester effluent COD increases. As discussed in Chapter 1, this could result in an increase in effluent concentration above a maximum admissible concentration of a discharge compliance. The need for a method of control to prevent this is highlighted by this set of data.

To this effect, experiments were conducted using a control system described in Chapter 3. Data from the adaptive control algorithm is presented in Figure 5.4 and

Figure 5.5 during a similar increase in concentration of COD of digester feed. As with the data presented in Figure 5.3 we would expect to see a delay in change to digester effluent COD from mixing with digester contents. In addition to this we would also expect a subsequent dilution with the contents of the mixing vessel containing the on-line suspended solids and conductivity probes.

Figure 5.4 presents data from an increase in digester feed COD from 5 g/l to 10 g/l, applied to the digester for 15 hours. The digester was operating at steady state with a hydraulic retention time of 18 hours. The digester effluent $COD_{(t)}$ data was derived from the on-line suspended solids and conductivity probes. Feed and effluent COD are shown in Figure 5.4. The digester effluent $COD_{(t)}$ concentration is seen to rise slightly above the original set point at 5 hours. However, the control algorithm reacts to the increase in feed and effluent $COD_{(t)}$ by reducing the pump speed (dilution rate) until 22 hours. Methane production rate was seen to decrease and increase relative to dilution rate. However, the methane production rate (q) increases to a rate higher than the original level. This increase, sustained from 23 hours to 44 hours, is due to the metabolism of the increased COD concentration. Once the increased COD is metabolised after 44 hours the methane production rate decreases and the digester effluent $COD_{(t)}$ decreases. In response to this the dilution rate gradually increases until it returns to its original level at 47 hours. The data presented in Figure 5.4 and Figure 5.5 compared to a similar uncontrolled digester feed concentration increase (Figure 5.3) demonstrate that the control system is capable of maintaining a constant effluent quality during fluctuations in digester feed concentration.
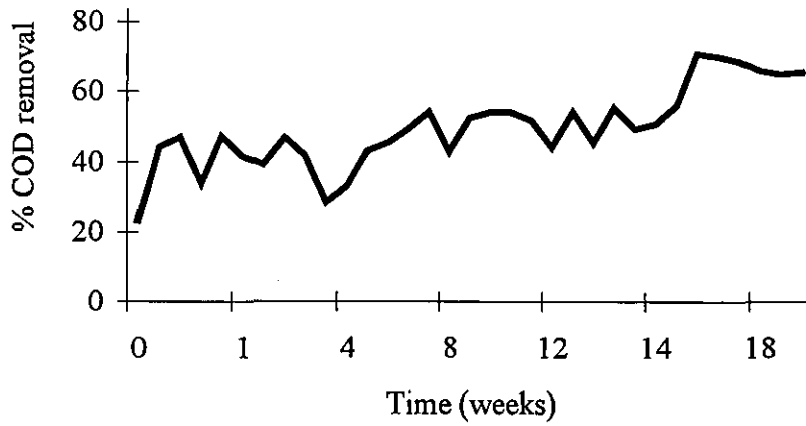
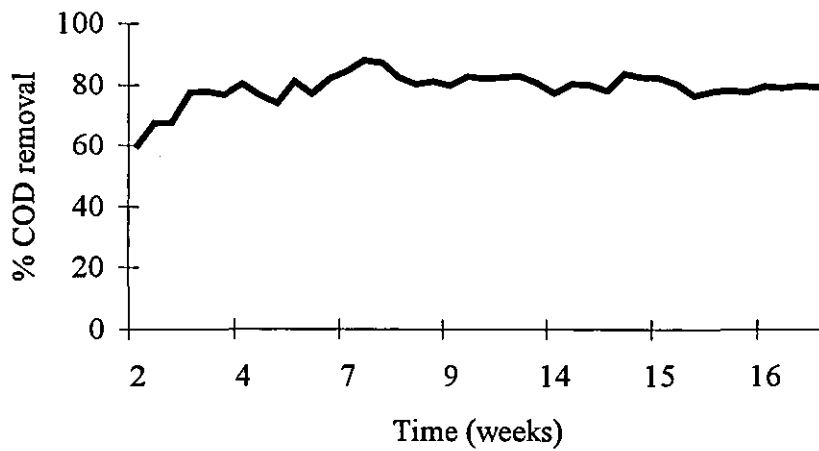Figure 5.1 Laboratory digester fed with coffee waste start-up data



Figure 5.2 Laboratory digester fed with yeast extract start-up data
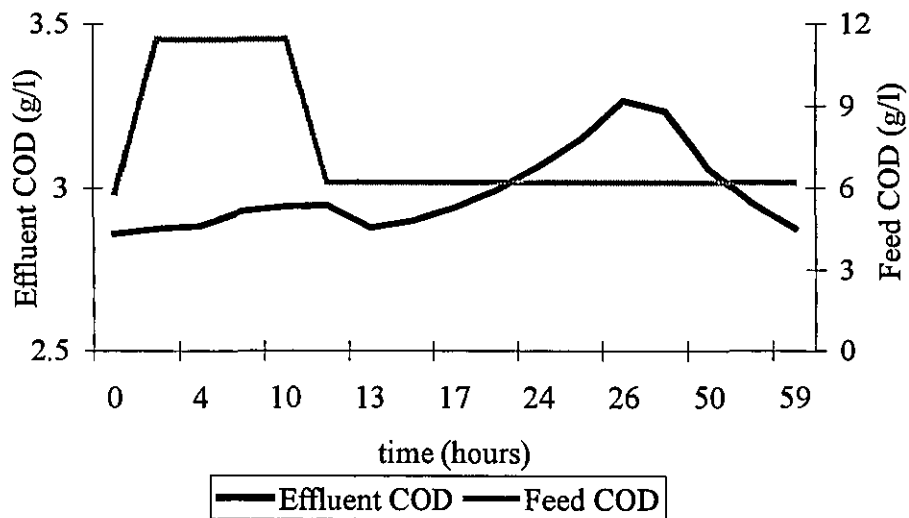


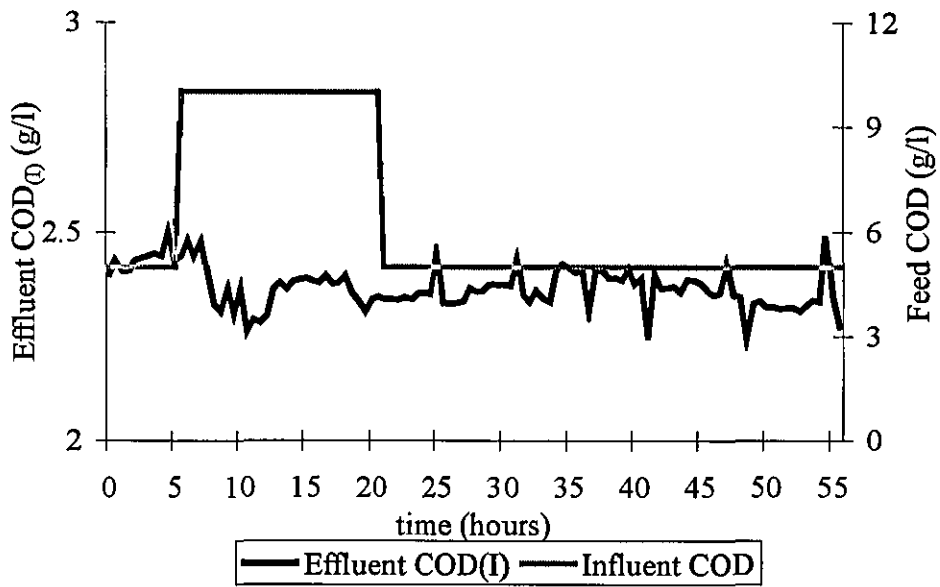Figure 5.3 Uncontrolled organic load increase (feed and effluent COD)

Figure 5.4 Controlled organic load increase (feed COD and effluent COD$_{(I)}$)
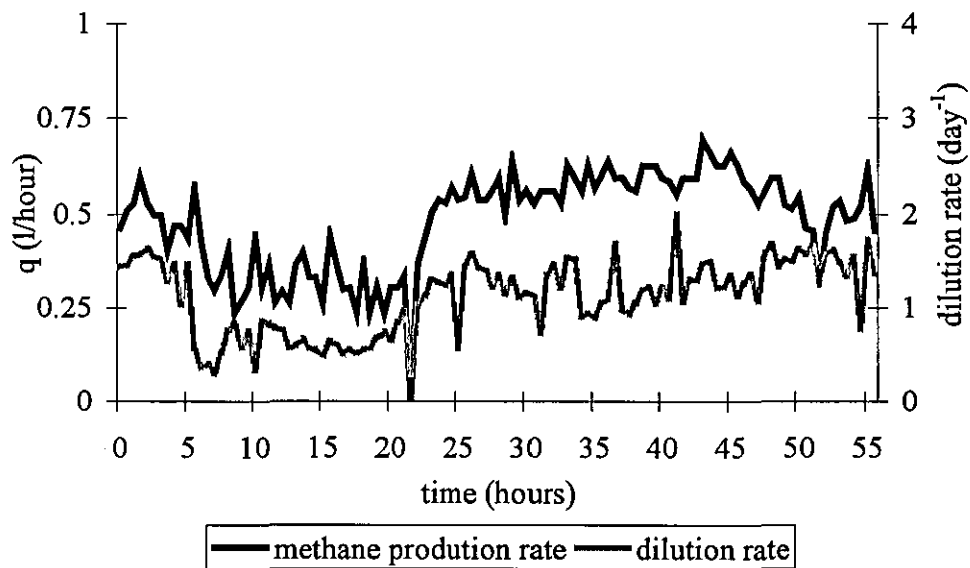


Figure 5.5 Controlled organic load increase (methane production rate and dilution rate)

## 5.2 Addition of toxic compounds to the laboratory scale digester – results

The control algorithm was demonstrated as being able to closely monitor the anaerobic digestion process and to control it by maintaining a constant effluent quality during organic load fluctuations in the previous section. As discussed previously (Chapter 2) production of instant coffee involves a roasting process which results in an effluent that contains a number of compounds that are potentially inhibitory to anaerobic digestion. It was decided, therefore, to investigate the effect of increasing the concentration of several potential toxins and to closely monitor and control the anaerobic digestion process using the control algorithm. This section describes the results from the addition of three toxins potentially present in instant coffee processing waste; pyrogallol, furan and pyrazine. Section 5.2.1 describes three additions of pyrogallol, at increasing concentrations, to a steady state anaerobic digester treating instant coffee processing effluent. Section 5.2.2 describes two additions of furan to a steady state anaerobic digester, also at increasing concentrations. The digester response is discussed and conclusions drawn from the data. Section 5.2.3 describes the addition of pyrazine to a steady state anaerobic digester. The results of these toxin additions are discussed and conclusions drawn.

### 5.2.1 Pyrogallol additions

Pyrogallol was first added to the influent stream of an anaerobic digester at 0 hours, the concentration was 0.25 g/l. The reactor was monitored and controlled by the adaptive control algorithm. Figure 5.6 and Figure 5.7 show data from this addition. Very little change in effluent quality is shown (an increase in effluent $COD_{(l)}$ of 20 mg/l). Methane production rate fluctuates around a steady state level. The addition of 0.25 g/l pyrogallol appears not to have a detrimental effect to the operation of continuous anaerobic digestion of instant coffee processing effluent.

Figure 5.8 and Figure 5.9 show data from a later experiment in which 1 g/l pyrogallol was added to the feed of the same digester. Compared with the previous addition of pyrogallol (0.25 g/l) there is a larger increase in effluent $COD_{(l)}$. The control algorithm reduced the dilution rate in response to this change. However, both the

increase in $COD_{(1)}$ (60 mg/l) and control response are small. Methane production rate is shown to decrease slightly, simultaneously with the increase in effluent $COD_{(1)}$ concentration, but otherwise remains unchanged throughout the experiment.

It was decided to increase pyrogallol concentration within the digester feed to 3 g/l. Figure 5.10 and Figure 5.11 show data from this addition, which shows some similarities with the previous addition of 1 g/l pyrogallol. The increased concentration of pyrogallol resulted in a increased effluent $COD_{(1)}$ concentration of 110 mg/l. The methane production rate decreases slightly at the same time as the increase in $COD_{(1)}$ concentration. The control algorithm reduces dilution rate in response to the increase in effluent $COD_{(1)}$.

Although the control algorithm did yield a large quantity of data relating to digester performance, there is not direct measurement of changes in alkalinity or volatile fatty acid levels within the digester. As discussed in Chapter 2 on-line measurement of these parameters is difficult. Therefore, it was decided therefore to monitor these parameters off-line in the following experiments in order to allow a comparison of on-line control parameters with these liquid phase indicators of digester stability.

Figure 5.6 0.25 g/l pyrogallol addition - $COD_{(I)}$ and dilution rate



Figure 5.7 0.25 g/l pyrogallol addition - methane production rate and $COD_{(I)}$

Figure 5.8 1.0 g/l pyrogallol addition - $COD_{(I)}$ and dilution rate



Figure 5.9 1.0 g/l pyrogallol addition - methane production rate and $COD_{(I)}$
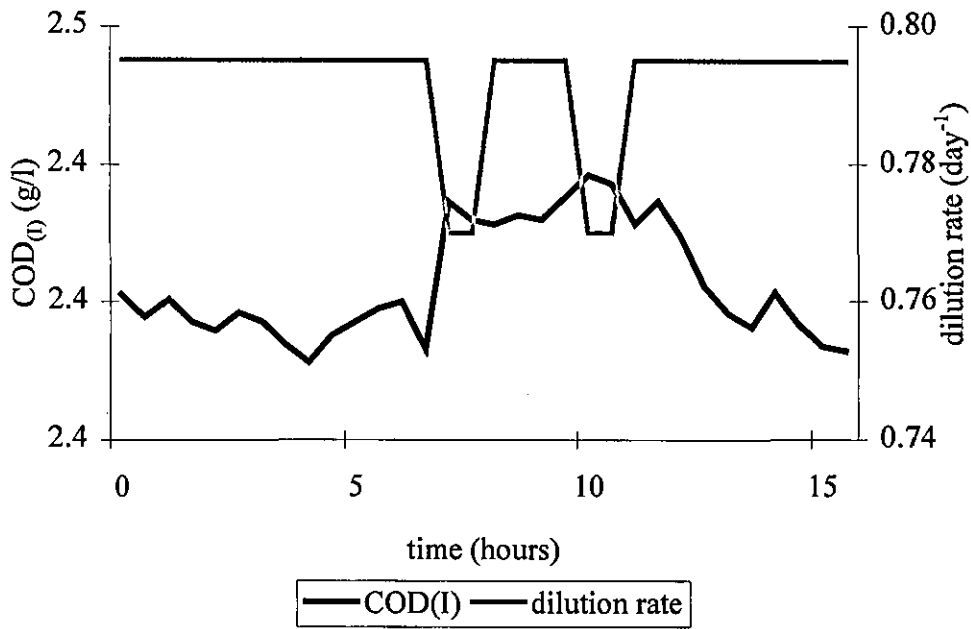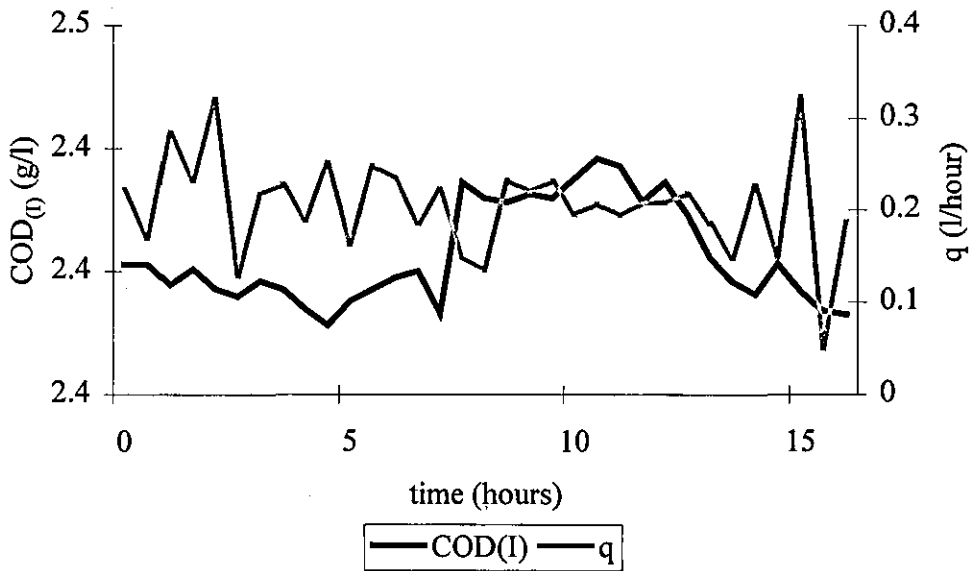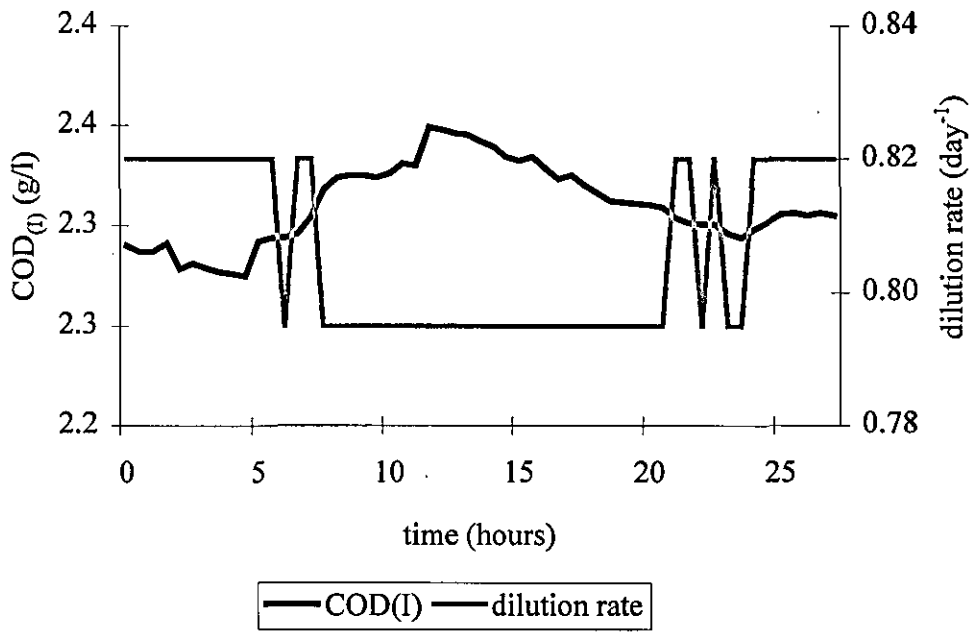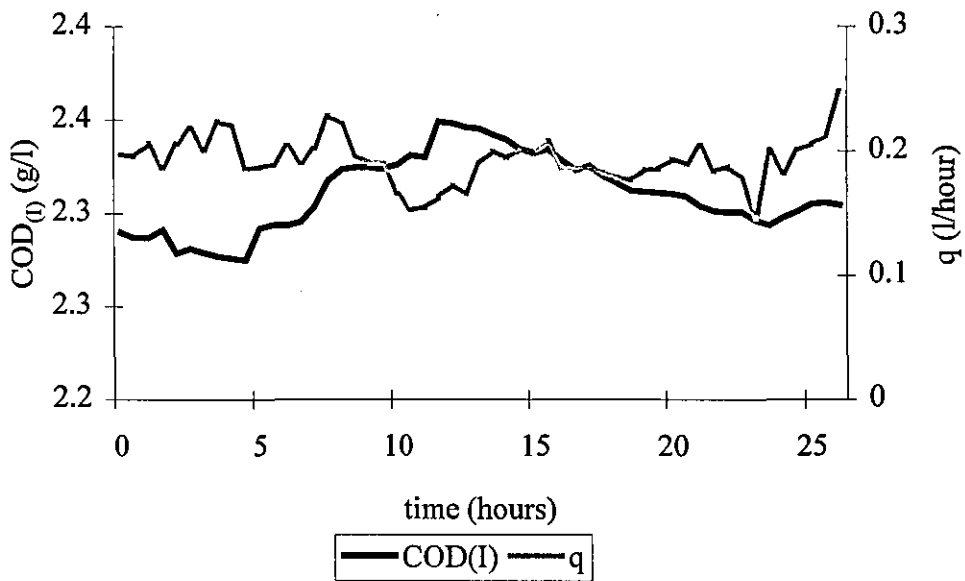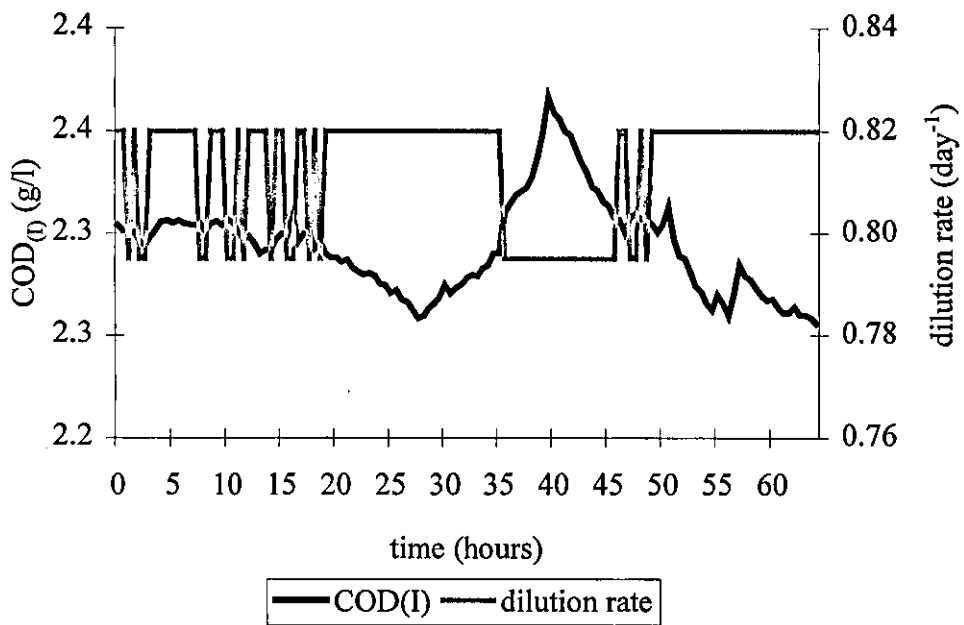
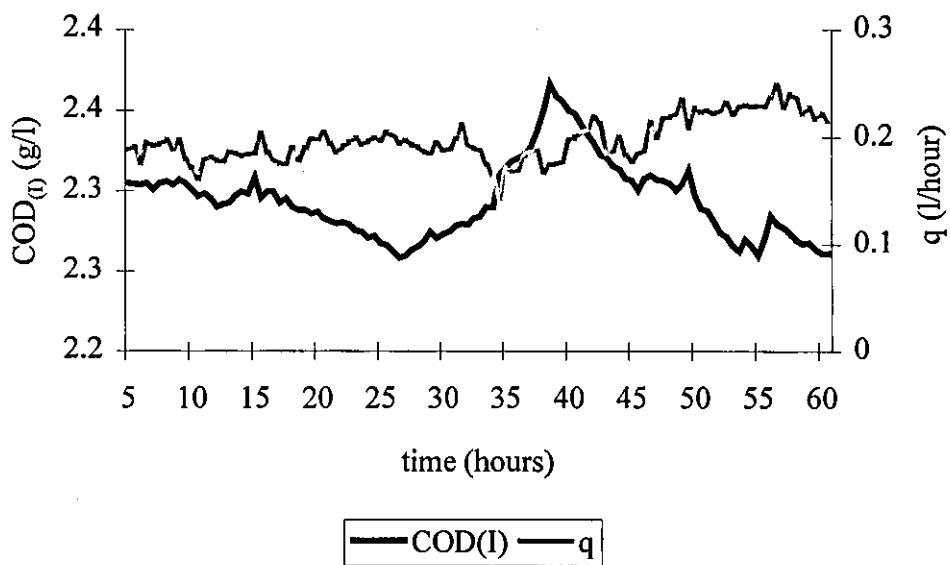Figure 5.10 3.0 g/l pyrogallol addition - $COD_{(I)}$ and dilution rate



Figure 5.11 3.0 g/l pyrogallol addition - methane production rate and $COD_{(I)}$

## 5.2.2 Furan additions

Experiments were conducted to determine the inhibitory or toxic effect of furan on the anaerobic digestion process. No previous publication describing the anaerobic digestion of furan could be found in literature searches. Therefore, two arbitrary concentrations of furan were added to the digester. The resulting changes in digester performance monitored using the control apparatus. The control action was switched off in order to determine the effect of toxin addition at a constant hydraulic retention time. Later experiments were planned with the control action switched on which could be used as a comparison to determine the efficiency of the control algorithm response to increased furan concentrations. However, addition of furan to the anaerobic digester proved problematic and therefore further additions of furan were not performed. Results from the first two additions of furan are presented showing digester performance which is discussed and conclusions are drawn.

Figures 5.12 and 5.13 present data from the addition of 2 g/l furan to the anaerobic digester feed. Data from methane production rate and digester effluent $COD_{(I)}$ are shown in Figure 5.12. Ripley's ratio and total VFA concentration are shown in Figure 5.13. The Ripley's ratio and total VFA concentration remains at steady state throughout the experiment suggesting that there is little or no inhibition of the anaerobic digestion process. Digester effluent $COD_{(I)}$ was seen to increase 17 hours after the addition of furan, from 2.13 g/l to a maximum of at 2.3 at 20 hours, before slowly decreasing again. There is no corresponding decrease in methane production rate which would have suggested inhibition of the anaerobic digestion process. The increase in $COD_{(I)}$ is likely to be from the additional COD of the furan. Therefore, from these results there is no evidence of a marked inhibition of continuous anaerobic digestion of instant coffee processing effluent. However, furan is a volatile compound, it was thought that the concentration of furan in a stirred feed storage container could be decreasing over time by volatilisation into the atmosphere. Furan is a carcinogen and is harmful to human health by inhalation. Concern regarding the volatility of furan lead to an alteration in the method of application of the toxin.
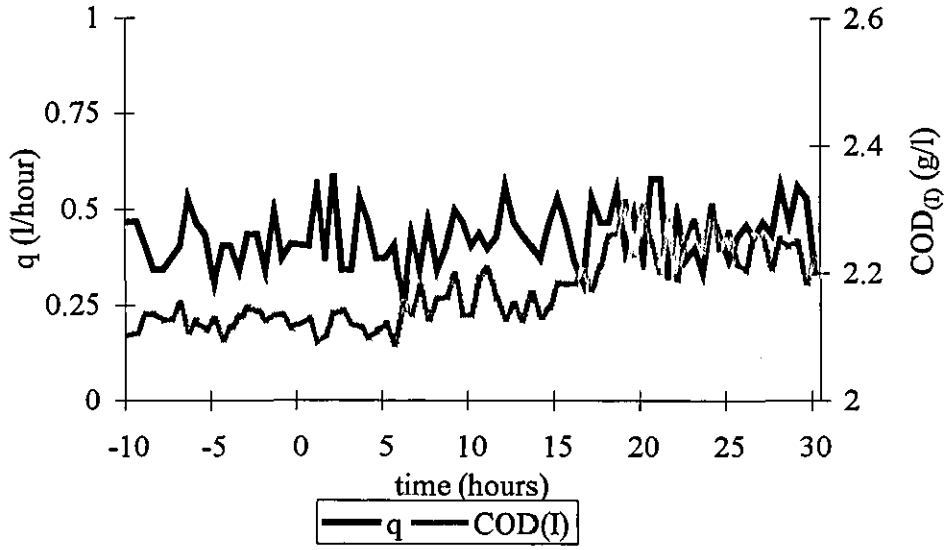
Figure 5.12 $COD_{(I)}$ and methane production during a 2g/l furan addition



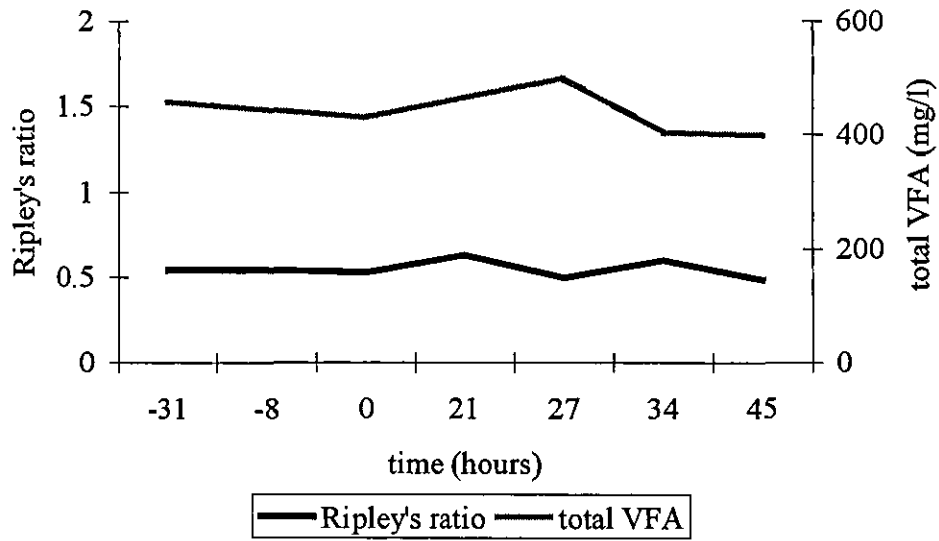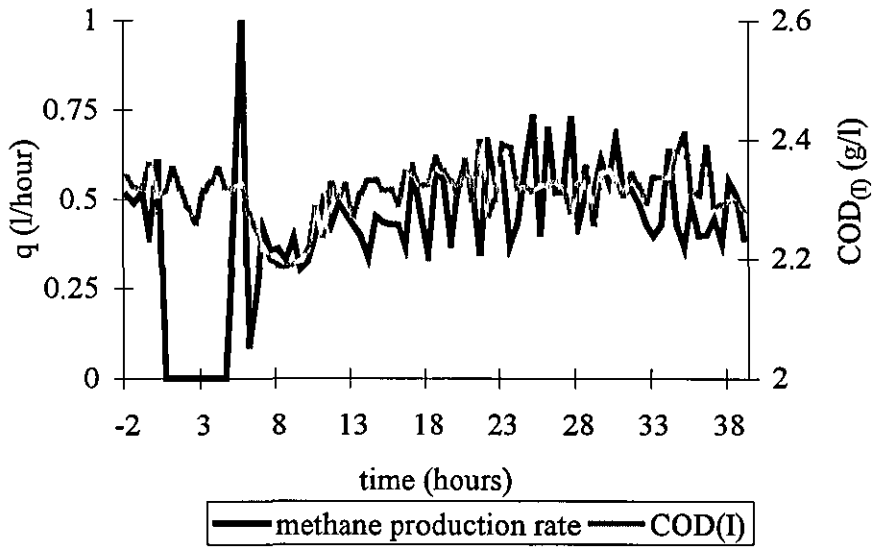Figure 5.13 Ripley's ratio and total VFA concentration during a 2 g/l furan addition

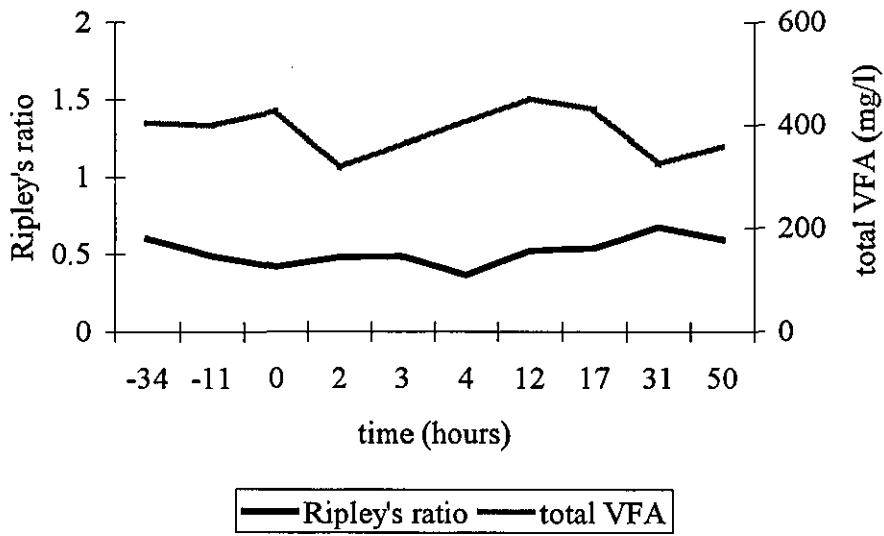Figure 5.14 $COD_{(I)}$ and methane production during a 10 ml furan addition



Figure 5.15 Ripley's ratio and total VFA concentration during a 10 ml furan addition

Direct injection at the feed entrance of the digester was employed to give a concentration of 1g/l within the digester. This dose of furan should in theory be lower then that applied previously via the digester feed.

However, the addition of 10ml in a single slug dose results in an instant concentration of furan inside the digester, which is likely to have a more rapid effect than addition via digester feed. Figure 5.14 and Figure 5.15 show the results from this slug addition of furan. As the furan was injected to the digester it volatilised rapidly, resulting in an instantaneous increase in gas evolved from the digester. The gas flow meter was off scale for between 0 and 5 hours after the addition of furan. The volume of gas vented resulted in a loss of water from the gas flow meter, which needed to be reset. Thereafter, between 5 and 10 hours after the addition of furan the methane production rate was lower than the original value (from 0.49 to 0.38 l/hour). The methane production rate increased back to original levels after 10 hours. The reduced production rate is thought to have been due to the volatilisation of furan resulting in a displacement of biogas from the support media within the digester. The $COD_{(I)}$ of the reactor effluent is shown to decrease from its steady original level of 2.31 g/l to 2.18 between 5 and 10 hours after the addition of furan. After 10 hours the digester effluent $COD_{(I)}$ returned to the original steady state concentration. The decrease in digester effluent $COD_{(I)}$ is not in agreement with the results from the previous addition of furan. We would expect an increase in digester effluent $COD_{(I)}$ to occur earlier than that which occurred for the previous furan addition due to the different method of application. The increased mixing that occurred after injection of furan due to its immediate volatilisation resulted in a loss of liquid volume contained by the digester. This resulted in the remaining contents gaining an increase in hydraulic retention time. This combined with the effect of increased mixing within the digester may account for an increase in COD removal. Figure 5.15 shows that the Ripley's ratio and total VFA concentration remained constantly low during the second addition of furan, indicating that the digester was not inhibited.

It is difficult to conclude much about the inhibitory effects from the slug addition of furan to the digester due to the changes produced by the physical effect of the

volatilisation of furan. These effects resulted in a loss of gas flow measurement data and an increase in hydraulic retention time. However, off-line monitoring of Ripley's ratio and total VFA concentration was shown to assist in the determination of whether the digester was undergoing inhibition.

### 5.2.3 Pyrazine addition

Experiments were conducted to determine the inhibitory or toxic effect of pyrazine on the anaerobic digestion process. As was the case with furan, no previous publication describing the anaerobic digestion of pyrazine could be found in literature searches. Therefore, a concentration of 1 g/l pyrazine was chosen arbitrarily to be added to the digester. This section describes the addition of 1 g/l pyrazine to the digester feed. The resulting changes in digester performance were monitored using the control apparatus. The control algorithm was controlling the anaerobic digester throughout this period.

Figure 5.16, Figure 5.17, Figure 5.18 and Figure 5.19 present data from the addition of 1g/l pyrazine (toxic load) to the instant coffee processing effluent. The results show a large increase in methane production (q) immediately after the addition of pyrazine to the reactor feed (Figure 5.17). As in the previous experiment the dilution rate was increased simultaneously with the increase in methane production. Figure 5.18 shows that the $COD_{(t)}$ of digester effluent increased above the set point 2.5 hours after the addition of pyrazine in response to the increased dilution rate. After 7 hours the effluent $COD_{(t)}$ decreases, indicating no sign of reactor stress until 15 hours, at which time the $COD_{(t)}$ fluctuates above its set point. The hydrogen results (Figure 5.17) show a rapid and marked increase in concentration. At 2.5 hours after addition of pyrazine, hydrogen started to increase from 65 to 240 ppm at 5 hours. After 15 hours the hydrogen concentration peaks at over 600 ppm. This compares with peak concentrations of 1250 and 1400 ppm for other additions of 1g/l pyrazine reported in Appendix 4. The dilution rate only started to decrease once the methane production rate had reduced at 15 hours. The sustained low dilution rate occurred at 16 hours. However, the control had to be switched off at 15.5 hours due to the reactor going 'sour' as indicated by elevated levels of volatile fatty acids (Figure 5.19). The Ripley's ratio was shown to be at a constant steady state of approximately 1.3 prior to

the addition of pyrazine. This slightly elevated level is not unusual in anaerobic filters treating industrial effluent (Hickson, 1995). After 15 hours the levels of Ripley's ratio and total VFA rose quickly and only decreased after addition of sodium bicarbonate.
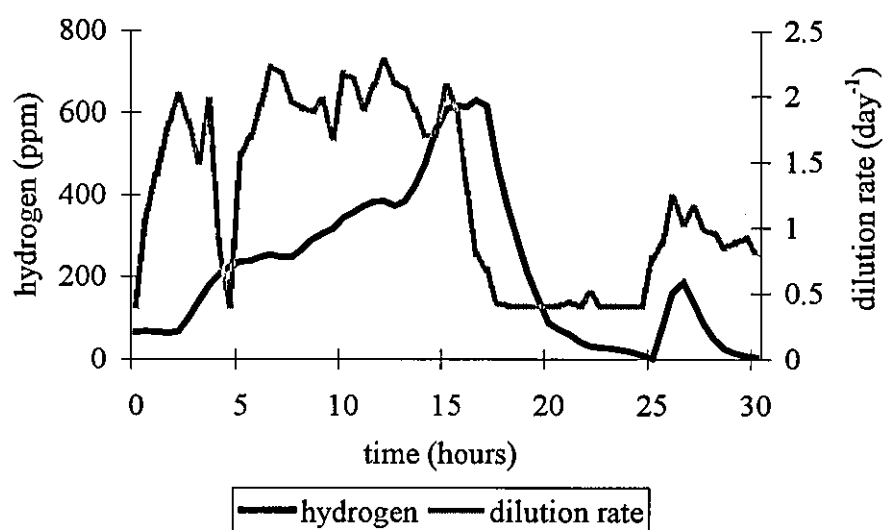
Figure 5.16 Hydrogen and dilution rate during a 1g/l pyrazine addition
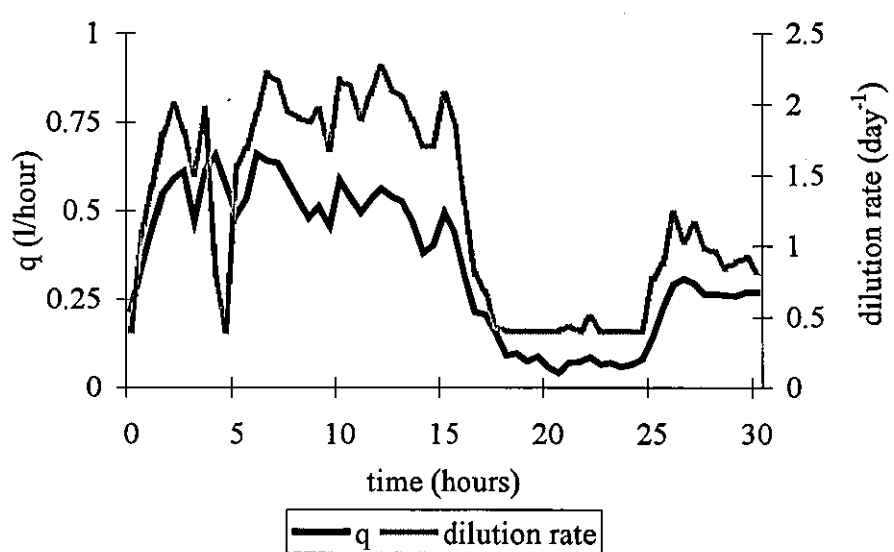


Figure 5.17 Methane production rate and dilution rate during a 1 g/l pyrazine addition
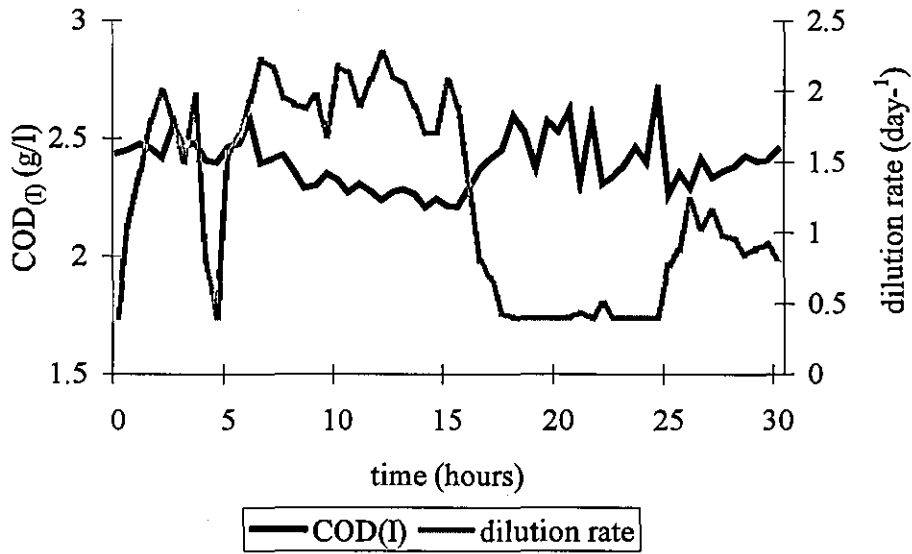
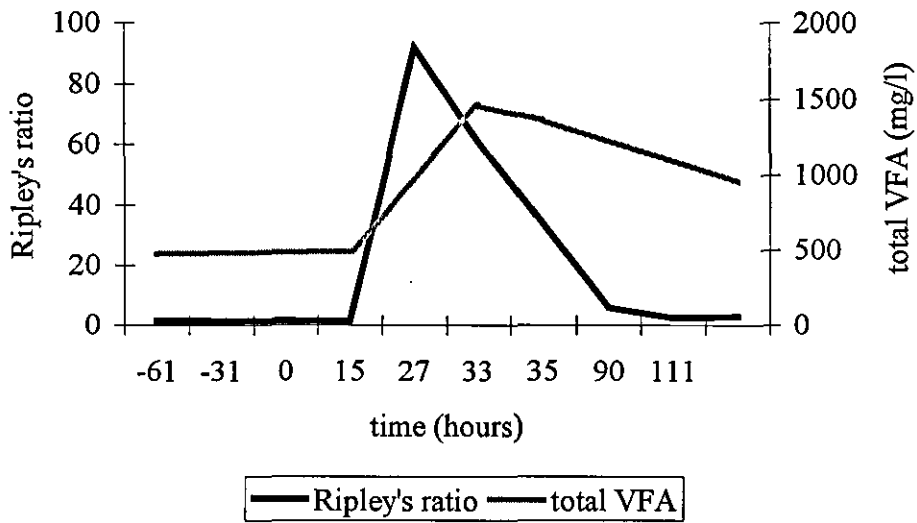Figure 5.18 $COD_{(I)}$ and dilution rate during a 1g/l pyrazine addition



Figure 5.19 Ripley's ratio and total VFA during a 1g/l pyrazine addition

## 5.3 Discussion from laboratory scale organic shocks and toxic compound additions

### Organic load experiments:

Dochain (1995) describes the use of the same control algorithm during an experiment where in a 60 litre CSTR pilot reactor the influent organic matter concentration is doubled from 30 g/l to 60 g/l COD. The controller was shown to maintain the effluent substrate concentration within 2.7% of its desired value by decreasing the dilution rate. As with the results reported here, the methane production rate does increase and decrease with fluctuations of dilution rate, however, the desired effluent $COD_{(I)}$ concentration is maintained relative to the previously reported uncontrolled organic load increase.

The control model used during these experiments and those reported by Dochain (1995) was based on that reported by Renard et al. (1988) and described in Section 3.2.4. Results from both Renard et al. (1988) and Dochain (1995) control experiments are comparable to those reported for organic load increases. However, the technique used for COD analysis differs. Renard et al. (1988) and Dochain (1995) analysed COD using a modified sulphuric acid – dichromate method for which the reflux heating time is reduced from 2 hours to 10 minutes. The COD results were then manually stored in the microcomputer used for control. The reduced reflux method of COD determination is fast enough to allow frequent analysis and will relate to the current state of the anaerobic digester. However, it relies upon continuous manual COD analysis and manual input of results, which is not practical for long term experiments (e.g. overnight or weekend) or application to an operating full scale anaerobic digester due to the cost of 24 hour a day manual monitoring. In contrast the procedures used for estimating $COD_{(I)}$ (discussed in Chapter 3) during the experiments reported for this research overcome these problems.

Other control models utilising various control parameters such as bicarbonate alkalinity (Wilcox et al., 1995), on-line VFA (Slater et al., 1990), or on-line TOC have been demonstrated to maintain reactor performance. However, these techniques require analysers that were either unavailable or required resources that were

unavailable for this research (i.e. the expense of dedicated GC or TOC analysis). Also, direct comparison with other control strategies is problematic as the control objective can be different. For example, the control objective of Wilcox *et al.* (1995) was to maintain steady bicarbonate alkalinity within the anaerobic digester or that of Pullammanappalilli *et al.* (1991) which was to maintain a consistent methane production rate. In comparison, this work aims to produce a consistent effluent quality.

### *Toxic compound additions*

### *Pyrogallol additions:*

The results do indicate that the anaerobic digestion process was affected by the two highest concentrations of pyrogallol. However, compared to previous research (reviewed in Chapter 2) undertaken on pyrogallol additions to anaerobic digestion the inhibition is less significant. This is in agreement with Field and Lettinga (1987) who found that additions of pyrogallol increased biogas production. Diffuse sludge used and defined by Bajwa and Forster (1988) showed inhibition of biogas production. The results of this study show that there was little inhibition of the anaerobic digestion process in an anaerobic filter. Azhar and Stuckey (1994), found that pyrogallol was 54% degraded by anaerobic sewage sludge. However, greater degradation efficiencies of pyrogallol could be possible with bacteria that have been retained within a digester long enough to acclimate to the presence of pyrogallol. Parkin and Speece (1982), modelled toxicity in anaerobic digesters; they found that that the anaerobic filter inherently provided a means of retaining biological solids while liquid is removed, a significant advantage when treating wastes which contain inhibitory compounds. When an anaerobic digester is inhibited, even when the biogas production has ceased, the rate of recovery is greatly increased once the inhibitor is removed. By retaining most of the biological solids attached to a support media, the anaerobic filter is ideal for industrial waste likely to contain varying levels of inhibitory compounds. Structural changes in UASB granules that have treated effluent containing 3 g/l pyrogallol have been reported by Quarmby and Forster (1995), however, it is not reported if there was a subsequent change in efficiency of the anaerobic digestion

process. In contrast to other work published and reviewed on the subject of pyrogallol degradation by anaerobic digestion, the bacteria within the controlled digester used during this research had been fed with coffee processing effluent for a period of two years, and could therefore have acclimated to unknown concentrations of the toxin. This is the most likely explanation for the lack of inhibition shown upon addition of pyrogallol to the digester. This would be in agreement with results from Demirer and Speece (1998) who demonstrated that an UASB reactor was able to utilise 3-carbon compounds its sole carbon source which had previously been shown to be inhibitory to acetate enriched *Methanosarcina* cultures. This ability was concluded to be due to acclimation achieved through careful control of the operating parameters such as step-wise increases in the influent concentration.

*Pyrazine additions:*

At 2.5 hours after addition of pyrazine, hydrogen started to increase from 65 to 240 ppm at 5 hours. After 15 hours the hydrogen concentration peaks at over 600 ppm. Further results reported in Appendix 4 show increases up to 1250 and 1400 ppm. This compares with Mosey and Fernandes (1989) who reported a rise in hydrogen concentration from 0 to 75 ppm after the addition of chloroform to a 2 litre capacity laboratory scale anaerobic digester (0.75 mg/l). Also, Hickey *et al.* (1987) added four organic toxicants [chloroform, bromoethanesulfonic acid (BES), trichloroacetic acid (TCAA) and formaldehyde]. Hickey *et al.* (1987) reported an increase of 250 ppm hydrogen for a 0.51 mg/l addition of chloroform and an increase of >1000 ppm for a 1.02 mg/l addition of chloroform to anaerobic batch tests. All of the organic toxicants added resulted in an increase in hydrogen concentration above levels in the controls. For the addition of chloroform, BES and TCAA samples where methane production was severely inhibited (<30% the rate of controls) demonstrated a rapid rise in hydrogen above 1000 ppm, while samples that were inhibited <70% exhibited a response pattern similar to but higher in concentration that control samples. Hydrogen and biogas response to formaldehyde was lower compared to the other toxicants. After formaldehyde additions hydrogen concentrations peaked and were observed to decline before recovery of methanogenesis was evident. Hickey *et al.*

(1987) reported that all toxicant additions resulted in both a faster rate of increase and higher reported concentration of hydrogen.

Results from the pyrazine experiment reported show a rapid increase in hydrogen before other parameters (VFA, Ripley's ratio, methane production rate and $COD_{(f)}$) indicated reactor disturbance (also Appendix 4 Figures 4-4 to 4-12), this is also reported by Mosey and Fernandes (1989) where hydrogen concentrations were seen to increase prior to biogas production responded to chloroform addition. They showed that daily additions of 1.5 mg of chloroform to a 2 litre capacity laboratory scale CSTR resulted in inconsistent rises in hydrogen concentration. Mosey and Fernandes (1989) concluded that increases in hydrogen acted like an event marker. Comparison of reaction rates of hydrogen concentration and biogas production reported by Hickey *et al.* (1987) is not possible due to infrequent analysis of biogas production, this is a consequence of the small samples available from batch test bottles used during their experiments.

As discussed in Chapter 2, the increase in hydrogen concentration is non-linear to the changes in reactor influent characteristics (Guwy *et al.*, 1997). This is supported by the variation in hydrogen response shown in this research to the same dose of pyrazine. Although hydrogen response was shown to be non-linear it has been reported that the rate of increase and final concentration is proportional to toxicity of the compound addition during batch tests (Hickey *et al.*, 1987). The idea of using hydrogen concentration as an indicator or event marker has been postulated by several researchers (Wolin and Miller, 1982, Archer *et al.*, 1986, Hickey *et al.*, 1987, Slater *et al.*, 1990, Labib and Ferguson 1992). Therefore, a control scheme including hydrogen as an additional control parameter would be beneficial. The failure of the anaerobic digester after a 1 g/l pyrazine addition during this research may have been prevented if faster control action was taken. The hydrogen concentration did appear to act as an event marker, increasing in response prior to other control parameters showed inhibition and decreasing back to background levels before the inhibition had finished. The incorporation of hydrogen as a control parameter into the existing control strategy would utilise the characteristics of hydrogen as an event marker to act on the

digester earlier than the original control system. After hydrogen levels decrease the other control parameters would still be influence the dilution rate if inhibition was still occurring. In this way digester failure could be prevented.

## 5.4 Summary and Conclusions from laboratory scale organic shocks and toxic compound additions

- This chapter has presented results from the treatment of instant coffee processing effluent using laboratory scale anaerobic filters. By comparison with the anaerobic digestion of other food processing effluents (discussed in Chapter 2) the removal efficiency of COD is low (65%). The relatively poor performance of anaerobic digesters treating instant coffee processing effluent is thought to be due to the presence of compounds which are recalcitrant or inhibitory to anaerobic digestion.

- Results from organic load increases are presented in this chapter. Data is compared from experiments in which digester feed concentration was increased; firstly with a constant hydraulic retention time. This resulted in an increase in digester effluent $COD_{(t)}$ concentration. Secondly, similar experiments were performed in which the feed pump was controlled. The adaptive control algorithm was shown to be capable of maintaining a constant effluent quality during fluctuations in concentration of digester feed COD.

- In contrast to results reported by other researchers (discussed in Chapter 2) the addition of pyrogallol to anaerobic digestion did not have an inhibitory effect. Bacteria within the digester used for this research have been shown to have acclimated to the presence of the pyrogallol over a period of time. This resulted in the ability to tolerate and degrade pyrogallol.

- Addition of a concentration of 2g/l furan to digester feed does not inhibit anaerobic digestion of instant coffee processing effluent. There is no previous work reported on furan to compare this result.

- Addition of 1g/l pyrazine to the anaerobic digester feed resulted in a marked inhibition of the anaerobic digestion process. The control algorithm did react to this inhibition but only after the 'souring' of the digester. A potential control parameter (hydrogen) was shown to be able to identify the occurrence of inhibition significantly quicker than those employed by the control algorithm.

- Changes in concentration of pyrazine in instant coffee processing effluent are expected (discussed in Chapter 2). Results presented from this chapter showing a marked inhibition of the anaerobic digestion process caused by an increase in concentration of pyrazine highlight the need for more detailed monitoring and control. In Chapter 2 the potential for incorporation of additional control parameters into a control strategy was identified. Gas phase parameters in particular were shown to have the benefits of being able to rapidly respond to digester stress caused by toxic and organic load fluctuations. Hydrogen was identified as being able to detect such changes while also being a relatively inexpensive parameter to monitor and able to provide on-line data. The monitoring of hydrogen provides additional information to identify the occurrence of inhibition to the anaerobic digestion process. Therefore, the next logical step was to characterise the response as measured by hydrogen to toxic shocks and organic load variations and to incorporate hydrogen into the existing control strategy.

## 5.5 Laboratory scale steady state operation

Steady state data is presented in Figures 5.20 to 5.23. This data is from a period when problems were being experienced with $COD_{(I)}$ probes. Experimentation on the performance of the laboratory anaerobic filters and the control system did not take place during this period.

Steady state data shows fluctuations in hydrogen concentration of the biogas between 0 and 80 ppm (Figure 5.20). These fluctuations can be considered normal background variation during digester operation. Figure 5.21 is from a pyrazine addition experiment, it is included to make a comparison with hydrogen variation during steady state operation. Methane production rate is relatively consistent at approximately 0.23 litres per hour (Figure 5.22). However, there is an increase at 265 hours. This sudden increase in biogas production rate is the result of a blockage in the biogas measurement device described in Chapter 3. The fault was detected and rectified manually soon after it occurred.

Figure 5.23 shows $COD_{(I)}$ over this period. $COD_{(I)}$ results show sharp decreases at 60 and 380 hours as a result of a faulty probe. A new probe was fitted and re-calibrated at 540 hours which results in a steady $COD_{(I)}$ output.

Hydrogen variations reported in the literature (discussed in Chapter 2) show that hydrogen can vary in concentration during steady state operation. Guwy et al. (1997) reported a variation in hydrogen content of biogas from 200 to 800 ppm during a change between batches of feed with a consistent COD. However, Guwy et al. (1997) did report that the older batch of feed was partly acidified. An increase in hydrogen production as a result of sudden increased volatile acid concentration has also been reported and discussed by Smith and McCarty (1989a and 1989b) and Furumai (1997). Premier et al. (1997) reports a method of avoiding this change in feed quality affecting digester operation during monitoring experiments. A concentrated feed was diluted at the point of delivery to the digester. However, this method would not allow the use of real effluent.

In contrast to the results from Guwy *et al.* (1997) showing a 200-800 ppm variation in hydrogen concentration, the data in Figure 5.20 shows relatively steady hydrogen concentration (0-80 ppm). Unlike Guwy *et al.* (1997) variations in biogas quality was not observed. A possible explanation for this is that during this research large batches of feed (instant coffee processing effluent) were stored in a cold room after periodic collection. In order to minimise the possibility of a change in feed quality affecting results a single batch was used throughout each experiment.
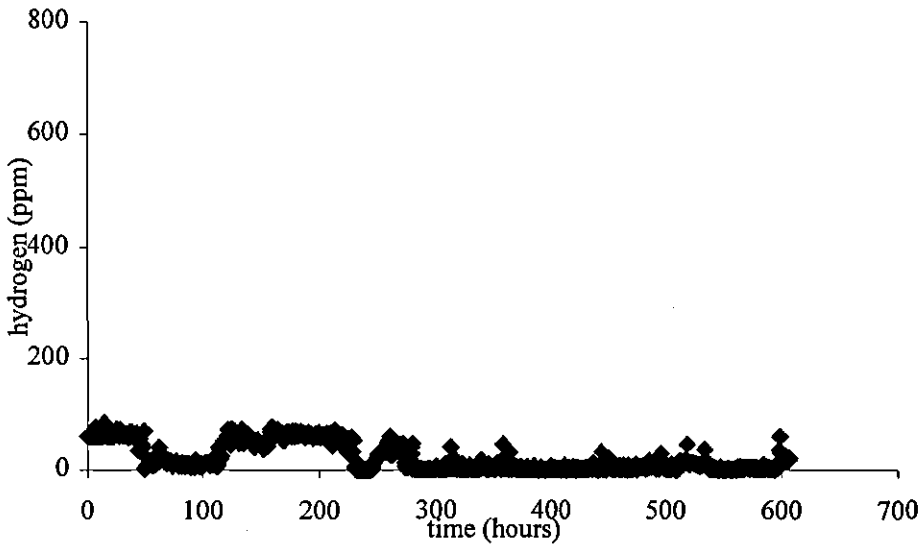
Figure 5.20 Steady state hydrogen concentration data

Figure 5.20 shows variation of hydrogen concentration in the biogas during
a steady state period while changes were carried out to the $COD_{(I)}$ probes.

Periods of stability are seen at various concentrations, however, hydrogen
concentration does not usually rise higher than 80 ppm. This is in contrast
to the concentrations shown in Figure 5.21 from the addition of 1 g/l pyrazine.

Table 5.1 Information from Figure 5.20

| Hydrogen (ppm) | |
|---|---|
| 21.62 | average/mean |
| 8.00 | median |
| 0.00 | min |
| 85.00 | max |
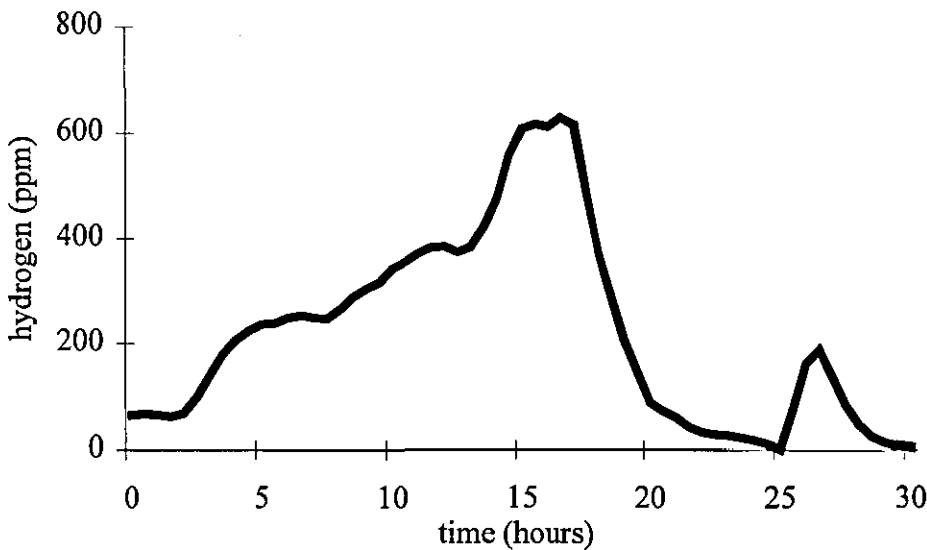


Figure 5.21 Hydrogen during a 1 g/l pyrazine addition for comparison

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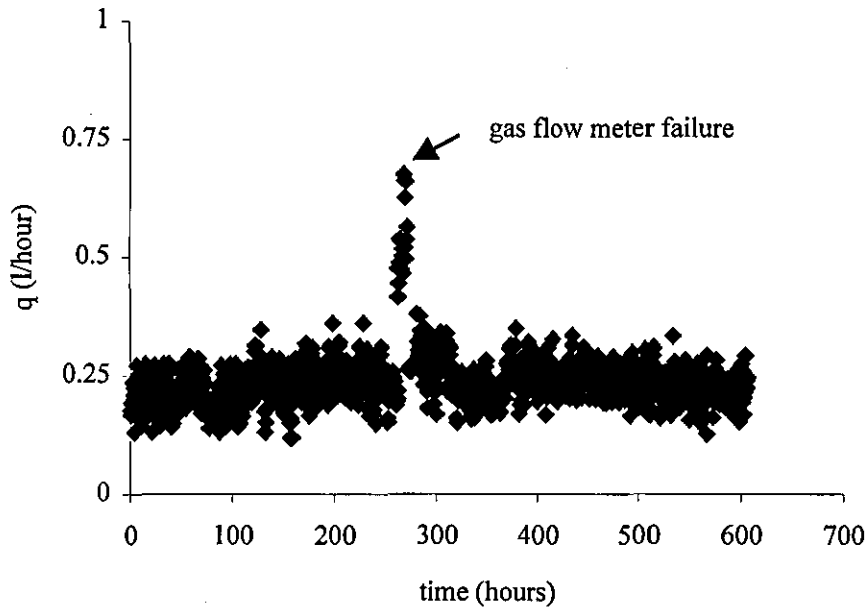
Figure 5.22 Steady state methane production rate data

Figure 5.22 shows methane production rate during a steady state period while changes were carried out to the $COD_{(I)}$ probes. A failure of the gas flow meter is indicated. This resulted in an increase in the reported methane production rate, until the flow meter was manually reset. Data in Table 5.2 only refers to data during the steady state period.

Table 5.2 Information from Figure 5.22

| q (l/hour) | |
|---|---|
| 0.236 | average/mean |
| 0.232 | median |
| 0.119 | min |
| 0.379 | max |
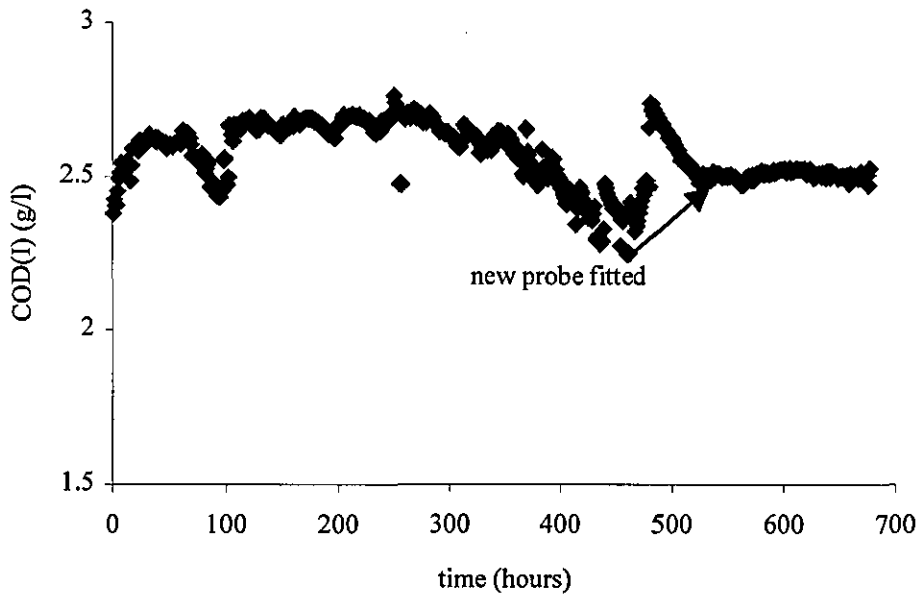
Figure 5.23 COD(I) data

Figure 5.23 shows $COD_{(I)}$ data during a period with a faulty suspended
solids probe, after 540 hours the probe was replaced and $COD_{(I)}$ is seen
to become stable. Data presented in table 10.3 only refers to after 540 hours.

Table 5.3 Information from Figure 5.23

| $COD_{(I)}$ mg/l | |
|---|---|
| 2.51 | average/mean |
| 2.51 | median |
| 2.48 | min |
| 2.53 | max |

# 6. INCORPORATION OF HYDROGEN AS A CONTROL PARAMETER

As mentioned previously in the literature review (Chapter 2), hydrogen is transferred in most stages of anaerobic digestion. Under steady operating conditions hydrogen concentration in the biogas remains low (usually 5-100 ppm). However instability of an anaerobic system due to the slow growth rates of the methanogens and acetogens compared to the hydrolysing and acidogenic bacteria, causes the hydrogen to increase markedly in the system. The build-up of hydrogen is thought to be the most rapid indicator of instability and has therefore been investigated as a control parameter for detecting organic and toxic imbalances.

The work presented in this chapter is divided into two distinct phases. Firstly, incorporation of hydrogen as a control parameter is described in section 6.1. Secondly, the new control strategy is tested in section 6.2. In section 6.1 results are presented from an increased organic load and addition of pyrazine to the feed to a controlled digester. Comparison is made between the original control algorithm and predicted results obtained from the new control algorithm which has hydrogen incorporated as a control parameter. The original control algorithm output is dilution rate (D), output from the new control algorithm is dilution rate incorporating hydrogen content of biogas ($D_{(H)}$). That is to say, the dilution rate is flow (l/d) over volume of reactor (l), and is thus quoted with the unit $d^{-1}$. This is the inverse of HRT i.e. volume of reactor (l) over flow (l/d) – see also Chapter 3. The equations to calculate $D_{(H)}$ are shown below.

Hfactor $= (H_2$ gas concentration $-$ steady state $H_2$ gas concentration$)/100$

$D_{(H)} = D_{(H)} - ( D_{(H)} * Hfactor)$

In section 6.2 the new control algorithm is tested and used to control anaerobic digestion undergoing identical increases in organic load and addition of pyrazine as presented in section 6.1. Differences in digester performance under the two control systems are discussed and conclusions are drawn.

## 6.1 Incorporation of hydrogen as a control parameter to existing adaptive control strategy

Hydrogen concentration was incorporated as empirical data (using results presented in Figures 6.1-6.6). Prior to this set of experiments the baseline concentration of hydrogen was approximately 65 ppm during normal digestion of the instant coffee processing waste. This concentration was, therefore, set as the normal baseline, when the hydrogen concentration was level or below this, then there was no action from the control system. When the hydrogen concentration increased above the baseline concentration, $D_{(H)}$ was reduced in proportion to the concentration of hydrogen (above baseline) in the biogas. The changed dilution rate calculation to determine $D_{(H)}$ is shown in the control program (Appendix I). In order to maintain the influence of all other control parameters, the hydrogen influence was limited to a 50% reduction of the original dilution rate. Any change in hydrogen up to the pre-set steady state concentration is assumed to be within normal variation. This variation is demonstrated in Section 5.4, where the concentration of hydrogen during steady sate operation is between 0 and 80 ppm. Other limits were also imposed on the $D_{(H)}$. $D_{(H)}$ was not allowed to decrease below 0.4 $d^{-1}$. This was to ensure a minimum velocity of effluent across the effluent probes. Additionally, $D_{(H)}$ was not allowed to increase above 2.0 $d^{-1}$. This maximum dilution rate is required to prevent washout of active biomass.

The data presented in the series of graphs in Figures 6.1-6.6 show the *predicted* effect of the new control algorithm incorporating hydrogen as a control parameter, in comparison with experimental results obtained using the original control algorithm. Data is presented in terms of hydrogen, methane production rate (q) and $COD_{(I)}$ (mg/l). Control response is represented by *dilution rate* (D day$^{-1}$) which controlled feed pump speed. The predicted response of the new control algorithm incorporating hydrogen concentration in the biogas is identified by $D_{(H)}$ (day$^{-1}$).

Figures 6.1, Figure 6.2 and Figure.6.3 present data from an increase in strength of digester feed from 16000mg/l to 33000 mg/l. The increase in organic loading was applied to the reactor between 0.5 hrs and 7 hours into the experiment. The data

compares the experimental data using the original control algorithm (without hydrogen incorporated), with the new control algorithm (predicted response) for comparison. As would be expected both strategies control the feed pump (by D and $D_{(H)}$) in an identical manner until there was an increase in hydrogen concentration above the critical 65 ppm. Although D and $D_{(H)}$ reduced as a result of the increased feed concentration the $COD_{(I)}$ of the effluent still increased at 11 hours into the experiment (Figure 6.3), due to the greater organic loading rate. The COD was metabolised and this resulted in an increase in methane production (q) between 15 and 27 hours (Figure 6.2). It is at this point (20 hours) that the response of the new control algorithm differs. The original adaptive control algorithm increases the D as the methane production increases due to the assumption, on the part of the control system, that the anaerobic digestion process has increased in efficiency. The $D_{(H)}$, on the other hand, was reduced due to the increase in hydrogen concentration. At this point the $D_{(H)}$ is slowing the feed pump to reduce stress to the hydrogenotrophic methanogens. Off-line analysis of Ripley's ratio and total VFA are shown in Figure 6.17. The Ripley's ratio was shown to be at a constant steady state prior to the increase in feed strength. An increase in Ripley's ratio was seen after the increase in hydrogen concentration at 20 hours. The Ripley's ratio was at steady state at 0.4 and peaks at 4 which as discussed in the methods chapter indicates firstly a well operating and later a stressed reactor. Ripley's ratio decreased only after a decrease in the dilution rate at 58 hours.

The original control algorithm was shown to be capable of maintaining a constant $COD_{(I)}$ set point. However, there is an accumulation of VFAs and an increase in Ripley's ratio which indicate digester upsets. Also, the control action does not prevent an increase in hydrogen above normal levels. The $D_{(H)}$ decreased during these times of elevated hydrogen concentrations. Therefore, we can hypothesise that if this new control strategy was fully operational it would result in a better control of the influent pump speed, thereby limiting the effects of the organic loading more effectively.

Figure 6.4, Figure 6.5 and Figure 6.6 present a set of data shown previously in Chapter 5. Data is from an addition of 1mg/l pyrazine (toxic load) to the instant

coffee processing effluent. As with the previous set of data the reactor was being controlled by the original adaptive control algorithm and results are presented from both online adaptive control and the new control algorithm (offline) for comparison. The results show a large increase in methane production (q) immediately after the addition of pyrazine to the reactor feed (Figure 6.5). As in the previous experiment the dilution rate was increased simultaneously with the increase in methane production. Figure 6.6 shows the $COD_{(I)}$ of digester effluent increased above the set point 2.5 hours after the addition of pyrazine in response to the increased dilution rate (D). After 7 hours the effluent $COD_{(I)}$ decreases, indicating no sign of reactor stress until 15 hours, at which time the $COD_{(I)}$ fluctuates above its set point. The hydrogen results (Figure 6.4) show a more rapid and marked increase in concentration than those recorded for the organic loading experiment (Figures 6.1-6.3). 2.5 hours after addition of pyrazine, hydrogen started to increase from 65 to 240 ppm at 5 hours. The $D_{(H)}$ decreases in response (at 5 hours) and remains low due to the continuing high hydrogen concentration. In contrast, the dilution rate (D) only started to decrease once the methane production rate had reduced at 15 hours. The sustained low dilution rate occurred at 16 hours. However, the control had to be switched off at 15.5 hours due to the reactor going 'sour' as indicated by elevated levels of volatile fatty acids beginning to interfere with pH. (Figure 6.18). The Ripley's ratio was shown to be at a constant steady state of approximately 1.3 prior to the addition of pyrazine. This elevated level is not unusual in anaerobic filters treating industrial effluent (Hickson, 1995). After 15 hours the levels of Ripley's ratio and total VFA rose quickly and only decreased after addition of sodium bicarbonate. It can be hypothesised that reactor failure could have been prevented if the control algorithm incorporating hydrogen had been used to more rapidly and accurately determine the condition of the anaerobic digester. Thus, with respect to both organic overloading and toxic shock loadings the new control algorithm has been shown to be capable of responding more rapidly to different types of potential operational problems.

Figure 6.7 presents an extended set of data to include the period of time during which the 'soured' reactor recovered. After the feed was switched off at 15.5 hours and the reactor was allowed to recover. The $COD_{(I)}$ versus dilution rate graph showed

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interesting events at 31, 37, 41 and 43 hours. The sharp increases in $COD_{(l)}$ are due to probe fouling. The probes were usually cleaned at regular intervals, but during the reactor recovery period they were not cleaned. This further demonstrates the problem of probe fouling, particularly when there is no flow. This is in conjunction with the delay between toxic shock load and increase in $COD_{(l)}$ highlights the problems of liquid phase probes in on-line control.
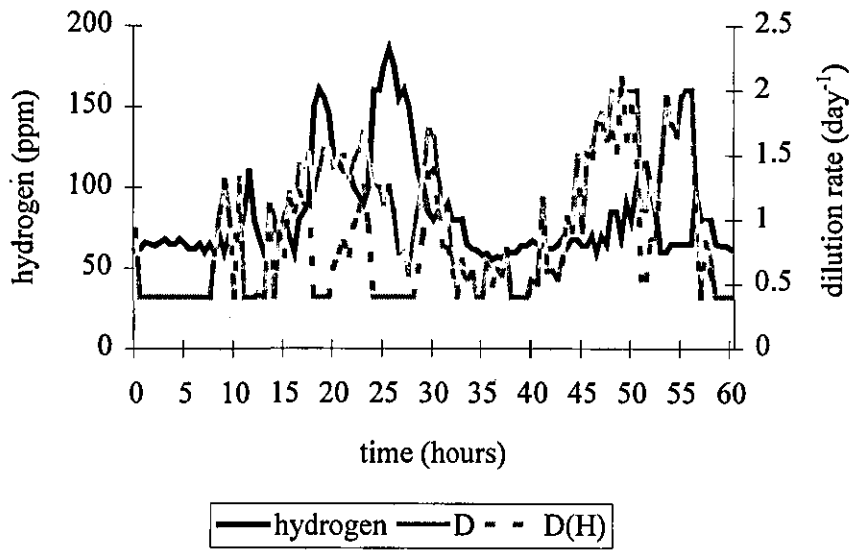
Figure 6.1  Hydrogen, D and $D_{(H)}$ rate during an organic load increase
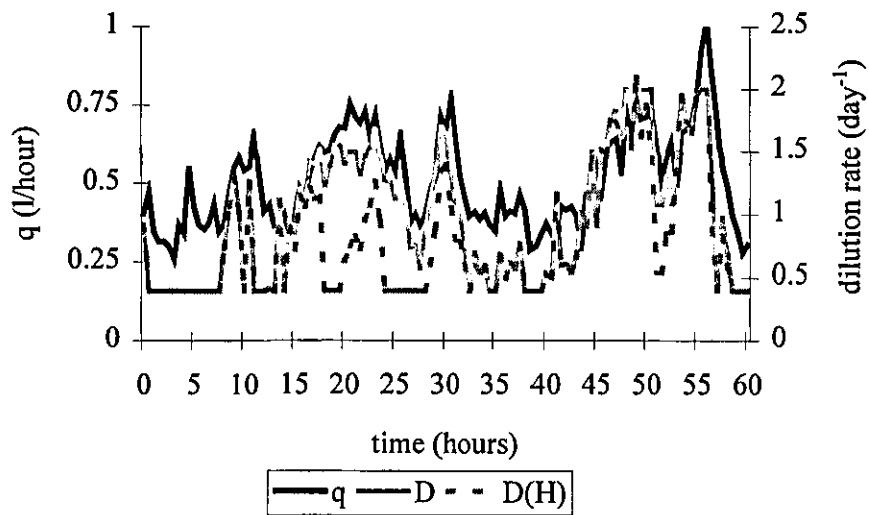


Figure 6.2  Methane production rate, D and $D_{(H)}$ during an organic load increase



Figure 6.3  $COD_{(I)}$, D and $D_{(H)}$ during an organic load increase

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Figure 6.4 Hydrogen, D and $D_{(H)}$ during a 1g/l pyrazine addition
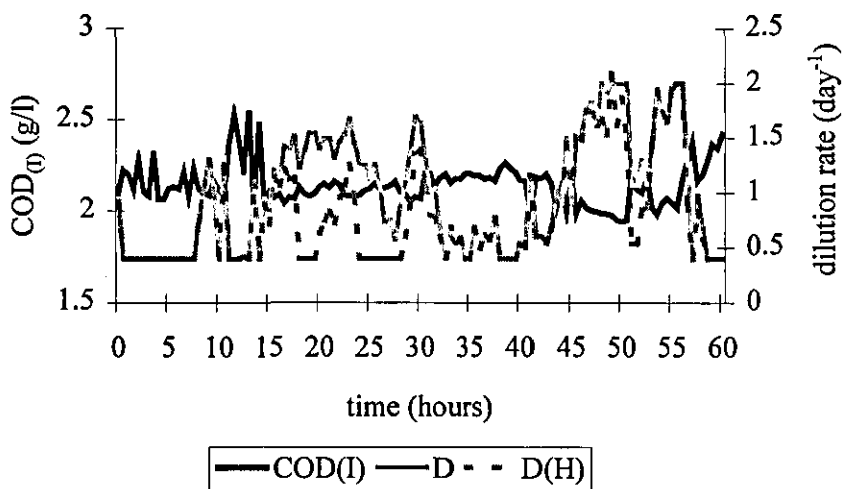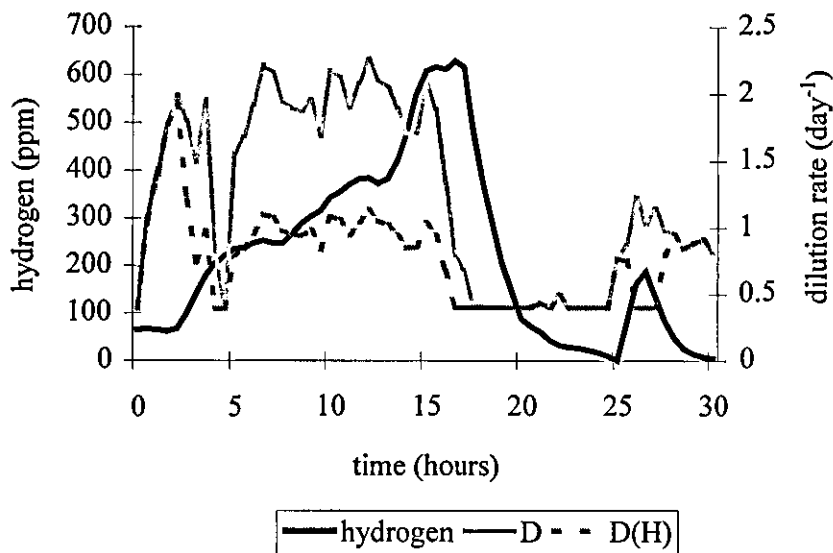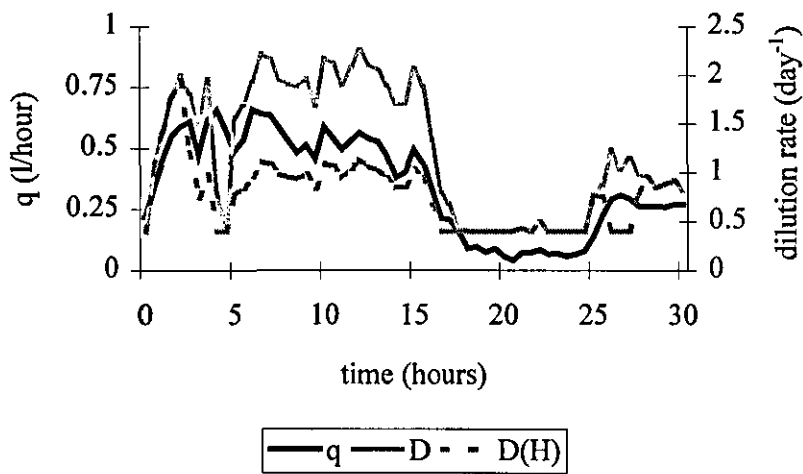


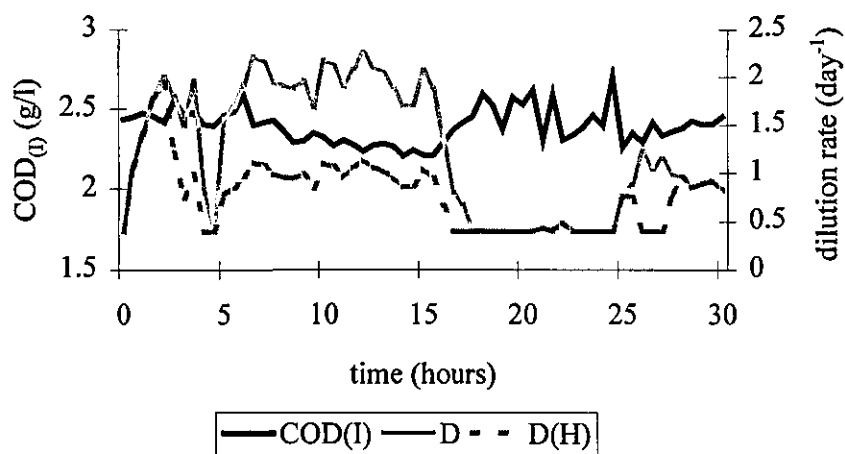Figure 6.5 Methane production rate, D and $D_{(H)}$ during a 1g/l pyrazine addition



Figure 6.6 $COD_{(I)}$, D and $D_{(H)}$ during a 1g/l pyrazine addition
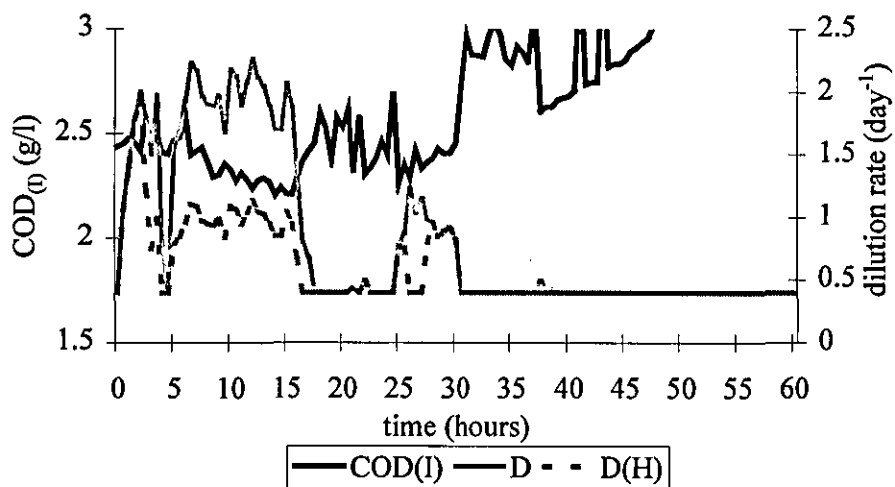
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Figure 6.7 1g/l pyrazine addition to feed, extended to show $COD_{(I)}$ probe fouling

## 6.2 Results from utilising hydrogen as a control parameter

The next set of experiments were conducted using the new control algorithm incorporating hydrogen (as discussed in Section 6.1) for on-line control of the anaerobic digester. For this series of experiments the steady state level of hydrogen was found to be 25 ppm. These concentrations of hydrogen and those reported for the previous set of experiments are both similar to those found by other researchers as discussed in Chapter 2. The hydrogen set point for the control algorithm was, therefore, set at this lower level (25 ppm), so that an increase above the background level would result in a control action. Figure 6.8, Figure 6.9 and Figure 6.10 present data from an addition of 1mg/l pyrazine to the instant coffee processing effluent. Compared to the previous addition of pyrazine, which showed it to be a toxic load (Figure 6.4, Figure 6.5 and Figure 6.6), the control of the anaerobic digester was improved with a more steady response; i.e. the $D_{(H)}$ in Figures 6.8-6.10 did not vary as widely as D in Figures 6.4 to 6.6. Figure 6.8 does show that hydrogen concentration within the biogas did increase, but not above 60 ppm and despite this, the $D_{(H)}$ decreased in response to increases in hydrogen concentration. The methane production rate did increase, but the corresponding increase in $D_{(H)}$ was relatively low due to the influence of increased hydrogen concentration. For instance, at 22 hours $D_{(H)}$ decreased due to an increase in hydrogen (Figure 6.8), this occurs as methane production rate is increasing (Figure 6.9), subsequently methane production rate decreases. Overall, compared to the previous experiments there is a lower dilution rate (and a longer hydraulic retention time), and the effects are more subtle. The data is therefore, shown over a larger time frame (60 hours). Fluctuations in hydrogen reduce over time as the pyrazine is washed out and degraded. The control algorithm with hydrogen incorporated as a control parameter is shown to keep all parameters better controlled than compared to the previous identical experiment with the original control algorithm. The Ripley's ratio is shown to be at a constant steady state of approximately 1.5 prior to the addition of pyrazine. Although the total VFA does not fluctuate significantly, the Ripley's ratio does increase from the initial value of 1.5 to 2.8 at 20 hours. This increase is relatively small compared to that shown in the

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previous addition of pyrazine and the Ripley's ratio is seen to decrease to levels below the original steady state levels due to the reduction in dilution rate. These results, compared to the previous set of data from a 1g/l pyrazine addition, support the hypothesis that a more sophisticated control incorporating hydrogen as an additional control parameter in the original algorithm would be beneficial to prevent reactor failure from toxic stress.

Data is presented from two further runs, aborted due to $COD_{(I)}$ probe failure. These additional results are shown in Appendix 4 (Figures 4-4 to 4-12). The data shows a similar pattern to that of the original control algorithm and that from the new control algorithm incorporating hydrogen. Results are shown for hydrogen, VFA and Ripley's ratio during two 1 g/l pyrazine additions. Due to a faulty $COD_{(I)}$ probe dilution rate rapidly decreased to the minimum rate in both experimental runs. This prevented digester failure, however, in the first aborted control experiment the $COD_{(I)}$ probe failure and resultant dilution rate reduction occurs earlier than the second. This results in the first aborted run showing greater reactor stability in terms of Ripley's ratio and VFA when compared to the second aborted experiment. The hydrogen concentration increase occurs later in the first aborted run where the $COD_{(I)}$ probe failed earlier in the experiment. The earlier failure of $COD_{(I)}$ probe and resultant decrease in dilution rate which is similar to the faster action taken by $D_{(H)}$ in Figures 6.4 to 6.6, results in a similar digester stability shown by the methane production rate, Ripley's ratio and total VFA production (Figures 4-4 to 4-7). In Figures 4-8 to 4-12 the later failure of $COD_{(I)}$ probe and resultant decrease in dilution rate is similar to the original control algorithm shown in Figures 5.15 to 5.18, and results in a similar digester instability shown by the methane production rate, Ripley's ratio and total VFA production. The data from Appendix 4 shows that the same response was seen from similar operating circumstances reported in Sections 5.2 and 6.2. The peak hydrogen concentration response was shown to vary despite identical doses of pyrazine. This finding is in agreement with results reported by Guwy et al. (1997) who reported that similar organic overloads did not give rise to a proportional increase in levels of biogas hydrogen concentration.

Figure 6.11, Figure 6.12 and Figure 6.13 present data from an increase in organic loading to the instant coffee processing effluent, during control with the new control algorithm. Compared to the previous increase in organic loading (Figure 6.1, Figure 6.2 and Figure 6.3) the control of the anaerobic digester is more steady. This is due in part to $D_{(H)}$ being at the minimum set point for a longer period of time. The dilution rate is seen to be influenced by increases in hydrogen, as the hydrogen concentration increases the dilution rate decreases. The dilution rate decreased in response to higher feed concentration. There is a delay shown before the increased concentration of feed, entering the reactor, results in an increased concentration of $COD_{(I)}$ within the reactor. The hydrogen concentration decreased at this point, this could be due to the metabolism of hydrogenotrophic methanogens. After 2.5 hours hydrogen increased again until 7.5 hours when the concentration of feed was returned to normal. The concentration of hydrogen in the biogas compared to that shown in Figure 6.1 is similar up until 15 hours after increase in feed concentration. The original control algorithm increased the dilution rate at 15 hours (Figure 6.1) which resulted in hydrogen concentrations above 150 ppm. The hydrogen concentration during $D_{(H)}$ control was lower in comparison (60 ppm).

This compares with further data shown in Appendix 4 (Figure 4-1 to 4-3) from an additional run aborted due to $COD_{(I)}$ probe failure. This shows hydrogen concentration increases up to 370 ppm during a similar organic load increase. The peak hydrogen response to similar organic load increases is shown to vary despite similar organic overloads, as found by Guwy *et al.* (1997).

Figure 6.12 shows that the methane production rate remained steady for the first 10 hours, after which methane production increased due to the increase of feed concentration. This experiment, however, has similarities with results from the hydrogen incorporated control of the addition of pyrazine, in that the $D_{(H)}$ increased from the increase in methane production, however, the increase in $D_{(H)}$ is checked by the influence of hydrogen concentration which increased simultaneously to methane production. In Figure 6.13 it can be seen that, after 11 hours, the digester effluent

$COD_{(I)}$ increased sufficiently to keep the $D_{(H)}$ low until the effluent $COD_{(I)}$ decreased at 55 hours.

There was a sustained low $D_{(H)}$ compared to that seen in the previous organic load increase using the original control algorithm shown in Figures 6.1 to 6.3 (without hydrogen used as a control parameter). The influence of hydrogen on the $D_{(H)}$ after the decrease in hydrogen concentration at 7.5 hours was relatively small, compared to that of the increase in $COD_{(I)}$. The increase in $COD_{(I)}$ in the reactor effluent combined with relatively low methane production rate suggests that the reactor is overloaded. Figure 6.20 shows the Ripley's ratio and total VFA concentration during this organic load increase. The Ripley's ratio was seen to be at steady state at 0.7. Although the increase to 2.2 is lower than that in Figure 6.17 (the previous organic load increase) the Ripley's ratio is slower to decrease again, despite the reduced dilution rate.

Figure 6.14, Figure 6.15 and Figure 6.16 present data from a second increase in organic loading to the instant coffee processing effluent (15000-33000 mg/l COD). Again, the reactor is steadier compared to the previous increase in organic loading controlled by the original control algorithm (Figure 6.1,Figure 6.2 and Figure 6.3). The timing of increase and decrease in hydrogen concentration is similar to that seen in previous runs, e.g. Figure 6.11, however hydrogen concentrations are much higher (340 ppm compared to 60 ppm). The methane production rate is initially at a lower rate than previous experiments. Methane production rate (Figure 6.15) increased in response to the increased feed concentration as shown in previous results (Figure 6.12), and after 7 hours it decreases and remains steady. $COD_{(I)}$ increased at 11 hours, dilution rate is subsequently kept low until the $COD_{(I)}$ decreased back to original levels at 40 hours. Ripley's ratio and total VFA concentration are shown in Figure 6.19. Ripley's ratio was at steady state at 0.7 prior to increasing to a maximum of 2.3. Ripley's ratio does decrease, however, it does not decrease back to the steady state level, but remains at 1.5.

Results from the two hydrogen incorporated, controlled experiments (Figures 6.11-16), compared to the previous set of data from an increase in organic loading (Figures 6.1-6.3), support the hypothesis that control incorporating hydrogen as a control

parameter in the original control algorithm would result in more stable digester operation.

## 6.3 Discussion from the incorporation of hydrogen for control

The results from this section have shown the benefits of the incorporation of hydrogen into a control strategy. The hydrogen concentration is shown to respond quickly to both organic load increases and toxic shocks. The incorporation of hydrogen into the control strategy overcomes the confusion between an increase in methane production rate being assumed to be beneficial, i.e. an increase in efficiency rather than as a short term result of an organic load increase. However, these elevated concentrations of hydrogen are not sustained throughout the period during which the anaerobic digester is under stress. Comparison of Figures 6.1 and Figure 6.17 (hydrogen concentration and Ripley's ratio during control of an increase in organic load) shows that the hydrogen responded quickly to the increased organic load, but also decreased back to baseline levels fairly rapidly (30 hours). The Ripley's ratio, on the other hand, was slower to respond initially but shows the digester to be under stress from the increased organic load as late as 60 hours. The usefulness of hydrogen as a rapid detection control parameter has been demonstrated, however, it should be emphasised that the relatively short lived response of hydrogen means that it will primarily be of use as one of several control parameters used in conjunction. This observation is in agreement with results published in current literature, reviewed in Chapter 2 (Pauss and Guiot, 1993, Slater *et al.*, 1990, Ehlinger *et al.*, 1994). For example Slater *et al.* (1990) concluded that the fast response and short term sensitivity of hydrogen to loading upsets, indicates that hydrogen concentration might be useful as a control variable. However, Slater *et al.* (1990) went on to say that further work would be needed to understand how hydrogen concentration could be combined with other variables to infer the state of the reactor. Also the long term perturbation experiments conducted by Ehlinger *et al.* (1994) showed that the hydrogen concentration increased as soon as the problem arose, but came back to its initial value despite the persistence of the problem. This pattern is also demonstrated by this research. Ehlinger *et al.* (1994) used an expert system type control strategy that used pH, hydrogen

concentration and biogas production rate as control parameters. He concluded that his control system was sufficient to automatically control the digester during short term overloads, but that further control parameters were required to detect long term instability.

Previous literature points to the advantage of using hydrogen as the quick response time to an upset to the digester, however the disadvantage of the relatively short term response of hydrogen to an upset must be compensated for by the involvement of other control parameters within the control strategy.

Direct comparison of these results with other research on control of anaerobic digestion utilising hydrogen as a control parameter is problematic because of the variety of other parameters used for any particular control strategy. Examples of previous research conducted on the control of anaerobic digestion is described in detail in the literature review (Chapter 2). For example, Holst *et al.* (1995) used only pH, methane production rate and hydrogen with an 'expert system type' control system (similar to that reported by Ehlinger *et al.*, 1994). This control system maximised the volume of effluent treated by increasing the dilution rate in steps until the methane and hydrogen concentration changed, indicating that the anaerobic digester was operating at an optimum loading rate. Holst *et al.* (1995) describes a controlled organic shock load applied to test the control system. A 200% increase in feed rate resulted in a decrease in feed pump speed in response to an increase in hydrogen concentration from 65 to 120 ppm. This increase in hydrogen concentration is similar to that reported during this research for organic load increases. Moletta *et al.* (1994) also used hydrogen concentration, pH and methane concentration for control using an expert system, with the aim of optimising reactor performance. Slater *et al.* (1990) and Slater *et al.* (1991) used hydrogen, carbon monoxide and methane production rate as gas phase control parameters and VFA concentrations to monitor the liquid phase for control by an adaptive control strategy. Ehlinger *et al.* (1994) used pH, biogas production rate and hydrogen with expert system based control algorithm to control the dilution rate during an increase of influent concentration from 20 to 60 g/l COD. Despite the difficulty of making a direct

comparison with these other researchers results it is possible to compare hydrogen response to organic load increases and organic toxicant additions. Hydrogen concentration increases reported by other researchers are comparable to those reported in Chapters 5 and 6. For example 80 to 600 ppm hydrogen during an organic over load reported by Ehlinger *et al.* (1994) and 0 to >1000 ppm hydrogen during the addition of organic toxicants (Hickey *et al.*, 1987).

The control algorithm used in this research differs from the above mentioned literature in that it incorporates the on-line measurement of digester effluent $COD_{(t)}$ as a control parameter. The control strategy is based on maintaining a specific concentration of $COD_{(t)}$ in the treated effluent to meet a defined consent. This is important for many on-site industrial effluent treatment plants where there is a discharge consent including COD. The control action when the gas phase indicators (methane production rate and hydrogen concentration) indicate that the feed pump speed can be increased, whether it is or not is still dependent on effluent $COD_{(t)}$ concentration. This control strategy has the advantage over that reported by Ehlinger *et al.* (1994) of being able to monitor effluent quality ($COD_{(t)}$ concentration) which would detect digester instability once hydrogen concentrations decreased and biogas production rates became stabilised after an organic overload or toxic inhibition event.

## *6.4 Conclusions from the incorporation of hydrogen for control*

From this set of experiments the following conclusions can be drawn

- Hydrogen concentration is an important control parameter to rapidly detect digester upset, particularly in the case of toxic inhibition.

- Hydrogen concentration is less useful in the case of increased organic loading in which case $COD_{(t)}$ is still the most important parameter.

- Hydrogen concentration responds rapidly which is its principal advantage – a rapid detection control parameter.

- The disadvantage of using hydrogen as a control parameter is that it decreases before the digester has fully recovered.

- Hydrogen concentration is therefore particularly useful when combined with other parameters, such as COD/VFA which do not respond as quickly, but are better indicators of longer term digester instability.
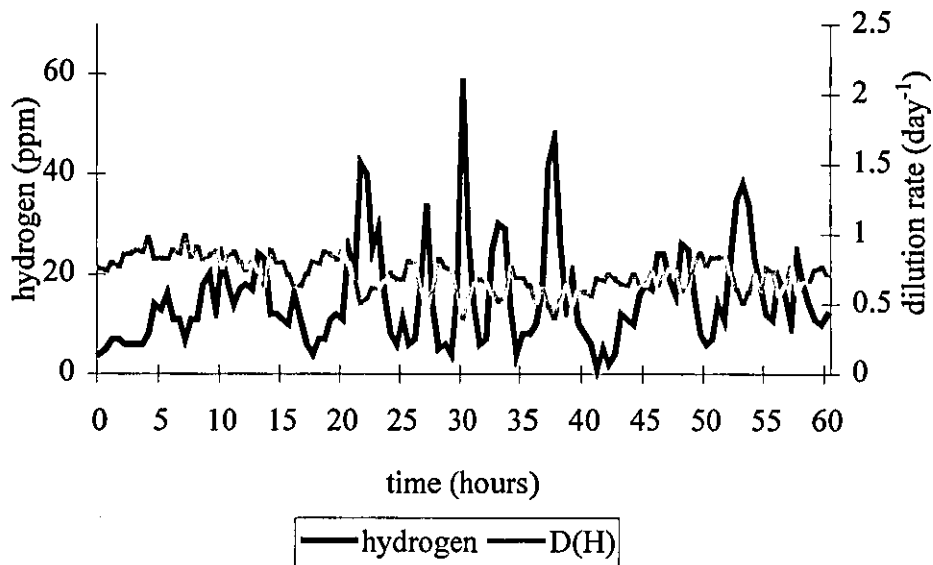
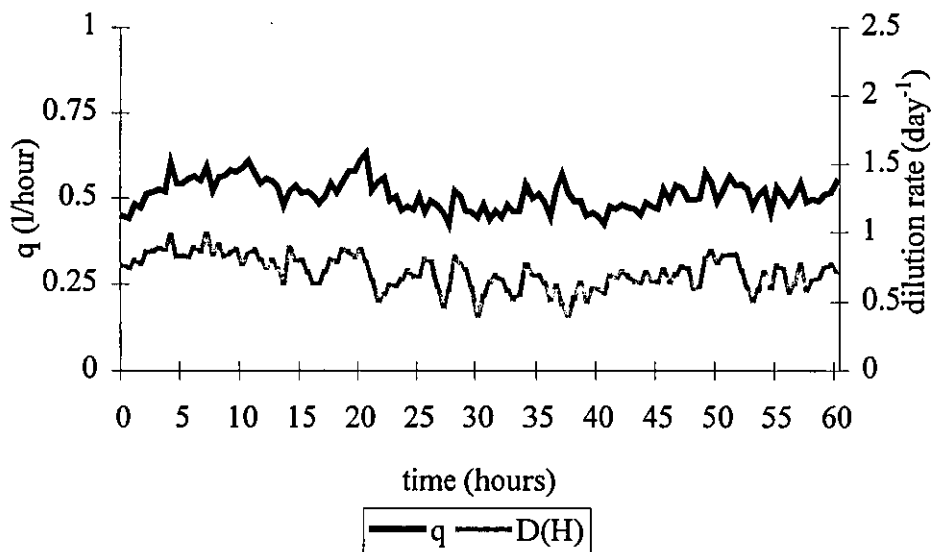Figure 6.8  Hydrogen and $D_{(H)}$ during a 1g/l pyrazine addition



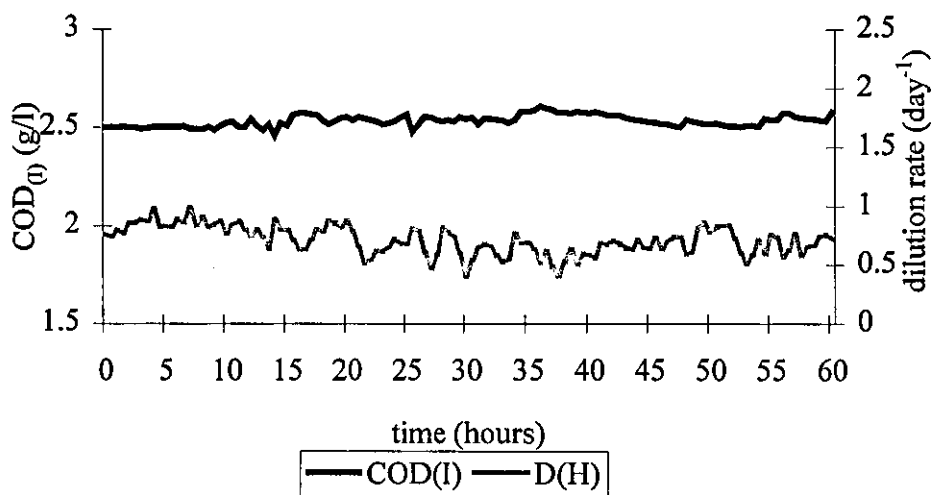Figure 6.9  Methane production rate and $D_{(H)}$ during a 1g/l pyrazine addition



Figure 6.10  $COD_{(I)}$ and $D_{(H)}$ during a 1g/l pyrazine addition
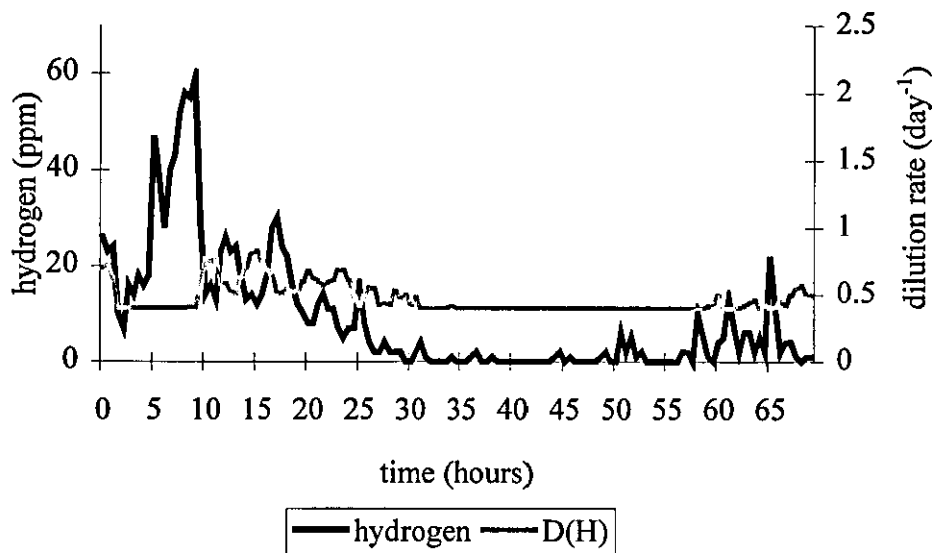
Figure 6.11 Hydrogen and $D_{(H)}$ during an organic load increase



Figure 6.12 Methane production rate and $D_{(H)}$ during an organic load increase
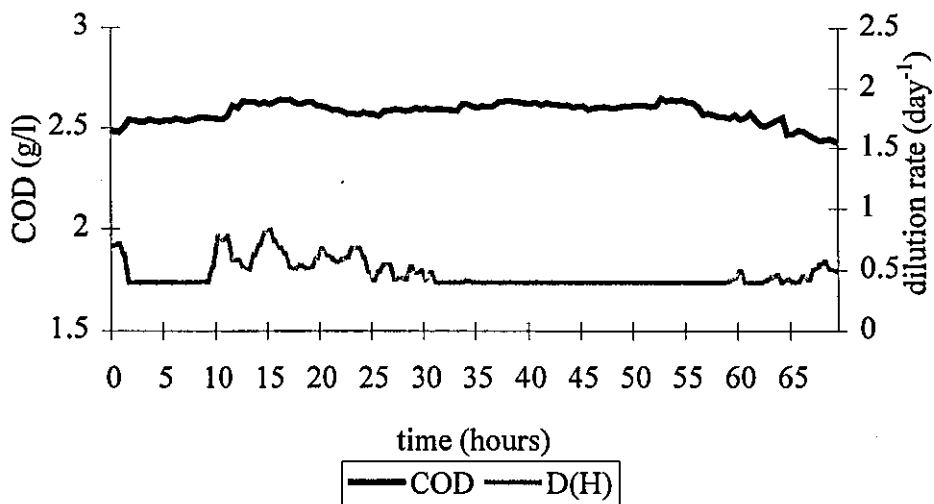


Figure 6.13 $COD_{(I)}$ and $D_{(H)}$ during an organic load increase
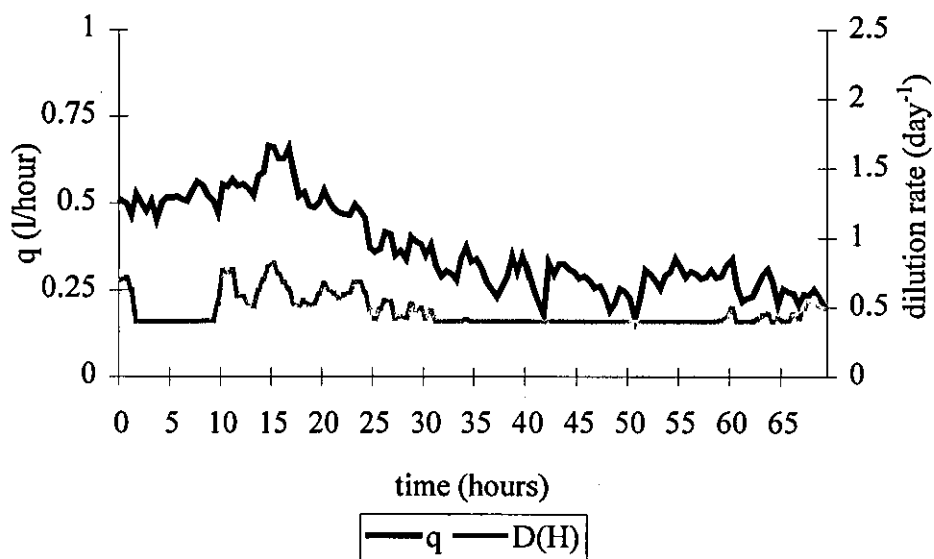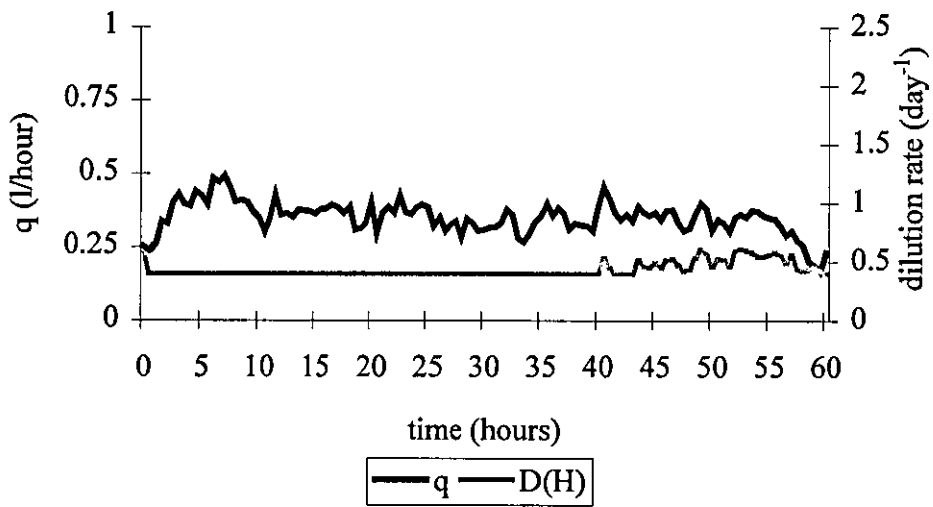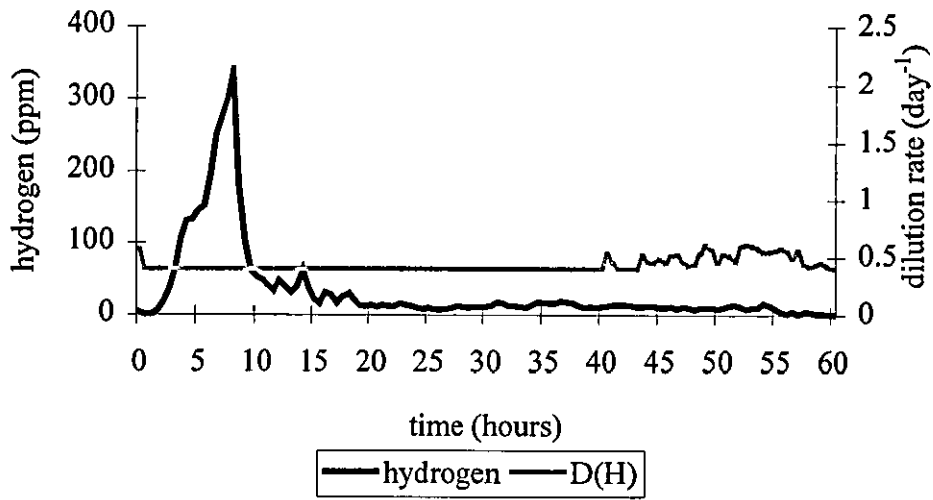
Figure 6.15  Methane production rate and $D_{(H)}$ during an organic load increase



Figure 6.16  $COD_{(I)}$ and $D_{(H)}$ during an organic load increase

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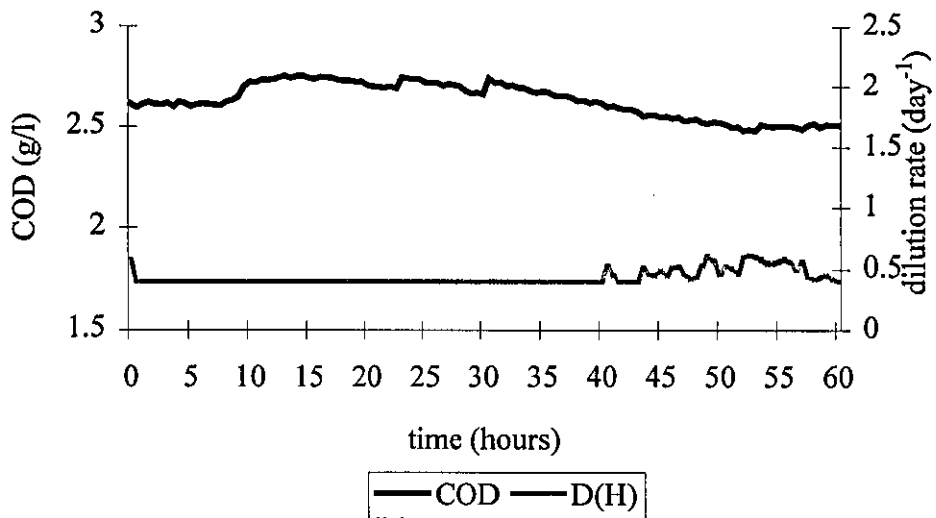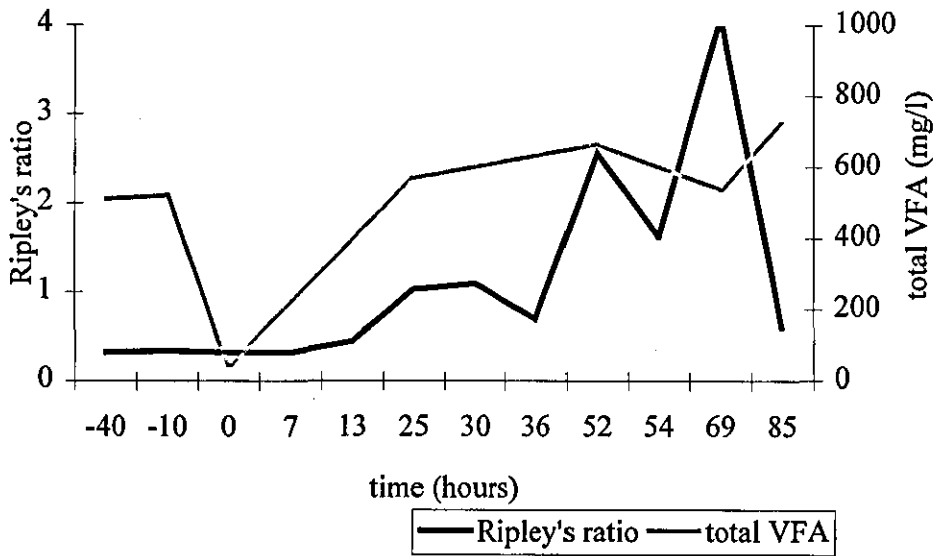
Figure 6.17 Ripley's ratio and total VFA during an organic load increase (original control)
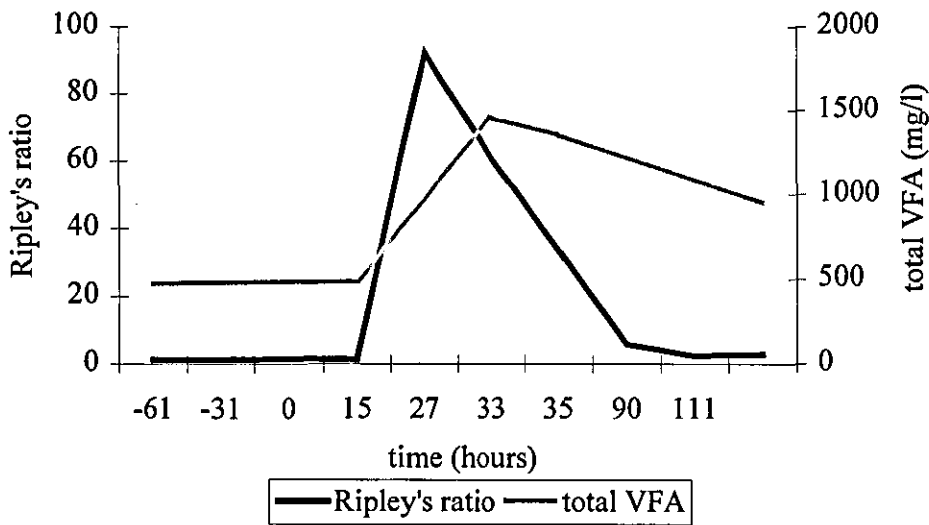


Figure 6.18 Ripley's ratio and total VFA during a 1g/l pyrazine addition (original control)
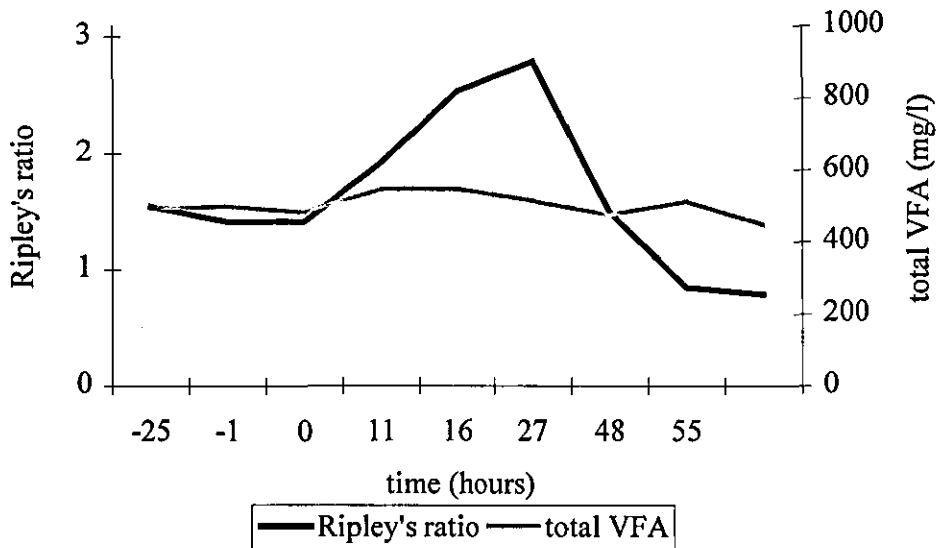


Figure 6.19 Ripley's ratio and total VFA during a 1g/l pyrazine addition (new control)
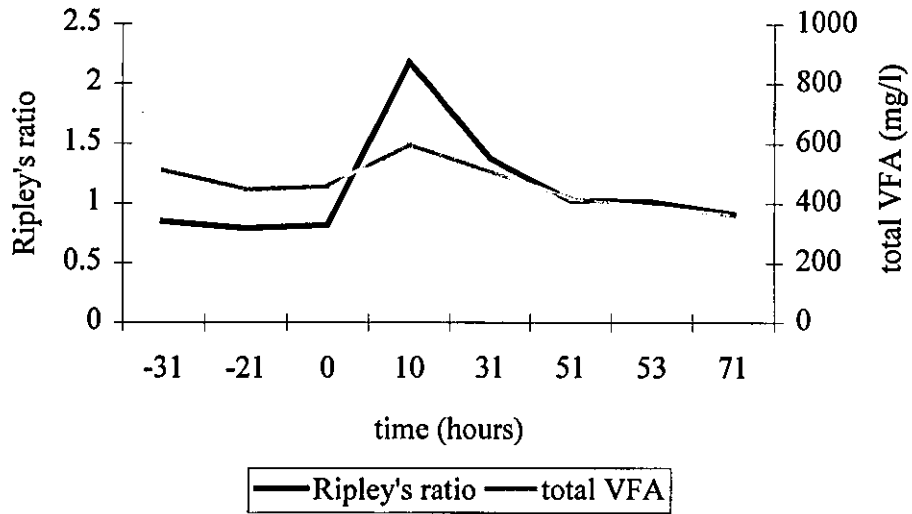
Figure 6.20 Ripley's ratio and total VFA during an organic load increase (new control)



Figure 6.21 Ripley's ratio and total VFA during a second organic load increase (new control)

## 7. NEURAL NETWORK TRAINING AND TESTING

Results presented in Chapters 5 and 6 show that effective control of an anaerobic digester treating coffee processing effluent of varying strength and composition often requires the intelligent interpretation of a combination of parameters. That is, different stress conditions, e.g. organic overloading or toxic shock may require different control responses, which can best be learn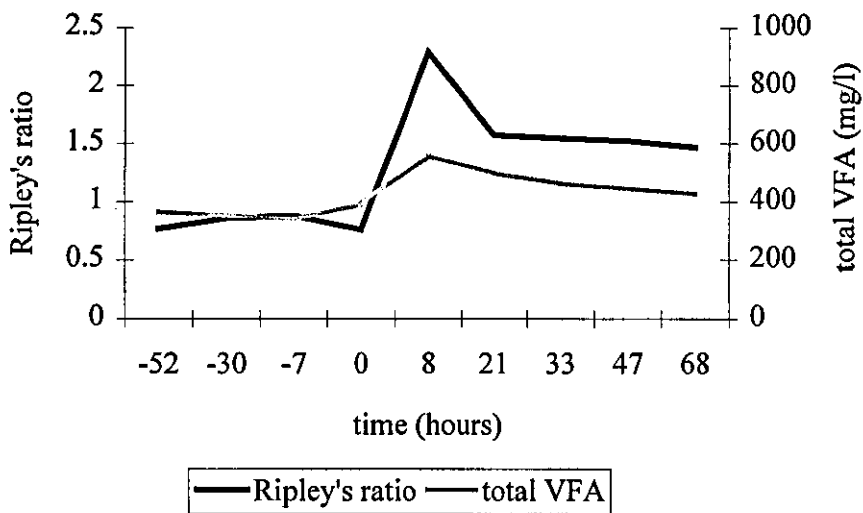ed from the experience gained during long-term operation. Artificial neural networks have the capacity to generate their own rules based on learned examples and are, therefore, a good choice for a complex system which is not fully defined, but has been well monitored resulting in good operating data. For this research, i.e. the control of an anaerobic digester treating waste containing potentially toxic and recalcitrant compounds, it was decided that the control strategy would be based on previously obtained experimental data. Artificial neural networks were therefore identified as a potential control strategy to be evaluated.

For this research a commercially available neural network package (Neuralware's Neural Explorer) was used to generate three identical back propagation neural networks (illustrated in Figure 2.8). The objective was to protect the laboratory scale anaerobic digester from shock loads and to maintain a consistent effluent quality. The inputs were $COD_{(t)}$ and methane production rate, the neural output was dilution rate. Different 20 hour sections of training data from a real time control experiment were input in order to establish the amount of training information required. The trained ANN was then tested using a 2 month period of data to test its capability to control a $5m^3$ pilot plant treating the same waste. One of the objectives being to determine whether the neural network required lengthy periods of time to gain experience, which could be a potential disadvantage.
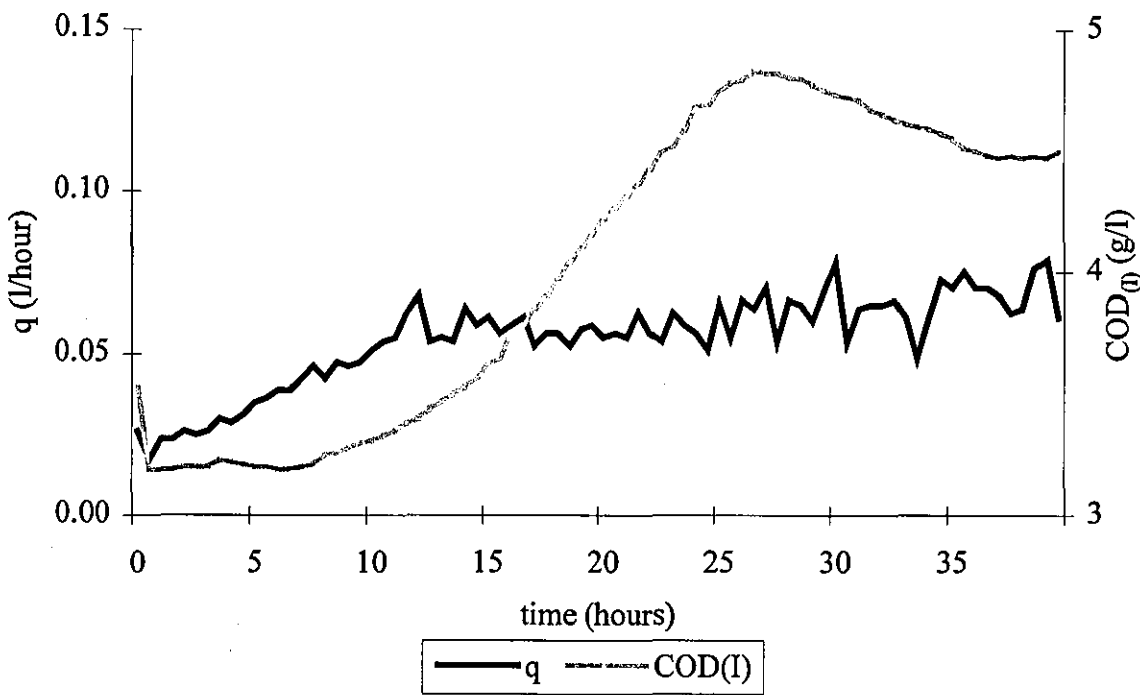
Figure 7.1 The data given to test the neural networks



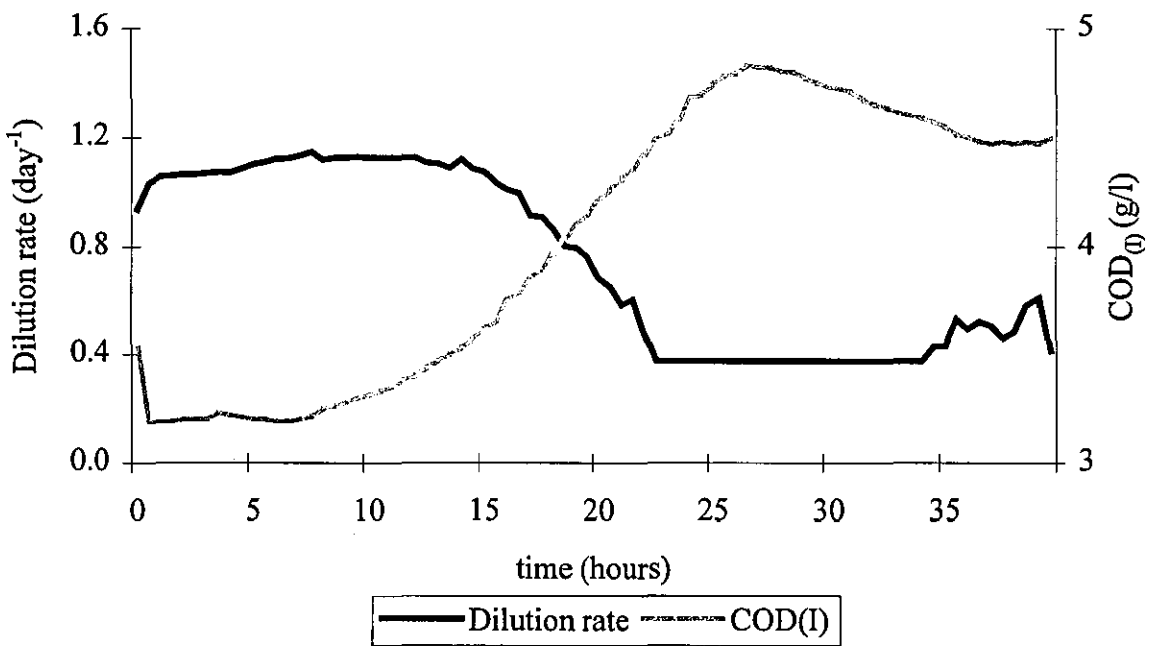Figure 7.2 Data from an adaptive control experiment

135
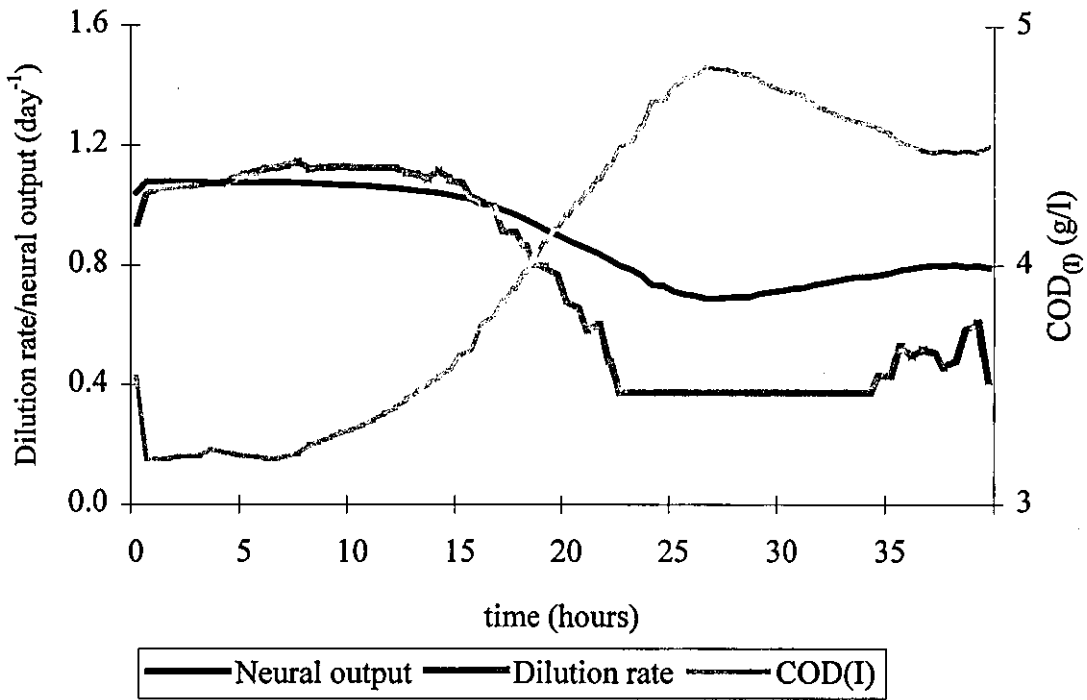
Figure 7.3 Output from the first neural network, trained over a narrow range of example data
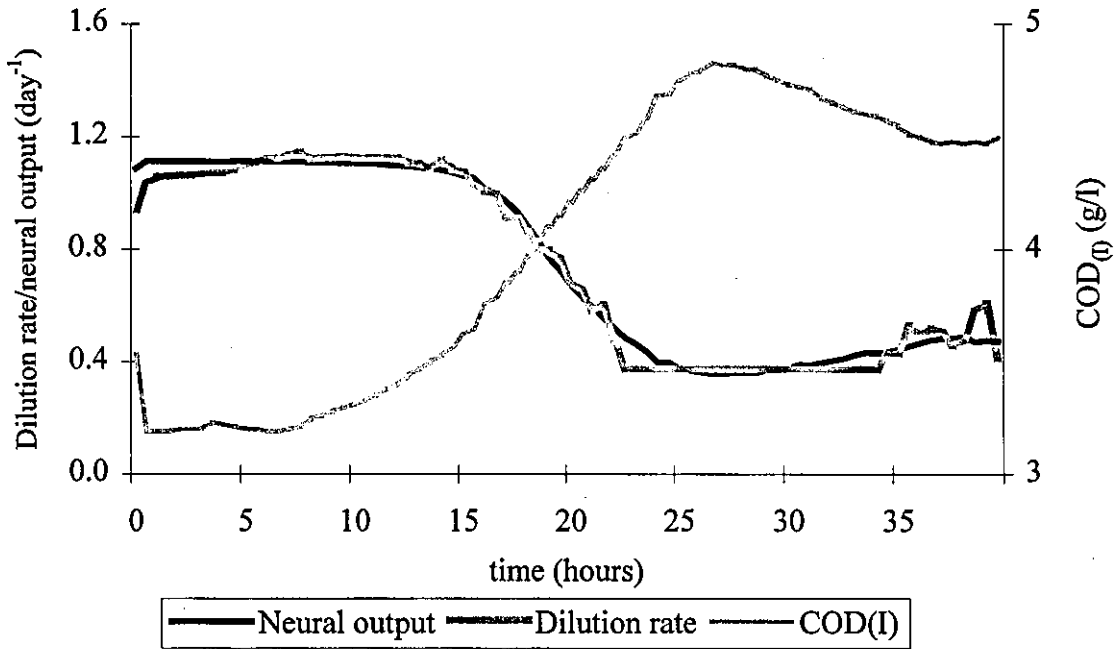


Figure 7.4 Output from the second neural network, trained over a wide range of example data

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## 7.1 Training and testing of neural networks

A typical set of data, showing an increase in $COD_{(I)}$ from 3.2 to 4.8 g/l over an arbitrary 40 h period was used to test the neural networks. Parallel experiments were conducted with the adaptive control algorithm to provide a set of experimental control data against which the neural networks were to be compared. The data used to test the neural networks with the adaptive control system are shown in Figure 7.1 and 7.2. The inputs of $COD_{(I)}$ and methane production rate are the only data that are input to test the neural networks. The response of the adaptive control to the increase in $COD_{(I)}$ is shown in Figure 7.2. As $COD_{(I)}$ increases dilution rate decreases in response.

In the first experiment the ANN received the first 20 hours training i.e. a range of $COD_{(I)}$ (3.2 - 4.0 g/l) of the data shown in Figure 7.2.

The output from the neural network shown in Figure 7.3 follows and repeats the output from the adaptive control model until the $COD_{(I)}$ rises above 4 g/l beyond which the ANN has no experience. After this point the ANN generalises using the rules learnt from the narrow range of data shown. As a result the pump speed does not decrease as much as the adaptive control model. This indicates that although the ANN was poorly trained and unable to respond precisely to the full range of test data it was able to predict the correct action, a reduction in pump speed.

The second ANN also received 20 hours of training data but which included the widest possible range of $COD_{(I)}$ and methane production rate. This data was from the middle 20 h period of the data set in Figure 7.2.

In Figure 7.4 the output from the NN and adaptive control model match each other closely (usually ± 2%) over the entire 40 hours. This demonstrates that the neural network develops the capability to control the anaerobic digester, once trained on a suitable range of data.

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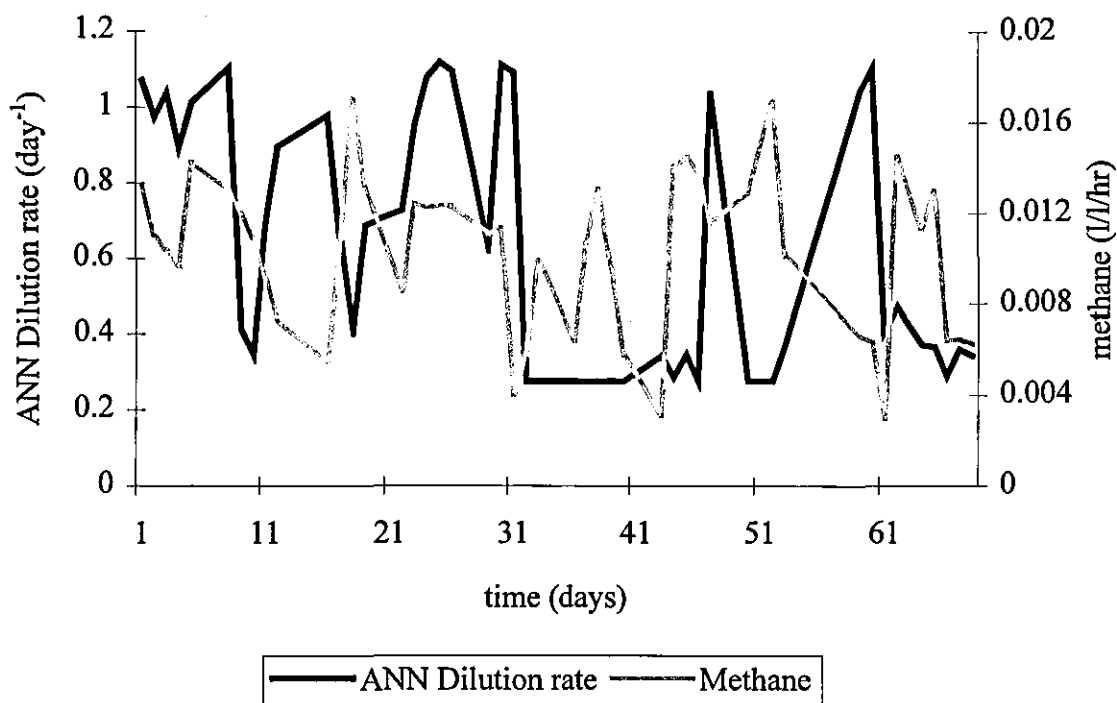
Figure 7.5 Pilot plant methane production data and ANN dilution rate output
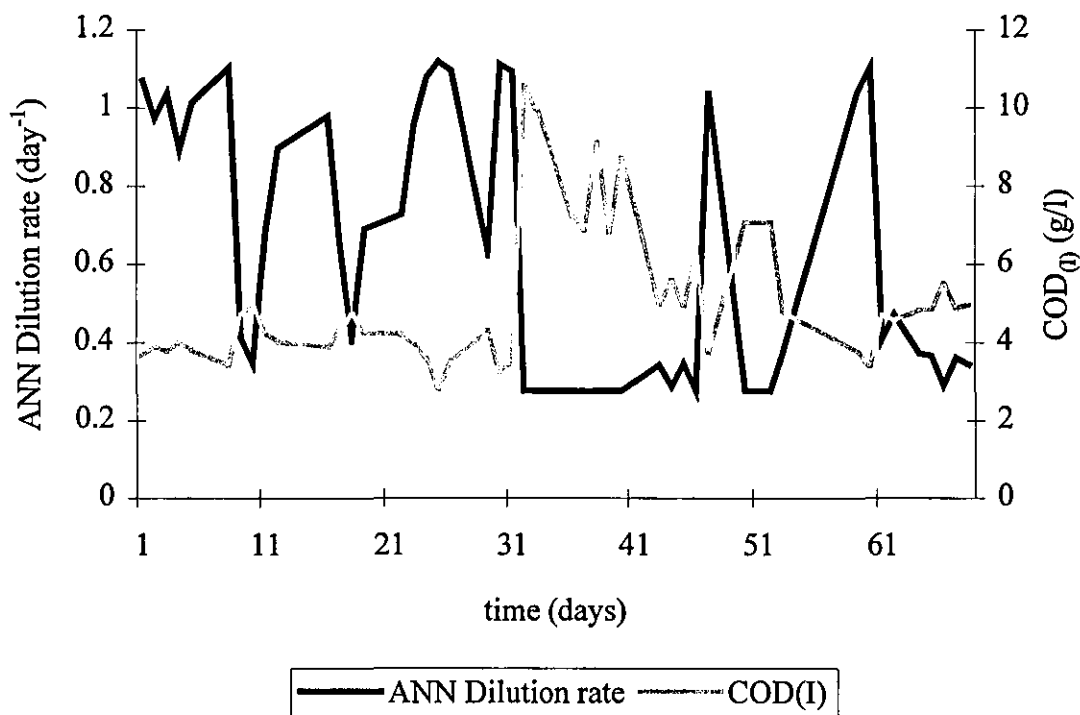


Figure 7.6 Pilot plant $COD_{(I)}$ data and ANN dilution rate output

## 7.2 Testing of the trained neural network on pilot plant data

The trained ANN was then applied to pilot scale data over a 2 month period (Figures 7.5 & 7.6). The data shows rapid changes of feed pump speed in sympathy with $COD_{(I)}$ concentration in the effluent.

## 7.3 Discussion of neural network training and testing results

The results from the laboratory ANN after the training period are comparable to those obtained from the tried and tested adaptive control. Johnson *et al.* (1995) noted in their work on the control of anaerobic digesters that there were potential problems for the simple rule based systems such as adaptive control if the characteristics of the waste changed. They concluded that these might be overcome by using a greater array of control parameters. Artificial neural networks have been shown to be at least as good as adaptive control and offer the possibility of simple addition of control parameters. They are commercially available and able to accept a large number of sensor inputs without a separate control strategy for each. The results presented show that programming does not require extensive or expert knowledge. It should therefore be possible to program a neural network during the routine commissioning of a plant. Thereafter, the control will improve as more system experience is gained from the operating data.

The neural network applied to the pilot plant data had previous laboratory scale experience of $COD_{(I)}$ variations from 3-5 g/l but at pilot scale encountered COD concentrations up to 10 g/l. The pilot plant data is from a period of time during which there appears to be an upset with the anaerobic filter. The $COD_{(I)}$ of effluent from the pilot-scale filter is steady until it increases on day 32, in response to which the ANN decreases the dilution rate until the effluent $COD_{(I)}$ decreases to 4 g/l. The pilot plant data shows sharp and highly variable gas production, this was not observed at laboratory scale and is undesirable. Further investigations into gas response times will be necessary. In the IAWQ model, for example, responses to particulate substrate took several hours (Henze *et al.*, 1987). This would give rise to a significant time

delay in the generation of gas. The laboratory waste was deliberately settled and a greater proportion of the $COD_{(I)}$ would have been as soluble COD from which the response time would have been much quicker. More input variables would be necessary with wastes containing significant amounts of solid substrate, potentially toxic components or other changing characteristics. These could be based on other control parameters such as alkalinity, hydrogen and hydrogen sulphide which will have advantages for shocks not linked to changes in organic load.

Wilcox *et al.* (1995) describe neural network control of an anaerobic digester using non-invasive alkalinity analysis. They attributed some small but continual fluctuations in the performance of the neural network to a lack of training. For simple control outputs, i.e. organic loads, our data shows very little training is required. The simulation experiments described here indicate that artificial neural networks are applicable for the control of anaerobic digestion and have the advantage of being able to learn from previous operating data, which should ultimately give a faster response than an adaptive control system due to ANNs having the capability to form associations between other inputs/sensors.

Emmanouilides and Petrou (1997) compared three types of neural network (back propagation, and two random optimisation techniques called chemotaxis and random search) using simulation results. It was reported that the random optimisation techniques were faster than the back propagation algorithm. They used a mathematical model of the anaerobic digestion process to demonstrate stability in the case of process input variations and that set points could be maintained. Emmanouilides and Petrou (1997) argue that the presence of a well constructed training data set is unnecessary, since the on-line nature of the networks improve modeling accuracy and control performance by adding significant flexibility to the control scheme. Emmanouilides and Petrou (1997) suggest that given a sufficient set of training data their ANN will have the ability to give a calculated response, despite having been presented with previously unseen input.

Premier *et al.* (1999) compared a non-linear neural network model with two other black box ARX (auto regressive with exogenous input) models, the first being a linear

single input single output (SISO) model, the second a linear multi-output (MIMO) model. The models were trained and validated using bicarbonate alkalinity, gas production rate and percentage carbon dioxide data collected from a laboratory scale fluidised bed anaerobic digester treating a synthetic bakers wastewater. The performance of the models were compared using correlation analysis of the residuals (one-step-ahead prediction errors) and it was found that the SISO model was the least able to predict the changes in the reactor parameters. Premier *et al.* (1999) report that the MIMO and neural models both performed well. The neural model was shown to have superior overall performance compared to the MIMO model. However, the MIMO model had the advantage of simplicity over the neural model, which would be a factor to consider when choosing between them. Premier *et al.* (1999) conclude that when the model is estimating one step (30 minutes) ahead the performance of the model is at a point that it can be considered a relatively accurate representation of the anaerobic system.

The ability of these models to predict the state of the anaerobic digester could be used to develop a control algorithm. The advantage of such a control algorithm would be that it would be based on past operating data specific to a given system, rather than being based on the biological, chemical and physical processes taking place during anaerobic digestion.

### *7.4 Conclusions from neural network section*

- The literature reviewed and data from experiments reported in this chapter have shown that a neural network can perform as well as the adaptive control system whilst requiring less expert input (and accepting more parameters in standard proprietary software).

- Neural networks have the potential to be trained on laboratory scale data and then used for control of pilot plant reactors without additional training being necessary.

- Only small periods of training (30-40 hours) have been shown to be necessary to control simple desired outputs, e.g. effluent quality and gas production from a waste of known treatability.

- Increasing acceptance of this technology and the reduction in computer hardware prices will result in artificial intelligence techniques being used increasingly in the future to achieve better operation and control of wastewater treatment plants.

## 8. CONCLUSIONS AND FURTHER RECOMMENDATIONS

The principal objective of this research was to develop a control strategy to improve the consistency of performance of an anaerobic digester treating liquid effluent from an instant coffee processing plant. The first stage in developing the control strategy involved a detailed study on the treatability of the effluent in question. A review of current and retrospective literature, combined with data from laboratory scale anaerobic filters and from a $5m^3$ pilot plant anaerobic filter, identified the following problems:

- Instant coffee processing effluent, in comparison with other food industry effluents, was found to contain recalcitrant and inhibitory fractions which resulted in a relatively low treatment efficiency and could be problematic with respect to toxicity.

- Organic load fluctuations resulting from process changes in the factory often resulted in increased effluent COD from the anaerobic digesters. This could result in an effluent COD concentration greater than the maximum admissible concentration of the factory discharge compliance.

A control strategy was identified that was able to respond to the above criteria and was tested extensively on laboratory-scale anaerobic filters treating instant coffee processing effluent. The control strategy involved the on-line measurement of methane, biogas production and effluent $COD_{(I)}$. On-line $COD_{(I)}$ measurements using suspended solids and conductivity probes were shown to be effective for the detection of fluctuations in digester effluent quality at both laboratory and pilot plant scale. The control system was shown to be effective at smoothing out organic load fluctuations to the digesters by controlling the feed pump, thereby reducing operational imbalances and ensuring a constant effluent $COD_{(I)}$ quality. Thus, it can be concluded that the original control system fulfilled the objective of ensuring a consistent quality of effluent, thereby enabling compliance with a known discharge consent.

However, parallel research conducted by Imperial College London found that, instant coffee processing effluent contained a number of substances that would be potentially

toxic or inhibitory to anaerobic digestion (Azhar and Stuckey, 1995). This research showed that acclimation of the anaerobic population to some of these substances (e.g. pyrogallol) enabled tolerance and degradation of the compounds. However, severe inhibition and failure of the digestion process was demonstrated to occur in the presence of pyrazine at concentrations of 1g/l. In this case the control system failed to react rapidly enough to prevent digester failure. At this point in the research it was concluded that the control system was not ideally suited to rapid detection of toxin-related inhibition in an anaerobic digester. Moreover, problems were identified with the liquid phase solids and conductivity probes; probe fouling was found to occur at the pilot plant and during laboratory experiments. It is recommended that the liquid phase probes are cleaned daily to ensure a good correlation between on-line and standard wet test COD readings, on which the discharge consents are based and monitored. Thus, it can be concluded that the use of liquid phase probes for control will be effective but will require a high level of maintenance to achieve consistently accurate results. A vital area of future research is, therefore, to investigate automated cleaning procedures for use with liquid phase probes.

The fact that the control system was not shown to be suitable for dealing with rapid inhibition of anaerobic digestion highlighted the need for incorporation of additional parameters into the control strategy. Gas phase parameters were identified as preferential due to the fouling problems associated with liquid phase probes. In particular, hydrogen in the digester biogas, which was measured on-line during this research, was identified as being able to respond rapidly to operational imbalances caused by both toxic inhibition and organic load fluctuations. Moreover, hydrogen was shown to be a relatively inexpensive parameter to monitor on-line.

Hydrogen was, therefore, incorporated as an on-line parameter in the original control system. Hydrogen concentration in the biogas was found to respond rapidly to digester stress and the new control system was shown to be capable of preventing digester failure in the presence of a pyrazine. As earlier experiments with pyrazine resulted in digester failure, in spite of the intervention of the original control system, it can be concluded that the incorporation of hydrogen is beneficial to control of

digestion in circumstances of toxic inhibition. Hydrogen concentration was found to be less useful in the case of increased organic loading in which case $COD_{(t)}$ was found to be the most important parameter in the control algorithm. A disadvantage of hydrogen as a control parameter was found to be that it decreases to normal operational levels before the digester has achieved steady-state operation according to parameters such as the acidity:alkalinity balance. It can, therefore, be concluded that hydrogen is advantageous as a rapid detection control parameter. Thus, hydrogen is primarily beneficial when combined with other parameters, such as COD/VFA which do not respond as quickly to inhibition, but are better indicators of longer term digester instability. It is recommended that further research be undertaken to investigate the benefits and disadvantages of the hydrogen incorporated control algorithm on different types of waste, particularly those wastes containing unpredictable loads of inhibitory substances.

Although the hydrogen-incorporated control system was found to be capable of dealing with inhibitory wastes, it was clear from the research that effective control of an on-site anaerobic digester required the intelligent interpretation of a combination of parameters to deal with the inconsistent quality of the instant coffee processing effluent. Artificial neural networks, being able to generate their own rules based on previous operational experience, were therefore investigated in the final phase of this project. Results showed that the neural network investigated could perform as well as the adaptive control system whilst requiring less expert input. It was shown that a principal advantage of neural networks were the relatively small periods of training (30-40 hours) required to enable control of simple desired outputs, e.g. effluent quality from a waste of known treatability. Moreover, the neural networks could be trained on laboratory-scale data and used for control of pilot plant reactors without additional training. It is thought that increasing acceptance of this technology and the reduction in computer hardware prices will result in artificial intelligence techniques being used increasingly in the future to achieve better operation and control of wastewater treatment plants.

## 9. REFERENCES

Addis, T. R. 1981

Definition of an expert system.

British Computer Society Specialist Group on Expert Systems Newsletter (3) Spring/Summer


Agardy, F. J., Cole, R. D. and Pearson, E. 1963

Enzyme activity as a parameter of digester performance.

in Proceedings of the 18th Purdue Industrial waste conference, Engineering extension series No 115, Purdue Uni. Lafayette, IN, 1963 51-65


Alatiqi, I. M., Dadkhah, A. A. and Nabil M. J. 1990

Dynamics and multivariable control analysis for anaerobic digestion.

The Chemical Engineering Journal 43 B81-B91


Alexiou, I. E., Anderson, G. K. and Evison, L. M. 1994

Design of pre-acidification reactors for the anaerobic treatment of industrial wastewaters.

Water Science & Technology 29 (9) 199-204


Anderson, G. K., Donnelly, R. and McKeown, K. J. 1982

Identification and control of inhibition in the anaerobic treatment of industrial wastewaters.

Process Biochemistry July/Aug 28-32


Anderson, G, K., Kasapgil, B. and Ince, O. 1994

Comparison of porous and non-porous media in upflow anaerobic filters when treating dairy wastewater.

Water Research 28 (7) 1619-1624

Anderson, G. K., Saw, C. B., Tebbutt, T. H. W., Forster, C.F. Hawkes, D.L. Lester, J. N. and Wheatley, A. D. 1988

Design of the SERC anaerobic digestion pilot plant facility.

5th Int. Symp. on AD Bologna Italy 1988 251-253


Andrews, J. F. and Kambhu, K. 1971

Thermophilic aerobic digestion of organic solid wastes.

Clemson University Environmental Systems Engineering Dept 79


Andrews, J. F. 1968

A dynamic model of the anaerobic digestion process.

Envir. Systems Engng Dept Clemson Univ., S. C., 52


Archer, D. B., Hilton, M. G., Adams, S. P. and Wiecko, H. 1986

Hydrogen as a process control index in a pilot scale anaerobic digester.

Biotechnology Letters **8** (3) 197-202


Ashley, N. V. and Hurst, T. J. 1981

Acid and alkaline phosphatase activity in anaerobic digested sludge: a biochemical predictor of digester failure.

Water Research **15** (5) 633-638


Azhar, N. G. 1994

Personal communication.

Department of Chemical Engineering, Imperial College London


Azhar, N. G. and Stuckey, D. C. 1993

The anaerobic treatment of liquid wastes containing refractory/toxic compounds; a case study of instant coffee wastes.

ICME conf. in Birmingham Jan 1993

Azhar, N. G. and Stuckey, D. C. 1994

The influence of chemical structure on the anaerobic catabolism of refractory compounds: a case study of instant coffee wastes.

Water Science and Technology **30** (12) 223-232


Baba, K., Enbutu, I., Matuzaki, H. and Nogita, S. 1990

Intelligent support system for water and sewage treatment plants which include a past history learning function-Coagulant injection guidance system using neural net algorithm.

Proceedings of the 5th International Association on Water Pollution Research and Control workshop, Yokohama and Kyoto, Japan. Pergammon Press 227-234


Bajwa, H. S. and Forster, C. F. 1988

The inhibition of anaerobic processes by vegetable tanning agents.

Environmental Technology Letters **9** 1245-1256


Barnett, M. W. and Andrews, J. F. 1992

Expert system for anaerobic digestion process operation.

Journal of Environmental Engineering **118** 949-962


Bastin, G. and Dochain, D. 1988

Stable adaptive controllers for waste treatment by anaerobic digestion.

In: Proceedings of the IEEE: Automatic Control Conference. Atlandt, GA, June


Bressani, R. and Braham, J. E. 1980

Utilization of coffee pulp as animal feed.

Institute of Nutrition of Central America and Panama (INCAP), Guatemala.


Boopathy, R. 1987

Effect of temperature on anaerobic fermentation of coffee waste.

Asian Environmental 9 (3) 13-18


Boscolo, A., Mangiavacchi, C., Drius, F., Rongione, F., Pavan, P. and Cecchi, F. 1993
Fuzzy control of an anaerobic digester for the treatment of the organic fraction of municipal solid waste (MSW).
Water Science and Technology 27 (2) 57-68


Bryant, C. 1993
Doing without Oxygen.
Biologist 40 (2) 58-61


Chang, A. C., Fairbank, W. C., Jones, T. E. and Warneke, J. E. 1983
Wastewater recycling in anaerobic digestion of beef cattle wastes.
Agricultural Wastes 7 (1) 1-12


Chynoweth, D. P., Svoronos, S. A., Lyberatos, G., Harmon, J., Pullammanappallil, P., Owens, J. M. and Peck, M. J. 1994
Real-time expert system control of anaerobic digestion.
Water Science and Technology 30 21-31


Chung. Y. C. and Neethling, J. B. J. 1988
ATP as an indicator of anaerobic digester activity.
Water Pollution Control Federation 60 107-112


Clark, R. J. and Macrea, R. eds 1985
COFFEE Volume 1. Chemistry.
Elsevier Applied Science Publishers Ltd
London and New York 1985
ISBN 0-85334-368-3


Collins, L. J. and Paskins, A. R. 1987

Measurement of trace concentrations of hydrogen in biogas from anaerobic digesters using an exhaled hydrogen monitor.
Water Research **21** (12) 1567-1572


Conrad, R., Phelps, T. J. and Zeikus, J. G. 1985
Gas metabolism in support of juxtapositioning of hydrogen-producing and methanogenic bacteria in sewage sludge and lake sediments.
Applied Environmental Microbiology **50** 595-601


Daoming, S. and Forster, C. F. 1993
An examination of the start-up of a thermophilic upflow sludge blanket reactor treating synthetic coffee waste.
Environmental Technology **14** 965-972


Daoming, S. and Forster, C. F. 1994
Inhibitory effects in the thermophilic anaerobic treatment of assimilated coffee wastewater.
Environmental Technology **15** (3) 287-292


De Haas, D. W. and Adam, N. 1995
Use of a simple titration procedure to determine $H_2CO_3$ alkalinity and volatile fatty acids for process control in waste-water treatment.
Water S.A. **21** (4) 307-318


Delcambe, L., Lenzen,. C. Dierickx, L., Fontaine-Delcambe, P., Joris, E., Gilles, A. and Joassin, L. 1983
Selection of a method of biomass measurement in anaerobic digesters in terms of their methanogenic activity.
Tribune du Cebedeau **36** (480) 495-504


Demirer, G. N. and Speece, R. E. 1998

150

Anaerobic biotransformation of four 3-carbon compounds (acrolein, acrylic acid, allyl alcohol and n-propanol in UASB reactors.

Water Research **32** (3) 747-759


Dinsdale, R. M., Hawkes, F. R. and Hawkes, D. L.  1996

The mesophilic and thermophilic anaerobic digestion of coffee waste containing coffee grounds.

Water Research **30** (2) 371-377


Disley, R. S., Walmsley, M. J. and Forster, C. F.  1993

Inhibition of gas production by thermophilic anaerobic sludges: the effect of organic compounds.

Environmental Technology **13** (12) 1153-1159


Dochain, D.  1995

Recent Approaches for the modelling, monitoring and control of anaerobic digestion processes.

Proceedings from the International workshop on monitoring and control of anaerobic digestion processes, December 6th and 7th, 1995, Laboratorie de biotechnologie de L'environment, INRA, Narbonne, France 23-29


Dochain, P. and Bastin, G. 1985

Stable adaptive controllers for waste treatment by anaerobic digestion.

Environmental Technology Letters **16** 584-593


Duarte, A. C. and Anderson, G. K. 1982

Inhibition modelling in anaerobic digestion.

Water Science and Technology **14** (6/7) 749-763


Ehlinger, F., Escoffier, Y., Couderc, J. P., Leyris, J. P. and Moletta, R.  1994

Development of an automatic control system for monitoring an anaerobic fluidized-bed.

Water Science and Technology **29** (10-11) 289-295


Emmanouilides, C. and Petrou, L. 1997

Identification and control of anaerobic digesters using adaptive, on-line trained neural networks.

Computers and Chemical Engineering. **21** (1) 113-143


Enbutsu, I., Baba, K. and Hara, N. 1991

Fuzzy rule extraction from a multilayered neural network.

Proceedings of IJCNN '91, Seattle


Enbutsu, I., Baba, K., Hara, N., Waseda, K. and Nogita, S. 1993

Integration of multi AI paradigms for intelligent operation support systems - fuzzy rule extraction from a neural network.

Water Science and Technology **28** (11-12) 333-340


Fenton, B. 1991

Treating low strength high volume effluent by anaerobic digestion.

Water & Waste Treatment **34**, (5) 18


Fernandez, N. and Forster, C. F. 1993

A study of the operation of mesophilic and thermophilic anaerobic filters treating a synthetic coffee waste.

Bioresource Technology **45** 223-227


Fernandez, N. and Forster, C. F. 1994

The anaerobic digestion of a simulated coffee waste using thermophilic and mesophilic upflow filters.

Transactions of the Institute of Chemical Engineering **72 B** 15-20


Field, J. A. and Lettinga, G. 1987

The methanogenic toxicity and anaerobic degradability of a hydrolyzable tannin.

Water Research **21** (3) 367-374


Field, J. A., Kortekaas, S. and Lettinga, G. 1989

The effect of auto-oxidation on the methanogenic toxicity and anaerobic biodegradability of pyrogallol.

Biological Wastes **30** 111-121


Furumai, H. 1997

Modelling of hydrogen behaviour and reduced product formation following perturbation with hydrogenic substrate in a methanogenic reactor.

Water Science and Technology **36** (6-7) 255-262


Graef, S. P. and Andrews, J. F. 1974

Stability and control of anaerobic digestion.

Journal of the Water Pollution Control Federation **46** 666-683


Guwy, A. J., Hawkes, F. R., Hawkes, D. L. and Rozzi, A. G. 1997

Hydrogen production in a high rate fluidised bed anaerobic digester.

Water Research **31** (6) 1291-1298


Hajipakkos, C. 1992

The application of a full scale UASB plant for the treatment of coffee waste.

Water Science and Technology **25** (1) 17-22


Hattingh, W. H. J., Thiel, P. G. and Siebert, M. L. 1967a

Determination of protein content of anaerobic digestion sludge.

Water Research **1** 185-189


Hattingh, W. H. J., Kotze, J. P., Thiel, P. G. and Toerrien, D. F. 1967b

Biological changes during the adaptation of an anaerobic digester to a synthetic substrate.

Water Research **1** 255-277


Hattingh, W. H. J. and Siebert, M. L. 1967

Determination of the deoxyribonucleic acid (DNA) content of anaerobic sludge.

Water Research **1** 197-203


Hawkes, F. R., Rozzi, A., Black, K., Guwy, A. and Hawkes, D. L. 1992

The stability of anaerobic digesters operating on a food-processing wastewater.

Water Science and Technology **25** (7) 73-82


Hawkes, F. R., Donnely, T. and Anderson, G. K. 1995

Comparative performance of anaerobic digesters operating on ice-cream wastewater.

Water Research **29** (2) 525-533


Hawkes, F. R., Guwy, A. J., Hawkes, D. L. and Rozzi, A. G. 1994

On-line monitoring of anaerobic digestion: application of a device for continuous measurement of bicarbonate alkalinity.

Water Science & Technology **30** (12) 1-10


Henson, J.M. Smith, P.H. White, D.C. 1988

Applied Environmental Microbiology **50** 1428-1433


Henze, M. and Harremoes, P. 1983

Review paper : Anaerobic treatment of Wastewater in fixed film reactors.

Water Science and Technology **15** (8/9) 1-101


Henze, M., Grady, C. P. L., Gujer, W., Marais, G. V. R. and Matsuo, T. 1987

A general model for single-sludge wastewater treatment systems.

Water Research **21** (5) 505-515

154

Hickey, R. F. and Switzenbaum, M. S. 1990

Behavior of carbon monoxide as a trace component of anaerobic digester gases and methanogenesis from acetate.

Environmental Science and Technology **24** 1642-1648


Hickey, R. F.and Switzenbaum, M. S. 1991

The Response and utility of hydrogen and carbon monoxide as process indicators of anaerobic digesters subject to organic and hydraulic overloads.

Research Journal of the Water Pollution Control Federation **63** (2) 129-140


Hickey, R. F., Vanderweilen, J. and Switzenbaun, M. S. 1989

The effect of heavy metals on methane production and hydrogen and carbon monoxide levels during batch anaerobic sludge digestion.

Water Research **23** 207-218


Hickey, R. F., Vanderwielen, J. and Switzenbaum, M. S. 1987

The effects of organic toxicants on methane production and hydrogen gas levels during the anaerobic digestion of activated sludge.

Water Research **21** (11) 1417-1427


Hickson, C. 1995

Performance effects of transition metal additions on anaerobic fixed film and fluidised bed reactors.

PhD Thesis Cranfield University


Hill, D. T. and Barth, C. L. 1977

A dynamic model for simulation of animal waste digestion.

Journal of Water Pollution Control Federation **4** (10) 2129-2143


Holland, K. T. Knapp, J. S. and Shoesmith, J. G. 1987

Anaerobic bacteria (tertiary level biology).

Chapman and Hall, New York


Holst, T. C., Ehlinger, F.,Clermont, E. and Pujol, R. 1995

An automatic control system for an anaerobic fluidized bed: Premier industrial application.

Proceedings from the International workshop on monitoring and control of anaerobic digestion processes, December 6th and 7th, 1995, Laboratorie de biotechnologie de L'environment, INRA, Narbonne, France, 36-40


Horowitz, A., Sufita, J. M. and Tiedje, J. M. 1983

Reductive dehalogenations of halobenzoates by anaerobic lake sediment microorganisms.

Applied and Environmental Microbiology **45** (5) 1459-1465


Ince, O. 1998

Performance of a two-phase anaerobic digestion system when treating dairy wastewater.

Water Research **32** (9) 2707-2713


Jenkins, S. R., Morgan, J. M. and Zhang, X. 1991

Measuring the usable carbonate alkalinity of operating anaerobic digesters.

Research Journal of the Water Pollution Control Federation **63** (1) 28-34


Johnson, K. A. 1991

Monitoring and control in anaerobic digestion.

M.Phil Thesis. Cranfield University


Johnson, K. A., Wheatley, A. D. and Fell, C. J. 1995

Control of anaerobic digestion of industrial effluent.

Transactions of the Institute of Chemical Engineering **73** 203-211

Johnson, K. A., Wheatley, A. D. and Monroy, O. 1994

Mixing solids accumulation in anaerobic filters. Two case studies.

Environ. Technol. **15** 263-270


Kaspar, H. F. and Wuhrmann, K. 1978

Product inhibition in sludge digestion.

Microbial Ecology **4** (3) 241-248


Kida, K., Sonoda, I. and Sonoda Y. 1992

Treatment of coffee waste by slurry-state anaerobic digestion.

Journal of Fermentation and Bioengineering **73** (5) 390-395


Kidby, D. W. and Nedwell, D. B. 1991

An investigation into the suitability of biogas hydrogen concentration as a performance monitor for anaerobic sewage sludge digesters.

Water Research **25** (8) 1007-1012


Kiely, G., Tayfur, G., Dolan, C. and Tanji, K. 1997

Physical and mathematical modelling of anaerobic digestion of organic wastes.

Water Research **31** (3) 534-540


Kordes, B. and Bauerle, U. 1986

Aerobic or anaerobic sludge stabilization? energy balance and economics.

Korrespondenz Abwasser 33 (2) 96-100 and 102-103


Kosko, B. and Isaka, S. 1993

Fuzzy logic.

Scientific American July 62-67


Kostenberg, D. and Marchaim, U. 1993a

Solid waste from the instant coffee industry as a substrate for anaerobic thermophilic digestion.

Water Science and Technology 27 (2) 97-107


Kostenberg, D. and Marchaim, U. 1993b

Anaerobic digestion and horticultural value of solid waste from manufacture of instant coffee.

Environmental technology 14 973-980


Labib, F., Ferguson, J. F., Benjamin, M. M., Merigh, M. and Ricker, N. L. 1992

Anaerobic butyrate degradation in a fluidized bed reactor: Effects of increased concentrations of hydrogen and acetate.

Environmental Science and Technology 26 369-376


Lane, A. G. 1983

Anaerobic digestion of spent coffee grounds.

Biomass 3 247-268


Lanting, J., Jordan, J. A., Schone, M. T., Kull, A., Carey, W. W. and Kitney, B. L. 1989

Thermophilic anaerobic digestion of coffee waste water.

43rd Purdue Ind. Waste Conf. Proceedings 513-524


Lapointe, J., Marcos, B., Veillette, M. and Laflamme, G. 1989

BIOEXPERT- An expert system for the wastewater treatment process diagnosis.

Computers and Chemical Engineering 13 619-630


Lenhard, G. 1968

A standardized procedure for the determination of dehydrogenase activity in samples from anaerobic treatment systems.

Water Research 2 161-167

Levenspiel, O. 1972

Chemical reaction engineering.

2$^{nd}$ Edition. John Wiley and Sons


Liwen, L., Rong, Y., Hui, Z., Yuansheng, X., Yibo, Q. and Yizhang, Z. 1988

Studies on (MV) hydrogenase activity of methonbacter.

In Poster Papers, Fifth International Symposium on Anaerobic Digestion 22-26 May 1988 (Tilche, T. and Rozzi, A., editors) Monduzzi Editore, Bologna, Italy, 53-59


Macario, A. J. L., Conway, D.E. and Macario, E. 1988

Quantitative immunologic analysis of the methanogenic flora of digestors reveals a considerable diversity.

New York State Department of Health, Albany

Applied and Environmental Microbiology 54 (1) 79-86


Marsili-Libelli, S. and Lasagni, M. 1985

Self-tuning control of the activated sludge process.

Environmental Technology 6 576-583


Mathieu, J. L. 1989

Applications and limitations of redox electrodes for controlling effluent discharges.

Tribune de l'Eau 42 (537) 21-31


Mathiot, S., Escoffier Y., Ehlinger F., Couderc J. P., Leyris J. P. and Moletta, R 1992

Control parameter variations in an anaerobic fluidized bed reactor subjected to organic shock loads.

Water Science and Technology 25 (7) 93-101


McAvoy, D. C., Eckhoff, W. S. and Rapaport, R. A. 1993

Fate of linear alkylbenzen sulphonate in the environment.

Environmental Toxicology and Chemistry 12 977-987

159

McCarty, P. L. and Mosey, F. E. 1991

Modelling of anaerobic digestion (a discussion of concepts).

Water Science and Technology **24** (8) 17-33


McCarty, P. L. 1964

Anaerobic waste treatment fundamentals. IV. Process design.

Publ. Wks N. Y **95** (12) 95-99


McCarty, P. L. 1982

One hundred years of anaerobic treatment.

Anaerobic Digestion 1981 (edited by D. E. Hughes *et al.*) Elsevier Biomedical Press BV, Amsterdam, 3-22


McCarty, P. L., Jeris, J. S. and Murdoch, W. 1964

The significance of individual volatile acids in anaerobic treatment.

Proc. 17th industr. Waste Conf. Purdue Univ. Engng Extn Ser. No. 112, 421-439


McFarland, M. J. and Jewell, W. J. 1989

In-situ control of sulfide emissions during the thermophilic (55°C) anaerobic digestion process.

Water Research **23** (12) 1571-1577


Moletta, R., Escoffier, Y., Ehlinger, F., Coudert, J. P. and Leyris, J. P. 1994

On-line automatic control system for monitoring an anaerobic fluidized-bed reactor: response to organic overload.

Water Science & Technology **30** (12) 11-20


Monroy, O., Johnson, K. A., Wheatley, A. D., Hawkes, F. and Caine, M. 1994

The anaerobic filtration of dairy waste: results of a pilot trial.

Bioresource Technology **50** (3) 243-251

Morgan, J. W., Goodwin, J. A. S., Wase, D. A. J. and Forster, C. F. 1990

The effects of using various types of carbonaceous substrate on UASB granules and on reactor performance.

Biological Wastes **34** 55-71


Mosey, F. E. 1983

Mathematical modelling of the anaerobic digestion process: regulatory mechanisms for the formation of short chain volatile acids from glucose.

Water Science and Technology **15** 209-232


Mosey, F. E. and Fernandes, X. A. 1984

Mathematical modelling of methanogenesis in sewage sludge digestion.

Soc. Appl. Bacterial. Tech. Ser. 19 MI **19** 159-168


Mosey, F. E. and Fernandes, X. A. 1988

Monitoring hydrogen in biogas during the anaerobic digestion of sugars.

5th Int Symp. on AD Bologna Italy 1988 219-222


Mosey, F. E. and Fernandes, X. A. 1989

Patterns of hydrogen in biogas from the anaerobic digestion of milk sugars.

Water Science and Technology **21** 187-196


Nyns, E-J. 1994

A guide to successful industrial implementation of biomethanisation technologies in the European Union – successes and guidelines.

Published by and to be obtained from DGXVII, European Commission, Brussels, Belgium


Parkin, G. F. and Speece, R. E. 1983

Attached versus suspended growth anaerobic reactors: Response to toxic substances.

Water Science and Technology 15 261-289

Parkin, G. F. and Speece, R. E. 1982

Modelling toxicity in methane fermentation systems.

Journal of the Environmental Engineering Division, Proceedings of the American Society of Civil Engineers 108 (EE3) 515-531

Pauss, A. and Guiot, S. R. 1993

Hydrogen monitoring in anaerobic sludge bed reactors at various hydraulic regimes and loading rates.

Water Environment Research 65 (3) 276-280.

Pauss, A., Guiot, S. and Samson, R. 1988

Sensors for anaerobic digestion management.

In poster papers, Anaerobic Digestion (Tilche, A. and Rozzi, A. eds.) Monduzzi Editore, Bologna, Italy, 231-234

Pauss, A., Samson, R., Guiot, S. and Beauchemin, C. 1990

Continuous measurement of dissolved $H_2$ in an anaerobic reactor using a new hydrogen/air fuel cell detector.

Biotechnology and Bioengineering 35 (5) 492-501

Pohland, F. G. 1994

Anaerobic treatment fundamental concepts, application, and new horizons.

In Water Quality Management Library Volume 7. Design of anaerobic processes for the treatmetn of industrial and municipal wastes (Malina, J. F. and Pohland, F. G. eds) Technomonic Publishing Company Inc. Lancaster, Pennsylvania, USA

Premier, G. C., Dinsdale, R., Guwy, A. J., Hawkes, F. R., Hawkes, D. L. and Wilcox, S. J. 1997

Simple black box models predicting potential control parameters during disturbances to a fluidised bed anaerobic reactor.

Water Science and Technology **36** (6-7) 229-237


Premier, G. C., Dinsdale, R., Guwy, A. J., Hawkes, F. R., Hawkes, D. L. and Wilcox, S. J. 1999

A comparison of the ability of a black box and neural network models of ARX structure to represent a fluidized bed anaerobic digestion process.

Water Research **33** (4) 1027-1037


Prodruzny, M. F. and Van den Berg, L. 1984

Development of a computer control system for anaerobic methane producing reactors.

Biotech. and Bioeng. **XXVI** 392-393


Pullammanappallil, P., Harmon, J., Chynoweth, D. P., Lyberatos, G. and Svoronos, S. A. 1991

Avoiding digester imbalance through real-time expert system control of dilution rate.

Applied Biochemistry and Biotechnology **28/29** 33-42


Quarmby, J. and Forster, C. F. 1995

An examination of the structure of UASB granules.

Water Research **29** (11) 2449-2454


Renard, P., Dochain, D., Bastin, G., Naveau, H. and Nyns, E. -J. 1988

Adaptive control of anaerobic digestion processes - a pilot-scale application.

Biotechnology and Bioengineering **31** 287-294


Ripley, L. E., Boyle, W. C. and Converse, J. C. 1986

Improved alkalimetric monitoring for anaerobic digestion of high strength wastes.

Journal of the Water Pollution Control Federation **58** (5) 406-411

Rittmann, B. E. and McCarty, P. L. 1980

Evaluation of steady-state biofilm kinetics.

Biotechnology and Bioengineering **22** (11) 2359-2373


Robinson, J. A. and Tiedje, J. M. 1982

Kinetics of hydrogen consumption by rumen fluid, anaerobic digester sludge, and sediment.

Applied and Environmental Microbiology **44** (6) 1374-1384


Ross, W. R., Novella, P. H., Pitt, A. J., Lund, P., Thomson, B. A., King, P. B. and Fawcett, K. S. 1992

Anaerobic digestion of wastewater sludge: operating guide.

Report to the Water Research Commission by the Sludge Management Division and Water Care Division of the Water Institute of Southern Africa. ISBN 1 874858 36 5


Rozzi, A., Di Pinto, A. C., Limoni, N. and Tomei, M. C. 1994

Start-up and operation of anaerobic digesters with automatic bicarbonate control.

Bioresource Technology **48** (3) 215-219.


Rozzi, A. Pinto, A. C. and Brunetti, A. 1985

Anaerobic process control by bicarbonate monitoring.

Environmental Technology Letters **6** 594-601


Rozzi, A. and Labellarte, G. 1984

Direct bicarbonate determination in anaerobic digester liquors by measurement of the pressure of carbon dioxide.

Process Biochemistry **19** 201-203


Samson, R., Guiot, S., Beaubiens, A. and Jolicoeur, C. 1988

In poster papers, Anaerobic Digestion (Tilche, A. and Rozzi, A. eds.) Monduzzi Editore, Bologna, Italy, 231-234

164

Sarner, E., Hultman, B. G. and Berglund, A. C. 1988

Anaerobic treatment using new technology for controlling $H_2S$ toxicity.

T.A.P.P.I. Journal **71** 41-45


Schmidt, J. E. and Ahring, B. K. 1993

Effects of hydrogen and formate on the degradation of propionate and butyrate in thermophilic granules from an upflow anaerobic sludge blanket reactor.

Applied and Environmental Microbiology **59** (8) 2546-2551


Slater, W. R., Merigh, M., Ricker, N. L., Labib, F., Ferguson, J. F. and Benjamin, M. M. 1990

A microcomputer based instrumentation system for anaerobic wastewater treatment processes.

Water Research **24** (1) 121-123


Smith, A. J. 1989

Computers and quantity surveyors.

McMillan Education Ltd Basingstoke (Hampshire) and London


Smith, D. P. and McCarty, P. L. 1989a

Energetic and rate effects on methanogenesis of ethanol and propionate in perturbed CSTRs.

Biotechnology and Bioengineering **34** 39-54


Smith, D. P. and McCarty, P. L. 1989b

Reduced products formation following perturbation of ethanol and propionate fed methanogenic CSTRs.

Biotechnology and Bioengineering **34** 855-895


Souza, M. E., Fuzaro, G. and Polegato, A. R. 1992

Thermophilic anaerobic digestion of vinasse in pilot plant UASB reactor.
Water Science and Technology 25 (7) 213-222


Sparling, R. and Gottschalk, G. 1990
Molecular hydrogen and energy conservation in methanogenic and acetogenic bacteria
Microbiology and biochemistry of strict anaerobes involved in interspecies transfer.
Edited by Belaich, J. P. et al. Plenum Press, New York.


Standard Methods for the Examination of Water and Waste water, 17th edition 1989.
ALPHA-AWWA-WPCF, Washington D.C. Edited by Clesceri, L., Greenburd, A.E.,
Trussell, R.R.


Stumm, W. 1967
in Advances in Water Pollution Research, Vol. 1 (Proceedings of the 3rd International
Conference, Munich)
Water Pollution Control Federation, Washington 283-308


Switzenbaum, M. S., Giraldo-Gomez, E. and Hickey, R. F. 1990
Monitoring of the anaerobic methane fermentation process.
Enzyme Microbiology and Technology 12 722-730


Thauer, R. F., Jungermann, K. and Decker, K. 1977
Energy conservation in chemotrophic anaerobic bacteria.
Bacteriological Reviews 41 (1) 100-180


Toerien, D. F., Siebert, M. L. and Hattingh, W. H. J. 1967
The bacterial nature of the acid-forming phase of anaerobic digestion.
Water Research 1 497-507.


Tong, R. M., Beck, M. B. and Latten, A. 1980
Fuzzy control of the activated sludge wastewater treatment process.

Automatica **16** 659-701

Ugurlu, A. and Forster, C. F. 1991

Thermophilic anaerobic treatment of ice cream wastes: a comparison of porous and non-porous support media.

Process Safety and Environmental Protection **69** (B1) 37-42

Ugurlu, A. and Forster, C. F. 1992

The impact of shock loadings on the performance of thermophilic anaerobic filters with porous and non-porous packings.

Bioresource Technology **39** (1) 23-30

Wilcox, S. J., Hawkes, D. L., Hawkes, F. R. and Guwy, A. J. 1995

The use of a neural network to monitor anaerobic digestion with an On-line bicarbonate alkalinity sensor.

Water Research **29** 1465-1470

Williams, C. M. and Shih, J. C. H. 1991

Enumeration of some microbial groups in thermophilic poultry waste digseteres and enrichment of a feather-degrading culture.

Journal of Applied Bacteriology **67** (1) 25-35

Wolin, M. J. 1975

Interactions between $H_2$ producing and methane producing species.

Proceedings of Symposium on microbial production and utilisation of gases, Gottingen 1-5 September 141-150

Wolin, M. J. and Miller, T. L. 1982

Interspecies hydrogen transfer: 15 years later.

ASM News **48** 561-565

Young, J. C. and McCarty, P. L. 1968

The anaerobic filter for waste treatment.

Dept civ. Engng Stanford Univ.Calif., Tech. Rep. No. 87, 252pp


Young, J. C. and Yang, B. S. 1990

Design considerations for full scale anaerobic filters.

Research Journal of the Water Pollution Control Federation **62** 296-299


Zeikus, J. G. 1977

The biology of methanogenic bacteria.

Bacterialogical Reviews **41** (2) 514-541


Zeikus, J. G. 1980

Microbial populations in digesters.

Anaerobic Digestion (edited by Stafford Wheatley and Hughes), Applied Science Publishers Ltd, London 1980 61-89


Zender, A. and Stumm, W. 1988

Geochemistry and biogeochemistry of anaerobic habits.

Biochemistry of Anaerobic Microorganisms, Edited by Zehnder, A. J. B. Wiley series in ecological and applied microbiology, Series editor Mitchell, R., John Wiley & Sons, New York.

**Control Program**

REM h2 control based on init h2 and ss based on large mid range probe 15 aug 95

REM program name = chnew22.bas

CLEAR

INPUT "enter time between samples in minutes"; min!

INPUT "enter name for file (e.g. data1.dat)"; filename$

INPUT "enter influent COD (g/l)"; influent!

INPUT " enter desired COD (g/l)"; target!

INPUT "enter initial value for gfm clicks "; flow!

INPUT "enter initial value for ch4% "; ch4%

INPUT "enter initial value for COD of effluent (g/l) "; cod!

INPUT "enter initial pump speed (l/d) "; speed!

INPUT "enter initial hydrogen (ppm)"; h2init%

INPUT "comments on run"; comment$


LET min! = min! * 60

ON TIMER(min!) GOSUB savedata


pm = (min / 60 / 60) / 24

flow! = flow! / 40: flow! = flow! / (min! / 60 / 60): flow2! = flow!: REM flow rate in litres per hour

flow2! = flow!

REM flow!(3) = flow!: flow!(2) = flow!: flow!(1) = flow!

Q! = (flow! / 100) * ch4%

OLR! = (influent! * speed!) / 10

dilrate! = OLR! / influent!: IF dilrate! < .4 THEN dilrate! = .4: IF dilrate! > 2 THEN dilrate! = 2

k! = dilrate! * (influent! - cod!) / Q!: kb4! = k!

OPEN filename$ FOR OUTPUT AS #1

PRINT #1, " time between samples = "; min; "   OLR = "; OLR!; "   Q = "; Q!; " influent cod = "; influent!; "   target cod = "; target!; "   initial cod = "; cod!; "   k estimate = "; k!; "   dilrate init = "; dilrate!; "   comments on run :"; comment$; "   "; DATE$; " "; TIME$

PRINT   #1,   "h2,ss,tds,gas,ph,ch4,gas,empty,litres,litres2,ph,flow2,q,cod,k,dil,date time,(5*(2900-N3)+O3*M3)/(7000-N3)"

CLOSE #1


GOSUB controlpump


c1 = 21: c2 = .1: REM ********** design parameters ***********

REM  kb4! = k: GFM% = 0: gfm2% = 0: litres2! = 0: LITRES! = 0: cdelay& = 0: CHECK% = 0: peat2% = 0: peat% = 0: SS% = 0: TDS% = 0: ph! = 0: pump& = 0: chris! = 0: flow! = 0: flow2! = 0

40 PRINT : PRINT :

70 GOSUB adinit: REM ********* initialise a-d board **********


GOSUB NSCREEN

290 C% = 0: GAIN% = 0:

321 LOCATE CURLIN%, 1: REM GOSUB setgain

330 TIMER ON

331 FOR I = 0 TO 7

340    REG% = MPX%: BYTE% = I: GOSUB 530' Set mpx channel

350    REG% = ADTRIG%: GOSUB 490       ' Dummy read to init. conv.

360    GOSUB WAITE                 ' wait for status

370    LONIBL% = INP(LBYTE&) \ 16: HINIBL% = INP(HBYTE&)

380    valu% = HINIBL% * 16 + LONIBL%

381 IF I = 0 THEN valu% = (valu% * .6) * 2: H2% = valu%: IF H2% > 1500 THEN H2% = 1500

382 IF I = 1 THEN valu% = ((valu% / 81.5) * (valu% / 81.5) * 2.2)-47

383 IF I = 1 THEN SS% = valu%

1-2

384 IF I = 2 THEN valu% = ((valu% * (valu% / 150)) + (valu% / .25)) / 2

385 IF I = 2 THEN TDS% = valu%: TDS% = (TDS% + TDS2% + TDS3% + TDS4%

+ TDS5% + TDS6% + TDS7% + TDS8% + TDS9%) / 9: TDS9% = TDS8%: TDS8%

= TDS7%: TDS7% = TDS6%: TDS6% = TDS5%: TDS5% = TDS4%: TDS4% =

TDS3%: TDS3% = TDS2%: TDS2% = TDS%

386 IF I = 4 THEN ph! = ((valu% * (valu% / 142500)) + (valu% / 139)) / 2

387 IF I = 5 THEN valu% = (valu% / 14) + 3: REM for ch4%

388 IF I = 5 THEN ch4% = valu%

390    PRINT valu%;

391    IF I = 3 AND valu% > 3 THEN peat% = 1

393    IF I = 3 AND valu% < 3 AND peat% = 1 THEN GOSUB GFM

400 NEXT I:

LITRES! = GFM% / 40: litres2! = gfm2% / 18.18

402 cod! = ((((SS% * 9.4) * .2) + ((TDS% * 1.11) * 1.8)) / 2) / 1000

406 PRINT : PRINT " GFM COUNT "; GFM%; "   LITRES "; LITRES!; "      gfm2

"; gfm2%; "   litres "; litres2!

407 PRINT : PRINT "  COD "; cod!; "    methane prodn rate l/h "; Q!; "    gas flow

rate l/h "; flow2!

408 PRINT : PRINT " pH "; ph!; " k "; k!; " dilrate "; dilrate!

409 PRINT : PRINT DATE$; " "; TIME$

410 CHAR$ = INKEY$: IF (LEN(CHAR$) = 0) GOTO 290

420 IF (ASC(CHAR$) = &H1B) THEN INPUT "enter influent COD (g/l)"; influent!

421 IF influent! = 0 THEN GOTO 460

430 C% = ASC(CHAR$)

440 IF ((C% > &H2F) AND (C% < &H34)) THEN GAIN% = C%

450 GOTO 290

460 CLOSE #1: STOP

470 REM ************** END OF PROGRAM **************


480 REM drd(reg%)

490    OUT ZBASE%, REG%

1-3

```
500    X% = INP(SFUNCT%)
510 RETURN

520 REM dwr(reg%,byte%)
530    OUT ZBASE%, REG%
540    OUT SFUNCT%, BYTE%
550 RETURN

560 REM delay(timedelay%)
570    FOR T% = 1 TO TIMEDELAY%
580       FOR J% = 1 TO 5
590       NEXT J%
600    NEXT T%
610 RETURN

620 setgain:      REM setgain(gain%)
630    BYTE% = GAIN% AND &H3
640    REG% = GAINLAT%: GOSUB 530'dwr(gainlat%,gain%)
650 RETURN

660 WAITE:         REM wait,stat
670    REG% = STATUS%
680    GOSUB 490
690    IF (X% AND &H1) GOTO 680 ' Loop while busy
700 RETURN

2070
2100 RETURN

GFM:
REM ********** gosub GFM **********
```

```
2500 GFM% = GFM% + 1: flow! = flow! + 1
2501 peat% = 0
2605 FOR cdelay& = 1 TO 50000: NEXT
2610 RETURN


2700 REM gfm2% = gfm2% + 1
2702 REM peat2% = 0
2705 REM FOR cdelay& = 1 TO 50000: NEXT
2710 RETURN


savedata:
REM ********** gosub SAVEDATA ***********
flow! = flow! / 40: flow! = flow! / (min! / 60 / 60): REM flow rate in litres per hour
flow! = (flow! + flow2!) / 2
REM flow!(3) = flow!(2): flow!(2) = flow!(1): flow!(1) = flow!
REM flow! = (flow!(1) + flow!(2) + flow!(3)) / 3
Q! = (flow! / 100) * ch4%
flow2! = flow!
k! = kb4! + pm * c2 * Q * (target! - cod!)
dilrate! = (c1 * (target! - cod!) + k! * Q) / (influent! - cod!)
Hfact! = (h2% - H2init% )/100: if hfact! > 0.5 then hfact! = .5: if hfact! < 0 then hfact!
= 0
dilrate! =dilrate!-(dilrate! * hfact!)
IF dilrate! < .4 THEN dilrate! = .4
IF dilrate! > 2 THEN dilrate! = 2
OPEN filename$ FOR APPEND AS #1:
        PRINT #1, H2%; ","; SS%; ","; TDS%; ","; ","; ph%; ","; ch4%; ",";
","; ","; LITRES!; ","; litres2!; ","; ph!; ","; flow2!; ","; Q!; ","; cod!; ","; k!; ",";
dilrate!; ","; DATE$; " "; TIME$
CLOSE #1
```

LET flow! = 0: REM *** resetting flow to zero for determination of flow rate ***

GOSUB controlpump

GOSUB NSCREEN

RETURN


NSCREEN:

REM ********** gosub NEWSCREEN ***********

CLS

PRINT "Control program for anaerobic reactors   CJF 95 ":

PRINT "Adjust gain with keys (0 - 3) : (0 = 10v) etc."

PRINT "Hit Esc to exit ": PRINT

PRINT "influent COD = "; influent!

PRINT "target COD = "; target!

PRINT "initial COD = "; cod!

PRINT "initial Q (methane production rate) = "; Q!: PRINT

PRINT "Filename = "; filename$

PRINT "comments = "; comment$


FOR I = 0 TO 7: PRINT USING "  #  "; I; : NEXT I: PRINT

CURLIN% = CSRLIN

RETURN


adinit:

4700 REM ********** gosub initialise a-d board ***********

 ZBASE% = &H180: REM base address

 SFUNCT% = ZBASE% + 1: REM special functions address

 LBYTE& = ZBASE% + 2: REM LS data address

 HBYTE& = ZBASE% + 3: REM MS data address

 ID% = &H81: REM offset value of board id register

 GRLED% = &H80: REM offset value of green user led register

 MPX% = &H0: REM channel mpx addr.

1-6

```
GAINLAT% = &H1: REM gain latch addr.

ADTRIG% = &H2: REM software A/D trigger addr.

STATUS% = &H3: REM read status addr.

REG% = ID%: GOSUB 490' x%=drd%(id%)

REG% = GRLED%: TIMEDELAY% = 50

FOR I% = 1 TO 5

    BYTE% = 0: GOSUB 530

    GOSUB 570   ' delay(timedelay%)

    BYTE% = 1: GOSUB 530

    GOSUB 570   ' delay(timedelay%)

NEXT I%

RETURN


controlpump:

5000 REM *********** gosub control pump speed sub routine... *********

7000 ZBASE2% = &H184: REM base address

8000 SFUNCT2% = ZBASE2% + 1: REM special functions address

9000 LBYTE2% = ZBASE2% + 2: REM LS data address

10000 HBYTE2% = ZBASE2% + 3: REM MS data address

11000 ID2% = &H81: REM offset value of board id register

12000 GRLED2% = &H80: REM offset value of green user led register

13000 DAC0% = 0: REM offset value for dac0


19000 REG2% = ID2%: GOSUB 58000

22000 REG2% = GRLED2%: TIMEDELAY2% = 50

23000 FOR I2% = 1 TO 5

24000    BYTE2% = 0: GOSUB 62000

25000    GOSUB 66000   ' delay(timedelay2%)

26000    BYTE2% = 1: GOSUB 62000

27000    GOSUB 66000   ' delay(timedelay2%)

28000 NEXT I2%
```

1-7

```
29010 volts! = dilrate! / .3456
32000 FOR CHAN% = 0 TO 3
33000 valu2% = (-4080 + (volts! * 406.4)): GOSUB poutput
34000 NEXT CHAN%
49000 REM at this point we should return to the main program...
49500 REM GOSUB adinit
50000 RETURN
55500 STOP


57000 REM drd(reg2%)
58000    OUT ZBASE2%, REG2%
59000    X2% = INP(SFUNCT2%)
60000 RETURN
61000 REM dwr(reg2%,byte2%)
62000    OUT ZBASE2%, REG2%
63000    OUT SFUNCT2%, BYTE2%
64000 RETURN
65000 REM delay(timedelay2%)
66000    FOR T2% = 1 TO TIMEDELAY2%
67000     FOR J2% = 1 TO 5
68000      NEXT J2%
69000    NEXT T2%
70000 RETURN
poutput:
71000 REM dacwr(chan%,data%)
72000    OUT ZBASE2%, CHAN%
73000    OUT LBYTE2%, (valu2% AND &HF0)' two byte data transfer
74000    OUT HBYTE2%, (valu2% \ 16) AND &HFF
74500 RETURN
```

1-8

**Papers (Published, posters and presented)**

Johnson, K. A., Wheatley, A. D. and Fell, C. J. 1995

An application of an adaptive control algorithm for the anaerobic treatment of industrial effluent.

Trans IChemE **73** (B) 203-211

Fell, C. J. and Wheatley, A. D. 1995

A comparison of adaptive and neural network control models for the anaerobic digestion of industrial effluents.

Paper presented to the International Workshop on Monitoring and Control of Anaerobic Digestion Processes, INRA, Narbonne, France, 6th and 7th December 1995

Sofikitis, E., Fell, C. J. and Wheatley, A. D. 1996

The use of powdered activated carbon to reduce inhibition in anaerobic digestion.

Poster paper presented at the 2nd Specialised Conference on the Pre-treatment of Industrial Wastewater, Athens, Greece

# AN APPLICATION OF AN ADAPTIVE CONTROL ALGORITHM FOR THE ANAEROBIC TREATMENT OF INDUSTRIAL EFFLUENT

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The paper describes the application of an adaptive algorithm for the monitoring and control of anaerobic digestion. Results are presented on the performance of the model for controlling shock loads applied to laboratory-scale anaerobic filters. Instrumentation and sensors used were on-line conductivity, suspended solids, gas flow and quality. Data are also presented on the steady-state performance of the upflow anaerobic filter for the treatment of dairy and coffee effluent.

*Keywords: Adaptive process control; anaerobic filter; on-line instrumentation; COD measurements; turbidity; conductivity; shock loads; dairy and coffee effluent.*

## INTRODUCTION

Anaerobic digestion is a widely used waste treatment process[1]. A common problem with the treatment of industrial effluents is instability caused by the generation of volatile carboxylic acids. These acids are important intermediates in the sequential breakdown of organic matter to methane but an imbalance between the stages leads to excessive acidity and inhibition of the process[2]. Two potential strategies for monitoring acidity have been described. One technique uses pH probes; for example, Colin[3] described the use of auto-titration for the on-line determination of alkalinity within anaerobic digestion. Powell and Archer[4] have also tried this system to control feed and alkali dosing pumps to a laboratory-scale anaerobic digester.

Difficulties arise however because of the contamination of pH probes by sulphides and other reduced compounds generated during the anaerobic process. The alternative approach is analysis of the gas phase carbon dioxide, which is in equilibrium with dissolved bicarbonate. Rozzi, et al.[5] described several possibilities for gas phase analysis of alkalinity including gas volume, gas pressure and infrared measurements of carbon dioxide.

The advantages of non-invasive gas analysis have also led to research on trace gas indicators of instability. Whitmore et al.[6] described the use of a small mass spectrometer for the on-line analysis of hydrogen in the biogas and Mosey and Fernandes[7] used a hydrogen analyser based on a fuel cell for monitoring the effects of shock loads on a laboratory digester.

A different approach, used in the research described in this paper, is to avoid excessive acidity by maintaining a constant organic loading rate. Direct and continuous measurement of organic carbon is difficult but indirect parameters such as turbidity and conductivity are shown in this work as able to represent dissolved and suspended organic load. The precision of this indirect approach was improved by combining these sensors with a self-tuning control model. Dochain and Bastin[8] have described the application of an adaptive control algorithm to anaerobic digestion, using off-line COD analysis as the input. Jones et al.[9] also reported on the success of the similar Kalman filter algorithms for controlling anaerobic digesters using gas chromatographic gas analysis. This paper describes the control of laboratory-scale (10 litre) upflow anaerobic filters to achieve a steady effluent quality when subjected to a series of shock loads. A feedback adaptive control model, based on the on-line determination of COD and gas production, was used to automatically vary the influent pumping rate and so avoid any imbalances and instability.

## MATERIALS AND METHODS

### Anaerobic Reactors and Waste

The digesters were of a standard design usually used by this laboratory (Figure 1(a)). The ten litre vessels contained two sizes of PVC support rings. A lower 150 mm layer of a larger 50 mm ring (Flocor R2 specific surface 150 m$^2$ m$^{-3}$) was included to aid distribution and provide for sludge accumulation. The remainder of the vessels were packed with a 25mm ring (Flocor R specific surface 200 m$^2$m$^{-3}$). The reactors were maintained at mesophilic temperatures 35–37°C. These type of units have been previously described in dimensional detail[10].

The reactors were inoculated with 1 litre of digesting municipal sludge from the local sewage works and made up to 10 litres with deaerated tap water. The reactors were fed with either a laboratory prepared diluted suspension of ice cream or real coffee processing wastewater. The research described here was part of a UK coordinated programme and the characteristics of these feeds have previously been described in detail[11]. The general features are shown in Tables 1(a) and 1(b). A
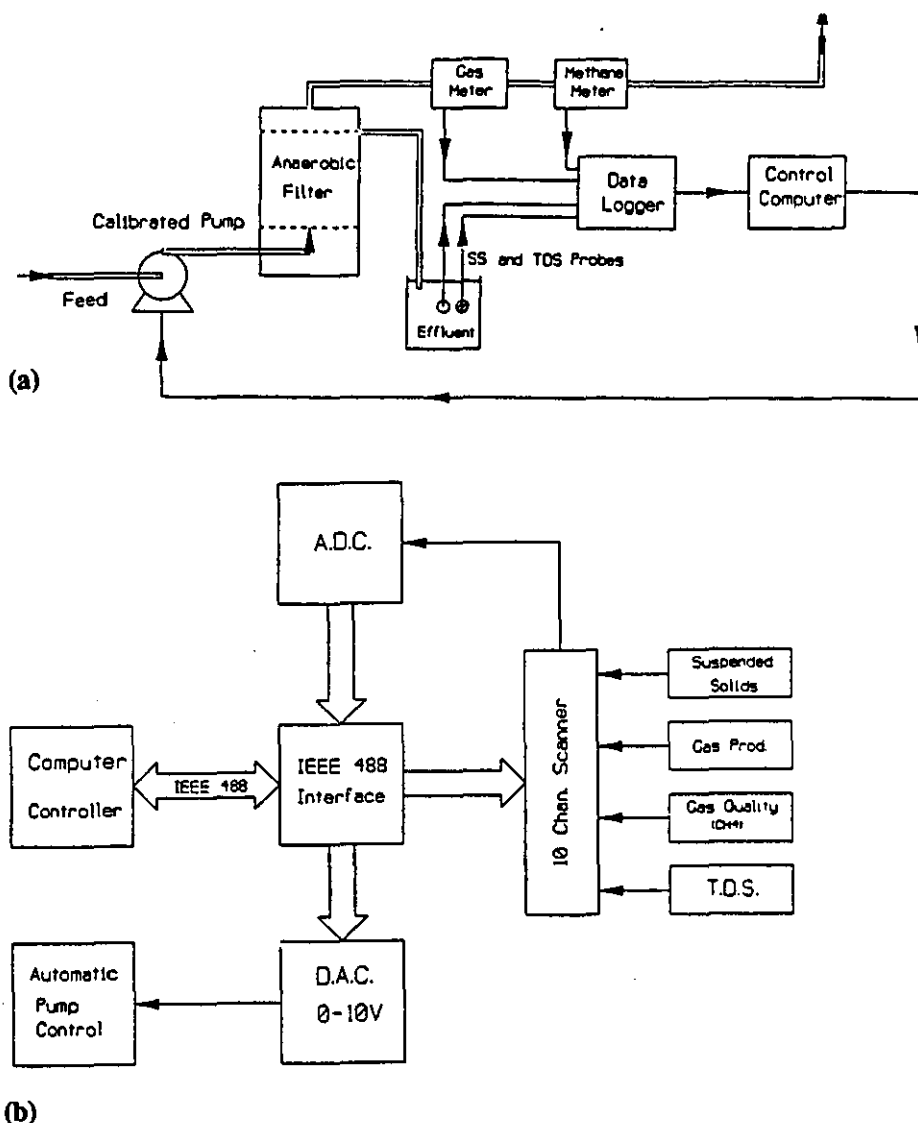
*Figure 1.* (a) Schematic flow diagram of the laboratory anaerobic digester system. (b) Schematic of data-logging and control equipment.

period of 20 weeks is usually allowed for these reactors to achieve steady-state performance measured as COD removal efficiency at a fixed organic load.

### Instrumentation

The data logging and control equipment were set up as shown in Figure 1(b). Commercially available probes were used to monitor suspended solids, dissolved solids and gas quality. Gas volume was measured by a workshop-built meter. A correlation between dissolved and suspended solids and COD was established by wet analysis.

### Suspended Solids

Suspended solids were measured with the MEX-3 meter and low solids concentration probe RD-120/25 (BTG United Kingdom Ltd, Surrey). The system operated on a four-beam infrared transmission principle, measuring changes in solids concentration while at the same time automatically compensating for probe foul-

ing. Calibration was carried out using solutions of known suspended solids concentrations for 100% and 50% of a full-scale deflection on the data-logging and control system.

### Total Dissolved Solids (TDS)

Total dissolved solids were monitored with a Series 55 conductivity meter and type D1 measuring cell (pHOX Systems, Shefford). Meter readout was dissolved solids in $mg\,l^{-1}$.

### Biogas Measurement

A special low flow gas meter was workshop-built using a conductivity type level controller (IMO Omron, London 61FGPY). A calibrated gas collection chamber (150 ml) was allowed to fill and empty by two three-way miniature solenoid valves controlled by stainless steel conductivity electrodes. The number of gas chamber 'fills' was recorded electronically.

Table 1(a). Analysis of the synthetic wastewater in $mg\,l^{-1}$

| Ice cream wastewater (2.5 year average) | |
| --- | --- |
| $COD_{total}$ | 4,934 |
| Number of values | 553 |
| $COD_{filtered}$ | 2,220 |
| Suspended solids | 1,120 |
| Oil and grease | 610 |
| Volatile acids | 630 |
| Organic nitrogen | 350 |

Table 1(b). Average analysis of coffee wastewater in $mg\,l^{-1}$.

| Coffee wastewater (6 month average) | |
| --- | --- |
| $COD_{total}$ | 10,380 |
| $COD_{filtered}$ | 9,055 |
| Suspended solids | 833 |
| Number of values | 175 |
| Volatile acids | 2,200 |

This coffee waste was taken from the first stage of a two-stage pilot plant after preacidification and settlement. The effluent was added to the reactor at a 50% dilution to allow organic shock loading tests to be performed.

Table 2. Components of the data-logging system.

IEEE 488 interface module (3700-02).
10 channel, 2 pole precision scanner module (3700-03B).
12 bit bipolar 4 range programmable Analogue to Digital Converter (ADC) with built in instrument amplifier (3700-11).
Single channel programmable Digital to Analogue Converter (DAC) with a 0-10V output and 12 bit precision (3700-09).

## Gas Quality (CH₄) Measurement

On-line methane measurements were made by a Crowcon 76TC gas tester which uses a thermal conductivity sensor (Crowcon Instruments Ltd, Abingdon, Oxfordshire).

## Data-Logging and Control Systems

The data-logging and control equipment was a 3700 series MAPS System (Harlyn Automation, Congleton, Cheshire). Four modules were used for the data-logging; these are shown in Table 2. The general system arrangement is shown in Figure 1(b).

## Wet Analysis

The wet chemical analysis was carried out according to UK standard methods[12].
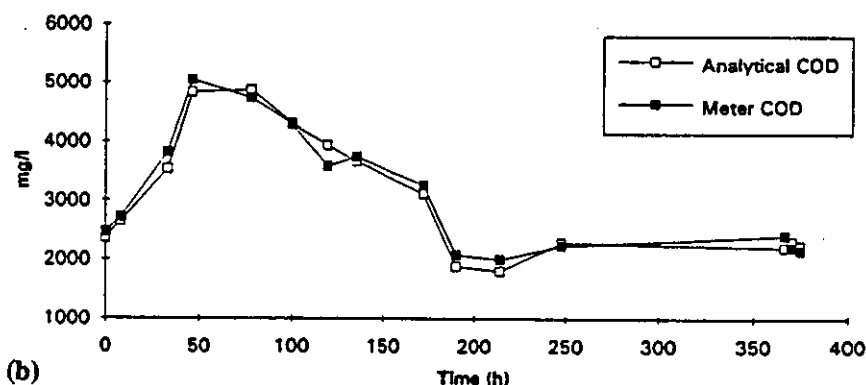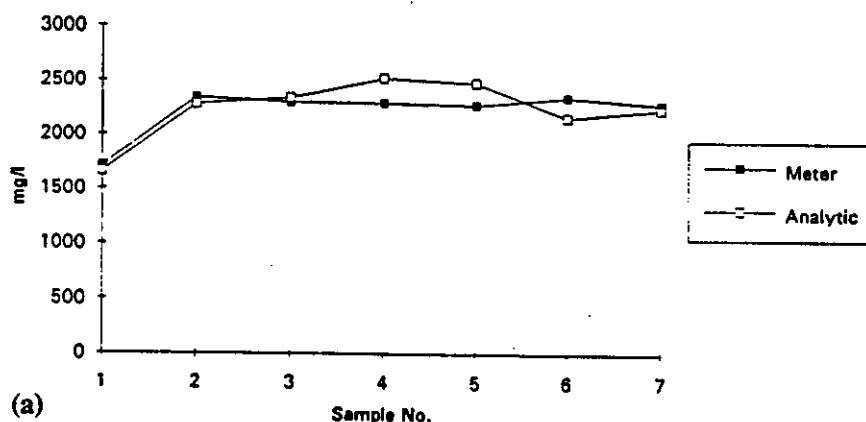


Figure 2. A comparison of the on-line derived COD with conventional wet analysis. (a) Analysis of ice cream wastewater. (b) Analysis of coffee wastewater.
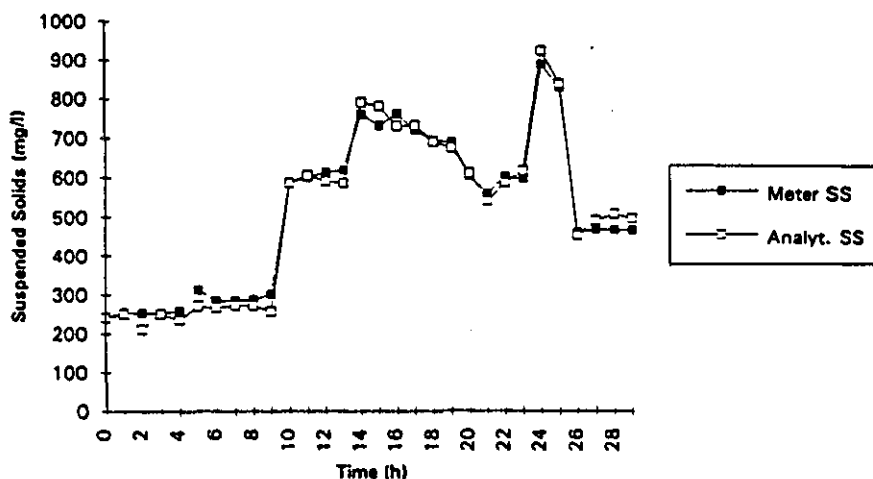
*Figure 3.* A comparison between the meter derived suspended solids and standard gravimetric analysis results.

## RESULTS AND DISCUSSION
### Estimation of On-line COD

Automatic determination of TOC is available but the equipment requires the continual preparation of reagents and is expensive. The strength of a waste as measured by COD is proportional to the dissolved and suspended solids, i.e.:
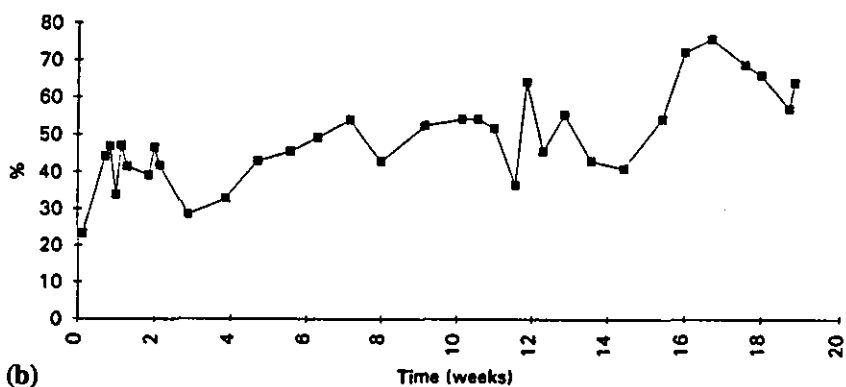
$$COD \; \alpha \; (SS + TDS)$$

where SS   = suspended solids
TDS = total dissolved solids
$\therefore$   COD  = $K_c$ (SS + TDS) where $K_c$ = constant
for a particular type of waste.

The value of $K_c$ was obtained by comparing the on-line values of SS + TDS with COD obtained conventionally
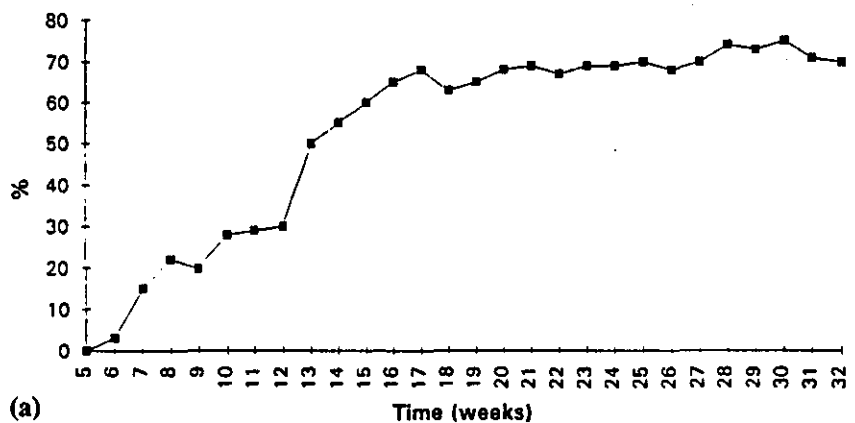


(a)



(b)

*Figure 4.* Start-up and steady-state performance of the anaerobic digesters. (a) Anaerobic filter treating ice cream wastewater. (b) anaerobic filter testing coffee wastewater.
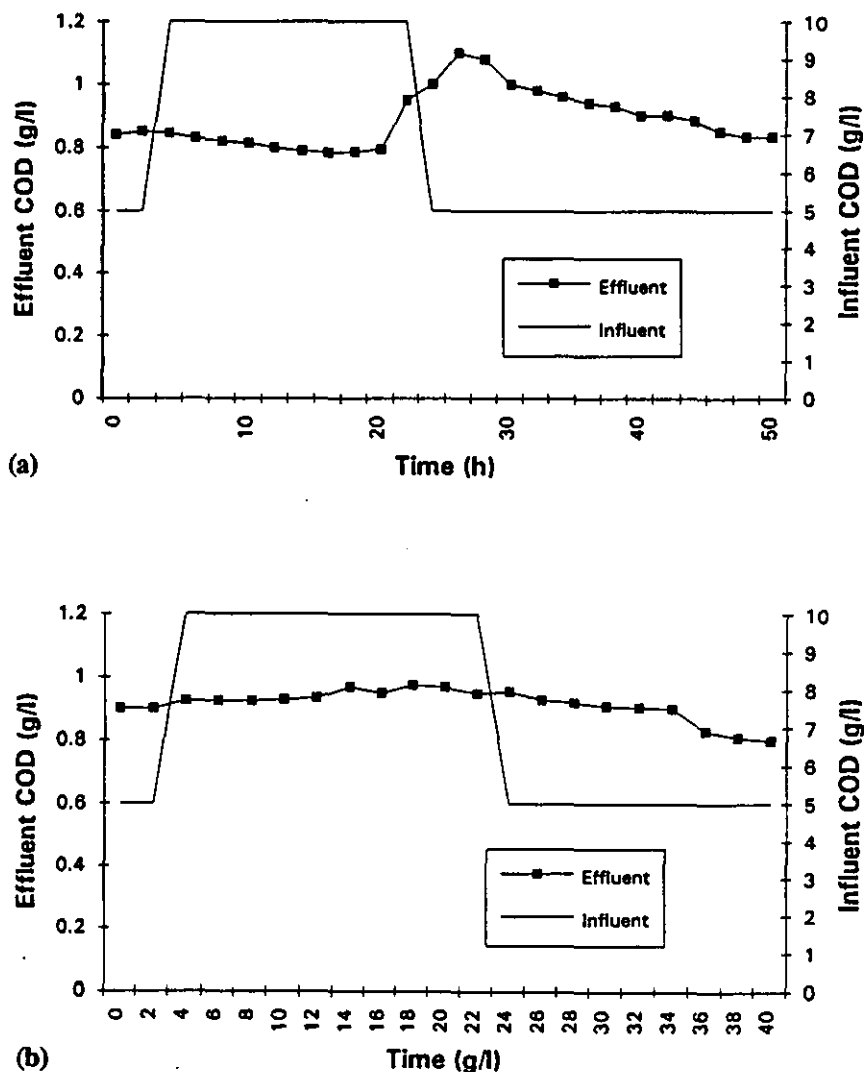
*Figure 5.* Examples of shock load experiments with ice cream wastewater. (a) Typical results showing influent concentration and controlled effluent COD. (b) a second similar experiment.

by wet analysis. Some representative results are shown in Figure 2(a) for the ice cream wastewater and 2(b) for the coffee waste. Figure 3 compares the suspended solids measured by meter and probe with the standard gravimetric method[12]. Using the combination of these two probes and regular cleaning (every 2 or 3 days) the COD could be obtained to within 5% of the wet analysis result. Problems with this approach would occur if there were changes in the inorganic content of the waste. The ratio between the TDS and SS would have to be continually checked by the model to identify, for example, caustic clean-downs.

The original intention was to use the on-line estimation of COD for feed-forward control but problems were encountered with probe fouling. It was found necessary to clean the probes every few hours with a damp cloth when using them in the feed. The main problem was the accumulation of fat; the automatic compressed air cleaning supplied with the probes was ineffective with this type of waste. The difficulty was overcome by using the probes in the treated effluent as part of a feed-back

control loop. Previous research[11] has established that reactors of this design are well mixed when gas production exceeds 1 volume of gas per volume of reactor.

### Feed-back Control Algorithm

The control model used in these experiments was based on that reported by Renard et al.[13] who used an adaptive algorithm to control a pilot anaerobic filter.

The objective of the control algorithm was to regulate the treated effluent COD concentration $(S)$ to a fixed predetermined level $(S^*)$. This was to be achieved regardless of fluctuations in the influent COD concentration $(S_{in})$ by control of the hydraulic and organic loading rate (dilution rate $D$).

The algorithm assumed that the reactor was well mixed and that ultimately the methanogenic step controls the removal of COD from the liquid phase. A mass balance of the reactor according to the well-known microbial growth equations was used (see Renard et al.[13] for details) to produce the dynamic control equation (1).

$$\frac{dS(t)}{dt} = -KQ(t) + D(t)S_{in}(t) - D(t)S(t) \qquad (1)$$

where:

$K$ $\quad = k_1/k_2$;

$X(t)$ $\quad$ = methanogenic bacterial (active biomass) concentration

$S(t)$ $\quad$ = substrate concentration in the effluent $(g\,COD\,l^{-1})$

$S_{in}(t)$ $\quad$ = substrate concentration in the influent $(g\,COD\,l^{-1})$

$Q(t)$ $\quad$ = methane gas production rate $(l\,h^{-1})$

$D(t)$ $\quad$ = dilution rate $(day^{-1})$

$\mu(t)$ $\quad$ = specific growth rate $(day^{-1})$

$k_1$ and $k_2$ = yield coefficients

This equation assumes that the growth rate is positive between 0 and $\mu_{max}$, the maximum specific growth rate, and also that there is no growth without substrate, i.e. $\mu(t) = 0$ when $S(t) = 0$.

Equation (1) is a dynamic equation for the substrate concentration $S(t)$, in which the measurable on-line variable $Q(t)$ has replaced the difficult to measure concentration $X(t)$ and specific growth rate $\mu(t)$ of the

methanogenic biomass. $K$ is then the yield coefficient for converting substrate, $S_{in}(t)$, into methane. Equation (1) was used as the basis for control. The yield coefficient $K$, was unknown and was replaced by an on-line estimate of $K$, i.e., $K(t)$ which was a function of time and continually updated and re-used for automatic control. Based on the adaptive theory of Dochain and Bastin[8] two discretized control equations could then be established:

$$\hat{K}_{t+1} = \hat{K}_t + TC_2Q_{t+1}[S^* - S_t] \qquad (2)$$

$$D_{t+1} = \frac{C_{1t+1}[S^* - S_t] + \hat{K}_{t+1}\hat{Q}_{t+1}}{S_{int} - S_t} \qquad (3)$$

where $\hat{K}_{t+1}$ was the present value of $\hat{K}$ which had been estimated from $\hat{K}_t$ the value of $\hat{K}$, $t$ hours earlier ($K_t$ at $t = 0$, the first value was arbitrarily chosen). The value $S_t$ was the on-line estimate of the effluent COD measured every $t$ hour period, $Q_{t+1}$ was the on-line measured methane production rate over this period. $C_1$ and $C_2$ are control or design constants adopted from Renard *et al.*[13]. These constants were tested empirically in the present experiments and also found to produce realistic results.

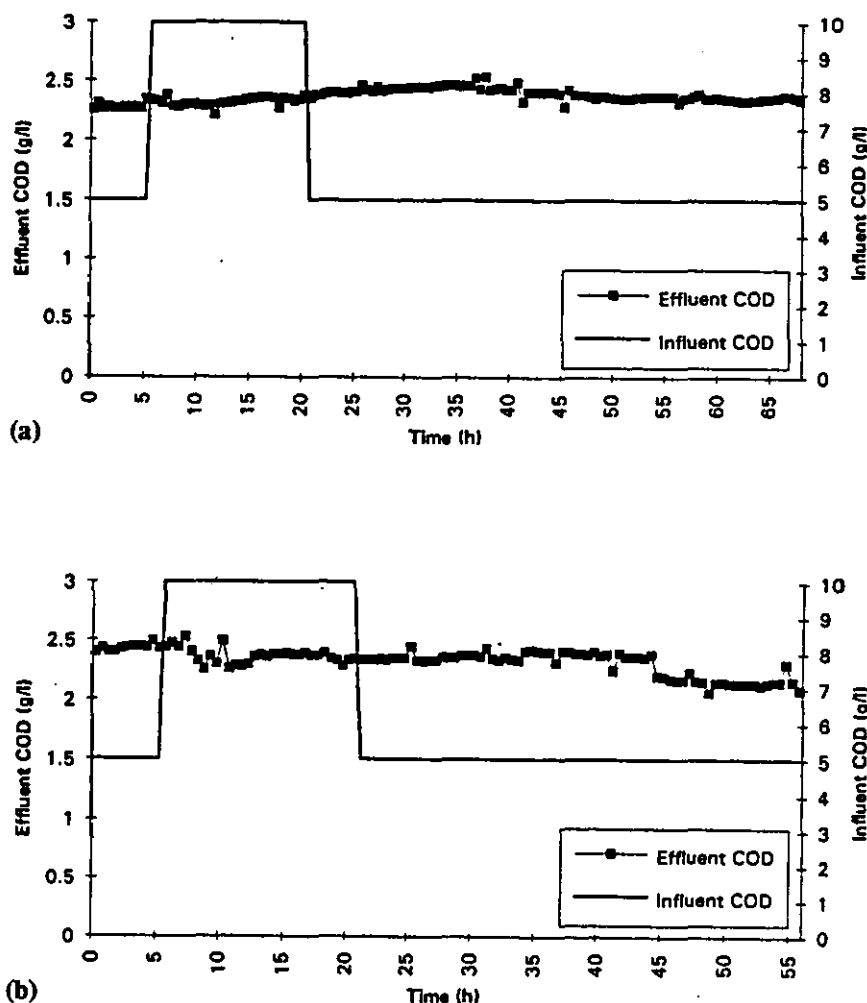The program runs by first calculating a value for



(a)



(b)

*Figure 6.* Examples of shock load experiments using coffee wastewater. (a) Typical results showing influent concentration and controlled effluent COD. (b) A repeat experiment over a shorter period.
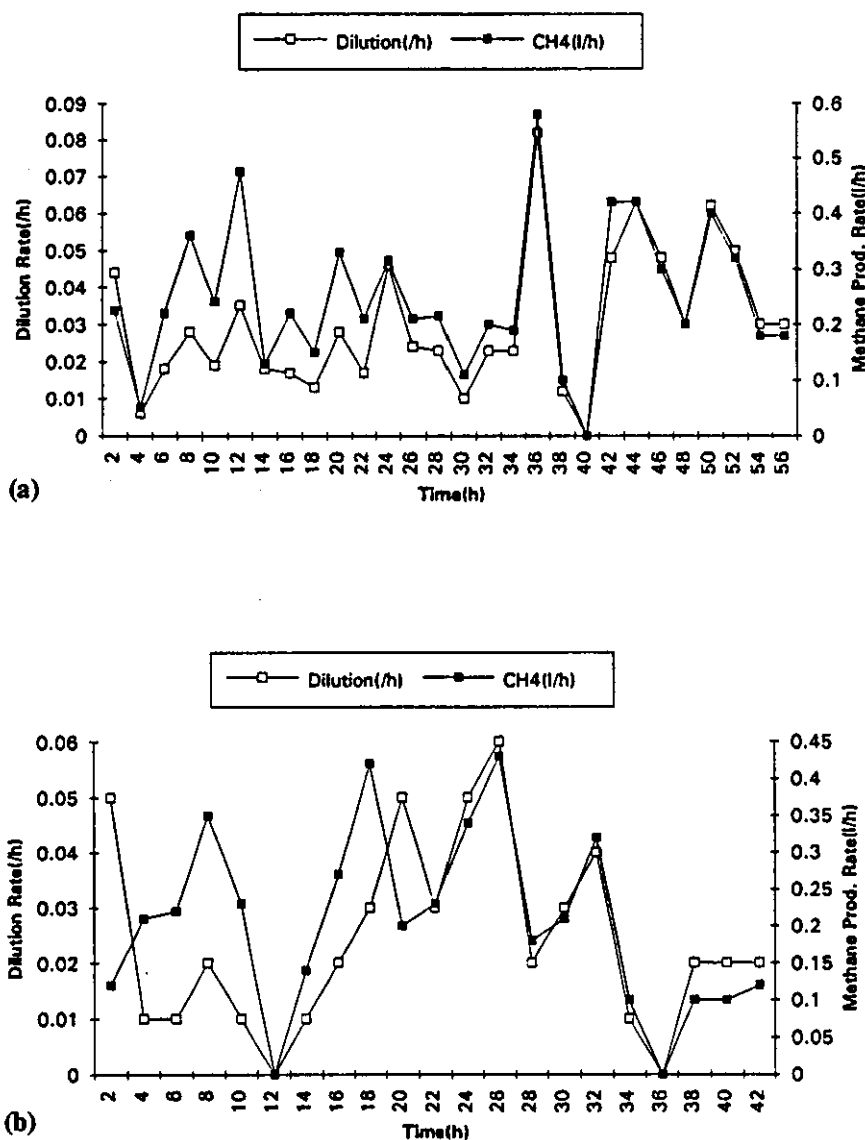
*Figure 7*. Methane production rate during shock loading. (a) Influence of methane production rate on dilution rate. (b) A second similar experiment.

effluent COD ($S_t$) from measurements of SS and TDS. The biogas production rate and % methane were derived directly from sensors. From these figures $\hat{K}_{t+1}$ was estimated by the application of equation (2). The dilution rate $D$ was then calculated by substituting the $\hat{K}_{t+1}$ value in equation (3) and used to control the pump speed (and hence dilution rate) via the DAC. The calculations were then continuously repeated to keep updating $\hat{K}_{(t)}$ to give an adaptive control.

### Shock-load Experiments

The reactor treating the ice cream wastewater attained steady state (Figure 4(a)) after about 20 weeks at an organic loading rate of 5 kg COD m$^{-1}$ day $^{-1}$ equivalent to a feed concentration of 4.6 g l$^{-1}$ COD. Performance after this period improved more slowly reaching a maximum at week 28. The average COD removal was 70–80% at this loading over the 2.5 years of the experiments. This performance is typical of anaerobic processes treating food industry wastes with hydraulic retention times of between 20–40 hours[11]. The performance of the anerobic filter treating the real coffee wastewater, at a similar loading rate (5 kg COD m$^{-1}$ day$^{-1}$), was not as good as would be expected from most food wastes (Figure 4(b)), and this has been commented on previously[14–16]. This earlier work on coffee effluents also noted that real coffee wastewaters are less treatable than those prepared from instant coffee. The reduced performance has been attributed to the presence of toxic ions and organics[14] or recalcitrant solids, particularly oils and greases[15].

The experimental objective was to use the adaptive control model to improve the consistency of the treated effluent quality compared to what might be expected from a variable industrial wastewater. Greater consistency from biological treatment plants will be necessary in the future to meet legally binding statistically based consents. The steady-state effluent qualities were selected as the control or desired performance against which the experimentally induced shocks could be evaluated ($\sim$900 mgl for the ice cream waste and $\sim$2400 mgl for

the coffee waste). For the shock experiments the influent COD concentration was doubled by an equivalent increase in the amount of ice cream used in the preparation of the feed or a reduction in the dilution of the coffee waste. This was then fed into the anaerobic reactor for 24 hours as a shock load.

The results of four typical transient responses to these shocks are shown in Figure 5 for the ice cream waste and Figure 6 for the coffee waste. The control algorithm responds to these shocks by reducing feed rate and holding waste up in the feed or balancing tank. Effluent quality is thus maintained in the desirable range. After 24 hours the influent COD was reduced to its original value when there was a corresponding increase in pumping rate (Figures 5 and 6). The results show that the control system is able to deal with different types of waste. The proportion of suspended COD in the feed ice cream waste was much higher than the coffee waste. The treatability of the ice cream waste was however greater.

These results compare well with previously published work. Cayless *et al.*[17], for example, also report on the performance of a laboratory anaerobic filter treating ice cream waste when subjected to load, temperature and pH shocks. They used a six-fold increase in waste strength, applied for eight hours, and monitored the results with standard wet analysis. Cayless *et al.* showed an increase in volatile carboxylic acids and a reduction in alkalinity and effluent quality in the first sample taken two hours after the start of the shock load. There are no previous reports on the effect of shock loads on the treatment of coffee wastewater but in the results reported at pilot scale[15,16], an increase in organic load was followed by a deterioration in effluent quality. In the results presented here effluent quality was successfully kept constant by the control model.

Practical problems for the application of this type of control to full scale were encountered. Experiance gained during the research showed that even with the probes in the treated effluent, cleaning with a cloth every two or three days was necessary.

Compressed air cleaning as supplied with the probes was insufficient. Probes with brush cleaning are now available and these are to be recommended for full-scale applications of this model. In the longer term, development of non-invasive gas analysis or water analysis based on reflectance or fluorescence could overcome these difficulties.

Changes in gas production and character are also immediately apparent when shock loads are applied. Cayless *et al.*[17], for example, were able to measure changes in gas production two hours after the application of the shock load. The volume of gas increased but the methane content was reduced. Gas production could be an alternative indicator of performance and used as the basis for a method of controlling industrial digesters to a fixed gas output to suit the downstream use of the gas. This would avoid the need for liquid phase analysis. Figure 7 shows the methane production rate during the shock experiments. Gas production rate closely follows changes in the hydraulic loading rate indicating the potential of this parameter for control. Hawkes *et al.*[18] give some results from the shock loading of a pilot plant treating ice cream waste. The organic loading rate was

tripled for eight hours and changes in both gas production and methane content were recorded in the first sample taken one hour after the start of the shock.

Mathiot *et al.*[19] conducted experiments with both short shock increases in load (15 minutes duration) and longer shock loads (lasting eight hours). In the case of the 15 minute shocks (when the COD concentration of the vinasse was increased 20 times), they found the gas production increased within a minute but then remained high for five hours. For the long shocks (lasting eight hours) the strength of the waste was increased six times. The response in gas production was again immediate with an increase which lasted over ten hours. There are no details of treated effluent quality but they do report increases in the concentrations of acetic and propionic acids. In another series of experiments Slater *et al.*[20] subjected an anaerobic fluidized bed reactor to continual changes in loading rate, but because of the protracted response of gas production, the effects of short shocks (lasting 30–60 minutes) were obscured. Our results (Figure 7) do not show extended changes in gas production if substrate loading rate is kept constant. There may be some advantages in using other more sensitive gas parameters such as hydrogen, hydrogen sulphide and carbon monoxide if the shocks are transient, superimposed or toxic[6,7].

## CONCLUSIONS

(1) Experiments have shown that measuring total dissolved solids by conductivity and suspended solids by light scattering can be used to estimate COD.

(2) The adaptive control system proposed, based on effluent quality and gas production, can avoid some of the costs and complexity of continuous monitoring of total organic carbon.

(3) Longer term tests are necessary to determine whether the algorithm is able to take account of slow progressive changes in the nature of the waste or characteristics of the biomass.

(4) The invasive probes used were unreliable with this type of raw waste because of fouling by fats. Further work is necessary on refining non-invasive analysis such as total gas production and qualitative gas analysis as possible alternatives.

## REFERENCES

1. Pauss, A., Depaepe, D. and Nyns, J., 1990, Review of anaerobic digestion plants in Europe, in *Proceedings of Eureka Euroenviron, Anaerobic Digestion Workshop*, Richards, G. E. (Ed) (Harwell, Oxford, UK), pp 11–21.
2. De Poli, F., Gamboni, M. and Tilche, A., 1988, Chemical and biological problems in full scale biogas plants: The Italian experience, in *The Fifth International Symposium on Anaerobic Digestion*, Hall, E. R. and Hobson, P. N. (Eds) (Pergamon Press, Oxford, UK), 389–396.
3. Colin, F., 1984, Development of automatic equipment for the study of acid-base equilibria for the control of anaerobic digestion, in *Anaerobic Digestion and Carbohydrate Hydrolysis of Waste*, Ferrero, G. L., Ferranti, M. P. and Naveau, H. (Eds) (Elsevier Applied Science, London), 381–394.
4. Powell, G. E. and Archer, D. B., 1989, On-line titration method for monitoring buffer capacity and total volatile fatty acid levels in anaerobic digesters, *Biotechnology and Bioengineering*, 33: 570–577.
5. Rozzi, A., Di Pinto, A. C. and Brunetti, A., 1985, Anaerobic

process control by bicarbonate monitoring. *Environmental Technology Letters,* 6(12): 594–601.

6. Whitmore, T. N., Lloyd, D., Jones, G. and Williams, T. N., 1987, Hydrogen dependent control of the continuous anaerobic digestion process. *Applied Microbiol and Biotechnology,* 26: 383–388.

7. Mosey, F. E. and Fernandes, X. A., 1989, Patterns of hydrogen in biogas from the anaerobic digestion of milk sugars. *Water Science and Technology,* 21(4/5): 187–196.

8. Dochain, D. and Bastin, G., 1985, Stable adaptive controllers for waste treatment by anaerobic digestion. *Environmental Technology Letters,* 6(12): 584–593.

9. Jones, R. M., MacGregor, J. F., Murphy, K. L. and Hall, E. R., 1992, Towards a useful dynamic model of the anaerobic wastewater treatment process. *Water Science and Technology,* 25(7): 61–71.

10. Wheatley, A. D. and Cassell, L., 1985, Effluent treatment by anaerobic filtration. *Water Pollution Control,* 84(1): 10–22.

11. Johnson, K. A., Wheatley, A. D. and Monroy, O., 1994, Mixing and solids accumulation in anaerobic filters. *Environmental Technology,* 15(3): 263–270.

12. Department of the Environment, Methods for the examination of waters and associated materials.
   (a) 1986, *The Chemical Oxygen Demand (Dichromate Value) of Polluted and Waste Waters,* 2nd edition (HMSO).
   (b) 1980, *Suspended, Settleable and Total Dissolved Solids in Waters and Effluents,* 1st edition (HMSO).
   (c) 1980, *The Measurement of Electrical Conductivity and the Determination of pH Value in Natural Waters,* 1st Edition (HMSO).

13. Renard, P., Dochain, D., Bastin, G., Naveau, H. and Nyns, E. J., 1988, Adaptive control of anaerobic digestion processes—a pilot scale application. *Biotechnology and Bioengineering,* 31: 287–294.

14. Fernandez, N. and Forster, C. F., 1994, The anaerobic digestion of a simulated coffee waste using thermophilic and mesophilic upflow filters. *Trans IChemE,* 72(B1): 15–20.

15. Lanting, J., Jordan, J. A., Schone, M. T., Kull, A., Carey, W. W. and Kitney, B. L., 1989, Themophilic anaerobic digestion of coffee wastewater, in *Proc 43rd Industrial Waste Conf, Purdue, Indiana* (Lewis Publishers), 513–524.

16. Hajipakkos, C., 1992, The application of a full-scale UASB plant for the treatment of coffee waste. *Water Science and Technology,* 25(1): 17–22.

17. Cayless, S. M., Motta-Marques, D. M. L. and Lester, J. N., 1989, The effect of transient loading, pH and temperature shocks on anaerobic filters and fluidized beds. *Environmental Technology Letters,* 10(11): 951–968.

18. Hawkes, F. R., Rozzi, A., Black, K., Guwy, A. and Hawkes, D. L., 1992, The stability of anaerobic digesters operating on a food-processing wastewater. *Water Science and Technology,* 25(7): 73–82.

19. Mathiot, S., Escoffier, Y., Ehlinger, F., Couderc, J. P., Leyris, J. P. and Moletta, R., 1992, Control parameter variations in an anaerobic fluidized bed reactor subjected to organic shockloads. *Water Science and Technology,* 25(7): 93–101.

20. Slater, W. R., Merigh, M., Ricker, N. L., Labib, F., Ferguson, J. F. and Benjamin, M. M., 1990, A microcomputer-based instrumentation system for anaerobic wastewater treatment processes. *Water Research,* 24(1): 121–123.

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## ADDRESS

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# A COMPARISON OF ADAPTIVE AND NEURAL NETWORK CONTROL MODELS FOR THE ANAEROBIC DIGESTION OF INDUSTRIAL EFFLUENTS.

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## ABSTRACT

Anaerobic digestion is being used increasingly for the treatment of industrial wastes due to the rising cost of waste disposal in the U.K. Industrial effluents can vary significantly in strength and composition (including inhibitory compounds) which results in instability of the digestion process. Thus, there is a need for closer control of anaerobic digestion. Results are presented from a comparison of two possibilities, adaptive control and artificial intelligence i.e. a neural network simulation for the control of the anaerobic digestion of a coffee processing effluent (from an instant coffee manufacturing plant in London). Both liquid and gaseous phase sensors have been used linked to control algorithms which balanced the organic loading rate by means of a variable speed pump.

## KEYWORDS

Adaptive control model; anaerobic treatment; industrial waste water; neural networks, monitoring and control.

## INTRODUCTION

Increasing charges (imposed by the water companies) for the treatment of industrial waste water from food processing factories is making on-site treatment more attractive. Industrial food processing produces wastes that can vary in quality and quantity over a short period of time. For these reasons monitoring and control of anaerobic digesters treating industrial waste waters is desirable (Switzenbaum et al., 1990). Furthermore, it is now common European practice to require a 90-95% compliance to a maximum admissible concentration (MAC) value, which reinforces the need for careful control. The control objective is to regulate final effluent quality at a prescribed level irrespective of fluctuating loads, by acting on the loading rate via the HRT (Dochain and Bastin, 1985). Researchers have developed control systems based on a variety of indicators relating to digester performance (see Table 1).

Table 1 Control system performance and control variables.

| Research team | Performance indicators | Controlled variable |
|---|---|---|
| Prodruzny and van den Berg, (1983) | gas flow rate | feed pump speed |
| Renard et al., (1988) | gas production rate, $CH_4$ in $CO_2$%, pH, temperature and manual COD values | feed pump speed (HLR) |
| Johnson et al., (1995) | gas production rate , SS, TDS, and $CH_4$ in $CO_2$% | feed pump speed |
| Alatiqi et al., (1990) | temperature and total organic carbon of effluent | heat input and feed pump speed |
| Slater et al., (1990) | $CH_4$, $CO_2$, $H_2$, CO, VFA ($C_1$-$C_4$) temperature, pH, ORP, and gas production rate | feed pump speed |
| Wilcox et al., (1995) | bicarbonate alkalinity | bicarbonate dosing pump |

The results presented in this paper are those of a study undertaken to investigate and develop a monitoring and control system applicable to the anaerobic digestion of coffee processing effluent. The initial stages of the project involved experimentation to establish the usefulness of on-line sensors for COD estimation, which were used with adaptive and neural network control models. The control model used was based on the equations described in Renard et al. (1988) and work done by Johnson et al. (1995). Adaptive control is attractive since it relies on continuous updating of the control constants by on-line monitoring.

Two approaches were followed in order to test the control system:

(1) To test the control system response under organic shock loading conditions.

Waste from the coffee factory was used to organically shock load the laboratory scale reactors in order to test the control system.

(2) To test the control system response to toxic components.

The roasting of coffee beans produces a number of complex heterocyclic compounds, many of which contain nitrogen. These compounds are frequently strongly coloured and resistant to breakdown during the residence times typically encountered in anaerobic digestion (Azhar and Stuckey, 1994). Clarke and Macreae (1985) found that anaerobic digestion of quinic acid (present in the liquid fraction of coffee waste) produced hydroquinone, pyrogallol, phenol and catechol as end-products. Pyrogallol has been shown to be 54% degraded under anaerobic conditions (Azhar and Stuckey, 1994). Thus, it was chosen as a potentially inhibitory compound with which to investigate the control of anaerobic digestion during toxic shock loads. The extent of inhibition was investigated by adding pyrogallol to a steady state, laboratory scale, upflow anaerobic filter being controlled by an adaptive control system.

The possible application of a back propagation based neural network (NN) for the control of anaerobic digestion was investigated. Neural networks and other forms of artificial intelligence have several advantages over traditional control methods. The network generates its own rules based upon learning examples. In supervised learning for each input a desired output signal is presented to the system and the network gradually configures itself to achieve that desired input/output. Neural networks also have a distributed associative memory, an item of knowledge is distributed across many of the memory units in the network and is shared with other items of knowledge stored in the network. The nature of NN memory leads to a reasonable network response even when presented with incomplete or previously unseen input. This property is referred to as *generalisation*. *Intelligent* responses to novel stimuli are possible by the combination of knowledge in the network layers. Neural networks have fault tolerance, so that even if a section of the network is destroyed it will not result in a breakdown. Neural networks therefore, have the ability to learn and build unique structures specific to a particular problem, such as the indications of a specific type of shock to an anaerobic system.

The use of gas phase indicators have been investigated in the later stages of the project as they have the advantage of significantly faster response times to stress of the anaerobic microorganisms than liquid phase indicators (Switzenbaum et al., 1990), as well as being less susceptible to probe fouling. Other researchers (Johnson et al. 1995) have found probe fouling to be a significant problem when monitoring lipid containing wastes. The possible gas phase indicators are: $CH_4$, $CO_2$, $H_2S$, $H_2$ and CO. Many researchers have investigated the role of hydrogen as an early warning indictor of digester overload (Kidby and Nedwell, 1991; Mosey and Fernandes, 1988; Hickey et al., 1987; Hickey and Switzenbaum 1990). Archer et al. (1986) found that $H_2$ gas concentration could be used to indicate reactor stress during shock loads.

Evaluation of a hydrogen analyser as a possible early indicator of reactor stress, under both an organic and toxic shocks, was undertaken.

## EXPERIMENTAL APPARATUS AND PROCEDURE

All experiments were carried out using laboratory scale 10 l biological anaerobic upflow filters containing randomly packed plastic media. The laboratory reactors were described previously in detail (Wheatley and Cassell 1985). The liquid volume of both reactors was 10 l and normally set to run with a hydraulic retention time of 40 hours. The reactors were located in a constant temperature room which was maintained at $37 \pm 0.5°C$. Effluent from instant coffee production was used as the feed (stored at $4 \pm 0.5°C$), the waste characteristics are shown in Table 2. This coffee waste was taken from the first stage of a two stage pilot plant after preacidification and settlement. The effluent was added to the reactor at a 50% dilution to allow organic shock loading tests to be performed.

Table 2. Instant coffee processing wastewater (6 month average)

| Parameter | mg/l |
|---|---|
| COD total | 10380 |
| COD filtered | 9055 |
| suspended solids | 833 |
| volatile acids | 2200 |

Reactor performance was routinely monitored by an adaptive control model. The control model used is based on adaptive equations described in Renard et al. (1988) and described in detail in Johnson et al. (1995).
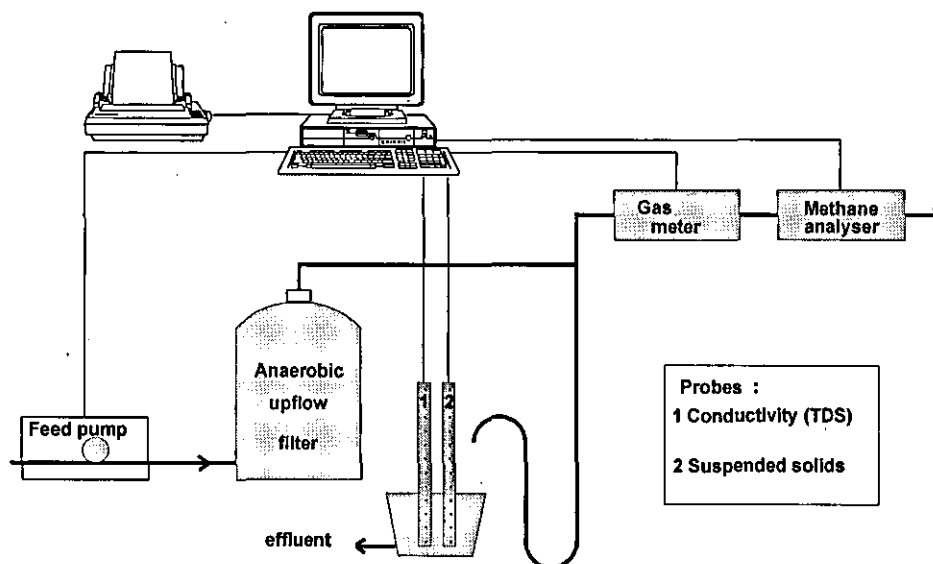


Fig. 2 Schematic diagram of the control system.

Fig. 2 shows the principal components of the control system. A variable speed pump is used to feed the anaerobic upflow filter. Gas and liquid effluent from the reactor are separated using a T-piece. Gas flow and methane concentration are determined and recorded by the computer prior to being vented to the atmosphere. The treated effluent stream enters a fixed volume header tank (3 l) continuously mixed by a magnetic stirrer. The SS and TDS probes are suspended in the header tank and connected to the computer, which in turn controls the variable speed pump.

Chemical oxygen demand was estimated on-line using a suspended solids (SS) and conductivity (TDS) probes (details of probes are given in Table 3). A correlation between SS, TDS and COD were established using the open reflux method for COD analysis (Standard methods, 1989).

$$COD = K_c \, (SS+TDS) \quad \text{Where } K_c = \text{constant for a particular waste.}$$

The rate of gas flow was determined by a work shop gas flow meter, which outputs a pulse to the computer for every 40 mls of biogas produced. The methane in carbon dioxide analyser was adversely affected by condensation of water vapour and high concentrations of hydrogen sulphide gas. Therefore, a buchner flask containing desiccant material and a drechsel bottle containing a solution of zinc acetate was located upstream of the gas analyser.

Table 3 Equipment used for adaptive control system

| Parameter | Equipment |
|---|---|
| data processor | IBM 286 PC |
| interface | Arcom PCDAC12-4 and PCAD12/16H |
| suspended solids meter | Eur-control mex 3, SS meter and RD 120/25 probe |
| total dissolved solids | pHOX series 55 conductivity meter with a D1 conductivity measuring cell |
| biogas quality | Crowcon 76 TC methane in carbon dioxide analyser |

Organic shock load

An organic shock load was applied to the reactor by increasing the strength of the influent (stored at $4 \pm 0.5°C$). Reactor performance during an organic shock load was monitored using the control model.

Toxic loading of the reactor.

Pyrogallol was added into the influent stream at three concentrations, 0.25, 1 and 3 g/l. Reactor performance was monitored with the control model. Pyrazine was also used at a concentration of 1 g/l and reactor performance was monitored using biogas hydrogen concentration and the control model.

Neural network training and testing.



Fig. 3 The structure of the neural network used.
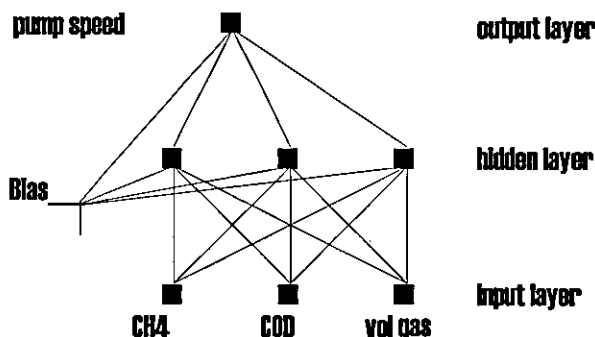
Three identical back propagation neural networks were set up using neuralware's Neural Explorer commercial program (illustrated in Fig. 3). The inputs were set as COD and methane production rate, output was pump speed. Different 20 h sections of training data from a real time control experiment were input in order to compare the output from untrained, poorly trained and well trained networks with those from adaptive control.

Hydrogen monitoring.

A GMI exhaled hydrogen analyser (based on the fuel cell principle) was calibrated before each experiment and used at a constant flow rate of 2.5 ml/minute. Output from the analyser was logged directly by computer. An increase in organic loading rate of the reactor was applied from 5 to 10 g/l/d for 15 hours and the response of the concentration of hydrogen within the biogas was closely monitored. Hydrogen was also monitored during a toxic shock using 1g/l pyrazine. The effects on hydrogen concentration from organic and toxic shocks were monitored with and without the application of the adaptive control model.

## RESULTS AND DISCUSSION

Organic shock load results
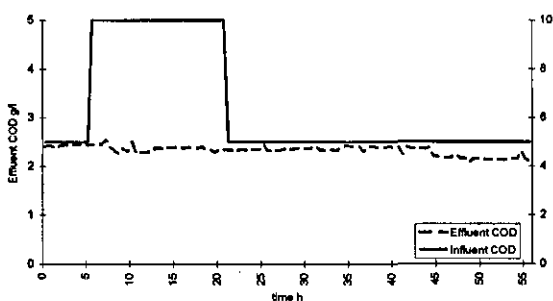


Fig. 4 Organic shock load.
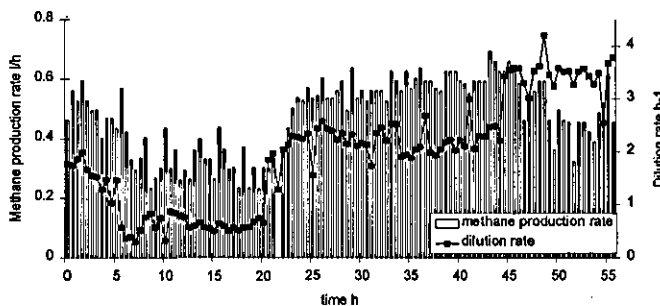


Fig. 5 Dil rate and methane production rate during organic load.

The results of increasing the feed strength from 5 to 10 g/l/d are shown in Fig. 4. The adaptive control system decreases pump speed in response. As influent COD decreases back to the initial level, pump speed is increased (see Fig. 5). The COD of the effluent remains constant. This indicates that the adaptive control system was able to detect and respond to fluctuations in COD and was attempting to minimise changes in effluent concentration

due to organic shock. The main operating difficulty would be the response time and lag in returning the effluent COD to a constant value.

## Pyrogallol Addition Results
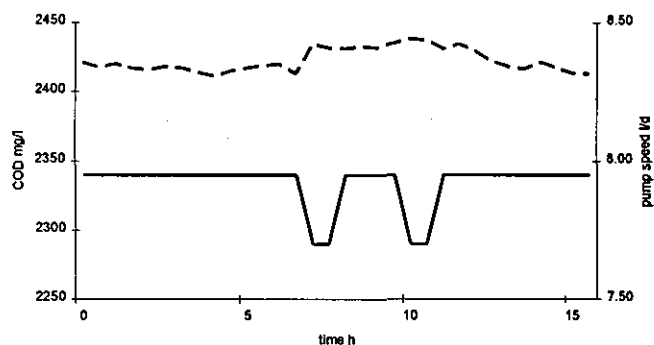


Fig. 6   0.25 g/l pyrogallol applied to reactor.

In Fig. 6 the results of introducing 0.25 g/l pyrogallol into the reactor feed are shown. The COD is seen to increase by 20 mg/l and pump speed to decrease simultaneously by 0.25 l/d for 2 h. This resulted in the effluent COD being returned to the steady-state concentration.
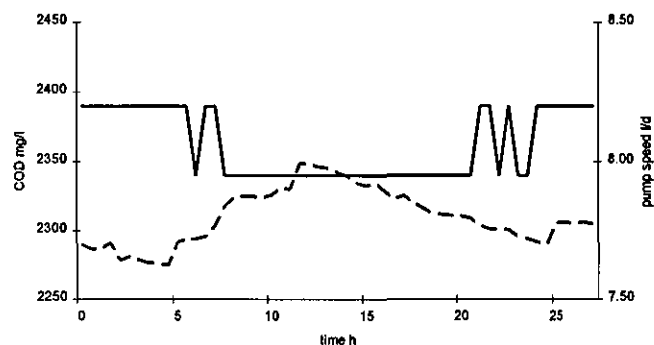


Fig. 7   1 g/l pyrogallol applied to reactor.

In Fig. 7 the pyrogallol concentration in the reactor feed was increased to 1 g/l. This resulted in a COD increase of 65 mg/l and the control system reduces pump speed by 0.25 l/d for 27.5 h, until the COD returns to the set value.
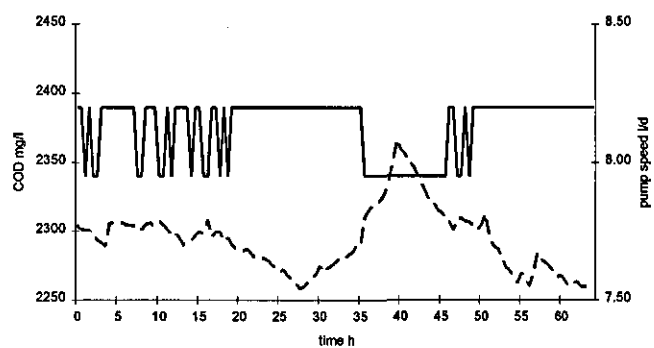


Fig. 8   3 g/l pyrogallol applied to reactor.

In Fig. 8 the pyrogallol concentration in the reactor feed was increased to 3 g/l. This resulted in a COD increase of 110 mg/l and the control pump speed to decrease simultaneously by 0.25 l/d for 32 h.

The pyrogallol results in contrast to previous work show no marked inhibition. The increases in COD of the effluent occurred approximately 50 hours after the pyrogallol was added into the waste. The COD increase was greatest with the highest dose. Azhar and Stucky (1994), found that pyrogallol was 54% degraded by anaerobic sewage sludge and at doses of 3 g/l pyrogallol, structural changes in UASB granules have been reported (Quarmby, 1995). However, the bacteria within the digester used during this research have been fed with coffee waste for two years and could, therefore, have acclimated to pyrogallol, and may be capable of increased degradation of the pyrogallol.

## Neural network training and testing.

A typical set of data, showing an increase in COD from 3.2 to 4.8 g/l over a 40 h period was used throughout the experiments to test the neural network. The data was taken from the existing adaptive control experiments and the response was a controlled reduction in pump speed (Fig. 9). This therefore was the well tried standard against which the neural network was to be compared. Two different 20 hour sections of this data were used to train two of the ANNs (Figures 12 and 14).
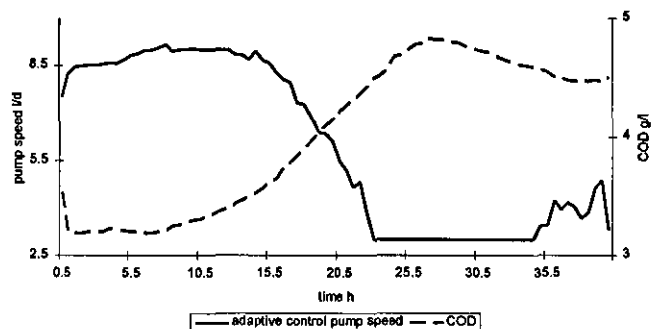
Fig. 9. Data from an adaptive control experiment. As COD increases pump speed decreases in response.

The input data used to test the ANNs is based on COD and methane production rate, shown in Fig. 10.
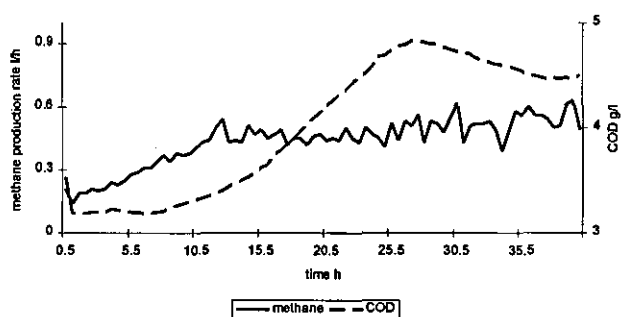


Fig. 10. The test data given to all three neural networks. The inputs of COD and methane production rate are the only data that are input to test the neural networks.

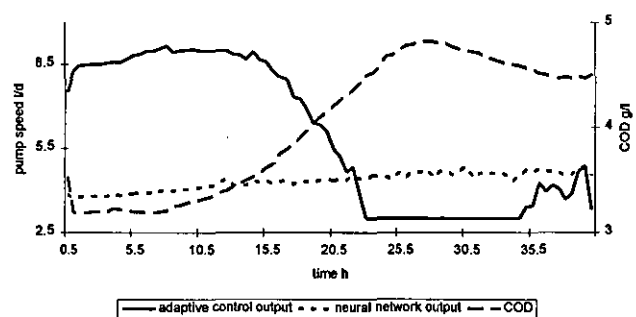The results from the first ANN which was untrained (i.e. it received no previous operating data) are shown in Fig. 11.



Fig. 11. Output from the untrained neural network.

In Fig. 11 there is no significant change in output from the neural network as would be anticipated. The results demonstrate that the untrained network has no capacity to control the feed pump speed correctly in response to a rise in effluent COD.

In a second experiment the ANN received training data from a narrow range of variation in COD (3.2 - 4.0 g/l), pump speed and methane production rate (not shown to simplify Fig.), i.e. the first 20 h period (shown in Fig. 12) from the data set in Fig. 9.
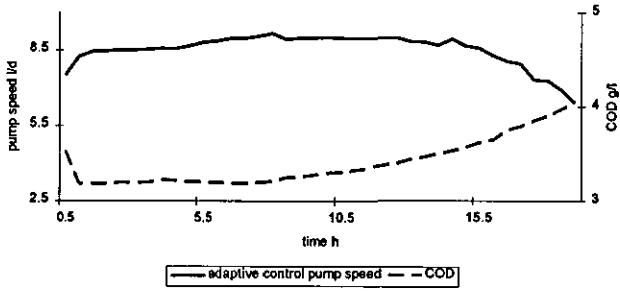
Fig. 12. The training data used to teach the second neural network.
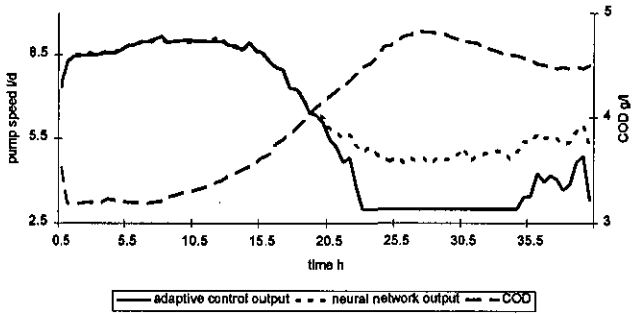


Fig. 13. Output from the second neural network, trained using data over a narrow range of sample data.

The output from the second neural network shown in Fig. 13 follows the output from the adaptive control model adequately until the COD rises above 4 g/l beyond which the ANN has no experience. After this point the ANN generalises using the rules learnt from the narrow range of data shown. As a result the pump speed does not decrease as much as the adaptive control model. This indicates that the ANN is poorly trained and therefore unable to respond adequately to the full range of test data.

The third ANN received training data with the widest possible range (Fig. 14). COD, pump speed and methane production rate (not shown in Fig. 14) were the inputs to train the third network over the wide range illustrated. In this case the data comes from the middle 20 h period from Fig. 9.
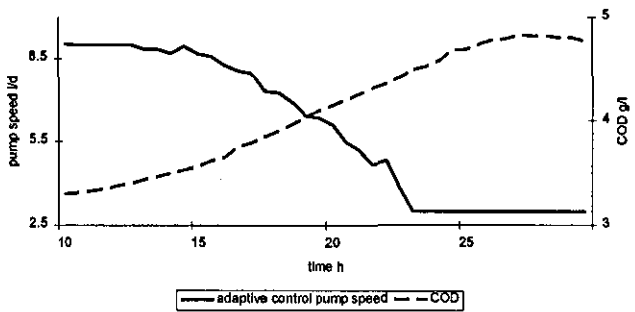


Fig. 14. The training data used to teach the third neural network.
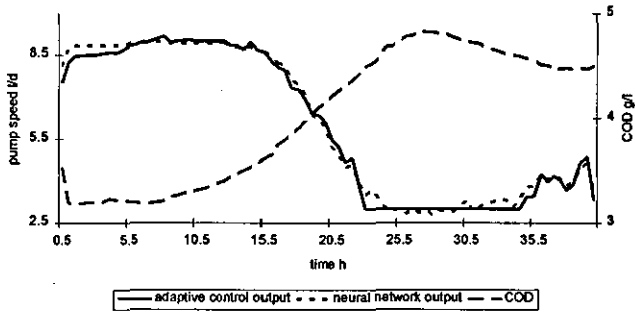
Fig. 15. Output from the third neural network, trained over a wide range of example data.

In Fig. 15 the output from the NN and adaptive control model match each other closely (usually ± 2%) over the experiment. This demonstrates that the neural network develops the capability to control the anaerobic digester, once trained on a suitable range of data.

The results have demonstrated the potential of neural networks to control organic loading and maintain a constant effluent quality and gas production. The results after the training period are comparable to those obtained from the tried and tested adaptive control. Johnson et al. (1995) noted in their work on the adaptive control of anaerobic digesters that there were potential problems for automatic control systems if the characteristics of the waste changed. They concluded that these might be overcome by using a greater array of sensors. Neural networks offer this possibility, they are commercially available and able to accept a large number of sensor inputs without a separate control strategy for each. Programming does not require extensive or expert knowledge. It should therefore be possible to program a neural network during the routine commissioning of a plant. Thereafter, the control will improve as more system experience is gained from the operating data.

Our results indicated that an approach based on methane production rate could lead to a faster response and be without the risk of probe fouling. More input variables would be necessary with wastes containing significant amounts of solid substrate, potentially toxic components or other changing characteristics. These could be based on other control parameters such as alkalinity, hydrogen and hydrogen sulphide which may have advantages for shocks not linked to changes in organic load.

Wilcox et al. (1995) describe neural network control of an anaerobic digester using a non-invasive analysis of alkalinity. They attributed some small but continual fluctuations in the performance of the neural network to a lack of training. For simple control outputs, i.e. organic loads, our data shows very little training is required. The simulation experiments described here indicate that artificial neural networks are applicable for the control of anaerobic digestion and have the advantage of being able to learn from previous operation data, which should ultimately give a faster response than the adaptive control system because due to ANNs having the capability to form associations with other inputs.

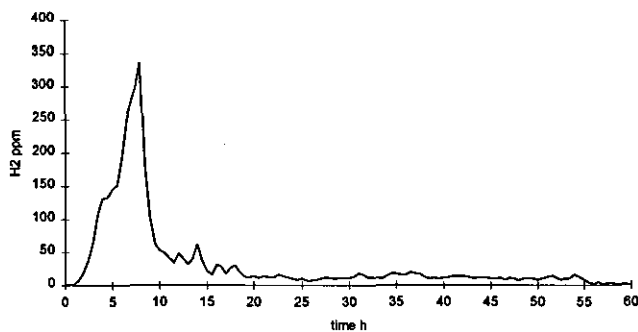## Hydrogen monitoring results.



Fig. 16 Hydrogen variations during an organic shock load.

8

In Fig. 16 hydrogen is seen to respond quickly to an increase in organic loading rate applied for 15 h. The hydrogen increase occurs within 2.5 h of the increase in organic loading rate. The response to fluctuations in reactor performance is markedly quicker than that demonstrated by the liquid phase parameter, i.e. estimated COD.
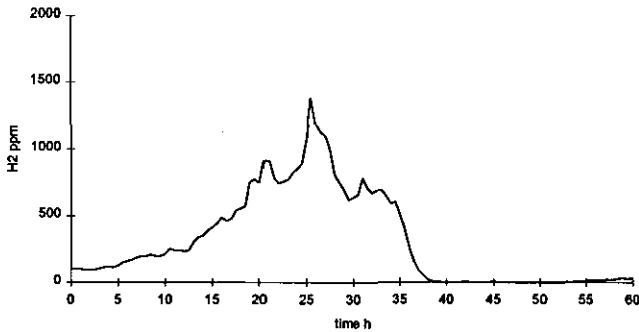


Fig. 17 Hydrogen variations during an uncontrolled pyrazine shock load.

Fig. 17 shows hydrogen increasing significantly 12 hours after the addition of pyrazine. The hydrogen gas increase starts after 5 hours and lasts for until 38 hours after which the reactor reverts back to its original state.
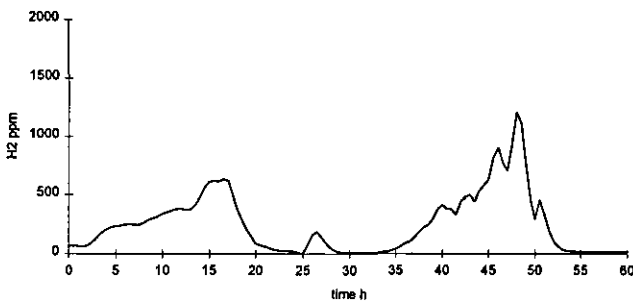


Fig. 18 Hydrogen variations during a controlled pyrazine shock load.

Fig. 18 shows a different pattern to Fig. 17, an increase in hydrogen production is seen to occur, at the same point as Fig. 17 but it is distributed over a wider time. The control system was at these times not using hydrogen as a control parameter but it is successful in preventing the hydrogen indicated disturbance from occuring in the same way as the uncontrolled example.

## CONCLUSIONS

The organic and pyrogallol loading of the anaerobic reactor showed that the adaptive control model is able to respond to changes in COD. However fluctuations in biogas production rate and quality are still present. Therefore, a faster acting control is desirable.

Hydrogen is shown to be a faster indicator of reactor stress than COD as it is measured in the gas phase. Liquid phase probes measuring COD detect a change slower and have the added disadvantage of being susceptible to fouling from the effluent.

The neural network experiments have shown that an ANN can perform as well as the adaptive control system whilst requiring less expert input (and accepting more parameters in standard proprietary software). Only small periods of training (30-40 hours) have been shown to be necessary to control simple desired outputs e.g. effluent quality and gas production from a waste of known treatability. It is likely that artificial intelligence techniques will be used increasingly in the future to achieve better operation and control of wastewater treatment plants.

The digester response to pyrogallol (shown in Figures 6,7 and 8) was better than expected from previous work, possibly due to acclimation of the anaerobic bacteria to pyrogallol concentrations normally found in the instant coffee processing waste.

The experiments using pyrazine show that the control model is capable of reducing reactor disturbances indicated by hydrogen fluctuations. Further experiments on new non-invasive gas analysis such as alkalinity linked to carbon dioxide, hydrogen and hydrogen sulphide could provide a comprehensive system capable of identifying potentially toxic and hazardous materials in the feed.


# FUTURE WORK

Further work is planned incorporating hydrogen and other gas and liquid phase parameters as indicators of reactor stress and to produce a faster acting control system using a neural network.


# ACKNOWLEDGEMENTS

# REFERENCES

Alatiqi, I.M. Dadkhah, A.A. Nabil M.J. (1990). Dynamics and multivariable control analysis for anaerobic digestion. The Chem. Eng. Journal 43, B81-B91

Archer, D.B. Hilton, M.G. Adams, S.P. Wiecko, H. (1986). Hydrogen as a process control index in a pilot scale anaerobic digester. Biotech. letts. 8 (3), 197-202

Azhar Ur-Rehman, N.G. Stuckey, D.C. (1994). The influence of chemical structure on the anaerobic catabolism of the refractory compounds; a case study of instant coffee wastes, Water Science and Technology 30 (12), 223-    232.

Clark, R.J. Macrea, R. (1985). COFFEE Volume 1. Chemistry
    Elsevier Applied Science Publishers Ltd. London and New York

Dochain, P. Bastin, G. (1985). Stable adaptive controllers for waste treatment by anaerobic digestion. Environ. Tech. letts 16, 584-593

Hickey, R.F. Switzenbaum, M.S. (1990). Behavior of carbon monoxide as a trace component of anaerobic digester gases and methanogenesis from acetate. Envoron. Sci. Tech. 24, 1642-1648

Hickey, R.F. Vanderwielen, J. Switzenbaum, M.S. (1987). The effects of organic toxicants on methane production and hydrogen gas levels during tha anaerobic digestion of activated sludge. Wat. Res. 21 (11), 1417-1427

Johnson, K. A., Wheatley, A. D. and Fell, C. J. 1995. Control of anaerobic digestion of industrial effluent. Trans. Inst. Chem. Eng. 73, 203-211.

Kidby, D.W. Nedwell, D.B. (1991). An investigation into the suitability of biogas hydrogen concentration as a performance monitor for anaerobic sewage sludge digesters. Wat. Res. 25 (8), 1007-1012

Mosey, F.E. Fernandes, X.A. (1988). Monitoring hydrogen in biogas during the anaerobic digestion of sugars
    In the 5th International symposium on anaerobic digestion Bologna Italy edited by Hall, E. R. Hobson, P.W. 219-222 Pergamon, Oxford

Prodruzny, M.F. Van den Berg, L. (1984). Development of a computer control system for anaerobic methane producing reactors. Biotech. and Bioeng. 26, 392-393

Quramby, J. and Forster, C. F. (1995). An examination of the structure of UASB granules. Wat. Res. 29 (11), 2449-2454

Renard, P., Dochain, D., Bastin, G., Naveau, H., Nyns, E. -J. (1988). Adaptive control of anaerobic digestion processes - a pilot-scale application. Biotech. and Bioeng. 31, 287-294

Slater, W.R. Merigh, M. Ricker, N.L. Labib, F. Ferguson, J.F. Benjamin, M.M. (1990). A microcomputer based instrumentation system for anaerobic wastewater treatment processes. Wat. Res. 24 (1), 121-123

Standard methods for the examination of water and waste water, 17th edition (1989). ALPHA-AWWA-WPCF, Washington D.C. Edited by Clesceri, L., Greenburd, A.E., Trussell, R.R.

Switzenbaum, M.S. Giraldo-Gomez, E. Hickey, R.F. (1990). Monitoring of the anaerobic methane fermentation process Enzyme Microb. Technol. 112 722-730

Wheatley, A. D. and Cassell L. 1985. Effluent treatment by anaerobic biofiltration. Water Pollut. Control Maidstone Engl 84 (1), 10-22

Wilcox, S. J., Hawkes, D. L., Hawkes, F. R. and Guwy, A. J. 1995. The use of a neural network to monitor anaerobic digestion with an On-line bicarbonate alkalinity sensor. Water Res. 29 (6), 1465-1470

# THE USE OF POWDERED ACTIVATED CARBON TO REDUCE INHIBITION IN ANAEROBIC DIGESTION

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## ABSTRACT

The use of anaerobic digestion for the treatment of industrial wastes is becoming more common throughout the world as confidence in the process increases and it becomes more economically feasible. The anaerobic digestion process is based on a mixture of synergistic bacteria that can be inhibited by a variety of compounds  common in industrial effluent, therefore much research has been performed to minimise inhibition. Detergents such as sodium lauryl sulphate are present in a wide range of effluents and have been shown to result in operational difficulties in anaerobic digestion. Activated carbon has been cited in various papers as a way of reducing inhibition, however the literature is often vague and contradictory. This paper describes experiments on the application of a commercially available activated carbon powder to the anaerobic digestion of sodium lauryl sulphate (SLS) and sodium dodecyl-benzene sulphonate (SDBS). Results are presented on the performance of anaerobic batch tests. Inhibitory concentrations of sodium lauryl sulphate were added to the batch reactors which were monitored for inhibition and beneficial effects of powdered activated carbon. The addition of powdered activated carbon did not provide any improvement to total gas production due to absorption. SLS and SDBS were found to be inhibitory at 750 mg/l, however, 1% PAC of sludge solids was found to stop inhibition up to 2000 mg/l.

### KEYWORDS

Anaerobic digestion; powdered activated carbon (PAC); inhibition; detergents; sodium lauryl sulphate; sodium dodecyl-benzene sulphonate: gas production; anaerobic batch tests.

### INTRODUCTION

Both laboratory and full scale field experiments from previous studies have provided results which demonstrate that the addition of activated carbon to the anaerobic digester process will provide many benefits.  The first reported use of activated carbon in anaerobic digestion was by Rudolfs and Trubnick (1935), the idea was later patented by Statham (1936).  The benefits that powdered activated carbon give to anaerobic digestion are reported as being: improved settling within the anaerobic digester (Adams, 1975b); up to 500% increase in methane production (Adams, 1975a); improvement in stability for overloaded digesters (Koch et al., 1978); reduced odours (Hunsicker and Almeida, 1976).

The literature demonstrates some disagreement with respect to optimal concentrations of activated carbon (Table 1). Concentrations of powdered activated carbon reported to be beneficial when added to the influent of anaerobic digesters vary from 3 mg/l (Statham, 1936) to 20 000 mg/l (Rudolfs and Trubnick, 1935). Other researchers have added PAC as a concentration of sludge solids within an anaerobic digester. These concentrations vary from 150 mg/l (McConville and Maier, 1978) to 100 000 mg/l (Adams, 1975a). Therefore a research programme was started to experimentally determine the optimum concentration for powdered activated carbon in anaerobic digestion. Koch et al. (1978) stated that PAC will not improve the performance of a well operated digester, but will improve performance and stability for overloaded digesters. The mechanism responsible for enhancement of the anaerobic digestion process is unclear, however it is thought that adsorption of inhibitory compounds plays a major part.  Therefore the effect of PAC on the anaerobic digestion of two inhibitory detergents commonly present in industrial effluent was tested.  These detergents are anionic surfactants: an alkyl sulphonate, sodium lauryl sulphate (SLS), and a linear alkylbenzene sulphonate: Sodium Dodecyl-Benzene Sulphonate (SDBS). Batch scale tests were performed to determine the optimum dosage of powdered activated carbon, the threshold inhibitory concentration of the detergents and the effect of activated carbon on microbial inhibition.

TABLE 1 Previous research investigating the use of activated carbon.

| Reference | Apparatus | dosage of PAC | observations |
|---|---|---|---|
| Adams (1975a) | lab-scale CSTR | unknown | 500% increase in methane production at 5% PAC of the sludge solids |
| | 2 MGD trickling filter plant with 2 stage digestion | ~10% of solids | No increase in gas production , but supernatant clarity improved |
| | 1.8 MGD as above | ~10% of solids | 31% increase in gas production after 2-3 months and supernatant clarity improved |
| | 2 MGD activated sludge plant with an overloaded 2 stage AD | ~10% of solids | gas increase reported, but not measured |
| Hunsicker and Almeida (1976) | 2 stage sewage sludge digester | 5% of solids | improved odours and increase in gas production (unmeasured, but bluer flame), |
| Koch et al. (1978) | 3.5 litre continuous CSTR | 2 and 5% of the total solids | PAC will not improve the performance of a stable digester, but will improve performance and stability for overloaded digesters. 2% was found to be best. |
| McConville and Maier (1978) | batch fed CSTR | 150-3000 mg/l sludge | 3-12% increase in biogas production at 15.2 d HRT to 253% increase at 4 d HRT. 150 mg/l found to be best. |
| Montalvo and Almeida (1992) | 5 l batch reactor | 50-250 mg/l waste | reduced inhibition giving 10% increase in efficiency. |
| Ng et al. (1988) | 125 ml batch tests | 500-4000 mg/l liquid volume | increased rate of methanogenisis under inhibition reduced inhibitory effects from absorbable toxins |
| Rudolfs and Trubnick (1935) | 1.5 l batch tests | 20-40 g/l sludge (10-20 g/l total volume) | accelerated the digestion of the fresh solids, less gas was produced with 40g than with 20g carbon, greatly improved the drainablility of the digested sludge. |
| Statham (1936) | unknown | 3-10 PPM of sewage | decrease HRT and volatile solids, increases digester temperature, BOD removal and gas production. |
| Takashima et al. (1991) | 125 ml batch tests and 2.5 litre continuous CSTR | 0.1-1 g/l and 4-40 g/l substrate | addition of PAC eliminated inhibition caused by heat treatment of human wastes |
| Ventetuolo and Adams (1976) | 11.4 MGD activated sludge with 2 stage AD | 5% of estimated sludge solids production | 10% increase in gas production and increased stability |

## MATERIALS AND METHODS

Powdered Activated Carbon
The powdered activated carbon used for this work was NORIT SA2, a commercially available PAC, commonly used in the waste water treatment industry.

Sodium Laryl Sulphate.
Sodium laryl sulphate (Sigma L5750) has an average molecular weight of 341. The detergent contains approximatelly seventy precent (70%) lauryl sulphate sodium salt and the balance made up of higher homologs

Dodecyl-benzene Sulphonic Acid.
The second detergent used was Dodecyl-benzene Sulphonic Acid (Sigma No. D2525). The detergent had approximatelly 80% purity and higher and lower homologs present.

Batch Scale Anaerobic Digesters.
The apparatus used in these experiments consisted of a 500 ml capacity bottle bioreactor, from which the evolved biogas was fed, via ten millimetre (10 mm) plastic tubing, to an inverted graduated 350 ml measuring cylinder, which collected the gas. Adapters, clips and stands are used where necessary to hold the apparatus steady. A schematic diagram of the apparatus is shown above in Fig. 1.
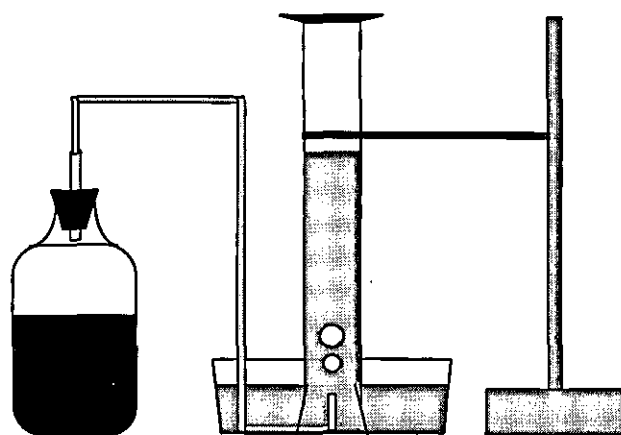
Fig. 1. Diagram of the laboratory apparatus used for the batch scale experiments.

The batch reactors were set-up with 300 grams of digested sludge, collected from Loughborough sewage treatment works, and kept in a constant temperature room at 37°C ± 1°C. For the duration of the experiment (6 days) the batches were agitated for one minute every day and the gas collected and analysed for percentage of methane.

The first batch scale experiment was undertaken to investigate the relationship between activated carbon dosage size and digester performance, in an attempt to find the optimum dosage of activated carbon. Activated carbon was added to batch anaerobic tests at 0, 0.076, 0.152, 0.228, 0.304 and 0.456% of wet weight of sludge.

A second batch test with higher concentrations of PAC (0, 0.5, 1, 1.5, 2, 2.5, 3 and 3.5%) was performed. To each of these batch reactors and all subsequent reactors was added 2.4 grams of yeast extract as feed to the digester. TOC analysis was performed at the end of the batch test. Samples were centrifuged to remove solids, and filtered through a Watman 502 filter to remove any PAC prior to analysis with a Sartec model DC-190 TOC analyser.

The third experiment investigated high concentrations of added activated carbon (0%, 2.5%, 5%, 7.5%, 10% and 15%).

The fourth experiment evaluates the effects of PAC on detergent addition to the bioreactor. Sodium lauryl sulphate was added at concentrations of 0, 750 1000, 1500 and 2000 mg/l. PAC was added at 0, 1 and 5% sludge solids to each concentration of detergent.

This experiment was repeated using SDBS at concentrations of 0, 500, 750, 1000, 1500, 2000 and 2500 mg/l. PAC was added at 0 and 1% sludge solids.

## RESULTS AND DISCUSSIONS

**PAC Optimisation Experiments**
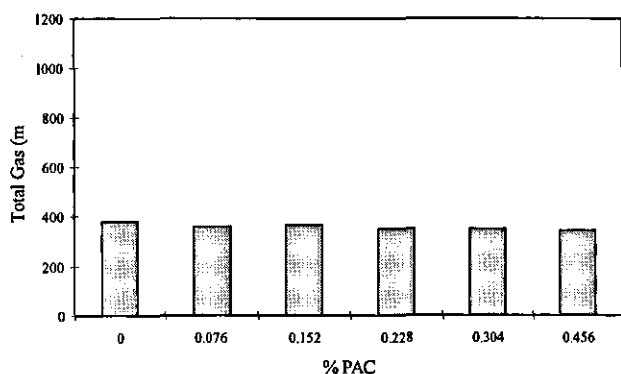


Fig. 2. Total gas production from low concentration PAC additions.

In Fig. 2 it is shown that low concentrations of PAC do not have a marked effect on biogas production. However, when concentrations of PAC are increased a decrease in total gas production can be seen (Fig. 3). In Fig. 4 TOC at the end of the batch test is seen to decrease as PAC concentration increases. This suggests that some of the TOC was absorbed by the PAC thereby making it inaccessible to the anaerobic bacteria. This could have contributed to the decrease in total gas production.
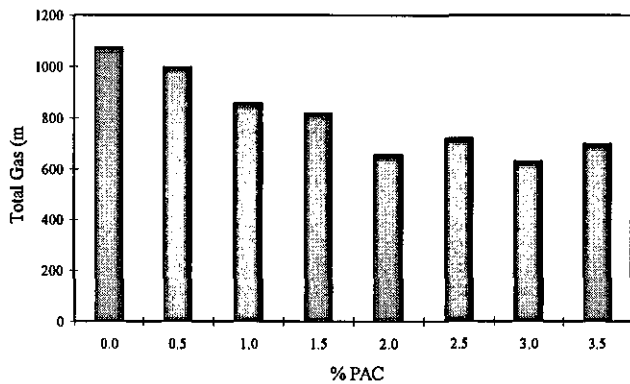
Fig. 3. Total gas production at PAC 0-3.5%
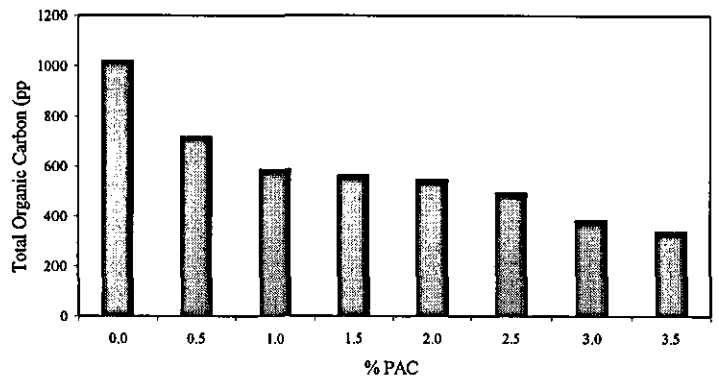


Fig. 4. TOC removal at PAC 0-3.5%

It is also possible that some of the biogas was itself absorbed by the PAC. Ng et al.(1987) performed tests to find the maximum adsorption of methane onto PAC, they found it to be approximately 3 ml methane/g PAC. Rudolfs and Trubnick (1935) demonstrated that $CO_2$ in sewerage was absorbed by PAC resulting in an increase in pH. However, Fig. 5 shows that the final pH of the batch tests actually decreased with the addition of PAC. There can be no doubt that biogas can be adsorbed to some extent, but this cannot be the only factor resulting in the reduced gas production shown here. An experiment was therefore performed to investigate whether PAC could absorb TOC prior to digestion.
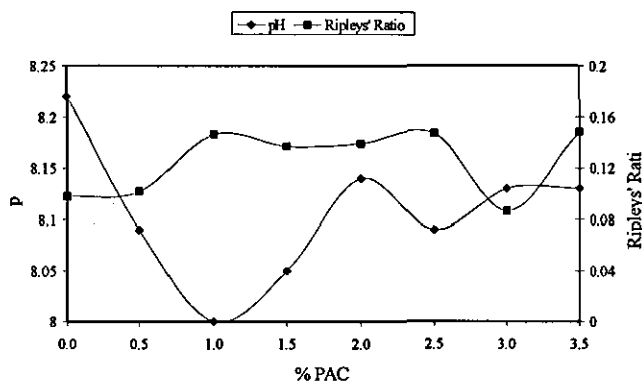


Fig. 5. pH and Ripleys' Ratio at end of batch test.
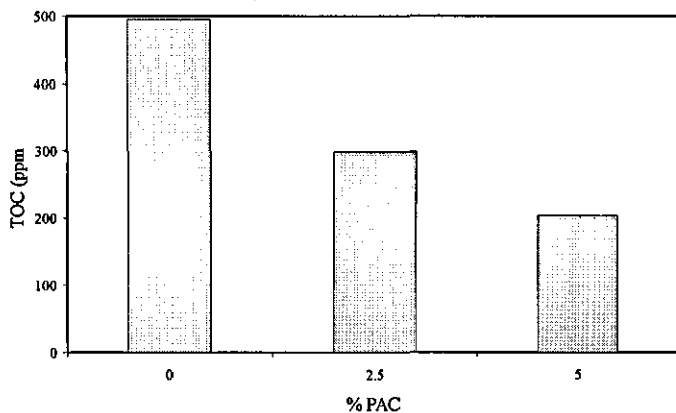


Fig. 6. TOC in batch reactors with PAC additions.

Fig. 6 demonstrates that PAC was found to absorb TOC from the yeast extract - digested sludge mixture before anaerobic digestion had started. If a quantity of TOC in the batch experiment is absorbed by the PAC it could account for the reduced total gas production. We would expect TOC to be slowly released from the PAC as the concentration of available TOC is reduced by the action of anaerobic digestion (Fox and Suidan, 1991) however some TOC would be retained.
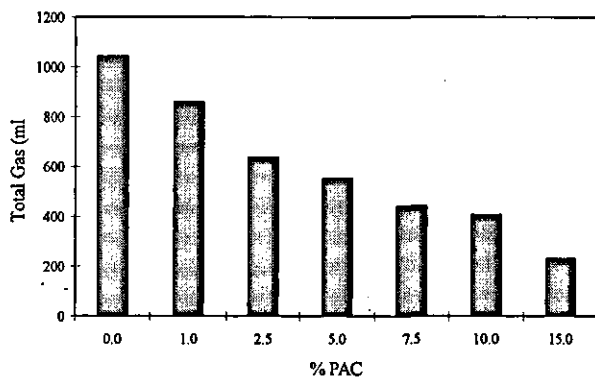
Fig. 7. Total gas production at higher PAC concentrations

When the experiments were repeated at even higher concentrations of PAC (Fig. 7) the trend seen in Fig. 3 becomes more pronounced, i.e. increasing concentration of PAC results in decreasing total gas production. These results demonstate that there is a difficulty in determining an optimum concnetration of PAC for an unstressed anaerobic digester.

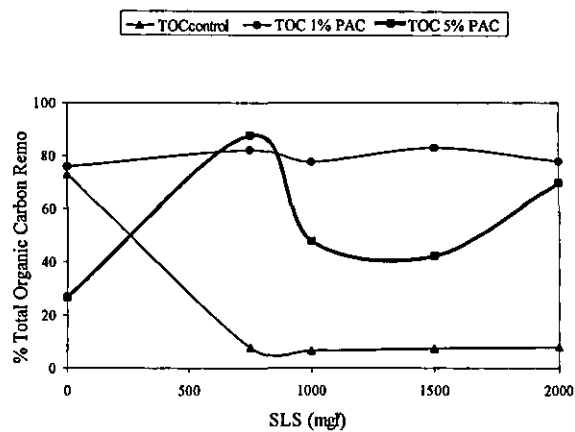**Inhibition Experiments**
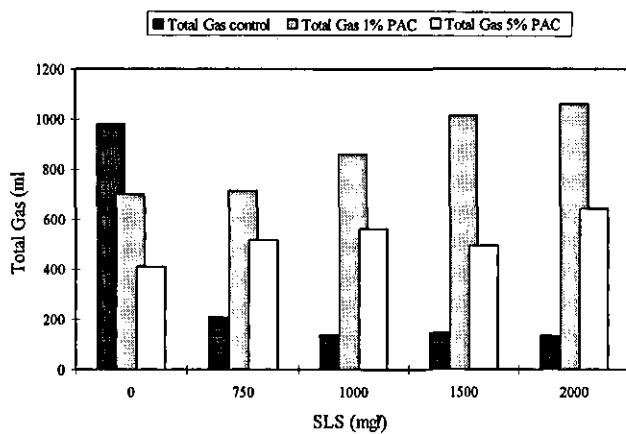


Fig. 8. Total gas production at 1 and 5% addition of PAC



Fig. 9. TOC removal at 1 and 5% PAC addition

In Fig. 8 inhibition is seen in the control (no PAC) at SLS concentration of 750 mg/l. The addition of PAC at both 1 and 5 % is shown to counteract the inhibitory effect of the detergent. Morover, at both concentrations of PAC it can be seen that gas production increases with increasing concentrations of SLS. This suggests that the SLS is not inhibitory and is in fact degraded in the presence of PAC. In the tests containing 5% PAC total gas production is lower than the tests with 1% PAC. This is probably due to absorption of biogas and TOC, as discussed previously. The success of PAC in the anaerobic digestion of inhibitory compounds was attributed by Fox and Suidan (1991) to the carbon acting as a buffer, maintaining a constant substrate concentration. In this way, organic and toxic shock loading can be prevented. As our results show that anaerobic digestion is not inhibited by SLS at concentrations below 750 mg/l, it is probable that 1% PAC was able to keep the available SLS concentration below 750 mg/l.

Fig. 9 shows percentage TOC removal in batch reactors containing 0, 1 and 5 % PAC. TOC removal can be seen to be consistently highest in reactors containing 1 % PAC, regardless of detergent concentration. Reactors without PAC show a loss in TOC removal related to inhibition by SLS. The results achieved with 5% PAC are contradictory to those expected, i.e. that higher PAC concentrations give rise to increased TOC removal. Tests are continuing to investigate these results.

It may not be possible to find one standard concentration of PAC applicable to all stressed anaerobic digesters as it is likely to be related to the type of inhibitor and reactor type.
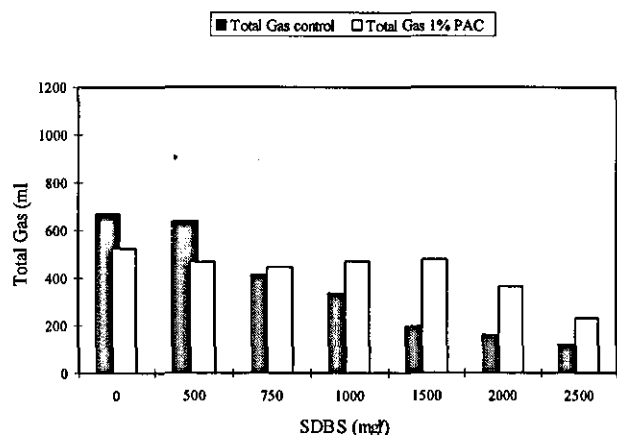
Fig. 10. Total gas production vs Concentration of SDBS.

Fig. 10 shows that the second detergent, SDBS, causes inhibition at 500 mg/l in the control (no PAC). The reactors containing 1% PAC were not inhibited until the SDBS concentration reached 2000 mg/l. Even at this concentration of SDBS the total gas production in the PAC reactors was more than twice that of the control.

The results presented within this paper confirm that PAC does absorb substrates and products of the anaerobic digestion process. The reduction of inhibition is demonstrated in Figs. 8, 9 and 10 but increasing the concentrations of PAC above 1% was not shown to result in better performance or a further reduction in inhibition.

To the best of our knowledge, no results have not been presented previously showing a reduction in biogas production resulting from the addition of PAC. Some researchers have reported little or no change: Ahlstrom and Spencer (1978) found that low-level, intermittent dosing did not significantly affect their sludge digester; Spencer (1979) did state that only very moderate increase in methane production are to be expected in unstressed, well operating digesters. The batch tests presented here were not under any stress or overloaded and no increase in methane production was seen. Conversely, anaerobic digestion of inhibitory or toxic compounds have been widely reported within the literature to be assisted by addition of PAC (Koch et al., 1978, Takashima et al., 1991, and Montalvo and Almeida, 1992). Our results were in agreement with these findings.

## CONCLUSIONS

1. Addition of PAC to an unstressed anaerobic digester will not result in any increase in efficiency of the process.

2. PAC absorbs available carbon and gases in solution.

3. Addition of PAC to an anaerobic digester containing inhibitory concentrations of SLS and SDBS counteracts inhibition. It is suggested that this is due to adsorption of the detergents onto the PAC.

4. The use of PAC in anaerobic digestion plants treating industrial wastewaters containing inhibitory compounds will result in enhanced process stability and thereby make the process more competitive in the future.

## REFERENCES

Adams, A. D. (1975a). Activated carbon: Old Solution to Old Problem (part I). Water and Sewage Works 7: 46-48

Adams, A. D. (1975b). Activated carbon: Old Solution to Old Problem (part II). Water and Sewage Works 8: 78-80

Ahlstrom, S. B. and Spencer, R. R. (1978). Assessment of powdered activated carbon addition to anaerobic digesters at Salt Lake City, Utah. Pacific Northwest Laboratory, Richland, Wash., Report PNL-2665, (07B AHL) 32

Fox, P. and Suidan, M. T. (1991). A fed-batch technique to evaluate biodegradation rates of inhibitory compounds with anaerobic biofilm attached to granular activated carbon. Water Science and Technology 23: (7/9) 13371346

Fox, P., Suidan, M. T., Pfeffer, J. T. (1988). Anaerobic treatment of a biologically inhibitory wastewater. Journal of Water Pollution Control Federation 60: (1) 86-92.

Hunsicker, M and Almeida, T. (1976). Powdered activated carbon improved anaerobic digestion. Water and Sewage Works 7: 62-63

Koch, C. M., Nelson, M. D and DiMenna, R. (1978). Wanted: More gas, less sludge - can PAC help? Water and Wastes Engineering 7: 27-29

McConville, T. and Maier, W. J. (1978). Use of powdered activated carbon to enhance methane production in sludge digestion, Biotechnology and Bioengineering Symp. No. 8, 345-359.

Montalvo, S. J. and Almeida, M. P. (1992). Anaerobic process of soluble wastes with addition of activated carbon. Biotechnology Letters **14:** (11) 1093-1098

Ng, W. J. and Chin, K. K. (1988). Treatment of piggery wastewater by expanded-bed anaerobic filters. Biological Wastes **26:** (3) 215-228.

Rudolfs, W. and Trubnick, E. H. (1935). Activated carbon in sewage treatment. Sewage Works Journal **7:** (5) 852-881

Spencer, R. R. (1979). Enhancement of methane production in the anaerobic digestion of sewage sludge. Biotechnology in energy production and conservation (edited by C. D. Scott), John Wiley & Sons, New York, Biotechnology and Bioengineering Symposium (8) 257-268

Statham, N. (1936). Method of Sewage Disposal. U. S. Patent 2 059 286

Takashima, M., Sugawara, Y., Ohkawa, T. and Ohkubo, Y. (1991). Effects of heat treatment on the high-rate anaerobic digestion of human wastes concentrates. Water Science and Technology **23:** 1137-1145

Ventetuolo. T. and Adams, A. D. (1976). Improving anaerobic digester operation with powdered activated carbon. WPCF Deeds & Data **7:** D1 and D4-D8.

**Tracer study and COD$_{(I)}$ probe graphs**
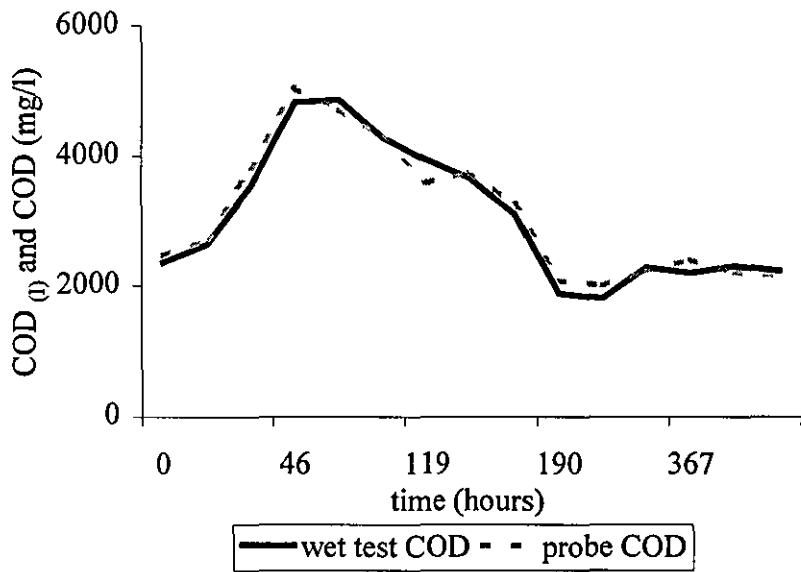
Figure 3-1 probe and wet test COD comparison
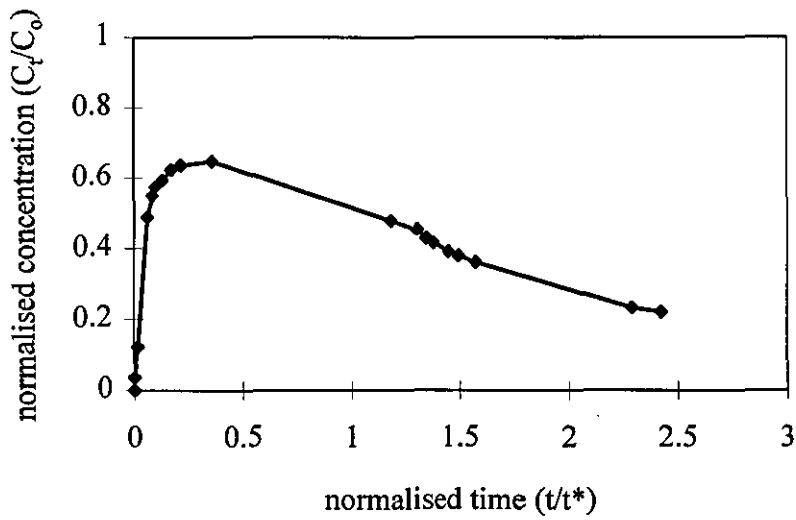


Figure 3-2 Tracer study for laboratory anaerobic filter

**Further Data**

Figures 4-1 to 4-3 hydrogen, methane production rate and $COD_{(I)}$ during an aborted control experiment where organic loading rate was increased. $COD_{(I)}$ probe failure resulted in the experiment being abandoned as dilution rate was rapidly reduced to minimum.

Figures 4-4 to 4-7 hydrogen, methane production rate and $COD_{(I)}$ during an aborted control experiment where 1 g/l pyrazine was added to digester feed. $COD_{(I)}$ probe failure in the first hour resulted in the experiment being abandoned as dilution rate was subsequently reduced to minimum.

Figures 4-8 to 4-11 hydrogen, methane production rate and $COD_{(I)}$ during a second aborted control experiment where 1 g/l pyrazine was added to digester feed. $COD_{(I)}$ probe failure at 6 hours resulted in the experiment being abandoned as dilution rate was subsequently reduced to minimum.
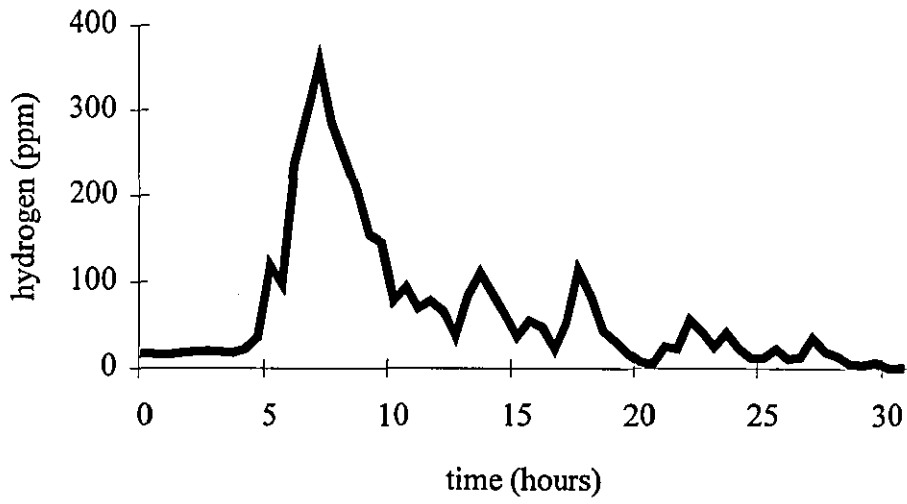
Figure 4-1 Hydrogen during an organic load increase (aborted original control)
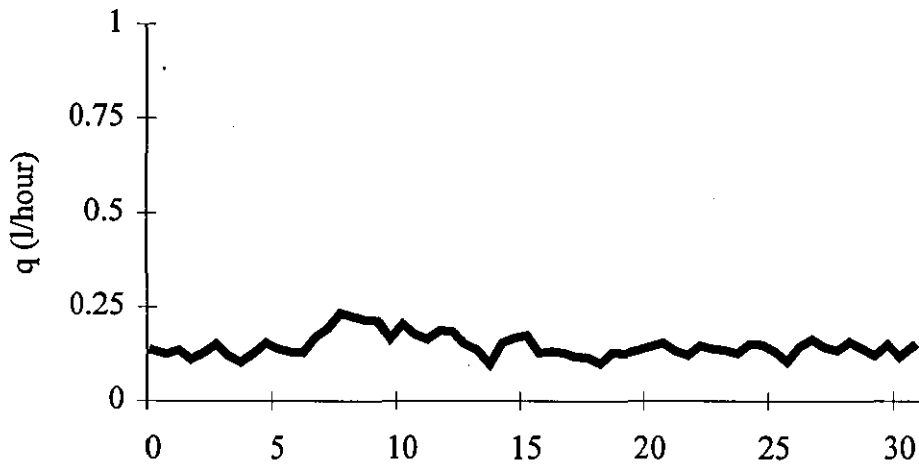


Figure 4-2 Methane production rate during an organic load increase (aborted original control)
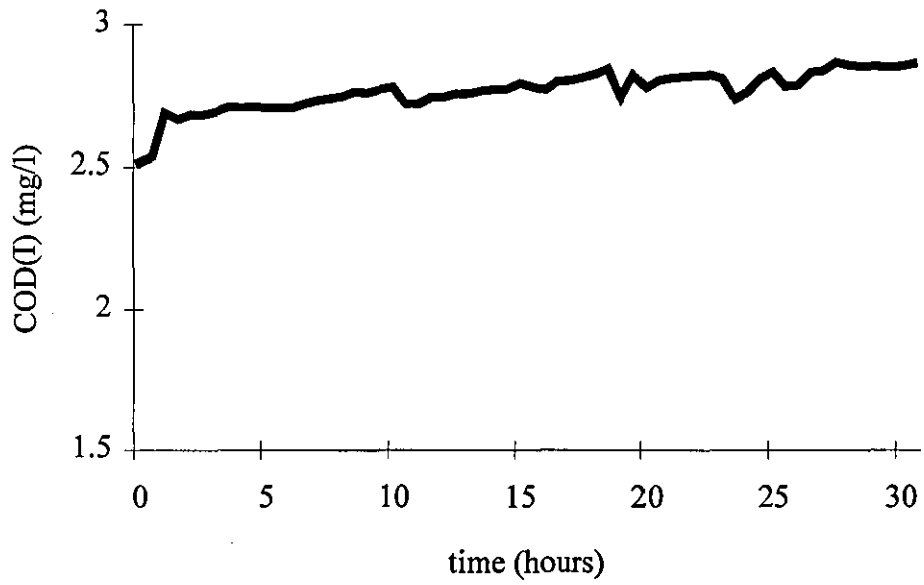
Figure 4-3 $COD_{(l)}$ during an organic load increase (aborted original control)
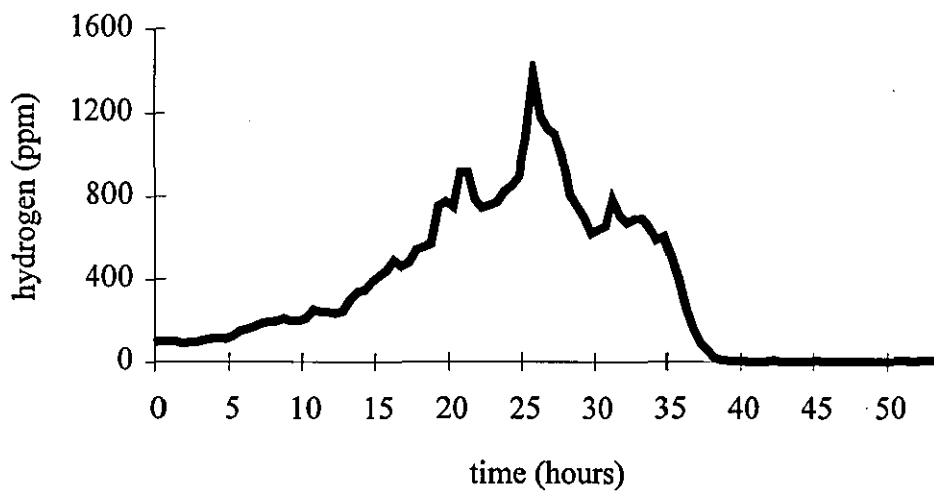
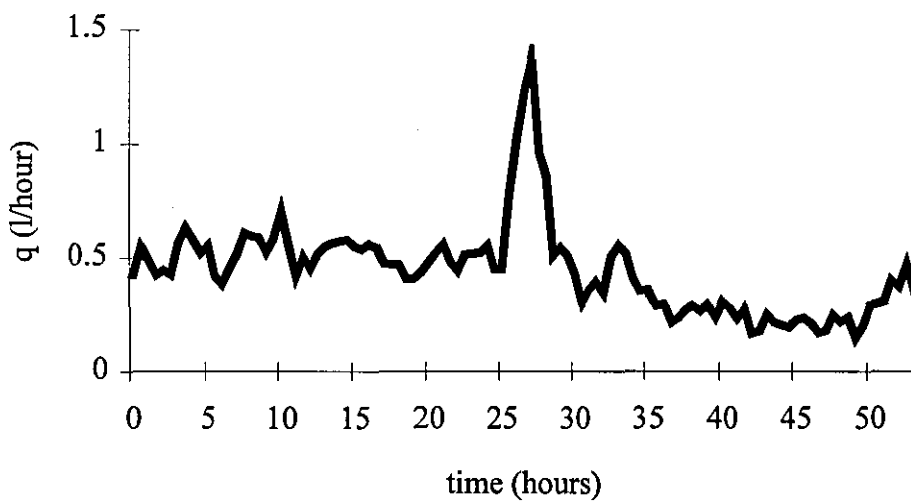Figure 4-4 Hydrogen during a 1 g/l pyrazine addition (aborted original control)



Figure 4-5 Methane production rate during a 1 g/l pyrazine addition
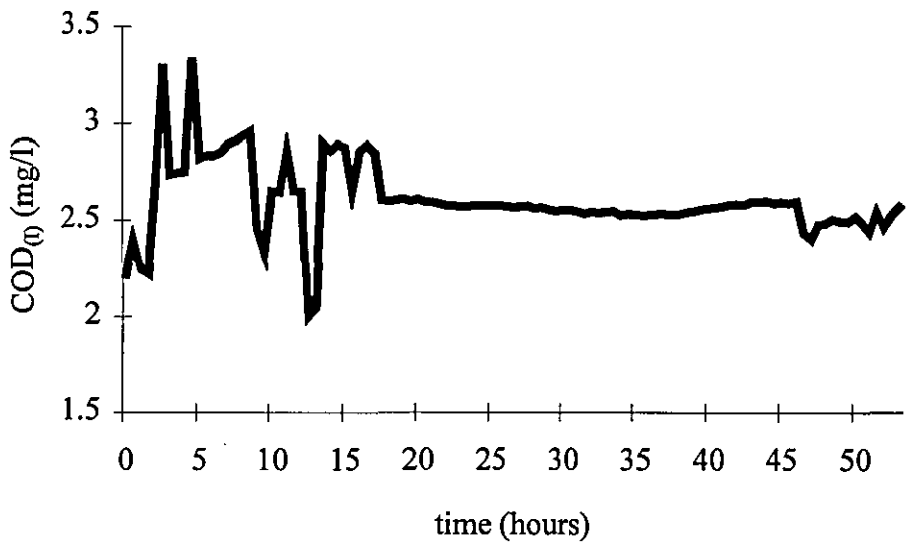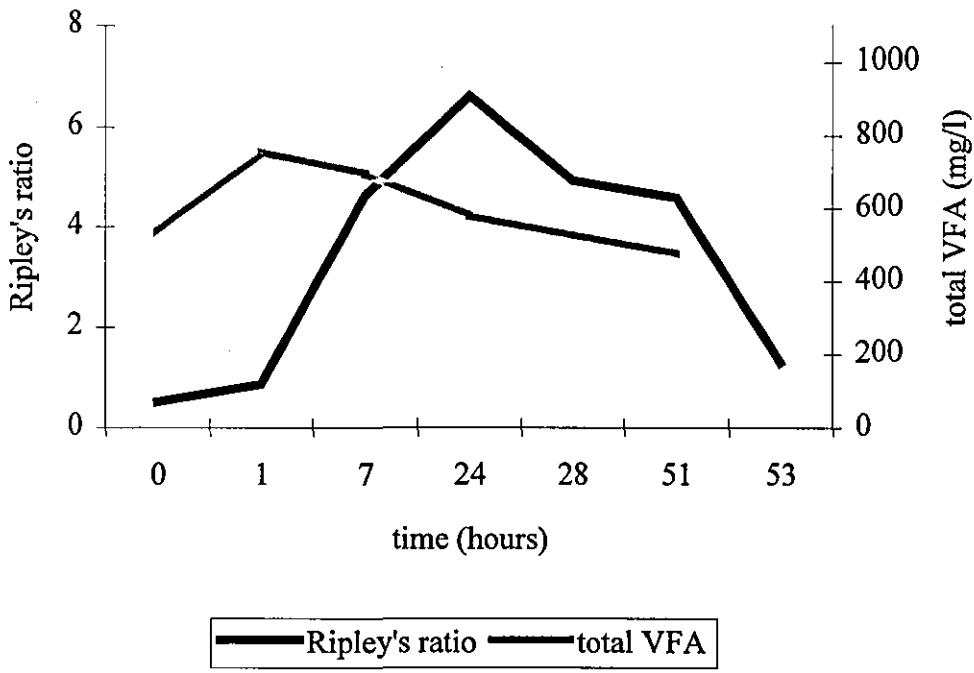(aborted original control)

Figure 4-6 COD$_{(I)}$ during a 1 g/l pyrazine addition (aborted original control)



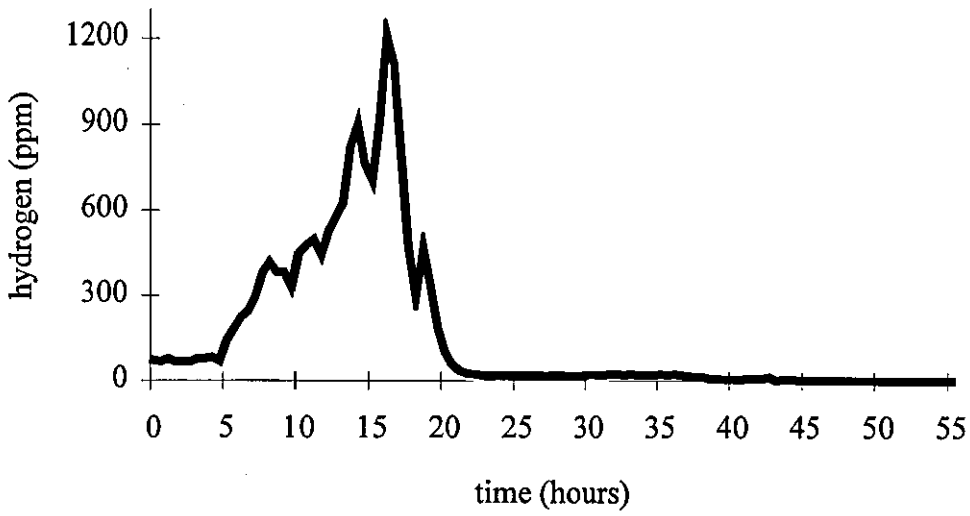Figure 4-7 Ripley's ratio and total VFA during a 1 g/l pyrazine addition (aborted original control)

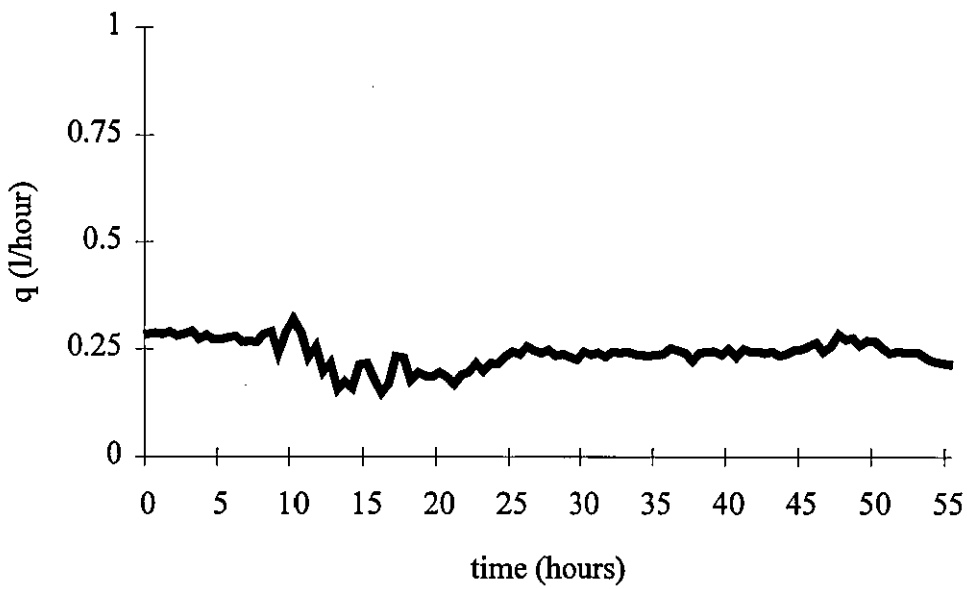Figure 4-8 Hydrogen during a 1 g/l pyrazine addition (2nd aborted original control)



Figure 4-9 Methane production rate during a 1 g/l pyrazine addition
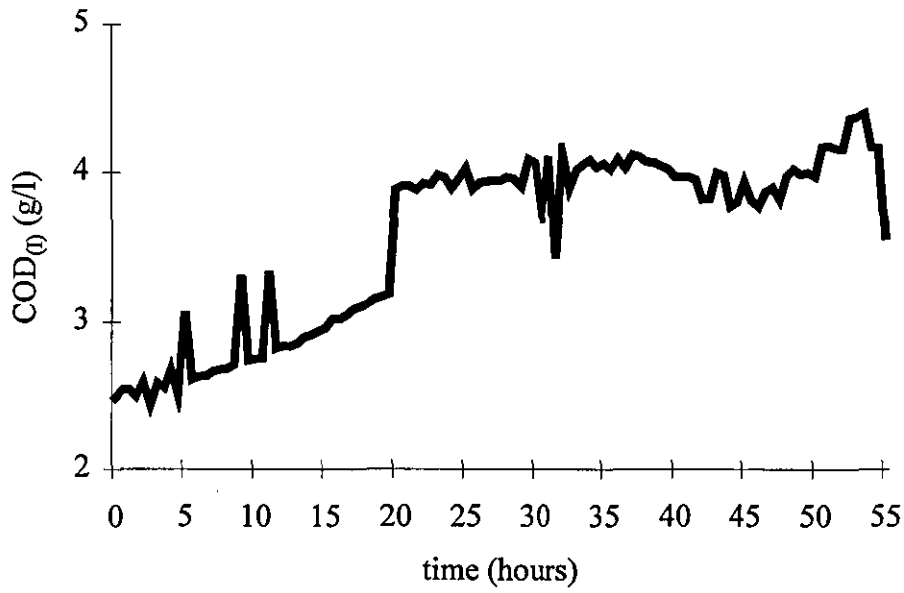(2nd aborted original control)

4-5

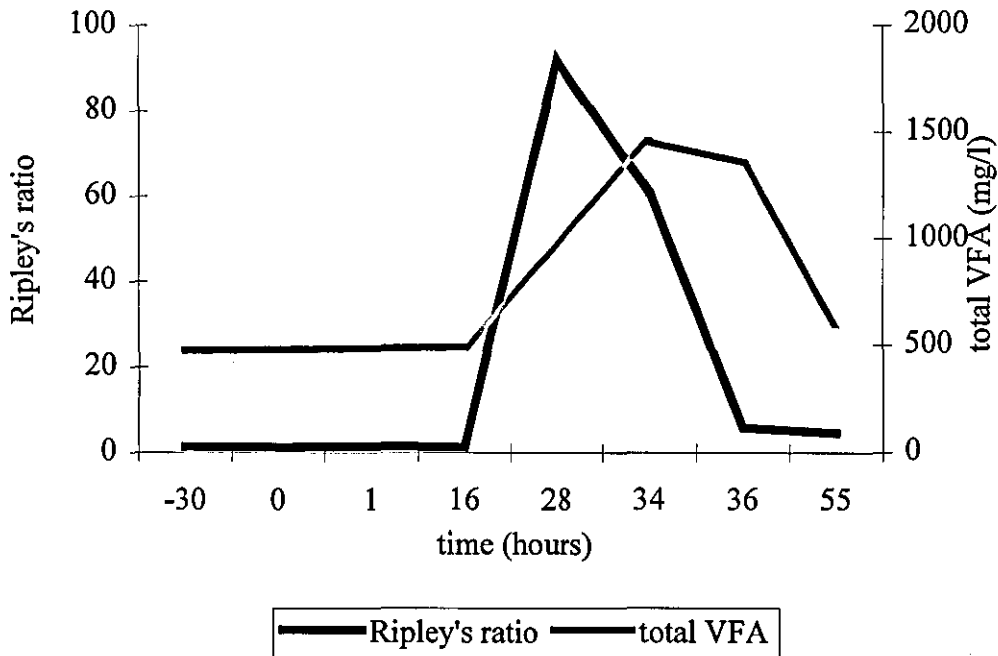Figure 4-10 $COD_{(l)}$ during a 1 g/l pyrazine addition (2nd aborted original control)



Figure 4-11 Ripley's ratio and total VFA during a 1 g/l pyrazine addition (2nd aborted original control)