ANAEROBIC TREATMENT OF HIGH STRENGTH WASTEWATER IN FLUIDIZED BED REACTORS

by

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ABSTRACT

The literature describing the sources and characteristics of waste-waters has been reviewed with particular reference to the meat and dairy industries. Available methods of treatment are examined with emphasis on anaerobic processes. The biochemistry and microbiology of anaerobic degradation is examined in detail.

Laboratory scale fluidized bed reactors were constructed and the performance of the reactors was examined at steady state whilst treating a synthetic milk waste-water at elevated temperature and a meat extract waste-water at ambient temperature. The reactors achieved good COD removals at COD loadings of up to 6 kg m^{-3} d^{-1} at 37°C and 3 kg m^{-3} d^{-1} at ambient temperature.

The performance of the reactors when subjected to transient changes in temperature, influent flowrate, influent COD and pH were also examined. Effluent quality generally deteriorated during a transient change but full treatment efficiency was regained within 24 hours. Long term operation at a low influent pH was considered to be inadvisable.

In a study concerned with optimising the process and evaluation of rapid start-up techniques the addition of methanol and manipulation of the loading regime over the first weeks of operation was found to accelerate the development of an active methanogenic bacterial population. The use of ion exchange resins as a support material was found to be unsuitable due to the lack of biological attachment to the particles.

Two phase anaerobic digestion with an initial acidification reactor followed by a methanogenic fluidized bed reactor has been compared with a single phase anaerobic fluidized bed reactor. Two phase anaerobic digestion was found to produce a superior quality final effluent with lower suspended solids concentrations and greater methane yields. In a study of the degradation of propionate and acetate in the two systems, degradation rates were found to be an order of magnitude greater than in a conventional system. Specific degradation rates indicated that the biomass in a separated phase system was better adapted to volatile acids degradation than in a single phase reactor.

Bacterial activity and substrate composition throughout a fluidized bed reactor were examined. Bacterial activity was found to be greatest in the central portion of the reactor with evidence of partial phase separation at one organic loading. Attached biomass was found to have a greater biological activity than free floating flocs.

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1. INTRODUCTION

Agriculture and the subsequent processing of its products for foodstuffs, represents one of the United Kingdom's largest industries, almost every agricultural product is refined or treated by the food processing industries before it reaches the consumer (Een, 1975). The consumption of water in these industries is very high and consequently they have a waste-water disposal problem. Although statistics show that waste from food industries is a small part of all the waste produced in industrialised countries, problems of disposal may be very acute locally, where food industries are concentrated.

With the increasing costs of water and waste-water treatment these industries have attempted to reduce their water consumption by introducing dry instead of wet methods and by recirculation of used water. Pollution problems may be alleviated by the reclamation of by-products (Jorgensen, 1979, Jones, 1975), however, many food manufacturing plants find it necessary to make a considerable investment in waste-water treatment facilities in order to comply with legal standards for effluent quality (Een, 1975).

Food manufacturing encompasses a wide variety of processes, however, meat and milk production produce waste-waters which typify the problems encountered in these industries.

In 1980, 15.2×10^9 l of milk were produced in the U.K. and virtually all of this was processed in some manner to produce a wide variety of dairy products (Milk Marketing Board, 1980). However, the processing of such large volumes of material inevitably produces a large quantity of waste-water, merely the transport and subsequent storage of the milk produces a waste with a Biochemical Oxygen Demand (BOD_5) of 0.7 kgm^{-3} of milk processed (Royal, 1977).

The effluents from milk processing originate from four sources (Royal, 1977). Washing of process and storage equipment, leaks and spillage, processing losses and deliberate wastage of low value products. Thus the waste-water is largely organic in nature and composed of a solution of milk, milk products and cleaning materials. Shabi and Cannon (1975) reviewed the effluent characteristics from a variety of processes, their results are summarised in Table 1.1 The waste-

Table 1.1. Characteristics of dairy effluent

Type of Plant	Volumetric Load m^3 effluent tonne milk processed^{-1}	BOD Load kg BOD tonne milk processed^{-1}	BOD_5 mg l^{-1}	COD mg l^{-1}	SS mg l^{-1}	pH
Milk Bottling	3.3	4.2	1300	-	-	-
Cheese	6.0	34.0	5700	-	-	-
Casein	1.8	27.0	15000	-	9000-14000	4.0-6.0
Butter	1.9	0.6	300	460	-	-
Mixed production	2.2	2.0	910	1400-3400	500-1000	6.5-9.0

water is extremely strong in comparison to domestic sewage (a typical sewage BOD_5 being 200 mg l^{-1} (Metcalf and Eddy, 1972)). Wide ranges of effluent characteristics are reported even from processes of a similar size and nature due to the differences in water management practised within the dairy.

In 1973, the meat industry in England and Wales handled 2.4×10^7 beasts with an estimated live weight of 2.2×10^6 tonnes. The annual volume of effluent produced has been estimated at 7×10^6 M^3 in addition 3×10^8 broiler chickens are processed anually with an estimated annual effluent discharge of 4.5×10^6 M^3 (Shabi and Cannon, 1975).

The industry may be divided into three main categories:

(i) Slaughterhouses or abattoirs - killing, cleaning, dressing.

(ii) Packing houses - killing, dressing, curing, cooling.

(iii) Processing plants - processing.

The above activities may be combined together in one complex, or exist as separate entities (Anon, 1978).

Effluents from meat and poulty processing industries are similar to domestic sewage, but with a strength of between two and ten times that of normal sewage (Jorgensen, 1979). The chief sources of polluting matter from the industry are: faeces and urine; blood; washings from carcases; floors and utensils; undigested foods; condensate from offal rendering; wastes from cooking; curing and pickling of meat (Dart, 1974). Thus the effluents are characteristically high in BOD, suspended solids (S.S) and grease, and may contain blood, flesh, feathers, manure, dirt and viscera, and be discharged at elevated temperatures. As with effluents from dairies, volumes and strengths of waste-waters may vary greatly due to differing manufacturing processes and local management techniques, the characteristics of a wide variety of metal industry effluents have been reviewed (Shabi and Cannon, 1975) and the data presented in Table 1.2.

Direct discharge of industrial waste-water to rivers, streams or lakes may lead to serious pollution problems with adverse consequences for public health and safety, the effect on aquatic life, the damage to property and other economic, recreational and aesthetic losses. A natural waterway has only a limited capacity for self puri-

Table 1.2. Characteristics of meat processing effluent

Type of Plant	Volumetric Load m^3 effluent tonne live weight^{-1}	BOD Load kg BOD tonne live weight^{-1}	BOD_5 mg l^{-1}	COD mg l^{-1}	SS mg l^{-1}	pH
Poultry	7.0	7.7	470	-	-	-
Beef	11.4	23.2	3600	5400	2240	6.4
General Meat Packing	7.5-20.3	8.1-23.0	2000-3000	-	200-3000	-

fication and may become polluted if this capacity is exceeded or destroyed. A particular problem associated with meat industry wastewaters is the transmission of disease. A number of diseases found in livestock are common to both animals and man, of which anthrax, bovine tuberculosis, salmonella infection and helminthic and fungal infections are of the greatest significance (Anderson, 1977, Hopwood, 1980). In the U.K., about one third of water abstracted for public supply comes directly from rivers. It is therefore clear that proper water management through the treatment of sewage and industrial wastewater, and the control of discharges to sewers and rivers is of the upmost importance (Government of Great Britain, 1978).

Legislation has been developed over the last half century to control the discharges into watercourses. The Public Health Act in 1936 (Government of Great Britain, 1936) empowered the water authority to construct sewers and sewage treatment works and laid controls on the nature of discharges into these sewers. The Rivers (Prevention of Pollution) Acts of 1951 and 1961 (Government of Great Britain, 1951, 1961) prohibited industrial or sewage effluents to pass into watercourses without consent. The 1951 Act applied to new or altered outlets, and the 1961 Act extended the controls to cover all discharges. The 1974, Control of Pollution Act (Government of Great Britain, 1974) contained a number of provisions that considerably strengthened the existing legislation on the control of water pollution to include nearly all discharge to inland and coastal waters. The Act also places powers and duties on the water authorities to forestall and remedy pollution of water, returning the stream and its fauna to its previous condition. If the polluting discharge was within the authorities consent limits then the water authority must bear the costs of the remedial work.

Some countries such as the USA and the USSR have set standards for a wide variety of water pollutants, but most set standards only for BOD_5, SS and in some cases pH, chloride, sulphate and ammoniacal nitrogen (McKnight et al., 1974). In the UK the standards recommended by the Royal Commission on sewage disposal (1898-1915) (20 mg l^{-1} BOD_5, 30 mg l^{-1} SS with a minimum of 1:8 dilution) have been the normal minimum requirement for effluent discharged to inland waters. In the future, greater emphasis will be placed on the use of the receiving water, in accordance with the European Economic Community (EEC) objectives (Department of the Environment, 1978).

Whenever circumstances permit, the discharge of industrial wastes into municipal sewers is generally considered the best practice (Imhoff et al., 1971, Klein, 1966). A large municipal sewage treatment plant can generally treat mixed domestic sewage more economically than any individual establishment treating and discharging its own waste into the nearest watercourse (Imhoff et al., 1971). However, standards are often applied to discharges into sewers, limits of 400 mg l^{-1} BOD_5, 400 mg l^{-1} SS and 100 mg l^{-1} grease are common (Shabi and Cannon, 1975).

Charges are usually imposed by the water authority to cover the treatment costs. The recommended guidelines for the control of and charging for industrial effluent discharged to the sewer produced jointly by the Confederation of British Industries and the Regional Water Authorities includes a charging formula as follows (Dart, 1977)

$$C = R_c + V_c + \frac{O_t}{O_s} B_c + \frac{S_t}{S_s} S_c \qquad - (1)$$

where C = Total charge per m^3 of industrial effluent

R_c = Reception and conveyance charge per m^3

V_c = Volumetric and Primary treatment cost per m^3

O_t = The Chemical Oxygen Demand (COD) (in mg l^{-1}) of the industrial effluent after one hours quiescent settlement at pH 7.

O_s = The COD (in mg l^{-1}) of settled sewage

B_c = Biological oxidation cost per m^3 of settled sewage

S_t = The total SS (in mg l^{-1}) of the industrial effluent at pH 7

S_s = The total SS (in mg l^{-1}) of crude sewage

S_c = Treatment and disposal costs of primary sludges per m^3 of sewage

The advantages of combined treatment include (Byrd, 1961):

(i) industrial wastes are generally more amenable to biological degradation when mixed with sewage, since domestic wastes provide dilution for the industrial wastes and supply deficient nutrients;

(ii) expert attention is available on a large centrally located sewage treatment plant;

(iii) less space at the industrial site is required.

However the industrial waste-water may overload the works and cause operational problems, in addition, by passing the waste effluents over to an outside agency to treat, the costs move outside the dischargers control (Dart, 1977).

The specific characteristics of the waste-water generated by the meat and milk industry have led to the evaluation of a variety of different treatment methods. Generally, the options available to the industry for the disposal of waste-water are:

(i) Disposal with no pretreatment;

(ii) Physicochemical treatment;

(iii) Biological treatment, either Aerobic or Anaerobic.

The disposal of liquid wastes from meat and milk processing to land by spray irrigation or by overland flow has become a common practice in the USA especially rural areas, however, this method is rarely reported in the UK. Disposal is achieved by percolation into the soil and to a lesser extent by evaporation (Gurnham, 1955), since the method relies on large land areas and suitable climatic conditions throughout the year, it is not generally used in this country. The advantages of the system are those of simplicity, low capital cost and the use of grasses grown for animal food. Natural soils have only a limited capacity for absorption and decomposition of organic material, thus there is a limit to the amount of polluting material that may be applied (Imhoff et al., 1971). There is also a danger that groundwater may become contaminated due to excessive application rates.

The 1974, Control of Pollution Act includes legislation to prevent contamination of groundwater and surface waters. Land treatment, however, may be more suitable as a tertiary treatment process (Dart, 1974) or after anaerobic pretreatment which would reduce fats and oils which may clog the soil (Wheatland et al., 1976).

Dennis (1953), has reported a spray irrigation method to dispose of a milk waste in Tennessee. The effluent flowrate was 47.8 m^3 d^{-1} and carried a BOD_5 load equivalent to 31.8 kg d^{-1}. A 0.8 hectare pasture was irrigated for a 24 hour period, followed by 9 days rest. Average application rates for dairy wastes are typically 25 mm over a 24 hr period followed by a 14 day rest (equivalent to an application rate of 17.8 m^3 ha^{-1} d^{-1}) (Borne, 1974).

According to Hopwood (1975) and others (Porges and Struzeski, 1962), one of the simplest methods of disposing of effluents from meat and poultry processing is by spray irrigation. Hopwood (1975) described the use of this system for a turkey processing effluent, at an irrigation rate of 7.78 m^{-3} ha^{-1} d^{-1} of a waste with a BOD_5 of 1100 mg l^{-1}. Porges and Struzeski (1962) reported that approximately 22 hectares are needed to deal with the waste waters produced as a result of processing 50 000 birds per week.

The land disposal of an effluent on a large scale for an anaerobic lagoon treatment process has been reported for a meat packing plant in the USA. Although the BOD_5 of the waste-water was low (25 mg l^{-1}) the effluent contained a high total dissolved solids (950 mg l^{-1}). The design flowrate was between 3250 and 5410 m^3 d^{-1} onto four irrigation sites with a total area of 163 hectares. This provided a nutrient addition to the soil of 28 kg ha^{-1} yr^{-1} of nitro gen and 45 kg ha^{-1} yr^{-1} of phosphorus. It was envisaged that the irrigated area would be sown with the mixture of grasses and soybeans (Dencker et al., 1977).

Effluents from meat and milk processing industries containing pollutants may be classified into three types; suspended, colloidal and dissolved, whereas dissolved matter is difficult and expensive to remove, suspended and colloidal matter may be removed relatively easily using mechanical (or physical) treatment processes. Some form of pretreatment is usually necessary whatever the disposal method used, to prevent process difficulties such as pump and pipeline blockages, in addition appreciable amounts of organic matter may be removed by such processes (Bruce, 1957, Imhoff et al., 1971).

The processes most commonly applied for pretreatment are:

(i) Screening, for removal of coarse suspended solids;
(ii) Grit Chambers, for removal of heavy, settleable solids;
(iii) Skimming (using grease traps or skimming tanks;
(iv) Flotation, chemical precipitation and fine screening, for removal of suspended solids

(Imhoff et al., 1971).

The proportion of settleable solids in waste-waters from different types of milk processing may vary considerably depending on

the products being made. Wastes from distribution centres generally contain little settleable matter and primary sedimentation is not usually necessary before any biological treatment. Wastes from butter and cheese manufacturing, and dried and condensed milk products usually contain sufficient solids to make settlement necessary before secondary treatment, however this does not generally bring large reductions in BOD_5. At a typical factory producing a variety of milk products settlement of waste-waters reduced the BOD_5 from 1420 to 1200 mg l^{-1} (Isaac, 1959).

Waste-waters from the meat industry generally contain higher concentrations of suspended material and an appreciable reduction in BOD_5 may be achieved by such physicochemical processes (Bruce, 1957, Imhoff et al., 1971).

Dissolved air flotation is generally a more efficient method of reducing solids and its use has been widely reported (Grant, 1977). The process involves dissolving between 4 and 6% (v/v) of air in water, beyond its normal solubility at atmospheric pressure; industrially it is common to use pressures between 275 and 345 K Nm^{-2}. Once the water is released to atmospheric pressure the air comes out of solution as small micro-bubbles with a diameter between 80-120 μm. These bubbles attach themselves to hydrophobic surfaces (e.g. fats and greases) as well as suspended solids to provide a buoyant two phase composite which rises to the surface where it may be skimmed off (Ramirez et al., 1976). Dissolved air flotation units usually operate at half the retention time of an equivalent settlement process (Wheatly and Denham, 1980).

In Omaha, eighteen meat packing establishments have arranged to have their effluents treated on a central site using sedimentation tanks followed by air flotation units. The wastewater flow rate averaged 68,190 m^3 d^{-1} with at least 63 tonnes of SS and 36 tonnes of animal fats per day. The sedimentation tanks provided 50% SS and 40% grease removal whilst the air flotation tanks were expected to remove 50% of the influent SS and 60% of the grease (Meier and Korbitz, 1968). A dissolved air flotation process was able to remove 91% of the BOD_5 and 94% of the SS and fats, oils and greases at an American slaughterhouse, where the influent contained 978 mg l^{-1} BOD_5, 573 mg l^{-1} SS and 278 mg l^{-1} fats, oils and greases (Ramirez et al., 1976).

Electroflotation is a similar process to dissolved air flotation. Microbubbles are formed electrolytically at the base of a mid-section of the tank. These then act in the same manner as the air bubbles in the dissolved air flotation process. The passage of an electric current may also have a destabilizing effect on a particle suspension. This is due to the fact that a suspension is often stabilized by particles possessing electrical charges and electrolysis tends to neutralize these charges aiding coagulation (Bockris and Nagy, 1974). Often electrocoagulation is practised in conjunction with electroflotation. In this process coagulent chemicals are formed electrolytically, usually by the dissolution of a metal electrode into an alkaline solution to form hydroxides. This is obviously an expensive method of adding chemicals but it can often be a useful side effect of electroflotation and other electrolytic effluent treatment processes (Bockris and Nagy, 1974).

A direct comparison has been carried out between dissolved air flotation and electroflotation (with and without prior electrocoagulation) treating a beef slaughterhouse waste and a dehairing liquor. There was little difference in performance between the two flotation systems treating the slaughterhouse waste. Both systems being able to remove 90% of the BOD_5 and 94% of the SS. However, once the dehairing liquor was added to the waste, the dissolved air flotation systems' BOD removal was reduced to 48% whilst the electrolytic system maintained a 90% removal. The poor results of the dissolved air system were attributed to the lower surface tension of the dehairing liquor and high turbulence in the flotation tank (Ramirez et al., 1976).

A laboratory experiment has been reported using electrocoagulation followed by electroflotation for the treatment of a dairy waste. Electrocogulation required a current density of $3mAcm^{-2}$ whilst electroflotation required 24 $mAcm^{-2}$ using Duralumin electrodes. Reduction in fats, suspended solids and COD were >95%, 86% and 62% respectively and the effluent polishing was by electrochemical oxidation (Feofanov and Kalinia-Shuvalova, 1977). In a similar experiment electrocoagulation was used for the removal of fats from a dairy waste-water and high fat removal efficiency was achieved (96-97%) with a BOD reduction from 3240 to 180mg l^{-1} (Prsyazhnyuk, 1977). A full scale system has been installed at a Russian dairy for treatment of

its waste-water, primarily for removal of lipids. The waste is first adjusted to pH 6-8 and then aluminium sulphate or calcium hydroxide is added and the waste electro-coagulated. The resulting sludge is dewatered by heat treatment to 4-11% solids and disposed of in municipal sludge digesters (Solymos, 1976).

The addition of varous chemicals to precipitate colloidal and dissolved material from meat processing wastes has been studied. The use of aluminium sulphate to precipitate protein from slaughterhouse effluents has been reported, the waste-water is first adjusted to pH 5.0-5.5 and aluminium sulphate is added at a concentration of 40 mg l^{-1}, typical COD and SS reductions were 62% and 25% respectively (Russell and Cooper, 1981). Lignin sulphonic acid has been used to remove proteins from waste-waters. The effluent is adjusted to pH 3 with the acid and then passed to flotation tanks, 60 to 90% recovery of the protein as a 5 to 15% dry solids sludge was achieved, however, the pH must be readjusted to 7 before being passed to any subsequent biological removal process (Hopwood, 1975).

Chemical coagulation systems have been reported for the treatment of dairy wastes especially for the reduction of fats prior to treatment in a percolating filter, however in the UK the use of such processes is not recommended (Wheatland, 1960).

Waste-waters from both the meat and milk processing industries have the potential for by-product recovery. The flotation methods reported previously do produce a solid containing high concentrations of proteins and these may be used for animal foodstuffs (Grant, 1977). Other processes exist that are specifically tailored to produce high value by-products, these processes include membrane separation techniques and ion exchange systems.

One of the more severe treatment problems encountered with the dairy industry that may be treated using these methods is the disposal of whey. This by-product from cheese manufacture contains 5% lactose, 0.8% protein and 0.8% minerals (Forbes, 1974). In the past it was common to feed whey to pigs; however, with the advent of plants producing up to 9×10^5 l of whey per day, it is now impossible to dispose of it fully using this method due to difficulties with transportion. Some companies have recovered the lactose or have

concentrated the whey and dried it to produce a solid with approximately 12% protein but with a similar concentration of minerals which affects the palatability and drying properties of the solids. Ultrafiltration is a process which may be used to concentrate the protein whilst selectively allowing the passage of lactose and minerals. A 20 fold concentration of whey with respect to protein would produce a solids (after spray drying) of 65% protein, 30-32% lactose and 3% minerals (Forbes, 1974). Moreover, using these methods it is possible to reduce the BOD_5 of the whey stream from 20 g l^{-1} to 50 mg l^{-1} (Ericksson, 1974).

Whey may also be demineralised by a process which utilizes both cationic and anionic ion exchange resins. After passing through a bed of each type of resin the treated whey is dried to a solid containing 13% protein, 86% lactose and 1% minerals which may be used in a variety of food products (Hervé, 1974).

An ion exchange resin treatment process has been developed for the removal of proteins from waste-waters. Whereas conventional resins have a negligible capacity for proteins, new resins have been developed that have capacities of up to 0.5 g of protein per gram of resin. Absorbed protein is easily desorbed by washing with alkaline sodium chloride. The method has been reported for the treatment of both milk and meat processing waste-waters (Palmer, 1977, Grant, 1977). The process is not an economic method of organic matter removal, however as the resin can be made selective for individual proteins it is potentially useful for the preparation of high value products such as bovine serum albumin and various enzymes (Grant, 1977).

Physico-chemical pretreatment cannot ensure an adequate degree of purification and as a consequence additional treatment processes have to be used. Secondary treatment is generally necessary for wastes containing appreciable concentrations of dissolved or colloidal organic matter, since soluble substances are generally not removed by primary treatment and may be a major source of pollution. The most commonly used secondary treatment method is biological treatment. This is defined as the removal of biodegradable material due to the action of micro-organisms (Curtis, 1970, Imhoff, 1971).

Biological treatment may be divided into two distinct types; aerobic and anaerobic. Aerobic biological methods of treatment are those where the micro-organisms responsible for purification require the presence of free or molecular oxygen (Klein, 1966). Anaerobic treatment does not require the presence of oxygen and will be described in detail later.

The organisms responsible for aerobic treatment processes possess the ability to decompose complex organic material and to use the energy so liberated for their cellular functions; reproduction, growth and maintenance. The part of the organic material used to produce energy is converted to stable end products such as carbon dioxide, water and nitrate, whilst the remainder is used to maintain existing cells or converted to new cells. Oxygen must be supplied continuously during the aerobic process since it acts as the terminal hydrogen acceptor for the oxidation of organic material and it is during this hydrogen transfer that there is a liberation of the energy which is used for synthesis and maintenance of cellular material (Imhoff, 1971, Isaac, 1959).

The micro-organisms responsible for aerobic decomposition of organic wastes include a complex and interlocked community of many different species. Bacteria comprise the dominant group and are of most importance in the decomposition process. Fungi, yeasts, algae and protozoa are the most common other groups of micro-organisms (Winkler, 1981). For successful growth of micro-organisms the presence of certain inorganic elements is necessary, particularly nitrogen and phosphorus. The cleaning agents used in dairies elevate the phosphate concentrations (Brown and Pico, 1979), whilst meat processing effluents are rarely deficient in nutrients (Gurnham, 1955).

Aerobic biological filters have been widely used in waste-water treatment since early this century and have acquired a reputation for stability of operation, simplicity of design and requiring a relatively unskilled level of operating staff (Winkler, 1981). Distinction may be made between low and high rate filtration, the low rate process passes the waste-water through the filter bed with little or no recycle, the rate of application is low enough to ensure almost complete decomposition of the organic material. Therefore the level of solids discharge is low and little sludge is produced. Hydraulic

loadings are typically in the range 0.07-0.15 $m^3\ m^{-2}\ h^{-1}$ and BOD_5 loadings in the range 0.08-0.4 kg $m^{-3}\ d^{-1}$ (Clark and Viessman, 1965). In a high rate process only a limited amount of biomass is built up on the surface of media, therefore, little oxidation and stabilization is achieved and large recycle flows must be used. Hydraulic loadings are typically in the range 0.39 to 1.17 $m^3\ m^{-2}\ h^{-1}$ and BOD_5 loadings between 0.4 to 1.12 kg $m^{-3}\ d^{-1}$ (Clark and Viessman, 1965).

Low rate biological filters were the first systems to be used for treating slaughterhouse waste-waters (Anderson, 1977), in conjunction with grease and SS removal processes this has been found to be a dependable treatment method for meat packing wastes, especially for large installations. Experiments have shown that biological low rate filters treating milk wastes soon become blocked at the surface by heavy accumulations of biological film and fat (Wheatland, 1974) causing a condition known as ponding. It is now generally accepted that low rate filtration cannot be used successfully for the treatment of milk wastes without prior treatment to remove fat and protein. The only exception is when the waste-waters are discharged intermittantly and the effluent is continuously recycled. This type of plant, however operates in a similar manner to the alternating double filtration (ADF) process (Isaac, 1957; Wheatland, 1974).

Low and high rate filters have been reported for treatment of meat processing and poultry wastes. A poultry packing waste-water has been treated by low rate filtration, the system operated with a 2:1 recycle, at a BOD_5 loading of 0.21 kg $m^{-3}\ d^{-1}$ and was able to produce an effluent with a BOD_5 of 15 mg l^{-1} and SS of 23 mg l^{-1} (Hopwood, 1975). However, high rate filtration using plastic type media is more economic and requires less land area and has proved more popular for recently constructed plants. High rate filtration can give excellent results providing less than 90% removal is required (Hopwood, 1975).

High rate filters are most effectively used as the first stage of a two stage biological process, since by themselves they cannot be economically used to produce the effluent quality required for discharge to a watercourse (Wheatland, 1974). The use of plastic media in high rate filters can considerably increase their capacity. Imperial Chemical Industries have described a number of plants using towers of 'Flocor' plastic media for partial treatment of dairy wastes

which achieve 60% removal of BOD_5 at BOD_5 loadings in the range 2.4 to 3.0 kg m^{-3} d^{-1} (Borne, 1974). Partial treatment of slaughterhouse and meat processing wastes with Cloisonyle high rate plastic filters has been reported (Shabi and Cannon, 1975) with removal efficiencies averaging 75% at mean filter BOD_5 loadings of 8.6 kg m^{-3} d^{-1}. The high efficiencies were attributed to the high specific surface of the media (220 m^2 m^{-3}), optimum operating temperatures (25-30°C) and the pretreatment (primary settlement, grease trap and balancing tank).

Alternating double filtration is a development of the conventional filtration process and has been used widely for the treatment of both meat and milk processing effluent (Anderson, 1977, Wheatland, 1974). Two filters are operated in series, the first being loaded at a high rate and its effluent after settlement is applied to the second filter. The film growth on the first filter is rapid and every 1 to 7 days before blockage occurs the order of the filters is reversed and the film on the former primary filter disintegrates rapidly. The process can raise the BOD_5 loading rate to over 0.25 kg m^{-3} d^{-1} (Mara, 1980). ADF treatment has been reported for the treatment of settled slaughterhouse waste-waters by Wheatland (1968). The process proved effective, with a BOD_5 reduction from 1260 mg l^{-1} to 10 mg l^{-1}. Raw waste-water was diluted with recirculated effluent such that the filter received a waste BOD_5 of 650 mg l^{-1} at a loading of 0.28 kg m^{-3} d^{-1}.

The ADF process is one of the most successful biological systems for the treatment of dairy wastes (Issac, 1957). The recommended BOD_5 design loading for an ADF process is 0.3 kg m^{-3} d^{-1} in the two filters together (Borne, 1974, Wheatland, 1974). This corresponds to a hydraulic loading of 1 m^3 m^{-3} d^{-1} when the waste-water has a BOD_5 of 300 mg l^{-1}. Several plants in the UK now use ADF and the performance of four of these is given in Table 1.3.

Another fixed film biological process is the Rotating Biological Contactor (RBC). This consists of a shaft supporting circular plastic (or another material) plates, immersed approximately 40% in a contoured tank and which is slowly rotated by power driven equipment. Micro-organisms grow on the disc surfaces, which are spaced such that during submergence waste-water can enter between the surfaces and when they are rotated out of the tank air enters the voids whilst the liquid runs over the biological growth. Excess microbial

Table 1.3. Mean operational conditions of four ADF plants treating dairy wastes

Plant	A	B	C	D
Volume of waste $m^3 d^{-1}$	590	91	272	181
BOD of waste mg l^{-1}	600	300	250	700
Recirculation ratio raw-recirculated	1:1	2:3	1:1	1:3
BOD loadings g m^{-3} d^{-1}	214	41	63	60
Effluent BOD mg l^{-1}	8	3	4	4

solids slough from the media and are carried out in the effluent for gravity separation in a final clarifier (Barnes et al. 1981). Although RBCs were developed in 1900 and tested in the USA during the 1920s using metal discs the results were not encouraging. However, during the 1960s further research continued using plastic discs (Antonie and Welsch, 1969, Birks and Hynek, 1971). The power requirements for the process are considerably less than those of other aerobic processes and there is a saving on capital investment as no recycle lines or pumps are required (Chittenden and Wells, 1971).

An RBC unit has been used to treat an effluent from a slaughterhouse which had been pretreated in anaerobic lagoons, a three stage system was used to treat up to 38 m^{-3} d^{-1} of a waste with an average BOD_5 of 250 mg l^{-1}, total BOD_5 removal was approximately 47% at a flow rate of 38 m^3 d^{-1} (corresponding to a disc area loading of 0.3 m^3 m^{-2} d^{-1}) and 83% at 19 m^3 d^{-1} (Chittenden and Wells, 1971). In another system an RBC was evaluated for secondary treatment of an abattoir and meat processing effluent. Primary treatment was by dissolved air flotation and produced an effluent with an average BOD_5 of 650 mg l^{-1} and SS of 450 mg l^{-1}. The system was tested at three different hydraulic loadings of 0.112, 0.53 and 1.06 1 m^{-3} d^{-1} and achieved average BOD_5 removals of 95%, 83% and 64% respectively. The effect of shock loading was studied by reducing the flow by 75% for

two days and then returning the flow to its normal value, no detrimental effect on effluent BOD_5 was observed (Johnson and Krill, 1976).

Prior to 1974 it had been reported that no RBC unit was in operation at a UK dairy (Wheatland, 1974), however, some units have recently been installed (Anon, 1981), the method has, however, been used in the USA for treatment of dairy wastes for some time (Birks and Hynek, 1971). In one such unit the waste-water was first held in an anerobic stage which helped degrade the fats and oils and then passed on to a four stage RBC unit. The typical waste strength was 1540 mg l^{-1} COD, (1000 mg l^{-1} BOD_5) at an average flowrate of 11.3 m^3 d^{-1}. The unit was able to provide 85% COD reduction (75% under shock loading conditions) (Birks and Hynek, 1971). A two stage RBC unit with intermediate settling tanks was used to treat wastes from a dairy process; the unit was able to remove up to 80% of the COD at a loading of 6.5 kg m^{-3} d^{-1}. The addition of ammonium hydrogen orthophosphate was required as a nutrient at high loadings (Antonie and Welch, 1969).

The rate of organic stabilization in an RBC system is generally limited by oxygen flux rather than substrate diffusion into the film (Huang and Bates, 1971). The oxygen flux may be increased by increasing the rotation speed but at the expense of a higher power consumption and the high hydraulic shearing forces tend to interfere with the development of a satisfactory biomass; for this reason a recommended maximum peripheral disc speed of 18 m min^{-1} is suggested. Another method of increasing the oxygen flux is to raise the oxygen partial pressure, either by pressurising the unit with air or by using a pure oxygen atmosphere. An experiment has been reported that compared the effect of these modifications on an RBC system treating a synthetic milk waste. As well as increasing the treatment capacity of the system pressurisation also improved the settling properties of the sludge. The use of pure oxygen produced a sludge that was dense and free of filamentous growths, however, the high oxygen concentration tended to inhibit nitrification (Huang and Bates, 1971).

The activated sludge process is the conventional alternative to biological filtration and has been successfully applied to the treatment of both meat and milk processing waste-waters (Steffen, 1968; Borne, 1974). Activated sludge plants generally have a lower capital cost than percolating filters and use less land, but may have a higher

running cost and require more skilled operators (Dart, 1974). A number of variations of the basic process have been developed which give the process a versatility which enables the system to be adapted to a wide range of operational circumstances (Winkler, 1981). In this process settled waste-water is led to an aeration tank where oxygen is supplied either by mechanical agitation or by diffused aeration. The waste-water is brought into contact with a mixed microbial population in the form of a flocculent suspension (the 'activated sludge'). Activated sludge acts on the waste-water by two distinct mechanisms, adsorption and oxidation. The gel structure of the zoogloeal bacterial floc is capable of adsorbing dissolved, colloidal and coarse suspended solids which are then subsequently oxidised. For successful operation of an activated sludge process the adsorption and oxidation reactions must be maintained in proper balance (Issac, 1957). The biomass which grows as part of the suspended solids is removed in a high rate secondary sedimentation tank. In order to maintain a high biomass concentration in the aeration tanks (2000-8000 mg l^{-1}) most of the sludge is recycled from the sedimentation tank to the aeration tank inlet. The supernatant is discharged as the final effluent (Dart, 1974; Mara, 1980).

Klein (1957) reported the use of the activated sludge process for the treatment of meat industry waste-waters in Chicago as early as 1916 and quoted a typical example of an American plant operating in 1938 which gave a BOD reduction from 758 mg l^{-1} to 9 mg l^{-1} (99.8%) and SS reduction from 1000 mg l^{-1} to 20 mg l^{-1} (98%). A more modern plant has been described by Stacey (1975), prior to activated sludge, treatment is carried out in the form of screening, balancing and grease removal by on-site grease traps followed by primary sedimentation. Reductions in BOD_5 from 690 mg l^{-1} to 21 mg l^{-1} and SS from 400 mg l^{-1} to 19 mg l^{-1} were reported.

Activated sludge effluents from the meat industry with a BOD_5 of less than 10 mg l^{-1} and an SS of over 40 mg l^{-1} are frequently encountered, this is due to the high grease concentrations of the waste which tend to interfere with settlement (US Environmental Protection Agency, 1971). This suspended solids figure is rather high for discharge to an inland waterway thus some form of tertiary treatment is required.

Saal (1977) described an activated sludge treatment system designed for a dairy plant effluent containing cottage cheese acid whey. This utilised high concentrations of lactose degrading bacteria obtained from the plants milk centrifuges which were added to the oxidation tank to increase the efficiency of the treatment system. The BOD reduction was from 15,000 mg l^{-1} to less than 300 mg l^{-1} (98%).

In the UK the use of conventional activated sludge processes for the treatment of dairy wastes is not favoured, experimental studies carried out in the 1930s on milk and whey washings showed that the performance of the process was influenced by the weather conditions, during cold weather the period of aeration had to be increased (Wheatland, 1974). Although the process can give favourable results if care is taken with process control, dairy wastewaters are more often treated by modifications of the basic activated sludge process (Borne, 1974).

Extended aeration is a common treatment method for food processing wastes as it offers certain advantages over conventional activated sludge (Klein, 1966). The extended aeration process operates on the principle of providing sufficient aeration time for oxidising the biodegradable portion of the sludge produced from the organics removed in the process. By the use of aeration periods of the order of 24 hours and a high sludge return rate (up to three times the volume of incoming waste-water) it is possible to achieve extensive oxidation of the activated sludge solids, such that the surplus sludge problem is virtually eliminated (Jorgensen, 1979).

A recently developed activated sludge system operating on the principles of extended aeration is the oxidation ditch. The waste-water is fed to mixed liquor in the ditch, where it is mechanically aerated using a caged rotor. The effluent is clarified and the settled sludge returned to maintain the desired Mixed Liquor Suspended Solids (MLSS) concentration. Dairy waste-waters have been successfully treated in oxidation ditches. The operation was on a fill and draw system and after sufficient time was provided for oxidation and settling the effluent was drawn off (Barnard, 1978). Borne (1974), has given data on the performance of oxidation ditches at Dutch dairies. At BOD_5 to sludge loadings of 0.05 kg kg^{-1} d^{-1} and 4000 mg l^{-1} MLSS the COD and BOD_5 of the wastes were reduced from 1700 mg l^{-1} to 50 mg l^{-1} and from 1000 to 10 mg l^{-1} respectively.

The oxidation ditch system has been reported for the treatment of meat processing waste-waters. The system consisted of screening, grit separation, settling and flotation for grease and solids reduction followed by two independent oxidation ditches. The first ditch received 35% of the total flow and operated at a sludge loading of 0.26 kg kg^{-1} MLSS and a detention time of 36 days. The COD removal averaged 87.3%, BOD_5 94.8% and grease 93.9%. The second ditch received the remaining 65% of the waste-water and operated at a loading of 0.56 kg kg^{-1} MLSS and a detention time of 1.9 days. COD removal was 53.2%, BOD_5, 67.1% and grease 6.6% (Paulson et al., 1972).

The contact stabilization process is another modification of the conventional activated sludge process which was developed to take advantage of the adsorptive properties of the activated sludge. The two stages of BOD removal are separated, the first absorptive phase taking place in a contact tank. The sludge is then separated from the treated effluent by sedimentation and then aerated in a stabilization tank where oxidation and metabolic growth occur (Metcalf and Eddy, 1972). Its value in industrial waste-water treatment is limited largely to wastes in which the organic material is not predominantly soluble. Aeration volume requirements are approximately 50% of those for a conventional activated sludge process (Mara, 1980, Metcalf and Eddy, 1972). The process has been used for meat processing waste-waters, but often an equalizing tank is required to moderate the effects of intermittent flow conditions (Willoughby and Patton, 1968). A treatment system has been described by Litchfield (1975) consisting of a rotary screen, dissolved air flotation, contact stabilization and final clarification. Removals of 99% BOD, 98% SS and 98% oil and grease were reported at an unspecified plant loading.

Milk waste with an average BOD_5 of 1500-2200 mg l^{-1} has been treated with the contact stabilization method on a pilot plant scale. The average hydraulic retention time (H.R.T) of the mixed liquor was 0.8 hours and of the recycled sludge in the aeration zone 3.3 hours. The plant operated at a BOD_5 sludge loading of 0.56-1.12 kg kg^{-1} d^{-1} and was designed for a BOD_5 removal of 60%. Sludge production was 0.49 kg kg^{-1} BOD_5 removed.

Wheatland (1967) examined the performance of the process to treat effluents from a factory producing condensed milk and milk

powder. The waste-water had a BOD_5 of 1500 mg l^{-1}. The plant operated at a BOD_5 loading of 0.93 kg kg^{-1} d^{-1} with a HRT of 1.6 hours in the contact tank. The plant achieved a BOD reduction of 67% with ultimate disposal to a municipal sewer.

Other modifications of the activated sludge process which have been reported for the treatment of food processing wastes include the high rate activated sludge process (Butts et al., 1977; Tenney et al., 1963), pure oxygen activated sludge (Bebin, 1976; Tolaney, 1975) and the deep shaft process (Bolton et al., 1976). These are all, however, fairly recent developments and little information is available regarding their application to meat and milk processing waste-waters.

Anaerobic treatment of food industry waste-waters is not a widespread practice, it is generally not considered suitable due to its low rate of organic removal and its extreme sensitivity to process fluctuations (Jewell et al., 1981). In aerobic systems oxygen transfer to the liquid phase is generally the rate limiting stage (Forster, 1980), high rate aerobic systems require the use of pure oxygen which not only adds to the treatment costs but places a heavy reliance on an external source of supply for a key element of the process (Forster, 1980). High strength waste-waters require such long residence times or high rates of aeration so that for increasing waste strength anaerobic processes become more economical than aerobic systems. Cillie et al. (1969) examined the operating costs of waste-water treatment systems and concluded that for waste-waters with a COD of 4000 mg l^{-1} or more anaerobic processes are the cheapest option whilst at a COD of 20,000 mg l^{-1} anaerobic systems cost a quarter of equivalent aerobic processes. Cillie et al. (1969) only considered conventional low rate reactors in this analysis, with the development of new high rate reactor types even dilute wastes may be treated economically (Jewell et al., 1981; Wheeldon and Bayley, 1981)

Anaerobic digestion is a complex process involving various groups of organisms including bacteria (Toerein and Hattingh, 1969) fungi (Cooke, 1965) and protozoa (Lackey, 1949) which have all been observed in the digestion process; however only bacteria are considered to be present in sufficient numbers to have a significant role in treatment (Toerein and Hattingh, 1969).

The anaerobic process may be arbitrarily divided into two phases; the non-methanogenic phase where complex organic compounds are hydrolyzed and fermented into simple compounds, usually short chain fatty acids, and the methanogenic phase where methane is produced from simple organic compounds (Toerein and Hattingh, 1969). The biochemical transformations in each of these phases are performed by two distinct groups of bacteria generally termed the acid formers and methane formers. It has recently been shown that there is another important group of organisms, the obligatory hydrogen producing acetogenic (OPHA) bacteria, which produce acetate from higher molecular weight fatty acids (Verstraete et al., 1981).

The non-methanogenic bacteria can utilize many complex organic substrates. Lipids (McCarty et al., 1962), proteins (Lackey and Hendrickson, 1958) and carbohydrates (Kotzé et al., 1968) are all successfully degraded to short chain organic acids. These diverse reactions require many different types of bacteria, the presence of different bacterial groups have been demonstrated by many authors (Toerein and Hattingh, 1969). Non-methanogenic bacteria are mainly obligate anaerobes and although facultative bacteria are found they typically account for less than 10% of the population (Toerein et al., 1967).

It is presently thought that methanogenic bacteria can utilize only formate, acetate, methanol, hydrogen and carbon dioxide as substrates (Balch, 1979) and thus the action of the OHPA bacteria is essential in breaking down longer chain organic acids to acetate (Kaspar and Wuhrmann, 1978a). It has been estimated that 54% of the acetate and hydrogen is formed through the action of the OHPA bacteria (Kaspar and Wuhrmann, 1978a). These two groups of bacteria must grow in close association with one another since the OHPA bacteria depend on the methanogens to remove the hydrogen they have produced to maintain ideal thermodynamic conditions (the pH_2 of an anaerobic system should ideally be maintained below 10 Nm^{-2} (Verstraete et al., 1981)). Although the methanogenic bacteria are generally considered to be the rate limiting step of the soluble phase of anaerobic digestion the OHPA bacteria generally have far greater doubling times (typically 2-6 days (McInerney et al., 1979; Boone and Bryant, 1980) than the methanogenic bacteria (0.2-2.0 days (Ghosh and Klass, 1978)) thus maintaining favourable conditions for growth of the OHPA bacteria is of

the utmost importance. A summary of the anaerobic digestion process is shown in Figure 1.1.

Both the OHPA and the methanogenic bacteria are obligate anaerobes, their precise physiological characteristics are difficult to define as it is hard to obtain pure cultures. However several methanogenic bacteria have been identified and they are listed in Table 1.4. (Mosey, 1982).

Methane is produced by two distinct mechanisms, approximately 70% originates from acetate;

$$CH_3COOH \longrightarrow CH_4 + CO_2$$

Stadtman and Barker (Stadtman and Barker, 1949) concluded from tracer studies that the methane was formed entirely from the methyl group and carbon dioxide from the carboxyl carbon of the acetate molecule.

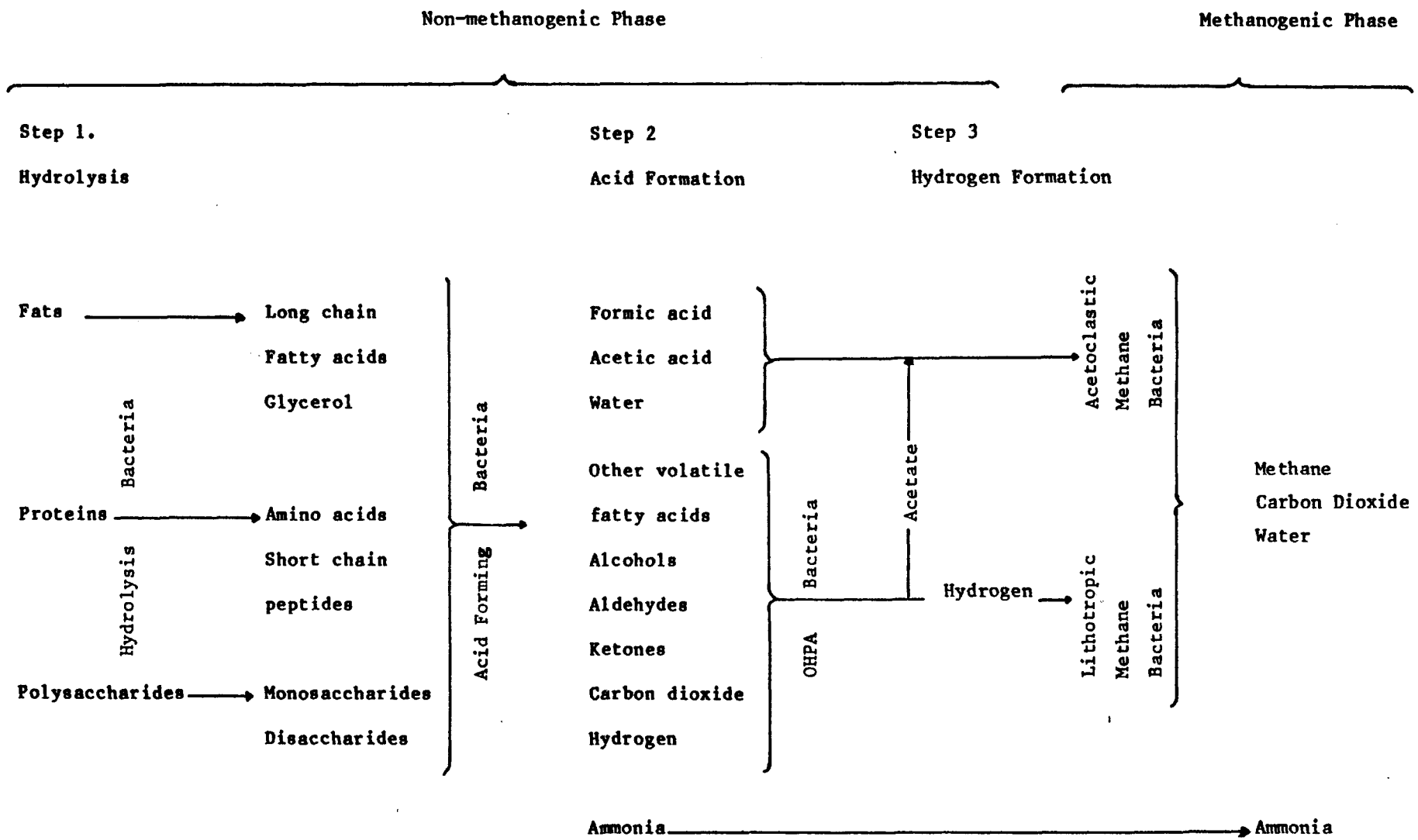
The remaining 30% of the methane is formed by the reduction of carbon dioxide;

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

It is the trace concentrations of hydrogen in an anaerobic digester that play an important role in determining the balance between the various biochemical reactions. The formation of pyruvic and acetic acid from complex organics and the degradation of butyric and proprionic acids to acetic acid are both retarded by increasing concentrations of hydrogen (Mosey, 1982). This regulation of the internal metabolism of the acid forming bacteria may be illustrated by examining the anaerobic degradation of glucose during an organic overload. The acid forming bacteria respond rapidly to the shock of producing large quantities of acetic acid;

$$C_6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH + 4H_2$$

This decreases the pH, inhibiting the action of the bacteria and liberates large quantities of hydrogen. The increased hydrogen partial pressure acts on the system in two ways, it slows the rate of acetic acid production and diverts part of the acetic acid production



1.1. Anaerobic degradation of organic material.

Table 1.4. Taxonomy of the methanogens (Balch, 1979)

Genus	Species	Substrates for growth and methane production
Methanobacterium	formicicum	$H_2 + CO_2$ formate
Methanobacterium	bryantii	$H_2 + CO_2$
Methanobacterium	bryantii strain MoHG	$H_2 + CO_2$
Methanobacterium	thermoautrophicum	$H_2 + CO_2$
Methanobrevibacter	ruminantium	$H_2 + CO_2$ formate
Methanobrevibacter	arboriphilus	$H_2 + CO_2$
Methanobrevibacter	arboriphilus strain AZ	$H_2 + CO_2$
Methanobrevibacter	arboriphilus strain DC	$H_2 + CO_2$
Methanobrevibacter	smithii	$H_2 + CO_2$ formate
Methanococcus vannielii		$H_2 + CO_2$ formate
Methanococcus voltae		$H_2 + CO_2$ formate
Methanomicrobium mobile		$H_2 + CO_2$ formate
Methanogenium cariaci		$H_2 + CO_2$ formate
Methanogenium marisnigri		$H_2 + CO_2$ formate
Methanospirillum hungatii		$H_2 + CO_2$ formate
Methanosarcina barkeri		$H_2 + CO_2$ methanol acetate
Methanosarcina barkeri strain 227		$H_2 + CO_2$ methanol acetate
Methanosarcina barkeri strain H		$H_2 + CO_2$ methanol acetate

to butyric acid. This reduces the acetic acid load on the system and provides time for the acetoclastic bacteria to metabolize the acetic acid. Under these conditions the digester is only in a mildly overloaded condition and will recover usually without pH control (Mosey, 1982).

However, under more severe conditions the increased concentration of hydrogen changes the thermodynamic conditions of the system to make the production of propionic acid more favourable.

$$C_6H_{12}O_6 + 2H_2 \longrightarrow 2CH_3CH_2COOH + 2H_2O$$

This reduces the hydrogen partial pressure and enables the acid forming bacteria to continue to produce acids thus further decreasing the pH of the system. The acetogenic bacteria are unable to utilize the accumulated propionic acid as the hydrogen partial pressure is too great, thus there is the possibility of a total failure of the digestion as the OPHA bacteria may be washed out of the system before the accumulated hydrogen is consumed by the lithotropic methane bacteria. This situation is unusual since hydrogen removal is rapid, in a typically loaded digester the hydrogen removal rate is only 1% of the maximum possible (Mosey, 1982, Kaspar and Wuhrhmann, 1978a).

Gas formation is inhibited by many substances in particular certain heavy metals such as cadmium, copper, chromium, zinc and iron and certain organic compounds such as chloroform (Mosey and Hughes, 1975; Mosey et al., 1971). Low concentrations of iron (0.2-2 mM) have, however, been shown to stimulate methane production especially in conjunction with sulphate ions (Hoban and Van den Berg, 1979; Van den Berg et al., 1980).

The somewhat delicate nature of the anaerobic digestion process has restricted its use for the treatment of industrial waste waters. The only established process is the anaerobic lagoon which is simply an open pond loaded to such an extent that anaerobic conditions prevail throughout the liquid volume. Excess undigested grease floats on the surface forming a natural cover for retention of heat and strict anaerobic conditions. Typical BOD loadings are low, typically in the range 0.16-0.4 kg m^{-3} d^{-1} with retention times of 4 days or more (Clark and Viessman, 1965). Anaerobic lagoons are generally used as a

pretreatment stage before final treatment, although they operate at very low organic removal rates they are reported for treatment of a wide variety of waste waters including fruit processing (Balakrishnan and Lisanti, 1974; Parker, 1966) and meat packing (Saucier, 1969) where the system is often more economical than equivalent aerobic systems (Camin, 1970).

Various basic equations occur frequently in theoretical models of biological unit operations discussed later. The growth rate of the biomass is assumed to be related to the biomass concentration;

$$\frac{dX}{dt} = \mu X \qquad - (2)$$

where X = biomass concentration

μ = specific growth rate.

The specific growth rate is not a constant but is related to the substrate concentration S. Monod (1949) developed a semi-empirical equation which predicts that

$$\mu = \frac{\mu_m S}{K_s + S} \qquad - (3)$$

where μ_m = maximum specific growth rate

K_s = half rate coefficient.

K_s is the substrate concentration at which the specific growth rate is half the maximum rate, thus giving an indication of how easily the substrate is assimilated by the biomass.

A similar relationship is used to relate substrate utilization rate to initial substrate concentration;

$$V = \frac{K_m S}{K_s + S} \qquad - (4)$$

where V = substrate utilization rate

V_m = maximum substrate utilization rate

Monod (1949) found that a constant relationship existed between the mass of bacteria produced and the mass of substrate utilised this led to the definition of the growth yield Y.

$$Y = \frac{\text{mass of organisms formed}}{\text{mass of substrate utilized}} \quad - (5)$$

This relationship may also be expressed as a differential (Moser, 1958);

$$\frac{dX}{dS} = -Y \quad - (6)$$

The growth yield has important implications for the economics of a particular process as it is an indication of the quantity of excess sludge that will be produced and which will need subsequent treatment and disposal.

The simplest reactor type reported for anaerobic degradation is the stirred tank reactor. This has been widely employed for the stabilization of sewage sludge and the treatment of industrial wastes containing high concentrations of solids such as palm oil wastes (Morris, 1979). In this type of reactor the solids retention time (S.R.T) is equal to the H.R.T and hence the use of such reactors for high rate treatment is not possible due to wash-out of the biomass (Atkinson and Davies, 1972). The anaerobic contact (or anaerobic activated sludge) process employs a setting tank after a contact reactor such that a portion of the settled sludge can be recycled (Schroepfer and Ziemke, 1959).

The anaerobic contact reactor has been used for the treatment of a wide variety of waste waters. Schroepfer and Ziemke (1959) evaluated the process for the treatment of packing house fatty acids, domestic sewage, a wood fibre, and synthetic milk waste waters. To aid settling in the second stage a vacuum degasification system was placed between the reactor and the settling tank. Typical BOD removals were between 69.9-97.9% for BOD loadings of between 0.44 and 2.5 kg m^{-3} d^{-1}. BOD removals when the reactors treated a domestic sewage were poorer, 74.5-69.9% for BOD loadings of 0.56-0.94 kg m^{-3} d^{-1}. The reactor configuration is widely reported for the treatment of higher

strength waste waters (Hemens and Shurban, 1959; Van den Berg and Lentz, 1977; Cillie et al., 1969) the treatment of dilute wastes generally being impractical due to the long retention times required (Simpson, 1971).

Anderson and Donnelly (1978a) derived a theoretical approach to predict the peformance of an anaerobic contact system by taking mass balances across the reactor, their reactor system is shown in Figure 1.2.

At steady state these balances reduce to

$$\mu = \frac{1}{\tau_s} + K_D \quad \text{for the biomass} \qquad - (7)$$

and

$$\frac{1}{\tau_s} \cdot \frac{1}{Y} + \frac{K_D}{Y} = \frac{Q\ (S_o - S)}{X\ V} \quad \text{for the substrate} \qquad - (8)$$

where τ_s = sludge age

K_D = endogenous respiration coefficient

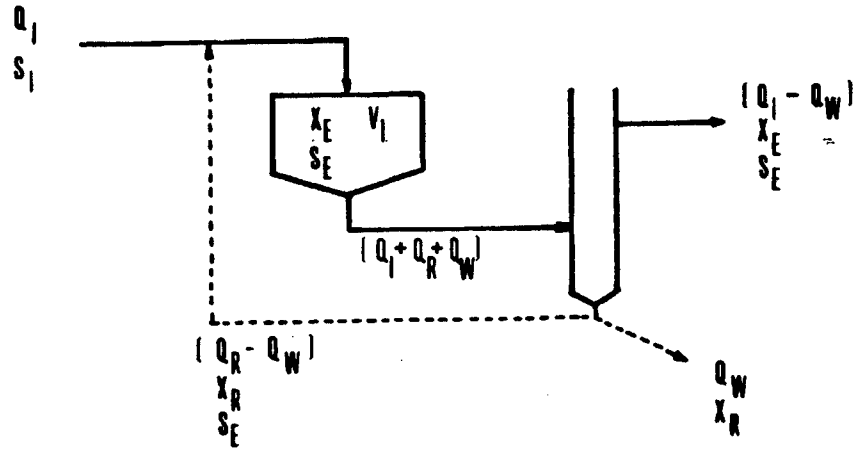


Figure 1.2. Mass balance over the anaerobic contact process

By operating laboratory scale digesters at steady state the kinetic coefficients μ, K_S, K_D and Y may be determined and used in the model to predict unsteady state operation.

Two digester systems were evaluated by this method, a semi-continuous system where sludge is wasted daily and a continuous system where a constant biomass volume was maintained in the settling tank. A simple substrate based on glucose was fed to the semi continuous digester whilst a more complex substrate with 40% of the COD obtained from a meat extract and peptone was fed to the continuous operation. The results obtained are summarised in Table 1.5. together with some comparative aerobic data.

The difference in K_D values for the two anaerobic systems is an indication of the relative biodegradability of the two substrates. It is also important to note the much lower yield coefficients for anaerobic systems as this indicates that smaller amounts of biomass will be produced and hence the sludge disposal problem will be diminished.

Table 1.5. Typical biological kinetic coefficients of aerobic and anaerobic systems

Reactor Type	Substrate Type		K_S mg l^{-1} COD	K_D days	Y mg USS mg COD^{-1}
Continuous Anaerobic Contact	Complex	0.274	2953	0.0215	0.192
Semi-Continuous Anaerobic Contact	Glucose	0.158	212	0.029	0.208
Activated Sludge	Sewage	5.0	40	0.06	0.4
Anaerobic Fluidized BOD	Whey Permeate	N.R.	N.R.	N.R.	0.24

Above a sludge loading of 0.25 kg COD kg VSS^{-1} d^{-1} the settling properties of sludge began to deteriorate and above a MLVSS concentration of 18000 mg l^{-1} separation of the biomass was impaired. These two difficulties are the basic limitation on the ultimate rate of the process (Anderson and Donnelly, 1977).

A novel anaerobic contact digestion system has been described which uses a gas mixed reactor followed by an upflow sludge blanket clarifier (Oleszkiewicz and Koziarski, 1982). The system was used to treat a piggery waste and was operated at COD loadings of up to 38 kg COD m^{-3} d^{-1} whilst still maintaining methanogenic conditions. Satisfactory treatment was obtained at COD loadings of 4 kg m^{-3} d^{-1} and a H.R.T. of 3-5 days. It was found that the effluent quality deteriorated linearily with the increasing organic loading and a close fit to the systems performance was obtained by the following equations

$$S_e = 1.5 + 0.151\ O \qquad - (9)$$

$$N = 89 - 1.01\ O \qquad - (10)$$

where O = organic loading (COD)

S_e = effluent COD

N = % COD removal

Kinetic coefficients were also derived in a similar manner to Anderson and Donnelly (1978a); the growth yield was 0.213 and the endogenous decay coefficient -0.016. It should be noted that the system was operated without sludge recycle which tends to result in higher yield coefficients than systems with recycle (Oleszkiewicz and Koziarski, 1982).

The separation of the biomass from the treated liquor is one of the main problems with the anaerobic contact reactor. To improve separation various modifications have been suggested. One system employs a cold thermal shock, reducing the temperature of the effluent from 35°C to 15°C. This arrests gasification in the settling tank and also encourages flocculation of the solids (Anderson and Duarte, 1980).

Some authors have reported the use of coagulent chemicals (Dague, 1970). A 90% reduction in effluent solids was possible by

treating the effluent with sodium hydroxide to pH 8.3 and then ferrous chloride at concentrations between 60 and 230 mg l^{-1}. An increase in gas production was found due to the increased recycle of active biomass (Dague, 1970).

The Anaerobic Sludge Blanket Reactor (ASBR) eliminates the need for a separate settling chamber and consists of a single reactor vessel, the waste enters at the base of the reactor and passes upwards through the biomass which takes the form of a 'sludge blanket'. Mechanical mixing and sludge recirculation are kept to a minimum to aid settleability of the sludge flocs. Since retention of the sludge depends on an effective separation of the gas produced, a gas-solids separation unit is included in the reactor. The reactor has been employed in laboratory, pilot plant and full scale systems generally treating high strength wastes (Lettinga et al., 1981; Lok, 1978).

Using an 18 l reactor the treatment of a skimmed milk type waste water with a COD of 1500 mg l^{-1} has been reported. COD reductions of 90% were obtained with COD loadings up to 7 kg m^{-3} d^{-1} and sludge loadings between 0.4 and 0.6 kg kg^{-1} VSS day^{-1}, the reactor was operated at 30°C (Lettinga and van Velsen, 1974). A sugar beet waste with a COD of between 5000 and 9000 mg l^{-1} has also been treated by the ASBR, with COD loadings of between 4 and 14 kg m^{-3} d^{-1}, 65-95% COD reductions were achieved (Lettinga et al., 1981; Lettinga, 1978).

Upflow sludge blanket reactors have been used typically for the treatment of high strength wastes at elevated temperatures. Pretorius (1971) reported the application of the process for the treatment of a raw sewage using a laboratory scale reactor followed by an anaerobic filter, both stages had a reactor volume of 8 litres. The digesters were maintained at a constant 20°C and the waste strength was adjusted to a constant COD of 500 mg l^{-1}. COD removals were typically 90-78% at total loadings of 0.25-0.47 kg m^{-3} d^{-1}, typical reactor VSS were 25000 mg l^{-1}. Following the laboratory experiments a small pilot plant was constructed with a reactor volume of 2000 litres, the unit gave almost identical results to the laboratory study. Apart from periodically breaking up the sludge layer in the conical section best results were obtained without mixing.

Somewhat lower removals have been found in a system treating an acetate rich waste water, COD removal was up to 70% without a primary settling tank, the optimum BOD loading for gas production was only 1.6 kg m^{-3} d^{-1}, however since the system was self scrubbing the gas contained up to 99% methane (Godwin et al., 1982).

To overcome the problems of settling and recycling of the biomass inherent in anaerobic free floating systems the anaerobic filter has been developed. This consists of a reactor filled with a coarse packing media such as rock or gravel; as with its aerobic equivalent the reactor name is a misnomer since treatment occurs mainly due to biological action rather than any filtration effect. The waste water enters at the base of the reactor and flows upwards through the filter bed. Anaerobic organisms appear to accumulate in the void spaces between the media as well as becoming attached to the media surface, thus the waste comes into intimate contact with a large active biomass as it passes through the reactor (Young and McCarty, 1969).

The anaerobic filter was initially tested in laboratory scale experiments where it was evaluated for the treatment of two synthetic substrates, a mixed volatile acids waste and a protein carbohydrate waste. The filter was packed with smooth quartzite stones 2.5-3.8 cm in diameter and dispersion rings were placed at 0.3 metre intervals up the column to prevent channelling of the flow. The filter was tested by applying COD loadings between 0.425 and 3.40 kg m^{-3} d^{-1} at an operating temperature of 25°C. The influent was diluted to give various waste strengths from 1500 to 6000 mg l^{-1} COD. BOD removals increased with increasing waste strengths at the same organic loading, highest removals were up to 80% over the range tested (Young and McCarty, 1969). The performance of the reactor could be predicted by the empirical equation;

$$E = \frac{100\ (1-1.8)}{HRT} \qquad - (11)$$

where E = BOD removal efficiency

Plummer et al. (1968) extended this work by using a filter to treat a carbohydrate waste which contained significant concentrations of suspended solids. The filter operated at 35°C and treated a waste with influent characteristics of 1508 mg l^{-1} SS and 8475 mg l^{-1} COD.

The anaerobic filter has also been reported for a wide variety of industrial waste waters including pharmaceutical wastes (Sachs et al., 1982), abattoir wastes (Arora and Routh, 1981), dairy wastes (Patterson, 1975) and vegetable processing wastes (Perkins et al., 1975).

The kinetics of substrate removal in an anaerobic filter employing a large recycle rate have been studied (DeWalle and Chian, 1975) due to the recycle the system was interpreted as a completely mixed reactor. By equating Fick's law of diffusion with the substrate utilization rate equation the following equation was obtained;

$$\frac{d^2S}{dz^2} = \frac{1}{D}\,\frac{UX}{K_s + S} \qquad - (12)$$

This equation does not have a simple solution and was solved by assuming S is either much smaller or larger than K_s. When S is larger and the expression for the thickness of the biofilm layer developed by other workers (Pirt, 1973; Saunders and Bazin, 1973) is substituted the mass transfer rate is given by,

$$\frac{dF}{dt} = k\sqrt{\frac{A}{V}\,Sb} \qquad - (13)$$

where $\frac{dF}{dt}$ = mass transfer rate

Sb = bulk substrate concentration

k = coefficient based on zero order kinetics

when S is much smaller than K_s the mass transfer rate is given by;

$$\frac{dF}{Vdt} = \frac{K_2 A\ Sb}{V} \qquad - (14)$$

where k_2 = coefficient based on first order kinetics.

By examining experimental data the authors found that equation 14 was more applicable, however insufficient data was available to make a final conclusion (DeWalle and Chain, 1975).

Using an anaerobic filter with a substantial amount of recycle enables the process to treat waste waters of a toxic nature which would be difficult to treat anaerobically in a single pass reactor. Chian and DeWalle (1977) used this reactor configuration to treat an acidic waste water with a pH of 5.4 and a COD of 54000 mg l^{-1}. The filter was 55 l in volume and packed with a commercial plastic packing with a porosity of 0.94. Reactor start up was initially attempted without any biological seeding material, however no significant biodegradation was noted. Following this experiment the filter was seeded with active digester sludge and the reactor successfully treated the waste water providing a sufficiently high recycle ratio was maintained. The reactor was evaluated over a range of retention times and it was found that COD removal rapidly decreased from over 95% to 52% when the retention time was less than 7.5 days (Chain and DeWalle, 1977).

Various packing materials have been evaluated for use in the anaerobic filter. These materials include gravel (Sachs *et al.*, 1982), crushed stone (Anderson and Ibrahim, 1978), rashig rings (Plummer *et al.*, 1968), and various commerical packings (Chian and DeWalle, 1977; Anderson and Ibrahim, 1978). Khan *et al.* (1982) compared two packing materials, a non porous anthracite coal and surface active granular carbon particles. The filters were used to treat a stripping bath waste water and a synthetic substrate, a typical influent COD was 1350 mg l^{-1}. It was found that the activated carbon packed filter gave removals superior to the anthracite packed filter (71-74% vs 58-69%), methane yields were up to 100% greater. The ability of the activated carbon surface to protect dense populations of bacteria was considered one of the main reasons for superior performance.

A similar reactor to the anaerobic filter has been described, known as 'the stationary fixed film reactor'. In its simplest form the reactor is merely a vertical glass tube through which the waste water is pumped (Van den Berg and Lentz, 1979b). In a downflow reactor biomass is retained almost entirely as a film on the reactor walls whilst in the upflow reactor biomass accumulates in the reactor as biological flocs. Initial experiments consisted of testing reactors with varying surface:volume ratios. COD removal efficiency increased with decreasing reactor diameter at the same volumetric loading. The reactor configuration was refined to consist of several small tubes contained in a larger vessel. Several materials were tested for use in the reactor including clay, polyvinyl chloride and needle punched polyester (Van den Berg and Kennedy, 1981). Red clay and needle punched polyester were found to be the most effective supports due to the ability of the bacteria to become entrapped on the surface.

Using fired clay support tubes (2.8 cm I.D., 3.8 cm O.D.) contained in a larger glass tube the reactor was able to effectively treat a waste water with a COD of 14000 mg l^{-1} at loadings of up to 17.9 kg COD m^{-3} d^{-1} at 35°C with COD reductions between 78-84%. The reactors were shown to be able to tolerate severe hydraulic overloading for 24 hours without serious problems (Kennedy and Van den Berg, 1982). Operation of the reactors was found to be more efficient when applying intermittent rather than continuous loading (Van den Berg and Kennedy, 1982).

The anaerobic rotating biological contactor (ARBC) is a similar reactor to the aerobic RBC however in its anaerobic mode the disk submergence is greater (>70%) and the reactor is in a closed vessel. The reactor was evaluated in a laboratory scale experiment treating a synthetic waste water with glucose as the sole carbon source (Tait and Friedman, 1980). The reactor consisted of four stages, each with ten 12.7 cm diameter disks constructed from polymethylmethacrylate, the total reactor volume was 5.25 l. During the start up procedure part of the glucose was replaced by methanol in order to encourage the growth of methanogenic bacteria. The reactor was operated over a range of TOC loadings from 1.44 to 12.06 kg m^{-3} d^{-1}. TOC removals varied from 96%-46%, effluent suspended solids were relatively high, between 296-361 mg l^{-1}.

Two approaches were used to describe the performance of the reactor. The first was an empirical solution where;

$$\ln S_e = \ln S_i - K_t T \qquad - (15)$$

where K_t = pseudo first order rate constant.
T = hydraulic residence time.

From the experimental data K_t was found to be $K_t = 0.3744 - 7.96 \times 10^{-5}$ Si. Although this approach gave good agreement with the experimental results it was only considered applicable to this particular reactor.

A different approach was used to develop a more general solution. The removal in each stage is described by;

$$M_N = \frac{kS_i^2}{K^i + S_i} \qquad - (16)$$

M_N = mass of organics removed per stage per unit time
k = rate constant
S_i = substrate concentration entering the stage
K^i = a constant.

This was developed from previous work on aerobic RBCs (Schroeder, 1977).

In the first stage it can often be assumed that $S_i >> K^i$ then the equation may be approximated by

$$Mn = KS_i \qquad - (17)$$

thus K may be calculated from experimental data and an approximation for K^i may be found. The model was found to agree closely with the experimental results however no independent data was available to verify the model.

It has been reported that rotation of the discs in an ARBC has virtually no effect on the efficiency of the process; thus an anaerobic baffled reactor has been developed through which the liquid flows

horizontally and around several baffles which serve to retain the biomass. Little reported information is available for this reactor configuration, however COD reductions of 60-80% for COD loadings of 10- 20 kg m^{-3} d^{-1} have been noted (Josephson, 1982).

The anaerobic treatment of waste-waters in fluidized and expanded bed reactors (AFBR and AEBR) is a relatively new technique in the waste-water treatment field. Fluidized beds can be considered to be a hybrid between fixed film and free floating reactor systems. A fluidized bed reactor consists of a bed of particles contained in a vertical column, through which waste water flows upwards (through the column) at a sufficient velocity to maintain the particles in constant motion, but with the flowrate adjusted to avoid particle carry-over in the effluent. This arrangement provides a large specific surface (m^2 m^{-3}) available for microbial growth as a thin film, typically 3000 m^2 m^{-3} for sand particles (Cooper, 1981). Thus high biomass concentrations may be developed which are not subject to diffusional limitations. An expanded bed reactor is a similar type of reactor except that the bed expansion is limited to approximately 5% and the particles remain in constant contact with one another.

Initial experience with the fluidized bed reactor for waste water treatment applications has been for the denitrification of treated sewage (Jeris et al., 1974; Jeris et al., 1977) and the use of aerobic reactors for COD removal (Cooper and Wheeldon, 1980). The use of the reactor for denitrification has been very successful however the use of aerobic fluidized beds for COD removal has experienced significant problems due to the difficulty in supplying sufficient oxygen to the biomass (Forster, 1980). The anaerobic fluidized bed has no such limitation and has been reported for the treatment of a dilute waste water (Switzenbaum and Jewell, 1980) and a domestic waste water (Jewell et al., 1981). These laboratory scale studies used 1 l volume reactors and were filled with either aluminium oxide pellets or polyvinyl chloride and expended ion exchange resins. In the domestic waste water treatment study (Jewell, 1981) the reactors were operated at 20°C and treated a waste water with an average COD of 186 mg l^{-1} and a suspended solids (SS) of 86 mg l^{-1}. The performance of the AEBR was studied at COD loadings of between 0.65 and 35 kg m^{-3} d^{-1}, effective treatment was obtained up to COD loadings of 4 kg m^{-3} d^{-1}. Above this loading treatment efficiency rapidly declined to less than 50% at

19 kg m^{-3} d^{-1}. Effluent suspended solids were generally very low, below 5 mg l^{-1} but rose rapidly at retention times of less than than 30 minutes.

The results from the synthetic substrate experiments were subjected to a kinetic analysis, the effluent concentration was given by

$$Se = K_1SiB \quad - (18)$$

$$Se = K_2SiA \quad - (19)$$

where B = net specific film growth rate
A = specific film utilization rate
K_1 K_2 = pseudo first order rate coefficients.

These equations are simplified forms of equations 2 and 3 and their pseudo first order nature relies on assuming K_s is high compared to the substrate concentration. Applying the experimental results to these equations gave a reasonably good fit with correlation coefficients between 0.76 and 0.96.

Matsui et al. (1979) reported on the treatment of a dilute waste water in a fluidized bed reactor. COD removals were generally very low (typically 23.8%) but a very high range of COD loadings were tested, between 18.6 and 131.6 kg m^{-3} d^{-1}. The use of particles with a diameter less than 0.42 mm was found to be less efficient due to the inability of biomass to adhere to the surface of the media.

The performance of the anaerobic expanded bed reactor whilst treating a domestic sewage has been studied. The TOC of the influent varied between 40 and 260 mg l^{-1}. It was found that operating under these conditions TOC removal was poor (17-52%) except when the TOC loading was low (<0.5 kg TOC mg^{-3} d^{-1}) and it was considered that under real operating conditions the reactor would be unsuitable for treatment of waste waters of this nature (Rockey and Forster, 1982).

Jewell and Morris (1982) subjected an anaerobic fluidized bed reactor to variations in temperature, flowrate and influent concentration. The substrate was based on glucose with added inorganic nutrients, the reactor was found to have excellent stability with COD

removal efficiency rarely decreasing below 90% even under conditions of combined 25°C temperature shocks with 100% influent COD increases.

The treatment of high strength whey permeate (2000-7000 mg l^{-1} soluble COD) in an anaerobic fluidized bed has been reported. Organic (SCOD) removal rates of up to 19.5 kg m^{-3} d^{-1} were obtained with a soluble COD removal of 70% at 35°C. At 15°C the reactor performance was considerably impaired with an organic (SCOD) removal rate of 3 kg m^{-3} d^{-1} at 50% removal efficiency. The nutrient requirement for the system was much lower than for an equivalent CSTR system thus no extra nitrogen or phosphorus was required. A first order substrate utilization model developed previously (Chen and Hashimoto, 1978) was found to give the most satisfactory prediction of reactor performance (Boening and Larsen, 1982).

$$Se/So = K'/(\tau_s \mu m - 1 + K') \qquad - (20)$$

where K' = a constant
τ_s = solids retention time
μm = maximum specific growth rate

Sutton and Li (1981) used the approach developed by Anderson (1978a) to evaluate the kinetic parameters in a fluidized bed process, the observed values for the reported kinetic values are shown in Table 1.5.

Two sand particle sizes (0.5 and 0.7 mm) were evaluated for use in the reactor. It was found that the smaller particles gave marginally superior COD reductions (68% compared to 63%).

The treatment of a beet molasses waste-water in a fluidized bed reactor has been described by Frostell (1982). The reactor treated a wastewater with an influent COD of 9100 mg l^{-1}. The average COD loading was 22.2 kg m^{-3} d^{-1} achieving a 43% COD to methane conversion. A solids recycle system was necessary to retain the biomass in the reactor (only 59% of the biomass was attached to the support material.

Rittman and McCarty (1980a; 1980b) has examined biofilm kinetics in detail and has used this analysis to compare four different reactor configurations (Rittman, 1982a). The analysis equates mass transport and the film substrate utilization

$$D_f \frac{d^2S_f}{dz^2} = \frac{KX_fS_f}{K_s + S_f} \qquad - (21)$$

and includes a term for mass transfer resistance from the bulk liquid into the biofilm surface.

$$J = (D/L)\ (S-S_s) = K_m\ (S-S_s) \qquad - (22)$$

where L = reactor length.

These equations may be simultaneously solved for J when the other kinetic parameters are known (Rittman and McCarty, 1980a; 1980b). Steady state biofilm thickness was found by assuming that total amount of biofilm mass is equal to that which can be supported by the substrate flux thus;

$$JY = 6X_fL_f \qquad - (23)$$

or $L_f = JY/6X_{cf}$.

General reactor performance is given by a mass balance over a control volume;

$$\frac{dS}{dt} = \frac{-vdS}{dx} + D\frac{d^2S}{dx^2} - aJ - \frac{\varepsilon kXS}{K_s + S} \qquad - (24)$$

These equations were solved numerically by a finite difference method. Five reactor types were compared, a completely mixed reactor and packed and fluidized beds with and without recycle.

The model predicted that a once through fluidized bed reactor would achieve superior performance as the biofilm is evenly distributed throughout the reactor whilst the liquid regime is 'plug flow'. Adding recycle to fixed and fluidized bed reactors makes performance approach that of completely mixed units which had the lowest removal efficiency.

Separated phase anaerobic digestion involves the use of two reactors to separate physically the non-methanogenic and methanogenic phases. The use of two separate reactors allows the two phases to operate at their ideal environmental conditions (e.g. pH, temperature and organic loading), and allows the delicate methanogenic and OPHA bacteria to be protected from process fluctuations. This reactor configuration also enables the components of the effluent from the first stage to be adapted to obtain the best possible substrates for the OPHA bacteria (Verstraete et al., 1981). Since these bacteria have the longest doubling times of the organisms found in anaerobic digestion use of suitable substrates can enhance the possible reaction rates. It has been shown for example that the OPHA bacteria operate more efficiently when treating a single acid substrate rather than a mixed acid substrate (Lescure and Bourlet, 1979).

Phase separation has been achieved by three methods; a dialysis technique (Hammer and Borchardt, 1969; Schaumberg and Kirsch, 1966), inhibition of the methanogenic phase by the addition of certain chemicals (Pohland and Mancy, 1969) or by kinetic controls in each reactor (Massey and Pohland, 1978).

Hammer and Borchardt (1969) utilized two completely mixed reactors separated by a vinyl dialysis membrane. This apparatus was used to determine the oxidation/reduction potential (E_c) and pH for acidification and methane fermentation of digester sludge. Optimum pH conditions were 6.9-7.0 and 7.05-7.2 and E_c -508 to -516 mV and -520 to -527 mV for the acidification and methane formation steps respectively. It was concluded that when an anaerobic digester operated under ideal conditions for the methanogenic phase the acidification step was rate limiting since it only operated at 75% of its optimum rate.

pH optima of 5.8 and 7.8 were found for a mixture of domestic refuse and sewage sludge. Near complete liquefaction was obtained in the range 20-240 kg VS m^{-3} d^{-1} at volatile solids concentrations of 11-13%. Some alkaline pretreatment had taken place previously (Ishida et al., 1979).

By adjusting the residence times and environmental conditions in a reactor, optimum conditions for acid and gas formation may be achieved.

achieved (Pohland and Ghosh, 1971a; Pohland and Massey, 1975).

This concept has been applied to the treatment of a glucose based waste and an effluent from a confectionery industry. With an influent COD of 3581 mg l^{-1} between 54 and 73% acidification was achieved at hydraulic retention times of between 10 and 23 hours in the first reactor. The methanogenic phase reactor operated at longer retention times of between 47.6 and 116.8 hours where conversion of the volatile acids varied between 61 and 19%. By connecting the gas phase of each reactor together improved COD removals were obtained. The biomass from the second stage reactor had poor settling properties and gravity sedimentation was not feasible (Massey, and Pohland, 1978).

Cohen et al. (1979; 1980) studied the anaerobic digestion of a 1% glucose substrate with separated acid and methane production. At a retention time of 10 hours in the acidic reactor over 96% of the glucose was degraded to hydrogen, carbon dioxide, butyrate and acetate at 30°C and pH 6.0 in the methanogenic reactor 98% of the organic substrates were converted to carbon dioxide, methane and biomass at a retention time of 100 hours. Approximately 11% of the glucose fed to the system was converted to biomass. The methanogenic reactor could be organically loaded 270% greater than an equivalent single phase system.

Zoetemeyer et al. (1982a; 1982b) studied the acidification of a 1% glucose solution to evaluate the effect of pH and temperature on the process. At pH 4.5-6.0 the predominant acid produced was butyric acid, however at pH values higher than 6.0 a mixture of acetic acid, ethanol and formic acid was produced. Maximum gas production and bacterial specific growth rate were found at pH 5.8 and 6.0 respectively. Two temperature optima were found for acid production, a mesophilic form at 37°C and a thermophilic peak at 52°C.

Stability of one and two phase systems treating glucose solutions has also been investigated under conditions of organic overloading (Cohen et al., 1981). In a single phase system accumulation of the volatile acids occurred, especially propionic acid, and degradation of these acids took up to 120 hours. Overloading the methanogenic phase of a two phase system with high concentrations of

volatile acids led to an immediate breakdown of the acids within 60 hours, indicating that the two phase system was more stable.

Two phase digestion of activated sludge in completely mixed reactors has been described. Acidification of the activated sludge took place at a pH of 5.7 and an E_c of -240 mV. Acid phase digestion could be operated satisfactorily at sludge loadings between 0.055 and 0.139 kg m^{-3} d^{-1} VS with retention times between 10 and 24 hours. The acidified activated sludge could be gasified efficiently in the methane digester at a retention time of 6.46 days. The performance of the system was favourably compared with a single phase system which operated at a retention time of 14 days (Ghosh et al., 1975).

It is apparent that there is significant potential for the development of high rate anaerobic processes for the treatment of waste-waters which have considerable advantages over their aerobic equivalents. These processes would seem particularly suitable for the treatment of higher strength waste-waters due to the high half rate coefficients (K_s) encountered in anaerobic degradation and the favourable economics of treatment at these concentrations. However many problems still exist with these reactor types such as their performance under fluctuating loadings, the retention of sufficient biomass to maintain high rates of organic removal and overcoming the slow start up times encountered. At present the fluidized and expanded bed type reactors offer the greatest potential for anaerobic waste-water treatment and an understanding of the process and its performance over a wide range of operating conditions is required to fully optimize the system.

Futher elucidation of the performance of separate phase systems particularly in combination with fluidized bed reactors may lead to further improvements. Better quality effluents may be expected due to the lower yield coefficients of the methanogenic bacteria found in the second reactor and the reactor configuration will also give wider opportunities for process control which may enhance reactor stability and operation.

2. OBJECTIVES

Food industries discharge significant quantities of waste-waters that are readily treated by both aerobic and anaerobic biological methods. Anaerobic processes have been shown to have economic advantages over aerobic systems when treating high strength wastes, but conventional anaerobic processes are limited by their low organic loadings and long retention times. In addition, they frequently require an energy input in the form of heat to maintain favourable conditions for the anaerobic biomass. Recent developments in anaerobic proceses have stimulated an interest in developing economically viable high rate treatment of industrial wastes. An important development in this context is the anaerobic fluidized bed reactor. Hence the primary objectives of this work were to:

1. Determine the organic loadings which could be tolerated by anaerobic fluidized bed reactors through an examination of the steady state treatment efficiencies attainable when treating synthetic high strength wastes.

2. Establish whether effective treatment can be obtained from a reactor operating without heat input which would reduce the energy requirements of the system.

3. Examine the general suitability of this reactor type for the treatment of different types of waste-water.

Industrial waste discharges are often characterised by intermittent variations in flow rate, temperature and pH. Therefore, in order to assess the limitations on the practical application of anaerobic fluidized bed reactors in the treatment of such discharges it was considered important to examine:

1. The response and long term stability of fluidized bed reactors when subjected to transient changes in influent COD and flowrate, influent pH and temperature of operation.

2. The ability of reactors to recover from long periods during which the organic loading is reduced to very low levels.

It is apparent that anaerobic degradation proceeds via at least two distinct biochemical phases, of which methanogenesis generally occurs quite slowly. As a result of this, many anaerobic processes do not proceed at maximum theoretical efficiency and the periods of time required for the full development of a stable process are often quite long. In order to overcome these disadvantages, the following aspects were considered worthy of evaluation:

1. The specific activities of the acidogenic and methanogenic populations within a fluidized bed.

2. Methodology whereby the establishment of an effective anaerobic biomass could be accelerated, such as the application of stepped organic loading or the provision of a readily metabolisable substrate for the methanogenic population.

3. The advantages of physical separation of the acidification and methanogenic phases in two different reactors and an examination of the kinetics of treatment in such a system to facilitate empirical comparison with single phase systems.

3. MATERIALS AND METHODS

3.1. Analytical Methods

Analysis of samples for their constituents or physical characteristics was generally undertaken in accordance with the standard methods of the Government of Great Britain (1972). Except where stated 'Analar' reagents were used throughout.

3.1.1. Chemical Oxygen Demand

The method adopted incorporated minor modifications of the Government of Great Britain (1972) standard method. The size of the sample was taken in accordance with Tables 3.1 and if necessary made up to 5 ml with distilled water.

Table 3.1. Sample size for COD Analysis

COD range mg l^{-1}	<200	200-600	600
Samples size ml	5	2.5	<1

The sample was boiled under reflux for two hours in a 250 ml round botton flask with 9.5 ml of oxidising reagent. This reagent was prepared by mixing 1500 ml of silver sulphate solution (10 g l^{-1} in concentrated sulphuric acid) with 400 ml potassium dichromate solution (7.6618 g l^{-1} in distilled water), 1 ml mercuric sulphate solution (200 g l^{-1} in 10% (v/v) sulphuric acid) was also added to the sample.

After cooling, 20 ml of distilled water was added through the condenser and the contents of the flask titrated against 0.0625 M ferrous ammonium sulphate in 2% (v/v) sulphuric acid using 2 drops of ferrous phenanthroline as an indicator.

The COD of the sample was determined from the relationship:

$$COD = \frac{(B-S) \times 500}{V}$$

where B = blank titration, ml.

S = sample titration, ml.

V = samples volume, ml.

3.1.2. Biochemical Oxygen Demand

The determination was undertaken over five days according to the method recommended by the Government of Great Britain (1972). The dissolved oxygen concentration was determined by the Winkler method (Government of Great Britain, 1972).

3.1.3. pH

The pH of the sample was determined electrometrically with a Pye Unicam Model 292 Mk2 pH meter, with compensation for temperature. Standardisation of the meter was carried out prior to each measurement using a pH 7 buffer solution (Gallenkamp Ltd., London), renewed weekly.

3.1.4. Alkalinity

The method adopted was based on the standard method using an electrometric titration. Total alkalinity was measured by titrating 40 ml sample against 0.05 M sulphuric acid to pH 4.5. The sample was continuously stirred throughout the titration using a magnetic stirrer.

The alkalinity of the sample was determined according to the relationship:

$$\text{Alkalinity} = \frac{T \times 5000}{V} \quad \text{mg } l^{-1}$$

where T = volume of 0.05 M titration reagent, ml.

V = volume of sample, ml.

3.1.5. Suspended and Volatile Suspended Solids

Suspended and Volatile Suspended Solids were determined according to the Standard Method. Samples (50 ml) were filtered using Whatman Glass Fibre 7.0 cm GF/C filters and the filter paper heated at 121°C and 550°C respectively.

3.1.6. Total Volatile Acids

A colorimetric method recommended by the Government of Great Britain (1972) was adopted. Absorbance was measured at 500 nm with a 1 nm slit width using 2 cm glass cells (Frost Instruments, Wokingham) on a Pye Unicam Model SP8-100 UV-visible spectrophotometer. Calibration was carried out using a distilled water blank and working standards prepared from a stock solution of 10,000 mg l^{-1} acetic acid.

3.1.7. Individual Volatile Acids

Individual volatile acid concentrations were determined on a Model 5700 A Gas Chromatograph (Hewlett Packard, Winersh, Berks) fitted with a flame ionization detector (F.I.D.). A 1.8 m, 5 mm I.D. glass column packed with Chromosorb 101 (J.J. Chromatography, Kings Lynn, U.K.) was used. Nitrogen, at a flowrate of 40 ml min^{-1} was used as a carrier gas, the flowrates of hydrogen and air were adjusted to optimize the detector's response to propionic and buyric acids. The chromatograph was operated with an injection port temperature of 200°C, oven temperature 170°C, and detector temperature 250°C.

A 2.5 µl sample was injected into the chromatograph using a 10 µ l syringe. An injection of 5 µl of 10% (v/v). Formic acid was made between each samples injection to eliminate hysteresis effects. A standard solution of 200 mg l^{-1} each of acetic, propionic, butyric and valeric acids was prepared from Analar grade reagents and used for calibration. Acid concentrations were determined by comparison of peak heights recorded on a Servogor 120 Chart recorder (Servoscript Ltd., Croydon, Surrey).

3.1.8 Hexose Sugars,

Hexose sugar concentrations were measured by the method of Dubois et al. (1956). Aliquots of 1 ml of 5% (w/v) phenol were added to a 2 ml sample and 5 ml of concentrated sulphuric acid were added rapidly. The mixture was thoroughly shaken after 10 min, then left to stand for 2 hours before measuring the absorbance at 490 nm.

3.1.9 Protein

Protein concentrations were measured by the method of Lowry et al. (1951); bovine serum albumen was employed as a standard. Aliquots of 5 ml of reaction mixture (50 ml, 2% $NaCO_3$ in 0.1 M NaOH added to 2 ml, 0.25% Cu $SO_4.5H_2O$ in potassium sodium tartrate) prepared on the day of analysis were added to 1 ml of sample. Folin reagent (0.5 ml) (Folin and Ciocalteus phenol reagent, (BDH Chemicals, Poole)) was diluted to 1 M with distilled water, and added and the mixture shaken thoroughly. Samples were allowed to stand at room temperature for 2 hours before absorbance at 750 nm was measured.

3.1.10.Turbidity

Turbidity was determined using a Hach 2100 A turbimeter (Camlab, Cambridge). Formazin Turbidity Unit (FTU) 10 and 100 standards prepared from latex solution and supplied with the instrument were used for calibration.

3.1.11.Gas Composition

A modified Gas Chromatograph (Gallenkamp Ltd.) adapted to contain two parallel packed columns (Chromosorb 102 and Molecular Sieve 5A) (Phasesep Ltd., Queensferry, Clwyd) each passing through opposing cells of a thermal conductivity detector, was used to determine methane, carbon dioxide, nitrogen and oxygen concentrations in the gas produced as described by Kirk et al. (1981). The chromatograph was calibrated using pure methane and a mixture of 40% nitrogen, 60% carbon dioxide (BOC Ltd., Special Gases).

3.1.12 Alkaline Phosphatase Activity

Alkaline phosphatase activity was determined at pH 9.5 as recommended by Ashley and Hurst (1981). Approximately 5 ml samples were taken from the reactors, the solids allowed to settle and the liquor was decanted off. The remaining solids were sonicated for 30 mins at 80W (± 5 W) in a Kerry 125 Ultrasonic Bath (Kerry Ultrasonic, Hitchin, Herts). The samples were shaken with 3 ml of distilled water and filtered through glass fibre filters (GF/C grade, Whatman, U.K.). The filtrate was then made up to 10 ml with distilled water.

Substrate (0.5 ml), a 1% (w/v) p-nitrophenol phosphate disodium (Sigma, Poole, U.K.) was added to 1.5 ml of pH 9.5 AMP buffer, (a 0.2 M 2-amino, 2-methyl-propanol solution) and 1 ml of filtrate added. All determinations were run in duplicate. The controls consisted of the substrate and the buffer to which 1 ml of heat deactivated filtrate was added. The tubes were incubated at 37°C for 90 minutes in a heated water bath. After incubation 1 ml was removed from each tube and added to 2 ml of 0.2 M NaOH. After 30 minutes assays were examined spectrophotometrically at 420 nm.

The solids remaining on the filter were retained and analyzed for SS and VSS as previously described.

3.1.13.Relative Methane Forming Activity

Methane production was determined using a modified method described by van den Berg and Lentz (1979b). A solids sample (3 ml) was incubated at 37°C in 1000 mg l^{-1} acetic acid solution (40 ml) adjusted to pH 7.4±0.2 with ammonium hydroxide solution. Gas production was measured over two days by the displacement of acidified water and the methane concentration determined by gas chromatograph as previously described.

3.1.14.Determination of Propionate and Acetate degradation parameters

Propionate and Acetate degradation parameters were measured, using the method of Kaspar and Wuhmann (1978a). Steady state acetate and propionate turnover rates were assumed to be 0.7 and 0.08 times the methane production rate respectively. Catabolic kinetic parameters during the saturated and concentration dependent phase were determined by increasing the concentration of acetate and propionate and measuring its degradation over a period of time. Lineweaver-Burke (1934) plots were used to determine the parameters K_s and V_m. An appropriate allowance was made for dilution by the influent due to the reactor configuration.

3.1.15.Settleability of Effluent Suspended Solids

A 250 ml sample of effluent was collected and a 50 ml aliquot immediately analysed for suspended solids as previously described. The remaining sample was allowed to stand for three hours. Each hour a 40 ml sample was carefully pipetted from the liquid surface and the suspended solids determined.

3.2. Laboratory Scale Fluidized Bed Reactors

3.2.1. Construction of Reactors

Each reactor system consisted of a fluidized bed reactor column with recycle and overflow chambers, together with recycle, feed and nitrogen purging systems. A schematic representation of the assembly is shown in Fig. 3.1.

The reactor assembly was constructed of extruded acrylic tube (Visijar Laboratories Ltd., Croydon) of height 2 m, 50 mm I.D. and wall thickness of 5 mm. This material was chosen since it is transparent and easy to machine. Two versions of base construction

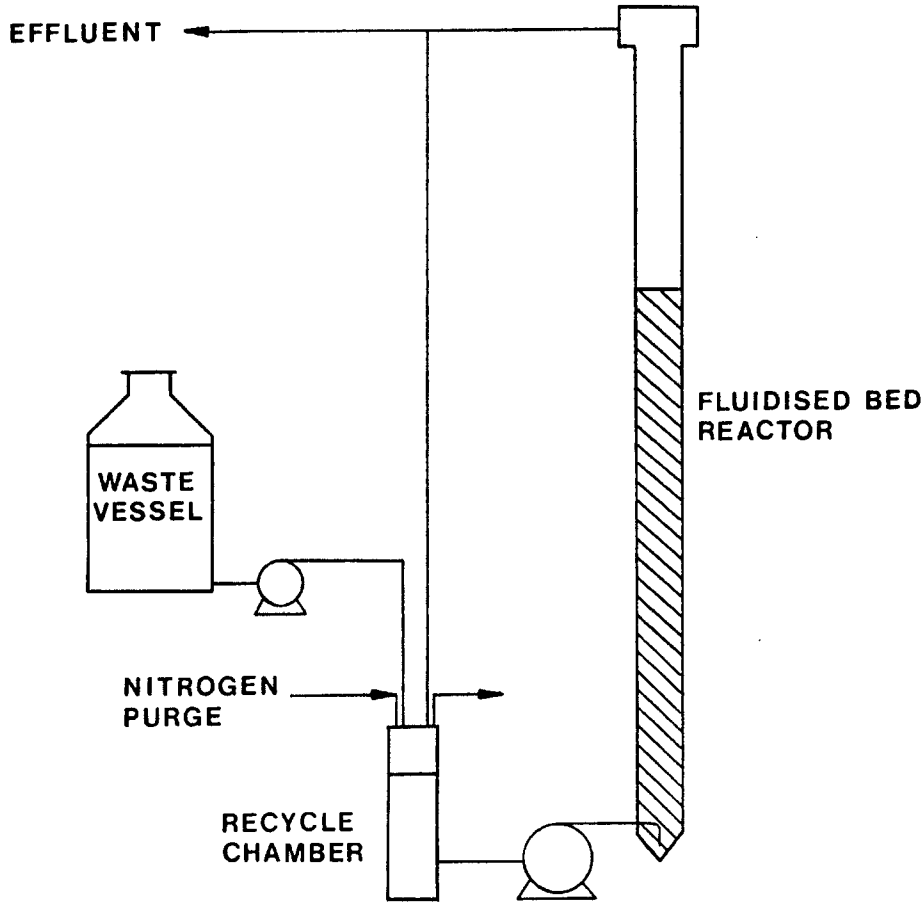


Figure 3.1. Schematic diagram of the fluidized bed reactor

were used during the experiments. Each was constructed from a block of acrylic plastic. In the first version the flow entered the base of the reactor through a 15 mm I.D. acrylic inlet tube and was distributed by a 15 cm layer of gravel with an approximate diameter of 10 mm, a plastic mesh prevented the gravel passing into the inlet pipe.

The second version utilized a conical base distribution system, a stainless steel inlet pipe with a 5 mm I.D. directed the flow to the apex of the cone to facilitate even distribution of the liquid. (see Fig. 3.2.) each version the column and the base unit were connected by a screw thread (12 TPI) with a plastic O-ring seal.

The top of the reactor incorporated an overflow system constructed of 5 mm acrylic sheet and was connected to the column in a similar manner to the base section (see Fig. 3.3).

Sampling inlets were set into the reactor at regular intervals and the assembly of these inlets is shown in Fig. 3.4.

The effluent left the overflow system by 25 mm I.D. flexible PVC tubing to a valve and water seal system constructed of rigid 12.7 mm I.D. PVC tubing. The flow left this system either by a valve to waste or returned to the recycle chamber by way of 5 mm I.D. PVC tubing.

The overflow and recycle chambers were constructed from acrylic tubing of height 300 mm, 60 mm I.D. and a wall thickness of 5 mm. In some experiments where the valve effluent system described above was used a 10 l aspirator replaced both chambers. The chambers were connected 50 mm from the base by a length of 5 mm I.D. silicone rubber tubing. The overflow chamber also included a L-shaped glass tubing overflow 200 mm from the base.

Synthetic waste-water was pumped to the recycle chamber using a LKB Multi-perpex pump (LKB Ltd., Croydon, Surrey). Two chambers (the 'overflow' and the 'recycle') were used to ensure the influent passed through the reactor rather than flowing directly out with the effluent. The tops of both chambers were sealed with rubber bungs, pressure was equalised between each chamber by an interconnecting PUC tube and the bung in the recycle chamber was also bored to allow the escape of the gases produced.

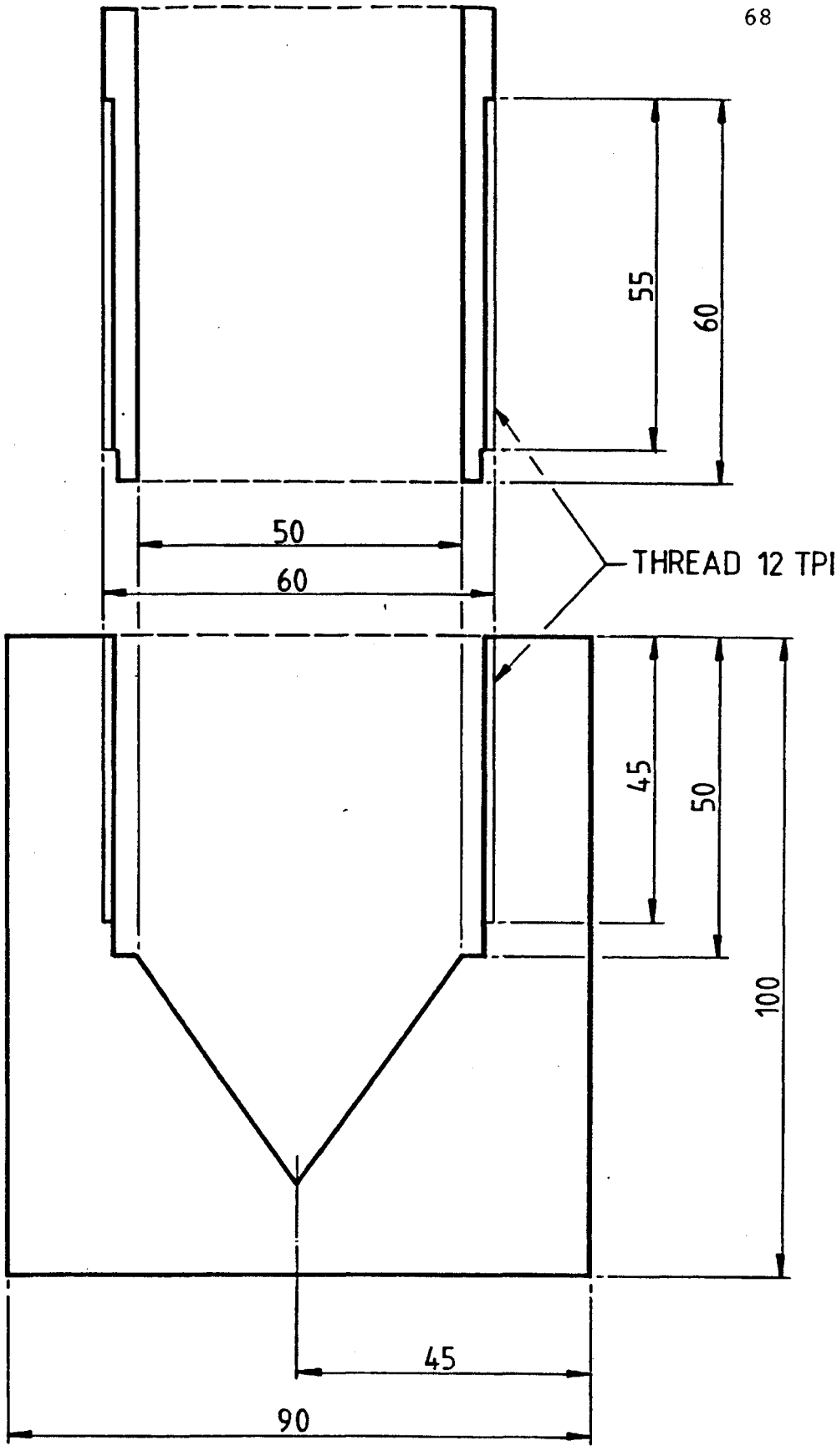


Figure 3.2. Conical base assembly of fluidized bed reactor

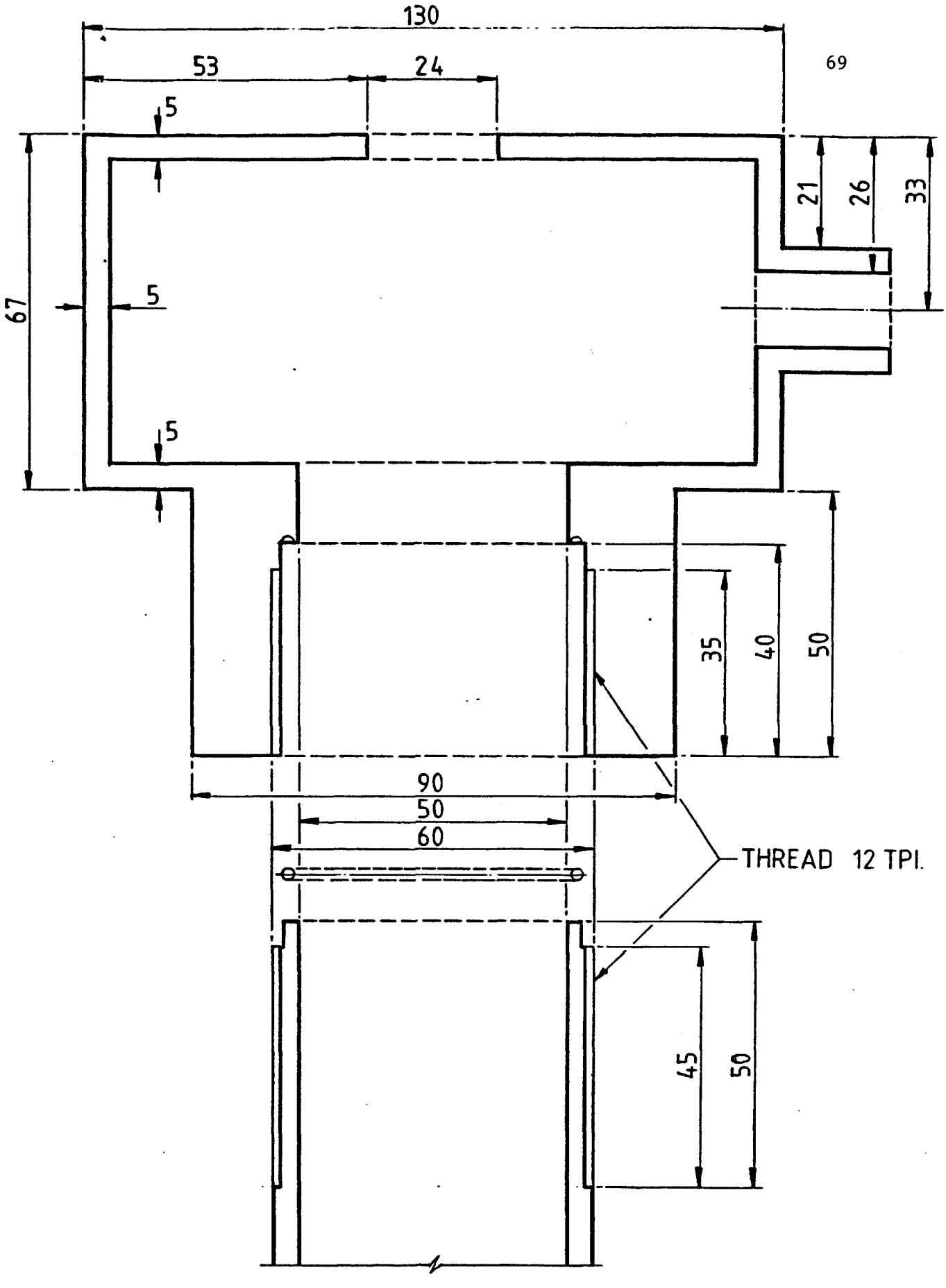


Figure 3.3. Overflow assembly of the fluidized bed reactor

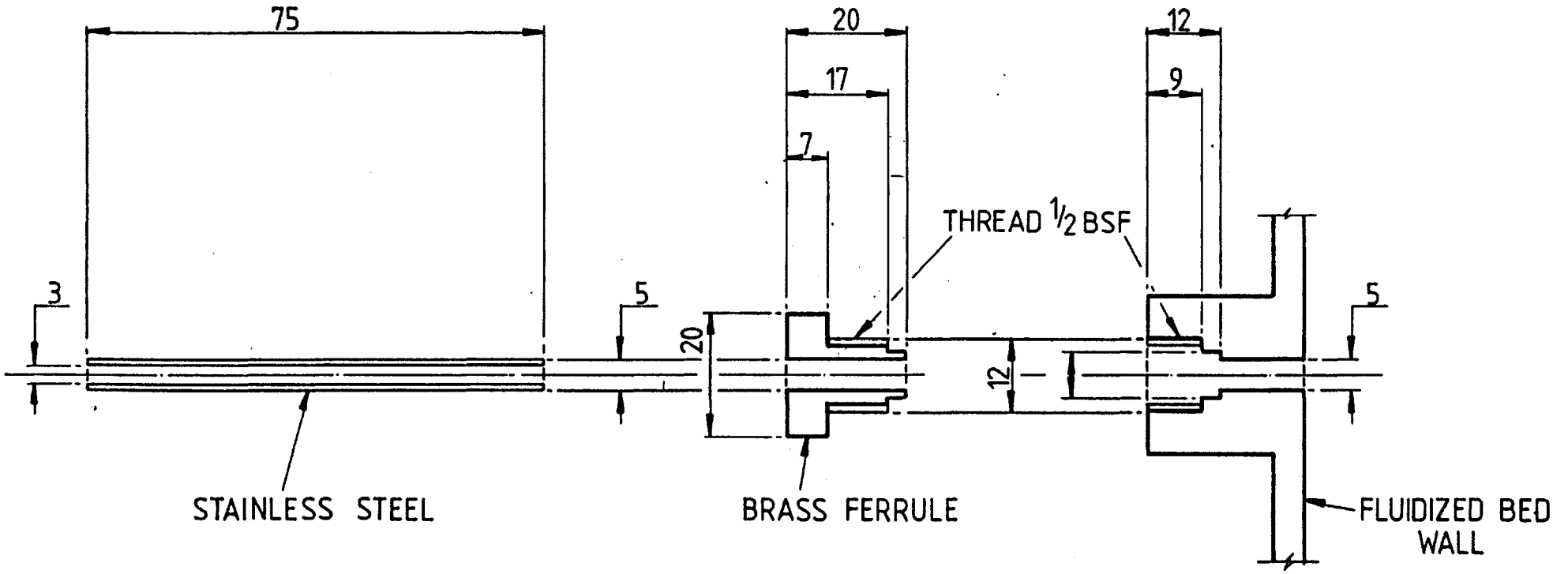


Figure 3.4. Sample tap assembly

Prior to entering the recycle chamber, the synthetic waste passed into a mixing chamber which also had an inlet for oxygen free nitrogen (BOC Special Gases) which was sterilized by passing through a steam sterilizable filter (Formaflow Ltd., Windlesham, Surrey). The nitrogen was maintained at a pressure of 200 Nm^{-2} to help maintain an anaerobic environment and also to prevent contamination of the synthetic waste by bacterial growth back along the feed line.

The mixed recycled effluent and synthetic waste-water was pumped up through the fluidized bed via a Watson Marlow HRSV 214 Flow inducer (Watson Marlow, Falmounth, Cornwall) fitted with either 4.8 mm or 6.3 mm I.D. silicone rubber tubing at a sufficient rate to maintain the required expansion. The silicone rubber tubing in the pump head was inspected regularly for wear and changed if necessary. The tubing and the pump head rollers were lubricated with glycerol to increase the tube life.

If required the influent was passed through a glass coil of approximately 2.5 M length placed in a heated water bath (Hearson Ltd., England) stirred with a Circotherm unit (Tecam, Cambridge, U.K.). The temperature of the water bath was adjusted to maintain the required temperature within the fluidized bed.

Gas production was measured by the displacement of acidified water from an inverted 1 litre measuring cyliner, samples for gas analysis were collected in a perspex cylinder fitted with a silicone rubber septum

Tube connections were polypropylene push-fit connectors (Gallenkamp Ltd.) and polypropylone non-return valves (Gallenkamp Ltd.) were fitted at the reactor column inlet and recycle pump outlet to prevent loss of column contents in the event of failure, or rupture of the recycle line. All other interconnecting pipework was 5 mm I.D. flexible PVC tubing.

3.2.2 Operation of Fluidized Bed Reactors

3.2.2.1 Synthetic waste-waters. Three synthetic waste-water types were used during the study, a milk waste based on that used by Schroepfer and Ziemke (1959), a meat waste-water based on meat extract

and glycerol together with essential inorganic nutrients and a glucose based waste-water reported by Anderson and Donnelly (1978a). The composition of each waste-water is given in Table 3.2.

Table 3.2. Composition of synthetic waste-waters.

Constituents	Grade	Concentration mg l^{-1}
Milk waste-water		
Milk Powder	-	2200
Sodium hydrogen carbonate	Analar	750
Meat extract waste-water		
Oxoid 'Lab Lemco' powder (L34)		1950
Glycerol	GPR	200
Ammonium chloride	Analar	360
Sodium chloride	Analar	50
Potassium dihydrogen phosphate	Analar	30
Calcium chloride (hydrated)	Analar	24
Magnesium sulphate (hydrated)	Analar	7.5
Glucose based waste-water		
Glucose	Analar	8000
Peptone (Oxoid, L29)	-	2400
Oxoid 'Lab Lemco' Powder (L31)	-	800
Potassium dihydrogen phosphate	Analar	240
Sodium hydrogen carbonate	Analar	320
Calcium chloride (hydrated)	Analar	22
Magnesium chloride (hydrated)	Analar	48

Each waste-water was prepared in 20l quantities with distilled water, the meat extract and the glucose based waste-water were sterilized at 121°C for one hour to maintain a consistent influent quality while the milk based waste-water which could not be autoclaved at this temperature due to coagulation of the proteins was partially sterilized by steaming at 100°C for 1 hour on two consecutive days.

3.2.2.2. Biomass support material. Two materials were evaluated as biomass support materials during this study, a silica sand (British Industrial Sands, Redhill, Surrey) and an ion exchange resin, Ambersep 359; their physical properties are given in Table 3.3.

Table 3.3 Physical properties of biomass support materials

	Ambersep 359	B15 Redhill 65
Mean particle size	5 mm	2.2 mm
Particle density	1.18	2.65
Bulk density	0.53	1.43

3.2.2.3. Operational Parameters. The main operational parameter used in this study was COD loading calculated from:

$$\text{COD Loading} = \frac{F \times C}{V} = \text{kg m}^{-3}\ \text{d}^{-1}$$

where F = influent flowrate, l d^{-1}

C = influent COD, g l^{-1}

V = bed volume m^3.

3.3. Laboratory Scale Acidification Reactor

3.3.1. Construction of Reactor

All parts of the reactor were constructed from borosilicate glass and silicone rubber. In the following description Quickfit (Corning, U.K.) reference numbers for each component are appended in brackets.

A flat bottom fermentation vessel (FV500) adapted by a side arm to maintain a constant volume of 300 ml was fitted with a five socket flange lid (MAF1/75), silicone grease being applied to the ground glass joint, prior to clamping the two securely together (JC75F). Influent was pumped into the vessel via a sterile mixing chamber connected via a cone to straight tubing connector (MF10/2). Effluent gases left the reactor via a cone to rubber tubing, right angle connector (MF10/2B) connected by PVC tubing to a water seal. A thermometer pocket (SH4A) facilitated temperature measurement.

The remaining sockets were sealed with closed end stoppers (SB19). Effluent left the reactor vessel via a U-tube (to maintain a positive pressure) to the recycle chamber of the fluidized bed reactor. Each vessel was supported above a magnetic stirrer (Stuart Ltd., U.K.) and equipped with a PTFE coated magnetic follower to maintain the vessel in a completely mixed state. A wrap around electric heating belt type SD/2 (Thermelec Manufacturing Congleton, Cheshire) was used to maintain the reactors at 35°C (±2°C).

3.4. Glassware

Prior to use all glassware was rinsed twice with tap water and then twice with distilled water. If heavily soiled the glassware was soaked overnight in chromic acid. Prior to enzyme analysis and methane activity determination all glassware was cleaned with a 10% (v/v) solution of Decon 90 detergent (BDH Ltd., Poole, Dorset).

Round bottom flasks for the COD determination were filled with dilute chromic acid when not in use, to avoid contamination. Pipettes were stored in a dilute solution of Decon 90 detergent.

4. RESULTS

4.1. Initial Reactor Start Up

The reactor construction described in Section 3.2.1 and the milk-based waste-water were used for the initial experiments. Four reactors were used, each containing approximately 2.2 litres of silica sand (BIS, Redhill, 65), the reactors were initially filled with tap water to their intended operating volume. Three grams of dried milk powder were added to two reactors and 500 ml of digester sludge previously acclimated for 60 days to a milk based substrate was added. The remaining two reactors were not seeded with anaerobic sludge but 20 ml of sour milk was added to each as an initial bacterial seed and carbon source in order to determine whether an active bacterial population could develop without initial innoculation from an anaerobic digester. The recycle pumps were adjusted to give a bed expansion of 20%, all reactors were operated at room temperature.

The reactors were initially operated in batch mode, additions of milk powder (1g) were made directly to the recycle chamber every three days to maintain an adequate substrate concentration. After fifteen days of operation, a feed with a COD of 2500 mg l^{-1} (see Table 3.2) was supplied to each reactor at a flowrate of 1 l d^{-1}. After forty days of operation the flowrate was increased to 4 l d^{-1} using a higher concentration of milk powder (50 g l^{-1}) diluted to the necessary strength with tap water in the mixing chamber. COD and pH were measured daily over this period, volatile acids were determined weekly. The COD during this period is shown in Fig 4.1.

Reactor operation over the entire attempted start up period was unstable, pH adjustment was frequently required. This was achieved by adding 1-2 g of calcium oxide to the recycle chamber. Over the first forty days COD reduction was moderate, typically between 40 and 50%, however no methane could be detected in the head space above the recycle chamber. It would appear unlikely that anaerobic degradation was responsible for the reduction in COD. Aerobic degradation (due to air leakage) or coagulation (due to the low pH) and settlement of the milk proteins are possible mechanisms of removal. After the influent flowrate was increased to 4 l d^{-1} effluent COD increased rapidly to approach the influent values.

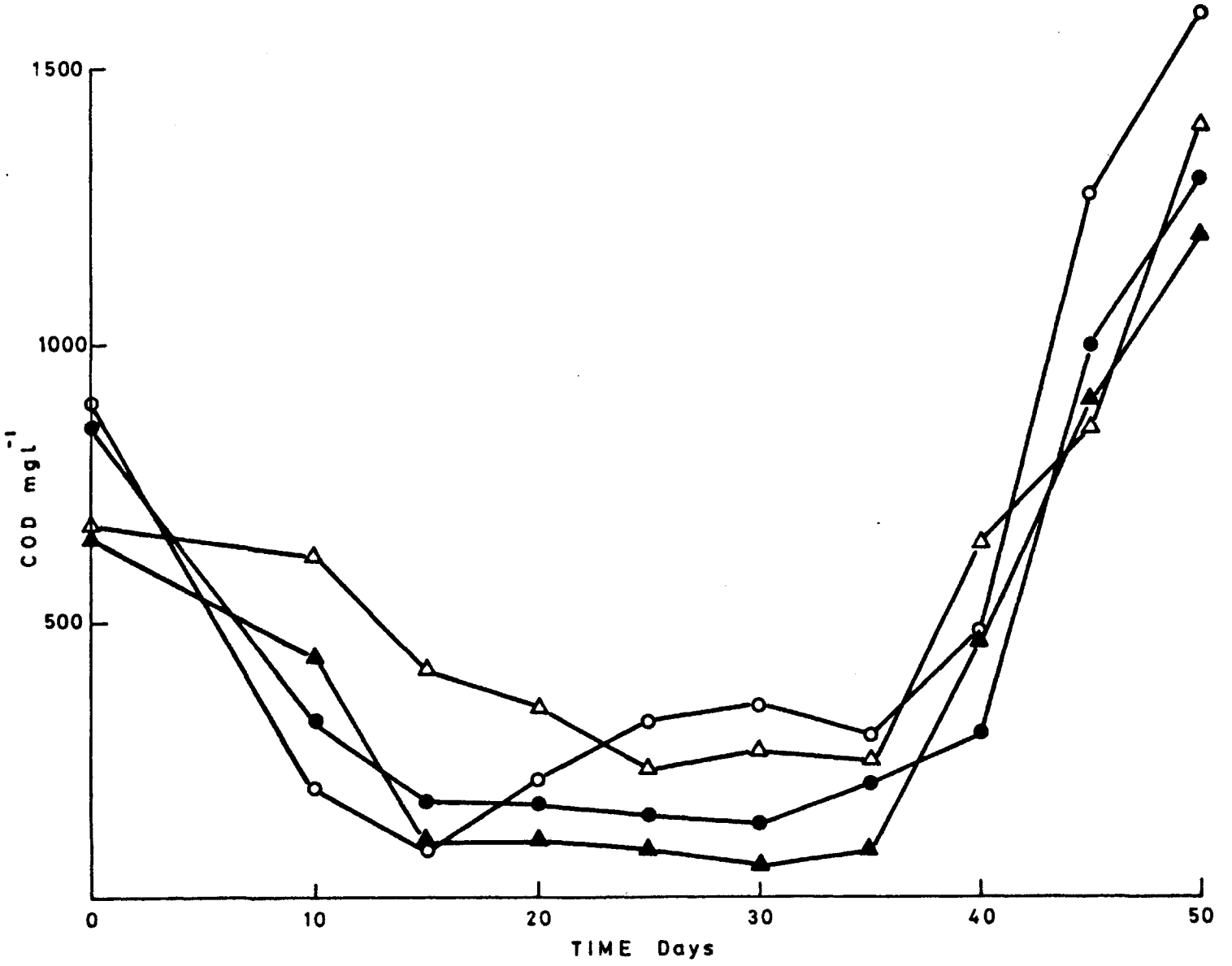


Figure 4.1. Effluent COD during initial start-up period (○ ●) seeded, (△▲) unseeded

Some operational problems were encountered with the design of the equipment. The gravel bed distributor system proved to be unsatisfactory since distribution was poor, evidenced by visible channelling in all four reactors and the void space in the gravel quickly became blocked with biological solids, on two occasions the reactors had to be dismantled and the gravel removed and washed.

The system of balancing the influent and effluent flowrate by adjusting the valve positions was highly unsatisfactory. It was difficult to accurately adjust the flowrates as was apparent from the large fluctuations in the fluid level in the recycle chamber. Frequent adjustments to the liquid volume had to be made either by wasting or adding fluid to the system. Due to these level fluctuations the gas volume of the system was not constant and it would have been impossible to accurately measure any gas production, thus the reactors were shut down and redesigned to give a constant gas and liquid volume, and to minimise the volume of the recycle chambers. The gravel bed distribution system was also replaced with the inverted conically shaped system described in Section 3.2.1.

4.1.2. Modified Reactor Start-Up Procedure

The reactors were refilled with 2.2 litres of fresh sand and two reactors were filled with the buffered milk waste at the required strength and were operated at 37°C. The two remaining reactors were filled with the meat extract waste-water and operated at room temperature. The reactor operating conditions and measured influent characteristics are given in Table 4.1

The recycle pumps were adjusted to give a 20% bed expansion and after the reactors had equilibrated at their appropriate operating temperature freshly collected digester sludge (20 ml) was injected into a lower sample tap of each reactor. The COD and pH were monitored daily. Once the COD began to decline waste was pumped to the recyle chambers at a low flowrate and the reactors were allowed to stabilize prior to further stepped increases in loading.

The difference in equilibration times between the ambient temperature and heated reactors in terms of effluent COD is shown in Fig 4.2., the reactor operating at ambient temperature took 80 days to equilibrate, at a COD loading of 2.6 kg m^{-3} d^{-1} which was 100% longer than the heated reactor.

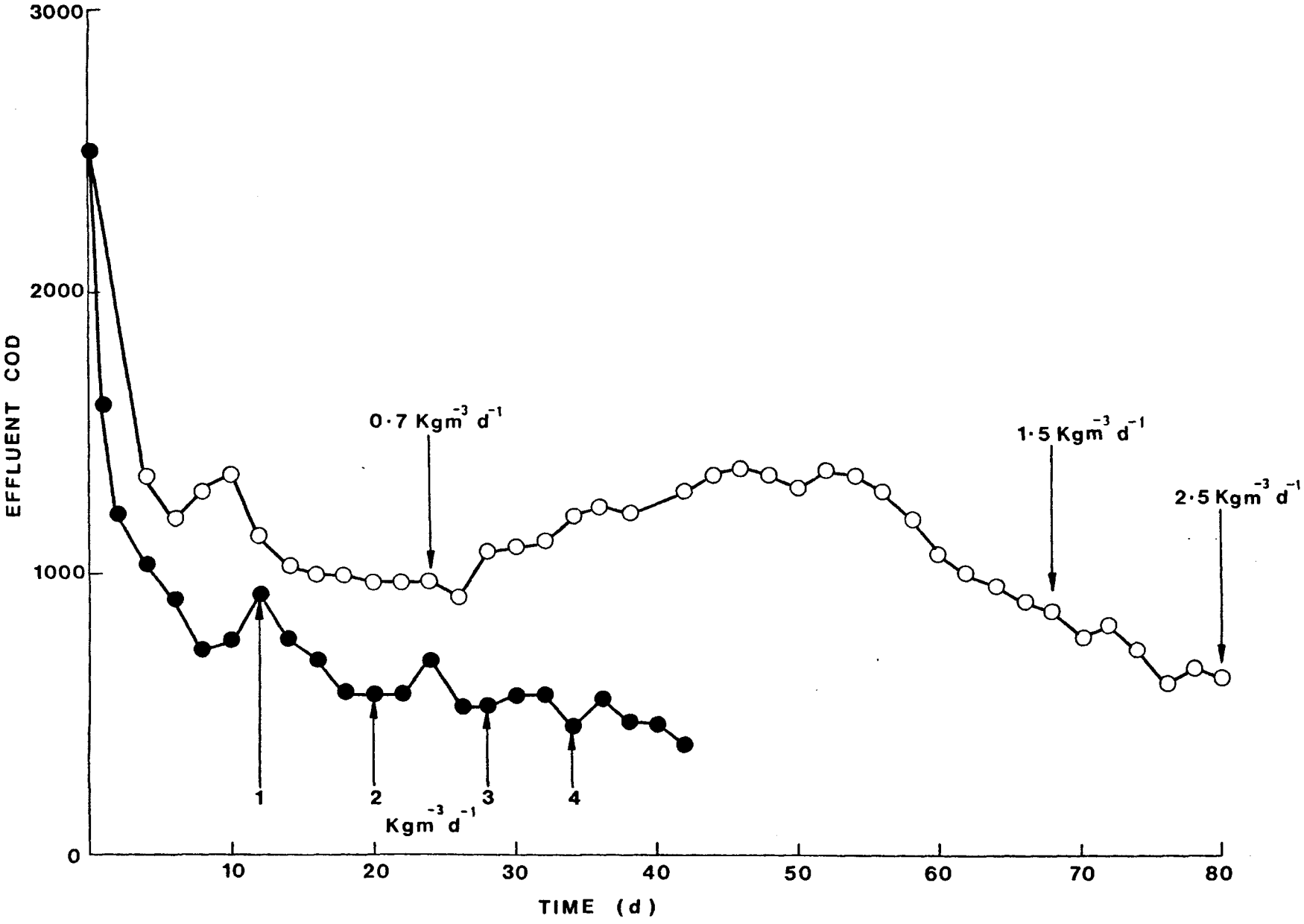


Figure 4.2. Equilibrium times of fluidized bed reactors (●) meat waste, (O) milk waste

Table 4.1. Fluidized bed reactor operating conditions

Reactor	1	2	3	4
Operating Temperature °C	37	37	20	20
Waste type	milk powder	milk powder	meat extract	meat extract
Influent COD mg l^{-1}	1250	2500	1250	2500
Influent BOD mg l^{-1}	590	1180	620	1240
Influent SS mg l^{-1}	0	0	0	0
Influent pH	6.0	6.0	6.1	6.1
Upflow velocity cm min^{-1}	7.62-12.7	7.62-12.7	7.62-12.7	7.62-12.7

4.2. Reactor performance at steady state

After a period of eighty days since initial reactor start-up had elapsed the performance of the reactors was studied over a range of COD loadings. The influent flowrates were adjusted for the required loading and a period equivalent to three hydraulic residence times or fourteen days was allowed to let the reactors stabilize. The effluent COD, volatile acids, SS, VSS and pH were measured daily for three days at each organic loading. The COD loading was increased until the reactors showed signs of impending failure, indicated by unstable pH and high volatile acids concentrations. The operating parameters at each COD loading are shown in Figs 4.3 and 4.4.

The COD removal in the heated reactors was greater than 80% over most of the loadings tested, whilst in the unheated reactors COD removal efficiency declined rapidly over COD loadings of 3 kg m^{-3} d^{-1} however, the stability of these reactors was good with no indication of volatile acid accumulation over the range tested. Effluent volatile acid concentrations were generally below 100 mg l^{-1} except at the higher loadings in the heated reactor, where there was some tendency

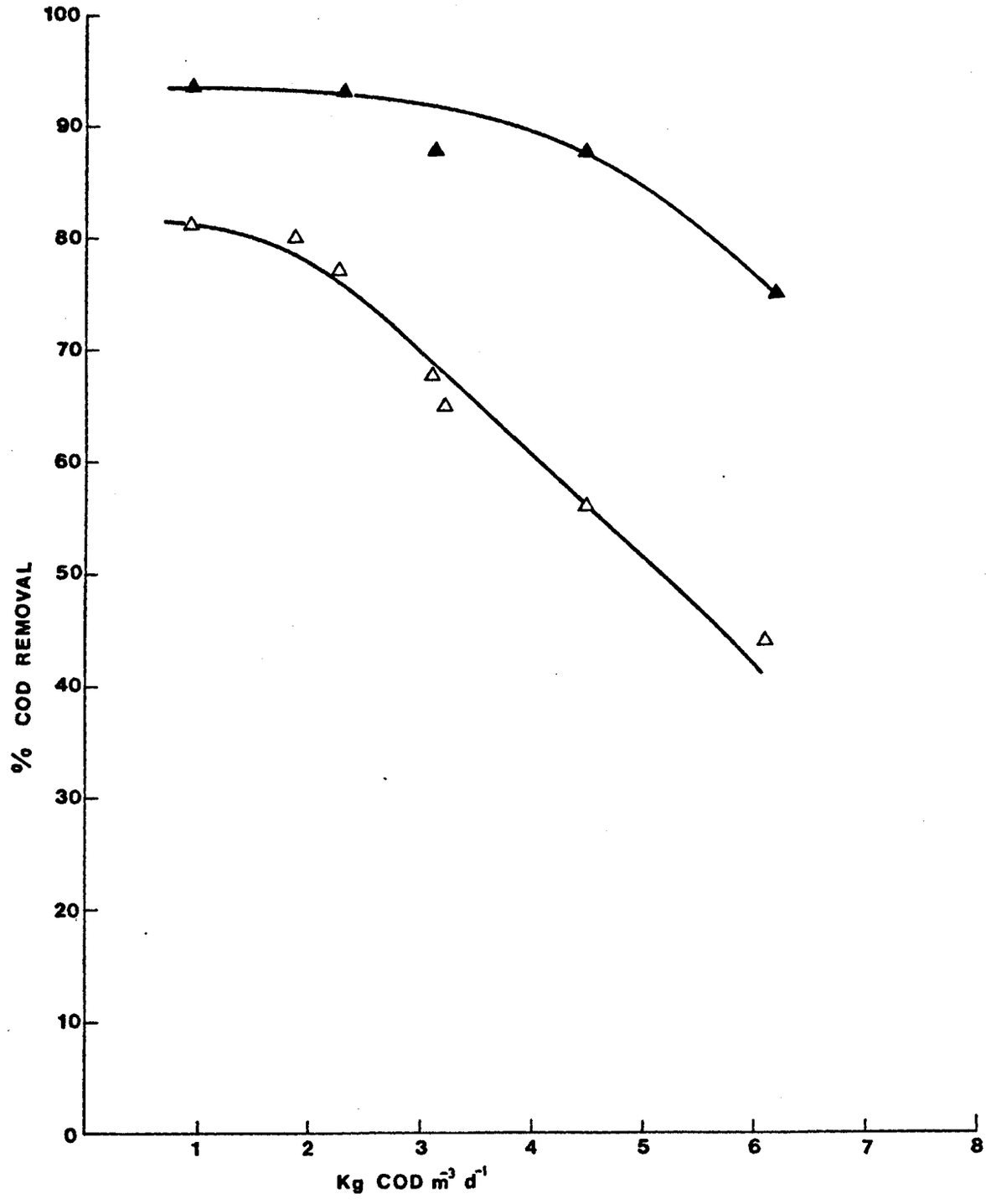


Figure 4.3. Influence of COD loading on effluent COD, (▲) milk waste, (△) meat waste

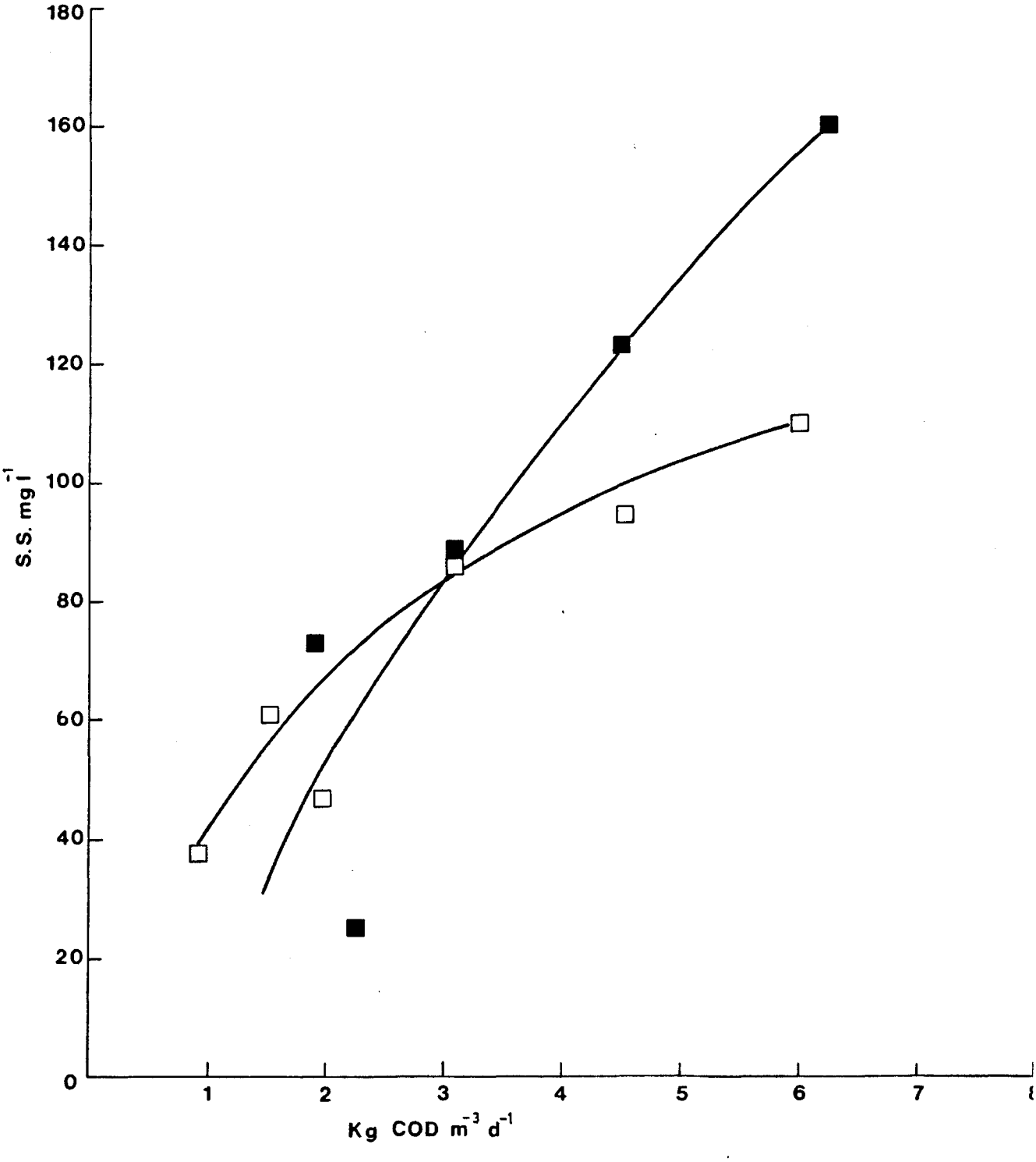


Figure 4.4. Influence of COD loading on effluent suspended solids (■) milk waste, (□) meat waste

for volatile acid accumulation, the reactor pH was corrected in this instance by the addition of 5 g of sodium hydrogen carbonate.

COD reduction at the same organic loading was largely independent of influent COD, however effluent suspended solids were lower at lower influent COD concentrations.

Effluent suspended solids concentrations exhibited a definite increase with organic loading although results at the lower COD loadings were somewhat erratic. The effluent suspended solids appeared to be of a very fine nature and thus the settlement tests described in section 3.1.15 were undertaken on the effluent from a heated reactor fed with the milk based waste-water with a COD of 2500 mg l^{-1}. The results are shown in Table 4.2. Little change in suspended solids concentrations over the three hour period of settling were noted except

Table 4.2. Investigation of the settleability of fluidized bed reactor effluent suspended solids

Initial COD Loading (kg m^{-3} d^{-1})	1	2.5	4.0
Time (hours)	Effluent Suspended Solids (mg l^{-1})		
0	58	68	105
1	60	66	95
2	60	78	95
3	62	66	98

at a COD loading of 4 kg m^{-3} d^{-1}, where there were some larger flocs visible, although the measured reduction was small (<10%). During the four months of the study at no time was it necessary to waste any biomass from the reactors. Settlement in the recycle chambers was minimal due to the fine nature of the solids.

Detailed gas analysis and measurements were not within the scope of this study, however an estimate was made of the gas yield from each reactor, these were 0.38 m^3 CH_4 per kg COD removed for the milk waste and 0.31 m^3 CH_4 per kg COD removed for the meat waste-water.

On two occasions with the heated reactors the recycle pumps were stopped and thus the reactor contents cooled to ambient temperature for 21 h. After restarting the flow and restoring the temperature to 37°C the reactors almost immediately started to produce methane and were operating with full efficiency within two days. The reactors thus showed good stability under unfavourable process conditions, a characteristic not generally expected of anaerobic reactors and an important feature of a process to be used commercially in an industrial situation, thus further examination of reactor performance under variable process conditions was made.

4.3. Performance of reactors under variable process conditions

In order to simulate the effects of transient or intermittent variations in waste characteristics which may arise from industries employing batch or semi-batch type production, intermittent cleaning operations or combinations of different production processes generating wastes of various strengths, the fluidized bed ractors were subject to transient changes in temperature influent flow rate, influent COD concentration and pH and their stability of operation monitored. These experiments were carried out on a heated fluidized bed reactor treating the buffered milk waste at an influent COD of 2500 mg l^{-1} and on the unhreated reactor treating the meat extract waste at an influent COD of 1250 mg l^{-1}. Analysis of the samples took place immediately with the exception of the determination of volatile acids concentrations.

4.3.1. Evaluation of methods of preserving samples for total volatile acids determination.

It was anticipated that during the series of transient changes in operating parameters that with sampling at hourly intervals it would not be possible to undertake immediate analysis of the volatile acids concentration. Effluent sub-samples would have to be stored for up to 48 h prior to analysis. Therefore an investigation was carried out to evaluate effects of preservation and storage on the volatile acids concentrations.

In a preliminary study with a filtered effluent sample, it was found that the addition of formaldehyde at a concentration of 0.2% (v/v) produced considerable interference with the analytical method, this form of storage was therefore not pursued in subsequent work. Table 4.3. summarises the results of these experiments.

Table 4.3. The effect of formaldehyde addition on the determination of volatile acids in filtered effluent samples

Filtered Sample Untreated		Filtered Sample + Formaldehyde	
Day 0	x	Day 0	x
Vol. Acids mg l^{-1}	n-1	Vol. Acids mg l^{-1}	n-1
8		172	
12	8.80	208	211.20
4		288	
8	3.34	192	44.84
12		196	

In a further comparison an unfiltered effluent sample was obtained from the reactor operating under steady state conditions at a COD loading of 2.6 kg m^{-3} d^{-1}. This sample was divided into a number of sub-samples, one of which was analyzed immediately. Two of the remaining subsamples were stored at 4°C in a refrigerator and at -10°C in a freezer. The remaining sub-sample was treated with a mercuric chloride solution to a concentration of 20 mg l^{-1}. Part of this sample was analyzed immediately and the remaining portion stored at 4°C. The sub-samples were analyzed at 3 days and 6 days after the time of sampling, the variations to the original volatile acids concentration are given in Table 4.4.

A similar experiment was carried out for a sample which was immediately filtered, the results are given in Table 4.5.

The filtered samples stored at -10°C were found to have the least variation in volatile acids measurement. A T-test carried out on the 0 day and 3 day sets of samples showed that the measurements were not significantly different at the 95% confidence level. This method of storage was therefore used during subsequent work.

Table 4.4. The effects of storage of unfiltered effluent samples on volatile acids analysis

Storage	Day 0 Vol. Acids mg l^{-1}	x n-1	Day 3 Vol. Acids mg l^{-1}	x n-1	Day 6 Vol. Acids mg l^{-1}	x n-1
4°C			5.6		0	
			0	7.32	0	0
			16.9		0	
	8.7	14.5	5.6	6.17	0	0
	17.4		8.5		0	
	14.5					
-10°C	14.5	3.55	14.1		0	
	17.4		2.8	18.6	0	3.94
			25.4		9.8	
			28.2	10.28	3.3	4.26
			22.5		6.6	
mercuric	52.2		15.2		0	
chloride	52.2	42.3	12.1	17.58	8.0	5.34
4°C	31.9		24.2		18.7	
	26.1	12.40	21.2	4.95	0	8.23
	49.3		15.2		0	

Table 4.5. The effects of storage of filtered effluent samples on volatile acids analysis

Storage	Day 0 Vol. Acids mg l^{-1}	x n-1	Day 3 Vol. Acids mg l^{-1}	x n-1	Day 6 Vol. Acids mg l^{-1}	x n-1
4°C			6.3		21.9	
			21.9	14.4	19.2	23.56
			9.4		16.4	
	11.3	16.34	12.5	7.18	21.9	8.60
	14.0		21.9		38.4	
	19.7					
-10°C	28.2	7.81	12.5		16.4	
	8.5		18.8	16.26	19.2	23.0
			12.5		30.1	
			21.9	4.09	19.2	6.58
			15.6		30.1	
mercuric	22.5		6.8		28.2	
chloride	33.8	27.04	10.2	14.24	36.6	32.12
4°C	25.4		13.6		36.6	
	22.5	5.13	20.3	6.03	28.2	4.24
	31.0		20.3		31.0	

4.3.2. Influence of transient temperature reductions on the performance of the heated fluidized bed reactor

Temperature reductions were carried out on a fluidized bed operated at a COD loading of 3.2 or 5 kg m^{-3} d^{-1}, at each COD loading the temperature was decreased by 10°C and 20°C. Each temperature reduction was maintained for 4 and 8 hours. Table 4.6 summarises the changes in performance of the reactor for each temperature reduction.

The effect of a temperature reduction was characterized by an immediate decrease in reactor pH, which stabilized at a new value between 0.2 and 0.3 pH units below the normal operating value. The pH was generally stable at this lower operating value during operation at the lower temperature. The decrease in pH was coincident with an increase in effluent volatile acids which continued to rise during operation at the reduced temperature to values up to 200% greater than the normal concentration; thus the reactor pH was only maintained by the buffering capacity of the system. This was indicated by a decrease in the alkalinity during the temperature reduction. Once the reactor temperature was increased to its former value the effluent volatile acids immediately began to decrease and attained their original values within 14 hours.

Typically, effluent suspended solids concentrations were unstable during a temperature reduction but showed a general increasing trend whilst after operation at the lower temperature they usually decreased and stabilized at a new value.

Effluent COD increased throughout each temperature reduction to values up to 143% greater than normal. To establish whether waste-water passed through the reactor unaffected by the treatment process, the concentration of protein in the effluent was determined (the milk based waste-water was analyzed and found to contain 850 mg l^{-1} of protein). Increases of up to 30% were found indicating that the first stage of anaerobic digestion (i.e. the acid formation step) was overloaded.

Gas production was severely retarded by the temperature reduction to minimum values of approximately 20% of those at normal temperatures (during 20°C decreases). The methane concentration of the gas produced also decreased immediately after the temperature was

Table 4.6. Summary of the effects of temperature reduction on fluidized bed performance

Initial Organic Loading COD m^{-3} d^{-1}	Temperature reduction °C	Duration Hours	Maximum % Increase COD	Volatile Acids	Suspended Solids	Maximum pH depression	Maximum % Decrease Alkalinity	Recovery Time Hours
3.2	10	4	30.1	110.7	50	0.3	7	6
3.2	10	8	56.2	133.3	54.8	0.3	8.5	6
3.2	20	4	105.0	100.0	75.0	0.38	14.3	7
3.2	20	8	143.0	271.0	54.6	0.31	11.5	10
5.0	10	4	33.0	118.0	31.6	0.2	3.6	6
5.0	10	8	31.0	172.0	45.0	0.15	8.1	6
5.0	20	4	51.7	135.0	22.0	0.25	7.1	7
5.0	20	8	121.8	184.0	41.9	0.2	14.9	20

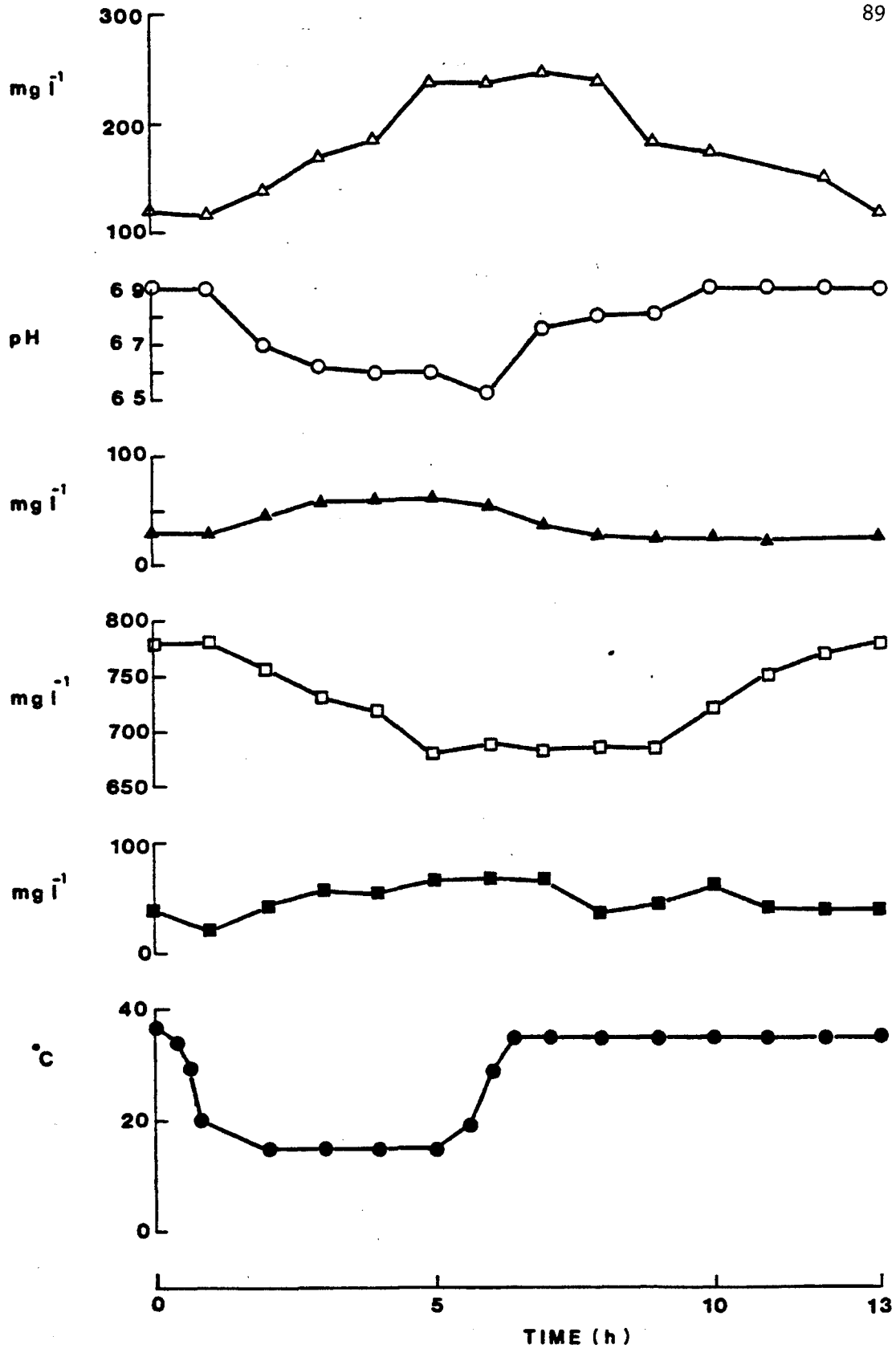


Figure 4.5. Effect of 4 h, 20°C temperature reduction on various process parameters of a heated anaerobic fluidized bed reactor (COD loading 3.2 kg m^{-3} d^{-1}) (△) effluent COD (○) pH, (▲) volatile acids, (□) alkalinity, (■) suspended solids, (●) reactor temperature

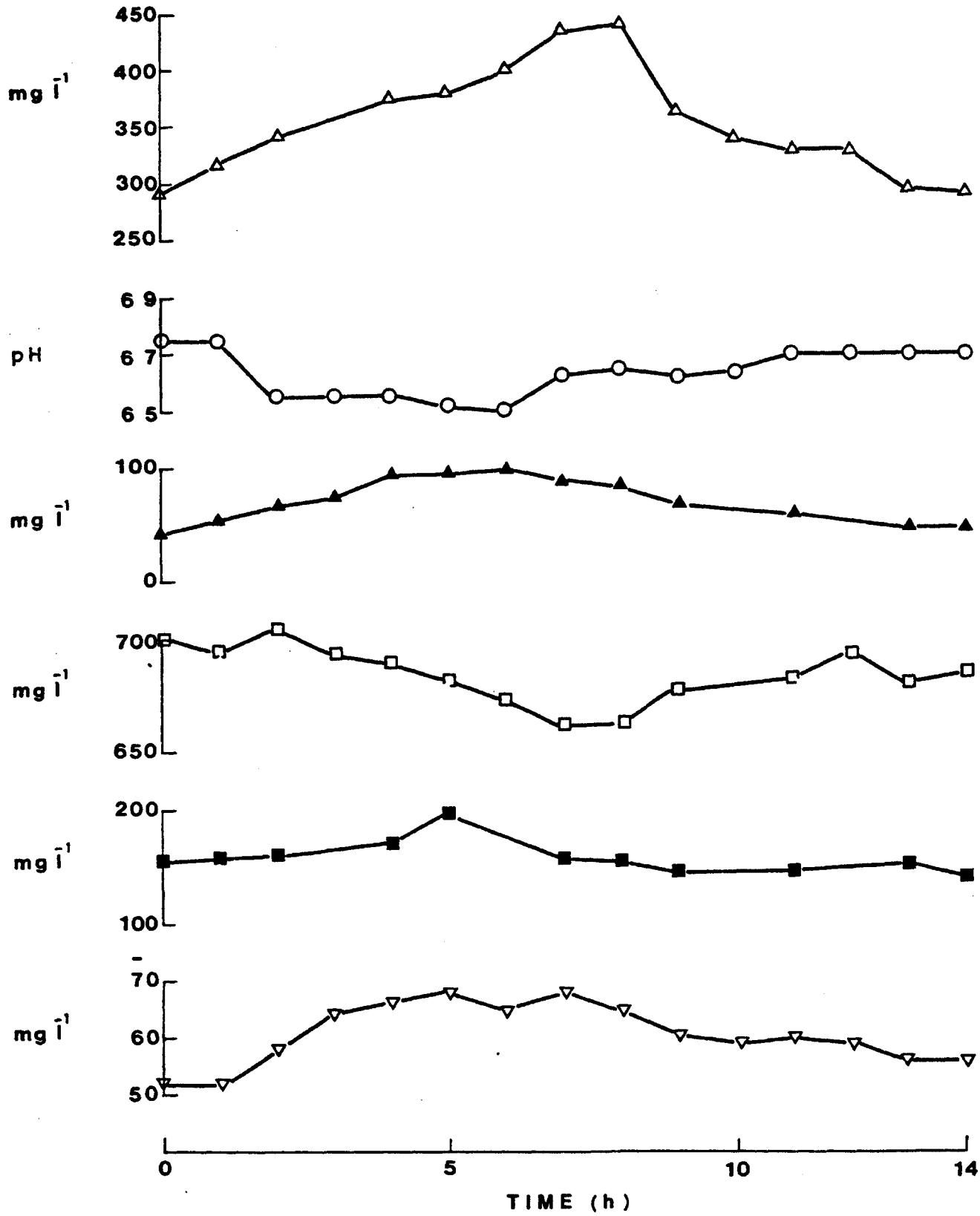


Figure 4.6. Effect of 4 h, 20°C temperature reduction on various process parameters of a heated anaerobic fluidized bed reactor (COD loading 5.0 kg m^{-3} d^{-1}) (△) effluent COD (○) pH, (▲) volatile acids, (□) alkalinity, (■) suspended solids, (▽) protein

returned to 37°C, gas production resumed, and an initial high rate of gas production was observed due to the high volatile acid concentrations.

It was also noted that due to the increased viscosity of the fluid at the lower temperatures, the bed expansion increased by up to 10% during a temperature reduction.

Figs 4.5. and 4.6. illustrate the changes in process parameters for a single four hour 20°C temperature reduction at COD loadings of 3.5 and 5 kg m^{-3} d^{-1} respectively. Temperature reductions carried out at the higher loading generally caused a greater degree of destabilization however, there was no difference in general behaviour of the reactor at the two loadings. The reactors demonstrated considerable resistance to adverse process conditions with no long term detrimental affects.

4.3.3. Influence of transient increases in influent flowrate on the performance of the heated fluidized bed reactor

A fluidized bed reactor operating at a COD loading of 5 kg m^{-3} d^{-1} was subjected to increases in influent flowrate of 100% and 150% each maintained for 4 and 8 hours. The results from each shock are summarised in Table 4.7.

In general the fluidized bed responded in the same manner as when the temperature was reduced (Section 4.3.2). A decrease in pH of 0.2-0.3 pH units during an increase in hydraulic load was found, effluent COD and volatile acids increased while there was a coincident decrease in alkalinity. Fig. 4.7. gives an example of the changes in process parameters during a single 4 hour, 150% flowrate increase. During the eight hour flow rate increase the effluent COD began to stabilize at a new value, although effluent volatile acids were still increasing slightly when a normal flowrate was resumed.

During the variations in organic load, effluent suspended solids increased to values of up to 45% greater than normal. The SS exhibited a definite upward trend in all cases rather than the erratic behaviour noted in the temperature reductions.

Table 4.7. Summary of the affects of increasing influent flowrate on the performance of the fluidized bed reactor

Initial COD Loading kg m^{-3} d^{-1}	Increase in COD loading	Duration Hours	Maximum % Increase COD	Volatile Acids	Suspended Solids	Maximum pH depression	Maximum % decrease Alkalinity	Recovery Time Hours
5	100%	4	42	160	22.8	0.25	5.2	8
5	100%	8	71.5	230	30.5	0.21	7.3	8
5	150%	4	115	245	22.8	0.47	15.8	12
5	150%	8	119	276	42.8	0.3	11.08	14

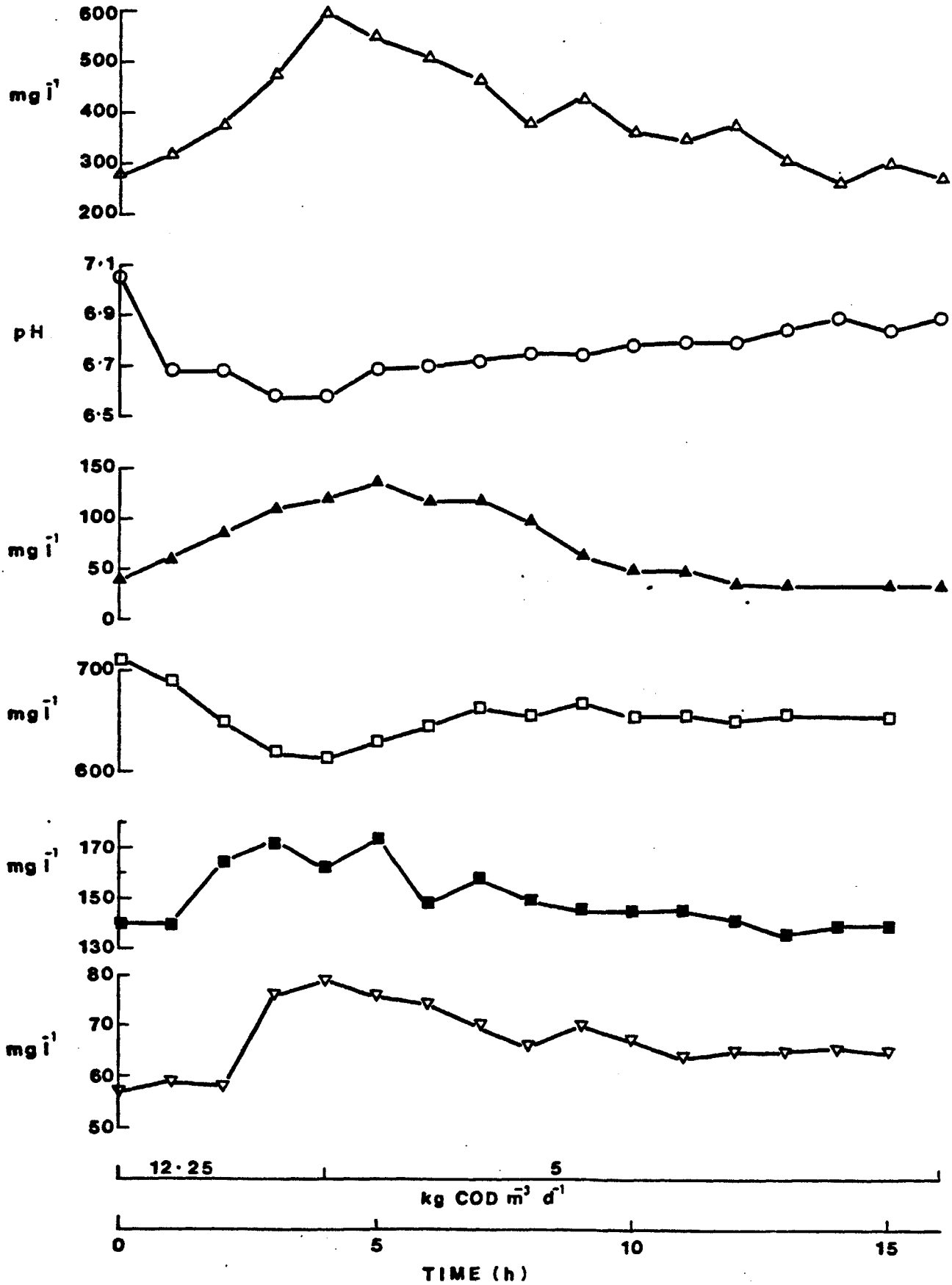


Figure 4.7. Effect of 4 h 150% hydraulic overloading on various process parameters of a heated anaerobic fluidized bed reactor (△) effluent COD (○) pH, (▲) volatile acids, (□) alkalinity, (■) suspended solids, (▽) protein

Gas production increased during the shock loading, although the methane concentration of the gas decreased with a coincident increase in carbon dioxide partial pressure.

After the influent flowrate was returned to its normal value all the measured parameters returned to their original values, and complete recovery took between 8 and 18 hours.

Although the reactor was destabilized during a hydraulic overloading no long term adverse affects were found and during all the flowrate increases the reactor maintained a COD removal of over 75%.

4.3.4. Influence of transient increases in influent COD on the performance of the heated fluidized bed reactor

Influent COD increases of 100% for 4 and 8 hours and 150% for 4 hours were applied to a reactor at a COD loading of 5 kg m^{-3} d^{-1}. The higher strength waste-waters were prepared by increasing each component of the waste by the same proportion. Table 4.8. summarises the effects of increased influent COD on reactor stability. The COD shock loads were characterised by a small, slow decrease in effluent pH, usually less than 0.1 pH unit, even though the volatile acids concentration rose rapidly. The pH appeared to be controlled by the increased buffering capacity of the influent as evidenced by the increased alkalinity of the effluent.

Effluent suspended solids increased rapidly during shock loads to values of up to 79% greater than normal, whilst effluent COD increased by up to 165%, the increases being generally more rapid and of a greater magnitude than found during equivalent influent flow rate increases. Fig. 4.8. illustrates the changes in process parameters during a single 4 hour, 150% influent COD increase.

Since the increased buffering capacity of the influent during the shock load was affecting process stability, a four hour, 150% COD increase was carried out without any increase in the sodium hydrogen carbonate concentration, the changes in process parameters during this increase are shown in Fig. 4.9.

Without the increased alkalinity the reactor demonstrated a greater degree of destabilization, the most significant aspect being

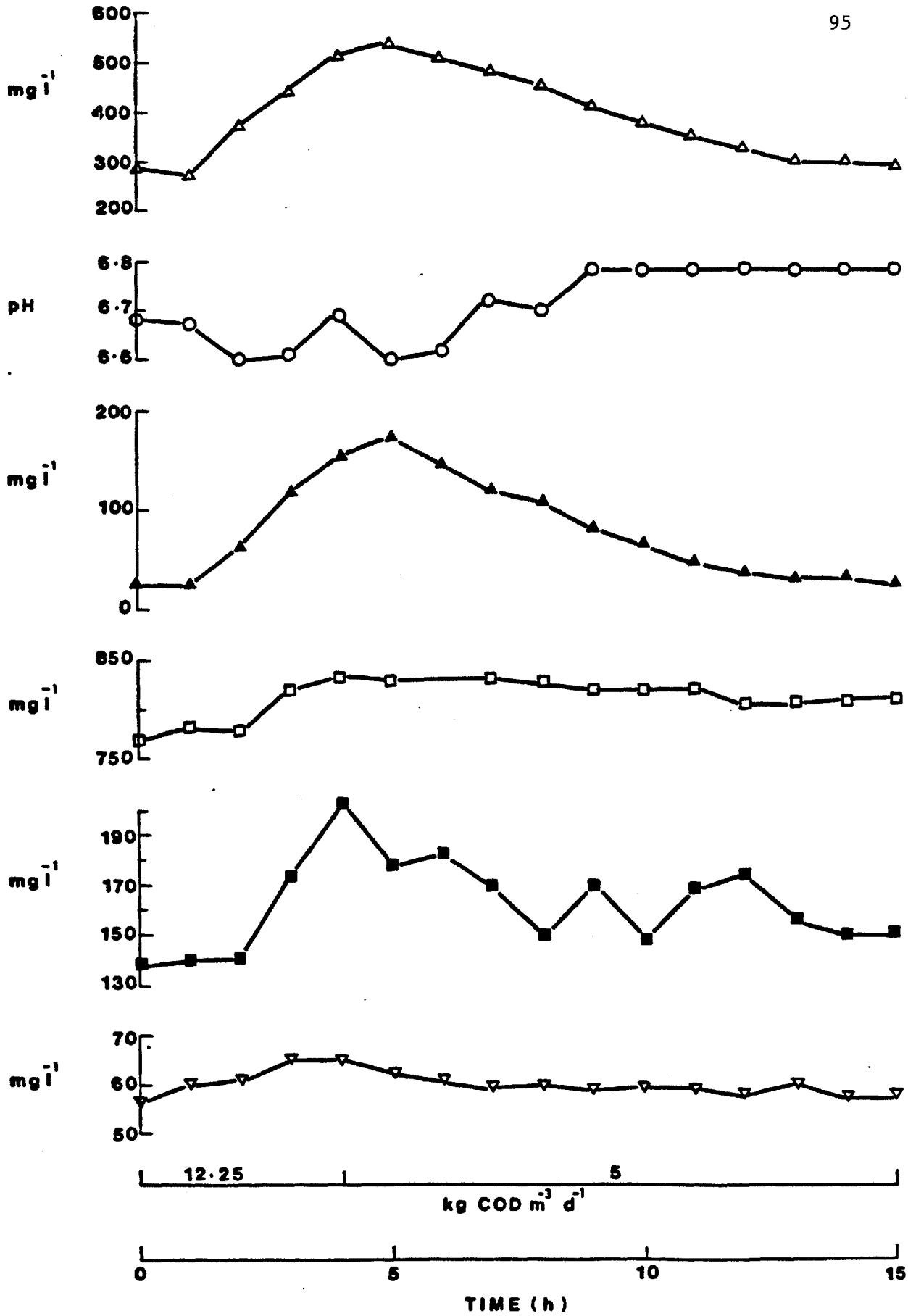


Figure 4.8. Effect of 4 h 150% influent COD increase on various process parameters on a heated anaerobic fluidized bed reactor (△) effluent COD (○) pH, (▲) volatile acids, (□) alkalinity, (■) suspended solids, (▽) protein

Table 4.8. Summary of the effects of increasing influent COD on fluidized bed performance

Initial COD Loading kg m^{-3} d^{-1}	Increase in Influent COD	Duration Hours	Maximum % Increase COD	Volatile Acids	Suspended Solids	Maximum pH from initial value	% Change in Effluent Alkalinity	Recovery Time Hours
5	100%	4	72.1	371	43.5	0.05	+ 6.6	9
5	100%	8	165.4	735	58.1	0.17	+14.2	17
5	150%	4	85.4	372	46.3	0.08	+ 5.5	11
5	150%*	4	96.8	402	78.5	0.13	+ 8.1	22

* Reduced Alkalinity Experiment

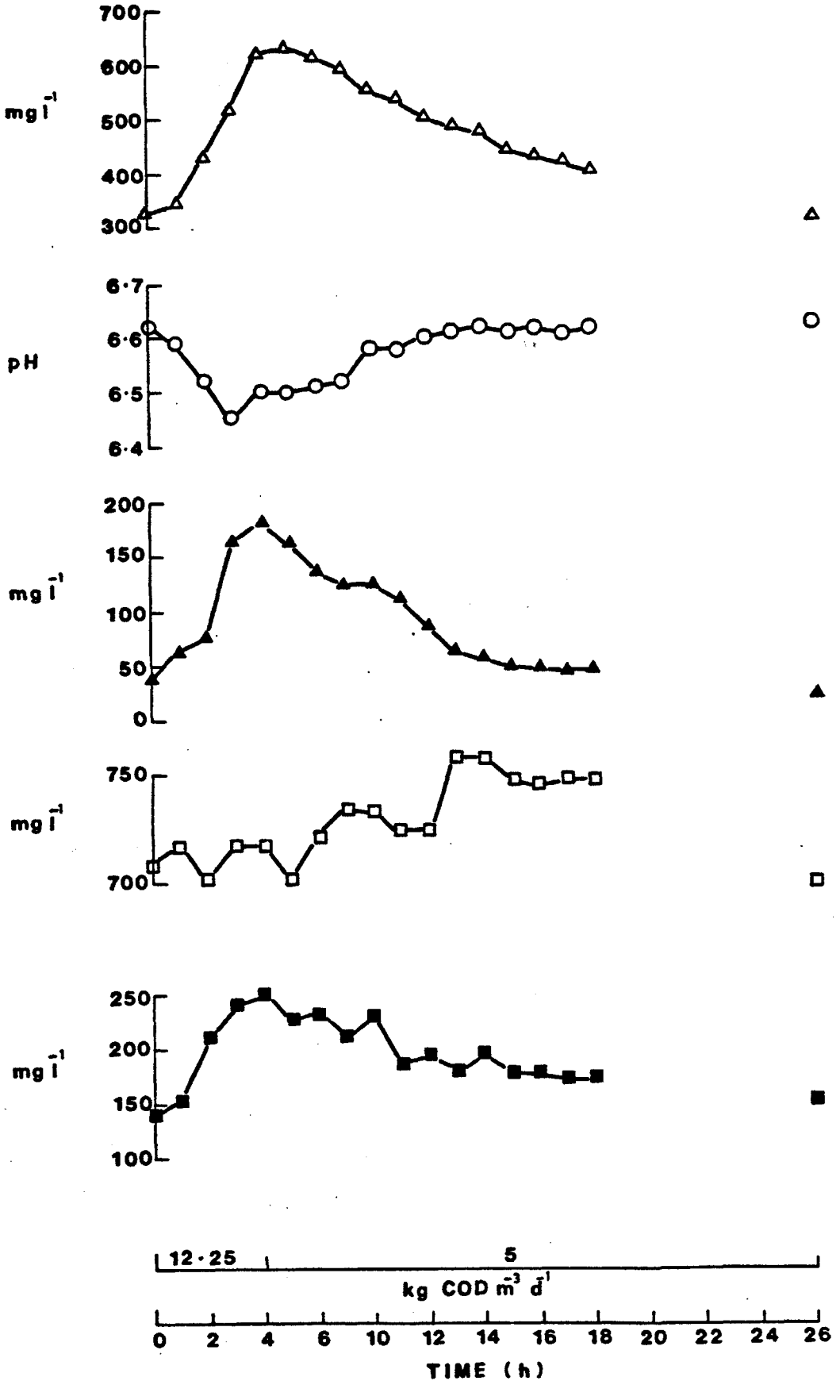


Figure 4.9. Effect of 4 h 150% influent COD increase (low influent alkalinity) on various process parameters of a heated anaerobic fluidized bed reactor (△) effluent COD (○) pH, (▲) volatile acids, (□) alkalinity, (■) suspended solids

the greater reduction in pH, decreased organic removal and a longer recovery period following the return to the original operating conditions. This could have important consequences if the reactor is treating a waste-water with a low influent alkalinity where organic overloading could lead to process failure.

4.3.5. Influence of transient increases in influent flowrate on the performance of the unheated fluidized bed reactor

Increases in influent flow rate of 100% and 150% each maintained for the 4 and 8 hours were applied to the fluidized bed reactor. The results are summarised in Table 4.9 Fig 4.10 shows the typical response of the reactor subjected to a single 150%, 4 hour increase.

In general, the increase in influent flow rate was characterised by an immediate drop in pH of between 0.15 and 0.25 pH units, with recovery to the original level immediately after the reactor was returned to its normal loading. The effluent COD increased during the shock load period by 40-57%, but started to decrease immediately when the flow rate was decreased, returning to original values within 8 hours.

The suspended solids exhibited a wide variation which did not coincide with the increase in flowrate and after the 8 hour shock period the suspended solids concentration continued to rise for up to eight hours following the return to normal operation conditions. The alkalinity remained virtually unaffected during the 100% increases but exhibited a general decline of between 15-18% during and following the 150% shock period.

4.3.6. Influence of transient increases in influent COD on the performance of the unheated fluidized bed reactor

Increases in influent COD of 150% and 300% both maintained for periods of 4 and 8 hours were applied to the reactor. Higher percentage organic load increases than those performed for the hydraulic overload experiments (Section 4.3.5) were chosen since the previous results indicated that the reactor could tolerate 100% organic loading increases with no major operating difficulties. The results from these experiments are summarised in Table 4.10.

Table 4.9. Summary of the effects of increasing influent flow rate on fluidized bed performance

Influent						Effluent		
Initial COD Loading kg m^{-3} d^{-1}	% Increase Influent Flow Rate	Duration Hours	Maximum COD	% Increase Volatile Acids	SS	Maximum pH Change	Maximum % Alkalinity Change	Recovery Time Hours
2.6	100	4	40	600	70	-0.24	+ 2	4
2.6	100	8	48	1100	220	-0.17	- 7	8
2.6	150	4	41	340	27	-0.20	-18	6
2.6	150	8	57	500	100	-0.15	-15	8

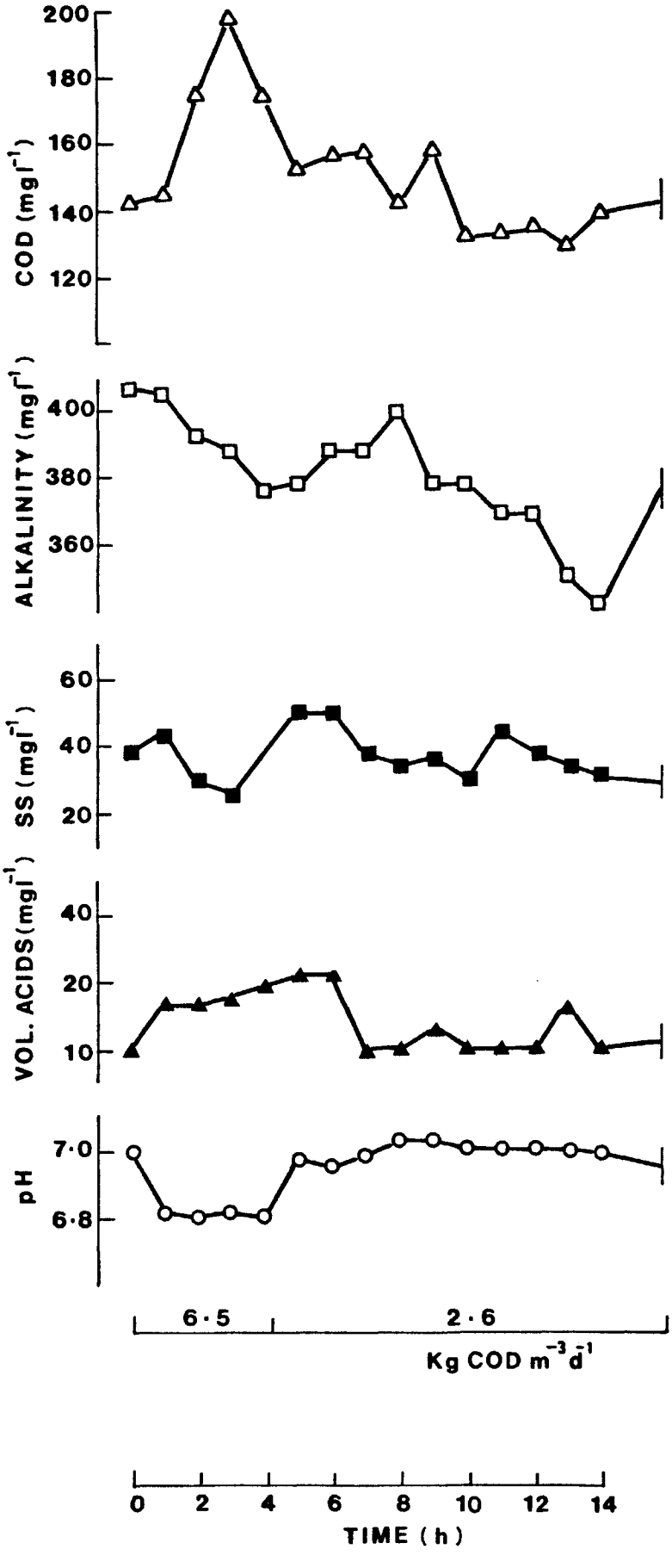


Figure 4.10. Effect of 4 h 150% influent flowrate increase on various process parameters on an unheated anaerobic fluidized bed reactor

Table 4.10. Summary of the effects of increasing influent COD on fluidized bed performance

Influent				Effluent				
Initial COD Loading kg m^{-3} d^{-1}	% Increase Influent Flow Rate	Duration Hours	Maximum % COD	% Increase Volatile Acids	SS	Maximum pH Change	Maximum % Alkalinity Change	Recovery Time Hours
2.6	150	4	35	680	25	-0.25	+15	4
2.6	150	8	44	860	59	-0.15	+28	4
2.6	300	4	160	1700	211	-0.04	+39	8
2.6	300	8	400	2260	166	+0.08	+75	9

The fluidized bed reactor responded to the 150% COD increases in a similar manner to the 100% and 150% increases in hydraulic load. However the 300% increases in influent COD resulted in much greater variations in all measured parameters with the exception of pH. Fig. 4.11. indicates the response of the reactor to a single 300%, four hour COD increase.

During a 300% increase the pH of the effluent remained stable during and following the short period. The volatile acids rose to concentrations of 80-100 mg l^{-1} and were still increasing at the conclusion of the short period. However they returned to their original values within four hours of the reactor being returned to its original loading. The alkalinity of the effluent increased during all the shock loads to values of up to 75% greater than usual and did not return to its original level after the shock period but stabilized at a new higher value. The suspended solids exhibited an increase during the shock period, with maximum values (up to 75% increase) being attained up to six hours after the reactor was returned to its original loading.

The effluent COD increased to values up to 400% greater than normal, with evidence during the eight hour shock period of some degree of stabilization. The COD returned to its original level eight to nine hours after the reactor was returned to its normal loading.

The reactor therefore behaved in a similar manner during COD increases to the heated reactor as reported in Section 4.3.3. The results cannot be directly compared since different substrate and operating conditions were used, but in general the unheated reactors responsed more slowly to an organic overload albeit at a lower organic removal rate.

4.3.7. Influence of transient changes in reactor operating temperature on the performance of an unheated fluidized bed reactor.

The operating temperature of the reactor was decreased to 10°C and increased to 35°C each for a four hour period. Transition periods of one hour before and after the shock periods allowed full temperature adjustment to take place. The major variations of the process parameters are summarised in Table 4.11.

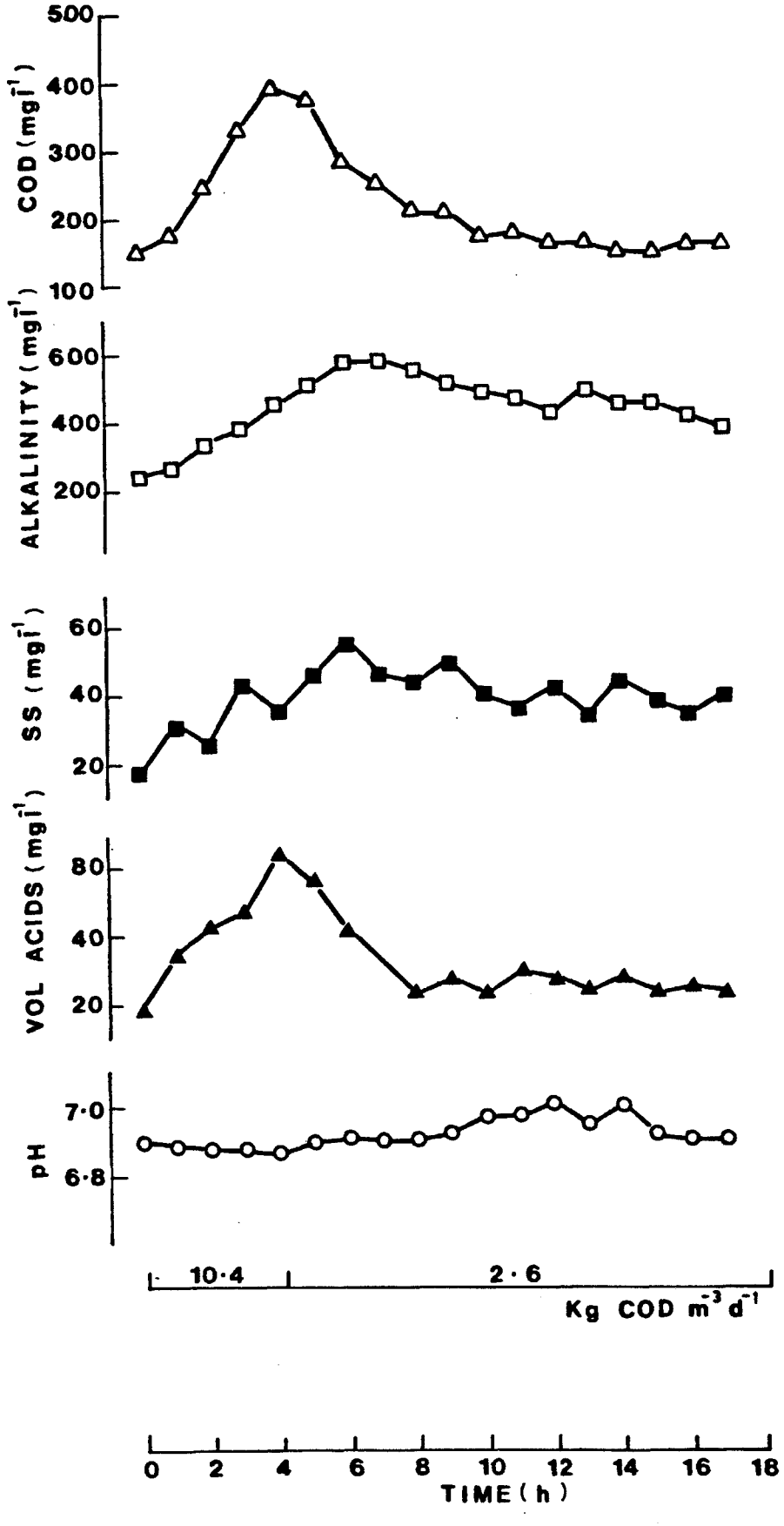


Figure 4.11. Effect of 4 h 300% influent COD increase on various process parameters of an unheated anaerobic fluidized bed reactor

The transient temperature reduction resulted in an effluent pH which remained steady throughout the shock period, with a small increase of 0.1 pH units two hours after the reactor was returned to room temperature. Volatile acids increased during the temperature change periods but stabilized during operation at the lower temperature. The alkalinity showed a gradual decrease during and after the shock period.

The suspended solids remained at a steady level throughout, although there was a gradual increase two hours after the temperature was restored. The COD was unstable during the temperature reduction, fluctuations continued two hours after the reactor was returned to its original operating temperature, return of the COD to its normal value was attained within four hours.

The transient increase in temperature of the reactor resulted in the pH remaining stable during and after the shock period with a small decrease following the return to room temperature. The volatile acids increased and were unstable during the shock period, returning to original values three to four hours after the temperature was returned to 20°C.

There was a high initial rise in both COD and SS immediately following the temperature change, however recovery during the shock period was observed.

It was therefore evident that small adverse affects occurred only during the temperature changes and the reactor continued to remove organic material at a typical rate at the reduced or increased temperature.

4.3.8 Influence of transient changes in influent pH on the performance of an unheated fluidized bed reactor

An influent pH decrease from 6.25 to 3.0 and an increase from 6.25 to 10 were each maintained for eight hours. The influent alkalinity was thus 0 mg l^{-1} at pH 3 and 233 mg l^{-1} at pH 10, the responses of the reactor to the pH changes are summarised in Table 4.12.

The increase in influent pH resulted in an increase in effluent pH of 0.18 over the eight hour period, with a gradual return to the

Table 4.11. Summary of the effects of increasing influent flow rate on fluidized bed performance

Influent						Effluent		
Initial COD Loading kg m^{-3} d^{-1}	Reactor Temperature °C	Duration Hours	Maximum COD	% Increase Volatile Acids	SS	Maximum pH Change	Maximum % Alkalinity Change	Recovery Time Hours
2.6	10	4	40	400	90	+0.09	-9	4
2.6	35	4	66	440	89	-0.06	-6	4

Table 4.12. Summary of the effects of increase and decrease of influent pH on fluidized bed performance

Influent						Effluent		
Initial COD Loading kg m^{-3} d^{-1}	Influent pH	Duration Hours	Maximum COD	% Increase Volatile Acids	SS	Maximum pH Change	Maximum % Alkalinity Change	Recovery Time Hours
2.6	10	8	22	400	40	+0.18	+5	4
2.6	3	8	8	300	40	-0.10	-15	5

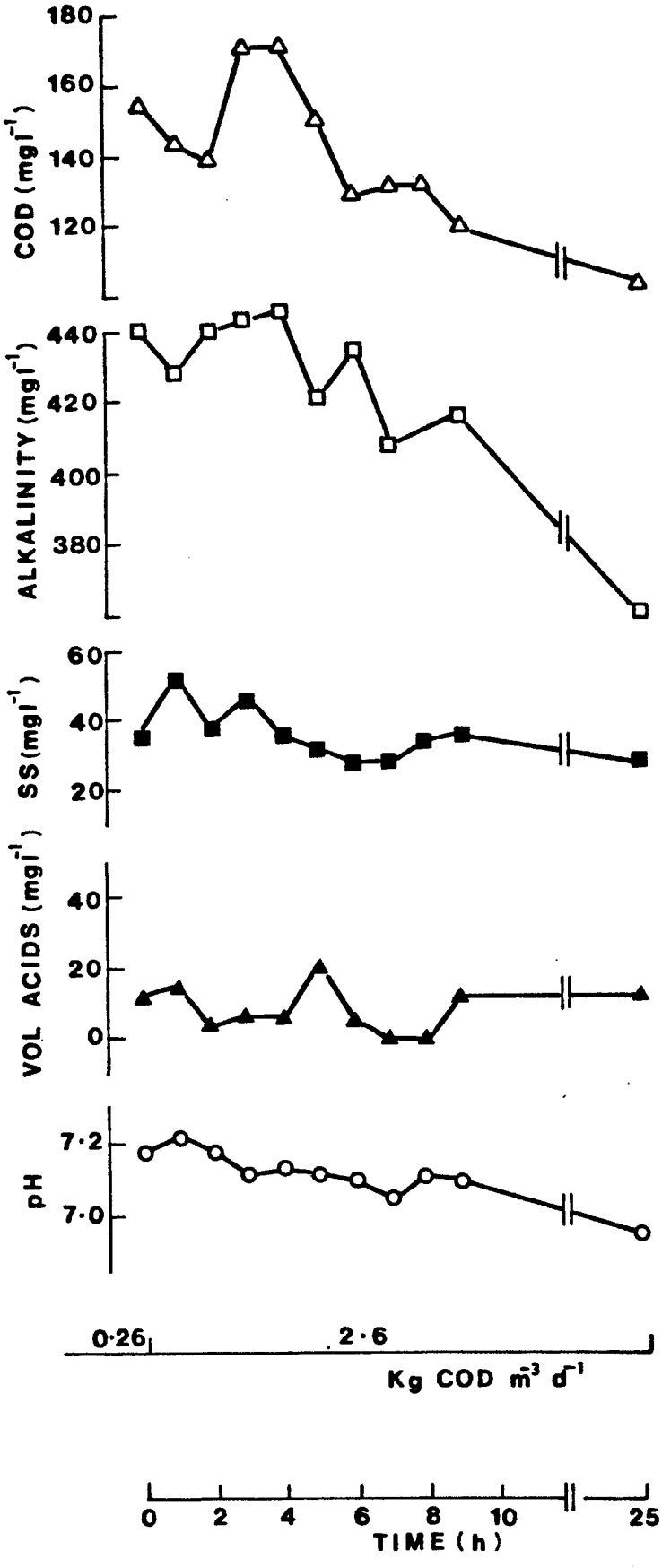


Figure 4.12. Effluent of simulated working week operation on various process parameters of an unheated fluidized bed reactor

original value 16 hours later. Alkalinity increased by 5% during the pH increase, remaining at this level for two hours after the influent pH was restored to 6.25, the alkalinity then decreased by 20% over the following 14 hours. COD, suspended solids and volatile acids all showed an initial increase, but no long term detrimental effect was noted.

During the eight hour pH decrease to pH 3, the alkalinity was the only parameter significantly affected. This showed a consistent decrease during the course of the pH shock but quickly increased after the influent pH was returned to 6.25, the pH of the effluent decreased by 0.1; COD, suspended solids and volatile acids were all unaffected.

4.3.9. Influence of long term influent flow rate decreases on the performance of the unheated fluidized bed reactor

To simulate the effects of reduced waste discharge at the end of a five day working week the reactor loading was decreased by 90% for two days and then returned to its original loading. The effects of this decrease are shown in Fig 4.12. Reactor operation was unstable with a decrease in pH over a period of 25 hours of 0.25. Alkalinity, COD, suspended solids and volatile acids were all unstable, however the fluctuations in these parameters were not severe and during the first day of operation at normal loading the reactor consistently removed more than 85% of the influent COD. This indicated that anaerobic fluidized bed reactors could be used in situations where intermittant interruptions to the flow of waste-water occur as a result of the nature of the industrial process used.

4.4. An evaluation of ion exchange resin as a biological support material

In order to minimize the recycle rate and therefore the pumping costs involved with the reactor system, lighter particles of ion exchange resin were evaluated in two fluidized bed reactors. Each reactor was filled with 2.2 litres of resin, and the remaining volume of the reactor was filled with the meat extract waste-water with a COD of 1250 mg l^{-1}. The recycle pump was adjusted to give an initial bed expansion of 20%, active digester sludge (20 ml) was injected into the lowest sample tap of each reactor, the reactors were operated at room temperature. Effluent COD and pH were monitored daily and once the COD began to decline, influent was supplied at a flow rate equivalent

to a COD loading of 0.25 kg m^{-3} d^{-1}. The effluent COD over the first forty days of operation is shown in Fig 4.13.

The reactors were operated over a period of 10 week, little biomass visibly developed on the particles and COD removal was poor even at the low loading selected for this study. There was no further improvement in COD removal during the final four weeks of operation, the use of ion-exchange resin was therefore considered unsatisfactory and discontinued.

4.5. An evaluation of four start-up regimes for anaerobic fluidized bed reactors

Following the initial experiments one of the disadvantages of the anaerobic fluidized bed reactor was recognized to be the the long periods required to attain efficient treatment at realistic organic loadings. Therefore attempts were made to improve start-up times by employing substrate amendment and continuous or stepped loadings.

Four reactors were used as described in Section 3.2.1, each containing 2.2 l of silica sand (BIS Redhill 65). Each reactor was filled with a substrate of the appropriate composition and the recycle pump adjusted to give a bed expansion of 20%, all reactors were operated at 37°C. The substrate used was the meat extract waste described in Section 3.2.2, with a COD of 2500 mg l^{-1}. Where appropriate up to half of the Lab Lemco components was replaced with its COD equivalent of methanol. The four regimes investigated were:

1. Continuous COD loading at 4.6 kg m^{-3} d^{-1}.
2. Continuous COD loading at 4.6 kg m^{-3} d^{-1} with 50% of the COD initially replaced by methanol.
3. Stepped COD loading over a period of 40 days.
4. Stepped COD loading over a period of 40 days with 50% of the COD initially replaced by methanol.

Where a substrate with methanol was used the NH_4Cl concentration was adjusted to 50 mg l^{-1}, the changes in operating conditions during the forty days of this study are summarised in Table 4.13.

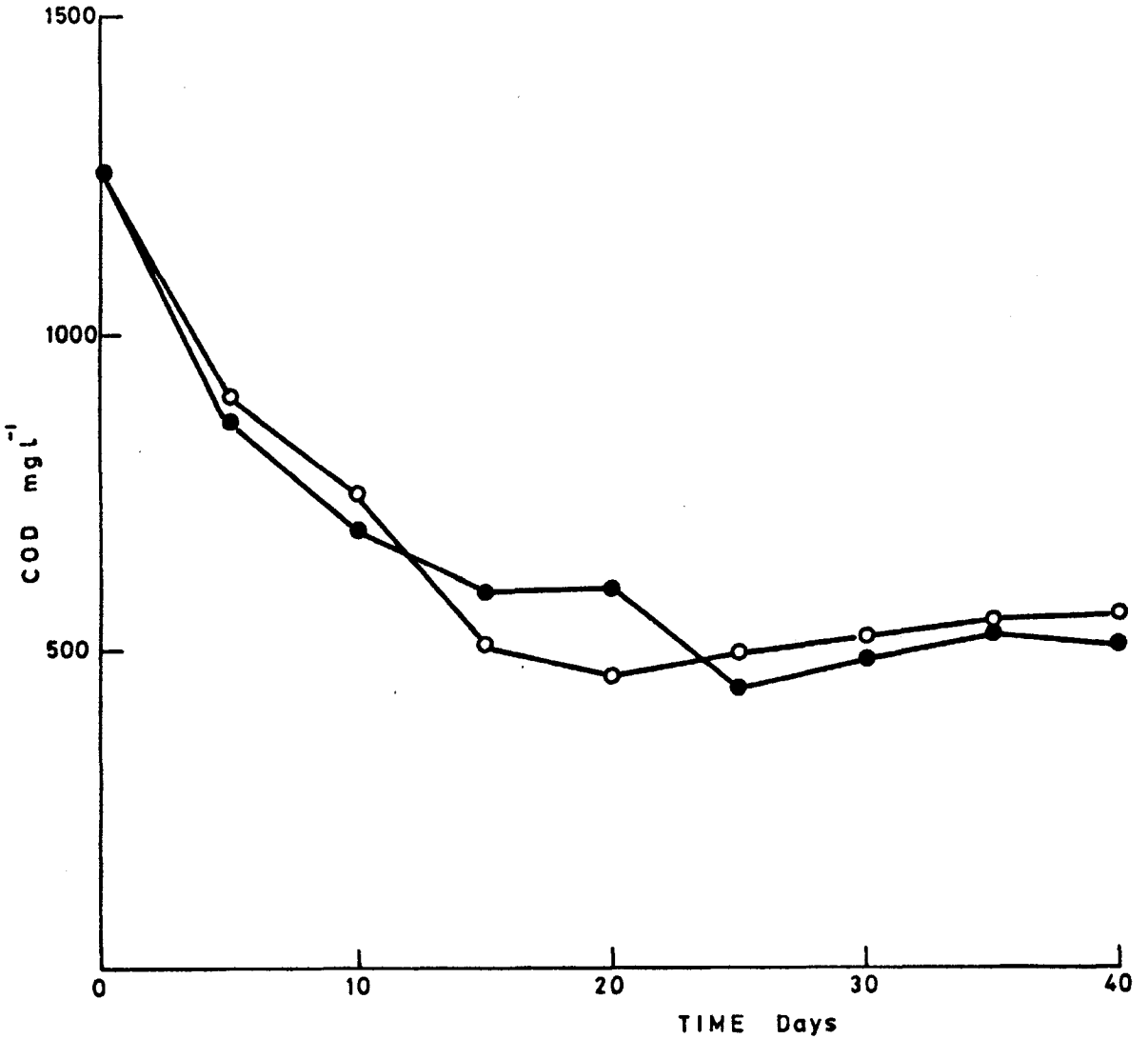


Figure 4.13. Effluent COD during initial start-up period of anaerobic fluidized bed reactors using ion-exchange resin as a biological support material

Table 4.13. Organic loading and influent methanol concentration (COD equivalent) for each reactor

Day	Reactor							
	1		2		3		4	
	COD Loading $kgm^{-3}d^{-1}$	Methanol COD mgl^{-1}	COD Loading $kgm^{-3}d^{-1}$	Methanol COD mgl^{-1}	COD Loading $kgm^{-3}d^{-1}$	Methanol COD mgl^{-1}	COD Loading $kgm^{-3}-1$	Methanol COD mgl^{-1}
0	4.6	1250	4.6	0	0.86	0	0.86	1250
10	4.6	1250	4.6	0	1.64	0	1.64	1250
20	4.6	1250	4.6	0	2.50	0	2.50	1250
25	4.6	625	4.6	0	4.00	0	4.00	625
30	4.6	625	4.6	0	4.00	0	4.00	625
35	4.6	0	4.6	0	4.60	0	4.60	0

Once the reactors had equilibrated at their operating temperature active digester sludge (20 ml) was inoculated into each reactor through the lowest sample tap. The feed to the reactor was then adjusted to give the required flowrate. Effluent COD, pH, total volatile acids and suspended solids (SS) were measured daily.

Effluent COD, volatile acids and pH during the first thirty days of the study are presented in Figs. 4.14, 4.15 and 4.16. There was an initial rapid decline in COD in all the reactors followed by a slight increase and then a slower decrease in COD. Stepped increase loading regimes gave the most rapid development in COD reduction, with methanol addition a 90% COD reduction was achieved within eight days of operation at a very low loading. The stability of both reactors operating at a constant loading was poor for the first 20 days of operation and the addition of sodium hydrogen carbonate was required daily to maintain the pH above 6.5. Again the addition of methanol gave a more rapid start-up for the constant loading regime.

The addition of methanol as a substrate also had the effect of reducing the effluent suspended solids concentration from these reactors. These concentrations gradually increased as the methanol concentration was decreased. Volatile acid concentrations generally

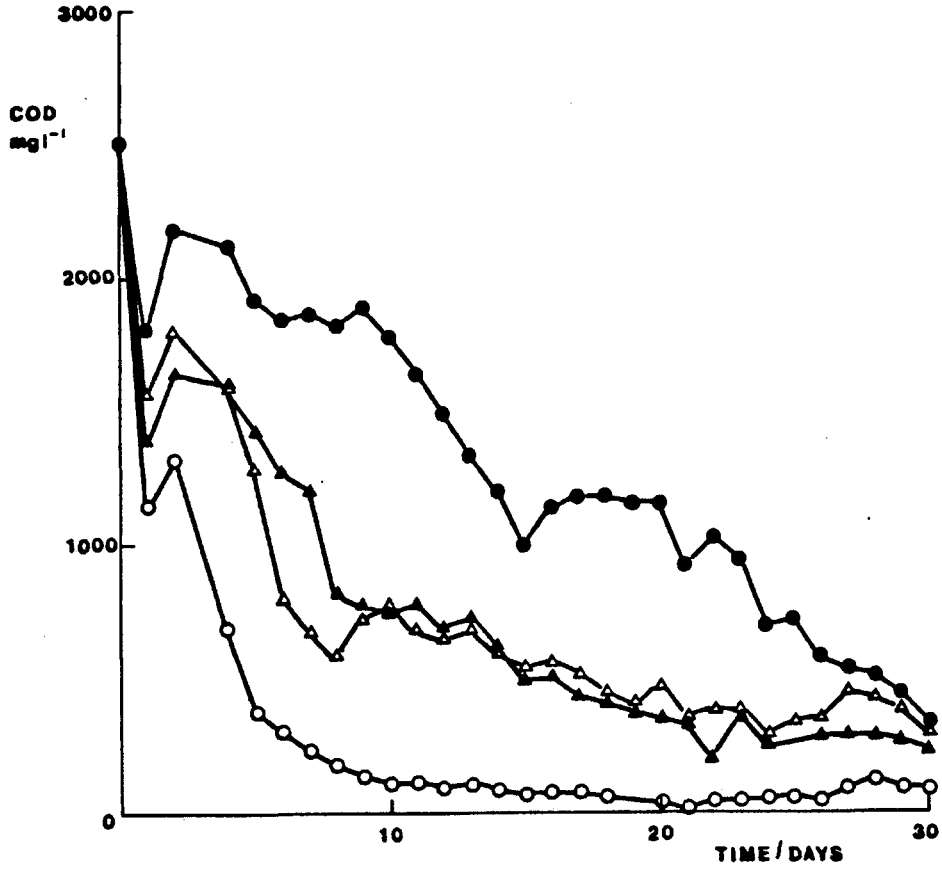


Figure 4.14. Effluent COD of anaerobic fluidized bed reactors during the first 30 days of operation (△) reactor 1, (●) reactor 2 (▲) reactor 3, (○) reactor 4

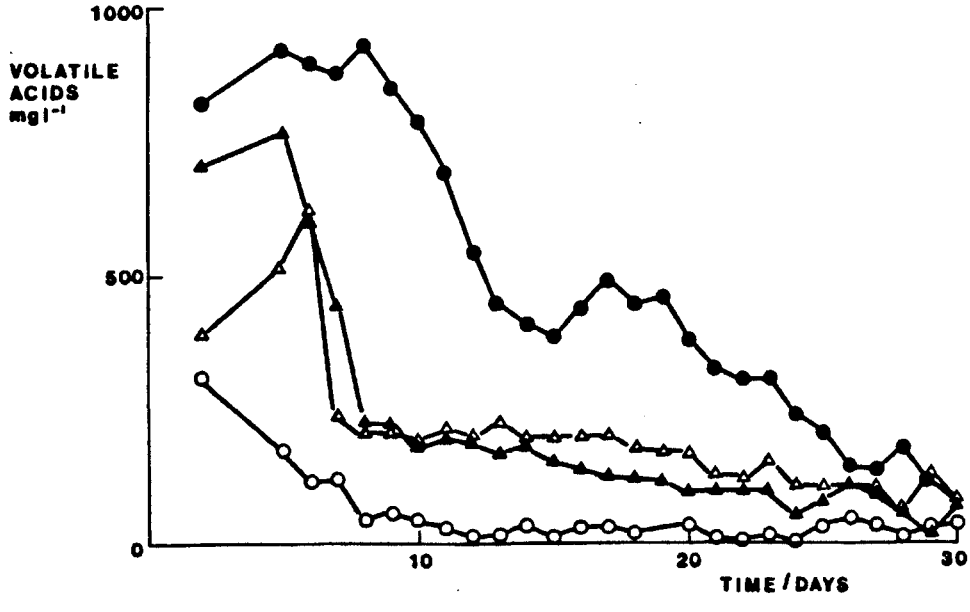


Figure 4.15. Effluent volatile acids of anaerobic fluidized bed reactors during the first 30 days of operation (△) reactor 1, (●) reactor 2 (▲) reactor 3, (○) reactor 4

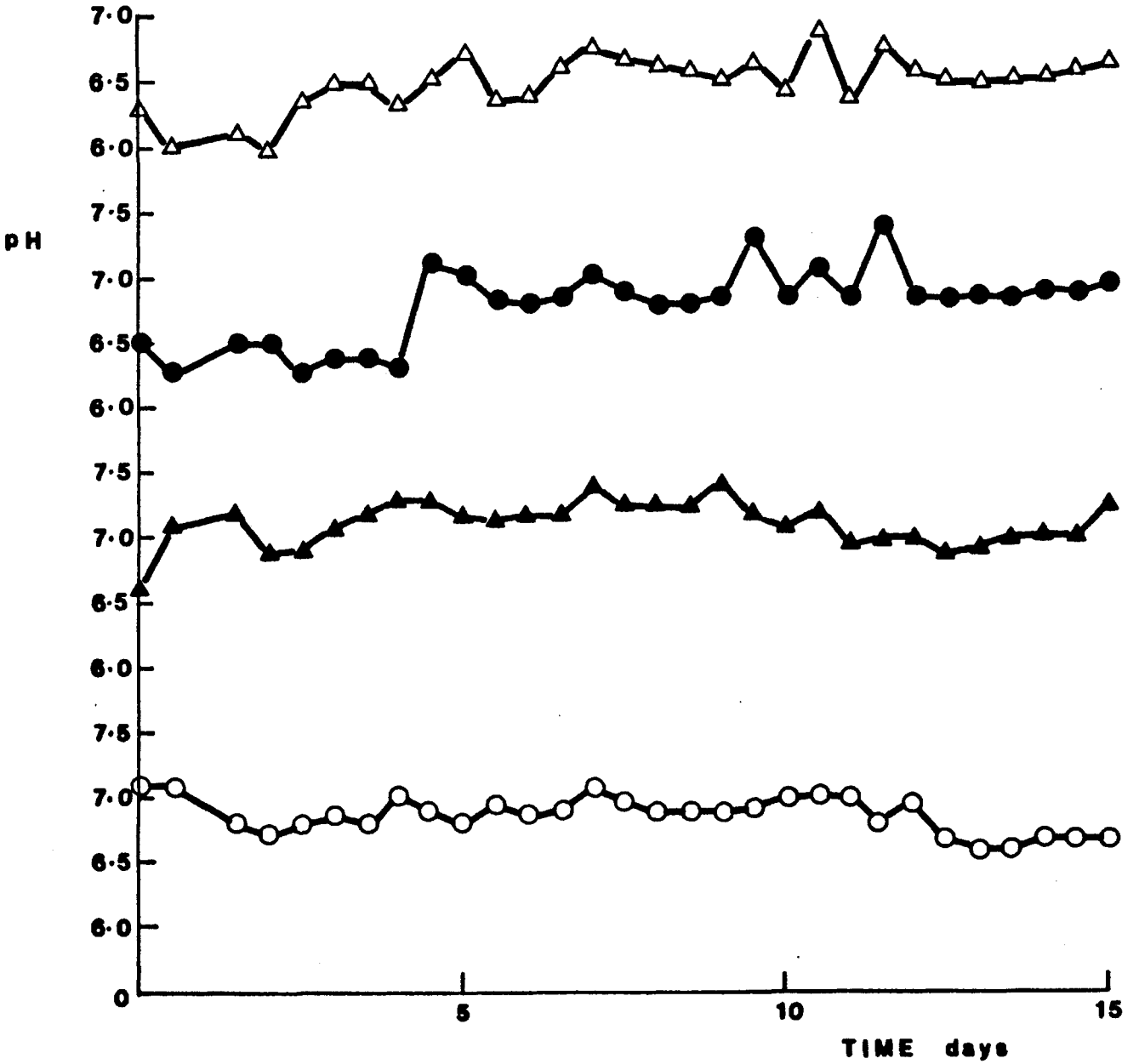


Figure 4.16. Effluent pH of anaerobic fluidized bed reactors during the first 30 days of operation (△) reactor 1, (●) reactor 2 (▲) reactor 3, (○) reactor 4 .

followed the COD concentration and except for the reactor operating at constant loading without methanol addition were usually below 250 mg l^{-1}.

Each reactor's performance 40 days after start-up was measured and the results given in Table 4.14. Little significant differences in performance can be noted except for higher methane concentrations in the gas produced from the reactors with a stepped loading regime.

Table 4.14. Effluent characteristics for each reactor on day 40

Reactor	1	2	3	4
Effluent COD				
filtered mgl^{-1}	126	163	138	124
unfiltered mgl^{-1}	172	195	207	199
Effluent S.S. mgl^{-1}	44	64	70	64
V.S.S. mgl^{-1}	44	60	64	64
Effluent pH	6.7	6.84	6.75	6.89
Effluent volatile acids mgl^{-1}	25	37	30	25
Effluent turbidity (FTU)	10.05	11	13.5	8.0
Gas Composition (% CH_4)	71	71	75	75

The experiment indicated that the start-up time of an anaerobic reactor can be decreased by the use of a methanol supplement and manipulation of the organic loading.

4.6. An evaluation of single and separated phase anaerobic digestion in fluidized bed reactors

4.6.1. Initial reactor stabilization

An influent based on glucose (see Table 3.2) was chosen for use in this study to allow the results to be compared to previously reported data. The reactors employed were the four used for the start-up evaluation experiments (Section 4.5). Two reactors were operated at an influent COD of 6000 mg l^{-1} whilst the remaining two operated with a COD of 12000 mg l^{-1}. At each influent strength one reactor was operated as a single phase reactor as previously described whilst the remaining two operated with an acidification reactor as

described in Section 3.3.1. Each reactor's operating conditions are included in Table 4.15.

Table 4.15. Single and separated phase reactor operating conditions

Reactor	1	2	3	4
Operating Temperature °C	37	37	37	37
Influent COD mg l^{-1}	12000	12000	6000	6000
Influent BOD mg l^{-1}	5800	5800	2900	2900
Influent pH	7	7	7	7
Phase	Single	Separate	Single	Separate
Recycle ratios	1:120-1:40			

The fluidized bed reactors used had already developed an active biomass during and following the start-up experiments described previously (Section 4.5.). The reactors were fed with waste-water of the required strength at 0.25 ml min^{-1} and the flow rate was increased step wise to achieve a COD loading of 12 kg m^{-3} d^{-1} over a period of eight weeks. No operational difficulties were encountered during this period.

4.6.2. A comparison of single and separated phase digestion over a range of COD loadings

Each reactor system was operated at six fluidized bed COD loadings in the range 3-18 kg m^{-3} d^{-1} at an influent COD of 12000 mg l^{-1} and 1.5-9 kg m^{-3} d^{-1} at an influent COD of 6000 mg l^{-1}. At the three highest loadings for each reactor the concentration of sodium hydrogen carbonate in the influent was increased by 100% to improve reactor stability. The influent flow rate was adjusted for the required loading and the reactors were allowed to stabilize for 14 days or three hydraulic residence times. The reactors operational parameters were measured daily over three days to ensure stabilization had taken place; the mean of the three measurements is reported. Parameters measured were fluidized bed effluent pH, COD (soluble and insoluble), volatile acids (total and individual), suspended and vola-

tile suspended solids, gas production (at three COD loadings), fluidized bed suspended and volatile suspended solids, acidification reactor effluent pH, volatile acids (individual and total), suspended solids, hexose and COD.

4.6.2.1. Performance of acidification reactors.

Prior to initial start-up the reactors were filled with waste solutions and the contents were allowed to stabilize at the required temperature. The reactors were both inoculated with 10 ml of freshly collected activated sludge and allowed to operate in a batch mode for 48 hours before waste-water was allowed to enter the reactor at a flow rate of 0.25 ml min^{-1} and the loading increased as previously described. An active bacterial population was rapidly established as evidenced by rapid increase in effluent suspended solids, and a reduction in pH. Since the reactors were connected in series with the fluidized beds they were then subjected to the same range of influent flow rates although the COD loading on the acidification reactors was proportionally higher due to their smaller volume.

Acidification reactor suspended solids were affected by both influent concentration and flowrate. The suspended solids were approximately twice as high in the reactor fed with the higher strength solution than in the reactor fed with the lower strength substrate. Suspended solids declined linearly with hydraulic residence time in both the reactors except at the two highest loadings in the high strength influent reactor. After 30 days operation both reactors developed a yeast type biomass (identified by direct visual microscopy, which at the higher loadings attached itself to the reactor walls. The reactors were emptied, cleaned and re-inoculated however this type of biomass still persisted to a limited extent although increasing the stirrer speed reduced wall growth. Acidification reactor suspended solids over the range tested are given in Fig. 4.17.

Reactor operating pH was between 3 and 5. At the lower loadings with the reduced buffering capacity the pH was relatively stable over the three COD loadings, with a typical value of 3.5. The operating pH increased to over 4.5 when the influent sodium hydrogen carbonate concentration was increased but declined with further increases in loading, these phenomena are shown in Fig. 4.18.

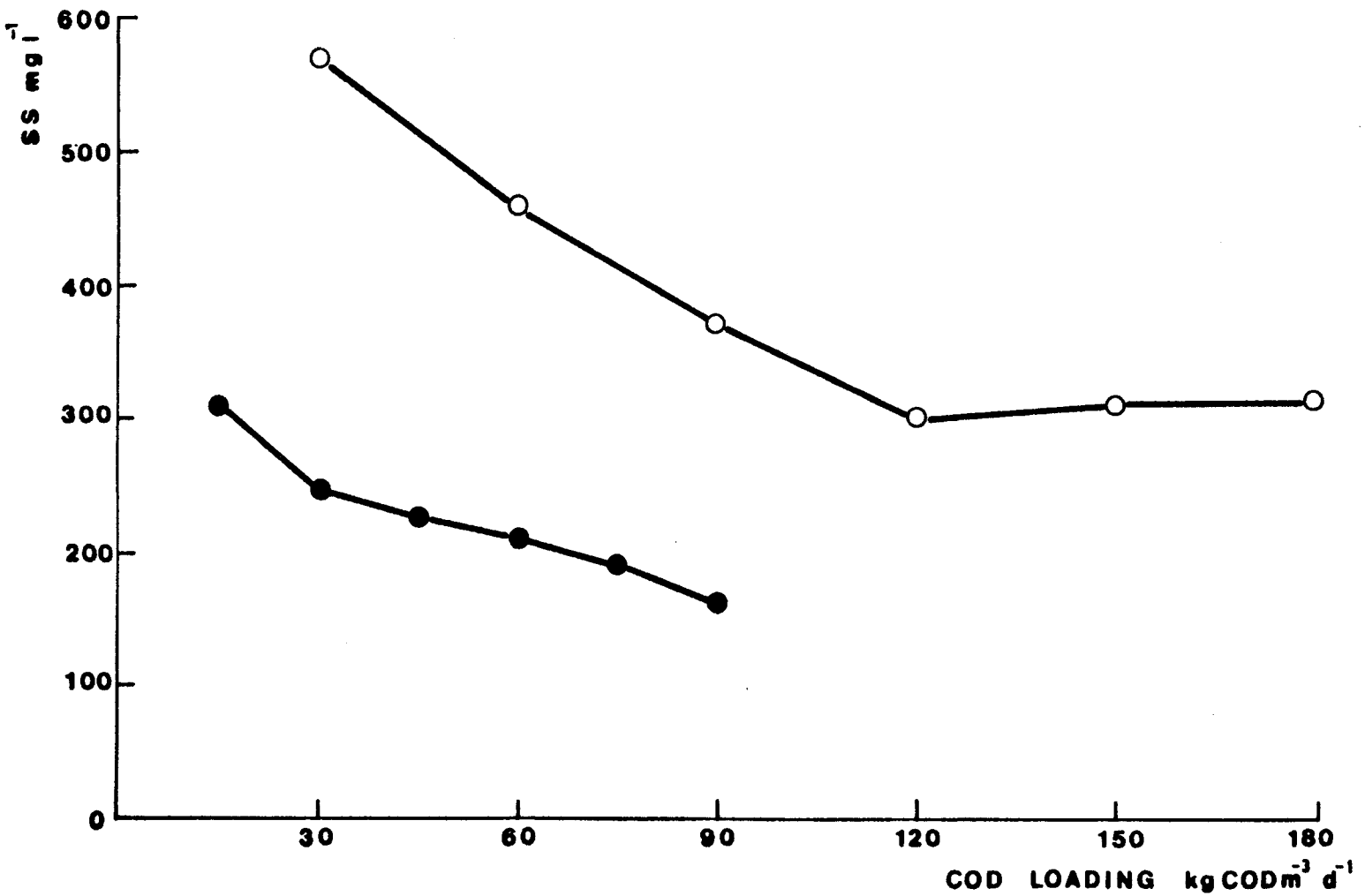
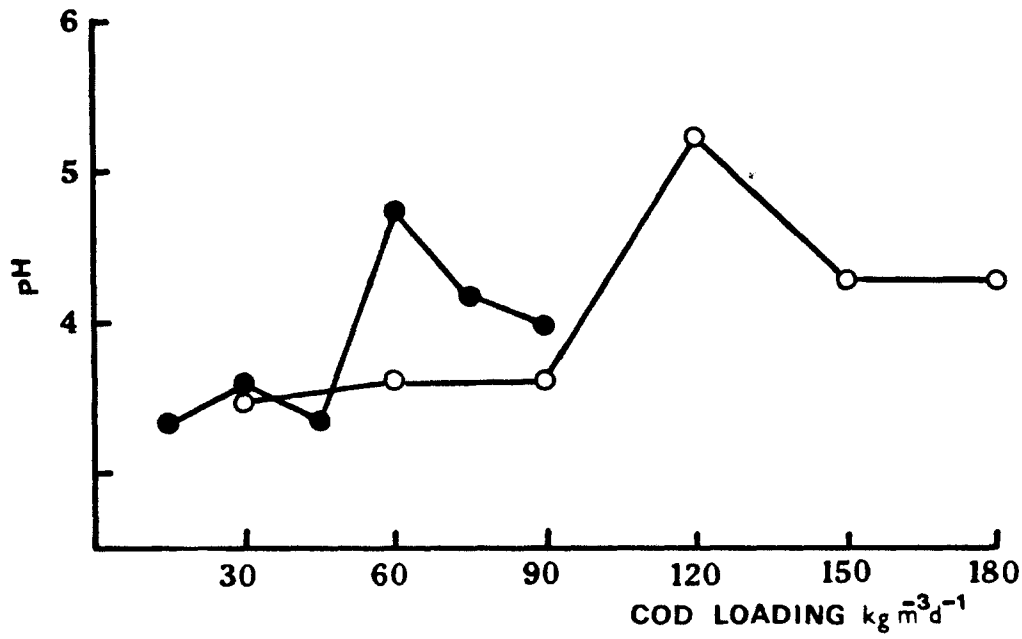


Figure 4.17. Influence of organic loading on acidification reactor suspended solids (●) influent COD 6000 mg l^{-1} (○) influent COD 12000 mg l^{-1}

Figure 4.18. Influence of organic loading on acidification reactor operating pH Influent COD (●) 6000 mg l^{-1} (○) 12000 mg l^{-1}



The total volatile acid concentrations generally reflected the changes in pH, showing a general decline with increasing organic loading. Higher concentrations were found when the sodium hydrogen carbonate concentration increased, but again these declined with increasing organic loading. Acetic acid was the main acid product usually accounting for over 90% of the total acids. Propionic and butyric acids were also detected in measureable concentrations, propionic acid concentrations in the high strength reactor generally increased with increasing loading whilst in the lower strengh reactor the concentration peaked at an intermediate loading. Butyric acid concentrations were low (<30 mg l^{-1}) and were relatively unaffected by the organic load. Higher molecular weight organic acids (such as valeric acid) were also detectable but not in measureable concentrations. Individual volatile acids are given in Table 4.16. Effluent hexose sugar concentration increased with increasing organic loading except in the reactor supplied with waste-water at a COD of 6000 mg l^{-1} where the effluent hexose concentration dropped at a COD loading of 60 kg m^{-3} d^{-1}, in both cases the concentration tended to reach a plateau at the higher loadings as shown in Fig. 4.19.

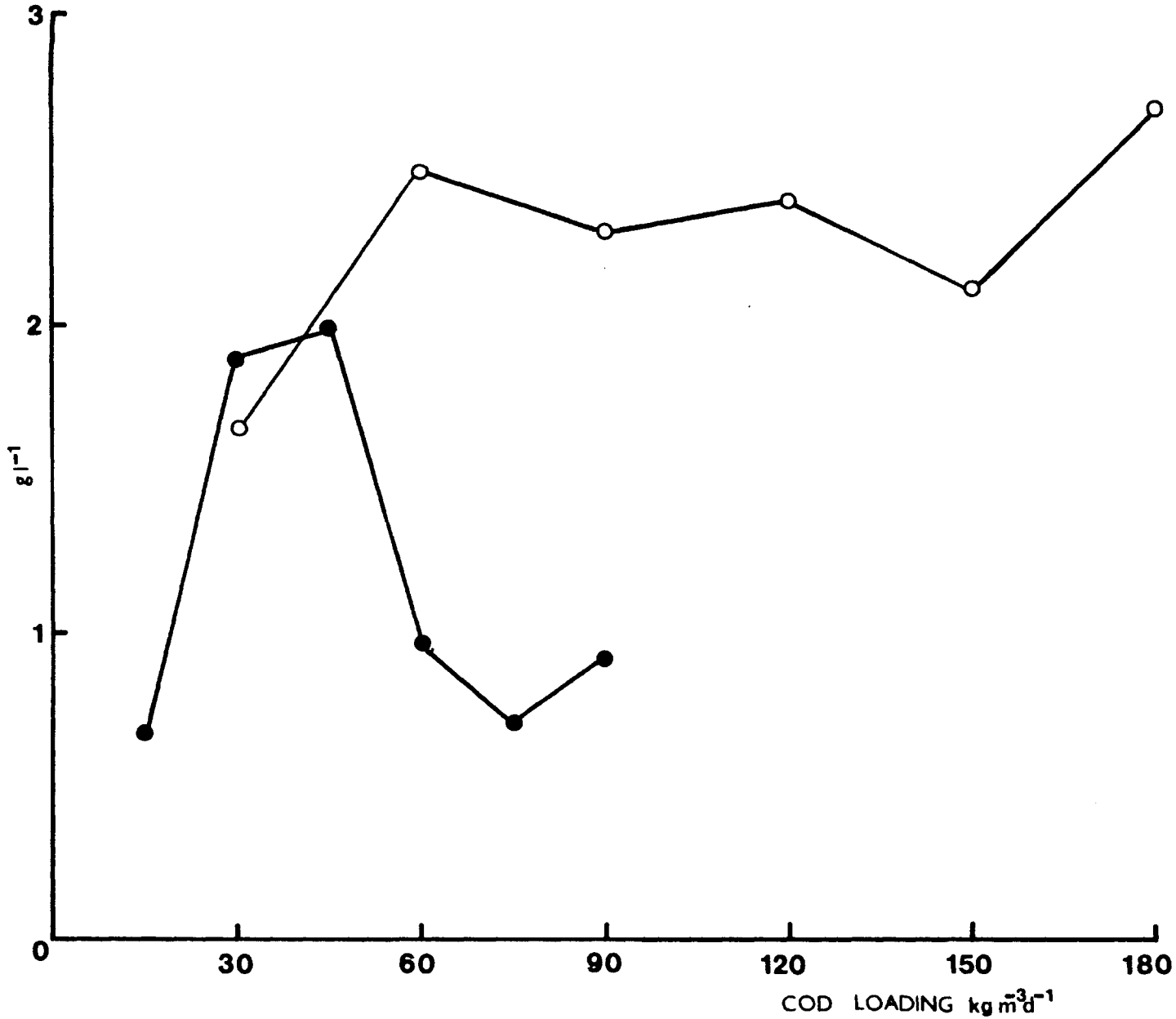


Figure 4.19. Influence of organic loading on acidification reactor effluent hexose concentration
Influent COD (●) 6000 mg l^{-1} (○) 12000 mg l^{-1}

Table 4.16. Individual volatile acids produced from the acidification reactors

Influent COD	Reactor					
	6000			12000		
HRT (hours)	Acetic	Propionic	Butyric	Acetic	Propionic	Butyric
	mg l^{-1}			mg l^{-1}		
10	833	23	11	1191	47	15
5	584	72	22	1102	39	21
3.33	415	99	10	1126	56	25
2.5	944	43	7	1419	47	15
2	786	56	15	1296	106	16
1.66	761	41	27	1258	130	22

Little COD reduction was achieved in the acidification reactor, with a maximum of 8% found in the reactor fed with the higher strength waste-water. Gas production was impossible to measure due to level fluctuations in the vessel and losses through the overflow line. However the gas produced consisted mainly of carbon dioxide (80%) with some hydrogen and nitrogen, methane was not detected.

4.6.2.2. Performance of fluidized bed reactors.

All reactors operated satisfactorily over the range of organic loadings except the dual-phase reactor treating the high strength waste which was found to have poor distribution at the base and tended to carry over large quantities of biomass and sand. This was traced and rectified when the reactor was operated at COD loadings at and above 9 kg m^{-3} d^{-1}.

Overall COD removal in fluidized bed reactors (both soluble and insoluble) is shown in Figs. 4.20 and 4.21. COD removal decreased with increasing organic loading. Filtered COD removal was over 75% at COD loadings up to and including 15 kg m^{-3} d^{-1}, but above this loading COD removal rapidly declined to less than 50%. In the reactors treating the higher strength influent there was a significant difference in performance between the single and separated phase reactors in both soluble and insoluble COD removals, the separated phase reactor con-

Figure 4.20. Influence of organic loading on fluidized bed reactor COD removal (soluble) (▲) single phase, (△) separated phase, (total) (●) single phase, (○) separated phase Influent COD: 12000 mg l^{-1}

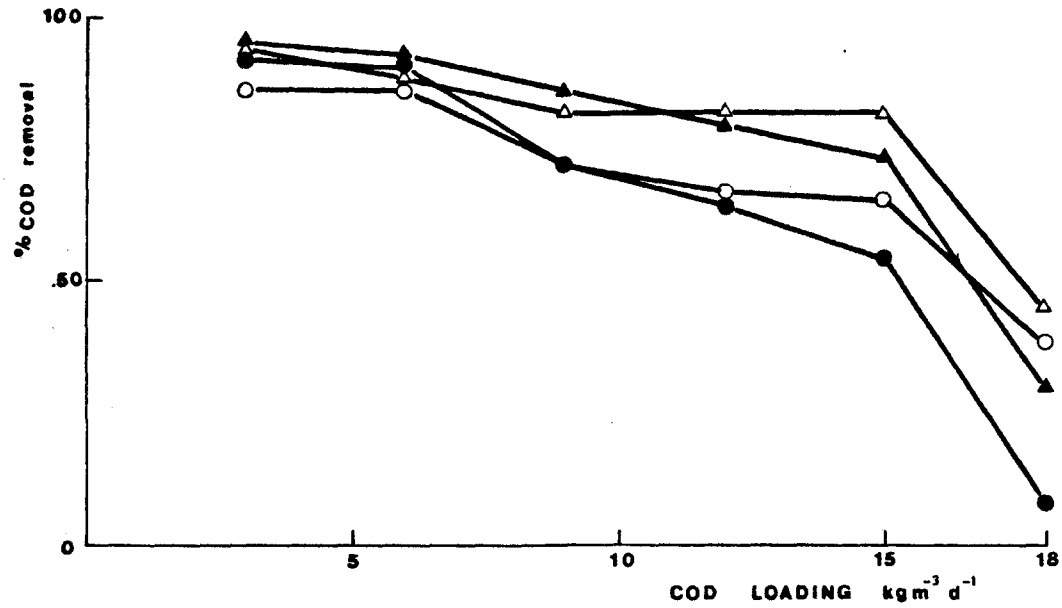
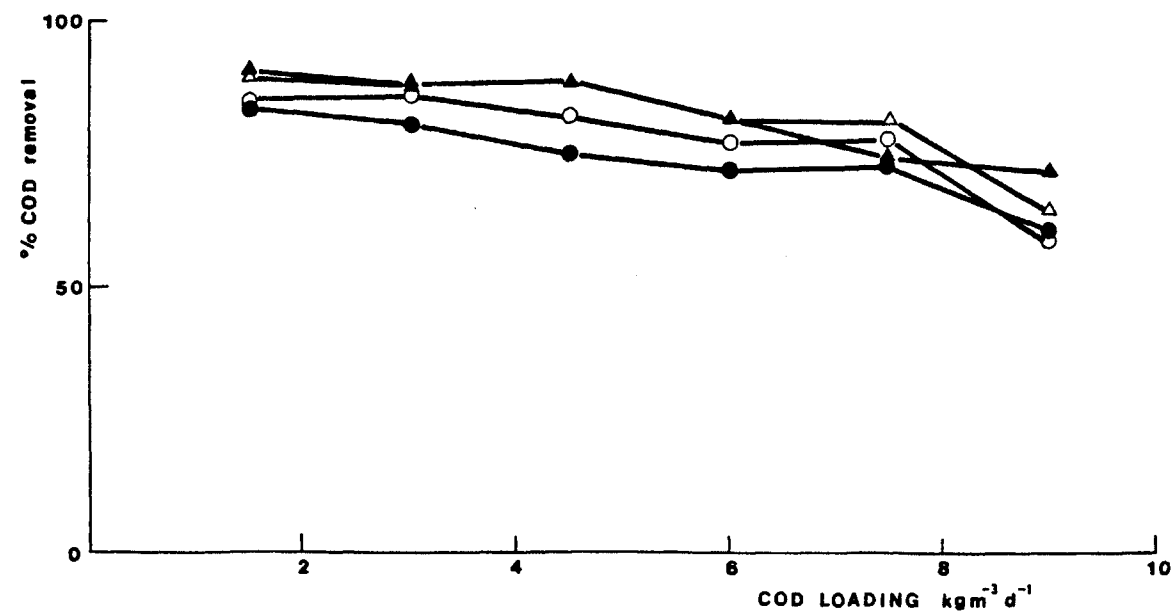


Figure 4.21. Influence of organic loading on fluidized bed reactor COD removal (soluble) (▲) single phase, (△) separated phase, (total), (●) single phase (○) separated phase Influent COD: 6000 mg l^{-1}



sistently giving an improved performance. With the reactors operating with the lower strength feed, the separated phase reactor achieved superior insoluble COD removal, however soluble COD removals were similar over most of the range tested. The reactors treating the higher strength waste-water gave superior removals at the same organic loading to the reactors operating with a lower strength waste-water.

Fluidized bed effluent suspended solids were very high even at the lower loadings, values below 150 mg l^{-1} were never recorded. With lower strength waste-water the suspended solids concentration increased with increasing organic loading up to a COD loading of 6 kg m^{-3} d^{-1} where the concentration decreased but rose again on further increases in the organic load. The reactors treating the high strength waste-water exhibited a sharp increase in effluent suspended solids at a loading of 6 kg m^{-3} d^{-1}, above this loading there were only relatively small changes in concentration on increasing the COD loading. Effluents from the separated phase fluidized bed reactors had considerably lower suspended solids concentrations, generally having a value approximately 60% of those from the single phase fluidized bed reactors, typically 95% of the solids were volatile. Fig. 4.22 shows the effluent suspended solids over the range of COD loadings examined.

As shown in Fig. 4.23, effluent pH was generally above 6.5 in all reactors except at the highest COD loading (18 kg m^{-3} d^{-1}) where values below 5 were noted. The separated phase fluidized bed reactors generally produced an effluent with a pH 0.2-0.3 higher than their single phase equivalents.

Volatile acids rose consistently with organic loading in all fluidized bed reactors, however, there was a sharp rise in volatile acids concentration at the highest COD loading tested. The organic acids consisted almost entirely of acetic acid, propionic acid concentrations were generally below 20 mg l^{-1} except at COD loadings above 15 kg m^{-3} d^{-1}. At a COD loading of 18 kg m^{-3} d^{-1}, propionic, butyric iso-butyric and valeric acid were all detected in concentrations above 200 mg l^{-1}. Total volatile acids from each reactor are shown in Fig. 4.24. Gas production and methane composition are given in Table 4.17, both methane production and methane composition decreased with increasing COD loading.

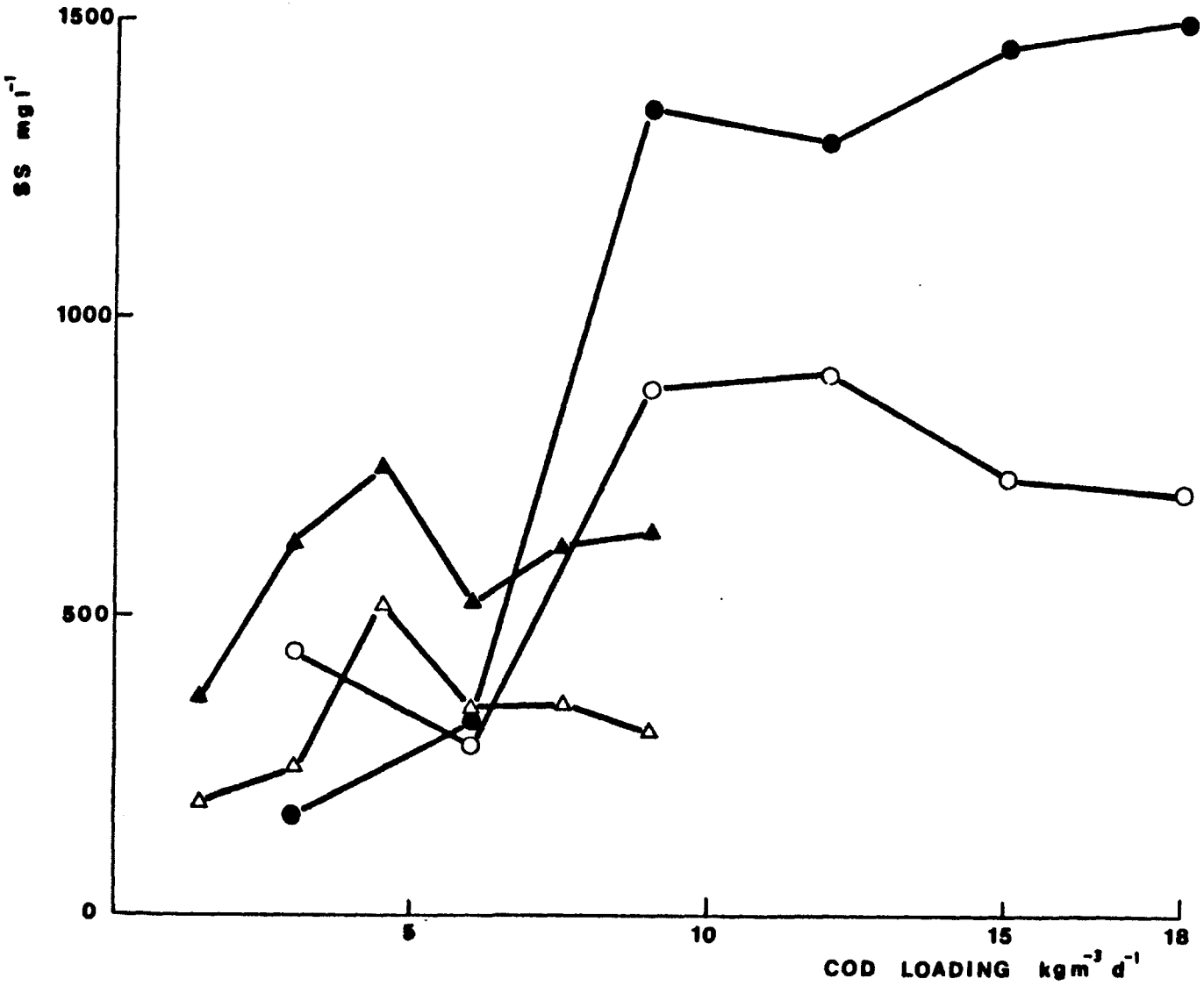


Figure 4.22. Influence of organic loading on fluidized bed reactor effluent suspended solids; Influent COD: 12000 mg l^{-1} (●) single phase, (○) separated phase Influent COD: 6000 mg l^{-1} (▲) single phase, (△) separated phase

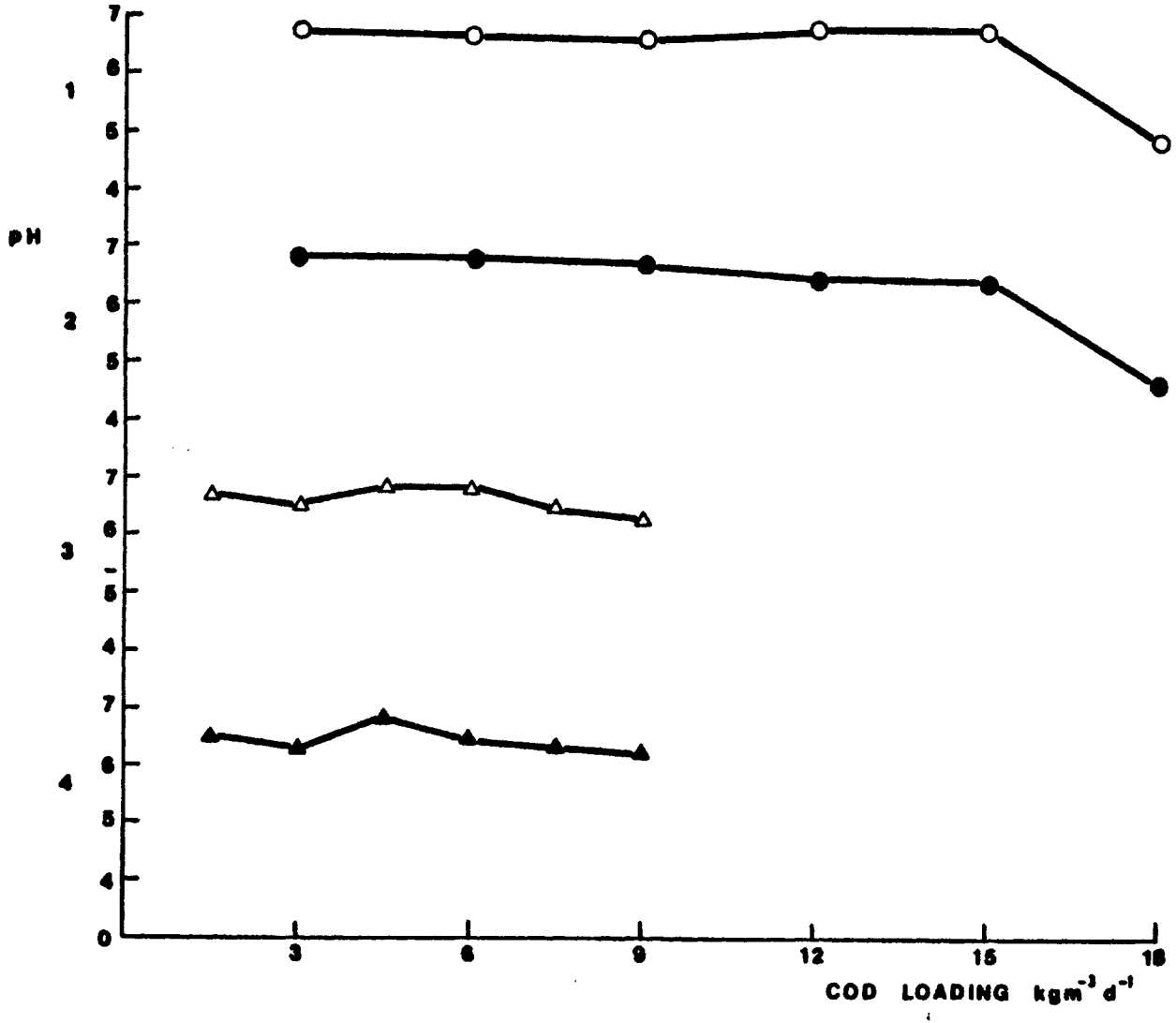


Figure 4.23. Influence of organic loading on fluidized bed reactor effluent pH Influent COD: 12000 mg l^{-1} (●) single phase, (○) separated phase Influent COD: 6000 mg l^{-1} (▲) single phase (△) separated phase

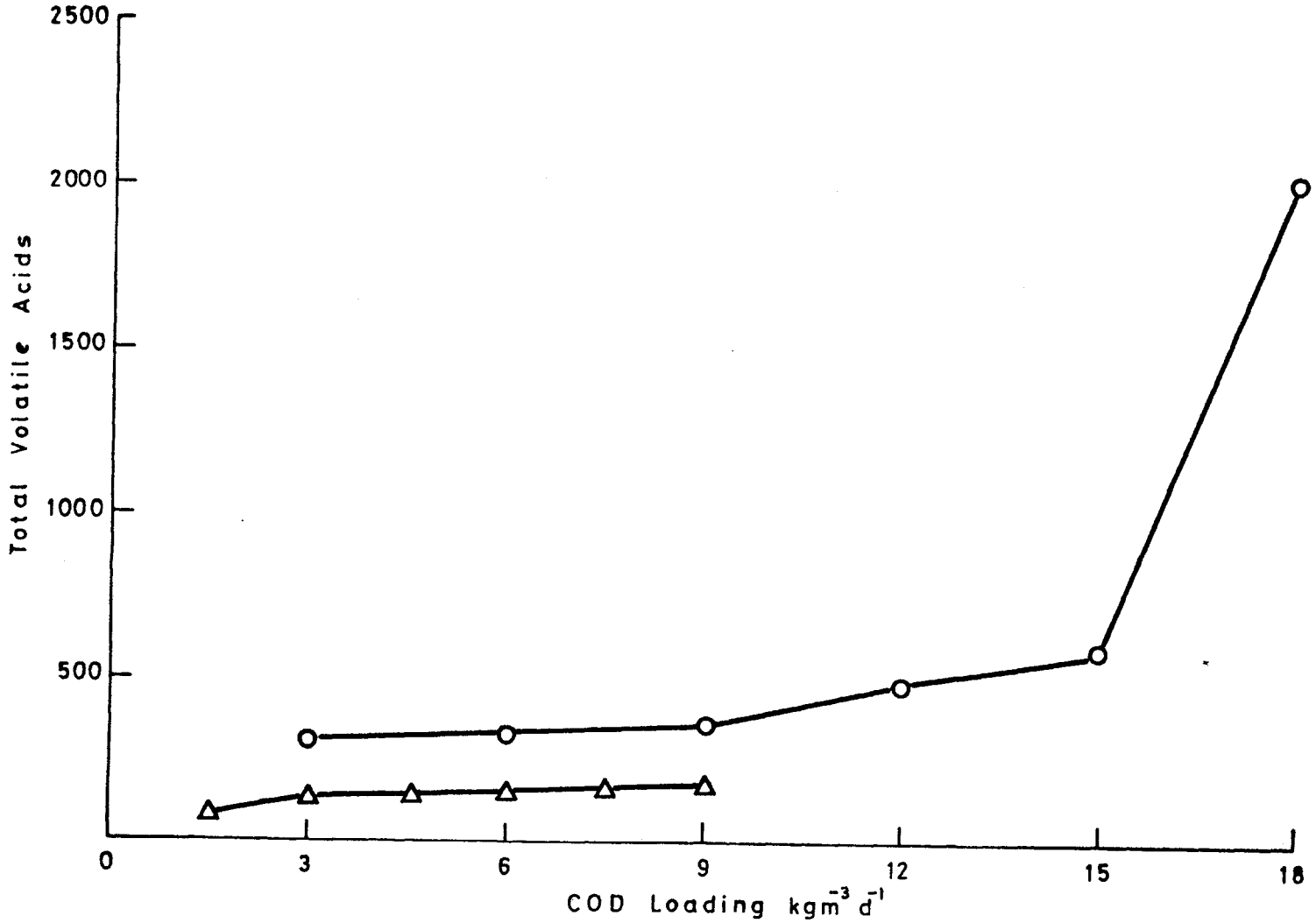


Figure 4.24. Influence of organic loading on fluidized bed reactor effluent total volatile acids
Influent COD (○): 12000 mg l^{-1} (△) 6000 mg l^{-1}

Table 4.17. Gas yield and methane composition from fluidized bed reactors

Low strength feed

COD loading kg m^{-3} d^{-1}	Single phase Gas yield m^3 CH_4 kg^{-1} COD	Single phase Methane Composition %	Separated phase Gas yield m^3 CH_4 kg^{-1} COD	Separated phase Methane Composition %
3	0.257	73	0.343	76
6	0.268	73	0.350	77
9	0.263	73	0.347	74

High strength feed

COD loading kg m^{-3} d^{-1}	Single phase Gas yield m^3 CH_4 kg^{-1} COD	Single phase Methane Composition %	Separated phase Gas yield m^3 CH_4 kg^{-1} COD	Separated phase Methane Composition %
6	0.271	72	0.349	77
12	0.213	68	0.322	71

At the two highest loadings biomass had to be wasted once from the fluidized bed reactors, approximately 200 ml of biomass being removed. Sludge also settled in the recycle and mixing chambers of the reactors, especially in the separated phase reactors and this periodically had to be removed to prevent line blockage.

In overall performance the separated phase systems achieved a superior effluent quality to a single phase fluidized bed reactor. The improvements in reactor performance were principally lower effluent COD, lower effluent suspended solids and a greater gas yield.

4.7. Influence of varying process conditions on the performance of single and separated phase fluidized bed reactors.

Experiments concerned with comparing the performance of single and separated phase reactors were carried out on the two reactors operating with an influent COD of 6000 mg l^{-1} with an initial COD loading of 6 kg m^{-3} d^{-1}. The experiments took place immediately after the conclusion of the steady state organic loading experiments. In these experiments the same techniques as described in Sections 4.3 and 4.3.1. were employed.

4.7.1. Influence of a transient temperature reduction on the performance of single and separated phase fluidized bed reactors

Each reactor was subjected to a four hour, 10°C temperature reduction, one hour was required for temperature changes to occur, the acidification reactor in the separated phase system was maintained at 35°C since it operated on a different heating system. Fig. 4.25 summarises the responses of the reactors to the temperature reductions.

The pH in the effluent from both reactor systems remained relatively stable during and after the temperature reduction, volatile acids increased during the reduction and only slowly returned to their original concentrations some 24 hours after the reactors were returned to their normal operating temperatures. The alkalinity of the effluents from both reactors reduced during the experiment and tended to stabilize at new lower values.

Effluent COD was unstable and increased especially in the single phase system. Return to typical values took longer in the single phase reactor, the effluent COD still tending to increase 10 hours after the reactor temperature was returned to 37°C. Suspended solids concentrations were also variable with a general increase in the single phase reactor. The separated phase reactor effluent suspended solids tended to decrease and stabilized at a slightly lower value after the temperature was increased.

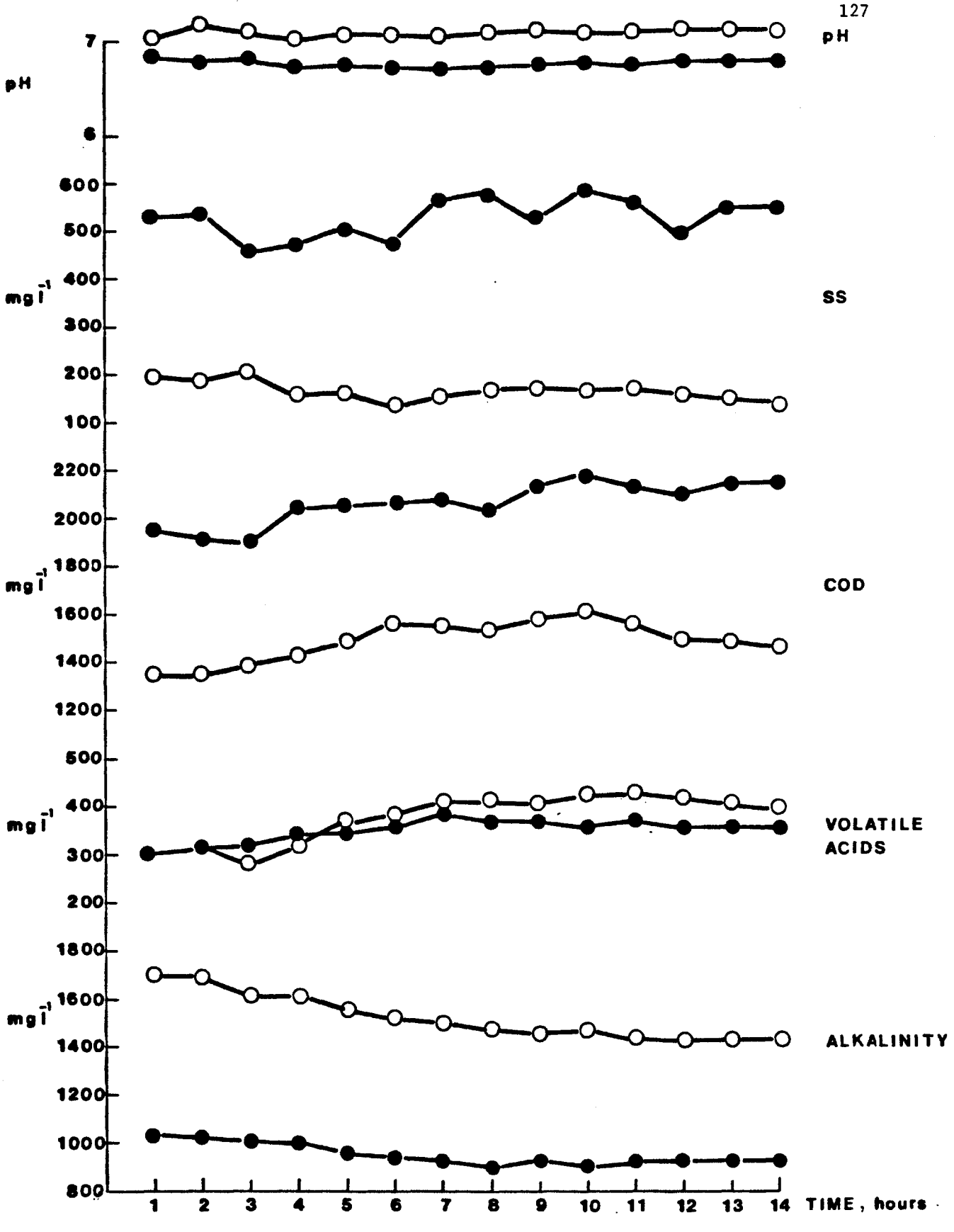


Figure 4.25. Effect of 4 hr, 10°C temperature reduction on various process parameters of single and separated phase fluidized bed reactors (O) separated phase, (●) single phase

4.7.2. Influence of a transient increase in influent flow rate on the performance of single and separated phase fluidized bed reactors

An increase in influent flowrate of 100% maintained for four hours was applied to both reactors, the effects on reactor performance are summarised in Fig. 4.26.

Increasing the influent flowrate produced an immediate decrease in effluent pH from both reactors of between 0.25-0.3. During and following the shock load the pH remained relatively stable at the lower value and increased slowly to its original value over 48 hours.

Total volatile acids concentrations followed the same trend in each reactor, an increase during and following the shock load reaching a peak one hour after the flowrate was returned to its original value. The effluent volatile acids concentration in each reactor then returned to its original value within 24 hours. Alkalinity decreased during the experiment especially in the separated phase reactor but remained stable after two hours following the return to usual operating conditions.

Effluent COD increased by similar values in both reactors reaching a peak an hour after the flowrate was returned to its original value. In both reactors effluent COD then decreased although the single phase reactor was less stable and took a longer period to restabilize than the separated phase reactor. Effluent suspended solids remained relatively stable from the separated phase reactor, whilst the single phase reactor effluent concentration was variable and generally increased during and after the shock period. In general the separated phase system was more stable, and hence more suited to industrial applications.

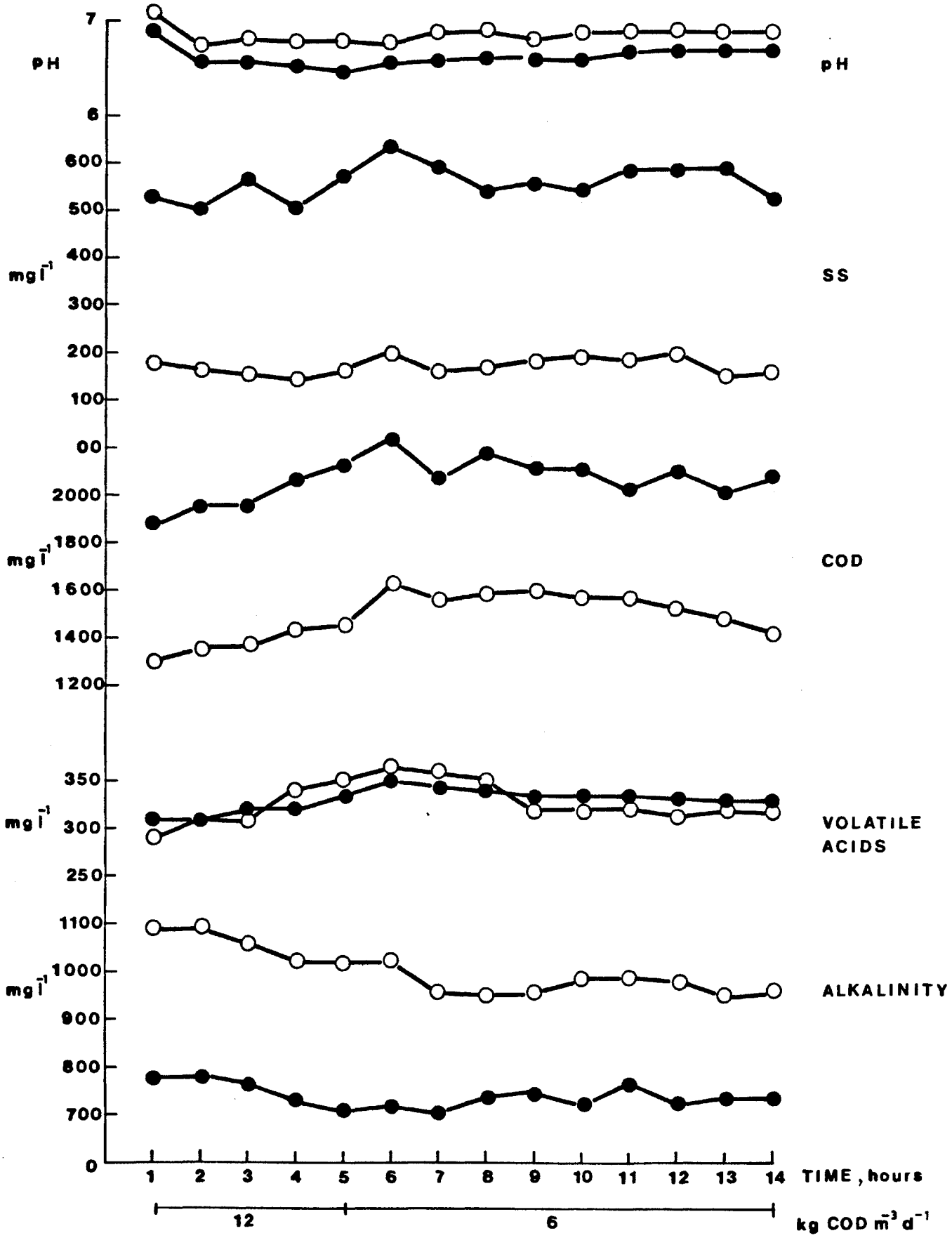


Figure 4.26. Effect of 4 hr, 100% influent flowrate increase on various process parameters of single and separated phase fluidized bed reactors (O) separated phase, (●) single phase

4.7.3. Influence of transient increases in influent COD on the performance of single and separated phase fluidized bed reactors.

An increase in influent COD of 100% maintained for four hours was applied to each reactor and the effects are summarised in Fig. 4.27.

During and following the COD increase the pH of the single phase reactor remained stable whilst the separated phase reactor exhibited a slight increase during the shock load although the pH stabilized at its original value three hours after the COD was returned to 6,000 mg l^{-1}.

Volatile acids concentrations increased at the same rate in each reactor and tended to stabilize at a new higher value three hours after the COD was restored to its original value. The volatile acids concentration decreased in the separated phase reactor five hours later but in the single phase reactor's concentration was stable or increasing slightly over this period. The alkalinity was largely unaffected although a slight decrease during the experiment was noted.

The effluent COD and suspended solids from both reactors increased for a period up to eight hours after the shock load, effluent COD increased faster in the single phase reactor but stabilized at a new value before the separated phase reactor, both reactors began to return to original operating parameters 4-5 hours after the shock period.

4.8. Determination of kinetic parameters of volatile acid degradation in fluidized bed reactors

In order to compare the relative rates of reaction in separated and single phase fluidized bed reactors the kinetic parameters of propionate oxidation and acetate degradation were determined. A concentrated solution (20 g l^{-1}) of the sodium salt of the acid was injected slowly into the fluidized bed through the lowest sample tap to achieve a concentration of 250 mg l^{-1} to permit the evaluation of degradation under conditions of substrate saturation or 100 mg l^{-1} to collect data for Lineweaver-Burk plots during concentration dependent conditions.

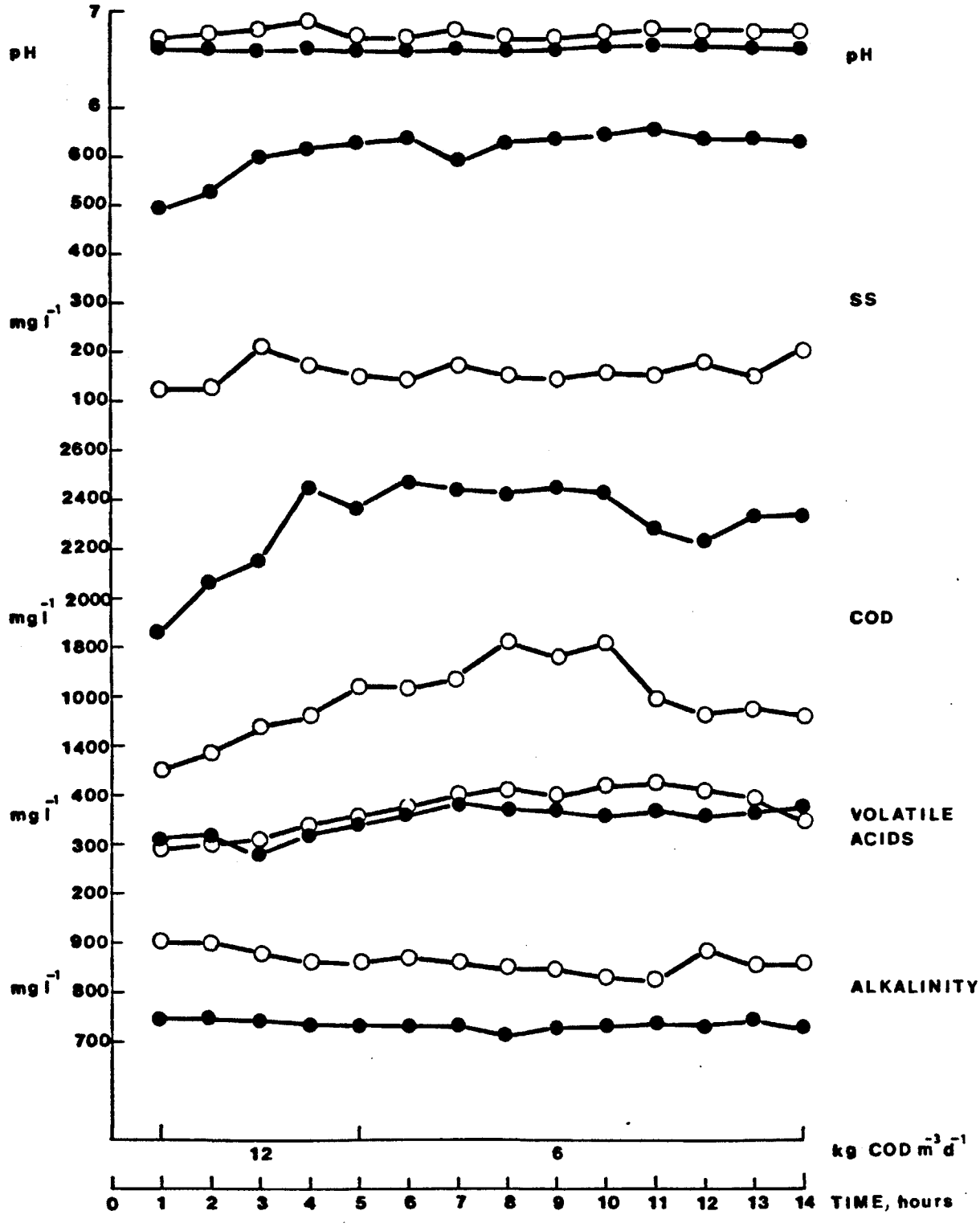


Figure 4.27. Effect of 4 hr, 100% influent COD increase on various process parameters of single and separated phase fluidized bed reactors (O) separated phase, (●) single phase

Effluent samples were collected hourly and the individual volatile acids concentration determined immediately by gas chromatography.

4.8.1. Determination of kinetic parameters of propionate oxidation in single and separated phase fluidized bed reactors.

Three 100 mg l^{-1} proprionate additions were made, the results from a typical 100 mg l^{-1} increase in each fluidized bed reactor are shown in Figs. 4.28 and 4.29. There appeared to be little difference in behaviour between the single and separated phase fluidized bed reactors. As the proprionate concentration decreased the acetate concentration rose for a period of up to two hours following the propionate increase. Satisfactory Lineweaver-Burk plots (a typical plot is given in Fig. 4.30) were drawn and values of the theoretical maximum degradation rate (V_{max}), the experimental maximum degradation rate (V_E), the steady state propionate turnover rate (V_o) and the half-rate coefficient are given in Table 4.18. Highest maximum theoretical degradation rates were found in the single phase system, whilst the highest experiment degradation rates lowest K_m values were found in the separated phase system indicating a more amenable substrate.

Table 4.18. Kinetic parameters of propionate oxidation

Single phase reactor

Expt. No.	V_o	V_{max} mmol l^{-1} h^{-1}	V_E	K_s mg l^{-1}	r^2
1	0.154	1.908	0.877	166	0.993
2	0.161	1.872	0.856	143	0.875
3	0.157	1.890	0.866	150	0.890

Separated phase reactor

Expt. No.	V_o	V_{max} mmol l^{-1} h^{-1}	V_E	K_s mg l^{-1}	r^2
1	0.215	1.589	1.115	125	0.947
2	0.210	1.670	1.078	130	0.870
3	0.217	1.620	1.092	130	0.832

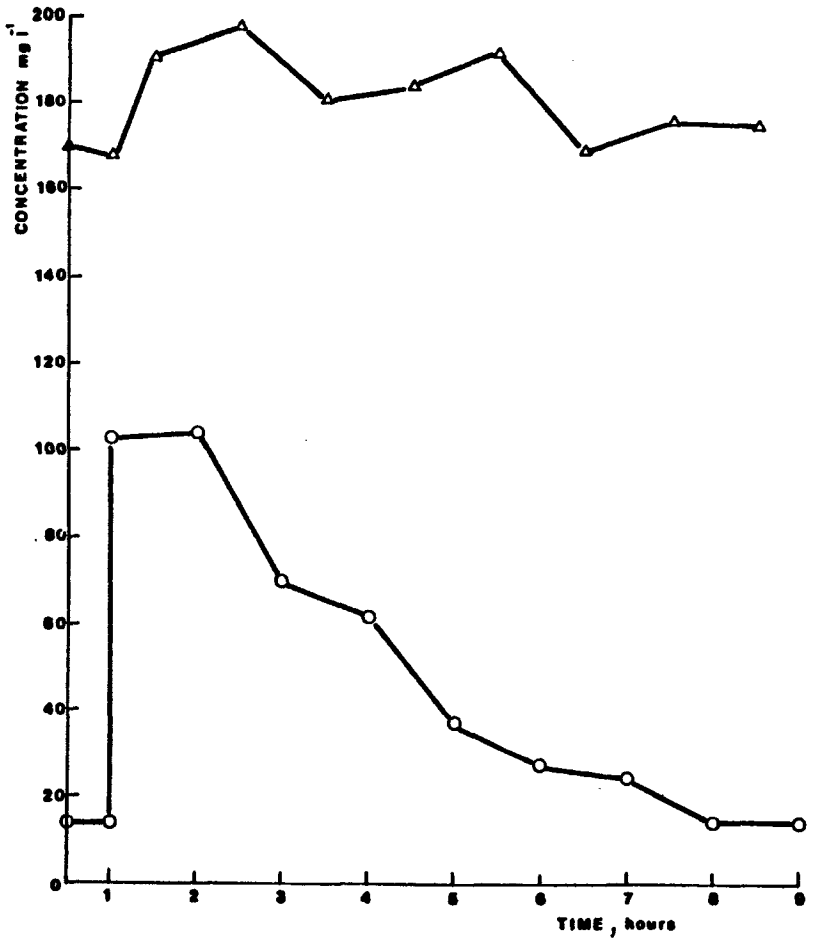


Figure 2.28. Effect of loo mg l^{-1} propionate increase in a single phase fluidized bed reactor on (O) propionate and (Δ) acetate concentrations

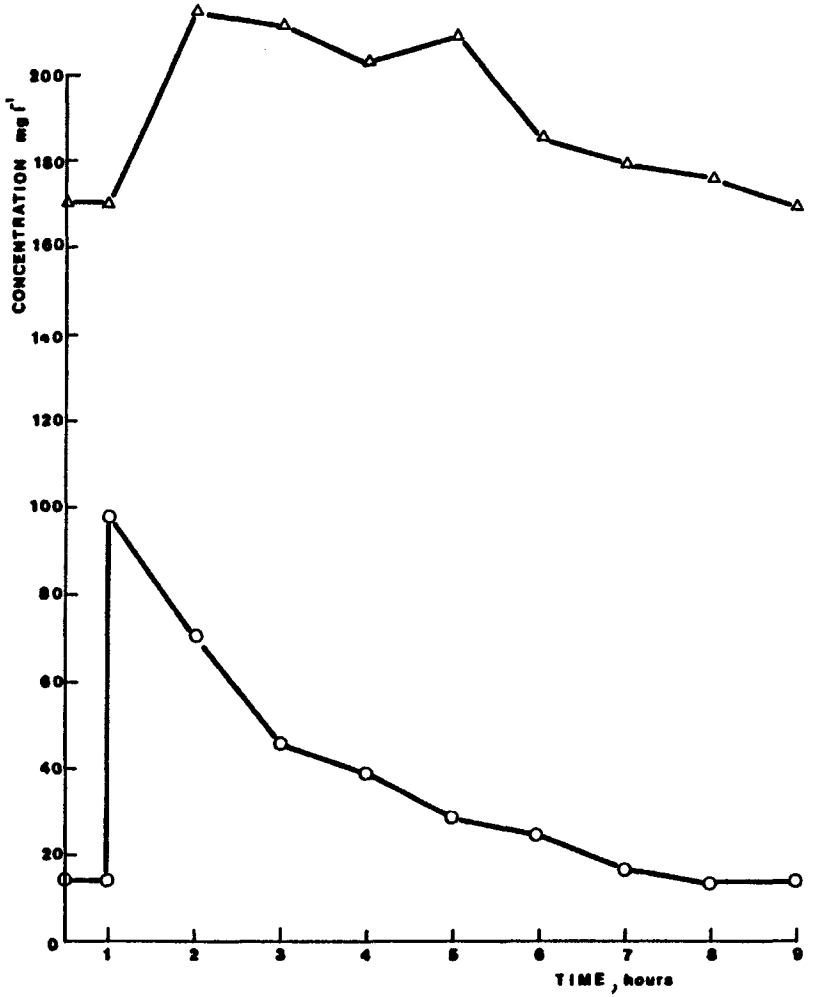


Figure 2.29. Effect of 100 mg l^{-1} propionate increase in a separated phase fluidized bed reactor on (O) propionate and (Δ) acetate concentrations

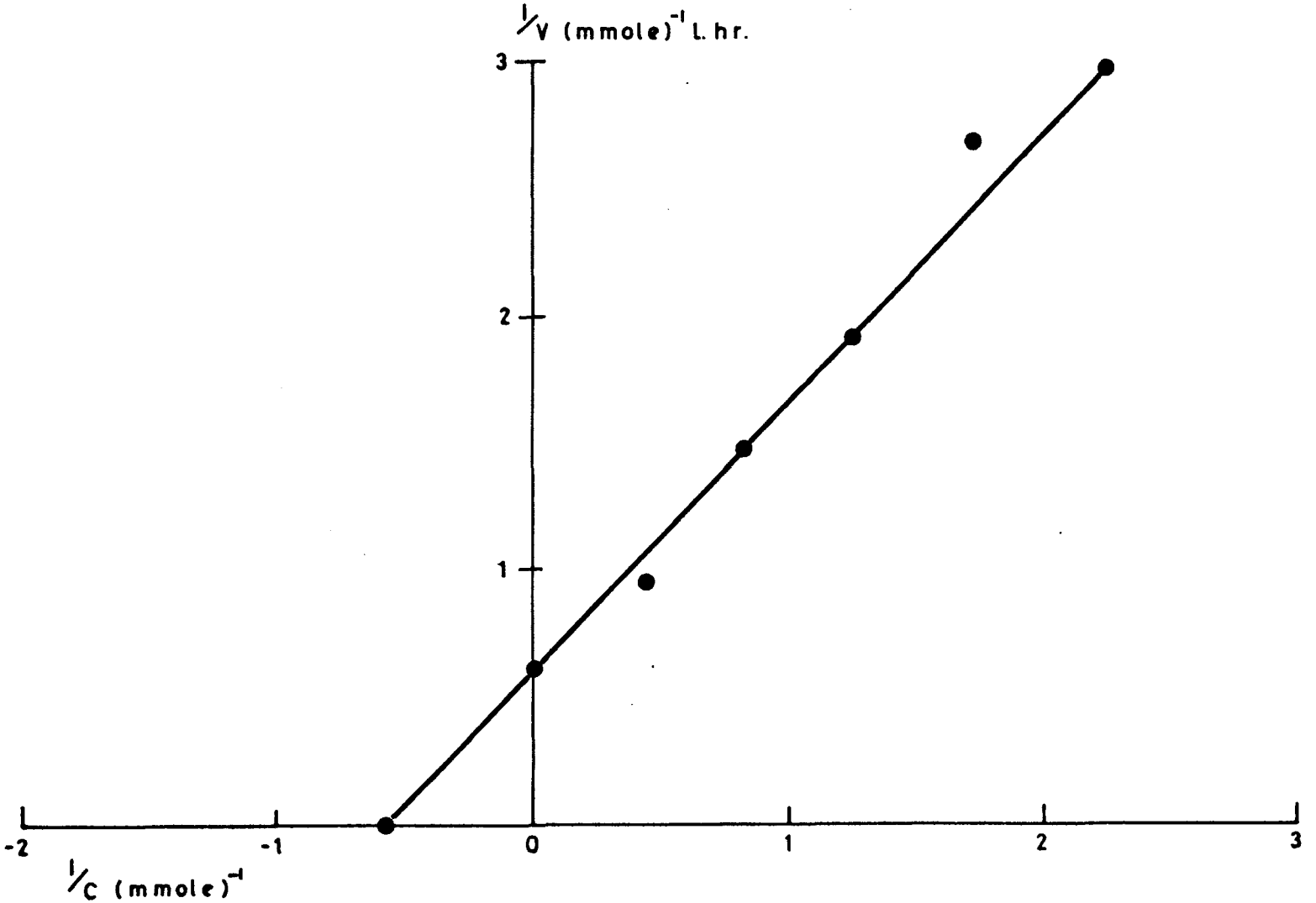


Figure 4.30. Typical Lineweaver-Burke plot for calculation of kinetic parameters of propionate degradation

4.8.2. Kinetic parameters of acetate degradation in single and separated phase fluidized bed reactors

Three 100 mg l^{-1} acetate increases were performed. It was found that degradation in the concentration dependent phase was so rapid that satisfactory Lineweaver-Burk plots could not be drawn due to insufficient data. Steady state degradation and experimentally measured maximum degradation rates are therefore given in Table 4.19. Again maximum experimental removal rates occurred in the single phase system.

Table 4.19. Kinetic parameters of acetate degradation

Expt. No.	Single phase reactor			Separated phase reactor		
	V_o	V_E	r^2	V_o	V_E	r^2
	mmol l^{-1} h^{-1}			mmol l^{-1} h^{-1}		
1	1.34	1.76	0.977	1.88	2.33	0.967
2	1.41	1.57	0.960	1.83	2.31	0.98
3	1.37	1.89	0.948	1.89	2.37	0.947

4.9. Determination of the distribution of bacterial activity in a single phase fluidized bed reactor

An investigation of bacterial distribution was conducted during the organic loading experiments described in Section 4.6. Bacterial activity was determined in a single phase fluidized bed reactor operating with an influent of 12000 mg l^{-1} at three COD loadings, 6, 12 and 18 kg m^{-3} d^{-1}. Samples were collected at five sample points at 25, 55, 95, 115 and 145 cm above the base of the reactor. Individual volatile acids, alkaline phosphatase activity and methane production were determined from each sample on two consecutive days at each loading, mean results are reported. In operation the biomass could be considered as two distinct phases; at the top of the reactor was an unattached portion, whilst throughout the rest of the reactor a direct microscopic examination of the bed contents indicated that virtually all of the biomass was attached to the sand particles. Biomass concentration increased with increasing reactor loading and also increased up the height of the bed, VSS:SS ratios up the column at the three organic loadings studied are given in Table 4.20.

Table 4.20. Volatile suspended solids: suspended solids ratios at three COD loadings

Height (cm)	COD Loading kg m^{-3} d^{-1} 6	12	18
25	0.0032	0.0037	0.0062
55	0.0023	0.0044	0.0098
95	0.0042	0.0044	0.0124
115	0.0048	0.0097	0.0167
145	0.0428	0.1430	0.0932

4.9.1. Distribution of alkaline phosphatase activity in a fluidized bed reactor

In Figure 4.31 the vertical distribution of relative phosphatase activity per unit mass of volatile suspended solids in the fluidized bed at each organic loading is presented. At a COD loading of 6 kg m^{-3} d^{-1} the activity was very low being detectable but not measurable throughout most of the reactor with the exception of the sample taken from the top of the bed. At COD loadings of 12 and 18 kg m^{-3} d^{-1} phosphatase activity was evident throughout the reactor with a marked peak approximately half-way up the bed. Highest relative activities were obtained at an organic loading of 12 kg m^{-3} d^{-1} where the reactor can be considered to be approaching failure. Relatively low activities were obtained from the flocculated material at the top of the column.

4.9.2. Distribution of relative methane production in a fluidized bed reactor

Methane production was only measurable at the lower two COD loadings however a very small amount of gas production was evident at the highest loading due to the appearence of some gas bubbles in the incubated samples. The vertical distribution of methane production is shown in Fig. 4.32. Gas production increased up the column to a peak near the centre of the column although in one case (at 6 kg COD m^{-3} d^{-1}) the peak was somewhat higher up the column. At the extremes of the column the relative activity of the biomass was rather lower. Hence again the flocculated material at the top of the bed had a relatively low activity.

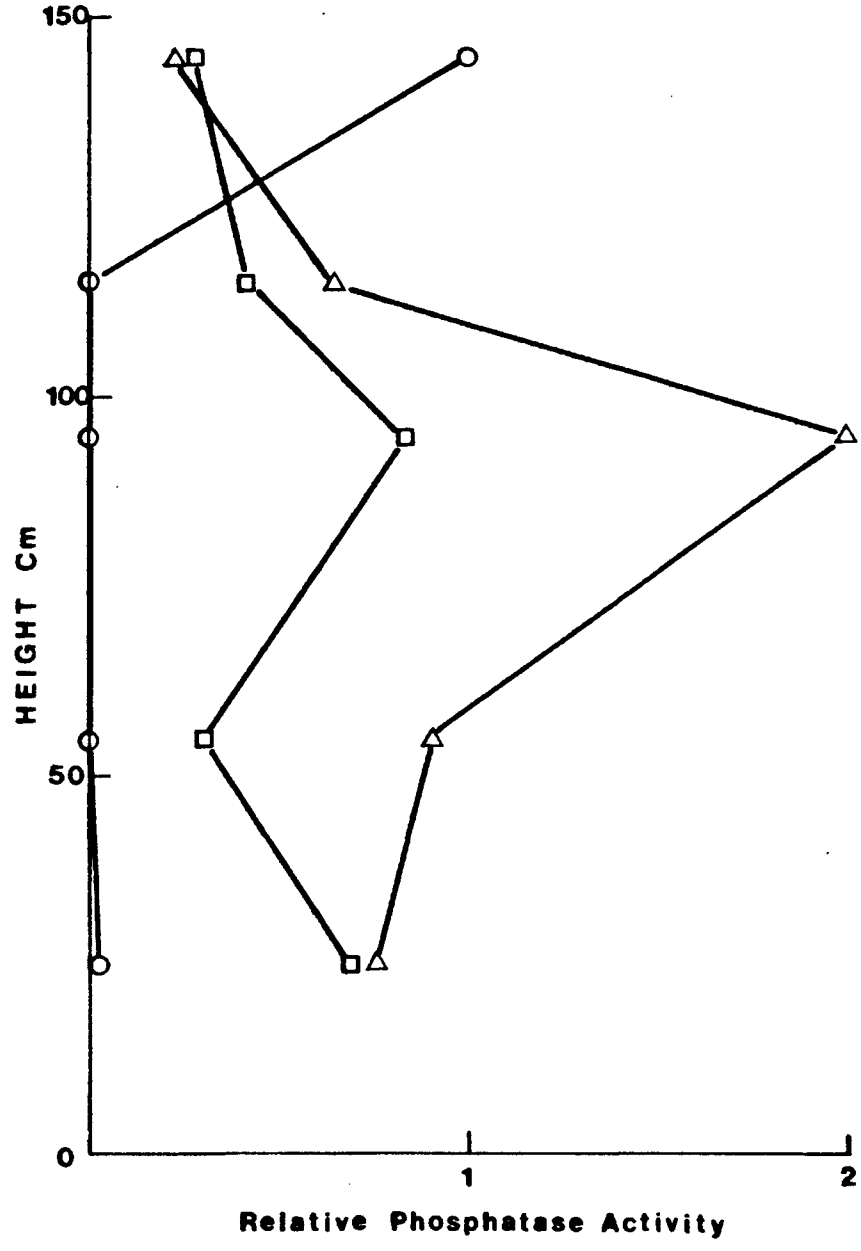


Figure 4.31. Phosphatase activity profiles in a fluidized bed reactor COD loading (○) 6 kg m^{-3} d^{-1}, (△) 12 kg m^{-3} d^{-1} (□) 18 kg m^{-3} d^{-1}

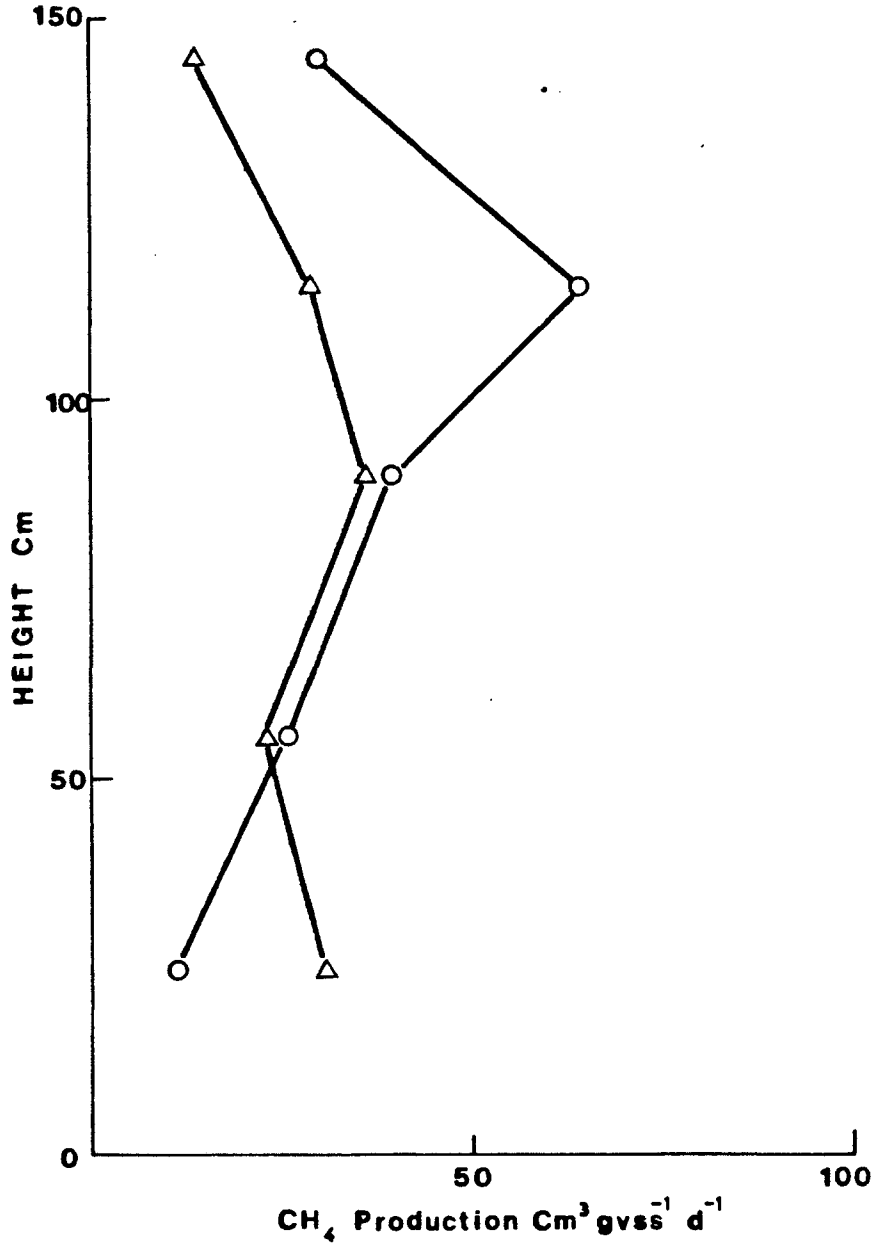


Figure 4.32. Relative methane forming activity profiles in a fluidized bed reactor COD loading (△) 6 kg m^{-3} d^{-1}, (○) 12 kg m^{-3} d^{-1}

4.9.3. Total volatile acid profiles in a fluidized bed reactor

Total volatile acids profiles for each organic loading are shown in Fig. 4.33. At the two lower COD loadings acetic acid was the only acid detected whilst at 18 kg m^{-3} d^{-1} propionic, iso-butyric, butyric and valeric acids were all detectable. At a COD loading of 6 kg m^{-3} d^{-1} there was very little change in the volatile acids concentrations up the reactor, however, at 12 and 18 kg m^{-3} d^{-1} there was a marked reduction in acids concentrations in the centre of the reactor and peaks in concentration were noted in the upper part of the reactor. Differences in acid concentrations were generally noted between the top and the base of the reactor indicating some acidification took place in the recycle chamber.

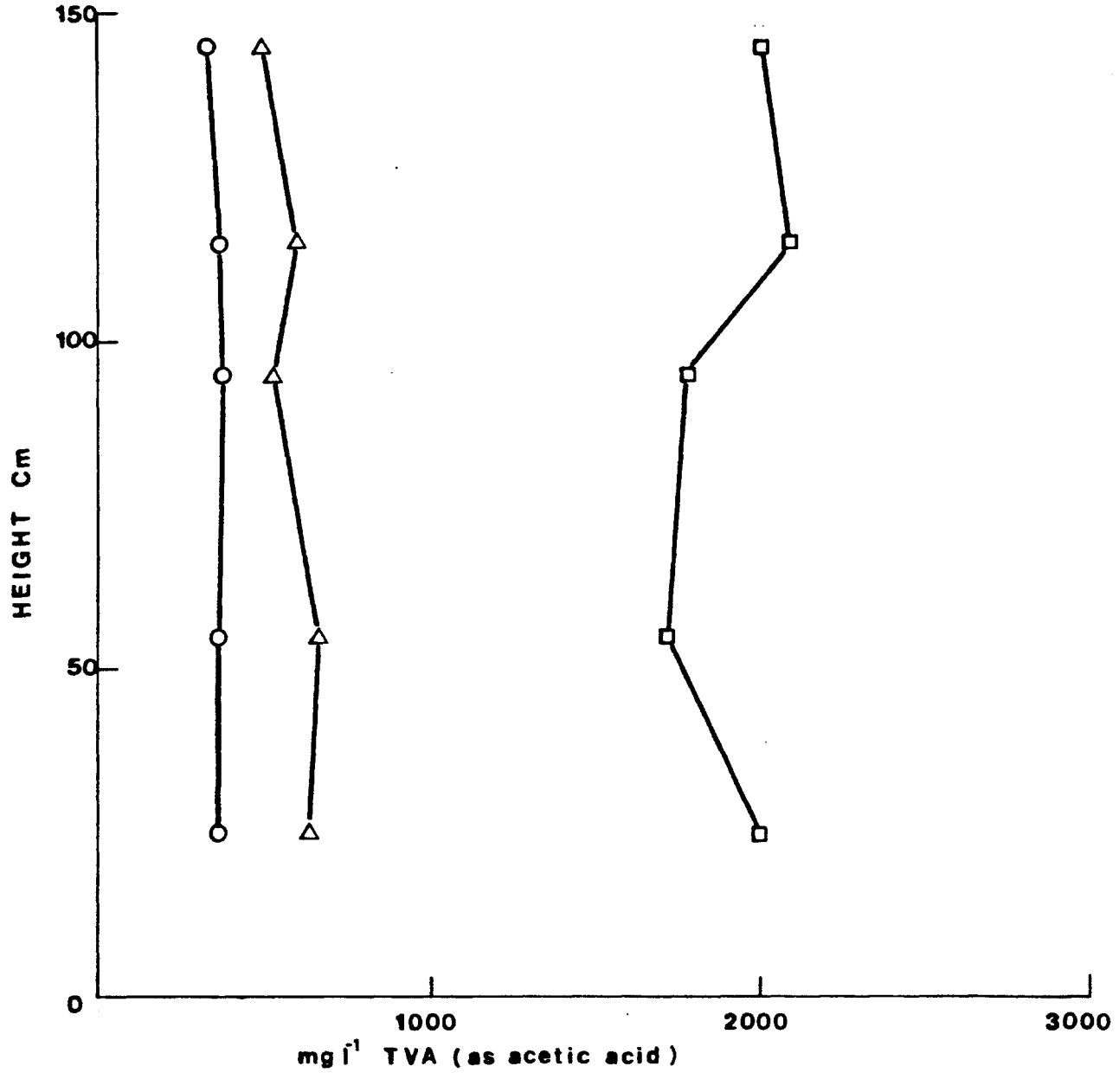


Figure 4.33. Total volatile acids profiles in a fluidized bed reactor COD loading (○) 6 kg m^{-3} d^{-1}, (△) 12 kg m^{-3} d^{-1} (□) 18 kg m^{-3} d^{-1}

5. DISCUSSION

In all food processing industries production costs must be minimized and this principle extends to the cost of disposal of waste effluents. Full treatment of food industry waste-waters will generally involve some form of biological secondary treatment. As secondary treatment constitutes a significant part of the waste-water treatment costs it is important to utilize and develop biological processes which can provide satisfactory treatment at the lowest cost. Conventional anaerobic treatment has been shown to have economic advantages over aerobic processes for higher strength wastes (> 4000 mg l^{-1} COD) (Cillie et al., 1969), however, improvements in reactor designs may increase the advantages of anaerobic systems, hence there has been an interest in the development of high rate reactors. Increasing degradation rates in biological reactors necessitates the development and retention of a sufficiently high biomass concentration within the reactor. This has been achieved by either utilizing external biomass recycle, as in the anaerobic contact reactor (Anderson and Duarte, 1980), or by using a retained biomass system such as the anaerobic filter (Mosey, 1978). Interest in the possibilities of using the anaerobic fluidized bed reactor for waste-water treatment developed following experiments concerned with aerobic fluidized bed reactors. These demonstrated that the reactor design could retain extremely high biomass concentrations, yet maintain high volumetric throughputs without biomass washout (Cooper and Wheeldon, 1980). Although anaerobic reactors have been reported for the treatment of dilute waste-waters the high half-rate coefficients (K_m) encountered mean that higher strength waste-waters are more suited to anaerobic treatment. In the preliminary study reported here the reactor design was developed from previously reported work (Cooper and Wheeldon, 1980, Jewell et al., 1981) and efficient COD removals were expected with COD loadings in the range 1-4 kg m^{-3} d^{-1}. Fluidized bed reactor design is relatively constrained since once the maximum organic loading, the influent COD and the bed expansion are defined the upflow velocities can be calculated from expressions such as the Kozeny equation (Cleasby and Kuo-shuh, 1981). With the upflow velocity and reactor volume defined the reactor dimensions can be chosen to maintain a practicable height to area ratio.

A 20% bed expansion was chosen to minimize the upflow velocity yet maintain a true fluidized bed (Cooper, 1981). The conical distribution system appears to be ideal for fluidized bed design since as long as the inlet pipe is properly aligned it does not suffer any of the blockage or poor distribution problems encountered in this study with a gravel bed distribution system.

Dairy waste-waters are generally acknowledged to be difficult to treat anaerobically and previously reported methods have generally been confined to pretreatment at low organic loadings (Vandamme and Waes, 1980 a,b) otherwise acid accumulation occurred. Although the combination of the high biomass concentration and the large recycle flows used in fluidized bed reactors in this study aids reactor stability, acid accumulation still occurred but at relatively high COD loadings compared to those reported previously.

Waste-waters from meat processing industries are generally considered to be ideal for anaeorobic treatment since they have been shown to be easily biodegradable and are often discharged at elevated temperatures thus aiding anaerobic degradation. These waste-waters are one of the few types of industrial effluents where anaerobic treatment is an established practice (Steffen and Bedker, 1961; Rands and Cooper, 1966). Following the difficulties encountered in the first reactor start-up attempts at ambient temperature a more amenable substrate than the milk waste was used for reactor evaluation. Anaerobic treatment at ambient temperatures has been previously reported, successful degradation of various substrates has been achieved but only at low organic loadings (Pretorius, 1971; Coulter et al., 1956) except in expanded bed reactors (Jewell et al., 1981). In these experiments similar COD removals were achieved to those reported in expanded bed reactors with good COD removals (> 70%) up to a COD loading of 3 kg m^{-3} d^{-1}. Although good soluble COD removals were achieved the major drawback of the process was the high effluent suspended solids concentrations.

This problem was especially pronounced when the reactors were treating the high strength glucose based waste-water. The high suspended solids in the effluent appear to be due to the fact that the biomass concentration in the reactor was self regulating, it being rarely necessary to waste any biomass. The biomass concentration

increased with increasing COD loading and increasing influent COD. This is in agreement with the experimental results of Switzenbaum (1978) and the theoretical predictions of Rittman and McCarty (1980). The fluidized bed reactor biomass concentration was however rather lower than other reactors such as the expanded bed (Switzenbaum and Jewell, 1980) and the upflow sludge blanket reactor (Lettinga et al., 1979). This is due to the higher bed expansions used in the fluidized bed reactor. Firstly, because anaerobic films in fluidized bed reactors are very thin (up to 15 μm (Switzenbaum, 1978)) the biomass concentration per unit volume will decrease with increasing bed expansion. Secondly, due to the higher upflow velocity biomass losses due to shear stress will be considerably greater. Rittman (1982) demonstrated that film loss in a fluidized bed reactor may be at least 50% greater than a static film reactor such as a gravel bed filter. However, running the reactor at higher expansions does have the advantage that blockage of the reactor with inert solids will not occur.

To achieve reliable treatment a biological system should be tolerant of fluctuations in process parameters such as influent COD, flowrate and temperature, since industrial effluents generally exhibit wide variations in such parameters. Anaerobic bacteria, particularly those in the methanogenic phase are adversely affected by even small changes in process parameters (Stein, 1980), however fixed film reactors such as the anaerobic filter are known to be more tolerant of shock loads since microbial washout under adverse conditions does not occur.

In this study anaerobic fluidized bed reactors operating at both ambient and elevated temperatures were subjected to various changes in process parameters either typical of, or greater than those found in industry. Temperature changes occur in industrial wastes because of intermittent operations such as steam cleaning (Moodie and Greenfield, 1978). Generally these variations are not large but loss of methane production due to a temperature shock is often reported (Jewell and Morris, 1981). This phenomenon can be used to good effect for example in the anaerobic contact reactor to improve biomass settling properties (Anderson and Duarte, 1980), however in a fixed film process treating an industrial waste it is desirable that the reactor is tolerant of any temperature changes (Jewell and Morris, 1981).

In this study the heated fluidized bed reactor showed no long term detrimental effects following 4 and 8 hour temperature reductions. The principal parameters affected by a temperature reduction were the gas production and gas composition. The increase in carbon dioxide content of the gas is due to the lack of conversion of volatile acids to methane whilst carbon dioxide was still produced by the reaction between bicarbonate and volatile acids (as reflected by the decrease in alkalinity) and as one of the products during acid formation from complex organics (Mosey, 1981; Kennedy and van den Berg, 1982). The accumulation of volatile acids found in most of the shock loading experiments is commonly reported during periods of reactor instability (Kennedy and van den Berg, 1981, Cohen et al., 1980). The concentrations found in the fluidized bed reactors would not cause process inhibition as long as the pH remained sufficently high (Andrews, 1969; Anderson and Duarte, 1980). Temperature changes in the unheated fluidized bed reactor appeared to only briefly affect the methanogenic bacteria, causing only small changes in effluent quality and gas production. The development of biomass at ambient temperature will produce a bacterial population of a different nature to that found at elevated temperatures (Hobson, 1981; Chen, 1983; Rimkus et al., 1982) and this type of population appears to operate satisfactorily over a wide range of temperatures (Switzenbaum and Jewell, 1980). In these experiments satisfactory COD removal was still attained whilst operating at low temperatures (< 10°C) an effect also noted by Jewell and Morris (1981).

Flowrates of industrial effluents vary widely throughout the day particularly where shift working is practised (Shabi and Cannon, 1975), these may be minimized by the use of a balancing tank. However, since the recommended balancing tank volume is up to four times the daily flowrate (Campbell and Strachen, 1976) if a process is tolerant of hydraulic overloads considerable land and capital savings may be achieved by either decreasing the volume of, or removing entirely the balancing capability. Due to the large recycle ratios used in the fluidized bed reactors in this study any physical effects (such as washout of biomass due to the increased upflow velocity) can be minimized by regulating the recycle flowrate and in the fluidized bed reactors the upflow velocity remains constant whatever the influent flowrate, therefore only biological overloading effects will be found. The reactors tolerated hydraulic over-loading with no long

term detrimental effects. The definite increases in effluent suspended solids noted during hydraulic loading were probably due to the increase in gas production where unattached biomass particles become attached to gas bubbles and are carried out in the effluent. Biomass may also be sloughed off the media due to increased gas production within the biofilm.

Deterioration in effluent quality was found to be greater during influent COD increases than for an equivalent hydraulic overloading to the same organic loading. This would be expected if it is assumed that the rate of organic removal at a constant loading is relatively independent of influent COD, then in this case effluent COD must rise with increasing influent COD.

The fluidized bed reactors appeared to be extremely tolerant of changes in influent pH. In an industrial process this is important since pH changes occur regularly particularly during cleaning operations, pH variations of 4-9 and 6-8 have been reported for dairy and meat-processing respectively (Shabi and Cannon, 1975). Although operating parameters such as COD and pH were relatively unaffected by a pH reduction the decreasing alkalinity indicated that it was the reactors' buffering capacity that was neutralizing the effects of the low pH. A prolonged influent pH decrease may have eventually caused the reactor operating pH to fall and inhibit methane fermentation (Anderson and Duarte, 1980). The high recycle ratio used in a fluidized bed reactor also will aid reactor stability when toxic materials enter the reactor, mainly due to the dilution effect caused by the recycle. Reactor configurations employing a high recycle ratio have previously been shown to be capable of anaerobically treating wastes with an unfavourable pH or containing inhibitory materials (Chian and DeWalle, 1977). It is for this reason that fluidized bed reactors or anaerobic filters (with recycle) are considered more resistent to adverse influent conditions than single pass reactors such as the upflow sludge blanket reactor (Olthef and Oleszkiewicz, 1982)

The increase in effluent COD in all types of transient changes in operating parameters may be attributed to three factors: (i) increases in effluent volatile acids; (ii) increases in suspended solids; (iii) influent passing through the reactor untreated due to overloading of the process. In Figure 5.1 the contribution to the

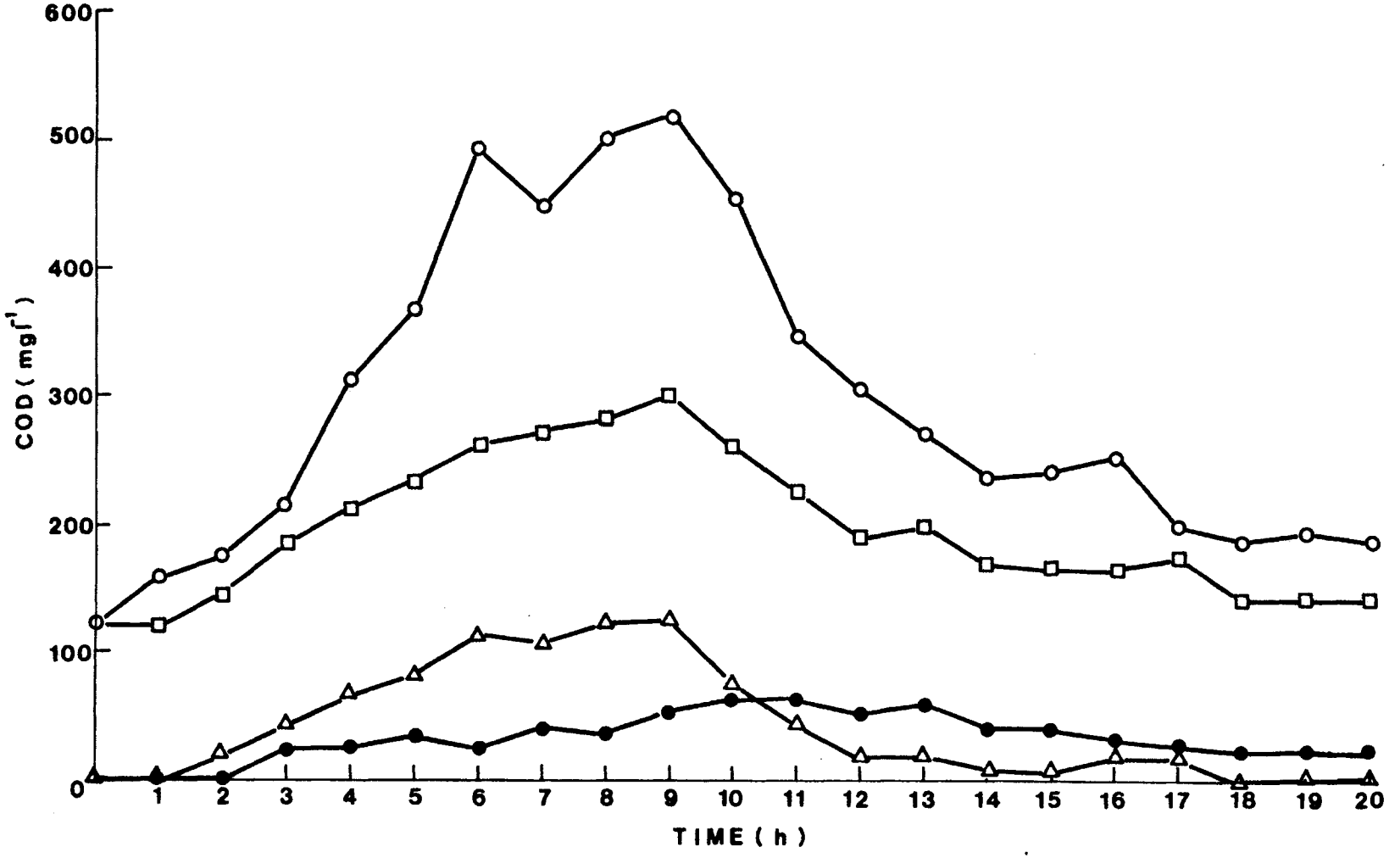


Figure 5.1. The contribution to effluent COD of volatile acids (△) and suspended solids (●) during an 8 h 300% influent COD increase (O) effluent COD, (□) initial COD + equivalent volatile acids and suspended solids COD

effluent COD of the volatile acids (equivalent COD = 1.05 x volatile acids concentration) and the suspended solids (equivalent COD = 1.42 x suspended solids concentration (Switzenbaum and Jewell, 1980)) has been plotted together with the expected increase in effluent COD if these two parameters were solely responsible for the rise in COD during an 8 hour, 300% influent COD increase applied to unheated fluidized bed reactor. At the highest effluent COD approximately 50% of the increase was accounted for by the rise in these parameters, the remaining contribution being due to untreated effluent passing through the reactor.

Resistance to organic over-loading in a fluidized bed reactor may be due to two factors, microbial resistance or dilution due to the large recycle ratios. The theoretical effluent COD increase during a COD shock if no increase in biological organic removal occurred may be determined from the equation:

$$C_e = C_s\ (1-e^{-t/\tau})$$

where C_e = increase in effluent COD
C_s = increase in influent COD
τ = hydraulic residence time
t = time

The expected effluent COD values for a COD shock load are given in Table 5.1 where it may be clearly seen that dilution of the influent is not a principal factor in resistence to organic over-loading otherwise a greater degree of destablization would be expected.

Table 5.1. Theoretical and experimental effluent COD increases for influent COD increase experiments

COD increase (%)	Duration (h)	Experimental COD increase (%)	Theoretical COD increase (%)
150	4	35	272
150	8	44	597
300	4	160	545
300	8	400	1194

The high degree of microbial resistance to organic over-loading in fixed film anaerobic reactors has been attributed to the high biomass concentration in the reactor and the maturity of the biological films (Morris and Jewell, 1981). It has also been found that variations in process conditions result in the development of a versatile biomass which can quickly degrade organic acids (Cohen et al., 1982).

In these experiments and others reported elsewhere (Morris and Jewell, 1981; Cohen et al., 1982; Kennedy and van den Berg, 1982) the basic composition of the waste-water is not changed thus the biomass is not subjected to any stress caused by a change of substrate. This type of experiment is an important progression from steady state operation experiments and fundamental operating problems under variable loading conditions may be found, however these experiments do not completely simulate a true industrial discharge where the physical and chemical characteristics of the effluent are variable. In the reduced alkalinity experiment process stability was found to be considerably affected by the influent composition and in another experiment in an expanded bed utilizing real sewage process performance was found to be considerably poorer than at a constant influent composition (Rockey and Forster, 1983). Therefore variable influent characteristics are an important factor affecting a biological process and care should be taken in extrapolating steady state data to industrial working conditions. However industrial waste streams will probably have a more consistent quality than mixed waste streams or domestic sewage.

Start-up of anaerobic reactors can be a serious problem in most types of reactor configuration (Olthof and Oleszkiewicz, 1982), periods of up to twelve months to achieve satisfactory degradation have been reported (van den Berg and Lentz, 1979; Switzenbaum and Jewell, 1980). The addition of methanol will provide a substrate that is easily assimilated by the methanogenic bacteria (Tait and Friedman, 1980; Mah, 1980) and hence encourage their growth. Attachment to solid surfaces by bacteria is believed to be influenced by the surface charge on the anaerobic bacteria and by the excretion of extracellular polymers, to encourage polymer production the C/N ratio should be increased (Wilkinson, 1958) which is another effect of the methanol addition.

The most striking effect of the addition of methanol was the low effluent suspended solids due to the decreased yield of the non-methanogenic bacteria. The higher carbon dioxide concentrations in the gas produced from the two reactors a constant organic loading is probably an indication of greater activity of the acid forming bacteria, increased carbon dioxide concentrations are often detected in reactors that have an unbalanced bacterial population (Kennedy and van den Berg, 1982; Ashley and Hurst, 1981).

The experiments concerned with separated phase digestion in fluidized bed reactors were intended to evaluate as practical a system as possible, hence the emphasis has been placed on reactor simplicity with only crude control of such parameters as pH. Although a synthetic substrate has been used this waste-water has typical kinetic properties of a high strength effluent (Anderson and Donnelly, 1978a). Reactor operation, particularly of the acidification reactor was somewhat less than optimum. The operating pH of those reactors (3.5-5) was considerably less than the optima of approximately 6 reported by Zoetemeyer et al. (1982a) and Ishida et al. (1979). Operation at this lower pH not only affects the reaction rates but also affects the product distribution from the reactor. In experiments concerning the anaerobic acidification of glucose over a range of operating pH the major acid component at pH 5.69 (the lowest pH reported) was found to be butyrate (Zoetemeyer et al., 1982a).

The high acetate and ethanol concentrations found in the acidification reactor effluents were probably a result of the high dilution rates and the lack of biomass recycle. Ethanol production under these conditions has been reported previously (Zoetemeyer et al., 1982). Pipyn and Verstraete (1981) found that operating an acidification reactor without biomass recycle favoured ethanol and lactic acid production rather than the smaller volatile acids. Ethanol is often reported as a product of acid fermentation, particularly in failed digesters (Zoetemeyer et al., 1982), however, it has been shown to degrade rapidly under anaerobic conditions (Kaspar and Wuhrmann, 1978 b).

The biomass concentration in the acidification reactors was typical of that reported in similar systems (Cohen et al., 1980) and the increase in biomass concentration with influent substrate concen-

tration found in these experiments has been reported previously (Cohen et al., 1980). The biomass in the acidification reactor was white and formed flocs of between 1-2 mm diameter, these flocs appeared to have good settling properties. Effluent hexose concentrations cannot be directly correlated with effluent glucose since intra- and extracellular polysaccharides will give a positive reaction to the test (Rudd et al., 1982), the hexose sugar concentration can give an indication of glucose degradation. This was relatively low in comparison to other reported systems (Cohen et al., 1981) and this is a consequence of the high organic loadings used and the unfavourable pH. Glucose acidification may be improved by recycling biomass but this would increase the complexity of the system and change the product distribution.

The fluidized bed reactors (both in the single and separated phase systems) achieved good COD removals and favourable conditions for methanogenesis up to a COD loading of 15 kg m^{-3} d^{-1}. Higher loadings have been achieved in anaerobic reactors, generally these have been operated with forms of pH control (Oleszkiewcz and Koziarski, 1982; Sutton and Li, 1981) or the reactors are capable of retaining higher biomass concentrations due to lower bed expansions or lower upflow velocities(Jewell et al., 1981; Lettinga et al., 1979). The fluidized bed reactors overall performance in terms of COD removal may be compared favourably to most reactor types; a comparison of maximum reported loadings in other anaerobic reactors is given in Table 5.2

Use of separated phase digestion appears to principally affect the insoluble phase and improves the gas yield. The improvements in effluent suspended solids from the separated phase reactors was probably due to two factors, firstly the superior settling properties of the acid reactor sludge. Due to the greater sludge build-up in the separated phase fluidized bed recycle chambers it is evident that more biomass was settling within the reactor system than in the single phase reactors. Effluent suspended solids from all the fluidized bed reactors were extremely fine and had poor settling properties thus it is important to reduce the solids concentration as much as possible to improve the final effluent quality.

Table 5.2. Comparison of anaerobic reactor performance

Type of reactor and waste-water	Cod loading range kg m^{-3} d^{-1}	COD removal %	Reference
Stationary fixed film reactor. Bean blanching waste.	up to 18.4	88	Kennedy and van den Berg (1982)
Anaerobic contact reactor.	0.55-2.25	95.5-98	Anderson and Donnelly (1978b)
Anaerobic filter. Mixed volatile acids.	0.424-3.392	79-98.4	Young and McCarty (1969)
Anaerobic expanded bed reactor. Domestic sewage	0.6-20	40-80	Jewell et al. (1981)

A second factor that improves effluent quality from the separated phase reactor is the substrate composition. Pipyn and Verstraete (1981) showed that formation of lactate and ethanol in the acid stage was preferable to volatile acid production since the former route distributed a greater proportion of the free energy change of anaerobic degradation to the methanogenic bacteria (see Table 5.3). In an experimental two phase process, biomass production was found to be 40% less if the fermentation in the acidification stage was directed to ethanol and lactate rather than volatile fatty acids and this was attributed to the difference in the free energy change distribution between the two possible routes. Since ethanol fermentation was occurring in the system reported here and although lactic acid was not measured it is generally found in equimolar quantities to ethanol in acid fermentation (Pipyn and Verstraete, 1981), this effect was probably also occurring in these experiments.

The anaerobic degradation rates of volatile acids allow a comparison to be made between the performances of different reactors. The maximum degradation rates in the fluidized bed reactors were extremely high in comparison to a conventional sludge digester; the data from the conventional digester is given in Table 5.4. The higher biomass

Table 5.3. Distribution of the total free energy change of the two phase anaerobic fermentation of glucose to methane over the different microbial groups
(after Pipyn and Verstraete, 1980)

End Acid Phase Product	Free Energy Change available for the fermentatives (%)	Free Energy Change available for the synthetic bacteria as H_2 gas[a] (%)	Free Energy Change available for the synthetic bacteria otherwise (%)
Acetic Acid	51.1	33.6	15.4
Propionic Acid	88.7	0.0	11.3
Butyric Acid	63.0	16.8	20.2
Ethanol	55.9	0.0	44.1
Lactic Acid	49.0	0.0	51.1

(a) potentially subject to loss if headspace gases are not reintroduced into the methane reactor

Table 5.4. Kinetics of volatile acid degradation in conventional anaerobic digesters (Kaspar and Wuhrmann, 1978a)

	V_o mmol l^{-1} h^{-1}	V_{max} mmol l^{-1} h^{-1}	V_E mmol l^{-1} h^{-1}	K_s mmol l^{-1}
Acetate	0.27	0.63	0.41	0.32
Propionate	0.03	0.233	0.19	0.094

concentration and the lack of any diffusional limitation in a fluidized bed probably account for the increases in degradation. The K_s values for propionate degradation in the fluidized beds were extremely high but this could be a reflection of the high maximum turnover rates. The lower K_s values found in the separated phase fluidized bed reactor indicate the superior ease of substrate assimilation in these reactors. Experimentally measured V_{max} values were higher in the separated phase reactors and they were operating closer to their maximum theoretical values than the single phase reactor. The data for propionate oxidation is presented as maximum specific turnover rates (mg propionate degraded per g of biomass per h) in Table 5.5 in order to facilitate comparison with the results of Cohen et al. (1982). Values of V_{max} in separated phase reactors were very similar, although the V_{max} values from single phase reactors were three times higher than those reported by Cohen et al. (1982), however this is again probably a reflection of the high reaction rates achievable in a fluidized bed reactor. The higher maximum specific

Table 5.5. Specific propionate and acetate degradation rates in single and separated phase fluidized bed reactor and conventional sludge digesters

Single phase fluidized bed mg l^{-1} biomass h^{-1}			Single phase sludge digester (data from Cohen et al. 1980)	
Expt.	$V_{E_{Prop}}$	$V_{E_{Ac}}$	$V_{E_{Prop}}$	$V_{E_{Ac}}$
1	8.2	13.25	1.84	2.89
2	8.0	11.82	1.54	1.74
3	8.1	14.15	2.18	3.62

Separated phase fluidized bed mg l^{-1} biomass h^{-1}			Separated phase sludge digester (data from Cohen et al. (1980)	
Expt.	$V_{E_{Prop}}$	$V_{E_{Ac}}$	$V_{E_{Prop}}$	$V_{E_{Ac}}$
1	16.15	27.3	17.42	20.94
2	15.62	27.06	14.03	13.02
3	15.82	27.77	12.34	20.31

turnover rates in the separated phase reactor indicate that the biomass was more adapted to volatile acids degradation, implying that the population of OHPA and methanogenic bacteria was greater or more active in this reactor than the single phase system. The accumulation of acetate during the oxidation of propionate indicates that in both reactors acetoclastic reactions were rate limiting, this is in agreement with the findings of Kaspar and Wuhrmann (1978), however Cohen et al. (1982) found that carbon dioxide reduction was the rate limiting step in their system. The rate limiting step has important consequences during organic overload. In this system with a substrate based on glucose a shock load will lead to rapid generation of $NADH_2$ by glycolysis. Reducing equivalents may be disposed of either by hydrogen transfer leading to reduction of carbon dioxide to methane or by electron-disposing fermentation leading to the formation of propionate or butyrate (Wolin, 1975, Thaver et al., 1977). Should carbon dioxide reduction be rate limiting acid accumulation will occur and with significant quantities of hydrogen in the digester gas inhibition of propionate and butyrate degradation will occur leading to a failed digester (Mosey, 1982). Since acetoclastic reactors were rate limiting in the fluidized bed reactor system reported here, the principal advantage of phase separation under shock load conditions will be the separated phase reactors' ability to remove volatile acids more quickly (due to the lower K_s values).

Cohen et al. (1982) found that V_{max} values increased after successive shock loads of a mixture of volatile acids, they assumed that the system adapted itself by increasing the population of acid degrading (OPHA) organisms to aid process stabilization during organic overloading. This effect was not found here but it is possible that a highly adaptable microbial population had developed during the preceding experiments when the reactors were subjected to wide ranges of operating conditions.

In the previous studies of bacterial activity and substrate profiles thoughout similar anaerobic reactors (e.g. the anaerobic filter) the greatest activity has generally been found at the base of the reactors (Young and McCarty, 1969; van den Berg and Lentz, 1979). In the study of bacterial activity reported here, activities of both groups of bacteria appeared to be at their greatest in the central portion of the fluidized bed. The different flow regimes resulting

from the high recycle ratio and the mobile nature of the inert support material probably account for this difference.

There was some evidence of partial phase separation in the fluidized bed reactor at one COD loading (12 kg m^{-3} d^{-1}) where the methane production was at its greatest slightly higher up the reactor than the peak in phosphatase activity. The profile of volatile acids appears to confirm this with highest concentrations coincident with the peak in relative methane production and appeared above the areas of greatest phosphatase activity. At other COD loadings peaks in both activities occurred in the central portion of the reactor and complete phase separation therefore appears unlikely in single phase reactors.

It would have been expected from previous work that the highest phosphatase activities would have been found when the reactor was in a failed condition (Ashley and Hurst, 1981), however, this was not the case. The most probable reason for this is that in fact acid production was greatest at the intermediate loading. By examining the COD removal efficiency and assuring 70% of the COD is removed with acetic acid as an intermediate (Kaspar and Wuhrmann, 1978a) and noting the effluent volatile acids concentrations, the rate of acid production at each loading may be estimated; these values are given in Table 5.6. It may be seen that acid production in the failed condition was only 66% of that of the immediate loadings. The low substrate pH, high concentrations of higher chain organic acids and possibly hydrogen in the gas produced would all lead to inhibition of the acid forming bacteria.

Table 5.6. Acetic acid production rates in a single phase fluidized bed ractor at three organic loadings

COD loading kg m^{-3} d^{-1}	Acetic acid production g l^{-1} d^{-1}
6	3.79
12	5.71
18	3.80

The flocculated material at the top of the fluidized bed had relatively low methane forming and phosphatase activity, it is probable that this material was largely composed of dead biomass which had sloughed off the support material. Morris and Jewell (1982) examined the attached and free bacterial phases in an anaerobic reactor and found that the attached portion of the biomass was largely responsible for soluble COD removal whilst the free biomass was associated with solids removal, the results reported here are in agreement with this work. The role of the unattached portion of biomass in the fluidized bed reactor is unknown, and process efficiency may be improved if this biomass was removed and replaced with sand (hence increasing the area available for biological growth as a film).

It is evident from these results that the fluidized bed reactor especially as part of a separated phase anaerobic treatment system is a practical method of organic removal from wastewaters. It is capable of maintaining methanogenic conditions and removing significant quantities of influent COD under steady state and variable process conditions at COD loadings of at least 15 kg m^{-3} d^{-1} with only crude control of reactor pH. As stated earlier the experimental system used in these experiments has been constructed and operated to achieve as simple a system as possible. It is clear from other reported results that higher COD loadings may be achieved in anaerobic fluidized bed reactors but at the cost of including certain control systems. The benefits of adding such controls must be carefully balanced against the additional cost and complexity of the process.

For operation at high organic removal rates three possible anaerobic reactor systems have been reported; the fluidized bed, the expanded bed and the upflow sludge blanket reactor. In a recent comparison of these reactor types none of them could be considered ideal for all types of waste-water and operating conditions (Olthof and Oleszkiewicz, 1982). The fluidized bed reactor's advantages can be considered as, the ability to operate at high organic removal rates with a high solids loading and to be capable of operating under conditions of variable process conditions and toxic shock loads, however, this is at the cost of higher power consumption (due to the higher upflow velocities used) than the other two reactor types. Due to the poor solids removal performance of all types of reported high rate anaerobic reactors together with the lack of ammonia removal these

reactor types would generally be used as the first stage of a biological system for high rate organic carbon removal and a second aerobic stage would be required for effluent polishing. However due to the high organic removal rates found in anaerobic fluidized bed reactors they have great potential for capital and operating cost savings to industry.

6. CONCLUSIONS

1. Food processing industries discharge significant quantities of waste-water containing high concentrations of soluble organic material. This effluent is amenable to biological methods of treatment, both anaerobic and aerobic. However, anaerobic processes have been shown to have economic advantages over aerobic methods especially at high influent COD concentrations.

2. An anaerobic fluidized bed reactor operating at 37°C, treating a milk based waste-water maintained stable anaerobic conditions and achieved COD removals of over 80% at COD loadings of up to 6 kg m^{-3} d^{-1}. Methanogenic conditions could be maintained at higher COD loadings but the reactor was unstable and required the addition of buffering agents.

3. An anaerobic fluidized bed reactor operating at ambient temperature successfully treated a meat extract based waste-water achieving COD removals of over 70% at COD loadings up to 3 kg m^{-3} d^{-1}. Above this loading COD removal efficiency rapidly decreased to less than 50%. Establishment of an active anaerobic biological population at ambient temperature took up to twice as long than that at elevated temperatures.

4. Solids yield from both the fluidized bed reactors was very low, at no point during the four months of the study was it necessary to waste any biomass from the system except for sampling purposes. Gas yields from all reactors were typical of other systems treating similar types of waste-water.

5. Anaerobic fluidized bed reactors operating at 35°C could tolerate 10°C and 20°C temperature reductions for 4 and 8 hours with no long term detrimental effects. Effluent quality deteriorated during a temperature reduction but returned to its normal value within 20 hours. Whilst operating at ambient temperatures 10°C temperature changes only briefly affected the performance of the reactor.

6. Under organic overloading, by increasing the influent COD or the influent flowrate effluent quality from both the unheated and heated reactors decreased but typical operating conditions were achieved within 22 hours. Analysis of both protein and volatile acid concentrations and summing COD equivalents indicated that both the non-methanogenic and the methanogenic phases were overloaded. The resistance of the fluidized bed reactor to biological overloading was shown to be due to increased biological activity rather than dilution due to the large recycle ratios. The stability of the raectors was found to be influenced by the influent alkalinity.

7. Transient increases and decreases for 8 hours in influent pH were tolerated by a fluidized bed reactor with little effect on effluent quality. Long term operation at a low pH may be inadvisable since inhibition of the methanogenic bacteria could occur.

8. An experiment where the influent flow rate was reduced for two days in order to simulate working week operation was carried out on an unheated fluidized bed reactor and was tolerated well with full treatment efficiency regained within six hours of return to normal operation.

9. The establishment of an active bacterial population in a heated fluidized bed reactor may be accelerated by the addition of a substrate (methanol) that may be directly assimilated by methanogenic bacteria and by manipulating the loading regime over the first weeks of operation. A more balanced bacterial population may also be achieved using these methods.

10. Anaerobic fluidized bed reactors treating a glucose based substrate achieved good COD removals of up to a COD loading of 15 kg m^{-3} d^{-1} with only crude pH control. Above this COD loading volatile acid accumulation occurred indicating failure of the reactors. COD removal efficiency increased with increasing influent COD, however, effluent suspended solids concentrations were higher at a greater influent COD.

11. The glucose based waste-water could be acidified in a stirred tank reactor at COD loadings between 15 and 180 kg m^{-3} d^{-1}. Fermentation was directed towards the production of lactate, ethanol and acetate rather than volatile acids. This was due to the lack of biomass recycle and the development of a yeast type biomass.

12. The acidification reactors operated at pH values considerably different from the optimum values. This affected both the product distribution and the rate of acidification, thus complete acidification of the waste-water was not achieved although an active bacterial population was always maintained.

13. The addition of an acidification reactor prior to a methanogenic fluidized bed improved final effluent quality compared to a single phase fluidized bed reactor. The separated phase reactor produced an effluent with lower suspended solids and total COD; gas yield from the separated phase system was also superior. The greater distribution of the free energy change to the methanogenic bacteria accounted for this improvement.

14. Under varying process conditions both the single and separated phase fluidised bed reactors had good stability. The separated phase system had an inherently greater stability but improvement in performance of the separated phase system over the single phase process was small although the separated phase system was generally destabilized to a lesser degree and recovered more rapidly.

15. Maximum degradation rates of propionate and acetate in fluidized bed reactors were an order of magnitude greater than for a conventional system. Experimentally measured degradation rates indicated that the separated phase fluidized bed system was operating nearer its theoretical maximum than a single phase system.

16. Specific degradation rates of propionate and acetate in fluidized bed reactors were similar to those reported for other systems. Greater specific degradation rates in the separated phase system indicated that a biomass had developed that was

more adapted to volatile acid degradation than in a single phase reactor.

17. During organic overloading and whilst evaluating propionate degradation parameters, acetoclastic rather than lithotrophic reactions were found to be rate limiting in both the single phase and separated phase systems.

18. Biological activity was found to be greatest in the central portion of the fluidized bed reactor. Determination of the activity of the non-methanogenic and the methanogenic bacteria indicated that partial phase separation may occur in an anaerobic fluidized bed reactor.

19. Biomass attached to a support particle was found to have a greater activity than free floating flocs and was considered to have a more important role in the removal of soluble organic material.

20. The anaerobic fluidized bed reactor has been shown to have great potential for the high rate removal of soluble organic material. However due to its poor solids removal performance and the lack of nitrogen removal in an anaerobic process its use will probably be confined to pretreatment prior to an aerobic system.

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