A BIOLOGICAL TREATMENT SYSTEM

FOR

FELLMONGERY WASTES

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MICHAEL DESMOND RYDER

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SUMMARY

Traditionally fellmongery wastes from freezing works have been treated by ponding before discharge to the nearest watercourse. Unfortunately, this does not always produce a satisfactory effluent.

These studies seek to provide a method of improving the quality of fellmongery effluent.

The lime and sulphide components of fellmongery wastes limited many of the chemical and biological systems considered. Biofiltration offered a simple and inexpensive method of treatment. Batch and continuous loadings were considered, the batch loadings being subjected to a range of recirculation ratios. Emphasis was directed at determining the mechanism of sulphide removal from the waste during treatment.

Batch operation (8 hour/day per 5 day-week) was shown to be marginally superior to a continuous operation on the basis of COD removal. Both systems exhibited 90 - 100% sulphide removal, which was shown to occur by a biological mechanism. Thiobacillus thioparus, an autotrophic sulphur-oxidising bacteria, was the main agent of sulphide removal, sulphate being the end product of the oxidation process. Thiorhodaceae, the purple sulphur bacteria, was also isolated from the filter during continuous operation. The mechanism of sulphide removal from fellmongery wastes was incompletely defined.

Effluent pH was shown to be independent of changes in influent pH. A decrease in pH during treatment was due to the increases in sulphate concentration and the precipitation of lime by carbonation reactions.

Biological filtration of fellmongery wastes provided a satisfactory method for the simultaneous reduction of COD, sulphide concentration and lime concentration.

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INTRODUCTION

INTRODUCTION

The fellmongery process involves the removal of wool from sheep and lamb skins prior to tanning. The pelts also must be free from epidermis, sweat and fat glands, muscle tissue, blood vessels, fat cells and collagen fibrous tissue. The process consists of the following operations:-

(1) Washing of pelts.
(2) Lime/Na_2S paint application.
(3) Wool removal; manual pulling.
(4) Liming; removal of residual wool, pelt conditioning, carried out in a "dolly" or drum.
(5) Deliming and bating; removal of lime liquor and extraneous pelt matter, "dolly" or drum processing.
(6) Pickling; preservation; "dolly" or drum processing.

Thirty-nine fellmongeries, which were operating in New Zealand at the end of 1972 (42), were all departments of meat processing works.

Fellmongering, as a completely separate process from tanning, is relatively unique to New Zealand. The majority of foreign fellmongeries are integrated with the tanning process. This situation arose from New Zealand's early trading role as a producer of raw materials for the more industrially developed countries of Western Europe. Thus New Zealand exports only partially processed pelts, although this is likely to change in the future. Approximately 36 million pelts, valued at $N.Z. 48.7 million, were exported in 1971; the majority to Britain, the U.S.A., the Netherlands and France (84).

The lamb and sheep kill of a meat processing works will influence the size of the associated fellmongery. The pelt throughput of the fellmongery determines the volume of effluent discharged.

The organic portion of fellmongery waste is represented by its high BOD, while the sulphide and lime components constitute the bulk of the inorganic fraction. The waste is characteristically alkaline. An effluent with such characteristics is not readily amenable to biological treatment, although biological filtration is an exception. Costly chemical treatments are required to achieve a satisfactory product for discharge.

After a primary sedimentation treatment the majority of fellmongery effluents are discharged to ponds or to the main meat processing waste stream. Additions of fellmongery effluent to existing effluent streams only serve to increase their respective volumes and organic loads. Treatment by ponding necessitates large land areas, and results in the emission of unpleasant odours during treatment.

Discharge of untreated fellmongery waste to sewer systems or receiving waters is undesirable owing to the toxic effect of the sulphide and lime components on biological life present in both systems. The corrosive effect is well recognised, and accordingly sulphide concentrations entering sewers are set at low limits by local authorities. The high BOD of the waste will cause severe depletion of dissolved oxygen in receiving waters if insufficient dilution is present.

With an increasing public awareness of environmental conservation, treatment of effluents such as fellmongery, will become mandatory. Waste treatment systems must be selected on the basis of economy and performance characteristics. In addition, maintenance and degree of attention must be minimal. A system with a specific mechanism for simultaneous removal of BOD, sulphide and lime is desirable. Several processes when combined together may accomplish this, but biological filtration exhibits the potential to accomplish these objectives in a single operation. Accordingly, these studies were concerned with the investigation of the performance of a biological filter treating fellmongery waste. The nature of the mechanism of sulphide removal and the alkalinity of the waste were also the subject of a detailed study.

CHAPTER ONE

LITERATURE REVIEW

1. LITERATURE REVIEW

1.1 CHARACTERISTICS OF FELLMONGERY WASTE

1.1.1 Introduction

Since the fellmongery process is unique to New Zealand, very little published data pertaining to the composition of fellmongery waste is available, and so the literature relating to tannery waste composition has been consulted. The two wastes differ by virtue of the additional constituents found in tannery wastes such as chrome salts, vegetable tannins, dyes and oils.

Table 1.1 presents a breakdown of the components of fellmongery effluent.

1.1.2 Physical Characteristics

Koziorowski and Kucharski (64) indicated that 86.5 per cent of the total water consumption in a tannery was attributed to fellmongery operations.

Water usage within a fellmongery will depend upon several factors:-

(i) Type of operation (drum or paddle processing)
(ii) Scale of operation
(iii) Water availability
(iv) Process management
(v) Discharge facilities

Southgate (106) quoted 20-30 gallons (91-136 litres) per skin, as water usage for a fellmongery unit in Great Britain. Water consumption of a New Zealand fellmongery (89) has been estimated at between 45-136 litres per pelt.

Individual waste waters originate from several operations within the fellmongery. In order of processing these are:-

(i) Soak and wash waters; dirt, fleshings, wool and dissolved proteins are present.
(ii) Lime liquors; large quantities of suspended matter, consisting of lime, wool and proteinaceous material

TABLE 1.1

COMPOSITION OF TANNERY AND FELLMONGERY WASTES

	Polish Chrome Tannery Waste[1]	Russian Tannery Waste[2]	N.Z. Fellmongery Waste[3]
pH	7.5 - 12.2		9.5 - 12.4
BOD_5 (mg/l)	235 - 2700	451 - 1239	1100 - 2400
Total Nitrogen (mg/l)	177 - 470	83 - 159	400
Chlorides (mg/l)	2140 - 3950	810 - 2210	3000
Sulphides (mg/l)	9 - 140		10 - 150
Total Suspended Solids (mg/l)	452 - 20,645	1320 - 2559	7360 - 15,097
Settleable Solids (mg/l)			539 - 1457
COD (mg/l)			760 - 5920

1. Perkowski, S., Mechaniczne i chemiczne oczyszanic sciekow garbarskich, Przegl. Skorzany, 13, (24), (1958).

2. Figures presented are average values of 10 tanneries. Konorova, E.F., Kozhevennye Zavody, in Proizvodstvennye Stochnye vody, Boldyrev, T.E. (Editor) Moscow 1948.

3. "Pelt Effluent Treatment with Reference to Islington Works" N.Z. Refrigerating Co. Ltd., Report, 1972.

are found. Very alkaline and high sulphide concentration.

(iii) Deliming and bating liquors; weak and slightly alkaline. Skin-proteinaceous material and fatty pelt substances may be present.

(iv) Pickle liquors; characterised by a low pH and the presence of sodium chloride.

Each of the above operations is followed by a washing stage. Soaking and wash waters and washings from the limed and delimed product are the major contributors to the overall waste (64).

From the above descriptions it is extremely difficult to define fellmongery wastes with any degree of exactness. This difficulty is further compounded by the fact that the respective waste streams are discharged at different times of the day, depending upon the operation in progress (64, 106).

Primary sludge production is considerable in fellmongery waste. Lime and wool are the most significant contributors. Additional sludge may arise as the pH decreases, since this will cause large amounts of protein and their degraded products to precipitate (122).

Fellmongery wastes produce very pungent, ammonia-like odours. Hydrogen sulphide, a very unpleasant odorous gas, is prevalent when a pH decrease occurs.

The wastes display a grey to green colouration caused by the sulphide-lime depilatory paint and liming liquors present.

1.1.3 Chemical Characteristics

One of the main characteristics of fellmongery waste is the high organic matter content. Large variations occur in recorded BOD and COD values for different fellmongery wastes (42). BOD values may range from 500 to 2400 mg/l, while variation in COD is greater - 760 to 5920 mg/l (42). These values correlate well with values presented for analyses

effected on total wastes from Polish tanneries (64), and figures for English tanneries (79). Moore's figures (79) indicated that liming and soaking wastes are the main sources of BOD.

Nitrogen levels of fellmongery wastes are also considerably high. Polish and Russian figures (64) show a range of 80 to 470 mg/l total nitrogen. Analysis of a New Zealand fellmongery waste yielded an average total nitrogen concentration of 400 mg/l (50). As with BOD, the main source of nitrogen is in the soaking and liming liquors (79). Wool and skin proteins, as well as their degraded products, contribute significantly to the nitrogen levels in the waste.

Sulphide is an important component of the total waste. Arising from the depilatory paint and liming liquors, sulphides, especially hydrogen sulphide, are very toxic, particularly to fish and biological life important in purification processes (42, 122). Some fish species will not tolerate a concentration of even 1 mg/l sulphide (18). The toxicity of sulphide is influenced markedly by variations of pH. Longwell and Pentelow (71) found that the duration of exposure for brown trout (Salmo trutta L.) was increased fifteen-fold by increasing the pH from 7.5 to 9.0. Hydrogen sulphide is poisonous if inhaled and concentrations of 0.06 to 0.08% will cause acute poisoning in a short time (114).

If fellmongery wastes flow into a sewer, the pH will decrease by virtue of dilution with other waters, particularly if they encounter a stream of acidic industrial waste. This will allow the liberation of hydrogen sulphide, which may penetrate into the pores of the concrete and exert a corrosive effect if converted to sulphuric acid by the action of groups of sulphur bacteria (26).

Sulphide concentrations encountered in fellmongery wastes range from 10 to 150 mg/l (42), depending upon the water consumption and the operation in progress at a particular time.

Another toxic compound present is lime, $Ca(OH)_2$, concentrations of which have been estimated as high as 3000 mg/l in fellmongery wastes (89). Bianucci and de Stefani (18) noted that the harm caused to fish may be due to the hydroxyl ion content, corresponding to pH 12-13. Since the optimum pH for fish ranges from 6 to 8.5, the discharge of large volumes of fellmongery effluent to receiving waters with small flows is not recommended.

Lime is the main component contributing to the high pH and alkalinity of the effluent. Sodium sulphide, a strong basic salt, will also contribute to the alkalinity portion of the waste. Since saturated lime solutions are utilised in the liming process, a reserve of lime is always present and is instrumental in maintaining a high pH.

Fellmongery wastes may often bring about a reduction in the cross-sectional areas of pipes, because of the lime sludge forming crusty deposits on the inside walls. If temporary hardness is present in the sewer water, this phenomenon proceeds more rapidly since calcium hydroxide present in the waste reacts with the temporary hardness yielding calcium carbonate. This "limestone" will deposit on pipe walls forming a hard crust (64).

The remaining inorganic compounds found in the effluent are sodium chloride, ammonium chloride, ammonium sulphate, small quantities of sulphuric acid and fungicides from the pickling operation. Sodium chloride may be present in concentrations of up to 2500 mg/l Cl^- (89). Salt-laden waters can deposit scales on municipal water-distribution pipe lines, thus increasing resistance to flow and lowering the overall capacity of the lines (49). Chloride concentrations similar to that reported do not affect biological life or treatment processes. Sawyer and McCarty (98) reported that water with chloride concentrations of 2000 mg/l may be used without the development of adverse effects, once the human system becomes adapted to the water. The remaining components will not be present in large concentrations and should cause no problem in treatment systems or receiving waters.

1.2 THE TREATMENT OF FELLMONGERY WASTE

1.2.1 Introduction

This section attempts to review both biochemical, chemical and physical methods of treating fellmongery waste. Tannery waste treatment methods have been incorporated and are used to supplement fellmongery waste data.

In many cases information has been obtained from abstracts, which while providing a brief description of a particular process, are often lacking in essential design and operating data.

Fellmongery effluent poses several problems when biological treatment is contemplated. The alkaline pH and high lime and sulphide concentrations are often thought to inhibit biological stabilisation.

Chemical treatment methods are normally used as pre-treatment processes, directed towards eliminating one specific component, e.g. sulphide. Although this is satisfactory in one sense, it is economically desirable to remove as many components in one process as is practically possible. Biological treatment lends itself to simultaneous BOD, sulphide and lime removal by a combination of microbiological and chemical mechanisms.

Both aerobic and anaerobic mechanisms of biological waste treatment are considered.

1.2.2 Biological Treatment Methods

1.2.2.1 Aerobic Treatment

Biological oxidation of an organic waste is a process whereby the indigenous heterotrophic microorganisms degrade the waste. Part of the waste acts as the substrate for respiration, producing the energy necessary for life processes. It is broken down to carbon dioxide, water and other end-products such as ammonia, sulphate and phosphate compounds. The remainder is used in the synthesis of new cells, which is seen as a build-up

of sludge in the form of a "film" on filter beds, or the microbial flocs of activated sludge. An excess of sludge is likely to occur which must be removed from the effluent prior to discharge. Large sludge quantities can block biological filters, and if discharged without removal from treated effluents, will impose biological loads on receiving waters. Sawyer (97) showed that 0.5 - 0.6 lb (0.23 - 0.27 kg) of sludge remained for every 1 lb (0.45 kg) BOD removed from the waste.

Inorganic compounds such as cyanides, sulphides, thiocyanates and thiosulphates may also be metabolised (52). Oxidation of these is accomplished by groups of autotrophic bacteria.

Dissolved oxygen acts as the source of oxygen for both heterotrophic and autotrophic microorganisms. Their metabolism will deplete dissolved oxygen concentrations which must be maintained at a certain level to prevent anaerobic processes from overcoming the aerobic ones. The most important mechanism for replenishment of dissolved oxygen is absorption from the atmosphere. Reaeration rates are dependent upon several factors:

(1) Degree of deficiency of dissolved oxygen based on saturation conditions.
(2) Surface area available for oxygen transfer.
(3) Resistance of the surface film to oxygen transfer.

Of the aerobic treatment methods available, biological filtration, activated sludge units, oxidation ditches, and oxidation ponds are the most commonly reported systems for the treatment of fellmongery and tannery wastes.

1.2.2.1.1 Biological Filtration

Besselievre (17) remarks that high rate filtration is especially applicable to the treatment of tannery wastes.

A biological filter is a packed bed of stones or other natural or synthetic media over which the waste is applied.

Over a period of time a growth of microbial film on the packing may be observed. As the liquid trickles over the medium, organic matter and oxygen diffuse into the film where they are oxidised to carbon dioxide, water and metabolic by-products. New slime is synthesized and the carbon dioxide and water diffuse out of the film.

Biological filtration is considered in more detail in Section 1.3 of this chapter.

1.2.2.1.2 Activated Sludge Units

Activated sludge systems are similar to trickling filters in that they bring air and liquid waste into intimate contact, and so promote the aerobic biological breakdown of the organic constituents of the waste. Contact between organisms, dissolved oxygen and substrate is achieved by turbulent mixing which is induced by turbine brushes or sparged air streams. The micro-organisms form flocculent growths that are suspended in the liquid phase. The effluent overflows from the aerated chamber after a certain residence time. The flocs are removed by sedimentation leaving the clear, treated effluent. Excess sludge is removed, the remainder recycled to maintain constant solids concentration.

Koziorowski and Kucharski (64) referred to the activated sludge treatment of tannery wastes in Germany and France. Dilution with domestic sewage in ratios of 1:1 and 1:2 respectively, was necessary in both cases for satisfactory treatment. The presence of lime was found to inhibit biological action. However, carbon dioxide production by the microorganisms will neutralise the excess lime, reducing this inhibitive effect. If insufficient carbon dioxide is produced, then biological treatment cannot be used. This is substantiated by the observation of Koziorowski and Kucharski (64), that long aeration periods are required for high lime concentrations. Poszto (91) confirmed this and stipulated that a 60% dilution with domestic sewage was required prior to activated sludge treatment of tannery waste.

Dilution with domestic sewage was found necessary by Hunter

and Sproul (56) to accomplish a 90% BOD reduction of tannery waste by activated sludge. The dilution was required to avoid the high pH effect. This contrasts with the proposition that dilution is necessary to achieve a satisfactory start-up process (64).

Increased aeration of tannery effluent in an activated sludge unit has been reported by Emerson and Nemerow (34) as a means of lime removal. The aeration caused the lime to precipitate as calcium carbonate, reducing the pH. They claimed that the production of carbon dioxide by the microorganisms is the key to the formation of calcium carbonate, since the carbon dioxide is then converted to carbonic acid which reacts with the lime to give calcium carbonate. Eye and Liu (38) made a similar observation and noted that combined tannery wastes are amenable to biological treatment provided that suspended lime is removed prior to treatment.

Rosenthal (94) achieved a 95% BOD reduction in an activated sludge system with a preliminary flue gas aeration. The activated sludge unit was loaded with 100 lb/1000 ft^3.day (1.6 kg/m^3.day) aeration capacity.

Thafaraj *et al* (119), in a comparison of the activated sludge treatment of tannery waste with lagooning, found that activated sludge gave better performance.

An activated sludge process with extended aeration was found to be effective for tannery waste treatment by Dobolyi (30), whose work was in agreement with that reviewed by Koziorowski and Kucharski (64). Dobolyi (30) also found that excessive foaming occurred in the presence of large quantities of suspended solids, high sulphide concentrations and over the pH range 7.0 - 12.0.

A U.S. Department of the Interior (U.S.D.I.) report (120) indicated that activated sludge treatment of tannery waste yielded a 90% BOD removal in addition to a 90% decrease in

suspended solids and 99 - 100% sulphide removals.

Pilot plant activated sludge studies in Czechoslovakia (118) showed 98% BOD removals and 77 - 85% COD removals in tannery waste. Although treatment was carried out without the addition of domestic sewage, it was found that the addition of phosphorus was necessary. Liquors were amenable to treatment by high rate (3 hr), conventional (6 - 9 hr) and extended aeration (> 24 hr) processes. Oxygen consumption and sludge production were dependent on the load removed and sludge concentration. In contrast, activated sludge treatment of fellmongery and tannery wastes in France (118) reduced the BOD by only 60%. The waste was applied at the rate of 0.6 kg/m^3. day. A 2 day residence time resulted in very poor sludge settling.

The previously cited works do not mention the effect of sulphides on efficiency of treatment. Dobolyi (30) found the sulphides present in the wastes were associated with excessive foaming. The U.S.D.I. report (120) indicated almost total removal of sulphide, suggesting that its presence does not affect the overall process of degradation of this type of effluent.

Aulenbach and Heukelekian (4) investigated the transformation and effects of reduced sulphur compounds in activated sludge treatment. They found that microflora solutions may be conditioned to treat wastes containing as much as 100 mg/l sulphide, similar concentrations as found in fellmongery and tannery effluents. The sulphide was completely oxidised to sulphate within 6 hours aeration. Elemental sulphur and thiosulphate intermediates were detected. The workers also investigated the effect of sulphide on BOD removal from the waste. It was found that activated sludge could purify sewage containing 25 mg/l sulphide without decreased performance. A sulphide concentration of 50 mg/l was tolerated for two weeks before BOD removal efficiency commenced to decrease. Additions of 100 mg/l sulphide resulted in rapid BOD removal efficiency decreases.

A higher sulphide concentration was tolerated by the activated sludge used by Dawson and Jenkins (27). Sulphide was found to depress oxygen uptake by the sludge only when its concentration exceeded 10,000 mg/l. This study, however, neglects to relate changes in sulphide concentration to the BOD removal ability of the microbial mass. The oxygen uptake recorded in the investigation may be attributed to endogenous respiration. There is no mention of an exogenous metabolisable substrate which would require additional oxygen. The ability of the organisms to metabolise an organic substrate in a 1% sulphide solution is doubtful.

Leafe et al. (69) found a lower sulphide concentration of 40 mg/l than the 100 mg/l quoted by Aulenbach and Heukelekian (4), decreased the performance of an activated sludge unit. 20 mg/l of sulphide had no effect on the performance. All sulphide added to the plant was converted to sulphate during treatment.

In contrast to the results published by Leafe et al (69) and Aulenbach and Heukelekian (4), Villa (124) demonstrated that a small, two-stage activated sludge unit, used to treat tannery wastes, tolerated sulphide concentrations up to 300 mg/l. Concentrations up to this value were not detrimental to the performance of the unit.

Since complete operating data of the afore-mentioned systems are not presented, it is difficult to judge the effect that the presence of sulphide has on activated sludge treatment. However, it is possible to conclude that activated sludge units will satisfactorily treat sulphide-bearing wastes with the simultaneous removal of the sulphide.

1.2.2.1.3 Oxidation Ditches

Oxidation ditches are very similar to activated sludge units. Both aeration and settling are carried out in the ditch. Based on an original design due to Pasveer (88), an oxidation ditch may be described in its simplest form as

consisting of a "race-track" type ditch, into which a revolving rotor of adjustable speed is placed across the path of the ditch. The brush promotes vigorous aeration of the liquor in the ditch and controls the rate of flow of waste through the ditch. Typical loading figures are 45 gm BOD/(kg D.M).day, which is only approximately 6% of the loading in an activated sludge system, with the result that endogenous respiration prevails in the ditch.

Van Vlimmeren (122) described a pilot plant oxidation ditch for the treatment of tannery wastes which had a pretreatment stage consisting of sedimentation for 30-45 minute periods. Retention time in the ditch varied from two to three days, depending upon the loading rate. Average BOD load was 22.2 g/m^3.hr., while the average oxygen capacity was 32.5 g/m^3.hr. BOD was reduced from 1000 mg/l to 20 mg/l. Waste flow was very low at nights and during weekends. He concluded that the system was a highly satisfactory method of treating tannery wastes. Capital costs evaluated on a 200,000 population equivalent (p.e.) basis were $1 million lower than those of a conventional activated sludge system. Operating costs per p.e. were 30 cents lower. He made no mention of sulphide removal.

Another Pasveer ditch system which includes a pre-settling stage has been described (32). A 900 mg/l to 20 mg/l BOD reduction with tannery waste was achieved. Operating parameters were not provided.

1.2.2.1.4 Oxidation Lagoons

Oxidation lagoons, with and without induced aeration, have been used to treat tannery wastes (64, 86, 103, 118).

Aerated lagoons primarily differ from activated sludge systems in the degree of system control. The microorganism population in the activated sludge system is controlled by recycling sludge from a secondary clarifier, whereas the aerated lagoon is strictly a "flow-through" aeration basin,

where the solids concentration is a function of the waste-water characteristics and basin detention time. Oxygen is supplied to the basin by mechanical or diffused systems. The induced turbulence level is sufficient to maintain an essential dissolved oxygen concentration but insufficient to keep all solids in suspension.

The use of an oxidation pond without induced aeration has been reported for tannery waste treatment (118). These systems differ from aerated lagoons in several ways. Oxidation ponds utilise the symbiotic growth of bacteria and algae to fulfil waste treatment requirements. Bacteria oxidise the available organic matter in the waste. Algae utilise the bacterial metabolic products in a photosynthetic process producing oxygen, which in turn is used by the aerobic bacteria.

Partridge (86) reported the use of a pilot plant aerated lagoon for the treatment of tannery effluent. He expressed a difficulty in maintaining a necessary sludge concentration. Contact stabilisation lagoons were also investigated and operated satisfactorily with long aeration periods.

In a French pilot plant lagoon (118) aeration of fellmongery and tannery effluent for a period of 20 days resulted in a 70% reduction in BOD for a system loading of 0.1 kg/m^3.day.

Italian work reported (118) involved the treatment of tannery wastes, diluted 25% with domestic sewage, in an oxidation pond. The pond depth was 0.9 m, and a residence time of 40 days was used. For vegetable tannery effluent, the BOD was reduced in 40 days from 802 to 219 mg/l, a 73% reduction.

French investigations presented in the 1971 IULCS report (118) demonstrated that a two stage pilot plant lagoon system could handle tannery wastes of 113 mg/l sulphide without altering the BOD removal performance. Additions of 199 mg/l sulphide resulted in zero BOD removals. The first lagoon operated with a one day residence time, and the second, three to five days.

An important factor not considered in any of the consulted papers on lagooning is the possibility of sulphide production within the pond, and the occurrence of mal-odours associated with operation of the system. The chemical compounds, most often associated with odours from ponds include: sulphides and mercaptans, both recognised components of tannery and fellmongery wastes, and also the amines and polyamines produced during bacterial decomposition of proteins (36).

Espino and Gloyna (36) stated that the most important sulphide source in a pond stems from the biological activities of the sulphate-reducing bacteria. These bacteria have been associated with pipe corrosion and odour problems in sewer lines and sewage plants.

1.2.2.2 Anaerobic Treatment

In an anaerobic treatment process, organic wastes are stabilised by microbial degradation to methane and carbon dioxide in an anaerobic environment. The growth of excess microorganisms is minimised, thereby reducing the amount of sludge to be disposed of, and the need for nutrients, such as nitrogen and phosphorus, which are required for cell synthesis. A promising system is the anaerobic filter in which bacteria grow on a suitable packing medium in an anaerobic environment. A long biological solids retention time is maintained.

Anaerobic treatment of tannery or fellmongery wastes seems to have few advocates. Ivanov (58) had an anaerobic stage prior to his aerobic process for treating tannery wastes. The raw influent exhibited variable characteristics:- pH 7.6 - 10.0, BOD 840 - 2350 mg/l. It was diluted with domestic sewage to a BOD of 380 mg/l prior to anaerobic conditioning. A residence time of 2 hours was maintained in the anaerobic tank. No reference to sulphide influence on the anaerobic digester performance was made.

Gates and Lin (44) also studied an anaerobic type system

which consisted of a model lagoon with an aerobic upper section and anaerobic lower section. Residence times of 2.64 days and 1.64 days in the anaerobic and aerobic sections respectively were maintained. Using a synthetic tannery waste, they achieved 92% COD reduction with loadings of 0.45 kg COD/m^3.day. The mean COD was 1000 mg/l. On varying the influent COD a relatively stable effluent COD was achieved. The aerobic section was used to control odours originating from the anaerobic unit.

The IULCS report (118) briefly mentioned the operation of an anaerobic treatment system for vegetable tanning liquors in Italy. The waste had a volatile solids content of 800 mg/l of digester capacity per day, and its BOD was reduced by 90%.

The use of an anaerobic filter for tannery effluent treatment has been reported (29) but no details accompany this report.

The effect of sulphides on anaerobic digestion is well documented (74). Sulphide concentrations of 50 - 100 mg/l have been tolerated with little adverse effect on the process (74). Concentrations above 200 mg/l are considered to be toxic. McCarty (74) noted that sulphides, as well as those entering the digester in the waste, can result from the biological reduction of sulphates and other sulphur-containing inorganic compounds. Anaerobic protein degradation is also a source of sulphide (36).

Sulphide may induce the precipitation of toxic heavy metals such as copper, zinc and nickel from the liquors (68). In addition to removal by precipitation, sulphides may remain in solution as soluble sulphides or be removed as a gas in the form of hydrogen sulphide (H_2S).

The large quantities of lime which are present in the fellmongery waste streams are likely to affect the operation of an anaerobic process. It has been demonstrated that high

concentrations of alkali and alkaline earth metal salts, such as those of sodium, potassium, calcium or magnesium are frequently the cause of inefficiency in, or failure of, anaerobic treatment (65, 66).

1.2.2.3 Aerobic/Anaerobic Treatment Comparisons

It is difficult to present a comparison of the aerobic and anaerobic methods reviewed, owing to the small amount of quantitative data accompanying the respective reports. On a cost basis, waste stabilisation ponds would prove the most attractive (45). However the problems associated with these, such as odour production and large land requirements, diminish their appeal. Activated sludge and associated methods seem to produce substantial BOD reductions and sulphide removal from fellmongery and tannery wastes. The application of anaerobic digestion to tannery and fellmongery waste treatment is not common. The high pH and sulphide components of the waste may be deterrents.

1.2.3 Physical and Chemical Treatment Methods

1.2.3.1 Physical

Physical treatment methods of tannery and fellmongery wastes are similar to the conventional methods applied to sewage and industrial wastes. The first step normally encountered is the removal of coarse suspended solids using grids and screens. Koziorowski and Kucharski (64) noted that grid spacings of 20-25 mm and screen meshes of 0.5 - 5 mm were used for tannery waste treatment. Boley (20) has described the satisfactory use of screens for tannery effluent.

Koziorowski and Kucharski (64) maintained that an equalisation tank is required following screening. This unit minimises hydraulic and organic fluctuations in subsequent treatments.

Primary sedimentation is a necessary operation in tannery and fellmongery waste treatment, since these wastes exhibit

high settleable solids concentrations. Willis (129) has reviewed the principles of sedimentation and flocculation and relates the design of sedimentation tanks to the different modes of particle settling.

Rands (42) investigated the use of hydrocyclones in primary fellmongery waste treatment. He concluded that they were ineffective because of the high moisture content of the separated solids. These findings contrast with claims of satisfactory suspended solids removal from tannery wastes using a large-scale hydrocyclone (93).

The practice of coagulation in aiding the sedimentation of fellmongery and tannery wastes has been extensively reported. Acids (16, 19, 64, 83), ferrous and ferric salts (19, 51, 64, 80, 104), polyelectrolytes (37, 39, 107), clays (16) and alum (51, 64, 73, 80) have been found to be successful coagulants. Koziorowski and Kucharski (64) showed that the acid coagulation of tannery wastes resulted in a 61.4% BOD reduction. 73% BOD removals were obtained by Niwa (83) with HCl and H_2SO_4. The optimal pH range for both processes was 4.5 - 6.0. Sierp (104) stated that acidification should be carried out in closed tanks; if necessary the hydrogen sulphide liberated may be used to regenerate sodium sulphide. Acids have been used successfully to complement treatment with clays (16), ferrous and ferric salts (19), and alum (64). Lime with subsequent carbon dioxide treatment has been used in conjunction with ferric, ferrous and aluminum salts (64). Lime contributed to improved sludge settling while the carbon dioxide reduced the pH.

Ferric sulphate, ferric chloride and aluminum sulphate effect BOD removals of 40 - 80% (39, 64, 73). BOD removal efficiencies are influenced by pH, coagulant concentration and the nature of the waste. A most effective coagulant is ferrous sulphate when used with carbon dioxide and calcium hypochlorite or lime (64). Hal'perin (51) reported that alum, used in comparable concentrations to ferrous sulphate (500 mg/l), gave satisfactory BOD removals.

1.2.3.2 Chemical

Chemical methods of sulphide elimination include:-

(i) catalytic and non-catalytic aeration.
(ii) acidification.
(iii) ferrous and ferric salt treatment.
(iv) flue-gas treatment.

The most common method of sulphide removal is by catalytic or non-catalytic oxidation. Oxidations are normally carried out in conventional aeration systems.

Manganese sulphate and manganese chloride are the most commonly reported of a wide range of catalysts that have been investigated (6, 15, 40, 133). Concentrations are found in the range 50-200 mg/l. Reaction products have been identified as thiosulphate and small quantities of sulphate (6). Eye and Clement (40) confirmed this, but proposed that a small amount of elemental sulphur could also be present. pH considerations led Berg et al (15) to surmise that oxidation converted sulphide to sulphate. They proposed that manganese forms $Mn(OH)_2$ in alkaline solutions, which they believed to be the active catalyst. The workers also stated that catalysts may be removed from the reaction by poisoning with hair and other proteinaceous material.

Catalytic agents are not confined to manganese salts. Eye and Clement (40) investigated the effect of potassium permanganate and found it to be more satisfactory than manganese sulphate. Schwab and Butterworth (101) reported the use of nickel and copper salts as catalysts, and claim good sulphide removal rates. They did not publish quantitative data.

Aeration without catalyst addition may be used to remove sulphide from waste streams (10, 43, 48). The data of Bailey and Humphreys (6) and Eye and Clement (40) indicated that long aeration times were required.

Oxidative sulphide removal has been accomplished in packed columns and pipe ejectors at elevated temperatures and pressures (1, 22, 115). Abegy (1) described a packed column operating at 115°C and under 3 atmospheres pressure. Sulphides were converted to sulphates, thiosulphates and thiols, and were subsequently removed with the spent air and burnt.

Jones and Pearson (61) and Collins and Roetman (24) reported that the acidification of wastes assists sulphide elimination. Collins and Roetman maintained that pH adjustment to a range of 8 - 10 is necessary. In contrast, Jones and Pearson acidified the liquors in the presence of an SO_2 radical to a neutral pH, to precipitate the sulphide. Pepper (90) cautioned the use of acidification for sulphide removal, and claimed that liberated hydrogen sulphide was undesirable.

In addition to their usefulness as coagulants, ferrous sulphate and ferric chloride have been extensively utilised in sulphide removal from tannery and fellmongery effluents (42, 51, 64, 77, 80, 87, 90, 92, 131).

Pepper (90), Rawns (92), Wolfe (131), Munteanu and Weiner (80), and Hal'perin (51) described the use of ferrous sulphate to remove sulphide as ferrous sulphide. In contrast to the other workers, Pepper (90) found that the precipitated ferrous sulphide was bulky and difficult to settle.

The use of ferric chloride has been proposed by Mehner (77) and Cooper (42) and also reported by Koziorowski and Kucharski (64). Mehner (77) found that a pH range 4.7-7.2 was necessary for satisfactory sulphide removal. Cooper (42) made no pH adjustment but used higher concentrations (900 mg/l compared with 500 mg/l quoted by Mehner) to achieve comparable removals.

Bianucci and de Stefani (19) and Koziorowski and Kucharski (64) described the use of ferric hydroxide as a sulphide-removing agent. Initial acidification assisted the process.

Biannui and de Stefani (18) described a tannery waste

treatment process which consisted of a flue gas treatment stage, the effluent pH was decreased to 7.5 and all the sulphides removed as hydrogen sulphide.

1.3 BIOLOGICAL FILTRATION

1.3.1 Introduction

Biological filters are one of the most widely used devices for industrial waste treatment. The bed provides support for the biological film that develops on application of the waste. Purification of the waste is accomplished by the biochemical activity of the film.

1.3.2 Definitions

The classification of biofiltration processes is based on three parameters:-

(i) organic loading
(ii) hydraulic loading
(iii) recirculation ratio

Eckenfelder and O'Connor (31) classified trickling filters into two broad categories:- high-rate and low-rate systems. The distinction is based on hydraulic and organic loading to the filter. Low-rate filters operated at hydraulic loadings of 1.2 - 3.3 m^3/m^3.day, with organic loadings of 0.55 - 2.77 kg/m^3.day. Hydraulic loadings for high-rate units were claimed to vary from 6.1 - 18.4 m^3/m^3.day. No range for organic loading was provided. They reported that high-rate filters may employ recirculation in single or two-stage units.

McKinney (75) classified biofiltration processes in a similar manner to the previous scheme, using recirculation ratio to assist classification. Low-rate organic loadings ranged from 0.16 - 0.41 kg/m^3.day, whereas high-rate loadings ranged from 0.60 - 1.19 kg/m^3.day. Organic loadings in excess of this were classified into a super-rate category. A low-rate filter was claimed to have no recirculation; high-rate

filters a recirculation ratio range 0.5 - 10:1; super-rate filters a range of 10 - 50:1.

Bruce and Merkins (23) stated that high-rate filtration is encountered when the hydraulic loading is in excess of 3 m^3/m^3.day, discounting recirculated flow, or when the organic load is greater than 0.6 kg BOD/m^3.day.

The efficiency of a trickling filter is computed from the BOD removed by the filter, expressed usually as a percentage of feed BOD. Efficiency is influenced by both waste characteristics and filter geometry.

Excellent reviews of the mathematical modelling of trickling filter operations are given by Behn (11), Behn and Monadjemi (12) and the National Research Council report (82).

1.3.3 Application of Biofiltration to Fellmongery and Tannery Wastes

Gurham (49) has reported that tannery wastes can be treated on trickling filters provided the wastes are adequately pretreated by sedimentation and possibly chemical coagulation. Coarse rock was recommended for the media, to minimise clogging from grease and fragments of flesh, hide and hair. He stated that the high alkalinity of tannery wastes requires a period of acclimation for the film microorganisms. Recirculation is needed to reduce the effect of excessive changes in alkalinity. Thafaraj et al (119) confirmed the report of Gurham, on the biological filtration of tannery wastes.

97% BOD removals were obtained by Akriska et al (3), when tannery effluent was applied to a stone packed filter at a hydraulic rate of 2 MGAD (6.2 m^3/m^3.day; calculated on a 1.83 m filter depth). The pH was adjusted to between 7 and 8 prior to treatment. They did not specify recirculation ratios or organic loadings. Sarber (96) reported 80 - 90% BOD removals with biological filtration of effluent from a sole leather tannery. Additional information was not provided.

Poszto (91) found that for satisfactory BOD removal, tannery wastes had to be diluted 90% with domestic sewage prior to biological filtration.

The packing used by Bailey et al.(7) in their studies of the biofiltration of fellmongery waste, was a plastic medium. It was housed in a 0.36 m^3 tower, 3.65 m tall. The tower was charged with 5000 l/day of effluent, with a BOD range 600 - 1000 mg/l. The method of feeding was not specified. They reported a 50% BOD removal with organic loadings of 2.95 kg/m^3.day, but made no mention of any changes in pH or sulphide concentration.

In a review of tannery waste treatment, Bianucci and de Stefani (18) regarded biological filtration as a secondary treatment, subsequent to all methods they cited. In particular, they described a filter column which was flushed prior to operation with a suspension of river mud, which was aerated in the presence of sulphide in order to provide an inoculum of sulphur-oxidising bacteria. Effluent was recirculated at a rate which was sufficient to ensure that not only was the medium in the filter adequately wetted, but also that the pH was reduced to the optimum required for the acid-tolerant sulphur-oxidising bacteria.

Biological filtration forms one part of an aerobic-anaerobic biological treatment plant for fellmongery effluent described by McDougall et al.(42). Effluent was pumped to the anaerobic unit, then subsequently recirculated through the filter. Typical daily readings showed 100% sulphide removals, 90% COD reductions and a fall in pH from 10.95 to 9.05.

1.3.4 Effect of Sulphides on Biofiltration

Green (46) has reported the effects of sulphide on biological filtration. Results indicated that his filter tolerated sulphide concentrations of up to 400 mg/l H_2S (corresponding to 0.1% Na_2S). A combined chemical-biological sulphide oxidation process was proposed. He postulated an atmospheric oxidation of sulphide to thiosulphate and a

biological oxidation of thiosulphate to sulphate. This mechanism does not conform to the postulate of Vishniac and Santer (126), that during biological thiosulphate oxidation by autotrophic sulphur-oxidising bacteria, the thiosulphate enters the cell as sulphide. According to the proposed mechanism of Green, sulphide would be chemically oxidised to thiosulphate, then biologically transformed back to sulphide, prior to oxidation to sulphate.

Hill (54) investigated relative sulphide removal rates from solution by biological and chemical mechanisms. He found that biomass obtained from a biological filter treating fellmongery effluent accelerated sulphide removals. Manganese additions at a 25 mg/l $MnCl_2$ concentration stimulated sulphide removals in uninoculated and inoculated solutions, greater rates being achieved in the inoculated system.

Results presented by Heukelekian and Lassen (53) confirm those of Hill (54). Inoculation of sulphide solutions with filter slime accelerated sulphide removals. Sulphate was found to be the terminal oxidation product.

Bailey (5) demonstrated that percolating filters can tolerate sulphide concentrations of up to 250 mg/l without apparent effect on BOD removal efficiency. This confirms the earlier work of Green (46).

Complete sulphide removal from tannery wastes was reported by Rosenthal (94). A 40% domestic sewage and 60% tannery waste mixture was treated by biological filtration. The influent sulphide concentration exhibited a mean value of 82 mg/l.

1.3.5 Effect of pH on Biofiltration

pH influence on biological filtration has received little consideration by workers. Walter (128), however, has examined the effect of a high pH waste on trickling filter efficiency. Although the described waste is textile effluent, its pH was

similar to that of fellmongery wastes. His study indicated that influent pH significantly influenced BOD removal and effluent pH. An optimum BOD reduction, 60%, was achieved over an influent pH range of 8.0 - 9.0. A 45% removal was obtained in the pH range 11.0 - 12.0. Walter claimed that carbon dioxide production by the filter microorganisms exerted a buffering action within the waste, inducing lower pH values.

1.4 CHEMICAL AND MICROBIOLOGICAL SYSTEMS PRESENT IN BIOLOGICAL FELLMONGERY WASTE TREATMENT

1.4.1 Introduction

The chemical composition of tannery and fellmongery wastes is complex. It has been established (Section 1.2.2) that lime and sulphide exercise a considerable influence on the biological treatment of fellmongery waste. The effects of the two components on the system chemistry and microbiology are examined more closely in this section.

1.4.2 Physio-Chemical Aspects

Alkalinity aspects of waters and industrial wastes have been considered theoretically and quantitatively by Sawyer and McCarty (98). They commented that the major contribution to the alkalinity of a solution was caused by three major classes of materials. These were ranked in order of their association with high pH values as follows:-

(1) Hydroxides
(2) Carbonates
(3) Bicarbonates

The following equations express the equilibrium between carbon dioxide, alkalinity and pH in water:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

$$M(HCO_3)_2 \rightleftharpoons M^{2+} + 2HCO_3^-$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

Lijklema (70) stated that in effluent, the main factors governing pH will be the equilibria of carbonic acid. Up to pH 8.3 the ionisation step is dominant; at 20°C

$$[H^+][HCO_3^-] = 4.17 \times 10^{-7} [CO_2]$$

In the pH region 8.3 - 10.5 the equilibrium

$$[H^+][CO_3^{2-}] = 4.20 \times 10^{-11} [HCO_3^-]$$

dominates, and above pH 10.5 the concentration of free OH^- ions determines the pH. Since industrial wastes are essentially non-ideal solutions, corrections for electrolytes and non-electrolytes would have to be made, e.g. the depression of the solubility of CO_2 by NaCl.

Waste water pH change is controlled by two factors:-

(1) The production of acid or alkaline substances during biological purification.
(2) The buffer capacity of the influent.

Lijklema (70) presented various chemical and biochemical reactions, characteristic of biological waste treatment systems, that cause changes in alkalinity values. The significance of nitrification and the production, absorption and desorption of CO_2 were closely examined.

Fellmongery and tannery wastes are highly alkaline because of the large quantities of lime used in processing. Also, the presence of Na_2S, a strong basic salt, contributes to the effluent alkalinity. A typical fellmongery waste pH range, 9.5 - 12.3 (89), indicated that carbonate and hydroxide components will largely determine the alkalinity, according to the scheme presented by Lijklema (70).

The other inorganic component demanding consideration is sulphide. The form of sulphide in solution has been found to be pH dependent (18, 98). The relationship between H_2S, HS^- and $S^=$ with changing pH is shown in Figure 1.1. Sulphides in tannery and fellmongery wastes will be present as SH^-

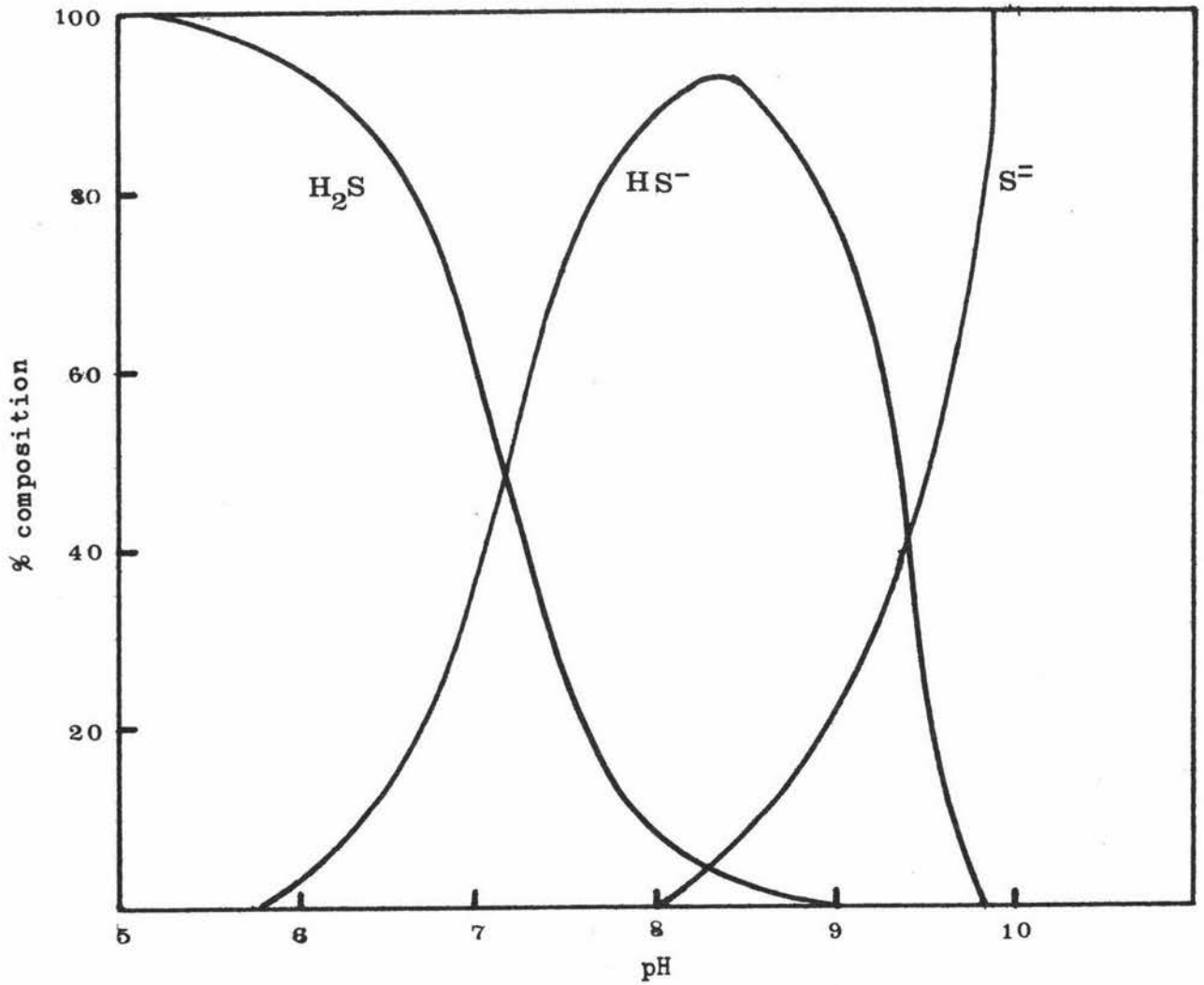

Figure 1.1 Effect of pH on Hydrogen Sulphide-Sulphide equilibrium (10^{-3} M Solution, 32 mg/l H_2S) (98).

and $S^{=}$ ions, by virtue of the pH range, 9.5 - 12.3, exhibited by the wastes.

The equilibrium-composition diagrams presented by Bianucci and de Stefani (18), and reproduced in Figure 1.2, assist in assessing the removal of sulphide from solution by oxidation. These S-H_2O system diagrams, which have pH and redox potential as coordinates, indicate that the type of system (either stable or metastable) and the form of sulphide in solution, will influence the reaction product formed on sulphide oxidation. The stable equilibrium diagram in Figure 1.2 (B), shows that if very strong oxidising agents such as chlorine in acid medium or hydrogen peroxide in alkaline medium are present, they overcome the considerable redox potential barrier involved, allowing sulphide to be oxidised directly to sulphate. The metastable diagram (A), however, shows that a weak oxidation, as that which can be obtained by aeration, gives a poor result, i.e. the conversion of sulphide into sulphur in acid medium and into thiosulphate in alkaline medium. The latter process characterises the aeration of fellmongery and tannery wastes. Several workers have confirmed that thiosulphate is produced on the aeration of tannery wastes containing sulphides (6, 18, 40).

1.4.3 Microbiological Sulphide Transformations

Jenkins (60) has reported that the nature of any effluent will profoundly affect the developing flora of a treatment process. He stated that inorganic compounds, toxic and non-toxic, in wastes entering a biological treatment system, will select groups of microorganisms that are capable of metabolising the compound. Products of metabolism will depend on substrate, type of microorganism, nature of waste and the operating characteristics of the system. The sulphide component of fellmongery waste exhibits the potential to select a group of microorganisms capable of sulphide metabolism, when the waste is biologically treated.

The transformations that sulphur undergoes in nature may

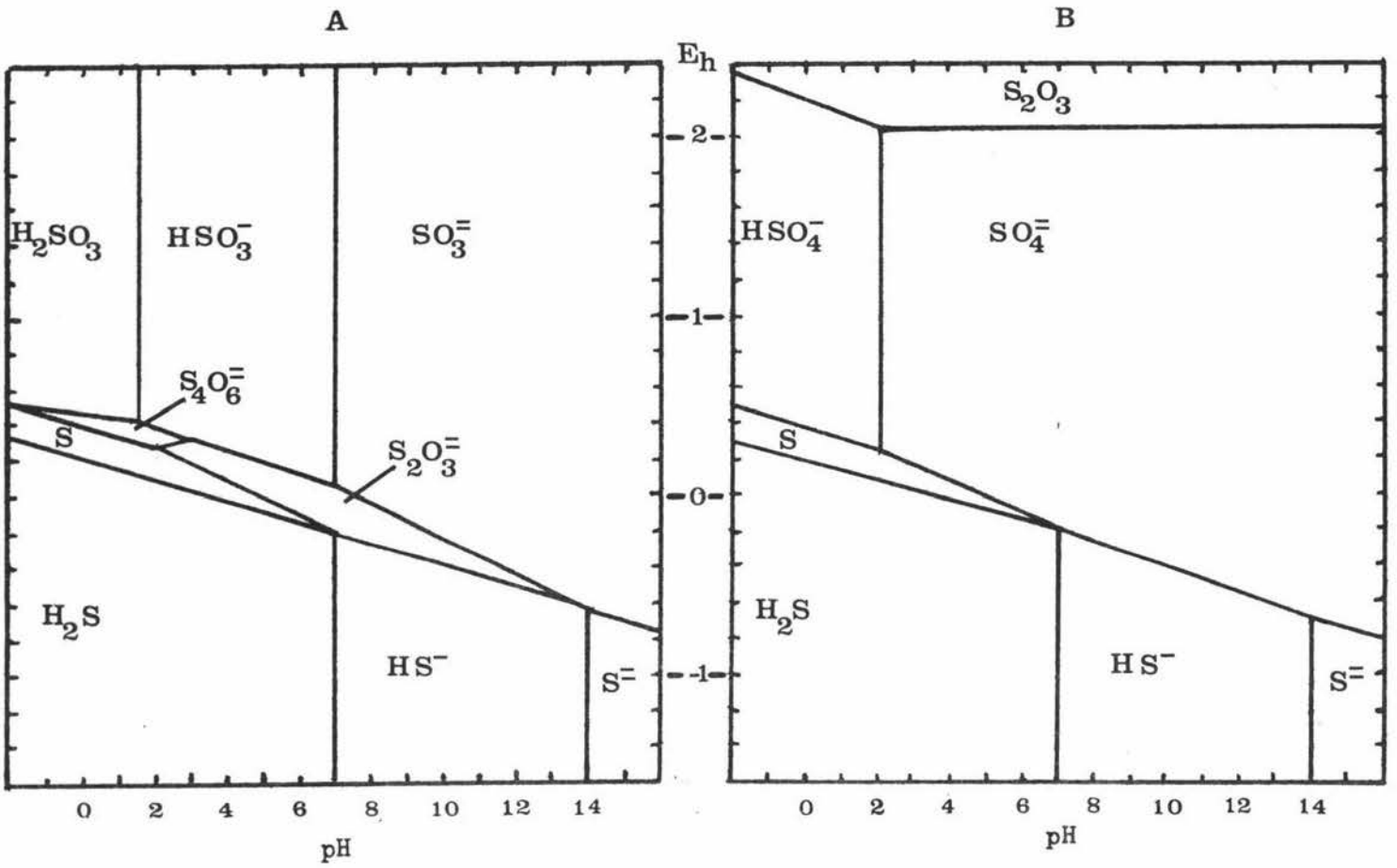

Figure 1.2 Equilibrium - Composition Diagrams for Metastable (A) and Stable (B) Equilibria (18)

be represented by a closed cycle, similar in concept to nitrogen and carbon cycles, which is shown in Figure 1.3 (36). Geochemical sources of sulphur are not included in this diagram; their contribution to biological waste treatment is minimal.

The microbial transformations of sulphur compounds have been described by several authors (36, 47, 98, 105). For these studies, it has been considered pertinent to examine all the microorganisms which may be implicated in the oxidation of sulphide from fellmongery wastes.

Thiobacillus thioparus is the most likely sulphur-oxidiser to develop in an aerobic biological system treating an alkaline waste (132). Starkey (111) and Sokolova and Karavaiko (105) confirmed this postulate. Data presented by Sokolova and Karavaiko (105) indicated that the optimum pH value for Th. thioparus growth fluctuated between 8.5 and 9.8. No bacterial growth was detected at pH 10.0. At pH values below 8, bacteria did grow but oxidised the substrate at a significantly lower rate.

According to Nathansohn (81), Beijerinck (13), Jacobsen (59) and Vishniac (125), Th. thioparus oxidises hydrogen sulphide and sulphides to sulphur and sulphate. Starkey (112) and Parker and Prisk (85) failed to confirm the oxidation of sulphides by growing cells of Th. thioparus.

Sokolova and Karavaiko (105) observed that the oxidation of sulphides by Th. thioparus is affected by the sulphide cation. Calcium sulphide was metabolised at greater rates than sodium sulphide. Sulphate was the metabolic product for both sulphides. A pH decrease accompanied the sulphate increase.

In contrast with the carbon assimilation of heterotrophs, where only 3% of the total carbon is gained from CO_2, the Thiobacilli utilise CO_2 as their sole carbon source (105). CO_2 fixation is linked to the energy-yielding oxidation of sulphur compounds. CO_2 produced by heterotrophic organisms

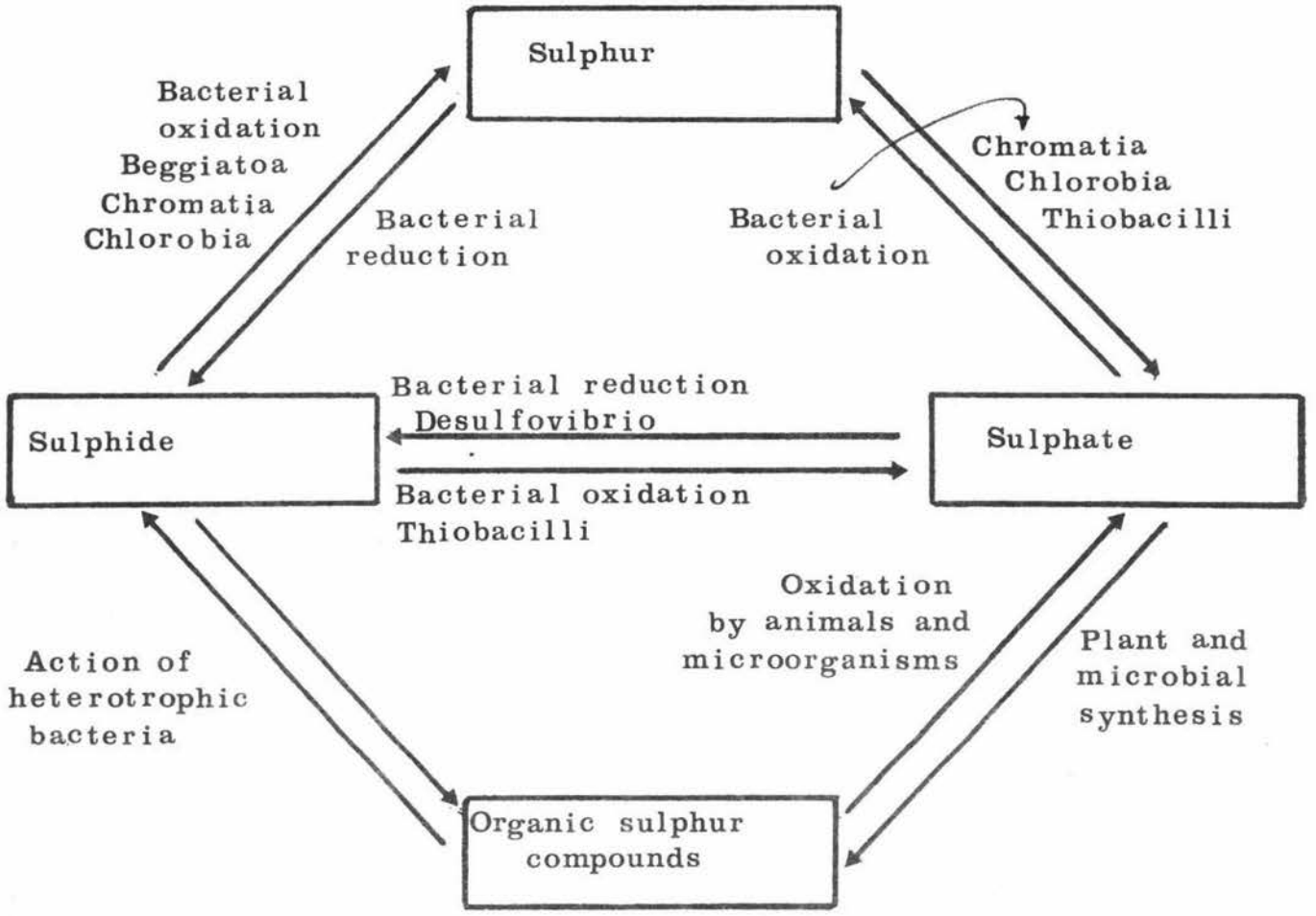

Figure 1.3 Microbiological Transformations of Sulphur (36)

could provide the Thiobacilli with a carbon source.

Th. thioparus is considered a strict aerobe. However, these bacteria have been isolated from environments where oxygen availability is restricted (105). Sulphide removal rates in such environments are relatively low.

The development of the purple sulphur bacteria, Thiorhodaceae, has been associated with anaerobic pond treatment of fellmongery effluents (21, 25). These bacteria are autotrophic anaerobes and require both light and sulphides. Zajic (132) listed the growth requirements as:-

(1) light
(2) minerals ($CO_3^{=}$, Fe, $S^{=}$, $PO_4^{=}$, Cl^{-})
(3) alkaline pH
(4) strict anaerobic conditions

The oxidation of hydrogen sulphide is carried out in two main steps (121):-

$$CO_2 + 2H_2S \xrightarrow{\text{light}} (CH_2O) + H_2O + 2S$$

$$2CO_2 + 2S + 5H_2O \xrightarrow{\text{light}} 3(CH_2O) + 2H_2SO_4$$

An important feature of this reaction is that no molecular oxygen is formed. Due to their photosynthetic activity, this group of bacteria does not help to reduce the BOD of the wastes treated, and may even tend to increase it (36). The sludge load imposed by these organisms on an effluent being treated in a system consisting solely of Thiorhodaceae, would cause an increase in waste BOD.

The development of Thiorhodaceae is favoured in the pH range 7 - 8.5, this range being slightly lower than the 8.5 - 9.8 range necessary for optimum Th. thioparus growth.

CHAPTER TWO

PRELIMINARY CONSIDERATIONS

2. PRELIMINARY CONSIDERATIONS

This chapter introduces the concepts behind the development of the experimental work described in the subsequent three chapters. Justifications for the process selection, and explanations of experimental development are presented.

The majority of New Zealand fellmongeries are associated with meat processing works where pelts are readily obtained. Effluent from fellmongery departments may enter the main works effluent stream or be treated separately. Separate treatment has many advantages. In a concentrated form the waste will require a smaller treatment unit. A plant designed for the treatment of sulphide wastes can be operated at conditions which produce optimum growth and activity of the sulphur-oxidising organisms. The discharge of sulphide waters into the meat processing effluent stream, which usually possesses a neutral or slightly acidic pH, may precipitate the liberation of hydrogen sulphide with the resulting corrosion and environmental problems.

A treatment system for fellmongery effluent must be selected on the basis of operating, environmental and cost considerations. An efficient and stable operation is necessary with minimal maintenance requirements. Health hazards, malodours and hydrogen sulphide evolution should not be prevalent. Finally a low capital and operating cost is desirable.

The methods most readily lending themselves to fellmongery waste treatment are activated sludge, anaerobic and aerobic lagoons and biological filters. Anaerobic digesters and oxidation ditches are not considered due to the lack of data regarding the operation of these systems with fellmongery or tannery wastes. Recent work, however, indicated that oxidation ditches may prove very satisfactory for tannery waste treatment. The presence of high lime concentrations in fellmongery and tannery effluents provide operational problems during anaerobic digestion. The sensitivity exhibited by activated sludge to shock loads and high sulphide concentrations precludes the use of the system.

Foaming associated with the aeration of alkaline liquors containing saponified grease and fat may similarly pose problems (30). Odour problems, large land requirements and sludge removal limit the use of oxidation ponds and lagoons (45). Health hazards may arise if the lagoons are adjacent to water supplies or ground wells.

Biological filtration is claimed to satisfactorily manage shock loads if subjected to them (2). Such loading is characteristic of fellmongery waste discharge (54). The selection of this system to treat fellmongery liquors was influenced mostly by the ability of biological filters to treat effluents with high sulphide concentrations, without adverse affect on their performance. Although the capital cost of biological filtration is large, running costs are minimal in comparison with activated sludge (2). Maintenance requirements are small but periodic checking of process efficiency, filter conditions, pumps and pipes are necessary.

This study is an extension of preliminary work on biological sulphide removal from fellmongery waste by Hill (54). The pilot plant used for the biological filtration studies was based upon the system described by McDougall et al.(42).

The objectives of this study were:-

(1) to investigate the mechanism and efficiency of sulphide removal in the pilot plant.
(2) to evaluate the COD removal efficiency of the pilot plant, and the influence of pH and sulphide on this efficiency.
(3) to study pH and alkalinity changes.
(4) to investigate the implications of the sulphur-oxidising bacteria in the system.

The operating procedure of the filter was selected from a consideration of the discharge characteristics of a typical New Zealand fellmongery. An 8 hour, 5-day week cycle is typical. Investigations with this cyclic loading were made

for a range of recirculation ratios, 5:1 - 35:1. In a second series of experiments, a continuous loading was imposed on the filter for each of three temperatures, 21, 31 and 34°C, with the aim of supplementing data collected for the sulphide oxidative studies. A constant recirculation ratio was maintained, the value of which was based on data obtained from the first series of experiments.

Initially the mechanism of sulphide oxidation in the system was not clear; doubt existed as to whether a chemical or biological mechanism, or both, was responsible for sulphide removal. Green (46) expressed similar doubts pertaining to sulphide removal in biological filters. Two experiments were designed to assist elucidation of this mechanism.

The first involved a sudden change in the temperature of the filter system, with subsequent monitoring of the effluent sulphide and sulphate concentrations. It was postulated that if a chemical oxidation mechanism existed, the sulphide and sulphate concentrations of the effluent would change quickly with temperature, since the rate and equilibrium of a chemical reaction is temperature dependent. If a biological oxidative mechanism was present, the temperature change would upset autotrophic metabolism with subsequent fluctuations in effluent sulphide and sulphate concentrations. Originally the filter was to be subjected to several sharp temperature increases, but heat losses set an upper temperature of 34°C and limited the number of changes.

The second series of experiments involved the aeration of pure sulphide, lime-sulphide and waste solutions, with and without filter biomass inocula. These investigations provided further data on the mechanism of sulphide removal from the waste, as well as information pertaining to the effect of waste components on the rate of chemical sulphide oxidation. As oxygen transfer to solution is required for both biological and chemical sulphide oxidation, these aeration studies were carried out in a laboratory-scale fermenter. Chemical and biological

oxidative mechanisms were compared by relative sulphide removal rates and subsequent sulphate increases. The increase in sulphate concentration served as an indicator of the degree of autotrophic metabolism.

The fermenter studies were completed prior to the experiments involving the temperature change to the filter system. Results obtained from the fermenter studies showed that filter biomass accelerated sulphide removals from fellmongery waste. Microbiological isolations of the organism, Thiobacillus thioparus, postulated to be primarily responsible in sulphide oxidation from the waste, were made from the biological filter. Isolations of this organism accompanied each temperature change. The metabolic rates of these organisms in the isolation medium were correlated with the sulphide and sulphate fluctuations of the pilot plant effluent following the temperature changes. The results obtained supplemented data previously compiled on biological sulphide oxidation from fellmongery waste.

CHAPTER THREE

BIOLOGICAL FILTRATION OF FELLMONGERY EFFLUENT

3. BIOLOGICAL FILTRATION OF FELLMONGERY EFFLUENT

3.1 Introduction

In this investigation a stone-packed biological filter and an equalisation/sludge concentration tank were used to treat fellmongery waste. The system was subjected to batch and continuous loadings. Batch investigations were conducted over a range of recirculation ratios at a constant feed input. Organic loadings varied over the experimental period, by virtue of the manner by which the waste was synthesized. A constant recirculation ratio characterised the continuous operation, during which the effect of three temperature changes were observed.

The batch process was evaluated on the basis of the change in COD, sulphide and nitrogen. In addition, data regarding sulphate production, and pH and alkalinity changes, were also collected, so that the influence of pH and sulphide on COD removal could be evaluated.

In contrast to the batch operation, the continuous loading investigations were of prime importance in elucidating the mechanism of sulphide oxidation in the system. COD removals and pH were also measured to supplement the data collected in the batch experiments.

Additional studies included chemical analysis of the sludge, sludge settling tests and evaluation of oxygen transfer within the filter.

3.2 Materials and Methods

3.2.1 Waste Source and Make Up

A source of fellmongery waste with reproducible characteristics was required. The large volumetric demand of the system, 66 litres per day, ruled out any collection and storage of actual fellmongery effluent, since such a procedure would have involved large transport costs and considerable storage facilities. Instead a synthetic effluent

was used.

Earlier work at the New Zealand Refrigerating Company (89) had yielded an approximate average composition for fellmongery waste (Table 1.1). The synthetic waste characteristics were based upon these results. Effluent characteristics will depend on the method of liming practised within a fellmongery. The traditional practice of lime liquor retention, in contrast to periodic discharge, determined the effluent composition in this investigation.

The waste used in these trials was prepared from a dilute solution of lime liquor. To this were added measured quantities of salts to give the desired composition.

A dilution of 3.5 litres of lime liquor in 66 litres of water produced a satisfactory waste feed for the filter. Wool fibres and skin material were screened out prior to use of the lime liquor. 25 mg/l Na_2S and 150 mg/l each of NH_4Cl and NaCl were added to the mixture.

Lime liquors were collected from three sources:-

(1) The Taikorea Fellmongery, Taikorea.
(2) The Longburn Freezing Works Fellmongery Department, Palmerston North.
(3) The New Zealand Leather and Shoe Research Association, Palmerston North.

Liquors were collected fortnightly in 45-litre quantities and stored in polythene containers at 8°C. Large variations in strength and composition of the liquors were recorded. These were attributed to the liquor age prior to collection and to the mode of operation of the dollies within the respective fellmongery sheds. The COD of the liquors lay in the range 30,000 - 66,000; nitrogen concentration varied in the range 1120 - 9650 mg/l, and sulphide concentrations within a range 1000 - 5000 mg/l. Further strength variation arose from lime precipitat-

ion, and the associated removal of suspended and colloidal solids, during storage. The precipitate formed a compact cake on the container bottom, which would not redissolve on agitation.

3.2.2 Pilot Plant Equipment and Operation

3.2.2.1 Equipment

The biological filtration system is shown in Figure 3.1. The filter and sump arrangement is indicated in Plate 3.1. Plate 3.2 shows the assembly of pumps, feed lines and temperature control equipment. Details of the individual components are described below.

(1) Feed Tank

A 0.61 m x 0.61 m x 0.61 m fibre-glass lined tank was used as the feed tank. Waste was pumped from the bottom of the tank to the sump through a muslin screen located over the outlet. This minimised the risk of wool fibres and precipitated lime entering the system.

(2) Sump

The sump was placed directly under the filter. It was constructed from a 44-gallon (200 l) oil drum. A plastic casing lined the drum to minimise corrosion.

Feed entered the sump directly above the recirculation take-off, 0.20 m from the sump base. Liquid then passed to the filter from this take-off.

Effluent discharge facilities were provided by a downcomer pipe attached to the side of the sump. Effluent was effectively removed from the centre of the sump, 0.32 m from the surface. Discharged wastes passed directly to a drain.

A baffle system was constructed to minimise the turbulence induced by the by-passed recirculation liquors. A bypass system was required to control the flow to the filter, since

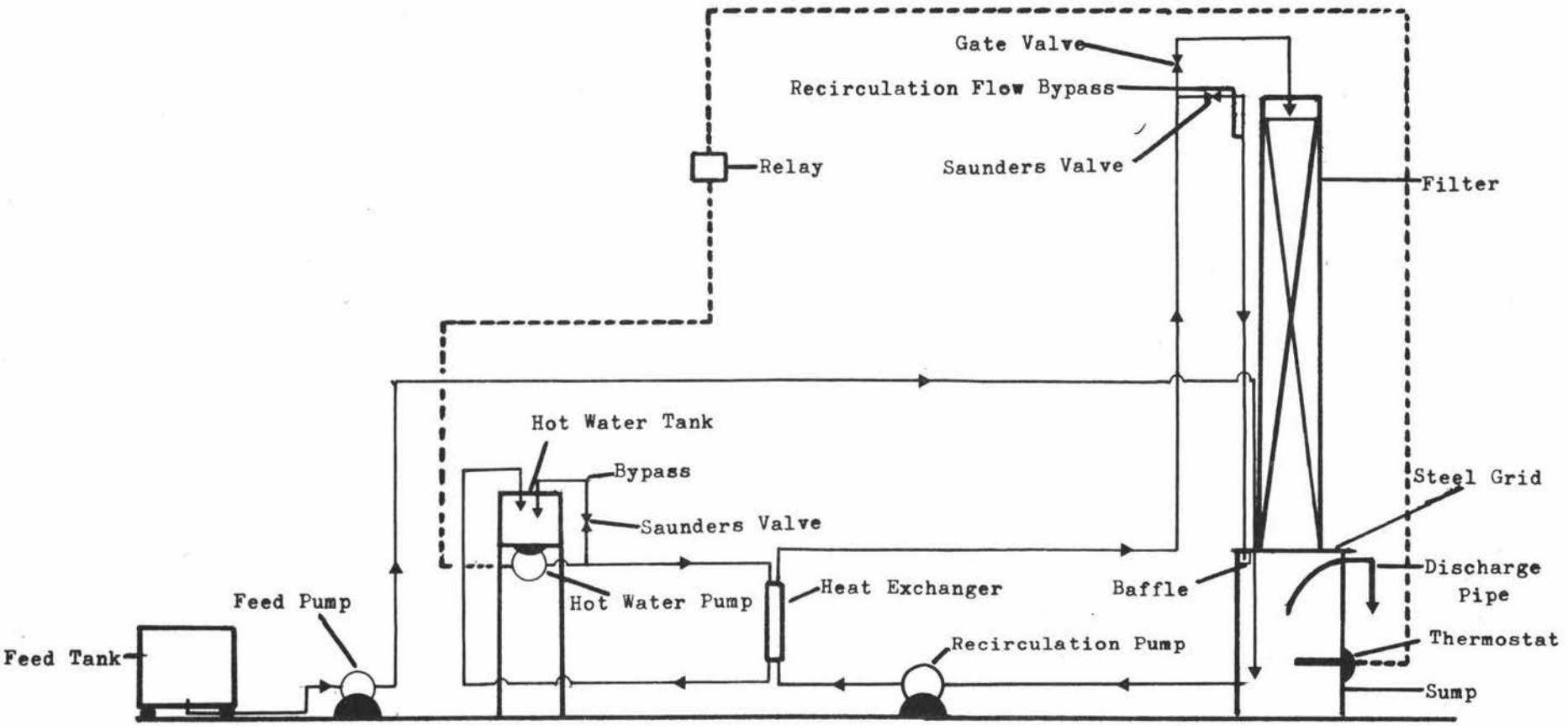

Figure 3.1 Line Diagram of the Biological Filtration System

Plate 3.1 Filter and Pump Arrangement

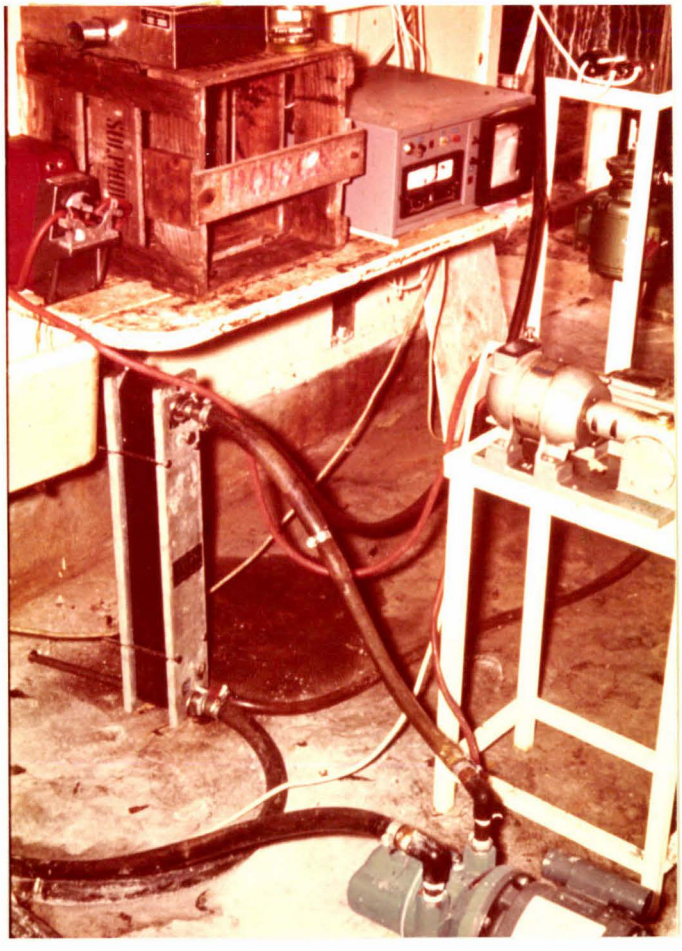

Plate 3.2 Pump and Feed Line Arrangement

the recirculation pump could not be sufficiently throttled down to give the required flow. The baffle consisted of a small stainless steel cubical container with perforated sides set in the sump as indicated in Figure 3.1.

(3) Filter Column

A 2.45 m high, 0.305 m I.D. concrete pipe packed with river bed stones, 0.051 - 0.064 m in diameter, was used as a biological filter. Sampling points, located 0.76 m and 1.52 m from the filter top, permitted biomass collection from different filter depths.

The stones were packed to a height of 2.25 m in the filter. Liquid was distributed over the packing by directing the flow over a perforated piece of metal placed over the top of the packing.

A 0.66 m x 0.55 m reinforced steel grill supported the filter structure over the collecting sump.

(4) Recirculation Pump and Lines

Recirculation of the waste was provided by a Dalhoff and King, 0.25 HP Mono pump, model DK/FA/3826.

The recirculation lines were constructed from 0.012 m I.D. transparent P.V.C. hosing. This pliable hosing permitted the removal of excess growth on the wall interiors. Simple squeezing or tapping of the lines released the adhered biomass.

Recirculated flows were controlled by a gate valve and a Saunders valve located on a bypass line on the pump delivery side. The bypass and valve arrangements are indicated in Figure 3.1.

(5) Feed Supply System

The freshly-made effluent was conducted to the system by one of two pumps. Initially, a Hughes DCL metering pump

No. 6-6305, was operated, but towards the end of the experimental period it developed mechanical problems (leaking sealing glands), and had to be replaced by a Sigma pump, Model T68H. Silicon reinforced rubber hosing was required for the latter. Normal rubber tubing was found to abrade rapidly and needed frequent adjustments.

(6) Temperature Control Unit

The sump liquors were maintained at a constant temperature with an Alfa-Laval countercurrent plate heat exchanger, Type P.20. The liquors were pumped countercurrent to a stream of hot water from a constant temperature bath. Sump temperatures were controlled with a thermostat located in the sump centre. A relay served to cut out the hot water pump when the preset sump temperature was attained.

The determination of oxygen transfer coefficients at different flow rates through the filter required alterations to the equipment. These are shown in Figure 3.2. The column had to be isolated from the sump prior to experiments. Liquid passing through the filter was collected in a funnel arrangement set in the sump and piped to an outlet set in the sump wall.

Sulphite solutions were pumped from a holding tank by a 0.25 HP Gryphon centrifugal pump (serial no. BS 2048) operating under a flooded suction head. Flows were controlled by the bypass arrangement shown in Figure 3.2

3.2.2.2 Operation

3.2.2.2.1 Batch Operation

The pilot plant was commissioned seven months prior to commencement of the experiments. An 8-hour, 5-day per week loading cycle was selected for reasons previously stated. Recirculation ratios of 5:1, 9.3:1, 14.5:1, 25.7:1 and 34.5:1 were used for the evaluation of filter performance. Recirculation ratio, C, is defined as:-

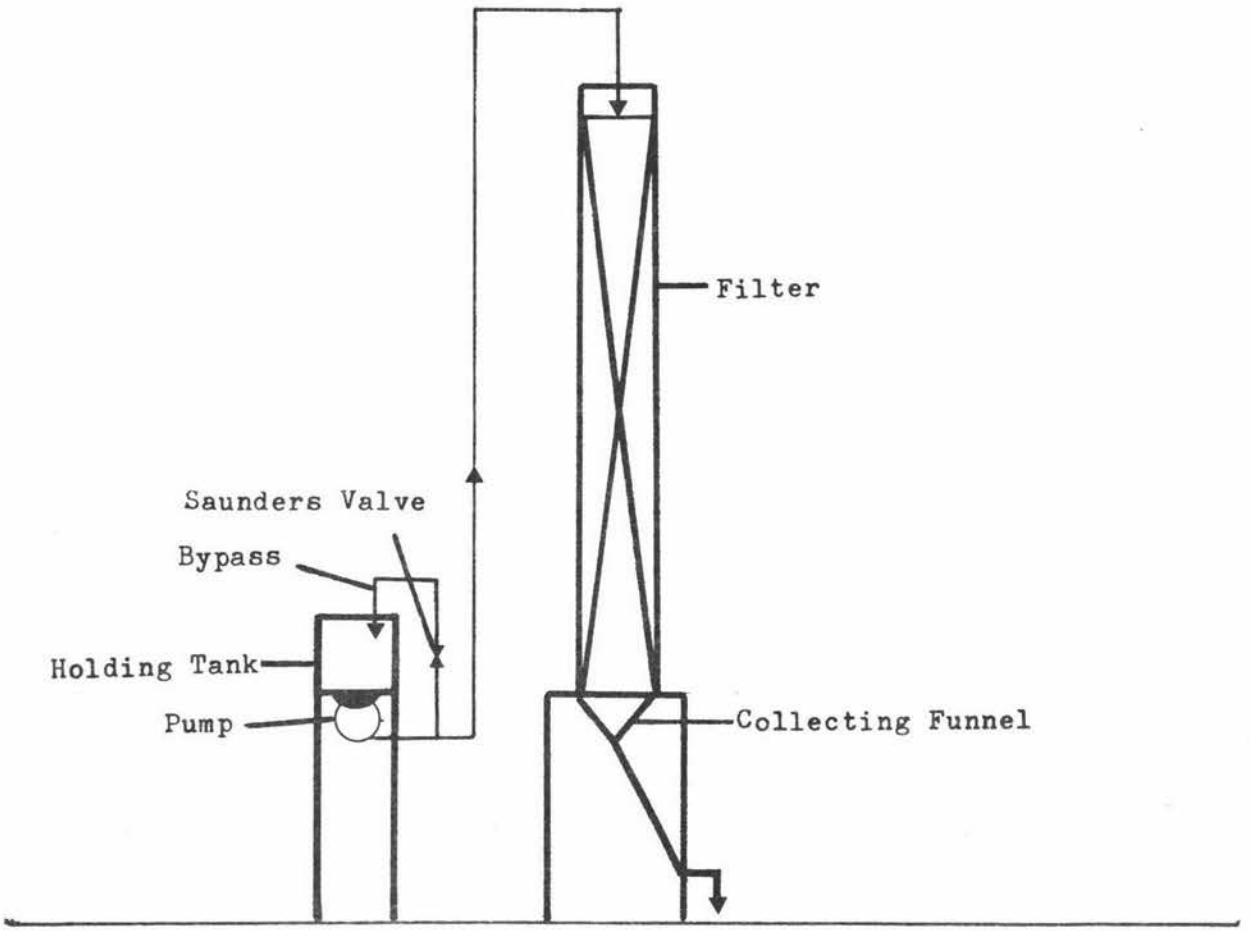

Figure 3.2 Equipment Arrangement for Oxygen Transfer Determinations

$$C = \frac{R - I}{I}$$

where:

R = flow to the top of the filter

I = flow to the system

(see Figure 3.3)

Originally ratios of 5:1, 10:1, 15:1, 25:1 and 35:1 were planned, however small flow variations produced slight deviations from these planned ratios. For convenience, the experimental recycle ratios are rounded off to the originally planned values. Excessive foaming at high flow rates prevented investigations of the higher recirculation ratios (40:1 and greater).

Each experiment consisted of maintaining the same recirculation ratio for 3 weeks. A week was allowed for the filter to attain equilibrium, data being collected during the remaining 2 weeks.

The waste feed and column flows were checked twice daily with a stop clock and measuring cylinder. Difficulty was experienced with column flow control particularly at recirculation ratios of 15:1, 25:1 and 35:1. Sludge particles lodged in the gate valve as well as the Saunders valve on the delivery side of the recycle pump, resulting in decreased flow rates. This decrease amounted to 40% of the set flow in two cases; 31.2 and 34% COD removals were recorded at these flows. This occurrence was attributed to the excessive turbulence, induced at higher recirculation flows, disturbing the sludge at the bottom of the tank and causing it to enter the recirculation line.

400 ml samples of influent and effluent were taken throughout the day and analysed separately after 30 min settling. Random sampling was not used since the number of, and time required to perform the analytical procedures, limited sampling to certain times of the day. For the same reasons sampling was

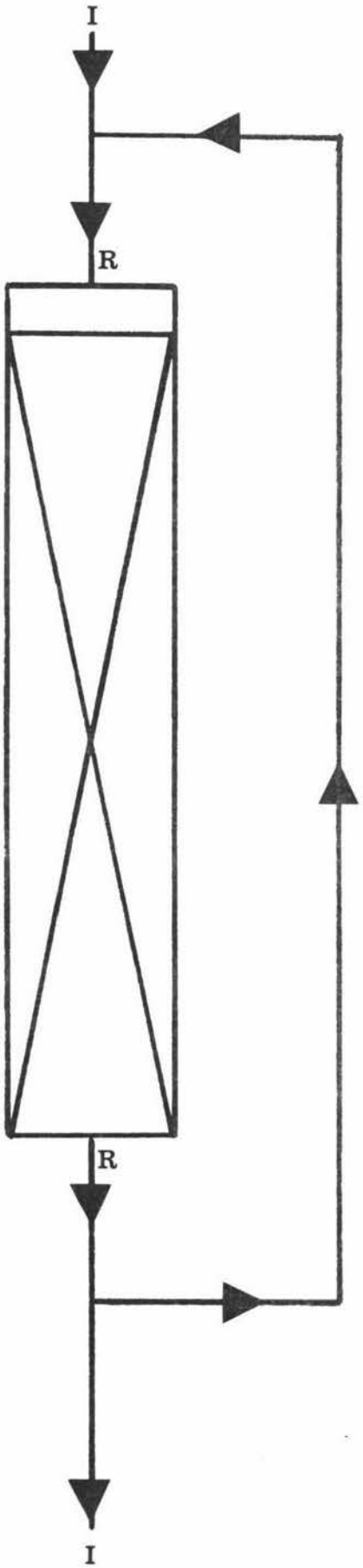

Figure 3.3 Filter Flows

not carried out on a daily basis.

The samples were analysed for:-

(i) COD
(ii) sulphide concentration
(iii) sulphate concentration
(iv) pH and alkalinity
(v) nitrogen concentration

The associated analytical procedures are described in Section 3.2.2.

3.2.2.2.2 Continuous Operation

In contrast to the batch operation, the filter was allowed to perform continuously at a lower hydraulic loading, but at a similar COD loading. This facilitated COD removal comparisons to be made between the two modes of operation for similar COD loadings.

However, the main objective of the continuous run was to study sulphide removals and sulphate increases at a range of system temperatures. Experiments were carried out at temperatures of 21°C, 31°C and 34°C. The unit operated for three weeks at each temperature. The recirculation ratio was constantly maintained at approximately 12:1. This particular ratio was selected since it gave a rate of flow through the filter, which at 21°C, provided a measurable sulphide concentration in the effluent.

Analysis was commenced immediately following the temperature changes with the result that the data are of a transient nature. Settled 400 ml samples of influent and effluent were analysed for the parameters, with the exception of nitrogen concentration, outlined in Section 3.2.2.2.1.

3.2.2.2.3 Oxygen Transfer Studies

Oxygen transfer coefficients were determined at the filter

flows used for the batch loading experiments. 22 l of sodium sulphite solution contained in a holding tank were pumped through the filter and collected at the sump base (Figure 3.2). The latter operation was accomplished with minimum agitation to prevent any undesired oxidation of the sulphite. Flow rates were checked before and after each experiment which were carried out in duplicate. 50 ml samples were also collected at the beginning and end of each run and were analysed for sulphite. The analytical procedure for sulphite determination is described in Section 3.2.3.

3.2.2.3 Sludge Removal

Settled sludge was removed from the sump base at the end of each batch experiment and at the conclusion of the continuous run. A Sigma pump, model T68H, was used to remove the sludge. Sludge samples were analysed for total solids concentration on collection, and then frozen before the subsequent analysis for ash and nitrogen. Unfortunately, samples collected at recirculation ratios of 5:1, 10:1 and 25:1 were lost during freezing, providing an incomplete sequence of results.

3.2.3 Analytical Techniques

3.2.3.1 Chemical Oxygen Demand

Chemical oxygen demand (COD) is defined as the amount of oxygen, expressed as mg/l, consumed under specific conditions in the oxidation of organic and oxidisable inorganic matter in waste water. Correction is made for the influence of chlorides. Samples are refluxed with known quantities of potassium dichromate and sulphuric acid, and the excess dichromate is titrated with ferrous ammonium sulphate. The amount of oxidisable organic matter is proportional to the dichromate consumed.

The method is described in full detail in Standard Methods (109).

3.2.3.2 Biological Oxygen Demand

Biological oxygen demand (BOD) indicates the quantity of oxygen that will be utilised by natural agencies in stabilising organic matter.

Samples were diluted with air-saturated dilution water, and subsequently analysed for dissolved oxygen before and after 5 day, 20°C incubation periods. Sample seeding was not required. Dissolved oxygen determinations were made according to the Alsterburg modification of the Winkler method.

The procedures followed were those described in Standard Methods (109).

3.2.3.3 Total Kjeldahl Nitrogen

Total Kjeldahl nitrogen includes ammoniacal and organic nitrogen, but not nitrite or nitrate nitrogen.

Procedures paralleled those presented in Standard Methods (109).

3.2.3.4 Sulphide

Sulphide concentrations were colorimetrically determined by the method reported by McMillan *et al* (76). This method is based on the reaction which takes place, under suitable conditions, between para-aminodimethylaniline, ferric chloride and sulphide ion, resulting in the formation of methylene blue. Ammonium phosphate is added prior to transmittance measurement to remove the colour due to the presence of ferric ion. Transmittance values of the solutions were determined with a Hitachi - model 101 Spectrophotometer at 730 mμ. A distilled water blank was used as a comparison.

Standard curves were obtained with sulphide solutions previously standardised by the zinc acetate titration method (109). These are shown in Appendix 1.

3.2.3.5 Sulphate

Vogel (127) has presented a turbidometric method for sulphate determinations which may be applied to wastes and sewage (109). This method is based on the precipitation of sulphate in a hydrochloric acid medium with barium chloride. Barium sulphate crystals of uniform size are formed, and the resulting increase in turbidity is determined colorimetrically. The sulphate ion concentration is determined by comparison of the reading with a standard curve. Determinations were made with the previously described spectrophotmeter at 420 mu. The standard curve is presented in Appendix 2.

3.2.3.6 pH and Alkalinities

pH was measured with an E350B Metrohm Herisam pH meter.

Phenolpthalein and total alkalinities were determined as described in Standard Methods (109).

3.2.3.7 Sludge Settling Tests

The degree of settling is determined by noting the position of the falling interface at regular intervals. This is expressed as a decreasing volume of sludge and will yield data for plotting settling rate curves.

Sludge settling characteristics were studied in a 1-litre glass measuring cylinder.

3.2.3.8 Ash and Calcium Determinations

Sludge ash concentrations were determined at 800°C, as described by Vogel (127).

In order to assess the quantity of lime entering the sludge, samples of the sludge were analysed for calcium. Calcium was determined as calcium oxide, by the oxalate method presented by Vogel (127).

3.2.3.9 Total Solids

Total solids were obtained by the aluminum dish method described in Standard Methods (109).

3.2.3.10 Sulphite Determination

An iodometric titration was utilised to determine sulphite concentrations in the oxygen transfer studies.

A 10 ml sample is placed in a flask with excess 0.1N iodine solution (25 ml). Sulphite present in the sample reduces the iodine, and excess iodine is back-titrated with 0.1N sodium thiosulphate solution, using a starch indicator. The titre reveals the quantity of reduced iodine and is a measure of the concentration of sulphite in solution.

3.3 Results

3.3.1 Batch Feed

The complete experimental data obtained from the filter are tabulated in Appendix 3. All subsequent calculations are derived from this table.

3.3.1.1 COD Loading and Removal

Sample calculations for determining the values of applied COD and COD removed are presented in Appendix 4. Where several samples were taken over the course of one day, a mean value was used. These values are presented in Table 3.1, which include average values for each recycle ratio.

Applied COD is plotted against COD removed in Figure 3.4 for each recirculation ratio. A linear regression curve of the type:-

$$Y = 0.97X - 0.44$$

where:

Y = COD removed

X = COD applied

was fitted to the data in Figure 3.4.

TABLE 3.1

SUMMARY OF COD MEASUREMENTS FOR BATCH LOADING

Date	C	COD					
		Influent	Effluent	Reml Eff	A	D	R
		mg/l	mg/l	%	kg/m^3.day		
8.1.73+	13.5:1	3335	775	76.8	1.35	0.31	1.03
9.1.73+	15:1	3560	1205	66.2	1.42	0.48	0.94
10.1.73+	15:1	3400	1235	63.7	1.33	0.48	0.85
11.1.73+	15:1	3975	1420	64.3	1.60	0.57	0.98
12.1.73	15:1	3840	1660	56.8	1.55	0.67	0.88
15.1.73+	14.5:1	2910	1240	57.4	1.17	0.50	0.67
17.1.73+	14.5:1	4305	1820	57.7	1.72	0.73	1.00
19.1.73	14.5:1	3580	1420	60.3	1.43	0.57	0.87
23.1.73	14:1	2580	1500	41.8	1.03	0.60	0.43
24.1.73+	14.5:1	2210	1520	31.2	0.89	0.61	0.28
26.1.73+	14.5:1	2850	1317	53.8	1.11	0.53	0.59
Average	14.5:1	3322	1374	57.3	1.33	0.55	0.77
7.2.73+	25.7:1	1640	760	53.7	0.65	0.30	0.35
8.2.73	"	2040	735	64.0	0.81	0.29	0.52
9.2.73	"	4500	1000	77.8	1.79	0.40	1.39
13.2.73+	"	4800	1195	75.1	1.87	0.48	1.39
14.2.73	"	4400	1470	66.6	1.75	0.58	1.16
15.2.73+	"	4950	1550	68.7	1.97	0.62	1.35
Average	25.7:1	3722	1118	67.7	1.47	0.44	1.03
26.2.73	34.5:1	2400	900	62.5	0.95	0.36	0.60
27.2.73	"	4270	1310	69.3	1.71	0.52	1.19
28.2.73	"	4225	1485	64.9	1.69	0.59	1.10
1.3.73	"	3680	1490	59.5	1.47	0.60	0.88
2.3.73	"	3900	1500	61.5	1.56	0.60	0.96
5.3.73	"	4940	1470	70.2	1.98	0.59	1.39
6.3.73	"	3720	1540	58.6	1.49	0.62	0.87
7.3.73	"	3930	1680	58.5	1.57	0.67	0.90
8.3.73	"	4210	1700	59.6	1.69	0.68	1.01
Average	34.5:1	3919	1453	62.7	1.57	0.58	0.99
22.3.73+	4.9:1	1665	725	56.5	0.67	0.29	0.38
22.3.73	5:1	2500	970	61.2	1.00	0.39	0.61
26.3.73+	5:1	2430	988	59.3	0.97	0.39	0.57
27.3.73+	5:1	2530	1130	55.3	1.01	0.45	0.56
28.3.73	5:1	2620	1730	34.0	1.05	0.69	0.36
Average	5:1	2349	1109	53.3	0.94	0.44	0.50
11.4.73+	9.3:1	3045	523	82.8	1.22	0.21	1.01
18.4.73	"	2910	1050	63.9	1.12	0.42	0.70
19.4.73	"	2330	1170	49.8	0.93	0.47	0.46
20.4.73	"	2500	1000	60.0	1.00	0.40	0.60
21.4.73	"	2900	985	66.0	1.16	0.39	0.77
Average	9.3:1	2737	946	64.5	1.09	0.38	0.71

\+ Mean daily value

A = Applied R = Removed

D = Discharged C = Recycle Ratio

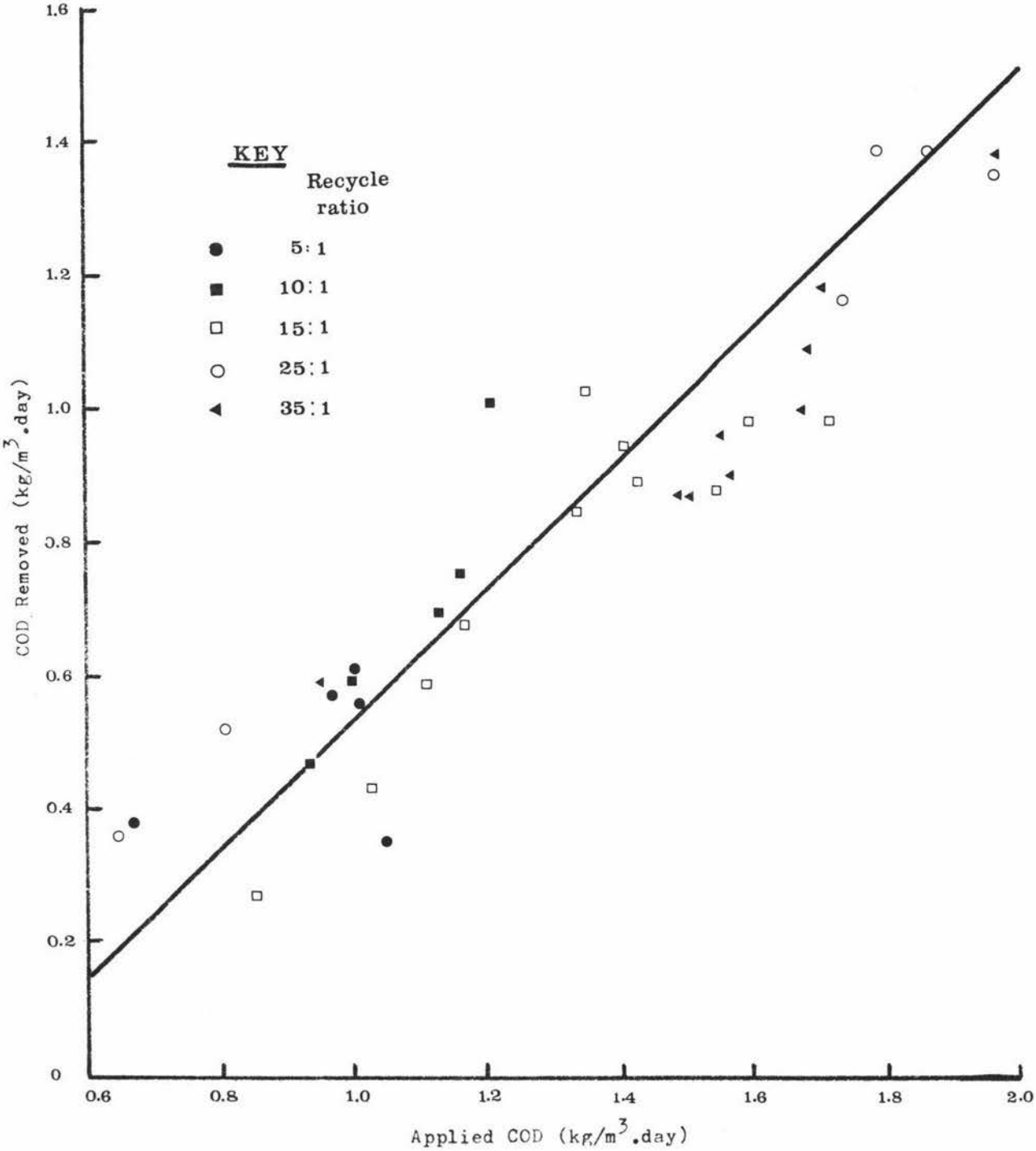

Figure 3.4 Applied COD versus COD Removed.
Filter; 8 hour feed

Figure 3.5 depicts the percentage COD reduction as a function of the COD applied. The curve suggests little major increase in COD reduction over the range of COD values investigated.

The effect of recycle ratio on percentage COD reduction is shown in Figure 3.6. COD removal appears to be independent of recirculation ratio over a range 5:1 - 35:1.

The effect of change in the pH and in the sulphide concentration of the influent on the percentage COD removal is shown in Figures 3.7 and 3.8 respectively. Data is taken from Appendix 3. Over the pH range investigated, 9.8 - 11.5, the influent pH appears to have little effect on the efficiency of removal. However, the influence of sulphide concentration in the range 60 - 120 mg/l is more pronounced. Maximum COD removal occurred in the range of sulphide concentrations 90 - 105 mg/l. Removal efficiency decreases slightly outside this range. The two points corresponding to 31.5 and 34% COD removal were obtained when blockages occurred in the recirculation line.

3.3.1.2 Sulphide Removal

Data for the parameters, sulphide removal and sulphate production are given in Table 3.2. The percentage sulphide removed for each recirculation ratio is presented as well as a ratio defined as:-

$$S = \frac{\text{decrease in sulphur concentration as loss in sulphide}}{\text{increase in sulphur concentration as gain in sulphate}}$$

A sample calculation of S is provided in Appendix 5.

Figure 3.9 shows a graph of percentage sulphide removal against recirculation ratio, data for which is taken from Table 3.2. Mean values of sulphide removal for each recirculation ratio are also plotted. Although a wide scatter of data was obtained in most instances, the average values show an exponential increase of sulphide removal with increase in recirculation ratio, maximum removal being obtained at a

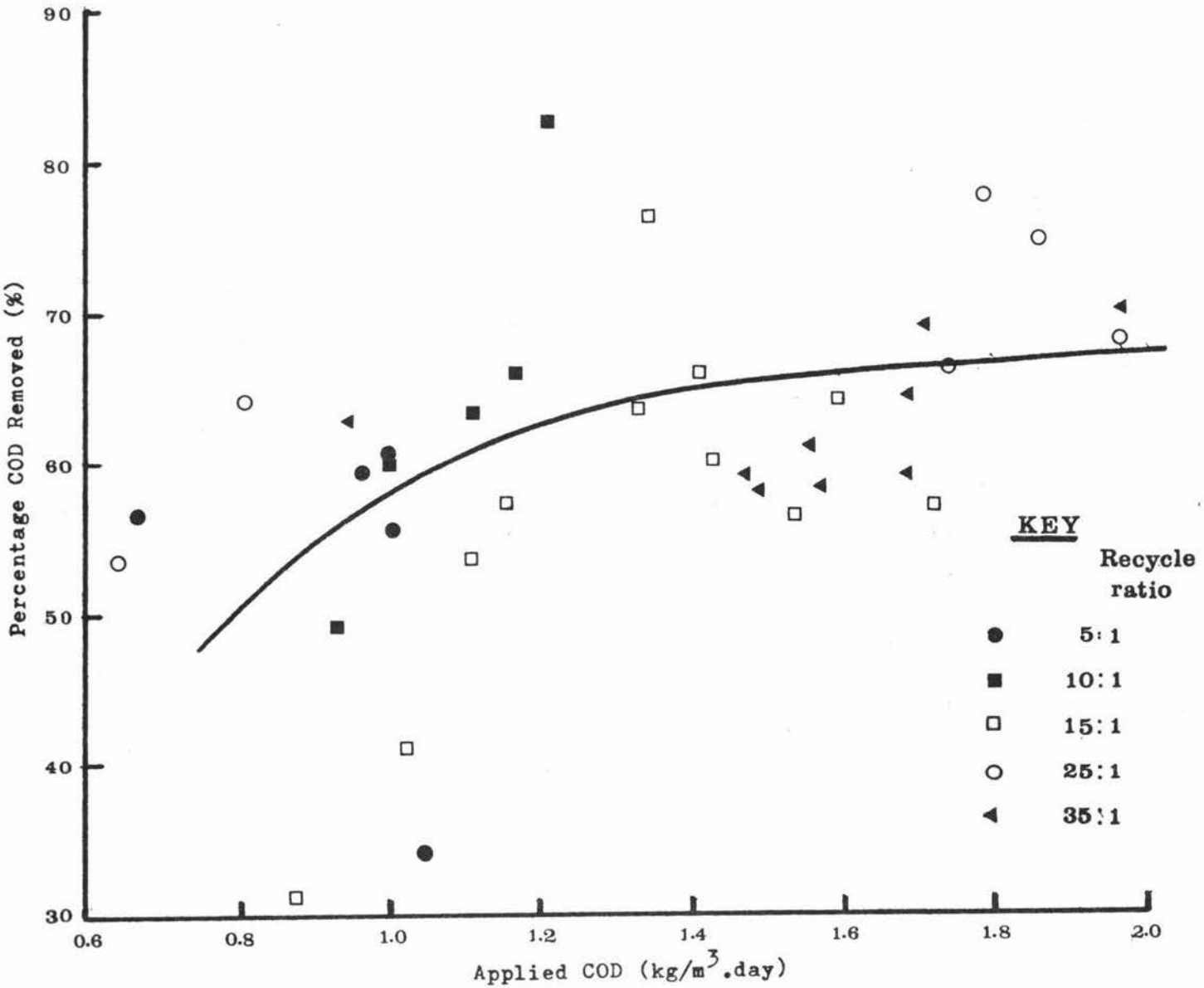

Figure 3.5 Applied COD versus Percentage COD Removed. Filter; 8 hour feed.

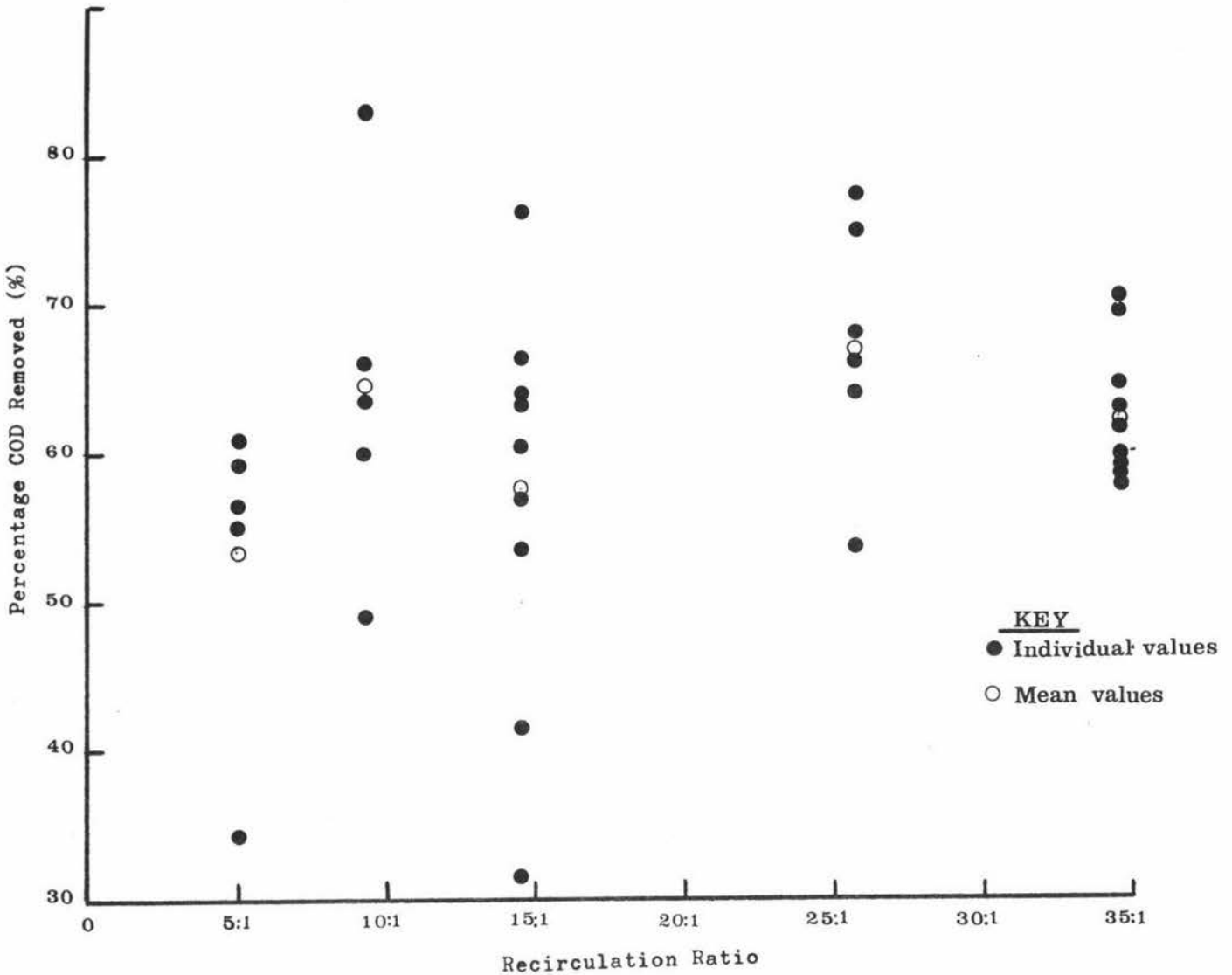

Figure 3.6 Recirculation Ratio versus Percentage COD Removal. Filter; 8 hour feed.

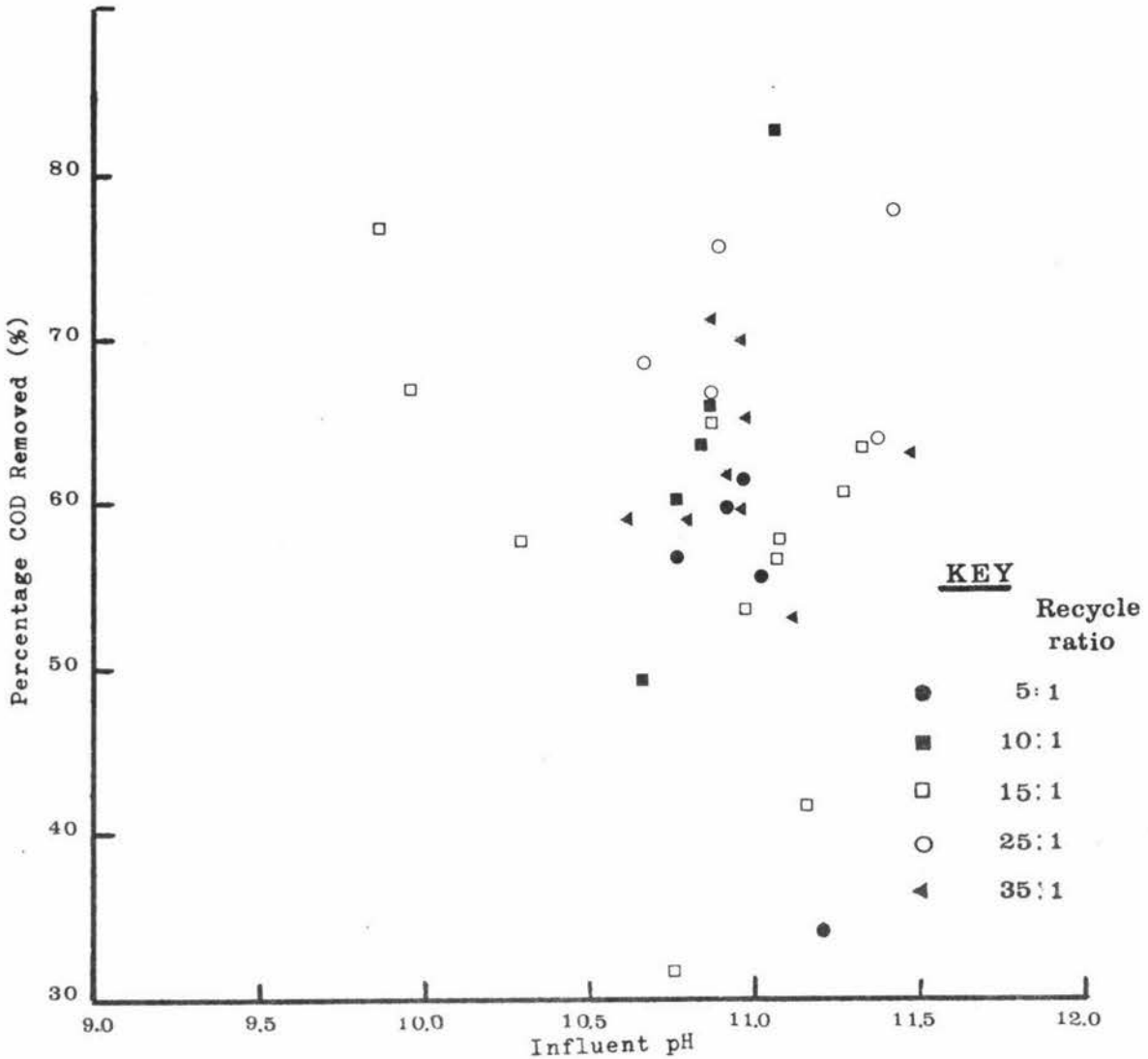

Figure 3.7 Influent pH versus Percentage COD Removed. Filter, 8 hour feed.

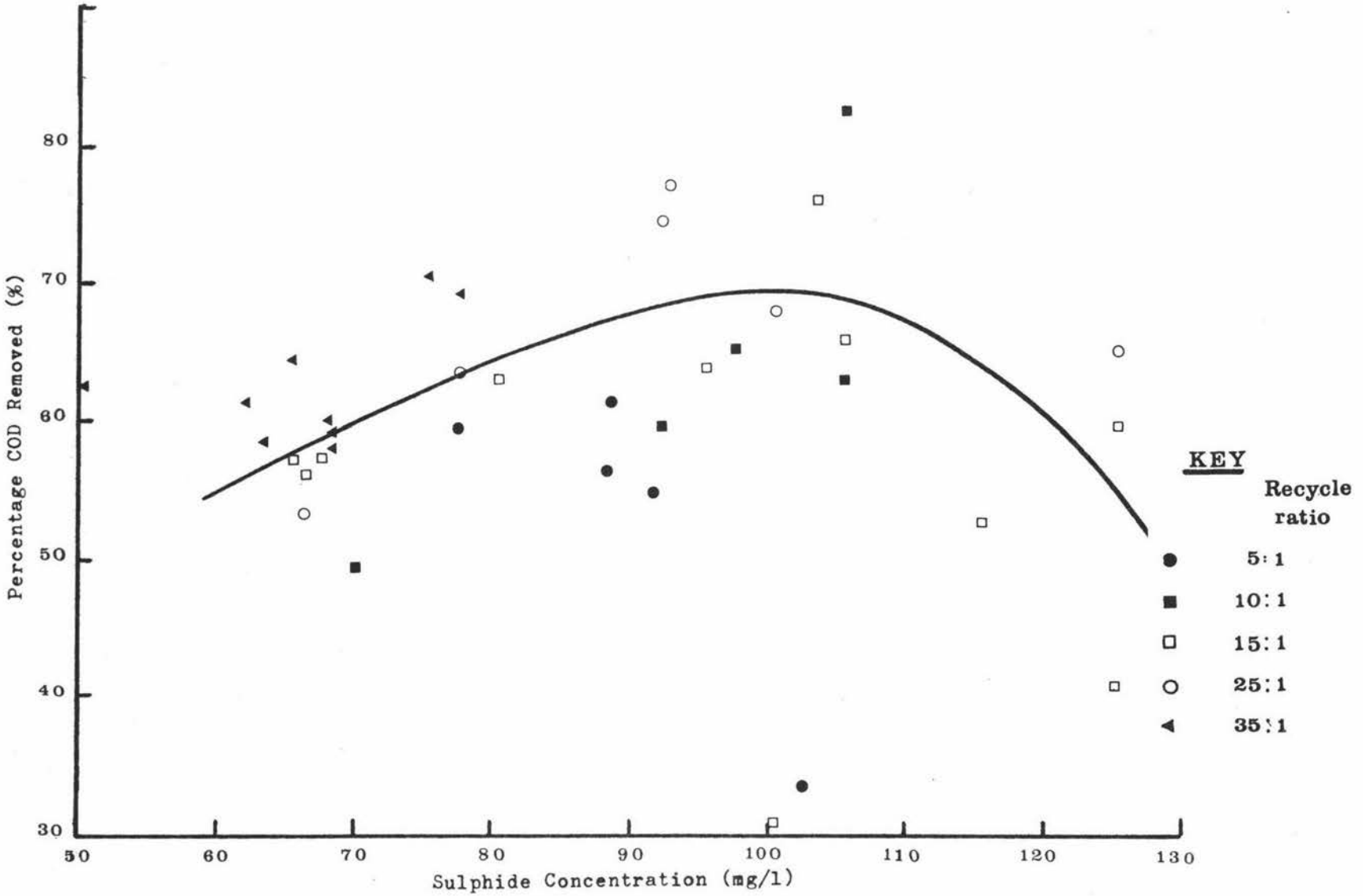

Figure 3.8 Sulphide Concentration versus Percentage COD Removed. Filter, 8 hour feed.

TABLE 3.2

SULPHIDE-SULPHATE MEASUREMENTS FOR BATCH LOADING

Date	C	Influent		Effluent		S^{2-} RML	S
		S^{2-}	SO_4^{2-}	S^{2-}	SO_4^{2-}		
		mg/l	mg/l	mg/l	mg/l	%	
8.1.73+	13.5:1	103		0		100	
9.1.73+	15:1	105		0		100	
10.1.73+	14:1	80		0		100	
11.1.73+	15:1	95		0		100	
12.1.73	15:1	66		0		100	
15.1.73+	14.5:1	67		4		94.03	
17.1.73+	14.5:1	64	31	4	405	93.75	0.48
19.1.73	14.5:1	125	56	7	480	94.90	0.83
23.1.73	14:1	125	57	6	450	95.20	0.91
24.1.73+	14.5:1	100	66	5	460	95.00	0.72
26.1.73+	14.5:1	115	74	8	475	93.04	0.80
Average	14.5:1	95	57	3	454	96.86	0.75
7.2.73+	25.7:1	66	73	3	438	95.45	0.53
8.2.73	"	77	83	2	480	97.40	0.57
9.2.73	"	92	103	0	470	100	0.75
13.2.73+	"	92	108	6	425	92.39	0.81
14.2.73	"	125	110	3	500	97.60	0.93
15.2.73+	"	100	61	0	450	100	0.73
Average	25.7:1	92	90	2	461	97.14	0.73
26.2.73	34.5:1	50	89	0	430	100	0.44
27.2.73	"	77	100	0	420	100	0.72
28.2.73+	"	65	81	0	512	100	0.45
1.3.73	"	68	77	0	430	100	0.58
2.3.73	"	62	75	0	420	100	0.54
5.3.73	"	75	77	0	500	100	0.53
6.3.73	"	63	74	0	520	100	0.42
7.3.73	"	68	67	0	480	100	0.49
8.3.73	"	68	70	0	490	100	0.49
Average	34.5:1	66	79	0	467	100	0.52
22.3.73+	4.9:1	88	28	10	428	86.64	0.59
23.3.73	5:1	88	30	4	400	95.45	0.68
26.3.73+	5:1	77	30	5	430	93.51	0.54
27.3.73+	5:1	91	40	13	395	85.71	0.65
28.3.73	5:1	102	40	9	420	91.18	0.73
Average	5:1	89	34	8	415	90.50	0.64
11.4.73+	9.3:1	105	34	2	383	98.10	0.89
18.4.73	"	105	23	2	490	98.10	0.66
19.4.73	"	70	23	8	490	88.57	0.42
20.4.73	"	92	25	9	490	90.22	0.54
21.4.73	"	97	29	6	485	93.81	0.60
Average	9.3:1	94	27	5	468	93.76	0.62

+ Mean daily values

S^{2-} = Sulphide

SO_4^{2-} = Sulphate

S^{2-} RML = Sulphide Removal

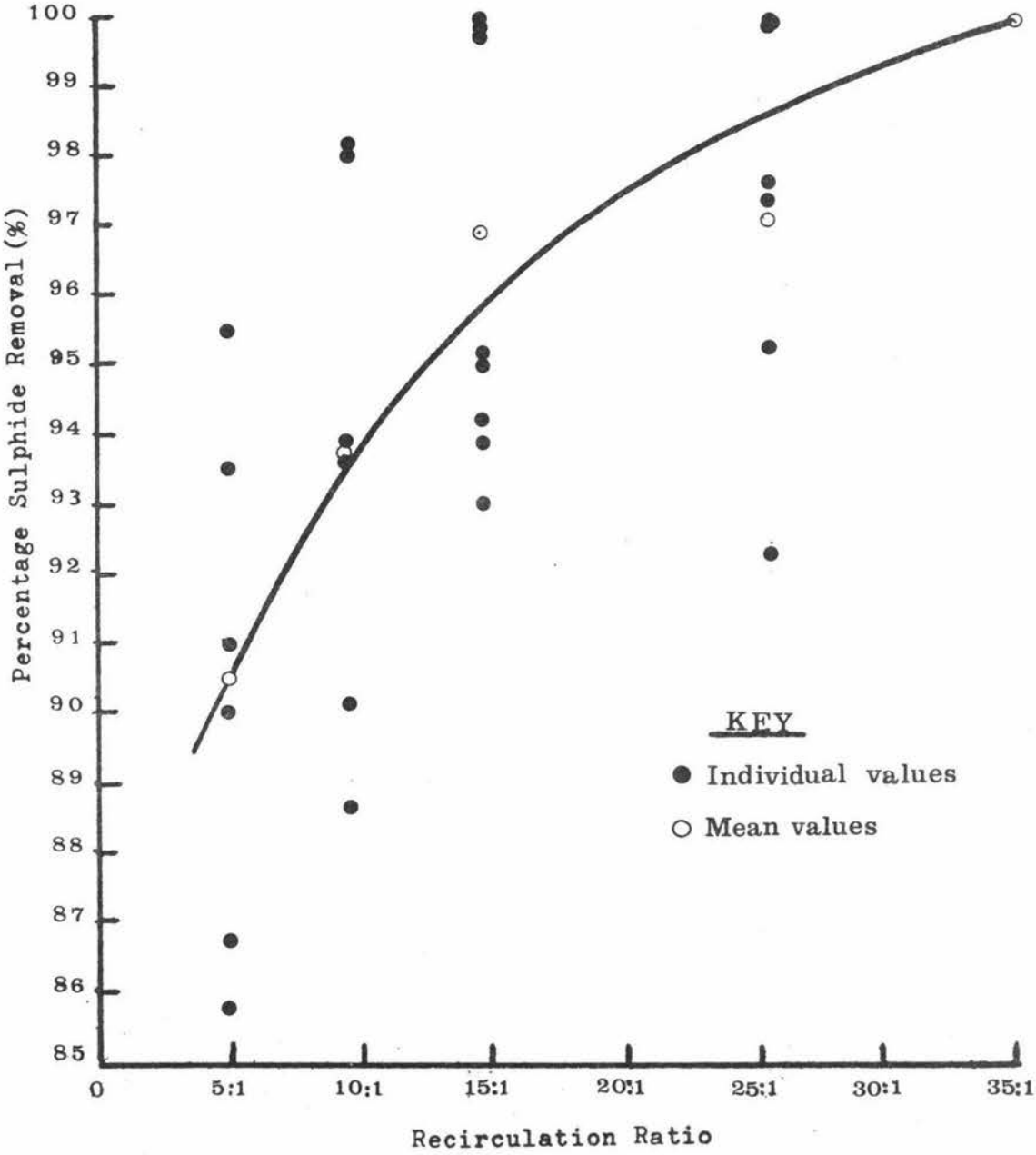

Figure 3.9 Percentage Sulphide Removal versus Recirculation Ratio. Filter, 8 hour feed.

a recycle ratio of 35:1.

There was no apparent relationship between the recirculation ratio and the ratio S. The increase in sulphur as sulphate does not correspond to the removal of sulphur as sulphide in any instance. Mean influent sulphide concentrations range from 66 - 95 mg/l, while the mean effluent sulphate concentration range is 415 - 468 mg/l. The stoichiometric conversion of sulphide to sulphate for the influent sulphide range presented, yields a sulphate concentration range of 198 - 285 mg/l. This is significantly lower than the experimental values obtained for sulphide and sulphate concentrations in the effluent. The concentration of sulphate in the influent is taken into account. The S ratio is less than unity over the flow range studied, which suggests that the sulphate present in the effluent may arise from sources other than the oxidised sulphide.

Effluent sulphide concentrations were also monitored at each recirculation ratio. These results are shown in Figure 3.10.

At a recycle ratio of 5:1 the effluent sulphide concentration increased steadily throughout the 8 hours of operations. On resumption of the feed sixteen hours later, 4 mg/l of sulphide were recorded in the effluent from the filter, a reduction of 10 mg/l from the previous day. This suggests a 2-stage mechanism in which, initially, the sulphide is adsorbed on to the biological film and then subsequently oxidised.

For recirculation rates of 10:1, 15:1 and 25:1, a sudden increase in effluent sulphide concentration was observed during the first four hours of operation, while the filter was seeking to establish equilibrium conditions. In each case, the steady-state value achieved fell to zero on reintroduction of the feed on the following day. At the highest recirculation ratio of 35:1, no sulphide appeared in the effluent stream at any time.

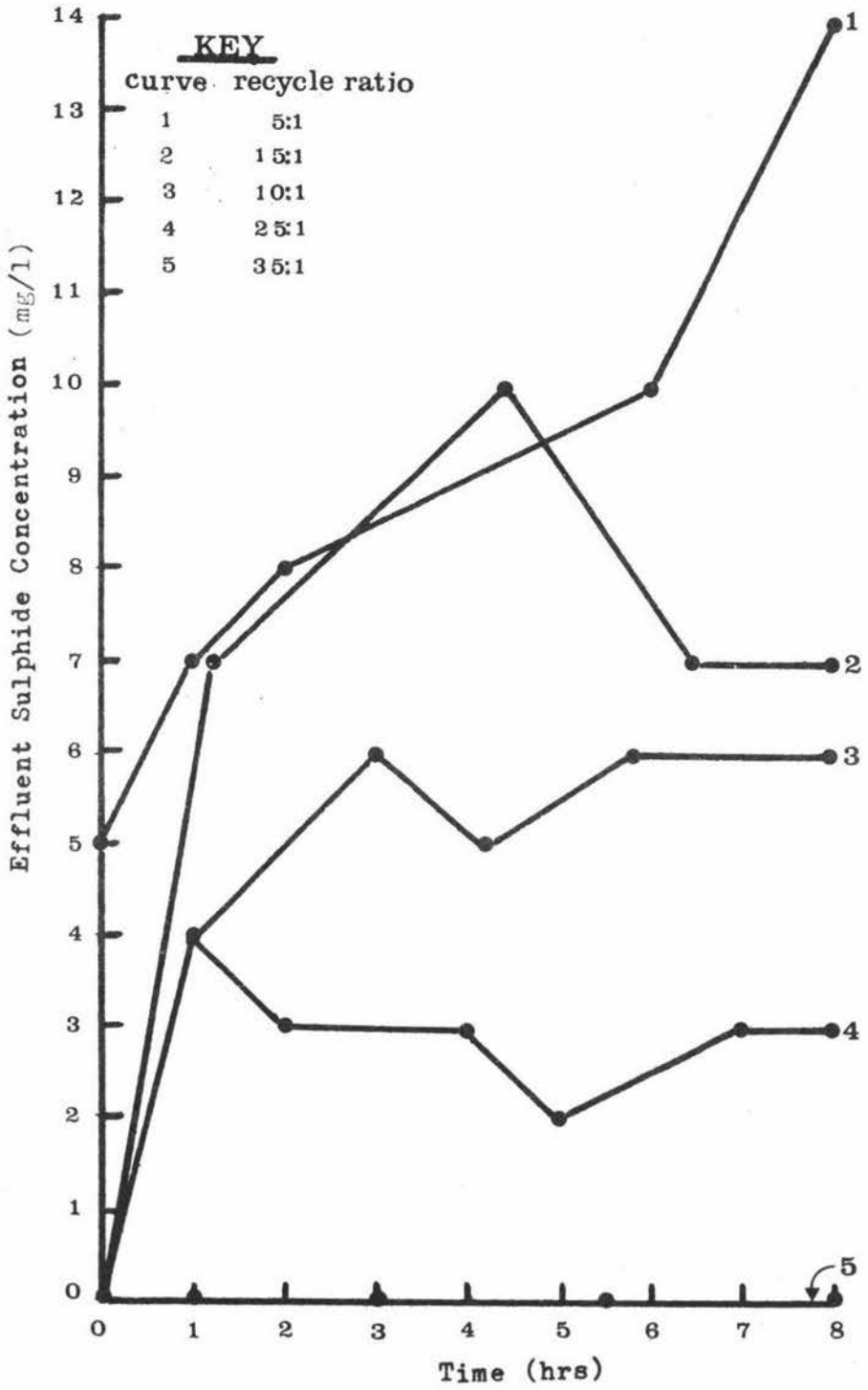

Figure 3.10 Monitoring of Effluent Sulphide Concentrations for Filter, 8 hour feed.

3.3.1.3 Nitrogen Removal

Table 3.3 summarises the average total nitrogen removal efficiencies of the system. Nitrogen values exhibited the greatest variation of any parameter measured throughout the experiment. An optimum removal occurs at a recirculation ratio of 10:1. It was not possible to collect data at a recycle ratio of 15:1.

3.3.1.4 pH/Alkalinity Considerations

The pH of the influent and effluent streams are recorded in Appendix 3 and plotted in Figure 3.11. Effluent pH values are plotted against the corresponding values of influent pH and show that influent pH appears to have little effect on effluent pH, in the influent pH range 9.7 - 11.5. The effluent pH varied between 8.05 and 8.80 over the batch feeding period.

Mean values of phenolpthalein alkalinity and total alkalinity for each run are presented in Table 3.4. These results allow the stoichiometric classification of the effluent in terms of bicarbonate, carbonate and hydroxide concentrations which are shown in Table 3.4 with the corresponding alkalinities. Carbonate represents the largest alkalinity fraction of the influent. Bicarbonate is the sole contributor to the effluent alkalinity.

3.3.2 Continuous Operation

Experimental data collected at 21°C, 31°C and 34°C are included in Appendix 6. Subsequent evaluations of parameters are derived from this appendix.

Emphasis within this section is placed upon the changes in effluent sulphide and sulphate concentrations.

3.3.2.1 COD Loading and Removal

COD loading and removal data for the three temperatures are shown in Table 3.5. A sample calculation of applied and removed COD is presented in Appendix 4. Data were collected

TABLE 3.3

AVERAGE NITROGEN REMOVALS FOR BATCH LOADING

C*	Nitrogen Concentration*		Nitrogen Removal*
	Influent	Effluent	
	mg/l	mg/l	%
5:1	252	182	27.6
10:1	290	161	44.7
25:1	410	262	33.5
35:1	452	328	27.2

* Mean values C = Recycle ratio

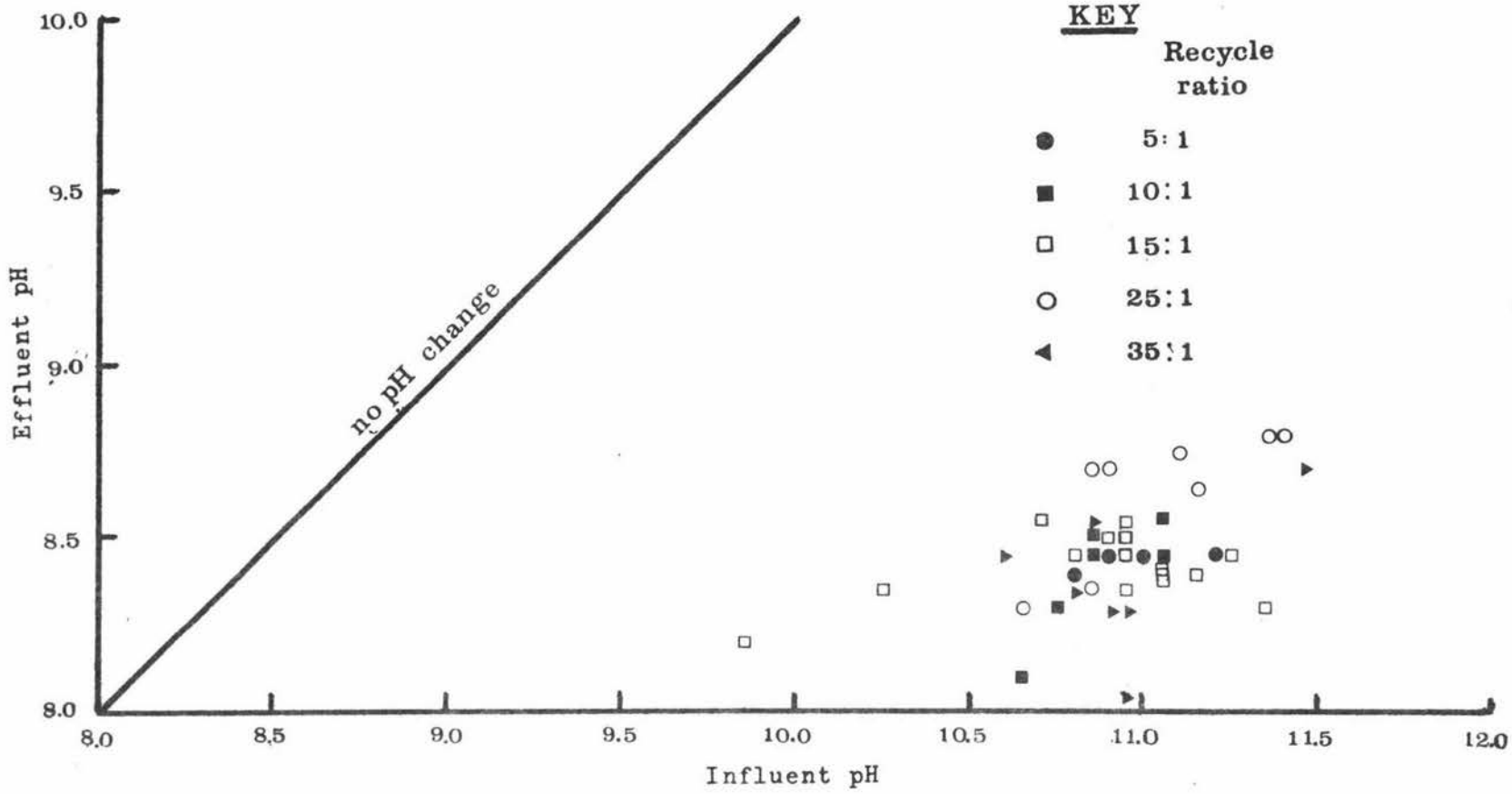

Figure 3.11 Effect of Changes in Influent pH on Effluent pH.
Filter, 8 hour feed.

TABLE 3.4

ALKALINITY DATA FOR BATCH LOADING

C	Alkalinity (as mg/l $CaCO_3$)									
	Influent					Effluent				
	P	T	OH^-	$CO_3^=$	HCO_3^-	P	T	OH^-	$CO_3^=$	$HCO_3^=$
5:1	363	934	0	726	208	0	583	0	0	583
10:1	340	931	0	680	251	0	427	0	0	427
15:1	472	1339	0	944	399	0	768	0	0	768
25:1	461	1323	0	922	401	0	523	0	0	523
35:1	583	1358	0	1164	294	0	682	0	0	682

P = Phenolphalein Alkalinity

T = Total Alkalinity

OH^- = Hydroxide Alkalinity = 0 when $P < \frac{1}{2}T$

$CO_3^=$ = Carbonate Alkalinity = 2P when $P < \frac{1}{2}T$

$HCO_3^=$ = Bicarbonate Alkalinity = (T - 2P) when $P < \frac{1}{2}T$

All parameters presented are mean values

TABLE 3.5

COD MEASUREMENTS - CONTINUOUS LOADING AT RECYCLE RATIO OF 12.2:1

Date	Temp	COD					
		Influent	Effluent	Removal Efficiency	A	D	R
	°C	mg/l	mg/l	%	kg/m^3.day		
28.5.73	21	4000	1560	61.0	2.4030	0.9370	1.4660
29.5.73	21	3720	1960	47.3	2.2357	1.1779	1.0578
30.5.73	21	4500	2020	55.1	2.6647	1.1961	1.4686
1.6.73	21	3720	2000	46.2	2.2357	1.1843	1.4804
2.6.73	21	3560	1950	45.2	2.1395	1.1547	0.9848
5.6.73	21	3160	1590	49.7	1.8712	0.9415	0.9297
7.6.73	21	3560	1480	58.4	2.1080	0.8764	1.2316
8.6.73	21	3750	1490	60.3	2.2205	0.8823	1.3382
Average	21	3746	1756	52.9	2.2347	1.0438	1.2446
12.6.73	31	2870	995	65.3	1.7248	0.5980	1.1268
13.6.73	30	2660	995	62.6	1.5986	0.5980	1.0006
26.6.73	31	3850	1120	70.9	2.3138	0.6731	1.6407
18.6.73	30	3870	1120	71.1	2.3258	0.6731	1.6527
20.6.73	31	3500	1020	70.9	2.1034	0.6130	1.4904
21.6.73	31	3740	980	73.8	2.2236	0.5890	1.6346
22.6.73	31	3940	960	75.6	2.3679	0.5769	1.7910
26.6.73	31	1490	385	74.2	0.8955	0.2313	0.6642
Average	31	3240	947	70.6	1.9442	0.5691	1.3751
9.7.73	34	955	188	80.3	0.5739	0.1130	0.4609
10.7.73	33	1200	202	83.2	0.7212	0.1214	0.5998
11.7.73	34	1240	187	84.9	0.7452	0.1124	0.6328
12.7.73	34	2110	297	85.9	1.2681	0.1785	1.0896
Average	34	1370	219	83.6	0.8271	0.1313	0.6958

A = Applied

D = Discharged

R = Removed

infrequently during the three temperatures owing to the greater consideration given to the sulphide studies.

Mean COD removal percentages from Table 3.5 indicate that removal efficiency increases with increase in temperature. The mean value obtained at 21°C at a recycle ratio of 12:1, 52.9%, when compared with the interpolated value of 61.6% from the batch operation (between recycle ratios of 10:1 and 15:1), indicates that the batch process is slightly more efficient than the continuous.

From individual removal percentages presented in Table 3.5, the filter appears to be undergoing a transient period of operation since at temperatures of 31°C and 34°C, COD removal percentages increase with time.

3.3.2.2 Sulphide Removal

Data for the change in the chemical state of sulphide is reproduced in Table 3.6, and is evaluated in a manner similar to that used in the sulphur studies of the batch process.

At 21°C, the mean effluent sulphide concentration, 9 mg/l, was greater than the interpolated concentration for the batch-fed system, 4 mg/l. This would imply that the continuous application of a waste with a high sulphide component is less desirable than a batch dosing.

On completion of the experiment at 21°C the system temperature was increased to 31°C. This led to an increased effluent sulphide concentration and a marked decrease in effluent sulphate concentration. This effect is portrayed in Figure 3.12. Sampling commenced two days following the temperature change and this datum point is designated as Day 0 in Figure 3.12. The system responded slowly in returning to equilibrium; sulphide concentration in the effluent fell to zero after 17 days, whereas sulphate concentration slowly increased over a period of 30 days, reaching a value of about 440 mg/l, which is similar to that achieved with batch

TABLE 3.6

SULPHIDE-SULPHATE DATA - CONTINUOUS LOADING

(Recycle Ratio - 12.2:1)

Date	Temp	Influent		Effluent		Sulphide Removal	S
		Sulphide	Sulphate	Sulphide	Sulphate		
	°C	mg/l	mg/l	mg/l	mg/l	%	
28.5.73	21	66	12	7	400	89.39	0.46
29.5.73	21	91	13	6	370	93.41	0.71
30.5.73	21	110	12	11	340	90.00	0.90
1.6.73	21	97	19	5	310	94.85	0.95
2.6.73	21	97	19	11	305	88.66	0.90
5.6.73	21	83	9	11	350	86.75	0.64
7.6.73	21	89	10	10	300	88.76	0.82
Average	21	90	13	9	339	90.26	0.78
12.6.73	31	102	7	28	130	72.55	1.80
13.6.73	30	81	9	21	120	74.07	1.62
14.6.73	31	93		20		78.49	
16.6.73	31	80	9	19	125	76.25	1.58
18.6.73	30	105	9	16	120	84.76	2.40
20.6.73	31	80	8	16	175	80.00	1.15
21.6.73	31	81	10	15	220	81.48	0.94
22.6.73	31	79	9	10	230	87.34	0.94
26.6.73	31	82	12	4	300	95.12	0.82
29.6.73	31	84	10	0	315	100	0.83
Average	31	87	9	15	193	83.01	1.34
9.7.73	34	67	11	0	375	100	0.56
10.7.73	33	73	11	0	395	100	0.57
11.7.73	34	81	12	0	380	100	0.66
12.7.73	34	102	6	0	405	100	0.77
Average	34	81	10	0	389	100	0.64

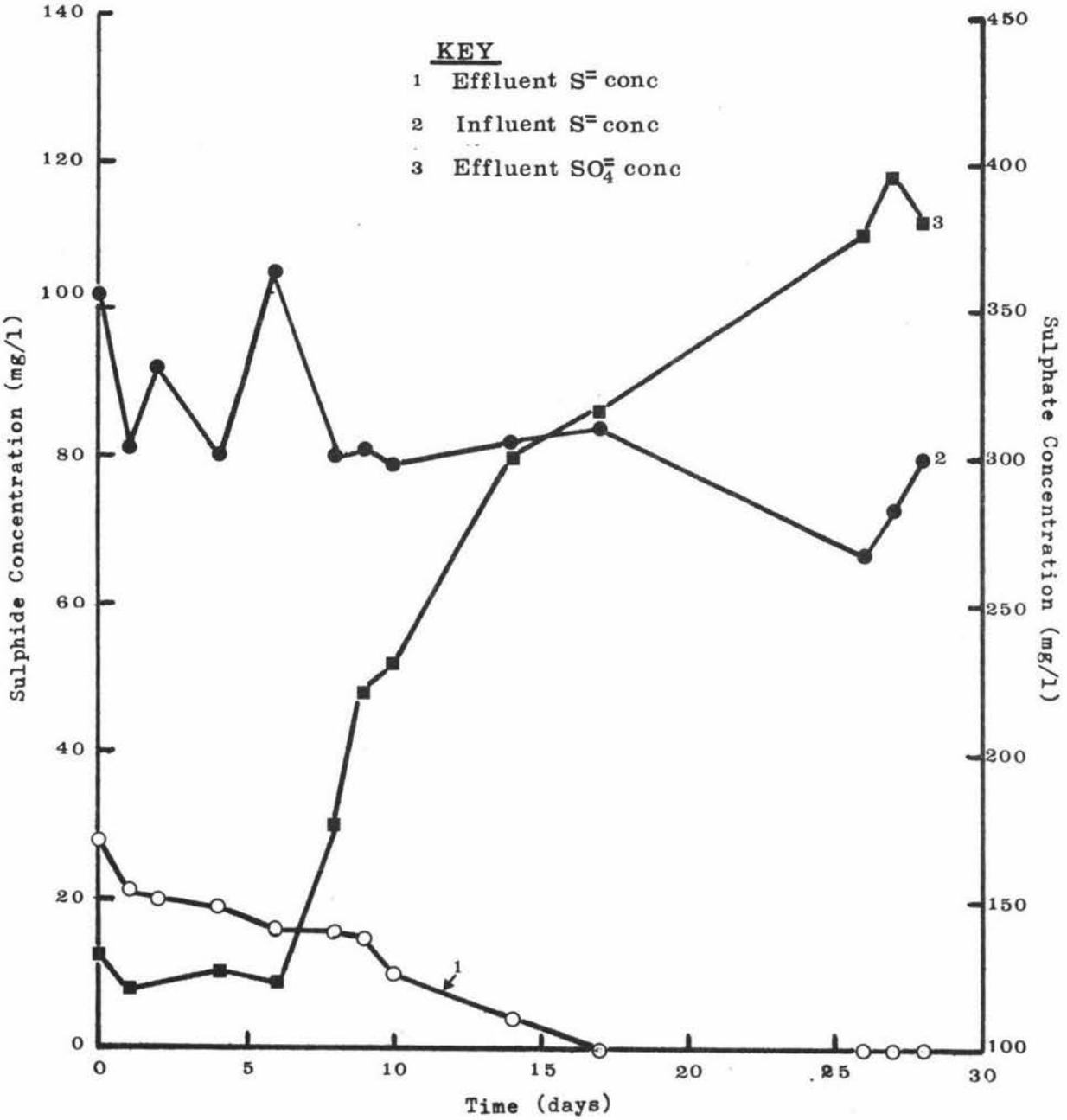

Figure 3.12 Changes in Effluent Sulphide and Sulphate Concentrations with Filter Temperature Change

operation.

An additional temperature increase of 3°C did not alter the sulphide removal from the system.

3.3.2.3 pH/Alkalinity Considerations

The effect of change in influent pH on effluent pH is shown in Figure 3.13. As for the batch fed system, change in influent pH over a range 9.7 - 11.2, has little influence on effluent pH. The effluent pH values range from 8.05 - 8.55 and appear to be independent of temperature.

Alkalinity data are reported in Table 3.7 and follow a similar pattern shown for the batch fed system. The total alkalinity of the effluent gradually approached that of the influent and eventually exceeded the influent value as the experiment progressed.

3.3.3 Sludge Analysis

3.3.3.1 Chemical Analysis

Nitrogen, total solids and ash determinations for the sludge samples are presented in Table 3.8. 75% of the ash from the continuous run was found to be calcium, determined as calcium oxide. This would suggest that the lime entering the system is precipitated, and contributing significantly to the ash content of the sludge.

The results obtained for the three samples in Table 3.8 are in good agreement with each other. The small number of samples prevented a statistical analysis of the results.

3.3.3.2 Sludge Settling Tests

The rates of sludge sedimentation are shown in Figure 3.14. The curve for the highest sludge solids concentration, 12,620 mg/l, indicates that hindered settling occurred. However, the curves for the other concentrations demonstrate unhindered particle settling, with extremely rapid settling rates.

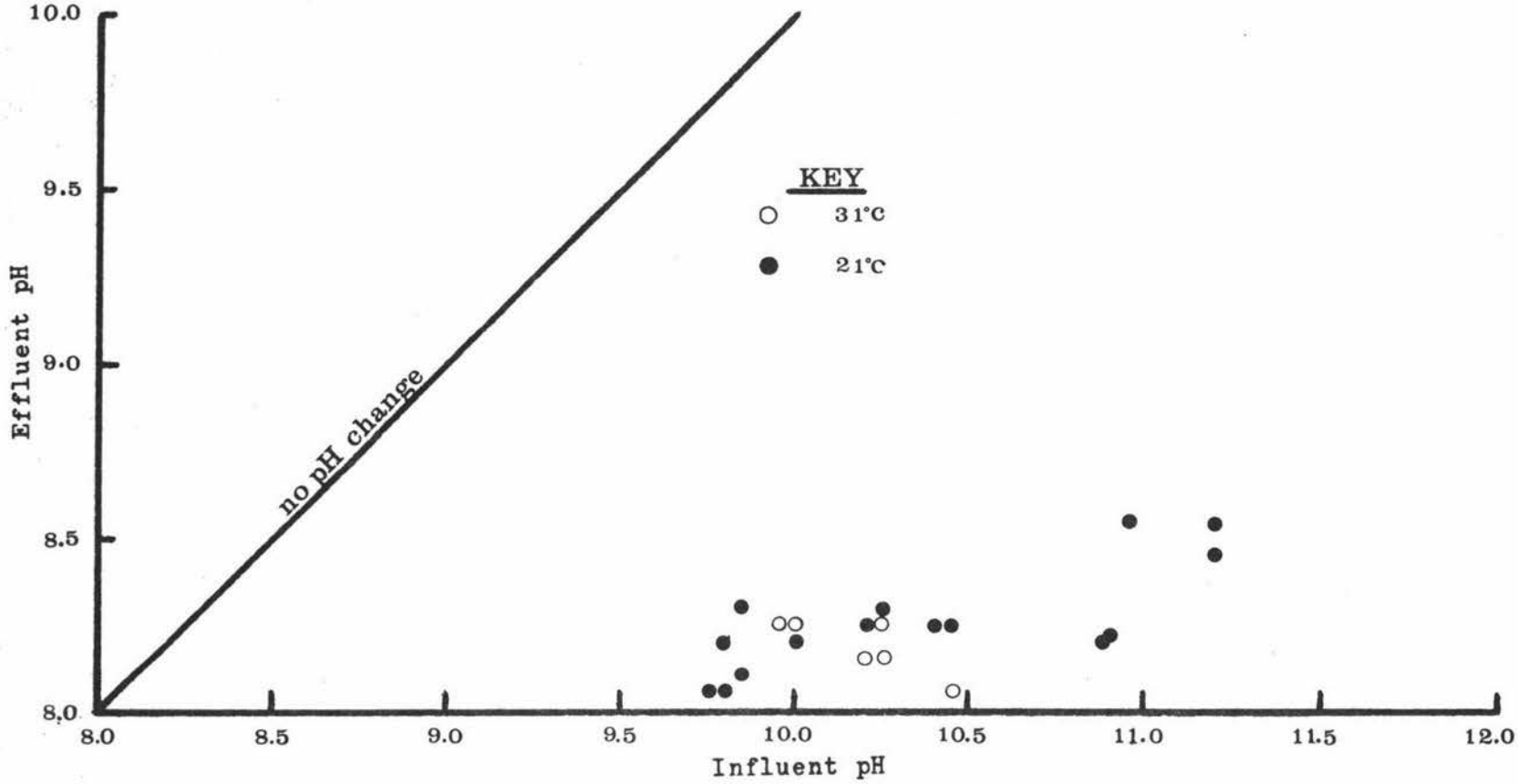

Figure 3.13 Effect of changes in Influent pH on Effluent pH. Continuous Feed.

TABLE 3.7

ALKALINITY DATA - FILTER CONTINUOUS OPERATION

(Recycle Ratio - 12.2:1)

Temp	Alkalinity (as mg/l $CaCO_3$)									
	Influent					Effluent				
^oC	P	T	OH^-	$CO_3^=$	HCO_3^-	P	T	OH^-	$CO_3^=$	HCO_3^-
21	226	1019	0	452	567	0	1086	0	0	1086
31	305	994	0	610	384	0	1037	0	0	1037
34	211	548	0	422	126	0	468	0	0	468

P = Phenolphalein alkalinity

T = Total alkalinity

OH^- = Hydroxide alkalinity = 0 when $P < \frac{1}{2}T$

$CO_3^=$ = Carbonate alkalinity = 2P when $P < \frac{1}{2}T$

HCO_3^- = Bicarbonate alkalinity = (T - 2P) when $P < \frac{1}{2}T$

All parameters presented are mean values

TABLE 3.8

SLUDGE COMPOSITION

Sample	Moisture Content	Total Solids	Nitrogen	Ash
	%	%	%*1	%*1
15:1	93.6	6.4	5.15	27.3
35:1	94.0	6.0	5.0	28.5
21°C C.L.	93.0	7.0	5.5	26.1

* : On dry weight basis

1 : Carried out by New Zealand Leather and Shoe Research Association, Palmerston North.

C.L. : Continuous Loading

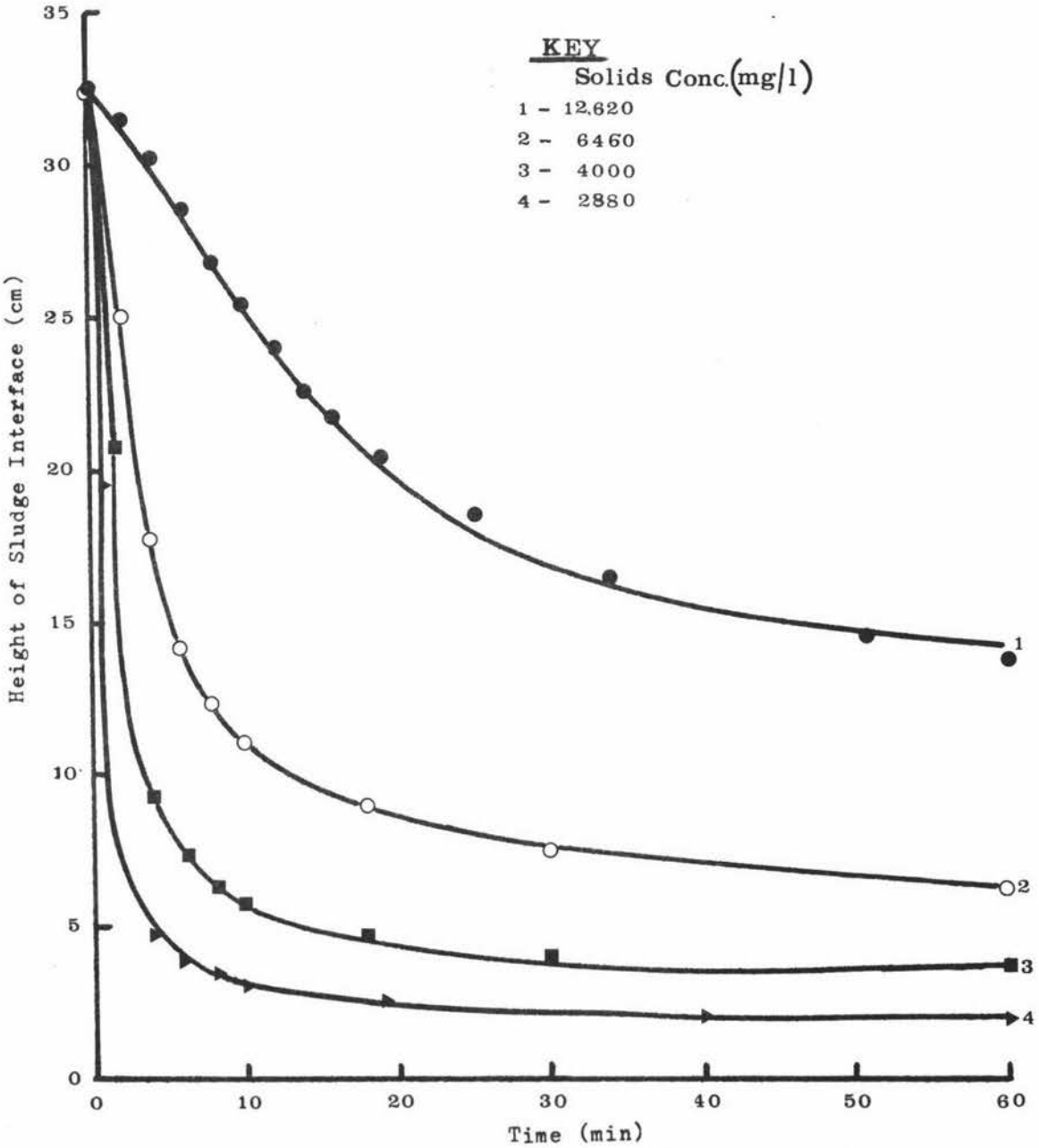

Figure 3.14 Sludge Settling Characteristics.

Approximately 100% sedimentation of settleable solids was obtained after 40 min for solids concentrations of 6460, 4000 and 2880 mg/l. These rates are greater than those presented by Fair and Geyer (41) for the sedimentation of domestic sewage. The rapid rates are probably induced by the presence of lime in the feed, since lime is reported as being a commonly used chemical for the sedimentation of sewage and industrial wastes.

3.3.4 Oxygen Transfer in the Biological Filter

$K_L a$ values were expressed in two forms:

(1) per unit volume of liquid,

(2) in the conventional manner for a packed column (True $K_L a$), i.e. per package volume.

Values for each hydraulic flow applied to the filter surface were as follows:

Flow Rate (l/hr)	48.6	84	126	180	288
$K_L a$/unit vol. at 10°C	73	58.7	43.6	33.6	17.9
True $K_L a$ (hr^{-1}) at 10°C	5.1	7.18	8.04	8.55	7.5

Sample calculations are presented in Appendix 7.

Experimental $K_L a$ values were obtained at 10°C. $K_L a$ values per unit liquid volume were corrected to yield values at the filter operating temperature (20°C) by using the equation due to Eckenfelder and O'Connor (31):-

$$K_L a_{(T)} = K_L a_{(20)} \cdot 1.024^{(T-20)}$$

where: $K_L a_{(T)}$ = mass transfer coefficient at temperature T

$K_L a_{(20)}$ = mass transfer coefficient at 20°C

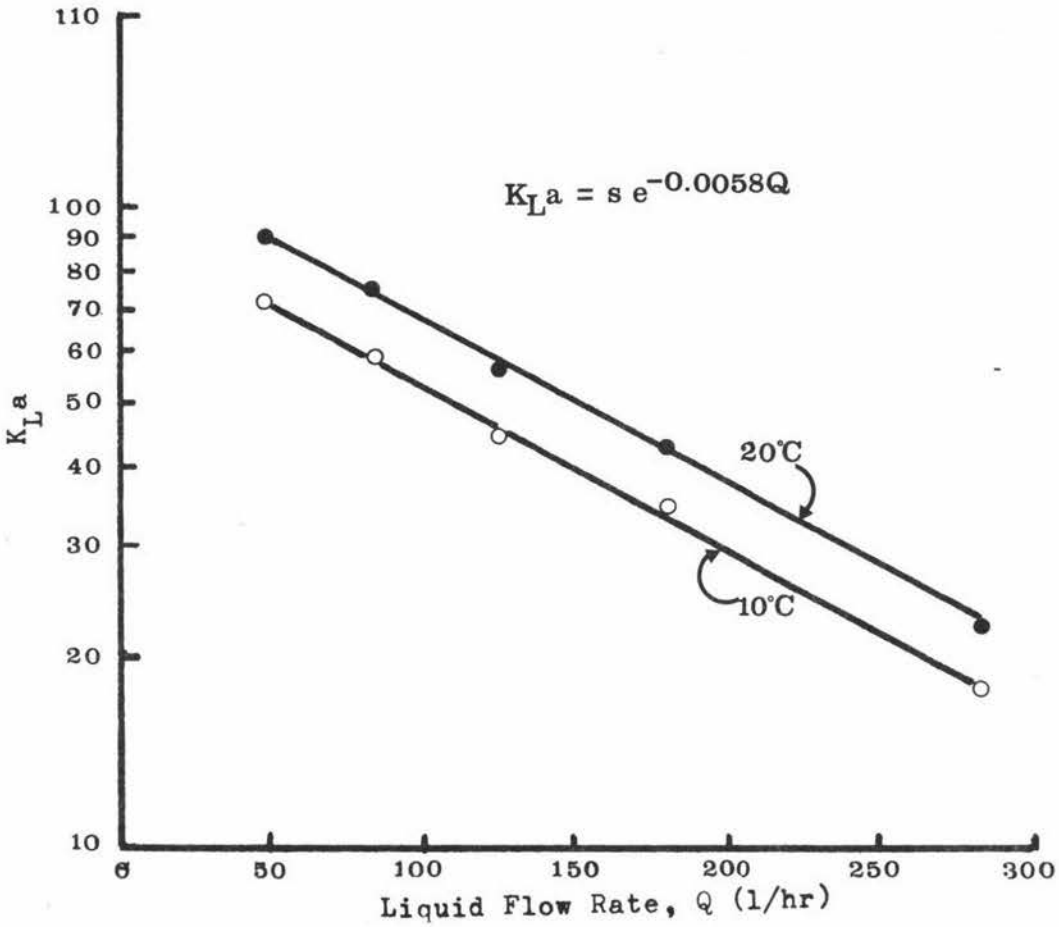

Figure 3.15 Filter Oxygen Transfer

T = temperature in ^{o}C.

Figure 3.15 shows K_La per unit liquid volume as a function of liquid flow rate. A linear relationship was demonstrated at each temperature, and was of the form:

$$K_La = Se^{-0.0058Q}$$

where: S = some function of temperature, system geometry and liquid properties.

Q = liquid flow rate (l/hr).

3.4 Discussion

3.4.1 COD Removal

The batch and continuous treatment of fellmongery waste by biological filtration provided a satisfactory reduction in COD. 0.50-1.03 kg COD/m^3.day were removed during batch operation, over a recycle ratio range 5:1-35:1. This represented a mean COD removal of 57.3-67.7%. On a BOD basis, this is a 57-70.5% decrease. Simultaneous BOD and COD analyses of the biological filter influent and effluent produced linear curves shown in Appendix 8. These were used to evaluate BOD decreases from corresponding COD data. The calculations are also located in Appendix 8. A linear relationship resulted on plotting COD removed against COD applied. Similar results, but in terms of BOD, have been obtained by many workers.

Data from the continuous operation at 21^{o}C show a mean COD decrease of 52.9% for an applied load of 2.23 kg COD/m^3.day and hydraulic loading of 1.82 m^3/m^3.day (4.45 m^3/m^2.day). Mean removals at 31^{o}C and 34^{o}C were 70.6 and 83.6% respectively. However, the filter appeared to be in a transient condition at these higher temperatures, since the COD removal progressively increased with time (Table 3.5).

Over the batch loading period, maximum COD removal occurred at a recycle ratio of 25:1. Figure 3.6 indicated no apparent relationship between COD removal and recycle ratio. Difficulty

in controlling recirculation flows resulted in low COD removals. In the last three runs at a recycle ratio of 15:1 for example, sludge particles were trapped in the valves in the recirculation lines. The resultant decrease in flow yielded COD removals with reduced values 41.8, 31.2 and 53.6% respectively.

The waste fed to the system exhibited a variable COD, which would account for the variations in COD removal during the batch and continuous experiments. Velz (123) and Stack (108) have stated that variations in applied loading will result in variable removal efficiencies. However, Schulze (100) demonstrated that the efficiency of a biological filter was independent of the organic load, provided that the hydraulic loading remained constant. Such was the case at each recirculation ratio in the present investigation. It is possible that the cyclic pattern of feed introduction to the plant, as well as the variable loading, may have influenced the performance of the system.

Removals are lower than those obtained from a biological filter treating a chemical waste, with a similar BOD to that of fellmongery waste. Majewski et al (72) achieved a 92-96% BOD reduction of a waste with an initial BOD of 1800 mg/l. Although these experiments were carried out during the summer, temperatures were not specified. The hydraulic loading was 4.9 m^3/m^2.day, with a 10:1 recycle ratio and an organic loading of 0.38 kg BOD/m^3.day. During winter operation, an applied BOD of 2200 mg/l and a 10:1 recycle ratio produced a 65% BOD removal. Their operating parameters, hydraulic loading 8.1 m^3/m^2.day and organic loading 0.77 kg BOD/m^3.day, are similar to those of this experiment. For the batch operation, BOD/COD correlations (Appendix 8) show an organic loading range of 0.23-0.75 kg BOD/m^3.day. Hydraulic loads ranged from 3.98-23.6 m^3/m^2.day during the batch experiments and were constantly maintained at 4.45 m^3/m^2.day for the continuous operation. The continuous experimental operating variables closely approximate those described by Majewski et al (72) for the summer operating conditions but a difference in results is apparent.

The graph of percentage COD reduction with applied COD for the batch loading, Figure 3.5, demonstrates that COD removal efficiency increased only slightly over the applied COD range 0.6-2.0 kg/m^3.day (0.23-0.75 kg BOD/m^3.day). A similar plot presented by Walter (128) for the biological filtration of an alkaline waste exhibited an identical pattern over the same BOD loading range.

The only data published on the biological filtration of fellmongery waste is that reported by Bailey (5). Using a plastic packing, he obtained a 50% BOD removal at a loading of 2.95 kg BOD/m^3.day. The hydraulic loading of the filter was not presented. Removals obtained in these experiments are higher than those reported by Bailey.

Akrishna et al (3) achieved a 97% BOD removal from tannery waste on a stone packed filter. The filter was operated at a hydraulic loading of 2.3 m^3/m^2.day. Preliminary pH adjustment to between 7 and 8 was necessary to attain this decrease. A pre-treatment of this nature would effect considerable coagulation and sedimentation of protein with subsequent reduction of BOD.

Influent pH changes were found to have no effect on the COD removal for the batch operation. Insufficient data prevented a study of the influence of pH on the performance of a continuously operated filter. Results obtained for the batch loading are contrary to those presented by Walter (128). His studies on the biological filtration of an alkaline waste demonstrated that BOD removal is strongly influenced by pH changes. A maximum BOD removal, 60%, occurred in the pH range 8-9. Outside this range removals decreased, with a 25% lower removal in the pH range 11-12.

Changes in the input sulphide concentration influenced the COD removals more significantly than pH changes. Figure 3.8 indicates that maximum removal occurred in the sulphide concentration range, 90-110 mg/l. The decrease

in performance at higher concentrations occurred probably as a result of the toxicity of sulphide to the filter organisms. Eckenfelder and O'Connor (31) observed that sulphide concentrations of less than 10 mg/l appear to have little effect on the oxidation process within a biological filter. However, the inferior performance at concentrations below 90 mg/l is more difficult to explain. It is proposed (refer Chapter 6) that a symbiotic relationship between the sulphur-oxidisers (if responsible for the sulphide elimination) and the heterotrophs was established in the filter. This relationship is most favoured in the sulphide concentration range 90-110 mg/l.

Bailey (5) and Green (46) subjected biological filters to greater sulphide concentrations. Bailey (5) reported that an experimental filter tolerated concentrations of up to 250 mg/l, without adverse effect on the BOD removals. Concentrations of 400 mg/l of sulphide or H_2S were accommodated without any deleterious effect by a filter described by Green (46). Both investigations, however, involved additions of sulphide to sewage effluent. However, fellmongery waste is more complex. An alkaline pH and high concentration of lime predominate which, it was thought, would adversely affect the metabolism of sulphur and organic compounds in a biological treatment unit. This was, in fact, found to be the case.

3.4.2 Sulphide/Sulphate Considerations

An exponential increase in sulphide removal with increasing recirculation ratio is demonstrated in Figure 3.9 for the batch loading experiments. Since the true mass transfer coefficient, K_La, exhibited very little increase over the recycle flow range investigated, the mechanism of sulphide removal appears unlikely to be chemical. Oxygen is required for the chemical oxidation of sulphide. This oxygen must diffuse from the gas phase into the bulk liquid phase prior to reaction with the sulphide component. The increased sulphide removals at higher recirculation ratios are not totally consistent with the notion of a chemical sulphide oxidation. The results may be explained in the light of a biological

mechanism of sulphide oxidation. The rate of sulphide application is constant. Thus at high recycle ratios, sulphide concentrations applied to the filter will be low with a possible resultant decrease in toxicity and increased removal rates. Higher concentrations are applied at low recycle ratios, exerting a greater toxicity and associated slower removal rates.

Sulphur studies for both batch and continuous operation (Tables 3.2 and 3.6) depict sulphate as the terminal product of sulphide oxidation. Sulphur balances show that sulphide was not stoichometrically converted to sulphate. In the batch loading experiments sulphate increases were in excess of those calculated for complete conversion from sulphide. Had 100% conversion occurred, a S value of unity would arise. Alternative potential sources of sulphate must have existed within the system. Roy and Trudinger (95) report that sulphate is liberated from the metabolism of sulphur-containing amino acids. Since proteinaceous wool products, of which cystine is a constituent amino-acid, exist in fellmongery waste, metabolism of cystine may increase sulphate concentrations. Table 3.3 yields an average waste nitrogen content of 350 mg/l, and hence a protein concentration of 2180 mg/l (nitrogen concentration x 6.25). Wool exhibits a sulphur content of 4%. Assuming all the protein present in the waste originated from wool products, the waste contains a sulphur concentration of 87 mg/l (excluding inorganic sulphide-sulphur). Direct metabolism of this component to sulphate would give concentrations of 261 mg/l $SO_4^{=}$. The average sulphate increase of the waste after treatment was 395 mg/l (Table 3.2). Consideration of a theoretical sulphate increase from protein sulphur degradation yields a sulphate concentration of 134 mg/l which arises from sulphide oxidation. A mean sulphide removal of 83 mg/l was obtained during the batch experiments (Table 3.2), which would have produced 249 mg/l $SO_4^{=}$, if stoichometrically oxidised. This is greater than the theoretically calculated 134 mg/l $SO_4^{=}$. However, the assumption that the waste is composed entirely of protein arising

from wool products is questionable. Degraded pelt proteins would contribute to the total protein content of the waste, thus lowering the theoretically estimated sulphate increase. Furthermore thiosulphate and polythionates were possibly present in the waste, autotrophic metabolism of which results in sulphate formation (105). These two sources may have contributed to the total sulphate concentration.

The results obtained are consistent with those of Heukelekian and Lassen (53), Aulenbach and Heukelekian (4) and Leafe et al (69). These workers demonstrated that sulphate was the terminal metabolite of biological sulphide transformation. Stoichometric sulphide oxidation was revealed in all cases. However, as with the work of Bailey (5) and Green (46), sulphide was the only sulphur source present.

Sulphide concentrations recorded in the effluent on typical operating days for the batch loading experiments (Figure 3.10), suggested a sulphide adsorption onto the biological film, with subsequent oxidation. Sulphide concentrations applied to the filter surface were a function of the recirculation ratio. The lowest concentrations were applied at the highest recycle ratio by virtue of the dilution volume. Effluent sulphide concentrations at a recycle ratio of 5:1 increased steadily over the feeding period. Concentrations at this recycle ratio were the highest applied to the filter surface, and the saturation concentration was exceeded, indicating that the max adsorption rate had been exceeded. Termination of the feed resulted in a decrease in sulphide concentration in the recycled liquors. Effluent sulphide concentrations at recycle ratios of 10:1, 15:1 and 25:1 attained equilibrium six hours after feed commencement. Adsorption rates in these cases reached steady-state values after an initial transient period. Since no sulphide was recorded in the effluent at a recycle ratio of 35:1, the low concentrations in the recycled liquors were such that the

maximum adsorption rate was not attained.

The sulphide/sulphate investigations implemented during the continuous loading experiments suggested that sulphide oxidation was a biological mechanism. A 10°C temperature increase was accompanied by an immediate effluent sulphide concentration increase and associated sulphate decrease. As the system regained steady-state conditions, effluent sulphide concentrations decreased slowly, while sulphate concentrations gradually attained a value of 380 mg/l, consistent with that present before the temperature change. Figure 3.12 indicates that sulphate increase lagged behind the sulphide disappearance, steady-state concentrations being reached in 28 days. Had a chemical oxidation mechanism been responsible for the sulphide removal, sulphide and sulphate concentrations would have reached equilibrium values at greater rates than those shown in Figure 3.12. The dependence of a chemical reaction on temperature would have produced an immediate change in reaction rate, with a subsequent product concentration change.

The results may be explained by the presence of a biological mechanism of sulphide removal. Section 1.4.3 of the literature review indicates that the autotrophic sulphur-oxidising bacteria, Thiobacillus thioparus is the most likely organism to oxidise sulphide to sulphate in an alkaline environment (105). The 10°C filter temperature change probably induced a metabolic shock, which required a readjustment of the associated growth cycle. This metabolic shock was accompanied by a sulphide concentration increase in the effluent, and a decreased sulphate concentration. As the microorganisms readjusted to the new operating conditions, sulphide utilisation gradually increased. The lag in sulphate increase is a characteristic of sulphide oxidation by Th. thioparus.

3.4.3 Nitrogen Removal

Maximum nitrogen removal at a recycle ratio of 25:1, evaluated for the batch loading, did not correspond to the maximum COD removal attained at a ratio of 15:1. A 44% total

nitrogen removal was recorded at the former recycle ratio.

Although nitrite and nitrate concentrations were not recorded, according to the pathway presented by Eckenfelder and O'Connor (31), nitrogen is removed in biological waste treatment via a nitrification process. Balakrishnam and Eckenfelder (8) demonstrated that nitrification increased with an increase in hydraulic loading. The results of Table 3.3 fail to confirm this observation, if the assumption of nitrogen removals reflecting nitrification is made. The pH range 8.05-8.85, exhibited by the treated wastes of the present system, is unlikely to have a deleterious influence on nitrogen removal (35).

3.4.4 pH/Alkalinity Considerations

pH and alkalinity investigations were made for batch and continuous operations. These factors have been linked with both chemical and biological sulphide oxidations (18, 105), the latter mechanism possibly implicated in the biological filter.

For both batch and continuous loading, effluent pH was independent of influent pH changes over the influent pH range 9.7-11.5 (Figures 3.11 and 3.13). Walter (128), however, demonstrated that effluent pH was dependent upon influent pH changes in a trickling filter. The effect was more pronounced in the pH range 9-12. Lijklema (70) indicated that alkalinity relationships governed effluent pH changes. Equilibrium relationships presented (Section 1.4.2) involving carbonate, bicarbonate and carbon dioxide, are implicated in the present system.

Tables 3.4 and 3.7 show that carbonate represented the largest portion of the influent, whereas the effluent alkalinity consisted solely of a bicarbonate portion. The pH of the recycled liquors, 8.05-8.75, favoured the conversion of feed carbonate ions to bicarbonate. The bicarbonate ions may participate in a further reaction (Section 1.4.2),

with carbon dioxide formation occurring. This reaction is favoured at pH values below 8.3. The preceding reactions were instrumental in maintaining a pH range in which biological waste stabilisation occurred.

Differences between batch and continuous operation alkalinity data are apparent. Effluent total alkalinity values for batch loading range from 40 to 60% of the corresponding influent values (Table 3.4), whereas effluent values associated with continuous operation (Table 3.7) are equal or slightly greater than corresponding influent total alkalinities. Continuous feeding ensured that the carbonate portion was continually converted to bicarbonate. However, the batch operation had periods of sixteen hours in which no feed was applied. This may have permitted the bicarbonate to participate in a further equilibrium reaction, with subsequent carbon dioxide production. An occurrence of this nature would assist a decrease in total alkalinity.

The pH decrease in both batch and continuous systems is also aided by the sulphate production from sulphide oxidation. Lijklema (70) stated that the production of acid substances during biological purification is a major factor influencing pH change.

3.4.5 Sludge Analysis

A high mean ash content of 27.2% (Table 3.8), of which 75% was calcium determined as calcium oxide, shows that significant lime quantities were precipitated from the influent during treatment. This would have occurred through a carbonation reaction.

Eckenfelder and O'Connor (31) reported that the ash content of most biological sludges is in the range 2-15%. Higher values are due to the presence of non-biological inert substances. Assuming all the calcium determined originated from the lime component, a 7% ash remains which is due to the presence of organic matter. This is in the range presented

by Eckenfelder and O'Connor.

The average nitrogen content of the sludge was 5.2%. Data provided by Hoover and Porges (55) for activated sludge from synthetic dairy waste, indicated a nitrogen content of 12.3%. However, a large non-biological sludge fraction occurred in the present studies, which lowers the true biological nitrogen concentration. An adjusted value of 6.5% is obtained, which is markedly lower than the value presented by Hoover and Porges (55). This difference may be attributed to the influence of pH and environmental factors on sludge composition (31).

Sludge settling investigations demonstrated that very rapid settling rates were obtained at a total solids concentration of 6460 mg/l and smaller. Figure 3.14 shows that hindered particle settling occurred at a solids concentration of 12,620 mg/l, unhindered settling being achieved at the remaining concentrations. The rapid settling rates are attributed to the lime component of the sludge.

3.4.6 Oxygen Transfer in the Filter

The oxygen transfer investigations were of prime importance in comparing the rate of sulphide removals in the biological filter and the fermenter. However, the relationship of liquid flow rate through the filter with overall mass transfer is briefly considered.

Determination of $K_L a$ based on a liquid volumetric basis revealed that $K_L a$ decreased with increased flow rate (Q) through the column. A relationship of the form

$$K_L a = S e^{-0.0058Q}$$

was obtained, where S is some function of temperature, system geometry and fluid properties. This increase may have occurred by virtue of the increased liquid hold-up in the filter with increasing liquid flow rate.

In contrast the true $K_L a$ values, based on the volume of packing, increased over the flow range studied to a maximum at a flow of 180 l/hr. The magnitude of these values, 5.1-8.55 hr^{-1}, was relatively low compared with that of the fermenter, 311 hr^{-1} (Section 4.3.6). This $K_L a$ increase with increased flow rate is similar to that reported by Sherwood and Holloway (102).

CHAPTER FOUR

COMPARISON OF CHEMICAL AND BIOLOGICAL REMOVALS OF SULPHIDE - FERMENTER STUDIES

4. COMPARISON OF CHEMICAL AND BIOLOGICAL REMOVALS OF SULPHIDE - FERMENTER STUDIES

4.1 Introduction

Data obtained from the biological filter continuous operation suggested that sulphide oxidation occurred by a biological mechanism. To assess the degree of biological oxidation the previous results were complemented with studies of the aeration of sulphide, lime-sulphide and fellmongery waste solutions. The effect of pH and filter biomass on sulphide removal rates were investigated. Little work has been published regarding the influence of pH on aerated sulphide wastes.

Factors affecting the rate of chemical oxidation of sulphide in the waste were also studied. For the chemical oxidation of sulphide, oxygen must be transferred from the gaseous phase to the bulk liquid, where it may undergo chemical reaction with the sulphide to form a product dependent upon the initial pH and type of reacting system (18). Eckenfelder and O'Connor (31) indicated that the components of a waste may have a marked effect on the degree of oxygen transfer in solution.

Additions of manganese in trace quantities to inoculated and uninoculated wastes were made to investigate the extent of its reported effect on the metabolism of the sulphur-oxidising bacteria (85).

Studies were carried out in a small laboratory fermenter. This had facilities for metered air flow, agitator and temperature control.

4.2 Materials and Methods

4.2.1 Solutions and Waste Samples

Three different systems were used in these investigations:-

(1) Pure sulphide solutions: made up from hydrated sodium sulphide and tap water.

(2) Lime-sulphide solutions: solutions comprising hydrated sodium sulphide in a concentration range 80 - 100 mg/l, and calcium hydroxide (lime) in concentrations of 50, 100, 200, 500 and 1000 mg/l. The solution pH was maintained at a constant value of 10.85.

(3) Waste: fellmongery effluent identical in composition to that treated in the biological filter was used.

The pH of the above solutions was adjusted by additions of HCl, NaOH, $NaHCO_3$ or Na_2CO_3.

For the biological aeration studies, inocula were prepared from biomass collected from the filter. The biomass was then incubated with 200 ml of waste, similar in composition and pH to the waste used in system (3), and subsequently placed in an orbital incubator at 23°C and 100 rpm, for 24 hours prior to inoculation.

Manganese was added in the form of manganese chloride at a concentration of 10 mg/l.

4.2.2 Fermenter Design and Operation

Aeration was carried out in a 5 litre glass fermenter, shown in Figure 4.1. The operating conditions for each experiment were:-

(1) Airflow = 0.033 m^3/sec (2000 cc/min) at 1.013 N/m^2
(2) Agitator speed = 215 rpm
(3) Temperature = 23°C

5 litre volumes were aerated for periods ranging from 360 to 420 minutes in each experiment. Samples were withdrawn at approximately 20 minute periods for analysis. The frequency of analysis was greater at the commencement of an experiment.

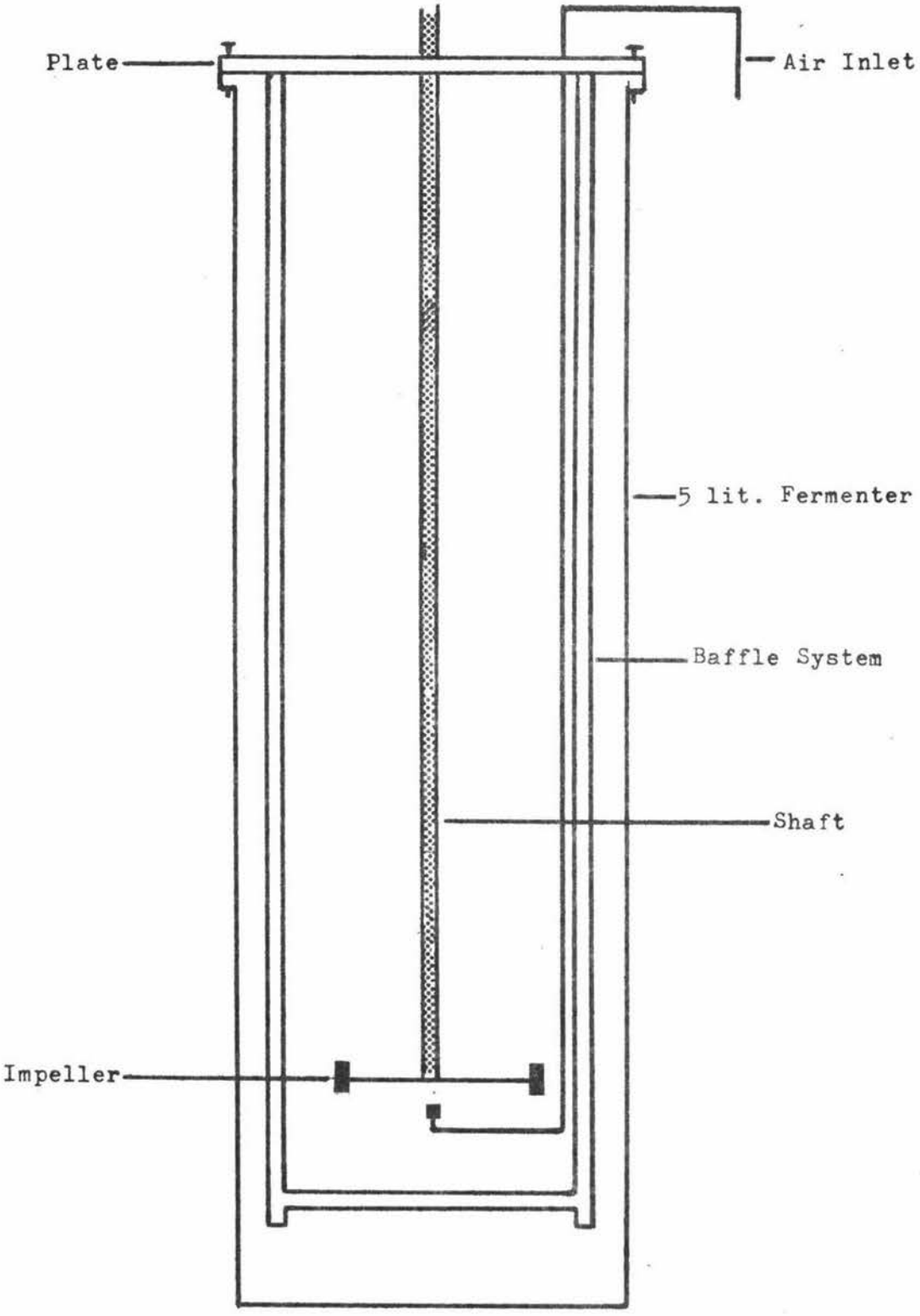

Figure 4.1 Laboratory-Scale Fermenter

4.2.3 Analytical Techniques

Sulphide, sulphate and pH values were determined as described in Section 3.2.3. Attempts were made to determine thiosulphate and sulphite concentrations in the solutions, but a satisfactory method was not found. Problems were encountered when sulphur compounds in solution interfered with each other on executing the analytical procedure. Several titrimetric methods were investigated, which, while proving satisfactory for pure solutions, were unsuitable for solutions with mixed sulphur components.

4.3. Results

This section is divided into five parts. The first three deal with the aeration of pure sulphide, lime-sulphide and waste solutions, while the remaining two involve the inoculation of the waste solutions with filter biomass.

4.3.1 Aeration of Pure Sulphide Solutions of Different pH Values

The change in sulphide concentration with time of aeration for pure sulphide solutions is presented in Figure 4.2. It shows that as the initial pH of the solution is increased, the rate of sulphide removal decreases. At pH 10.85, the highest value tested, the rate of sulphide removal decreased to zero, no removal being observed for the first 77 minutes of aeration.

The same results were replotted in Figure 4.3 on a semi-logarithmic scale to determine a rate constant, K (logarithmic rate), for the reaction. K values obtained at each pH are shown below:

Initial pH	9.00	9.40	9.85	10.20	10.85
Log. Rate K(mg/l.min)	0.0137	0.010	0.008	0.00275	0.0026

Table 4.1 summarises the data obtained from this experiment

in terms of the S ratio, defined in Section 3.3.2, at the end of each run.

Sulphate concentrations were found to increase for all the initial pH values investigated. However, examination of the values indicates a relative decrease in formation of sulphate with increasing pH values.

4.3.2 Aeration of Constant pH Lime-Sulphide Solutions of Varying Lime Concentrations

The effect of a varying lime concentration on the oxidation of sulphide in solution was investigated in a manner similar to that described in the previous section. The pH of the solutions was maintained at a constant value of 10.85. pH values below this are conducive to lime precipitation and are liable to cause variations in initial lime concentrations.

Sulphide concentrations are plotted against aeration time in Figure 4.4 and curves similar to those observed in Section 4.3.1 were obtained. For all lime concentrations, the rate of logarithmic sulphide decrease is given by K = 0.00315 mg/l. min (Figure 4.5). This rate is greater than those presented for pure sulphide solutions at pH 10.20 and 10.85, 0.00275 and 0.0026 mg/l.min respectively, since carbon dioxide in the air stream caused the lime in solution to precipitate, thereby lowering the system pH. This progressive pH lowering resulted in greater sulphide removals, as shown in Section 4.3.1.

The semi-logarithmic plot of the results in Figure 4.5 indicated an average time of 80 minutes before the reaction started. The mean value closely corresponds to 77 minutes obtained for pure sulphide solution of pH 10.85.

S values for the aeration of the lime solutions shown in Table 4.2 are similar to the value of 5.08 achieved for the pure sulphide solution at an initial pH of 10.85.

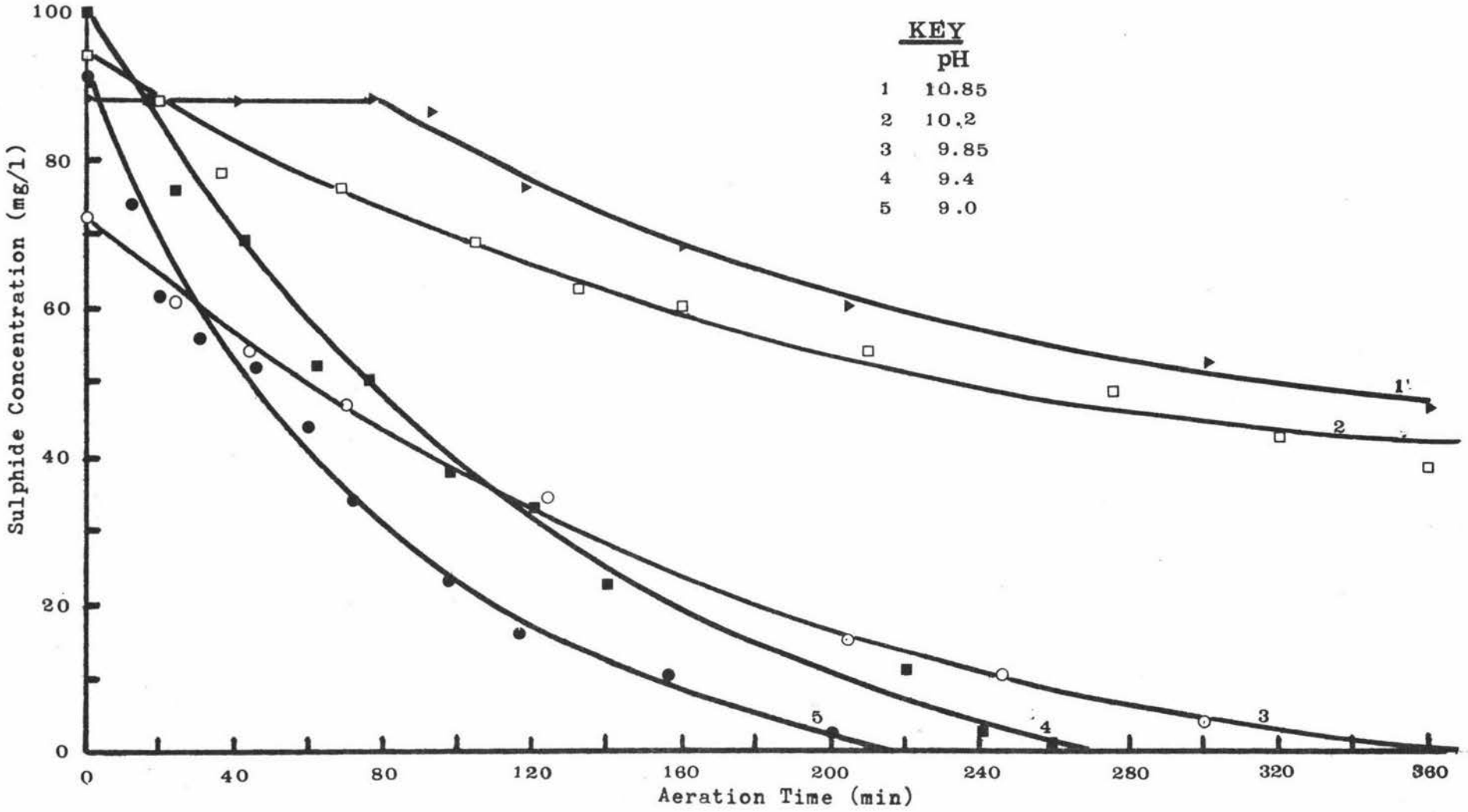

Figure 4.2 Sulphide Concentration versus Aeration Time: Pure Sulphide Solutions

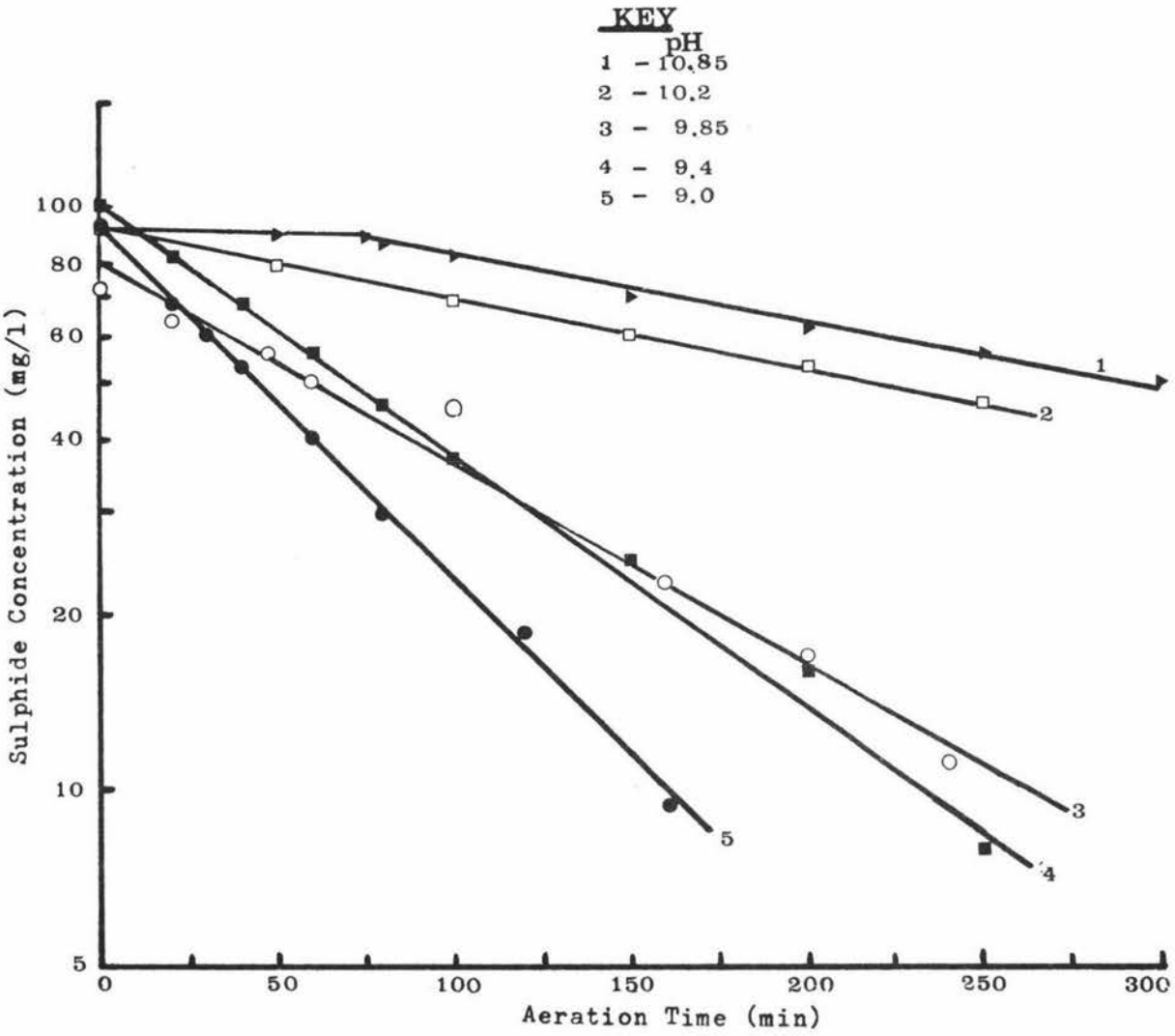

Figure 4.3 Logarithmic Sulphide Removals for the Aeration of Pure Sulphide Solutions

TABLE 4.1

A DATA SUMMARY FOR THE AERATION OF PURE SULPHIDE SOLUTIONS

Initial Data			Final Data				
Sulphide	Sulphate	pH	Aeration Time	Sulphide	Sulphate	pH	S
mg/l	mg/l		min.	mg/l	mg/l		
92	14	9.00	200	3	160	7.85	1.84
102	19	9.40	240	2	140	8.10	2.48
76	16	9.80	320	2	100	8.90	2.64
94	16	10.20	360	39	70	9.40	3.06
89	17	10.85	370	67	30	9.95	5.08

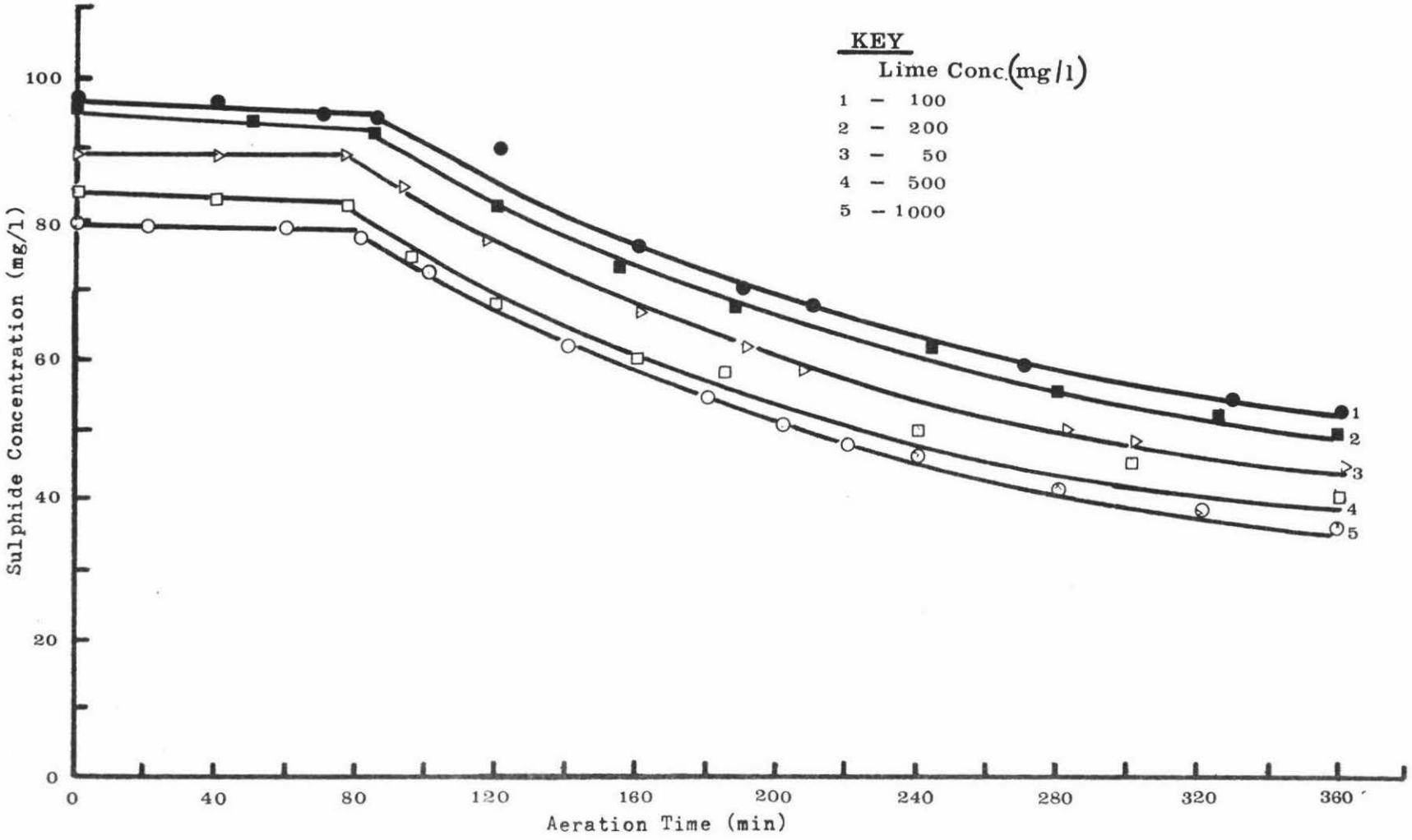

Figure 4.4 Sulphide Concentration versus Aeration Time: Lime-Sulphide Solutions

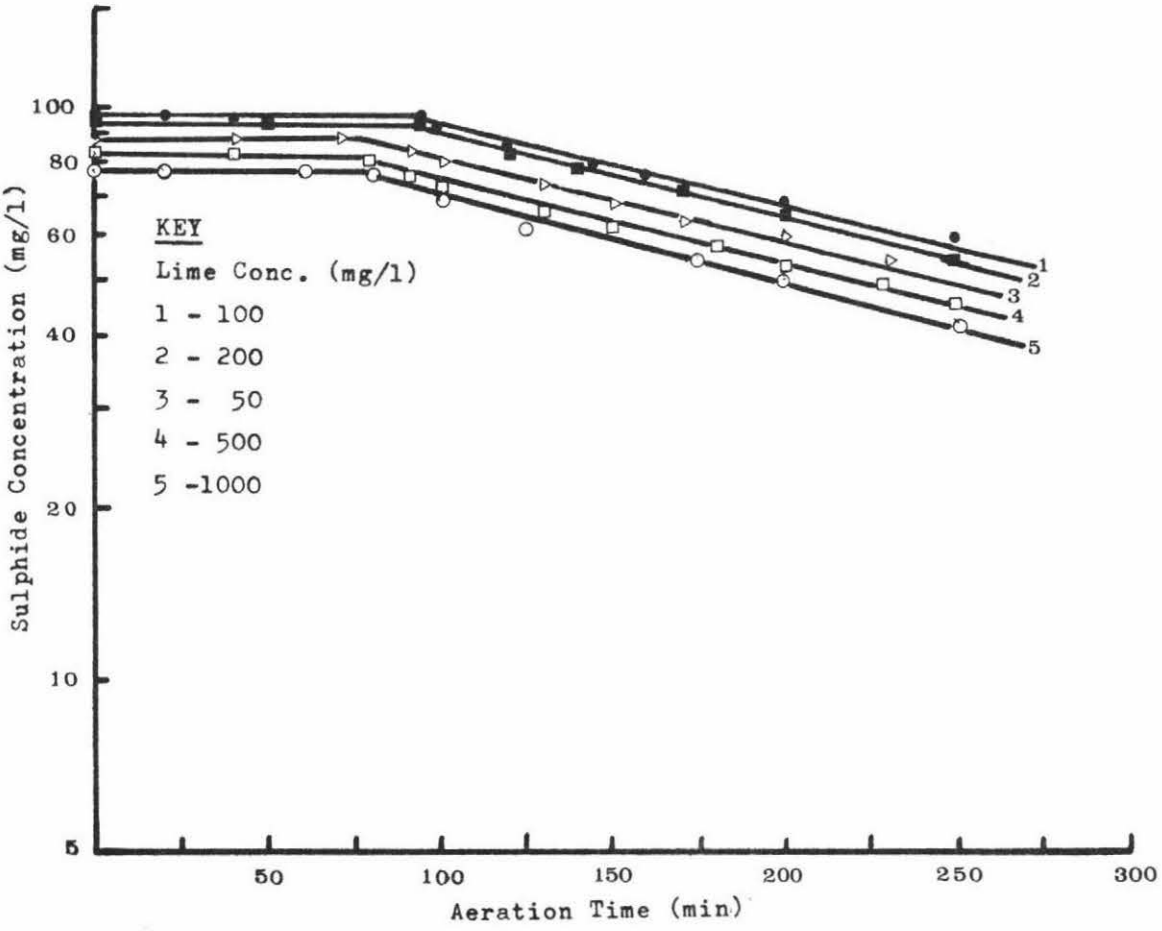

Figure 4.5 Logarithmic Sulphide Removals for the Aeration of Lime-Sulphide Solutions

TABLE 4.2

A DATA SUMMARY FOR THE AERATION OF LIME-SULPHIDE SOLUTIONS

(Constant initial pH 10.84)

Initial Data			Final Data			S
Sulphide	Sulphate	Lime	Aeration Time	Sulphide	Sulphate	
mg/l	mg/l	mg/l	min.	mg/l	mg/l	
89	16	50	380	44	40	5.61
98	18	100	380	52	45	5.10
97	18	200	380	50	40	6.41
84	15	500	380	41	35	6.05
80	17	1000	380	36	45	4.70

4.3.3 Aeration of Fellmongery Wastes of Varying pH

The elimination of sulphide from fellmongery waste by aeration was studied in the same way as for pure sulphide solutions (4.3.1) and lime-sulphide solutions (4.3.2).

Graphs of change in sulphide concentration with aeration times are shown in Figure 4.6. Semi-logarithmic plots of sulphide concentration with time are presented in Figure 4.7. Logarithmic removal rates, K, calculated from the gradients of Figure 4.7 are tabulated as follows:

Initial pH	9.15	9.55	9.95	10.50	10.85
Log Rate K(mg/l,min)	0.0092	0.00465	0.0018	0.00063	0.00038

The logarithmic removal rates are substantially lower than those obtained in the two preceding series of experiments for similar initial pH values. The times required before any reaction occurred (shown in Figures 4.6 and 4.7) diminish as the initial pH of the solution is decreased.

Over the pH range investigated no significant net increase in sulphate concentration of the solutions was observed (Table 4.3). A decrease in pH observed during each run may be attributed to the precipitation of lime by carbon dioxide present in the air. A sediment formed on the bottom and sides of the fermenter which may have been precipitated lime.

4.3.4 The Effect of the Addition of Column Biomass on the Removal of Sulphide from Fellmongery Waste at Varying pH

The effect of biomass inoculation on sulphide removal from wastes of varying initial pH is shown in Figure 4.8. Figure 4.9 is a graph of the logarithmic sulphide concentration against aeration time. At the initial pH values 9.55 and 10.20, there are two linear portions of the semi-logarithmic plots. The first portion is termed K_a and the second K_b.

This is contrary to the shape of the curves for the aeration of fellmongery waste with no inoculum and at similar initial pH values. The graphs of change in logarithmic sulphide concentration with aeration time were of one slope during aeration for the remaining pH values.

Logarithmic removal rates from Figure 4.9 had the following values:-

Initial pH	9.55		10.20		10.40	10.90
Log. rate K(mg/l.min)	K_a	K_b	K_a	K_b		
	0.0056	0.0139	0.0042	0.0077	0.0021	0.00082

It is reported that the time of the appearance of sulphate in the medium will lag behind that of sulphide disappearance (105). Consequently, two experiments were run for extended periods to verify this. An initial waste pH of 9.55 was maintained for samples with and without inocula. This pH was chosen as being most likely to permit sulphide oxidation by a biological mechanism (105). With both runs, aeration was terminated after 400 mintues owing to excessive foaming. However, agitation was maintained. A direct result of this change would have been to decrease the rate of oxygen supply to the solutions, with possibly a consequent decrease in biomass metabolic activity. This may have extended the time of sulphate synthesis by the organisms.

Figure 4.10 demonstrates sulphide and sulphate concentrations of the inoculated and uninoculated systems as a function of time over the first 1100 minutes of the experiment. Sulphide removal is complete in the inoculated sample, but little change in sulphate concentration is observed over this time. Figure 4.11 presents the relative sulphate increase of the inoculated and uninoculated systems over the total experimental period, 5 days. The uninoculated sample showed a sulphate concentration increase of only 35 mg/l over 5 days, whereas an increase of 247 mg/l was obtained in the

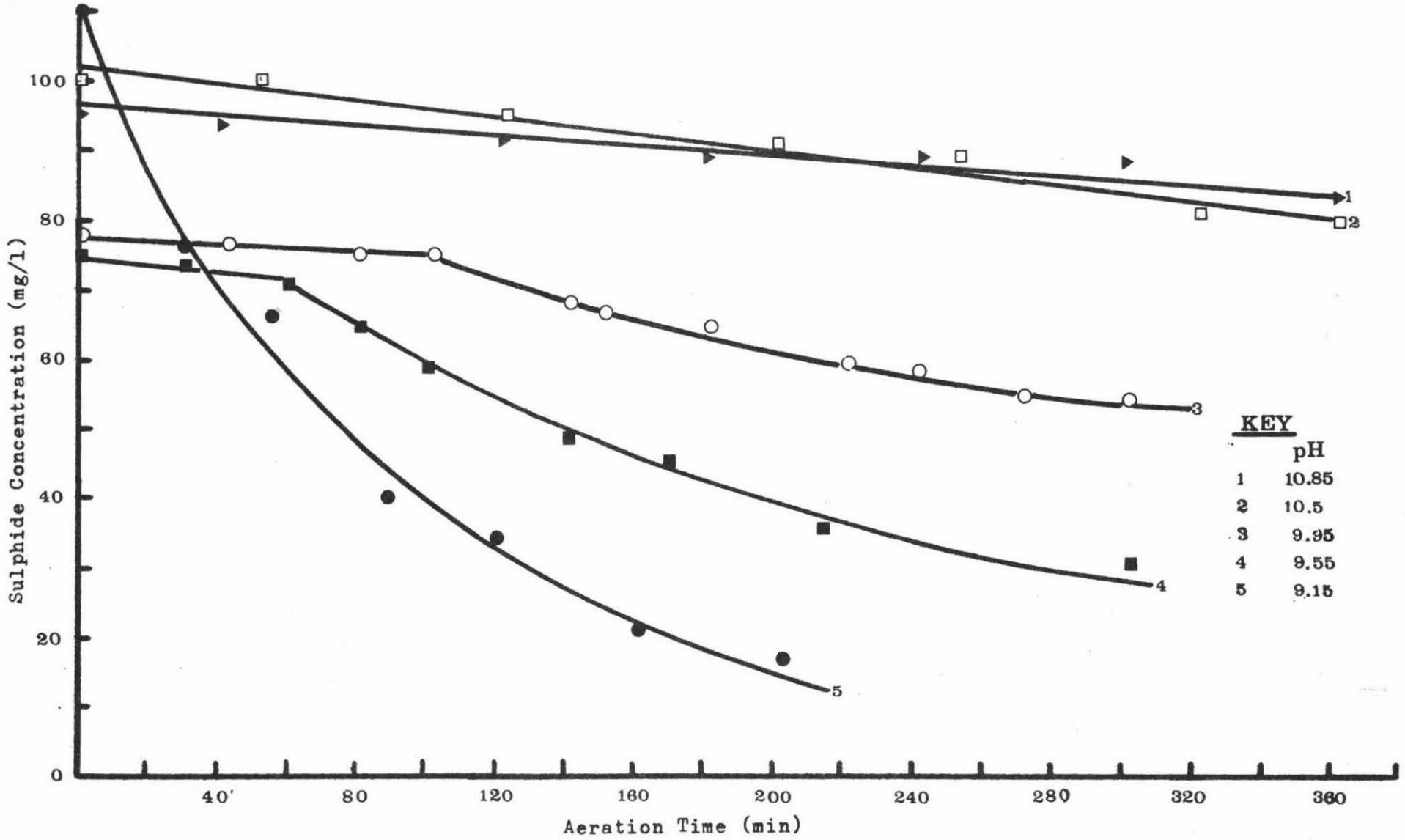

Figure 4.6 Sulphide Concentration versus Aeration Time: Fellmongery Wastes

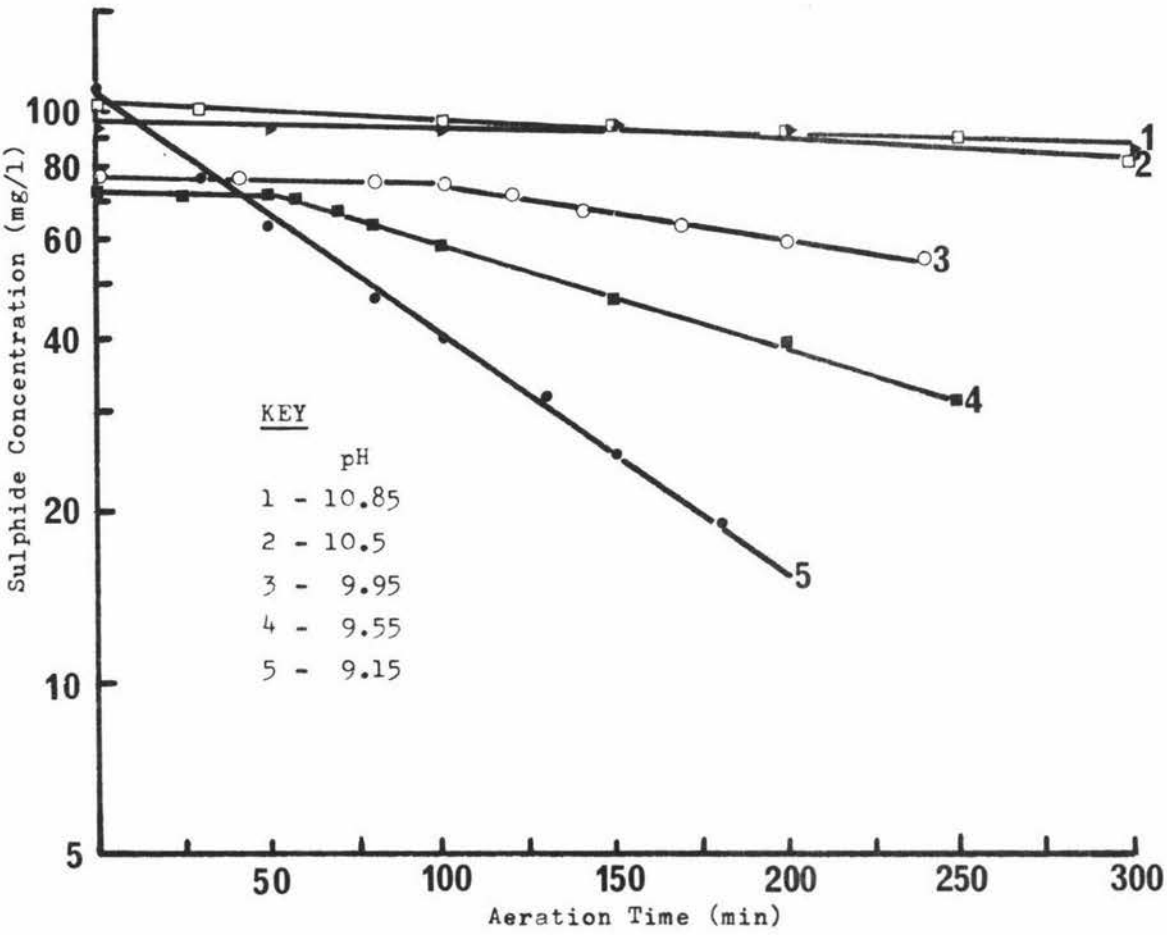

Figure 4.7 Logarithmic Sulphides Removals for the Aeration of Fellmongery Wastes

TABLE 4.3

A DATA SUMMARY FOR THE AERATION OF FELLMONGERY WASTES

Initial Data			Final Data				S
Sulphide	Sulphate	pH	Aeration Time	Sulphide	Sulphate	pH	
mg/l	mg/l		min.	mg/l	mg/l		
110	100	9.15	200	17	136	8.90	7.63
73	96	9.55	300	31	111	9.15	8.40
77	107	9.95	300	55	112	9.50	13.20
100	53	10.50	420	80	53	10.15	∞
95	94	10.85	420	83	94	10.55	∞

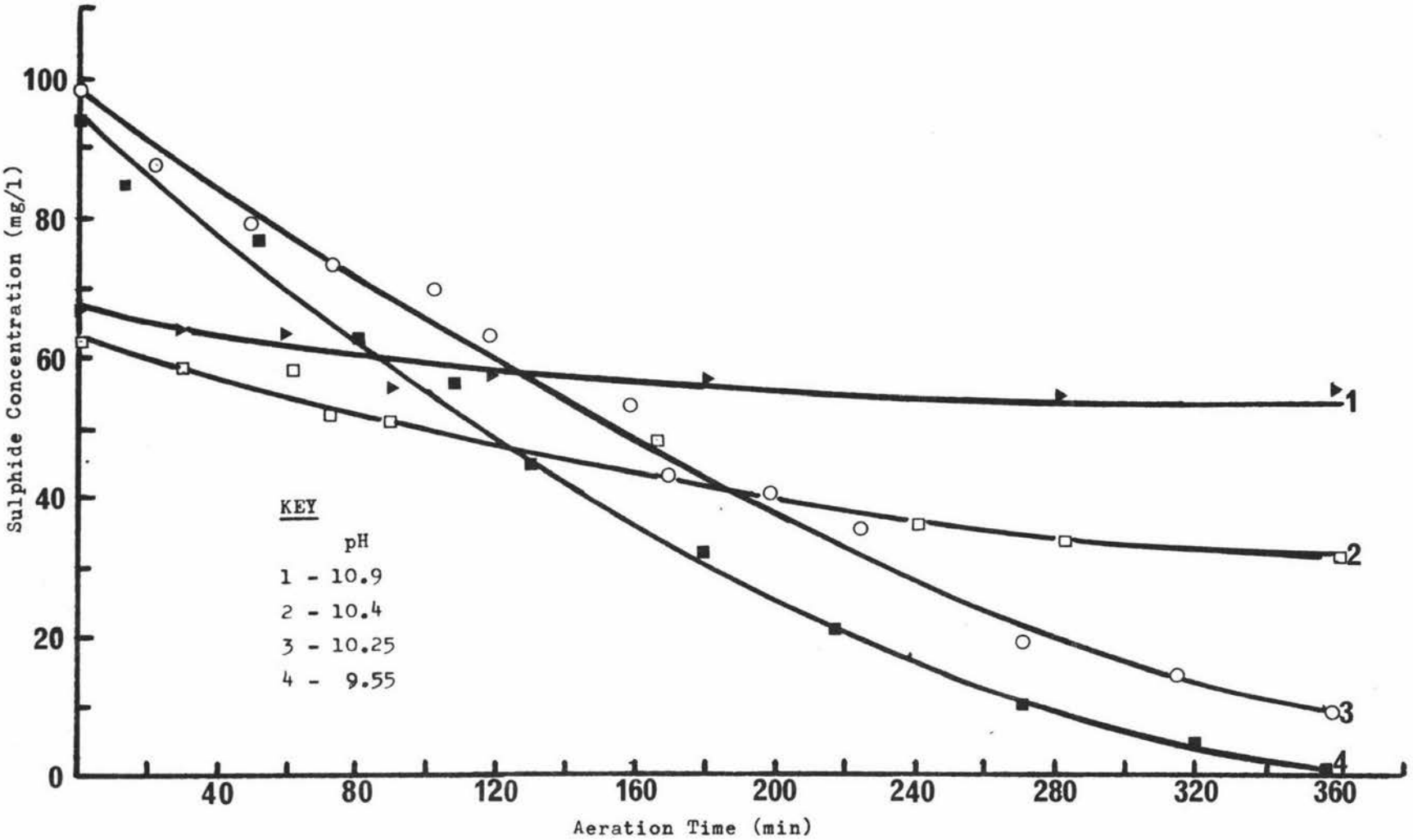

Figure 4.8 Sulphide Concentration versus Aeration Time: Inoculated Fellmongery Wastes

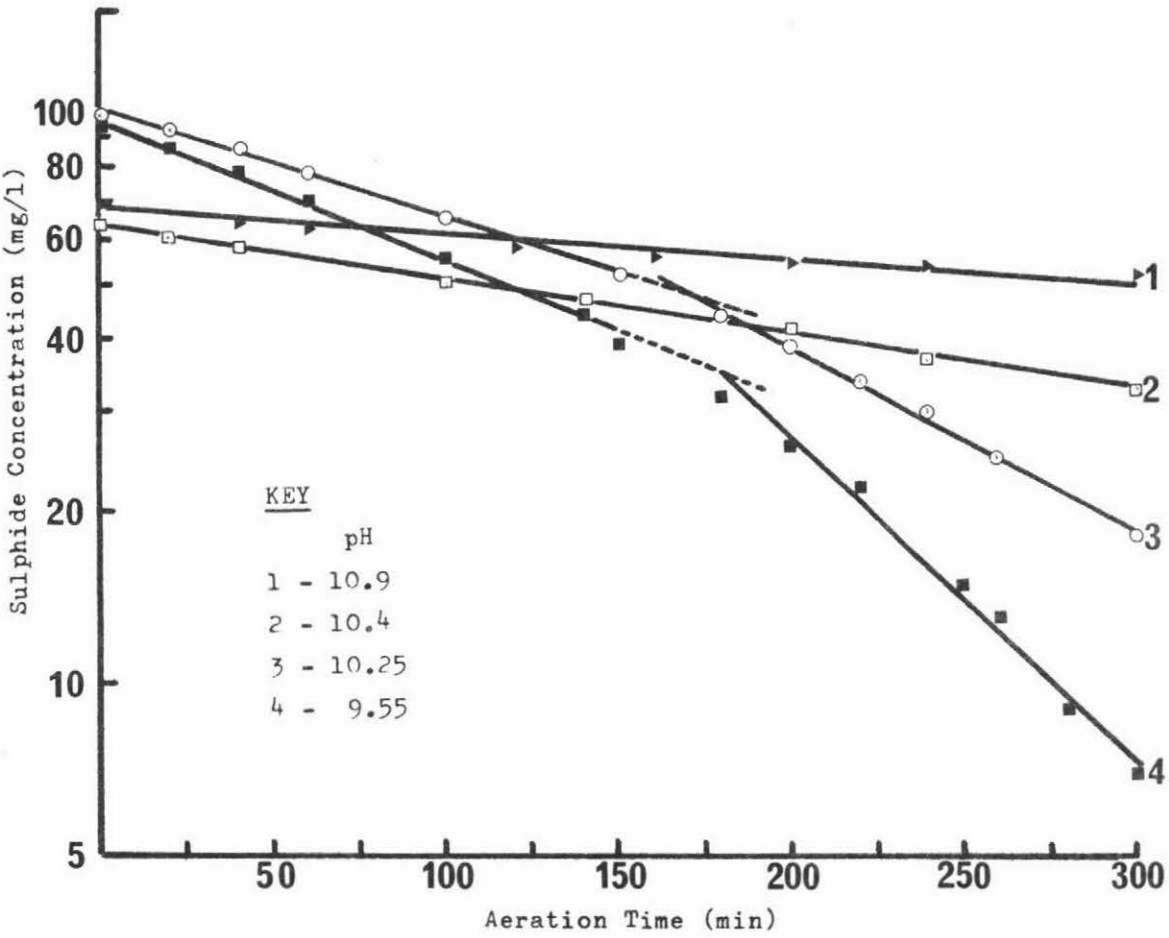

Figure 4.9 Logarithmic Sulphide Removals for the Aeration of Inoculated Fellmongery Wastes

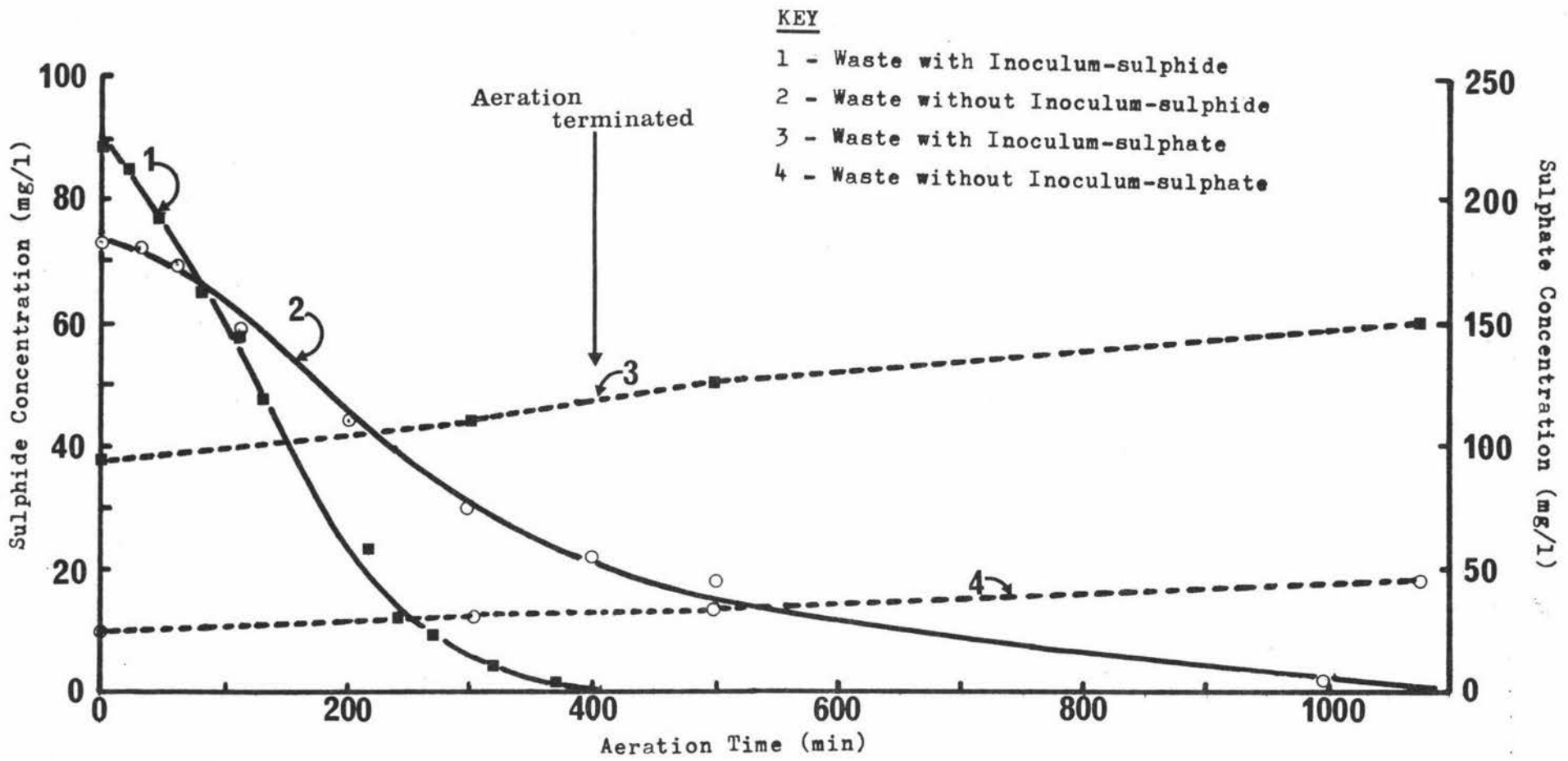

Figure 4.10 Changes in Sulphide and Sulphate Concentrations with Aeration Time for Inoculated and Uninoculated Fellmongery Waste of Initial pH 9.55

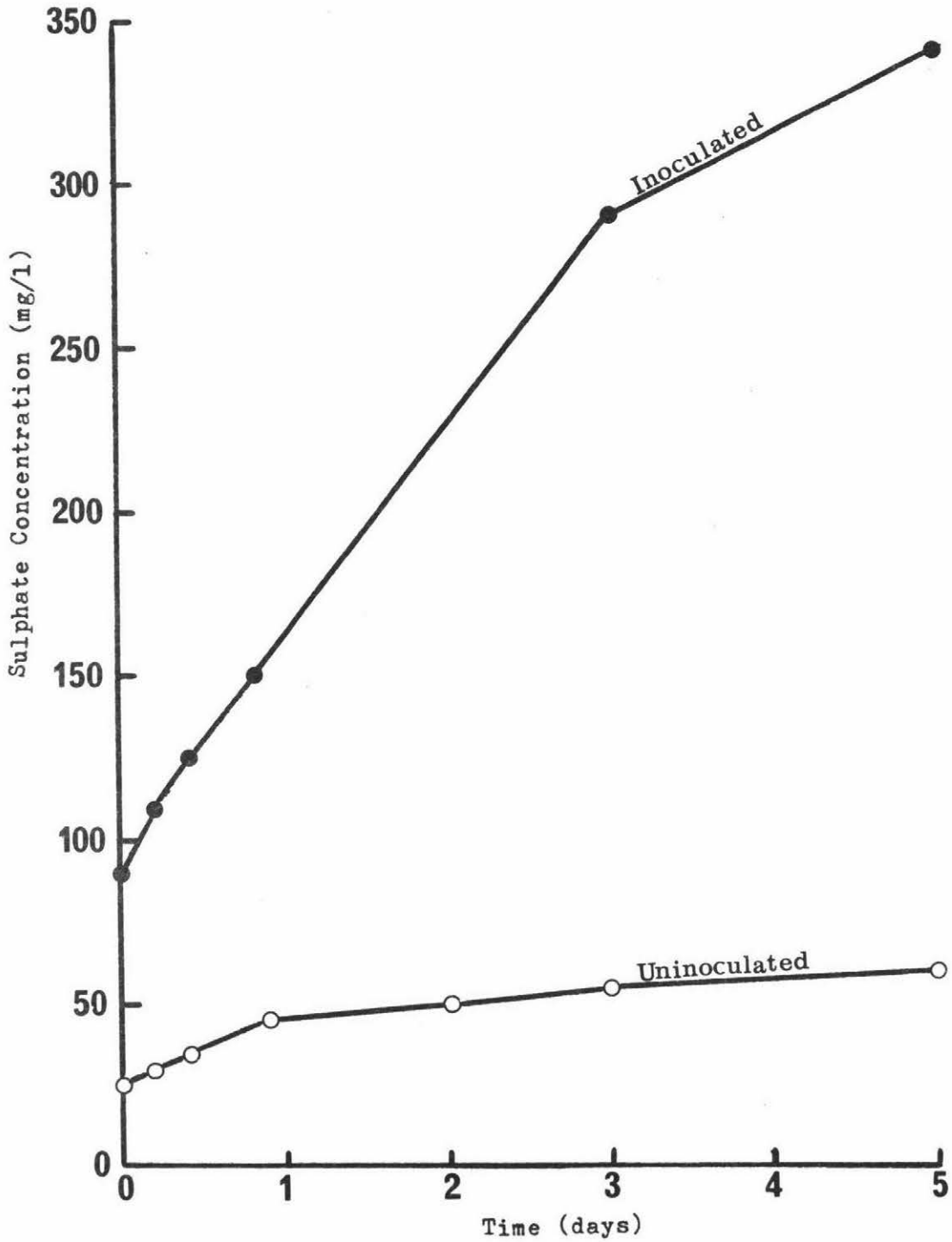

Figure 4.11 Sulphate Increases for Inoculated and Uninoculated Fellmongery Wastes of Initial pH 9.55

inoculated sample. This resulted in S values of 1.06 and 4.9 for the inoculated and uninoculated systems respectively. pH values after 5 days were 8,55 for the uninoculated and 7.50 for the inoculated. Lime precipitation occurred in both samples and accounted for the fall in pH. The lower pH of the inoculated sample may be attributed to the high sulphate concentration.

4.3.5 The Influence of Manganese on the Chemical and Biological Removal of Sulphide in Fellmongery Wastes

A procedure similar to that described in Section 4.3.4 was pursued to determine the effect of manganese on the rate of sulphide removal from samples of waste, half of which were inoculated with column biomass. The uninoculated fraction of these samples were control systems for the inoculated samples.

Results are shown in Figures 4.12, 4.13, 4.14 and 4.15. Logarithmic sulphide removal rates, calculated from Figures 4.12 and 4.13 are different from the corresponding values in the previous experiments (Sections 4.3.1, 4.3.2, 4.3.3 and 4.3.4).

Figure 4.15 shows that with a waste at an initial pH 9.60, containing manganese and inoculum, the logarithmic sulphide removal is non-linear. This is contrary to the behaviour demonstrated in the experiments with no manganese addition. Linear plots were obtained at the other pH values investigated. Although the shape of the graph for the initial pH of 9.60 prevented the calculation of a meaningful logarithmic rate constant, it does show that the removal rate is greater than others presented for pH 9.55 - 9.60 (Figures 4.3, 4.7, 4.9 and 4.14).

Graphs of logarithmic sulphide concentration versus time for solutions of pH 9.60, 10.20, 10.50 and 10.90 without inocula (controls) are presented in Figure 4.14. These similarly exhibit an unusual pattern. All the graphs consist of two linear portions, the first of which has a slope greater

than the second.

Logarithmic sulphide removal rates for both systems are presented below; K_a and K_b are described as in Section 4.3.4.

	Initial pH	9.60		10.20		10.50		10.90
C	Log.rate K(mg/l. min)	K_a	K_b	K_a	K_b	K_a	K_b	$\rightarrow 0$
		0.0045	0.00295	0.00305	0.00092	0.0021	0.00075	
I	Log.rate K(mg/l. min)	not determined		0.0074		0.00245		$\rightarrow 0$

C = Control; I = Inoculated

Sulphate increases in the control and inoculated samples at pH 9.60, shown in Figure 4.15, follow the same pattern as shown in Figure 4.11. A lag in the appearance of sulphate, following sulphide removal, occurred in the inoculated sample, but little sulphate increase occurred in the control. Although the experiment was run for 5 days, aeration was terminated after 7 hours owing to foaming. An S value of 1.02 resulted for the inoculated sample and a value of 5.7 for the control.

Terminal pH values for the control and inoculated sample were 8.45 and 7.30 respectively. These correspond with the values of 8.55 and 7.50 obtained in the studies of biological oxidation without manganese addition (Section 4.3.4).

4.3.6 Determination of $K_L a$ for the Fermenter

To compare the oxygen transfer capabilities of the fermenter and biological filter, a $K_L a$ determination was carried out in the fermenter at 23°C, 2000 cc/min air flow rate, 215 RPM agitator speed and a liquid volume of 5 l. The sulphide oxidation method described in Section 3.2.3.10 yielded a value of 311 hr^{-1} for the oxygen transfer coefficient. This coefficient is based on the liquid volume.

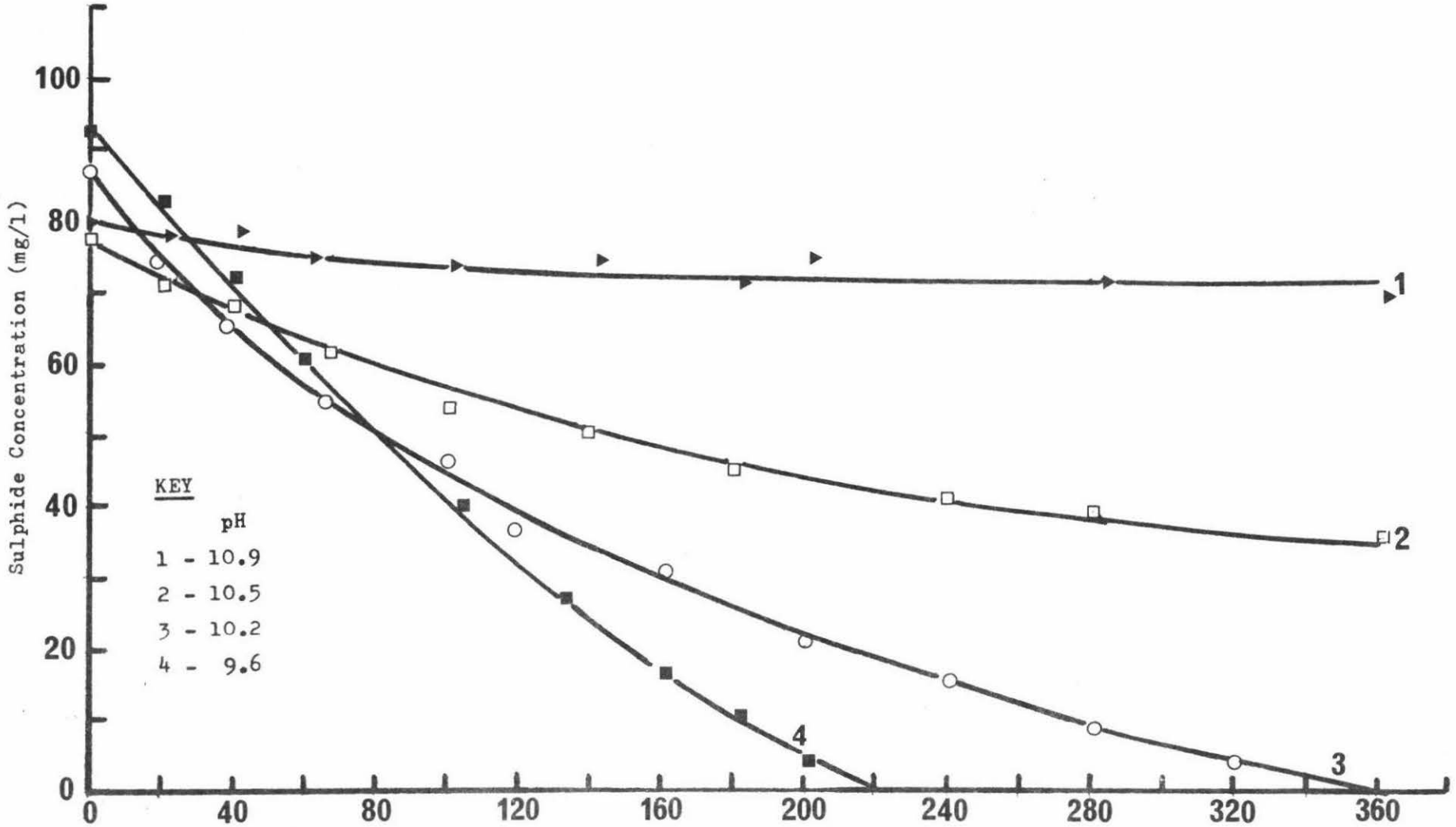

Figure 4.12 Sulphide Concentration versus Aeration Time: Manganese Additions to Inoculated Fellmongery Waste

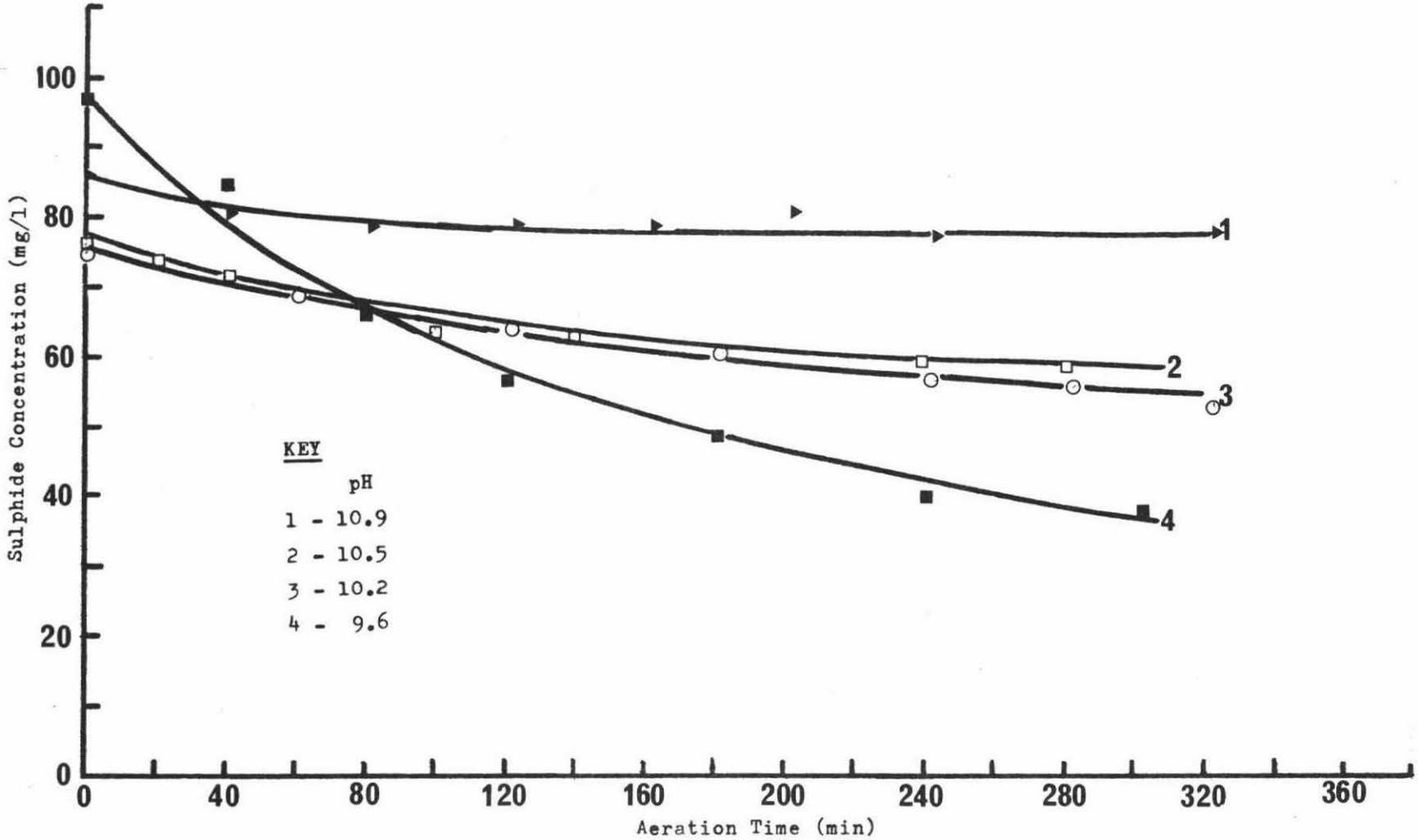

Figure 4.13 Sulphide Concentration versus Aeration Time: Manganese Additions to Uninoculated Fellmongery Waste

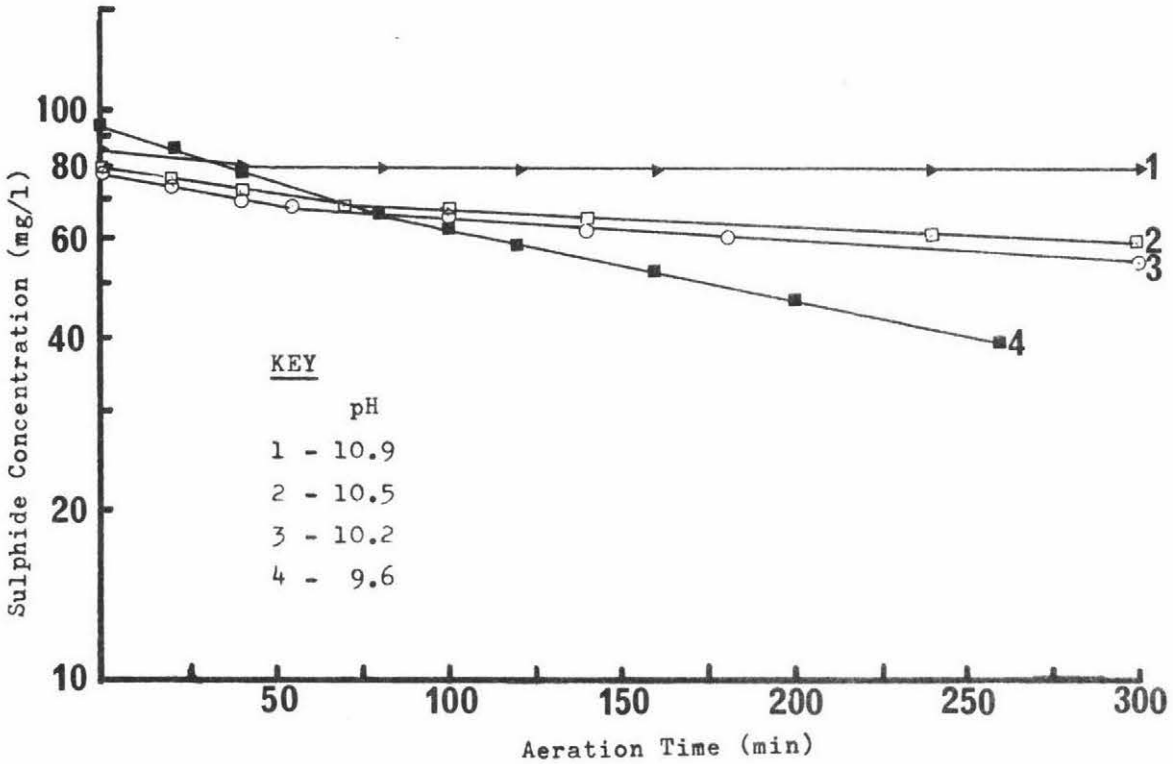

Figure 4.14 Logarithmic Sulphide Removals for Manganese - Uninoculated Fellmongery Wastes

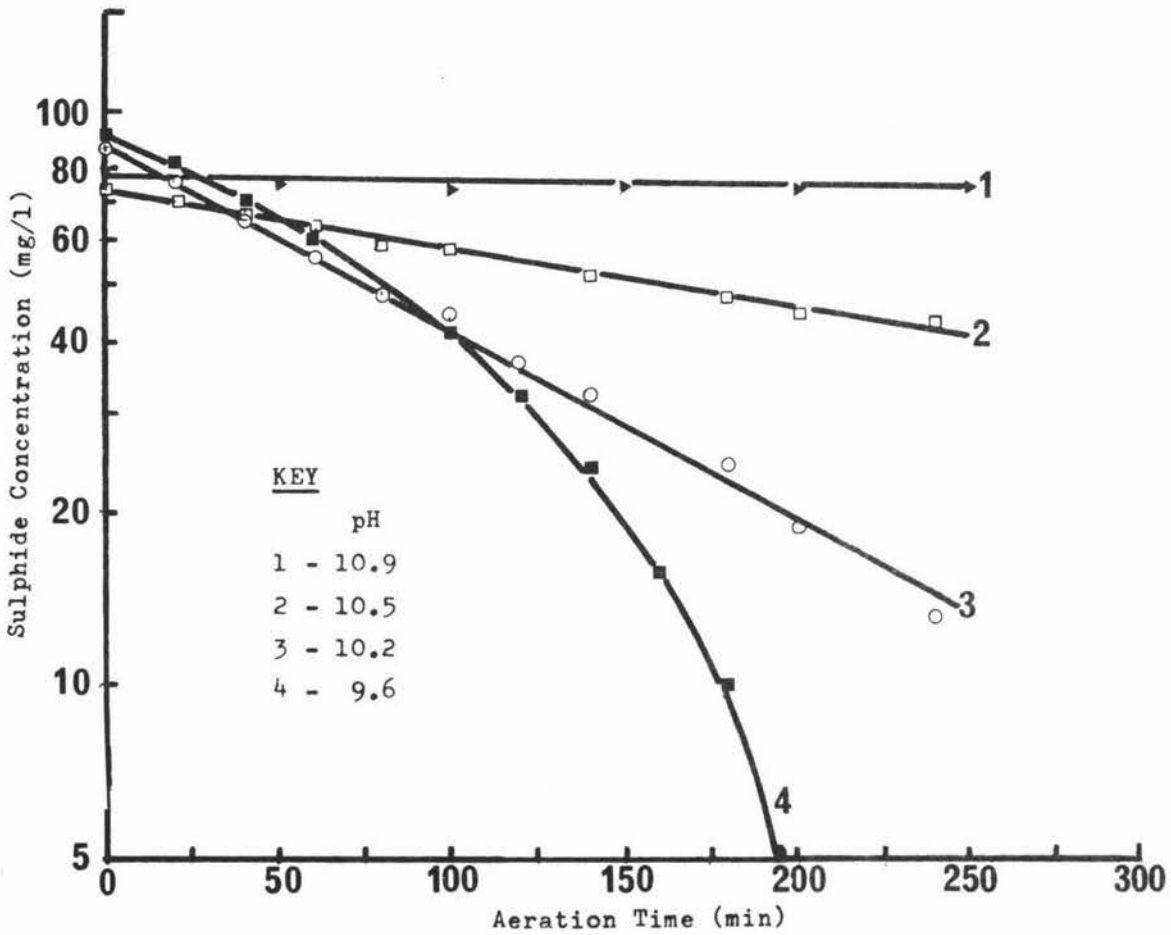

Figure 4.15 Logarithmic Sulphide Removals for Manganese - Inoculated Fellmongery Wastes

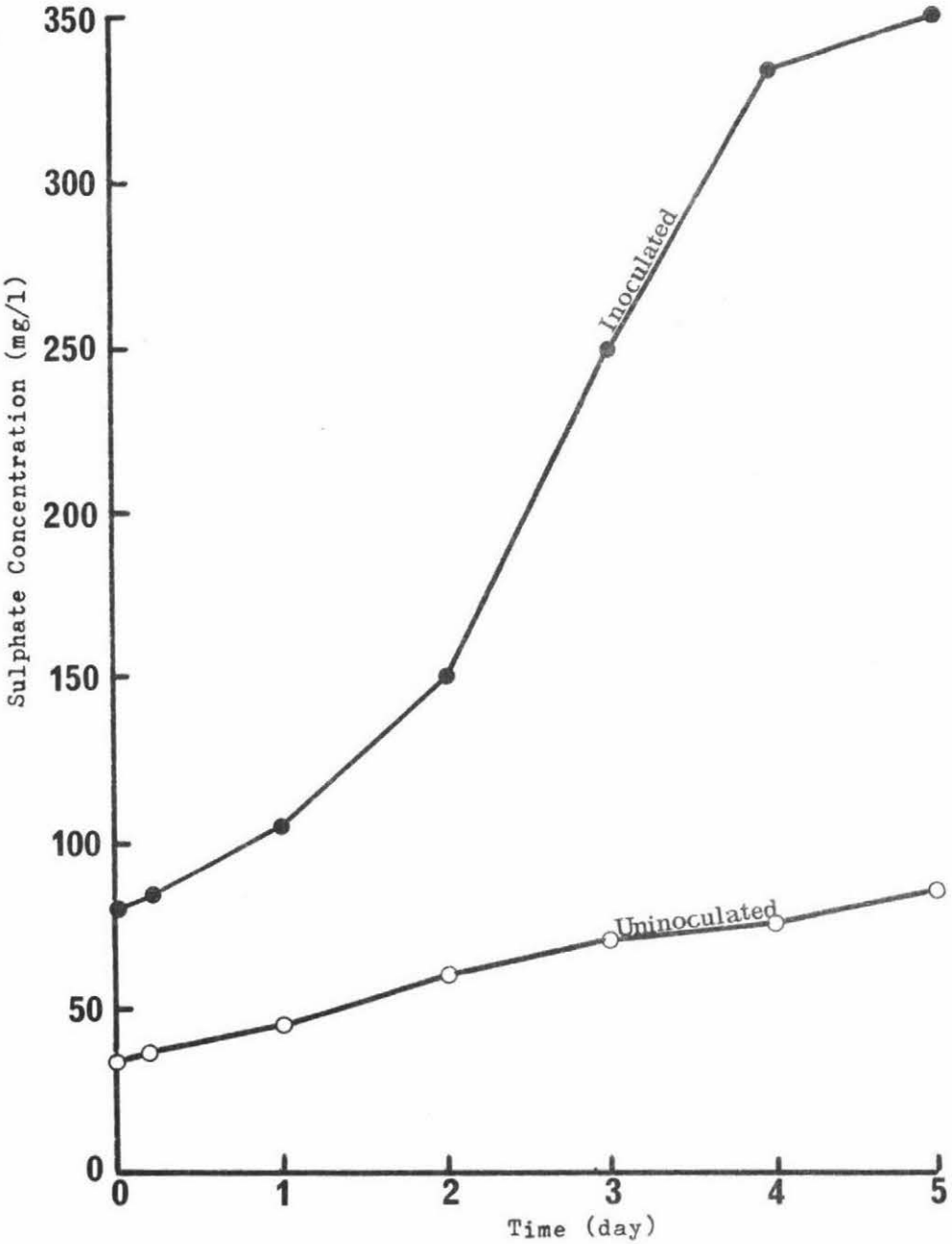

Figure 4.16 Sulphate Increases for Manganese Inoculated and Uninoculated Fellmongery Waste of Initial pH 9.60

4.4 Discussion

4.4.1 Aeration of Pure Sulphide, Lime-Sulphide and Fellmongery Waste Samples

The aeration of pure sulphide, lime-sulphide and fellmongery waste solutions permitted an investigation to be made of the effect of individual components of the waste on the rates of chemical and biological oxidation of sulphide. Within this framework the effect of initial pH of the solution was also studied. Graphs of changes in logarithmic sulphide concentration with aeration time, similar to those used by Espino and Gloyna (36), yielded linear curves, the gradients of which characterised the rate of sulphide decrease. These gradients designated K (mg/l.min) were a measure of the oxidative rate in a respective system.

Aeration of pure sulphide solutions indicated that the initial solution pH influences the rate of sulphide removal (Figure 4.2). The curve obtained with an initial pH 10.85, differs from those achieved at pH values of 9.00, 9.40, 9.85 and 10.20. There was no decrease in sulphide concentration for the first 77 minutes of aeration at the pH 10.85. This was not observed at the remaining pH values. The literature revealed no data on this process and it is suggested that this period of zero rate of decrease is a function of alkalinity and pH.

S values reflected a decrease in sulphate concentration with increase in initial solution pH (Table 4.1). On a sulphur basis, a 54% conversion of sulphide to sulphate was achieved at pH 9.00, and 19.5% conversion resulted at pH 10.85. Solution pH values decreased as a result of the presence of sulphate and also, the alkalinity reactions involving Na_2SO_3, which was used to adjust the initial pH. The alkalinity reactions follow those described by Lijklema (70), involving carbonate, bicarbonate and carbon dioxide interactions.

Equilibrium water-sulphide diagrams, shown in Figure 1.2, indicate that pure sulphide solutions, when aerated, fall into

a stable system classification. This is demonstrated by the conversion of sulphide to sulphate in quantities dependent upon the initial pH. Sulphate is not an oxidation product of a metastable system.

Sulphide removal rates in lime-sulphide solutions were evaluated to determine the effect of varying lime concentrations. Lime, an important component of fellmongery waste, contributes to its high alkalinity. The logarithmic removal rates determined from Figure 4.5, for lime concentrations of 50, 100, 200, 500 and 1000 mg/l, were identical. The K value obtained, 0.00315 mg/l.min, was greater than the value of 0.0026 mg/l.min for the pure sulphide solution with an initial pH 10.85. This difference is attributed to the relative alkalinities present in each solution. Na_2CO_3 was used to adjust the pH of the pure sulphide solutions, whereas the lime provided the alkalinity portion of the lime-sulphide solutions. Precipitation of the lime, on aeration, results in an alkalinity decrease, which, from pure sulphide solution studies, is conducive to greater sulphide removal rates.

The average period of zero sulphide decrease for the lime-sulphide solutions was 80 minutes, which was almost the same as the 77 minutes shown for a pure sulphide solution of initial pH 10.85.

The average value of S was 5.57 for lime-sulphide solutions. This corresponds to an18% conversion of sulphide to sulphate on a sulphur basis and compares closely with the 19.5% conversion achieved for a pure sulphide solution of initial pH 10.85.

These results indicate that lime concentrations in the range 50-1000 mg/l do not alter the rate of removal of sulphide from solution.

A comparison of the rates of removal of sulphide from fellmongery waste and those previously discussed, shows that

some component or components of the waste, other than lime or sulphide, markedly affected the relative removal rates. Rates for all the waste pH values studied were lower than those for corresponding values of pH of pure sulphide and lime-sulphide solutions. It is suggested that these reduced rates, obtained from Figure 4.7, are due to the restriction of oxygen transferred into solution. Dissolved oxygen is essential for the chemical oxidation of sulphide in these systems. The effect of various substances on the oxygen transfer coefficient has been discussed by Eckenfelder and O'Connor (31). Surface-active substances concentrate at the liquid-air interface and apparently create a barrier to oxygen diffusion. Grease and fats in an alkaline environment may form soap-like substances, which exhibit surfactant properties. Proteinaceous material may display similar properties. These components are recognised constituents of a fellmongery waste.

Figures 4.6 and 4.7 demonstrate a diminishing period of zero sulphide removal with decreasing initial pH of the waste. These results differ from those obtained for pure sulphide and lime-sulphide solutions with a corresponding initial pH. The period of zero sulphide decrease was achieved only for an initial pH of 10.85 in the latter two systems. It appears that certain waste constituents, as well as pH, determine the length of this period during aeration of fellmongery wastes.

Table 4.3 demonstrates that insignificant quantities of sulphate were formed. No increase in sulphate was recordded for initial waste pH values of 10.50 and 10.85. This contrasts with results obtained for the aeration of pure sulphide solutions, where sulphate concentrations increased during sulphide removal.

4.4.2 Biological Removal of Sulphide from Fellmongery Wastes

Figure 4.9 shows that inoculation of fellmongery waste with column biomass accelerated the rates of removal of sulphide at the initial pH values 9.55, 10.20 and 10.40, when compared with the rates obtained without inoculation. The

value of K achieved at pH 10.90, 0.00082 mg/l.min, was very low, and corresponds to the low value, 0.0038 mg/l.min, obtained for the latter system.

Graphs of the logarithmic change in sulphide concentration with aeration time, for initial waste pH values of 9.55 and 10.20, exhibit different characteristics to those for pure sulphide, lime-sulphide and fellmongery waste solutions with the same pH values. The curves possess two linear portions, the gradient of the first portion being less than that of the second. This may have been due to the period required by the biomass to acclimatise to the new system. Biomass from the filter column was incubated in an orbital incubator with waste, prior to the fermenter studies. The operating characteristics of the incubator and the fermenter were different, and may have accounted for the lag in sulphide utilisation by the biomass. Once the biomass had adapted to the new operating conditions, sulphide removal rates increased to a higher value.

An extended run at pH 9.55 demonstrated that sulphate was the terminal sulphide oxidation product of an inoculated system. Figure 4.11 shows little sulphate increase in an uninoculated control compared with an inoculated waste sample. An increase in sulphate concentration of 250 mg/l occurred in the inoculated system, while only a 35 mg/l increase resulted in the control. On a sulphur basis, this reflects an 88% conversion of sulphide to sulphate in the inoculated system, and a 16% conversion in the control. These results are consistent with those reported by Aulenbach and Heukelekian (4) and Heukelekian and Lassen (53) for sludge samples and sulphide-sewage solutions. The former workers showed that biomass in a system, similar to the fermenter, could be acclimatised to oxidise at least 100 mg/l sulphide completely to sulphate within six hours aeration. The present results indicated a greater time lag for the increase in sulphate concentration, following sulphide disappearance. This may be attributed to the media of the present studies consisting of

a high lime concentration with associated high pH. The inoculum size, aeration rate, source of inoculum and in addition, the fact that aeration was curtailed after 400 min, probably contributed to the longer lag period for sulphate formation.

Parker and Prisk (85) and Zajic (132) report manganese to be an essential compound in the autotrophic metabolism of the sulphur oxidising bacteria. The results obtained when manganese was added to inoculated fellmongery waste samples demonstrate that the removal rates of sulphide were increased. At a waste pH of 9.60, a non-linear logarithmic sulphide removal curve was obtained, which indicated progressive increases in logarithmic sulphide removal rates with time. The presence of manganese eliminated the initial slow removal portion of the semi-logarithmic plots evident in inoculated samples without manganese.

Sulphate was again found to be the final oxidation product for an initial waste pH of 9.60 (Figure 4.16). Aeration was terminated after 7 hours owing to the presence of foam. S was found to have a value of 1.02 for the inoculated-manganese system, which represented a 98% conversion of sulphide-sulphur to sulphate-sulphur. The presence of manganese did not alter the rate of sulphate production and appears only to influence the sulphide removal rate. Sokolova and Karavaiko (105) indicated that two distinct processes constitute the sulphide oxidation of aerobic sulphur-oxidising bacteria.

(1) The removal of sulphide from solution by the micro-organisms and subsequent intracellular oxidation to an intermediate compound.
(2) The production of sulphate from this intracellular compound which is accomplished after a significant lag period.

Manganese appears to have an influence on process (1) in

the present system.

The additions of manganese to uninoculated waste samples yielded semi-logarithmic curves, of change in sulphide versus aeration time, with two linear portions. The gradient of the first portion being greater than the second (Figure 4.14). This behaviour is different from that exhibited by aerated waste samples with no manganese addition, the corresponding curves for which are shown in Figure 4.7. Manganese is a commonly used catalyst, for the oxidation of sulphides in tannery and fellmongery wastes (6, 15, 40). However, while proving effective at concentrations of 100 mg/l (6), manganese is ineffective at low concentrations (15). Berg et al. (15) demonstrated that when added to tannery wastes, manganese is rapidly removed from solution by a poisoning mechanism, involving adsorption onto proteinaceous material. This is particularly prevalent at low manganese concentrations. Once poisoned, the manganese does not participate in the oxidation of sulphide, and sulphide removal rates are decreased. Such a mechanism is postulated for the uninoculated samples. The first part of the curves represents the initial rapid removal rate involving a catalytic oxidation of the sulphide, while the second portion of the curve characterises the reduced rate of sulphide removal, resulting from the poisoning mechanism.

An extended run made at an initial pH of 9.60 demonstrated that sulphate was present in insignificant quantities, compared with the inoculated system of similar initial pH with manganese. In this, S had a value of 5.7, corresponding to an 18% conversion of sulphide to sulphate on a sulphur basis. A conversion of 16% was achieved for waste aeration without inoculation or manganese addition (Section 4.3.2) at initial pH 9.55

CHAPTER FIVE

MICROBIOLOGICAL STUDIES - WITH REFERENCE TO SULPHIDE REMOVAL

5. MICROBIOLOGICAL STUDIES - WITH REFERENCE TO SULPHIDE REMOVAL

5.1. Introduction

The previous experiments firmly indicate biological oxidation to be a major mechanism in sulphide removal from fellmongery wastes. However, the physio-chemical characteristics of the waste are such that only select heterotrophic and autotrophic microbial populations would develop in a treatment unit.

Since the experimental system is aerobic, treating an alkaline sulphide-bearing waste, the most likely sulphur-oxidising bacteria to have been present is Thiobacillus thioparus (105). This microorganism was in fact isolated during the operation of the filter, and the ability of the organism to metabolise sulphide determined.

The presence of the purple sulphur Thiorhodaceae was also observed in the plastic recirculation line, six weeks prior to termination of the filter operation. The anaerobic conditions, required for development of this organism, were provided under the outer slime layer of the interior of the recirculation line. Thiorhodaceae is a photosynthetic microorganism and the necessary light was transmitted to the organism through the transparent hosing. Sulphides and an alkaline environment were provided by the recirculated waste. This photosynthetic microorganism was isolated from samples of film taken from the recirculation hose.

5.2 Materials and Methods

5.2.1 Media Composition

Thiobacillus thioparus was isolated on Beijerinck's medium, which had the following composition:

Component	Quantity: g/l
Sodium thiosulphate pentahydrate	5
Sodium bicarbonate	1

Disodium hydrogen phosphate	0.2
Magnesium chloride	0.1
Ammonium chloride	0.1
Ferrous sulphate	trace

The medium was made up with distilled water and the pH adjusted to 9.2 - 9.4. Thiosulphate, bicarbonate and ferrous sulphate components were sterilised separately and after cooling were added to the salt solution.

The presence of Th. thioparus is indicated by the gradual development of turbidity and the formation of a white pellicle consisting of droplets of amorphous sulphur, as well as the presence of minute, rod shaped, Gram-negative bacteria (105).

For the isolation of Thiorhodaceae van Niel's medium of the following composition was used:

Component	Quantity: g/l
Ammonium chloride	1
Magnesium chloride	0.4
Dihydrogen potassium phosphate	0.8
Sodium bicarbonate	5
Hydrated sodium sulphide	1
Sodium chloride	0.1

The medium, prepared with tap water, was sterilised separately from 10% solutions of sodium bicarbonate and sodium sulphide. Medium pH was adjusted to 8.5 after sterilisation with a 10% solution of sodium carbonate.

5.2.2 Experimental Procedures

5.2.2.1 Thiobacillus thioparus Isolations

Four series of isolations were carried out during the operation of the biological filter. The first and second were made when the system was operating at 21°C, the third a day following the temperature change from 21 to 31°C, and the fourth two weeks after this temperature change.

Samples for the first isolation were taken from:

(1) The top stones of the filter.
(2) Stones 0.76 m from the filter surface.
(3) Stones 1.52 m from the surface.
(4) The sump liquors.

The samples for the remaining three isolations were taken from one site - any two stones 1.52 m from the filter surface. Different stones were utilised for each study. Biomass was taken from the rocks with a sterile spatula and suspended in 100 ml of sterile water. For each isolation, 10 ml of this suspension was used to inoculate 300 ml of Beijerinck's medium. This procedure was assumed to provide an equal size inoculum in all cases. It was assumed that under continuous operating conditions, the film thickness would remain constant and the film be evenly distributed. A constant weight of film would characterise each stone and consequently standard inoculum sizes be obtained.

Control flasks of 10% formalin were used for all experiments. Flasks were incubated at 21 on 31°C as indicated in Section 5.3.1. Incubation was carried out under both stationary and agitated conditions. The agitated flasks were held in an orbital incubator operating at 150 rpm.

Development of elemental sulphur within the medium, turbidity and pH decrease were used as growth indicators, in accordance with the descriptions of Sokolova and Karaviako (105). Turbidity was assessed visually, since the large particles present made spectrophotometric determinations difficult. Sulphur was identified by the characteristic blue flame exhibited on ignition, by its solubility in CS_2 and by its typically strong odour. Gram stains provided morphological data.

Photographs of slide preparations were made with an Olympus Tokyo, Photomax 200046 microscope and mounted camera.

A magnification of 1500 with oil immersion was used for examination and photography. Morphological dimensions were determined with a calibrated slide and eyepiece.

5.2.2.2 Growth of Thiobacillus thioparus in Fellmongery Waste and Sulphide Solutions

Two systems were investigated, each at two pH values:

(1) pure solutions of sodium sulphide (control)
(2) samples of fellmongery waste.

Three 500 ml conical flasks were used for each experiment. 300 ml of Beijerinck's medium was added to the flasks. To the first was added heat destroyed inoculum as a control. The other two were inoculated with a 25 ml suspension of 7-day old Th. thioparus culture from Beijerinck's medium. Flasks were incubated at 21°C in a stationary incubator.

Sulphide, sulphate and pH were determined as described in Section 3.2.3.

5.2.2.3 Thiorhodaceae Isolations

A small section of the filter recirculation line was removed, from which an inoculum was aseptically obtained. This inoculum was aseptically transferred to 250 ml bottles which were subsequently completely filled with van Niel's medium. The bottles were sealed with glass stoppers and placed in a 25°C incubator, 20 cm from a 60-watt bulb. Thiorhodaceae growth was indicated by a red colouration of the medium.

5.3 Results

5.3.1 Thiobacillus thioparus Isolations

5.3.1.1 Initial Isolations

These isolations were made from samples taken from various filter sites, and were carried out in stationary and orbital incubators.

Two days after inoculation an increase in the turbidity of the media was observed in the shaken flasks. The control flasks remained clear. Little turbidity had developed in the stationary flasks.

On the fourth day, examination of the stationary flasks revealed a white layer of elemental sulphur on the liquid surface. The pH of these flasks had fallen from 9.2 to 8.1, whereas the clear control flasks exhibited no pH decrease.

An even greater turbidity was observed in the agitated inoculated flasks, compared with the corresponding stationary flasks. The controls again exhibited no turbidity. The pH of the experimental flasks had decreased from 9.2 to 5.2. No decrease had occurred in the controls.

The results are presented in Plates 5.1 and 5.2. Plate 5.1 shows a control, a stationary and an agitated flask after 5 days incubation. Flask 1 is a control, flask 2 is from the stationary incubator and flask 3 from the orbital incubator. Flask 3 is more turbid than flask 2, although both exhibit sulphur coating on the liquid surface. This is shown more clearly in Plate 5.2. These photographs compare very favourably with those presented by Sokolova and Karavaiko (105).

To obtain a purer culture of Thiobacillus thioparus, a further passage was made through freshly sterilised medium. Gram stains of preparations from the resulting culture were carried out. The slides, on microscope examination (Plate 5.3), revealed the sole presence of a small Gram-negative, rod-shaped organism, with slightly rounded ends. The average dimensions of the cells were measured as 1.2 - 1.5 microns by 0.3 - 0.5 microns. Several organisms were observed prior to division, which occurred transversely.

5.3.1.2 Isolations made in Conjunction with Filter Temperature Changes

The remaining isolations of Th. thioparus were carried

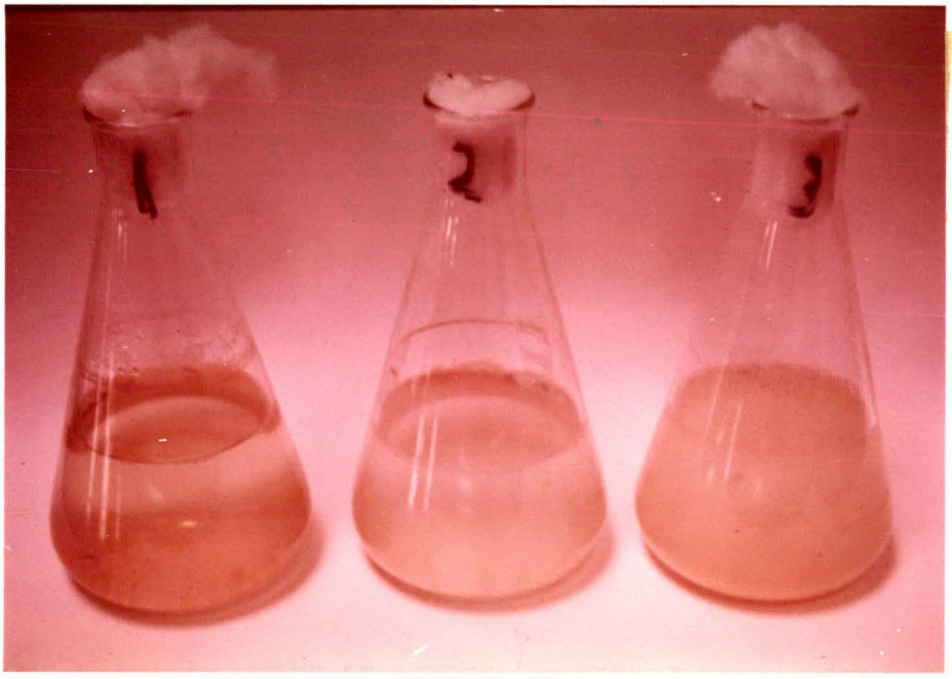

Plate 5.1 Thiobacillus thioparus Growth in Beijerinck's Medium

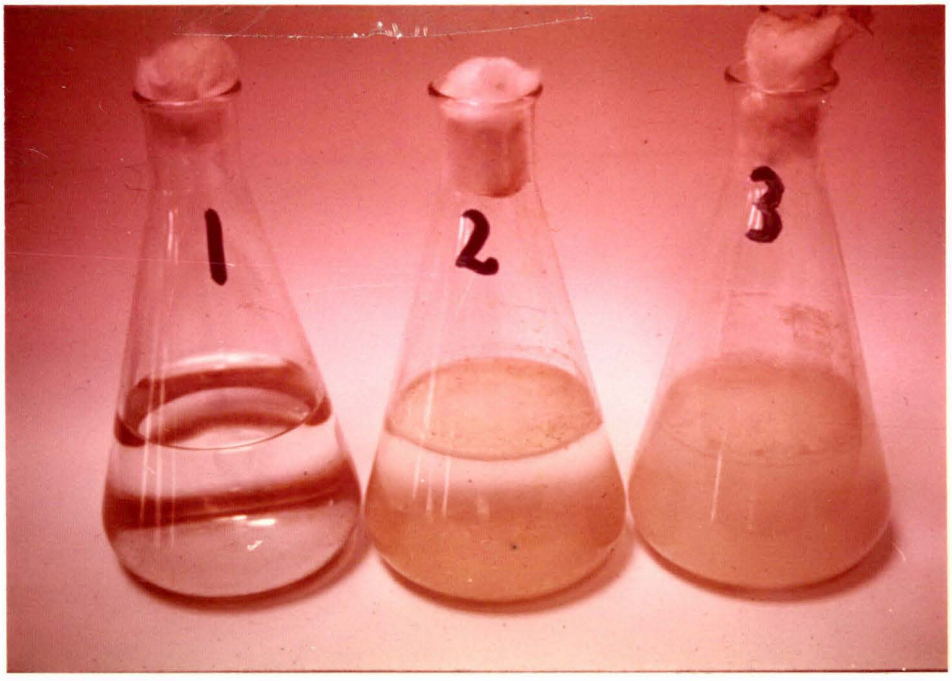

Plate 5.2 Thiobacillus thioparus Growth in Beijerinck's Medium-Sulphur Coating

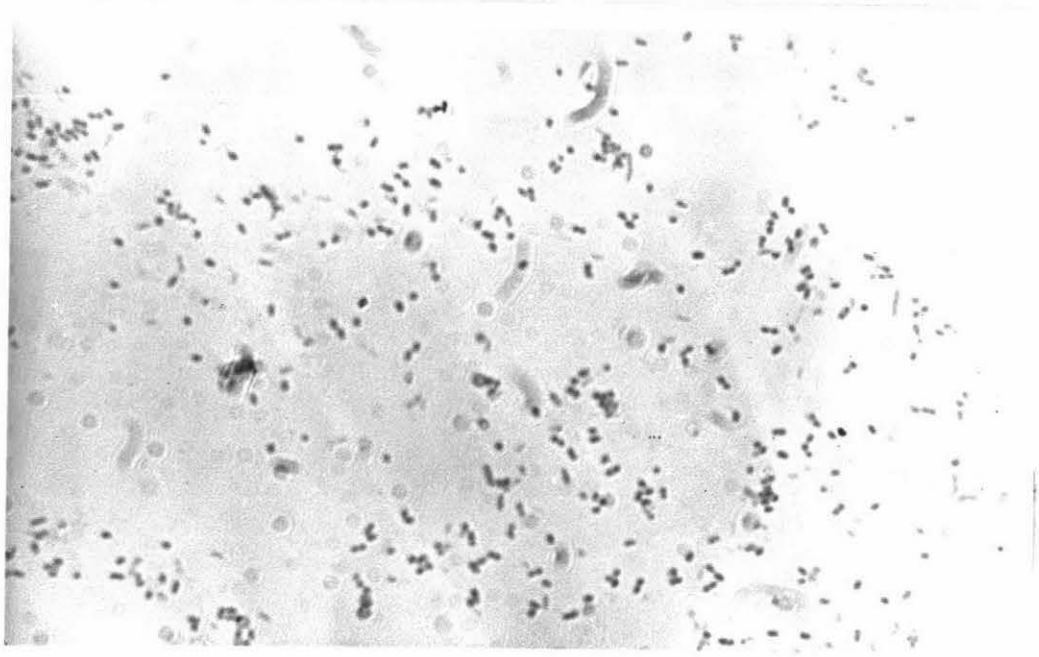

Plate 5.3 Thiobacillus thioparus - Gram Stain (x 1500)

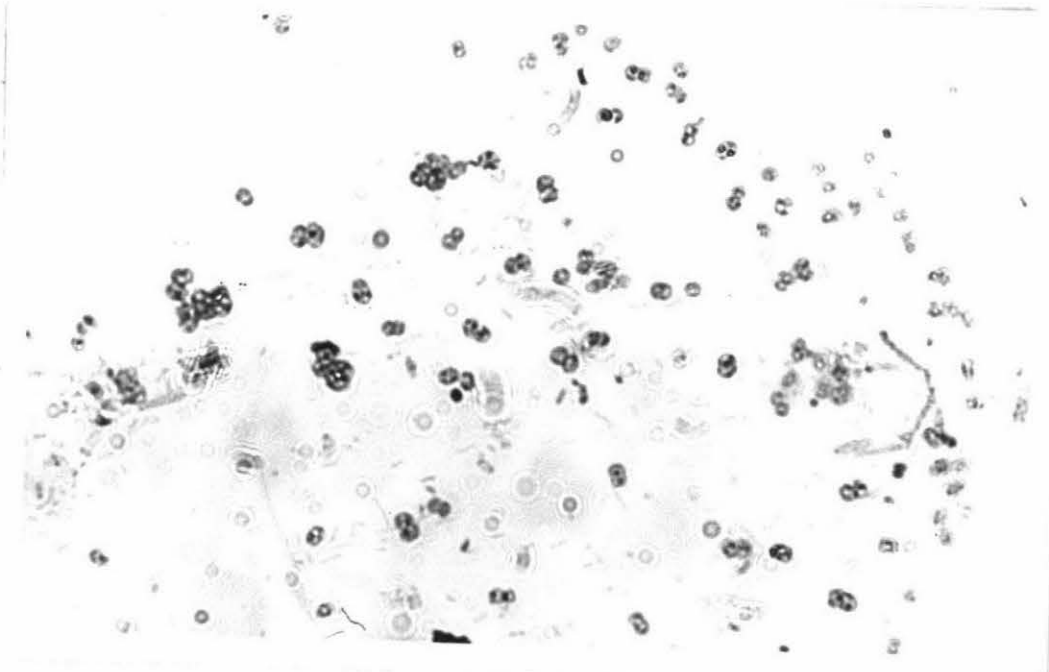

Plate 5.4 Thiorhodaceae - Gram Stain (x 1500)

out to ascertain whether a change in the temperature of the filter system would alter the metabolic activity of the organism. Isolations were made during the period of temperature change, and the metabolic upset of the sulphur-oxidising bacteria was measured by the extent of sulphur deposition and the reducti n in pH. The subsequent results all depend upon the assumption that the inoculum size for each isolation was approximately the same.

The results presented in Table 5.1 correlate favourably with the assumptions made regarding a metabolic disturbance with a temperature change. The sample isolated one day after the temperature change took significantly longer to metabolise the thiosulphate substrate than a sample isolated a day prior to the change. However two weeks after the temperature change, a further sample displayed a much higher rate of thiosulphate metabolism. This was demonstrated by the development of turbidity one day following incubation of the inoculum. This rapid turbidity development was recorded only for this isolation. These results demonstrate that following two weeks filter operation at 31°C, Th. thioparus metabolise thiosulphate at greater rates than those recorded for a filter temperature of 21°C.

5.3.1.3 Sulphide Removal from Fellmongery Waste and Sulphide Solutions by Th. thioparus

The previous microbiological studies involved the determination of Th. thioparus metabolism by thiosulphate utilisation in Beijerinck's medium. These studies did not indicate whether Th. thioparus could metabolise a sulphide substrate.

The metabolism of sulphide by Th. thioparus in waste samples at an initial pH of 9.75 and 8.95 was compared with that in pure sulphide control solutions at an initial pH of 9.85 and 9.30. Sulphide removals for each system are presented in Figure 5.1. Only data obtained at pH 9.85 are presented for the pure sulphide solutions, since similar rates resulted

TABLE 5.1

GROWTH OF THIOBACILLUS THIOPARUS

Day	Medium Appearance		
	Sample 1[1]	Sample 2[2]	Sample 3[3]
0	Initial pH 9.3. Clear medium	Initial pH 9.3. Clear medium	Initial pH 9.3. Clear medium.
1	Clear medium	Clear medium	Turbidity commencing
2	Clear medium	Clear medium	Turbid, white sulphur droplets on surface
3	Clear medium	Clear medium	Very turbid, surface completely covered with sulphur. pH 8.60
4	Slightly turbid	Clear medium	
5	Turbid with sulphur deposits on surface	Clear medium	
6	Very turbid with surface completely covered with sulphur. pH 7.90	Slightly turbid medium, pH 8.95	Very turbid, sulphur droplets completely throughout medium, pH 6.90
7		Turbid, sulphur droplets on surface, pH 8.80	

1. Sample 1 : Isolated 1 day prior to the filter temperature change. Incubated at 21°C.

2. Sample 2 : Isolated 1 day after the filter temperature change. Incubated at 31°C.

3. Sample 3 : Isolated 14 days after the filter temperature change. Incubated at 31°C.

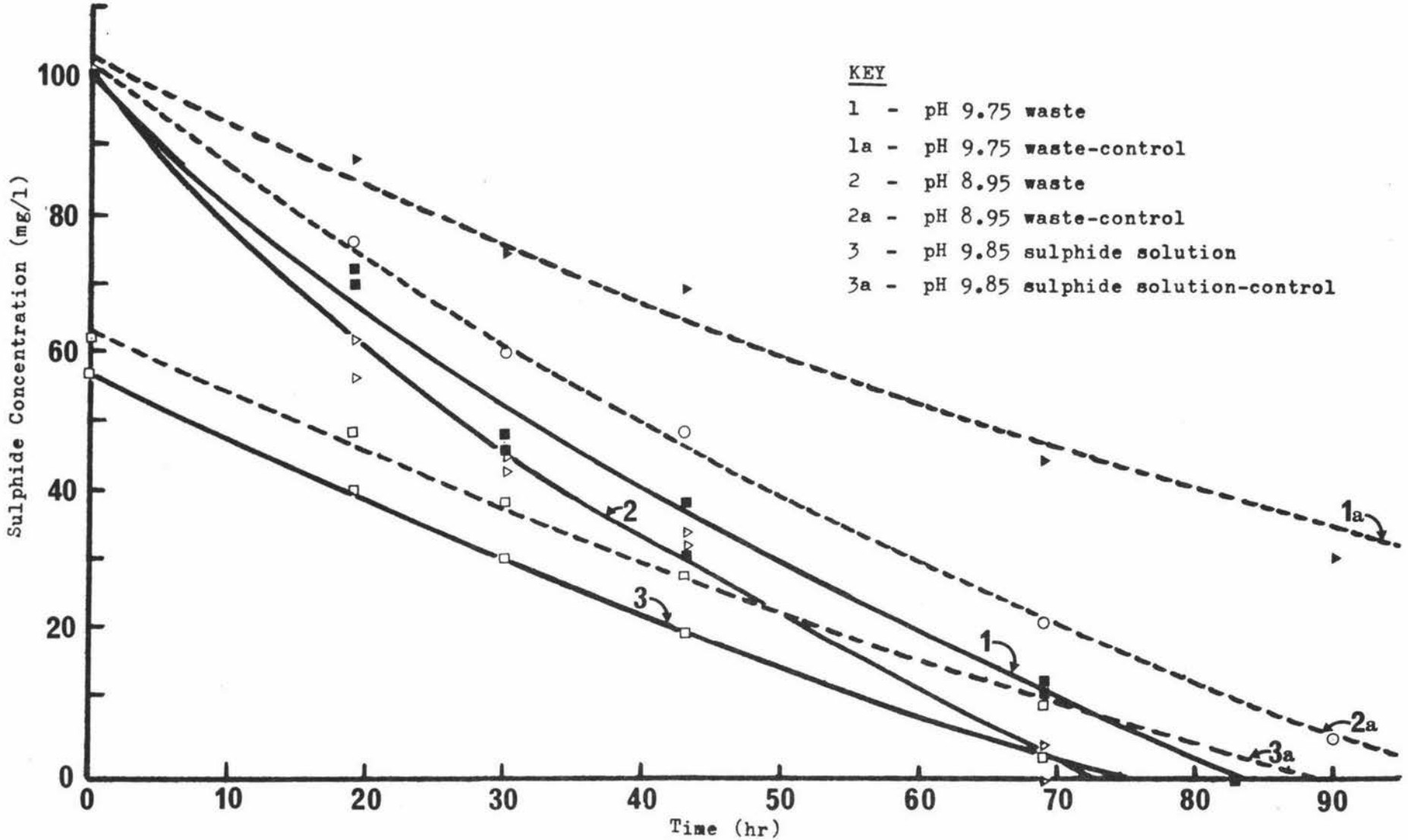

Figure 5.1 Thiobacillus thioparus Growth in Pure Sulphide and Fellmongery Waste Solutions.

at pH 9.35. Tables 5.2 and 5.3 summarise the experimental data.

Identical sulphide removal rates were obtained in both the control and the inoculated flasks for the pure sulphide solutions (Figure 5.1). Table 5.2 indicates a very small sulphate increase in the medium for this system. A pH decrease accompanied this small sulphate increase.

Graphs of sulphide concentration against time, Figure 5.1, show that Th. thioparus accelerated the removal of sulphide from fellmongery waste. This was more pronounced at pH 9.75 than 8.95.

Table 5.3 shows that large increases in sulphate concentration occurred for inoculated wastes. Little increase resulted in the controls. The values of S achieved for the inoculated system, 0.87 - 0.96, fall in the S range obtained for the batch filter operation. The pH decrease of the inoculated flasks was slightly greater than that of the controls.

5.3.1.4 The Isolation of Thiorhodaceae

Examination of a cross-sectional cut from the plastic recirculation line revealed that the red colouration adjacent to the interior wall was a red microbial growth and was located beneath an outer coating of dark slime. This is shown in Figure 5.2.

Van Niel's isolation medium was used to obtain pure cultures of the organism. Growth of Thiorhodaceae was apparent after two weeks by the red colouration in the medium. This description of growth of Thiorhodaceae agrees with that of Kondrat'eva (63).

Two successive passages were made through van Niel's medium to free the culture of alien microorganisms. A Gram-stain was made on the culture resulting from the second passage

TABLE 5.2: THIOBACILLUS THIOPARUS METABOLISM IN PURE SULPHIDE SOLUTIONS

	Initial pH 9.85									Initial pH 9.35								
	1			2			C			1			2			C		
	$S^=$	$SO_4^=$	pH	$S^=$	$SO_4^=$	pH	$S^=$	$SO_4^=$	pH	$S^=$	$SO_4^=$	pH	$S^=$	$SO_4^=$	pH	$S^=$	$SO_4^=$	pH
	mg/l	mg/l		mg/l	mg/l		mg/l	mg/l		mg/l	mg/l		mg/l	mg/l		mg/l	mg/l	
Initial value	61	162*	9.85	57	164*	9.85	62	25	9.90	59	162*	9.35	59	162*	9.35	61	25	9.30
Value after 69 hr	6	210	8.95	3	220	8.40	8	80	8.95	2	235	8.20	0	230	8.10	3	85	8.05
$S^=$ decrease	55			54			56			57			59			58		
$SO_4^=$ increase		48			56			55			73			68			60	
S	3.44			2.88			3.05			2.34			2.61			2.90		

$S^=$ = Sulphide concentration

$SO_4^=$ = Sulphate concentration

1, 2 = Viably inoculated samples

C = Control

* = Initial sulphate concentrations high by virtue of viable inoculum carry over

TABLE 5.3: THIOBACILLUS THIOPARUS METABOLISM IN FELLMONGERY WASTE

	Initial pH 9.75									Initial pH 8.95								
	1			2			C			1			2			C		
	$S^{=}$	$SO_4^{=}$	pH	$S^{=}$	$SO_4^{=}$	pH	$S^{=}$	$SO_4^{=}$	pH	$S^{=}$	$SO_4^{=}$	pH	$S^{=}$	$SO_4^{=}$	pH	$S^{=}$	$SO_4^{=}$	pH
	mg/l	mg/l		mg/l	mg/l		mg/l	mg/l		mg/l	mg/l		mg/l	mg/l		mg/l	mg/l	
Initial value	100	170*	9.75	100	175*	9.75	105	25	9.75	103	180*	8.95	105	180*	8.95	105	30	8.95
Value after 69 hr	10	480	8.80	12	450	8.60	43	30	9.45	0	550	6.65	5	500	7.00	20	30	8.25
$S^{=}$ decrease	90			88			62			103			100			85		
$SO_4^{=}$ increase		310			275			5			370			320			0	
S	0.87			0.96			3.7			0.84			0.91			∞		

$S^{=}$ = Sulphide concentration

$SO_4^{=}$ = Sulphate concentration

1, 2 = Viably inoculated samples

C = control

* = Initial sulphate concentrations high by virtue of viable inoculum carry over

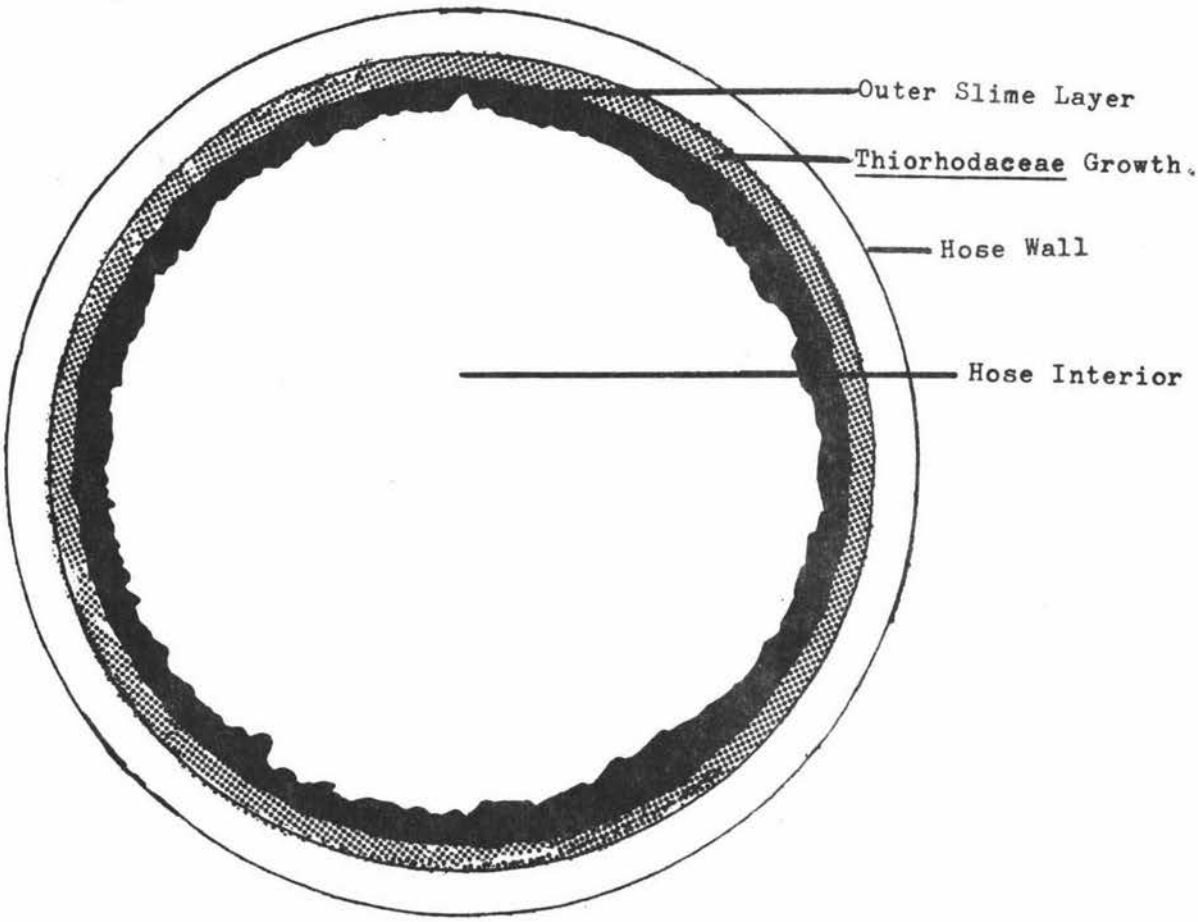

Figure 5.2 Thiorhodaceae Growth in Recirculation Hose

medium. The stained organism was Gram-negative and was encapsulated in a slimy pink membrane. Plate 5.4 shows the morphological characteristics exhibited by the organism. The culture appeared to be free from contamination.

The organism diameter range was 1 - 4 microns. Several cell aggregates were observed within the encapsulating membrane; aggregate cells numbered 1 - 3 per membrane.

Attempts to isolate this organism from the sump liquors and the filter media were unsuccessful.

5.4 Discussion

5.4.1 Thiobacillus thioparus Studies

Isolations of Thiobacillus thioparus from the filter column and sump liquors were accomplished in Beijerinck's thiosulphate medium. Turbidity development, sulphur deposition and pH decrease were used to assess the metabolic activity of the organism. Thiosulphate is metabolised to elemental sulphur and sulphate by Th. thioparus (105). The appearance of elemental sulphur within the medium provides a reliable indicator of growth (105).

The organism exhibited an ability to proliferate in fixed bed (the filter column) and fluidised bed (the sump) reactors, treating sulphide-bearing effluent. Sokolova and Karavaiko (105) indicated that Th. thioparus is commonly found in sulphide-containing waters and deposits. They also report that other workers have isolated Th. thioparus from similar environments.

The alkalinity, salinity and concentration of sulphides and ammonium salts in the waste provided favourable conditions for the growth of Th. thioparus in the biological filter and in the sump. Carbon required by these autotrophs for cell synthesis originates entirely from CO_2 (105). The main sources of CO_2 are atmospheric CO_2, the product of respiration by the heterotrophs, and also that resulting from alkalinity

reactions occurring in the waste.

The rate of metabolism of samples placed in an orbital incubator was greater than that of samples in a stationary incubator. This is contrary to the findings of Sokolova and Karavaiko (105) in which greater rates of thiosulphate oxidation were achieved at low aeration rates. Their experiments indicated that redox potential was a critical growth parameter. However, this behaviour was probably a function of the strain of Th. thioparus used by the workers. It was apparent from the literature reviewed by them that large differences in metabolic physiology occur between different strains of Th. thioparus. The strain isolated from the biological filter metabolised the thiosulphate of Beijerinck's medium at a greater rate in aerated, agitated samples when compared with the rates of a stationary culture.

Morphological examination of the isolated organism compares favourably with descriptions reported by other workers (85, 105). The general morphological features of the organism closely resemble those presented by Sokolova and Karavaiko (105), Beijerinck (13) and Parker and Prisk (85). All reported strains conformed to the description of minute, Gram-negative, thin rods. The rounded-end characteristic exhibited by the isolated organism was displayed by strains examined by Sokolova and Karavaiko (105). Cell dimensions are similarly in agreement with published data. The strain isolated from the biological filter had dimensions of (1.2 - 1.5) x (0.3 - 0.5) microns. Organisms isolated by Sokolova and Karavaiko (105) possessed the dimensions (1.0 - 1.1) x (0.45 - 0.5)microns, while those described by Parker and Prisk (85) measured (1.0 - 1.5) x 0.5 microns. The observation of cell multiplication by transverse division is similar to that reported by Sokolova and Karavaiko (105) for Th. thioparus.

Th. thioparus isolations made in conjunction with the filter temperature change of 21 to 31°C indicated that the change initially affected the metabolism of thiosulphate by the organism (Table 5.1). This was inferred from the length

of time taken to achieve the expected turbidity, sulphur deposition and pH decrease in Beijerinck's medium. The organisms isolated one day following the 10°C change required the longest time to display metabolic activity, the medium becoming turbid six days after inoculation. These results differed from those obtained with organisms isolated one day before, and 14 days after, the temperature change. Th. thioparus isolated before the change, developed turbidity 4 days after inoculation, while the latter isolation showed turbidity one day following inoculation. Decreases in medium pH followed a similar pattern, with the slowest decrease recorded in the sample isolated one day following the change.

The above results may be linked to those obtained in the filter by considering the modes of metabolism of sulphide and thiosulphate. Assuming that sulphide metabolism changes follow similar patterns to those of thiosulphate metabolism, the biological filter results (Figure 3.12) demonstrate that the sudden change in filter sulphide removal paralleled a decrease in Th. thioparus activity. This assumption is justified by the pathway for thiosulphate metabolism, presented by Vishniac and Santer (125), in which thiosulphate is converted to sulphide prior to entering the cell. The conversion is accomplished by enzymes probably located on the cell surface. The suggestion of sulphur reduction at the cell surface was in agreement with the earlier findings of Suzuki and Werkman (116). Starkey (113) put forward the hypothesis that sulphur compounds enter the cell only in the form of SH^- groups. Figure 1.1 indicates that the sulphur in fellmongery waste is largely present in this form.

Th. thioparus cultures from Beijerinck's medium were used to inoculate pure sulphide and fellmongery waste solutions of varying pH, in order to determine the ability of the organisms to metabolise sulphide. Figure 5.1 demonstrates that sulphide was utilised more easily by the bacteria in the waste solutions in contrast to that of the pure sulphide solution controls. Greater sulphide removal rates were achieved at a waste pH of 9.75 compared to those obtained at pH 8.95. The initial pH

of the isolation medium 9,50, may have influenced this result. Sokolova and Karavaiko (105), however, reported data which correlated the metabolism of Th. thioparus with pH change. Optimum activity lay in the pH range 7 - 10 for one strain, while the narrow range of pH 8,5 - 9,8 was required by another. The optimum activity for the latter strain tended to the higher end of the pH range. These results compare favourably with the present findings, where the highest rate of elimination of sulphide occurred at pH 9,75.

Initial and final sulphate concentrations indicated that sulphide was oxidised to sulphate in the inoculated waste solutions during the incubation period. This was not observed in the control flasks. Nathansohn (81), Beijerinck (13), Jacobsen (59), Vishniac (125), and Sokolova and Karavaiko (105) have demonstrated that sulphate is the end product of Th. thioparus sulphide metabolism. S values of 0.87 - 0.96, obtained for the inoculated waste samples, correlated with those of the batch filter operation, 0.42 - 0.93, shown in Table 3.2. This strongly suggested that Th. thioparus was responsible for sulphide removal in the biofiltration of fellmongery waste.

A pH decrease accompanies the formation of sulphate when Th. thioparus oxidises sulphide. The data of Table 5.3 indicate that a greater pH decrease occurred in flasks with inocula of Th. thioparus compared with the pH decrease of the control waste flasks. The pH decrease of both systems was caused by lime precipitating from the waste. The high sulphate concentrations account for the slightly lower pH of the inoculated flasks. Sokolova and Karavaiko (105) presented data which confirm the above findings.

As anticipated, no difference in sulphide removal rates between controls and inoculated flasks was apparent with the pure sulphide solutions. The absence of large sulphate concentrations indicates that Th. thioparus did not utilise the sulphide of this system (Table 5.2). Figure 5.1 depicts

a reduction in sulphide concentration during the incubation period. This reduction may be attributed to a chemical oxidation by dissolved oxygen. Values of S obtained for the pure sulphide solutions of this experiment were in the range 2.3 - 3.4. They were similar to those found for the aeration of similar solutions in the fermenter studies: 2.4 - 2.6 (Table 4.1). The pH decrease shown for all samples (Table 5.2) is attributed to the slight increase in sulphate concentrations. Since nitrogen and phosphorous sources were absent, autotrophic metabolism could not proceed, and Th. thioparus was unable to utilise the sulphide.

5.4.2 Thiorhodaceae Investigations

The presence of Thiorhodaceae was detected only during the continuous operation of the filter when a red colour was observed in the recirculation line. Espino and Gloyna (36) reported that these photosynthetic sulphur bacteria impart a red colouration to their environment. They stated that the colouration may be used to indicate the presence of the organism. Bavendamn (9) suggested that the habitats of these microorganisms be divided into three groups. Of these, the first group be described included sulphide-bearing waters with a constant chemical composition and constant temperature, and in which purple sulphur bacteria are found in abundance. This environment closely corresponds to that provided by the recycled liquors of the biological filter treating fellmongery waste.

Van Niel (121) divided the Thiorhodaceae into two groups. The first group exhibit activity in the pH range 8.4 - 10.5, and an H_2S concentration range, 150 - 200 mg/l, whereas the second group tolerate a wider pH range, 6.5 - 9.5, but lower sulphide concentrations. Van Niel noted that when the H_2S concentration increased to 150 - 200 mg/l, the latter group only grew within a pH range of 8.5 - 9.0. The species proliferating in the filter recirculation line would qualify for Van Niel's second grouping, since a low sulphide concentration and a pH of 8.5 characterised the recycled liquors.

The organisms were isolated in van Niel's medium for purple sulphur bacteria. Growth of the organisms was extremely slow in the isolation medium - two weeks passed before the medium was completely red.

Gram-staining of pure cultures obtained revealed that the isolated organism was a Gram-negative, encapsulated bacteria. A slimy membrane enclosed the cell, and in many cases encapsulated up to 3 cell aggregates. Organism diameters averaged 1 - 4 microns. This range of diameters compares favourably with a similar range presented by Kondrat'eva (63) for aggregating purple sulphur bacteria. Morphological characteristics were similar to those described by Winogradskyi (130) and those presented by Kondrat'eva (63) from the micrographs of Schlegel and Pfennig (99) for an aggregated Thiorhodaceae genus. Van Niel (121) reported that this genus was termed Ameobobacter in the Seventh Edition of Bergey's Manual (14).

Observations have demonstrated that large cell aggregates are found primarily in media with a high alkalinity (63). This is consistent with the environment in which the isolated species grew. The bicarbonate and carbonate alkalinities which are present satisfy the essential mineral requirements of the organism (63).

It was apparent that Thiorhodaceae only developed in the recirculation line interior, whereas Th. thioparus populated the entire system. Since sulphide utilisation studies of these photosynthetic organisms were not attempted, it is impossible to establish their contribution to the removal of sulphide from the waste. However, their presence indicated some degree of sulphide removal. Sulphide removed from the waste by these bacteria is stored intracellulary as sulphur granules. When sulphide concentrations decrease, these granules are oxidised to sulphate and released from the cell. Espino and Gloyna (36) indicated that the red colour associated with the growth of these organisms is correlated with a decrease in both sulphide concentration and cellular oxidation of internally

stored sulphur granules. A brown colour occurred at high sulphide concentrations which was said to characterise intracellular sulphur storage. These findings were obtained from a waste stabilisation pond investigation. However, the metabolic physiology of Thiorhodaceae is unlikely to be influenced by the type of treatment system operated. The observations of Espino and Gloyna (36) suggest that the purple sulphur bacteria were possible inhabitants of the system prior to their detection.

CHAPTER SIX

GENERAL DISCUSSION

6. GENERAL DISCUSSION

The important aspects of the preceding three chapters are integrated in this discussion to provide an overall interpretation of the biological filtration of fellmongery waste. Emphasis is placed upon the influence of sulphide on the process, and the mechanism of its removal during treatment.

Sulphide removal mechanisms were investigated with the aid of three series of experiments:-

(1) The effect of a 10°C temperature increase on the effluent sulphide and sulphate concentrations of the biological filter.
(2) Waste aeration studies in a fermenter, to evaluate relative rates of sulphide oxidation by biological mechanisms.
(3) Microbiological investigations involving the implications of sulphur-oxidising bacteria in the biological filtration of fellmongery wastes.

The first experiment was conducted during the continuous operation of the filter at 21°C and the effect of a subsequent 10°C step change observed. Results tentatively indicated a biological mechanism of sulphide removal. Had a chemical mechanism predominated, constant sulphide and sulphate (if a chemical oxidation product) concentrations would have characterised the effluent for constant values of the operating variables. This was contrary to that achieved.

Microbiological experiments were carried out in conjunction with the filter temperature change. The literature reviewed indicated that Thiobacillus thioparus was the sulphide-oxidising organism most likely to inhabit the filter environment. This organism was isolated and identified from the biological filter. Isolations of this organism prior to, and after, the filter temperature change, revealed that the organism metabolism was altered by the change.

The Th. thioparus metabolic changes correlate with the decreased sulphide utilisation and the decrease in effluent sulphate concentration experienced after the temperature change - the decreased metabolism in Beijerinck's medium paralleled the decreased sulphide elimination from the system.

The previous experiments did not indicate whether Th. thioparus could metabolise the sulphide of fellmongery waste. Beijerinck's medium employed thiosulphate as the substrate, and consequently provided limited data on the use of sulphide as a substrate. Inoculation of fellmongery waste samples with Th. thioparus increased the sulphide removal rates from solution. Sulphate was the terminal sulphide oxidation product of Th. thioparus.

In the second series of experiments, samples of fellmongery waste were aerated in a fermenter. Some of these were inoculated with column biomass. Sulphide removal rates were taken as a measure of the difference in the degree of sulphide oxidation between the inoculated samples and those that were not. Rates obtained in the fermenter were accomplished at a K_La value of 311 hr^{-1}. K_La values for the filter ranged from 5.1 to 8.55 hr^{-1}. The higher value of K_La for the fermenter indicates that oxygen availability was not a limiting factor in the oxidative mechanism in the fermenter studies. Chemical oxidations in these investigations were markedly lower than corresponding biological rates (Sections 4.3.3 and 4.3.4). Excellent sulphide removals, 90.5-100%, were achieved in the filter over the recycle ratio range 5:1-35:1. Oxygen transfer in this case was lower than that shown for the fermenter. This enhances the possibility of a biological mechanism of sulphide oxidation in the filter. The fermenter experiments also demonstrated that sulphate was not the end product of chemical sulphide oxidation. Had chemical sulphide oxidation occurred during the biological filtration of fellmongery waste, effluent sulphate concentrations would have been considerably lower than those obtained.

The biological filter operation was characterised by two modes of microbial metabolism - heterotrophism and autotrophism. Heterotrophic metabolism was reflected in the BOD/COD decrease of the waste, whereas biological sulphide oxidation suggested an autotrophic metabolism. An important product of heterotrophic metabolism is carbon dioxide resulting from organic matter oxidation.

Sokolova and Karavaiko (105) reported that carbon dioxide provides the sole carbon source for the sulphur-oxidising bacteria. The "mixed-culture" nature of the biological film of the filter suggests that heterotrophically produced carbon dioxide would occur in an environment populated by autotrophs. This carbon dioxide would be readily available to the sulphur-oxidising bacteria. The described situation would preclude a gaseous diffusion into the recycled liquors, with subsequent absorption back to the film for autotrophic metabolism requirements. Gaseous diffusion through adjacent microbial membranes could possibly have occurred. This would imply that the metabolism of the autotrophs was linked to that of the heterotrophs. The previous comments do not consider the possible role of atmospheric carbon dioxide in the process. It is postulated that the most readily available carbon dioxide source would be more likely to be involved in the autotrophic process.

No published data relating to the influence of sulphide concentration on carbon dioxide assimilation was revealed. Figure 3.8 indicates that optimum COD removal lay in the sulphide concentration range 90-110 mg/l. This sulphide concentration may have provided optimum energy for Th. thioparus carbon dioxide assimilation. Lower concentrations would not have met the energy demands of the populations, with resulting lower growth rates, and associated decreased carbon dioxide utilisation. This postulated situation may have affected the metabolism of the heterotrophs, with a resulting decrease in organic matter degradation. Concentrations above 110 mg/l possibly exerted a metabolic toxicity

on the heterotrophs. This would account for the decreased COD removals exhibited.

The energy yielded from autotrophic sulphide oxidation is used for the synthesis of cellular material. Carbon dioxide acts as the carbon source. This process is dependent upon environmental factors such as pH, temperature, redox potential and mineral content of the medium (105). Optimum pH for the metabolism of sulphide by Th. thioparus is 8.5-9.8 (105), which is maintained by the waste liquors recycling through the system. They also act as the source of nitrogen and dissolved oxygen.

The role of carbon dioxide in the system is masked by several other mechanisms. Dissolved air and alkalinity reactions provide additional carbon dioxide. The relative contribution to the total carbon dioxide concentration of the liquors, by the diffused air, would be minimal. An atmospheric carbon dioxide concentration of 0.03% results in low diffusion rates. In addition to autotrophic utilisation, carbon dioxide may be eliminated from the system by two further mechanisms. Carbon dioxide exhibits the ability to neutralise the lime component of the waste. Carbon dioxide in solution is converted to carbonic acid, which reacts with the lime to give calcium carbonate. Lijklema (70) reported that carbon dioxide may be lost from solution by a desorption process, which involves air stripping of carbon dioxide from the waste.

Isolation of Thiorhodaceae from anaerobic sections of the recirculation line demonstrated that Th. thioparus was not the sole biological agent of sulphide oxidation. Thiorhodaceae developed when continuous filter operation was commenced, suggesting that growth was favoured in a steady-state environment. Van Niel (121) showed that carbon dioxide was the sole carbon source for this group of organisms. As with Th. thioparus, carbon dioxide utilisation is linked with sulphide oxidation to achieve synthesis. The metabolic

difference between the two groups is in the use of sulphide by Thiorhodaceae as a carbon dioxide reductant. The reaction is characterised by a photosynthetic catalysis, and an absence of oxygen.

Thiorhodaceae were located beneath a surface slime layer. The metabolism of organisms constituting the slime would provide a carbon dioxide source for the Thiorhodaceae. Sulphides were present in the recycled liquors, and would have reached the Thiorhodaceae by diffusion through the outer slime layer.

The previous discussion highlights the intricate carbon dioxide and sulphide pathways that may have been occurring within the biological filter when treating fellmongery wastes.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Fellmongery waste is a complex effluent resulting from the preparatory processes in the tanning of pelts. It is very difficult to characterise.

The biological filter investigated, when treating fellmongery waste, compares favourably with other reported systems. For recycle ratios in the range 5:1 - 35:1, the following were achieved:-

(1) 57 - 67% COD removal
(2) 90 - 100% sulphide removal
(3) 27 - 45% nitrogen removal
(4) pH reduction from initial values in the range 10 - 11.5, to the range 8.05 - 8.55

COD removals were unaffected by change in influent pH. Maximum COD removal was achieved in an optimum sulphide concentration range 90 - 110 mg/l.

The mechanism of sulphide oxidation in a biological filter has been investigated by other workers with inconclusive results. These studies tended to show that sulphide removal was accomplished by a biological oxidative mechanism, rather than by a chemical oxidation. The sulphur-oxidising bacteria, Thiobacillus thioparus, was primarily responsible for the biological oxidation. Sulphide was converted to sulphate by an incompletely defined mechanism.

The effluent pH decreased as a result of the presence of sulphate and the removal of lime by carbonation reactions. The latter mechanism appeared to be the most significant one.

Batch operation is marginally superior to continuous

operation on the basis of COD removal, where batch operation is considered to be 8 hour/day per 5 day week.

Biological filtration offers considerable potential as a method of treating fellmongery wastes.

Recommendations for Further Work

It is suggested that future studies be directed at:-

(1) Evaluating the relative contributions of the packed filter and that of the sump to the overall performance of a system similar to that described.

(2) Confirming the relationship between the autotrophic and heterotrophic populations in a biological filter treating fellmongery waste.

(3) Evaluating the influence of the components of fellmongery waste on the metabolism of sulphide by Th. thioparus.

(4) Examining the role of Thiorhodaceae in the biological treatment of fellmongery wastes.

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APPENDIX 1

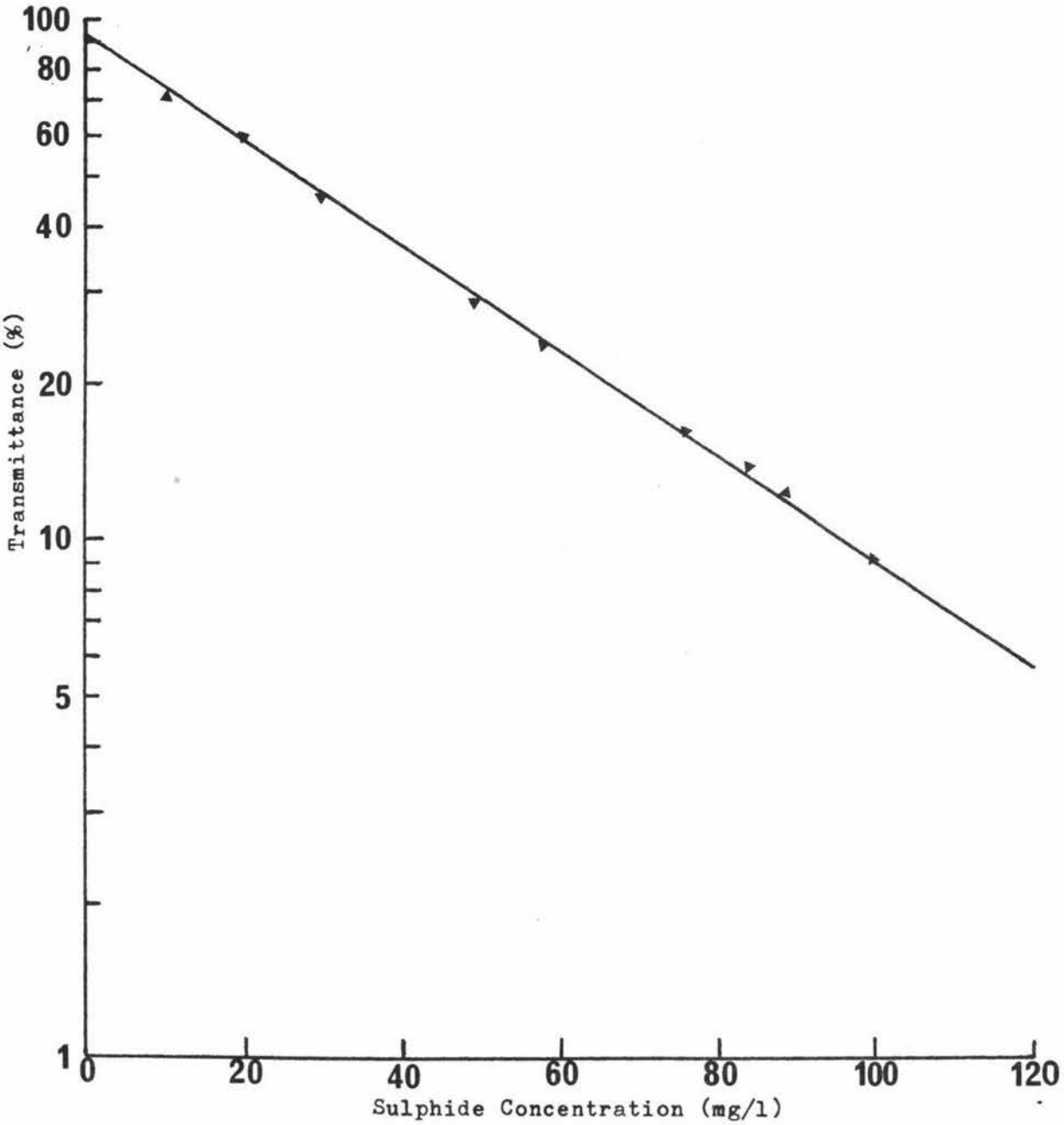

Figure A.1.1 Calibration Curve for Spectrophotometric Determinations of Sulphide. Concentration Range 10 - 100 mg/l

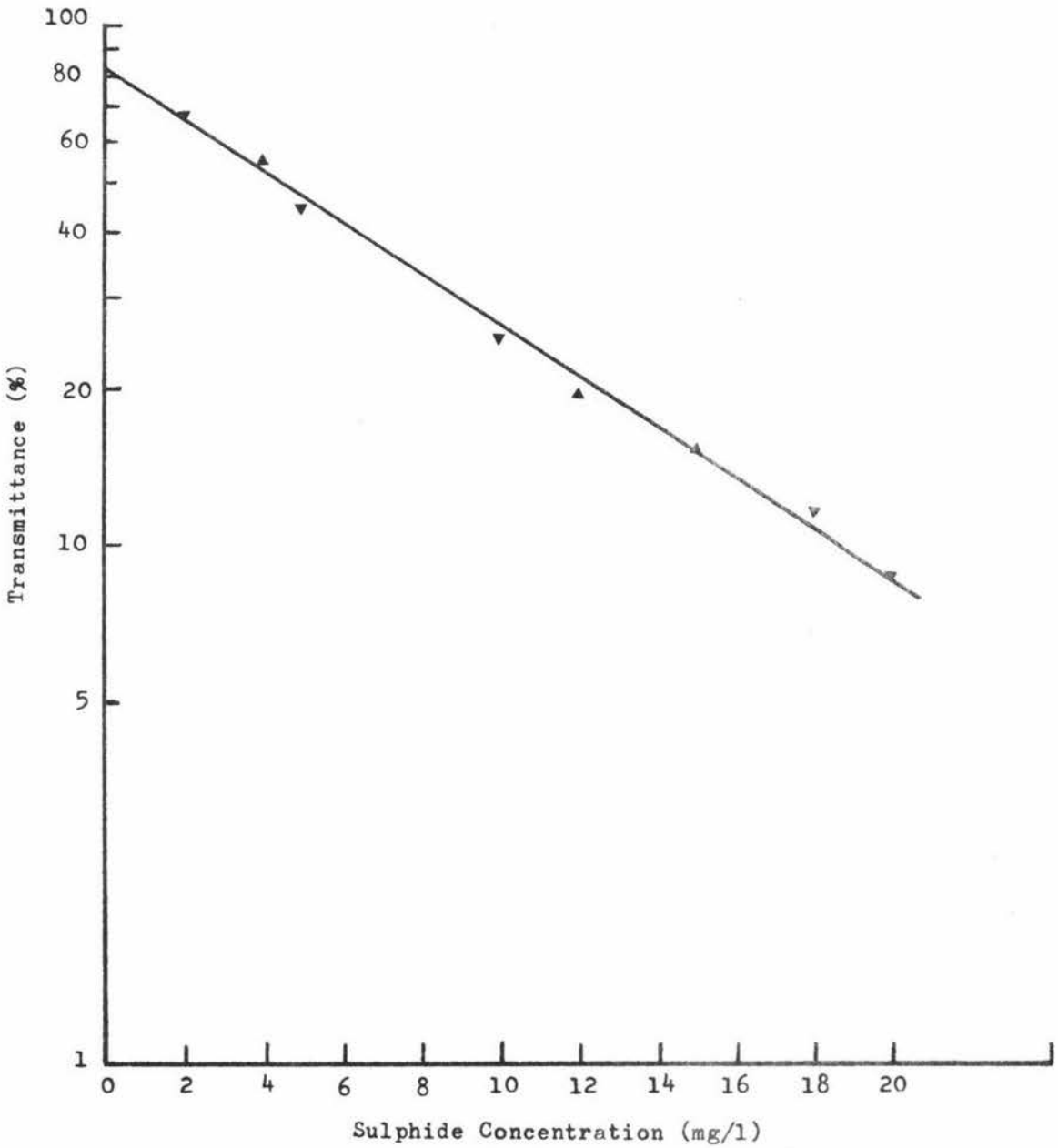

Figure A.1.2 Calibration Curve for Spectrophotometric Determinations of Sulphide. Concentration Range 1 - 20 mg/l

APPENDIX 2

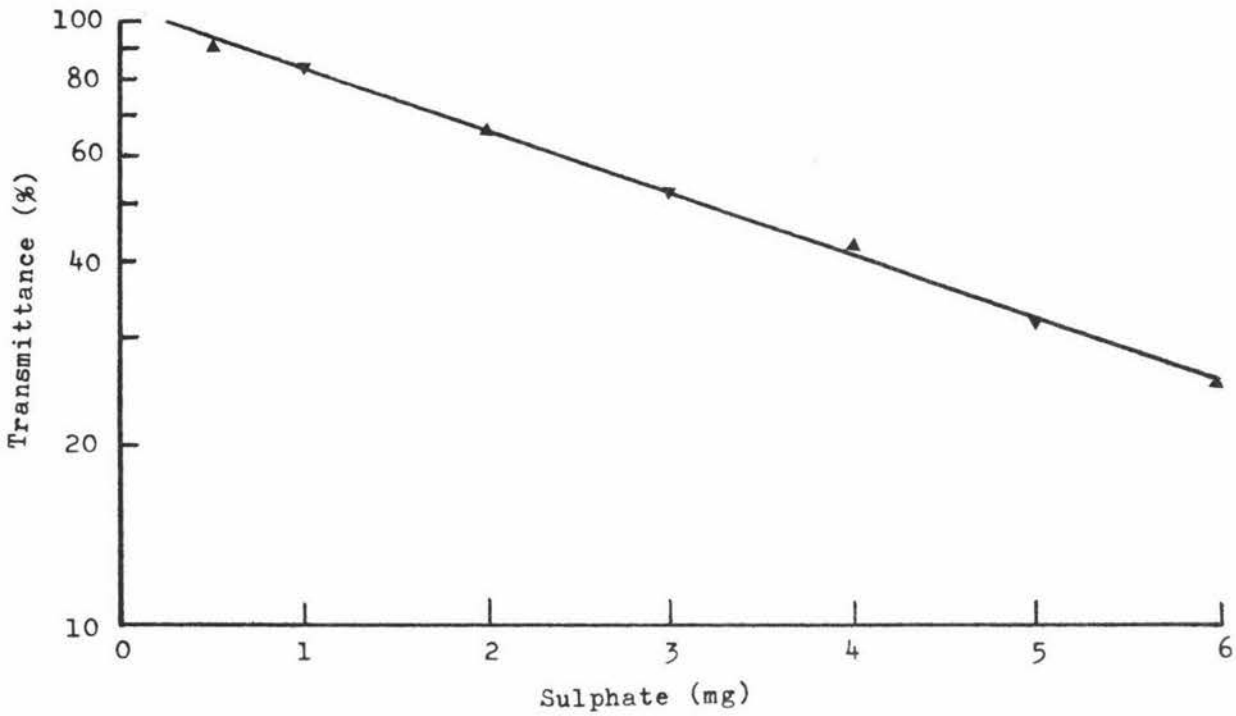

Figure A.2 Calibration Curve for Sulphate Determinations

APPENDIX 3

TABLE A.3: BIOLOGICAL FILTER - PILOT PLANT RESULTS - 8 HOUR FEED

		Operating Variables				Influent							Effluent						
Date 1973	Time	I	R	C	Te	COD	pH	$S^{=}$	$SO_4^{=}$	P	T	N	COD	pH	$S^{=}$	$SO_4^{=}$	P	T	N
	hr	mls/min			°C	mg/l		mg/l					mg/l		mg/l				
8.1	10.52	137	1987	13.5:1	21	3350	9.85	100		412	1280		720	8.20	0		0	628	
"	14.05	137	1990	13.5:1	21	3320	9.85	105		426	1540		830	8.60	0		36	630	
9.1	11.05	135	2165	15:1	21	3560	10.00	105		542	1680		1230	8.35	0		0	680	
"	13.55					3560	9.90	105		477	1550		1180	8.40	0		0	740	
10.1	11.05	133	1990	14:1	24	3400	11.30	79		690	1560		1160	8.25	4		0	750	
"	13.55					3400	11.35	80		710	1680		1310	8.35	7		0	790	
11.1	11.05	137	2190	15:1	22	3990	10.90	95		380	1340		1360	8.35	0		0	740	
"	14.05	137	2200	15:1	22	3940	10.80	95		346	1200		1480	8.35	0		0	740	
12.1	13.55	137	2200	15:1	20	3840	11.05	66		505	1320		1660	8.40	0		0	730	
15.1	11.05	136	2100	14.5:1	20	2700	11.05	67		454	1170		1200	8.40	0		0	770	
"	14.00	136	2100	14.5:1	20	3150	11.00	67		400	1140		1280	8.40	7		0	750	
17.1	11.00	136	2100	14.5:1	21	4300	10.25	64	30	357	1190		1300	8.35	0	420	0	800	
"	14.20	136	2100	14.5:1	21	4310	10.30	64	32	350	1180		1840	8.35	7	390	0	800	
19.1	10.30	136	2100	14.5:1	21	3580	11.25	125	56	800	1820		1420	8.45	7	480	0	850	
23.1	15.00	135	2025	14:1	21	2580	11.15	125	57	520	1460		1500	8.40	6	450	0	550	
24.1	13.00	136	2100	14.5:1	19	2210	10.80	100	63	335	1110		1520	8.45	4	470	0	990	
"	15.00					2210	10.70	100	68	335	1090		1400	8.55	5	450	0	900	
26.1	10.15	136	2100	14.5:1	20	2750	10.90	115	70	470	1200		1380	8.50	7	500	0	830	
"	13.25					2900	10.95	115	78	470	1200		1470	8.50	10	450	0	800	
"	15.30					2800	10.95	115	74	460	1200		1230	8.45	7		0	830	
"	16.50	136	2100	14.5:1	20	2950	10.95	115	77	465	1210		1190	8.50	7		0	840	
7.2	11.00	135	3600	25.7:1	21	1640	11.15	66	73	285	1120		770	8.65	3	450	0	480	
"	15.00	135	3600	25.7:1	21	1640	11.10	65	73	363	1470		750	8.75	3	425	0	500	
8.2	14.50	135	3600	25.7:1	22	2040	11.35	77	83	472	965		735	8.80	2	480	0	452	
9.2	13.30	135	3600	25.7:1	22	4500	11.40	92	103	570	1450		1000	8.80	0	470	0	470	
13.2	11.30	135	3600	25.7:1	19	4850	10.85	92	108	494	1400		1020	8.70	4	430	0	480	
"	14.15	135	3600	25.7:1	19	4750	10.90	92	108	465	1440	400	1370	8.70	9	420	48	550	280

TABLE A.3: BIOLOGICAL FILTER - PILOT PLANT RESULTS - 8 HOUR FEED (CONT.)

14.2	14.30	135	3600	25.7:1	22	4400	10.85	125	110	400	1300	590	1470	8.35	3	500	0	500	330
15.2	15.50	135	3600	25.7:1	21	4950	10.65	100	61	635	1440	240	1550	8.30	0	450	0	750	177
26.2	14.10	135	4795	34.5:1	24	2400	11.45	50	89	1900	2640		900	8.70	0	430	58	605	
27.2	14.30	136	4835	34.5:1	23	4270	10.95	77	100	510	1340	445	1310	8.30	0	420	0	600	284
28.2	09.15	136	4835	34.5:1	23	4250	10.95	65	81	490	1310		1380	8.05	0	525	0	630	
"	14.15	136	4835	34.5:1	23	4200	10.90	65	80	445	1260	470	1590	8.30	0	500	0	635	324
1.3	14.15	136	4835	34.5:1	25	3680	10.75	68	77	344	1040	427	1490	8.30	0	430	0	665	314
2.3	14.15	136	4835	34.5:1	25	3900	10.90	62	75	500	1190	430	1500	8.30	0	420	0	775	330
5.3	14.15	136	4835	34.5:1	24	4940	10.85	75	77	443	1310	510	1470	8.55	0	500	0	705	350
6.3	13.30	136	4835	34.5:1	22	3720	10.60	63	74	420	1210	440	1540	8.45	0	520	0	750	339
7.3	13.00	136	4835	34.5:1	20.	3930	10.80	68	67	393	1140	426	1680	8.35	0	480	0	715	343
8.3	13.15	136	4835	34.5:1	21	4210	10.95	68	70	384	1140	466	1700	8.35	0	490	0	740	342
22.3	09.00	137	800	4.9:1	21	1730	10.80	88	25	334	1030	216	685	8.35	5	465	0	620	157
"	10.00							88							7				
"	11.00							88							8				
"	14.00							88							10				
"	17.00	137	800	4.9:1	21	1600	10.65	88	30	300	835	210	765	8.40	15	390	0	680	140
23.3	10.00	136	810	5.0:1	21	2500	10.95	88	30	332	920	317	970	8.35	4	400	0	590	247
26.3	09.15	135	810	5.0:1	21	2400	10.90	77	30	394	920		590	8.40	0	455	0	595	
"	11.15					2460	10.85	177	30	380	925	230	1060	8.45	4	435	0	628	205
"	13.20					2400	10.90	77	30	335	930		1170	8.50	5	430	6	590	
"	17.05	135	810	5.0:1	21	2460	10.95	77	30	354	900		1130	8.45	9	400	0	610	
27.3	12.20	136	810	5.0:1	21	2530	11.00	91	40	383	980		1130	8.45	6	400	0	384	
"	17.05	136	810	5.0:1	21	2580	11.05	91	39	334	940	260	2000	8.65	19	390	0	578	182
28.3	12.00	136	810	5.0:1	21	2620	11.20	102	40	480	960	276	1730	8.45	9	420	0	555	161
11.4	10.30	136	1395	9.3:1	21	3140	11.05	105	32	413	980	273	416	8.45	0	390	0	305	85
"	13.00	136	1395	9.3:1	21	2950	11.05	105	36	400	1050		630	8.55	3	375	0	324	
18.4	13.00	136	1395	9.3:1	21	2910	10.85	105	23	344	935	276	1050	8.50	2	490	0	443	159
19.4	17.00	136	1395	9.3:1	21	2330	10.65	70	23	285	805	300	1170	8.20	8	490	0	510	178
20.4	17.00	136	1395	9.3:1	21	2500	10.75	92	25	290	905	290	1000	8.35	9	490	0	500	185
21.4	16.00	136	1395	9.3:1	21	2900	10.85	97	29	310	910	310	985	8.45	6	485	0	480	200

TABLE A.3: BIOLOGICAL FILTER - PILOT PLANT RESULTS - 8 HOUR FEED (CONT.)

I = Feed rate to system

R = Flow to filter surface

C = Recirculation ratio

$S^{=}$ = Sulphide

$SO_4^{=}$ = Sulphate

P = Phenolphthalein Alkalinity (as $CaCO_3$)

T = Total Alkalinity (as $CaCO_3$)

Te = Temperature

N = Nitrogen

APPENDIX 4

APPENDIX 4

Sample calculations for COD applied and COD removed

(1) For batch filter loading (8 hour feed) - Table 3.1

Consider COD results of 17.1.73

Mean influent COD = 4305 mg/l

Mean effluent COD = 1820 mg/l

Feed rate (influent) = 136 ml/min = 8.15 l/hr

Filter volume = 0.163 m^3

Take unit "day" as 8 hr.

Hence COD applied

$$= 4305 \frac{mg}{l} \times 10^{-6} \frac{kg}{mg} \times \frac{1}{0.163} \frac{l}{m^3} \times 8.15 \frac{l}{hr} \times 8 \frac{hr}{day}$$

$$= 1.72 \text{ kg/m}^3\text{day}$$

Effluent flow rate is equal to influent flow rate,

Hence COD discharged

$$= 1820 \frac{mg}{l} \times 10^{-6} \frac{kg}{mg} \times \frac{1}{0.163} \frac{l}{m^3} \times 8.15 \frac{l}{hr} \times 8 \frac{hr}{day}$$

$$= 0.73 \text{ kg/m}^3\text{.day}$$

COD removed = COD applied - COD discharged

= (1.72 - 0.73) kg/m^3.day

= 0.99 kg/m^3.day

(2) For continuous filter loading - Table 3.5

Consider COD results of 28.5.73

Influent COD = 4000 mg/l

Effluent COD = 1560 mg/l

Feed rate (influent) = 68 ml/min = 4.08 l/hr

Filter volume = 0.163 m^3

Unit "day" is 24 hr.

Hence COD applied

$$= 4000 \frac{mg}{l} \times 10^{-6} \frac{kg}{mg} \times \frac{1}{0.163} \frac{l}{m^3} \times 4.08 \frac{l}{hr} \times 24 \frac{hr}{day}$$

$$= 2.40 \text{ kg/m}^3\text{.day}$$

Effluent flow is equal to influent flow rate

$\therefore$ COD discharged

$$= 1560 \frac{mg}{l} \times 10^{-6} \frac{kg}{mg} \times \frac{1}{0.163} \frac{l}{m^3} \times 4.08 \frac{l}{hr} \times 24 \frac{hr}{day}$$

$$= 0.94 \text{ kg/m}^3\text{.day}$$

$\therefore$ COD applied = $(2.40 - 0.94)$ kg/m^3.day

$= 1.46$ kg/m^3.day

APPENDIX 5

APPENDIX 5

Sample calculation of S.

$$S = \frac{\text{sulphur removed as sulphide}}{\text{sulphur increase as sulphate}}$$

Consider sulphide and sulphate measurements of 19.1.73 for the batch filter loading (Table 3.2)

Influent sulphide concentration	=	125 mg/l
Effluent sulphide concentration	=	7 mg/l
∴ Sulphide removed	=	118 mg/l

Since sulphide has a similar molecular weight to that of sulphur (32.06),

Sulphide removed as sulphur	=	118 mg/l

Influent sulphate concentration	=	56 mg/l
Effluent sulphate concentration	=	480 mg/l
∴ Sulphate removed	=	424 mg/l
Molecular weight of sulphate	=	96.06

$$\therefore \text{ Sulphate removed as sulphur} = 424 \frac{mg}{l} \times \frac{32.06}{96.06}$$

$$= 142 \frac{mg}{l}$$

$$\therefore \quad S = \frac{118 \text{ (mg/l)}}{142 \text{ (mg/l)}} = 0.83$$

APPENDIX 6

TABLE A.6: BIOLOGICAL FILTER:- PILOT PLANT RESULTS - CONTINUOUS FEED

Date 1973	Operating Variables				Influent							Effluent						
	I	R	C	Te	BOD	COD	pH	$S^=$	$SO_4^=$	P	T	BOD	COD	pH	$S^=$	$SO_4^=$	P	T
	ml/min			°C	mg/l			mg/l		mg/l		mg/l			mg/l		mg/l	
28.5	68	900	12.2:1	21		4000	10.25	66	12	196	925		1560	8.25	7	400	0	755
29.5	68	900	12.2:1	21		3720	10.45	91	13	265	955		1960	8.05	6	370	0	835
30.5.	67	900	12.2:1	21	1760	4500	10.25	110	12	275	1200	720	2020	8.20	11	340	0	1150
1.6.	67	900	12.2:1	21		3720	10.00	97	19	206	1030		2000	8.25	5	310	0	1260
2.6	68	900	12.2:1	21	1150	3560	10.20	97	19	246	1120	960	1950	8.20	11	305	0	1230
5.6	67	900	12.2:1	21	1180	3160	9.95	83	9	196	900	690	1590	8.25	11	350	0	1190
7.6	67	900	12.2:1	21	1350	3560	10.25	89	10	200	1000	630	1480	8.25	10	300	0	1180
8.6	67	900	12.2:1	21	1400	3750						500	1490					
12.6	68	900	12.2:1	31	1170	2870	11.20	102	7	405	1240	290	995	8.45	28	130	0	1260
13.6	68	900	12.2:1	30	1000	2660	11.20	81	9	304	1060	370	995	8.55	21	120	0	1260
14.6	68	900	12.2:1	31			10.95	93						8.55	20			
16.6	68	900	12.2:1	30	1480	3850	11.20	80	9	304	1060	390	1120	8.55	19	125	0	1160
18.6	68	900	12.2:1	31	1500	3870	10.20	105	9	304	930	410	1120	8.25	16	120	0	1120
20.6	68	900	12.2:1	31	1380	3500	10.45	80	8	344	1070	280	1020	8.25	16	175	0	1040
21.6	68	900	12.2:1	31	1460	3740	10.25	81	10	326	1030	340	980	8.30	15	220	0	1000
22.6	68	900	12.2:1	31		3940	10.40	79	9	305	1070		960	8.25	10	230	0	1010
26.6	68	900	12.2:1	31		1490	10.00	82	12	148	490		385	8.20	4	300	0	443
29.6	68	900	12.2:1	31			9.80	84	10					8.25	0	315		
9.7	68	900	12.2:1	34		955	9.85	67	11	127	422		188	8.30	0	375	0	410
10.7	68	900	12.2:1	33	510	1200	9.75	73	11	137	410	66	202	8.05	0	395	0	373
11.7	68	900	12.2:1	34	480	1240	9.85	81	12	138	400	69	187	8.10	0	380	0	382
12.7	68	900	12.2:1	34	820	2110	10.90	102	6	442	960	105	297	8.02	0	405	0	500

I = Feed rate to system R = Flow to filter surface C = Recirculation ratio

Te = Temperature $S^=$ = Sulphide $SO_4^=$ = Sulphate P = Phenolphthalein Alkalinity (as $CaCO_3$)

T = Total alkalinity (as $CaCO_3$)

APPENDIX 7

APPENDIX 7

$K_L a$ Calculations for Filter Column

The basic equation which gives the rate of diffusion of oxygen from a gas stream to a liquid is of the form

$$Q = K_L a\ (C^* - C_L) \qquad \ldots\ldots\ (1)$$

Q = rate of diffusion of oxygen from gas to liquid.
$K_L a$ = volumetric mass transfer coefficient.
C^* = saturation dissolved oxygen concentration of liquid at the temperature and barometric pressure of the test.
C_L = concentration of dissolved oxygen in bulk solution.

When the sulphite oxidation method is used to evaulate oxygen transfer, the rate of dissolution of oxygen is the controlling factor, and since the back pressure of dissolved oxygen is negligible in the solution ($C_L = 0$), $K_L a$ is given by:

$$K_L a = \frac{Q}{C^*} \qquad \ldots\ldots\ (2)$$

(1) Sample calculation of $K_L a$ per unit volume for a column flow rate of 810 ml/min

$SO_3^=$ concentration before run = 5390 mg/l
$SO_3^=$ concentration after run = 1200 mg/l

∴ Amount of $SO_3^=$ oxidised to $SO_4^=$ = 4190 mg/l

The oxidation undergone by sulphite is

$$SO_3^= + \frac{1}{2} O_2 \xrightarrow[\text{catalyst}]{Co} SO_4^=$$

Consequently 5 mg/l of $SO_3^=$ are required to remove 1 mg/l of oxygen.

$\therefore$ Amount of oxygen removed $= \frac{4190}{5}$ mg/l

$= 838$ mg/l

Convert to a molar basis:

Amount of oxygen removed $= 0.0261$ g moles O_2/l

Volume of solution passed through column per hour

$= 48.6$ l

$= 2,710$ g moles

Amount of oxygen transferred per hour $= 0.261 \frac{\text{g mole}}{\text{l}} \times 48.6$ l

$= 1.27$ g mole

Equilibrium concentration of oxygen in water in contact with air at 1 atmosphere and 10°C is calculated from Henry's Law

$$x = \frac{\bar{p}}{H}$$

where: $\bar{p}$ = partial pressure of gas

H = Henry's Law constant

$\bar{p}_{O_2} = 0.21$ atm

$H = 3.27 \times 10^4$ atm/mole fraction

$\therefore x = \frac{0.21}{3.27 \times 10^4} = 6.42 \times 10^{-6} \frac{\text{g mole } O_2}{\text{g mole } H_2O}$

This is equivalent to C* in Equation (2)
Substituting respective values in (2):

$$K_L a = 1.27 \left(\frac{\text{g mole}}{\text{hr}}\right) \times \frac{1}{2.71 \times 10^{-3}} \left(\frac{\text{hr}}{\text{g mole } H_2O}\right) \times \frac{1}{6.42 \times 10^{-6}} \left(\frac{\text{g mole } H_2O}{\text{g mole } O_2}\right)$$

$= 73$

$\therefore K_L a$ per unit liquid volume $= 73$
This $K_L a$ value is dimensionless

(2) Sample Calculation of true $K_L a$ for a column flow rate of 810 ml/min (= 48.6 l/hr)

Packing volume = Vp = 680 l

$K_L a$ per unit liquid volume for 810 ml/min = 73

$$K_L a \times Q = 73 \times 48.6 \frac{l}{hr}$$

$$= 3500 \frac{l}{hr}$$

$$K_L a \times \left(\frac{Q}{p}\right) = 3500 \frac{l}{hr} \times \frac{1}{680\ l}$$

$$= 5.1\ hr^{-1}$$

∴ $K_L a$ based on packing volume = $5.1\ hr^{-1}$.

APPENDIX 8

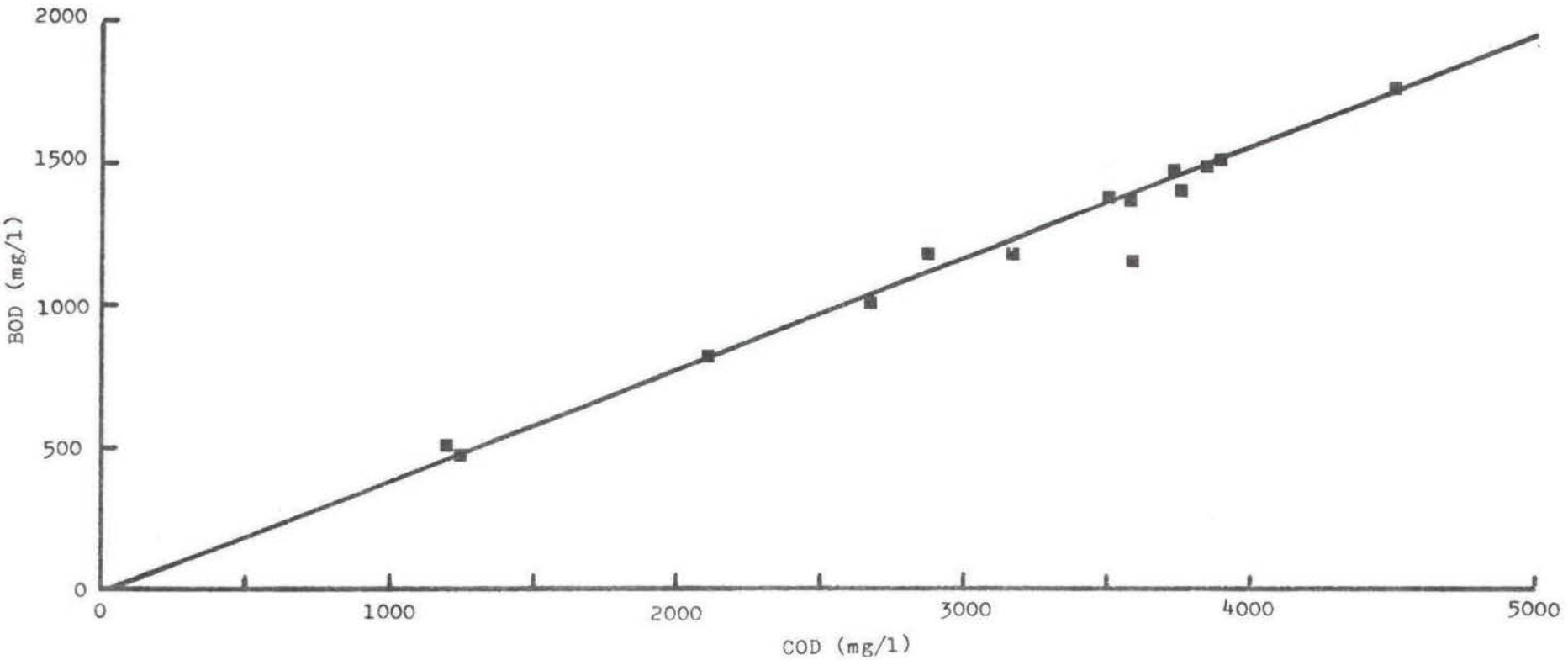

Figure A.8.1 BOD/COD Relationship for Filter Influent

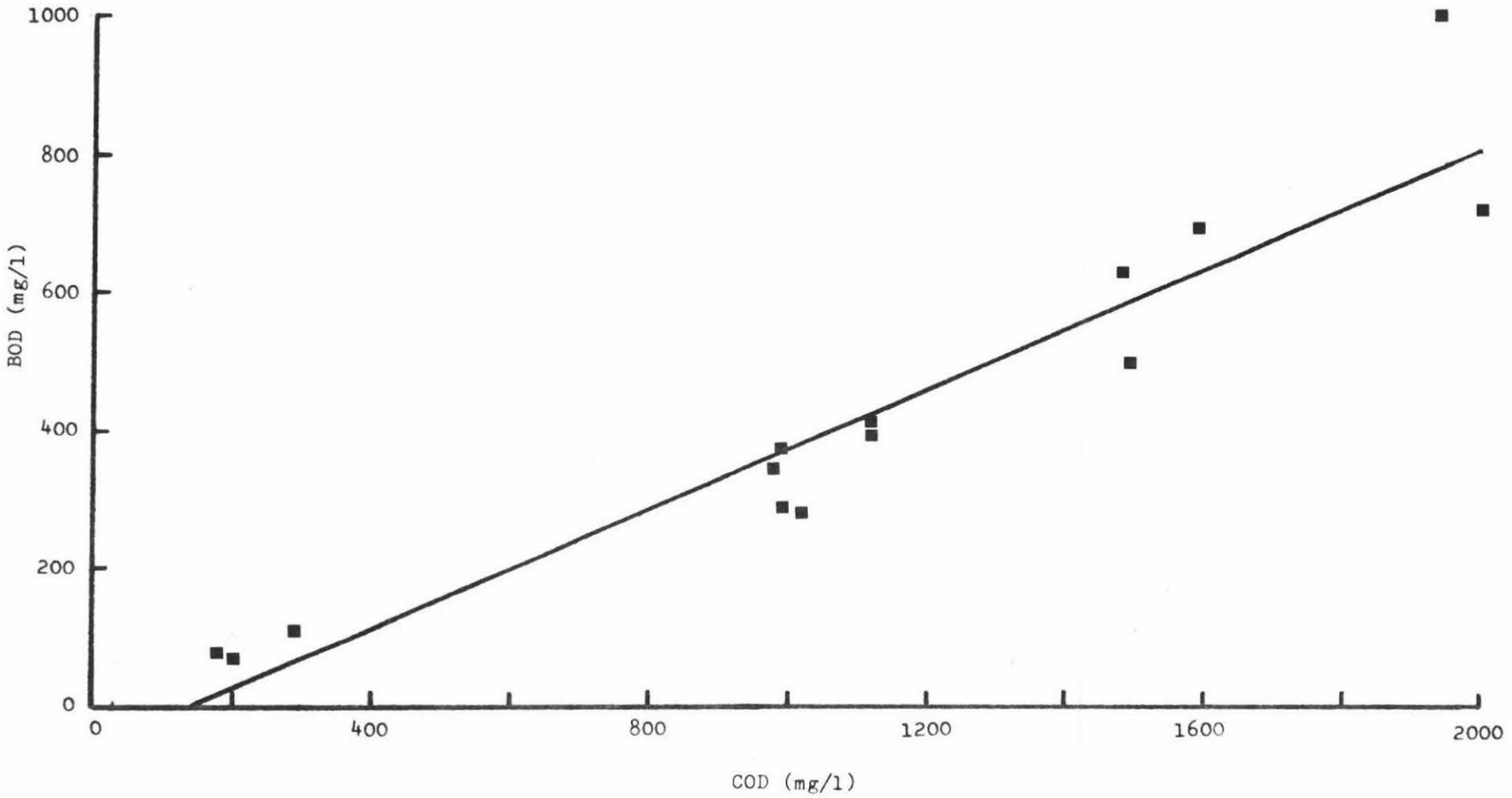

Figure A.8.2 BOD/COD Relationship for Filter Effluent