PREFERMENTATION AND SEQUENCING BATCH REACTOR TREATMENT OF FARM DAIRY EFFLUENT FOR BIOLOGICAL NUTRIENT REMOVAL

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ABSTRACT

In order to meet the requirements of regional councils' Water Quality Plans implemented under the Resource Management Act (1991), many farmers in New Zealand are now irrigating effluent farm dairy effluent. However there are situations where irrigation is not practicable and it is considered that a sequencing batch reactor (SBR) treatment system may provide a highly treated effluent able to be discharged directly to waterways.

The objectives of this research were to develop an SBR operating strategy to optimise biological nutrient removal from farm dairy effluent, monitor the effectiveness of a pilot-scale SBR at removing nitrogen and phosphorus, and assess whether the untreated effluent could be made more readily biodegradable by prefermentation.

An operating strategy was designed to enable biological nutrient removal, with the aim of achieving low phosphorus, ammonia and nitrate effluent concentrations. The SBR operating strategy is Fill, Anaerobic, Aerobic I, Anoxic, Aerobic II, Settle, and Decant.

Phosphorus is released in the anaerobic phase, using the readily biodegradable carbon. The first aerobic phase is used for nitrification and phosphorus uptake. Remaining readily biodegradable carbon is also oxidised thus the denitrification occurring in the anoxic phase depends entirely on endogenous carbon. The final aerobic phase operates as a polisher.

The results show that the SBR did not achieve biological nutrient removal: there was no apparent reduction in nitrogen and phosphorus levels in the effluent. The most likely reason for the SBR's failure to operate as expected is that it was operated on settled effluent rather than raw farm dairy effluent.

The prefermentation trial aimed to increase the readily biodegradable carbon to improve phosphorus removal. The results showed that the optimal time for prefermentation of raw farm dairy effluent at 20°C was eight to ten days, when VFA oxygen demand peaked at about 2,100 mg/L. The prefermentation trial showed a lag phase of 0 to 2 days. The VFA proportions obtained in this experiment were 1.0 : 0.3 : 0.14 : 0.08 acetic : propionic : butyric : valeric acids.

The SBR is likely to operate as part of a total treatment system, designed to enhance BNR and provide a high quality effluent. It is considered that screened farm dairy effluent would be held in a prefermentation pond with a hydraulic retention time of at least 8 to 10 days. Prefermented effluent would be treated in the SBR. The effluent would then be polished using wetlands.

KEYWORDS:

Sequencing batch reactor; prefermentation; farm dairy effluent; nitrogen removal; phosphorus removal; volatile fatty acids.

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1. INTRODUCTION

1.1 New Zealand's dairy industry

Dairy farming is a major industry in New Zealand which provides some 20% of total export earnings ($2,982.2 million in the year to June 1996, (Department of Statistics, 1997)). Ninety to 95% of all milk produced is exported as milk powder, cream products, cheese, or protein products (Department of Statistics, 1997).

The number of dairy cows in New Zealand has been rising over the last decade, reaching 4.090 million in the year to June 1996. Around 1.58 million ha, or 11%, of farmland was used for dairy farming at 30 June 1995, consisting of about 69,000 dairy farms. Milk production for the year ended May 1996 reached a record high of 788,000 tonnes of milk solids and this was expected to be topped in the year to May 1997 (Department of Statistics, 1997).

1.2 Farm dairy effluent

Dairy herds in New Zealand generally graze pasture year-round. Manure collection and treatment is an issue only for the time that the cows are in the yard for milking, typically 1.5 to 3 hours per day, equating to about 6 to 12% of daily manure production (Ministry of Agriculture and Fisheries, 1994).

There are three major components of farm dairy effluent: excreta, washdown water (for udder, plant and yard), and spilt or waste milk. The volume of waste produced is a function of herd size, milking time, and water use and conservation practises. There is

evidence that more effluent is produced during milking than at other times, due to the animals being stressed (Heatley, 1995). Vanderholm (1984) gives a range of 20 to 90 litres per cow per day as the volume of waste produced during milking, with an average of 50 L/cow.day, while Southland Regional Council (1993) suggests an average of 70 L/cow.day

Farm dairy effluent is a high strength waste. It is high in oxygen demanding substances (COD and BOD) and nutrients (nitrogen and phosphorus), and has a high solids content. The concentration of nutrients in the waste is related to nutrient levels in the animals' feed (Southland Regional Council, 1993). Some New Zealand data on the composition of farm dairy effluent is presented in Table 1.1.

Table 1.1 Nutrient characteristics of raw farm dairy effluent

Source: Heatley (1995)

Nutrient	Quantity per cow per day (g)		Annually per 100 cows (kg)
	Typical	Range	
BOD_5	120		
TKN	22.0	7.0 - 30.0	590
TP	2.5	0.5 - 4.5	70
TK	20.0	5.5 - 26.0	540
TS	3.0	1.0 - 4.0	80
Calcium			220
Chloride			180
Magnesium			100
Sodium			70
COD*	330	up to 570	
Total solids*	360	165 - 495	
Volatile solids*	250	120 - 360	

*Source: Vanderholm (1984)

A comparison of farm dairy effluent production and daily domestic sewage production shows that, depending on the contaminant of interest, the effluent produced per cow is equivalent to that produced by between two people (for BOD production) and eight people (for total nitrogen production) (Southland Regional Council, 1993). Given that there are 4.090 million dairy cows in New Zealand, this is equivalent to a population of 8 to 32 million people.

1.3 Environmental effects

The potential for pollution from farm dairy effluent is dependent on waste volumes, the method of treatment and disposal, and the receiving water. Pollution of waterways through the discharge of farm dairy effluent is specifically identified as an area of concern in New Zealand's *Environment 2010 Strategy* (Ministry for the Environment, 1994).

Davies-Colley (1996) identifies eleven different types of pollutant referred to, or implied, by the Resource Management Act 1991. These are oxygen demanding substances, suspended solids, infectious microbiota, acids and bases, heat, toxic materials, nutrients, malodorous substances, tainting substances, light attenuating materials and unsightly materials. He states that pollutants from all the above categories are to be found in farm dairy effluent ponds, with the exception of heat, and acids and bases.

Davies-Colley concludes that priority pollutants are faecal indicators; ammoniacal nitrogen, primarily as a toxicant, but also as a nutrient and an oxygen demanding substance; and suspended solids, for their effects both on stream life and on clarity of receiving waters.

Nitrogen and phosphorus are of particular concern as they stimulate excessive phytoplankton growth, which is responsible for the eutrophication of water bodies (Randall *et al*, 1992; Ministry of Agriculture and Fisheries, 1993). Eutrophication causes low oxygen levels, poor water clarity, odours, and may lead to fish kills in streams and lakes. Development of catchments, particularly into fertilised pasture, appears to be causative (Ministry of Agriculture and Fisheries, 1993). Some 2.2 million tonnes of phosphorus-based fertiliser was applied to farmland in New Zealand in 1996 (Department of Statistics, 1997).

Nitrogen and phosphorus enter waterways through point sources, such as sewage outfalls, or from diffuse sources, such as stormwater or pasture runoff. Phosphorus is generally considered to be a conservative substance that accumulates within a system, either in biomass or in sediments (Randall *et al*, 1992), however there is evidence that a small fraction is released to the atmosphere as phosphine (Kadlec and Knight, 1996), as is shown in the wetland model given in Figure 1.1. Phosphorus is released when thermal stratification occurs in a lake or reservoir and the lower layer of water becomes anaerobic. When the lake turns over, these minerals mix with the rest of the water causing high nutrient levels and thus eutrophication (Randall *et al*, 1992).

The importance of considering nutrients in wastewater is highlighted by the fact that the COD of the biomass required to assimilate nitrogen and phosphorus in wastewater is far higher than the COD of the original wastewater. Generally phosphorus is considered to be the limiting nutrient in controlling eutrophication in freshwater and nitrogen is the limiting nutrient in marine and estuarine environments (Randall *et al*, 1992).

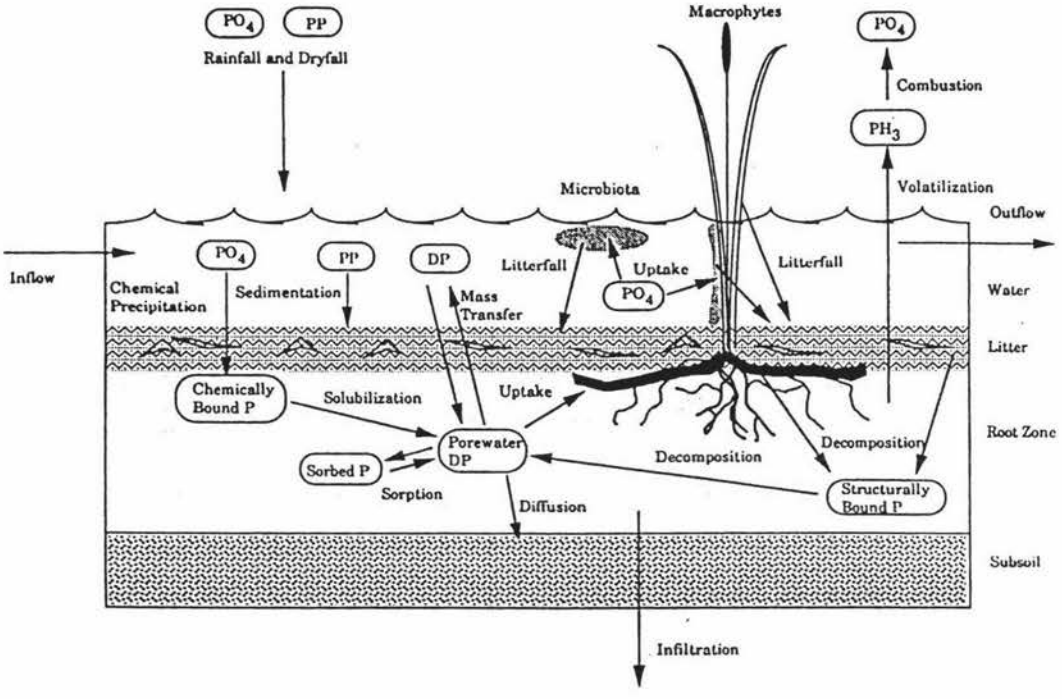

Figure 1.1 Phosphorus storages and transfers in the wetland environment

PO_4 = orthophosphate, PP = particulate phosphorus, DP = dissolved phosphorus, PH_3 = phosphine. PP may consist of all the forms shown in the root zone.

Source: Kadlec and Knight, 1996, Figure 14-1

1.4 Legislative requirements

The statutory framework for managing water quality and controlling discharges to water in New Zealand is the Resource Management Act 1991 (the Act). The purpose of the Act is "to promote the sustainable management of natural and physical resources".

Treatment of farm dairy effluent (and other farm effluents) has become an increasingly important issue for farmers since the introduction of the Act in 1991. The Act requires

that any discharge to water not affect the quality of the receiving water (Sections 70 and 107 and Third Schedule). Section 15 of the Act states that:

> "(1) No person may discharge any-
>
> (a) Contaminant or water into water; or
>
> (b) Contaminant onto or into land in circumstances which may result in that contaminant (or any other contaminant emanating as a result of natural processes from that contaminant) entering water; ... unless the discharge is expressly allowed by a rule in a regional plan, and in any relevant proposed regional plan, a resource consent, or regulations."

Section 30 identifies regional councils as being responsible for the maintenance of water quality in lakes and rivers. Regional councils may produce regional plans which identify the adverse environmental effects on a specific resource. Regional plans describe the issues involved, the objectives, policies and methods for addressing the issues and the rules relating to resource consent requirements and conditions for applications (Manawatu-Wanganui Regional Council, 1995a).

The objective of the Proposed Manawatu Catchment Water Quality Regional Plan is "to enhance surface water quality ... to a level which meets the needs of all people and communities while safeguarding the life-supporting capacity of the water" (Manawatu-Wanganui Regional Council, 1995b, pg. 26). This is to be achieved by limiting the quantities and concentrations of contaminants entering the water and, where appropriate, promoting discharges to land rather than water.

Restrictions are placed on the following discharges to water in the Proposed Manawatu Catchment Water Quality Regional Plan (Forsyth, 1996):

- discharges of untreated wastewater or treatment by physical processes only;

- dissolved carbonaceous BOD, ammonia and phosphorus levels;
- discharges that cause changes in horizontal visibility, hue and euphotic depth.

The receiving water limits for ammonia and phosphorus in the Proposed Manawatu Catchment Water Quality Regional Plan are less than 1.1 g/m^3 (at temperatures of 15°C or less) or less than 0.8 g/m^3 (at temperatures greater than 15°C), and less than 0.015 g/m^3, respectively. These limits apply after reasonable mixing of effluent in the receiving water, the definition of which is site-specific (Forsyth, 1996).

Other regional councils have set minimum treatment requirements with respect to farm effluents, such as the two pond system (Auckland, Waikato, Bay of Plenty, Taranaki, and West Coast) and/or barrier ditch (Waikato, Bay of Plenty, and Taranaki), along with either receiving water (Auckland and West Coast) or effluent quality minimum standards (Waikato, Bay of Plenty, and Taranaki). At June 1996, several regional councils had not yet notified a regional plan or not specified minimum standards (Forsyth, 1996).

1.5 Treatment of farm dairy effluent

1.5.1 Waste stabilisation ponds

Recognition of degraded water quality led catchment authorities to encourage the two-pond treatment system as the best practicable treatment option in the early 1970s (Ministry of Agriculture and Fisheries, 1994). Prior to this, untreated farm dairy effluent was disposed of into a nearby drainage ditch or waterway, or by land treatment (Mason, 1996).

The standard design for stabilisation ponds treating farm dairy wastewater in New Zealand is a two pond system consisting of an anaerobic pond followed by a facultative

(commonly known as aerobic) pond. Design guidelines were originally produced by the Ministry of Works and Development (1972) and republished in 1975 and 1985, with minor modifications, by the Ministry of Agriculture and Fisheries (Sukias *et al*, 1996). The design guidelines were based on American data for anaerobic ponds treating manure-based wastewaters and facultative ponds treating domestic sewage (Southland Regional Council, 1993; Ministry of Agriculture and Fisheries, 1994).

The ponds were designed to remove 90 to 95% of BOD_5 and suspended solids. Although the system was not designed for the removal of nitrogen or phosphorus, about 85% of total nitrogen and 70% of total phosphorus may be removed if the ponds are functioning well (Ministry of Agriculture and Fisheries, 1994). The system had the advantage of being low capital cost, with very low operation and maintenance cost (Ministry of Agriculture and Fisheries, 1994).

The treated effluent from the two-pond system was usually discharged into farm drainage systems or streams and rivers. More recently, in order to meet the water quality requirements of Regional Plans, land application has become a common method of disposal and is allowed as a permitted activity in some regions, for example, the Waikato region (Selvarajah, 1996).

According to Sukias *et al* (1996) anaerobic ponds treating farm dairy wastewater operate well, with greater than 70% removal of BOD_5, but facultative ponds are not performing very satisfactorily. Design guidelines for farm dairy ponds suggest that facultative ponds should achieve 80% removal of BOD_5, however in practice they appear to be achieving about 40 to 50% removal (Sukias *et al*, 1996). Facultative pond design was based on ponds treating domestic effluent, which did not allow for differences in effluent composition. Light penetration, needed for oxygen production by algae in facultative ponds, is minimal in farm dairy facultative ponds, which reduces their effectiveness (Mason, 1996).

Effluent quality has been found to be variable among the pond systems (Southland Regional Council, 1993; Ministry of Agriculture and Fisheries, 1994). Reasons for poor performance may be attributed to system design or use. Design problems include (Ministry of Agriculture and Fisheries, 1994):

- pond specifications are based on average waste loads, which may differ from actual waste loads depending on washdown/milking practices;
- recommended loading rates are based on broad geographical assumptions for climate which may be inadequate in some areas;
- incorrect location of inlets and/or outlets;
- infiltration to ponds by groundwater;
- drainage or runoff entering ponds.

Incorrect usage of ponds may cause overloading or reduced operation by any of the following reasons (Ministry of Agriculture and Fisheries, 1994):

- increased herd size without a corresponding increase in pond size;
- crusting developing to such an extent that flow is restricted or stopped;
- sludge build up;
- outlet clogged or not operating correctly.

1.5.2 Land treatment

Land disposal, or land treatment, is "the controlled application of effluent onto land and its treatment through the natural physical, chemical and biological processes within the soil-water-plant matrix" (Carnus, 1997, pg. 29). It may provide a viable, culturally acceptable and sustainable alternative to discharging effluent into surface waters (Carnus, 1997), providing the system is properly managed.

In many places, land treatment of farm dairy effluent provides an improved treatment method to the two pond system. Discharge of farm dairy effluent to land is a permitted activity in the Waikato region (Selvarajah, 1996), whereas it is a controlled activity in the Manawatu-Wanganui region (Manawatu-Wanganui Regional Council, 1995b).

Effluent may be irrigated daily or stored in ponds and then spray irrigated when weather and soil conditions are suitable. Effectiveness of land treatment is dependent on proper management of the system: hydraulic and nutrient loading rates must be correctly determined and adhered to to avoid contamination of groundwater, ponding or runoff (New Zealand Land Treatment Collective, 1993). Some soil types, such as the silty-clays of the Manawatu, are not free draining and thus irrigation is possible for only a few months of the year.

Whilst land disposal of effluent may be promoted for the protection of waterways, inappropriate application or poor management of the system, for example irrigating when soil is at field capacity, or spraying too close to waterways, may mean that nutrients still enter waterways. There is also the possibility of overloading the plants' and soil's capacity for the nutrient, which may lead to leaching to groundwater. This is of particular concern with nitrate, which may cause methaemoglobinaemia (blue baby syndrome) if levels in drinking water are sufficiently high (New Zealand Land Treatment Collective, 1993).

Land treatment requires a system of harvesting the nutrients in the biomass to avoid nutrient recycling. As the majority of land treatment is onto pasture, harvesting may be done by hay/feed production or by grazing. An alternative method under investigation is irrigating farm dairy effluent in eucalyptus and willow short rotation forestry (Roygard *et al*, 1997).

1.5.3 Alternative treatment methods

1.5.3.1 Pond upgrading

Treatment pond performance may be enhanced by modifying or extending the existing treatment scheme. Sukias *et al* (1996) categorise these as follows:

- "Add-ins" to existing pond facilities, e.g. mechanical aeration, baffling, biofilm attachment surfaces;
- "Add-ons" to otherwise unchanged existing pond facilities, e.g. maturation ponds, rock or sand filters, overland flow, constructed wetlands, land irrigation, rotating biological contactors; or
- Redesigned or reconfigured pond facilities, e.g. increased pond size, improved inlet/outlet structures, reduced water level.

Each of these methods will improve a pond's treatment performance, however as ponds are designed for BOD and suspended solids removal only, there will be limited improvement in nutrient removal. Attached growth processes, such as rock filters, constructed wetlands, and rotating biological contactors, may contribute significantly to nitrogen removal.

1.5.3.2 Wetlands

Constructed wetlands are simple, natural treatment systems that may provide cost-effective, low maintenance treatment of treated pond effluent (Tanner and Sukias, 1996). Effluent may be treated by either surface or sub-surface flow. Wetlands may also be planted. Features of wetland treatment processes are (Tanner and Sukias, 1996):

- low flow velocities and tortuous pathways allow sedimentation;
- contact between water, sediments and biofilms is high due to large surface areas created by vegetation;
- high plant productivity and thus high nutrient uptake; and
- a mixture of aerobic, anaerobic and anoxic zones created by plant photosynthesis.

Tanner *et al* (1995a&b) have conducted in-depth research on the use of wetlands for tertiary treatment of farm dairy effluent treated in oxidation ponds. Reductions of 50 to 80% of carbonaceous BOD_5, and 75 to 85% of suspended solids were achieved. It was also noted that changes in the influent concentrations were reflected in the effluent concentrations.

Planted wetlands have shown greater overall removal of nitrogen (48 to 75%) and phosphorus (37 to 74%) than unplanted wetlands (12 to 41% nitrogen removal and 12 to 36% phosphorus removal) (Tanner *et al*, 1995b). Higher removal occurred at the longer retention times (seven days). Influent quality varied markedly during the trial, with carbonaceous BOD_5 of 20 to 300 mg/L, suspended solids of 60 to 250 mg/L, total nitrogen of 10 to 110 mg/L and total phosphorus of 8 to 18 mg/L.

Treatment efficiency for phosphorus decreases over time, as sorption sites in the sediments and organic matter become saturated, and the wetlands mature (Tanner and Sukias, 1996).

Wetlands have the additional benefits of providing a wildlife habitat and providing a more culturally acceptable treatment method.

1.5.3.3 Adsorption/filtration

Several types of solid media are being investigated for the removal of nutrients from treated farm dairy effluent by adsorption or filtration.

Research at Massey University, Palmerston North, is using *Pinus radiata* bark to remove nutrients from farm dairy effluent. Treated effluent is applied to columns of bark. Although there is some preferential flow through the columns, preliminary results show that the bark retains nitrogen at 8.4 g/kg bark, phosphorus at 1.6 g/kg bark and potassium at 23.4 g/kg bark (Bolan *et al*, 1996). Thus for a herd of 250 cows on seasonal production, 450 m^3 of bark would be required per annum to retain the nutrients in the effluent.

A two-year trial using a scoria-like by-product of the steel-making process in a wetland system has shown 80% removal of suspended solids and 90% phosphorus removal (Curtis, 1996). The medium (marketed as "Ecoflow") is similar in composition to river gravel and is porous.

Naturally occurring zeolites (hydrated aluminium-silicate minerals) have been tested for ammonium and phosphate removal from effluent. The zeolites have been shown to have a significant capacity to remove phosphate and ammonia. Using synthetic and natural wastewaters, phosphorus removal of 14 to 84%, and ammonia removal of 67 to 98% was achieved, depending on the zeolite source and particle size (Nguyen, 1996). Desorption of ammonia from the zeolite into water was low (6 to 23%), but 34 to 100% of phosphorus was desorbed.

The capacity of these systems is likely to depend on the method of contaminant removal, clogging of the system by suspended solids, the size of the media and treatment bed, and the capacity of the media for adsorbing the nutrients.

1.5.3.4 Sequencing Batch Reactor (SBR)

A sequencing batch reactor (SBR) is an activated sludge treatment process that operates in batch mode, rather than the more conventional continuous mode. SBRs may be operated to remove carbon, nitrogen, phosphorus and toxins.

SBR treatment is a relatively simple method for treating farm wastes. SBR technology is particularly suitable for farm dairy effluent as the effluent is produced in batches (twice-daily milkings), and the set-up cost for a single tank treatment plant is more attractive than that for a continuous activated sludge treatment plant, which requires a separate tank for each step of the treatment process.

2. LITERATURE REVIEW

2.1 Biological nutrient removal (BNR)

2.1.1 Nutrient removal processes

Biological nutrient removal (BNR) is the term given to secondary wastewater treatment that uses micro-organisms to remove nitrogen and phosphorus species from wastewater.

Traditionally in New Zealand, any BNR that occurs during treatment has been incidental to the primary purpose of reducing the BOD and suspended solids of the wastewater, however several cities have implemented BNR treatment systems in the last decade, including Rotorua and Porirua, and more are likely to in the next decade as Water Quality Regional Plans become operative.

In Europe, population density has, for a long time, put significant pressure on land and water resources, and thus many countries have been using BNR techniques since the 1960s (Henze, 1996).

While activated sludge systems have come to the fore in BNR, other systems, such as trickling filters, are capable of nitrogen removal. BNR requires a combination of anaerobic, anoxic and aerobic conditions in order to promote nitrogen and phosphorus removal.

2.1.1.1 Nitrogen removal

Nitrogen removal is a two-step process involving nitrification and denitrification, which are carried out by different micro-organisms. Nitrification is the first step in removing nitrogen from the effluent; denitrification is required to convert the nitrified products to nitrogen gas which, unlike other compounds of nitrogen, is relatively unavailable for biological growth.

Nitrogenous pollutants, in the form of ammonia, are first converted into nitrite by *Nitrosomonas* bacteria and then to nitrate by *Nitrobacter*, under aerobic conditions, using alkalinity as the carbon source (Randall *et al*, 1992). The equations for the conversions are (Randall *et al*, 1992; Henze *et al*, 1995):

Nitrosomonas

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O \qquad (2.1)$$

Nitrobacter

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \qquad (2.2)$$

The nitrification process has an optimal pH range of 8 to 9, and a dissolved oxygen level greater than 1 mg/L is required. The optimum temperature for nitrification is 30°C (Henze *et al*, 1995).

Nitrate is subsequently converted to nitrogen gas by the heterotrophic denitrification bacteria (several different genera may be involved) under anoxic conditions. The reactions for denitrification are (Metcalf and Eddy, 1991; Henze *et al*, 1995):

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (2.3)$$

Denitrification generally requires a readily biodegradable carbon source, although endogenous carbon may be used at a slower reaction rate (Metcalf and Eddy, 1991). The optimal pH range for denitrification is 7 to 9, although both nitrification and denitrification processes may adapt to lower pH ranges over time (Henze *et al*, 1995). Denitrification is also sensitive to dissolved oxygen and temperature, with dissolved oxygen concentrations less than 1 mg/L required. A dissolved oxygen level of 0.2 mg/L is sufficient to inhibit denitrification by *Pseudomonas* culture (Randall *et al*, 1992). Denitrification may occur thermophilically (Henze *et al*, 1995).

Henze *et al* state that the optimum C/N ratio for denitrification is 3 to 3.5 kg BOD/kg N or 4 to 5 kg COD/kg N, whereas Randall *et al* suggest a ratio of COD : TKN of 8. Narkis *et al* (1979) determined that a critical ratio of BOD/NO_x-N of 2.3 was required to ensure full denitrification.

Nitrification and denitrification reaction rates for various sources are given in Table 2.1. The rates show that nitrification rates are generally low compared with denitrification using readily biodegradable carbon, whereas denitrification using endogenous carbon is significantly slower than using readily biodegradable carbon.

Table 2.1 Nitrification and denitrification reaction rates for domestic effluent

Reaction	Reaction rate (g N/g MLVSS.day)		Source
	Range	Typical	
Nitrification	0.03 - 0.06	0.05	Metcalf and Eddy, 1991
		0.08	Randall *et al*, 1992
Denitrification	0.03 - 0.11	0.04	Metcalf and Eddy, 1991
	0.05 - 0.4		Randall *et al*, 1992
Denitrification using	0.017 - 0.048		Metcalf and Eddy, 1991
endogenous carbon	0.015 - 0.06		Randall *et al*, 1992

2.1.1.2 Phosphorus removal

Phosphorus may be present in wastewater as orthophosphoate, polyphosphate or organic phosphorus. Of these, orthophosphate is the easist to remove. Polyphosphates and organic phosphorus are coverted to othophosphate by hydrolysis and bacterial decomposition, respectively (Surampalli *et al*, 1997).

Fuhs and Chen (1975) identified the bacteria responsible for phosphorus removal as strains of the *Acinetobacter* group, although other bacteria including some denitrifying bacteria have also been found to be phosphate-accumulating. *Acinetobacter* is an obligate aerobe which, under anaerobic conditions, can use the energy produced by the hydrolysis of polyphosphate within the cell to store low molecular weight organics, particularly acetic acid. Phosphate, the hydrolysis product, is released through the cell membrane to the water.

In a subsequent aeration phase the stored organics are metabolised, producing energy and allowing bacteria to take up the phosphate, which is again stored inside the cell as polyphosphate. Phosphorus uptake is in excess of the bacteria's normal requirements, in preparation for a future anaerobic phase (Fang and Ling, 1995). Phosphorus is concentrated in the bacterial cells and removed from the system during sludge wasting. Luxury phosphorus uptake is maximised when the dissolved oxygen level is greater than 2 mg/L (Surampalli *et al*, 1997).

Gerber *et al* (1986) state that phosphorus release is primarily dependent on the carbon source, rather than the existence of anaerobic conditions. They determined that phosphorus release occurred under anoxic conditions when the substrate used was formate, acetate or propionate. Substrates such as citrate, succinate, glucose and ethanol required anaerobic conditions for phosphorus release.

Phosphorus removal is generally reported as requiring anaerobic conditions, and being inhibited by the presence of nitrate. However, Kuba *et al* (1996) suggest that nitrate may be used as an electron acceptor for phosphorus removal instead of oxygen, giving rise to the concept of denitrifying dephosphatation. Carucci *et al* (1994) report that the performance of the phosphorus removal process is highly sensitive to the competition between phosphorus accumulating and denitrifying organisms for organic substrate.

Randall *et al* (1992) state that phosphorus removal is relatively insensitive to temperature, although temperatures below 12°C should be avoided, however Marklund (1993) achieved phosphorus removal at wastewater temperatures of 3 to 8°C. A mean treated effluent concentration of 1.57 mg/L was achieved, corresponding to a 74% reduction in phosphorus.

Phosphorus uptake rates of 0.02 to 0.03 g P/g SS.h were measured by Kuba *et al* (1993) but they do not state the order of the reaction. The method or model used to determine the rate is not given, and thus the information cannot be readily used. Kuba *et al* also give phosphorus release rates of 0.03 to 0.05 g P/g SS.h. Phosphorus uptake at the rate of 4.1mg/L.h, was reported by Fang and Ling (1995), resulting in a 75.2% reduction in phosphorus concentration over the 11.5 h aerobic phase.

Phosphorus removal requires a soluble COD to phosphorus released ratio of 1.2 : 1 (Fang and Ling, 1995). Manning and Irvine (1985) achieved greater than 95% phosphorus removal with a COD : TKN : TP ratio of 25 : 3 : 1. Randall *et al* state that to determine the extent of phosphorus removal, COD :TP should be compared with BOD_5 : TP: if COD : TP is significantly higher than 40 and BOD_5 : TP is significantly less than 20, then the wastewater has not undergone substantial fermentation and phosphorus removal will be minimal. An influent BOD_5 : TP of at least 20 should result in effluent phosphorus being less than 1 mg/L (Randall *et al*, 1992). The effect of this ratio on effluent total phosphorus is shown in Figure 2.1.

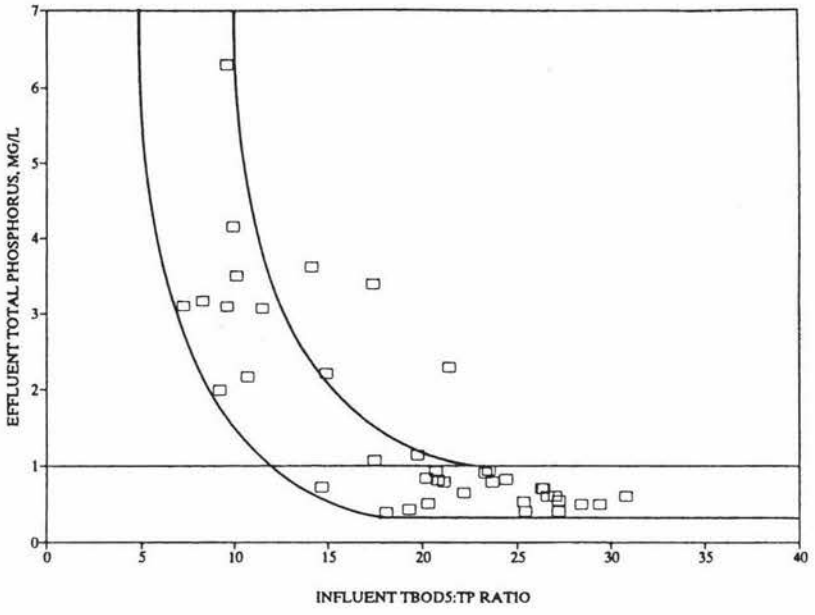

Figure 2.1 Effect of process influent $TBOD_5$: TP ratio on effluent total phosphorus

Source: Randall *et al* (1992) Figure 1.16

2.1.2 The roles of anaerobic, aerobic and anoxic phases in BNR

2.1.2.1 Anaerobic phase

An anaerobic phase requires that no oxygen be present in the wastewater, either as dissolved oxygen or chemically bound, for example, nitrate.

The anaerobic stage is required for phosphorus removal: aerobic bacteria, in order to survive the anaerobic conditions, release phosphorus, in the form of polyphosphates, in exchange for low molecular weight organic compounds, such as volatile fatty acids (Fuhs and Chen, 1975). This stage must be high in readily biodegradable carbon to ensure

phosphorus removal occurs, as this is the only form of carbon that the phosphate removing bacteria can utilise.

The anaerobic stage is generally the first stage for the secondary treatment. Unless prefermentation has occurred, it is likely that some of the larger organic molecules may begin to breakdown (ferment) into smaller molecules, such as VFAs, during the anaerobic period. This gives an increased supply of readily biodegradable carbon for phosphorus release (Randall *et al*, 1992).

2.1.2.2 Anoxic phase

The anoxic stage is essential for denitrification. This stage differs from the anaerobic stage in that chemically bound oxygen is present in the form of nitrate and nitrite, which are reduced to N_2O and N_2 gases by denitrifying bacteria. These bacteria require carbon as their energy source, and as the readily biodegradable carbon supply is generally diminished during the anaerobic phase in a BNR system, the carbon source may be endogenous or added externally, for example methanol or acetate.

2.1.2.3 Aerobic phase

For biological nutrient removal, the primary purpose of the aerobic stage is the conversion of ammonia to nitrate. This process occurs independently of carbon oxidation, as the carbon source for nitrifying bacteria is alkalinity, which is used at a ratio of 7.14 mg $CaCO_3$/mg NH_4 (Randall *et al*, 1992). Lime or soda ash dosing may be required to keep the alkalinity at a level sufficient for nitrification. It is essential to ensure sufficient alkalinity remains following nitrification so that the pH of the mixed liquor is not reduced (Surampalli *et al*, 1997).

Aeration causes the phosphorus removing bacteria to take up excess phosphorus, which is stored in preparation for a future anaerobic stage. However, phosphorus uptake does not occur until all VFAs have been utilised (Randall *et al*, 1992).

During this stage hydrolysis of carbon also occurs. The aggressive mixing ensures that any gases produced in the anaerobic and anoxic stages, such as N_2O and N_2, are volatilised.

2.1.3 BNR in continuous flow treatment systems

2.1.3.1 A^2/O process

The A^2/O process for BNR is based on the A/O mainstream phosphorus removal process. A schematic diagram of the process is given in Figure 2.2.

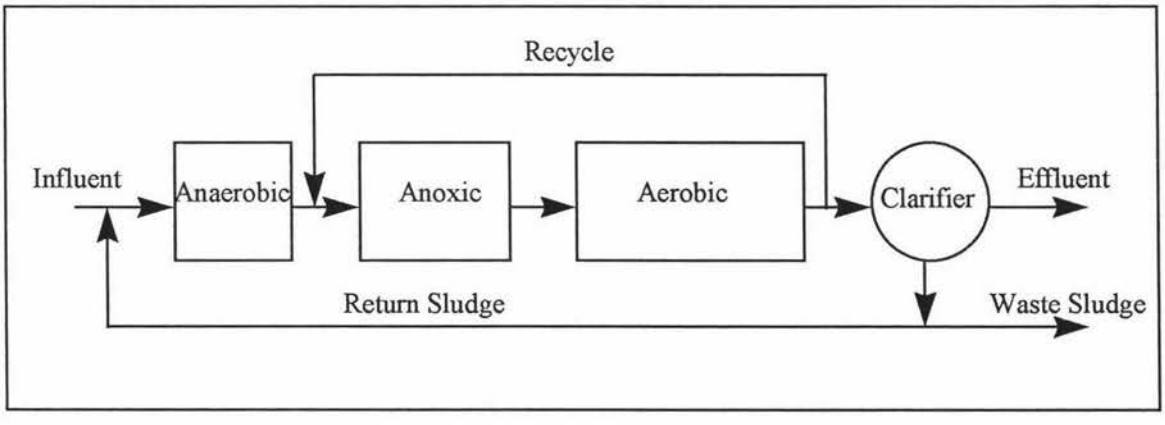

Figure 2.2 Schematic diagram of the $A^2/0$ process

Source: Metcalf and Eddy (1991) Figure 11-24

In the A^2/O process, phosphorus is released in the anaerobic phase, using the readily biodegradable carbon in the effluent. The effluent moves into the anoxic stage, where nitrate is added by a recycle stream which takes nitrified effluent from the end of the

aerobic stage. The nitrate is then denitrified using remaining readily biodegradable carbon and endogenous respiration (Randall *et al*, 1992). In the aerobic stage the wastewater is aerated to ensure nitrification and phosphorus uptake occurs.

This process produces an effluent that has a relatively high nitrate concentration. Generally, wastewater is high in carbon, phosphorus and ammonia, but low in nitrate. By the end of the A^2/O process, the carbon and phosphorus have been removed but the nitrogen has been converted to nitrate in the final aerobic phase. Although the recycle stream treats a portion of the nitrate, a considerable amount remains in the effluent and will require tertiary treatment for its removal (Metcalf and Eddy, 1991).

2.1.3.2 5-Stage Bardenpho process

This process is a modification of the 4-stage Bardenpho process for nitrogen removal, also known as the "Phoredox modification". A schematic of the 5-stage Bardenpho process is shown in Figure 2.3.

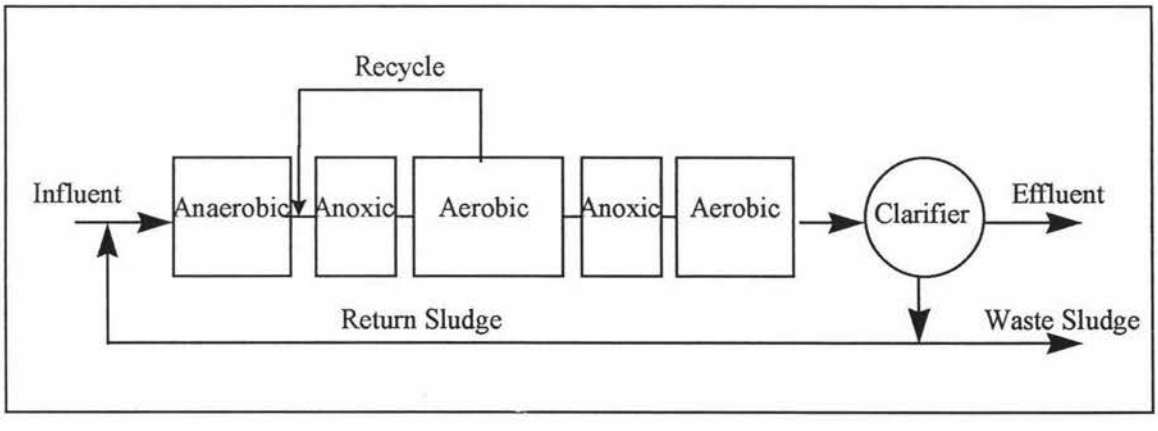

Figure 2.3 Schematic of the 5-stage Bardenpho process

Source: Metcalf and Eddy (1991) Figure 11-24

As in the A^2/O process, phosphorus is released in the anaerobic phase, using the readily biodegradable carbon in the effluent. The effluent then moves into the first anoxic stage,

where nitrate is added by a recycle stream which takes nitrified mixed liquor from the first aerobic stage (Metcalf and Eddy, 1991). The nitrate is then denitrified using readily biodegradable carbon and endogenous respiration.

The length of the first aerobic stage ensures that nitrification and phosphorus uptake go to completion (or to a predetermined end-point). The recycle stream returns a portion of the nitrate to the first anoxic stage while the remainder is denitrified in the second anoxic stage, which relies completely on endogenous respiration for the carbon source (Randall *et al*, 1992).

The use of two anoxic stages could be questioned, as it would seem that just the second anoxic period would suffice. The advantage of having the two anoxic periods is that there is readily biodegradable carbon available in the first anoxic stage that would not be available if only the second anoxic stage was used. Relying completely on endogenous organic carbon as the carbon source for denitrification would significantly lengthen the time required, as denitrification rates using endogenous respiration are slower than for a readily biodegradable carbon source (as is shown in Table 2.1).

The second aerobic stage is essentially a polishing stage and is shorter than the first aerobic stage. The wastewater is aerated to drive off any gases, such as N_2, to complete carbon oxidation, and to minimise secondary phosphorus release in the clarifier. This system gives an effluent low in ammonia, nitrate and phosphorus (Randall *et al*, 1992).

2.1.3.3 UCT process

The UCT process is named for the University of Cape Town, where it was developed. It is similar to the A^2/O process, the differences being the location of the return activated sludge and a recycle of mixed liquor from the anoxic stage to the anaerobic stage. The process is shown in Figure 2.4.

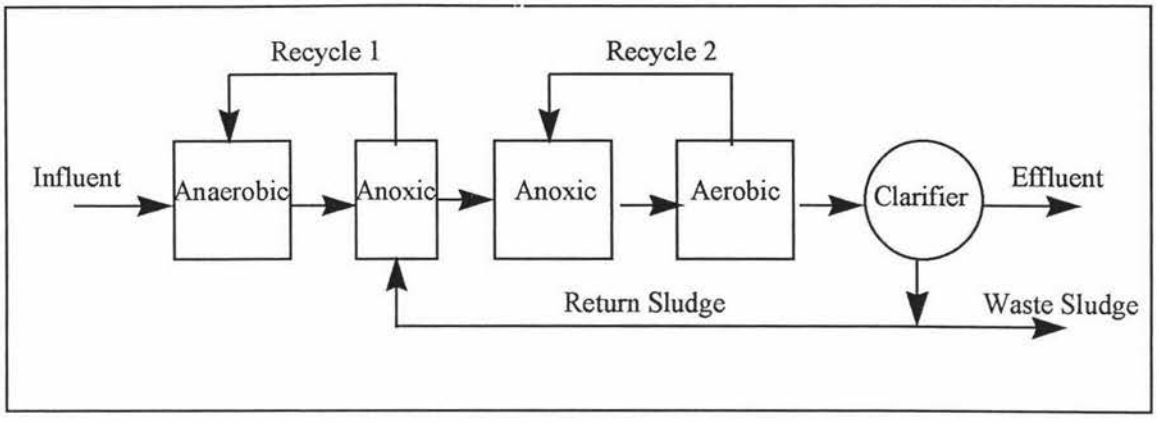

Figure 2.4 Schematic of the UCT process

Source: Metcalf and Eddy (1991) Figure 11-24

This process offers higher phosphorus removal levels than the other processes (Metcalf and Eddy, 1991). As in the previous methods, phosphorus is released in the anaerobic stage. By not introducing the return activated sludge (RAS) into the anaerobic stage, nitrate concentrations are minimised, improving phosphorus release. The mixed liquor recycled from the first anoxic stage has low amounts of nitrate but is high in readily biodegradable carbon, again improving phosphorus release.

The first anoxic stage denitrifies nitrate returned in the activated sludge, using readily available carbon. The second anoxic stage utilises remaining readily available and endogenous carbon to denitrify nitrate that is recycled from the aerobic stage (Randall *et al*, 1992).

The aerobic stage is used for nitrification and phosphorus uptake. As with the A^2/O process, an effluent low in carbon, phosphorus and ammonia, but high in nitrate, is produced.

2.1.3.4 VIP process

The VIP process is similar to the A^2/O and UCT processes. It was first trialled at the Virginia Initiative Plant in Norfolk, Virginia, hence the name.

The basic difference between this process and the UCT process is the use of a single anoxic phase, in which denitrification of recycled mixed liquor and RAS occurs, and from which a recycle stream to the anaerobic phase is taken. As the recycle stream to the anaerobic phase is taken from the outlet of the anoxic zone, it should be low in nitrate but is also likely to be lower in carbon that the UCT process, as more will have been used in the denitrification process. A schematic diagram of the process is given in Figure 2.5.

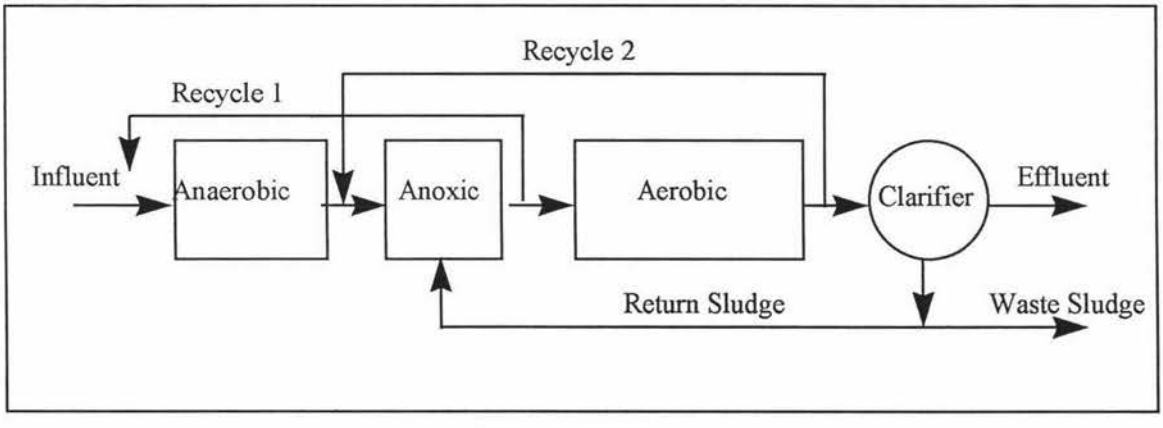

Figure 2.5 Schematic of the VIP process

Source: Metcalf and Eddy (1991) Figure 11-24

2.1.3.5 Recent developments in BNR

Besides the conventional continuous flow BNR methods, many other methods have been developed in laboratories and using pilot plants. Some of these observations defy convention, such as aerobic denitrification and denitrifying dephosphotation.

v. Munch *et al* (1996) observed a significant amount of aerobic denitrification, or simultaneous nitrification and denitrification, in bench-scale SBRs. The denitrification rate was highest at the beginning of the aerobic phase and decreased with time. It was determined that at a dissolved oxygen concentration of 0.5 mg/L the nitrification rate was equal to the denitrification rate, which would lead to complete simultaneous nitrification and denitrification.

Full-scale dynamic sand filtration for denitrification is being used in the Netherlands. The system uses a sand filter bed under anoxic conditions with denitrifying bacteria contained in the filter. The bacteria use an external carbon source (such as methanol) to convert nitrate to nitrogen gas and water. A trial filter showed an average removal efficiency of greater than 90% (Muller *et al*, 1997).

SHARON is a continuous stirred tank reactor (CSTR) process and stands for Single reactor system for High activity Ammonia Removal Over Nitrite. It is a pretreatment or sidestream treatment system and is most appropriate for nitrogen-rich flows (influent levels in the vicinity of 1,000 mg/L) (Mulder and van Kempen, 1997).

One of the main features of SHARON is that there is no sludge retention, contrary to conventional nitrification theory which requires sludge ages of several days. This allows ammonia concentrations to be reduced to about 100 mg/L, prior to secondary BNR treatment. SHARON promotes the conversion of ammonia to nitrite rather than nitrate, which can save up to 25% on oxygen input and energy consumption during nitrification, and 40% of the carbon source during denitrification (Mulder and van Kempen, 1997).

Two full-scale SHARON plants were under construction in the Netherlands in early 1997 for treatment of rejection water from sludge dewatering. The average nitrogen load for these plants is 420 to 540 kg N/day and 90% nitrogen removal is expected (Mulder and van Kempen, 1997).

Denitrifying dephosphotation uses nitrate as an electron acceptor instead of oxygen, i.e. phosphorus uptake occurs during an anoxic phase using denitrifying phosphorus removing bacteria, which have been identified in activated sludge. The occurrence of denitrifying dephosphotation has been studied in laboratory and full-scale plants (Vlekke *et al*, 1988; Kuba *et al*, 1996; Ostgaard *et al*, 1997; Sorm *et al*, 1997). Ostgaard *et al* operated a full-scale UCT process with anoxic phosphorus removal.

Denitrifying dephosphotation has been shown to give similar results to conventional anaerobic/aerobic phosphorus removal, with the possible advantage of reduced COD and aeration requirements (Kuba *et al*, 1996). Kuba *et al* achieved an average removal efficiency of 98% for phosphorus and 89% for nitrogen in a two-SBR system, where one SBR was operated under aerobic conditions and the other under anaerobic/anoxic conditions.

2.2 Operation of Sequencing Batch Reactors (SBRs)

2.2.1 The SBR treatment process

SBR systems have five steps in common that are carried out in the following sequence (Metcalf and Eddy, 1991):

1. Fill: Effluent is added to the reactor. Long fill times may operate as part of the react stage.
2. React: The nutrient removal stage. The react stage may include aerobic, anoxic and anaerobic phases, depending on the treatment objectives.
3. Settle: Solids separation occurs, providing a clarified supernatant.
4. Draw: Clarified supernatant is removed from the reactor.

5. Idle: A optional period between drawing off the clarified effluent and the next fill stage.

Sludge wasting normally occurs during the settle or idle phases but can occur during the react and draw phases (Metcalf and Eddy, 1991). Surampalli *et al* (1997) state that, when operating for phosphorus removal, sludge wasting must occur under aerobic conditions to avoid secondary release of phosphorus.

Unlike continuous treatment processes SBRs do not have the capacity to recycle effluent from one part of the process to another. This is primarily because SBRs are a time-oriented treatment process rather than space-oriented: parts of the process occur in the same tank sequentially, whereas in continuous flow plants they occur in separate tanks concurrently (Metcalf and Eddy, 1991).

A recycle stream would be possible in the form of a holding tank to hold a portion of effluent from one phase to be added to a later phase, however during the holding time further reactions will occur in the holding tank, which may influence the treatment.

Recycle streams are not practicable for supplying nutrients or readily biodegradable carbon to a treatment phase. An alternative often used in laboratory scale plants is the addition of an external carbon supply, such as methanol, acetate or sludge (Abufayed and Schroeder, 1986; Tam *et al*, 1994), however in full-scale plants this is expensive in terms of automated dosing equipment and the chemical itself. Thus it is necessary to rely on endogenous carbon respiration to complete the biological nutrient removal process. As readily biodegradable carbon is essential for phosphorus removal, then denitrification must use endogenous carbon, which is a substantially longer process (Metcalf and Eddy, 1991).

The decant volume of 40 to 60% is usually chosen, as the readily available carbon is replenished by effluent added during fill, enabling nitrogen and phosphorus removal go to desired end-point.

If a lower decant volume was used (e.g. 10 to 30%) the readily available carbon is not sufficiently replenished which means that nutrient removal will not occur as desired (Randall *et al*, 1992). A larger decant volume (70 to 90%) may begin to draw the settled sludge in the lower part of the tank, which would cause raised BOD and suspended solids levels in the treated effluent (Metcalf and Eddy, 1991; Randall *et al*, 1992). A decant volume of 40 to 60% is thus preferred to maximise treated effluent quality.

SBR design, operation and performance is discussed in detail by Irvine and Ketchum (1989), Metcalf and Eddy (1991), Ketchum (1997), and, with respect to farm effluents, Ellwood (1997).

2.2.2 SBR operation for biological nutrient removal

The SBR operating strategy used affects the amount and types of pollutants removed from the effluent. Different combinations of aerobic, anaerobic and anoxic phases target the removal of different nutrients.

Tam *et al* (1994) operated a bench-scale SBR to denitrify domestic wastewater. The operating strategy during the react stage was 4 h aeration, 3 h anoxic and 1 h aeration. An external carbon source was added in the anoxic phase to increase denitrification. Methanol, acetate and propionate were each tried as an external carbon source, of which propionate was found to be the most effective.

Tam *et al* found that the use of an external carbon source significantly reduced the time required for denitrification and also improved the nitrification efficiency. A high carbon

dose could achieve 95% denitrification within 1 hour, compared with 3 hours for a lower dosage.

Surampalli *et al* (1997) evaluated the performance of three full-scale SBRs operating for biological nutrient removal from municipal wastewater. The performance data showed that SBR treatment can achieve BOD_5 and suspended solids concentrations of less than 10 mg/L, and nutrient levels of 1 to 2 mg/L ammonia, and less than 1 mg/L phosphorus. In each of the case studies presented, the SBR operating strategy is not fixed: ot changes according to flowrate, season or as conditions require.

Imura *et al* (1993) treated domestic effluent for BNR. They achieved average removal rates of more than 90% for BOD_5, suspended solids, ammonia and phosphorus, and more than 80% nitrogen removal. Their operating strategy consisted of an anaerobic fill time of 1.75 h, followed by 2.25 h aeration and 2 h settle and decant.

Irvine *et al* (1985) operated two SBRs with different organic loadings, for phosphorus removal. The phosphorus loads of 7 mg/L were reduced by more than 80%, using anaerobic retention times of 0.6 to 1.3 h. Slightly better effluent quality was achieved in the SBR with the lower loading.

Figure 2.6 shows the relationship between phosphorus removal and anaerobic hydraulic retention time. The graphs show that increasing the hydraulic retention time does not improve phosphorus removal efficiencies. It is also clear that the higher TCOD : TP ratios result in increased phosphorus removal. Although the data is for continuous flow systems, it also applied to SBRs, as reaction rates are unchanged.

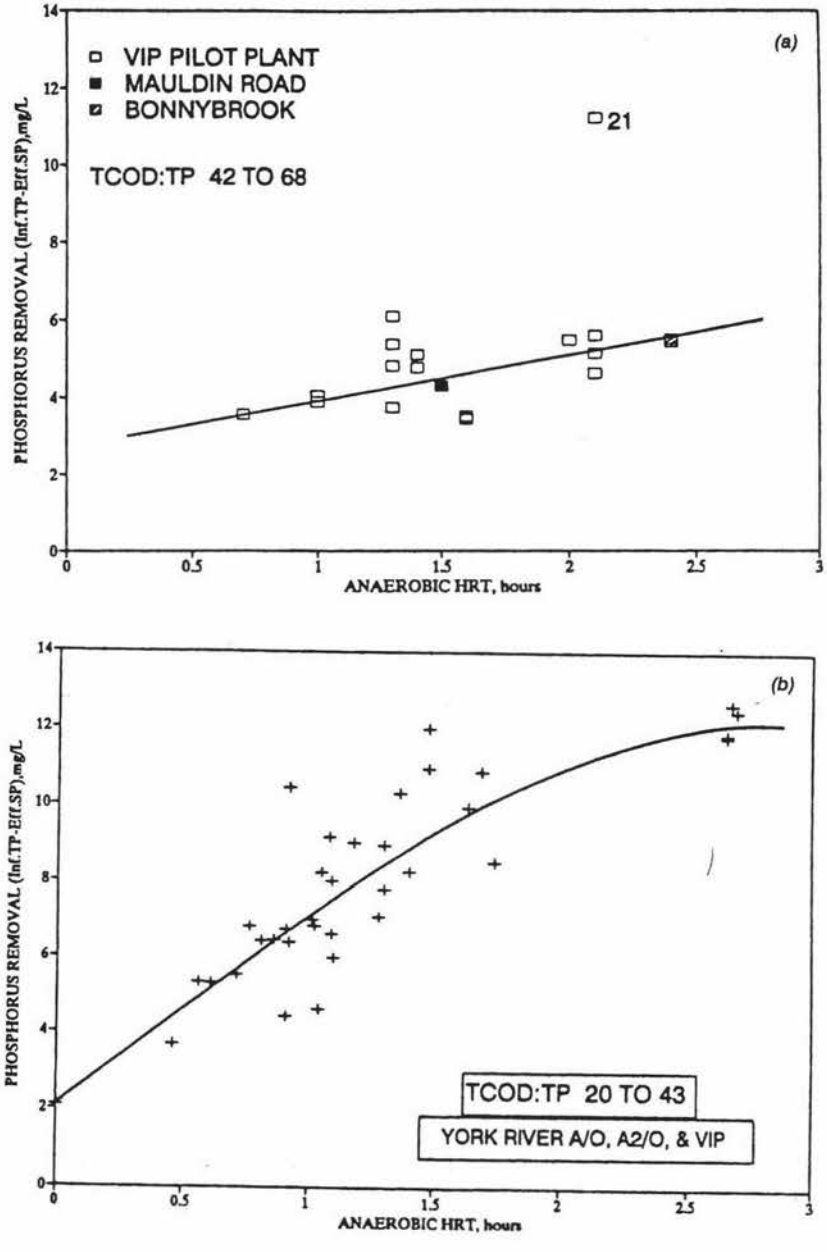

Figure 2.6 Effect of anaerobic hydraulic retention time on biological phosphorus removal

(a) high TCOD : TP ratio, and (b) low TCOD : TP ratio

Source: Randall *et al* (1992) Figure 4.2

2.2.3 Treatment of farm dairy effluent using an SBR

2.2.3.1 Farm dairy effluent data

Data obtained by Lo *et al* (1985; 1988) and Ellwood (1997) provide some of the only information available on nutrient levels and reaction kinetics for farm dairy effluent. Ellwood's data is particularly relevant as it is the most recently collected and is for the same farm dairy as used in this study. The data given in Table 2.2 was collected by Ellwood using yard effluent obtained as grab samples on several days during his trial period. The samples were taken during washdown of the yard and thus are not representative of an entire milking.

Table 2.2 Yard effluent data

Source: Ellwood (1997)

Parameter	Concentration (mg/L)	Concentration standard deviation (mg/L)
total COD	11,274	3,638
soluble COD	4,775	2,123
ultimate BOD	7,213	3,478
five day BOD	4,238	1,480
readily biodegradable BOD	957	
VFA	378	205
alkalinity	1,370	748
TKN	682	523
NH_4-N	210	200
NO_3-N	4	2
TP	101	52

There are several conditions necessary to ensure nitrogen and phosphorus removal occur. Phosphorus removal requires a soluble COD to phosphorus released ratio of 1.2 : 1 (Fang and Ling, 1995) and Manning and Irvine (1985) achieved greater than 95% phosphorus removal with a COD : TKN : TP ratio of 25 : 3 : 1. Using the data in Table 2.2, these ratios are 47 : 1 and 112 : 7 : 1, respectively. The COD : TP ratio is over 100 and the BOD_5: TP ratio is 41. According to Randall *et al* (1992) this effluent should be sufficiently fermented for phosphorus removal.

Denitrification requires BOD_5: NO_3-N to be at least 2.3 : 1 (Narkis *et al*, 1979); the ratio from the data in Table 2.2 is 20 : 1 (BOD_5 : NH_4-N), which assumes 100% nitrification. Alkalinity levels are insufficient for full nitrification. Randall *et al* state a requirement of 7.14 mg alkalinity per mg ammonia, and thus alkalinity levels would be completely used during nitrification, resulting in a reduced pH. This indicated that lime dosing is required.

2.2.3.2 SBR research using farm dairy effluent

Lo *et al* (1985; 1988) and Ellwood (1997) achieved excellent carbon oxidation and nitrification efficiencies (generally greater than 80%), although limited denitrification and phosphorus removal were achieved.

Ellwood used a pilot tank to treat farm dairy effluent that had been pretreated in an anaerobic pond, and thus had a low BOD. The SBR achieved 88% reduction of ammonia after 3 hours aeration. As the BOD : NO_3 ratio was low (less than 2.3 : 1), little denitrification was expected, and so the operating strategy was not designed to encourage it. No time was allocated in the cycle for phosphorus release as it was expected that it would be inhibited by the high nitrate concentration.

A pilot SBR treating farm dairy effluent was operated by Lo *et al* (1985). The SBR was operated in two modes, the major difference between them being the reduction in settling

time from 165 to 50 minutes per cycle. Nutrient removal efficiencies were BOD_5, 86.5%; suspended solids, 90.8%; and ammonia, 82.5%. No significant differences in treatment efficiencies were found when analysing the results for the two operating strategies.

Farm dairy effluent was treated in three 5 L bench scale SBRs, using different ambient temperatures and different cycle times, by Lo *et al* (1988). They achieved removal efficiencies of 90-97% BOD_5, 51-96% ammonia and 79-95% suspended solids. The lower efficiencies occurred in the tank operating at 10.5°C, whereas the different cycle times had little effect on efficiencies. The difference between the cycle times was predominantly the length of the aerobic phase, which varied between 1.75 and 3.5 hours.

2.2.3.3 Farm dairy effluent kinetics

Lo *et al* (1988) derived a first order model to estimate the time required for nitrification. The following equation is for the first order removal of substrate from the reactor:

$$\frac{dS}{dt} = kSX \qquad (2.4)$$

After integration this becomes:

$$\ln S_o - \ln S = kXt \qquad (2.5)$$

where S = substrate concentration, mg/L

t = time, h

k = first order reaction rate constant, mg NH_4-N/mg VSS .h

X = biomass concentration, mg/L

S_o = initial substrate concentration, mg/L

It is questionable whether the nitrification reaction rate constant of 1.28 mg N/g VSS.h determined by Lo *et al* (1988) is applicable in this study, as Ellwood's (1997) operating conditions and results were significantly different. For example, equation 2.5 uses a VSS of 1,000 mg/L, whereas a higher MLVSS is expected in this study as Ellwood had a mixed liquor suspended solids concentration of approximately 6,000 mg/L. This equates to a VSS concentration of 4,800 mg/L, using a MLVSS : MLSS ratio of 0.8 (Metcalf and Eddy, 1991).

Ellwood's first order nitrification rate constant was found to be 0.71 h. This held for the first three hours of the aerobic period, during which 88% of the ammonia was removed. The removal rate reduced significantly when the ammonia concentration reached about 10 mg NH_4-N/L; the final two hours of the aerobic phase saw little change in the ammonia concentration.

Several assumptions are made in the use of this model. The model assumes that there are no sources of ammonia other than the influent and no reactions other than nitrification. Fernandes (1994) states that the ammonia concentration in the fill stage is increased by the influent, and hydrolysis and ammonification of nitrogen-containing organic matter. Ammonia is assimilated during both the fill and aerobic stages. Nitrification will reduce ammonia levels in the aerobic phase, whilst hydrolysis and ammonification will continue to produce ammonia.

Of these five influences on ammonia concentration, it is generally assumed that the feed concentration and nitrification are dominant, however, this does not infer that the other factors can be ignored (Fernandes, 1994).

Equation 2.6, from Ellwood (1997), can be used to calculate the substrate concentration at the end of the fill time. It assumes that no reactions occur during fill time.

$$S_{o,actual} = S_o(1 - f_T) + f_T.S \qquad (2.6)$$

where $S_{o,actual}$ = actual effluent concentration at end of fill, mg/L

S_o = fraction of tank volume remaining after decanting, mg/L

f_T = influent concentration, mg/L

S = concentration in tank, mg/L

Neither Lo *et al* (1988) nor Ellwood achieved denitrification, and thus denitrification rates for farm dairy effluent are not available. Piggery effluent, like farm dairy effluent, has a lower C : N ratio than domestic effluent, and so the denitrification time calculated using piggery data is likely to be more relevant than that determined using domestic effluent data.

Metcalf and Eddy (1991) give typical denitrification rates as being between 0.03 and 0.11 mg NO_3-N/mg VSS.d for domestic effluent. Equation 2.7, from Metcalf and Eddy, can be used to calculate the denitrification time. A comparison of equations 2.5 and 2.7 shows that denitrification differs from nitrification in that it is it is a zero order, not a first order reaction (with respect to substrate)

$$t = \frac{S_o - S}{U.X} \qquad (2.7)$$

where U = zero order reaction rate constant, mg NO_3-N/mg VSS .d

Fernandes (1994), working with piggery effluent, proposed equation 2.8 for denitrification during the fill stage:

$$\frac{d(N_{NOX\text{-}N}.V)}{dt} = Q.N_{NOX\text{-}N,o} - k_{DN}.X.V \qquad (2.8)$$

where N_{NOX-N} = nitrite/nitrate nitrogen concentration in reactor, mg/L

V = reactor effective volume, L

Q = influent flow rate, L/h

$N_{NOX-N,o}$ = nitrite/nitrate nitrogen concentration in influent, mg/L

k_{DN} = maximum specific denitrification rate constant, h^{-1}

X = biomass concentration, mg/L

In this study, fill time will be minimal and denitrification will occur in the anoxic phase. Thus the equation reduces to:

$$\frac{dN_{NOX-N}}{dt} = - k_{DN}.X \qquad (2.9)$$

if Q = 0 and V is constant

After integration and rearranging, this becomes equation 2.7. Fernandes (1994) determined denitrification rate constants of 6.7×10^{-5} h^{-1} at 5°C, 0.0019 h^{-1} at 10°C and 0.0044 h^{-1} at 21°C. Fernandes' rate constant at 10°C converts to 0.046 d^{-1}, which is slightly lower than the reaction rates using endogenous carbon given by Metcalf and Eddy (1991) of between 0.017 and 0.048 d^{-1}.

Fernandes' rate constant is likely to be more realistic for this study than Metcalf and Eddy's data, as the composition of farm dairy effluent is closer to piggery than domestic effluent: both dairy and piggery effluents have high ammonia concentrations. The average effluent temperature is likely to be closest to 10°C, rather than 5 or 21°C, and thus Fernandes rate constant of 0.0019 h^{-1} is most appropriate.

2.3 Carbon characterisation and prefermentation

2.3.1 Carbon characterisation

Design and optimisation of wastewater treatment systems requires an understanding of the microbiological and chemical processes occurring in the wastewater. Such an understanding is usually obtained through the use of a model. Henze (1992) has developed a method of characterising organic matter in domestic wastewater for use in a model.

The organic matter in effluent can exist in many forms, which are characterised by their rate of degradation. These fractions are inert soluble, inert suspended, readily biodegradable, rapidly hydrolysable, and slowly hydrolysable organics. By assessing the quantities of each fraction present in the waste, it is possible to estimate the overall reduction in COD by treating the waste, as some fractions (inert soluble and inert suspended organic matter) will not be removed by bacterial activity.

Experiments can be conducted to measure the proportion of each of these types of carbon, in order to assess the extent of carbon and nutrient removal that can be anticipated (Henze, 1992). The total inert carbon may be found using Equation 2.10. This is carbon that will not be removed by biological treatment.

$$\text{Total inert carbon} = COD_t - BOD_u \qquad (2.10)$$

Inert soluble organics are present in untreated wastewater and are also produced by the activated sludge process (Henze, 1992), thus effluent concentrations are higher than influent concentrations. The inert soluble carbon is defined as the minimum COD of effluent that has been treated. The following equation is suggested by Henze:

$$\text{Inert soluble carbon} = \text{total soluble carbon} - 1.5 \cdot \text{soluble 5 day BOD}$$
$$= COD_{soluble} - 1.5 \cdot BOD_{5,soluble} \quad (2.11)$$

The BOD method needs to have suppressed nitrification, ensuring that only the carbonaceous BOD is measured.

Inert suspended carbon is not degraded by activated sludge treatment. A portion is also produced by the treatment. The method used by Ellwood (1997) to calculate this is given in equation 2.12, below:

$$\text{Inert suspended carbon} = \text{total inert carbon} - \text{soluble inert carbon} \quad (2.12)$$

Readily biodegradable carbon represents small molecules, such as VFAs, simple carbohydrates, alcohols, peptides, and lower amino acids, which can be directly metabolised, particularly for nitrogen and phosphorus removal. This fraction represents 10 to 15% of raw municipal wastewater total COD (Henze, 1992).

Readily biodegradable carbon can be specifically tested for, by testing for VFAs, glucose, ethanol, etc. Ellwood (1997) used VFA analysis and data from the first 12 hours of carbonaceous BOD measurement to determine the readily biodegradable carbon content.

Rapidly hydrolysable carbon accounts for 15 to 25% of the total COD of raw municipal wastewater (Henze, 1992). Both this and readily biodegradable carbon may be reduced significantly during transport in sewers, where they may be hydrolysed or consumed by suspended biomass and biomass on the walls. This is particularly relevant for domestic wastewater which may travel a considerable distance to a wastewater treatment plant, whereas farm dairy effluent is likely to travel only a few hundred metres.

Henze states that the rapidly hydrolysable carbon is the total COD, less the inert soluble and readily biodegradable fractions. Ellwood estimated it using the carbonaceous BOD

value after 24 to 36h, as Eckenfelder (1989) suggested that most readily degradable substrate was used in this time.

Slowly hydrolysable carbon is 40 to 60% of raw municipal waste water total COD. The method used by Ellwood to estimate it is given in equation 2.13:

$$\text{Slowly hydrolysable carbon} = BOD_u - \text{rapidly hydrolysable fraction} - \text{readily biodegradable fraction} \quad (2.13)$$

Whilst the model developed by Henze was for domestic wastewater, it is likely that the equations developed will be relevant for farm dairy effluent. The same types of carbon will exist in the wastewater, it is the proportion of each that will differ.

2.3.2 Prefermentation

Prefermentation is the breakdown of large organic compounds in the effluent to simple organic compounds (for example, volatile fatty acids) by anaerobic digestion, prior to activated sludge treatment. The intention of prefermenting the waste is to provide an increased concentration of readily biodegradable carbon for use by the bacteria in nitrogen and phosphorus removal, thus extending the reactions and producing a higher quality effluent.

Fermentation is the anaerobic decomposition of organic matter. It can be described as a two step process, as is shown in Figure 2.7. Firstly, acid forming bacteria breakdown high molecular weight organics to short chain fatty acids, then methane bacteria convert the fatty acids to methane. Randall *et al* (1992) state that 70 to 85% of the products formed in the first stage of fermentation are acetates, with the remainder consisting of propionates, butyrates and hydrogen, as well as other higher order fatty acids.

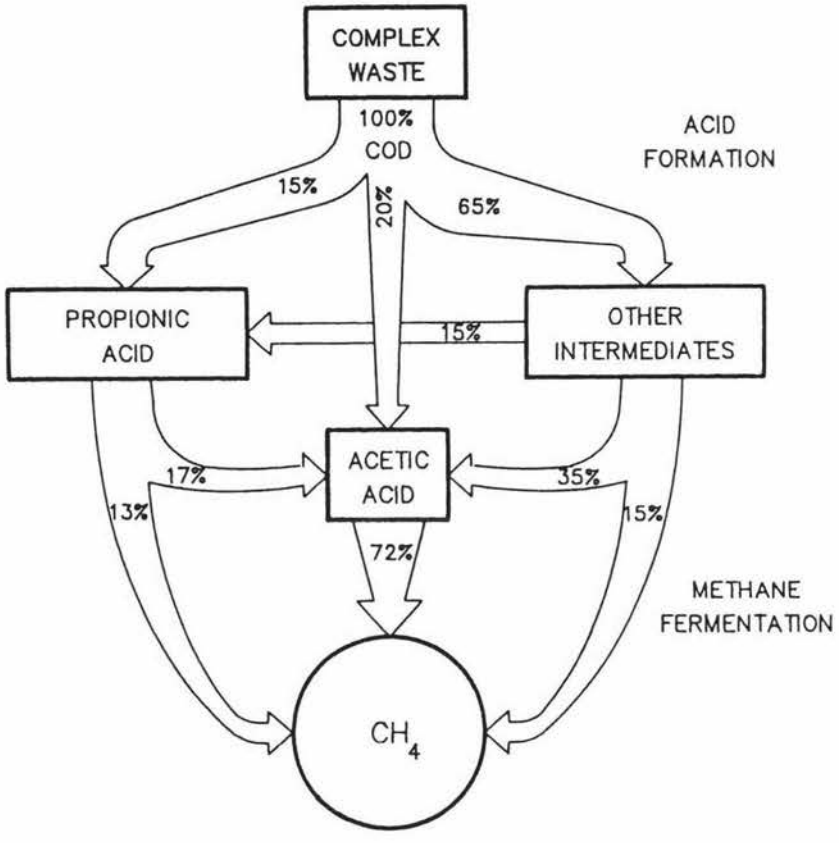

Figure 2.7 Biological pathways of methane fermentation

Source: Randall *et al* (1992) Figure 3.2

Acid fermentation occurs at a redox potential of more than -300 mV and methane fermentation requires a redox potential of less than -550 mV (Randall *et al*, 1992). In a fermenter, acid fermentation will occur initially and as the redox potential reduces methane fermentation will occur. Eventually an equilibrium is reached so that acid products are fermented at the same rate as they are produced. In the case of prefermentation, the objective is for VFA production to be optimised without the conversion to methane occurring.

Fuhs and Chen (1975) identified the bacteria responsible for phosphorus removal, *Acinetobacter*, and their requirement for short chain volatile fatty acids, particularly acetic acid, in order to release phosphorus in the first part of the phosphorus removal

process. Readily biodegradable carbon compounds, particularly short chain fatty acids, appear to be the preferred substrates for both denitrification and phosphorus removal (Gerber *et al*, 1986). Tam *et al* (1994) showed that addition of acetate or propionate prior to the anoxic phase could substantially reduce the time required for denitrification.

Prefermentation of farm dairy effluent to provide a waste high in short chain volatile fatty acids which would enhance phosphorus removal. Methods exist for prefermentation of domestic wastewater; and the design and operation of such reactors is discussed by Randall *et al* (1992).

Randall *et al* report that batch prefermentation tests show a lag phase of 0 to 7 days before acid production began, with a peak acid concentration achieved after 6 to 9 days. The VFA proportions obtained were 1.0 : 1.0 : 0.08 : 0.07 acetic : propionic : butyric : valeric acids. As batch tests progressed, more long chain acids were produced. In semi-continuous reactors there was no lag phase in VFA production. The VFA proportions in the effluent were 1.0 : 1.0 : 0.3 : 0.1 acetic : propionic : butyric : valeric acids.

Danesh and Oleszkiewicz (1997) operated a two-stage anaerobic-aerobic SBR system which consisted of a fermentation reactor followed by an SBR with an operating strategy for phosphorus removal. The two-stage system had a significantly higher phosphorus removal efficiency than a standard SBR operating in parallel. VFA concentrations were increased in the two-stage reactor and an improved water quality resulted. The use of the fermentation reactor also decreased the anaerobic time required in the SBR.

v. Munch and Koch (1997) identified four prefermenter types commonly used in domestic wastewater treatment. These are:

- Activated Primary Tank (APT). The ATP receives the entire wastewater flow. This is essentially a primary clarifier with a high sludge blanket than normal. Sludge is drawn off from the bottom and recycled into the influent of the ATP to wash out the VFAs.

- Complete-mix prefermenter. This reactor receives primary sludge. The prefermenter is well mixed, and the hydraulic and sludge retention times are equal.
- Static prefermenter. This prefermenter receives primary sludge and is not mixed. VFAs are produced in the sludge blanket and flow out in the overflow.
- Complete mix with dedicated thickener prefermenter (two-stage prefermenter). This also receives primary sludge. It consists of a complete-mix tank followed by a thickener, so the sludge and hydraulic retention times are independent.

v. Munch and Koch propose the following equation for comparing the efficiency of prefermenters. It determines the rate of VFA production, and is applicable to a continuous prefermenter at steady state:

$$r = \frac{C_{eff} - C_{in}}{HRT} \qquad (2.14)$$

where r = rate of VFA production (mg/L.h)

C_{eff} = VFA concentration in prefermenter effluent (mg/L)

C_{in} = VFA concentration in prefermenter influent (mg/L)

HRT = hydraulic retention time (h)

Hydraulic retention times for nine full-scale prefermenters in operation in Australia and Canada ranged from 6 to 165 days, however the majority were less than 20 days. Rates of VFA production in the prefermenters were from 1.4 to 28 mg/L.h, with an average rate of production of 15 mg/L.h.

A static prefermenter at Kelowna, Canada, was the most efficient. The least efficient was an Activated Primary Tank, however v. Munch and Koch state that low efficiencies in an APT may still be acceptable since the entire waste stream is being treated and thus a small increase in VFA concentration may represent a large mass of VFAs being produced.

Raper *et al* (1997) studied the installation and operation of an APT at West Wodonga, Australia. The ATP was followed by a 3 stage Bardenpho plant; and the combination was capable of providing a treated effluent phosphorus concentration of less than 0.5 mg/L, from influent concentrations of up to 40 mg/L. They also state that efficient prefermentation improved the nitrogen removal efficiency of the plant (in excess of 90% removal).

There is no documented use of a prefermenter in conjunction with an SBR., although Randall *et al* (1997) conducted batch tests to quantify the effects of VFAs on phosphorus removal. They stated that VFAs were important for inducing phosphorus removal in the SBR, and that addition of VFAs improved removal rates in SBRs where phosphorus removal was already occurring.

3. OBJECTIVES

The objectives of this research are to:

1. Determine an SBR operating strategy to optimise the removal of nitrogen and phosphorus from farm dairy effluent.

2. Monitor the effectiveness of the SBR at removing nitrogen and phosphorus.

3. Assess whether the untreated effluent can be made more readily biodegradable by prefermentation.

4. MATERIALS AND METHODS

4.1 Research site and plant

4.1.1 Research site

The farm dairy used in this research was at Massey University No. 4 Dairy Farm (Lovelock Block), Tennent Drive, Palmerston North, New Zealand. The farm is owned and operated by Massey University for seasonal milk production and as a research facility. The herd comprised approximately 470 pasture-fed Friesan cows (Massey University, 1997).

4.1.2 Pilot plant

The SBR pilot plant used in this research was that designed and installed by Ellwood (1997).

The SBR itself was a 4.5 m^3 fibreglass tank, 1.8 m high and with a diameter of 1.8 m at its widest point. It was built by the business partner to the research, Fibre-form NZ Ltd (Palmerston North, New Zealand).

The holding tank was a Devan 3000 polyethylene tank (Devan Plastics, Tauranga, New Zealand). It's capacity was 13.65 m^3, and was 3.5 m in diameter.

The four pumps used in the SBR operation were Tsurumi HS3-4, 0.4 kW, semi-torque flow, submersible pumps (Tsurumi Manufacturing Co Ltd, Japan). The aerator was a

Tsurumi 15 TR2, 1.5 kW, submersible aerator (Tsurumi Manufacturing Co Ltd, Japan). The collection pump was operated by a timer, whereas the other pumps (holding tank, mixing and decant) and the aerator were operated by a programmable logic controller (PLC), which was a Micro^3 micro programmable controller (Idec Izumi Corporation, Japan), housed in a shed adjacent to the SBR.

The layout of the pilot plant at Massey University No. 4 Dairy Farm is shown in Figure 4.1.

4.2 SBR operation

4.2.1 Plant operation

It was intended to install a collection channel capable of diverting all effluent produced in an entire milking to the holding tank. The collection channel was a 3 m long fibreglass channel (built by Fibre-form NZ Ltd, Palmerston North, New Zealand). The effluent pipe from the farm dairy fed into the channel, which emptied into the anaerobic pond.

A penstock near the outlet to the pond could be closed when effluent was required for the SBR. The effluent accumulated behind the penstock and was pumped to the holding tank. However due to spatial and design restrictions, the storage capacity of the channel was insufficient and it was decided to use effluent from the anaerobic pond, collected during milking from near the pond inlet. The pump was suspended in a float to reduce blockages.

(a)

(b)

Figure 4.1 Pilot plant layout

(a) SBR, left, with shed for PLC and holding tank on the right, and (b) inlet to anaerobic pond, showing collection channel and pump in float

The collection pump operated for 0.5 h, twice daily: 8.30 am and 5.30 pm, during the washdown period of the milking. The effluent was pumped about 50 m around the side of the anaerobic pond to the holding tank, where it was held until the SBR refilled.

The SBR operation was controlled by a PLC. Float switches determined the high and low water levels in the SBR. The low level float switch was positioned such that the decant volume was about 40%. The high level float switch allowed a 0.3 m freeboard. The PLC was programmed so that the mixing pump and the aerator would operate only when the SBR was full.

The SBR was filled by a pump in the holding tank, which turned on when the low level switch turned off and stopped when the high level float switched on. Once the SBR was full, the aerator and mixing pump operated according to the programme sequence, creating the aerobic, anoxic and anaerobic phases required for biological nutrient removal. The aerator only operated during the aerobic period, and the mixing pump only operated during the anaerobic and anoxic periods.

Following the biological nutrient removal sequence, the tank was completely quiescent to allow settling. The SBR was then emptied by the decant pump. This pump switched off when the low level switch turned off. The cycle then repeated.

4.2.2 Start-up procedure

The SBR was started up on 8 September 1997 using effluent collected adjacent to the inlet to the anaerobic pond. The start-up program used was designed to promote bacterial growth to the level required for biological nutrient removal, which was indicated by a mixed liquor suspended solids concentration of about 5,000 mg/L. The cycle consisted of fill, aerate (8 h), settle (1.5 h), and decant. The aerator was originally operated on a 4 min on/5 min off cycle, but this was reduced to 1 min on/2 min off cycle

during the aeration period, to minimise foaming and increase the time during which oxygen levels were elevated.

The required mixed liquor suspended solids level was reached on 10 October 1997 and the nutrient removal operating strategy was implemented.

4.3 Process design

4.3.1 Operating strategy design

SBR operating strategies can be designed to carry out BNR, with the aim of producing an effluent with low concentrations of nitrogen and phosphorus. Anaerobic, anoxic and aerobic phases are all possible but as the process is time-oriented, recycle streams are not practicable.

The A^2/O, UCT and VIP processes, as discussed in Section 2.1.3, all rely heavily on the internal recycle systems to ensure carbon is available for reactions and that nitrate is returned to anoxic zones. All three produce an effluent relatively high in nitrate.

The nutrient removal mechanisms used in the Bardenpho process can be adapted to work in an SBR, as is shown in Figure 4.2.

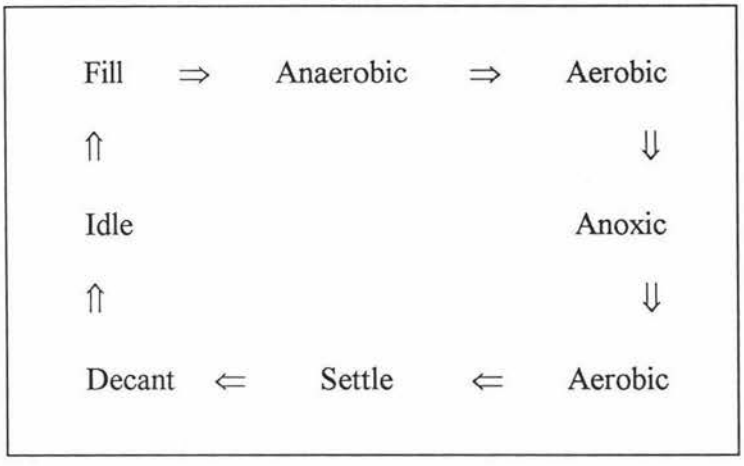

Figure 4.2 Theoretical SBR operating strategy for BNR

As in the continuous flow processes, phosphorus is released in the anaerobic phase, using the readily biodegradable carbon. No recycle facility is available, so it is not possible to go directly to an anoxic phase, as occurs in the Bardenpho process.

The first aerobic phase is used for nitrification and phosphorus uptake. It also oxidises remaining readily biodegradable carbon, thus the denitrification occurring in the anoxic phase depends entirely on endogenous carbon. The final aerobic phase operates as a polisher, as in the Bardenpho process.

Nitrogen and phosphorus removal dynamics during proposed SBR treatment are shown in Figure 4.3. 'High' and 'low' indicate a static concentration during the phase, at the relative level, and ↑ and ↓ indicate increasing and decreasing concentrations in the treatment phase.

High levels of ammonia enter the system in the influent and remain until nitrification occurs in the first aerobic phase, where it is converted to nitrate. Low quantities of

nitrate are added in the effluent but increase during the first aerobic phase. The nitrate is denitrified in the anoxic phase and the concentration is low in the treated effluent.

Phosphorus levels are increased by addition of influent, and increase further when phosphorus release occurs in the anaerobic phase. Luxury phosphorus uptake then reduces the phosphorus concentration in the aerobic phase.

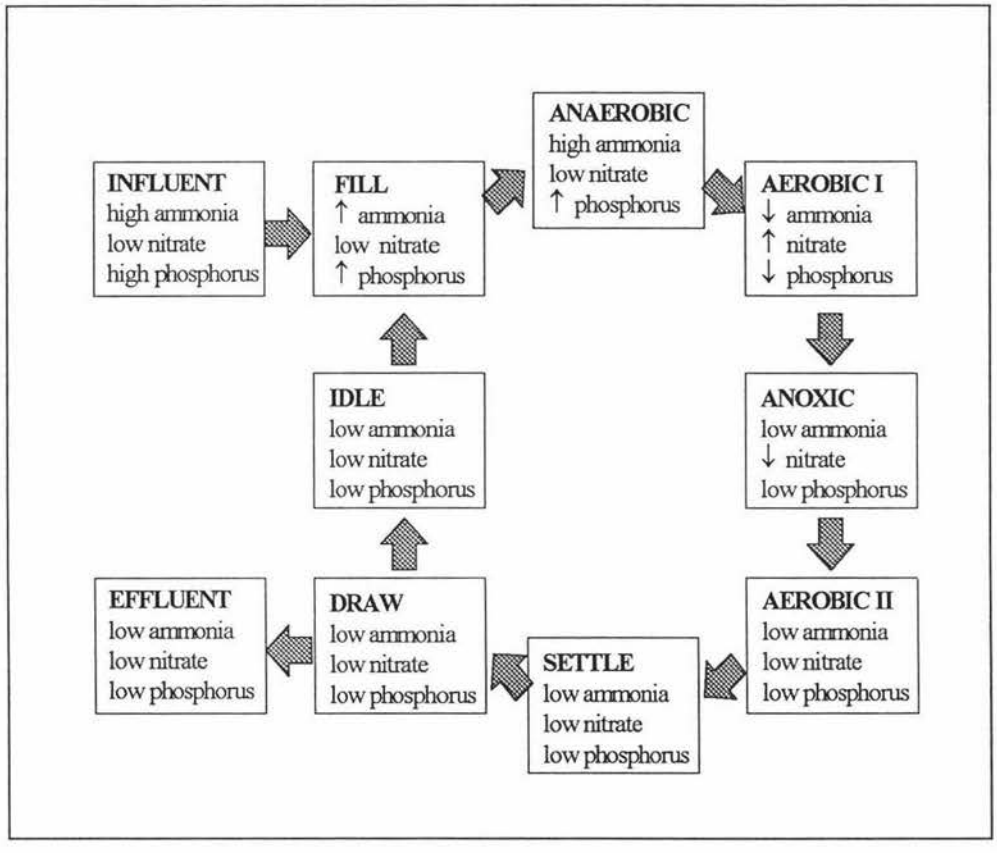

Figure 4.3 Nitrogen and phosphorus removal dynamics in each phase of SBR treatment

4.3.2 Calculation of treatment times

The length of the anaerobic period is determined by the time required for phosphorus release. From the data presented in Figure 2.6, it would appear that allowing a 1.5 h anaerobic time should ensure that a high level of phosphorus removal occurs.

The first aerobic phase is primarily for nitrification. In order to use the nitrification rate measured by Ellwood (1997), it is assumed that there will be an 88% reduction in ammonia. Thus using equations 2.5 and 2.6, the reaction time was found to be 3.1 h, marginally longer than the aerobic time required for 88% removal by Ellwood.

Using a denitrification rate of 0.0019 h^{-1} (0.046 day^{-1}) as determined by Fernandes (1994), in the zero order model given in equation 2.7, the anoxic time required for denitrification was 4.6 h.

As the second aeration period is used for polishing the effluent, its length is somewhat arbitrary. A time of 0.75 h was similar to hydraulic retention times used in Bardenpho operations and that used by Tam *et al* (1994).

A settle time of 1.0 h was considered adequate: a longer time could result in phosphorus release, and a shorter time, insufficient settling, and it was in keeping with the settle time used by Lo *et al* (1988).

The fill and decant times were controlled by the pumps' capacities.

The theoretical SBR operating strategy is given in Table 4.1. The operating strategy was designed to achieve biological nutrient removal, providing an effluent low in ammonia, nitrate and phosphorus.

Table 4.1 Theoretical operating strategy for nitrogen and phosphorus removal

Treatment Phase	Theoretical operating strategy (h)
Fill	0.15
Anaerobic	1.5
First Aerobic	3.1
Anoxic	4.6
Second Aerobic	0.75
Settle	1.0
Decant	0.15
Total	11.25

4.3.3 Summary of assumptions

The following is a list of assumptions used in the calculations in Section 4.3.2.

- Ammonia consumption is first order: this is supported by work on farm dairy effluent by Lo *et al* (1988) and Ellwood (1997), who both obtained first order rate constants.
- Denitrification is a zero order reaction, as described in Metcalf and Eddy (1991).
- No reactions occur during fill time. As fill time is a comparatively short period of time, any reactions will be negligible.
- There are no sources of ammonia other than the influent. This disregards any ammonia produced by hydrolysis. As hydrolysable carbon makes up a large proportion of COD, this may not hold.
- The biomass concentration (VSS) is 4,800 mg/L, as used by Ellwood (1997) in the same SBR. This is within the 1,500 to 5,000 mg/L range recommended by Metcalf and Eddy (1991).
- Phosphorus uptake in the first aerobic phase occurs concurrently with nitrification.

- True anaerobic conditions exist for phosphorus release.
- The second aerobic phase acts only as a polisher and does not directly contribute to the nutrient removal.

4.4 Cycle analysis

The cycle monitoring was conducted when the SBR's operating strategy had been optimised for nitrogen and phosphorus removal. It was to be carried out on two full operating cycles, several weeks apart. The first run was conducted on 9 December 1997. The second was due to be done on or about 12 January 1998, however an isolator tripped during the Christmas break, turning off the SBR's power supply for several days. The bacteria did not recover sufficiently prior to the completion of the research for the second run to be carried out.

Grab samples, in 120 mL polyethylene containers, were taken from the reactor every 10 minutes, from the beginning of the anaerobic phase through to the end of the settle phase. Samples were also taken of the untreated and treated effluent, and the sludge.

Temperature, pH and redox potential measurements were made immediately after collection. A Hanna Hi 9025c hand held meter was used to measure pH and redox potential. Samples were then stored in ice until they were removed to the laboratory freezer.

The dissolved oxygen concentration was measured using a YSI model 58 dissolved oxygen meter (Yellow Springs Instrument Co Inc, Yellow Springs, Ohio), and recorded by a Picolog data logger (Pico Technology Ltd, Hardwick, Cambs, UK), every 10 seconds for the duration of the cycle.

Samples were analysed within two days for total and soluble COD, suspended solids and alkalinity, and two months' later for ammonia, nitrate, total Kjeldahl nitrogen, total phosphorus.

4.5 Prefermentation experiments

4.5.1 Sample collection

A 10 L flow proportional sample of raw farm dairy effluent was collected for each experiment. Initial observations showed that the quantity and composition of the effluent produced during milking differed according to the stage of the milking, i.e. during milking, during yard washdown and following washdown. A quantitative analysis showed that effluent was produced according to the schedule in Table 4.2.

Table 4.2 Effluent production during milking

Activity	Duration (min)	Flowrate (L/min)	Volume (L)	% Total Volume	Sample Vol. (L)
During milking	120	55	6,600	20	2
Scraper	10	350	350	10	1
Washdown	30	550	16,500	50	5
Cleaning / milk waste	20	350	7,000	20	2
TOTAL	180		33,600	100	10

4.5.2 Laboratory procedures

4.5.2.1 Preliminary prefermentation trial

The research was conducted using a flow proportional sample of raw farm dairy effluent. Seven sealed 500 mL flasks of effluent were kept at 20°C and allowed to ferment.

Fresh effluent was tested for VFAs, COD and BOD. Every 24 hours one flask was sampled for VFAs.

4.5.2.2 Prefermentation trial

A flow proportional sample of raw farm dairy effluent was used. Sealed 500 mL flasks were kept at 20°C. The trial ran for 20 days with one flask being sampled every two days and every fifth day, i.e. samples were taken on days 0, 2, 4, 5, 6, 8, 10, etc.

This trial was also extended to include settled effluent, which was collected from the holding tank. Samples were taken every five days.

BODs were done on both the raw and settled effluents every ten days. VFA and COD analysis was also conducted on each sample.

4.5.2.3 Prefermentation semi-continuous reactor

The experiment was conducted in duplicate. Three sets of reactors were operated: one using raw farm dairy effluent, one using settled effluent, and the third using settled effluent but seeded with fresh effluent (described below).

The prefermenters were 500 mL flasks, filled with effluent, sealed, and kept at 20°C. After one week, the reactors were decanted, removing about 450 mL, and leaving the solids. The reactors were refilled with fresh raw or settled effluent, sealed, and kept at 20°C for two weeks (this was an extended period due to the Christmas break). The reactors were decanted and refilled with fresh effluent on a further two occasions, at one week intervals.

The reactor that was seeded with raw effluent had an initial volume of raw effluent which was replaced with settled effluent there after.

VFA samples were taken from each batch of fresh effluent, from the decanted effluent and from the refilled reactors. Soluble CODs were conducted on the same samples.

4.6 Analytical procedures

4.6.1 Ammonia and nitrate

Ammonia and nitrate were measured using a version of the automated phenate method, described by Greenberg *et al* (1992), and modified by the Fertiliser and Lime Research Centre, Massey University, Palmerston North, New Zealand.

Samples were thawed on the day of analysis. Ammonia was analysed using 1:25 dilutions, and nitrate undiluted. NH_4NO_3 standard solutions of concentration 0, 0.25, 0.5, 1, 2, 4, 8, and 12 mg/L were used. A Technicon autoanalyser was used for the analysis.

4.6.2 Total Kjeldahl nitrogen and total phosphorus

Total Kjeldahl nitrogen and total phosphorus analysis was conducted on a 5 mL sample, to which 4 mL of digestion acid was added. The digestion acid consisted of 2.5 L H_2SO_4, 250 g K_2SO_4 and 2.5 g selenium powder. Samples were heated to 350°C until water had evaporated. Samples were cooled, then diluted to 50 mL. Samples were analysed using a Technicon autoanalyser.

A standard solution of NH_4SO_4 at concentrations 0, 20, 40, 60, 80, 100, 120, and 150 mg/L was used for TKN and KH_2PO_4 at concentrations of 0, 2, 4, 6, 8, 10, 12, and 15 mg/L for phosphorus.

4.6.3 COD

COD was determined using the closed reflux method (Greenberg *et al*, 1992). Analyses were done in duplicate. Samples for soluble COD were filtered through Whatman GF/C filter paper, prior to treatment.

4.6.4 Suspended solids

Suspended solids were determined by filtering 1 mL samples through 4.5 cm diameter Whatman GF/C filter paper. Analyses were done in triplicate.

4.6.5 Alkalinity

Alkalinity was measured by the titration method (Greenberg *et al*, 1992) using a 25 mL sample and 0.02 N HCl. An endpoint of 4.5 was used.

4.6.6 Carbonaceous BOD

Carbonaceous BOD was measured using the respirometric method given by Greenberg *et al* (1992). The instrument used was a Hach BODTrak (Hach Co., Loveland, Colorado). Nitrification was inhibited by adding Hach Nitrification Inhibitor.

4.6.7 Volatile fatty acids (VFAs)

In the preliminary prefermentation trial, 5 mL samples were treated with a protein precipitant, centrifuged at 3000 rpm (1000 rcf) for 15 minutes using an IEC Centra GP8-R refrigerated centrifuge (International Equipment Co., Needham Heights, Massachusetts), and the supernatant decanted and frozen until analysis.

The protein precipitant was made up of 375g metaphosphoric acid dissolved in 900mL distilled water, 500mL of 100% formic acid was then added and the solution made up to 2L with distilled water.

As some of the VFA peaks were not clear using the previous method, for the following two experiments two extra 5 mL samples were also taken. One was treated with 1 mL of internal standard (10.5 mL caproic acid diluted to 2 L with deionised water) and the other was left untreated. All samples were centrifuged at 3000 rpm (1000 rcf) for 15 minutes, and the supernatant decanted and frozen for analysis.

Samples are analysed for acetic acid, propionic acid, n-butyric acid, iso-butyric acid, iso-valeric acid and valeric acid, using a Carlo Erba HRGC 5300 Mega Series gas chromatograph, using an internal standard. The adsorption column was a Stabilwax-Da column packed with Carbowax-PEG matrix. The column was 15 m long with an internal

diameter of 0.53 mm. A 5 μL sample was manually injected and carried by hydrogen gas at a flowrate of 0.5 kg/cm^2. VFAs were detected using a flame ionisation detector (FID).

Samples analyses were conducted in duplicate and concentrations were calculated in mmol/100 mL and were converted to mg/L using the molecular weights given in Table 4.3.

Table 4.3 VFA molecular weights

VFA	Molecular weight (g/mole)
Acetic acid	60.05
Propionic acid	74.08
Butyric acid	88.10
Valeric acid	102.13

5. RESULTS

5.1 SBR cycle analysis

5.1.1 Dissolved oxygen

The dissolved oxygen concentration during the SBR cycle is shown in Figure 5.1.

The dissolved oxygen fell from 0.5 to about 0.2 mg/L during the anaerobic phase. For the first hour of the first aerobic phase the concentration was between 0.25 and 0.75 mg/L. Following the first hour of aeration, the dissolved oxygen concentration was maintained between 1 and 2 mg/L.

The dissolved oxygen concentration dropped to about 0.2 mg/L almost immediately when aeration stopped at the beginning of the anoxic stage and remained unchanged until the second aerobic phase, when the concentration was between 1 and 2 mg/L. The dissolved oxygen concentration reduced to 0.15 mg/L in the settle phase.

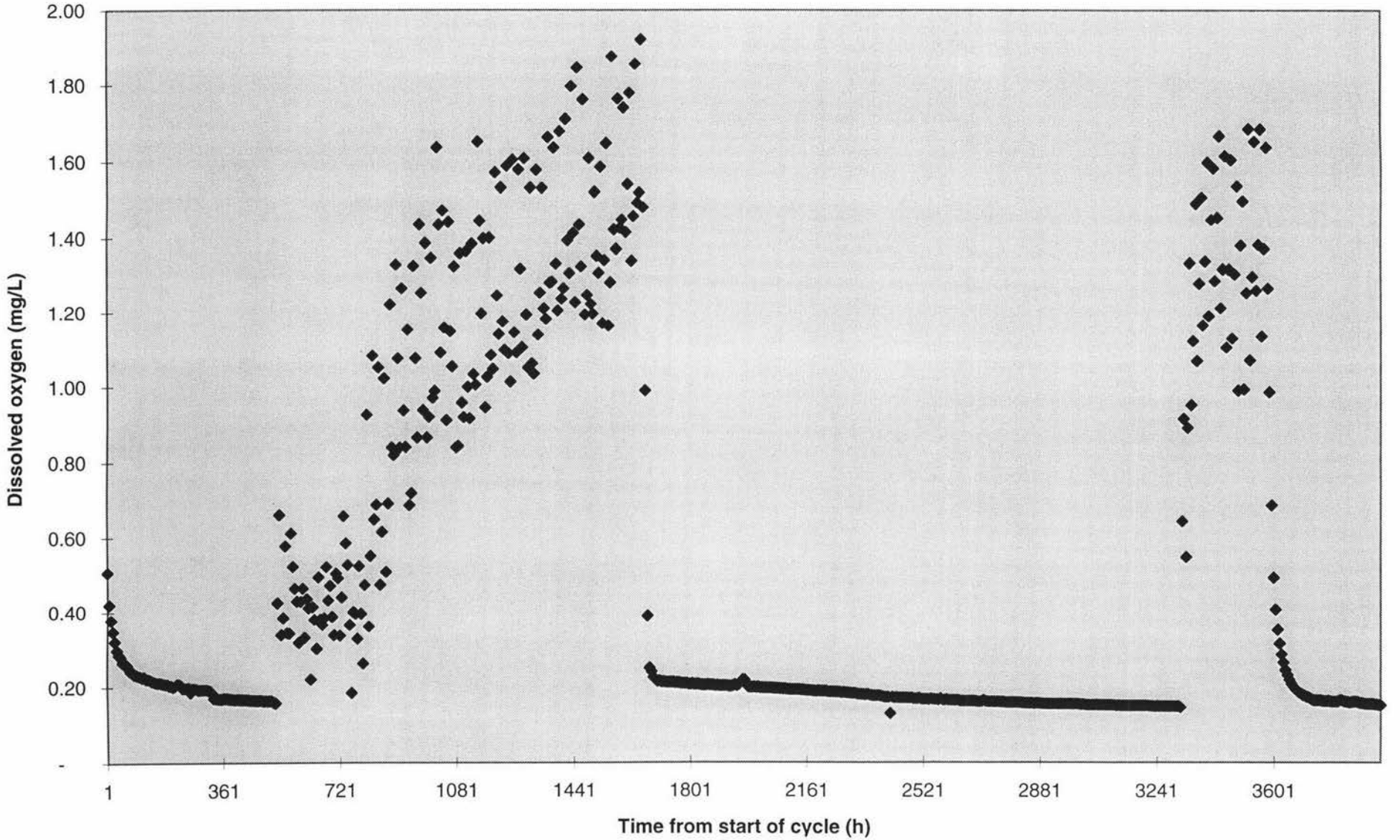

Figure 5.1 Dissolved oxygen concentration

5.1.2 Redox potential, pH and alkalinity

The redox potential, shown in Figure 5.2, was only measured during the anaerobic phase, as it is an indicator of acid and methane fermentation. The redox potential was relatively constant during the anaerobic phase at -40 to -43 mV but fell quickly to -50 mV when aeration began.

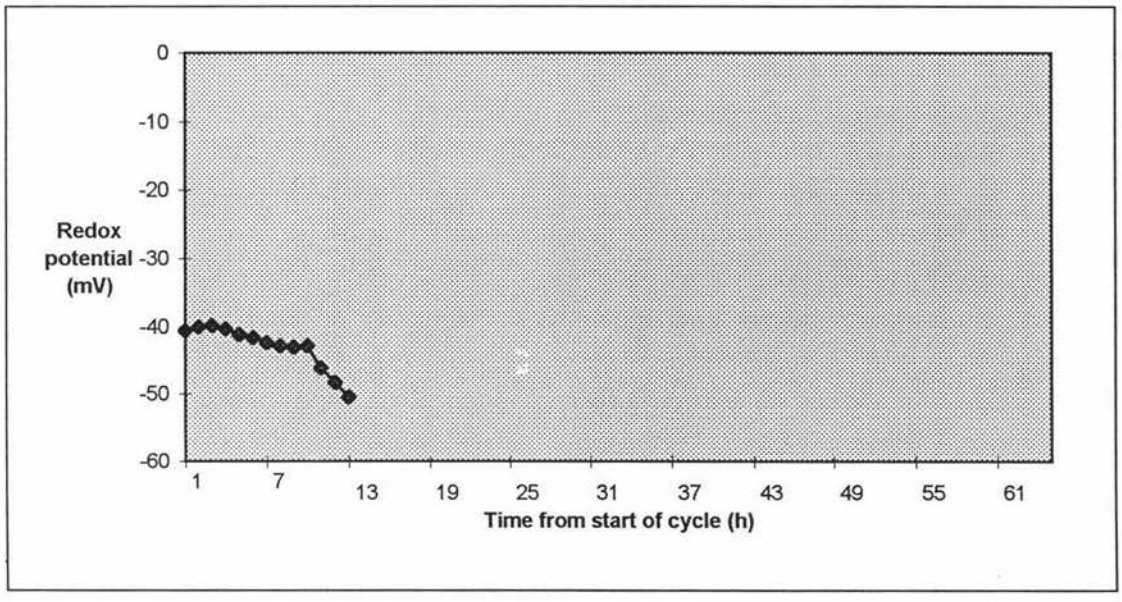

Figure 5.2 Redox potential during anaerobic phase

The pH is useful as an indicator of the alkalinity of the system. The pH and alkalinity are shown in Figures 5.3 and 5.4, respectively.

The pH of the system was constant throughout the cycle, at around 7.7. Alkalinity varied between 1,110 and 1,590 mg/L (as $CaCO_3$), with an average of 1,360 mg/L. There does not appear to be any trend associated with the alkalinity level.

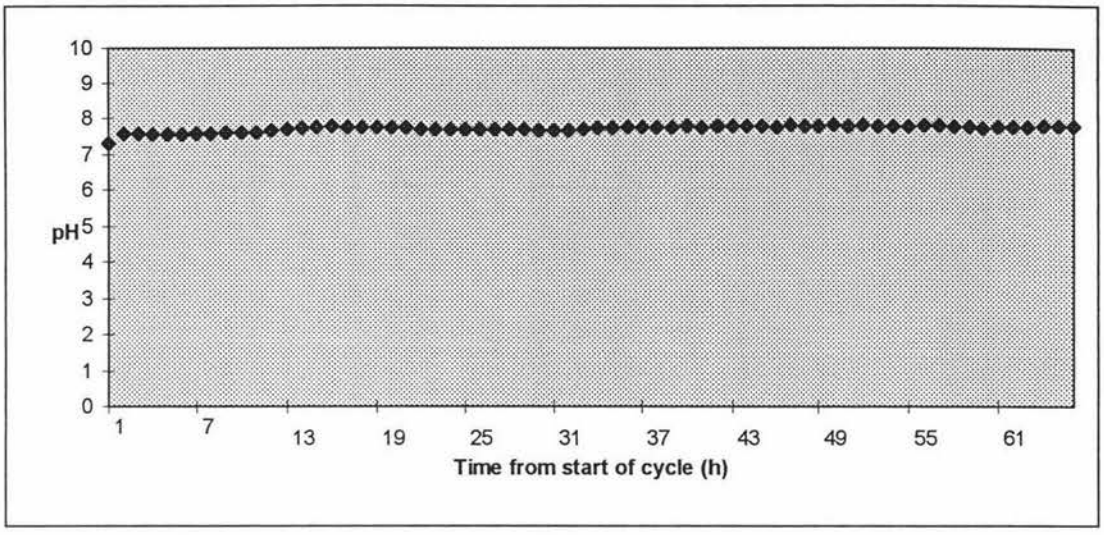

Figure 5.3 pH

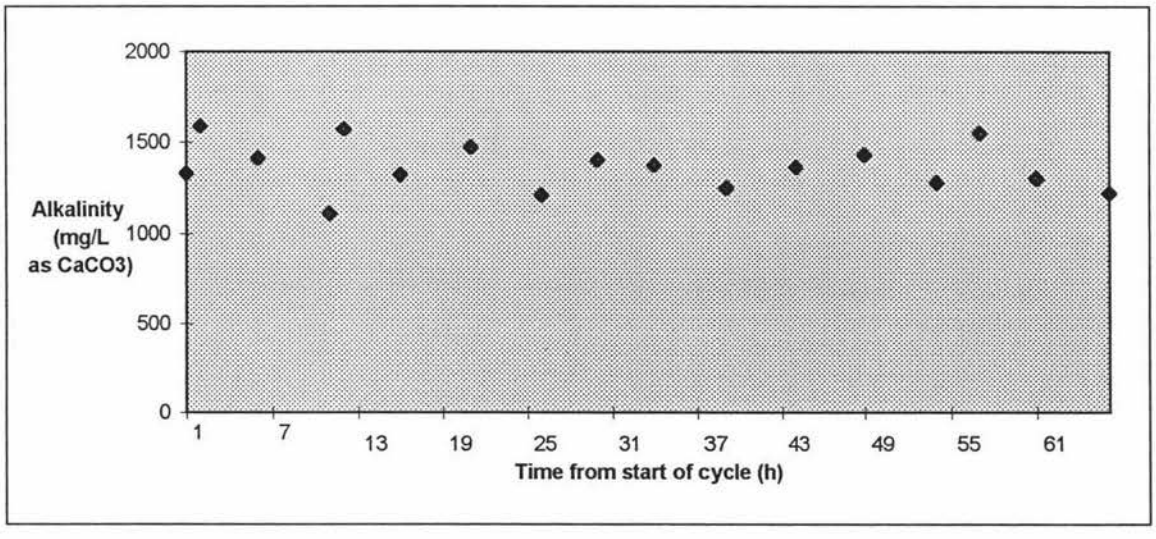

Figure 5.4 Alkalinity

5.1.3 Nitrogen

The total Kjeldahl nitrogen (TKN) concentration over the treatment cycle is shown in Figure 5.5. The concentration fluctuated between 240 and 760 mg/L and there is no apparent trend in the data, which indicates that biological nutrient removal did not occur.

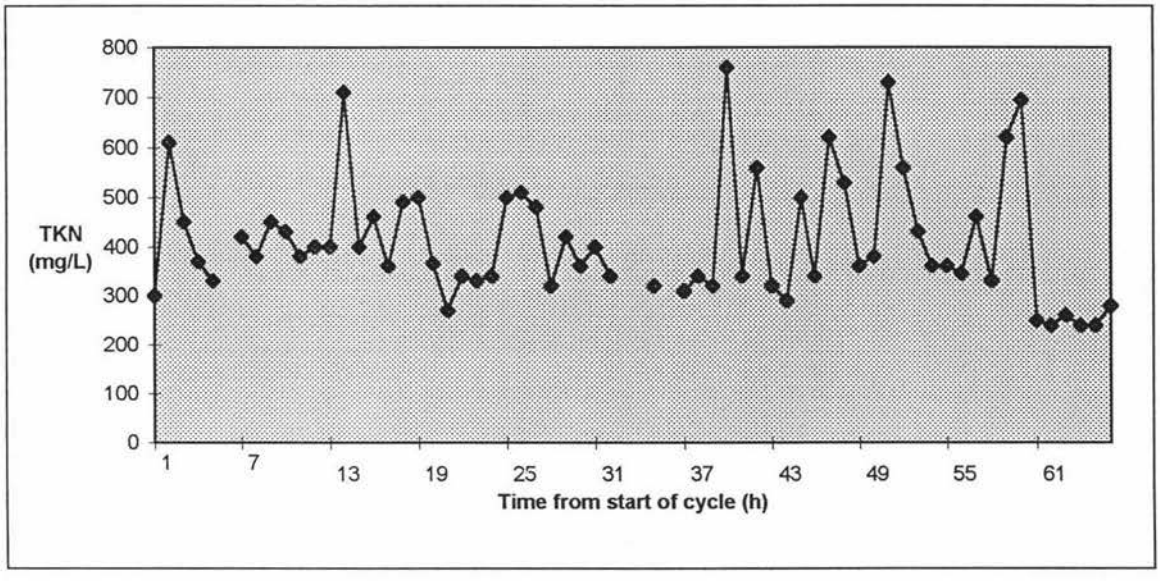

Figure 5.5 TKN concentration

The ammonia concentration is shown in Figure 5.6. The average concentration was 161 mg/L, ranging between 100 and 300 mg/L. While the ammonia levels fluctuated widely, they did not appear to be decreasing during the cycle, as would be expected if nitrification occurred.

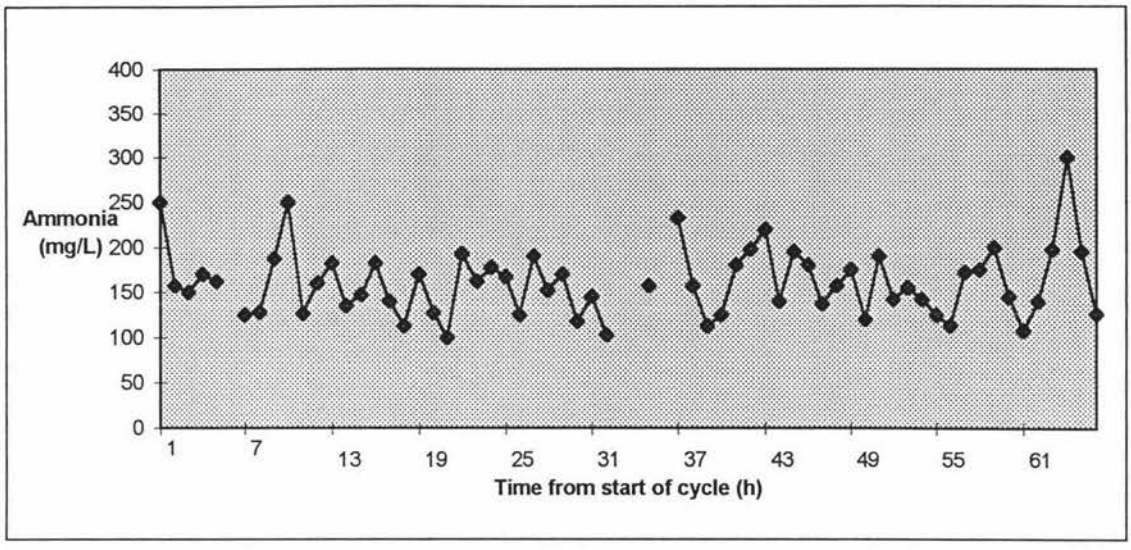

Figure 5.6 Ammonia concentration

Due to technical difficulties, nitrate levels were only measured over part of the cycle. The nitrate concentrations, as shown in Figure 5.7, were very low, less than 1 mg/L. If nitrification had occurred during the cycle, this would have been clear from Figure 5.7, as the data points shown are from the first aerobic phase.

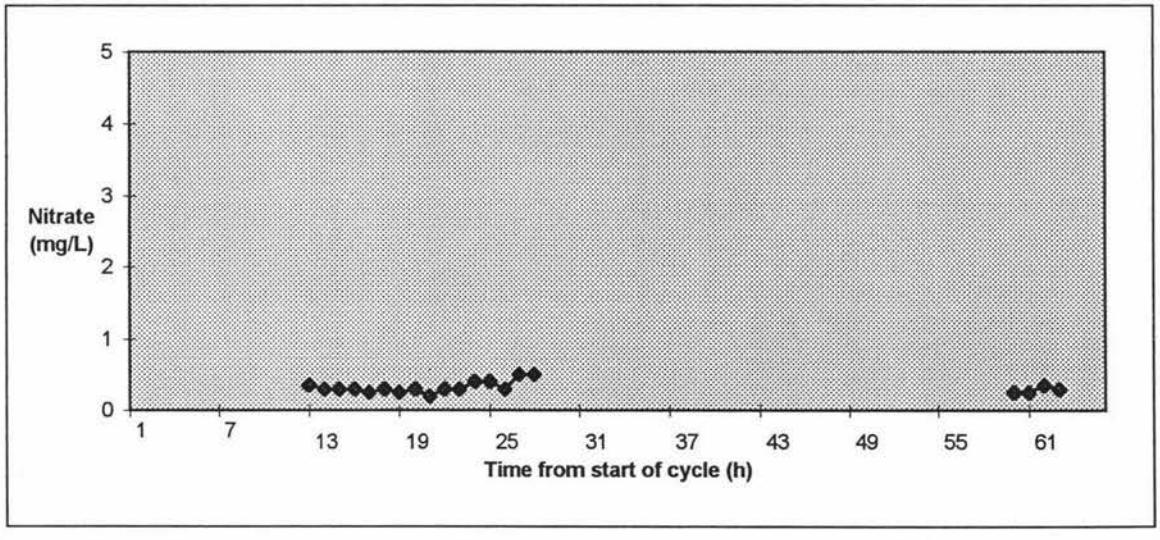

Figure 5.7 Nitrate concentration

5.1.4 Phosphorus

The phosphorus concentration during the treatment cycle (shown in Figure 5.8) averaged 57 mg/L, with a range of 19 to 107 mg/L. There was no discernible reduction in the phosphorus levels during the treatment.

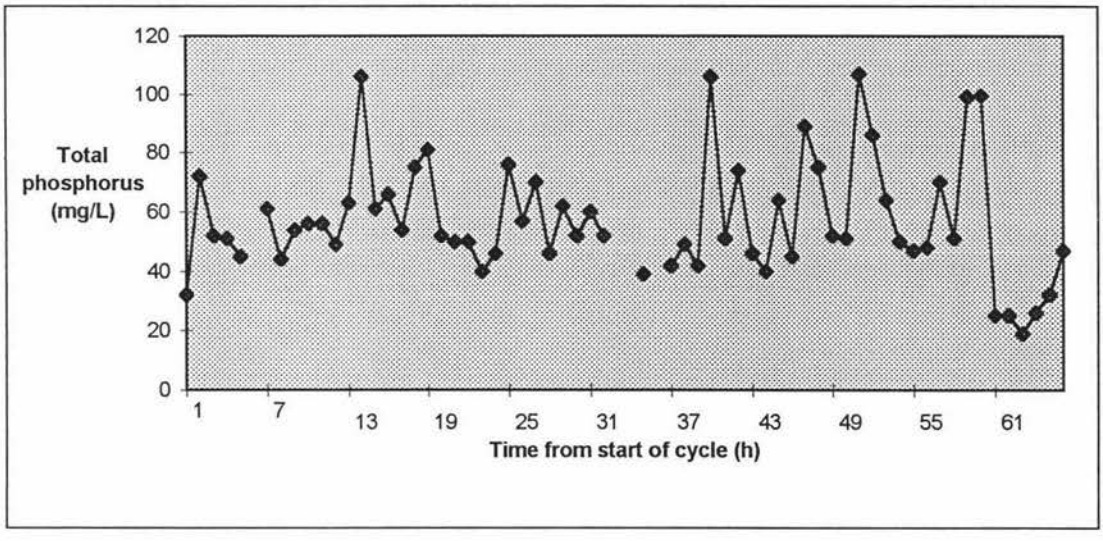

Figure 5.8 Phosphorus concentration

5.1.5 Suspended solids

Mixed liquor suspended solids levels were between 1,100 and 4,810 mg/L, with an average of 2,700 mg/L. Influent suspended solids were 900 mg/L and effluent suspended solids, 980 mg/L. Suspended solids are shown in Figure 5.9.

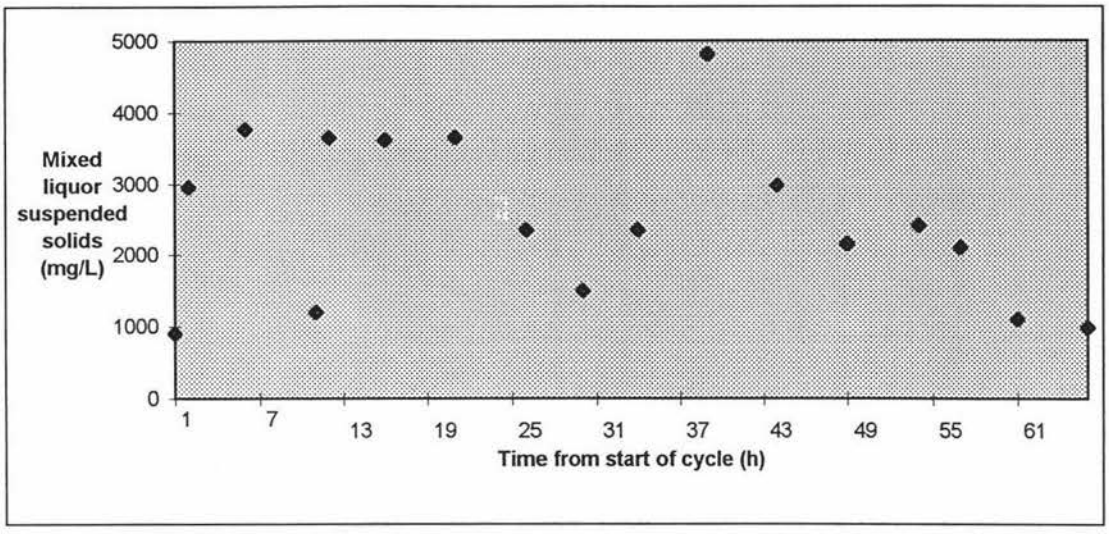

Figure 5.9 Mixed liquor suspended solids

5.1.6 COD

Figure 5.10 shows the soluble COD during the treatment cycle. There is no clear reduction over time. The average COD was 990 mg/L, with a range of 340 to 1,260 mg/L. The average total COD was found to be around 2,000 mg/L.

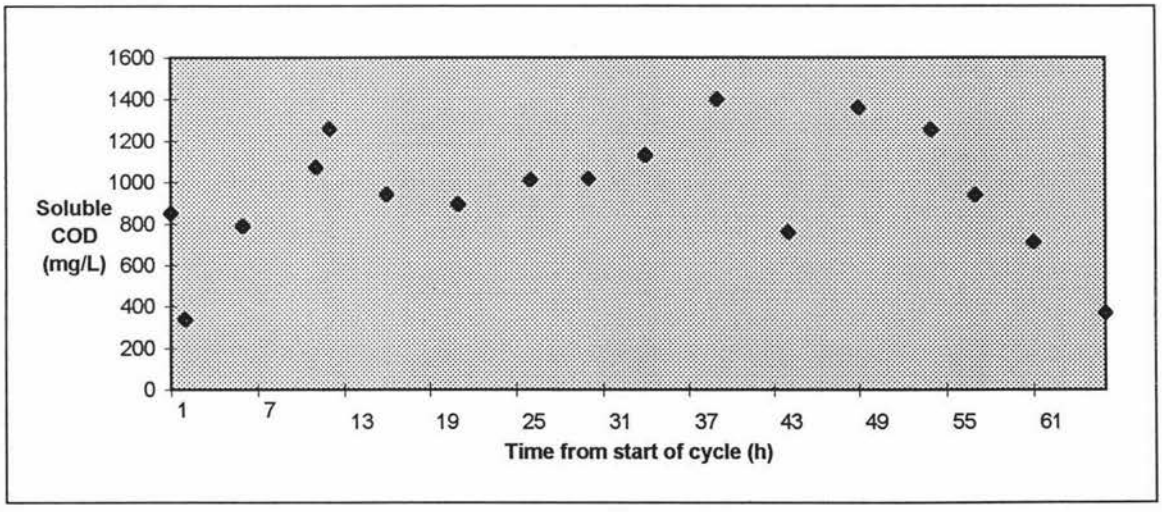

Figure 5.10 Soluble COD

5.2 Prefermentation

5.2.1 Preliminary prefermentation trial

5.2.1.1 VFA production

VFA quantities in the effluent have been expressed in terms of their theoretical oxygen demand, or COD, as is the convention (v. Munch and Koch, 1997).

The preliminary prefermentation trial confirmed that VFA production occurred in farm dairy effluent. Figure 5.11 shows the COD of VFAs produced in raw farm dairy effluent over a six day period. Low VFA levels existed in the fresh effluent: a total oxygen demand of 259 mg/l, consisting of propionic and butyric acids. After six days' fermentation the VFA oxygen demand had increased to 2,072 mg/L, with acetic and propionic acids comprising 700 and 790 mg/L respectively.

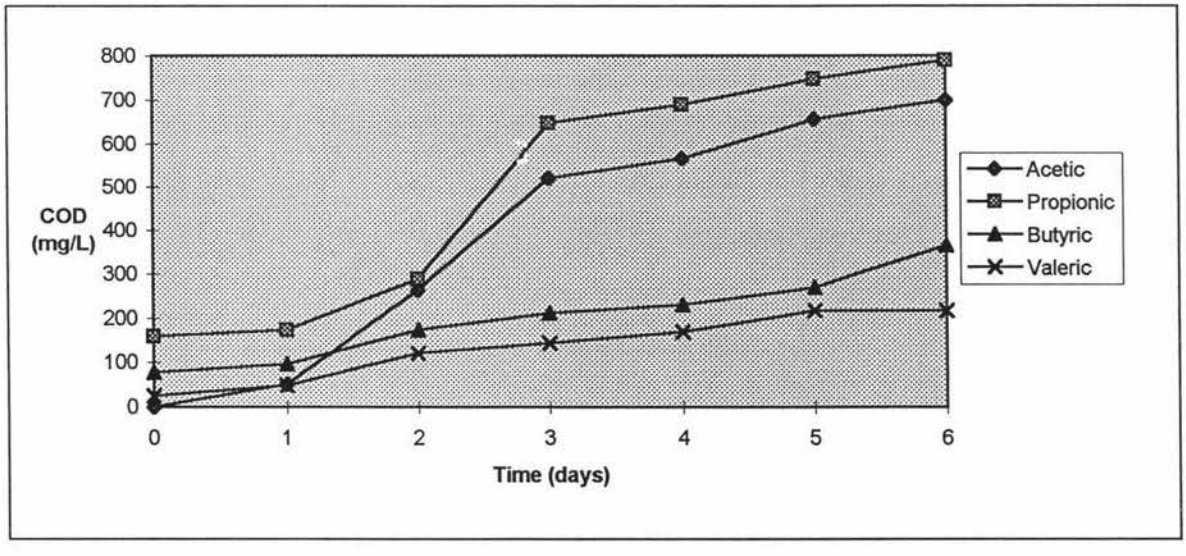

Figure 5.11 VFA production in raw farm dairy effluent over 6 days

5.2.1.2 BODs

Figure 5.12 shows the BOD curve for fresh farm dairy effluent. The breaks in the curve are due to a fault in the datalogger. The effluent had a BOD_5 of 4,900 mg/L and a BOD_u of 5,730 mg/L. Figures 5.13, 5.14 and 5.15 show the effluent BOD following two, four, and six days of fermentation. BOD_5 was reduced to 4,300 mg/L after two days' fermentation, 3,700 mg/L after four days' fermentation, and 3,000 mg/L after six days' fermentation.

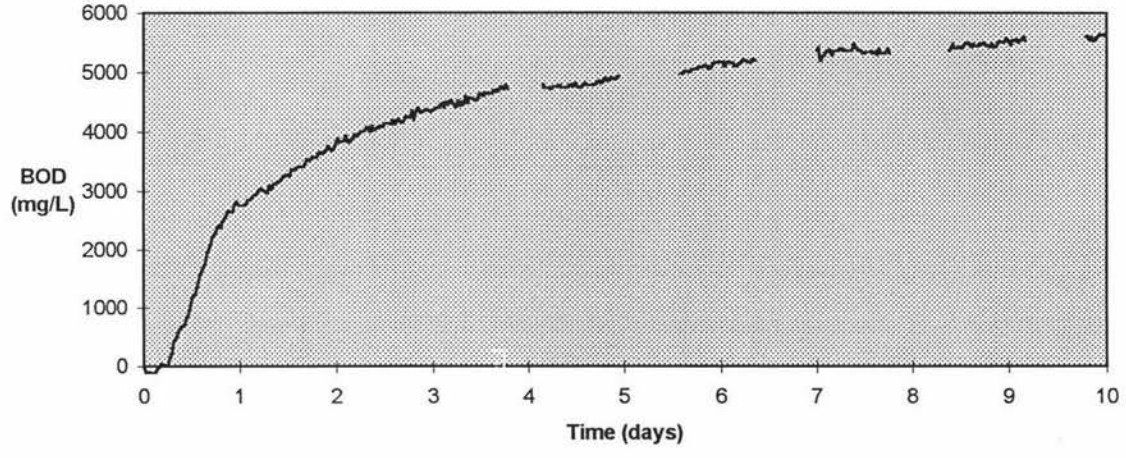

Figure 5.12 BOD curve for fresh farm dairy effluent

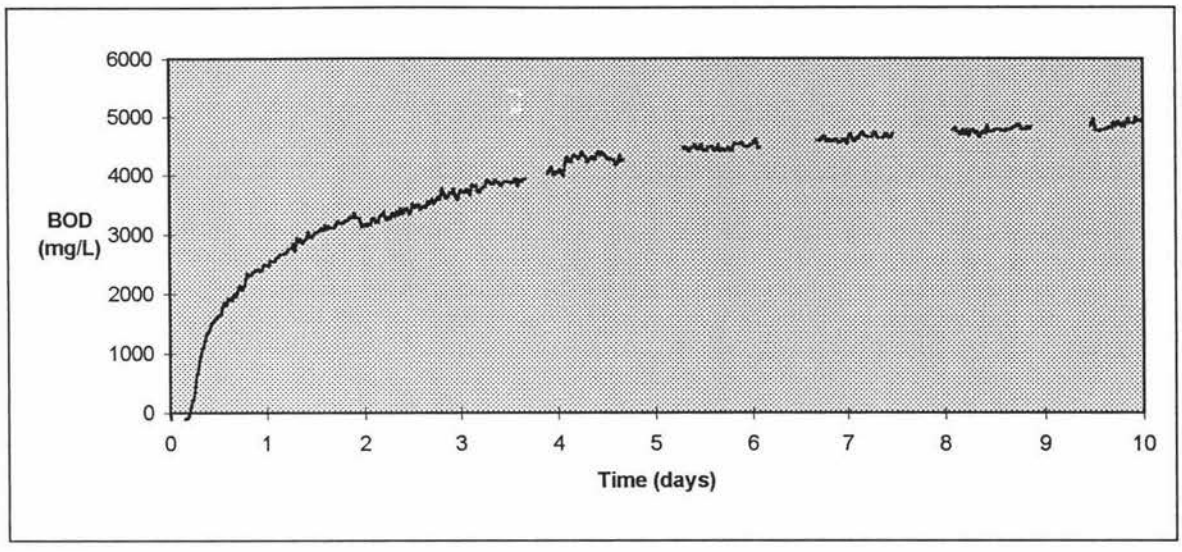

Figure 5.13 BOD curve for farm dairy effluent after fermentation for two days

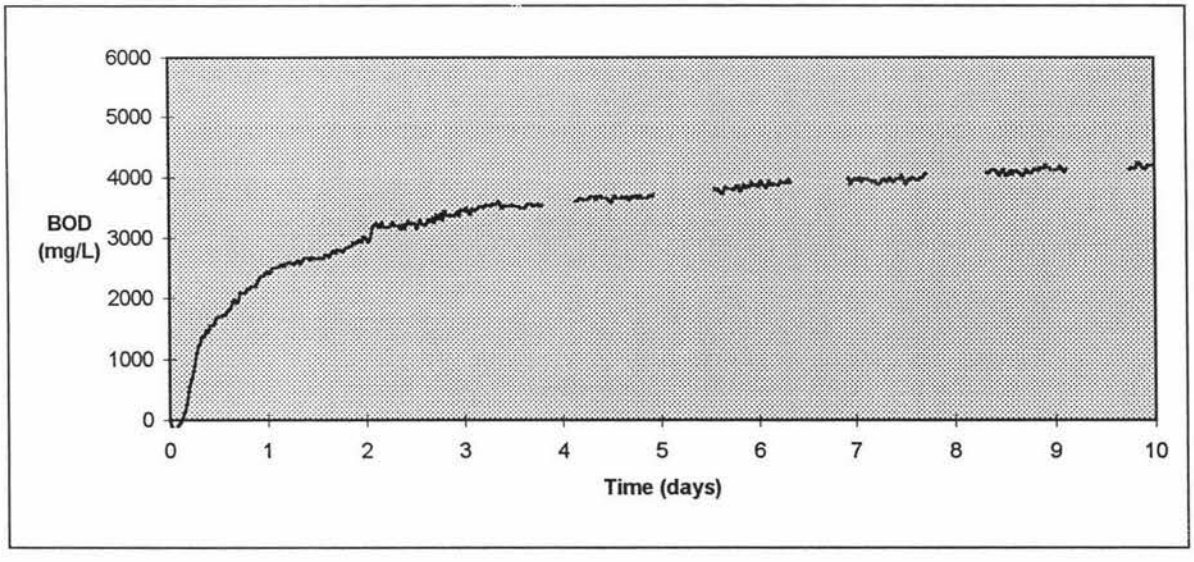

Figure 5.14 BOD curve for farm dairy effluent after fermentation for four days

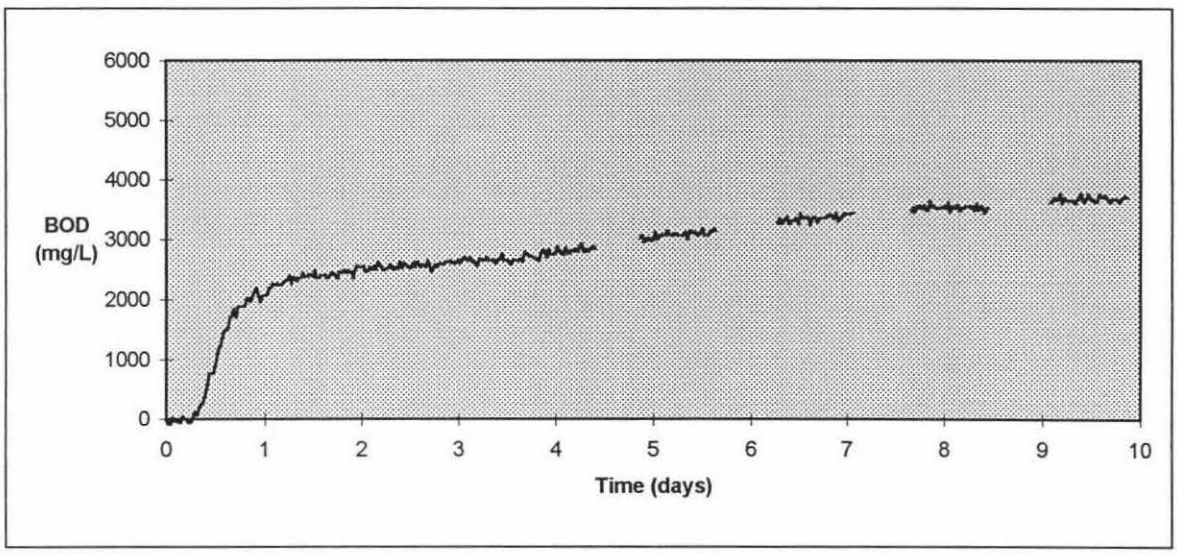

Figure 5.15 BOD curve for farm dairy effluent after fermentation for six days

5.2.2 Prefermentation trial

5.2.2.1 VFA production in raw effluent

Figure 5.16 shows the COD of VFAs produced in raw farm dairy effluent over a 20 day fermentation period. The highest VFA concentration occurred on day 15, however the shape of the curve suggests that the data points at day 15 are incorrect and it is more likely that the peak occurred around days 8 to 10.

Low VFA levels existed in the fresh effluent: a total oxygen demand of 315 mg/l, consisting of 96 mg/L acetic, 72 mg/L propionic, 134 mg/L butyric, and 12 mg/L valeric acids.

The total COD had increased to 2,144 mg/L after eight days and 2,174 mg/L after ten days. Acetic acid production peaked at 1,089 mg/L, and butyric acid at 317 mg/L, on day 8. Propionic acid peaked at 604 mg/L on day 10, and valeric acid peaked at 216 mg/L.

VFA levels decreased by less than 20% by day 20, although levels fluctuated widely between days 14 and 20.

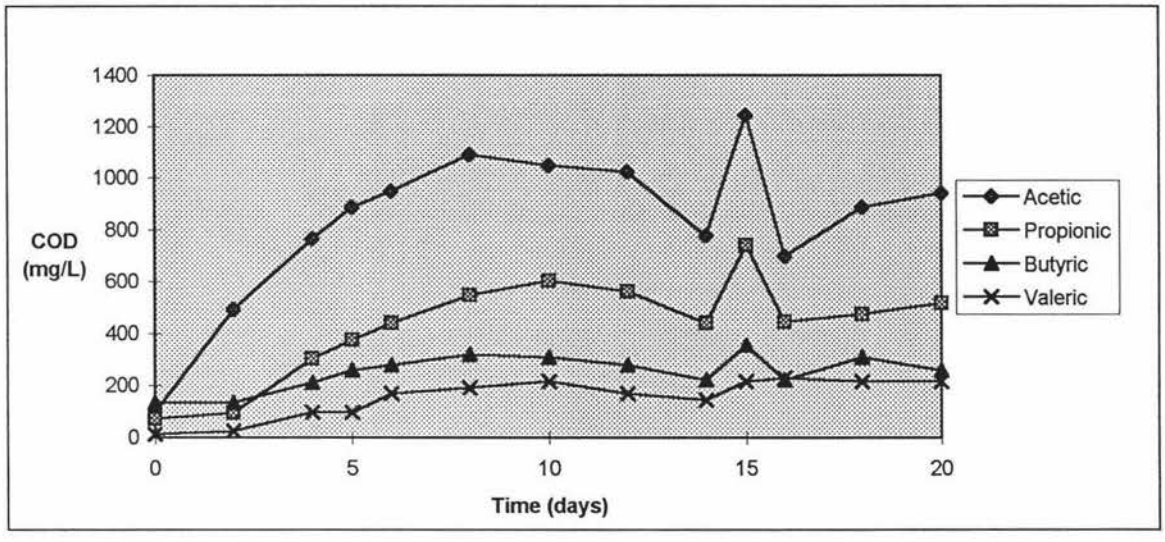

Figure 5.16 VFA production in raw effluent

5.2.2.2 VFA production in settled effluent

Figure 5.17 shows the COD of VFAs produced in settled farm dairy effluent over a 20 day fermentation period. VFA concentrations increased between days 0 and 5, to a total oxygen demand of 196 mg/L, with propionic and butyric acids making the largest contributions (79 and 58 mg/L respectively). COD decreased virtually to zero for all acids by day 10 (trace amounts of acetic and butyric acids were present). Butyric acid was present on day 15, and the COD levels were similar on day 20 as on day 0.

Very low VFA levels existed in the fresh effluent: a total oxygen demand of 82 mg/l, consisting of 19 mg/L acetic, 50 mg/L propionic, and 12 mg/L valeric acids.

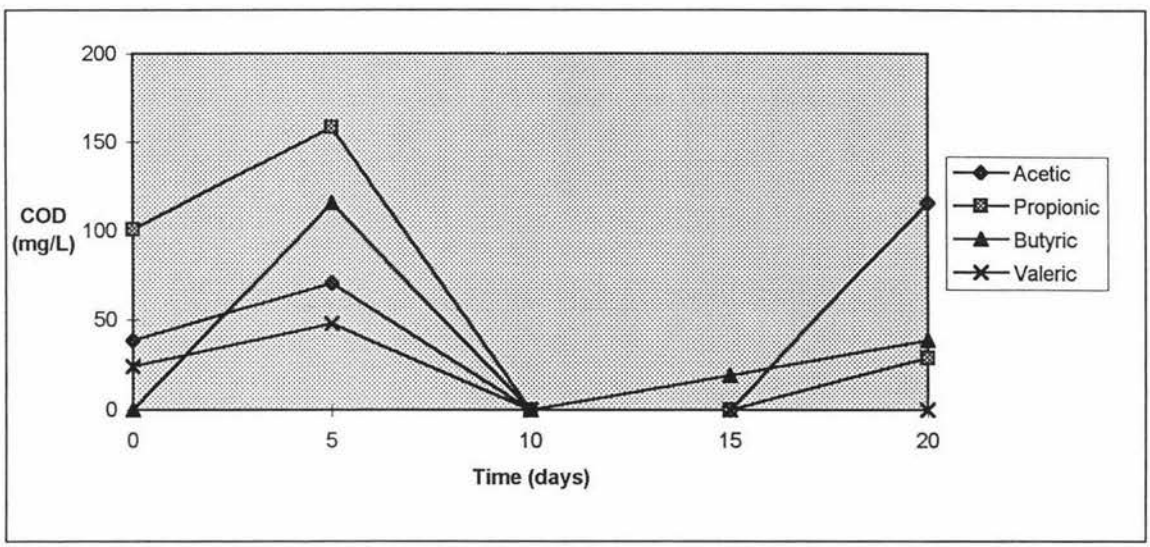

Figure 5.17 VFA production in settled effluent

5.2.2.3 BODs

The BOD of raw and settled farm dairy effluent after 0, 10 and 20 days' prefermentation is shown in Figure 5.18 to Figure 5.23. The fresh raw effluent had a BOD_5 of 4,900 mg/L, which decreased to around 3,200 mg/L after 10 days, and was similar at 20 days (3,300 mg/L).

Settled effluent had a significantly lower BOD than raw effluent: on day 0 the settled effluent had a BOD_5 of 700 mg/L, which reduced to around 250 mg/L on days 10 and 20.

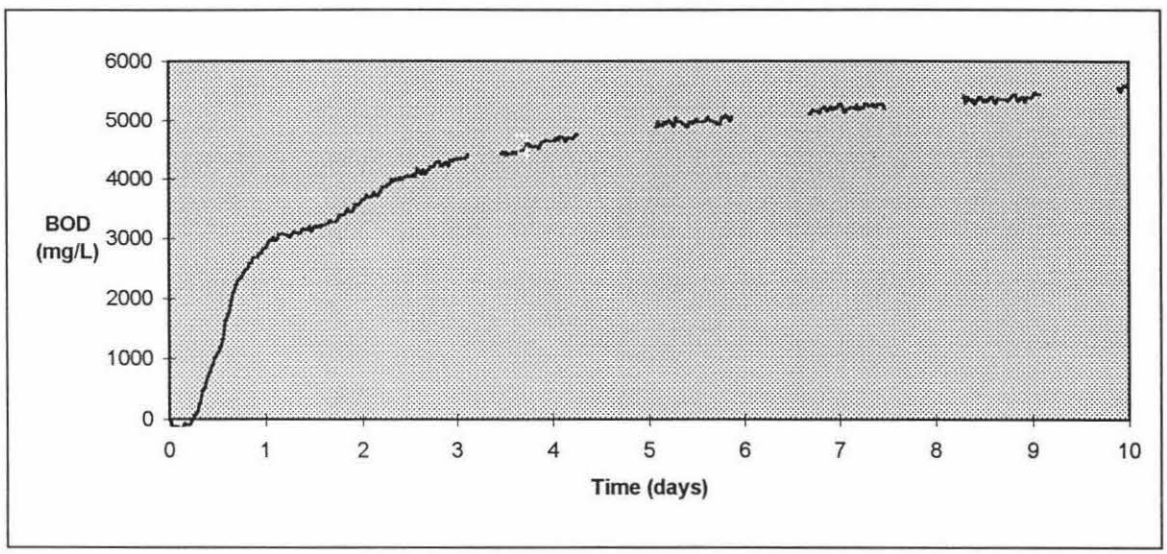

Figure 5.18 BOD of fresh raw effluent

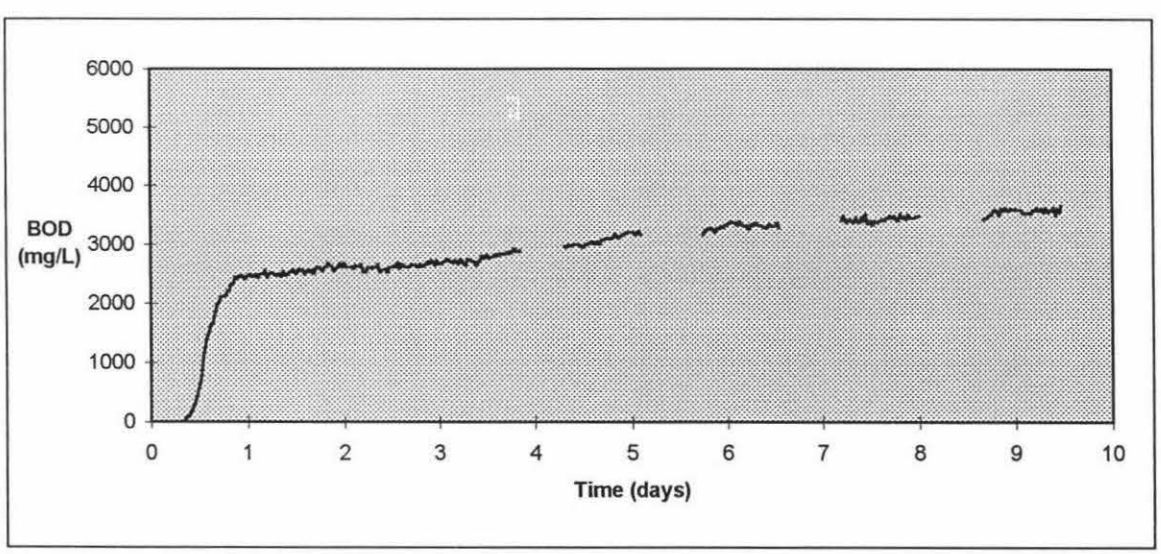

Figure 5.19 BOD of raw effluent after 10 days' prefermentation

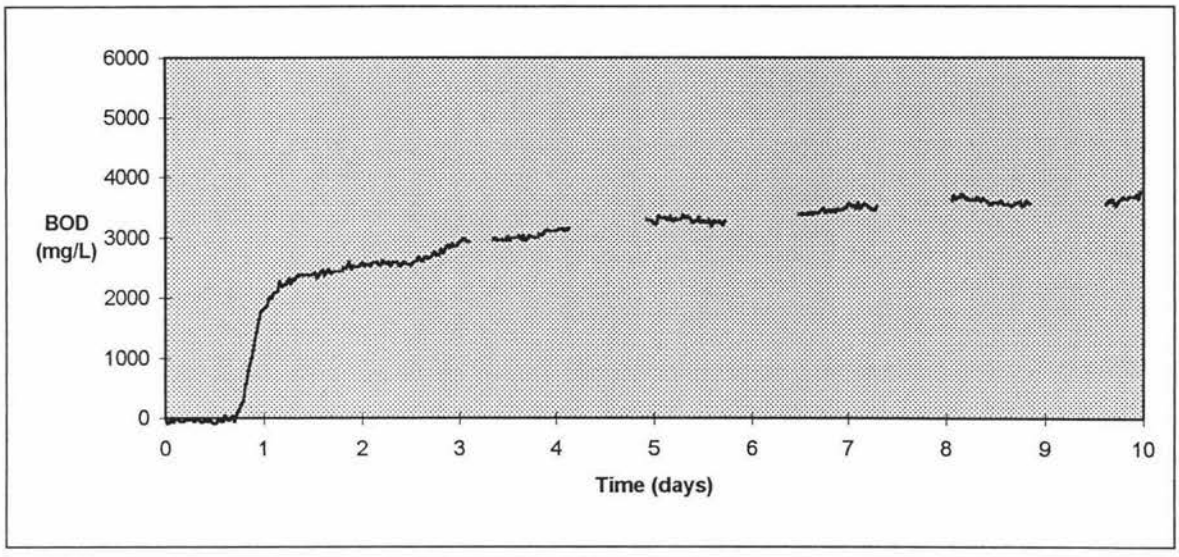

Figure 5.20 BOD of raw effluent after 20 days' prefermentation

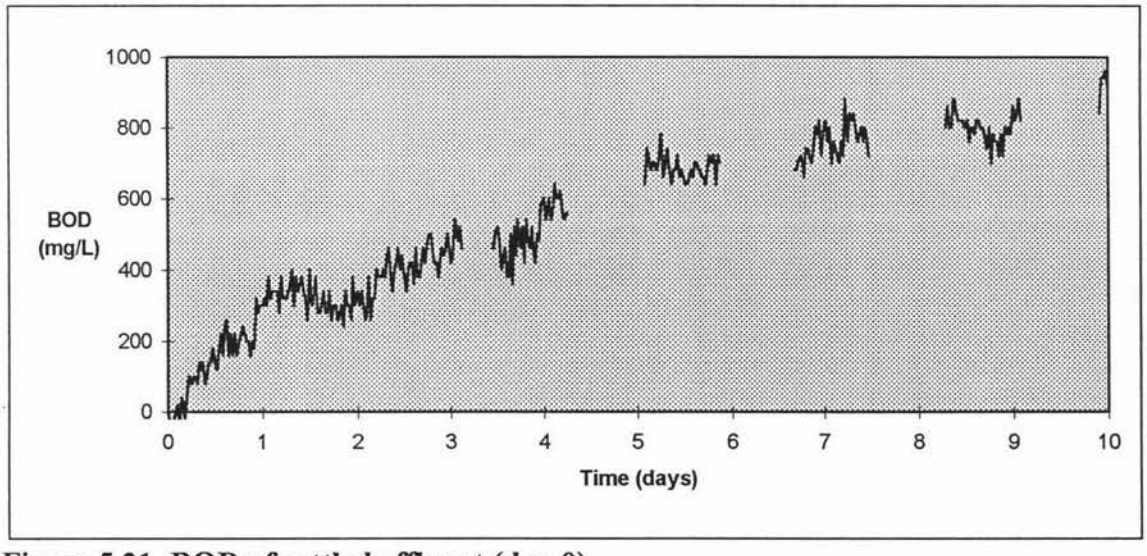

Figure 5.21 BOD of settled effluent (day 0)

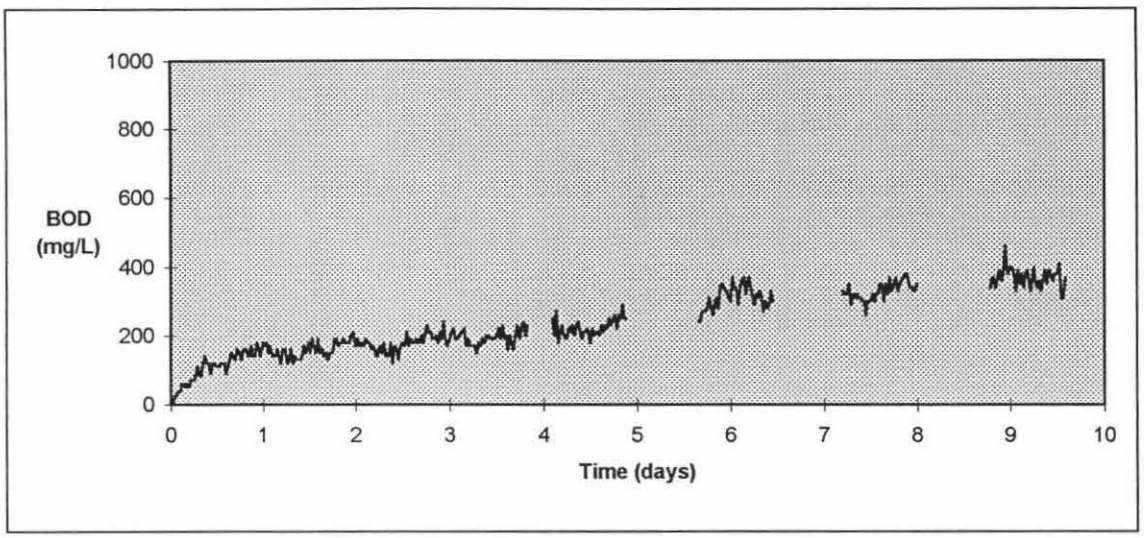

Figure 5.22 BOD of settled effluent after 10 days' prefermentation

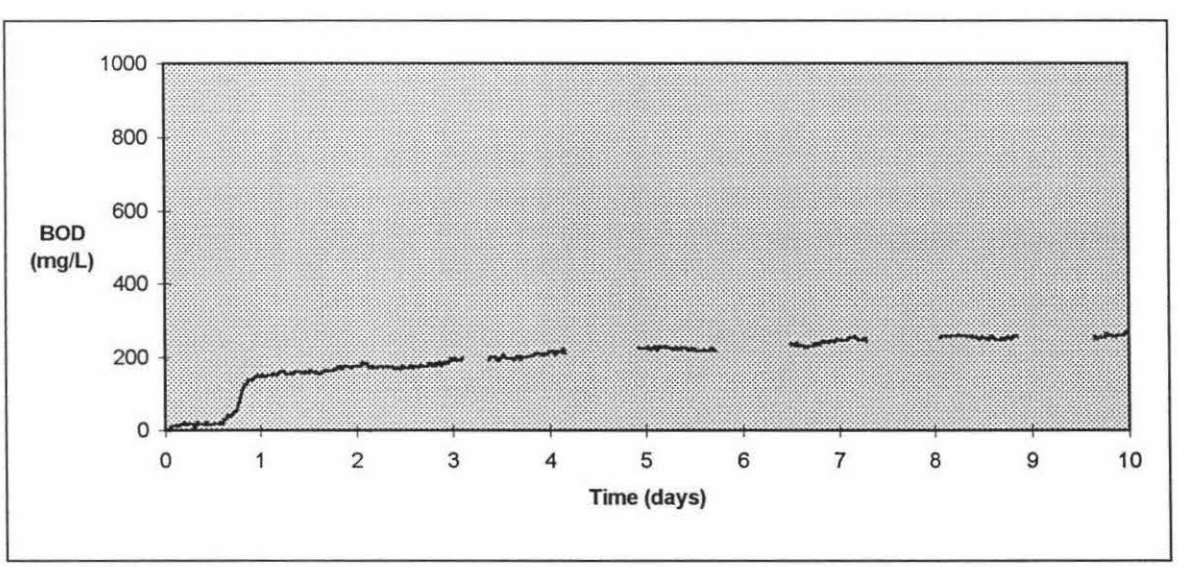

Figure 5.23 BOD of settled effluent after 20 days' prefermentation

5.2.3 Prefermentation semi-continuous reactors

5.2.3.1 Raw effluent reactors

The results in Figure 5.24 and Figure 5.25 show that VFA production in the semi-continuous reactors using raw effluent increased over the first three batches but was negligible in the final batch. The initial oxygen demands of VFAs in the reactors increased over the first three batches, due to VFAs in the raw effluent and retained in the solids from the previous batch.

VFA oxygen demands increased from 373 mg/L to about 1,000 mg/L in batch 1. Batch 2 oxygen demands increased from around 700 to 2,200 mg/L. In batch 3 the oxygen demands rose to over 2,500 mg/L from about 1,250 mg/L, and in batch 4 they changed slightly to give a final oxygen demand of around 1,000 mg/L.

Proportions of the four acids remained similar throughout the experiment, with acetic acid being the most prevalent, followed by propionic acid, then butyric acid and finally valeric acid.

The total oxygen demand of the VFAs in the raw effluent added to the reactors, shown in Figure 5.26, varied considerably between batches, most noticeably, though, the final batch had an VFA oxygen demand of 67 mg/L compared with more than 300 mg/L in the other batches. Effluent used in batch 4 also contained no acetic acid, which made up a large proportion of batches 1 and 2.

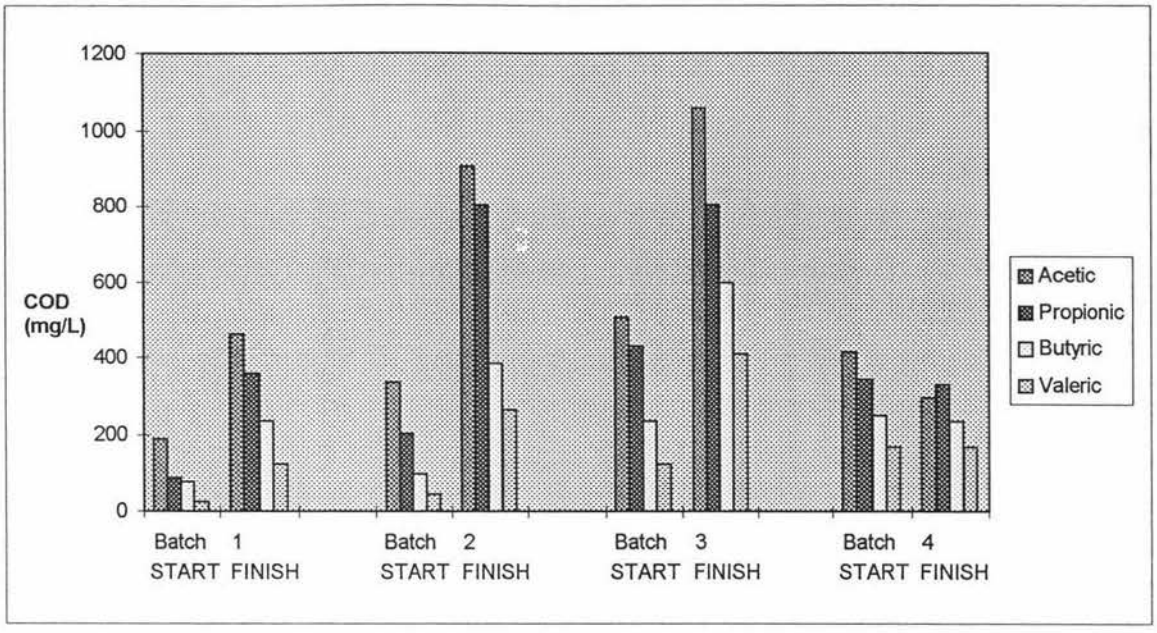

Figure 5.24 VFA production in raw effluent (reactor a)

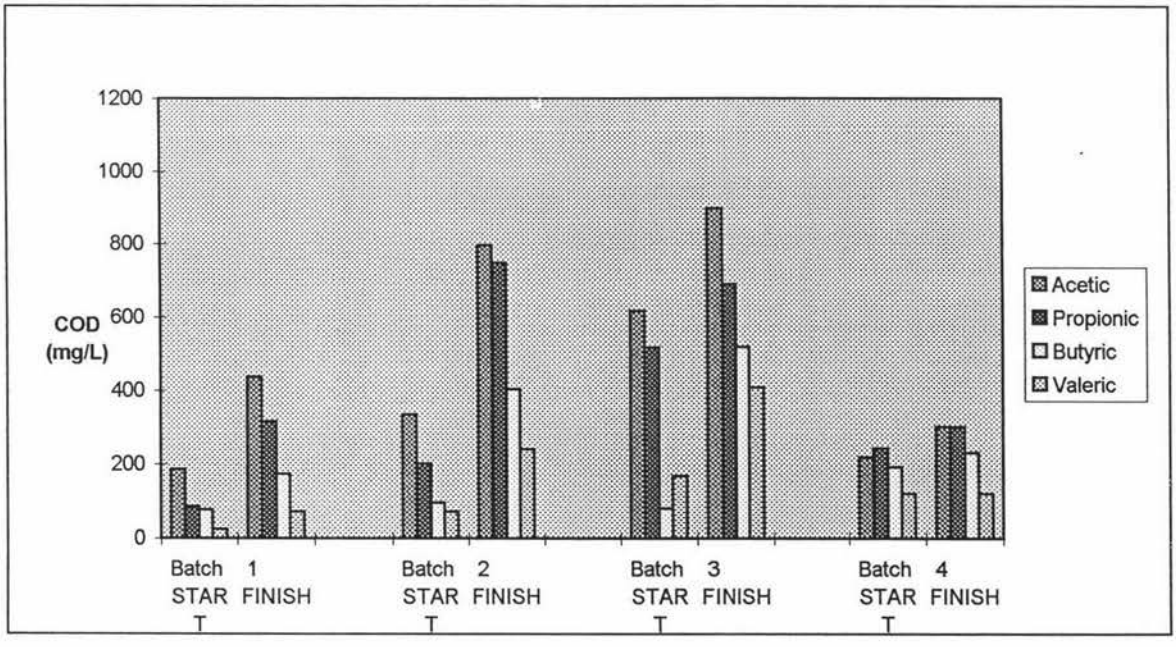

Figure 5.25 VFA production in raw effluent (reactor b)

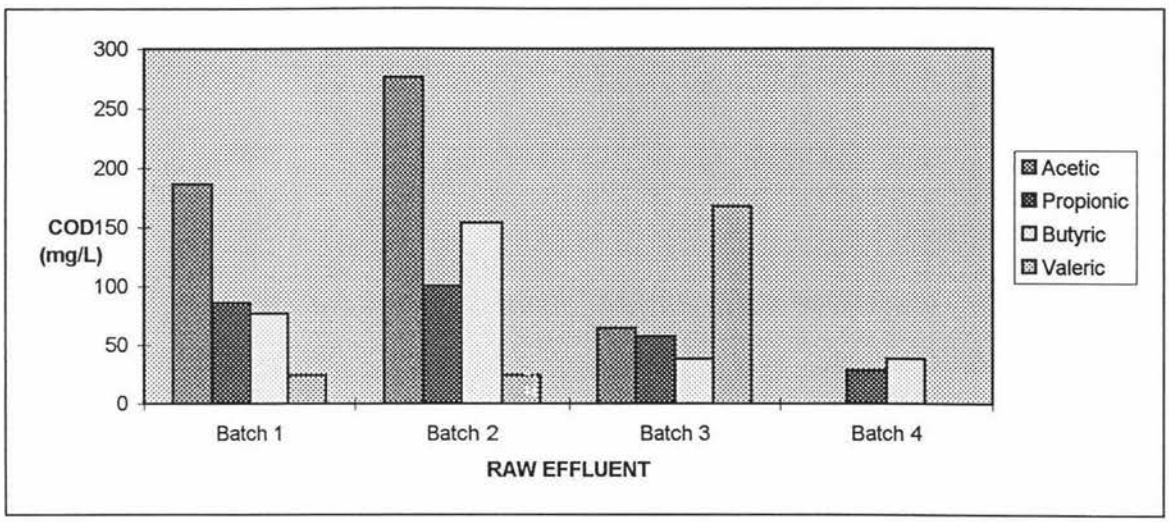

Figure 5.26 VFA concentrations in raw effluent

5.2.3.2 Settled effluent reactors

The results for VFA oxygen demand in the reactors using settled effluent show that VFA production was minimal (given in Figures 5.27 and 5.28). VFA oxygen demand increased marginally in batch 1: from 67 to 80 mg/L in reactor a, and there was no change in reactor b. Concentrations dropped from 67 to 34 mg/L (reactor a) and 53 (reactor b) in batch 2 and decreased to zero by the end of batch 3. No VFAs were recorded in batch 4.

The VFA demand of the settled effluent added to the reactors ranged from 0 to 91 mg/L. Figure 5.29 shows that the initial VFA composition in the settled waste is significantly different to that of the raw effluent. The dominant VFAs are propionic and butyric acids, compared with acetic and propionic acids in raw effluent. Similarly, the VFA production in the reactors was for propionic and butyric acids, with no valeric measurable and little acetic acid being produced.

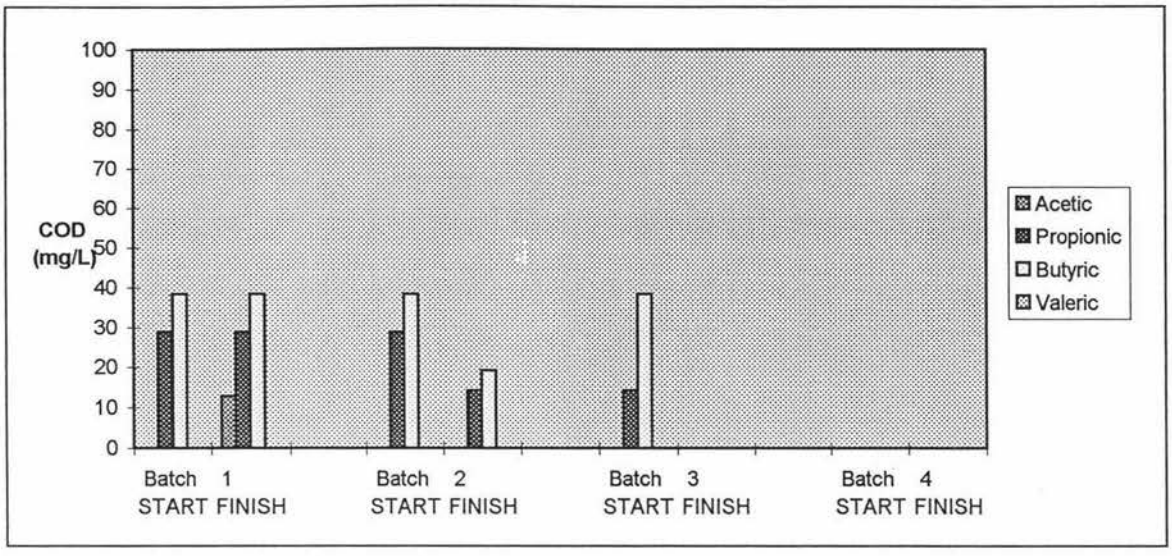

Figure 5.27 VFA production in settled effluent (reactor a)

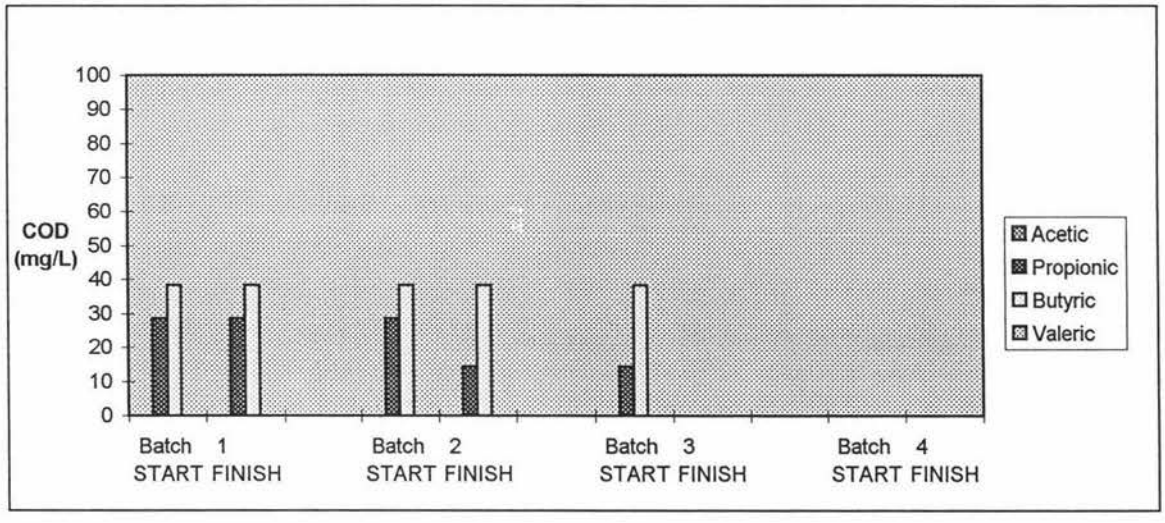

Figure 5.28 VFA production in settled effluent (reactor b)

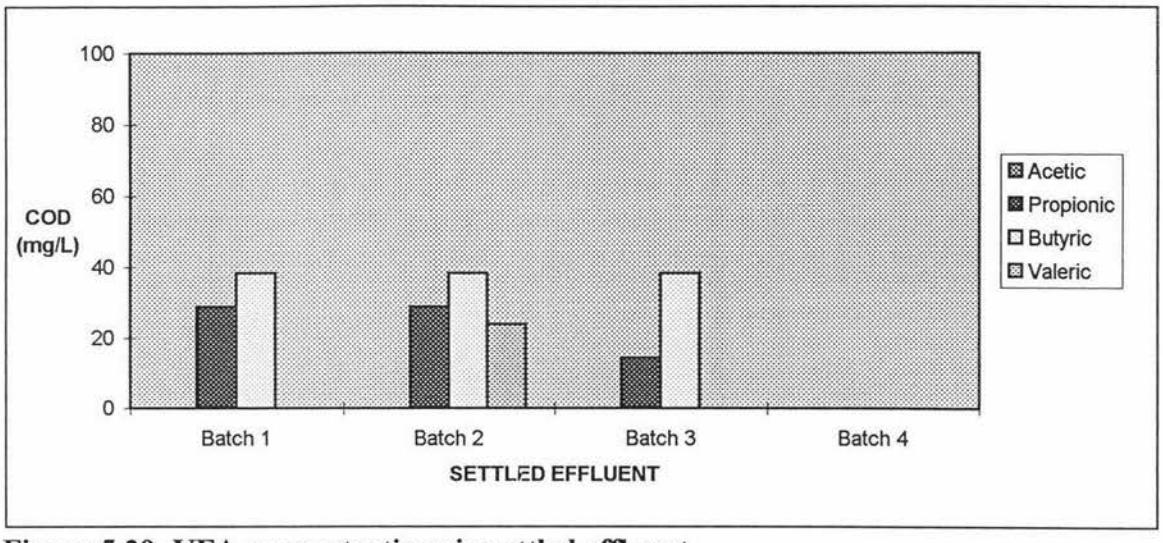

Figure 5.29 VFA concentrations in settled effluent

5.2.3.3 Seeded settled effluent reactors

Figures 5.30 and 5.31 show the effect of seeding the reactors with raw effluent. Batch 1 results are similar to those of the raw reactors, with an initial oxygen demand of 373 mg/L and a final oxygen demand around 1,000 mg/L. Initial concentrations in batch 2 were considerably lower than for the raw effluent reactors (about 350 mg/L), an indication of the low levels in the settled effluent. At the end of batch 2, reactor a oxygen demand was high (964 mg/L) but reactor b was unchanged.

Batch 3 results showed no increase in reactor a, but were anomalous in reactor b, as there was an unexpectedly high initial concentration, however the final concentration was low. The VFA production was minimal in batch 4 for both reactors (initial concentrations 34 mg/L and from 19 to 67 mg/L, final). Only propionic and butyric acids were measurable in batch 4, whereas all acids were present in the previous batches.

Figure 5.32 shows the initial and final soluble COD for each batch of each reactor. There are no obvious trends in the data, apart from the seeded reactors, in which the soluble

COD decreases from batch 1 to batch 4. The soluble COD does not consistently increase or decrease between the initial and final reading for each batch.

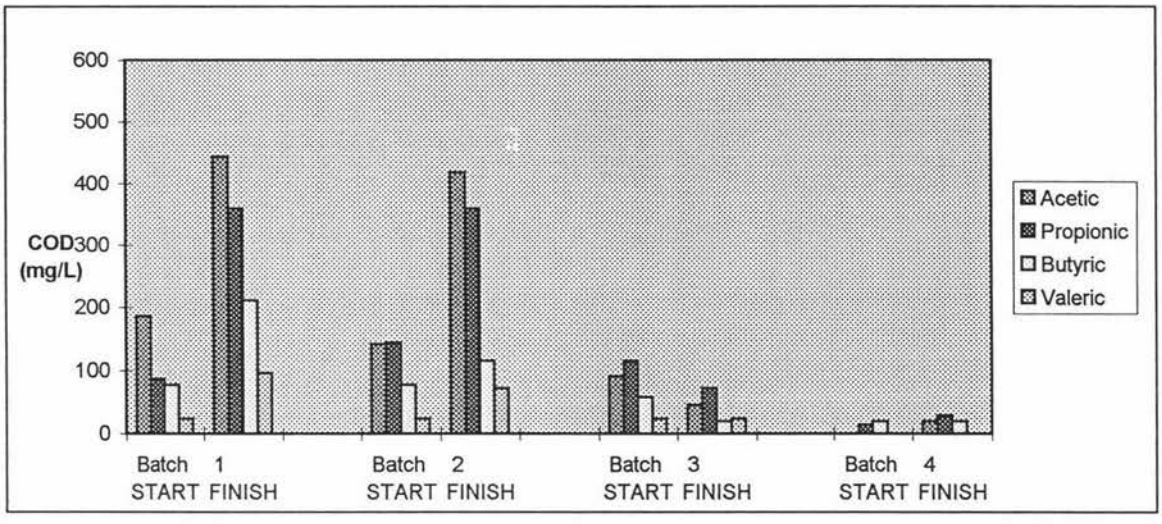

Figure 5.30 VFA production in settled effluent with raw effluent seed (reactor a)

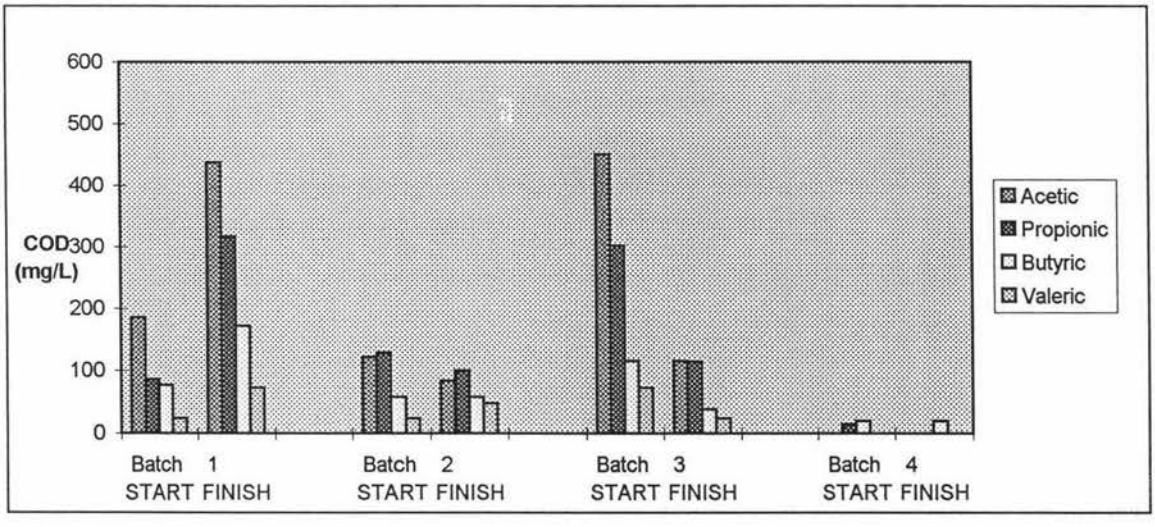

Figure 5.31 VFA production in settled effluent with raw effluent seed (reactor b)

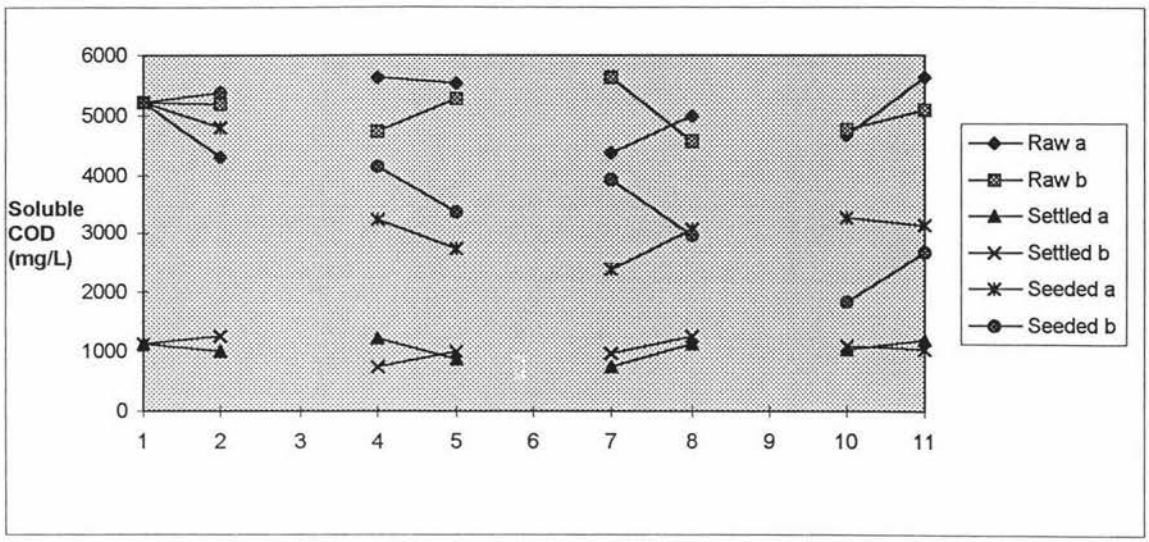

Figure 5.32 Initial and final soluble CODs for each treatment

6. DISCUSSION

6.1 SBR operation

The results show that the SBR did not achieve biological nutrient removal, as there was no apparent reduction in nitrogen and phosphorus levels in the effluent, according to Figures 6.5 to 6.8. Had BNR occurred, the total nitrogen, ammonia, and total phosphorus curves would have gradually reduced over the course of the treatment and the nitrate would have increased during the first aerobic phase and decreased during the anoxic phase.

The dissolved oxygen levels during the anaerobic and anoxic phases were less than 0.5 mg/L, which should not have inhibited phosphorus release or denitrification. It took approximately one hour for the dissolved oxygen concentration in the first aerobic phase to reach 1 mg/L, the requirement for nitrification, so the time available for nitrification was actually about two-thirds of the 3.1 h calculated as being required. However it is unlikely this contributed to nitrification not occurring, as this would simply cause the reaction to be incomplete.

The redox potential was sufficiently high (greater than -300 mV) for acid fermentation, however it is likely that any fermentation would have taken place in the holding tank, as effluent was held for up to two days prior to SBR treatment.

The average pH was 7.7, which is slightly lower than the optimal for nitrification of 8 to 9, but within the optimal range for denitrification (7 to 9). It is likely that pH would have been more varied had nitrogen removal occurred, as nitrification consumes alkalinity, which is a pH buffer, and denitrification releases it. Henze *et al* (1995) state that acid fermentation also consumes alkalinity, and so, had BNR occurred in the SBR, the

alkalinity may have been removed during prefermentation to such an extent that nitrification was reduced.

Suspended solids concentration in the SBR was considerably lower than the 5,000 mg/L measured at the end of the start-up phase. This could indicate that the bacteria were not thriving under the operating strategy imposed for biological nutrient removal. This may have been due to the low carbon level in the effluent coupled with the high energy requirement for substrate uptake during anaerobic periods. Intermittent operation of the aerator to minimise foaming may have also affected microbial growth by making the dissolved oxygen level limiting.

Soluble COD data does not indicate any trends COD levels during the treatment process, although it is considered likely that the closed reflux method used did not produce accurate results. It appears that the spectrophotometer may not have been working properly, as absorbance results obtained for the same sample were highly variable. Investigation into the reliability of the method is required.

The most likely reason for the SBR's failure to operate as expected is that it was operated on settled effluent rather than raw farm dairy effluent. All calculations for the SBR's operating strategy and theoretical ability to achieve BNR were based on Ellwood's (1997) yard effluent data, which had significantly different characteristics to the settled effluent that was used.

It was originally intended that raw effluent from an entire milking session would be collected for treatment in the SBR. However logistical difficulties concerning its collection meant that effluent was instead collected from the anaerobic pond adjacent to the inlet from the farm dairy. Collection took place during washdown, when the highest flows were entering the pond. It was anticipated that this would enable collection of relatively unmixed effluent, however the characteristics of the settled effluent suggest that it was closer in composition to anaerobic pond effluent than raw effluent.

Reworking the nitrogen and phosphorus removal ratios given in Section 2.2.3.1 using the settled effluent data may indicate why BNR did not occur. Henze *et al* (1995) state that the optimum C/N ratio for denitrification is 3 to 3.5 kg BOD/kg N or 4 to 5 kg COD/kg N, whereas Randall *et al* (1992) suggest a ratio of COD : TKN of 8. Denitrification requires BOD_5: NO_3-N to be at least 2.3 : 1 (Narkis *et al*, 1979).

The ratios, using settled effluent data for COD : N, BOD_5 : N, and BOD_5 : NO_x-N, are 5, 1.7, and 4.3 respectively. These would indicate that the likelihood of denitrification occurring using settled effluent was marginal: only the BOD_5 : NO_x-N ratio is exceeded.

Randall *et al* state a requirement of 7.14 mg alkalinity per mg ammonia. This would indicate a requirement of 1,150 mg/L, which is slightly less than the average concentration in the SBR (1,360 mg/L). Thus alkalinity levels would be almost completely used during nitrification, possibly resulting in a reduced pH. Dosing with limestone, or similarly slow-dissolving rock, to increase alkalinity was intended, however the order did not arrive until after the cycle analysis had been conducted.

Phosphorus removal requires a soluble COD to phosphorus released ratio of 1.2 : 1 (Fang and Ling, 1995) and Manning and Irvine (1985) achieved greater than 95% phosphorus removal with a COD : TKN : TP ratio of 25 : 3 : 1. Using the data for settled effluent, these ratios were 17 : 1 and 35 : 7 : 1, respectively. The BOD_5: TP ratio was 12, which, according to Randall *et al,* is too low for successful phosphorus removal.

Thus it would appear that the carbon content and the alkalinity of the settled effluent are marginal for nitrogen and phosphorus removal. Addition of carbon and alkalinity may have ensured that BNR took place using the settled effluent.

6.2 Prefermentation

6.2.1 Preliminary prefermentation trial

6.2.1.1 VFAs

The purpose of the preliminary prefermentation trial was to confirm the production of VFAs in farm dairy effluent and to give an indication of the quantity produced. The VFA oxygen demand in the fermenting effluent increased from 259 to 2,072 mg/L over the 6 day trial, and production did not appear to have reached a peak at day 6.

Randall *et al* (1992) reported that batch prefermentation tests, using domestic effluent, showed a lag phase of 0 to 7 days before acid production began, with a peak acid concentration achieved after 6 to 9 days. Although there were VFAs present in the fresh effluent, there appeared to be a 1 day lag before the concentrations started to increase.

Randall *et al* (1992) obtained VFA proportions of 1.0 : 1.0 : 0.08 : 0.07 acetic : propionic : butyric : valeric acids, and noted that as batch tests progressed, more long chain acids were produced. The VFA proportions (based on concentration, not oxygen demand) in this experiment were 1.0 : 0.7 : 0.2 : 0.1. These proportions are significantly different to those obtained by Randall *et al*, which is likely to be a reflection of the different compositions of domestic and farm dairy effluent.

6.2.1.2 BODs

Prefermentation for six days caused a 40% reduction in the BOD_5 of raw farm dairy effluent.

Farm dairy effluent BOD curves are characterised by a steep rise for the first half to one day, followed by a much gentler rise over the remainder of the BOD curve. It was hypothesised that the initial steep part of the curve was due to readily biodegradable carbon sources, and thus may be extended by the increase in VFAs by prefermentation of the effluent. However the BOD curves given in Section 5.2.1.2 show a reduction in that part of the curve over the six days of prefermentation.

The graphs show that although the steep part of the curve reduces over the prefermentation period, the proportion of VFAs contributing to that part of the curve increases from around 10% in fresh effluent to 100% in fermented effluent.

The steep part of the curve ends at about 2,500 mg/L in Figure 5.12, fresh, raw effluent of which 259 mg/L were VFAs. Following two days fermentation the VFA oxygen demand was approximately half of the height of the steep part of the curve. On days 4 and 6 the steep part of the curve was around 1,500 to 2,000 mg/L, as was the VFA concentration.

6.2.2 Prefermentation trial

6.2.2.1 VFAs

The 20 day prefermentation trial aimed to determine the optimal time for prefermentation. This appeared to be after eight to ten days, when VFA oxygen demand peaked at about 2,100 mg/L.

The prefermentation trial showed a lag phase of 0 to 2 days: slightly longer than in the preliminary prefermentation trial. Peak production occurred after 8 to 10 days. The VFA proportions obtained in this experiment were 1.0 : 0.3 : 0.14 : 0.08 acetic : propionic : butyric : valeric acids, which is slightly lower than those obtained in the

preliminary prefermentation trial, particularly the propionic acid concentration, which was greater than acetic in the preliminary trial.

The VFA proportions increased to 1.0 : 0.3 : 0.17 : 0.11 on day 20. Although it is difficult to say with certainty, the longer chain fatty acid (butyric and valeric) concentrations appeared to be increasing by the end of the trial.

6.2.2.2 BODs

The effect of 20 days' prefermentation on the raw effluent BOD was not markedly different from that following 6 days' prefermentation, as discussed in Section 6.2.1.2. The BOD_5 was reduced by 35% over the treatment period.

The steep part of the BOD curve was reduced from around 3,000 to 2,000 mg/L by prefermentation. VFA concentrations rose from 315 mg/L in the raw effluent to about 2,000 mg/L after 10 and 20 days prefermentation, which corresponds to an increase from 10 to 100% of the steep part of the curve.

Settled effluent BOD_5 was reduced by 65% over the 20 day treatment period. The steep section of the curve is not as pronounced in the settled effluent curves however it appeared to have halved in the BOD curves of the prefermented effluent (Figures 5.22 and 5.23). VFAs made up about one third of the steep part of the curve in fresh effluent and around 100% of the prefermented effluent on day 20.

6.2.3 Prefermentation semi-continuous reactors

The semi-continuous reactors were based on the idea of having a small prefermentation pond or tank prior to the SBR, as part of a treatment system on a farm. It is likely that such a pond would operate continuously, rather than semi-continuously, which would

cause some dilution of the VFAs. The choice of a one week retention time was based on Randall *et al*'s (1992) information and the preliminary prefermentation trial, as the results from the prefermentation trial were not available.

Randall *et al* stated that in semi-continuous reactors there was no lag phase in VFA production and that the VFA proportions obtained in the effluent were 1.0 : 1.0 : 0.3 : 0.1 acetic : propionic : butyric : valeric acids. VFA proportions in the raw effluent reactors were 1.0 : 0.5 : 0.3 : 0.2 and in the seeded reactors 1.0 : 0.6 : 0.2 : 0.2. These results are comparable with the domestic effluent results, apart from the propionic acid levels, which are much lower in the farm dairy effluent.

High initial concentrations for each batch suggests that the reactor solids retained a portion of the VFAs. This is confirmed by v. Munch and Koch (1997), who state that in full-scale prefermenters elutriation of VFAs from sludge blankets is required.

The low concentration of VFAs produced in the settled effluent, and the high proportion of longer chain VFAs produced, suggests that the settled effluent had already undergone significant prefermentation and that little easily hydrolysable carbon was available in the waste.

The results of the seeded reactors show some VFA production in batch 2, using settled effluent, but little in batches 3 or 4. It is possible that the VFA production in batch 2 is attributable to easily hydrolysable carbon remaining in the solids from batch 1, rather than carbon added in batch 2. Alternatively, the solids retention time may have been too long. The solids in the reactor remained from batch 1 throughout the experiment, and were not replenished by the effluent added in each batch, as the settled effluent had a low solids content.

6.3 *Implications for full-scale SBR treatment of farm dairy effluent*

6.3.1 Process design

Although BNR was not achieved in this research, the process design appears to be accurate for achieving an effluent low in ammonia, nitrate and phosphorus. This operating strategy extends on the work done by Lo *et al* (1985;1988) and Ellwood (1997) in developing SBR treatment for nitrogen removal.

The next stage of process development would be to operate the SBR on raw farm dairy effluent. It was intended to use raw effluent in this research but the site layout meant that the physical works required were beyond the limits of the research. The logistics of obtaining an effluent sample representative of an entire milking for SBR treatment will need to be overcome, as a suitably sized holding tank or pond for the farm dairy used in this research would need to have had a volume in the vicinity of 30 m^3.

Further research is required to accurately size an aerator for the SBR. The submersible aerator used in this research was selected because its dirty water mass transfer of oxygen (0.68 kg/h) was greater than the estimated requirement of 0.5 kg/h for farm dairy effluent treatment (Ellwood, 1997).

The oversized aerator caused excessive foaming in the SBR, particularly during start-up. Foaming was minimised by operating the aerator intermittently, on a 1 minute on, 2 minutes off basis. Figure 5.1, the dissolved oxygen concentration over the duration of the cycle, indicates that dissolved oxygen may have been limiting for at least the first hour of the first aerobic phase, and thus an aerator operating constantly at a lower mass transfer may be more effective. Intermittent operation also consumes more electricity than

continuous operation as the as the electricity demand for starting a motor is higher than during normal operation.

The results indicate that the alkalinity in farm dairy effluent is insufficient for complete nitrification, without causing a reduction in the pH. Farmers are unlikely to want a system that requires daily maintenance such as dosing with calcium carbonate, so some method of maintaining the alkalinity needs to be developed. This may be an automated mechanism for dosing daily, or as required, however this may be cost-prohibitive. The use of a slow-dissolving alkalinity source such as limestone may provide a cheaper option. Alternatively, reduced nitrification may be an acceptable compromise where treatment such as wetlands follows the SBR.

6.3.2 SBR treatment system

It is envisaged that the SBR treatment process will be utilised by farmers who are unable to irrigate effluent due to climatic or soil conditions, or in situations where the receiving water quality is critical and a highly treated effluent is essential.

The SBR is likely to operate as part of a total treatment system, designed to enhance BNR and provide a highly polished effluent. Figure 6.1 shows the treatment process most likely to provide a high quality effluent with low maintenance requirements.

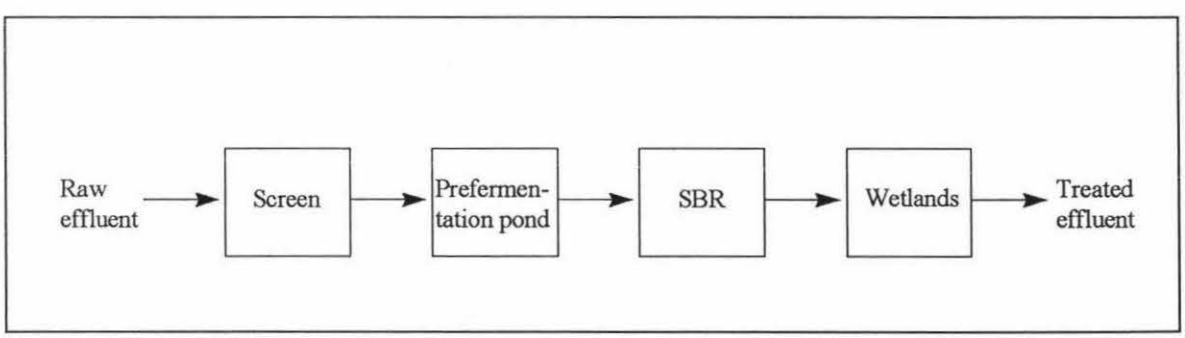

Figure 6.1 Flow diagram of treatment process

Raw effluent from the farm dairy would pass through a screen to remove large non-biodegradable objects such as syringes, stones and other waste materials. Cleaning of the screen would need to be incorporated with the cleaning of the yard to prevent blockages. The effluent would flow from the farm dairy to a prefermentation pond.

Of the four types of prefermenter discussed in Section 2.3.2, only the Activated Primary Tank (ATP) is suitable in this situation. Whereas the ATP receives the entire wastewater flow, the other three methods treat only primary sludge, which will not be produced by this process.

This research has shown that VFA production peaks after about 8 to 10 days at 20°C. The average effluent temperature is likely to be lower than 20°C, and as fermentation is temperature dependent (Henze *et al*, 1995) the optimum retention time may be increased in a prefermentation pond. Thus the prefermentation pond will need to be of sufficient size for a hydraulic retention time of at least 8 to 10 days. Further research is required to determine the time required to optimise VFA production at ambient temperatures.

It is important that the prefermentation pond be correctly sized. An oversized pond would increase the retention time, which may cause the development of methane producing bacteria, thus becoming an anaerobic pond as currently used. This would result in an effluent similar to that treated in this research, with insufficient VFAs available for phosphorus removal. An undersized pond may result in incomplete prefermentation, so phosphorus removal would not be maximised.

Effluent from the prefermentation pond would be treated in the SBR using the operating strategy developed in this research for nitrogen and phosphorus removal. The SBR would be sized to enable treatment of the equivalent of the effluent from an entire milking session.

The SBR would be controlled by a PLC which would enable it to operate unattended. As discussed in Section 6.3.1, an automated dosing system or slow-dissolving alkalinity source is required. These two factors would allow the SBR to operate without excessive input from the owner. The use of a screen and prefermentation pond would also have the advantage of removing larger solids which may block pumps.

The treated effluent would be polished using wetlands, which would further reduce BOD, suspended solids, nitrogen and phosphorus levels. Tanner *et al* (1995a &b) found that wetlands treating effluent from a two-pond system declined in efficiency over time. It is expected that the nutrient loading from SBR treated effluent would be significantly less than that from the two pond system and thus the life time of the wetlands would be extended.

Effluent from the wetlands would be sufficiently treated in terms of carbon, nitrogen and phosphorus levels to be disposed of directly into a waterway.

7. CONCLUSIONS AND RECOMMENDATIONS

7.1 SBR operation

An operating strategy was designed to enable biological nutrient removal from farm dairy effluent using an SBR. Drawing on the nutrient removal mechanisms used in continuous flow BNR processes, the operating strategy shown in Figure 7.1 was developed to achieve low phosphorus, ammonia and nitrate effluent concentrations.

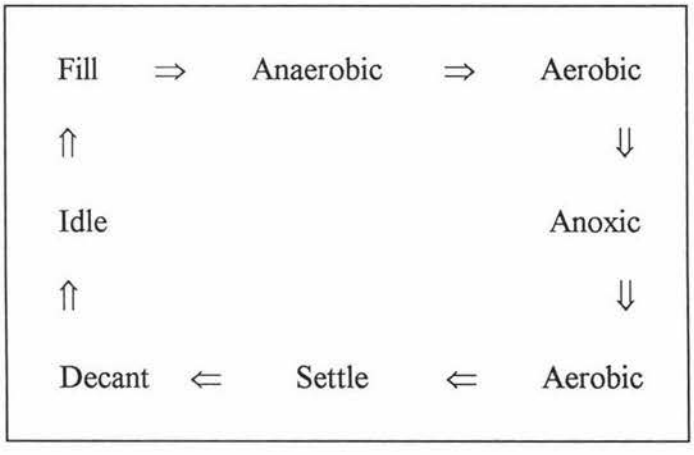

Figure 7.1 SBR operating strategy for biological nutrient removal

As in continuous flow processes, phosphorus is released in the anaerobic phase, using the readily biodegradable carbon. The first aerobic phase is used for nitrification and phosphorus uptake. It also oxidises remaining readily biodegradable carbon, thus the denitrification occurring in the anoxic phase depends entirely on endogenous carbon. The final aerobic phase operates as a polisher.

The results show that the SBR did not achieve biological nutrient removal, as there was no apparent reduction in nitrogen and phosphorus levels in the effluent. However, the process design appears to be accurate for achieving an effluent low in ammonia, nitrate and phosphorus.

The most likely reason for the SBR's failure to operate as expected is that it was operated on settled effluent rather than raw farm dairy effluent. All calculations for the SBR's operating strategy and theoretical ability to achieve BNR were based on Ellwood's (1997) yard effluent data, which had significantly different characteristics to the settled effluent that was used.

The average alkalinity in the SBR was 1,360 mg/L, slightly more than was required for complete nitrification. Thus alkalinity levels would be almost entirely used during nitrification, possibly resulting in a reduced pH.

Thus it would appear that the carbon content and the alkalinity of the settled effluent are marginal for nitrogen and phosphorus removal. Addition of carbon and alkalinity may have ensured that BNR took place using the settled effluent.

COD tests using the closed reflux method used did not produce accurate results. It appears that the spectrophotometer may not have been working properly, as absorbance results obtained for the same sample were highly variable. Investigation into the accuracy of this method is required.

7.2 Prefermentation

The prefermentation trial showed that the optimal time for prefermentation at 20°C was after eight to ten days, when VFA oxygen demand peaked at about 2,100 mg/L. The

prefermentation trial showed a lag phase of 0 to 2 days. The VFA proportions obtained in this experiment were 1.0 : 0.3 : 0.14 : 0.08 acetic : propionic : butyric : valeric acids.

The BOD_5 was reduced by 35% over the treatment period. The VFA data shows that although the initial steep part of the BOD curve reduces over the prefermentation period, the proportion of VFAs contributing to that part of the curve increases from around 10% in fresh effluent to 100% in fermented effluent.

The steep part of the BOD curve was reduced from around 3,000 to 2,000 mg/L by prefermentation. VFA concentrations rose from 315 mg/L in the raw effluent to about 2,000 mg/L after 10 and 20 days prefermentation.

Settled effluent BOD_5 was reduced by 65% over the 20 day treatment period. The steep section of the curve is not as pronounced in the settled effluent curves however it appeared to have halved in the BOD curves of the prefermented effluent. VFAs made up about one third (82 mg/L) of the steep part of the curve in fresh effluent and around 100% of the prefermented effluent on day 20 (91 mg/L).

VFA proportions in the raw effluent semi-continuous reactors were 1.0 : 0.5 : 0.3 : 0.2 acetic : propionic : butyric : valeric acids, and in the seeded reactors 1.0 : 0.6 : 0.2 : 0.2. These results are comparable with domestic effluent results, although the propionic acid levels are lower in the farm dairy effluent.

High initial concentrations for each batch suggests that the reactor solids retained a portion of the VFAs. The low concentration of VFAs produced in the settled effluent, and the high proportion of longer chain VFAs produced, suggests that the settled effluent had already undergone significant prefermentation and that little easily hydrolysable carbon was available in the waste.

The results of the seeded reactors show some VFA production. It is possible that the VFA production in batch 2 is attributable to easily hydrolysable carbon remaining in the solids from batch 1, rather than carbon added in batch 2. Alternatively, the solids retention time may have been too long.

7.3 Implications for full-scale SBR treatment of farm dairy effluent

The next stage of process development would be to operate the SBR on raw farm dairy effluent.

Further research is required to accurately size an aerator for the SBR. The submersible aerator used in this research was selected to ensure that the dissolved oxygen concentration was not limiting. However, the oversized aerator caused excessive foaming in the SBR, particularly during start-up.

The results indicate that the alkalinity in farm dairy effluent is insufficient for complete nitrification, without causing a reduction in the pH. A method of maintaining the alkalinity needs to be developed, such as an automated mechanism for dosing daily the use of a slow-dissolving alkalinity source such as limestone may provide a cheaper option.

The SBR is likely to operate as part of a total treatment system, designed to enhance BNR and provide a highly polished effluent. Figure 7.2 shows the treatment process most likely to provide a high quality effluent with low maintenance requirements.

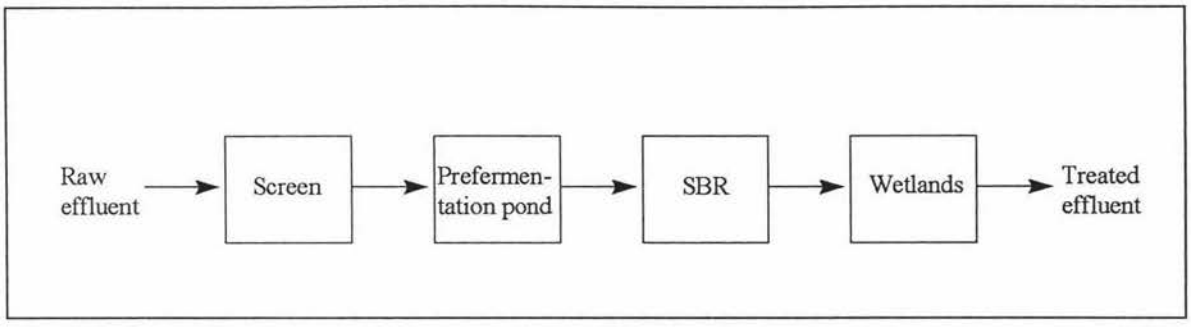

Figure 7.2 Flow diagram of treatment process

Raw effluent from the farm dairy would pass through a screen to remove large non-biodegradable objects such as syringes, stones and other waste materials. The effluent would flow from the farm dairy to a prefermentation pond.

The prefermentation pond will need to be of sufficient size for a hydraulic retention time of at least 8 to 10 days. Further research is required to determine the time required to optimise VFA production at ambient temperatures.

Prefermented effluent would be treated in the SBR. The SBR would be controlled by a PLC which would enable it to operate unattended. The treated effluent would be polished using wetlands, which would further reduce BOD, suspended solids, nitrogen and phosphorus levels. It is expected that the nutrient loading from SBR treated effluent would be significantly less than that from the two pond system and thus the life time of the wetlands would be extended.

Effluent from the wetlands would be sufficiently treated in terms of carbon, nitrogen and phosphorus levels to be disposed of directly into a waterway.

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9. APPENDICES

A Cycle analysis data

B Preliminary prefermentation trial data

C Prefermentation trial data

D Prefermentation semi-continuous reactors data

A Cycle analysis data

PHASE	SAMPLE	TIME h	AMMONIA mg/L	NITRATE mg/L	TOTAL N mg/L	TOTAL P mg/L	pH	REDOX mV	MLSS mg/L	CODs mg/L	ALKALINITY mg CaCO3/L
untreated	0	0.00	250		300	32	7.32		900	850	1330
anaerobic	1	0.17	158		610	72	7.57	-40.6	2950	340	1590
	2	0.33	150		450	52	7.57	-40			
	3	0.50	170		370	51	7.56	-39.8			
	4	0.67	163		330	45	7.55	-40.3			
	5	0.83					7.56	-41.2	3770	790	1410
	6	1.00	125		420	61	7.58	-41.6			
	7	1.17	128		380	44	7.59	-42.4			
	8	1.33	188		450	54	7.6	-42.8			
	9	1.50	250		430	56	7.61	-43			
	10	1.67	126		380	56	7.61	-42.8	1200	1071	1110
aerobic I	11	1.83	160		400	49	7.68	-46.1	3650	1259	1570
	12	2.00	183	0.35	400	63	7.71	-48.3			
	13	2.17	135	0.30	710	106	7.74	-50.4			
	14	2.33	148	0.30	400	61	7.77				
	15	2.50	183	0.30	460	66	7.8		3620	942	1320
	16	2.67	140	0.25	360	54	7.77				
	17	2.83	113	0.30	490	75	7.77				
	18	3.00	170	0.25	500	81	7.76				
	19	3.17	127	0.30	365	52	7.76				
	20	3.33	100	0.20	270	50	7.76		3650	895	1470
	21	3.50	193	0.30	340	50	7.69				
	22	3.67	163	0.30	330	40	7.7				
	23	3.83	178	0.40	340	46	7.71				
	24	4.00	168	0.40	500	76	7.71				
	25	4.17	125	0.30	510	57	7.71		2350	1012	1210
	26	4.33	190	0.50	480	70	7.7				
	27	4.50	153	0.50	320	46	7.7				
	28	4.67	170		420	62	7.69				

PHASE	SAMPLE	TIME h	AMMONIA mg/L	NITRATE mg/L	TOTAL N mg/L	TOTAL P mg/L	pH	REDOX mV	MLSS mg/L	CODs mg/L	ALKALINITY mg CaCO3/L
anoxic	29	4.83	118		360	52	7.68		1500	1020	1400
	30	5.00	145		400	60	7.66				
	31	5.17	103		340	52	7.66				
	32	5.33					7.71				
	33	5.50					7.72		2350	1130	1370
	34	5.67	158		320	39	7.74				
	35	5.83					7.75				
	36	6.00	233		310	42	7.75				
	37	6.17	158		340	49	7.75				
	38	6.33	113		320	42	7.76		4810	1401	1250
	39	6.50	125		760	106	7.78				
	40	6.67	180		340	51	7.75				
	41	6.83	198		560	74	7.79				
	42	7.00	220		320	46	7.8				
	43	7.17	140		290	40	7.78		2980	760	1360
	44	7.33	195		500	64	7.78				
	45	7.50	180		340	45	7.77				
	46	7.67	138		620	89	7.83				
	47	7.83	158		530	75	7.78				
	48	8.00	175		360	52	7.8		2150	1361	1430
	49	8.17	120		380	51	7.81				
	50	8.33	190		730	107	7.8				
	51	8.50	143		560	86	7.82				
	52	8.67	155		430	64	7.8				
	53	8.83	143		360	50	7.8		2410	1254	1280
	54	9.00	125		360	47	7.78				
	55	9.17	114		345	48	7.81				

PHASE	SAMPLE	TIME h	AMMONIA mg/L	NITRATE mg/L	TOTAL N mg/L	TOTAL P mg/L	pH	REDOX mV	MLSS mg/L	CODs mg/L	ALKALINITY mg CaCO3/L
aerobic II	56	9.33	173		460	70	7.83		2100	940	1550
	57	9.50	175		330	51	7.8				
	58	9.67	200		620	99	7.78				
	59	9.83	145	0.25	695	100	7.77				
settle	60	10.00	108	0.25	250	25	7.78		1100	714	1300
	61	10.17	140	0.35	240	25	7.78				
	62	10.33	198	0.30	260	19	7.79				
	63	10.50	300		240	26	7.81				
	64	10.67	195		240	32	7.81				
treated	65	10.83	126		280	47	7.82		980	374	1220

B Preliminary prefermentation trial data

PRELIMINARY PREFERMENTATION TRIAL DATA

SAMPLE	ACETIC			PROPIONIC			ISO-BUTYRIC	N-BUTYRIC	BUTYRIC	
day	mmol/100ml	mg/L	COD mg/L	mmol/100ml	mg/L	COD mg/L	mmol/100ml	mmol/100ml	mg/L	COD mg/L
0	0.00	0	0	0.11	81	158	0.01	0.03	35	77
1	0.08	48	51	0.12	89	172	0.01	0.04	44	96
2	0.41	246	263	0.20	148	287	0.02	0.07	79	173
3	0.81	486	520	0.45	333	647	0.03	0.08	97	211
4	0.88	528	565	0.48	356	690	0.03	0.09	106	230
5	1.02	613	655	0.52	385	747	0.04	0.10	123	269
6	1.09	655	700	0.55	407	790	0.07	0.12	167	365

SAMPLE	ISO-VALERIC	N-VALERIC	VALERIC		TOTAL VFAS	
day	mmol/100ml	mmol/100ml	mg/L	COD mg/L	mg/L	COD mg/L
0	0.01	0.00	10	24	127	259
1	0.01	0.01	20	48	201	368
2	0.04	0.01	51	120	525	844
3	0.05	0.01	61	144	978	1522
4	0.05	0.02	71	168	1061	1654
5	0.06	0.03	92	216	1213	1888
6	0.06	0.03	92	216	1321	2072

C Prefermentation trial data

RAW EFFLUENT **SAMPLE A**

SAMPLE	ACETIC			PROPIONIC			ISO-BUTYRIC	N-BUTYRIC	BUTYRIC	
day	mmol/100ml	mg/L	COD mg/L	mmol/100ml	mg/L	COD mg/L	mmol/100ml	mmol/100ml	mg/L	COD mg/L
0	0.14	84	90	0.04	30	57	0.02	0.05	62	134
2	0.69	414	443	0.06	44	86	0.01	0.06	62	134
4	1.15	691	739	0.21	156	302	0.03	0.08	97	211
5	1.39	835	893	0.27	200	388	0.04	0.1	123	269
6	1.51	907	970	0.32	237	460	0.04	0.11	132	288
8	1.79	1075	1150	0.40	296	575	0.04	0.13	150	326
10	1.64	985	1054	0.42	311	604	0.03	0.12	132	288
12	1.55	931	996	0.38	282	546	0.03	0.11	123	269
14	1.16	697	745	0.29	215	417	0.03	0.08	97	211
15	1.85	1111	1189	0.49	363	704	0.04	0.14	159	346
16	1.04	625	668	0.29	215	417	0.03	0.08	97	211
18	1.31	787	842	0.31	230	446	0.04	0.11	132	288
20	1.44	865	925	0.35	259	503	0.04	0.09	115	250

SAMPLE day	ISO-VALERIC mmol/100ml	N-VALERIC mmol/100ml	VALERIC mg/L	VALERIC COD mg/L	TOTAL VFAS mg/L	TOTAL VFAS COD mg/L
0	0.01	0.00	10	24	186	306
2	0.01	0.00	10	24	531	688
4	0.03	0.01	41	96	984	1348
5	0.03	0.01	41	96	1199	1646
6	0.04	0.03	71	168	1347	1886
8	0.06	0.03	92	216	1613	2268
10	0.04	0.03	71	168	1500	2113
12	0.04	0.02	61	144	1397	1955
14	0.04	0.02	61	144	1070	1517
15	0.05	0.03	82	192	1714	2431
16	0.05	0.02	71	168	1008	1464
18	0.06	0.03	92	216	1240	1791
20	0.06	0.03	92	216	1330	1894

RAW EFFLUENT **SAMPLE B**

SAMPLE	ACETIC			PROPIONIC			ISO-BUTYRIC	N-BUTYRIC	BUTYRIC	
day	mmol/100ml	mg/L	COD mg/L	mmol/100ml	mg/L	COD mg/L	mmol/100ml	mmol/100ml	mg/L	COD mg/L
0	0.16	96	103	0.06	44	86	0.01	0.06	62	134
2	0.84	504	540	0.07	52	101	0.01	0.06	62	134
4	1.23	739	790	0.21	156	302	0.03	0.08	97	211
5	1.37	823	880	0.25	185	359	0.03	0.10	115	250
6	1.44	865	925	0.29	215	417	0.03	0.11	123	269
8	1.6	961	1028	0.36	267	517	0.03	0.13	141	307
10	1.62	973	1041	0.42	311	604	0.04	0.13	150	326
12	1.63	979	1047	0.40	296	575	0.03	0.12	132	288
14	1.26	757	810	0.32	237	460	0.03	0.09	106	230
15	2.02	1213	1298	0.54	400	776	0.04	0.15	167	365
16	1.13	679	726	0.33	244	474	0.03	0.09	106	230
18	1.45	871	932	0.35	259	503	0.05	0.12	150	326
20	1.49	895	957	0.37	274	532	0.04	0.10	123	269

SAMPLE day	ISO-VALERIC mmol/100ml	N-VALERIC mmol/100ml	VALERIC mg/L	VALERIC COD mg/L	TOTAL VFAS mg/L	TOTAL VFAS COD mg/L
0	0.00	0.00	0	0	202	323
2	0.01	0.00	10	24	628	799
4	0.03	0.01	41	96	1032	1399
5	0.03	0.01	41	96	1163	1585
6	0.04	0.03	71	168	1274	1779
8	0.04	0.03	71	168	1440	2021
10	0.05	0.06	112	264	1546	2235
12	0.05	0.03	82	192	1489	2102
14	0.04	0.02	61	144	1161	1644
15	0.06	0.04	102	240	1883	2679
16	0.05	0.07	123	288	1151	1719
18	0.06	0.03	92	216	1372	1977
20	0.06	0.03	92	216	1384	1974

AVERAGE COD OF RAW EFFLUENT SAMPLES

SAMPLE day	ACETIC mg/L	PROPIONIC mg/L	BUTYRIC mg/L	VALERIC mg/L	TOTAL mg/L
0	96	72	134	12	315
2	492	93	134	24	743
4	765	302	211	96	1374
5	887	374	259	96	1616
6	948	438	278	168	1833
8	1089	546	317	192	2144
10	1047	604	307	216	2174
12	1022	560	278	168	2029
14	777	438	221	144	1581
15	1243	740	355	216	2555
16	697	446	221	228	1592
18	887	474	307	216	1884
20	941	517	259	216	1934

SETTLED EFFLUENT **SAMPLE A**

SAMPLE	ACETIC			PROPIONIC			ISO-BUTYRIC	N-BUTYRIC	BUTYRIC	
day	mmol/100ml	mg/L	COD mg/L	mmol/100ml	mg/L	COD mg/L	mmol/100ml	mmol/100ml	mg/L	COD mg/L
0	0.03	18	19	0.03	22	43	0.00	0.00	0	0
5	0.06	36	39	0.05	37	72	0.00	0.03	26	58
10	0.00	0	0	0.00	0	0	0.00	0.00	0	0
15	0.00	0	0	0.00	0	0	0.00	0.00	0	0
20	0.06	36	39	0.01	7	14	0.01	0.00	9	19

SAMPLE	ISO-VALERIC	N-VALERIC	VALERIC		TOTAL VFAS	
day	mmol/100ml	mmol/100ml	mg/L	COD mg/L	mg/L	COD mg/L
0	0.01	0.00	10	24	10	24
5	0.01	0.00	10	24	10	24
10	0.00	0.00	0	0	0	0
15	0.00	0.00	0	0	0	0
20	0.00	0.00	0	0	0	0

SETTLED EFFLUENT **SAMPLE B**

SAMPLE day	ACETIC mmol/100ml	ACETIC mg/L	ACETIC COD mg/L	PROPIONIC mmol/100ml	PROPIONIC mg/L	PROPIONIC COD mg/L	ISO-BUTYRIC mmol/100ml	N-BUTYRIC mmol/100ml	BUTYRIC mg/L	BUTYRIC COD mg/L
0	0.03	18	19	0.04	30	57	0.00	0.00	0	0
5	0.05	30	32	0.06	44	86	0.00	0.03	26	58
10	0.00	0	0	0.00	0	0	0.00	0.00	0	0
15	0.00	0	0	0.00	0	0	0.01	0.00	9	19
20	0.12	72	77	0.01	7	14	0.01	0.00	9	19

SAMPLE day	ISO-VALERIC mmol/100ml	N-VALERIC mmol/100ml	VALERIC mg/L	VALERIC COD mg/L	TOTAL VFAS mg/L	TOTAL VFAS COD mg/L
0	0.00	0.00	0	0	0	0
5	0.01	0.00	10	24	10	24
10	0.00	0.00	0	0	0	0
15	0.00	0.00	0	0	0	0
20	0.00	0.00	0	0	0	0

AVERAGE COD OF SETTLED EFFLUENT SAMPLES

SAMPLE day	ACETIC mg/L	PROPIONIC mg/L	BUTYRIC mg/L	VALERIC mg/L	TOTAL mg/L
0	19	50	0	12	82
5	35	79	58	24	196
10	0	0	0	0	0
15	0	0	10	0	10
20	58	14	19	0	91

D Prefermentation semi-continuous reactors data

RAW DAIRYSHED EFFLUENT **REACTOR A**

		ACETIC			PROPIONIC			ISO-BUTYRIC	N-BUTYRIC	BUTYRIC	
		mmol/100mL	mg/L	COD mg/L	mmol/100mL	mg/L	COD mg/L	mmol/100mL	mmol/100mL	mg/L	COD mg/L
Batch 1	START	0.29	174	186	0.06	44	86	0.01	0.03	35	77
	FINISH	0.72	432	463	0.25	185	359	0.03	0.09	106	230
Batch 2	START	0.52	312	334	0.14	104	201	0.01	0.04	44	96
	FINISH	1.41	847	906	0.56	415	805	0.04	0.16	176	384
Batch 3	START	0.79	474	508	0.3	222	431	0.02	0.10	106	230
	FINISH	1.65	991	1060	0.56	415	805	0.05	0.26	273	595
Batch 4	START	0.65	390	418	0.24	178	345	0.02	0.11	115	250
	FINISH	0.46	276	296	0.23	170	331	0.02	0.10	106	230

		ISO-VALERIC	N-VALERIC	VALERIC		TOTAL VFAS	
		mmol/100mL	mmol/100mL	mg/L	COD mg/L	mg/L	COD mg/L
Batch 1	START	0.01	0.00	10	24	264	373
	FINISH	0.03	0.02	51	120	774	1172
Batch 2	START	0.01	0.01	20	48	480	679
	FINISH	0.06	0.05	112	264	1550	2359
Batch 3	START	0.03	0.02	51	120	853	1289
	FINISH	0.07	0.10	174	408	1852	2868
Batch 4	START	0.03	0.04	71	168	754	1180
	FINISH	0.03	0.04	71	168	624	1025

RAW DAIRYSHED EFFLUENT **REACTOR B**

		ACETIC			PROPIONIC			ISO-BUTYRIC	N-BUTYRIC	BUTYRIC	
		mmol/100mL	mg/L	COD mg/L	mmol/100mL	mg/L	COD mg/L	mmol/100mL	mmol/100mL	mg/L	COD mg/L
Batch 1	START	0.29	174	186	0.06	44	86	0.01	0.03	35	77
	FINISH	0.68	408	437	0.22	163	316	0.02	0.07	79	173
Batch 2	START	0.52	312	334	0.14	104	201	0.01	0.04	44	96
	FINISH	1.24	745	797	0.52	385	747	0.05	0.16	185	403
Batch 3	START	0.96	576	617	0.36	267	517	0.03	0.01	37	81
	FINISH	1.40	841	900	0.48	356	690	0.04	0.23	238	519
Batch 4	START	0.34	204	218	0.17	126	244	0.02	0.08	88	192
	FINISH	0.47	282	302	0.21	156	302	0.02	0.10	106	230

		ISO-VALERIC	N-VALERIC	VALERIC		TOTAL VFAS	
		mmol/100mL	mmol/100mL	mg/L	COD	mg/L	COD
Batch 1	START	0.01	0.00	10	24	264	373
	FINISH	0.02	0.01	31	72	681	998
Batch 2	START	0.02	0.01	31	72	491	703
	FINISH	0.05	0.05	102	240	1417	2187
Batch 3	START	0.04	0.03	71	168	952	1383
	FINISH	0.07	0.10	174	408	1608	2516
Batch 4	START	0.02	0.03	51	120	469	775
	FINISH	0.02	0.03	51	120	595	954

SETTLED DAIRYSHED EFFLUENT **REACTOR A**

		ACETIC			PROPIONIC			ISO-BUTYRIC	N-BUTYRIC	BUTYRIC	
		mmol/100mL	mg/L	COD mg/L	mmol/100mL	mg/L	COD mg/L	mmol/100mL	mmol/100mL	mg/L	COD mg/L
Batch 1	START	0.00	0	0	0.02	15	29	0.01	0.01	18	38
	FINISH	0.02	12	13	0.02	15	29	0.01	0.01	18	38
Batch 2	START	0.00	0	0	0.02	15	29	0.01	0.01	18	38
	FINISH	0.00	0	0	0.01	7	14	0.00	0.01	9	19
Batch 3	START	0.00	0	0	0.01	7	14	0.01	0.01	18	38
	FINISH	0.00	0	0	0.00	0	0	0.00	0.00	0	0
Batch 4	START	0.00	0	0	0.00	0	0	0.00	0.00	0	0
	FINISH	0.00	0	0	0.00	0	0	0.00	0.00	0	0

		ISO-VALERIC	N-VALERIC	VALERIC		TOTAL VFAS	
		mmol/100mL	mmol/100mL	mg/L	COD mg/L	mg/L	COD mg/L
Batch 1	START	0.00	0.00	0	0	32	67
	FINISH	0.00	0.00	0	0	44	80
Batch 2	START	0.00	0.00	0	0	32	67
	FINISH	0.00	0.00	0	0	16	34
Batch 3	START	0.00	0.00	0	0	25	53
	FINISH	0.00	0.00	0	0	0	0
Batch 4	START	0.00	0.00	0	0	0	0
	FINISH	0.00	0.00	0	0	0	0

SETTLED DAIRYSHED EFFLUENT **REACTOR B**

		ACETIC			PROPIONIC			ISO-BUTYRIC	N-BUTYRIC	BUTYRIC	
		mmol/100mL	mg/L	COD mg/L	mmol/100mL	mg/L	COD mg/L	mmol/100mL	mmol/100mL	mg/L	COD mg/L
Batch 1	START	0.00	0	0	0.02	15	29	0.01	0.01	18	38
	FINISH	0.00	0	0	0.02	15	29	0.01	0.01	18	38
Batch 2	START	0.00	0	0	0.02	15	29	0.01	0.01	18	38
	FINISH	0.00	0	0	0.01	7	14	0.01	0.01	18	38
Batch 3	START	0.00	0	0	0.01	7	14	0.01	0.01	18	38
	FINISH	0.00	0	0	0.00	0	0	0.00	0.00	0	0
Batch 4	START	0.00	0	0	0.00	0	0	0.00	0.00	0	0
	FINISH	0.00	0	0	0.00	0	0	0.00	0.00	0	0

		ISO-VALERIC	N-VALERIC	VALERIC		TOTAL VFAS	
		mmol/100mL	mmol/100mL	mg/L	COD mg/L	mg/L	COD mg/L
Batch 1	START	0.00	0.00	0	0	32	67
	FINISH	0.00	0.00	0	0	32	67
Batch 2	START	0.00	0.00	0	0	32	67
	FINISH	0.00	0.00	0	0	25	53
Batch 3	START	0.00	0.00	0	0	25	53
	FINISH	0.00	0.00	0	0	0	0
Batch 4	START	0.00	0.00	0	0	0	0
	FINISH	0.00	0.00	0	0	0	0

SEEDED SETTLED DAIRYSHED EFFLUENT REACTOR A

		ACETIC			PROPIONIC			ISO-BUTYRIC	N-BUTYRIC	BUTYRIC	
		mmol/100mL	mg/L	COD mg/L	mmol/100mL	mg/L	COD mg/L	mmol/100mL	mmol/100mL	mg/L	COD mg/L
Batch 1	START	0.29	174	186	0.06	44	86	0.01	0.03	35	77
	FINISH	0.69	414	443	0.25	185	359	0.03	0.08	97	211
Batch 2	START	0.22	132	141	0.10	74	144	0.01	0.03	35	77
	FINISH	0.65	390	418	0.25	185	359	0.02	0.04	53	115
Batch 3	START	0.14	84	90	0.08	59	115	0.01	0.02	26	58
	FINISH	0.07	42	45	0.05	37	72	0.01	0.00	9	19
Batch 4	START	0.00	0	0	0.01	7	14	0.01	0.00	9	19
	FINISH	0.03	18	19	0.02	15	29	0.01	0.00	9	19

		ISO-VALERIC	N-VALERIC	VALERIC		TOTAL VFAS	
		mmol/100mL	mmol/100mL	mg/L	COD mg/L	mg/L	COD mg/L
Batch 1	START	0.01	0.00	10	24	264	373
	FINISH	0.03	0.01	41	96	737	1110
Batch 2	START	0.01	0.00	10	24	252	386
	FINISH	0.02	0.01	31	72	659	964
Batch 3	START	0.01	0.00	10	24	180	287
	FINISH	0.01	0.00	10	24	98	160
Batch 4	START	0.00	0.00	0	0	16	34
	FINISH	0.00	0.00	0	0	42	67

SEEDED SETTLED DAIRYSHED EFFLUENT REACTOR B

		ACETIC			PROPIONIC			ISO-BUTYRIC	N-BUTYRIC	BUTYRIC	
		mmol/100mL	mg/L	COD mg/L	mmol/100mL	mg/L	COD mg/L	mmol/100mL	mmol/100mL	mg/L	COD mg/L
Batch 1	START	0.29	174	186	0.06	44	86	0.01	0.03	35	77
	FINISH	0.68	408	437	0.22	163	316	0.02	0.07	79	173
Batch 2	START	0.19	114	122	0.09	67	129	0.01	0.02	26	58
	FINISH	0.13	78	84	0.07	52	101	0.01	0.02	26	58
Batch 3	START	0.70	420	450	0.21	156	302	0.02	0.04	53	115
	FINISH	0.18	108	116	0.08	59	115	0.01	0.01	18	38
Batch 4	START	0.00	0	0	0.01	7	14	0.01	0.00	9	19
	FINISH	0.00	0	0	0.00	0	0	0.01	0.00	9	19

		ISO-VALERIC	N-VALERIC	VALERIC		TOTAL VFAS	
		mmol/100mL	mmol/100mL	mg/L	COD mg/L	mg/L	COD mg/L
Batch 1	START	0.01	0.00	10	24	264	373
	FINISH	0.02	0.01	31	72	681	998
Batch 2	START	0.01	0.00	10	24	217	333
	FINISH	0.01	0.01	20	48	177	290
Batch 3	START	0.02	0.01	31	72	659	939
	FINISH	0.01	0.00	10	24	195	293
Batch 4	START	0.00	0.00	0	0	16	34
	FINISH	0.00	0.00	0	0	9	19

REACTOR SOLUBLE COD (mg/L)

		RAW EFFLUENT		SETTLED EFFLUENT		SEEDED SETTLED	
		A	B	A	B	A	B
Batch 1	START	5220	5220	1130	1130	5220	5220
	FINISH	4310	5180	990	1250	4790	5370
Batch 2	START	5640	4750	1240	750	3240	4150
	FINISH	5550	5280	880	1020	2750	3360
Batch 3	START	4370	5650	760	970	2410	3940
	FINISH	5000	4570	1140	1280	3090	2970
Batch 4	START	4680	4770	1050	1100	3260	1840
	FINISH	5640	5100	1200	1030	3150	2680