OPTIMIZATION OF VFA PRODUCTION IN AN ATAD REACTOR WITH RESPECT TO AERATION RATES AND REMOVAL OF PHOSPHORUS, INCORPORATING A MAGNESIUM AMMONIUM PHOSPHATE (MAP) CRYSTALLIZER FROM THE ATAD SUPERNATANT.

by

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to the required standard.

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Abstract

Previous researchers have demonstrated that a mixture of primary and secondary sludge provides increased production of VFA in ATAD. Experiments were carried out at the UBC pilot plant, in two phases, using a 35/65 mixture of primary/secondary sludge, to determine the optimum aeration rate with respect to production/generation of VFA, and to investigate the removal of phosphorus by forced formation of struvite in an up-flow crystallizer. The source sludge for the research was obtained from an on-site modified UCT process, and mixed in the correct ratios prior to feeding on an hourly basis to the 125-L tanks. The tanks, were configured in parallel and operated as individual first stage reactors, one of which was the control tank.

During the first stage, the control tank was maintained at a constant aeration rate of 50 ml/min (as suggested by EPA). The aeration rate in the test tank was varied from 0 ml/min (nitrogen was supplied) to 100 ml/min, at increments of 25 ml/min. Throughout the entire experimental period, temperatures were in the thermophilic range, between 47°C and 58°C inside the tanks; feed solids were maintained around 1.4% TSS, and ORP was consistent between –300 mV and –450 mV. There was higher production of VFA at lower aeration rates, the highest occurring when 25 ml/min air was supplied. Analysis of nutrients confirmed that there was a high release of stored phosphorus and an increase in ammonia nitrogen. The ratio of VFA: PO_4-P was the highest when 25 ml/min air was supplied.

Formation of struvite is highly dependent on the existence of the correct chemical conditions (molar concentrations of $Mg:PO_4$-$P:NH_4$-N at 1:1:1). In the second phase of this research, experiments were done with synthetic sewage and ATAD effluent to examine the removal of soluble PO_4 incorporating the Crystallizer. Removal was affected by the pH, the optimum pH being between 8 and 10. Presence of a high solids concentration in the ATAD effluent did not seem to affect the removal.

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Chapter 1

Introduction

1.1 Background

With the growth of world population at the current rate, our natural resources are strained to the limits. Humanity exploits these resources and in the process pollutes the surroundings. Within the next half a century the three major elements air, earth and water are bound to get severely polluted if corrective measures are not taken. The onus is on the scientific community to develop techniques and methods to control or minimize this pollution. A great deal of research has already been carried out in all these fields. The scope of this research is limited to a small but very important subject of wastewater treatment, the recovery and reuse of phosphorus.

The primary objective of wastewater treatment is to remove the various nutrients and thereby reduce the impact on the receiving water. The widespread application of advanced sewage treatment processes, aimed at removing the biological nutrients, has resulted in a generation of higher volumes of sludge. The treatment of sewage incorporating the Biological Nutrient Removal (BNR) process produces effluent low in nutrients, by concentrating them in the solids fraction of the biological sludge. Worldwide, the focus in environmental engineering is shifting to the treatment of the sludge and ultimate disposal in a safe manner.

One of the foremost processes for treatment of wastewater sludge is to digest it under aerobic conditions, especially under elevated temperatures of >45°C. Since it's first inception in Germany and USA in the 1960's (USEPA, 1990), Autothermal Thermophilic Aerobic Digestion (ATAD) has been investigated under various working conditions to optimize its efficiency. Various researchers have previously established that there is a high production of Volatile Fatty Acids (VFA) in the ATAD, which is a beneficial product for the BNR process. The production of VFA has been theorized to be a result of oxidation, fermentation and lysis of cells, as a result of the oxygen-restricted environment and the mechanical agitation inside the tank. From previous research, it was seen that the operation of ATAD, at a feed ratio of primary to secondary at 35:65, produces optimum results in terms of VFA production and solids destruction (Fothergill, 1996).

In a BNR process due to the luxury uptake by the bio-solids, the phosphorus is concentrated in the sludge. In ATAD, because of the biological and mechanical activity, this excess phosphorus from the solids fraction is released. Numerous research projects are done to remove soluble phosphorus (PO_4) from the effluent of ATAD before final reuse. There are various techniques in removing PO_4, one of them being crystallization. In crystallization, the PO_4 is removed by the formation of struvite which happens when phosphorus, magnesium and ammonia are present in the correct molar ratio (Dempsey, 1998). The resultant product is called 'Magnesium Ammonium Phosphate' or 'MAP'.

This research was done in two stages. The first stage was to investigate the effect of various aeration rates in the production of VFAs in pilot-scale ATAD units. The second stage mainly examined the removal of phosphorus incorporating the Crystallizer. Prior to this work, there has been little or no work done on removal of phosphorus from the ATAD effluent.

1.2 Research Objectives

Research was conducted at the UBC wastewater research pilot plant, where there are pilot scale ATAD units that can be worked in different configurations.

1.2.1 Primary objectives

(a) Optimise the VFA production at different aeration rates varying from 0 (no-air) ml/min to 100 ml/min (with increments of 25 ml/min) at a constant primary: secondary sludge ratio of 35:65.

(b) Investigate the removal of phosphorus incorporating the Crystallizer, promoting MAP formation.

1.2.2 Secondary objectives

(a) Evaluate the efficiency of solids destruction at the aeration rates.

(b) Determine the effect of aeration rates on the species of VFA generated.

(c) Determine the relationship of solids concentration in the removal of phosphorous in a Crystallizer.

Chapter 2

Background and Literature Review.

From previous studies and research, it has been established that there is a production of VFAs in thermophilic aerobic digestion. The relationship between VFA production and the aeration rate, along with the ratio of the phosphorus release, is very important with respect to the enhanced biological waste treatment process. Moreover, in ATAD there is a release of the stored phosphorus, which has a tremendous potential for recovery and reuse. Before presenting a detailed summary of the research findings, a brief description of the BNR process, thermophilic aerobic digestion and the operating conditions, along with the forced removal of phosphorus, is provided.

2.1 Biological Nutrient Removal

Biological nutrient removal is a relatively low-cost means of removing nitrogen and phosphorus from wastewater (Metcalf & Eddy, 1995). Biological nutrient removal refers to processes that utilise biological mechanisms, instead of chemical mechanisms, to remove phosphorus and nitrogen from wastewater (Randall, *et al.* 1992). The microbes that are present in the wastewater requires a simple carbon food source - termed Volatile Fatty Acids (VFAs) such as acetic acid or propionic acid - so they can efficiently perform their tasks. VFAs are a simple and consumable carbon source necessary for nutrient reducing microbes to thrive and thereby perform their intended function of nitrogen and phosphorus removal.

The exact mechanism of Biological Phosphorus Removal (BPR) is a topic that still intrigues a lot of researchers. The dry mass of a typical bacterium is about 90 percent organic, of which 0.95 percent P, is found in the nucleic acids, proteins, membranes and energy metabolism system of the cell. These forms of phosphorus account for about 0.86 percent of dry weight of a dry bacterium. This indicates that about 2.3% of the sludge mass is phosphorus (Randall *et al.* 1997). This percentage is highly dependent on the type of sewage and might vary from 2 to 5 percent (Metcalf & Eddy, 1995). Phosphorus is also stored in the cell as polyphosphate represented as $Me_{n+2}P_nO_{3n+1}$ (Jardin and Popel, 1994); this accounts for an average of 2.2 % of dry cell mass.

2.2 Autothermal Thermophilic Aerobic Digestion (ATAD)

All bacteria that are present in the sludge are, in reality, a natural resource. Out of convenience, microbiologists have categorised bacteria on the basis of the temperature they thrive in, into three different groups. These categories include psycrophilic bacteria with a temperature range of $-10^{o}C$ to $30^{o}C$ (optimum 12-18^{o}C), mesophilic bacteria with a temperature range of 20-50^{o}C (optimum 25-40^{o}C) and thermophilic bacteria which have a high temperature range of 35-70^{o}C with the optimum temperature between 50-65^{o}C (Metcalf and Eddy, 1995).

It is the digestion of sludge utilising these thermophilic bacteria, under an aerobic environment, that is called ATAD. ATAD is first, and foremost a digestion process, the primary purpose of which is to decompose a portion of the waste organic sludge generated from the wastewater treatment process. These solids which are generated from primary sedimentation and biological treatment process have a high concentration of pathogens. These factors result in the need to process the collected matter so that potential health hazards and objectionable environmental conditions do not result when the sludges are disposed of.

ATAD systems are usually two stage systems under thermophilic conditions and without the addition of supplemental heat. It is used to produce Class-A bio-solids (Kelly, 1990) for reuse. ATAD offers several advantages which include:

- Higher rates of digestion, resulting in smaller digestion volumes and lower capital costs. In comparison to mesophilic anaerobic digestion reactor the volumes are approximately ¼ the size (Kelly et al, 1995). According to a study of the South-West sewage treatment works, Chicago, Illinois, aerobic thermophilic operation doubled the plant's sludge handling capability and also achieved energy self-sufficiency (Rimkus, 1982).
- Compared to composting, lime conditioning and extended aeration treatment, digestion time is reduced from months to days (Bruce et al, 1987).
- Heat is released from energy release of organic decomposition and hence there is no requirement for heat above that needed for mixing.
- Relatively simple technology that is easy to operate.

- Increased destruction of pathogenic organisms, which is of special significance when land disposal is being practised.
- Lower volume of sludge generated to be disposed.
- With advanced design, off-gas heat loss can be reduced by up to 80% thus achieving higher critical reactor temperatures; this eliminates auxiliary boilers and ensures pathogen destruction in the winter months in cold areas.
- No electrical equipment such as motor drivers is situated inside the units, which makes maintenance much easier.
- Any tank geometry is suitable, even retrofits.
- ATAD units are effective in communities (effective upto treatment of sludge generated from 250,000 people, Kelly (1999)) where installing a large aerobic or anaerobic digester can be uneconomical.

From previous work, it has also been demonstrated that thermophilic aerobic digestion is also a pre-treatment step for anaerobic mesophilic digestion. The temperatures in the thermophilic stage provide the necessary pasteurisation that is otherwise absent in mesophilic treatment and provide better VFA production for the next step. This pre-treatment, otherwise called Aerobic Thermophilic Pre-treatment (ATP) has enhanced anaerobic digester performance with respect to feed stability, gas production, foam reduction and supplemental heat requirements (Fothergill, 1995). In another study of thermophilic pre-acidification of anaerobic treatment, it was demonstrated that a significant degree of acidification (22-38%) was observed (Dinsdale, 1997).

2.2.1 ATAD development

Studies in thermophilic digestion were started in the United Sates as early as the 1960's. Initially developed in the 1970s in Canada, Great Britain, Scandinavia, Switzerland, South Africa and Germany, it has found great fast application Germany as an alternative digestion treatment to meet strict regulations. It has tremendous application in Europe, with more then 40 units in Germany alone. It has found application world-wide. Various experiments were done to in optimizing and adapting to various regional needs and the ATAD system has come a long way since its initial conceptualization 30 years ago. Early thermophillic digestion research began in Germany in the research stations of Fuchs gas und Wassutechnik GMB, to treat animal manure in tanks 20 – 45 m^3. From that early work, it was found that temperatures of 60°C could be achieved in 20 m^3 tanks. These initial studies used a self-aspirating aeration device sold by DeLaval Inc. This produced odor free, pathogen free bio-solids that could be disposed off easily and fell within regulatory requirements.

Interest in auto-heating of sludge accelerated in North America during the early 70's. In 1972, research was started by Union Carbide on a pilot plant scale using pure oxygen for aeration in a research facility in New York (Matsch and Drnevich, 1977). ATAD using air, instead of pure oxygen, began in 1977 in Germany. The first ATAD in installed in North America, was in Ladysmith, BC which used a Fuchs™ system and the second was at Gibsons, BC using a venturi-pump, both these units were commissioned in

1989. Since then much research has been done in Canada and USA, and the pilot plant at UBC has been prominent in a number of these projects. Successful installation of ATAD units have been done in Salmon Arm, Whistler and Parksville just to name a few in British Columbia.

2.2.2 Process Description

ATAD can be operated in single stage or multistage configuration. Normally, they are a two-stage aerobic process. There are four possible ways of operating them. They can be batch, semi-batch, semi-continuous or continuous fed. With adequate supply of oxygen, microorganisms and nutrients ATAD can degrade these substances to end products, including water and carbon-dioxide. Some of the energy released by microbial activity is used to form new cellular matter and much of it is released in the form of heat. Typical heat production values reported (or assumed) range from 14,190 to 14,650 kJ/kg O_2 (USEPA, 1995). According to design parameters set forward by USEPA, the required feed Total Solids (TS) range should be 4-6% (40- 60 g/L), with a minimum reaction time of 20 hours. According to Fuchs™, of the TS present in the feed, at least 25 % (≥25g/L) are biodegradable volatile solids.

A schematic of the heat balance in a thermophilic digester is shown in Figure 2.1. Operating temperature, biodegradable solids reduction and digestion kinetics are all interrelated. For example, a higher operating temperature increases the rate of digestion. More biodegradable solids are converted to heat and therefore the temperature increases.

The same mechanism can decrease the operating temperature for the reverse case, when the solids concentration is lower in the feed.

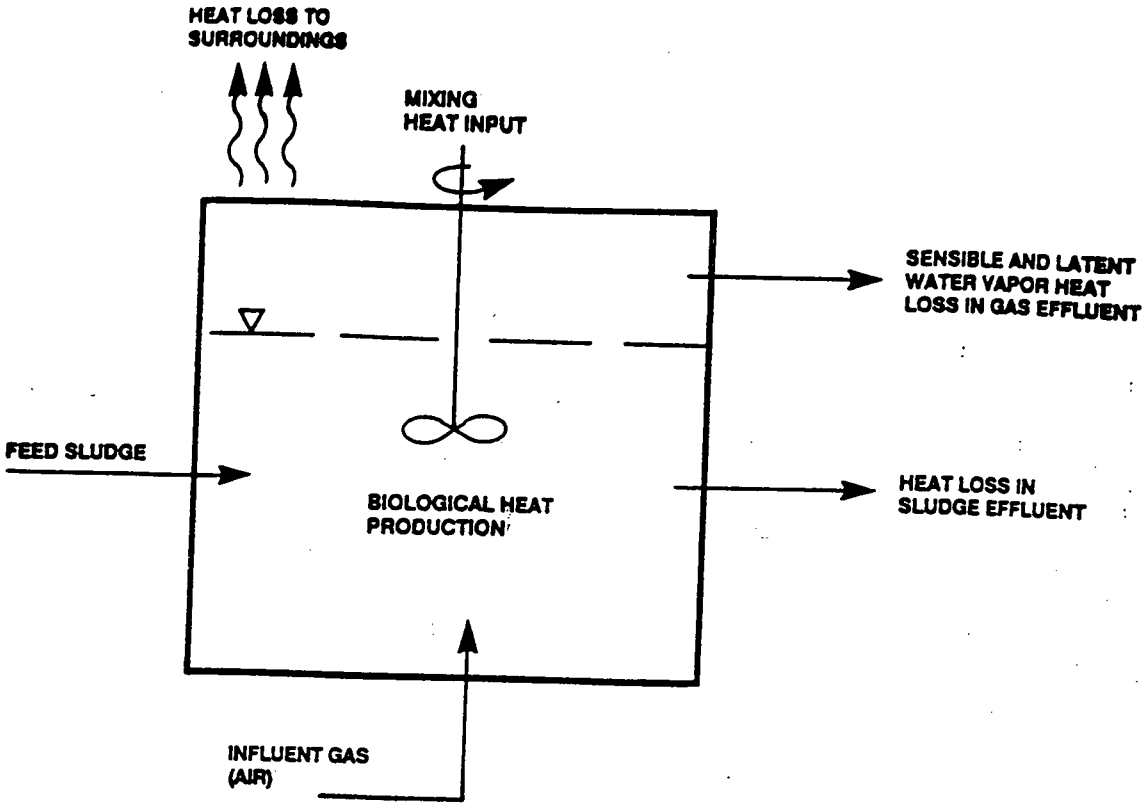


Figure 2.1 Heat balance in an ATAD (USEPA, 1995)

2.2.2.1 Pathogen Destruction

Any organisms that are capable of producing disease either directly or indirectly in humans, other animals, plants etc. is considered to be pathogenic. Such organisms can enter the waste stream from infected individuals or from previously contaminated waters; during wastewater treatment, these organisms become concentrated in the by-product sludge, where the concentrations can be several orders of magnitude higher then in the inlet waste stream. Essentially four main groups of pathogens can be found in

wastewater streams viz. *Bacteria, protozoa, helminths* and *viruses* (Mason et. al, 1992). The range of temperature-induced site specific damage, alteration and metabolic changes for *E.Coli* are shown in Figure 2.2. In aerobic thermophilic sludge pasteurization, the mesophilic organisms present in the process feed are subjected to a marked temperature shock that deactivates them. At the same time, autolytic mechanisms and/or the action of exo-enzymes, particularly protease, produced by the thermophilic process culture causes lysis (Haner et. al 1994). The aerobic thermophilic treatment process makes use of thermophilic organism whose growth substrates are the lysis products of the bacteria and the hydrolysis products of other solids present in raw sewage.

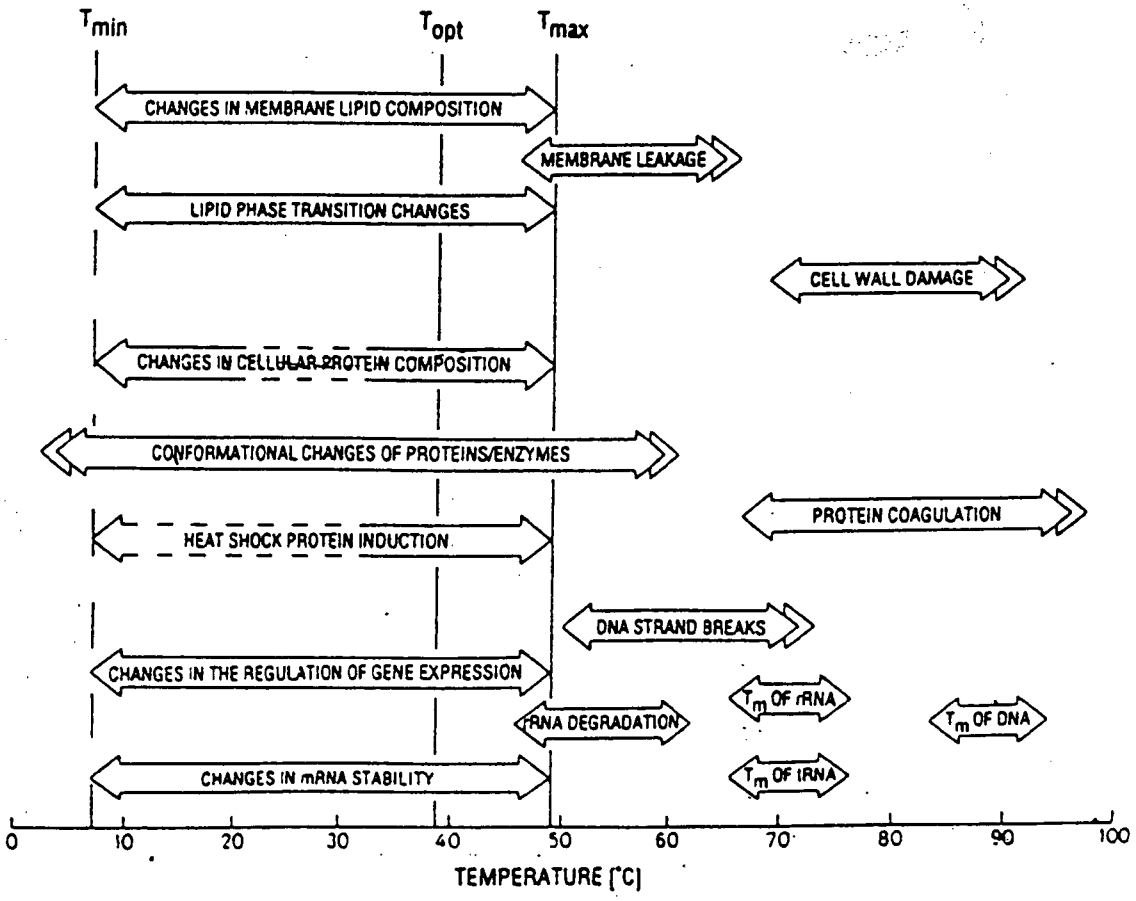


Figure 2.2 Damage to *E-coli* at increasing temperature.

2.2.3 Volatile Fatty Acids (VFA)

As the name itself suggests, VFA are short chain compounds formed primarily by fermentative processes, breaking down organic molecules and producing simpler organic end products. Fermentative bacteria use the organic molecules as final electron acceptors. Fatty acids are defined as mono basic acids containing only carbon (C), Hydrogen (H) and oxygen (O) and an alkyl group (CH_3, C_2H_3, etc.) attached to a carboxyl group ($COOH^-$) (Sharp, 1990). The lower weight species of fatty acids , loosely classified as short chained compounds, are referred to as VFA. VFA are one of the numerous biodegradable materials utilized by the microorganisms as substrate in wastewater treatment. Previous research (Rabinowitz, 1985) demonstrated that acetic and propionic acids are the most effective substrates in the enhanced biological phosphorous removal.

Enhanced biological phosphorus removal (EBPR) refers to processes operated in such a way as to stimulate the growth of poly-phosphate (poly-P) accumulating organisms, which have the ability to store large amounts of phosphorus as Poly-P. The process of biological phosphorus removal is a modification of a conventional activated sludge process, which consists of an anaerobic zone followed by an aerobic zone. The anaerobic zone induces the recycle biomass to release phosphorus into the solution to be used later on, in the aerobic zone. In the aerobic zone, the biomass recovers the phosphorus released in the anaerobic zone, as well as the initial phosphorus in the raw sewage, by oxidising the stored carbon reserves; this results in an accumulation of

phosphorus. According to models proposed by Comeau et al (1986) and Wentzel et al. (1986) the bacteria responsible for phosphate accumulation store polyhydroxyalkanoate. This model explains the beneficial effects of simple acetate and propionate additions to the anaerobic zone.

ATAD processes have the potential to provide the required acetate in the Bio-P process. Previous research has shown that the percentage of acetate could be as high as 95%, when a mixture of primary and secondary sludge (35/65) is used as the feed sludge, which had an initial acetate percentage of 55% (Fothergill, 1995). Acidic odours at a full scale thermophilic plant in UK was the first indication that VFA were being produced in this process (Morgan, 1984).

2.2.3.1 Generation of VFA

Utilizing bench scale studies, a model for production of VFA was put forward by Mason & Hamer (Mason et al. 1987). It was confirmed that VFA were produced only in an oxygen deprived environment. The species did vary with retention time, but it was evident that acetic acid was always pre-dominant, at least 5 to 10 times higher then propionic acid. It was also found that more acetate was formed when the supply of oxygen was reduced. This led to the development of the model that said that acetate was produced simultaneously with the enzymatic degradation of substrate bacteria, as a result of fermentative bacteria. This model also predicted the sequential disappearance of VFA as "preferred" substrates reach exhaustion, although it did not predict accumulation of

VFA (Hamer 1987). From other work, it was found that acetic acid production does not occur over an oxygen partial pressure of 25.6mm Hg, which was referred to as excess oxygen state. Below this partial pressure, acetate production increased progressively with an additional sharp increase below a partial pressure of 5.9mm Hg (Chu, 1995).

In his research, Chu (1995) demonstrated that SRT and aeration rates both affected the formation of VFA. Acetate production of 70-80% in the thermophilic digesters made it different from normal fermentative processes. He also suggested that the production of acetate may be due to inefficient coordination or uncoupling of the oxidative (TCA cycle and electron transport chain) and non-oxidative (glycolysis) phases of glucose metabolism, resulting in acetyl-coA being converted to acetate.

All this previous research has definitely indicated that VFA production is higher when the aeration rates are low. The main focus of this research was therefore, to determine the potential optimum aeration rate with respect to VFA production.

VFA production is know to be related to a lot of parameters, viz. temperature, aeration (oxygen supplied), solids content, retention time etc. The following sections describe the effect of the aforementioned parameters in the generation of VFA.

2.2.4 Temperature

In a dual ATAD digestion system where there are 2 stages, the target temperature in the first reactor should be from 35-50°C and 50-65°C in the second reactor (USEPA, 1995). As a product of biological activity VFA production is definitely a function of temperature; this has been shown just from the influent in the UBC wastewater pilot plant, where there was an increase from 8-25 mg/L VFA in the months of November – February (average temperature 9°C) to 18-35 mg/L during the summer months (average temperature 15°C).

ATAD systems can be batch fed, semi-batch fed, continuous fed or semi-continuous fed. In either option, there is a drop in the temperature after a new volume of feed is added to the reactor. Deeny et al. (1990) reports that, during batch feeding of two tanks in series, the temperature in the first vessel can be expected to drop 5° to 10°C per day, with a recovery of 1°C per hour. In the second vessel, he predicted a temperature drop of 4°C to 6°C with a higher recovery rate. The generation of heat in the ATAD units is from both biological activity and from the energy input for mixing and aeration. At full scale plants, with high (5-6%) solids content and a higher fraction of easily bio-degradable substrates, the generation of heat due to of biological activity makes up a major fraction, about 70-80%. This type of heat production is not as evident at a smaller scale, such as the UBC pilot plant. This is compensated by higher energy input from over-designed mixing equipment. From previous research (Chu, 1995) it has been shown that a mere increase of 10 rpm in the Turburator™ aeration device results in a sharp

increase in temperature (pilot plant studies at UBC). The USEPA manual for operation of ATAD recommends 9-15 kWh/m^3 as the mixing energy requirement (USEPA, 1995).

2.2.5 Solids

To maintain high temperature in ATAD, the feed must contain a high concentration of solids. Typically a 4-6% total solids concentration in the feed provides enough volatile content to generate heat in the thermophilic range. The results of using both primary and secondary sludge as feed in ATAD had been studied in previous works. The rate of stabilization of primary sludge is initially slower and may result in unstable digestion, because of its irregular composition. On the other hand, secondary sludge is theorized to be more suitable for ATAD operation, as it is closer to the oxidative state of a thermophillic culture (Mason et al. 1987); this is due to the presence of more biomass (as compared to just higher volatile content in primary sludge), providing the substrates in the required ratios. The final reduced sludge mass, results from destroying a portion of the volatile suspended solids that occur during digestion. The percentage of VSS destruction that is achievable by digestion varies depending on the feed make-up and operating conditions in the overall treatment plant. For ATAD systems treating a mixture of primary and waste activated sludge VSS reduction is expected to be between 35 % to 45%. VSS reduction of 40% with 4.5 days retention time has been reported from the Whistler ATAD plant. Jewell and Kabrick (1980) showed that, in batch tests and full-scale continuous operation, about 33% reduction of VS can be achieved. A very useful tool in determining whether the desired reduction of VSS has been achieved is the Koers-

Mavinic curve (Koers 1977). This curve was plotted from data from bench-scale, pilot-scale and full-scale cryogenic aerobic digestion plants that used lower operating temperatures. This curve is shown in Figure 2.3. The values reported by Jewell falls into the curve. Taking into consideration the advantages and disadvantages of both the sources of sludge, it was decided to use a mixture of primary and secondary sludge at a ratio of (35/65).

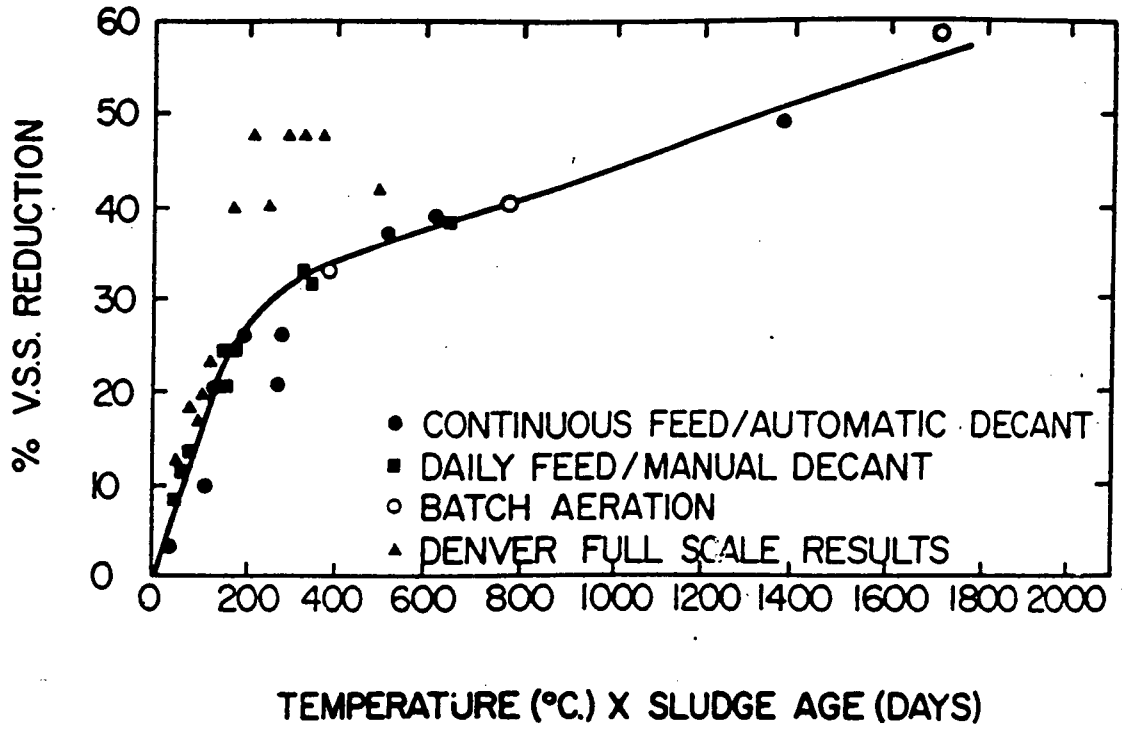


Figure 2.3 Koers-Mavinic curve for VSS reduction vs. Degree-days.

2.2.6 Aeration

Efficient air supply is an important parameter in ATAD operation. In the initial studies of ATAD, it was desirable to have a measurable level of DO. But this created a

lot of operational and measurement problems mostly because the aeration rates required to maintain that high amount of DO also resulted in cooling of the system. Moreover most DO probes are not equipped for adequate temperature compensation above 45°C; also, the high mixing in side the tank can be a deterrent in measuring on line DO and the accuracy in measuring low DO is not very reliable. Various studies have been conducted and it was demonstrated that compressed air can be employed instead of pure oxygen and get better results.

In his research Chu (1995), demonstrated that VFA production at lower aeration rates was higher. In his experiment, he used 2 reactors in series and the results indicated more generation of VFA at lower rates. Later on, he switched to a parallel system and ran the units at different airflow rates between 0-165 ml/min. Net production of VFA was the maximum with the lowest supply of air. Continuing on from that research, the optimization of the maximum production of VFA at the lower range of aeration (0 -100 ml/min) rates were studied in this work at four aeration rates.

2.2.7 Release of PO_4

The EBPR process has already been mentioned and how the excess phosphorus is stored in the secondary sludge. It has also been proven by earlier researchers that secondary sludge is more readily biodegradable and made available through lysis. The conversion of substrate can be represented by the equation which illustrates that VFA production is enhanced by the addition of secondary sludge (Hamer 1985).

$$CH_{1.4}O_{0.4}N_{0.2} + a(O_2) \rightarrow b(CH_{1.8}O_{0.43}N_{0.23}) + c(CO_2) + d(H_2O) + e(NH_3) + f\underline{(C_nH_{2n+1}COOH)}$$

The concern over using secondary sludge in aerobic digestion is the release of the nutrients, due to the EBPR process. Phosphorus, in particular, is readily released from aerobic sludge under thermophilic aerobic conditions (Boulanger 1995). This release of nutrients occurs in both aerobic and anaerobic processes, requiring further treatment of the supernatant before recycle. In countries like Japan, the sludge from the EBPR process containing on an average 7-10% P on a dry weight basis, is typically incinerated; however this results in incinerator ash with high concentrations of P, which, in turn can leach out. Thus disposal and recovery methods of P from sewage sludge may prove to be of interest where no safe disposal alternatives exist.

2.3 Struvite

Phosphorus present as various forms of phosphates, is of central concern to a wide variety of biological and chemical processes in natural waters, wastewater and water treatment. Phosphate is a nutrient required for the growth of all living protoplasm that contains approximately 2% phosphorus on a dry weight basis. Phosphate has various used in the treatment of industrial wastewater, including softening where their ability to form sparingly soluble calcium salts are capitalized upon. Phosphates can be present in four main groups

Orthophosphates	PO_4
Polyphosphates	P_2O_7 and P_3O_{10}
Metaphosphates	P_3O_9
Organic phosphates	Various sugars, nucleotides, etc.

In domestic sewage the molar ratio of nitrogen and phosphorus is around 8:1 with the phosphorus normally being present as the soluble orthophosphate. Since orthophosphate is not volatile (unlike ammonia) and is of similar molecular size, the only viable approach to its recovery in a concentrated form is precipitation as an insoluble (or slow release) salt. This approach is utilized in the removal technique of phosphorus using Fe salts, to precipitate $FePO_4$. However this salt completely ties up the phosphorus and make it unavailable as a nutrient.

All the groups mentioned above have different ionization constants. The group of interest here are the orthophosphates. A major problem caused by the presence of phosphorus in hard wastewater is the formation of scales in the pipe and digesters. Precipitation of Magnesium Ammonium Phosphate ($MgNH_4PO_{4(s)}$), also known as **struvite,** is a recognized problem in sludge digesters. These problems occur at the end of pipings, elbows and at the suction side of the pumps. This happens at these locations because they are regions of reduced pressure and there is a release of CO_2 from the solution. This causes a rise in the pH of the digester supernatant with an accompanying increase of in the k_{sp} (Solubility product).

The solubility product of struvite plays a major role in the precipitation and has intrigued many researchers. Bube (1910) reported a solubility product of 2.5×10^{-13} which is used in most water chemistry texts. Another value that was reported by Taylor (1963a) was 7.08×10^{-14}. The reaction of producing $MgNH_4PO_4.6H_2O$ is expressed in Eq.(1). It is produced when magnesium is mixed in water which is rich in phosphorus and nitrogen at a optimum pH. This reaction proceeds in alkaline solutions.

$$\mathbf{Mg^{2+} + NH^{+} + HPO^{2-} + OH^{2-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O \downarrow + H_2O} \quad (1)$$

Based on this equation, Tsuno et al. (1991) calculated another solubility product (k), which is shown in Eq. (2).

$$\mathbf{k = [Mg^{2+}][NH_4^{+}][HPO_4^{2-}][OH^{-}] = 7.8 \times 10^{-15}\ ((mol/L)^4)} \quad (2)$$

There are various advantages of investigating the usage of struvite and its application in the real world. At least three potential outlets for struvite have been identified (Schuiling, 1998).

1. As a secondary phosphate ore.
2. A raw material for other industrial uses. Struvite has already been used in cement building materials and has found its way into usage in the production of a high-density ceramic matrix.
3. As a slow fertilizer. Struvite is an excellent slow release, non-burning fertilizer that can be either produced from raw materials (which proved to be very expensive) or can be recycled from sewage where there is always an abundance of phosphorus, specially in secondary sludge. It has shown excellent agronomic properties. The problem of pathogen re-growth and pasteurization is not an issue if the sludge used is from a thermophilic digester.

2.3.1 Crystallization

Crystallization is a process by which a chemical is separated from solution as a high-purity, definitely shaped solid. A crystal may be defined as a solid composed of atoms in an orderly, repetitive array. The inter-atomic distances in a crystal of any definite material are constant and a characteristic of that material. Since the pattern or arrangements of the atoms is repeated in all directions, there are definite limitations on

the shapes which crystals may assume. For wash chemical compounds, there are unique physical properties differentiating that material from others. So the formation of a crystalline material from its solution or mother liquid, is accompanied by unique growth and nucleation characteristics.

Removal of phosphorus by crystallization has been studied by various organizations and much headway has been made in removing phosphorus from the wastewater treatment process in the sidestream and from the supernatant of anaerobic digesters. In a study by Sasai et. al (1995), it was found that there was more then 80% removal of phosphate and 14% removal of ammonium. The advantages and disadvantages for the various P-recovery and removal processes are shown in Table 2.1.

Process	Advantages	Limitation
MAP granule Formation process	Easy Operation. No pretreatment required. Product is valuable. Ammonium is also utilized. Low operation cost. No dehydration process.	Ammonium should be coexisted. Not feasible for low concentration of P
Calcium Crystallization process	Low operation cost. Low sludge generation.	Pretreatment required Management of seed crystal is difficult Product is less valuable Salt content of treated water is high
Coagulation settling process	Easy operation. High P removal.	High operation cost High volume of sludge
Simultaneous coagulation in aeration tank	No special vessel necessary. Easy operation. P is stable in sludge.	Production of excess volume of sludge Activity of Microorganism may be disturbed.
Bio-P removal	Volume of sludge does not change.	Operation needs careful monitoring P is released in sludge treatment

Table 2.1 Comparison of Various P removal and recovery process (Katsura, UNITIKA).

2.3.2 Process Development

In 1987, the engineering consultants, DHV, studied the dephosphorisation of pre-treated veal calf manure in a Crystalactor™. The process involves the crystallization of calcium phosphate on an inert carrier (grains of sand) in a fluidized bed. An advantage of this process, over the simultaneous dephosphorisation process, is that it results in a purer phosphorus product. This consisted of 80% calcium phosphate. The difficulty in removing the phosphorus from the bonded calcium phosphate is the main problem of phosphorous recovery by this method. In another experiment by DHV (Versteeg, 1992), where the experimental setup was the same to the one used in this research, calcium was used as the chemical to precipitate phosphorus. The molar ratio of Ca:P was 2.5:1 and removal up to 85 % was demonstrated, when P enriched tap water was used as the feed.

There are various other organizations that are actively doing research in the field of recovery of phosphates by crystallization. In South Africa, CSIR had also developed a fluidized bed Crystallizer column at laboratory scale for the removal of phosphorus from a variety of influent streams. Phosphate can be removed either as hydroxy-apatite or struvite, according to the make-up of the feed stream, and retention times in the range of 3-10 minutes result in about 90% removal of P at pH between 8.0 to 9.5. The pioneers in this kind of research are Kurita Water works (Japan), DHV (Netherlands) and CSIR (South Africa).

In his full-scale study, Fukase (1997) of Kurita waterworks Ltd., demonstrated that the phosphorus removal from the anaerobically digested, excess biological sludge

was higher then 80% when using an up-flow MAP Crystallizer. The phosphorus concentration in the supernatant of the anaerobically digested sludge was in between 80 to 120 mg/L. The P concentration in the effluent was consistently less then 20 mg/L. The recovered MAP granules had a diameter between 2 to 5 mm. These granules were formed without the presence of a nucleating body. The granules were formed by themselves in the granulating zone when the conditions were right with respect to pH and molar concentration of Mg, P and NH_4. The flow diagram of the process is shown in Figure 2.4.

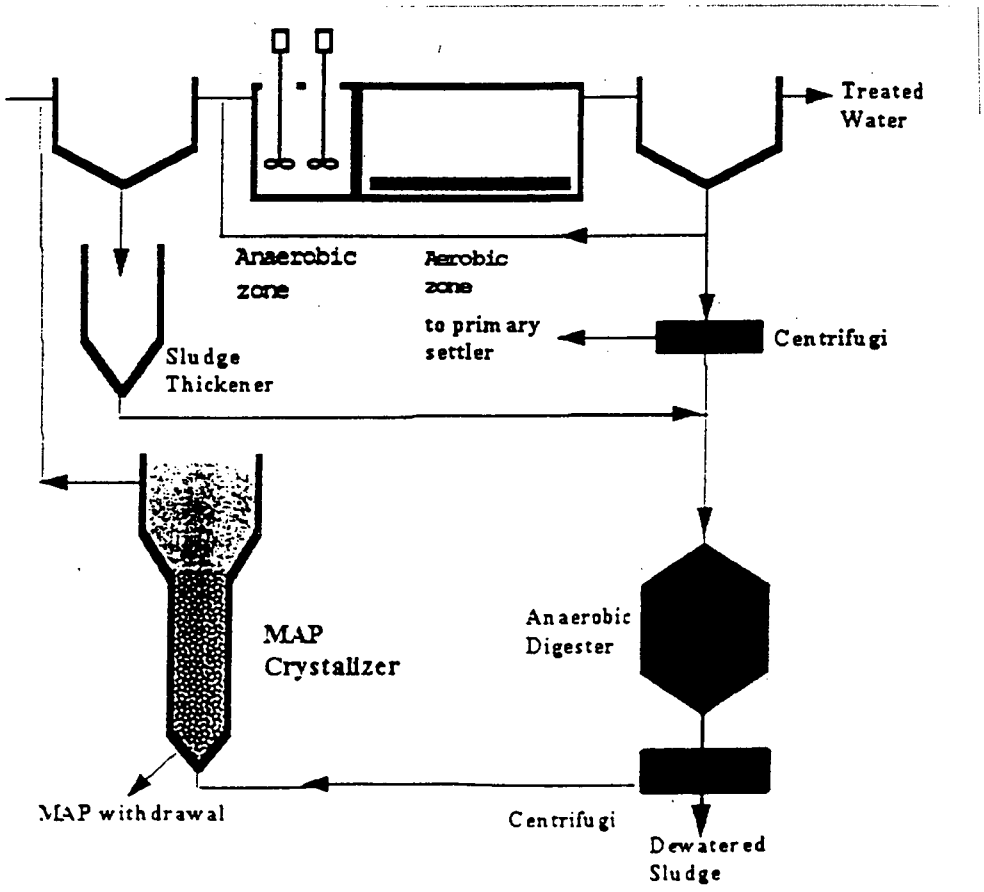
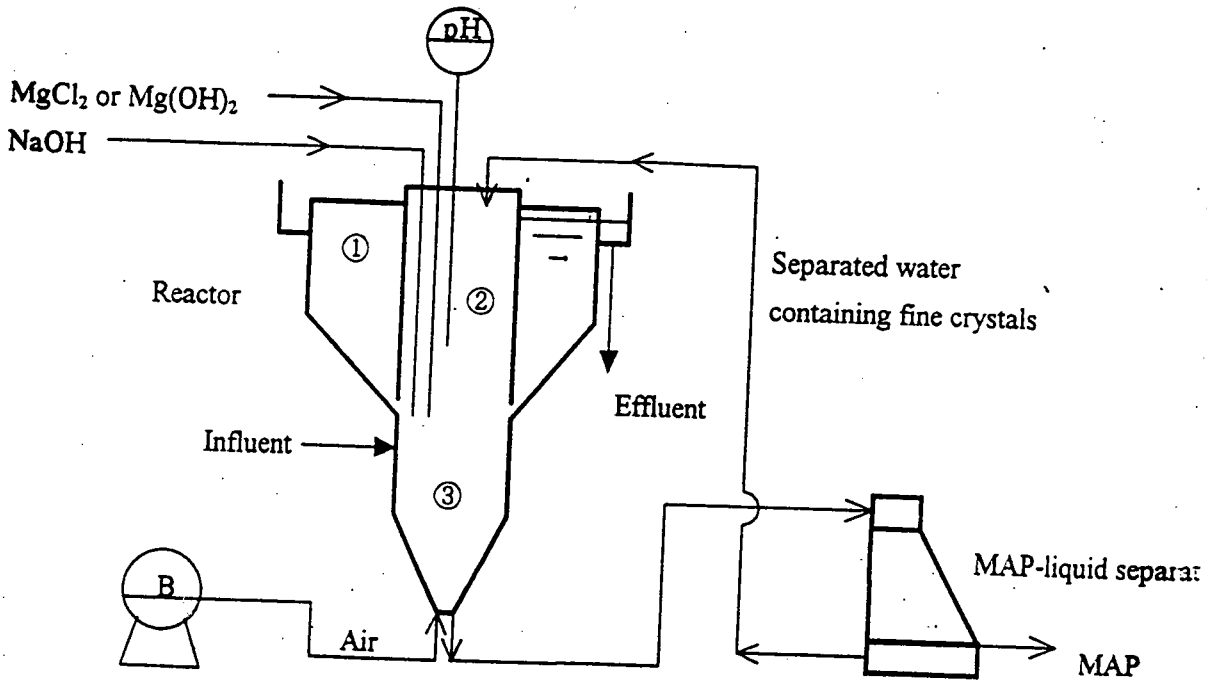


Figure 2.4 Flow diagram of Fukase's experiment (Fukase, 1997)

The MAP reactor in Sasai's experiment was divided into two zones such as separation and crystal forming (reaction and granulation). The crystal forming column was 0.96 m in diameter and 4.0 m long. MAP was crystallized and the granulated particles were deposited by gravity in the column. A flow sheet of the recovering process is shown in Figure 2.5.



① Separation zone, ② Reaction zone ③ Granualtion zone

Figure 2.5 Map recovery process flow diagram.

From the solubility products, it has been seen that the precipitation of struvite is dependent on the pH of the feed. Previous work has shown that the removal of P is highly dependent on the molar ratio of Mg and P. When the molar ratio of Mg/PO_4-P

was more then 1.0, it was found that PO_4-P removal ratio was more then 80% at pH = 8 and more then 90% at pH =9 (Sasai et. al 1995). For this research, the pH range therefore was kept between 8 and 10. Both $Mg(OH)_2$ and $MgCl_2$ can be used as chemicals as sources of magnesium. The advantage of using $MgCl_2$ is that pH can be controlled independently. pH can be controlled by using another chemical having an hydroxyl (OH) group.

The concentration of P can change substantially in the effluent of digested thermophilic sludge. As a result, the removal of phosphorus in the Crystallizer can be affected if the molar ratio between Mg and PO_4 is not maintained at the optimum level. To avoid this problem, the control method uses phenomena of pH and electric conductivity changes in accordance with MAP reaction. When $MgCl_2$ is added to an alkaline sample as a dropping liquid, electric conductivity increases as chloride ion concentration increases. However, its increasing ratio up to the achievement of MAP reaction is smaller then that after the equivalence point. On the other hand, hydroxide ion is used and pH value decreases as MAP reaction proceeds, with $MgCl_2$ dropping; that is the bending point of the pH curve is indicated, at the end of the MAP reaction. This method can be used as an accurate method for injecting $MgCl_2$ into the Crystallizer. With proper software and measuring methods, the required concentration of Mg to be added can be calculated in a matter of 10 minutes (Sasai, 1995). A typical graph of a conductivity test is shown in Figure 2.6.

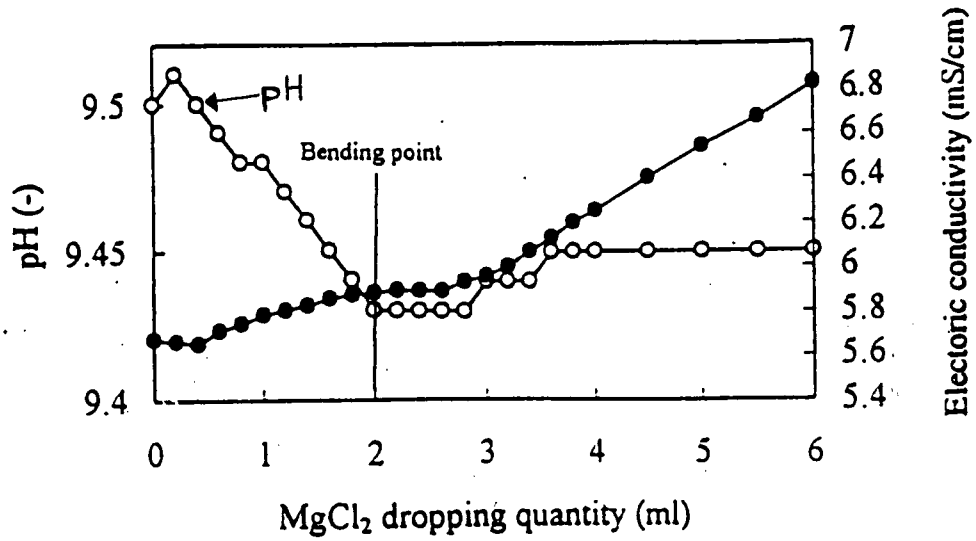


Figure 2.6 Mg conductivity graph vs. pH (Sasai, 1995)

All previous work was done on the supernatant of anaerobically digested sludge or incorporated as a side-stream treatment in the biological process. Since there was no available literature on MAP crystallization of thermophilic aerobic sludge, it seemed to be a very interesting area of study, especially with the high amounts of soluble phosphorus released during the cell lysis occurring alongside the release of VFA.

Chapter 3

Methods and Materials

3.1 Experimental set-up

This chapter deals with the methods and materials that were in incorporated in this research work. All experiments were carried out at the University of British Columbia's pilot plant situated on the south side of the campus. The plant is configured to treat $3000Ld^{-1}$ in two separate parallel 3-stage BNR streams. A schematic of the whole pilot plant layout and the process layout are shown in the Figure 3.1 and Figure 3.2 respectively. The collection of the sewage is done from the sewer that connects the UBC residences to the Vancouver sewage collection system. To achieve adequate solids loading to the process, sewage is pumped twice daily into three equalizing tanks of 1200 L capacity at the head of the plant and then subsequently pumped into the primary clarifier inside the plant a rate of 12 to 16 $L.min^{-1}$. The raw sewage is buffered daily by addition of approximately 500mg sodium bi-carbonate daily to compensate for the low alkalinity (approx. 100 $mg.l^{-1}$) in the Vancouver area (to bring the pH up to around 7). All the effluent and discharges from the plant are returned to the main sewage line, leading to the Annacis Island wastewater treatment plant.

The pilot scale ATAD system (Figure 3.3) consists of 2 sealed, insulated, stainless steel reactors of 128.6-L capacity, each that can be run parallel or in series. In this research, the tanks were always run in parallel. The tanks were covered by a fiberglass

jacket that was further insulated with a 10-mm thick closed cell foam to maintain minimum heat loss. Five experimental runs were done in the first stage to find the optimum VFA production at the different aeration rates.

The aeration rates were selected to cover the whole range from 0 air to 100 ml/min. The sludge ratio characteristics were kept as constant as possible; these are discussed later. The sludge mix ratio of 35:65 for primary:secondary was selected based on suggestions from previous research (Fothergill 1995)

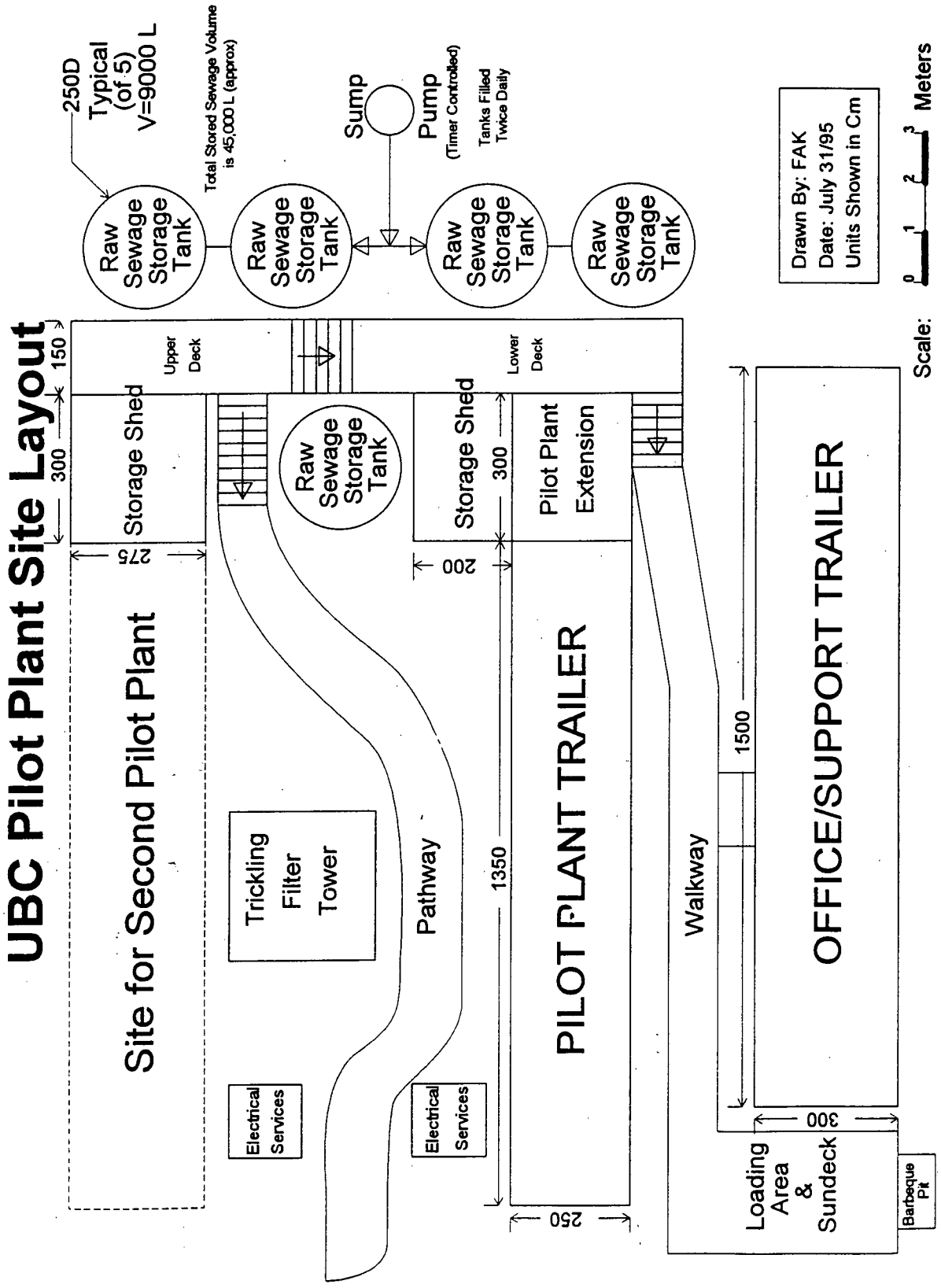
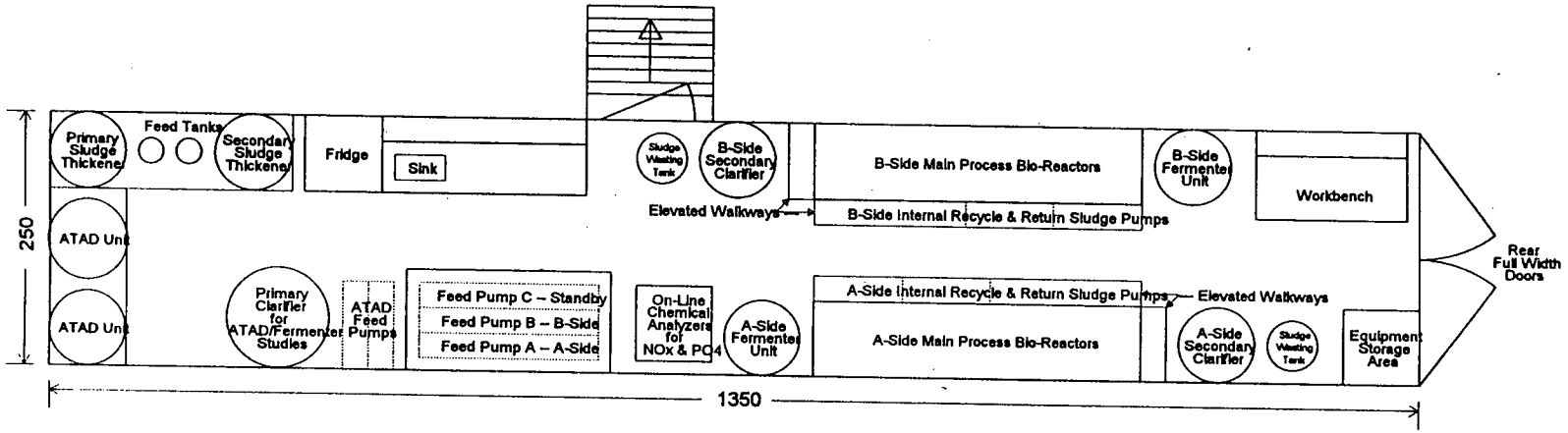


Figure 3.1 Pilot Plant Site layout

UBC Pilot Plant Trailer Layout

Pilot Plant is Housed in Fruehauf-Type, Full Length Truck Trailer
All Existing Equipment Shown in Approximate (Fixed) Position
Scale on this drawing may not be completely accurate



Insert Figure 3.2 Pilot plant process layout

Drawn By: FAK
Date: July 31/95
Units Shown in Cm

Additional Information Describing Main Process Bio-Reactor Tankage:

Total Useable Process Volume = 2500 L (approx)
Volume of Primary/Secondary Clarifiers = 450 L
Volume of IMUC Prefermenters = 400 L
Process Flowrates = 2.5 to 5.0 L/Min
(Note: Secondary Clarifiers become overloaded at higher flowrates)
In typical study applications: A-Side is used as Experiment and B-Side is used as Control

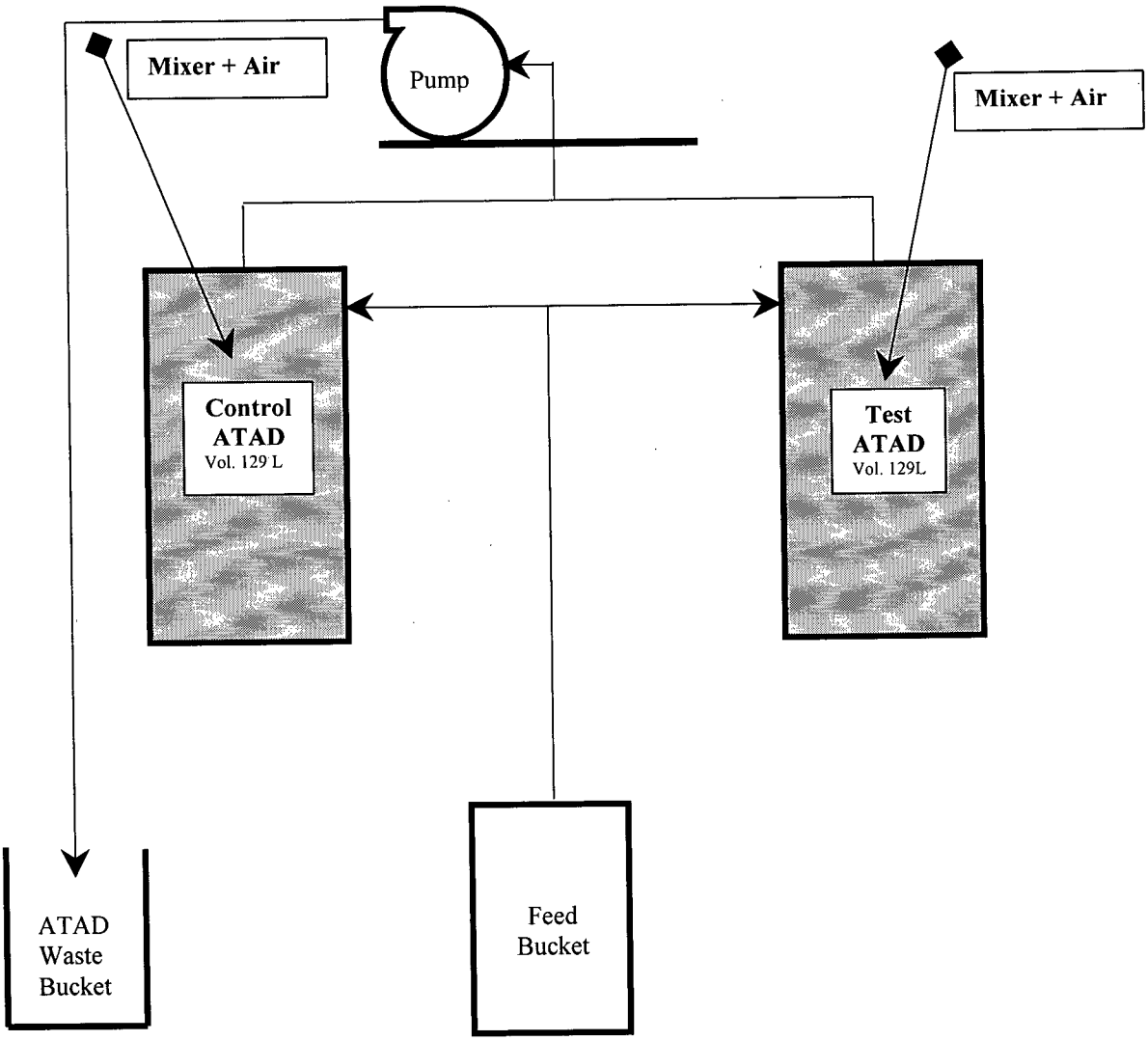


Figure 3.3 Schematic of ATAD pilot plant

3.2 Sludge Source

The thickened primary sludge is transferred from the primary clarifier to the primary thickener, from which the thickened primary sludge is taken to be mixed at the preset ratio of 35:65 for primary:secondary. The primary sludge was pumped from the primary clarifier to a second clarifier for further storage and thickening. The secondary sludge was obtained from the wasting tanks, where the daily wasting was done to maintain consistent sludge age. The secondary sludge was first wasted from the aerobic zone of the UCT process. Every 24 hours, 60 L was transferred to a pre-thickener where the sludge was collected and allowed to sit in the wasting tank for 45 minutes. The volume to be wasted was initially determined from the wasting chart; later on, to maintain constant waste volume, it was decided to waste 60L each day. The sludge wastage charts were designed based on the mean cell-residence time (θc), defined as the mass of organisms in the reactor divided by the mass of organisms removed from the system each day (Metcalf and Eddy, 1991).

$$\theta c = \frac{(V_r \times MLSS)}{(V_w \times MLSS) + (Q \times TSS)}$$

where V_r and V_w are vol. of reactor and vol. wasted respectively

This allowed more thickening of the secondary sludge to increase the solids in the feed. The settled solids were then manually sucked off with the help of a vacuum pump.

The mixed feed was then stored in feed tanks and was stirred continuously to prevent it from going anaerobic. The feed was made everyday and the sampling was

done simultaneously to remove the chances of generation of VFA in the feed. The feed was fed into the ATAD units, with the help of variable speed pumps at a rate of 1L/hr. This rate was monitored every run to maintain feed rate consistency. The feeding was done at this rate to configure this process as a semi-continuous process, instead of a batch process. A process schematic is shown in Figure3.3.

3.3 ATAD reactors

The process consisted of two 129L stainless tanks (Plate 1) fitted within insulated fiberglass tank, which was again insulated with a 10 mm thick closed cell foam. The tanks were sealed with a lid perforated to accommodate online monitoring of temperature and ORP and to allow the passage of the shaft, sludge inlet pipe and air exhaust port. All these perforations were well sealed to maintain minimum heat loss.

Both these tanks were fed with Moyno progressive cavity pumps (model 33101). The sludge from the ATAD units were removed each day with a Masterflex peristaltic pump (model 7585-50). The pump was situated on top of the units and the sludge was wasted to a bucket to measure the amount wasted. During wasting, the sludge was sucked out through the same inlet pipe.

Plate 1: Picture of ATAD units

The retention time of 3 days for the entire set of experiments was chosen based on previous research work (Chu, 1995). During regular operations, 24 liters were wasted once a day and the sludge volume in the tanks ranged between 60 and 84 L. The tanks were run under test conditions at different aeration rates for 10 days prior to sampling. The contents of the tanks were intermixed after each run, to prevent growth of facultative organisms and to ensure consistency in sludge characteristics in both tanks.

The mixing and aeration was done with the mixer/aerators, which were modified versions of the Turburator axial flow, manufactured by Turburator Technologies Ltd.™. Air is introduced through the hollow shaft and thoroughly mixed by the rotation of an patented impeller in the sludge. The aerators were belt driven and fitted with a variable speed DC motor. This same technology is used in the Salmon Arm facility in BC. The supply of compressed air into the aerators was controlled by Cole-Palmer flowmeters. Both the flowmeters were stainless steel float types, which had a range of 0-145 ml/min at 14.7 psi (model No. 32-15). The calibration curve for this flowmeter is shown in Figure 3.4. The air was supplied from the same source and split before entering either flowmeter. This was done to eliminate the usage of excess air by either unit because of higher rpm of the shafts, in the event of using only one flowmeter. These meters were monitored daily to reduce variability of air supply. This was the main variable in the first stage of the research. Exhaust ports for air were provided in both the tanks. Care was taken to prevent external air from entering the system, but due to the movement of the shaft and the gaps that were present in the insulation, total containment was, practically, not possible.

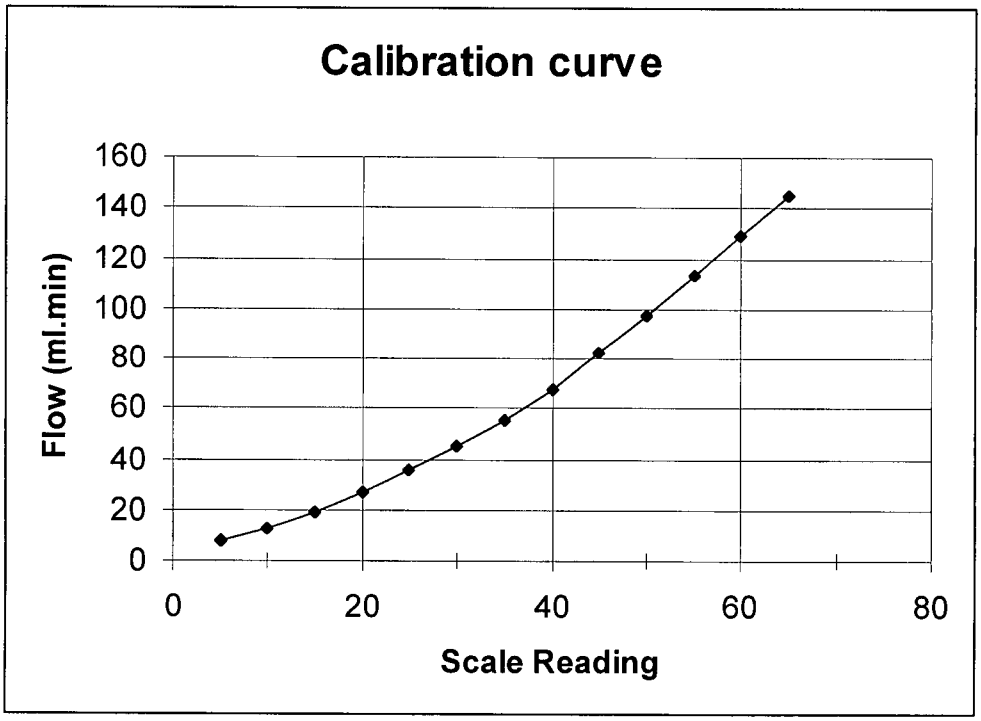


Figure 3.4 Calibration curve for Cole-Palmer flowmeter (Model 32-15) at 14.7 psi.

3.4 Monitoring Variables

To maintain process stability and performance the following variables were monitored throughout the experimental period.

3.4.1 ORP

Oxidation Reduction Potential (ORP), or Redox potential, was monitored as an indicator of oxygen levels. ORP has been advanced by previous researchers as a useful state of the system (i.e., anaerobic or aerobic) or the degree of treatment (i.e., extent of biological oxidation of organics in wastewater) (Snoeyink, 1980). ORP is basically a measure of the activity of the electrons involved in the oxidation-reduction reactions

within an aqueous environment and it can be used to accurately define the ranges of respiratory activity and indicate the presence or absence of various electron acceptors (Peddie, et al, 1990). The ORP probes in both tanks were capable of registering signals in-between -5000 to 5000 mV, within a temperature range of –5 to 135 –^{o}C. From previous research, ORP values between 0 to –300 mV were considered to be in ATAD environment. In all of the runs the ORP was negative, indicating a highly reduced environment in the ATAD units. There were two probes used in both tanks to ensure higher degree of accuracy (since the temperature was high). Prior to the start of the experimental runs, the probes were calibrated with AgCl.

3.4.2 Temperature

The high temperature in the reactors was mainly due to mixing, aeration and biological activity. Both the ATAD units were monitored on-line with probes which were accurate to 1 ^{o}C. The temperature data was connected to a data-logger (software XtGold) and readings were taken every 10 seconds and averaged every 5 minutes. Temperature measured by a thermometer was inaccurate, since the mercury dropped rapidly as the thermometer was taken out of the tank.

3.4.3 Turburator speed

Because of the small scale of the pilot plant and the high power usage of the Turburators™, the surface area to volume ratio was much smaller then full-scale plants.

The mixing and aeration equipment provide a major portion of the heat generation. To maintain the same mixing conditions, both Turburators™ were operated within the same range. Because of individual characteristics, this resulted in differences in the temperature in both tanks. The mixers were fitted with individual speed controllers and a high-speed motor. These units had to be stopped and cleaned everyday during operational days. to prevent build-up of solids inside the hollow shafts.

3.4.4 Total Solids.

Total solids were determined by evaporating a known volume of sample of ATAD influent (feed) and digested ATAD sludge (effluent) in a Fisher-Isotemp (model 350) forced draft oven at a temperature of 104^0C for 24 hours. From pre-run analysis it was noticed that there was no difference in the total solids content of the feed into the ATAD units; therefore the solids analysis for the feed was done only once. Analysis was performed as outlined in Standard Methods (A.P.H.A et al 1989). Since the feed was made up totally on the basis of sludge volume, there was a certain degree of variance in the feed sludge. To determine the solids destruction in both the feed and the ATAD solids analyses were done every 12 hours during experimental runs.

The MLSS was also determined for the process once a week, to confirm that the process was operating properly with respect to sludge age. These results are not discussed in this work.

3.4.5 Aeration rates.

The aeration rates for the entire experimental period were controlled by the flowmeters. The control ATAD unit was operated at 50 ml/min, as this was the recommended rate according to USEPA (EPA /625/10-90/007) for the volume of tankage in this work. According to the EPA, the recommended aeration rate is $4m^3/hr/m^3$, which converts to almost 50 ml/min in this work. However, this value is highly over-compensated, and according to some experts the aeration rate can be lower than this.

The experimental design of the research work is summarized in Table 3.1

	Test ATAD	**Control ATAD**	**Dates**
Run 1	50 ml/min	50 ml/min	24/03 to 29/03
Run 2*	25 ml/min	50 ml/min	19/05 to 25/05
Run 2a++	25 ml/min	50 ml/min	23/07 to 28/07
Run 3**	75 ml/min	50 ml/min	08/06 to 12/06
Run 4	100 ml/min	50 ml/min	29/06 to 04/07
Run 5***	0 ml/min	50 ml/min	17/08 to 22/08

* First run after the plant was started again
** Run curtailed because of plant problems. Discussed in results and discussions.
*** Compressed nitrogen gas was used instead of air for operational reasons.
++ This run was done to verify the results of Run 2.

Table 3.1: Experimental program for VFA optimization.

3.4.6 pH

The pH of the feed, process and the ATAD units were measured every second day during non experimental periods and the pH of the feed and ATAD were monitored everyday during experimental runs. The pH was measured with a Fisher Scientific Accument pH meter (model 25) and a 3 point calibration was done with buffers of 4, 7 and 10. The sample was constantly stirred with a electrical stirrer. Temperature correction was applied later on.

3.5 Experimental Variables

Depending on the point of sampling varying volumes were taken for sampling. The various sampling points and the frequency of sampling is discussed later on and the sampling schedule is shown in Figure 3.4. The parameters that were monitored were: VFA, PO_4-P, NO_3-N, Total P and TKN

The preservation of the samples for the respective analysis was done at the time of sampling. For the ATAD and feed sludge, the samples were taken when wasting was done from the units and the inlet of the feed source. 500 ml were taken from each point and later filtered and preserved.

3.5.1 Volatile Fatty Acids (VFA)

Samples from pre-set sampling points were collected and prepared immediately. The digested sludge was centrifuged at a high speed (approximately 16,000 rpm) for about 7 minutes. The centrifuge used was an IEC Clinical Centrifuge (Model CL). Even after centrifuging, the supernatant of the digested sludge was very colloidal in nature (See Plate 2). The supernatant was then filtered through a Whatman 4 filter under the influence of gravity. This filtrate was then again filtered through 25 mm dia 1.5μ (934-AH) filter paper using a syringe. Care was taken to make sure that there was no tear in the filter paper when it was put in the filtering unit and after the filtrate came out. In case a tear occurred, (which happened a few times) another filter paper was used and the whole process was repeated. This filtrate was then sampled with a dedicated dropper which dispensed 1 ml into 2ml clear glass GC vials (HP model 5181-3375) and preserved by 0.1 ml 3% phosphoric acid (HPO_4). After this, the vials were stacked in properly labeled racks and refrigerated at 4^0C.

The VFA analysis was done in the Environmental Engineering Laboratory, Dept. of Civil Engineering. The specifications and settings of the instruments are shown in Tabular form in Table 3.2

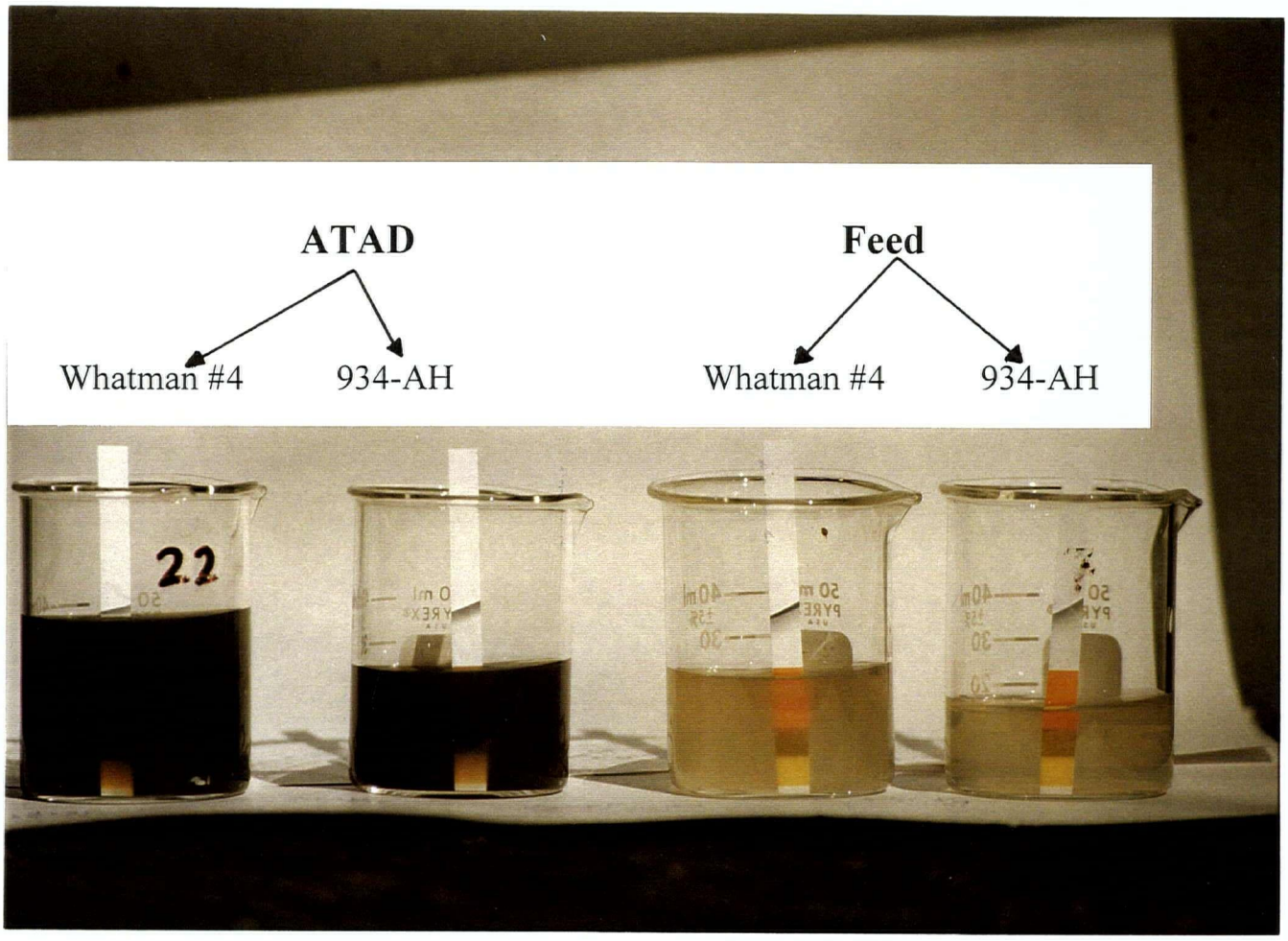


Plate 2: Filtrate sample using different filter paper.

Instrument	Gas Chromatograph
Model Number	Hewlett-Packard 5880-A
Automated Sampler	Hewlett-Packard 7672-A
Oven Temperature	120^0C
Injection port temperature	180^0C
Detector Temperature	200^0C
Detector type	Flame Ionization Detector (FID)
Carrier gas	Helium
Gas flow rate	20 ml/min
Column length	4ft, 2mm dia.
Column material	Glass
Column packing	60/80 CarbopackC/0.3% Carbowax 20M/0.1% H_3PO_4

Table 3.2 Specification of the Chromatograph.

The quantitation of the response peaks were done by comparison with external grade standards. All samples were analyzed for acetic acid, propionic acid, iso-butyric acid, butyric acid, 2-methyl butyric, 3-methyl butyric acid and valeric acid. Of all these species, acetic acid was found to be the most predominant species according to previous researchers (Chu, 1995).

Due to the volatile nature of the samples, the time between sampling and preservation was kept to a minimum. Moreover, from previous work, it was also found that volatilization of VFA occurs even at very low temperature (-2^0C). Because of this, the time period between sampling and analysis was kept to a minimum. All the analysis was done in duplicate, (triplicates, in some cases, to ensure the accuracy of the machine).

3.5.2 Soluble Orthophosphate (PO_4) and Nitrates (NO_x)

Samples for PO_4 as P and NO_x as N were prepared on site after centrifuging feed sludge and digested sludge. The filtration was the same for VFA analysis and PO_4-P and NO_x-N The sample size was 8 ml and stored in plastic tubes, which were preserved with 2 drops of phenyl mercuric acetate. All samples were done in duplicate, then stored in properly marked racks and later analyzed in the Environmental Engineering laboratory. For all nutrients, the samples were thawed under refrigeration, to avoid potential volatilization of sample constituents.

3.5.3 Total Phosphorus (TP) and Total Kejdhal Nitrogen (TKN).

TP and TKN were measured daily and required digestion before analysis. All samples were unfiltered and acidified to pH<2 using H_2SO_4 and sample size was approximately 60 ml before freezing. In the laboratory, after defrosting, the samples were blended using a Braun Hand Mixer to homogenize the contents and get a representative sample. Since the range of the samples was very high, known standards were also prepared. An aliquot from each bottle was withdrawn and placed in a 75 ml micro-Kejdhal flask. Boiling chips and 10 ml of digestion solution were placed in the flask. These flasks were then digested for 7 hours, the first 3.5 hours at 140^0C and the later 3.5 hours at 360^0C. The samples were later diluted with distilled water and made to 75 ml with continuous mixing.

A 10 ml sample from each flask was then withdrawn and analyzed on the Lachat Quickchem AE Automated Analyzer which had XYZ sampler on it. The methods used were Quickchem method No. 10-107-06-2 D for TKN and Method No. 10-115-01-1-1 for TP. Calibration checks were performed intermittently to maintain the integrity of the data.

3.6 Sampling points

Sampling was done for both the experimental and monitoring variables at : raw sewage, thickened primary sludge, thickened secondary sludge (after wasting and allowing to sit), secondary sludge supernatant, feed sludge and ATAD effluent

A detailed sampling chart for the VFA optimization phase is shown in Figure 3.5. Feed sludge samples were collected from a valve that was situated at the bottom of the Plexiglass tanks, which were graduated upto 40 liters. The feed was always in excess, to cover up the extra time in case sampling could not be done on time in the morning. This graduation also helped in determining the exact volume of sludge to be wasted everyday. The feed tanks were fitted with mixers that kept the sludge in a homogenous and aerobic state. Both the mixers were set at the same rpm and the feed tanks were identical in diameter. The sampling for the ATAD units was done from the wasting line, while mixing was done to keep the sludge inside the tanks completely mixed. After wasting was completed, the Turburator™ shafts were cleaned everyday.

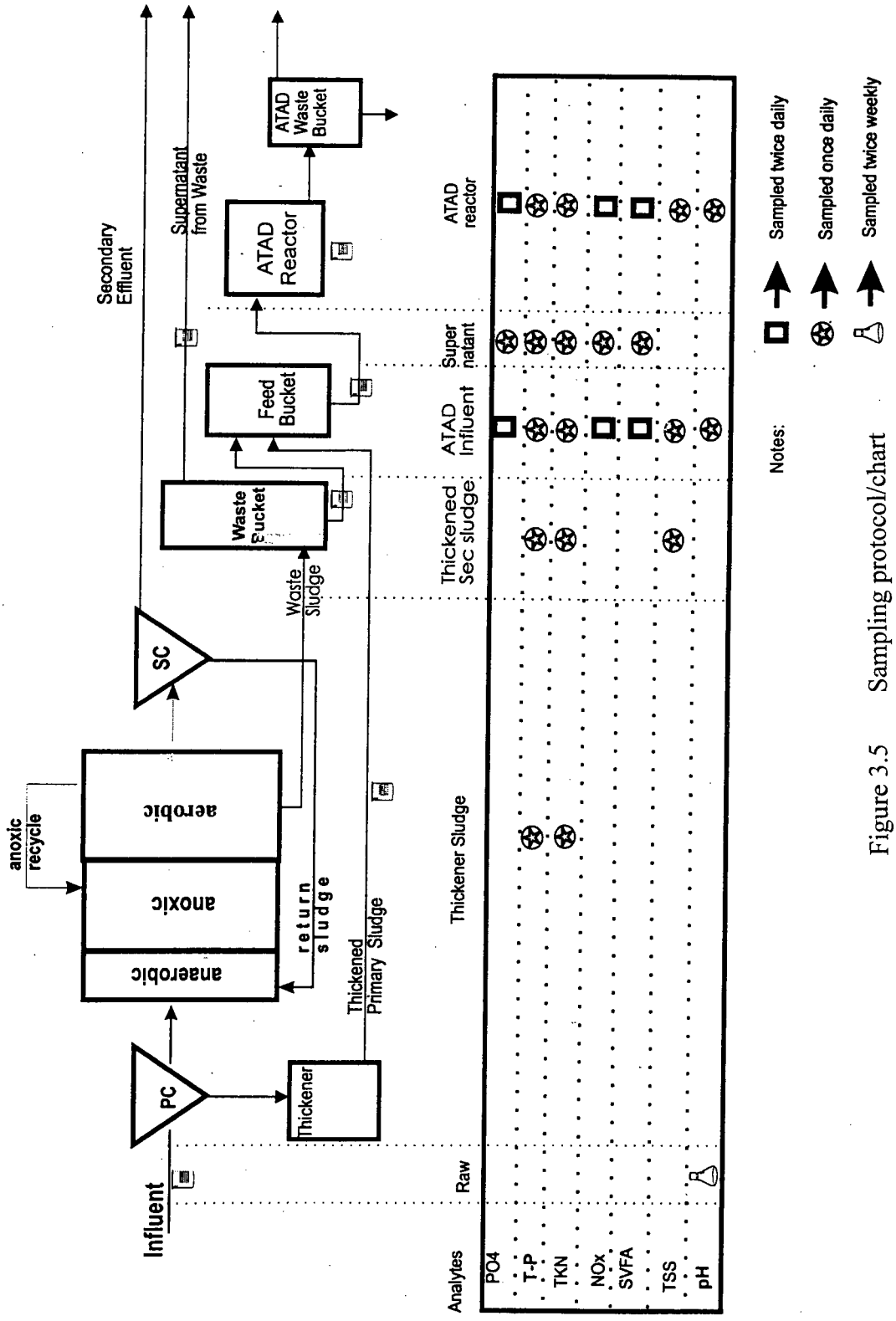


Figure 3.5 Sampling protocol/chart

The thickened primary sludge was taken while the feed was being made. The sludge was allowed to run for some time before the calculated volume was pumped into the mixing tank. The thickened secondary sludge sample was collected when the sludge was pumped by a vacuum pump into the mixing bucket. The secondary effluent was basically the final effluent of the process, but instead of collection from the final clarifier, the sample was collected from the top of the wasting tank for the process (where the sludge was allowed to sit for 45 minutes to further thicken). The raw sewage was taken from the influent pump and was sampled immediately for pH.

3.7 Crystallizer

This part deals with the materials that were used in the second part of the research work. After the initial phase of optimization of VFA, an attempt was made to remove the phosphorus from the ATAD effluent. In this phase, only one ATAD unit was used as the second one had a defective driver and had to be shut down. This did not effect the operation, as the required volume of sludge was met with only one unit.

After wasting, the ATAD sludge was allowed to sit in a graduated cylinder (in this case it was the feed tank for the non-operational ATAD unit). On verbal discussion with Dwayne Doucette (Kruger Inc.) it was decided to apply post-mesophilic aeration at a rate of 80 ml/min to the sludge. This helped the sludge to settle better and to overcome the thermal currents inside the tank at a faster rate. This reduced the solids content in the supernatant, that was the top part of the tank, by 50 % (approx.). The supernatant was

later screened off using a manual screen. There was no alteration to the inherent characteristics of the ATAD effluent on doing this.

The schematic of the setup and the reactor used during the experiments is shown in Figure 3.6. It consisted of a Perspex pipe 100 mm dia and 190 cm tall. The reactor was configured so as to allow injection of chemicals at the bottom of the reactor. The feed was pumped in at the bottom of the reactor and the column was filled with sand as the seeding material. Instead of a nozzle plate, as would be the ideal case, the bottom 15 cm of the column was filled with gravel and covered with a plastic net to prevent sand from entering the inlet pipe and clogging the system. The reactor was then filled up with commercially available silica sand, which was obtained from the UBC stores, up to a height of 85 cm. There were four inlets at the bottom of the reactor where the gravel was situated. This was considered to be the mixing zone and it was assumed (visual testing with Rhodamine dye) that the chemicals were all mixed up in this region, before coming into contact with the sand bed.

The chemicals for pH control (NaOH) and Magnesium Chloride ($MgCl_2.6H_20$) were injected via needles and pumped at the calculated rates with two Masterflex pumps (model No. 7553-30) with speed controllers. The calculations for the flow rates and the molar concentrations of the chemical added are shown in Appendix C. The feed was pumped in at a rate of 350 ml/min through a port with a Masterflex pump (18" head) and there was a recycle of 700 ml/min (2xQ) to increase the contact time. The pump used to

recycle was a Masterflex pump (model 7529-00). This also helped increase the fluidization of the bed.

Prior to experimentation with ATAD effluent, the reactor was run with synthetic sewage. This sewage was made up, using tap water, and spiked with PO_4 and NH_4 at a known concentration, similar to that of ATAD effluent and made up to the required molar ratio for the formation of struvite. The chemical used for PO_4 was $NaH_2PO_4.H_2O$ and NH_4Cl was used for NH_4. The rationale behind doing this was to study the removal of phosphorus without the presence of a high concentration of solids in the ATAD effluent and to get a better understanding of the chemistry of struvite formation. Moreover, this helped in correcting any flaws in the reactor set-up, because the volume of sludge was limited.

There were two sampling points, the influent and the effluent. The pH was constantly monitored with a hand held pH meter manufactured by HORIBA instruments. The model was D-13 and the range was 0-14 with a pH resolution of 0.01 with a repeatability of 0.01. The pH probe was fitted on top near the effluent port with proper gaskets, so as not to allow any leakage and to facilitate continuos monitoring. On doing a Rodhamine dye test to determine the up-flow velocity, it was noticed that there was some short-circuiting and the time taken for the dye to first appear was 16 seconds. This was ignored in the experiment and an assumption was made that there was little or no short circuiting.

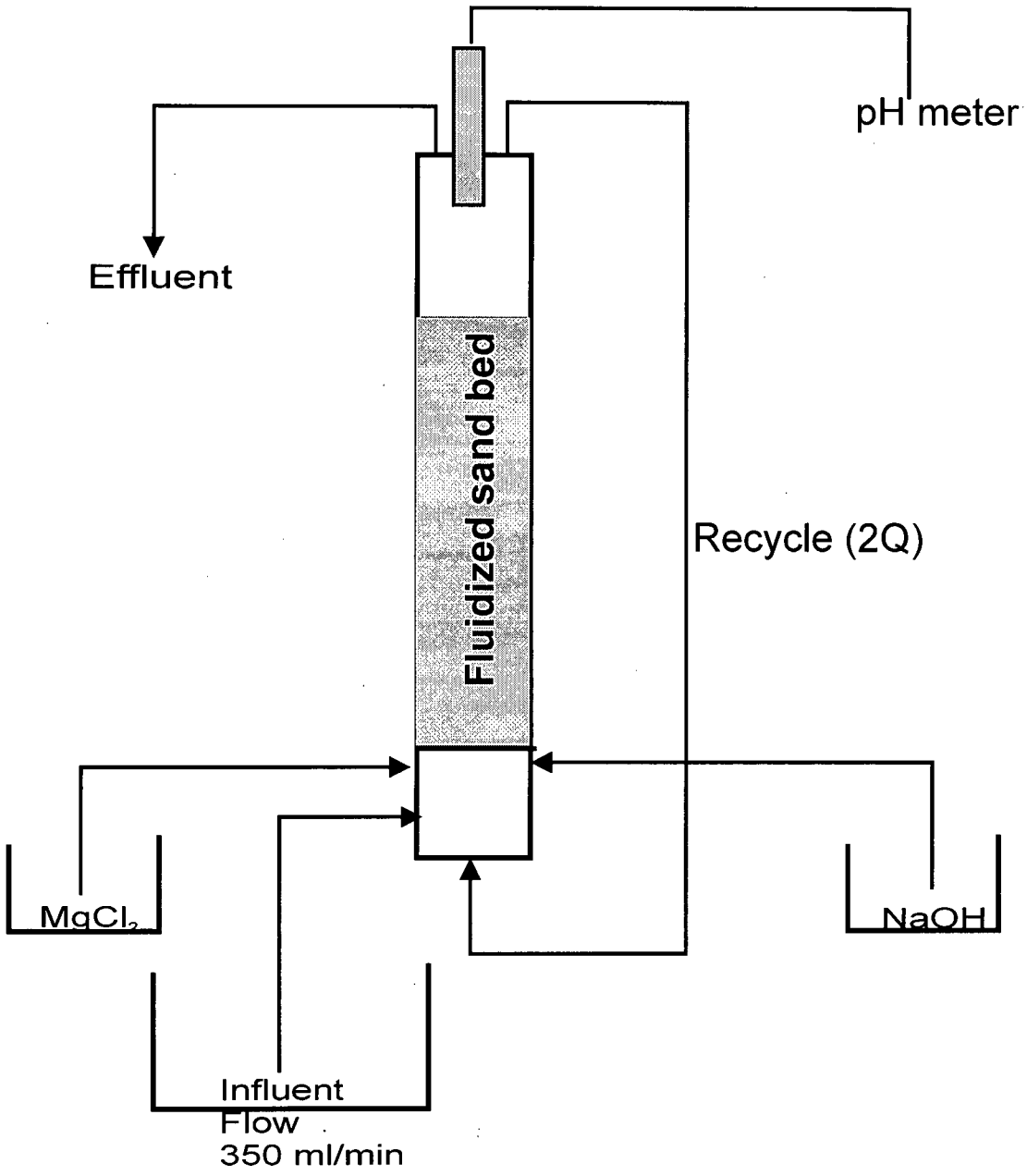


Figure 3.5 Schematic of Crystallizer layout.

3.7.1 Experimental Program

The pH range of the runs was decided based on previous work which demonstrated that the optimum pH range for formation of struvite was between 8 and 10 (Sasai, 1995).

	pH
Run 1	8.62
Run 2	9.04
Run 3	9.35
Run 4	8.5
Run 5	8
Run 6	10
Run 7	8.6

Table 3.3 Averaged pH values during all runs.

The pH values shown in Table 3.3 were set after the influent was run through the column. NaOH was injected at a very controlled rate and it took a couple of minutes for the pH to reach the desired level. It was intended to study the Crystallizer at pH increments of about 0.5. The runs were conducted for at least 60 minutes. Samples were collected in duplicates from both the sampling points and pH readings were taken every 5 minutes. After every run, the water was drained out and a fresh influent was run through. It was assumed that no residual phosphorus was released into the feed in a later run.

Two more runs were carried out to study the effect of an increasing trend in the pH to the removal of P from the same influent, over the same period, and to look into the removal percentage over a longer period.

3.8 Data interpretation

There are many possible sources of error in reporting environmental data including, sampling error, error associated with processing a sample (i.e. filtering, preservation, storage), handling error, and analytical error. To better analyse and represent the facts the data acquired has to be screened for outliers. In this research, there were two tanks that were run constantly with the same feed. The control tank was run to maintain a standard, so that the inherent differences can be corrected. It was expected that both tanks would demonstrate similar results, when operated at the same aeration rate.

The tables and data presented in the Results section are based on average of the data collected. For VFA samples, the sampling was done in duplicate and the analysis was also done in duplicate. Total VFA values are actually the averaged values of all the six species sampled and reported as acetic acid. Paired t-test for sample means were performed to determine if the differences were statistically different.

Chapter 4

Results and Discussion

The results of the all the experiments are discussed in this chapter in two separate sections. Section 4.1 deals with the results from the VFA optimization study with respect to aeration rates and includes the monitoring variables and the experimental variables. Section 4.2 discusses the removal of phosphorus from the ATAD supernatant in the Crystallizer, using both synthetic feed (water and chemicals) and ATAD effluent.

4.1 VFA optimization

As noted earlier in Table 3.1, there were 6 runs at different aeration rates. The control tank was run at 50 ml/min, throughout the entire period. The experiments were spread over a 5-month period. Initially, the experimental design was intended to be over in a much smaller period and only 5 runs were to be performed. All the runs were scheduled to be 6 days long, which provides for two full retention cycles. The acclimatization period between runs was usually more then 6 days, to account for the interchanging of the sludge between tanks and equipment maintenance. As is evident from the experimental chart, the periods for these runs, especially the acclimatization periods, are very irregular. This happened because of various problems that occurred in the plant; these are discussed later on in this section. Some of the delays experienced, included clogging and failure of pumps, Turburator™ motors, power failure and complete closure of the plant because of the failure of the main sewage pump. During

the experimental period, because of regular visits to the plant at least twice a day, most of the defects were rectified immediately; however there were certain things that could not be repaired on time and that led to unforeseen delays.

All the batch experiments, with different aeration rates, were done to find the maximum production of VFA. Effort was made to make the sludge source as consistent as possible. The supply of air was kept constant throughout the individual runs. The main sewage sump pump, which transfers sewage from the sewer to the pilot plant, broke down on the evening of April 22nd 1998; temporarily halting the operation of the entire plant. The pump was replaced and the plant was back in operation on May 3rd. This event disrupted an experimental run, since the entire plant had to be shut down for more then a week. Because of this failure, the sludge pumps were clogged and there was less solids content in the process. All these effects were evident in the subsequent runs, and the results are discussed later on. Moreover, the results of Run 2* (Table 3.1) undertaken just after the shut down, are not discussed in detail, due to inconsistent results specially for the solids concentration. To rectify this, Run 2 was repeated at the same aeration rate (Run 2a) at a later date, when the plant was fully operational. The results of this run are discussed in detail.

4.1.1 ORP

The redox potential for both the tanks was monitored on line with two probes in each tank. Table 4.1 summarizes the data base and Figure 4.1 illustrates the relationship

between ORP and aeration rates, that was evident in the two tanks. The averaged values of both the probes for each run are plotted in Figures 4.2 to 4.6. All the runs demonstrated the typical saw-tooth pattern, which is related to the feeding cycle. There was a distinct deflection whenever the sludge was wasted on a daily basis. The average ORP remained between – 300 mV to – 450 mV. This proves that micro-aerobic conditions existed inside the tanks (Chu, 1995). The ORP values were consistent during all the runs. From the graphs, it is evident that ORP is definitely affected by the aeration rates. During Run 1, where the supply of air to both the tanks was the same, the averaged ORP values for both the test and the control tank were similar. It has been found that ORP is sensitive to changes in substrates (Chu, 1995). In the subsequent runs, where the rate of air supply has been changed and the other operating conditions including solids content were kept as consistent as possible, there is a distinct trend of aeration rates affecting the ORP. Although the ORP readings (average) of the control ATAD unit in all the runs were different, there is a possibility that this was caused by the variations in the bio-solids present in the feed.

Aeration rates	Test		Control		Difference
	Average	Std Dev	Average	Std Dev	
0 ml/min	-375	22	-330	10	-45
25 ml/min	-383	17	-342	12	-41
50 ml/min	-368	9	-361	9	-7
75 ml/min	-380	9	-392	9	12
100 ml/min	-362	9	-416	11	54

Table 4.1 Average ATAD ORP.

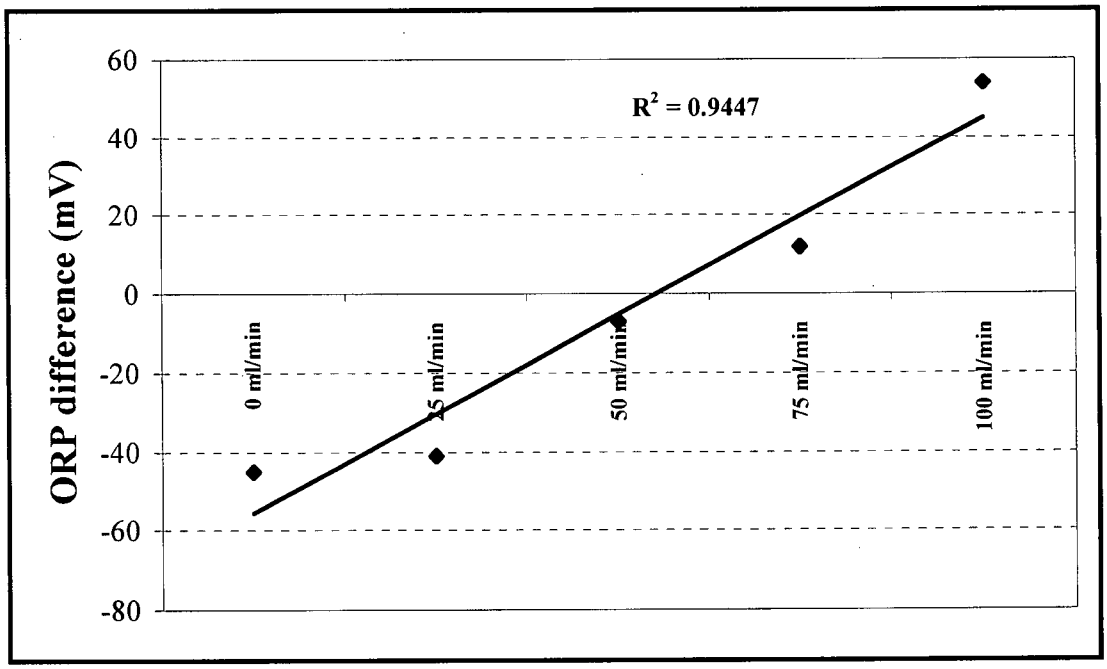


Figure 4.1 Difference in ORP at the different aeration rates

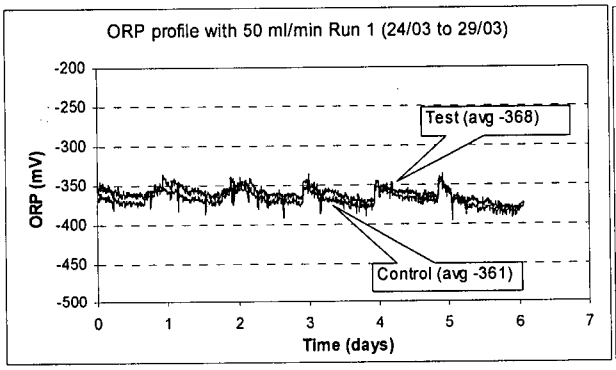


Figure 4.2 ORP profile Run 1

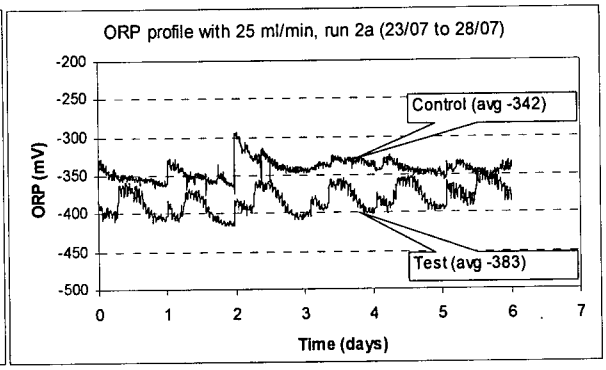


Figure 4.3 ORP profile Run 2a

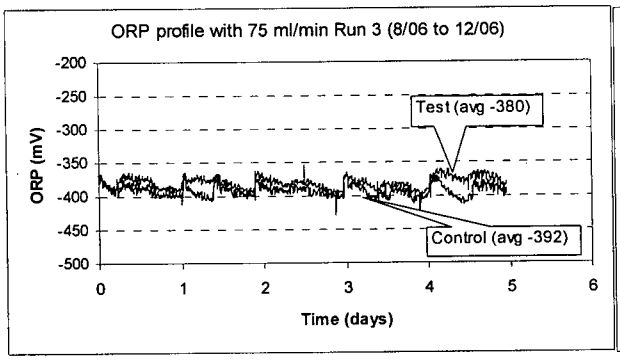


Figure 4.4 ORP profile Run 3

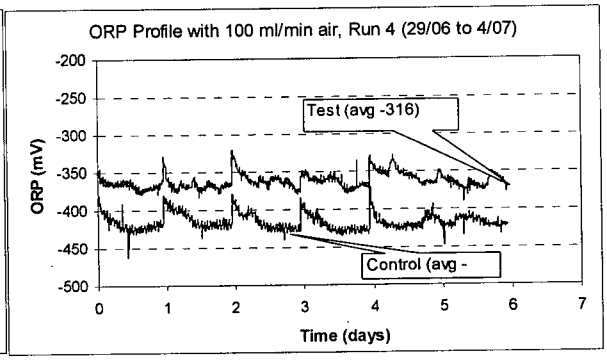


Figure 4.5 ORP profile Run 4

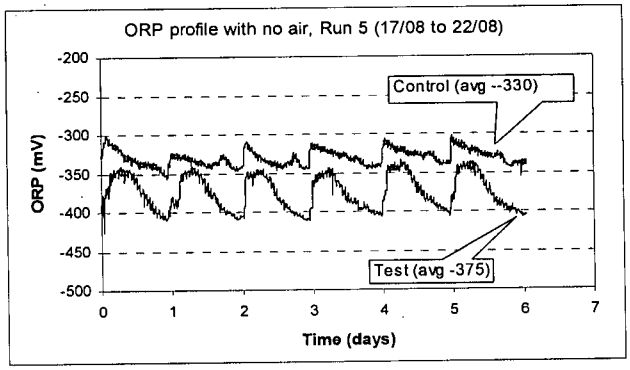


Figure 4.6 ORP profile Run 5

From Figure 4.1 and the R squared value, it is evident that there is a strong relationship between aeration rates and ORP in the ATAD units, at the pilot plant. The lower the aeration rate, the lower is the redox potential. The saw-tooth pattern is a phenomenon that happens whenever there is batch feeding; this happens because of utilization of substrates whenever new feed is added to the tank. At the same time, the ORP drops whenever wasting is completed.

4.1.2 Temperature

The profiles of the temperatures, in all the runs, are shown in Figures 4.7 to 4.11. The temperature was consistently in the lower optimum thermophillic range (over 45°C). The effect of the exterior temperature was very evident in Run 3 (Figure 4.8), when and the interior temperature in the trailer dropped. Temperature was also very dependent on the feeding cycle and the wasting cycle. The same saw tooth pattern, similar to the ORP profiles, was also demonstrated. There was also a drop in the temperature every day when the temperature dropped during the night. This might be due to imperfect insulation or lowering of the temperature of the feed. The temperatures in both the tanks were monitored on line, readings were taken every 10 seconds and averaged every 5 minutes.

There was a constant difference of 1°C (average) between the control and the Test ATAD units in Runs 2 through to Run 5, the maximum being 1.6 (Run 5) and minimum being 0.3 (Run 1). The probes were interchanged to determine if the probes were faulty

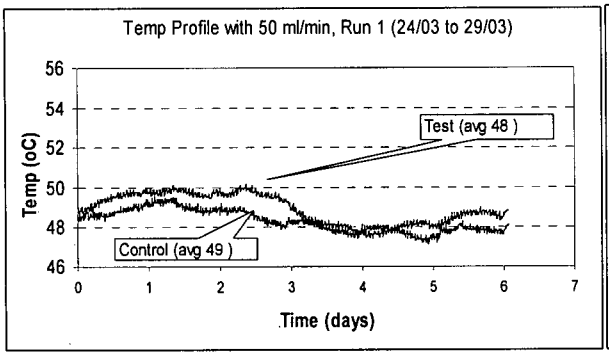


Figure 4.7 Temperature profile Run 1

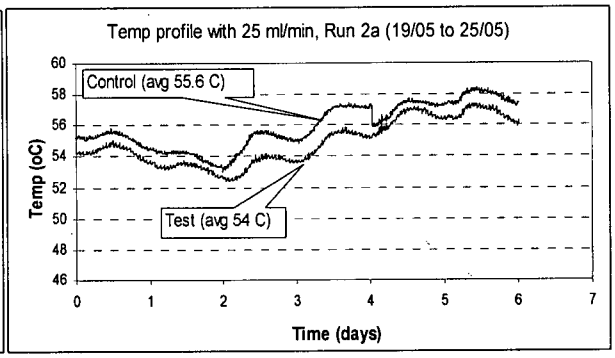


Figure 4.8 Temperature profile Run 2a

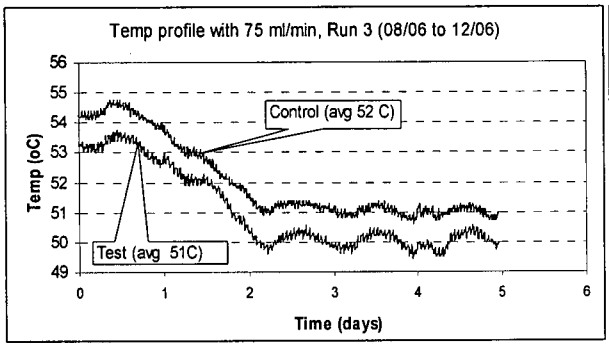


Figure 4.9 Temperature profile Run 3

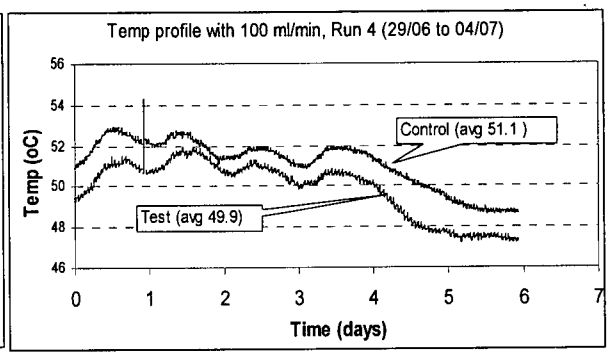


Figure 4.10 Temperature profile Run 4

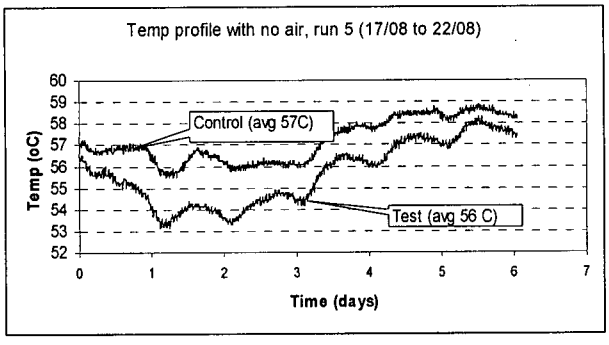


Figure 4.11 Temperature profile Run 5

but the same results were obtained. This difference was evident throughout all these runs and is shown in Table 4.2. The probable reason for this might be the different configuration of each unit. Fothergill (1995), also reported this phenomenon in her work, using the same ATAD system. However, this temperature difference was not very prominent, although it was noticed when the aeration rates in both the tanks were the same (Run 1). Initially, during the second run it was thought that the temperature changed with the aeration rate; however this was ruled out since the temperature was consistently higher in the control tank, regardless of the aeration rate. Therefore, the probable cause was the configuration of the Turburator™ disc. Since these units were over designed for a tank of that size, any small physical variation could have been the reason behind it. This difference could have been rectified by adjusting the rpm of the Turburator™; however, this would have resulted in more shear in the test tank or lowering the temperature in the control tank. Therefore, this adjustment was not done and the rpm reading was kept the same for both tanks.

Aeration rates	**Test**		**Control**		**Difference**
	Average	Std Dev	Average	Std Dev	
0 ml/min	55.6	1.44	57.2	1.00	1.6
25 ml/min	54.9	1.42	55.9	1.44	1.0
50 ml/min	48.2	0.76	48.5	0.56	0.3
75 ml/min	51.0	1.34	52.0	1.33	1.0
100 ml/min	49.9	1.43	51.1	1.23	1.2

Table 4.2 Averaged ATAD Temperature

There was a drop of 4°C over a period of 2 days in Run 3. The weather during this run was quite warm and so it cannot be attributed to this factor. The cause for this drop might have been a lower concentration of primary sludge in the feed mixture. Other

pilot scale studies had demonstrated that lower temperatures are attained only when secondary sludge is fed, instead of a mixture of primary and secondary sludge (Trim & McGlashan, 1984). The primary sludge pump, from the primary clarifier to the primary sludge thickener, had clogged overnight, and as a result, there was a buildup of solids in the clarifier (that was later pumped into the thickener). However, the feed was already made up and this could have resulted in uneven solids concentration in the feed. This effect could have effected the process for 2 days, since it is evident that the temperature leveled off by the 3rd day.

There was another decrease in the temperature during Run 4 towards the end of the run. The probable cause for this, could have been a lower concentration of secondary solids in the feed, which might have happened for two separate reasons. Firstly, there was a leak in the sludge return pump on one side of the process; as a result, solids were lost overnight. Moreover, there was a heavy rain event overnight, thereby decreasing the overall temperature of the plant and the feed.

4.1.3 Turburator™ speed

The speeds in both the tanks were maintained at the same rpm throughout the entire experimental period, to eliminate any effect of the rpm on the production of VFA or temperature. The average rpm for the Test tank was 952 and that of the control was 942.

4.1.4 Solids

Total solids were done for the feed and the ATAD effluent everyday in duplicate. The complete data sheet for the entire experimental period is shown in Appendix B. The solids for the rest of days are not shown. As mentioned earlier, the plant had to be shut down due to mechanical failure. The solids in the process were very low after the plant was fully operational. This is evident in the concentration in the feed sludge for Run 2. (The graphs for all the runs are shown in Figures 4.14 to 4.19.)

4.1.4.1 Feed Solids

The feed going into both tanks was the same mixture, originating in the mixing tank before being divided into the two feed tanks. The solids were analyzed only when the feed was made up during the daytime. The feed solids concentration was similar throughout all the runs except Run 3 (75 ml/min). The overall average feed solids was about 13.7 g/L., the lowest being 10.9 g/L during Run 3 (Table 4.3). This can be seen from Figure 4.12, where it is evident that the feed solids were fairly consistent (except Run 3). The solids for the first run (Run 2*), after the start up of the plant, is shown in Figure 4.15. The feed concentration was less then 10 g/l (average 9.1 g/l) throughout this entire experimental run. This resulted in lower heat production and generation of VFA. The average temperature in both the tanks was less then 45°C and the ORP profile was also very erratic (+75 to –300 mV). This indicated that low solids concentration could

indeed affect the operation of ATAD, where the whole process is, to a large extent, dependent on high solids concentration.

	Run 5	Run 2*	Run 2a	Run 1	Run 3	Run 4
	0 ml/min	25 ml/min	25 ml/min	50 ml/min	75 ml/min	100 ml/min
Test	11.30	7.21	11.50	11.45	8.74	11.21
Control	11.50	7.20	11.04	11.91	9.39	11.80
Feed	14.30	9.13	14.14	14.43	10.90	14.52

Table 4.3. Averaged TSS (g/L) for all experimental runs.

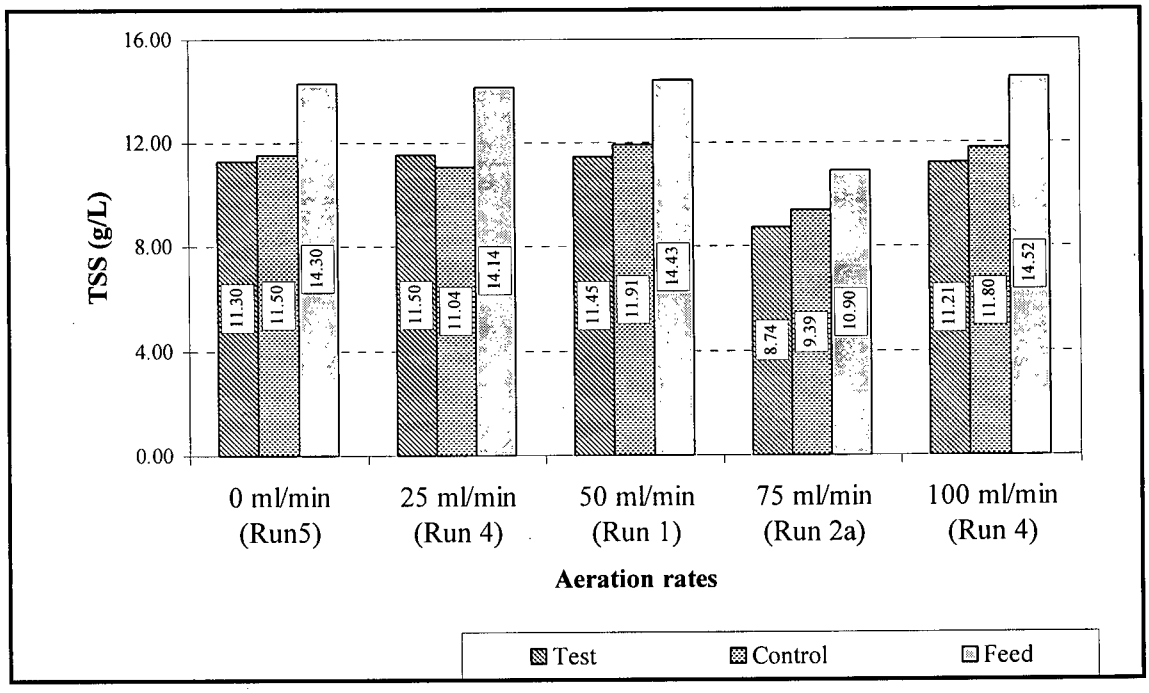


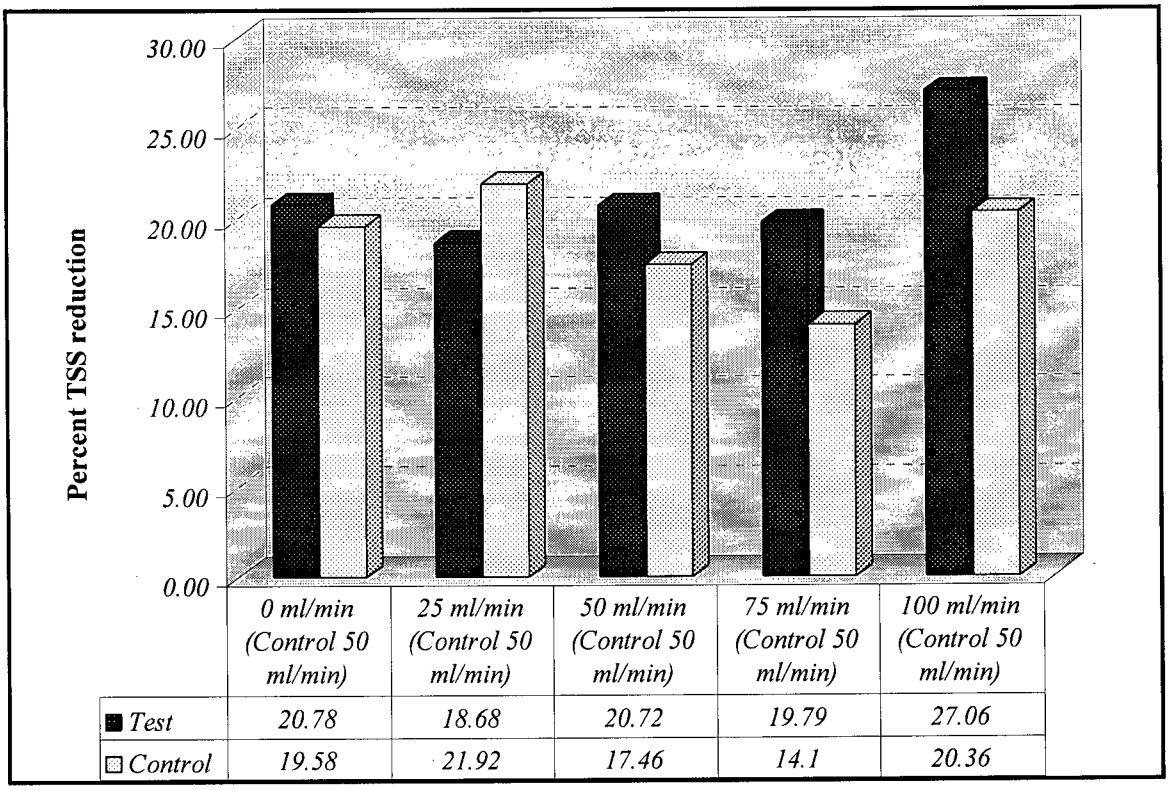
Figure 4.12 Average Total Suspended Solids in all ATAD runs and feed

Total solids variability is normal in full-scale plants, but it does affect performance and destruction efficiency (Kelly et al., 1993). However, TSS is not a measure of the biodegradable portion of the sludge, although it has been assumed that 55% to 80% of TSS is biodegradable. This percentage is different from process to process and is very dependent on the source sewage. Since there is no grit removal or screening incorporated in the pilot plant, the percentage of biodegradable content in the primary sludge would be lower then the secondary sludge. After the startup of the plant, the MLSS in the process was not at its optimum level and therefore the mixture of 35:65 primary/secondary feed contained comparatively less biodegradable material. Since the VFA production during Run 2 was very erratic and the solids concentration was also low, it is evident that solids concentration definitely affected VFA production.

4.1.4.2 Solids Destruction

The solids destruction efficiencies for all the experimental runs are shown in Figure 4.13. in a tabular and graphical form. There was a range of destruction efficiencies in the test ATAD, between 18% and 27%. There was also a change in the solids destruction in the control tank (average of 18%), although the aeration rate was the same throughout the entire period. Since these tanks were both run at 50ml/min (Run 1), the expectation was that the destruction efficiency would be similar. However, it was found that there was a difference of 3% (average) in the solids destruction. Previous researchers who used these same units (Chu, 1995 and Fothergill, 1995) also reported this

difference. Again Figures 4.14 to 4.19 show all the TSS data for all runs for the feed, test and control reactors.



	0 ml/min (Control 50 ml/min)	25 ml/min (Control 50 ml/min)	50 ml/min (Control 50 ml/min)	75 ml/min (Control 50 ml/min)	100 ml/min (Control 50 ml/min)
Test	20.78	18.68	20.72	19.79	27.06
Control	19.58	21.92	17.46	14.1	20.36

Figure 4.13 Averaged Solids destruction efficiencies at different aeration rates

From the results, it is evident that the solids destruction in the test ATAD was somewhat greater then the control tank, except in Run 2a. There was no apparent relationship between the aeration rate and the destruction efficiency. The maximum reduction of solids in the test ATAD was 27%, when the airflow rate was 100 ml/min. As discussed earlier, the percentage of biodegradable content in the TS is much higher and therefore the above values indicate a much higher reduction of volatile solids. In full-scale plants, the VS (volatile solids) destruction ranges between 35-45% when a mixture of primary and secondary sludge is used with a retention time of 6 days (Deeney, 1991). From actual reported values, a range of 35 – 66% VSS has been demonstrated for mixed feed sludge. These values are representative of a two stage ATAD treatment unit and Deeney also generalizes that 60% of VS destruction occurs in the first reactor. Since the tanks in this work are more representative of the first stage, of a minimum two-stage system, comparison to the first stage is more appropriate.

In full-scale plants with an initial feed concentration averaging between 30 to 40%, the total suspended solids (TSS) destruction ranges between 35-40%. In comparison to other pilot scale studies, where low initial feed solids tend to additionally reduce ATAD efficiency, destruction efficiencies were similar to this work. Chu (1995) reported 8-20% reduction when he used primary sludge as his feed and Boulanger (1995) achieved 20% reduction with a 44/56 sludge mix ratio. In his work, Trim (1984) reported 27% reduction when using a 50/50 mix ratio. Boulanger (1995) demonstrated that increasing aeration rates to increase dissolved oxygen levels did not effect destruction efficiency. In this work, the destruction efficiencies are within the same range reported

by previous researchers. The average percent reduction of TSS in the four runs (excluding Run3), in the control tank, with constant aeration rates of 50 ml/min, was about 20%.

There is a significant increase in the TSS reduction (at 27%) in the run with 100 ml/min. The low destruction rate in Run 3 is self explanatory, because of the lower concentration of solids in the initial feed. To better understand the effect of aeration rate in the destruction of solids, the operating conditions in the process should be the same and constant as much as possible. To negate the effect of the physical configuration of the ATAD tanks, parallel experiments should be done, at least for a few experimental runs to determine what is the magnitude of this effect. This can later be incorporated in all the results and a more accurate picture can be attained. Moreover, measurements of TS, VS and biodegradable VS on both feed and effluent is necessary for accurate assessment of solids destruction. This variation can also be controlled, if the primary sludge is screened, thereby increasing the biodegradable percentage in the feed and maintaining better consistency (which, in turn, increases the VS destruction).

From the results shown in this work, it is not evident that there is a pattern in the rate of solids reduction at aeration rates approaching 0 (no) air. There was no significant variation in the reduction rates at the lower rates. But, again, the apparent difference in the two reactors must be eliminated before any definite conclusions can be made about the effect of aeration rates on solids destruction.

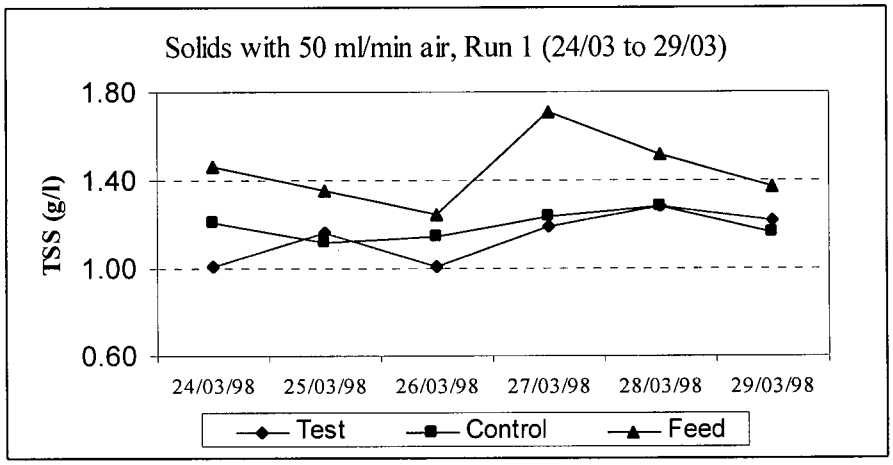


Figure 4.14 Solids in Run 1 (50 ml/min)

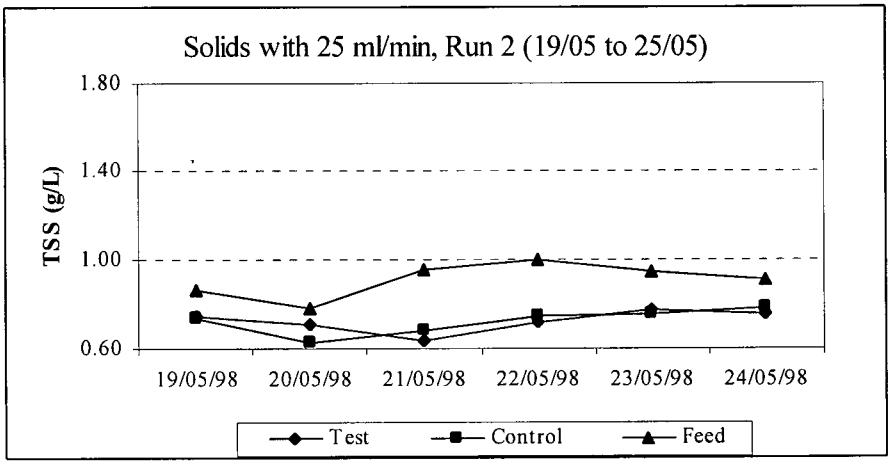


Figure 4.15 Solids in Run 2 (25 ml/min)

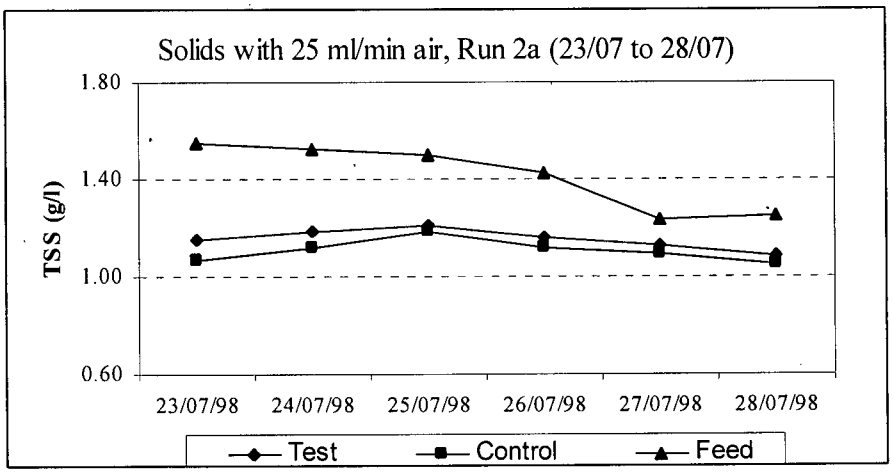


Figure 4.16 Solids in Run 2a (25 ml/min)

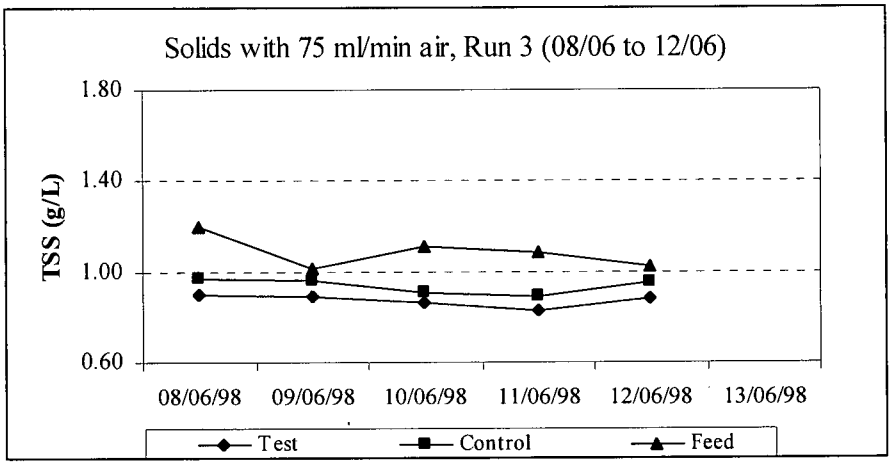


Figure 4.17 Solids in Run 3 (75 ml/min)

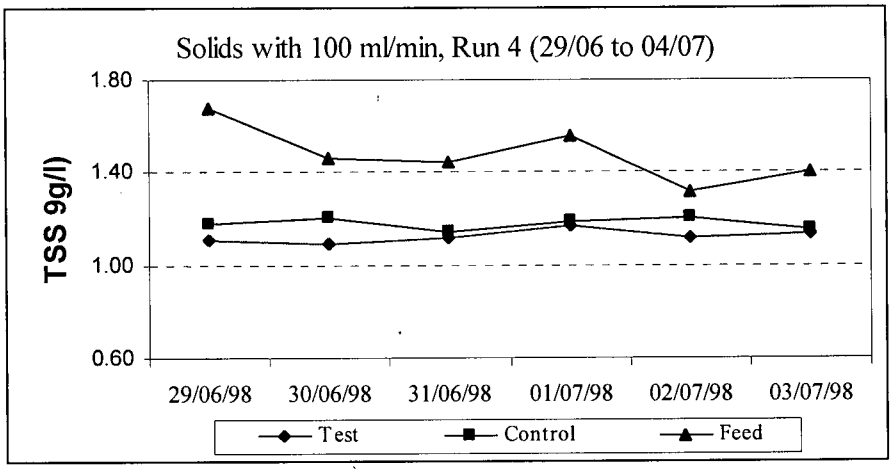


Figure 4.18 Solids in Run 4 (100 ml/min)

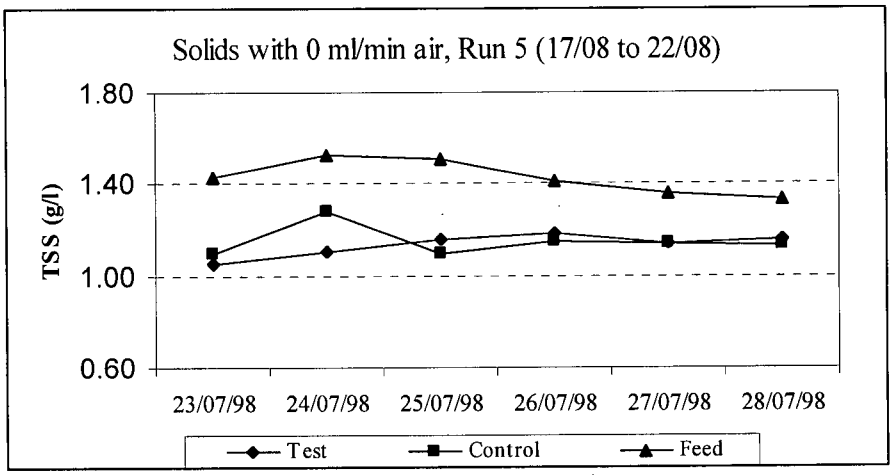


Figure 4.19 Solids in Run 5 (0 ml/min)

4.1.5 pH

The pH of the ATAD reactors remained between neutral and slightly acidic during the entire experimental period, indicating fairly stable operation. A temperature correction was applied to the effluent pH, since the pH was measured right after it was wasted from the tanks, when the temperature was higher then the calibrated temperature for the probe. The averaged values for all the runs are shown in Table 4.4. The pH in the raw sewage was maintained by addition of sodium bicarbonate in the main holding tanks.

Run	Aeration rate	Test	Control	Feed	Raw sewage
5	**0 ml/min**	7.05	6.92	6.11	6.01
2a	**25 ml/min**	6.99	6.85	6.02	5.98
1	**50 ml/min**	6.93	6.78	5.88	5.85
3	**75 ml/min**	6.65	6.68	5.60	5.60
4	**100 ml/min**	6.77	6.82	6.11	6.00

Table 4.4 Averaged pH for all runs

Deeney (1991) reported pH values for feed and ATAD sludge of 6.5 and 7.2 respectively, in full-scale operations. Previous researchers, using the same plant facility, at UBC reported values of 7.0 with a mixture of 44/56 and 35/65, primary/secondary (Boulanger, 1995; Fothergill, 1996). In his research, Chu (1995) reported that aeration rate did effect the pH. He observed that pH decreases with the aeration rate when the ATAD units were run with primary sludge. He also suggested that there is a point where available oxygen is limited and a drop in pH is attributed to VFA accumulation. ATAD is inherently stable with respect to pH, primarily because of the inhibition of nitrification; at the same time, any weak acid (acetic acid) or base (NH_4OH) may act as a buffer

(Kelly, 1990). In addition the production of CO_2 increases the buffering capacity and thereby increases the alkalinity. It is assumed that the pH rises rapidly during the first 3 to 5 hours, followed by a slow decrease over the remaining holding time in the feed tanks (Knezevic, 1993)

The pH was recorded at 24 hour intervals and, therefore, the increase in the feed pH during the storage period was not recorded nor was the rate of decrease. Moreover, the pH of the raw sewage was recorded twice every week and the average of those values are presented here. The results in this experiment demonstrated a slight increase in the pH during lower aeration rates. The slight difference that is recorded in this work is not significant, since the correction applied to the pH was not always accurate(due to the rapid cooling of the effluent when the pH was being read). The drop in temperature was quite rapid and the recorded temperature might not have been the exact temperature inside the ATAD unit; as a result, a slight misreading of the temperature might have resulted in a greater variation of the pH. The measurement of the pH in the feed was also hampered by the presence of more solids, which sometimes covered the probe and resulted in minor interference in the reading. In Run 3, it is seen that the pH was quite low in all the sampling points, due to the missed addition of Na_2CO_3 for a few days, after the startup of the plant.

4.1.6 VFA

In all experimental runs, VFA (reported as acetic acid) was detected in the ATAD tanks. There was also VFA present in the feed. VFA was analyzed for ATAD effluent, feed sludge and waste supernatant. The results of the waste supernatant were of minor importance compared to the VFA produced in the ATAD and those present in the feed sludge. The waste supernatant was selected as a sampling point to see if there was any production of VFA in the treatment process and to ascertain the contribution of the secondary sludge to the VFA concentration in the feed. The sampling was carried out on the clear supernatant that was available after the secondary sludge was allowed to settle for 45 minutes. The VFA from this source was less then 7 mg/L throughout the experimental period and therefore, are not discussed in any detail. Therefore, it was evident that the VFA in the feed was mainly due to the primary sludge. Fothergill (1996), reported that the average feed VFA was 8 mg/L when secondary sludge was used. From her work, it was clear that secondary sludge diluted the VFA concentration in the feed, but enhanced VFA production in the ATAD.

4.1.6.1 Feed VFA

The differences in the VFA present in the feed streams are illustrated in Figure 4.20 and summarized in Table 4.5. The concentrations of VFA in all the runs (except Run 1 and 5)are similar (fall in the same range). The feed VFA in the Run 1 (50 ml/min) was very high compared to the other 5 runs, the main reason being that, during Run 1, the feed was

stored in a mixing tank from one day in advance. As a result, when sampling was carried out the next day there was already a high concentration of VFA, due to pre-fermentation of the sludge in the tank (where it was mixed at a very slow rate to just keep it in suspension). The stored sludge was then pumped into the feed tanks from where the sampling was undertaken the next morning. This procedure was put in place, initially, to maintain a backup of feed sludge, in case of plant operational problems.

Run	Aeration rate	VFA (mg/L)
Run 5	0 ml/min	124
Run 2	25 ml/min	81
Run 2a	25 ml/min	89
Run 1	50 ml/min	270
Run 3	75 ml/min	98
Run 4	100 ml/min	106

Table 4.5 Averaged feed VFA in all the runs.

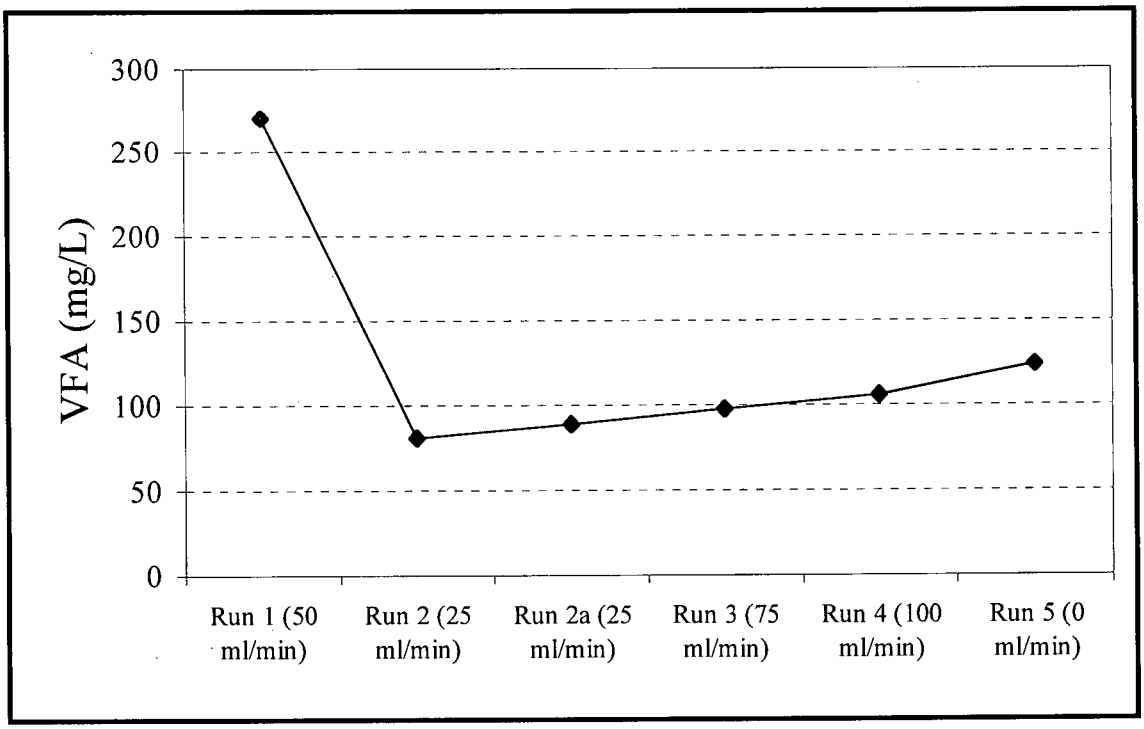


Figure 4.20 Averaged feed VFA in all runs (chronological order).

The variability of VFA in the feed on a day to day basis is shown in Figure 4.21. It is also seen that the VFA increased in the feed after Run 2, when the plant was restarted.

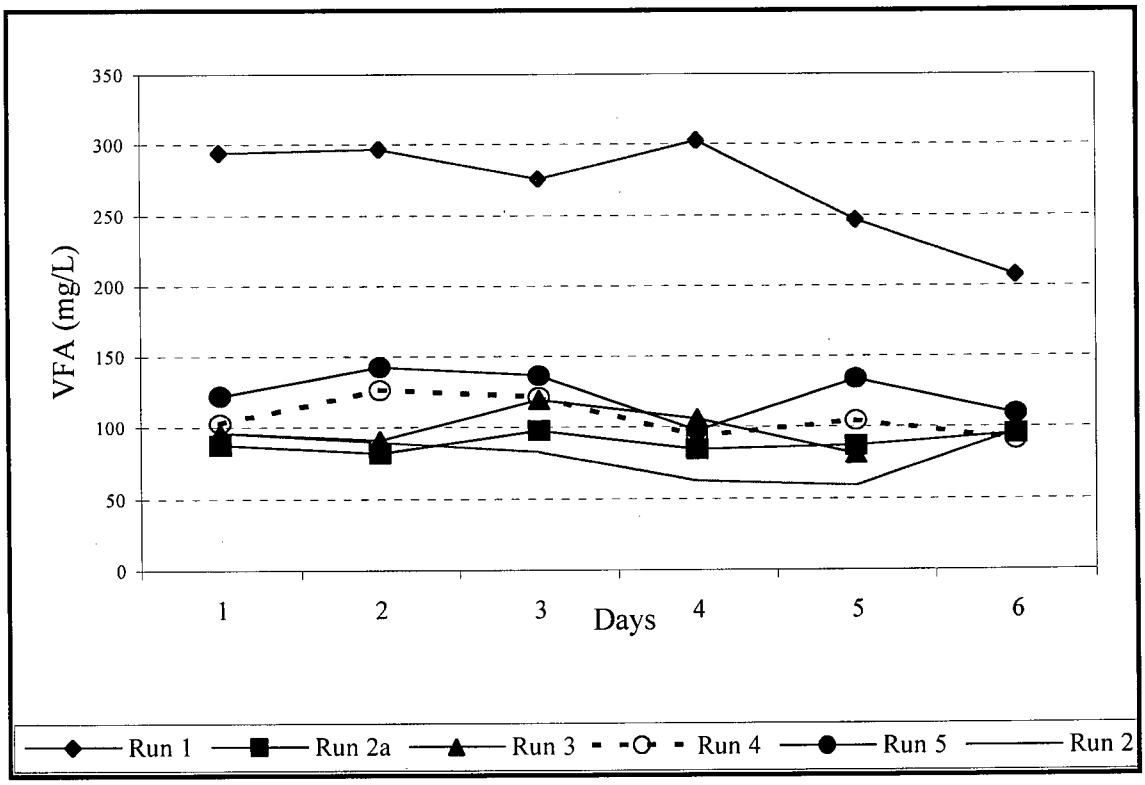


Figure 4.21 Variability of feed VFA in all runs.

During the first three runs, sampling was carried out twice at 12-hour intervals. The concentration of VFA was always higher at night, due to fermentation going on in the feed tanks. The values presented in the graphs are the averaged values of the two daily readings.

4.1.6.2 VFA in the ATAD units.

During the digestion of sludge, VFA was produced and consumed in a few instances. The accumulation of VFA in the test tank was greater as the aeration rate decreased and approached zero. The net production of VFA was the difference between the feed and the effluent. As discussed earlier, there is an inherent difference in the production of VFA between the control and the test tank. This was especially evident when the tests were done with 50ml/min of air flow. The highest net production of 530 mg/L was achieved in the test ATAD when 25 ml/min (Run 4) air was supplied. The maximum production in the control, of 550 mg/L, also occurred during the same run.

The net production profile of VFA in the control ATAD is shown in Figure 4.22. Figure 4.23 demonstrates the level of variation in the VFA production in the test tank. There was a large difference in the production of VFA from the control tank in all runs (all performed at an aeration rate of 50 ml./min). A comparison of production of VFA in both the test and the control units are shown in Figures 4.24 to 4.28.

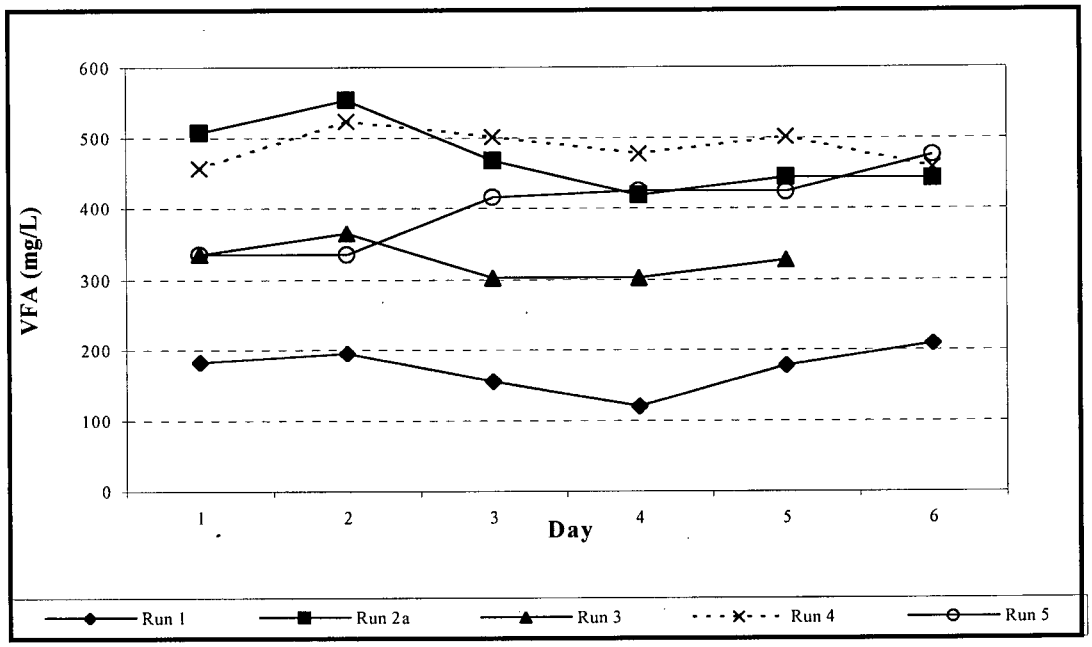


Figure 4.22 Net production on VFA in the control tank (airflow 50 ml/min)

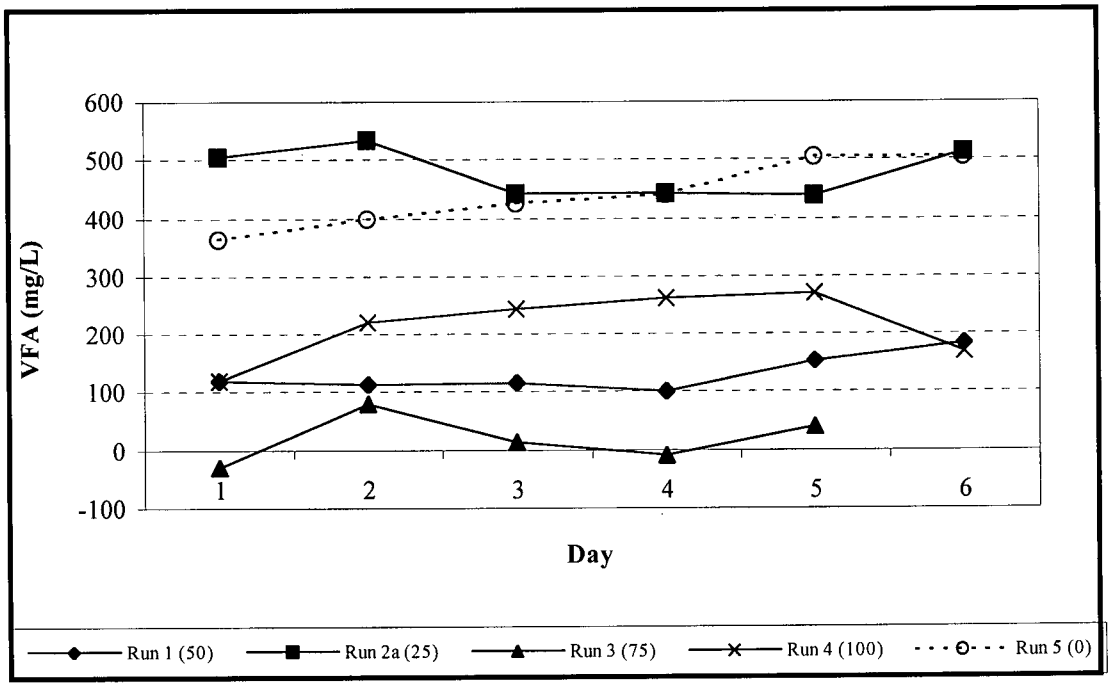


Figure 4.23 Net production of VFA in the test tank

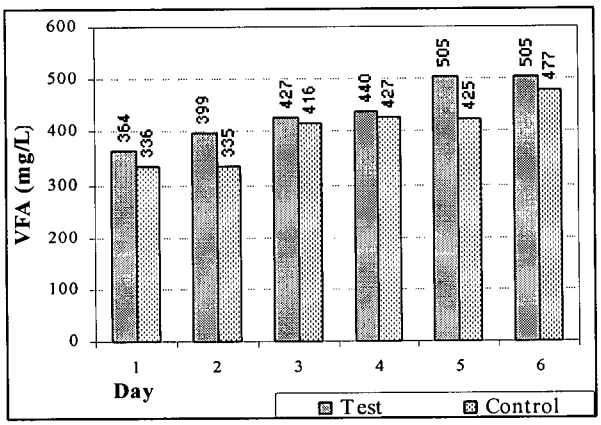


Figure 4.24 Net VFA production, Run 5

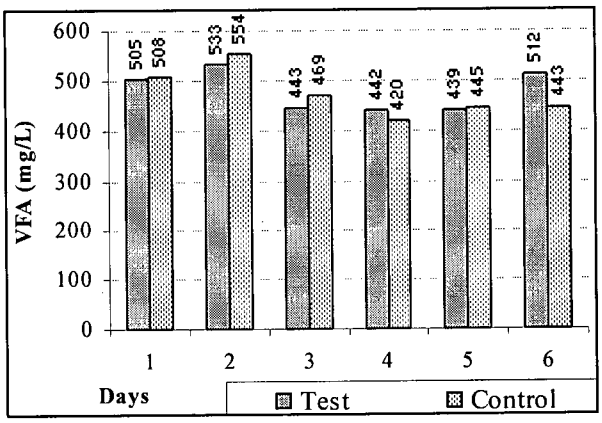


Figure 4.25 Net VFA production, Run 2a

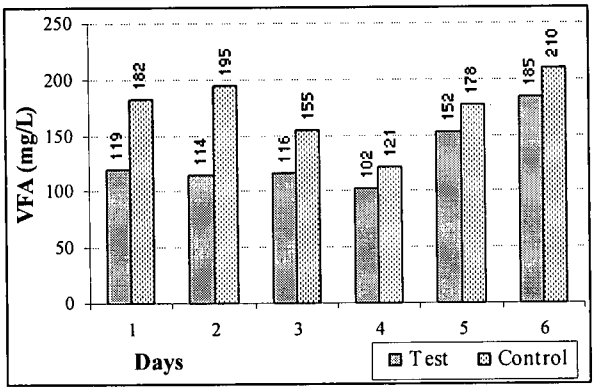


Figure 4.26 Net VFA production, Run 1

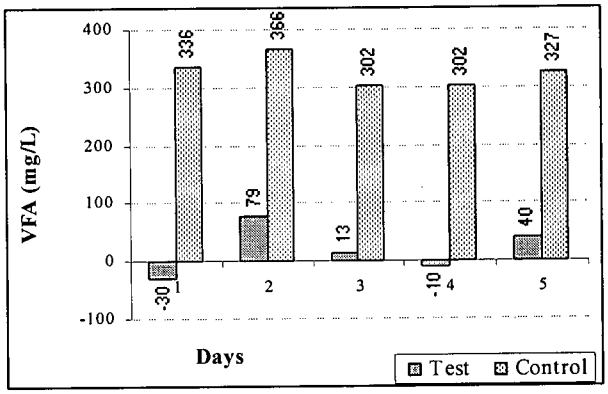


Figure 4.27 Net VFA production, Run 3

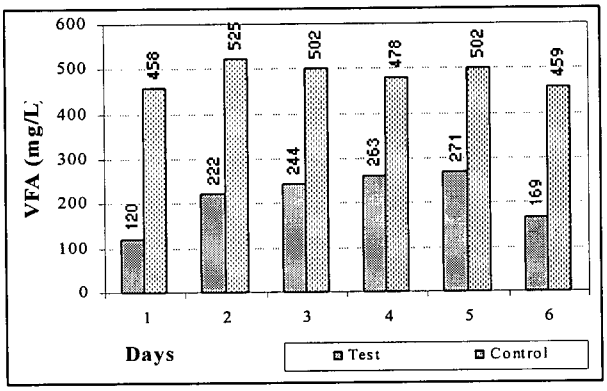


Figure 4.28 Net VFA production, Run 4

When comparing the net accumulation of VFA in the tanks, it is seen that the accumulation was maximum in both tanks during Run 4, when 25 ml/min of air was supplied. The term accumulation is used here because it is debatable whether the VFA are actually produced or released, due to lysis in the tanks (caused by high mixing in the tanks). Figure 4.29 shows the averaged accumulation of VFA in both the tanks for all the runs. To investigate this possibility further, a sonification test was done on the sludge and sewage collected from different sampling points. These results are discussed later in Section 4.1.6.3.

During the first three runs, sampling was undertaken every 12 hours, to develop a better understanding of the pattern of increase in VFA. While doing so, it was noticed that the accumulation of VFA in all the three sampling points, viz., test, control and feed showed an increase in the level of VFA present during the evening period. This increase was more evident in the feed sludge. However, for discussion purposes in this thesis, the averaged values were taken. As such, the average production during Run 1 would have been 224 mg/L, instead of 131 mg/L (which is used here) if only the morning values were taken for discussion purposes.

As noted earlier in Figure 4.12, the feed solids were constant at 1.4 %, except Run 2. Figure 4.30 shows the relationship between VFA production and solids destruction at the different aeration rates. There appears to be no relationship between solids destruction and the generation of VFA, with respect to aeration rates, in this research.

Moreover, the aeration rates did not affect the solids destruction, although the solids concentration in the feed did have a significant effect (as noted earlier).

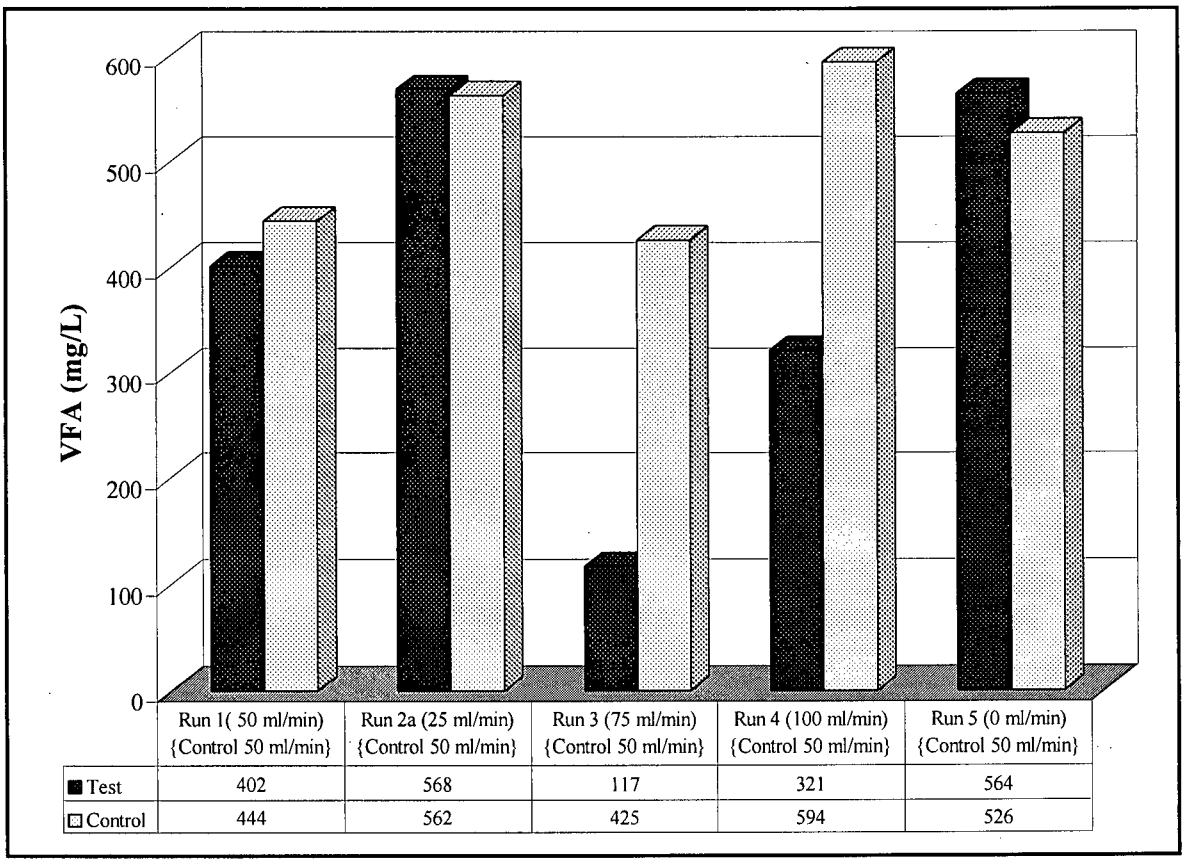


Figure 4.29 Averaged accumulation of VFA in all runs

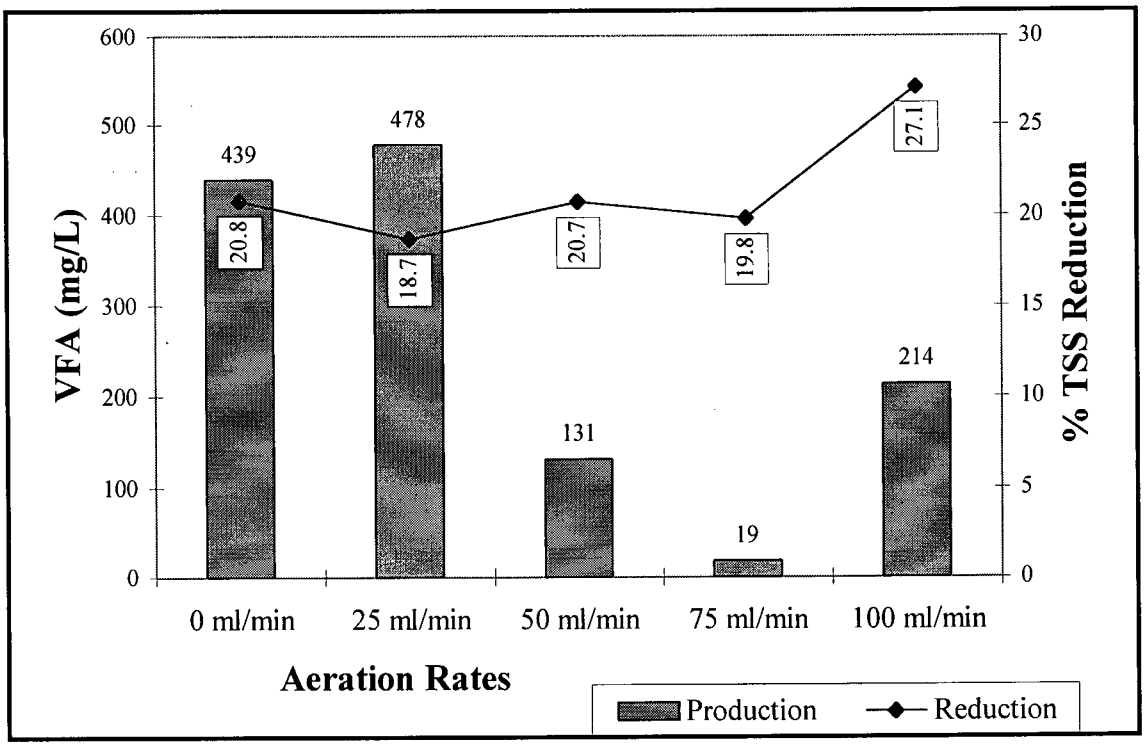


Figure 4.30 Relationship of VFA production to solids reduction.

4.1.6.2.1 VFA species

GC analysis was done for six lower chains of fatty acids. In the samples, acetic acid was the predominant species. The total value of VFA reported in the previous tables and graphs is the converted value of all the lower chains to acetic acid. The percentages of the different species present in the test tank at all the aeration rates are shown in Table 4.6.

	Acetic	Propionic	Iso-Butyric	Butyric	2-me butyric	3-me butyric	Valeric
0 ml/min	77.2	4.6	6.7	0.3	5.3	5.5	0.5
25 ml/min	76.2	3	6.7	0.6	5.7	7.5	0.3
50 ml/min	71.2	4	9.4	0.5	5.2	9.4	0.4
75 ml/min	91.9	0	4.5	0.2	1	0.5	2
100 ml/min	82.6	2.1	6.7	0.7	3.3	4.2	0.5

Table 4.6 Percentage of VFA species at different aeration rates.

In the feed, the average percentage of acetic acid was 66% and propionic acid was 27%, of the total VFA. From Table 4.6, it is evident, that there was a large consumption of propionic acid and conversion to acetic and lower chain fatty acids, at the expense of propionic acid. Total consumption of propionate occurred during Run 3 (75 ml/min). This also resulted in net consumption of VFA in the test tank.

Acetate production is a symptom of a change in the cellular physiological state. It is possible that the accumulation in the ATAD process is, at least, partially due to an inefficient coordination or uncoupling between the oxidative and non-oxidative systems (i.e. acetate overflow phenomenon), rather then simply due to pure fermentation (Chu,

1995). Fermentation of sludge generates an acetate to total VFA ratio of 40% (Rabinowitz, 1995). In previous research and findings of full-scale operational thermophillic aerobic digestion plants, it was reported that acetate percentage constituted 80-90% of the total VFA. The results obtained in this work are slightly less then reported values (which can be explained in part, by the inconsistent source sludge and low solids concentration in the feed). No distinct relationship was evident between the consumption of propionic acid and the different aeration rates.

The ratio of acetate to propionate is shown in Figure 4.31. The maximum difference between the ratio of acetic to propionic acid in the feed (average 2.2) to that in

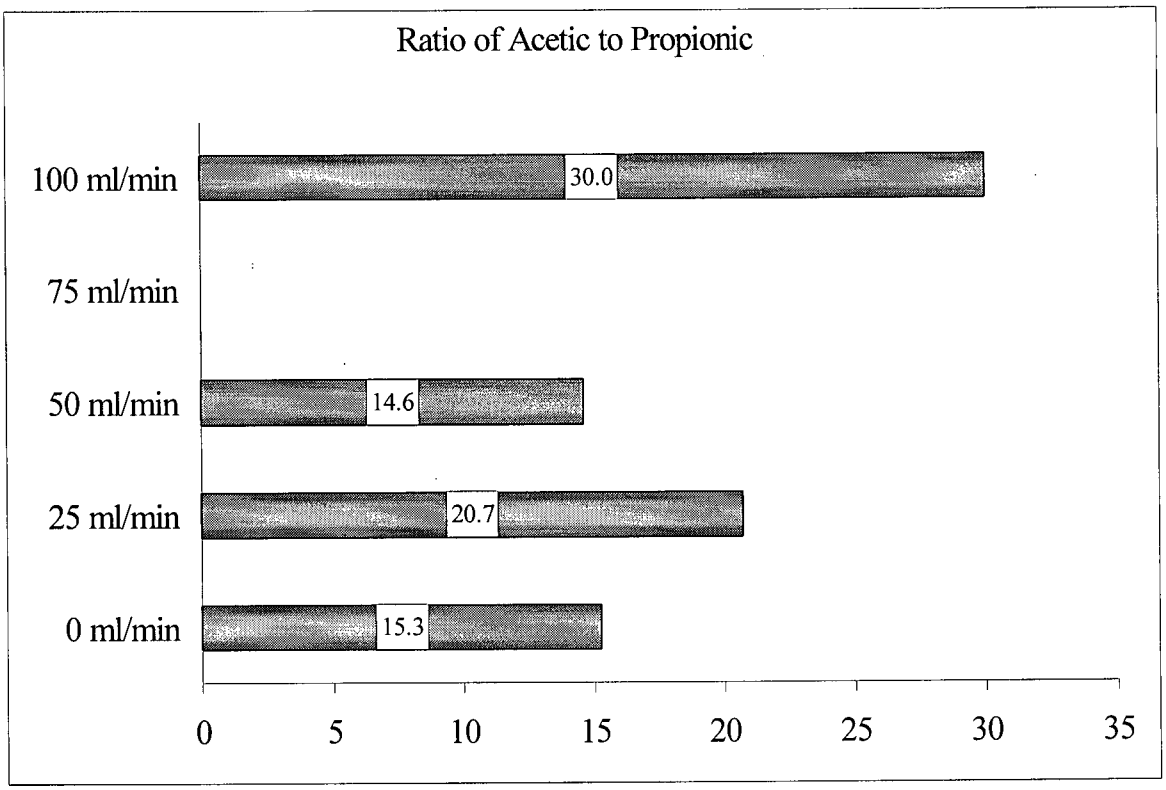


Figure 4.31 Ratio of concentration of acetic to propionic with respect to aeration rates.

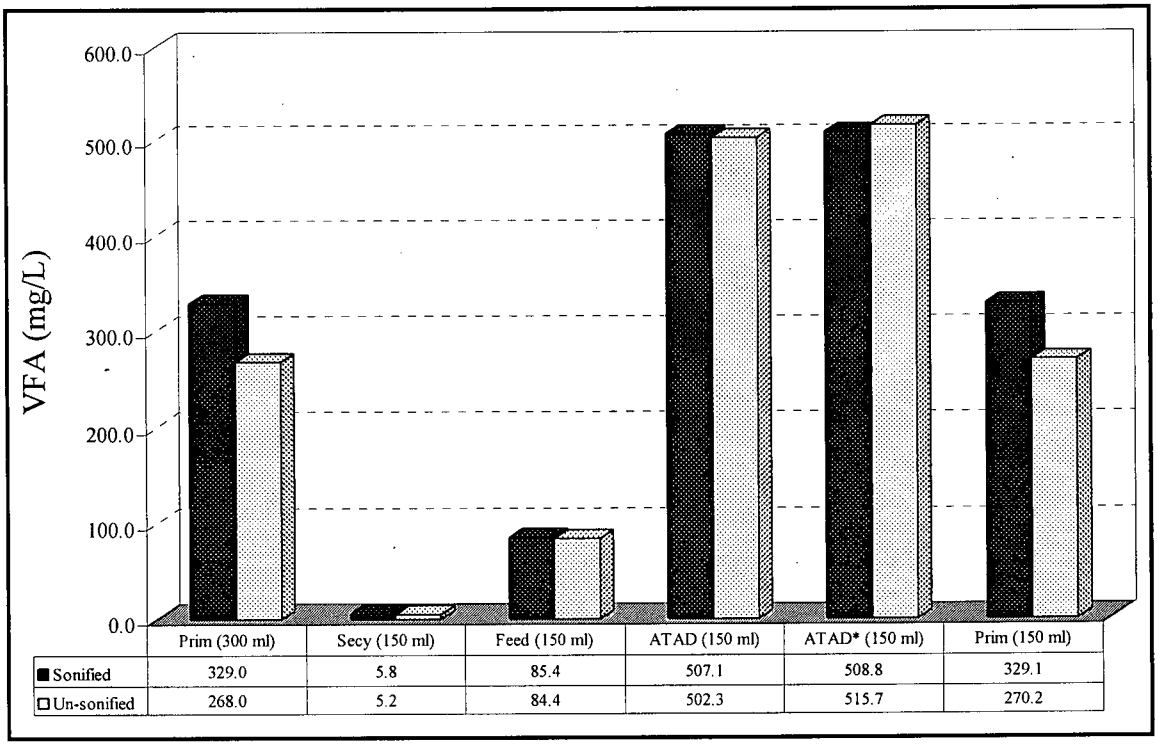
the ATAD effluent, occurred when the air supplied was 100 ml/min, with the ratio in the test being 30. This effect of an increase in the acetate percentage could also account for the sequential utilization of VFA, and is consistent with known biochemical properties of pure cultures of bacteria.

4.1.6.3 Sonification

To determine the possible source of generation of VFA in the ATAD tanks, a sonification test was done. The results are shown in Figure 4.32. Sonification was carried out for primary sludge, thickened secondary sludge, ATAD effluent and stored ATAD effluent (ATAD*). The rationale for doing this test reflected the concern, that due to the high mixing power input into the tanks, there was possible disruption of cellular matter inside the tanks, thus resulting in a premature release of VFA. This test was done after the VFA optimization phase was over. As discussed before, the ATAD effluent was stored for the second part of this project. Sonification was done in a Fisher scientific Disembrator (Model 300). A large probe (calibration 60) was used. This was the maximum size available. Sample volumes of 150 ml each were sonified 5 times each, in a time sequence of 1 minute off and 1 minute on. This was done in order to prevent overheating of the probe.

When sonified, the VFA in the primary sludge (using 2 different sample volumes) increased significantly, demonstrating that sonification did result in the release of VFA from the bacterial bio-mass (which was torn apart because of the high frequency being

applied). There was no such evident change in the VFA concentration in the feed and ATAD effluent. Therefore, it is clear that there was, indeed production, instead of just release, of VFA in these thermophillic digesters.



	Prim (300 ml)	Secy (150 ml)	Feed (150 ml)	ATAD (150 ml)	ATAD* (150 ml)	Prim (150 ml)
■ Sonified	329.0	5.8	85.4	507.1	508.8	329.1
□ Un-sonified	268.0	5.2	84.4	502.3	515.7	270.2

Figure 4.32 VFA before and after sonification

There was no contribution of VFA from the secondary sludge, even after sonification. It is speculated that the nature of solids in the primary sludge was the prime cause of the easy disruption of the cellular material. More research in this area is recommended, to fully understand this phenomenon.

4.1.7 Nutrients (phosphorus and nitrogen)

Along with the generation and release of VFA in the ATAD process, there is also the release of nutrients from digesting the biomass. Boulanger (1995) reported that when a phosphorus-rich, waste activated sludge from a Biological Nutrient Removal (BNR) process was digested with thickened primary sludge in an ATAD, most of the stored phosphorus was released into the solution form. About 79% of phosphorus was released when the ATAD was run in oxygen-deprived conditions during her work. The results from this research support the conclusions from that previous work. One purpose of producing VFA in ATAD is for recycle and possible use in the BNR process. However, in the process of producing VFA, there is also the release of phosphorus, which is not desirable for the overall treatment process. To make the most out of the recycle concept, the ratio between VFA and phosphorus should be as high as possible.

4.1.7.1 Phosphorus (total and Ortho)

Since phosphorus is a conservative element, total phosphorus (TP) levels were almost the same in the ATAD effluent and the feed. Prior to the experimental period, ortho-P (PO_4-P) was being added to the anaerobic zones of both the sides, of the BNR process for ongoing research in the main UBC pilot plant. This was done to ensure that ortho-P (PO_4-P) was left in the process effluent, thereby providing insight into the full capacity of the process for phosphorus removal. Adhering to the experimental design of that project, it was decided to double the ortho-P entering the process by adding 3.0 mg/L

soluble phosphorus, as mono-sodium phosphate (NaH_2PO_4 H_20), to the anaerobic zones of both sides of the BNR process and continue the P addition throughout the ATAD research program. This resulted in higher concentration of P in the feed, since all of the phosphorus was stored in the secondary sludge. Figure 3.4 shows the different sampling points for TP and PO_4.

Most of the variations in the feed concentration was due to the variations in the secondary sludge solids concentration. During Run 1, the PO_4-P concentration in the feed was quite high, due to the accumulation of ortho-P in the secondary sludge. Ortho-P was present in lower concentrations after the start-up of the plant. This resulted in a lower concentration of P in the feed during Run 3. Moreover, as the secondary sludge was mixed from both the sides of the process, a slight upset in one side could also result in a deviation in the feed P concentration. During Run 3, the recycle lines on both sides of the process were interchanged to mix the MLSS of the process. However, because of uneven flow, there was an accumulation of solids on one side and none on the other. This resulted in uneven distribution of P. Fothergill (1995) demonstrated that P concentration increased with the addition of secondary sludge.

There was no relationship between the aeration rate and the release of P in the ATAD. The maximum release of phosphorus occurred during run 5 in both the tanks. The lowest release of P occurred during Run 3, which can be explained by the low concentration in the feed. Table 4.7 summarises the average ortho-P (PO_4-P) concentration in the feed and the ATAD units in all the runs. Dissolved phosphorus

fractions in the ATAD units were much higher then in the influent mixed sludge. Boulanger (1995) implied that more phosphorus will be released in an oxygen deprived condition than in an oxygen excess condition, and the release will be minimum in an oxygen satisfied condition. However, in this research, the difference was not evident in the micro-aeration variations.

	0 ml/min	25 ml/min	50 ml/min	75 ml/min	100 ml/min
Test	124.5	101.23	89.98	79.21	85.11
Control	127.4	105.33	87.39	75.45	94.92
Feed	30.4	42.36	33.97	19.25	25.45

Table 4.7 Averaged PO_4 (mg/L -P) in all runs.

The ratios of the VFA to the PO_4-P concentration at the different aeration rates are illustrated in Figure 4.33.

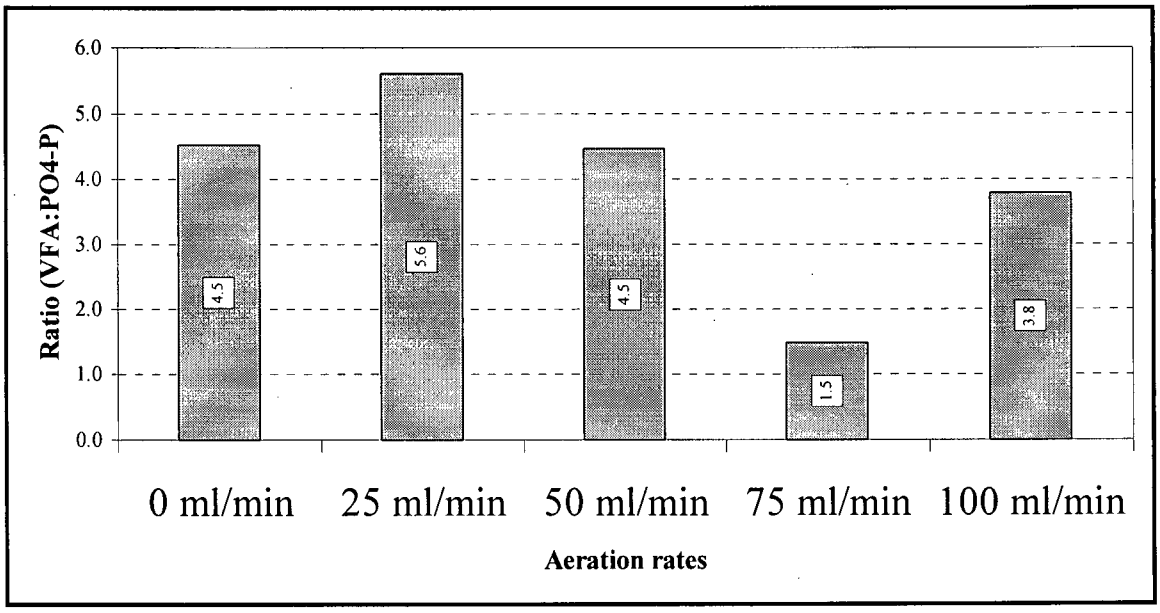


Figure 4.33 Ratio of VFA to PO_4

The maximum ratio was recorded during Run 2a, when the air supply was 25 ml/min. Although the release of PO_4-P was low in Run 3, the ratio was also low due to the lower concentration of VFA. The higher release of P during run 5 (0 air) resulted in a lower ratio of VFA: PO_4-P. The release of phosphorous seemed to be more dependent on the feed characteristics; this is evident from the near identical release of P from both the control and the test ATAD units in all the runs.

There was some fluctuation in the concentration of TP in the feed sludge and the ATAD effluent, as well. This was mainly attributed to sampling and analytical error, (because of the nature of the feed and ATAD effluent, where the solids concentration was not homogenous). The fraction of dissolved phosphorus was, on an average, 43% of the TP. This falls within the lower 50-70% range that Popel (1994) identified as the amount of TP in Bio-P sludge, which is contained in poly-P storage. This suggests that most of the poly-P phosphorus was released during ATAD digestion. Table 4.8 shows the amount of TP and PO_4 in all the runs.

	0 ml/min	**25 ml/min**	**50 ml/min**	**75 ml/min**	**100 ml/min**
Test	233	200	181	156	229
Control	246	234	177	172	291
Feed	303	202	194	206	210
% PO_4-P	41.1	50.1	46.3	38.4	40.5

Table 4.8 Averaged TP (mg/L) for all aeration rates.

The percentage of PO_4-P to TP (calculated as {PO_4-P/TP X 100%}) was maximum during Run 2a, when the aeration rate was 25 ml/min. The concentration in

the secondary sludge was the main contributor to the TP in the feed with an average of 350 mg/L. The data for all nutrients are shown in Appendix D.

4.1.7.2 Nitrogen (Nitrate, TKN and Ammonia)

TKN was quite high in the feed, as well as the ATAD effluent. It was generally conserved between the feed and the effluent. Less then complete conservation and recorded increases in the TKN values could have been a result of sampling and analytical errors. Nitrate levels were constantly lower than 2 mg/L, indicating that nitrification was inhibited by the thermophilic temperatures maintained throughout the experimental period.

Ammonia-N has been demonstrated to accumulate under an oxygen limited environment in ATAD (Mason, 1987 b). In this research, ammonia-N levels were monitored intermittently in the ATAD effluent during the first phase, since it was of importance in the second phase. Since it was not recorded on a regular basis, the results are not discussed here. When stored ATAD effluent was sampled, the concentration of NH_4-N was, on an average, 150 mg/L.

4.2 Phosphorus removal

Attempt was made to remove the soluble phosphorus from the ATAD effluent. This was done, by incorporating the Crystallizer that was previously discussed in Section 3.7. As mentioned earlier in the same section, there were two parts in this phase. Initially synthetic feed was used and then finally ATAD effluent was put through the system. The results are discussed accordingly

Removal of phosphorous and ammonia occurred in all the runs, both with the synthetic sewage and ATAD effluent, at different levels. Samples were taken at the influent and the final effluent points and analyzed for PO_4-P and NH_4-N. pH was monitored continuously at the top of the Crystallizer. The schematic is shown in Figure 3.5.

4.2.1 Synthetic sewage

It was noticed in all runs that, the time taken for maximum removal of phosphorus was, on an average, 60 minutes, after which it reached equilibrium. However, removal on a lower scale was evident immediately; in fact, the first sample that was collected in most runs (except Run 5, when the pH was low), demonstrated some removal. Previous researchers reported that MAP formation took place within a very short period of time if the conditions were right. Sasai et.al. (1995) reported that reaction was conducted within 15 minutes. Other researchers (Kuba, 1997) reported removal at less then 3 minutes.

The solubility of MAP decreases as the pH increases and so the pH of system should be maintained above pH 8 for efficient removal. Borgerding, (1972) and the results of this work demonstrated the same results in his published works. The pH value of the tap water used in the UBC study, was usually between 5.10 to 5.85; therefore it had to be increased to the desired level by using NaOH.

The individual graphs for all the runs, demonstrating the pattern of reduction are shown in Figure 4.34 to 4.41. In all runs, the sewage was made up and the chemicals had to be added at the appropriate molar ratio. The difficulty that was experienced, while doing this, was the addition of Mg. Since there was no conductivity meter available, the control was purely left to the theoretical calculations. There were 9 runs that were undertaken with water. During Run 1, the pH control was not consistent and, as a result, the removal percentage is not very accurate. As discussed earlier, the pH control was done by the addition of NaOH and this was done by injecting the chemical, using a Masterflex pump. During Run 1, the concentration of OH^- radicals was very high and whenever a drop was introduced into the Crystallizer, the pH of the system increased and decreased in "jumps". For these reasons the results from this run are not discussed here.

The concentration of phosphorus in the influent also plays an important role in the removal percentages; the higher the concentration, the better is the removal. Table 4.9 shows the influent concentration, effluent concentration and the removal percentage after 60 minutes. Figure 4.42 demonstrates this graphically.

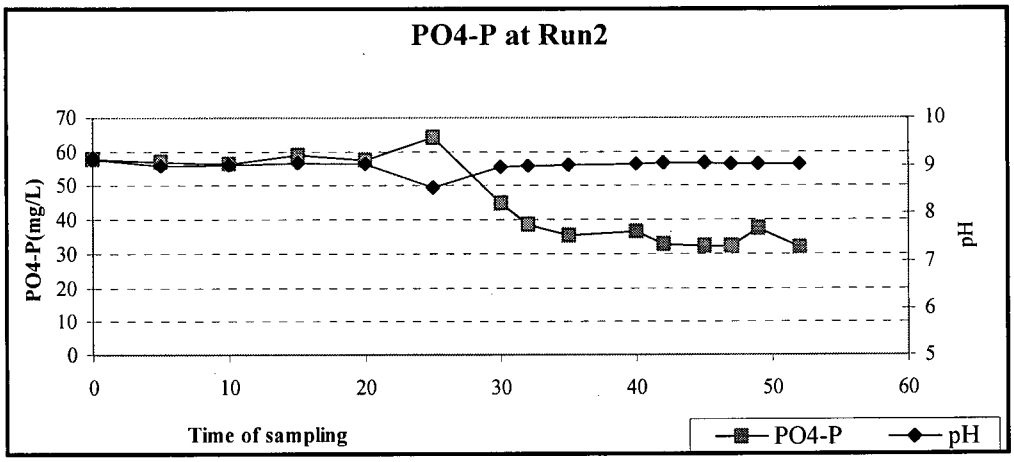


Figure 4.34 PO_4-P in Run 2

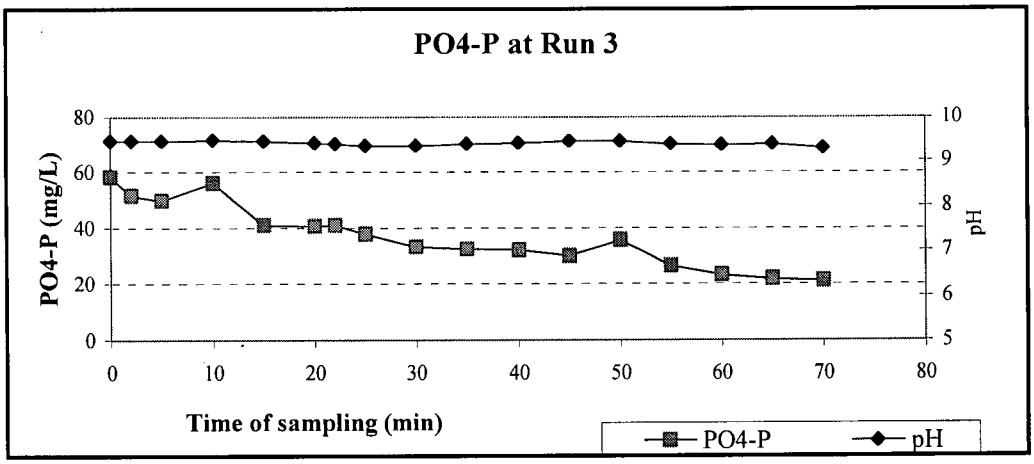


Figure 4.35 PO_4-P in Run 3

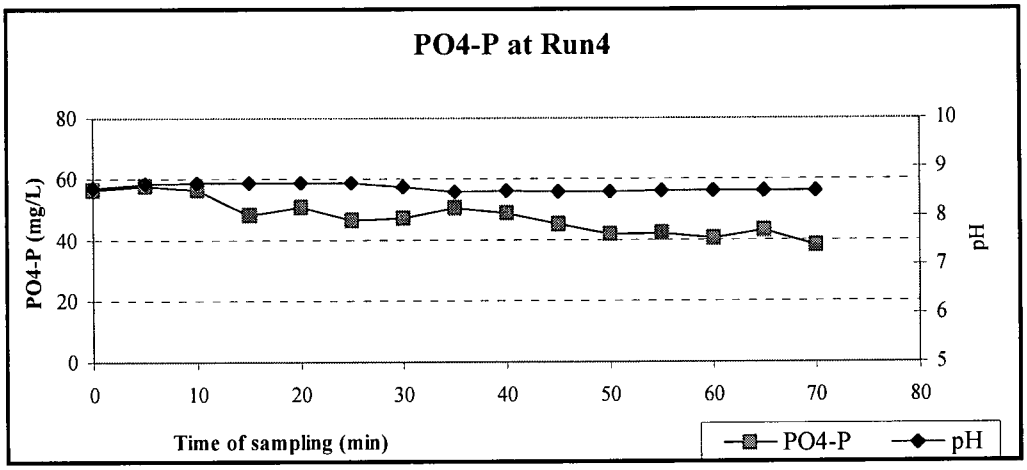


Figure 4.36 PO_4-P in Run 4

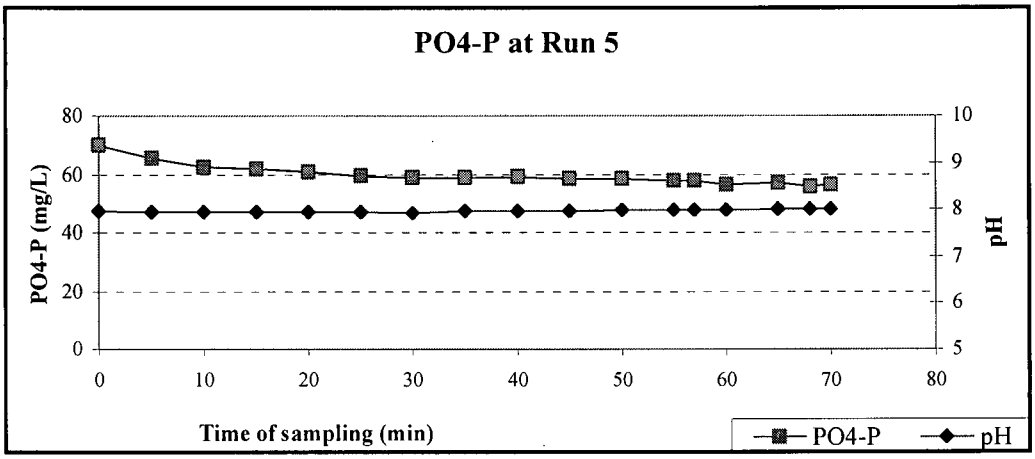


Figure 4.37 PO_4-P in Run 5

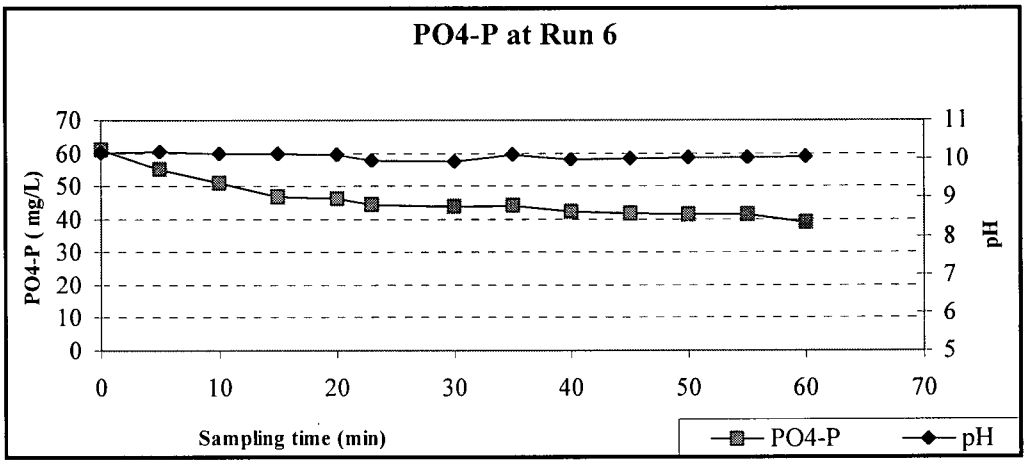


Figure 4.38 PO_4-P in Run 6

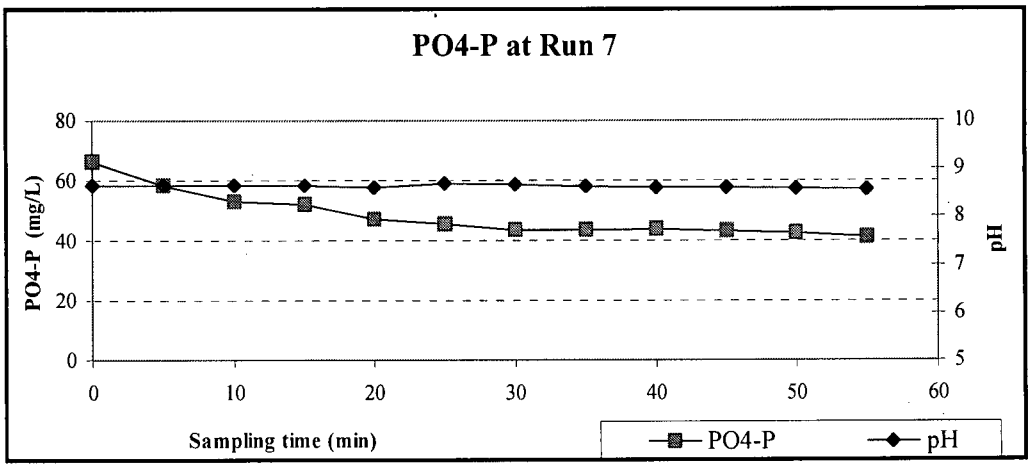


Figure 4.39 PO_4-P in run 7

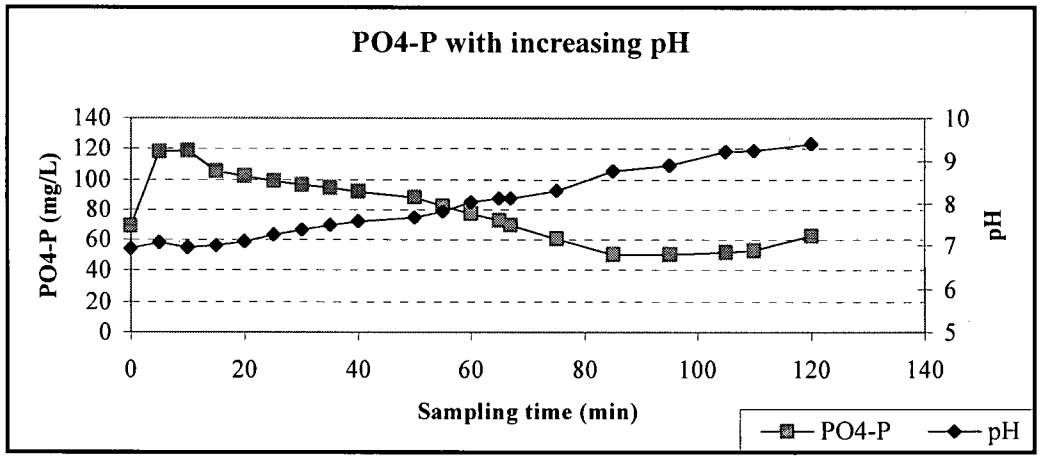


Figure 4.40 PO_4-P with increasing pH

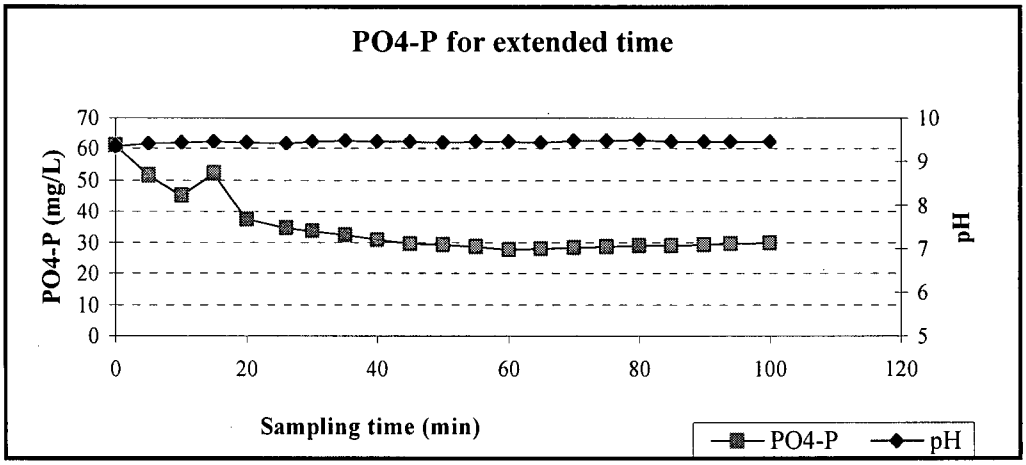


Figure 4.41 PO_4-P over 100 minutes

Run	pH	% removal	Influent
		PO_4-P	PO_4-P (mg/L)
5	7.98	13.0	64.89
4	8.51	37.1	64.77
7	8.6	55.3	88.56
2	9.04	53.7	69.26
3	9.3	65.4	60.64
9	9.45	56.2	63.29
6	10.06	43.2	68.89

Table 4.9 PO_4 removal at different pH

In a study done on dewatering filtrate of an anaerobic digestion process, Abe (1995) reported the phosphate removal efficiency to be higher then 80%, when the concentration of influent was higher then 100 mg/L and lower then 75%, when the concentration was less. However, this study was done without the incorporation of sand as the nucleating media.

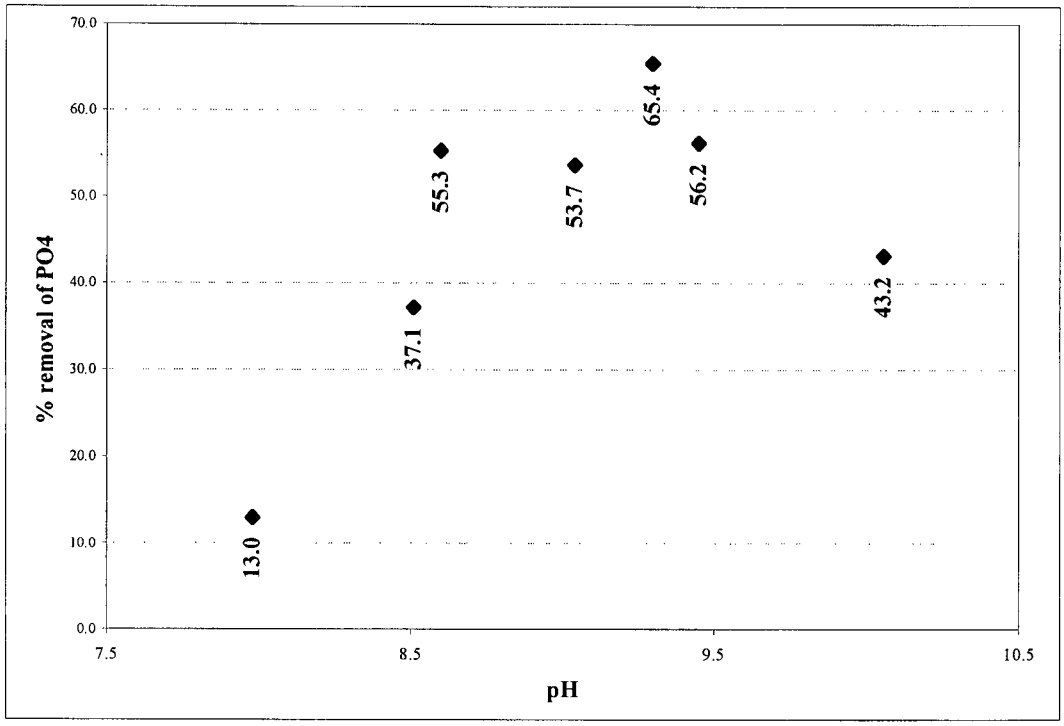


Figure 4.42 Removal percentage of phosphorus at different pH, after 60 minutes

The highest removal percentage of 65.4 % was seen during Run 3, when the pH was 9.3. The Mg was added in all the runs after the pH had reached a stable state, after which sampling was done. The expected concentration of PO_4 in the ATAD effluent was the reason for choosing the concentration in the synthetic feed; although theoretically, the concentration should have been about 100 mg/L, the resultant concentration in the feed was always less the expected. This might have been due to an incorrect dilution factor, since the feed was made from a stock solution. Moreover, it is always preferable to maintain a higher concentration of NH_4-N in the feed. Sasai et.al. (1995) reported that the phosphate phosphorus (PO_4-P) and ammonium nitrogen (NH_4-N) were reduced from 105 to 15 mg/L and 289 to 249 mg/L, respectively. In his work, it was found that molar NH_4-N removal mole was equivalent to that of PO_4-P.

There was no observed *significant* increase in the size of the sand particles in the Crystallizer, although it was agreed upon by myself and Fred Koch (Research associate at the pilot plant), that the colour of the sand particles had indeed changed to a dirty brown colour. Moreover, the particles at the bottom of the column were significantly bigger then the particles at the top of the column. This could have been caused by accumulation of phosphorus. During all the runs, the effluent turned milky white after 15 minutes (approx.). This coincides with a drop in the PO_4 concentration in the effluent. Since there are numerous types of MAP, with different solubility products, the milky white substance could have been a type which did not adhere to the sand particles. After the final effluent was allowed to settle for a few hours, the precipitate settled to form a white layer in the storage tank. Due to lack of time and resources, it was not possible to do any analysis on this precipitate to find out the purity and concentration of phosphorus.

4.2.2 ATAD effluent

Table 4.10 and Figure 4.43 show the removal of PO_4-P when using ATAD effluent in the Crystallizer. 3 runs were done at different solids concentration. Phosphate was spiked in the first 2 runs to increase the P concentration.

Solids	Sample Time (min)										
	0	5	10	15	20	25	30	35	40	45	Influent
Solid 135 mg/L	101.7	95.6	94.7	86.2	72.5	68.2	65.8	52.2	44.2	36.0	105.0
Solids 230 mg/L	126.5	108.0	92.1	96.2	85.4	87.5	66.0	61.0	52.0	50.0	123.0
Solids 430 mg/L	96.2	95.6	73.2	74.2	68.5	56.7	53.2	50.3	48.3	54.1	105

Table 4.10 PO_4-P in effluent at different solids concentration

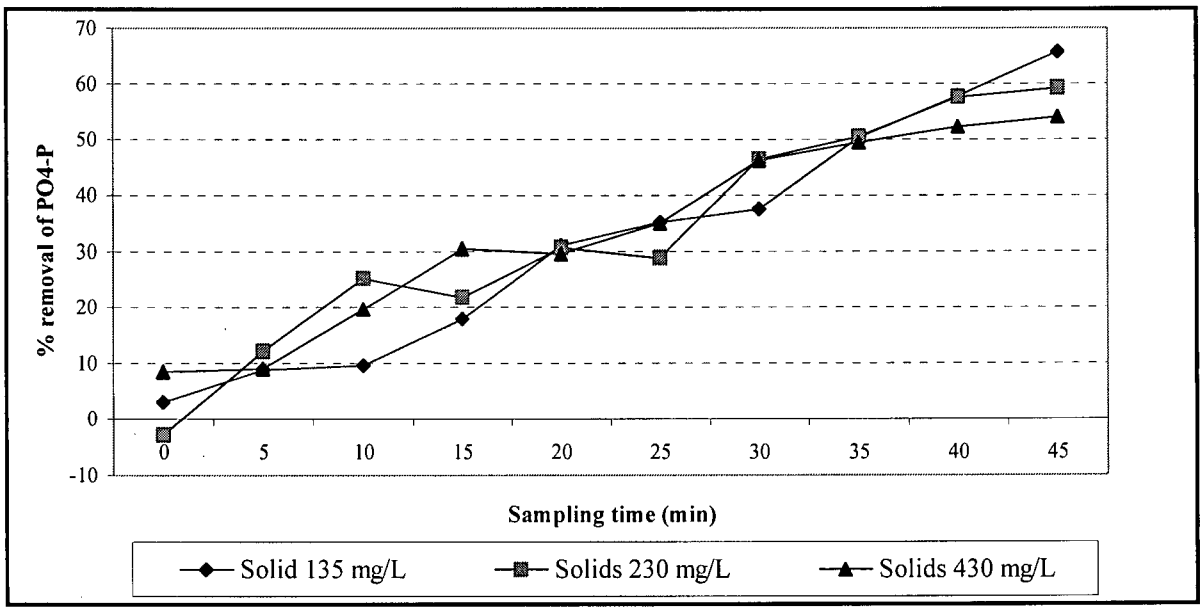


Figure 4.43 Percent removal of PO_4-P

There appears to be no significant difference in phosphorus removal levels with respect to initial solids concentration. High removal percentages were demonstrated at all solids

levels. As was the case with synthetic sewage, there was removal on a lower scale when Mg was added. Due to shortage of ATAD effluent, the runs could be extended to only 45 minutes. From the earlier section (Figure 4.34 and 4.35) it is evident the maximum removal occurs after 60 minutes. Figure 4.37 shows an increasing trend in the removal of PO_4 even after 45 minutes. Figures 4.44 to 4.46 demonstrates the effect of pH on the removal.

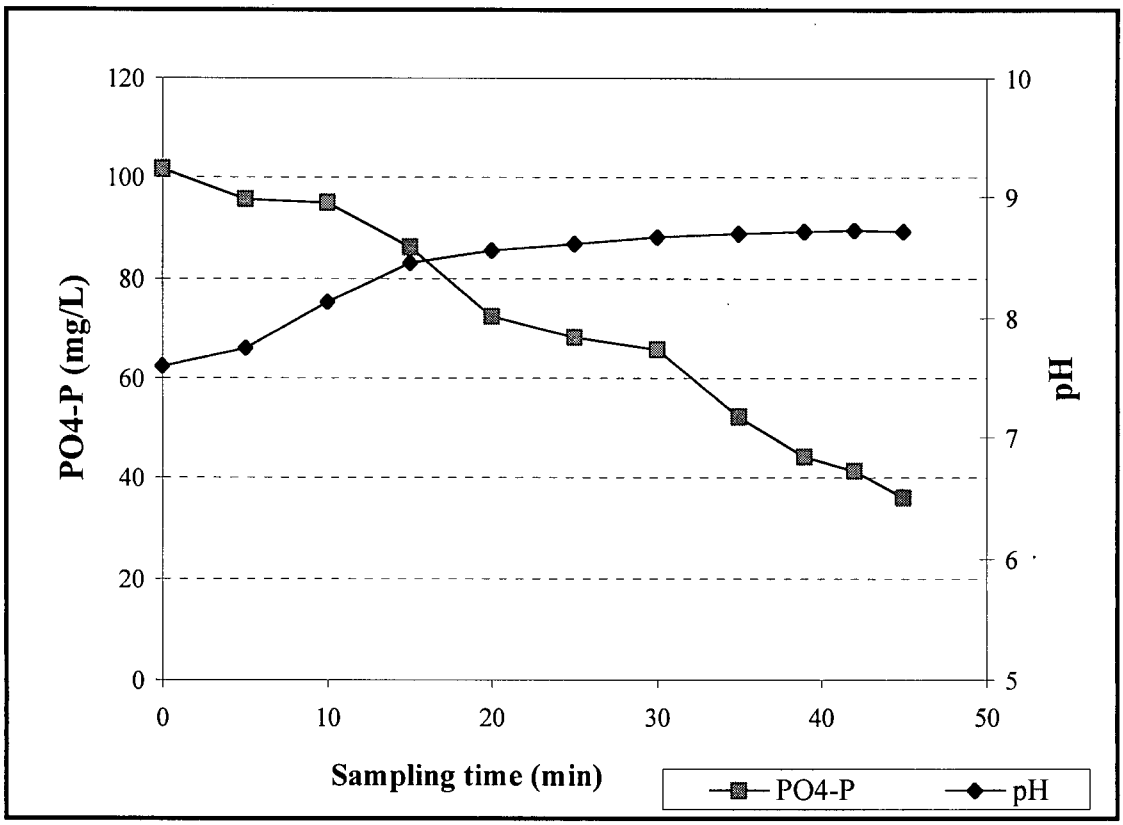


Figure 4.44 PO_4 removal, Run 1, with 135 mg/L solids level (diluted 1:4)

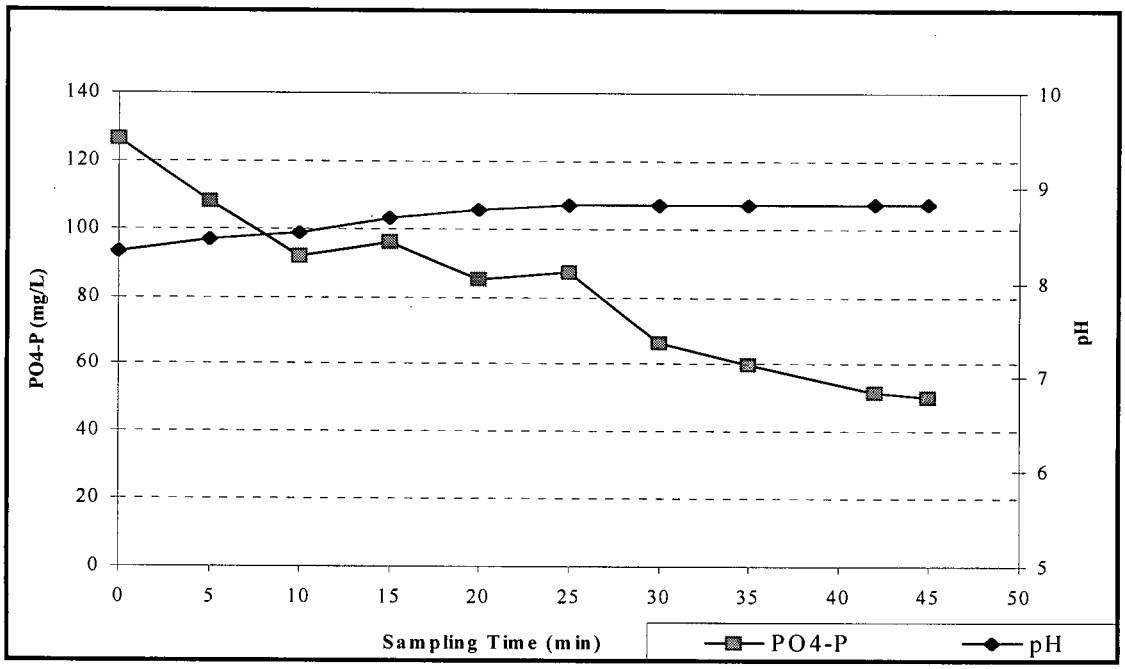


Figure 4.45 PO_4 removal, Run 2, with 230 mg/L solids level (diluted 1:2)

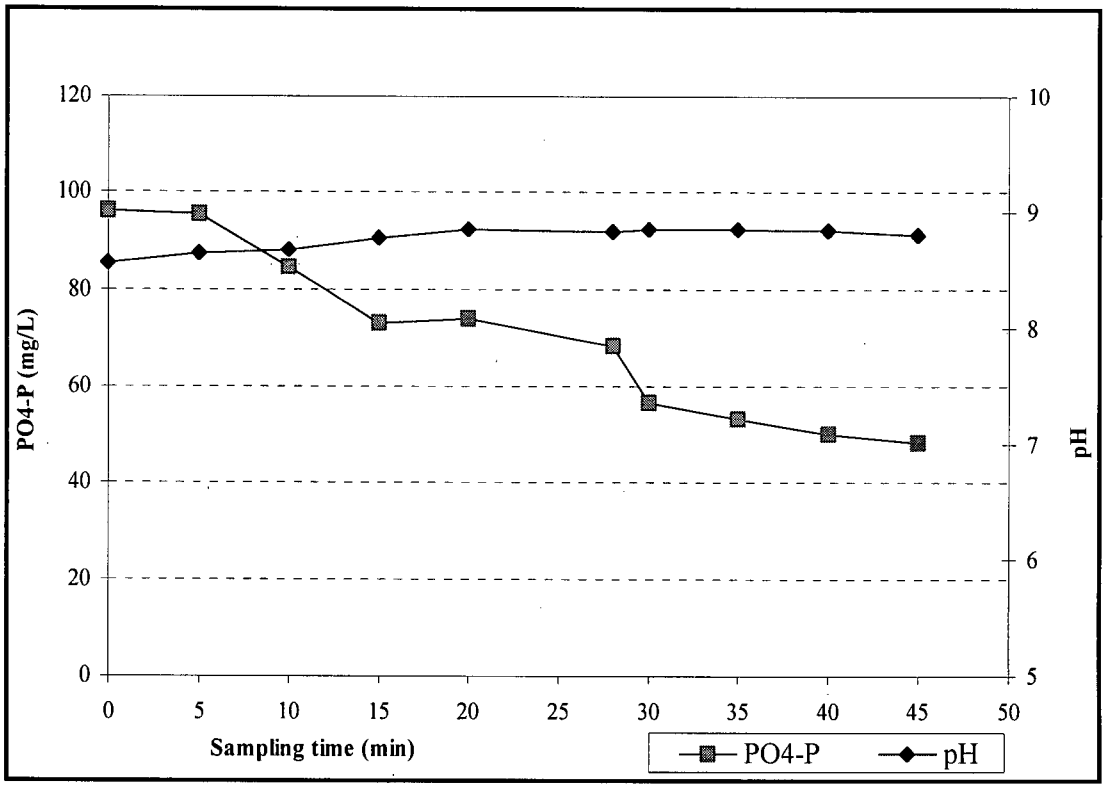


Figure 4.46 PO_4 removal, Run 3, with 430 mg/L solids level (undiluted)

From these figures and database, it is evident that the pH affects the removal rate. There is a sharp decrease in the concentration of phosphorus in the effluent, at the point, when the pH increases above 8. This is evident in all the 3 runs. Samples were taken for total solids in each run in triplicates. In Run 1(ATAD), water was added to 5L of ATAD effluent and no stock for ammonia-N was added.

The concentration of ammonia in the ATAD supernatant was enough to produce struvite. The average concentration of NH_4-N was 56 mg/L, 98 mg/L and 206 mg/L in Run 1 (dilution 1:4), Run 2 (dilution 1:2) and Run 3 (undiluted ATAD effluent). This was much higher then the average NH_4-N concentration when the Crystallizer was run with synthetic sewage. The influent concentration was 34 mg/L (averaged) in all the runs with water.

VFA samples were also taken of the influent and the a few effluent samples. The VFA concentration in the influent was 500 mg/L (see Figure 4.32). The results shown in the sonification test are representative of the concentration in the influent. Based on these results, it can be concluded that the removal of phosphorus along with the reduction of solids, from the ATAD effluent, and the high concentration of VFA in the Crystallizer effluent, presents a picture where it would be beneficial for the Bio-P process as well.

The sand, which would be struvite coated, can be extracted automatically from the column and used as a slow release fertilizer. This can be done once the sand or nucleating

media has grown in sufficient diameter. The column could be configured to allow removal of the particles from the bottom, where the largest particles will be present. In previous studies (Sasai, 1995), where the struvite was removed without a sand bed, the self forming struvite particles grew up to 1 mm in diameter. This size also reflects the expected size of the phosphorus rich sand particles, when they are finally removed and applied as a fertilizer. Taking into consideration all the potential beneficial qualities of the Crystallizer, it would be worthwhile to do further research with respect to ATAD effluent.

Chapter 5

Summary and Conclusions

5.1 VFA optimization - Summary

This research consisted of batch operations that were conducted at the UBC ATAD pilot plant, and consisted of two units. Tests were done with 35/65 mixed feed (35% primary and 65% thickened secondary sludge) at preset micro-aeration rates of 25 ml/min, 50 ml/min, 75 ml/min, 100 ml/min and no air (nitrogen had to be supplied because of operational reasons). One of the tanks was the control tank, which was operated at 50 ml/min throughout the experimental period. Thermophilic temperatures between 45°C and 55°C were maintained throughout the experimental period. The operating variables that were maintained demonstrated a stable nature, except for one run (which is not discussed in detail). Operating ORP was within the range of –300 to –450 mV. Airflow rates were monitored regularly, to ascertain that the air supply was being supplied at the rate set.

There was an inherent difference between the test and control reactors with respect to temperature and ORP, even at identical aeration rates, even though the feed supplied was the same to both tanks. The differences in ORP, at the different aeration rates demonstrated a distinct relationship between the ORP and aeration rate.

The feed solids were, on average 1.4%, except for one run, when the concentration of feed solids dropped to 1.09%. The range of solids destruction was between 18% to 27%. The highest reduction occurred when air was supplied at 100 ml/min. There seemed to be no relationship between solids destruction and aeration rate. The pH was stable and neutral in all the runs.

VFA production was, indeed, affected by both the aeration rate and solids content. From this research, it was evident that the lower aeration rate resulted in greater total production of VFA; net production of VFA was demonstrated in all the runs. Acetate was the dominant species in both feed and the ATAD units. The ratio of acetic acid to propionic acid in the ATAD units was 20 (averaged). There was also a conversion/consumption of propionic acid present in the feed (at a higher percentage) to more complex fatty acids in the ATAD units. Also, during Run 1, because of the storage of the feed mix for one day, there was a higher concentration of VFA in that feed; this resulted in the generation of VFA in the feed due to the fermentation process already underway in the tanks. As such, the net production of VFA was low, although the accumulation of VFA was high. The production of VFA was affected by the solids concentration in the feed. The production of VFA was lower when the concentration was lower. This was evident in Run 3, when the influent had 1.09% solids, compared to 1.4% in the other Runs.

There was a significant release of phosphorus in the process of digestion in the ATAD tanks. To maintain a recycle component of the effluent into the process, the

VFA:PO_4-P ratio would have to be as high as possible. The maximum ratio observed in this research was 5.6, when 25 ml/min air was supplied.

Nitrification was inhibited in the ATAD environment, resulting in the accumulation of ammonia-N. The inhibition of nitrification also resulted in minimal nitrate-N concentration, an expected result. This could be viewed as a positive aspect of ATAD sludge, that is, it can be disposed of without the worry of groundwater contamination, (if the application of the final sludge is done during the growing season and the plants uptake the nitrogen at a faster rate, to prevent eventual conversion to NO_3-N) due to nitrates.

5.2 Phosphorus Removal by Crystallization - Summary.

Two separate sets of experiments were carried out with a Crystallizer column, the purpose of which was to remove the soluble phosphorus from the supernatant of the ATAD effluent, in the form of struvite. The first set employed synthetic sewage and the second set with ATAD supernatant, at different dilutions (to study the effect of solids). The pH during the first set of experiments was maintained between 8 and 10 (since this is the optimum range for struvite formation) by the injection of NaOH. Magnesium was added in the form of $MgCl_2$. The phosphorus removal percentage varied with pH and the maximum removal was 65%, at a pH of 9.3. Phosphorus removal was noticed almost immediately, but was more prominent after 15 minutes, when a milky-white precipitate formed.

ATAD effluent (supernatant) was diluted and run through the Crystallizer at different solids concentration. Higher phosphorus removal was observed when actual ATAD effluent was used. The presence of more NH_4-N could be the reason for better removal. Solids levels did not seem to have any affect on the removal of PO_4-P. The reduction of PO_4-P also increased the VFA:PO_4-P ratio, thereby making it possible to recycle the entire effluent back to the main process.

5.3 Overall conclusions

Based on the results from this research the following specific conclusions can be drawn.

1) VFA production in ATAD systems increased at lower aeration rates.

2) Maximum VFA production occurred when 25 ml/min air was supplied; the accumulation and production in this run was even better then the one with no air being supplied.

3) Consumption and conversion of propionic acid (HPr → HAc)occurs in ATAD, with acetic acid being the predominant species.

4) The VFA to PO_4-P ratio was the highest when only 25 ml/min of air was supplied. On examining the results, it can be concluded that 25 ml/min of air was the **"optimum"** aeration rate for the production of VFA. Although 0 air (nitrogen) also produced substantial amounts of VFA, it was not as great as the 25 ml/min run.

5) Initial solids concentration in the feed affected the production of VFA

6) The nature of solids in the primary sludge contributed to the easy disruption of the cellular material in the sonification test, resulting in greater VFA. However, there was production in the ATAD, instead of just shearing and release of VFA from cell lysis (simulated by the sonification test).

7) Thermophilic aerobic sludge digestion results in release of phosphorus stored in the bio-solids.

8) Inhibition of nitrification occurs in ATAD resulting in accumulation of ammonia-N.

9) The Crystallization process employed in this work removed phosphorus from ATAD effluent very well, with the process being highly dependent on pH and occurring only above pH 8. The time taken for the reaction to take place is very short, if the operating conditions are right.

10) Removal of phosphorus from ATAD effluent demonstrated better efficiency with a higher concentration of NH_4-N present. However, the solids concentration did not seem to affect the removal of PO_4-P in the Crystallization process.

Chapter 6

Implications and Recommendations

6.1 Implications of results

The aeration rate at 25 ml/min proved to be the best aeration rate, in terms of production of VFA and release of PO_4. The present EPA guideline states that the air input into an ATAD system should be 4 $m^3/hr/m^3$ of active reactor volume which, converts to 50 ml/min (approx.) in this experimental setup. 25 ml/min converts to only 2.08 $m^3/hr/m^3$. As such, this would result in a substantial reduction in cost and power requirements in full-scale plants, where the volume of sludge treated is also very high and so are the solids concentration.

The Crystallizer process employed here, seems to be a useful tool in removing the accumulated phosphorus form the ATAD effluent. Since the solids are also reduced, due to post mesophilic aeration and there is a high concentration of VFA, the Crystallizer effluent shows promise as an addition to the main process stream.. From a commercial perspective, the **ATAD + Crystallizer** combination could be utilized to produce pathogen-free, slow-release fertilizer, that can be produced on a continuous basis and extracted from the process. If the need be, the phosphorus could be recovered by stripping it from the sand by an acid bath and the phosphorus could be used for other purposes. There are already a lot of patented Crystallizers and most of them incorporate

the same technology. However, there are no such products incorporating settled ATAD effluent as the feed.

6.2 Recommendations

From the results and the various technicalities that were faced while completing this research, the following recommendations with regards to future research and modification are made.

- Detailed study of performance of ATAD with 25 ml/min at different influent solids and phosphorus concentrations.
- Determination of VS and VSS, instead of just TSS, to get a better idea of the solids reduction efficiency.
- Investigate the Crystallizer performance while monitoring the concentration of Mg, PO_4 and NH_4 more accurately. Studies should also be done in a larger scale and on a continuous basis, instead of a batch fed system.
- Upgrading of the UBC pilot plant and investigate the inherent differences in the two ATAD tanks.

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Appendices

Appendix A

VFA data

VFA data for Run 1 (50 ml/min)

Feed Sludge

	3/24/98				3/25/98				3/26/98				3/27/98				3/28/98				3/29/98	
	morn		evening		morn		evening		morn		evening		morn		evening		morn		evening		morn	
Acetic	137.3	134.8	176.3	178.5	149.4	130.3	189.1	185.8	138.3	138.7	166.5	167.5	144.1	140.0	185.8	188.3	117.7	107.3	146.2	151.0	121.4	121.0
Propionic	81.8	82.4	116.3	120.0	82.9	83.5	108.6	107.7	76.1	77.6	104.2	105.1	89.0	86.5	122.2	124.8	75.3	73.2	102.6	103.3	69.0	68.5
Iso-butryic	5.3	5.8	7.6	7.4	6.1	4.2	10.6	10.2	6.2	5.9	7.3	7.4	5.0	4.8	6.6	6.0	4.3	4.4	5.7	5.3	3.5	3.0
Butryic	14.8	14.8	24.0	24.7	16.5	6.2	23.4	23.1	13.3	13.6	17.7	17.8	14.8	14.3	22.7	23.3	11.5	11.2	16.3	16.3	11.0	10.8
2-ME Butryic	1.7	1.5	1.9	1.6	1.6	1.0	3.5	3.4	1.6	1.5	1.6	1.6	0.9	0.8	1.3	0.9	0.8	0.9	1.5	1.1	0.0	0.0
3-Me Butryic	3.9	3.7	4.3	4.1	3.3	2.7	6.5	6.3	3.5	3.2	3.6	3.8	2.7	2.6	3.5	3.1	2.0	2.1	2.8	2.4	1.9	1.6
Valeric	3.3	4.9	7.2	7.3	5.5	0.7	7.3	7.2	4.6	4.8	5.8	5.7	2.0	4.6	6.6	4.1	4.0	3.9	5.4	5.4	1.2	1.3
Average		247.9		340.6		247.0		346.3		244.5		307.9		256.1		349.6		209.3		282.5		207.2

Test

	morn		evening		morn		evening		morn		evening		morn		evening		morn		evening		morn	
Acetic	319.0	307.5	301.4	300.6	284.0	422.8	269.7	278.5	286.3	294.1	264.4	265.3	289.7	293.9	275.6	264.7	279.1	283.7	251.2	253.4	257.7	262.0
Propionic	14.7	13.8	19.1	19.4	11.9	15.1	15.1	16.0	13.6	14.4	12.6	12.7	17.9	18.1	15.2	15.1	21.9	22.5	14.1	14.2	16.2	16.6
Iso-butryic	34.1	33.9	36.5	36.1	38.4	9.3	40.5	39.0	40.2	40.9	38.8	39.8	42.0	42.7	40.9	39.6	40.6	40.1	39.7	40.2	41.0	42.0
Butryic	5.0	4.9	3.3	3.1	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.4	1.4	5.5	5.4	2.8	2.8	2.4	2.5
2-ME Butryic	13.9	13.6	15.9	15.9	18.1	0.9	19.9	20.3	22.0	22.2	22.8	23.0	25.0	25.4	25.6	24.7	25.1	25.1	25.0	25.4	26.0	26.3
3-Me Butryic	35.2	34.7	35.9	36.1	36.8	30.0	37.6	38.2	39.0	39.3	38.2	38.7	40.1	40.7	40.0	38.6	38.7	38.7	38.1	38.6	39.1	39.5
Valeric	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.9	6.0	6.0	6.6	5.8
Average		415.2		411.7		434.1		387.4		406.0		378.1		417.7		391.5		417.1		378.7		391.8

Control

	morn		evening		morn		evening		morn		evening		morn		evening		morn		evening		morn	
Acetic	343.6	334.6	302.3	309.3	316.4	492.0	291.9	297.2	296.4	295.3	272.6	280.3	292.3	288.7	284.0	275.0	287.0	285.0	274.7	285.0	274.7	282.8
Propionic	24.7	24.5	19.2	20.4	21.6	10.0	14.4	15.1	18.5	18.5	11.2	12.2	15.2	15.2	12.7	12.9	17.8	17.5	14.9	15.2	13.9	14.7
Iso-butryic	45.7	44.4	44.9	44.4	47.5	40.7	48.1	46.9	46.8	46.8	46.3	45.6	46.6	46.5	47.0	44.9	44.2	44.0	42.3	44.0	43.4	43.3
Butryic	17.4	17.0	15.6	16.0	15.5	1.6	12.3	12.2	10.8	11.0	5.9	5.9	4.1	4.2	2.8	2.7	3.8	3.8	3.3	3.4	3.4	3.4
2-ME Butryic	26.1	25.6	25.9	26.2	27.6	20.3	28.8	29.2	28.5	28.7	29.3	29.2	30.2	30.1	31.3	29.5	29.1	29.4	28.1	29.3	28.7	28.9
3-Me Butryic	40.4	39.7	40.0	40.3	42.2	33.8	43.4	43.1	42.6	42.7	43.3	43.2	44.3	44.2	45.7	43.1	42.4	43.0	41.1	42.6	41.7	42.1
Valeric	4.4	4.4	4.5	4.7	4.7	1.3	4.0	4.2	3.3	3.7	2.2	2.2	1.2	1.2	0.0	0.0	0.0	8.3	7.5	6.9	5.5	7.1
Average		496.3		456.9		537.6		445.4		446.8		414.7		431.9		415.8		427.6		419.2		416.8

VFA Data for Run 2a (25 ml/min)

Test

	23/7		24/7		25/7		26/7		27/7		28/8	
	morn	evening	morning	evening	morn	evening	morn	evening	morn	evening	morn	evening
Acetic	439.4	461.2	462.3	474.8	405.5	418.2	402.5	395.5	398.2	402.0	474.1	457.2
Propionic	19.3	19.9	17.5	19.1	14.2	15.0	16.2	16.4	14.8	14.4	18.8	19.0
Iso-butryic	38.7	40.7	41.4	41.9	36.4	37.7	35.1	35.8	36.5	35.7	40.6	39.4
Butryic	2.8	3.0	4.7	4.6	4.3	4.5	4.5	4.5	2.4	2.2	2.0	2.0
2-ME Butryic	33.9	35.2	34.1	34.1	30.6	31.5	30.4	30.2	30.7	29.8	34.5	33.1
3-Me Butryic	42.4	43.9	44.3	44.3	40.7	41.7	40.7	40.6	41.5	40.8	46.2	44.7
Valeric	0.6	3.6	3.2	3.5	1.0	0.5	0.8	1.2	1.0	1.1	1.1	1.2
	577.1	607.3	607.4	622.3	532.6	549.0	530.3	524.2	525.0	526.0	617.4	596.6
Average		**592.2**		**614.8**		**540.8**		**527.2**		**525.5**		**607.0**

Control

	morn	evening	morning	evening	morn	evening	morn	evening	morn	evening	morn	evening
Acetic	459.2	467.7	527.9	457.7	435.5	427.2	386.0	392.7	393.8	432.0	421.5	417.1
Propionic	14.8	14.3	16.7	14.5	14.0	14.0	12.4	12.4	15.3	16.2	13.5	13.1
Iso-butryic	34.3	35.4	39.5	34.3	34.9	34.5	33.2	32.5	31.2	32.7	32.6	30.5
Butryic	7.8	7.8	11.4	10.0	11.5	11.3	1.5	1.8	2.2	2.3	1.8	1.7
2-ME Butryic	31.6	32.0	35.2	30.6	30.5	30.2	28.9	28.7	28.6	30.2	30.4	29.2
3-Me Butryic	40.8	41.6	47.3	40.7	41.5	41.3	38.2	37.8	37.7	39.7	41.1	39.7
Valeric	1.0	1.6	3.9	2.1	3.5	5.0	1.2	1.6	1.5	1.4	1.0	2.3
	589.5	600.6	681.9	589.9	571.3	563.6	501.5	507.6	510.3	554.4	541.9	533.7
Average		**595.1**		**635.9**		**567.4**		**504.5**		**532.4**		**537.8**

Feed

	morn	evening	morning	evening	morn	evening	morn	evening	morn	evening	morn	evening
Acetic	60.6	57.0	61.1	60.3	70.2	72.2	61.5	58.7	66.0	60.6	67.9	63.0
Propionic	22.9	21.9	19.1	18.8	22.8	23.5	22.4	21.7	20.3	20.2	23.8	24.1
Iso-butryic	3.0	2.8	2.4	2.4	3.7	3.8	2.6	2.6	3.5	3.5	4.8	4.9
Butryic	6.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-ME Butryic	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-Me Butryic	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Valeric	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.9
	93.2	81.7	82.6	81.4	96.7	99.5	86.6	82.9	89.8	84.2	96.9	92.8
Average		**87.4**		**82.0**		**98.1**		**84.8**		**87.0**		**94.9**

VFA data for Run 3 (75 ml/min)

Test

	8/6/98	9/6/98	10/6/98	11/6/98	12/6/98
Acetic	60.6	156.9	122.8	88.7	110.3
Propionic	0.0	0.0	0.0	0.0	0.0
Iso-butryic	1.5	8.0	6.6	4.0	6.1
Butryic	0.0	0.0	0.0	0.9	0.0
2-ME Butryic	0.7	1.5	1.3	1.1	1.3
3-Me Butryic	0.6	1.1	0.3	0.1	0.6
Valeric	2.2	2.7	2.4	2.2	2.2
Total	65.5	170.3	133.4	96.9	120.6

Control

	8/6/98	9/6/98	10/6/98	11/6/98	12/6/98
Acetic	350.1	364.7	337.6	323.6	320.0
Propionic	11.0	11.6	10.5	9.8	10.4
Iso-butryic	27.9	30.2	28.0	27.4	28.5
Butryic	1.1	2.7	3.6	5.1	7.0
2-ME Butryic	17.1	19.2	17.6	17.6	17.2
3-Me Butryic	21.8	24.4	21.5	21.4	20.7
Valeric	3.0	4.2	3.2	3.9	4.1
Total	431.8	457.1	422.0	408.7	407.8

Feed

	8/6/98	9/6/98	10/6/98	11/6/98	12/6/98
Acetic	63.2	65.1	79.3	71.6	66.7
Propionic	26.6	21.3	35.5	29.5	13.4
Iso-butryic	1.5	1.3	1.6	1.6	0.5
Butryic	1.9	1.1	1.9	1.7	0.0
2-ME Butryic	0.4	0.4	0.6	0.6	0.0
3-Me Butryic	2.1	1.8	0.9	1.8	0.0
Valeric	0.0	0.0	0.3	0.0	0.0
Total	95.7	91.0	120.1	106.7	80.6

VFA data for Run 4 (100 ml/min)

Test ATAD

	6/29/98	6/30/98	7/1/98	7/2/98	7/3/98	7/4/98
Acetic	189.4	279.2	301.7	291.0	304.0	204.9
Propionic	4.1	7.0	9.2	8.0	9.1	1.7
Iso-butryic	12.7	20.8	22.2	24.3	25.5	22.4
Butryic	0.0	3.1	5.6	2.4	2.5	0.0
2-ME Butryic	3.7	7.5	10.2	12.7	14.6	13.8
3-Me Butryic	4.0	9.6	13.6	16.7	18.8	16.6
Valeric	1.5	1.9	3.0	1.4	0.7	1.0
total	215.5	329.1	365.4	356.4	375.2	260.3

Control ATAD

Acetic	417.9	467.3	464.4	430.3	454.7	420.7
Propionic	18.0	23.0	28.0	19.7	22.0	11.7
Iso-butryic	42.3	47.0	43.6	43.6	46.5	45.5
Butryic	6.6	12.7	17.6	12.2	10.7	1.1
2-ME Butryic	26.4	30.0	28.2	28.7	30.9	30.5
3-Me Butryic	33.2	39.8	36.7	34.9	38.7	40.4
Valeric	1.5	3.2	4.7	2.9	3.0	0.6
Total	545.9	623.0	623.3	572.3	606.6	550.4

Feed Sludge

Acetic	129.4	134.2	88.0	71.0	78.2	73.4
Propionic	47.9	47.6	26.6	19.8	22.1	16.1
Iso-butryic	3.7	3.2	1.6	2.5	3.2	0.0
Butryic	7.6	7.8	4.3	0.0	0.0	1.3
2-ME Butryic	0.9	0.7	0.0	0.0	0.0	0.0
3-Me Butryic	1.1	1.1	0.1	0.1	0.2	0.3
Valeric	1.6	1.8	0.9	0.4	0.6	0.0
total	192.1	196.4	121.6	93.8	104.3	91.1

VFA data Run 5 (0 ml/min)

Test ATAD

	17-Aug		18-Aug		19-Aug		20-Aug		21-Aug		22-Aug	
Acetic	379.6	367.2	384.2	444.3	458.6	401.3	410.4	414.7	497.3	486.7	501.6	439.1
Propionic	14.8	14.3	19.5	23.0	30.8	26.7	22.6	22.5	29.5	27.9	29.3	25.5
Iso-butryic	37.1	35.8	36.1	42.3	41.8	36.2	36.0	37.0	43.7	41.7	45.8	39.8
Butryic	0.0	0.0	0.0	0.0	0.0	0.0	6.2	6.2	2.3	2.2	0.0	0.0
2-ME Butryic	32.1	31.0	31.2	36.9	34.1	29.4	29.3	29.4	34.8	32.8	36.5	31.7
3-Me Butryic	30.0	29.0	28.9	34.1	33.5	29.3	30.6	30.7	38.3	36.1	40.4	35.3
Valeric	1.1	1.5	1.9	0.0	3.0	2.2	0.0	0.0	2.6	2.6	1.9	1.8
	494.8	478.8	501.8	580.6	601.7	525.2	535.0	540.6	648.5	630.0	655.5	573.3
Average		486.8		541.2		563.4		537.8		639.2		614.4

Control ATAD

	17-Aug		18-Aug		19-Aug		20-Aug		21-Aug		22-Aug	
Acetic	344.8	362.0	347.8	336.1	429.0	438.0	392.5	426.1	437.3	437.2	469.3	454.9
Propionic	9.9	10.3	57.6	57.4	20.3	20.5	16.1	17.5	19.2	18.7	21.9	21.6
Iso-butryic	34.9	35.8	26.5	26.6	36.5	36.6	34.4	37.9	37.6	37.8	38.5	37.2
Butryic	0.0	0.0	8.6	8.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-ME Butryic	29.2	30.1	20.2	20.1	28.8	29.3	27.5	29.5	29.2	28.4	30.4	29.6
3-Me Butryic	27.4	28.1	19.7	19.3	29.1	29.6	29.5	31.8	32.9	32.0	35.3	34.2
Valeric	2.0	2.1	3.1	3.1	4.0	3.3	2.4	4.3	3.4	3.8	0.0	0.0
	448.1	468.4	483.6	471.1	547.8	557.4	502.3	547.1	559.5	558.0	595.5	577.5
Average		458.2		477.3		552.6		524.7		558.8		586.5

Feed Sludge

	17-Aug		18-Aug		19-Aug		20-Aug		21-Aug		22-Aug	
Acetic	77.3	74.5	92.0	92.4	94.2	87.9	66.0	66.2	94.2	90.7	72.6	75.8
Propionic	35.4	33.9	39.1	39.1	38.9	39.6	28.1	29.2	36.5	35.9	30.3	31.0
Iso-butryic	2.0	1.8	2.1	2.0	0.0	0.0	3.0	3.2	4.4	4.4	3.9	4.0
Butryic	5.8	5.6	6.1	6.1	4.3	4.4	0.0	0.0	0.0	0.0	0.0	0.0
2-ME Butryic	1.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-Me Butryic	1.1	1.1	1.2	1.2	0.7	0.6	0.0	0.0	0.4	0.0	0.0	0.0
Valeric	2.0	1.9	2.3	0.7	1.4	1.5	0.0	0.6	0.9	1.1	0.7	0.8
	124.6	118.8	142.8	142.4	139.5	134.0	97.1	99.2	136.4	132.0	107.5	111.6
Average		121.7		142.6		136.7		98.1		134.2		109.6

Appendix B

Data sheet for solids for all runs

Total Solids for Run 1 (50 ml/min)

date		Vol	Empty (g)	Dried (g)	TSS (mg/L)
3/24/98	Test	20	40.479	40.6802	10060
	Control	20	44.1971	44.4393	12110
	Feed	20	51.7958	52.0893	14675
3/25/98	Test	20	47.3058	47.5394	11680
	Control	20	47.0473	47.2713	11200
	Feed	20	46.9079	47.1779	13500
3/26/98	Test	20	51.797	51.9993	10115
	Control	20	50.3082	50.5365	11415
	Feed	20	44.198	44.4477	12485
3/27/98	Test	20	46.3849	46.6223	11870
	Control	20	40.4802	40.7267	12325
	Feed	20	47.1931	47.5343	17060
3/28/98	Test	20	50.3069	50.5629	12800
	Control	20	47.3046	47.5605	12795
	Feed	20	46.8762	47.1803	15205
3/29/98	Test	20	44.197	44.44	12150
	Control	20	46.9064	47.1395	11655
	Feed	20	47.1916	47.4655	13695

Total Solids for Run 2a (25 ml/min)

date		Vol	Empty (g)	Dried (g)	TSS (mg/L)
7/23/98	Test	20	40.4827	40.7124	11485
	Control	20	47.3079	47.5214	10675
	Feed	20	44.2007	44.511	15515
7/24/98	Test	20	46.9088	47.1452	11820
	Control	20	47.1947	47.4178	11155
	Feed	20	46.8779	47.1836	15285
7/25/98	Test	20	50.3117	50.553	12065
	Control	20	46.3875	46.6243	11840
	Feed	20	47.0501	47.3505	15020
7/26/98	Test	20	47.1954	47.4267	11565
	Control	20	44.204	44.4276	11180
	Feed	20	46.8783	47.1638	14275
7/27/98	Test	20	51.8001	52.0248	11235
	Control	20	47.3089	47.5275	10930
	Feed	20	40.4841	40.7481	13200
7/28/98	Test	20	50.3117	50.5285	10840
	Control	20	47.0504	47.26	10480
	Feed	20	46.3881	46.6375	12470

Total Solids for Run 4 (75 ml/min)

Note: there was no sampling done on the last day.

date		Vol	Empty (g)	Dried (g)	TSS (mg/L)
6/8/98	Test	20	47.0487	47.2287	9000
	Control	20	46.3873	46.5809	9680
	Feed	20	50.3098	50.5504	12030
6/9/98	Test	20	47.1947	47.3734	8935
	Control	20	51.7993	51.9913	9600
	Feed	20	46.9229	47.1266	10185
6/10/98	Test	20	50.3108	50.4834	8630
	Control	20	46.3883	46.5708	9125
	Feed	20	47.0499	47.2728	11145
6/11/98	Test	21	47.3079	47.4819	8286
	Control	20	40.4817	40.6592	8875
	Feed	20	44.2017	44.4193	10880
6/12/98	Test	20	47.1944	47.3715	8855
	Control	20	46.9086	47.0991	9525
	Feed	20	51.7978	52.0028	10250
6/13/98	Test				
	Control				
	Feed				

Total solids for Run 4 (100 ml/min)

date		Vol	Empty	Dried	TSS (mg/L)
6/29/98	Test	20	46.3885	46.6109	11120
	Control	20	47.196	47.431	11750
	Feed	20	50.3119	50.6482	16815
6/30/98	Test	20	46.9104	47.1289	10925
	Control	20	51.7994	52.0417	12050
	Feed	20	47.0495	47.3416	14605
31/06/98	Test	20	47.1945	47.4189	11220
	Control	20	46.3858	46.6151	11465
	Feed	20	50.3098	50.5985	14435
7/1/98	Test	20	40.4825	40.7163	11690
	Control	20	47.3083	47.5455	11860
	Feed	20	44.2009	44.5127	15590
7/2/98	Test	20	50.3114	50.5357	11215
	Control	20	46.3871	46.6274	12015
	Feed	20	47.1957	47.4597	13200
7/3/98	Test	20	51.8003	52.0278	11375
	Control	20	46.911	47.141	11500
	Feed	20	47.0507	47.3317	14050

Total Solids for Run 5 (0 ml/min)

date		Vol	Empty (g)	Dried (g)	TSS (mg/L)
8/17/98	Test	20	46.9095	47.1201	10530
	Control	20	47.3071	47.5261	10950
	Feed	20	50.3096	50.5948	14260
8/18/98	Test	20	47.1963	47.4177	11070
	Control	20	40.4833	40.7395	12810
	Feed	20	46.8784	47.1836	15260
8/19/98	Test	20	44.204	44.4353	11565
	Control	20	51.8027	52.0208	10905
	Feed	20	47.052	47.3541	15105
8/20/98	Test	20	46.3914	46.627	11780
	Control	20	50.307	50.5372	11510
	Feed	20	47.307	47.5898	14140
8/21/98	Test	20	46.9124	47.1398	11370
	Control	20	46.8809	47.1091	11410
	Feed	20	47.1979	47.4695	13580
8/22/98	Test	20	47.0518	47.2827	11545
	Control	20	50.3129	50.539	11305
	Feed	20	51.8018	52.0682	13320

Appendix C

Calculations for concentration of chemicals in crystallizer feed

Calculation for mixing chemicals for synthetic feed in the Crystallizer.

Chemical used	Molecular weight
$NaH_2Po_4.H_2O$	137.90
NH_4Cl	53.49
$MgCl_2.6H_2O$	203.31

For the optimum condition for the formation of struvite the ratio of PO_4:NH_4:Mg should be 1:1:1.

$PO_4/(NaH_2PO_4.H_2O)$ = 0.68

$Mg/(MgCl_2.6H_2O)$ = 0.119

NH_4/ NH_4Cl = 0.33

Concentration of stock solutions for required molar ratio are:

PO_4 = **40 g/L** (add 58.12 g/l of chemical)

Mg = **10 g/l** (add 84 g/l of chemical)

NH_4 = **8 g/L** (add 24.2 g/l of chemical)

This gives a molar ratio of **1:0.96:1.04::PO_4:Mg:NH_4.**

Projected feed concentration of phosphorous = 100 mg/L

Same molar ratio of NH_4= 20 mg/L

As Mg is pumped at a much slower rate the concentration should be higher. Based on flow diagrams and the injection rate of 6 ml/min of Mg, the concentration of the feed is 1400 mg/L.

Appendix D

Nutrient data

Phosphorous data with no air (Run 5)

Raw data

Date	8/17/98	8/18/98	8/19/98	8/20/98	8/21/98	8/22/98		Average	Median	Std Dev.
Test	116.8	121.3	123.9	127.2	126.8	131.2	Test	124.52	125.32	5.02
Control	118.8	131.1	123.6	129.1	129.7	132.0	Control	127.36	129.41	5.14
Feed	37.0	52.8	22.7	19.1	29.2	21.7	Feed	30.42	25.92	12.72
Waste sup	9.1	10.3	9.9	9.9	11.4	10.5	Waste Sup	10.18	10.11	0.77

Net production (mg/L)

PO4-P test	79.8	68.5	101.2	108.0	97.6	109.4	94.10	99.40	16.43
PO4-P control	81.8	78.3	100.9	110.0	100.5	110.2	96.94	100.72	13.82

Phosphorous data with 100 ml/min air (Run 4)

Raw Data

	7/23/98	7/24/98	7/25/98	7/26/98	7/27/98	7/28/98		Average	Median	Std. Dev.
Test	94.43	92.45	89.35	83.85	76.62	73.98	Test	85.11	86.60	8.44
Control	104.22	103.22	96.13	96.18	84.83	84.96	Control	94.92	96.16	8.48
Feed	56.2	35.36	16.67	17.23	13.94	13.32	Feed	25.45	16.95	17.14

Net Production

Test	38.23	57.09	72.68	66.62	62.68	60.66	Test	59.66	61.67	11.78
Control	48.02	67.86	79.46	78.95	70.89	71.64	Control	69.47	71.27	11.48

Phosphorous data with 50 ml/min air (Run 1)

Raw data

Date	3/24/98	3/25/98	3/26/98	3/27/98	3/28/98	3/29/98		Average	Median	Std. Dev
Test	93.4	88.5	89.7	95.9	95.7	77.0	Test	90.03	91.54	7.10
Control	87.1	86.7	86.6	87.1	88.4	88.5	Control	87.40	87.13	0.80
Feed	38.2	33.1	32.6	33.7	33.6	33.3	Feed	34.07	33.42	2.04

Net Production

Test	55.26	55.31	57.05	62.24	62.18	43.7	Test	55.96	56.18	6.79
Control	48.96	53.57	54.02	53.44	54.79	55.17	Control	53.33	53.80	2.24

Appendix E

Crystallizer data

Run 1

Time/point	pH	PO4 (mg/L)	NH3 (mg/L)
0	8.3	27.8	13.2
1	7.5	26.4	15.4
5	7.1	28.2	14.2
10	7.3	28.1	14.1
15	7.9	28.3	14.1
20	8.2	28.9	14.5
25	8.5	29.3	14.6
30	8.6	29.4	14.9
32	8.6	29.4	15.1
35	8.6	29.3	14.7
38	8.6	29.6	14.9
40	8.7	29.0	15.2
45	8.6	29.6	15.2
48	8.7	29.7	15.0
50	8.7	29.9	14.9
53	8.8	29.4	14.9
55	8.8	29.7	15.1
57	8.8	29.7	14.8

Run 2

Time/point	pH	PO4 (mg/L	NH3 (mg/L)
0	9.1	58.0	31.3
5	9.0	57.1	34.0
10	9.0	56.5	32.4
15	9.1	58.9	32.4
20	9.0	57.5	30.8
25	8.5	64.3	38.4
30	9.0	44.9	31.3
32	9.0	38.7	33.6
35	9.0	35.4	23.6
40	9.0	36.7	21.9
42	9.1	33.0	21.4
45	9.1	32.4	20.5
47	9.0	32.2	20.3
49	9.0	37.5	20.6
52	9.0	32.1	20.1

Run 3

Time/point	pH	PO4 (mg/L)	NH3 (mg/L)
0	9.44	58.2	29.2
2	9.45	51.4	29.8
5	9.45	49.9	28.4
10	9.47	56.0	28.0
15	9.45	40.9	27.1
20	9.41	40.5	25.3
22	9.38	40.9	24.1
25	9.33	37.7	28.9
30	9.34	33.2	24.3
35	9.39	32.6	22.1
40	9.41	31.9	22.9
45	9.44	29.8	21.9
50	9.44	35.7	22.4
55	9.39	26.4	22.6
60	9.37	23.3	20.4
65	9.38	21.7	19.4
70	9.3	21.0	22.5

Run 4

Time/point	pH	PO4 (mg/L)	NH3 (mg/L)
0	8.57	56.3	30.0
5	8.64	57.8	30.1
10	8.66	56.4	29.7
15	8.66	48.4	29.6
20	8.67	50.7	29.7
25	8.66	46.4	30.6
30	8.58	47.1	28.6
35	8.49	50.5	28.8
40	8.5	48.8	28.2
45	8.49	45.3	26.6
50	8.49	41.9	25.7
55	8.51	42.3	25.3
60	8.51	40.7	24.2
65	8.5	43.1	23.7
70	8.5	38.3	23.6

Run 5

Time/point	pH	PO4 (mg/L	NH3 (mg/L)
0	8.0	69.9	33.3
5	8.0	65.5	31.7
10	7.9	62.7	31.4
15	8.0	61.8	30.3
20	8.0	60.9	30.6
25	7.9	59.4	30.2
30	7.9	58.8	29.8
35	8.0	58.9	30.1
40	8.0	59.3	29.9
45	8.0	58.5	30.1
50	8.0	58.5	29.9
55	8.0	57.8	30.4
57	8.0	57.8	29.7
60	8.0	56.5	27.7
65	8.0	57.3	30.1
68	8.0	55.9	29.6
70	8.0	56.5	30.1

Run 6

Time/point	pH	PO4 (mg/L	NH3 (mg/L)
0	10.2	61.0	35.1
5	10.2	55.0	30.4
10	10.1	51.0	30.1
15	10.1	46.9	30.0
20	10.1	46.2	30.0
23	10.0	44.4	30.3
30	9.9	43.9	32.4
35	10.1	44.0	31.1
40	10.0	42.3	31.0
45	10.0	41.8	31.2
50	10.0	41.3	31.2
55	10.0	41.4	31.0
60	10.1	39.2	31.1

Run 7

Time/point	pH	PO4 (mg/L	NH3 (mg/L)
0	8.66	66.37	30.49
5	8.65	58.58	30.03
10	8.66	53.19	27.89
15	8.65	52.12	27.65
20	8.62	47.13	26.66
25	8.69	45.56	25.58
30	8.67	43.57	25.09
35	8.63	43.63	25.35
40	8.62	43.82	25.29
45	8.61	43.18	25.16
50	8.58	42.4	24.38
55	8.57	41.23	24.24
60	8.6	39.63	31.29

Run 8 (Increasing pH)

Time/point	pH	PO4 (mg/L	NH3 (mg/L)
0	6.93	69.36	24.94
5	7.07	118.26	50.18
10	6.96	119.01	54.51
15	7	105.64	51.22
20	7.11	102.55	48.29
25	7.25	99.2	50.55
30	7.38	96.54	45.69
35	7.5	94.54	52.28
40	7.57	92.14	52.11
50	7.67	88.38	51.2
55	7.8	82.22	49.08
60	8.04	77.58	48.5
65	8.12	73.01	40.06
67	8.12	69.99	37.13
75	8.32	60.43	35.12
85	8.77	50.77	34.52
95	8.91	50.7	28.66
105	9.23	51.58	36.4
110	9.25	52.89	28.33
120	9.41	62.66	35.19