ASSESSMENT OF A BIOLOGICAL NUTRIENT REMOVAL PROCESS FOR THE REMEDIATION OF EDIBLE OIL EFFLUENT

SANDILE PSYCHOLOGY MKHIZE

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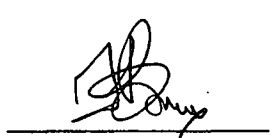
Dissertation submitted in compliance with the requirements of the Master's Degree in Technology in the Department of Biotechnology, Technikon Natal , Durban



Supervisor:
Mr. Faizal Bux
(M. TECH: BIOTECHNOLOGY, TECHNIKON NATAL)

10-5-2002
Date

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Declaration

I hereby declare that the dissertation is my own work, unless stated to the contrary in the text, and that it has not been submitted in part, or in whole to any other Technikon/University.

Sandile P. Mkhize
April 2002

Dedication

THIS DISSERTATION IS DEDICATED TO MY FAMILY

ABSTRACT

Eutrophication is a natural process that is greatly aggravated by the action of man in the natural environment. Deterioration of South Africa's natural water resources results directly or indirectly from the discharge of industrial effluent rich in nutrient nitrogen and phosphorus. The South African edible oil refineries generally discharge poor quality effluent which impacts negatively on the water resources and wastewater treatment installations. The main aim of this study was to assess the capacity of a laboratory scale effluent treatment process that will produce final effluent of acceptable quality with regards to organic load and phosphate concentration prior to its discharge into the municipal sewerage system. The study was conducted in three stages: wastewater characterization, treatability studies, and laboratory scale treatment investigations. After analysing various effluent parameters, treatability studies were conducted using an aerobic-anaerobic sequencing batch reactor with a total hydraulic retention time of 24 hours. The results showed an average of 75 % reduction of COD and more than 90 % removal of fats, oils and grease (FOG). Based on the results of effluent characterisation and treatability studies, a laboratory scale activated sludge effluent treatment process was designed and operated with two bioreactors (aerobic and anaerobic) in series. The system was operated for a period of one-month resulting in 70 % removal of COD and 4% reduction in phosphate (PO_4-P). After some structural and operational changes from the original design configuration, the system was the operated continuously for the duration of the study period. An optimum COD removal of 75 % and 107 mg/l PO4-P reduction was achieved during the last operational phase of the system. More than 95 % reduction in fats, oils and grease (FOG) had been achieved in both semi-continuously and continuously operated systems.

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JOURNAL PUBLICATIONS

Part of the work presented in this report has been presented and published in National and International Conferences and Journals.

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Authors: SP Mkhize, BW Atkinson and F Bux

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Glossary of Terms

BEPR	Biological excess phosphorus removal
BNR	Biological nutrient removal
BOD_5	Five day biochemical oxygen demand
COD	Chemical oxygen demand
DAF	Dissolved air floatation
DO	Dissolved oxygen
FOG	Fats, oils and grease or separable fatty matter (SFM)
FFA	Free fatty acids
HRT	hydraulic retention time
ML	Mixed liquor
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
PAO	Polyphosphate accumulating organisms
PHA	Polyhydroxyalkanoate
RBCOD (S_{bs})	Readily biodegradable COD
SBCOD (S_{bp})	Slowly biodegradable COD
SCFA	Short chain fatty acids or VFAs
SWI	Specific water intake
TSS	Total suspended solids
TKN	Total Kjeldal Nitrogen or Total nitrogen (TN)
VFA	Volatile fatty acids
UCT	University of Cape Town

List of Symbols

B_x	Organic loading rate
CO_2	Carbon dioxide gas
f_{xa}	Anaerobic sludge mass fraction
f_{xn}	Anoxic sludge mass fraction
f_{xt}	Anaerated sludge mass fraction ($f_{xa} + f_{xn}$)
F/M	Food to microorganism ratio or B_x
NO_x	Nitrate and nitrite fraction of Wastewater
N_2	Nitrogen gas
O_2	Oxygen gas
θ_c	Sludge age
θ	Hydraulic retention time (hrs)
S_u	Unbiodegradable COD
S_{up}	Unbiodegradable particulate COD sub-fraction
S_{us}	Unbiodegradable soluble COD sub-fraction
S_{ti}	Total influent COD
Q_i	Influent flow rate (l/d)
V_r	Total reactor volume excluding settler volume
V_{an}	Volume of the anaerobic reactor

CHAPTER 1

INTRODUCTION

1.1 THE SOUTH AFRICAN EDIBLE OIL INDUSTRY

South Africa has about 16 edible oil processing plants that are managed by 10 separate groups. These industries refine and process approximately 300 000 tons of crude vegetable oil per year, with production increasing annually by about 3 %. The amount of oil that is produced locally depends very much on the climatic conditions. Good rains lead to good maize, groundnut and sunflower crops, which results in good oil seed production. However, drought has negative impact in the industry, resulting in decline raw material production. To make up for the short fall in local oil production, the balance of oil is imported, in crude form, to be refined in the South African refineries (Steffen *et al.*, 1989).

Vegetable oil production can be divided into two distinct stages, which are: crude oil production in an oil mill, and crud oil processing which is conducted in a refinery. Thus the vegetable oil industry can be divided into two main groups based on the main production process being used. The milling industry produces crude oil from raw materials such as seed, and the refining industry purchases and refines crude oil into final products. In South Africa, the two stages of processing are usually conducted on the same site. Marine oils and animal fats are purchased in crude form and refined on site (Steffen *et al.*, 1989).

The principal product of edible oil refining is liquid oil, which may be sold as cooking or salad oil, or may be further processed to increase the market value of the final product, for example, margarine, peanut butter and mayonnaise manufacturing. Vegetable oil may be obtained from large variety of monocotyledonous and dicotyledonous seeds. The most commonly produced oil bearing crops in South Africa are the sunflower, groundnuts, and maize although other seeds such as cotton and soya, are also processed. (Steffen *et al.*, 1989).

The processing of vegetable oil, both milling and refining, is dependant on water availability. The edible oil processing industry consumes approximately 2 million cubic meters of water annually. A typical oil plant discharges about 40 % of the incoming water to the sewer system and the remainder of 60 % is either vaporised in the many cooling circuits, or else leaves the site in one of the secondary products or by-products. Hence, the specific water intake (SWI) for the edible oil industry is very high when compared to other industries in South Africa.

In a study that was conducted by Steffen, Robertson and Kirsten (Steffen *et al.*, 1989), they found that specific water intake (SWI) ranged between 2.1 and 3.1 m^3 per ton for milling, and between 3.2 and 4.6 m^3 per ton for refining of edible oils. Based on the results of this study, a target SWI of 2.0 m^3 per ton for milling and 3.0 m^3 per ton for refining was proposed. In addition to the proposed figure for each process, a further 5.0 m^3 per ton SWI for a plant milling and refining all products on site was proposed. It was then concluded that an improved SWI could be achieved by improving water management by the edible oil industry. (Steffen *et al.*, 1989).

1.2 THE ORIGINS OF EFFLUENT/WASTEWATER

Sealake Industries is situated in Pietermaritzburg, in the middle of the KwaZulu-Natal region. The factory used to buy both local and imported crude oil to be refined on-site. Sealake Industries was thus mainly a refining factory. But at the beginning of September 1999, milling was introduced at the factory, which converted the factory into both a milling and refining industry. The principal products of the factory are refined sunflower oil, soaps and candles. The factory also produces and sells acid oil, which is a one of the by-products of soap production.

The factory is subdivided into four main plants, which are all located on the same premises. Three plants are involved in production while the fourth is an effluent treatment plant. The three main production plants are: the refinery plant, which produces the refined oil; the acid oil plant, which produces soap stock and acid oil from fatty acids and sulfuric acid; and soap plant which produces soap from soap stock as well as candles. In addition to the abovementioned plants, there is a fifth subsidiary plant (packaging plant) that is responsible for the packaging of the final product into containers.

All the three production plants plus the packaging plant are responsible for the production of different kinds of effluents at variable quantities and strength as shown in Figure 1.1.

The volumes of effluents produced per plant vary on weekly basis depending on the refinery process employed as shown in Table 1.1. To understand the overall quality and quantity of effluent produced by the factory, it is better to consider individually the unit operations of each plant, its main products and effluents.

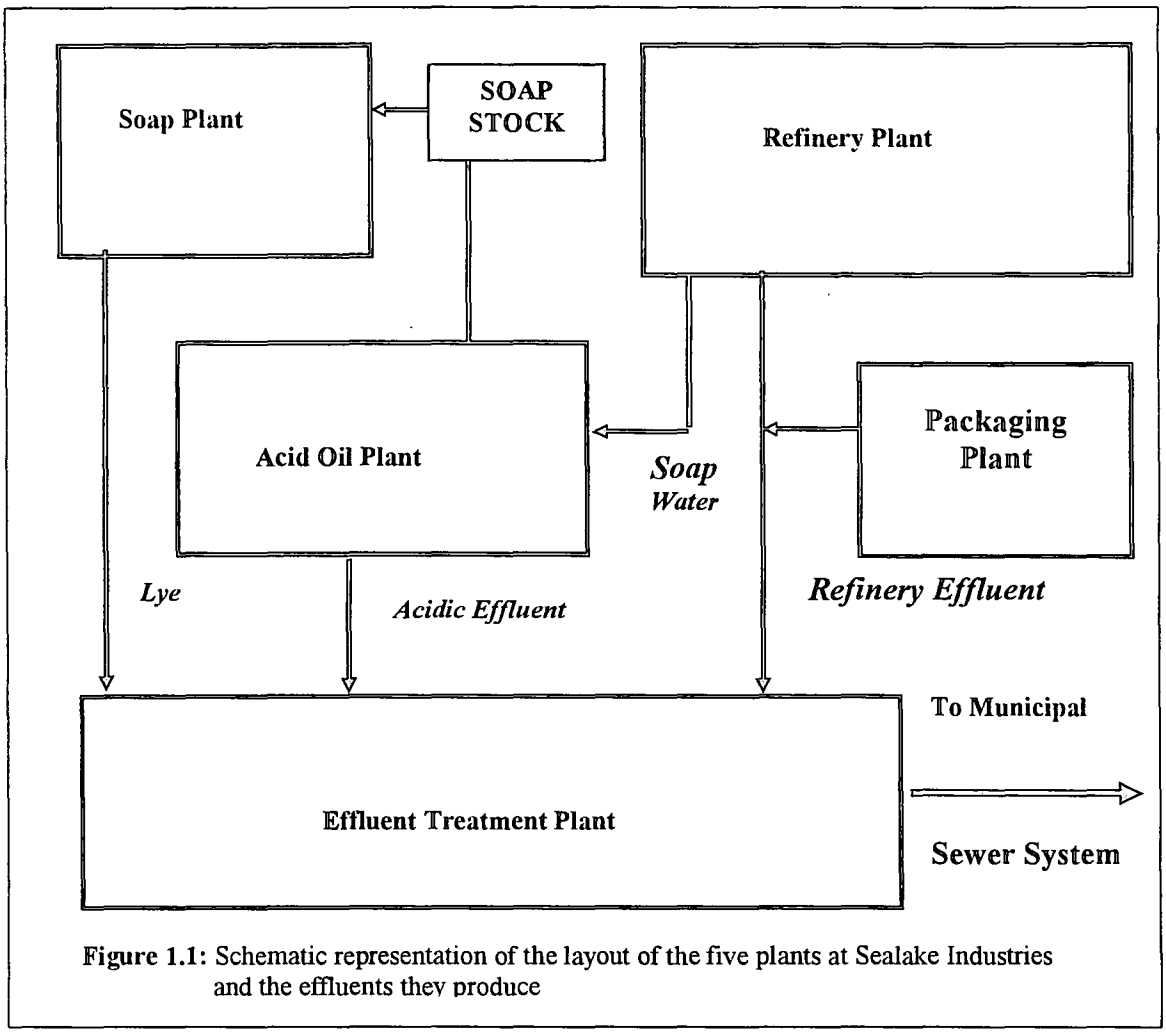

Figure 1.1: Schematic representation of the layout of the five plants at Sealake Industries and the effluents they produce

Table 1.1: Typical effluent volumes produced by each plant per week (19 April 1999 to 23 April 1999)

DAY (24 HOURS)	REFINERY EFFLUENT (tons/day)	LYE (tons)	ACID WATER (tons)
MONDAY	96	15	15
TUESDAY	96	10	15
WEDNESDAY	96	20	15
THURSDAY	96	7	15
FRIDAY	NIL	NIL	15

1.2.1 Refinery process and its effluents

The refinery is associated with the removal of phospholipids, colour bodies and other soluble and insoluble impurities from crude oil. The production of refined vegetable oil can be divided into two alternative processes or stages viz., chemical refining and physical refining. The two processes are different from each other and thus produce effluents of different quality and character. Nevertheless, the product in both processes is similar in quality i.e. refined vegetable oil ready for commercial use. Both the physical and the chemical refining processes for crude vegetable oil are shown schematically in Figure 1.2 below.

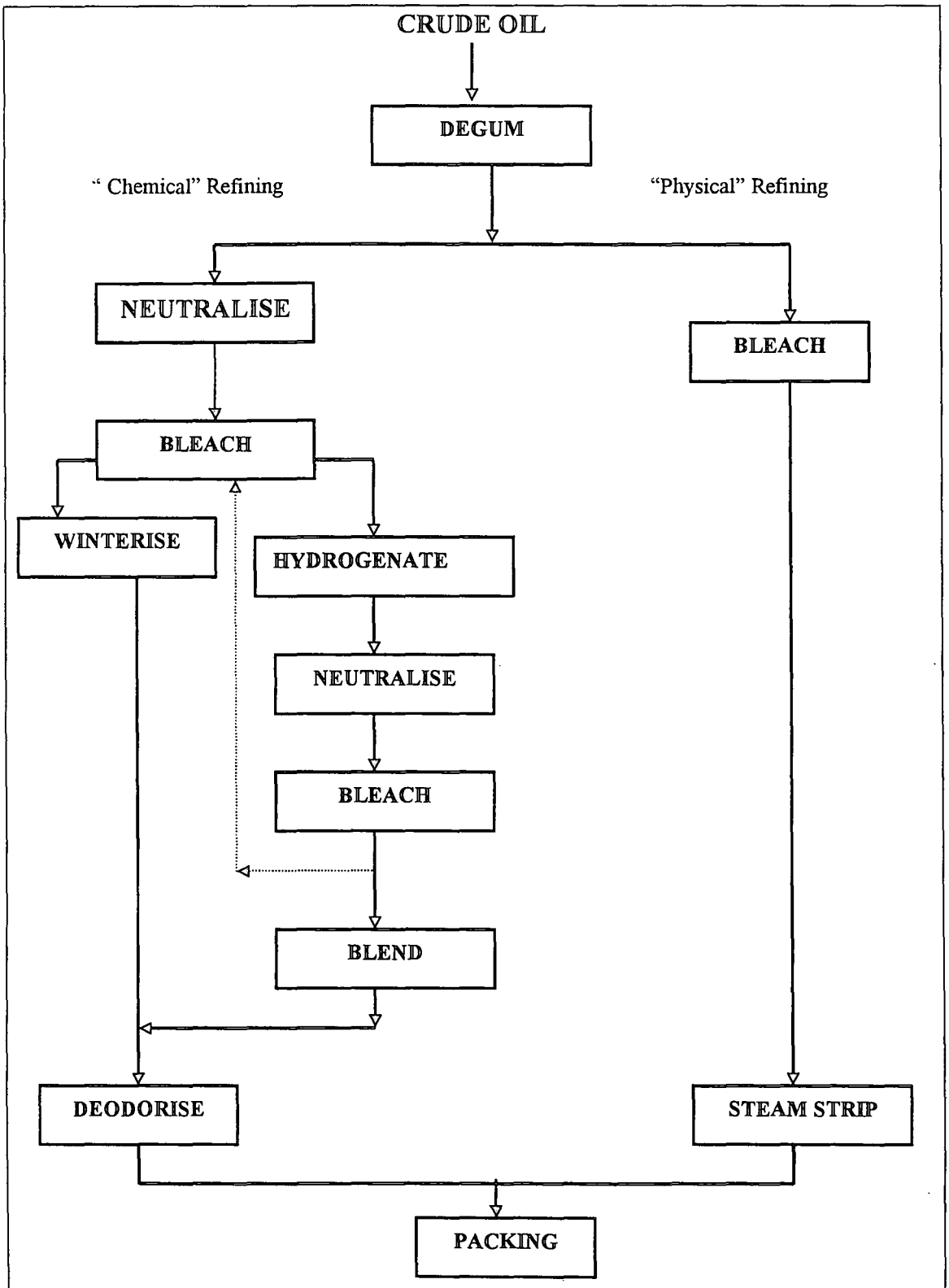

Figure 1.2: Physical and chemical refining process for Edible oil (Steffen *et al.*, 1989).

1.2.1.1 Degumming

Degumming may be considered the first step in the refining process that is designed to remove the phosphatides from the crude oil that interfere with subsequent processing. Oils high in phosphorus such as soybean, corn and sunflower, may require degumming prior to the refining process. But the degumming process is not always necessary, as the phosphatides can generally be effectively removed in subsequent processes. There are two types of gums viz. hydratable and the non-hydratable types. The primary reason for degumming is to either provide crude degummed oil suitable for storage or long transit; to prepare oil for physical refining; or to produce lecithins. There are three main problems that are associated with the presence of gums in the crude oil, which are:

(a) Decreased oil-water separation in the acidulation process, caused by the emulsifying properties of phospholipids when released as soap stock, resulting in product loss.

(b) The tendency of gums to impart deep brown colouring to finished oil during the deodorising stages due to high temperature that are employed.

(c) Adverse impact on product stability due to formation of complex compounds with certain trace metals.(Steffen *et al.*, 1989).

Water degumming is effective only for water-hydratable phosphatides ie. those having a great affinity for water phase existence then the remaining oil phase. The addition of hot water and subsequent separation of the swollen insoluble gums in the centrifuge equipment easily removes them. For non-hydratable gums, pretreatment of

the oil with phosphoric acid or citric acid is required to render them hydratable. The resultant hydratable gums are subsequently removed through addition of small amounts of water followed by centrifugation or by use of an activated adsorbent coupled with a filter. Many variations on this two-stage process exist. (Horan, 1991).

The effluent that is produced during the degumming stage tends to contain large quantities of phospholipids, inorganic phosphates (from use of phosphoric acid) and fats, oils and grease (FOG).

1.2.1.2 Chemical Refining

Chemical refining, also known as caustic refining, generally refers to the process designed to neutralise free fatty acids present in the oil by introduction of an alkali, followed by centrifugal separation of the heavy phase insoluble material. Caustic neutralization is the traditional first step for edible oil processing if degumming is not included as a pretreatment step. Caustic refining is made up of five inter-related processes and each process produces its own unique effluent. The five processes are neutralization, bleaching, hydrogenation, winterizing and deodorizing. The advantage of caustic refining over the alternative method is that it is less sensitive to the type of feedstock used.

(a) Neutralization

Crude oil naturally contains a percentage of free fatty acids (FFA). The free fatty acids or carboxilic acids are a resultant product of natural degradation of triglycerides.

Dilute caustic soda solution of up to 4N strength is usually used for neutralisation. The oil-alkali solution is thoroughly agitated to ensure intimate contact, normally using an inline high-shear mixer. Both the oil and caustic soda should be cooled to less then 38 °C. A careful control of the operating conditions is required at this stage because of the strong caustic soda used, which tends to saponify the neutral triglyceride with the consequent loss of neutral oil (Hui, 1996).

The neutralisation process also helps with the removal of metals, particularly magnesium (Mg) and calcium (Ca). Apart from saponification of free fatty acids in the crude oil, caustic addition tends to be more effective in hydration of gums than addition of hot water only. Thus it is possible for crude oil containing low gum contents to be processed chemically without the need for the degumming pretreatment step (Hui, 1996).

The immiscible soap or soapstock that is produced upon neutralisation is separated from the neutralised oil using centrifuges or gravitational settling, depending whether the operation is continuous, semi-continuous or batch process. Phosphoric acid may be added in the wash water to reduce the residual soap in the refined oil, and to provide a better split between the oil and the aqueous phase. The soapstock is further treated in the acid oil plant (on-site) to produce acid oil (Steffen *et al.*, 1989; Hui, 1996).

Chemical refining with caustic soda gives rise to the most potent effluent generated at an oil processing plant. The resultant effluent stream is known as soapy water and

contains quantities of free fatty acids, free oils, gums or phospholipids, sodium ions and phosphates (Eroglu *et al.*, 1990).

(b) Bleaching

Bleaching is the adsorptive process that is associated with edible oil refining process. While the degumming operation is designed to remove phosphatides and caustic refining converts water soluble free fatty acids into soluble soaps, adsorptive bleaching provides the last practical opportunity to reduce the quantities of the remaining impurities, especially colour and phospholipids, to acceptable levels. The major colour pigments found in edible oil are chlorophyll (green) and caretenoids (orange) (Hui, 1996).

Bleaching, like neutralisation process, may be conducted in a batch, semi-continuous or continuous mode. This step in edible oil refining process is conducted under vacuum at raised temperatures (Steffen *et al.*, 1989). In practice, the oil to be bleached may require pretreatment with acid (known as the dry degumming process for crude oils), which may be followed by dosing with bleaching clay and/or other agents in a slurry tank. The clay-oil mixture is agitated in a compartmentalised bleacher for several minutes before it is filtered to remove solids. Sometimes clay may be added in two stages, an inactivated clay is added first absorbs soaps whilst a more expensive activated clay absorbs trace metals, pigments and various other products which would otherwise cause reduced product shelf life. Bleaching produces the least effluent compared to other stages in edible oil refining (Hui, 1996). The effluent that is

produced at this stage is mainly acidic water from the acid pretreatment operation (Steffen *et al.*, 1989).

(c) Dewaxing

Dewaxing which is sometimes called winterising, refers to the removal of high melting point waxes extracted from certain oil seeds such as corn, sunflower and canola. The refined oil is cooled to approximately 5 °C thus causing high melting point esters and waxes to crystallise. These fat crystals are subsequently removed through filtering usually with the assistance of diatomaceous earth as a filter aid (Hui, 1996). The winterising process is only necessary for the oil that is going to be marked as such without further processing. It is usually not necessary to winterise the oil that is to be hydrogenated. This stage of edible oil refining has little contribution, if any, to the final effluent stream both qualitatively and quantitatively (Steffen *et al.*, 1989)

(d) Deodorising

This is typically the last step in the edible refining process. This step is included in almost all-refining operations regardless of other unit operations selected. The deodorisation process is intended to remove the relatively volatile odoriferous compounds from the refined oil. This process involves steam distillation under vacuum which results in the removal of residual free fatty acids, aldehydes and ketones that are responsible for unacceptable odours and flavours in the final refined oil. Removal of pigments is through thermal decomposition. The decomposition products from the pigments are subsequently distilled off from the final oil product. After the deodorisation process has been completed, the refined oil is cooled in the

lower tanks before being pumped for storage in the storage tanks. Small quantities of citric acid may be added during the cooling stage as an anti-oxidant to prevent oxidation of the cooled oil (Hui, 1996).

Deodorisation produces the second largest volume of effluent after the neutralisation process. Most of the effluent which is produced at this stage is the distillate from oil which contains volatile compounds responsible for the oil's characteristic odours as well as any remaining free fatty acids. A large quantity of water is also used during this stage for cooling purposes, which increases the specific water intake (SWI) of the plant. Some of the stripping stream and the remaining free fatty acid water vapours are mixed with the cooling water. After this has been recirculated over cooling towers, it is then discharged down the drain to join the main effluent stream (Steffen *et al.*, 1989).

1.2.1.3 PHYSICAL REFINING

Physical refining refers to the process whereby the free fatty acids in the crude or degummed oils are removed by evaporation rather than by being neutralised and subsequently removed as soap stock as is done during an alkali refining process. In design and operation, the deodoriser is very much like the physical refiner, with the major exception being the higher load of free fatty acids removed in physical refining process. Whilst some deodorising system designs can use carbon steel for certain non-contacted parts, the high levels of fatty acids generally demand that a physical refining system be made from stainless steel or other material not affected by contact

with fatty acids to prevent corrosion. The physical refining technique has two primary advantages over the conventional caustic refining route i.e. reduction in oil losses and the elimination of soapstock and its associated treatment problems (Hui, 1996, Steffen *et al.*, 1989).

Physical refining process has, however, one very important requirement, which is that the feedstock or crude oil should be rigorously pretreated to ensure it is free from phosphatides, impurities, trace metals and earth-removable pigments. If these impurities were allowed to remain in the oil, the high temperatures used in the process would darken the oil and hence resulting in poor quality product. The extent of pretreatment necessary depends on the particular oil type and its quality. Pretreatment of high fatty acid containing oils such as maize and sunflower, prior to physical refining, may comprise the addition of phosphoric acid or citric acid at temperatures of approximately 70 °C followed by high speed centrifugation to remove the hydrated gums. The centrifuged oil is then dried, bleached and winterised before physical refining. Both continuous and semi-continuous units may be used for physical refining (Hui, 1996).

The effluent streams that result from physical refining are similar in quality to those produced during degumming and deodorizing stages of caustic refining. But the quality and quantity of the effluent thus produced is superior to that produced during caustic refining due to the elimination of the neutralisation step and its associated effluent stream. Thus the final effluent from chemical refining will contain phospholipids or gums, inorganic phosphate from the pretreatment phase, volatile

organic compounds that are responsible for the oil's characteristic odours, as well as any residual free fatty acids and oil.

1.2.2 THE ACID OIL PLANT AND ITS EFFLUENTS

The main product of the acid oil plant is the acid oil, which is produced from a feedstock commonly known as soapstock. Soapstock is the byproduct of crude oil neutralisation with caustic soda during chemical refining process. As a result both the oil and the water phases have very high concentrations of fats, oils and grease (FOG), total suspended solids (TSS), biological oxygen demand (BOD), chemical oxygen demand (COD) loads, and including potentially valuable glycerin and free fatty acid sources, most processors include acidulation as part of the integrated facility. (Abou-Elela and Zaher, 1998).

Acidulation is one of the least desirable processes in the integrated facility. The process is rather difficult to perform effectively and it is generally the most cost ineffective process since it has no significant financial returns. The acidulation system is based on gravity separation that can be performed in either a continuous or a batch operation. The process involves collecting soapstock into equalization or holding tank. The mixture is heated and then treated with sulfuric acid (H_2SO_4) at controlled pH of about 2 to 2.2 units. After the reaction with the acid, the mixture enters a series of holding and settling tanks where the oil and the aqueous phases separate. Acid oil is skimmed from the top surface, which is followed by drying. The acid oil may be sold as it is or may be passed through an evaporative heat exchanger to remove excess

water. The product is sold as a feed ingredient or may also be used as a feedstock for soap and other industrial applications (Hui, 1996).

The acid water that is produced during acidulation may be neutralized with lime or other alkaline material prior to its discharge to the main effluent stream. This stream (acid water stream) is heavily polluted, with high concentrations of COD, BOD, TSS and sulfates. The concentrations of most of the contaminants in this stream far exceed the municipal discharge standards.

1.2.3 THE SOAP PLANT AND ITS EFFLUENTS

At Sealake industries, the main product of the soap plant is bar soap. No powdered soap is produce or manufactured on site. The soap manufacturing process may be performed as either a batch or continuous operation. The acid oil, which contains fatty acids from the acidulation phase, is neutralised using strong caustic hydroxide solution. The free fatty acids that results from the acid oil reacts with excess sodium hydroxide (NaOH) to form sodium salts which precipitate out of solution. After centrifugation and further treatment, the soap is then molded into desired shapes before being sold (Hui, 1996).

The effluent stream that is produced in this plant is generally known as lye water. It usually contains quantities of oils, free fatty acids, sulfates, and some sodium salts of free fatty acids. This stream is usually combined with acid oil water prior to its discharge to the final effluent stream.

1.2.4 WASH DOWN AND MISCELLANEOUS EFFLUENTS

Wash-down effluents are those effluents that emanate from regular cleaning of the edible oil factory. This cleaning is generally performed after a week's production or between changes of feed stock. Batch equipment may be cleaned after each batch has been processed. The cleaning of vessels is usually performed using live steam and hot water, to ensure maximum use of steam and the reduction in effluent volumes. Floor cleaning is conducted using hot water as necessary, which improves hygiene and reduces manual labour. The fats and oil bearing effluent stream resulting from cleaning is discharged to the main effluent stream via fat traps. The oil rich scum from the fat traps is recovered and recycled for reworking (Hui, 1996).

The miscellaneous effluents, which are a bulk of the remaining effluent, in terms of volume, emanate from the boiler house. Large volumes of effluent are generated from the ion exchange water softening units that are used for steam generation purposes. A considerable amount of effluent also comes from the return oil rich condensate from various vessels in the oil-processing factory. These steams combine with cooling tower blow down to form a significant volume of comparatively salty or saline effluent (Hui, 1996).

1.3 ON-SITE EFFLUENT TREAMENT METHODS AT SEALAKE INDUSTRIES

The three main effluent streams that are generated from the four main plants (see Figure 1.1) are channeled to the on-site effluent treatment plant. This plant is for treatment or pretreatment of incoming effluent prior to its discharge into the municipal sewer system. The three main effluents are the effluent from the refinery and packaging plants; the acidic effluent from the acid oil plant; and lye from the soap plant. The effluent plant comprises of two large holding tanks, pH correction tank, dissolved air floatation (DAF) unit and two settling tanks which are operated in series (Fig. 1.3).

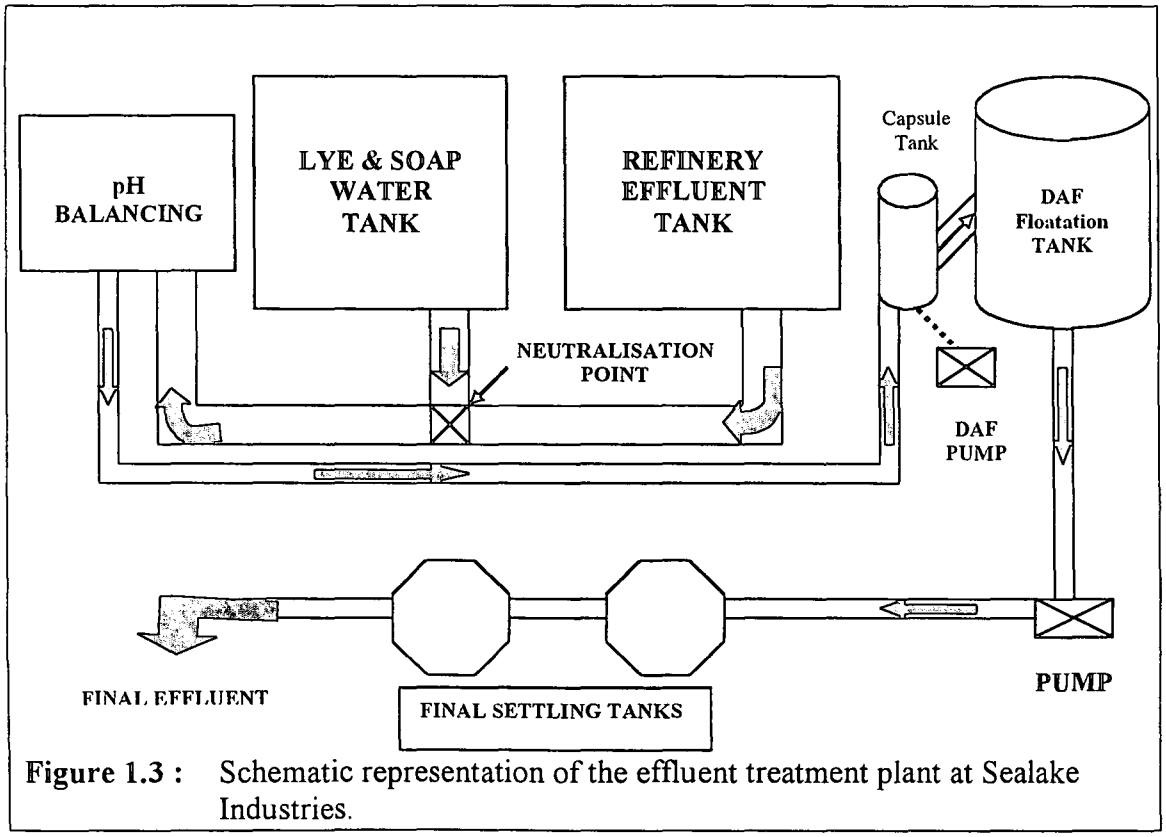

Figure 1.3 : Schematic representation of the effluent treatment plant at Sealake Industries.

Acidic effluents i.e. lye and acid water, are pumped and mixed together in the first holding tank. This effluent has a low pH of about 1-2 and is highly aggressive to concrete because of its sulfate content. On the other hand the refinery effluent has a high pH content ranging between 12 and 13. This effluent is pumped to the second holding tank. There are two processes for effluent treatment that are currently being used at Sealake Industries. The two effluent treatment processes are pH correction and physical separation of oil and grease using dissolved air floatation (DAF) method. After DAF treatment, lime and/or ferric chloride ($FeCl_3$) is added to the effluent, which is followed by settling in the two settling tanks in order to remove precipitated particles. The resultant effluent is discharged to the sewer system to be treated by Darvill Wastewater Works.

1.3.1 pH CORRECTION

The effluents from the two holding tanks are mixed together into a single effluent stream. Because of the pH differences in between the two effluent streams, the two streams are mixed at different volume ratios by controlling the flow rates from the two tanks such that the desired final pH of between 5.5 and 8.5 is archived in the final combined effluent stream. This effluent is finally directed to the acid equalisation tank for final pH adjustment. The effluent at this stage may be dosed with a polyelectrolite such as lime or ferric chloride to coagulate fats and to precipitate phosphates. This effluent is now ready for DAF treatment.

1.3.2 DISSOLVED AIR FLOATATION (DAF)

Dissolved air floatation process is a separation technique that employs the production of micro size (10-100 μm diameter) air bubbles to separate solids from liquids. A DAF system consist of three main unit processes, which are the pressurization system in the capsule, the floatation tank and the recycle system (see Figure 1.3).

The effluent from the pH correction tank is pumped into a capsule. Air is pumped into the capsule tank at high pressure (typically 350-450 kPa) resulting in the liquid becoming supersaturated with air. The supersaturated effluent is released to the floatation tank at atmospheric pressure. The sudden drop in pressure results in micro air bubbles being formed in water. The release of air bubbles is designed to take place in the presence of solids to be floated. The released air bubbles attach themselves to the oil particles imparting buoyancy, thus causing oil particles to rise to the surface of the floatation tank. Surface scrapers are used to remove the surface scum that is formed at the top of the floatation tank. People may mechanically or manually operate the surface scrapers (Metcalf and Eddy, 1991). Most of the fats (FOG) and inorganic phosphates are removed at this stage and hence reducing the organic and phosphorus load of the final effluent steam that is discharged to the sewer system. The pretreated effluent leaves the DAF system for final settling of the settleable solids in the two settling tanks. When both tanks are full, the effluent is then discharged to the

municipal sewer system for final treatment and disposal back to the water resource (river).

1.4 THE EFFLUENT PROBLEM AND LEGISLATION

Out of an estimated total of 16 edible oil factories in South Africa, only one factory was reported to be treating its effluent using only biochemical means. The rest of the edible oil plants generally use dissolved air floatation (DAF) for physical removal of oils and grease and pH correction (Steffen *et al.*, 1989). Even after application of these treatment processes, the remaining emulsified grease tends to clog the sewer pipes and pumps. The high organic (BOD and COD) and phosphorus loads create shock-loading problems for the receiving wastewater treatment installations (Eroglu *et al.*, 1990, Sokolovic *et al.*, 1992).

At present the Department of Water Affairs and Forestry regulates water resources pollution from point sources through legislation stipulating that the effluents from industries must comply to uniform discharge standards that are set at technologically attainable levels. These controls or regulations limit the rate of deterioration of the receiving water bodies, and are set down in the National Water Act, 1998 (Act 36 of 1998). The National Water Act, 1998 (NWA) repeals the old Water Act, 1956 (Act 54 of 1956), and was motivated by the need for new legislation that would reflect democratic principles and equitable access to water resources by al symbolised by the

slogan "Some for all, Forever" (Department of Water Affairs and Forestry, 1997). The Act provides for the compulsory purification of effluents by the user to specified standards and its subsequent disposal in a manner that will make it available for reuse.

The local authorities (the Pietermaritzburg-Msunduzi Transitional Local Council in this case) and the municipal sewage treatment plants (Darvill Wastewater Works) have increased pressure on industries to increase the efficiency of in-house effluent handling and treatment methods. Due to this increased pressure, Sealake Industries is taking steps towards investigating viable biological treatment processes to be implemented on-site to supplement the existing physico-chemical effluent treatment methods.

1.5 PROJECT AIM AND OBJECTIVES

The aim of this study was to design and operate a laboratory scale activated sludge treatment process that would produce the final effluent having a regulatory acceptable COD and phosphate loads prior to its discharge to the municipal sewer system. The study was guided by the following objectives:

1. To characterise the main pollution parameters in the edible oil final effluent
2. To conduct a preliminary effluent treatment investigation
3. To design and operate a laboratory scale effluent treatment process
4. To optimise the system operation for COD and Phosphorus removal.

CHAPTER 2

LITERATURE REVIEW

2.1 THE EUTROPHICATION PROBLEM

Eutrophication is a natural ageing process that occurs regularly in lakes over hundreds of years and is usually limited to quiescent bodies of water such as lakes and impoundments (Lilley *et al.*, 1997). The natural eutrophication process results from continuous enrichment of impoundments with nutrients, notably phosphorus (P) and nitrogen (N). This natural process is however greatly accelerated by human activities in the catchment areas of lakes and impoundments, through the increased input of nutrients (Bolitho, 1976).

Gross eutrophication is marked by massive increase in algal growth in the catchment area. This condition is met when the inorganic soluble nitrogen (N) and phosphorus (P) loads to impoundments reaches concentrations in excess of 0.3 mgN/L and 0.05 mgP/l, respectively (Lilley *et al.*, 1997). The algal species that are associated with eutrophication can be divided into four broad groups, namely, the blue green algae (Cyanobacteria), the green algae (Chlorophyta), the Diatoms, and the Flagellates. These organisms may be taken as effective indicators of eutrophication when they form the majority of species present (Rudd, 1979).

The symptoms of eutrophication have various effects. Although algae forms an essential part of the aquatic environment, their excessive growth is detrimental to the aquatic ecosystem. When the alga blooms die in large numbers and decay, a large pool of nutrients is released into the water body, which results in accelerated growth of other organisms. Consequently the oxygen content of the water body is depleted and the lower water (hypolimnion) becomes anaerobic due to thermal stratification. As a result eutrophication may constitute a health hazard to vertebrate animals (Dillon and Molot, 1996).

Studies on causes and control of eutrophication (Chutter, 1990; Dillon and Molot, 1996) have shown that eutrophication can be effectively controlled if the nutrient loads to the receiving waters is strictly regulated. Because of the ability of some blue-green algae to fix atmospheric nitrogen gas to support primary production, it is therefore virtually impossible to control eutrophication by limiting nitrogen. Therefore in most cases phosphorus has been shown to be the limiting nutrient (Chutter, 1990; Dillon and Molot, 1996; Orhon and Artan, 1994; Wentzel *et al.*, 1990).

In South Africa the eutrophication problem is particularly serious due to the long storage times of dams and reservoirs, with resultant accumulation of phosphate and nitrate, and the high summer temperatures, which promote algal growth (Bolitho, 1976). Eutrophication is a major threat to South African water resources for various reasons. These include a rapid increasing population, irregular rainfall often leading to drought conditions, irrigation demands by agricultural industry, industrial

requirements, and loss of source supply due to degradation of rivers. The prime example of the eutrophication problem in a South African context is the deterioration of the Hartbeespoort Dam during the mid 1970's, such that during 1977 to 1979, R200 000 was spent by the Department of Water Affairs (DWA), which is responsible for management and development of the national water resources of South Africa, on various rehabilitation programs (Rudd, 1979). Joska and Bolton (1994) reported that South Africa was spending approximately 400 thousand Rands anually for controlling macroalgae, especially in the former Transvaal region. *Cladophora glomerata* was reported to the major problematic algal weed in South Africa (Joska and Bolton, 1994)

In 1980, a special standard was promulgated in South Africa limiting the soluble ortho-phosphate ($O\text{-}PO_4^{3-}$) concentration from point source discharge to less than 1 mg/L for certain sensitive catchment areas. A five years grace period was allowed before enforcement, to allow for phosphorus removal technology to be developed and implemented. This stimulated considerable research in South Africa towards the understanding of the mechanisms that are involved in the biological phosphorus removal process and towards further development and refining the technology for practical implementation (Wentzel *et al.*, 1990).

2.1.1 Source of Nutrients (Phosphorus)

Nutrients that cause rapid eutrophication are introduced to the water environment by human activity from both diffuse and point sources. In this study more attention was focused on the nutrient phosphorus (P).

2.1.1.1 Diffuse Sources

Phosphorus is introduced to the environment in relatively small concentrations over large areas due to run-offs from rural and urban areas. The widespread use of agricultural fertilizers has a major contribution to this source of P pollution. In most instances, control and treatment to remove P from this source is not economically feasible, especially P originating from rural run-offs. For urban run-offs, natural and artificial reed beds are used as systems for phosphorus removal from contaminated water. In these systems the soluble P in waste stream is converted to P trapped in the reeds that grows in the beds. The entrapped P in reeds is removed when reeds are harvested. Some soluble P is not removed from the reed beds but remains trapped in the sediments lying at the bottom of the reed bed. This soluble P accumulates continually in the sediments (Wentzel *et al.*, 1990; Lilley *et al.*, 1997)

2.1.1.2 Point Sources

This P pollution is mainly due to industrial and domestic effluent discharges. In South Africa 80% to 90% of nutrients in water originate from point sources. These are usually, but not always, the main contributors of P pollution to the environment. This type of P pollution is easy to control because pollutants from the residential and industrial areas are concentrated to a point by means of sewers and treatment methods are readily available (Wentzel, 1992).

The edible oil industry in South Africa is both a major water consumer and polluter (Steffen *et al.*, 1989). In anticipation of water shortages in South Africa the then Water Act, (Act 54 of 1956), which was later replaced by the National Water Act, 1998 (Act 36 of 1998), made provision for the compulsory purification of effluents by industries (including municipal wastewater treatment works) to specified standards and its subsequent disposal in a manner that would make it available for reuse (DWAF, 1997). To comply with the effluent discharge standard of 1 mgP/L, the Darvill Wastewater Works (DWW) is increasing pressure on the industries in the Pietermaritzburg area to implement cleaner production technologies and some form of an in-house effluent treatment system prior to discharge to the sewer system. As a result, the current study was initiated in conjunction with Sea-Lake industries to find a biological solution to reduce the phosphorus load in the effluent, prior to its discharge to Darvill Wastewater Treatment Works for final purification.

2.2 Treatability of Edible Oil Effluent

Food processing effluent including effluent from the edible oil processing industry are a complex mixture of floating, settleable, suspended and dissolved materials. Complete treatment of these effluents requires a combination of physical, chemical and biological treatment processes (Dalzell,1994). The physical nature of fatty material is of great concern when considering any purification method. The fatty contaminants in the edible oil effluent can be characterized in three ways viz.: by polarity, biodegradability and physical characteristics. Polar contaminants are usually derived from animal and vegetable sources such as food industry operations, including the edible oil processing industry. The non-polar contaminants are derived from petroleum and mineral sources and are generally non-readily biodegradable (Grant, 1980; McDermott, 1982; Sutton *et al.*, 1994)

It used to be a common practice to group effluents from the edible oil processing industry, which has polar and readily biodegradable fatty components, with effluents originating from the petrochemical industry. This was because some pollution control authorities failed to recognise that there is a difference between fatty effluents from food industry and those from petrochemical industry (Grant, 1980; Tano-Debrah, 1999). As a result of this joint grouping of petrochemical effluents and the effluents from the food industry, the vegetable oil processing industry has since been widely perceived as problematic (Grant, 1980).

2.2.1 Physical Treatment

The effluent from edible oil processing industry carries an appreciable quantity of fatty material (or fats, oils and grease (FOG)). Prior to any form of treatment, it is desirable to install an oil-water separation system as the first phase. This will reduce the pollution load being discharged and also yield a recovery of potential usable fat. The separation of water phase and the oily phase from the edible oil effluent can be archived using two simple processes, which are gravity settling and dissolved air floatation (DAF).

2.2.1.1 Gravity Settling or Fat Traps

The removal of separable fatty matter (SFM) or FOG from both domestic and industrial effluents has for many years been archived through the use of fat traps. The gravity fat trap is usually installed as standard equipment on all process effluent steams and is the simplest form of physical treatment (Eroglu *et al.*, 1990). Fat traps are designed to produce a slow and gentle uniform flow through a tank, which allows density difference to bring the fatty material to the surface without disturbing any accumulated scum and sludge. In the homemade interceptors, fat removal can be done manually using surface scraping but it is important that a good platform access be provided to allow easy performance of this task. Removable and adjustable retaining baffles can also be hung on the walls of the tank. The purpose-built units, as oppose to the homemade built tanks, normally include a moving scraper and an endless chain with a trigger to activate a scum removal valve (Dalzell, 1994; Grant, 1980).

Traditionally, settlement tanks have been built of reinforced concrete. The edible oil effluent contains high sulfate concentrations, which makes it highly aggressive to concrete even after neutralization. As a result gravity fat traps for the edible oil effluent has to be constructed with a material that is resistant to the high sulfate content (Eroglu *et al.*, 1990). Fat traps are designed according to general settlement principle. According to Dalzell (1994) a typical fat trap has a length to width ratio of 2:1, a retention time of 10-40 minutes and the loading of $0.4m^3/m^2$ per hour to 3 m^3/m^2 per hour at maximum flow rate. Table 2.1 shows some typical examples from literature.

Table 2.1: Some examples of loading rates of fat traps (Dalzell, 1994)

Product	Retention time (minutes)	Surface loading (m^3/m^2 per h)
Margarine processing	**20-40**	**3**
Soap	**40**	**1**
Milk, Butter and Cheese	**30**	**1**
Milk processing	**20**	**0.4**

The usual problem with fat traps is that they are expensive and occupy a large surface area, which makes them not suitable for industrial application, especially for small industrial establishments (Dalzell, 1994; Grant, 1980). The disadvantage of using gravity fat traps is that they are unable to reduce emulsified fatty material content of

wastewater under 500mg/L, which is high to discharge to municipal sewer system (Eroglu *et al.*, 1990).

2.2.1.2 Dissolve Air Floatation (DAF)

The common problem with fat containing effluents is precipitation and emulsification due to pH, temperature, pumping and detergents. Under such circumstances, gravity separation with a simple fat trap rarely gives satisfactory results, as has been mentioned before. The alternative to circumvent this problem is to use assisted floatation, in this case, dissolved air floatation (DAF). DAF relies on the introduction of supersaturated water into the effluent. Micron size (10-100 μm) air bubbles are produced from the release of gas (air) at atmospheric pressure from liquid that has been supper saturated with air under pressure in a saturation vessel. (Lilley *et al.*, 1997; Oztark *et al.*, 1990)

The release of air bubbles is designed to take place in the presence of solids to be floated fore example emulsified fat droplets. There is a hydrophobic mutual attraction between the bubbles and the suspended oil particles that leads to the floatation of solids through imparted buoyancy. This causes the sludge particles to rise to the surface from where they can be removed by surface scrapers. The compaction of layer upon layer of rising sludge forces the float above water surface (Dalzell, 1994; Lilley *et al.*, 1997; Ozturk *et al.*, 1990).

The main advantage of using dissolved air floatation is its speed. Floatation rates are usually two to three times those of gravity fat traps and the tank sizes are much smaller, thus making it ideal for industrial application where space is of vital importance. DAF also has the advantage of avoiding potential anaerobic conditions that are common with gravity fat traps, which reduces the odor nuisance. The efficiency of process like gravity separation is dependent on particle size, but is also affected by bubble attachment and the efficiency of gas transfer (Dalzell 1994).

Dissolved air floatation is more difficult to operate when compared to the gravity fat trap and therefore more skilled labour is required (Lilley *et al.*, 1997). The other disadvantage of DAF is that it has higher operating cost than that of a simple gravity fat trap and the relatively complex technology is not well suited to effluent with variable characteristics (Dalzell, 1994). Several studies (Grant, 1980; Eroglu *et al.*, 1990; Tünay *et al.*, 1998) have shown that a well-operated DAF system has a better performance than the gravity fat trap. Eroglu *et al.*, (1990) using a full scale DAF unit at 6.6 hours hydraulic retention time (HRT), reported a fatty material removal of more then 80% and FM recovery of 65kg/d, which is a valuable by-product that can be used for soap production.

2.2.2 Chemical Treatment

Chemical treatment can improve the performance of most of the physical and biological processes used in the effluent treatment. This involves subjecting industrial wastewater to strong reducing or oxidizing agents. The most commonly used

chemical methods for effluent treatment are pH correction and coagulation to improve settlement rates by increasing particle size density (Dalzell 1994; Lilley *et al.*, 1997; Eroglu *et al.*, 1990).

In South Africa, all but one edible oil manufacturers use chemical treatment as the sole effluent treatment method to reduce pollution load prior to discharge to the municipal sewer system or the river body (Steffen *et al.*, 1989). Chemical treatment is used mainly for carbonaceous material and phosphorus removal from wastewater. Lime is the most widely used chemical coagulant for both COD and phosphorus reduction (Lilley *et al.*, 1997). Chemical phosphorus removal through phosphate precipitation can also be achieved using iron (Fe^{3+}) and aluminum (Al^{3+}) salts such as ferrous sulphate; ferric sulphate; ferric chloride; aluminum chloride; and aluminum sulphate (Dalzell, 1994; Loots *et al.*, 1994; Wentzel *et al.*, 1990; Lilley *et al.*, 1997; Grant, 1980).

At Sealake industries, lime and ferric chlorides are added to the neutralized effluent up-stream of the DAF unit. Eroglu *et al.*, (1990) reported that ferric chloride was the most effective coagulant during physicochemical treatability studies, and that it resulted in a BOD_5 reduction of 36%. Dart (1974) (as cited from Ozturk *et al.*, 1990) reported a 60% BOD and 88% fats oils and grease (FOG) removal through lime addition of 1500 mg/L, after pH adjustment to pH 10 by addition of sodium hydroxide, for a water containing 1040 mg/L BOD_5 and 800 mg/L FOG respectively. But the study did not include chemical phosphorus removal.

2.2.2.1 Advantages of Chemical Treatment

Chemical phosphorus removal in wastewater is reliable, and with proper control and dosages, a consistently low effluent phosphorus concentration can be archived (Lilley *et al.*, 1997). Chemically bound phosphorus is not easily dissociated in water, which prevents the release of the bound phosphorus back into the water body (Loots *et al.*, 1994). When alum is used as a coagulant, it is possible to recover both aluminum and fatty material from fat/alum flocks through acid splitting (Pope *et al.*, 1975 as cited from Grant, 1980).

2.2.2.2 Disadvantages of Chemical Treatment

The chemicals that are used during chemical treatment are corrosive in nature (strong oxidizing agents) and hence great care is required when handling them, which necessitate the use of more expensive equipment that is resistant to corrosion (Lilley *et al.*, 1997). Chemical treatment of effluent is expensive due to high chemical costs. According to Pitman (1988), estimated costs to the Johannesburg City Council at 1988 levels would be in the region of 10 million rands per annum, were they to persist in using chemical treatment alone. The other problem associated with chemical usage is increased mineralization of water through the release of ions. Chemical coagulants usually contain chlorides or sulphates, which remain in solution thus increasing the conductivity or the salinity of the receiving water body. This is of particular importance in South Africa where water is reused several times before entering the oceans (Wentzel *et al.*, 1990). Paul, 1999 (personal communication) expressed a

concern that there was increase pressure on Sealake Industries by the Pietermaritzburg-Msunduzi Transitional local council to reduce the effluent conductivity levels.

2.2.3 Biological Treatment

Biological treatment technology offers an efficient and a cost-effective means for treating edible oil industrial wastewater. Biological treatment of edible oil effluent may be carried out under either aerobic or anaerobic conditions, or a combination of both (Hui, 1996; Eroglu *et al.*, 1990; Grant, 1980; Seng, 1980).

2.2.3.1 Anaerobic Treatment Process

Anaerobic digestion has long been practiced as a stabilization process for waste sewage treatment sludges, but the process has not been widely adopted for effluent treatment, with only very high strength industrial effluent being seriously considered (Grant, 1980). The effluent from the vegetable oil refining industry is loaded with sulphates, fats and organic matter, which makes anaerobic treatment an attractive alternative prior to any aerobic treatment process (Lens *et al.*, 1995; Ozturk *et al.*, 1990; Eroglu *et al.*, 1990). Studies by Eroglu *et al.*, (1990) have shown that lime addition and activated sludge treatment does not bring about appreciable decrease in the sulphate concentration from acidic effluent.

In the anaerobic digestion of high strength industrial waste containing high level of sulphate, the two process of concern are sulphate reduction and methane production, the latter being inhibited by the former (Eroglu *et al.*, 1990). In their study, Eroglu *et al.*, 1990) reported a 60 % sulphate reduction in the anaerobic filter reactor with a concurrent reduction of 60 % for COD. From this study the conclusion was that anaerobic treatment of acidic effluent from the edible oil refining industry may be used to replace chemical treatment as a pretreatment step.

2.2.3.2 The Activated Sludge Treatment Process

The activated sludge treatment is generally considered to have its origin in the aeration experiments which were carried out by Ardern and Lockett at Manchester in 1914 (Droste, 1997). The activated sludge treatment process is a suspended growth system which could be defined as a suspension of microorganisms, both dead and living, in wastewater (Aitken *et al.*, 1994).

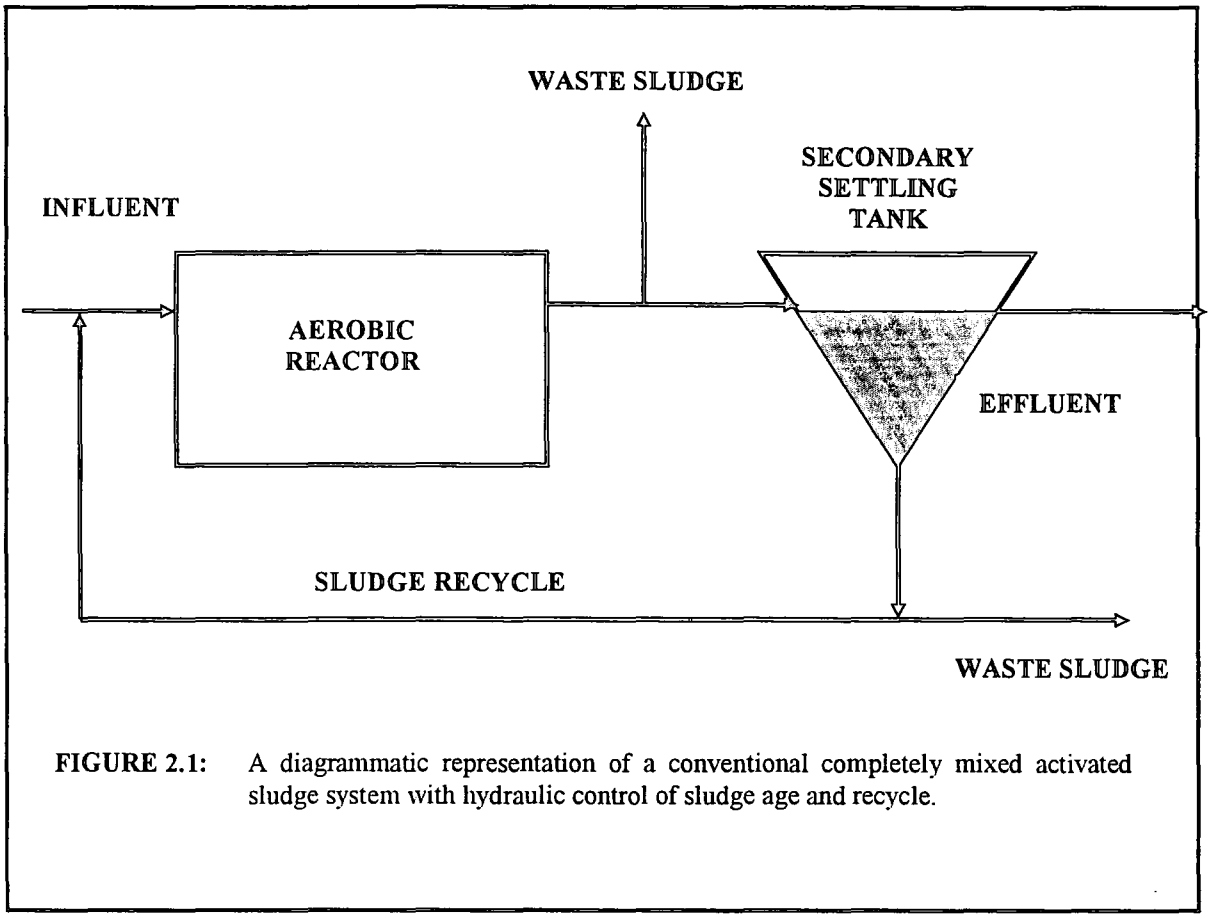

FIGURE 2.1: A diagrammatic representation of a conventional completely mixed activated sludge system with hydraulic control of sludge age and recycle.

Since its inception, the activated sludge process has become one of the main methods used world wide for the purification of wastewater containing biodegradable organic compounds, its most important application being in the treatment of domestic sewage (Horan, 1991; Droste, 1997). The conventional activated sludge treatment process involves two distinct operations usually performed in two separate basins; (i) aeration in the aeration chamber and (ii) settling in a secondary settling tank (Fig. 2.1).

The principal unit in all the activated sludge process is the aeration tank or the aerobic reactor. The contents of the aeration tank comprise an aerated mass of microorganisms, termed flocs, surrounded by the influent wastewater (or the mixed

liquor). The activated sludge flocs are made up of aggregate of microorganisms, inorganic and organic colloidal material and larger particulate matter, all held together in a compact organic matrix. A large number of protozoa, free-swimming ciliates and flagellates are found both in the mixed liquor and in the floc matrix (Horan, 1991). The flocs are mixed with incoming sewage in the presence of oxygen, which is supplied through aeration. In the aeration basin, some of the substrate is completely oxidized into harmless end products of CO_2, H_2O, and other inorganic substances that are required to proved energy for the growth of microorganisms (Horan, 1991; Bitton, 1994; Droste, 1997).

The second operation in the activated sludge treatment process is the separation of the biomass and other suspended solids from the treated wastewater. This is accomplished in a secondary settling tank. Under the quiescent conditions of the secondary settling tank the activated sludge flocs settle rapidly to yield the sludge with high solids concentration. The settled sludge is pumped back to the aeration tank via a recycle steam while some portion of it is removed from the system through wastage on continuous or intermittent basis. Consistent wastage of sludge ensures that the concentration of biomass in the aeration chamber remains constant within the desired range (Droste, 1997; Horan, 1991). The clarified effluent at this stage is relatively devoid of any suspended particles and may be discharged into a watercourse after tertiary treatment, which may include chlorination or irradiation.

Proper operation of a conventional activated sludge process depends on the manipulation of the three basic design parameters, which are: organic loading rate

(B_x) (or the sludge age, (θ_s) as an alternative); the operating value of MLVSS; and dissolved oxygen (DO) concentration in the mixed liquor (Horan, 1991). The organic loading rate is frequently used in place of sludge age as a key design parameter, since its use allows the determination of the required biomass without the need to make reference to the process kinetic coefficients.

The choice of limiting values that may be assigned to the main design parameter to archive a particular level of performance in the purification of a particular wastewater is most reliably made through pilot plant operation. The quality of the treated effluent is always a key consideration in the design and operation of any activated sludge process although other operational factors or parameters also influence the choice of sludge age and organic loading rate. The more important factors are the desired degree of stabilization of the sludge biomass and the need to produce a sludge biomass with good settling properties (Horan, 1991)

2.3 BIOLOGICAL NUTRIENT REMOVAL TREATMENT PROCESS

Biological nutrient removal refers to the removal of the primary nutrients (carbon, nitrogen and phosphorus) from wastewater which cause eutrophication (Wentzel and Ekama, 1997; Lilley *et al.*, 1997). The activated sludge process configuration is manipulated to create environmental conditions in the modified system favorable for the optimal growth and activity of the microorganisms responsible for removal of nutrients from wastewater (Wentzel and Ekama, 1997), in order to achieve maximum efficiency. These modifications may include the addition of anoxic (no oxygen, but

nitrate and nitrite present as electron acceptors) and anaerobic (no oxygen and no nitrate or nitrite present) zones in the system.

Biological nutrient removal is mediated by highly diverse mixed cultures that develop in the modified activated sludge process. These mixed cultures work in sequence to remove different nutrient components at different stages of the process (Wentzel and Ekama, 1997). Table 2.2 summarises the activities that take place in different zones or stages in a biological nutrient removal process.

Table 2.2: Principal organism groups in Biological Nutrient Removal System, their function and the zones in which these functions are performed (Wentzel and Ekama, 1997)

ORGANISM	BIOLOGICAL PROCESS	ZONE OF ACTIVITY
Ordinary heterotrophs (unable to accumulate P)	COD removal (organic degradation; DO uptake)	Aerobic
	Ammonification (organic N $\rightarrow$ NH_4^+)	Aerobic
	Denitrification (organic degradation; $NO^-_3 \rightarrow NO^-_2 \rightarrow N_2$)	Anoxic
	Fermentation (RBCOD $\rightarrow$VFA)	Anaerobic
Poly-P heteretrophs (accumulate poly-P)	P release (VFA uptake; PHA storage)	Anaerobic
	P release (VFA uptake; PHA storage)	Anoxic
	P uptake (PHA degradation)	Anoxic
	P uptake; P removal (PHA degradation; DO uptake)	Aerobic
Autotrophs (nitrifiers)	Nitrification ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$; DO uptake)	Aerobic

RBCOD : Readily Biodegradable COD
VFA : Volatile Fatty Acids
PHA : Polyhydroxyacetate
DO : Dissolved Oxygen

2.3.1 Carbonaceous Energy (COD) Removal

Carbon in wastewater streams occurs in organic and inorganic forms. Heterotrophic organisms use organic compound for their metabolism while the inorganic compounds are metabolized by a group of organisms collectively termed autotrophs. Both forms of carbon are removed from wastewater through a series of oxidation and reduction (redox) reactions, oxidizing the carbon source to carbon dioxide CO_2 and water (H_2O). The carbon dioxide then escapes to the atmosphere, thus removing carbon from wastewater (Ubisi *et al.*, 1997; Orhon and Artan, 1994).

In the bioreactor of the non-nitrifiying aerobic activated sludge systems the mixed liquor organic suspended solids or biomass is made up of three components viz: heterotrophic active biomass; endogenous residue; and inert material. In the nitrifying aerobic and anoxic/aerobic activated sludge systems, a fourth mixed liquor organic suspended solids component is included, which is the autotrophic active biomass. During the biodegradation processes of COD removal and denitrification in the mixed liquor component of the activated sludge, more heterotrophic organisms are produced through the synthesis of living heterotrophic organisms on biodegradable organic substrate (Ubisi *et al.*, 1997).

The inert material or the unbiodegradable particulate organics from the influent wastewater, on entering to the bioreactor, are enmeshed in the mixed liquor organic suspended solids, which are then removed from the system together with heterotrophic biomass through sludge wastage from the aerobic reactor or from the

return activated sludge underflow (Dold *et al.*, 1991; Ubisi *et al.*, 1997; Wentzel *et al.*, 1995).

The energy content of wastewater can be expressed using common substrate parameters, which are 5-day biological oxygen demand (BOD_5) and/or chemical oxygen demand (COD) (Orhon *et al.*, 1998; Lilley *et al.*, 1997). The COD test is the most popular monitoring method used at treatment works since it is quicker and gives a more accurate reflection of the energy content of the system then the BOD_5 test (Ekama *et al.*,1984; Lilley *et al.*, 1997). Because COD is a chemical test, biologically undegradable fractions of the wastewater are included in the measurement, while the (BOD_5) measures only the fraction which is biodegradable.

In a biological nutrient removal process, the carbonaceous material or the COD content of system is divided into three main fractions viz: the unbiodegradable; biodegradable; and heterotrophic active biomass (Wentzel *et al.*, 1995; Orhon *et al.*, 1998; Dold *et al.*, 1991). The unbiodegradable COD(S_u) has two subfractions (Fig. 2.2), the unbiodegradable particulate (S_{up}) and the unbiodegradable soluble (S_{us}). The biodegradable COD also has two subfractions, the slowly biodegradable (SBCOD) or (S_{bs}), and the readily biodegradable RBCOD or (S_{bs}) fractions. Both the RBCOD and SBCOD fractions are based wholly on the dynamic response observed in an activated sludge system (Dold *et al.*,1980, as cited from Wentzel *et al.*, 1995).

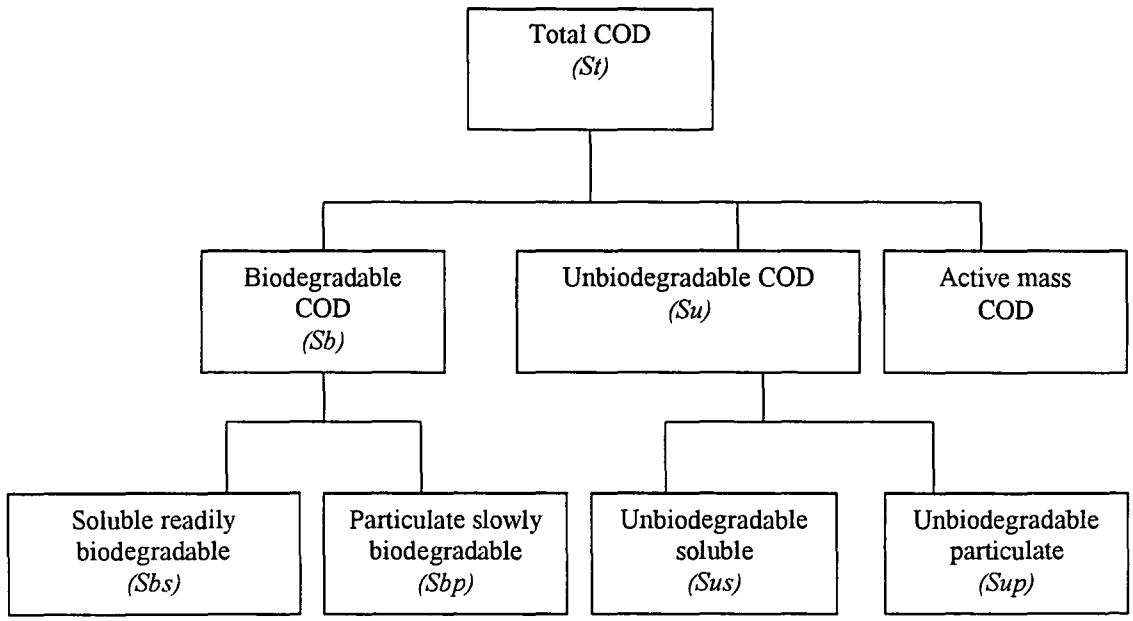

Figure 2.2: Division of influent COD into its constituent fractions (Dold *et al.*, 1991 as cited from Wentzel *et al.*, 1995)

2.3.2 Nitrogen Removal Process

Nitrogen in wastewater may be divided into two main fractions: free & saline ammonia and organically bound nitrogen (Ekama *et* al., 1984; Wanner, 1997). Like the COD fractions, the organically bound nitrogen may be subdivided further into non-biodegradable and biodegradable fractions, with both these fractions having soluble and particulate sub-fractions (Lilley *et al.*,1997). Generally domestic wastewater does not contain any nitrate (NO_3^-) or nitrite (NO_2^-) in the influent, but some industrial wastewater does contain appreciable quantities of nitrates and/or nitrite, depending on the characteristic and nature of that particular effluent. Thus for industrial wastewater it is important that, in addition to the Total Kjeldal Nitrogen (TKN) test and free/saline ammonia test, the nitrate and nitrite test be conducted to determine the quantity of each nitrogen fractions in the influent stream.

The first step in the nitrogen removal process is the nitrification stage. In this process, free and saline ammonia, which results from the hydrolysis of organic nitrogen, is oxidized first to nitrite (NO_{2-}) and thereafter to nitrate (NO_{3-}). The oxidation process takes place in the presence of oxygen in an aeration reactor. The autotrophic bacteria are responsible for the oxidation process (Ubisi *et al.*, 1997). These organisms have quite different behavioral characteristics when compared to the ordinary heterotrophs (Lilley *et al.*, 1997). There are two important autotrophs that are responsible for nitrogen oxidation, which are: *Nitrosomonas* spp. which converts the free and saline ammonia to nitrite (NO_2^-); and the *Nitrobacter* spp. which converts nitrites to nitrates (NO_3^-) (Ekama *et* al., 1984; Lilley *et al.*, 1997).

2.3.2.1 The Anoxic Zone

The anoxic zone is a zone or the bioreactor of the activated sludge process that is virtually free of oxygen but which contains nitrates and nitrites or has a substantial input of nitrates. The anoxic zone constitutes the second step in biological nutrient removal. Nitrified mixed liquor (rich in NO_x) is recycled from the aerobic reactor to the anoxic reactor through the A-recycle. The A-recycle is a return flow line between the aerobic and the anoxic reactor, which is responsible for returning oxidized mixed liquor from the aerobic reactor to the anoxic reactor for denitrification (see Fig. 2.3).

In the anoxic zone, the absence of oxygen allows the none-poly-P organisms or the ordinary heterotrophs to use the nitrates as a terminal electron acceptor during respiration, thus reducing it to nitrogen gas in a process called denitrification (Ekama and Wentzel, 1999; Wentzel *et al.*, 1992, Pitman 1988; Pitman *et al.*, 1991). The elemental nitrogen thus formed escapes to the atmosphere, thus completing the nitrogen removal process. The detailed mechanism of the biological nitrogen removal is beyond the scope of this project and will not be discussed further.

2.3.3 Biological Phosphorus Removal

Biological phosphorus removal is a well-documented phenomenon that is applied to reduce phosphorus in wastewater. Soluble ortho-phosphate in wastewater is converted into stored phosphorus (trapped) in the biological sludge mass of the activated sludge system. The stored phosphorus (P) is then removed from the system with the sludge

that is wasted daily (Wentzel *et al.*, 1990; Ekama *et al.*, 1984; Bdrjanovic *et al.*, 1997).

Biological excess phosphorus removal (BEPR) process refers to the biological uptake and subsequent removal of phosphorus (P) by the activated sludge in excess of the amount that is removed by "normal" completely aerobic (or conventional) activated sludge system. This process is as the result of cooperation of different groups of bacteria, primarily fermentation bacteria, phosphorus accumulating bacteria (poly-P bacteria), other heterotrophs and autotrophs in the same systems (Danesh and Oleszkiewcz, 1997).

Traditionally, bacteria of the genus *Acinetobacter* spp. were considered to be mostly responsible for the excess phosphorus removal process (Fuhs and Chen, 1975; Buchan, 1980; Buchan 1983). Other studies (Lötter and Murphy, 1985; Sidat *et al.*, 1999; Atkinson, 1999) have shown that in addition to *Acinetobacter* spp., other bacterial species including Gram-positives such as *Pseudomonas* spp., have the propensity to accumulate phosphorus in excess of their metabolic needs.

To stimulate the growth and dominance of the poly-P organisms in an activated sludge system to achieve excess biological phosphorus removal, two conditions are required:

(a) An anaerobic-aerobic sequence of reactors

(b) Presence of volatile fatty acids (VFA) or short chain fatty acids (SCFA) (e.g. acetic acid) in the anaerobic reactor (Comeau *et al.*,

1986; Wentzel *et al.*, 1986; 1991; Bdrjanovic *et al.*, 1997; Lilley *et al.*, 1997).

Successful design and operation of an activated sludge plant for bio-P removal entails creating conditions in the plant which favor propagation and proliferation of these organisms over the organisms which do not have this propensity (Lilley *et al.*, 1997). For brevity these organisms will be referred to here as poly-P organisms as opposed to non-poly-p organisms, which are unable to accumulate phosphorus beyond their metabolic requirement.

A number of mainstream processes have been developed for both nitrogen and phosphorus removal. These processes have evolved from the activated sludge process through the incorporation of the unaerated sludge mass fraction (anaerobic and/or anoxic zones) at the upstream end of the aerobic zone.

In South Africa, the 5 stage Bardenpho process, 3 stage Phoredox process, the Johannesburg process, UCT process, and the Modified UCT processes are the wastewater treatment process that are commonly used for domestic wastewater treatment (Fig. 2.3) (Lilley *et al.*, 1997). Table 2.3 summarises the advantages and disadvantages of using each process for wastewater purification purposes. The general mechanism of biological excess phosphorus removal process is discussed in detail in the following section.

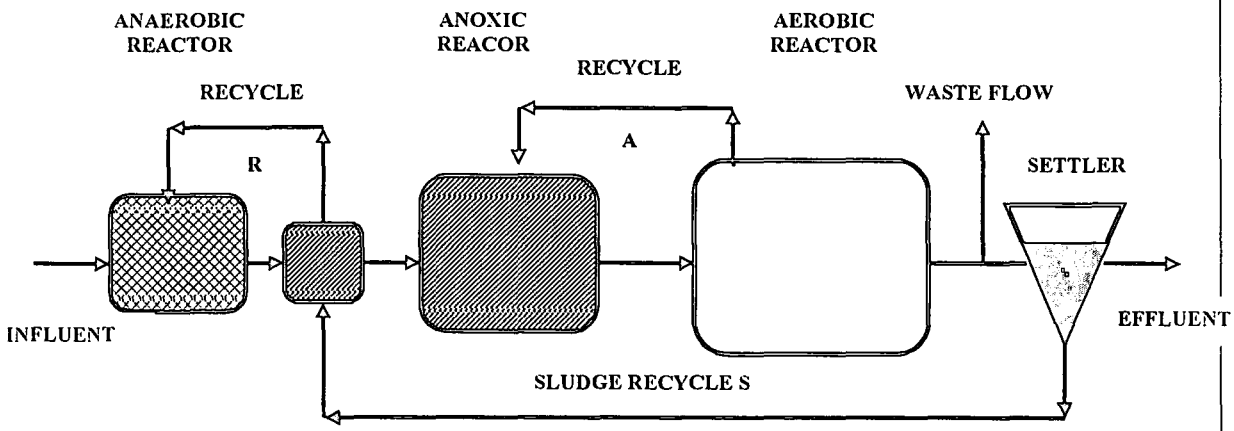

Figure 2.3a: The Modified UCT process for biological nitrogen and phosphorus removal

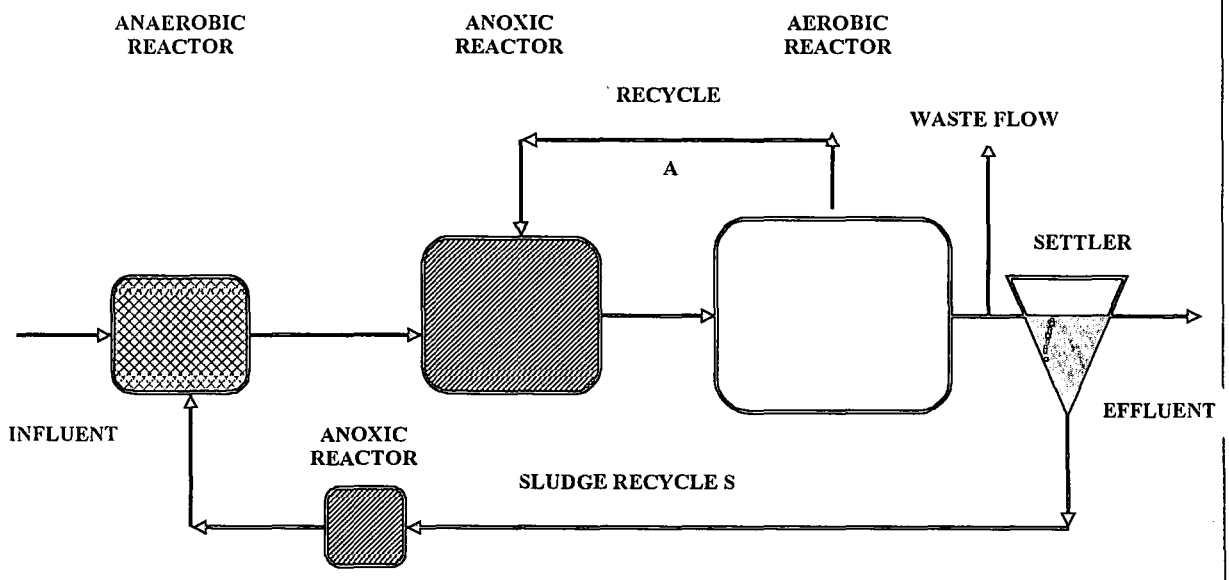

Figure 2.3b: The Johannesburg process for biological nitrogen and phosphorus removal

Figure 2.3: Configurations of commonly used Biological Nutrient Removal (BNR) processes in South Africa (Lilley *et al.*, 1997)

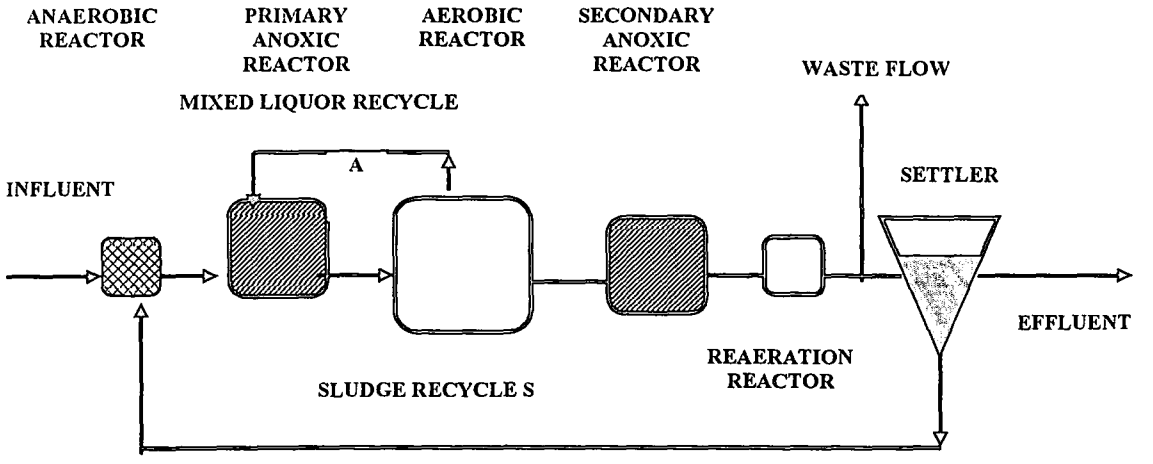

Figure 2.3c: The Phoredox process for biological nitrogen and phosphorus removal

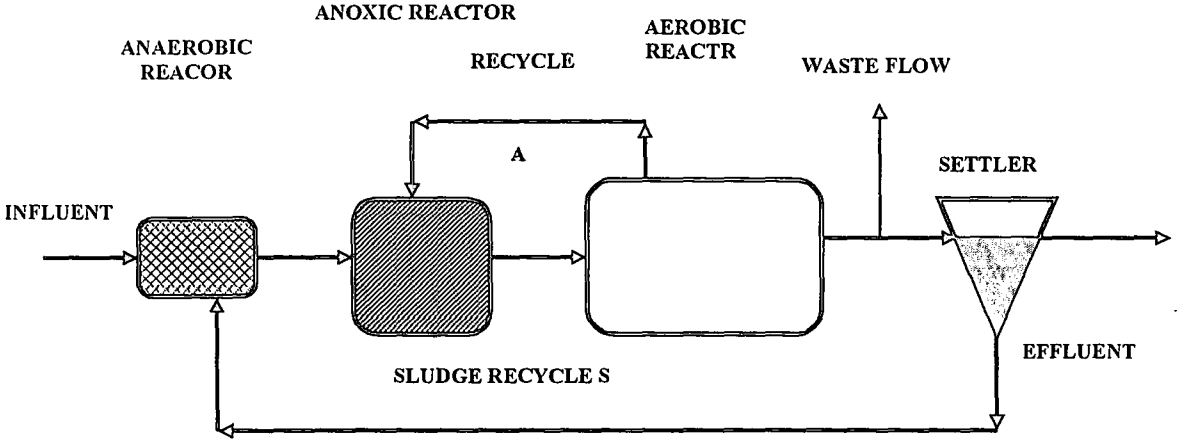

Figure 2.3d: The 3 stage Phoredox process for biological nitrogen and phosphorus removal

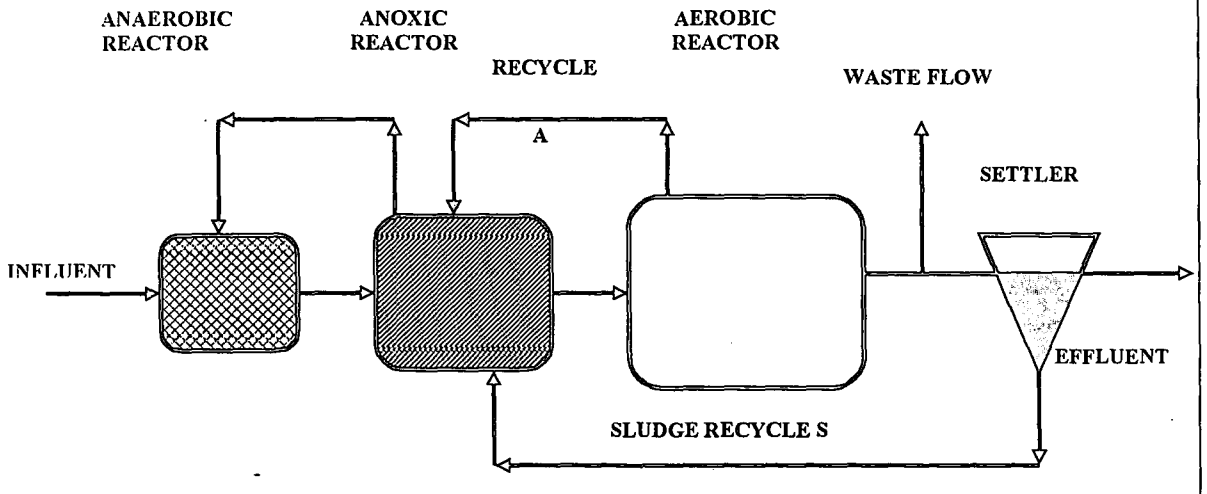

Figure 2.3e: The UCT process for biological nitrogen and phosphorus removal

Table 2.3: Advantages and disadvantages of each of the BNR processes commonly used in South Africa (Lilley *et al.*, 1997)

PROCESS	ADVANTAGES	DISADVANTAGES
Phoredox	Optimal nitrogen removal due to maximum use of the anoxic volume.	The S-recycle discharges directly into the anaerobic zone and thus any nitrate in the effluent will decrease the effectiveness of the anaerobic zone.
UCT	The R-recycle should be very low in nitrate and oxygen and thus near optimal use of the anaerobic reactor is achieved. Because the sludge concentration in the anaerobic reactor is low for the same unaerated volume the overall unaerated sludge mass fraction is less than the Phoredox and Johannesburg processes, and is thus less likely to develop a bulking sludge or lose nitrification in winter.	The A-recycle rate must be carefully controlled so as not to overload the anoxic zone with nitrate which will be returned to the anaerobic zone. The introduction of a third reclycle complicates the operation of the plant. Complete denitrification is not possible.
Modified UCT	The same as for UCT system except that the first anoxic zone is exclusively for denitrifying the S-recycle. Careful control of the A-recycle is less critical.	The same as for the UCT process except by utilising the first anoxic zone for denitrifying the S-recycle the overall plant ability to reduce nitrate is further reduced.

Johannesburg	The anoxic zone between the settler and the anaerobic zone is exclusively for denitrifying the S-recycle. This results in the return flow to the anaerobic zone being very low in oxygen and nitrogen and near optimal use of the anaerobic reactor is achieved. The volume of the underflow anoxic reactor is small.	The anoxic volume available for denitrification of the A-recycle is reduced due to the exclusivity of the underflow anoxic zone. As the S-recycle has a higher solids concentration that the reactor, the overall unaerated mass fraction is increased for the same overall volume. This could increase the propensity for developing a bulking sludge and also increase the chances of nitrification loss in winter. The denitrification rate of the underflow in the anoxic reactor is low due to the lack of readily available carbon.

2.3.4 Mechanisms of Biological excess P removal

All the bio-P removal processes are based on the circulation of the activated sludge biomass through a sequence of anaerobic and aerobic conditions or reactors (Kuba *et al.*, 1993). The exposure of the activated sludge to the alternating conditions stresses the poly-P organisms such that their release and uptake of phosphorus is above the normal levels required for metabolism. The phosphorus present in wastewater is not only used for cell maintenance, synthesis, and energy transport, but is also store for subsequent use by the poly-P organisms (Metcalf and Eddy, 1991).

2.3.4.1 The Anaerobic Zone

The anaerobic zone (or reactor) is that zone in the non-conventional activated sludge process, which is deficient of nitrates, nitrites (NO_x) and dissolved oxygen (DO) (Ekama *et al.*, 1994). The anaerobic reactor of the BEPR system serves two primary functions, that is:

(i) To stimulate the conversion or readily biodegradable COD (RBCOD) into volatile fatty acids (VFA) through fermentation by the non poly-P (heterotrophs) organisms.

(ii) Enables the poly-P organisms to take up and store VFAs as polyhydrxyalkanoate (PHA), a process termed sequestration.

The prerequisite for the BEPR process to take place is the presence or the introduction of VFAs in the anaerobic reactor, up stream of the aerobic zone (Wentzel *et al.*, 1988).

In the normal municipal wastewater or sewage from South Africa, very few or no VFAs are present, yet substantial biological phosphorus removal is achieved with this influent (Wentzel *et al.*, 1990). Upon entering the anaerobic reactor, the RBCOD fraction of the total influent COD is rapidly absorbed by the non-poly-P bacteria. Because of the absence of the terminal electron acceptors (O_2 and NO_x) in the anaerobic zone, none poly-P organisms are unable to metabolize the absorbed RBCOD to energy and for new cell synthesis. The RBCOD is then converted to VFAs through a fermentation process, which provides the non-poly-P organisms with enough energy to stay alive (Wentzel *et al.*, 1990).

The released VFAs (or the fermentation product) are then taken up by the poly-P organisms and stored internally through the linkage of VFA into long chain carbon molecules (polymer) called polyhydroxyalkanoate (PHA), specifically, the polyhydroxybutyrate (PHB). Once store internally, this substrate is no longer available to other heterotrophic organisms, but is reserved by the poly-P organisms for their exclusive use in the subsequent aerobic reactor.

The energy for substrate transfer and storage is derived from the hydrolysis of the energy rich polyphosphate (poly-P) bonds within the poly-P bacteria (stored-P). The hydrolysis of the polyphosphate molecules leads to the release of phosphorus into the environment (anaerobic zone). This phenomenon is known as P-release. The uptake and storage of VFAs with the subsequent P-release by the poly-P bacteria is called sequestration. The phosphorus release associated with the transfer and storage of

VFAs is referred to as primary release, where as P-release that is not associated with VFA uptake is called the secondary release (Danesh and Oleszkiewicz, 1997).

According to Wentzel *et al.*, (1990), 1 mole of P is released per mole of VFA sequestrated, that is, 0.5 mg P is released per mg VFA (as COD) sequestrated. Thus in the anaerobic reactor, ordinary heterotrophic bacteria convert the RBCOD to VFAs, which are then taken up by the poly-P bacteria to be stored in the form of PHB (Wentzel *et al.*, 1990; Ekama and Wentzel, 1999, Banister and Pretorius, 1998).

2.3.4.2 The Aerobic Zone (Reactor)

In the subsequent aerobic reactor down stream of the anaerobic zone, the poly-P organisms are unable to compete with non poly-P organisms for substrate (food source) such as glucose or other saccharides. The inability of the non-poly-P organisms to compete for food source in the aerobic zone/reactor is due to the presence of the terminal electron acceptor (O_2) (Lilley *et al.*, 1997). The poly-P organisms then use the stored PHB as a carbon and energy source for cell function and for the generation of new cells. The stored PHB is also utilized by the poly-P organisms as an energy source for taking up phosphate (P) from the bulk of the solution. The uptake of phosphate helps to remanufacture the polyphosphate that was broken down in the anaerobic zone and to make polyphosphate in the new cells that are generated. This gives rise to the phenomenon known as excess P uptake, which occurs in the aerobic environment.

The uptake of P to manufacture cellular polyphosphate in the new cells generated results in P being taken up in the aerobic reactor in excess of the P that was released in the anaerobic reactor, thus resulting in the net P removal from the liquid phase to the activated sludge biomass (Wentzel *et al.*, 1988; 1990; Ekama and Wentzel, 1999; Mino *et al.*, 1998). Thus in the aerobic reactor, the PHB is metabolised by the poly-P organisms and more P is taken up than required for the normal metabolic purposes (net P removal).

The excessive uptake and storage of P by the poly-P bacteria at this stage does no amount to P removal from the system, but a mere displacement of phosphorus (P) from wastewater to the biomass. Phosphorus is finally removed from the system through daily sludge wasting from the aerobic reactor or from the return sludge line (Wentzel *et al.*, 1990). Wentzel *et al.*, (1990) reported that at steady state, the biomass of poly-P wasted per day equals the mass of new poly-P organisms generated per day. Thus the mass of poly-P organisms in the biological system remains constant, which implies that in the activated sludge process at steady state there is neither a build up nor a loss of poly-P organisms (Wentzel *et al.*, 1990).

There are two factors of utmost importance in the design and operation of EBPR system which are based on the discussed mechanism viz:

1. RBCOD, that is, the magnitude of phosphorus removal that can be achieved is directly related to the amount of RBCOD present in the influent.
2. Recycling of oxygen and NO_x to the anaerobic zone.

The introduction of oxygen and/or nitrates/nitrites to the anaerobic reactor through the sludge recycle (S-recycle) should be avoided since the non-poly-P organisms tend to rapidly metabolise the RBCOD in the presence of the terminal electron acceptor such as oxygen. For every 1 mg O_2 recycled to the anaerobic reactor, 3 mg COD as RBCOD are consumed. The same applies for nitrogen, for every 1mg N as NO_3- recycled, 8.6 mg COD as RBCOD is consumed by the non-poly-P organisms for energy generation and new cell synthesis. This results in the RBCOD that is consumed by heterotrophs being unavailable for conversion to VFAs during the fermentation process. Hence the amount of VFAs generated and released to the solution will be reduced by the same amount of RBCOD that was consumed by the heterotrophic bacteria (Wentzel *et al.*, 1990).

CHAPTER 3

WASTEWATER CHARACTERISATION AND TREATABILITY STUDIES

3.1 INTRODUCTION

Before a wastewater treatment plant can be designed for biological phosphorus removal, it is necessary to characterise the effluent qualitatively and quantitatively. For this purpose, extensive monitoring of the effluent production is required, which includes the use of proper sampling techniques. Flow rates and water quality changes continuously, and these changes may affect the ability of a wastewater treatment plant to achieve consistent biological phosphorus removal.

Obtaining effluent samples that are representative of the effluent flow rate throughout the months and years to come is difficult at its best. Periodic and diurnal fluctuations occur in concentration and flow volume. Given the variable nature of the edible oil effluent that results from the varying nature of edible oil refining process, and the necessity of attaining consistent phosphorus removal, it is necessary to collect samples that will represent "average" characteristics and approximate characteristics under more extreme conditions (Steffen *et al.*, 1989). According to Novotny (1998), a desirable sampling method is to collect 3-4 hour composite samples. This would

provide data that may be considered representative of average effluent characteristics throughout the day. Usually a careful review of flow monitoring records and reports generated by the effluent plant over the past couple of years, if present, tend to be helpful in assessing the periodic and seasonal characteristics of wastewater throughout the year (Novotny, 1998).

3.2 MATERIALS AND METHODS

3.2.1 SAMPLING

Composite wastewater samples were collected monthly over a period of five months (June, 1998 to October, 1998) from Sealake Industries in Pietermaritzburg, about 92 km north west of Durban. The combined effluent samples (final effluent after pre-treatment at the effluent treatment plant before final discharge to the municipal sewerage system) were collected using 25 litre containers, which were then transported to Technikon Natal for immediate analysis. The remainder of the samples after analysis were stored in the cold room below 4 °C to prevent biological activity that could result in the change of effluent quality. The stored effluent samples were later used to conduct treatability studies.

3.2.1.1 Sample Preservation

The samples were always analysed immediately on arrival at the laboratory so that no preservation was required. It is important that the samples are not allowed to deteriorate from time of sampling. If it is not possible to analyse collected samples immediately, the samples should be preserved according to generally accepted methods (Standard Methods, 1989). Biological activity such as microbiological respiration and reproduction, and the chemical activity such as precipitation or pH changes, and the physical changes such as aeration and high temperatures should be

kept to a minimum. Preservation methods may involve cooling, pH control, and chemical addition. Freezing is usually not recommended (Novotny, 1998).

3.2.1.2 Sample Analysis Methods

The effluent samples were analysed for parameters considered necessary for wastewater treatment purposes (see Table 3.1 for effluent samples analysis results). Samples were first diluted to the desired concentration ranges with de-ionised water prior to analysis. A colourimetric method, using spectrophotometer SQ 118 from Merck, was used for measuring chemical oxygen demand (COD), ortho-phosphate (PO_4-P), total nitrogen (TN), ammonium nitrogen (NH_4^+), nitrates NO_3^- and sulphates (SO_4^{2-}). All the samples were analysed in triplicate except for phosphate which was done in duplicates (Appendix 1-6). The total suspended solids (TSS), Fats, oils and grease (FOG), and alkalinity as $CaCO_3$ were all analysed using standard methods (Standard Methods, 1989) (Appendix 7-9).

3.3 RESULTS

Table 3.1: Wastewater characteristics from Edible oil refining industry (Sealake Industries) for a period of five months (June 1998 to October 1998).

Parameter (mg/ℓ except pH)	June		July		August		September		October	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
PH	4.95 5.89	**5.55**	8.76 10.6	**9.8**	5.71 6.99	**6.5**	7.1 8.05	**7.7**	7.61 9.93	**8.6**
COD	7 590 7 680	**7 630**	7 550 8 710	**8 160**	1 025 1 270	**1155**	7 240 7 590	**7 400**	11 700 11 810	**11 763**
PO_4^{3-} (-P)	500 590	**550**	910 1 140	**1 020**	1 640 1 680	**1 660**	4 320 4 510	**4 400**	2 110 2 180	**2 140**
TKN (-N)	6.08 7.96	**6.93**	3.21 6.26	**4.78**	6.54 7.19	**6.82**	6.98 8.67	**7.65**	4.36 5.81	**4.98**
NH_4^+ (-N)	0.98 1.51	**1.25**	0.41 0.76	**0.6**	1.39 2.62	**2.0**	1.09 1.21	**1.15**	2.09 3.6	**2.69**
SO_4^{2-}	4 980 5 910	**5 550**	5 280 5 830	**5 600**	3 410 3 530	**3 470**	5 690 5 980	**5 800**	1 170 1 400	**1 260**
Lipids (FOG)	248.8 266.5	**255.6**	102.8 120.8	**111.1**	324.8 352.1	**339.9**	581.4 630.8	**627.8**	297.2 319.3	**308.2**
TSS	239.2 281.1	**265.2**	379.3 387.8	**383**	97.7 134.1	**111.5**	255.6 274.2	**265.2**	309.2 340.2	**322.3**
Alkalinity	487 542	**520**	465 492	**480**	1 670 1 760	**1 720**	616 649	**630**	742 778	**766**

3.4 TREATABILITY EXPERIMENTS

After the effluent was properly analysed for all relevant parameters, a treatability experiment was conducted to determine toxicity effects of the effluent to the biomass of the activated sludge process.

A 5 L bench scale sequencing batch reactor was designed with the maximum working volume of 4 litres. The bioreactor was seeded with concentrated mixed liquor (sludge), which was taken from the aerobic zone of Darvill Wastewater Works in Pietermaritzburg. The final mixed liquor suspended solid concentration in the bioreactor was adjusted to between 4100 to 4500 mg/l (MLSS) through addition of 50% diluted influent. After dilution with tap water the effluent to be treated had the following average chemical composition as shown in Table 3.2:

Table 3.2: Influent chemical parameters after dilution with tap water

PARAMETER	CONCENTRATION (mg/l)
COD	3535
PO4-P	550
TKN	7.0

The sequencing bioreactor was then operated with 24 hour cycles as follows: 2 hours of anaerobiosis, 21.5 hours of aerobiosis and 30 minutes of settling and decanting. An aquarium air pump was connected to the air diffuser (air stone) through a small silicon tube. The fine air bubbles from the air stone were responsible for the aeration and mixing of mixed liquor of the treatment process during aerobiosis stage. The dissolved oxygen (DO) was measured at random intervals using a portable laboratory scale dissolved oxygen (DO) meter. During the aerobiosis period the DO was maintained between 2.0 and 5.0 mgO_2/l through increasing and decreasing the aeration pumping rate of the aquarium air pump. The air pump was switched off during anaerobiosis and the magnetic stirrers were used to maintain homogeneous conditions in the mixed liquor. The DO of the mixed liquor dropped to below 1.0 mgO_2/l after the air pump was switched off thus ensuring that the anaerobic conditions prevailed in the system.

After the set up was completed the reactor was then operated for 7 days without any effluent analysis being done, to allow for the biomass to acclimatise to the influent. Acclimatisation was achieved a through gradual increase of the influent strength every day until the desired influent strength (3535 mgCOD/l) was achieved. The process was then operated for a further 7 days using a fill and draw method (Borja *et al.*, 1995). Two litres of effluent (filtered through 0.45 μm Glass-wool fibre filters) was collected and analysed each day for total COD, whereas the FOG analysis was performed three times a week.

3.4.1 Results of Treatability experiments

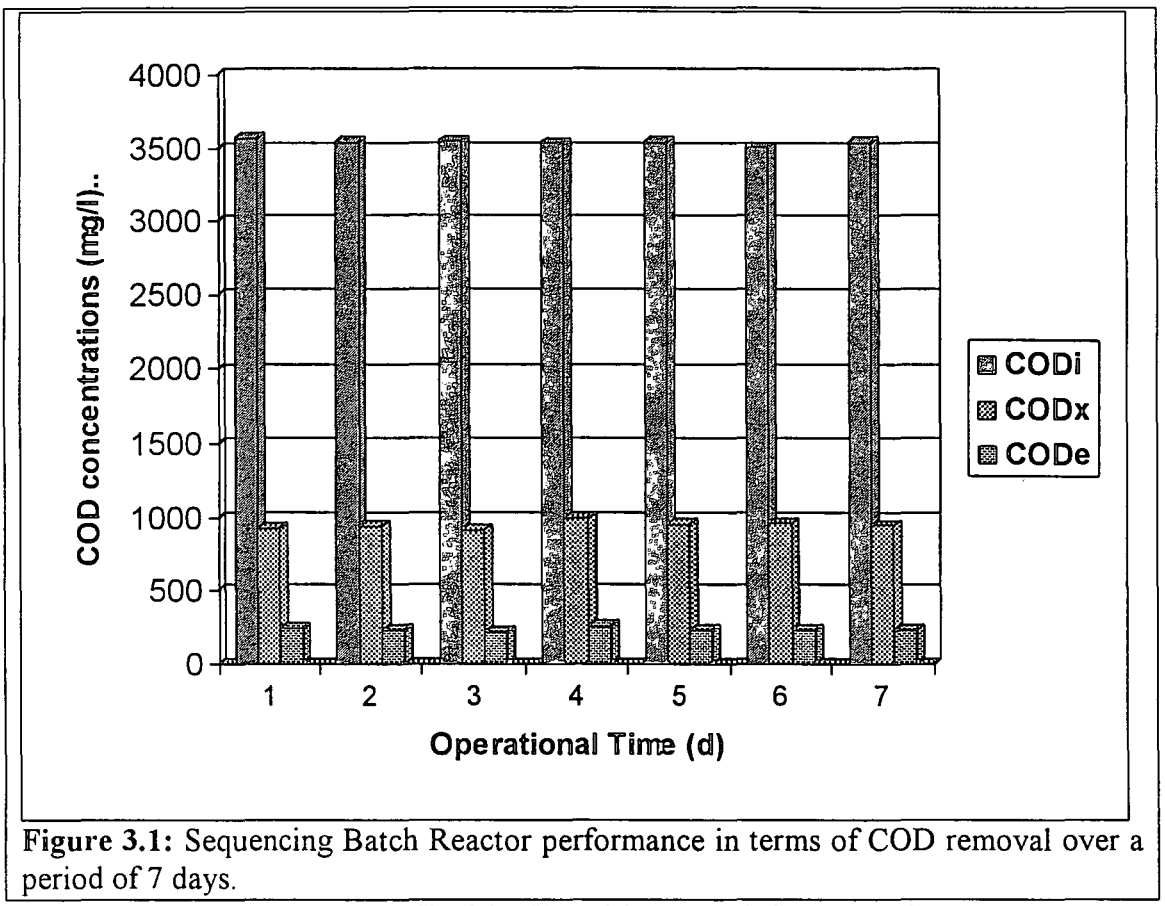

Figure 3.1: Sequencing Batch Reactor performance in terms of COD removal over a period of 7 days.

CODi = COD concentration (mg/l) of the filtered (0.45 μm) influent samples.

CODx = COD concentration of the mixed liquor samples from the aerobic reactor after filtration through 0.45 μm filter to remove suspended solids.

CODe = COD concentration in the final process effluent. This COD represent the unbiodegradable but soluble portion of the soluble influent COD before treatment.

COD removal efficiency of the process over the 7 day period remained constant and stable. On average 75 % if the influent COD was removed by the treatment process from an average of 3500 mgCOD/l to less then 300mgCOD/l.

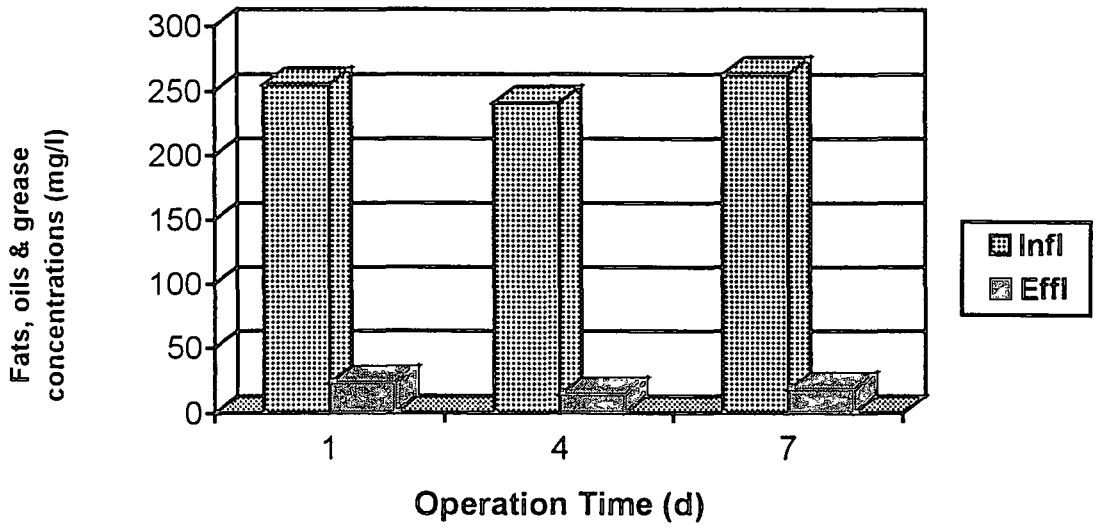

Figure 3.2: Removal of FOG by the Sequencing Batch Reactor over a period of 7 days

Infl = Concentration of fats, oils and grease (FOG) (mg/l) in the diluted influent samples.
Effl = Concentrations of fats, oils and grease (FOG) (mg/l) in the effluent after biological treatment through the Sequencing Batch Reactor (SBR).

On average the influent had FOG concentrations of 250 mg/l and the effluent was consistently below 25 mgFOG/l. This reduction represent more than 90 % FOG removal from the influent samples.

3.5 DISCUSSION

No previous effluent monitoring data was present at the beginning of this study due to lack of onsite effluent monitoring by the Effluent Plant at Sealake Industries. Hence off site effluent monitoring had to be conducted as the first step towards effluent treatment technique development. Effluent monitoring was conducted over a period of five (5) months so as to characterise the edible oil effluent. Characterisation of effluent is necessary for an optimal design and operation of a biological treatment process.

Wastewater characterisition studies of composite monthly effluent samples revealed that effluent characteristics vary widely throughout the month depending on the refining method currently being employed, i.e. whether chemical or physical refining method. The effluent contained both high organic (BOD & COD) and inorganic loads. In addition to the organic and inorganic loads, this effluent had high quantities of free fats.

The organic load in the effluent is due to the presence of large quantities of fats, oils & grease (FOG) in the final effluent, and is also due to the chemical nature of the vegetable oil. The hydrolysis products of the edible oil, which are the long chain fatty acids; glycerol and glycerides; and the proteins, all add to the organic load of the edible oil effluent. Eroglu *et al.*, 1990; Ozturk *et al.*, (1990) estimated the organic load of the edible oil wastewater to be in the range of 0.85 to 1.42 Kg BOD_5 /ton edible oil produced. In their investigations Ozturk *et al.*, (1990) discovered that there was a

strong correlation between BOD_5 and TSS, BOD_5 - COD, COD – FOG parameters. The relationship between FOG and COD was proven earlier by Dart (1974) and later by Grant (1980) who both reported that 60 % to 64 % of BOD_5 was removed from edible oil wastewater after the removal of 88 % to 91 % of FOG during their physico-chemical studies.

The inorganic constituents of concern in the edible oil wastewater are phosphates (PO_4^{3-}) and sulphates (SO_4^{2-}). Phosphate in the effluent originates mainly from the use of phosphoric acid during the degumming stage and to a minor extent from the hydrolysis of phospholipids. Hui, (1996) reported that crude oil, particularly soybean oil, contains significant quantities of organic phosphorus (P) in the form of phosphatides, which are subsequently translocated from the oil phase to the water phase during the crude edible oil refining process. After acidification of the refinery wastewater, phosphatides get hydrolysed and the resulting phosphates are then released to the water phase.

Sulphates constitute a measure part of the inorganic constituents in the edible oil wastewater. They results from the use of strong concentrated sulphuric acid during acid splitting of soap stock that results in the free fatty acids being separated from the medium. Eroglu *et al.*, (1990) and Hui, (1996) reported, from separate studies, that the resulting effluent from acid splitting has an average pH of 1.7 and that it contains sulphate concentrations of 4000 mg/l.

During this study, the sulphate concentration of the edible oil effluent was found to range from 1260 mg/l to 5800 mg/l SO_4^{2-} with a mean average of 4340 mg/l SO_4^{2-} during the five-month characterisation period. These results are comparable with other findings reported in the literature (Eroglu *et al.*, 1990; Ozturk *et al.*, 1990; Hui, 1996; Steffen *et al.*, 1990).

The other inorganic problem that is associated with edible oil effluent is salinity. Salinization of wastewater results from the use of divalent (M^{2+}) and trivalent (M^{3+}) inorganic salts during physico-chemical treatment of wastewater to reduce waste loads of the final effluent. Salinity is indicated by the increase in conductivity of wastewater. Sealake Industries reported that conductivity was one of their major effluent problems and that the municipality was demanding that the conductivity levels in the final effluent be brought down to acceptable levels as a mater of urgency.

The conductivity problem can be solved through the optimisation of chemical effluent treatment methods after the effluent has been subjected to a biological pre-treatment procedure. Optimisation of dosing technique, pH level and flocculation period should result in a decrease in excess ions being released to the final effluent hence resulting in a decrease in both conductivity levels and waste loads in the final effluent that is discharged to the sewerage system. During this study no attempt was made to determine the conductivity of the final effluent, nor was any attempt made to break down the fatty acid composition of the final effluent except the measuring of FOG from the final effluent.

The nitrogen content of the edible oil final wastewater both as total Kjeldahl nitrogen (TKN) and ammonium nitrogen (NH_4^+) was found to be below 10 mgN/l. This shows that nitrogen is the limiting nutrient for the edible oil effluent. In an edible oil study by Ozturk *et al.*, (1990) it was reported that the edible oil effluent BOD_5: N: P ratios were about 100: 4.4: 23, which indicated that nitrogen (N) was the critical factor and could be a growth limiting nutrient. During the present study, the N/COD ratio was found to be much smaller than that reported by Ozturk *et al*, (1990) from their study (see Table 3.1 for final edible oil effluent samples analysis in terms of N/COD ratios and Table 3.2 for diluted effluent samples prior to use as influent feed for the treatment process).

This effluent, due to its chemical composition, is not suited to treatment using traditional three stage or five-stage biological excess nutrient removal (BEPR) processes. The effluent would therefore either require nitrogen supplementation or treatment using a two-stage nutrient removal process incorporating carbon and phosphorus (P) removal. Hui, (1996) reported that vegetable oil effluent could be effectively treated in a full-scale wastewater treatment installation when diluted with domestic wastewater. Characterisation results of the raw oil wastewater samples during this stage are presented in Table 3.1.

Before the design of a laboratory scale wastewater treatment plant was initiated, a laboratory scale treatability study was conducted to determine the toxicity or the suitability of the edible oil wastewater to activated sludge treatment. More information is available in literature about the phytotoxicity of olive oil wastewater to

activated sludge due to the presence of phenolic and polyphenolic compounds in the final effluent (Beccari *et al.*, 1998; Borja *et al.*, 1995; Tünay *et al.*, 1998). Inhibition of methane production or methanogenesis in the anaerobic reactors was reported to be due to saturation of unsaturated long-chain fatty acids (LCFAs) in the olive oil mill effluent. There is no study that was found during literature review that reported the toxicity of edible oil effluent to biomass and hence an investigation was conducted to this effect due to some similarities existing between the two types of effluent substrates.

Treatability studies showed no toxicity effect of edible oil effluent to the activated sludge biomass during the experimental period over which the study was conducted (Figure 3.2). This was confirmed by the observed consistent removal of COD and FOG without any observable deterioration to the system biomass characteristics (Figure 3.2 and Figure 3.3, respectively). During the treatability studies, the system results showed an average reduction in COD level of 75 % and more than 90 % removal of FOG from an average of 253mgFOG/L to below 25mgFOG/L. These results confirms the treatability of edible oil wastewater using the activated sludge method as reported by Eroglu *et al.*, (1990) and Ozturk *et al.*, (1990).

CHAPTER 4

LABORATORY SCALE BIOREACTOR DESIGN AND OPERATION

4.1 INTRODUCTION

In the design of an activated sludge process, both for nutrient and non-nutrient removal, the characteristics of wastewater to be treated is of prime importance. Wastewater characteristics govern both the selection of process and the removal efficiencies of COD, nitrogen and phosphorus attainable in a process (Ekama *et al.*, 1984; Metcalf and Eddy, 1991). With proper analysis and optimal control of environmental conditions, almost all wastewater can be treated biologically. Biological processes such as the activated sludge treatment systems are used to convert finely divided and dissolved organic matter in wastewater into flocculent settleable biological and inorganic solids that can be removed in the sedimentation tanks through excess sludge wasting.

In many cases, these processes which are also known as secondary treatment processes, are employed in conjunction with other physical and chemical processes that are used for preliminary or primary treatment of wastewater. For domestic

wastewater, the major objectives are to reduce organic load (BOD_5 and COD) and to remove inorganic compound such as PO_4-P, NH_3 NO_3^- (Metcalf and Eddy, 1991).

To achieve biological nutrient removal (BNR) of nitrogen and phosphorus, the process must incorporate an anaerobic zone, anoxic zone and aerobic zone in series (Ekama *et al.*, 1984; Bdjanovic *et al.*, 1997; Starkenburg *et al.*, 1993, Wentzel *et al.*, 1990). For biological phosphorus removal only, as in the case of this presented study, the anoxic zone is not necessary since it is specifically used for the denitrification or nitrogen removal from influent wastewater. But the anaerobic zone is of major importance for the achievement of biological phosphorus removal in a system. This zone is of fundamental importance since it allows for competitive selection of microorganisms (bacteria) that are principally responsible for excess biological phosphorus removal process and enables the polyphosphate accumulating organisms (poly-P bacteria) to proliferate in the system (Kuba *et al.*, 1993).

The objective of this part of the study was to design and operate a laboratory scale biological treatment process, and to determine optimum conditions required for the treatment of edible oil effluent, by manipulating various process operation parameters. This part of the study was divided into 3 principal phases, with each phase having a unique set of operating parameters. The purpose of the three phases was to determine a combination (set) of operating conditions required to optimise the process treatment operation towards final edible oil effluent remediation.

4.2 MATERIALS AND METHODS

4.2.1 PHASE 1: 17 OCTOBER 1998 TO 20 NOVEMBER 1998

4.2.1.1 Unit set-up

Based on the results from wastewater characterisation studies, a two-stage activated sludge process was selected for edible oil effluent treatment. The laboratory scale bioreactor was designed and modelled upon the modified 3-stage Phoredox process for biological phosphorus removal (Figure 4.1).

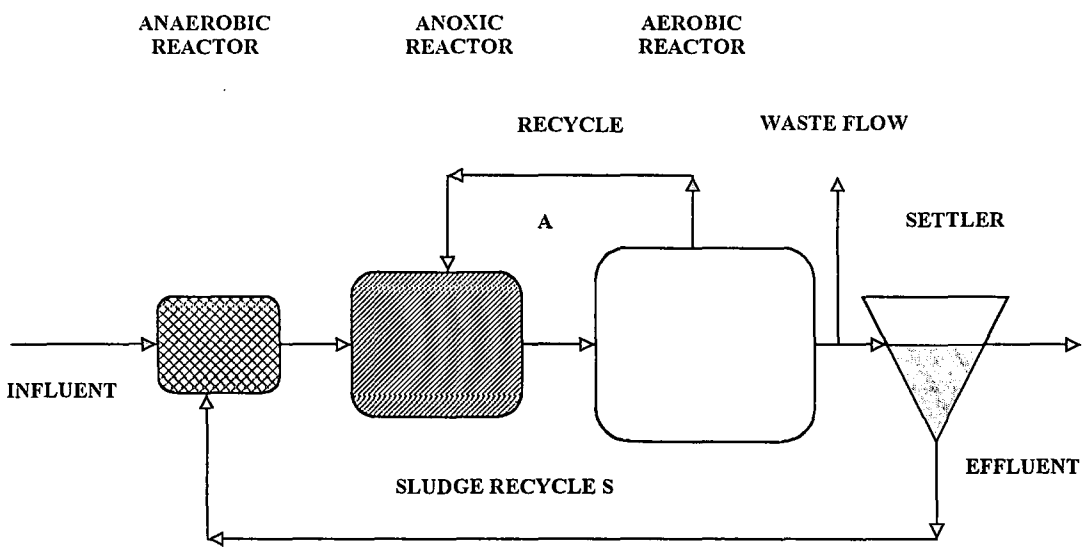

Figure 4.1: Schematic diagram of a modified 3 stage Phoredox Process for biological nitrogen (N) and phosphorus (P) removal

This modified 3-stage Phoredox process was altered to biological phosphorus removal system only by omitting the anoxic zone and the A-recycle from the original design (Figure 4.2).

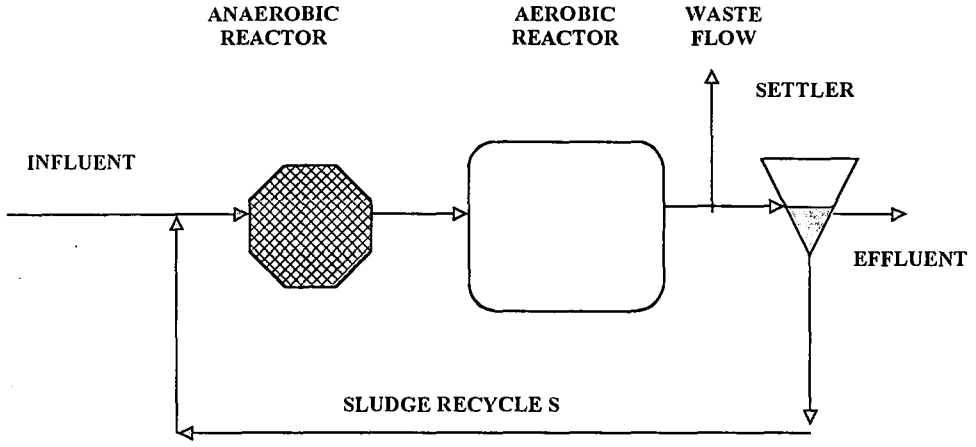

Figure 4.2: Schematic representation of a 2-stage Modified Phoredox process for biological phosphorus (P) removal.

A 5 litre calibrated plastic beaker was converted into an aerobic reactor by drilling two parallel holes underneath. The two holes were fitted with Perspex glass nozzles to which silicon tubing was connected. The anaerobic reactor was designed using a 1 litre calibrated conical shaped plastic aspirator bottle with a lid. The anaerobic reactor had one outlet and two inlets, one on top through the lid for influent inflow, and one underneath for return activated sludge (S-recycle) inflow. The mixed liquor from the anaerobic reactor flowed directly to the aerobic reactor through an outlet that was located underneath the anaerobic reactor, parallel to the return activated sludge (S-recycle) inlet.

The silicon tubing joining the anaerobic reactor and the aerobic reactor was connected by a Y-connector. Thus, the volume of the anaerobic reactor could be varied independently of the aerobic reactor volume by raising and lowering the position of the Y-connector on the retort stand.

The secondary settling tank was designed and placed immediately after the aerobic reactor. This reactor was designed using the 2 litre funnel shaped plastic bottle with the mouth facing downwards. The base of the plastic bottle was cut open to allow airflow and to prevent anaerobic conditions from developing in the secondary settling tank (settler). The mixed liquor inlet from the aerobic reactor to the secondary settling tank was located at the bottom of the reactor about 0.5 litres above the S-recycle sludge outlet point. The effluent overflow outlet was located opposite the mixed liquor inlet at about 1.3 litres above it. The aerobic reactor and the secondary settling tank were connected with each other through the 1.5-meter long 15-mm diameter silicon tubing. Settled sludge was pumped from the secondary settling tank through the variable speed peristaltic pump into the anaerobic reactor via a 2.5-meter long silicon tube (20mm diameter).

The flow though the system was maintained by two peristaltic pumps, one pumping the influent to the system and the other one pumping the settled sludge back to the anaerobic reactor. The internal flow rate was maintained through speed adjustment of the S-recycle line peristaltic pump, where as the effluent overflow rate depended on the speed of the influent flow line peristaltic pump. The bioreactors and the peristaltic

pumps that were used during these experiments were supplied and manufactured by the Instrumentation Centre at Technikon Natal, Durban.

4.2.1.2 Bioreactor Operation

During this phase of the study, the reactor was operated semi-continuously for a period of 20 days at a hydraulic retention time (HRT) of 24 hours and at a sludge age (θ_s) of 30 days. Concentrated settled activated sludge from the secondary settling tank was recycled through the return activated sludge recycle (S-recycle) to the anaerobic reactor at the rate three times the influent flow ($3Q_i$) The organic loading rate or food to microorganism ratio (F/M) of the system was maintained at 1.0 kg COD/kg MLSS/d.

The reactor was seeded with the mixed liquor from the aerobic zone of Darvill Wastewater Works in Pietermaritzburg. Darvill sludge was chosen because the plant is designed for biological nutrient removal processes, and is based on the modified Johannesburg process for treatment of industrial/domestic effluents (see figure 2.3b). Mixed liquor in the aerobic reactor was adjusted to 4300 mg MLSS/l. This value was maintained throughout the experiment by wasting a predetermined quantity of mixed liquor (0.133 litres) daily from the aerobic reactor.

The amount of mixed liquor or waste sludge to be wasted each day in order to maintain a certain sludge age was calculated using the following equations (Metcalf and Eddy, 1991):

$$\theta_c = \frac{V_r X}{Q_w X + Q_e X_e} \quad \text{.....(4-1)}$$

$$\theta_c = \frac{V_r X}{Q'_w X_r + Q_e X_e} \quad \text{.....(4-2)}$$

Where: θ_c = Sludge age (d)

V_r = Aeration reactor volume (l)

X = Suspended solids (VSS or MLSS) in the aerobic reactor (mg/l)

X_r = Suspended solids concentration (VSS or MLSS) in the return activated sludge from the secondary settler (mg/l)

X_e = Suspended solids concentration (VSS or MLSS) in the treated effluent from the secondary settling tank overflow (mg/l)

Q'_w= Waste sludge flow rate from the return sludge (s-recycle) underflow (l/d)

Q_w = Waste sludge flow rate from the aerobic reactor (l/d)

Q_e = Treated effluent flow rate from the secondary settling tank overflow (l/d)

The biological treatment process was operated using the following reactor working volumes:

0.34 L anaerobic reactor;

4.0 L for aerobic reactor; and

1.8L for secondary settling tank

Because of the high strength of the edible oil final effluent, the influent was diluted with tap water to a desired COD concentration before being fed through the system. The influent flow rate to the treatment process was maintained at 2.17 l/h for a period of 2 hours by carefully controlling the speed of the peristaltic pump. This flow rate resulted in a total of 4.34 litres being pumped into the system for treatment each day. Mixing or agitation of the mixed liquor was stopped during the influent pumping period to prevent dilution of the treated effluent and the untreated influent. The influent that was fed to the reactor was prepared daily in a 5 litre influent tank. The final influent composition is summarised in Table 4.1.

Table 4.1: Final influent composition after dilution with tap water.

PARAMETER	VALUE
pH	6.10
COD (mg/l)	3850
PO4-P (mg/l)	2144
TKN (mg/l)	< 7.0

Aerobic conditions in the aerobic reactor were achieved by pumping in diffused air though aquarium air pump with two nozzles. Bubbling of air in the aerobic zone was sufficient to keep the mixed liquor well mixed and hence no mixing devices or stirrers were used for mixing. The dissolved oxygen (DO) was measured at random intervals using a portable laboratory scale DO meter. The DO was maintained between 2.0 and 5.0 mgO_2/l to ensure that the aerobic conditions were achieved throughout in the aerobic reactor. The anaerobic reactor mixed liquor was mixed using a magnetic stirrer that was rotating at 50 revolutions per minute (rpm). The mixed liquor was kept rotating through the system (recycled) for 24 hours by the peristaltic pump that was connected to the S-recycle line. After 24 hours of treatment the effluent was collected and analysed for COD (daily), soluble P (daily), and FOG (at 3 day intervals). The results of treatment process operation during phase 1 are shown in Figures 4.3a, 4.3b and 4.3c.

4.2.1.3 Results

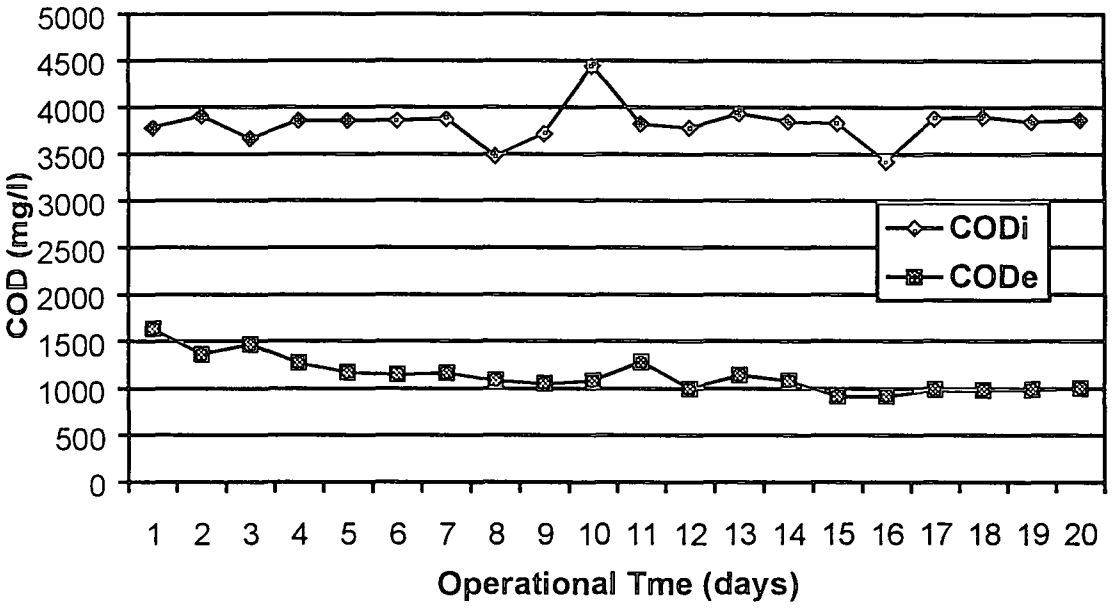

Figure 4.3a: Influent and Effluent total COD profiles for a semi-continuously operated biological treatment process at an F/M ratio of 1,0 (Phase 1)

CODi = COD concentration (mg/l) of the filtered (0.45 μm) influent sample after dilution with tap water

CODe = COD concentration (mg/l) of filtered (0.45 μm) effluent samples after biological treatment.

There was an observed gradual increase in COD removal efficiency from day 1 to day 7. After day 7, the process showed stabilisation with constant COD removal efficiency. The treated effluent COD was consistent to about 1000 mgCOD/l from an average of 3800 mgCOD/l.

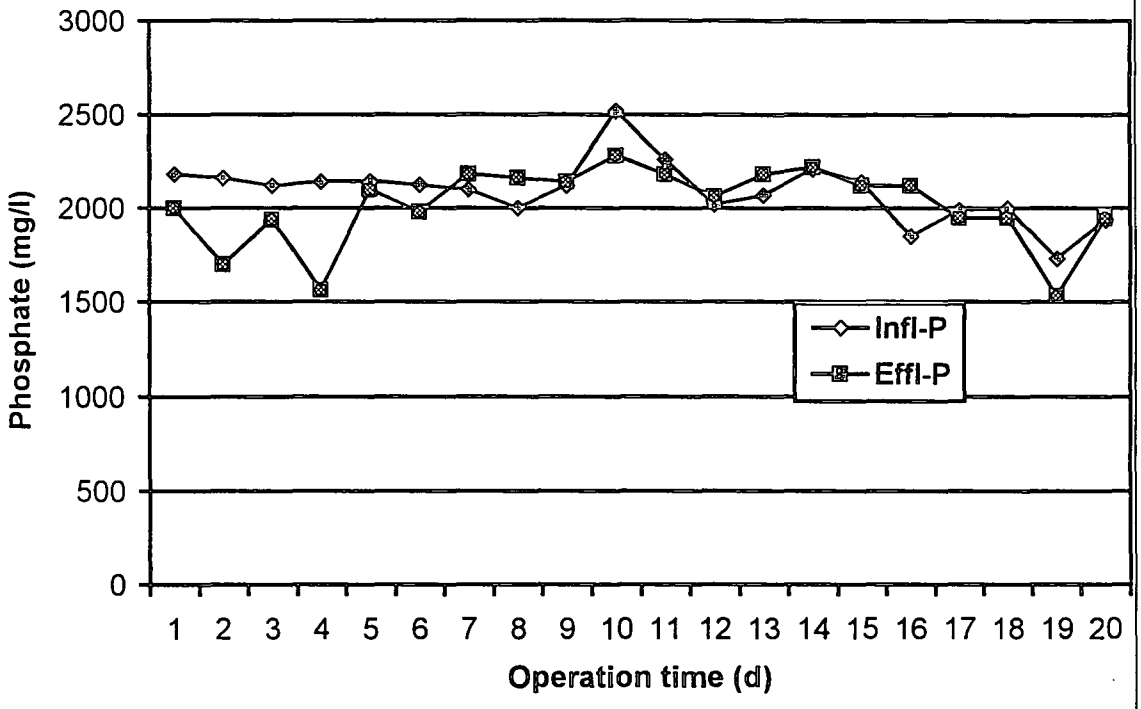

Figure 4.3b: Influent and Effluent soluble P profiles for a semi-continuously operated biological treatment process at F/M ratio of 1.0 (Phase 1)

Infl-P = Phosphate concentration (mg/l) of filtered (0.45 μm) influent samples after dilution with tap water.
Effl-P = Phosphate concentration (mg/l) of filtered effluent samples after biological treatment

From day 1 to day 6, phosphate removal of about 330 mgP/l was observed, with the highest and lowest P removal of 580 mgP/l and 43 mgP/l, respectively.

After day 6 until day 18, phosphate release instead of removal was observed. The highest P release over the 12 day period was 279 mgP/l, with the lowest P release recorded at 10 mgP/l.

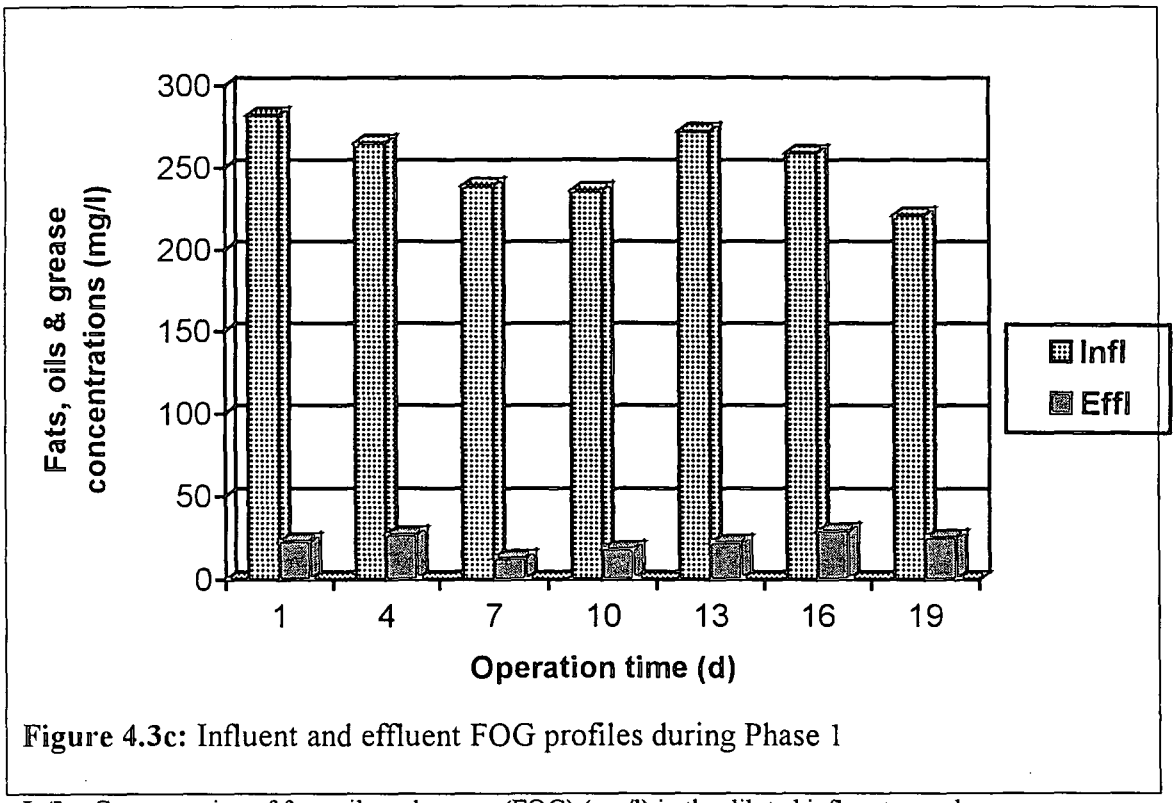

Figure 4.3c: Influent and effluent FOG profiles during Phase 1

Infl = Concentration of fats, oils and grease (FOG) (mg/l) in the diluted influent samples.
Effl = Concentration of fats, oils and grease (FOG) (mg/l) in the effluent after biological treatment.

FOG removal efficiency was constant through out the treatment process operation. More than 95 % FOG reduction was observed from an average of 259 mgFOG/l to below 25mgFOG/l.

4.2.2 PHASE 2: 22 November 1998 to 31 December 1998

4.2.2.1 Unit Set-up

At the end of phase one prior to the beginning of phase two the reactor was stopped and the experiment was started afresh using new design parameters. All the mixed liquor from the previous experiment, reactors and tubes were cleaned to prepare for the next phase of the study. The 1.8 litres (working volume) secondary settling tank was removed and was replaced with a 0.45 litres (working volume) secondary settling tank. The new settling tank resulted in 75 % reduction of the settler volume, which resulted in improved overall performance. The mixed liquor inlet from the aerobic reactor into the secondary settling tank was moved closer to the sludge recycle (S-recycle) outlet. The new arrangement resulted in an improved and rapid settling rate of the sludge in the secondary settling tank.

The volume of the anaerobic reactor was also increased from 0.34 litres to 1.0 litre by raising the position of the Y-connector on the retort stand. The increase in the anaerobic reactor working volume was equivalent to 20 % increase of the anaerobic sludge mass fraction. Mixing of the sludge was maintained using the magnetic stirrer operating at 50 rpm. The volume and operation of the aerobic reactor remained unchanged at 4.0 litres. Aeration and agitation of the mixed liquor was maintained by using diffused air into the system. A portable dissolved oxygen (DO) meter was used to monitor dissolved oxygen in the system at irregular intervals from time to time. The desired dissolved oxygen content of the aerobic reactor was kept within the range

of 2 - 5 mg O/l through switching the aquarium air pumps on and off as deemed necessary.

Fresh seed sludge was collected from Darvill Wastewater Works to be used as an inoculum to the reactor. New batches of final edible oil effluent were collected from Sealake Industries in 25 litre containers for this part of the study. The effluent was analysed for polluting parameters as previously described. After the effluent analysis the rest of the effluent was stored in the cold room at between 0 °C and 4 °C to prevent or reduce microbial activity. This batch of effluent was kept in the cold room for the duration of this phase of study.

4.2.2.2 Unit Process Operation

During phase 2 of the study the reactor operation mode was changed from semi-continuous mode to a continuous mode. Hydraulic retention time (HRT) of the system was maintained at 24 hours through constant pumping of the diluted influent at a flow rate (Q_i) of 5.0 l/d. The concentrated settled activated sludge from the secondary clarifier was recycled back to the anaerobic reactor trough the peristaltic pump connected along the S-recycle at a rate of $2Q_i$. The organic loading rate or food to microorganism (F/M) ratio was increased from 1.0 to 1.50 kg COD/kg MLSS/d by increasing the diluted influent strength from 3850 to 5500 mg COD/L. The fresh batch of effluent had a relatively low concentration load of phosphorus, which ranged from 430 to 450 mg PO4-P/l after effluent dilution with tap water. Mixed liquor (MLSS) concentration was kept between 3500 and 4000 mg MLSS/l while the sludge

age (θ_s) was reduced from 30 days to 15 days. A predetermined amount of mixed liquor was wasted daily from the aerobic reactor to achieve the desired sludge age (equation 4-1). The treatment process was operated at ambient laboratory temperatures, which ranged from 24 °C to 29 °C (Durban summer season). The pH of the aerobic reactor was monitored at irregular time interval using Backman portable pH meter fitted with a glass electrode. The pH in the aerobic reactor was maintained at around pH 7.0 through manual dosing of 1M hydrochloric acid (1M HCl) at irregular intervals, as needed.

A new influent preparation and storage tank with 25-litre capacity was used to replace the previous 5.0 L influent tank. Because of the new bigger influent tank, the influent was no longer prepared on daily basis but was prepared once in 5 days. The reactor was operated for 8 days using step feeding to allow for the biomass to acclimatise to the influent prior to the beginning of actual analysis period. The treatment process operating parameters during phase 2 are shown in Table 4.2. Parameters monitored were: influent and effluent COD (daily), soluble influent and effluent ortho-phosphate (daily), and FOG (was determined at 3 days intervals). The results of treatment process operation during phase 2 are shown in Figures 4.4a, 4.4b and 4.4c.

Table 4.2: Operational parameters for the treatment process during phase 2.

PARAMETER	VALUE
$COD_{influent}$ (mg/l)	5500
$PO_4\text{-}P_{influent}$ (mg/l)	430 – 450
$TKN_{influent}$ (mg/l)	< 7.0
MLSS (mg/l)	3500 – 4000
F/M (kgCOD/kgMLSS.d)	1.5
θ (hrs)	24
θ_c (d)	15
Temp (°C)	Room
pH	6.5 – 7.5
V_r (l)	5
Q_i (l/d)	5

4.2.2.3 Results

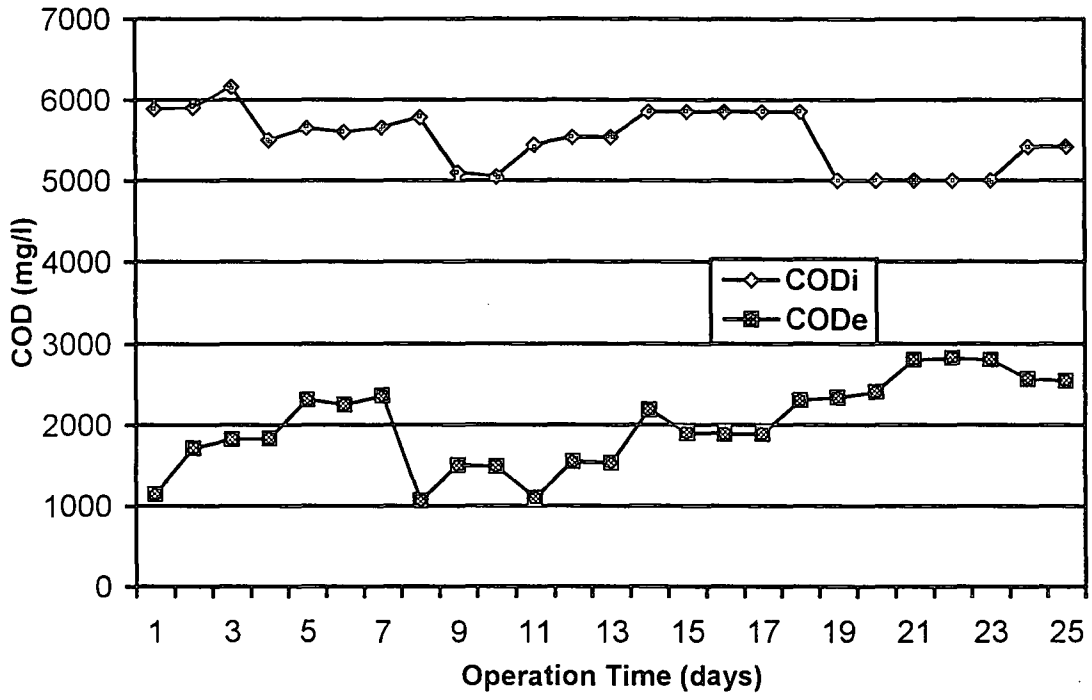

Figure 4.4a: Influent and Effluent total COD profiles for continuously operated biological treatment process at F/M ratio of 1.5 (Phase 2).

CODi = COD concentration (mg/l) of the filtered (0.45 μm) influent sample after dilution with tap water

CODe = COD concentration (mg/l) of filtered (0.45 μm) effluent samples after biological treatment.

From day 1 to day 7 there was an observed decline in COD removal efficiency. The COD removal efficiency increased from day 8 to day 16. This increase in COD removal efficiency represents COD removal of between 68 and 69%.

The inconsistency in the effluent strength quality was due to varying influent strength between day 8 and day 16.

After day 16, a gradual decline in COD removal efficiency was observed although the influent strength had dropped by more then 500 mgCOD/l.

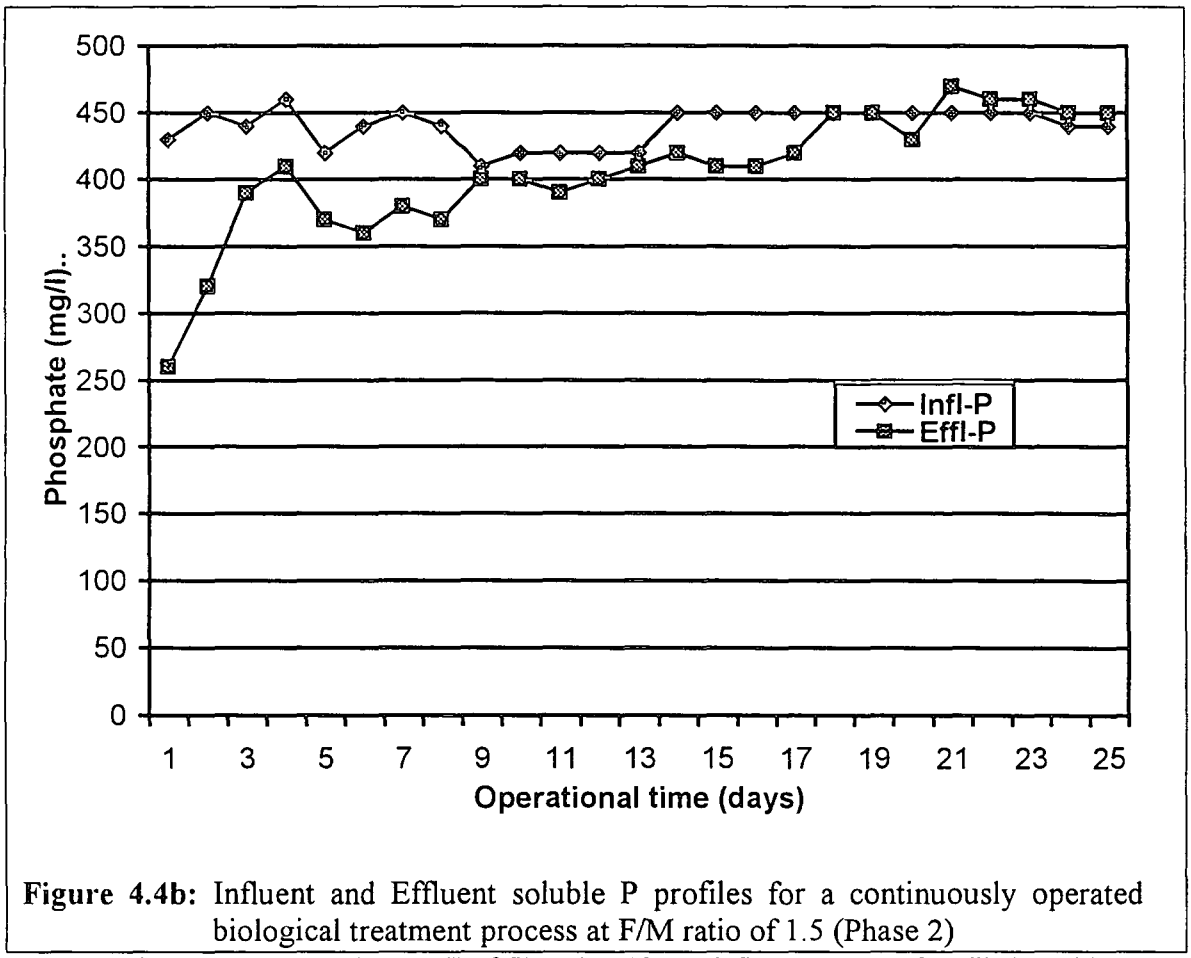

Figure 4.4b: Influent and Effluent soluble P profiles for a continuously operated biological treatment process at F/M ratio of 1.5 (Phase 2)

Infl-P = Phosphate concentration (mg/l) of filtered (0.45 μm) influent samples after dilution with tap water.

Effl-P = Phosphate concentration (mg/l) of filtered effluent samples after biological treatment

From day 1 to day 8 an average phosphate removal of 84 mgP/L was observed, with the highest P removal of 170mgP/l in day 1 and the lowest at 50 mgP/l during day 3, 4 and day 5.

From day 9 to day 17, there was an appreciable decrease in P removal efficiency from an average of 84 mgP/l to an average of 25 mgP/l. Between day 18 and day 19 there were no P removal observed. From day 21 to day 25, P release at an average of 12 mgP/l was observed.

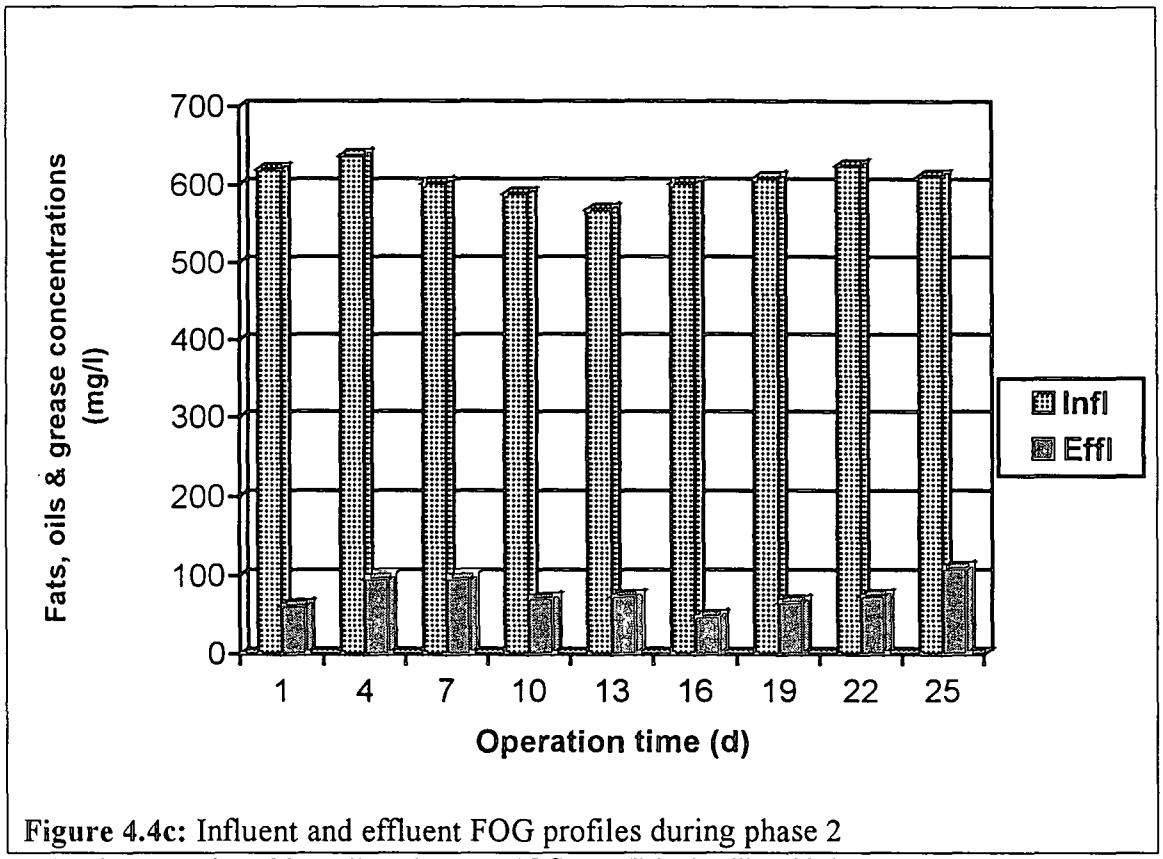

Figure 4.4c: Influent and effluent FOG profiles during phase 2

Infl = Concentration of fats, oils and grease (FOG) (mg/l) in the diluted influent samples.
Effl = Concentration of fats, oils and grease (FOG) (mg/l) in the effluent after biological treatment.

FOG removal efficiency remained constant through out the 25 day treatment period. On average 87 % FOG reduction was observed, from an average of 600 mgFOG/l to below 100 mgFOG/l except for day 25 which had effluent concentration of 110 mgFOG/l.

4.2.3 PHASE 3: 15 JANUARY 1999 TO 02 MARCH 1999

4.2.3.1 Bioreactor set-up and operation

The reactor design and set-up it remained the same as it was during phase 2. The anaerobic reactor, the aerobic reactor, and the secondary settling tank volumes remained unchanged at 1.0 litre, 4.0 litres, and 0.45 litres, respectively. Only the operating parameters were altered during this phase of the study. The study was started up using fresh seed sludge from Darvill Wastewater Works. Mixed liquor was maintained between 4100 and 4200 mg MLSS/l but the organic loading rate (F/M ratio) was decreased from 1.5 to 0.5 kg COD/kg MLSS/d. The sludge age (θ_s) was maintained at 15 days through wastage of predetermined quantities of mixed liquor from the aerobic reactor every day (see equation 4-1). Hydraulic retention time (HRT) was kept at 24 hours by constantly pumping the diluted influent at a rate (Q_i) of 5.0 l/d into the anaerobic reactor. Feed supplementation with 0.01M sodium acetate was initiated in order to determine the effects of artificially increasing the VFA load on biological phosphorus removal in the edible oil effluent.

4.2.3.2 Feed Preparation and Process operation

The same batch of edible oil final effluent that was used during phase 2 was also used during phase 3 of the study. Raw undiluted effluent stocks were kept in the cold room until required. The influent feed was prepared once every four days by diluting the predetermined volume of edible oil final effluent with tap water to make up a final

volume of 20 litres. Thirty five grams of sodium acetate trihydrate ($NaCH_3C00.3H_20$) was added to 20 litres (1.75 g/l) of diluted influent to give the final acetate concentration of 0.01M $NaCH_3C00.3H_20$. After addition of sodium acetate, the influent had a soluble COD concentration of 2000 mgCOD/l after being filtered through 0.45 μm filter. Operation parameters during phase 3 are summarised in Table 4.3 below.

Table 4.3: Process operation parameters during Phase 3 of the treatment process.

PARAMETER	VALUE
$COD_{influent}$ (mg/l)	2270
PO_4-$P_{influent}$ (mg/l)	190
$TKN_{influent}$ (mg/l)	< 7
MLSS (mg/l)	4100 – 4200
F/M (kgCOD/kgMLSS.d)	0.5
θ (hrs)	24
θ_c (d)	15
Temp (°C)	Room
pH	6.5 – 7.5
V_r (l)	5
Q_i (l/d)	5

4.2.3.3 Results

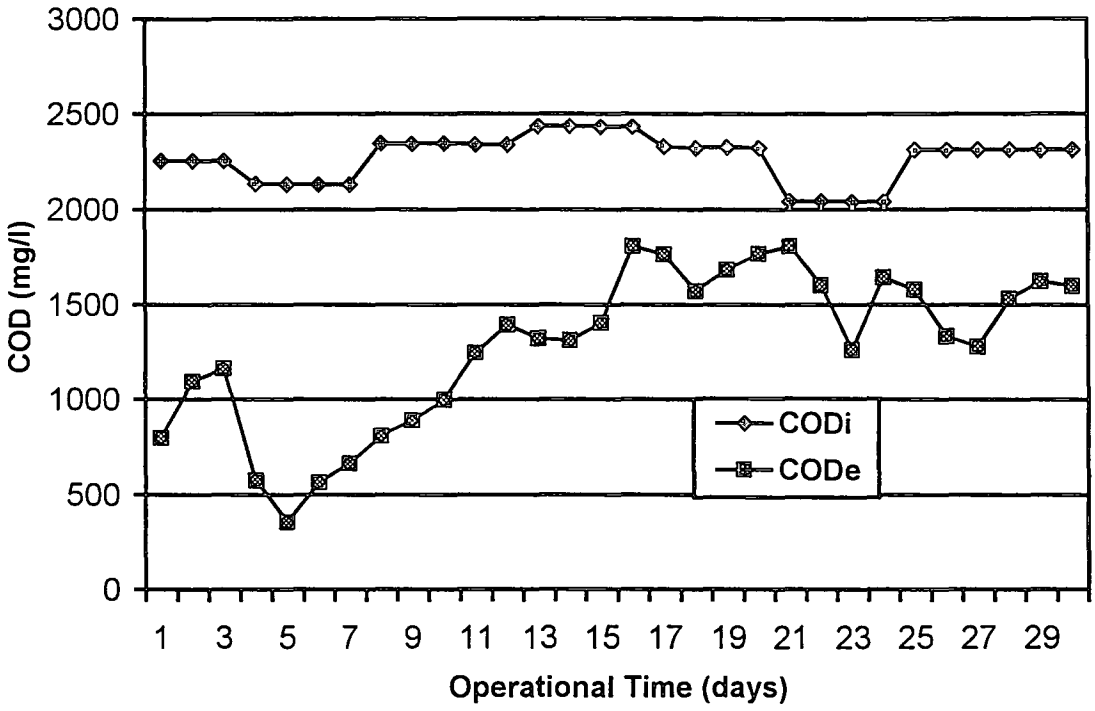

Figure 4.5a: Influent and Effluent total COD profiles for a continuously operated biological treatment process at F/M ratio of 0.5 (Phase 3)

CODi = COD concentration (mg/l) of the filtered (0.45 μm) influent sample after dilution with tap water

CODe = COD concentration (mg/l) of filtered (0.45 μm) effluent samples after biological treatment.

From day 5 to day 21, gradual decline in COD removal efficiency was observed.

Stabilization of COD removal efficiency started after day 21 until day 30.

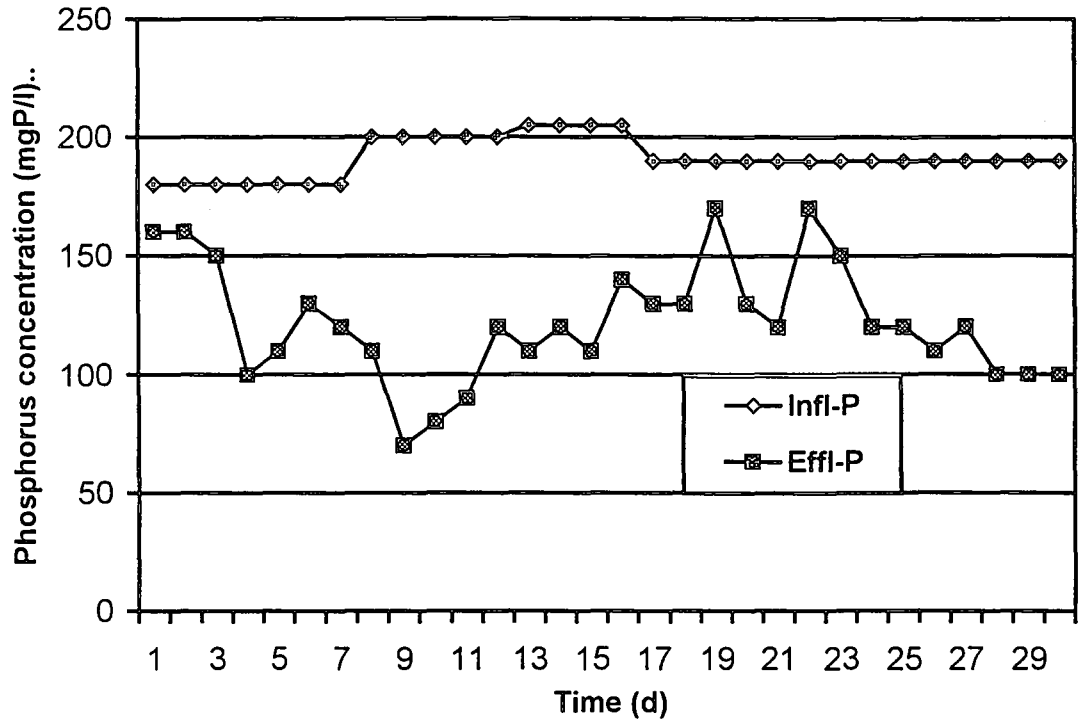

Figure 4.5b: Soluble influent and effluent orthophosphate profile for continuously operated biological treatment process at F/M ratio of 0.5 (Phase 3)

Infl-P = Phosphate concentration (mg/l) of filtered (0.45 μm) influent samples after dilution with tap water.

Effl-P = Phosphate concentration (mg/l) of filtered effluent samples after biological treatment

From day 1 to day 5 there was a fluctuating increase in P removal efficiency. On average 76 mgP/l was removed by the treatment process.

From day 16 to day 20, there was an observed decline in P removal efficiency from an average of 76 mgP/l to an average 53 mgP/l.

After day 20, P removal increased again to an average of 76 mgP/l.

No P release was observed throughout this phase.

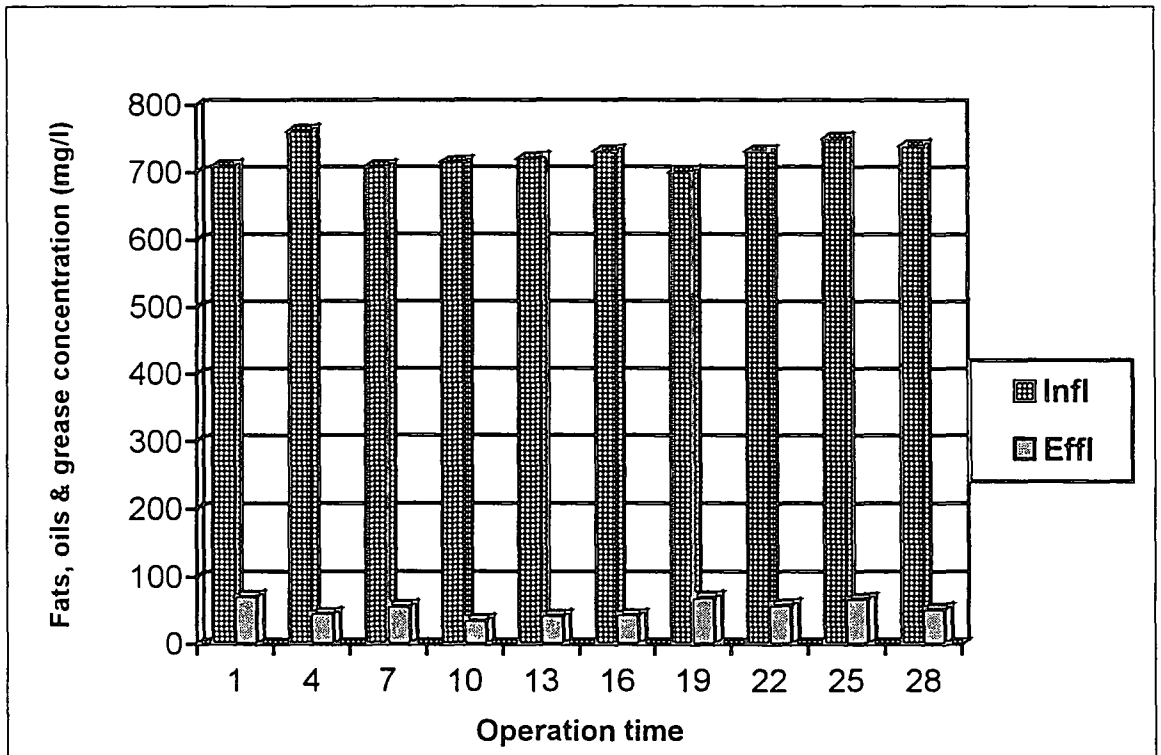

Figure 4.5c: Influent and effluent FOG profiles during phase 3

Infl = Concentration of fats, oils and grease (FOG) (mg/l) in the diluted influent samples.
Effl = Concentration of fats, oils and grease (FOG) (mg/l) in the effluent after biological treatment.

FOG removal efficiency remained consistent throughout the 30 day treatment period. On average 93 % of FOG was removed from the influent average of 727 mgFOG/l to below 71 mgFOG/l.

4.3 GENERAL DISCUSSION

Phase 1

During phase 1, the system had shown improved capability to remove COD and P (Figure 4.3a and 4.3b, respectively) as compared to the preliminary investigation phase. No signs of overloading were initially observed from the treatment process although the influent organic load was higher than the normal organic loads generally applied in domestic/industrial wastewater treatment processes, which are around 0.2-0.3 kgCOD/ kgMLSS/d as compared to 1.0 kgCOD/kgMLSS/d (Ekama *et al.*, 1984).

The system showed an average COD (S_{ti}) removal of 70 % [($COD_{influent} - COD_{effluent}$) X $100/COD_{influent}$] but a negligible removal of P of about 4.4 % was observed (see 4.3a and 4.3b, respectively). During the first six days of the system operation following the acclimatisation period of 15 days, an average P removal of around 330 mgP/l was observed, with the highest removal of 580 mgP/l and the lowest at 43mgP/l. This P removal was not consistent and varied considerably. After day six, a sudden change in the P removal pattern was observed. Phosphorus release instead of the expected P uptake and removal was observed from day 7 to day 18 after which the process was stopped and this phase abandoned. During the 12 days of the observed P release, an inconsistent P release pattern similar to that which was observed for P removal, was also observed. The highest P release was recorded at 270 mgP/l and the lowest at 10 mgP/l. On average the process showed a P release of about 93 mgP/l as compared to P removal of 331mgP/l.

Although it may appear as if the percentage of phosphate removal was minimal (ca 4.4 percent), in real terms the system was actually removing about 238 mgPO_4-P/l, a result which may have possibly been amplified due to phosphate analytical method error caused by the high dilution rates required for detection to be within the instrument's analytical range.

The reduced P uptake and removal capability of the system was partly attributed to the insufficient anaerobic sludge mass fraction of 0.08 or 8 % of the total system volume. It is likely that synthesis of short chain fatty acids (SCFAs) or volatile fatty acids (VFAs) from the fermentation of influent readily biodegradable COD fraction (RBCOD) was incomplete and the full acetate complement (Ekama *et al.*, 1984) was not produced.

The reduced P removal could also be attributed to the influence of the secondary settling tank size. The observed P released after day 6 coincided with the observed activated sludge blackening that was occurring in the anaerobic reactor. The sludge blackening in the anaerobic reactor was followed by the appearance of black sulphur deposits on the sides of the secondary settling tank due to the prevailing anaerobic conditions. The prevailing anaerobic conditions in the secondary settling tank resulted in the reduction of sulphate ions to sulphur which was further reduced to sulphide ions. The onset of anaerobiosis in the secondary settling tank was confirmed by the strong smell of hydrogen sulphide (H_2S), which has a characteristic smell, coming from the secondary settling tank.

The anaerobic conditions in the secondary settling tank have been reported by Simpkins (1979) to trigger the secondary phosphorus release in the biological nutrient removal (BNR) systems. Although the anaerobic conditions were observed in the secondary settling tank, no verification was attempted to verify it was responsible for the observed P release in the process after day six. The influence of the secondary settling tank on the P release of the system could be verified by taking mixed liquor from the outlet of the aerobic reactor towards the secondary settling tank inlet. The collected mixed liquor should be filtered through a 0.45 μm filter paper and the filtrate analysed immediately for P. The results of this analysis should be compared with the results of sample analysis of the final effluent samples taken from secondary settling tank overflow outlet. For the current study, this comparison was not conducted due to time and chemical constraints.

Phase 2

Changing the operation parameters such as sludge age, anaerobic sludge mass fraction and secondary settling tank volume, resulted in an improved consistency of phosphate (P) removal by the treatment process. The average P removal was observed to be 8 % of the total influent P of about 430-450 mgPO_4-P/l (see Figure 4.4b).

The improvement in P removal during phase 2 was thought to be due to the increased anaerobic sludge mass fraction and the reduced sludge age. Increasing the size of the anaerobic sludge mass fraction to 20 % of the total reactor volume (Vr) has been reported to increase the fermentation of RBCOD to VFAs in the anaerobic zone of the

domestic wastewater treatment plants (Rustrian *et al.*, 1999; Ekama *et al.*, 1984; Wentzel *et al.*, 1990). The decrease in sludge age is known to have an improved effect on phosphorus removal efficiencies in BNR of domestic wastewater treatment systems (Wentzel *et al.*, 1990). This is due to the increased removal frequency biomass including the PAO from the system. The increased removal frequency of PAO together with waste activated sludge is thought to result in more cells that contain accumulated P being removed from the system and thus stimulating the rapid reproduction of new biomass (PAO) that has enhanced P uptake capabilities. The P and COD removal efficiencies were calculated using the following methods:

$$\text{P removal efficiency (\%)} = \frac{(P_{influent} - P_{effluent})}{P_{influent}} \times 100$$

$$\text{COD removal efficiency (\%)} = \frac{(COD_{influent} - COD_{effluent})}{COD_{influent}} \times 100$$

During phase 2, a gradual decline in COD removal efficiency was observed (see Figure 4.4a). This decline in COD removal started after day 16 when the COD removal efficiency suddenly dropped from an average of 69 %-68 % COD removal to an average of 50 %, which remained there for the duration of the experimental phase. The observed decline in COD removal efficiency coincided with the observed decline in P removal efficiency of the treatment process. At about the same time when the COD removal efficiency dropped, a phosphorus (P) release in the system was

observed instead of the expected P uptake and removal. The decline in COD removal efficiency of the treatment process was partly attributed to the increased operational F:M ratio (food to microorganism ratio) that was maintained at 1.5 kgCOD/kgMLSS/d. Increasing the F:M ratio of the system is reported to have an overloading effect to the biomass which results in the overall poor system substrate metabolism performance (Wentzel and Ekama, 1997; Casey *et al.*, 1995).

The overall decline in the process COD and P removal efficiency after day 16 (Figure 4.4a and 4.4b, respectively) may also be attributed to the high sulphate (SO_4^{2-}) concentration of the original edible oil effluent. Although sulphates were not monitored in this study, their contribution to the process failure was evident from the observed sludge darkening in the anaerobic reactor and in the secondary settling tank, although its size had been reduced in order to reduce residence time in the secondary settling tank. Increased production of H_2S gas was observed after day 16 which was accompanied by an increased oxygen demand of the activated sludge in the aeration reactor. This effect was similar to the process failure that was observed during phase 1 of the treatment process operation.

The increase in sulphate concentration of the influent may be directly responsible for the decrease in P removal efficiency of the system. Because of the oxidising nature of the sulphur in the sulphate ion (S^{6+} in SO_4^{2-}), other heterotrophic microorganisms (heterotrophs) such as sulphur reducing bacteria may have utilized the sulphate ions in the influent as a terminal electron acceptor in the anaerobic reactor. The presence of sulphate ion as a terminal electron acceptor for some heterotrophs in the anaerobic

zone is thought to have resulted in the utilization of RBCOD by these heterotrophs, thus giving them a competitive advantage with regard to substrate utilization, a similar situation to that which occurs when oxygen or nitrates/nitrites (NO_x) are present or introduced into the anaerobic reactor of the BNR system.

The idea of existence of sulphate ions as terminal electron acceptor in the anaerobic reactor is supported by the observed production of the H_2S gas by the system after day 16 of treatment process operation. The reduction of sulphate ion to hydrogen sulphide is known to take place under anaerobic conditions in the presence of sulphur reducing bacteria such as *Desulfotomaculum* according to the equation shown below (Pelczar *et al.*, 1993; Metcalf and Eddy, 1991):

$$10H^{+}_{(aqua)} + SO_4^{2-}{}_{(aqua)} + 8e^{-} \longrightarrow H_2S_{(g)} + 4H_2O_{(l)}$$

In the presence of ferric ions in the mixed liquor (solution), the reduction of sulphate ions result in the formation of both ferric sulphide (Fe_2S_3) precipitate, which is black, and hydrogen sulphide (H_2S) gas, which is colourless, according to the following equation (Metcalf and Eddy, 1991):

$$34H^{+} + 2Fe^{3+}{}_{(aqua)} + 4\ SO_4^{2-}{}_{(aqua)} + 32\ e^{-} \longrightarrow H_2S_{(g)} + Fe_2S_{3\,(s)} + 16H_2O_{(l)}$$

Phase 3

During this phase of the study the only process treatment parameters that were changed were the organic loading rate, which was reduced from 1.5 kg COD/kg

MLSS/d in phase 2 to 0.5 kg COD/kg MLSS/d through influent dilution with tap water and the RBCOD of the diluted influent which was increased through feed supplementation with sodium acetate. The P/COD ratio remained constant between phases 2 and 3 since the same batch of edible oil effluent that was used previously as the treatment process feed influent (during phase 2) was also used during phase 3, thus resulting in no change in P/COD ratio after feed influent dilution with tap water.

The results after changing the process parameters in phase 3 showed an improvement in terms of P removal efficiency, which was almost constant through out the experimental phase (Fig. 4.5b). However, improved P removal efficiency was coupled with the observed gradual decline in COD removal efficiency, which had a similar pattern as was observed during phase 2 of this study. The improvement in P removal efficiency may be partly attributed to the sulphate ion concentration being lower in the influent due to dilution, thus resulting in a general decrease in concentration of sulphate ions as terminal electron acceptor.

The supplementation of influent with sodium acetate is strongly believed to have contributed to the increase in P removal efficiency of the treatment process during this phase. This could be attributed to the dominance of PAOs over non-PAO heterotrophs in the activated sludge biota. The increase in VFAs in the anaerobic reactor is thought to have resulted in the increased dominance and proliferation of PAOs in the whole system, thus giving them a competitive advantage over the sulphur reducing bacteria with regard to substrate utilisation in the anaerobic reactor.

The sulphur reducing bacteria are slow growers that exhibit a slow growth rate (K_s) (Metcalf and Eddy, 1991). The slow growth rate of sulphate reducing bacteria is evident from the previous two experimental phases (phases 1 & 2) that was shown by the delayed onset of their effect in the treatment process efficiency. No evidence of the presence of the sulphate reducing bacteria was observed during the third phase of the treatment process study. The symptoms of sludge blackening, increased DO demand and the production of H_2S gas were not observed during this phase.

The gradual reduction in COD removal efficiency is hypothesised to be due to the dominance of PAO over non-PAOs in the entire activated sludge biota. Non-PAOs metabolise both readily and slowly biodegradable substrate (COD) in the presence of a terminal electron acceptor (e.g. O_2, NO_3^- and SO_4^{2-}), where as the PAOs take up and store readily biodegradable in the anaerobic zone (RBCOD from acetate supplementation of the influent). The uptake of readily biodegradable substrate in the anaerobic reactor by the PAOs is thought to have resulted in poor removal of slowly biodegradable COD in the subsequent aerobic reactor.

After the three effluent treatment experimental phases (Phases 1-3) it is thus hypothesised that PAOs were unable to effectively and efficiently utilise the initial biodegradable COD factions in the influent wastewater. It is further hypothesised that high sulphate concentrations in the influent had had a negative impact on the wastewater treatment process efficiency in general (for both COD and P removal).

The removal of fats, oils & grease (FOG) was observed to be consistent throughout the treatment experimental phases, which was above 95% FOG removal. The removal of fats from the influent wastewater by the treatment process may be due to adsorption of fats onto the activated biomass, rather then through biochemical metabolism of fats into simpler organic molecules that could be utilised by microorganisms to increase their biomass.

CHAPTER 5

TREATMENT PROCESS OPTIMISATION (PHASE 4)

5.1 INTRODUCTION

A number of operating parameters have a profound influence on the degree of biological excess phosphorus removal (BEPR) from a wastewater treatment process. Manipulation of design and process operation can be used to optimise the BEPR process performance.

In determining the effect of different operation parameters on the magnitude of BEPR, Wentzel *et al.*(1990) used a steady state model to predict phosphorus (P) removal for various changes in parameters, such as sludge age, influent COD concentration, HRT, etc. Parameters that were noted in the preceding experiments to be important for biological excess phosphorus removal (BEPR) from the vegetable oil effluents are: the size of the anaerobic zone/reactor; number of anaerobic reactors; sludge age; and influent characteristics (C:N:P ratio and RBCOD concentration).

5.1.1 Size of Anaerobic reactor

The anaerobic reactor is sized using the anaerobic mass fraction (f_{xa}), which can be represented by the following formula:

$$f_{xa} = \frac{\text{mass of sludge in the anaerobic reactor}}{\text{mass of sludge in the system}}$$

For selected sludge ages, Wentzel *et al.*, (1990) demonstrated that an increase in the anaerobic sludge mass fraction (f_{xa}) resulted directly to an increase in P removal in biological nutrient removal (BNR) processes. The increase in P removal was attributed to the increased conversion rate of RBCOD to VFAs in larger anaerobic sludge mass fractions. Should nitrification and denitrification be included in the treatment process, care should be taken when increasing the anaerobic sludge mass fraction. Unilateral increase of the anaerobic sludge mass fraction results in the decrease in the mass fraction of the aerobic and anoxic zones. This could lead to poor overall system performance. Casey *et al.*, (1994) reported that an increase in the size of the anaerated mass fraction (f_{xt}), i.e. anaerobic (f_{xa}) and anoxic (f_{xn}) mass fractions, above 50 % was not favourable since it would result in low F/M filamentous bulking in biological nutrient removal (BNR) activated sludge systems.

5.1.2 Number of Anaerobic reactors

Biological phosphorus removal is reported to increase with the increase in the number of anaerobic reactors from 1 to 2 reactors in series (Wentzel *et al.*, 1990). Increasing the number of anaerobic reactors above 2 was reported to result in only slight improvement in P removal (Wentzel *et al.*, 1990). The improvement in P removal with the increasing number of anaerobic reactors from 1 to 2 was said to be due to the increased RBCOD conversion rate to VFAs. The RBCOD conversion to VFAs was reported to take first order kinetic conversion rate. This view was supported by the observations made in full-scale BNR systems, that plug flow operation of the anaerobic reactor gave better P removal than that found in an anaerobic reactor operated as a single completely mixed reactor (Wentzel *et al.*, 1990).

5.1.3 Sludge Age

The effects of sludge age (θ_s) on biological P removal are complex. Phosphorus removal in BNR systems was reported to increase with the increase in sludge age from θ_s = 1 day to θ_s = 3 days, which was then followed by a decrease in P removal with each increase in θ_s above 3 days. The decrease in bio-P removal with increase in θ_s above 3 days was reported by Wentzel *et al.*, (1990) to be due to the decrease in the active biomass and its associated P content that was wasted per day. This would tend to indicate that BNR systems should be operated at shorter sludge ages. But the sludge age can not be changed or reduced in an *ad hoc* fashion, since there is a minimum sludge age that is necessary to obtain compete nitrification with selected

unaerated sludge mass fractions (f_{xt}) (Ekama *et al.*, 1984). The requirements of N, P, and COD (S_{ti}) removal should be balanced. (Wentzel *et al.*, 1990).

5.1.4 Influent COD (S_{ti}) characteristics

Wentzel *et al.*, (1990) reported (from pilot plant experiments) that an increase in the influent COD of domestic wastewater resulted in an increase in phosphorus (P) removal (P removed/S_{ti}) efficiency. The observations of pilot plant experiments were confirmed by the observations that were made in full-scale Biological Nutrient Removal (BNR) processes. Wentzel *et al.*, (1990) associated the increase in P removal efficiency to an increase in RBCOD of the influent which resulted from a general increase of influent total COD (S_{ti}).

This part of the study (Phase 4) was aimed at optimising the process operation for both COD and P removals based on the operation parameters examined in the previous 3 phases.

5.2 MATERIALS AND METHODS

5.2.1 BIOREACTOR LAY-OUT AND OPERATION

The general reactor configuration of a two-stage modified Phoredox process was maintained throughout the experimentation period. Only the anaerobic configuration was altered to allow for more increase in the anaerobic mass fraction (f_{xa}). The anaerobic sludge mass fraction was calculated as follows:

$$\text{Anaerobic sludge mass fraction } (f_{xa})\ (\%) = \left(\frac{V_{anaerobic}}{V_{anaerobic} + V_{aerobic}}\right) \times 100$$

Where: $V_{anaerobic}$ = Volume of sludge in the anaerobic reactor (l)

$V_{aerobic}$ = Volume of sludge in the aerobic reactor (l)

$V_{anaeroboic} + V_{aerobic} = V_{total}$ = Total volume of sludge in the aerobic and anaerobic reactor

The 1-litre conical flask shaped anaerobic reactor was removed and replaced by a 5-litre rectangular polyethylene anaerobic reactor. The influent and mixed liquor flow pattern remained unchanged, ie. the influent flow entered through the top of the reactor whilst the returned sludge (S-recycle) and out-going mixed liquor flowed through the bottom inlet and outlet, respectively.

The reactor was seeded with 50 % mixed liquor from the aerobic zone and 50 % from the anaerobic zone of Darvill Wastewater Works. The anaerobic sludge mass fraction (f_{xa}) was increased from 1 litre (during phase 3) to 3 litres (total volume of the system increased from 5 litres to 7 litres), which represented the increase in the anaerobic sludge mass fraction of 23%, from 20% to 43 % of the total sludge in the process (3 l V_{an}/7 l V_{total}).

A new batch of effluent was collected in 25 litre containers from Sealake Industries prior to commencement of this fourth phase of the study. The effluent samples were stored in the cold room at between 0 °C and 4 °C after the necessary analyses were completed to prevent deterioration due microbial and chemical activity.

The influent was prepared in a large influent container (25 litre) once every 4 days through dilution of the industrial effluent with tap water to give the desired final COD concentration. The influent supplementation was maintained at 1.75 g/l through the addition of sodium acetate trihydrate ($CH_3COONa.3H_2O$). The hydraulic retention time (HRT) remained unchanged at 24 hours by maintaining the influent flow rate (Q_i) at 7 l/d. The sludge age was also kept at 15 days through daily wastage of predetermined quantities of mixed liquor from the aerobic reactor. Aeration and agitation of mixed liquor in the aerobic reactor was achieved by an aquarium air pump pumping air through two diffusing nozzles. A potable laboratory scale dissolved oxygen (DO) meter was used to measure the dissolved oxygen (DO) in the aerobic reactor. The DO concentration in the aerobic reactor was maintained between 2.0 – 5.0 mgO_2/l through on and off switching of the aquarium pump when necessary.

The anaerobic reactor contents were maintained in a well mixed condition through the operation of the magnetic stirrer unit at lowest speed (ca. 50 rpm) so as to simulate a plug flow pattern. The treatment process was operated for 15 days without any analyses being done to allow for acclimatisation of the biomass to the influent substrate (ie. achieve steady state). After the acclimatisation period was completed the system was then operated continuously for 82 days with sampling and analyses conducted daily as was done during phase 3 of the study. Table 5.1 shows the summary of the operation parameters of the treatment process during phase 4 of the study.

Table 5.1: Summary of the process operating parameters during phase 4

PARAMETER	VALUE
$COD_{influent}$ (mg/l)	2650
PO_4-$P_{influent}$ (mg/l)	600
$TKN_{influent}$ (mg/l)	< 7.0
MLSS (mg/l)	4100 – 4200
F/M (kgCOD/kgMLSS.d)	0.5
θ (hrs)	24
θ_c (d)	15
Temp (°C)	Room
pH	6.5 – 7.5
V_r (l)	7
Q_i (l/d)	7

5.3 RESULTS

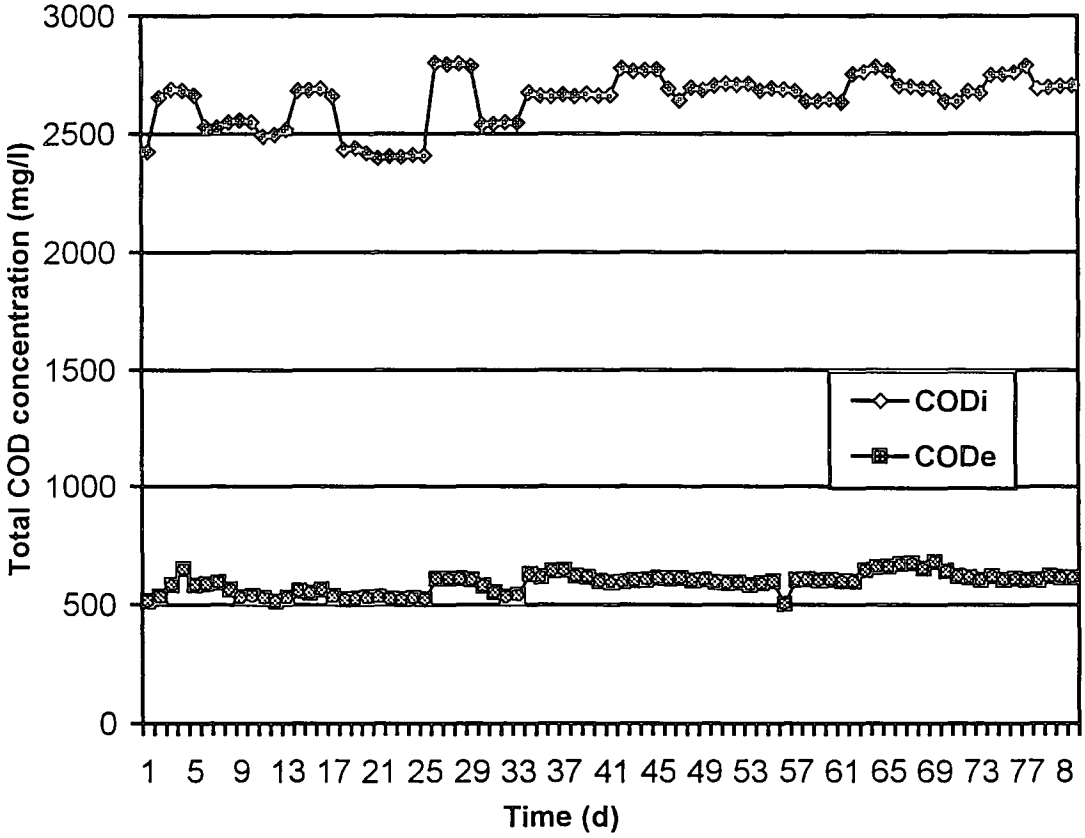

Figure 5.1: Total influent and Effluent COD profiles for continuously operated biological treatment process at 0.5 F/M ratio (Phase 4)

CODi = COD concentration (mg/l) of filtered (0.45 μm) influent samples after dilution with tap water.

CODe = COD concentration (mg/l) of filtered (0.45 μm) effluent samples after biological treatment.

From day 1 to day 29, variation of influent COD strength was observed. Influent COD strength varied between 2800 mgCOD/l and 2400 mgCOD/l.

The COD removal efficiency remained stable despite the fluctuating influent COD strength.

On average the COD removal efficiency remained 76 % throughout the process operation.

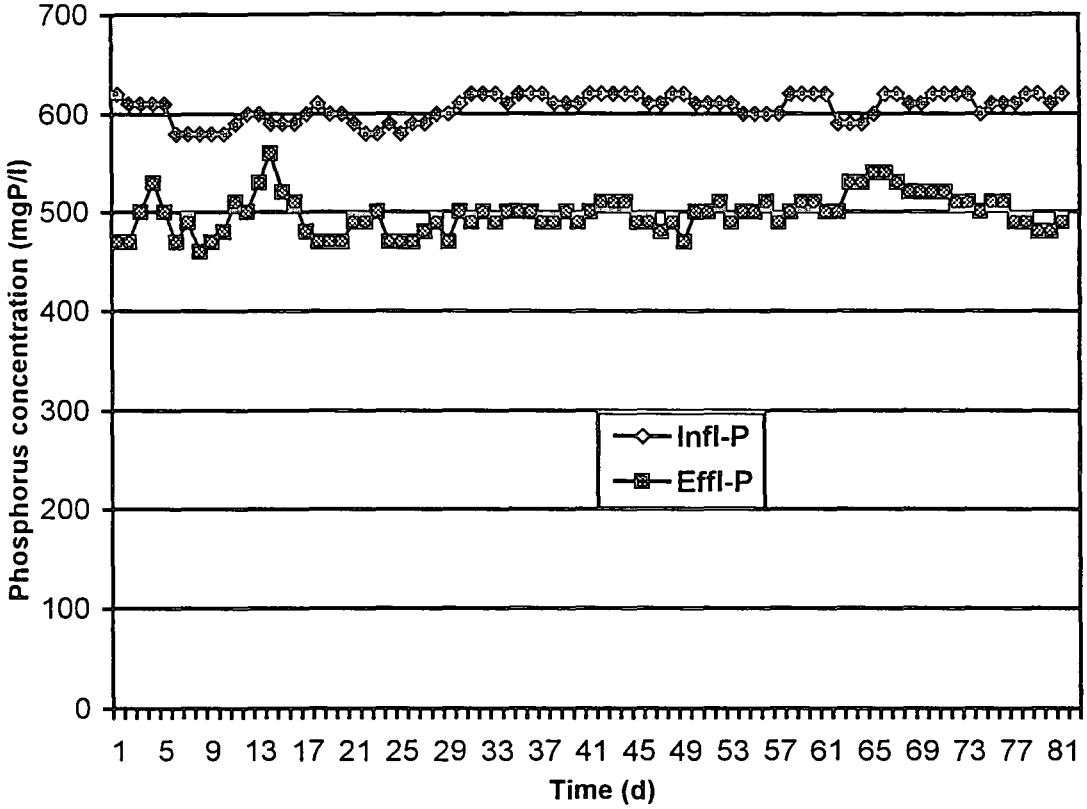

Figure 5.2: Soluble influent and effluent orthophosphate profiles for a continuously operated biological treatment process at 0.5 F/M ratio (Phase 4)

Infl-P = Phosphate concentration (mg/l) of filtered (0.45 μm) influent samples after dilution with tap water.

Effl-P = Phosphate concentration (mg/l) of filtered (0.45 μm) effluent samples after biological treatment.

From day 1 to day 16, P removal efficiency was fluctuating. On average 103 mgP/l was removed from the influent during day 1 to day 16.After day 16 until day 61, P removal efficiency improved to 116 mgP/l. From day 62 to day 69, a decline in P removal efficiency was observed. P removal efficiency dropped from 116 mgP/l to 76 mgP/l on average.Between day 70 and day 81, P removal efficiency improved to 114 mgp/l on average.

No release was observed throughout the treatment process operation at this phase.

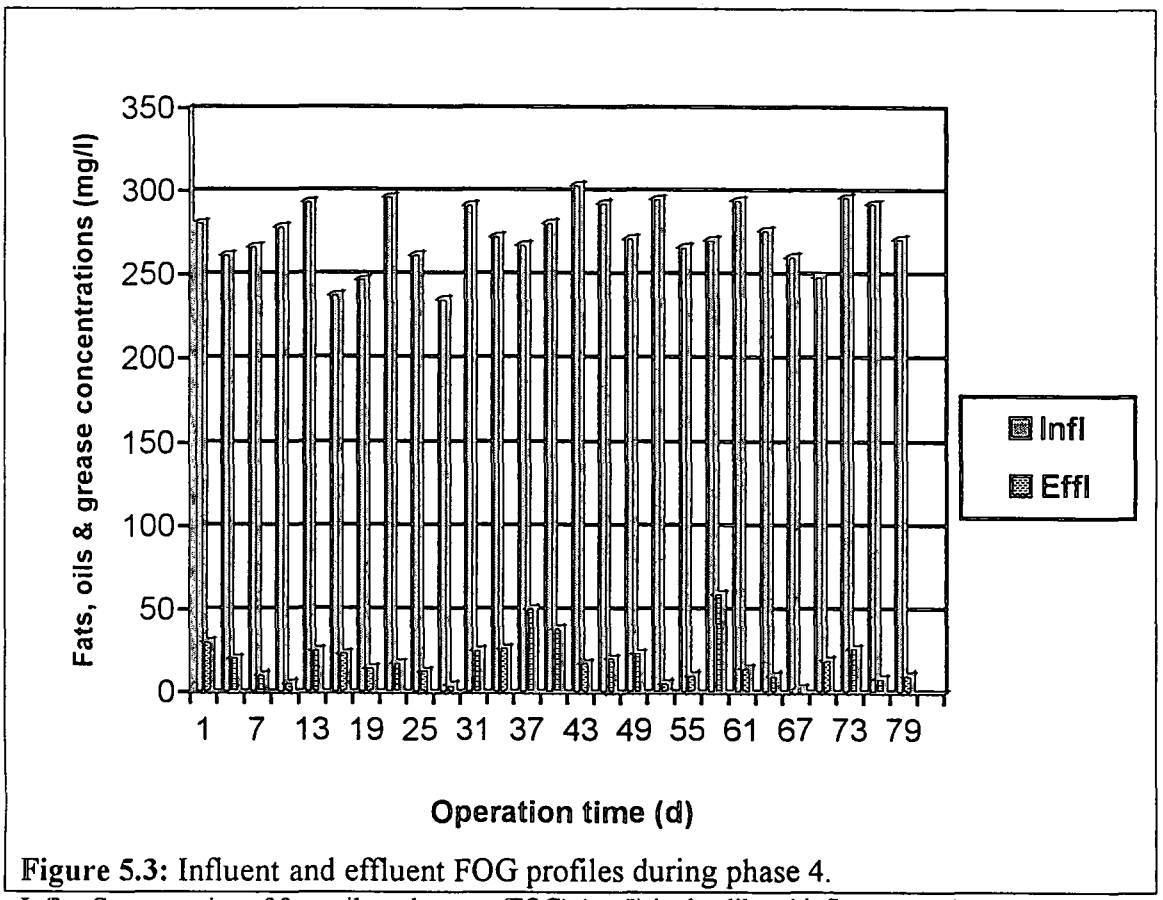

Figure 5.3: Influent and effluent FOG profiles during phase 4.
Infl = Concentration of fats, oils and grease (FOG) (mg/l) in the diluted influent samples.
Effl = Concentrations of fats, oils and grease (FOG) (mg/l) in the effluent after biological treatment.

On average FOG removal efficiency remained stable despite the fluctuating influent FOG concentrations throughout the process operation during this phase.

Effluent FOG concentrations were observed to be below 30 mgFOG/l, from an average influent FOG of 275 mgFOG/l, except for day 1, 37, 40 and 61 which had effluent FOG concentrations of between 31 and 60 mgFOG/l.

5.4 DISCUSSION

Increasing the anaerobic sludge mass fraction from 20 % to 43 % while maintaining a 0.5 kg COD/kg MLSS/d organic loading rate to the treatment process resulted in the general improvement in the treatment process performance in terms of both COD (Fig. 5.1) and P removal (Fig. 5.2).

The treatment process showed a consistent P removal efficiency which remained at a total average of 17 %. This P removal is equivalent to the P uptake and removal of 104 mgP/l from the influent wastewater. The increase in P removal efficiency was attributed to the increase in the anaerobic sludge mass fraction, which resulted in the increased contact time of the influent substrate with the systems biomass.

The increased contact time between the substrate and the biomass is postulated to have increased the fermentation rate of RBCOD to VFAs, which were subsequently sequestrated by poly –P organisms. This increased contact time in the anaerobic reactor is thought to have allowed more time for anaerobic, non-fermentative bacteria to metabolise the slowly biodegradable COD content of the influent substrate into readily biodegradable COD. The increased production of RBCOD made more substrate to be available to the anaerobic-fermentative bacteria for conversion into VFAs. Influent supplementation with 0.01 M sodium acetate may also have enhanced the dominance of PAOs in the anaerobic reactor over the non-PAO heterotrophic bacteria, as was postulated during phase 3 of this study.

The improved P removal performance (Figure 5.2) was coupled to the observed improvement in the total soluble COD removal performance (Figure 5.1) of the treatment process. The COD removal improved from a total average of 64 % to a total average of 76 %. There was no observed decline in the treatment process performance over time, as was observed during the preceding experimental phases (Phases 2 and 3).

The improved overall treatment process performance may also be attributed to the influent substrate chemical composition. The new effluent batch that was used during phase 4 of this study had different chemical characteristics to the effluent batch that was used during phases 2 and 3 of this study. This effluent batch had an increased P/COD ratio due to high concentrations of final effluent P and relatively low concentrations of COD (combined or final edible oil effluent samples collected from Sea Lake Industries). There was a noticeable decrease in sulphate concentrations of the edible oil effluent (industrial effluent sample) batch that was used during this experimental phase. Although the sulphate concentrations of the influent and effluent were not monitored as part of this study, the previously observed conditions of sulphate interference with the treatment process performance were not observed during this experimental phase.

The lack of observed sulphate presence in the influent during the preceding experimental phases, may confirm the postulated role of the sulphate reducing bacteria towards the previously observed poor performance of the treatment process. The mixed liquor of the treatment process remained dark brown (chocolate brown)

throughout this experimental operational phase, a condition that is usually observed in properly operated wastewater activated sludge treatment systems treating domestic effluent (Lilley *et al.*, 1997; Ekama *et al.*, 1984)

The improved reduction of COD with the increased anaerobic sludge mass fraction that was observed during this experimental phase, as opposed to the decreased COD removal efficiency that was observed during phase 3, is thought to be due to the increased activity of the anaerobic non-fermentative organisms and the fermentative microorganisms in the increased anaerobic reactor volume.

The increased activity of the non-fermentative bacteria in the anaerobic reactor is thought to have increased the rate of metabolism of slowly biodegradable COD to RBCOD, which otherwise could have escaped from the anaerobic reactor to the aerobic reactor and thus subsequently ending up in the final treatment process effluent. This could explain the dominance of poly-P organisms over the heterotrophic non-poly-P organisms with the increase in the anaerobic sludge mass fraction, as was reported for phase 3 of this study, did not have an effect on the systems performance in terms of COD removal.

The observed consistency of COD removal by the treatment process at a reduced organic load rate of 0.5 kgCOD/kgMLSS/d is comparable to the observation that was made by Eroglu *et al.*, (1990) and Ozturk *et al.*, (1990) from their edible oil effluent treatment study using conventional activated sludge treatment techniques. A consistent BOD removal of 85 % was reported by Eroglu *et al.*, (1990) and Ozturk *et*

al., (1990) from their activated sludge system that was treating vegetable oil effluent and was operated at an organic loading rate of 0.45 kgBOD/kgMLSS/d. The decrease in sludge age from 30 days to 15 days is thought to have a minimal contribution in the treatment process performance in terms of COD removal, since the COD removal performance in 15 days and 30 days (θ_s) operated systems showed no significant difference from each other (+/- 15% difference in performance efficiency).

The sludge age reduction from 30 days to 15 days is thought to have contributed to the system performance improvement in terms of P removal efficiency. This improvement in P removal efficiency with the decrease in sludge age (θ_s) is consistent with the findings of Wentzel *et al.*, (1990) who reported an increase in P removal efficiency of the treatment process treating domestic wastewater. The reported increase in P removal efficiency was said to decrease with the increase in sludge age above 3 days (Wentzel *et al.*, 1990). The difference in the observed performance between the two processes (Wentzel *et al.*, 1990 and that of this study) may be due to the different nature of the influent substrate that was treated and the difference in process design configurations.

Throughout the treatment process operation, the removal of fats, oils & grease (FOG) was observed to be constant and consistent. Figure 5.3 shows that the removal efficiency of FOG was always above 95 %. The reason for the consistent removal of FOG is thought to be due to fatty material being adsorbed rather then absorbed by the bacterial biomass.

The operating conditions in the fourth phase seems to be the optimal and ideal conditions required for successful treatment of edible oil effluent for both COD and P reduction from the final effluent (combined edible oil effluent streams at the final discharge point to the municipal sewerage system) using biological techniques.

CHAPTER 6

GENERAL CONCLUSIONS AND RECOMMENDATIONS

From the above experiments and other experiments reported from the literature, it is clear that edible oil effluents can be successfully treated using biological methods as a form of pre-treatment. Although the total effluent COD (S_{ti}) values were considerably reduced during the present study, the effluent would require further polishing treatment to ensure that the regulatory discharge standards or municipal by-laws are successfully adhered to. The edible oil effluent requires dilution with domestic wastewater prior to its subjection to activated sludge treatment. Dilution of the edible oil effluent with domestic wastewater will ensure that the final effluent characteristics are favourable for biological remediation techniques through the balancing of the TKN/COD ratio, P/COD ratio and RBCOD/ S_{ti} ratios.

Effluent parameters are strongly dependent on the quality and type of crude oil and on the refining method (physical or chemical/caustic refining) being currently employed for that particular batch of crude oil being refined. Additional P removal from the final effluent using chemical precipitation methods may be required after the final effluent has been subjected to on site biological treatment, prior to its discharge to the municipal sewer system. This would reduce the shock loading to the municipal treatment works.

It is recommended that industrial establishments with additional space available should have an anaerobic pre-treatment process installed upstream of the activated sludge treatment process, prior to the final edible oil effluent mixing with the domestic sewage. Installation of an anaerobic treatment process upstream of the activated sludge treatment process will result in the reduction of sulphate concentrations and COD load entering the activated sludge process. The proposed set-up will reduce the concentration of slowly biodegradable COD, which will be later replaced by more RBCOD from the domestic sewage after mixing. This will result in the increased RBCOD/P ratio of the influent, thus resulting in improved overall treatment process performance in terms of removal efficiency.

It is further proposed that the contribution and effects of sulphates and FOG concentrations in the final edible oil effluent be investigated in the laboratory systems. These investigations should be accompanied by a detailed microbiological study of the biomass characteristics so as to determine the principal organisms that are responsible for treatment of edible oil effluent.

The presence of high loads of phosphates in the effluent could be addressed by changing the use of phosphoric acid during the degumming phase of crude oil refining. Phosphoric acid could be replaced with acetic acid, which more readily biodegradable that the former. There is further information in the literature on the use of acetic acids as an alternative degumming agent to phosphoric acid. The reduction in the phosphate content of the edible oil effluent would result in less complex treatment methods being required for the treatment of edible oil effluent.

Optimisation of the DAF unit operating parameters needs to be further investigated which will result in increased removal of solids, FOG and COD from the effluent stream prior to its onsite treatment.

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APPENDICES

Appendix 1

Chemical Oxygen Demand (COD) determination.

Introduction:

The estimation of the oxygen requirement of organic matter by determination of oxygen consumed from boiling acidic potassium dichromate solution has advantages over measurement of permanganate value. A much higher degree of oxidation of organic matter is achieved which means that the scope for serious errors is reduced. It should be noted that COD is not the measure of organic carbon, though the same chemical reactions are involved.

Principle of the Method:

The sample is heated to boiling level with potassium dichromate and silver sulphate catalyst in strong sulphuric acid. The absorbance of the resultant coloured solution is measure using a photometer.

Method:

Spectroquant analysis method 14541 for 100 – 1500 mg/l COD and 14555 for 500 – 10000 mg/l COD using SQ 118 Merck photometer.

Appendix 2.

Ortho-phosphate (PO_4-P) determination.

Introduction:

Phosphate in water and wastewater may be present in two main forms: the organically bound phosphate, and the inorganic phosphate. The inorganic phosphate is further divided into two main forms based on its reactivity and its availability for utilization as a nutrient source by plants. The polyphosphate which is a polymeric form is inert in water and is not available as a plant nutrient. Yet the orthophosphate form on the other hand, is readily available in water and wastewater as a plant nutrient. This is the form of phosphate that needs to be monitored and controlled to prevent eutrophication of water resources.

Principle of the Method:

The sample is mixed with a reagent that reacts with the orthophosphate group in water, which produces a distinct yellow solution the absorbance of which can be measured using a spectrophotometer.

Method:

The samples were first diluted with deionised water to a desired concentration range. Spectroquant analysis method 14842 for 1.0 – 30.0 mg/l PO_4-P using SQ 118 Merck photometer.

Appendix 3

Total Nitrogen (TKN) determination.

Introduction:

Nitrogen in wastewater appears both as oxidized nitrogen and reduced forms. Both the ammonium (free and saline) and the organic forms are present in wastewater and constitute the total nitrogen.

Principle of the Method.

The sample is mixed with reagent 1 in the presence of a catalyst. After heating in a thermal block, the sample is mixed with the second reagent, which results in immediate colour development. The resultant coloured solution is measure using a photometer.

Method:

Spectroquant analysis method 14537 for 0.5 – 15.0 mg/l N using SQ 118 Merck photometer.

Appendix 4

Free and Saline Ammonia (NH_4^+)

Introduction:

The free and saline ammonium nitrogen is readily available in wastewater as a plant nutrient that is responsible for eutrophicaction phenomenon. Free and saline ammonia may result in wastewater from biodegradation of organic nitrogen. Hence it is important to determine both the organic and ammonium nitrogen in wastewater in order to control and prevent the mineralization of water resources.

Principle of the Method:

Ammonia is quantitatively separated from other forms of nitrogen in wastewater through sample distillation under alkaline conditions. The ammonia is then determined colorimetrically after addition of Nessler's reagent.

Method:

Spectroquant analysis method 14739 for 0.01 – 2.0 mg/l NH_4-N using SQ 118 Merck photometer.

Appendix 5.

Nitrate (NO_3^-) determination.

Introduction:

Nitrate is the oxidized form of nitrogen. It is not usually found in domestic wastewater influents. But industrial wastewater may contain appreciable amount of nitrates that results from the oxidation of the total nitrogen in wastewater due to chemical processes and harsh environmental conditions that industrial water may be subjected to during manufacturing and processing. As a result it is important to test for this form of nitrogen from industrial effluents although it is not necessary to do the same for domestic wastewater.

Principle of the Method:

The sample is reacted with a colour-forming reagent in the presence of a strong oxidizing acid. The resultant coloured solution is measured against the blank using a photometer.

Method:

Spectroquant analysis method 14542 for 2.0 – 80.0 mg/l NO_3^- using SQ 118 Merck photometer.

Appendix 6

Sulphate (SO_4^{2-}) determination.

Introduction:

Sulphate is widely distributed in nature and may be present in natural water in concentrations ranging from a few to several thousand milligrams per litre. Mine drainage waste and some selected chemical industrial wastewaters may contribute large amounts of point source sulphate deposition.

Principle of the Method.

The sample reacts with Barium chloride at low pH that results in the formation of Barium sulphate. At high pH excess Barium reacts with Methylthymol blue to produce a chelate. The uncomplexed Methylthymol blue is gray. The gray uncomplexed Methylthymol blue indicates the concentration of sulphates.

Method:

The samples were first diluted with deionised water to a desired concentration ranges. Spectroquant analysis method 14564 for 100 – 1000 mg/l SO_4^{2-} using SQ 118 Merck photometer.

Appendix 7

Total suspended solids (TSS) determination.

Introduction:

Solids refer to matter suspended or dissolved in water or wastewater. Solids may affect water or effluent quality adversely in a number of ways. Highly mineralised waters are unsuitable for many industrial applications. Waters high in suspended solids may be esthetically unsatisfactory for such purposes as bathing. Hence solids analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory limits.

Principle of the Method:

A well-mixed sample is filtered through a weighed standard glassfiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105 °C. The increase in weight of the filter represent the total suspended solids.

Method:

The samples were analysed in duplicates.20 ml of sample was analysed according to Standard Method 2540 D (Standard Methods, 1989) for total suspended solids dried at 103 - 105 °C. All the calculations were according to the given method.

Appendix 8

Fats, oils and grease (FOG) determination.

Introduction:

In determination of fats, oils and grease, an absolute quantity of a specific substance is not measured. Rather, groups of substances with similar physical characteristics are determined qualitatively on the basis of their common solubility in trichlorotrifluoroethane or in diethyl ether. FOG is any material recovered as a substance soluble in trichlorotrifluoroethane or in diethyl ether. It includes other solvent extractable material from acidified samples such as sulfur compounds, certain organic dyes, and chlorophyll) and not volatilised during the test. This method of FOG analysis is suitable for biological lipids and mineral hydrocarbons, and is also suitable for most industrial wastewaters or treated effluents containing these material.

Principle of the Method:

Soluble metallic soaps are hydrolysed by acidification. Any oils and solids or viscous grease present are separated from the liquid samples by filtration. After extraction in the Soxhlet apparatus with trichlorotrifluoroethane or diethyl ether, the residue remaining after solvent evaporation is weighed to determine the Fats, oils and grease content. Compounds volatilised at or below 103 °C will be lost when the filter is dried.

Appendix 8 continue

Method:

Diethyl ether was used as a solvent instead of trichlorotrifluoroethane. The analysis was done in duplicate. 100 ml effluent samples were analysed using Standard Method 5520 D (Standard Methods, 1989). The calculations were done according to the given method.

Appendix 9

Alkalinity as $CaCO_3$ determination

Introduction:

The methods for the determination of alkalinity in natural or treated waters are also used for wastewaters. Although methods for the relative proportions of hydroxide, carbonate and hydrogen carbonate alkalinity are given, they are rarely required in the case of wastewaters. Colour and turbidity in the sample make the use of indicators difficult or impossible, hence the simplest alternative is to use an electrometric method.

Principle of the Method:

The alkalinity of natural or treated waters is usually due to the presence of hydrogen carbonate, carbonate and hydroxide compounds of calcium, magnesium, sodium and potassium. The total alkalinity is determined by titration of the sample to the end-point of a suitable indicator having a colour change at pH 4.5. titration to an end-product of ph 8.3 determines approximately the alkalinity contributed by hydroxide and half of carbonate present (pH 8.3 is approximately that of a dilute hydrogen carbonate solution). The use of these two titrations enables an approximate calculation to be made of the concentrations of the three forms of alkalinity.

Method:

The samples were analysed in duplicate. 100 ml filtered samples were place in a conical flask. The conical flask was placed over a white surface. 3 drops of phenolphthalein

indicator were added to the solution. The pink sample was titrated with 0.1 N sulphuric acid solution to colourless end-point. Few drops of methyl orange indicator were added to the solution. The yellow coloured solution was titrated with the standard acid until the first perceptible colour change towards orange was achieved.

Calculation of results:

Alkalinity for 100 ml sample as mg $CaCO_3$/l = Volume of 0.1 N sulphuric acid (ml) x 50

Appendix 10

Effluent analysis results from June 1998 to October 1998. Sampling was done once a month from Sealake Industries and the composite wastewater samples were collected in 1 hour interval for three hours a day.

PARAMETER	JUN.	JUL.	AUG.	SEPT.	OCT.
pH					
1hr	5.89	10.6	5.71	7.10	8.26
2hr	5.81	8.76	6.80	7.79	7.61
3hr	4.95	10.04	6.99	8.05	9.93
Average	**5.55**	**9.80**	**6.50**	**7.70**	**8.60**
COD (mg/l)					
1hr	7680	8710	1025	7240	11700
2hr	7590	8220	1270	7590	11810
3hr	7620	7550	1170	7370	11779
Average	**7630**	**8160**	**1155**	**7400**	**11763**
PO_4-P (mg/l)					
1hr	560	1010	1680	4510	2180
2hr	590	910	1640	4320	2130
3hr	500	1140	1660	4370	2110
Average	**550**	**1020**	**1660**	**4400**	**2140**
SO_4^{2-} (mg/l)					
1hr	5760	5280	3410	5690	1210
2hr	4980	5690	3470	5730	1170
3hr	5910	5830	3530	5980	1400
Average	**5550**	**5600**	**3470**	**5980**	**1210**
TKN (mg/l)					
1hr	6.08	3.21	6.73	8.67	4.36
2hr	6.75	4.87	6.54	7.30	5.81
3hr	7.96	6.26	7.19	6.98	4.77
Average	**6.93**	**4.78**	**6.82**	**7.65**	**4.98**
NH_4-N					
1hr	0.98	0.63	1.99	1.21	2.09
2hr	1.26	0.41	1.39	1.15	3.60
3hr	1.51	0.76	2.62	1.09	2.38
Average	**1.25**	**0.60**	**2.00**	**1.15**	**2.69**
TSS (mg/l)					
1hr	281.1	379.3	102.7	265.8	340.2
2hr	275.3	381.9	134.1	274.2	317.5
3hr	239.2	387.8	97.7	255.6	309.2
Average	**265.2**	**383.0**	**111.5**	**265.2**	**322.3**
FOG (mg/l)					
1hr	248.8	109.7	324.8	630.8	308.1
2hr	251.5	102.8	352.1	617.2	329.2
3hr	266.5	120.8	342.8	581.4	319.3
Average	**255.6**	**111.1**	**339.9**	**627.8**	**308.2**
Alkalinity as $CaCO_3$/l					
1hr	531	492	1730	649	778
2hr	542	483	1670	625	742
3hr	487	465	1760	616	778
Average	**520**	**480**	**1720**	**630**	**766**

Appendix 11

Results of the treatment process operated in a semi-continuous mode (phase 1), 1998.

DAY	$COD_{influent}$ (mg/l)	$COD_{effluent}$ (mg/l)	FOG_{infl} (mg/l)	FOG_{effl} (mg/l)	PO_4P_{in} (mg/l)	PO_4P_{ef} (mg/l)	pH influent	pH ML	MLSS (mg/l)	Temp °C
02/11/98	3780	1625	282	23	2180	2000	6.01	6.77	1800	23.1
03/11/98	3908	1360	_	_	2160	1700	6.07	6.81	1350	23.0
04/11/98	3668	1465	_	_	2120	1940	6.02	7.04	1975	24.5
05/11/98	3858	1267	265	27	2140	1560	6.01	7.01	1895	24.0
06/11/98	3858	1167	_	_	2143	2100	6.01	7.05	1920	23.0
07/11/98	3858	1143	_	_	2125	1980	6.02	7.03	2150	23.4
08/11/98	3877	1160	239	13	2100	2180	6.05	7.05	4000	23.3
09/11/98	3480	1081	_	_	2000	2160	6.05	7.02	3960	24.0
10/11/98	3719	1047	_	_	2120	2140	6.05	7.01	2820	23.1
11/11/98	4442	1080	236	18	2520	2280	6.18	6.95	4040	25.4
12/11/98	3824	1279	_	_	2660	2180	6.02	7.00	3740	25.4
13/11/98	3782	995	_	_	2020	2060	6.14	6.98	4920	25.2
14/11/98	3936	1136	272	22	2070	2180	6.17	6.97	3740	26.1
15/11/98	3851	1079	_	_	2210	2220	6.23	7.00	4480	26.3
16/11/98	3833	977	_	_	2140	2120	6.20	7.01	3640	26.1
17/11/98	3423	916	259	29	1850	2120	6.15	7.00	4860	26.2
18/11/98	3885	984	_	_	1990	1950	6.05	7.01	5580	24.9
19/11/98	3897	978	_	_	2000	1950	6.89	7.05	4920	25.4
20/11/98	3844	986	221	25	1730	1530	6.87	7.05	5120	24.5
21/11/98	3865	998	_	_	1940	1950	6.50	7.05	4960	26.50

Appendix 12

Results of the treatment process operated in a continuous mode (phase 2), 1998.

DAY	$COD_{influent}$ (mg/l)	$COD_{effluent}$ (mg/l)	FOG_{infl} (mg/l)	FOG_{effl} (mg/l)	PO_4P_{in} (mg/l)	PO_4P_{ef} (mg/l)	pH influent	pH ML	MLSS (mg/l)	Temp °C
07/12	5886	1144	620	62	430	260	5.46	7.71	4640	24.5
08/12	5906	1717	_	_	450	320	5.62	7.56	4640	24.5
09/12	6154	1824	_	_	440	390	6.85	7.35	4360	25.3
10/12	5497	1836	638	96	460	410	5.35	7.25	3860	25.2
11/12	5646	2310	_	_	420	370	5.33	7.93	3920	26.5
12/12	5602	2249	_	_	440	360	6.78	7.68	2960	26.8
13/12	5655	2356	602	96	450	380	6.69	7.28	3260	27.0
14/12	5785	1066	_	_	440	370	6.78	7.31	3180	27.0
15/12	5090	1498	_	_	410	400	6.73	6.91	3060	27.1
16/12	5046	1485	589	71	420	400	6.71	6.88	2780	26.8
17/12	5441	1094	_	_	420	390	6.75	6.98	2480	27.0
18/12	5540	1548	_	_	420	400	6.73	7.99	1400	27.0
19/12	5540	1532	568	74	420	410	6.75	7.77	_	26.5
20/12	5856	2182	_	_	450	420	6.75	7.02	3420	27.0
21/12	5856	1896	_	_	450	410	6.75	7.01	3400	26.8
22/12	5856	1888	602	48	450	410	6.75	7.02	3560	26.5
23/12	5856	1890	_	_	450	420	6.75	7.03	2980	27.1
24/12	5856	2307	_	_	450	450	6.75	6.99	2989	27.5

25/12	5001	2338	609	67	450	450	6.34	7.00	3500	28.1
26/12	5001	2409	–	–	450	430	6.34	6.98	3630	27.0
27/12	5001	2808	–	–	450	470	6.34	6.92	3620	26.5
28/12	5001	2826	625	75	450	460	6.34	7.81	3580	28.1
29/12	5001	2805	–	–	450	460	6.34	7.30	3480	28.0
30/12	5420	2566	–	–	440	450	6.34	7.30	3500	27.6
31/12	5420	2539	612	110	440	450	6.62	6.66	3420	27.2

Appendix 13

Results of the treatment process operated in a continuous mode (phase 3), 1999.

DAY	$COD_{influent}$ (mg/l)	$COD_{effluent}$ (mg/l)	FOG_{infl} (mg/l)	FOG_{effl} (mg/l)	PO_4P_{in} (mg/l)	PO_4P_{ef} (mg/l)	MLSS (mg/l)	Temp °C
02/02	2256	798	710	71	180	160	4680	23.2
03/02	2255	1096	_	_	180	160	4600	23.6
04/02	2256	1163	_	_	180	150	4620	26.5
05/02	2134	572	762	46	180	100	4550	26.7
06/02	2132	354	_	_	180	110	4500	25.3
07/02	2130	563	_	_	180	130	4380	26.9
08/02	2131	665	709	57	180	120	4250	28.2
09/02	2345	808	_	_	200	110	4730	27.3
10/02	2343	891	_	_	200	70	5630	26.9
11/02	2345	998	716	36	200	80	3720	25.8
12/02	2341	1246	_	_	200	90	3910	29.1
13/02	2340	1396	_	_	200	120	3950	28.6
14/02	2437	1326	721	43	205	110	4170	26.4
15/02	2437	1316	_	_	205	120	3160	24.3
16/02	2435	1404	_	_	205	110	4420	22.3
17/02	2433	1807	732	44	205	140	3690	22.6
18/02	2328	1764	_	_	190	130	2250	26.5
19/02	2323	1570	_	_	190	130	3940	24.3

20/02	2325	1681	701	70	190	170	4303	27.3
21/02	2322	1766	_	_	190	130	4020	27.5
22/02	2043	1808	732	59	190	120	3980	26.8
23/02	2042	1600	_	_	190	170	4021	28.1
24/02	2041	1263	_	_	190	150	4060	29.7
25/02	2040	1642	751	68	190	120	4089	29.8
26/02	2314	1577	_	_	190	120	4010	26.5
27/02	2314	1336	_	_	190	110	4030	28.3
28/02	2311	1282	740	52	190	120	3980	28.6
01/03	2312	1531	_	_	190	100	3990	28.3
02/03	2310	1620	_	_	190	100	4057	28.4
03/03	2313	1598	_	_	190	100	4040	26.9

Appendix 14

Results of a continuously operated treatment process during phase 4, 1999.

DAY	$COD_{influent}$ (mg/l)	$COD_{effluent}$ (mg/l)	FOG_{infl} (mg/l)	FOG_{effl} (mg/l)	PO_4P_{in} (mg/l)	PO_4P_{ef} (mg/l)	MLSS (mg/l)
10/06	2425	514	281	31	620	470	4250
11/06	2655	531	–	–	610	470	4200
12/06	2690	580	–	–	610	500	4180
13/06	2684	650	262	21	610	530	4190
14/06	2664	581	–	–	610	500	4100
15/06	2530	587	–	–	580	470	4120
16/06	2529	592	267	11	580	490	4160
17/06	2549	562	–	–	580	460	4100
18/06	2558	530	–	–	580	470	4130
19/06	2550	534	279	6.0	580	480	4170
20/06	2489	527	–	–	590	510	4130
21/06	2497	513	–	–	600	500	4120
22/06	2520	529	294	26	600	530	4160
23/06	2683	557	–	–	590	560	4180
24/06	2687	549	–	–	590	520	4200
25/06	2691	561	238	24	590	510	4170
26/06	2659	534	–	–	600	480	4130
27/06	2433	522	–	–	610	470	4130

28/06	2441	524	247	15	600	470	4120
29/06	2419	529	_	_	600	470	4150
30/06	2397	531	_	_	590	490	4140
01/07	2405	525	297	18	580	490	4120
02/07	2403	520	_	_	580	500	4160
03/07	2410	526	_	_	590	470	4130
04/07	2408	522	262	13	580	470	4180
09/07	2801	608	235	5.0	590	470	4200
10/07	2795	609	_	_	590	480	4190
11/07	2799	607	_	_	600	490	4180
12/07	2788	602	292	26	600	470	4190
13/07	2539	579	_	_	610	500	4190
14/07	2543	552	_	_	620	490	4190
15/07	2550	531	273	27	620	500	4190
16/07	2547	540	_	_	620	490	4200
17/07	2675	626	_	_	610	500	4190
18/07	2663	617	268	51	620	500	4190
19/07	2660	641	_	_	620	500	4180
20/07	2668	643	_	_	620	490	4190
21/07	2660	619	281	39	610	490	4200
22/07	2671	614	_	_	610	500	4190
23/07	2663	598	_	_	610	490	4190

24/07	2665	592	304	18	620	500	4190
25/07	2778	595	_	_	620	510	4180
26/07	2765	599	_	_	620	510	4180
27/07	2770	602	293	21	620	510	4190
28/07	2773	610	_	_	620	490	4200
29/07	2693	607	_	_	610	490	4200
30/07	2644	610	272	24	610	480	4190
31/07	2696	601	_	_	620	490	4180
01/08	2687	603	_	_	620	470	4190
02/08	2706	593	296	6.0	610	500	4190
03/08	2715	589	_	_	610	500	4180
04/08	2708	591	_	_	610	510	4190
05/08	2713	580	281	11	610	490	4190
06/08	2684	588	_	_	600	500	4190
07/08	2694	597	_	_	600	500	4190
08/08	2690	601	267	11	600	510	4200
09/08	2681	602	_	-	600	490	4200
10/08	2640	606	_	_	620	500	4180
11/08	2639	601	271	60	620	510	4180
12/08	2647	602	_	_	620	510	4190
13/08	2634	598	_	_	620	500	4190
14/08	2754	596	295	15	590	500	4200

15/08	2763	645	_	_	590	530	4200
16/08	2784	657	_	_	590	530	4180
17/08	2769	660	277	11	600	540	4190
18/08	2704	670	_	_	620	540	4180
19/08	2701	673	_	_	620	530	4180
20/08	2693	651	261	3.0	610	520	4180
21/08	2698	679	_	_	610	520	4190
22/08	2641	642	_	_	620	520	4190
23/08	2638	620	249	20	620	520	4190
24/08	2681	615	_	_	620	510	4190
25/08	2672	603	_	_	620	510	4200
26/08	2748	613	297	27	600	500	4200
27/08	2751	602	_	_	610	510	4200
28/08	2759	609	_	_	610	510	4200
29/08	2739	603	293	9.0	610	490	4190
30/08	2693	604	_	_	620	490	4190
31/08	2698	619	_	_	620	480	4190
01/09	2702	613	272	12	610	480	4190
02/9	2705	614	_	_	620	490	4190