PROPANE DEHYDROGENATION WASTEWATER TREATMENT USING SEQUENCE BATH REACTORS

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CIVIL ENGINEERING
UNIVERSITI TEKNOLOGI PETRONAS
JANUARY 2010

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engineering futures

Propane Dehydrogenation Wastewater Treatment using Sequencing Batch Reactors

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Civil Engineering)

Approved.

MAY 2010

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AKOSUA ABONGILE KADE DANSO

ABSTRACT

The purpose of this study was to determine the effectiveness of using a Sequencing Batch Reactor (SBR) in treating PDH wastewater, to determine the effect of various organic loading rates on SBR performance and lastly, to determine the optimum operating conditions for the SBR. Industrial wastewaters commonly contain high organic loads as well as toxic and inhibitory substance such as sulphide. Therefore, the conventional activated sludge process is inefficient in treating wastewater of this nature. The wastewater sample was collected from a Propane Dehydrogenation (PDH) plant in Kuantan, Pahang. The initial wastewater characteristics of the sample before treatment were determined. Biomass obtained from the Sewage Treatment Plant (STP) at Universiti Teknologi Petronas (UTP), which was cultured for three months in a reactor in the Environmental laboratory, was used to inoculate the wastewater in the SBR. The performance of the SBR in treating the PDH wastewater was investigated with a suspended biomass configuration and operating under the following sequence: fill, react, settle and decant. The effects of four different organic loading rates were investigated. Two sequencing batch reactors were operated simultaneously, each initially having a total cycle period of 24 hours and respective organic loading rates of 0.7 kgCOD/m^3/day and 1.5 kg COD/m^3/day, which were respectively reduced to 0.35 kgCOD/m^3/day and 0.183 kgCOD/m^3/day after 30 days of operation. The performance of the SBR was assessed by measuring the COD, BOD and sulphide concentrations after each cycle, among other parameters. It was determined that the optimum operating conditions for the SBR were a 0.35 kgCOD/m^3/day organic loading rate with a subsequent HRT of 20 days and a 24 hour cycle period, where the COD, BOD and sulphide removal efficiencies of up to 96%, 98% and 97% respectively were achieved. Results showed that a high organic loading rate inhibited the SBR performance. The sulphide concentration was sufficiently reduced to meet the Environmental Quality (sewage & industrial effluent) Regulations, 1979 under the 3rd schedule Environmental Quality Act, 1974, where the sulphide limit is 0.5 mg/L for both standard A and B.

ACKNOWLEDGEMENTS

I would like to gratefully acknowledge Assoc. Prof. Dr. Mohamed Hasnain Isa for his supervision and guidance. I am also very grateful to the technicians in the Environmental Laboratory at Universiti Teknologi Petronas for their technical assistance. Lastly, I am thankful for the assistance and camaraderie of my colleagues Mr. Ceasar Bidal Clement and Natasha Ramdass.

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SBR	–	Sequencing Batch Reactor
DO	–	Dissolved Oxygen
BOD	–	Biochemical Oxygen Demand
COD	–	Chemical Oxygen Demand
STP	–	Sewage Treatment Plant
UTP	–	Universiti Teknologi Petronas
PDH	–	Propane Dehydrogenation
OCR	–	Oxygen Consumption Rate
HRT	–	Hydraulic Retention Time
ASP	–	Activated Sludge Process
MLSS	–	Mixed Liquor Suspended Solids
VSS	–	Volatile Suspended Solids
TSS	–	Total Suspended Solids

CHAPTER 1

INTRODUCTION

1.1 Background Study

There are various types of wastewaters, which originate from different sources, i.e. domestic or industrial activities. These wastewaters have different characteristics and thus cannot always be treated using the same method. It is important to have knowledge of the physical and chemical constituents of the wastewater in order to determine a suitable treatment method, as well as a comprehensive understanding of the pollutants of concern in wastewater and their impact on the environment (Burton et al., 2004).

Industrial wastewaters vary in composition, depending on the activities at the source. These wastewaters can have much higher organic and inorganic contents in comparison with domestic wastewater. As a result of the presence of inhibitory/toxic pollutants and the complex nature of some industrial wastewater, conventional biological treatment methods may not be efficient. Hence, different wastewater treatment technologies have been developed in recent years; one such being the Sequencing Batch Reactor.

Petrochemicals are defined by Ruggles (1959), as those compounds which are derived in whole or in part from petroleum and natural gas hydrocarbons and which are used mainly in chemical markets rather than being primary sources of fuel and lubricants. A basic petrochemical process is one where hydrocarbons obtained from oil and gas refineries are used to produce new chemicals. Therefore, the production of propylene from propane in the propane dehydrogenation (PDH) process can be classified as a basic petrochemical process.

Sulphide is one of the toxic compounds commonly found in sewage and industrial wastewaters, such as petrochemical waste. It is a poisonous by-product of the anaerobic decomposition of organic matter. In Malaysia, the Environmental Quality (sewage & industrial effluent) Regulations, 1979 under the 3rd schedule Environmental Quality Act, 1974 states the parameter limits of effluent for Standard A and B. The limit for sulphide under this standard is 0.5 mg/L, the COD limit is 50 mg/L and 100 mg/L and BOD is 20 mg/L and 50 mg/L for standard A and B respectively (see Appendix A1). Some form of pretreatment is often required by industries in order to reduce the high organic load as well as reduce the concentrations of toxic substances, such as sulphide, before the effluent is discharged to a Sewage Treatment Plant (STP) (Burton et al., 2004).

There are many problems associated with the presence of sulphide compounds in wastewater systems, such as the following (Bows et al., 2003):

- pungent odour;
- emission of toxic H_2S gas into the atmosphere;
- corrosion of sewage pipes;
- fish mortality.

Sulphide has a high oxygen demand; therefore its presence in industrial effluent discharged into rivers depletes the oxygen required in the river resulting in fish mortality (Ng, 2006). Therefore, the removal of sulphide from wastewater is instrumental in environmental protection.

1.2 Problem Statement

PDH wastewater typically contains inhibitory/toxic compounds such as sulphide and high organic loads which would be toxic to aerobic bacteria in the conventional biological treatment process (Petrovskaya and Rajalo, 1996). Therefore, this process would not be efficient in treating this type of wastewater. The problem with conventional biological treatment processes is that the reactor volume remains constant; therefore shock loading is an inhibitory factor. Most STPs do not maintain a long sludge age due to the cost of operation; thus the microorganisms do not have sufficient time to acclimatize to the toxicity of the wastewater (Elefsiniotis et al., 2008).

The conventional biological treatment process is shown in Figure 1.1 (earthpace resources, n.d.) below. A healthy culture of suspended microorganisms is maintained in the aeration tank. These microorganisms are responsible for the degradation of organic matter, under the provided contact time.

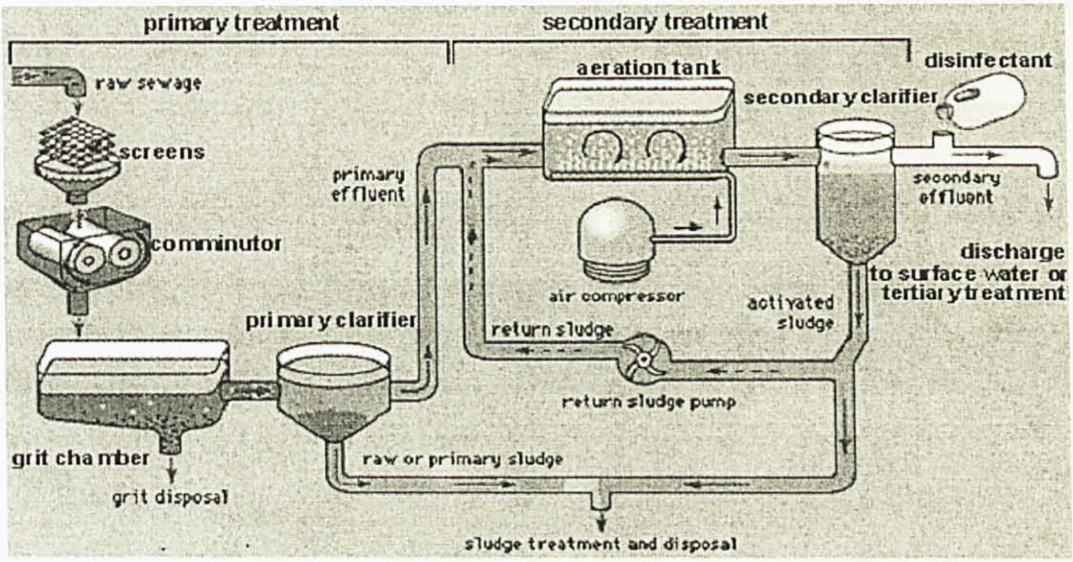


Figure 1.1: Conventional biological treatment process

“The objective for industrial wastewater treatment is to remove or reduce the concentration of organic and inorganic compounds” (Burton et al., 2004). In the treatment of industrial wastewater the problem occurs in the secondary treatment phase where the concentration of toxic compounds present in the industrial wastewater could inhibit the ability of the microorganisms to oxidize the organic matter. It is possible for the microorganisms to acclimatize to different levels of toxicity; however this requires a certain period of time (acclimatization period), depending on the concentration and type of toxic compounds (Ng, 2006). This acclimatization period may be insufficient in conventional biological treatment systems.

Sequencing Batch Reactor technology has been developed to address the shortcomings of conventional biological treatment processes. An SBR operates on the basis of a number of cycles in a day, each cycle having up to five phases: fill, react, settle, decant and idle. The following are advantages of an SBR (Chin et al., 2005; Irvine et al., 1989):

- ability to keep biomass in the system for extended periods of time;
- ease of operation;
- low operational cost
- tolerance to shock loadings
- ability to adapt to process control technologies.

The use of SBR technology for the treatment of industrial wastewaters with complex chemical constituents and high toxicity has been proven to be effective through extensive research by experts in the field (Chandrashekara Rao et al., 2005; Elefsiniotis et al., 2008).

1.3 Objectives and scope

The objectives of this study are to:

- determine the effectiveness of using an SBR in treating PDH wastewater
- determine the effect of various Organic Loading Rates on SBR performance
- determine optimum operating conditions for an SBR treating PDH wastewater.

This study will be conducted based on the treatment of wastewater from a Propane Dehydrogenation (PDH) plant in Kuantan, Pahang. The wastewater from such petroleum-related activities is expected to have a high organic load as well as contain other toxic compounds such as sulphide. The wastewater sample will be characterized by measuring the initial COD, BOD and sulphide concentrations, among other parameters, prior to treatment. A comparison will be made between the concentrations of these parameters prior to treatment and after treatment in the SBR.

CHAPTER 2

LITERATURE REVIEW

Propane Dehydrogenation is defined as a catalytic dehydrogenation technology to produce propylene from propane (www.hmcpolymers.com/technology.pdh.html). Natural gas and crude distillates such as naphta from petroleum refining are used as feed stocks to manufacture a wide variety of petrochemicals that are in turn used in the manufacture of consumer goods. The activities at these petrochemical plants release some carcinogenic and toxic compounds into the air, i.e. ethylene and propylene which can lead to the formation of extremely toxic oxides. Petrochemical plants generate solid wastes and sludges, some of which may be considered hazardous, because of the presence of toxic organics and heavy metals (World Bank Group, 1998). "Wastewater generated by the catalytic hydrocracking and refining of various crude-oil fractions, contains, in addition to hydrocarbons, large amounts of nitrogen and sulphur, in the form of ammonia (NH_3) and hydrogen sulfide (H_2S), respectively" (Aivasidis et al., 2005).

Industrial effluents contribute significantly to the contamination of surface water system. Many different types of industries discharge their effluents into rivers therefore their environmental impacts vary. Industrial wastewaters generally have high organic and inorganic loads. "A wide range of organic contaminants, comprising for example pesticides, mono- and polycyclic aromatic hydrocarbons, polychlorinated biphenyls (PCBs) as well as many phosphorous- and sulphur-containing compounds have been identified in industrial wastewaters" (Castillo et al., 1998; Alonso and Barcelo´ , 1999; Frintrop et al., 1999; Guerra, 2001; Crowe et al., 2002; Dsikowitzky et al., 2004; Zhang et al., 2008; Heim and Schwarzbauer, 2005).

There are two principal biological processes used for the treatment of wastewater; suspended growth and attached growth processes. The objectives of biological treatment of domestic wastewater are as follows (Burton et al., 2004).

- transform dissolved and particulate biodegradable constituents into acceptable end products;
- capture and incorporate suspended and nonsettleable colloidal solids into a biological floc or biofilm;
- transform or remove nutrients, i.e. nitrogen and phosphorus;
- in some cases, remove specific trace and organic constituents and compounds.

In the suspended growth process, a fixed concentration of microorganisms are maintained in a liquid suspension (Mixed Liquor Suspended Solids, MLSS) in the aeration tank for a set period of time, known as the Sludge Retention Time (SRT) before being wasted to the clarifier (Burton et al., 2004).

In conventional biological wastewater treatment, the SRT is often short therefore the microorganisms are not provided with sufficient contact time to acclimatize to toxic compounds such as those found in industrial wastewaters. The processes involved in the conventional biological treatment process, i.e. sedimentation, aeration, etc., occur in different tanks, which make the operation of a treatment plant costly.

"The Sequencing Batch Reactor process utilizes a fill-and-draw reactor with complete mixing during the batch reaction step (after filling) and where the subsequent steps of aeration and clarification occur in the same tank" (Burton et al., 2004).
Table 2.1, extracted from Burton et al. (2004), describes the operational steps for a SBR.

Table 2.1: Description of operational steps for the sequencing batch reactor (SBR)

Operational step	Description
Fill	During the fill operation, volume and substrate (raw wastewater or primary effluent) are added to the reactor. The fill process typically allows the liquid level in the reactor to rise from 75% of capacity (at the end of the idle period) to 100%. When two tanks are used, the fill process may last about 50% of the full cycle time. During fill, the reactor may be mixed only or mixed and aerated to promote biological reactions in the influent wastewater.
React	During the react period, the biomass consumes the substrate under controlled environmental conditions.
Settle	Solids are allowed to separate from the liquid under quiescent conditions, resulting in a clarified supernatant that can be discharged as effluent.
Decant	Clarified effluent is removed during the decanting period. Many types of decanting mechanisms can be used, with the most popular being floating or adjustable weirs.
Idle	An idle period is used in a multitank system to provide time for one reactor to complete its fill phase before switching to another unit. Because idle is not a necessary phase, it is sometimes omitted.

There are several treatment methods currently practised for the removal of sulphide from wastewater, using processes such as chemical precipitation and electrochemical oxidation, to name a few (Petrovskaya and Rajalo, 1996; Bows et al., 2003). However, a thorough literature search showed that not many investigations have been conducted to directly associate the treatment of PDH wastewater with SBR technology, thus far.

In a study conducted for the treatment of four industrial wastewaters; landfill leachates, textile, seafood and slaughterhouse effluent in Thailand, the success of the SBR in treating complex industrial wastewaters is evident. The treatment was done using three identical SBR systems operating in parallel. The SBRs were operated on a 24 hour cycle period, including a 5 hour fill period and a 3 hour settle-draw-idle period. Three SRTs of 60, 70 and 80 days were used and an HRT of 48 hours. The average acclimation period for the three SRTs was 60 days. The results yielded TKN and COD removal efficiencies in excess of 81% for all four wastewaters and TP removal ranged from 57% to 94%. An increase in SRT resulted in a decrease in TP removal from the textile and leachate wastewaters (Elefsiniotis et al., 2008).

Another significant study experimented with the treatment of complex chemical wastewater in a SBR. The characteristics of the wastewater used as feed in the SBR showed sulphides and sulphates concentrations of 35 mg/l and 1750 mg/l respectively. The SBR was operated with varying organic loading rates of 0.8, 1.7 and 3.5 kg COD/m^3/day in suspended growth configuration. The total cycle period of 24 hours consisted of: 15 minutes of filling phase, 23 hours of aerobic reaction phase with recycling, 30 minutes of settling phase and 15 minutes of withdrawal phase. The results showed 8% sulphate reduction at all organic loading rates. A conventional aerobic system cannot reduce sulphates, as it requires an anoxic/anaerobic environment to bring about conversion. An important conclusion from this study showed that the performance of the SBR is dependent on organic loading rate. The optimum organic loading rate was 1.7 kg COD/m^3/day; an increase in organic loading rate inhibited the performance. In the study, a comparison was also made between the SBR and a conventional ASP operated with the same complex chemical wastewater. Table 2.2 shows the comparative performance of the conventional ASP and the SBR (Rao et al., 2005).

Table 2.2: Comparative performance of conventional ASP and SBR

Reactors	Configuration	Organic loading rate (kgCOD/m3/day)	HRT (day)	% COD removal	% BOD removal	Sludge age (days)	VSS in mixed liquor (mg/l)
ASP	Suspended growth (aerobic)	1.1	5	55.0	67	12	2000-2250
SBR	Suspended growth (aerobic & anoxic)	0.8	1	66.4	92	10	2000-2250

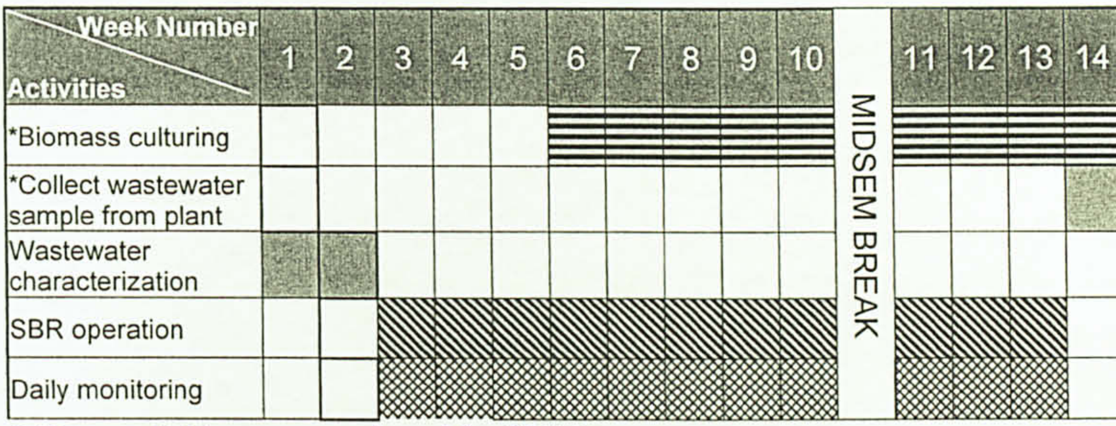
"Sequencing batch reactor technology has been developed on the basic scientific assumption that periodic exposure of the microorganism to defined process conditions is effectively achieved in a fed batch system in which exposure time, frequency of exposure and amplitude of respective concentrations can be set independently of any inflow condition" (Irvine et al., 2001).

Freshwater is essential for natural biota and human life, which has rapidly become a limited resource. The pollution of waterbodies has detrimental effects on the environment, particularly on the decline of water quality. This can be directly linked to industrial wastewater effluents containing toxic and inhibitory substances being discharged into lakes and rivers (Ng, 2006). The use of technology such as the SBR in treatment of industrial wastewaters, instead of the conventional biological treatment processes, will ensure that concentration of toxic compounds in the effluent discharged into rivers meet the required standards.

CHAPTER 3

METHODOLOGY

The Gantt chart below shows the important activities that were conducted in this study and their respective durations.



** These activities were conducted for FYP I*

Figure 3: Gantt chart for activities

3.1 Biomass and wastewater characteristics

In preparation for the experiment, biomass was cultured for a period of three months in the environmental lab at Universiti Teknologi Petronas (UTP). The biomass was stored at room temperature (±25 °C) in a 21 L reactor and constantly aerated. Twice a week, a supernatant volume of 10 L was decanted from the reactor and fed with 10L of fresh wastewater collected from the STP. This was done to ensure a healthy biomass culture is available for the reaction phase in the SBR. The VSS is an indication of the biomass solids in the reactor. The VSS concentration in the reactor at the time of SBR startup was 9650 mg/L.

The wastewater used in this study was collected from the effluent (before in-house treatment) at a PDH plant in Kuantan. The detailed characteristics of the wastewater used in this study as feed are shown in Table 3.1. The low BOD/COD ratio (< 0.015), high sulphate and relatively high sulphide concentrations show the complex chemical characteristics of the wastewater.

Table 3.1: Characteristics of wastewater used as feed in SBR

Characteristics of wastewater sample from PDH plant	
Parameters	**Concentrations**
pH	10.6
BOD (mg/l)	1106
COD (mg/l)	73100
Sulphide (mg/l)	21.4
Sulphate (mg/l)	9100
VSS (mg/l)	109
TSS (mg/l)	250
TKN (mg/l)	21
Total Phosphorus (mg/l)	120
Nitrate (mg/l)	1630

3.2 SBR configuration and operation

The sequencing batch reactors used were taken from the laboratory. The properties of the reactors are as shown in Table 3.2.1 below.

Table 3.2.1: Physical properties of SBR

Material	Perspex
Internal diameter (m)	0.14
Height (m)	0.525
Capacity (L)	8.15
H/D ratio	3.75
Liquid Volume (L)	5.0

The SBR was operated under the following configuration:

- Suspended growth configuration;
- Room temperature (25 ± 2°C);
- Initially, a 24 hour cycle period consisting of the filling phase, reaction phase, settling phase and decanting phase was used. By this trial-and-error method as shown in Table 3.2.2, the optimum operating conditions for the SBR were determined;
- The HRT and organic loading rate in each reactor will be varied;
- The sequence of the SBR operation was manually controlled;
- Dissolved Oxygen (DO) was maintained at a constant concentration throughout the reaction phase;
- A target VSS of approximately 4 000 mg/L was maintained in both reactors throughout;
- The pH of the influent wastewater was adjusted to 7.0 ± 2 before the filling phase.

Table 3.2.2: Proposed operating conditions for SBR by trial and error.

Operating conditions	Trial 1		Trial 2		Air supply
	SBR 1	SBR 2	SBR 1	SBR 2	
Filling (min)	10	10	10	10	Off
Reaction (hrs)	23	23	23	23	On
Settling (min)	40	40	40	40	Off
Decanting (min)	10	10	10	10	Off
Organic loading rate (kg COD/m^3/day)	0.7	1.5	0.35	0.183	
Hydraulic retention time (days)	10	5	10	20	
Feed volume (L)	1.0	2.0	0.5	0.25	

Figure 3.2 shows the experimental setup of the two sequencing batch reactors. The source of air is an electric (RS-248 A) aquarium air pump, which has a maximum flow of 2.5 L/min. The decanting of the effluent was done using the mechanical plastic pump.

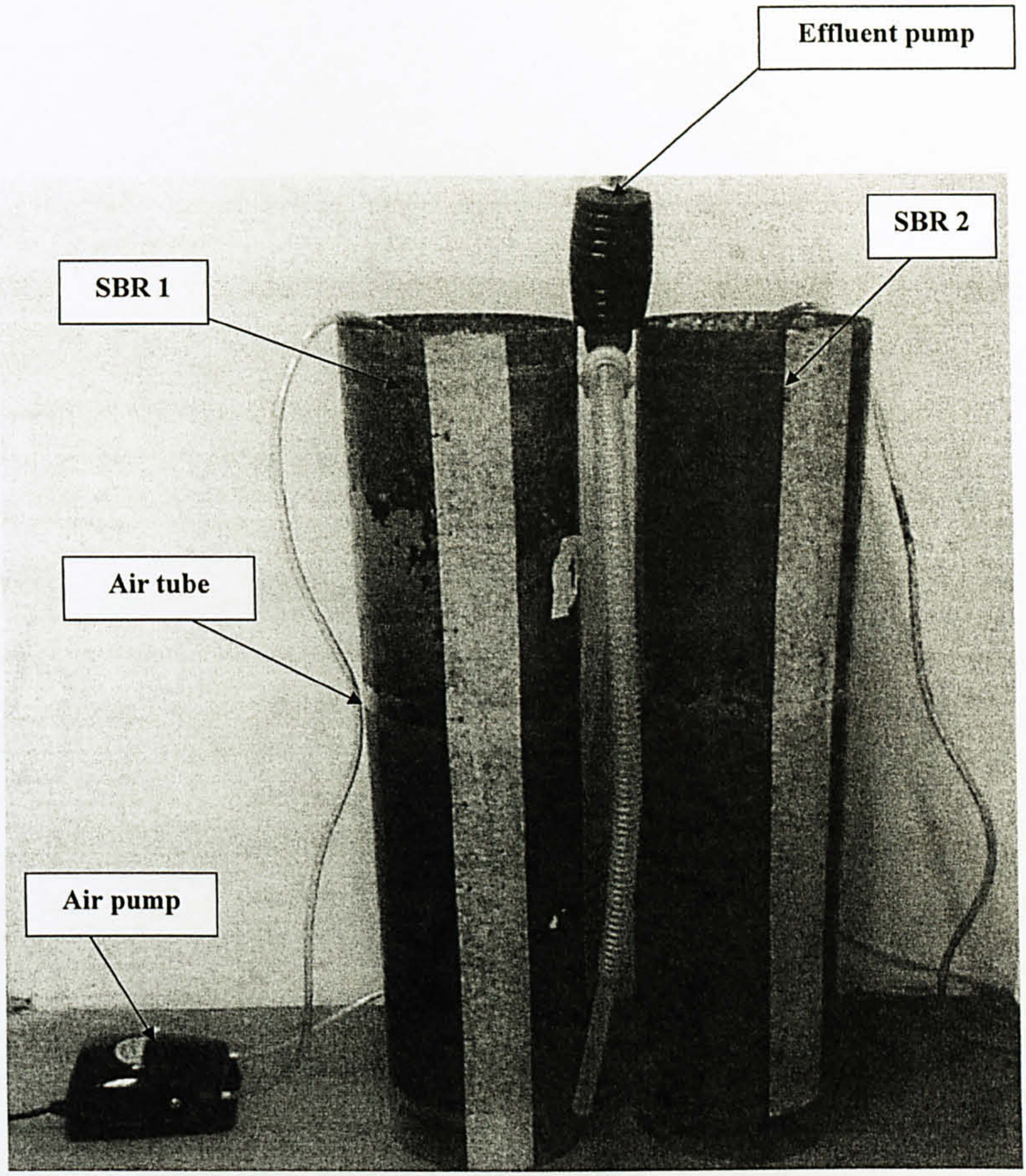


Figure 3.2: SBR experimental setup

3.3 Start up of SBR

The SBR was inoculated with the biomass cultured in the reactor, which was collected from the STP at Universiti Teknologi Petronas (UTP).

The two reactors were operated simultaneously, with varying organic loading rates; 0.7 kg COD/m^3/day and 1.5 kg COD/m^3/day respectively. The reactors were started with a liquid volume of 5 L; 2 L of biomass and 3 L of wastewater in each. The effluent from the PDH plant was diluted 1:10 before being fed into each SBR. This was done in order to reduce the toxicity of the sample and prevent shock-loading. During the decanting phase, 1 L was decanted manually (by pump) from the reactor with the higher organic loading rate (1.5 kg COD/m^3/day) and 0.5 L from the other reactor. The same volumes were respectively (manually) filled during the filling phase and recirculated by aeration during the reaction phase. The initial organic loading rates were reduced to 0.35 kgCOD/m^3/day and 0.183 kgCOD/m^3/day in SBR1 and SBR 2 respectively after 30 days of operation. Both reactors were operated for an overall period of 80 days.

3.4 Analytical Procedures

The SBR will operate continuously for a period of approximately three months. Table 3.4 shows the parameters that will be monitored and the respective methods to be used to measure them. These methods have been adapted from *Standard Methods for the Examination of Water and Wastewater*.

Table 3.4: Process performance parameters

Parameters	Standard Methods
COD	Reactor Digestion Method
BOD	Modified Wrinkler's Method
pH	pH meter
DO	Modified Wrinkler's Method (using DO meter)
Sulphide	Methylene Blue Method
Sulphate	SulfaVer 4 Method (using powder pillows), HACH
VSS	Gravimetric Method
TKN	Automated colorimetry with preliminary distillation/digestion
Total Phosphorus	Molybdovanadate Method with acid persulfate digestion

CHAPTER 4

RESULTS AND DISCUSSION

4.1 SBR performance

Two sequencing batch reactors were operated simultaneously, each initially having a total cycle period of 24 hours and respective organic loading rates of 0.7 kg $COD/m^3/day$ and 1.5 $kgCOD/m^3/day$. They were closely monitored in order to determine the most efficient SBR operating conditions. The performance was assessed by monitoring COD, BOD, sulphide, sulphate, TKN and Total Phosphorus concentrations throughout the reactor operation.

The variation of COD and BOD concentrations over time in both reactors are shown in figures 4.1 to 4.4. With continued operation, both reactors showed enhanced performance with respect to COD and BOD removal. The fluctuation in the results obtained within the early days of SBR operation, as shown in the graphs, is as a result of the bacteria still acclimatizing to the toxicity of the new substrate conditions as they had become acclimatized to the domestic wastewater from the STP prior to SBR operation. Lower BOD and COD concentrations were achieved in SBR 1 within a shorter period as compared to SBR 2, thus showing a superior performance is achieved at lower organic loading rates.

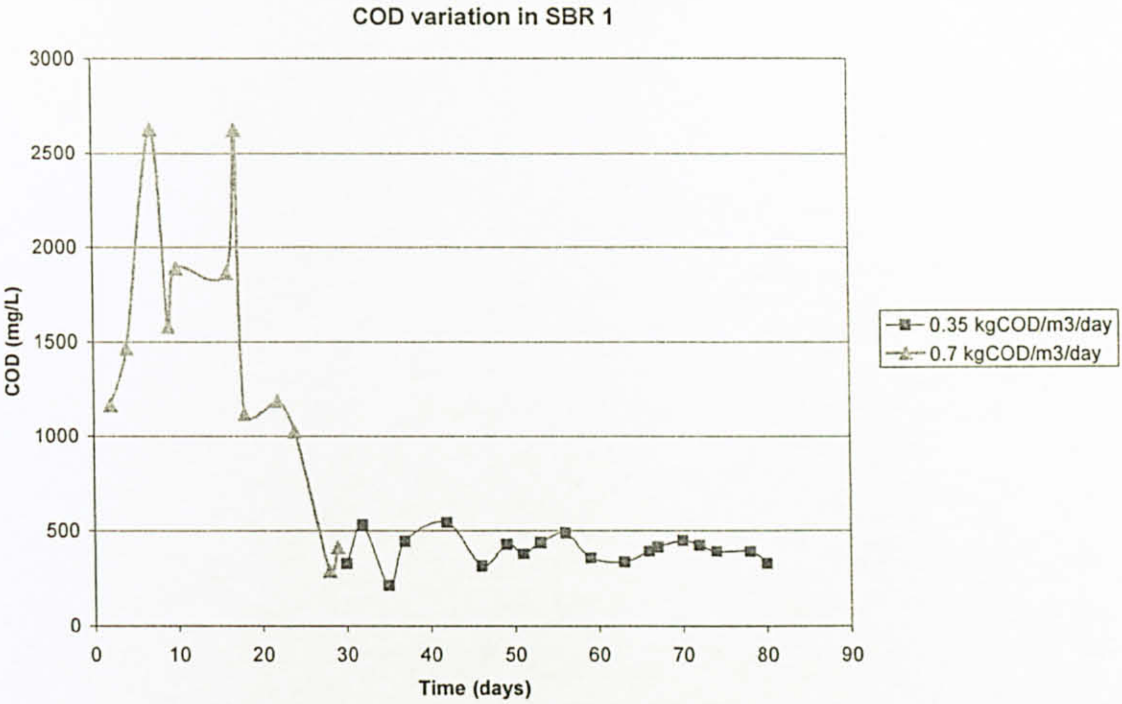


Figure 4.1: COD variation in SBR 1 at varying organic loading rates

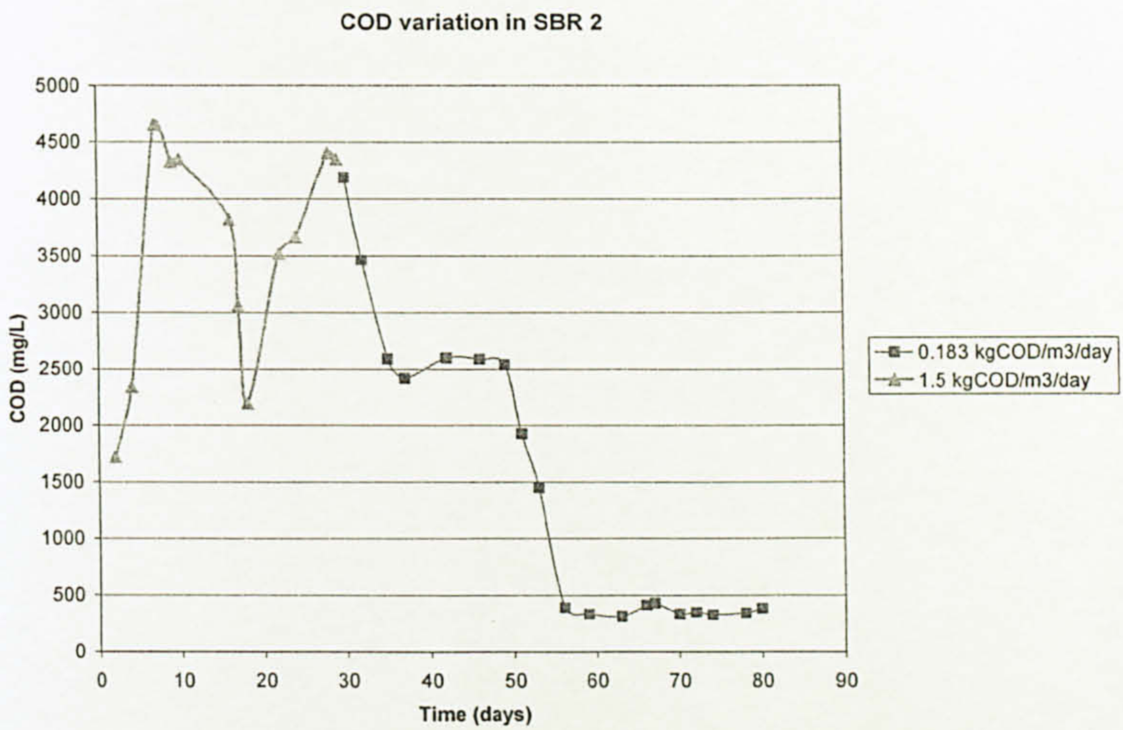


Figure 4.2: COD variation in SBR 2 at varying organic loading rates

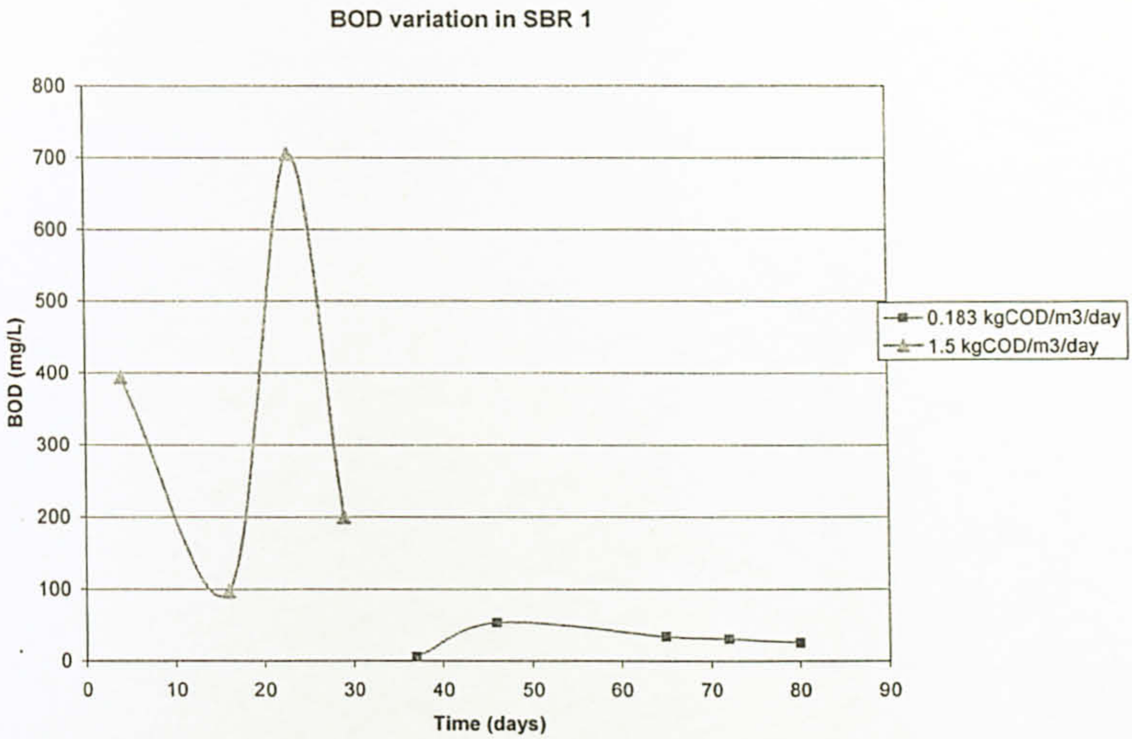


Figure 4.3: BOD variation in SBR 1 at varying organic loading rates

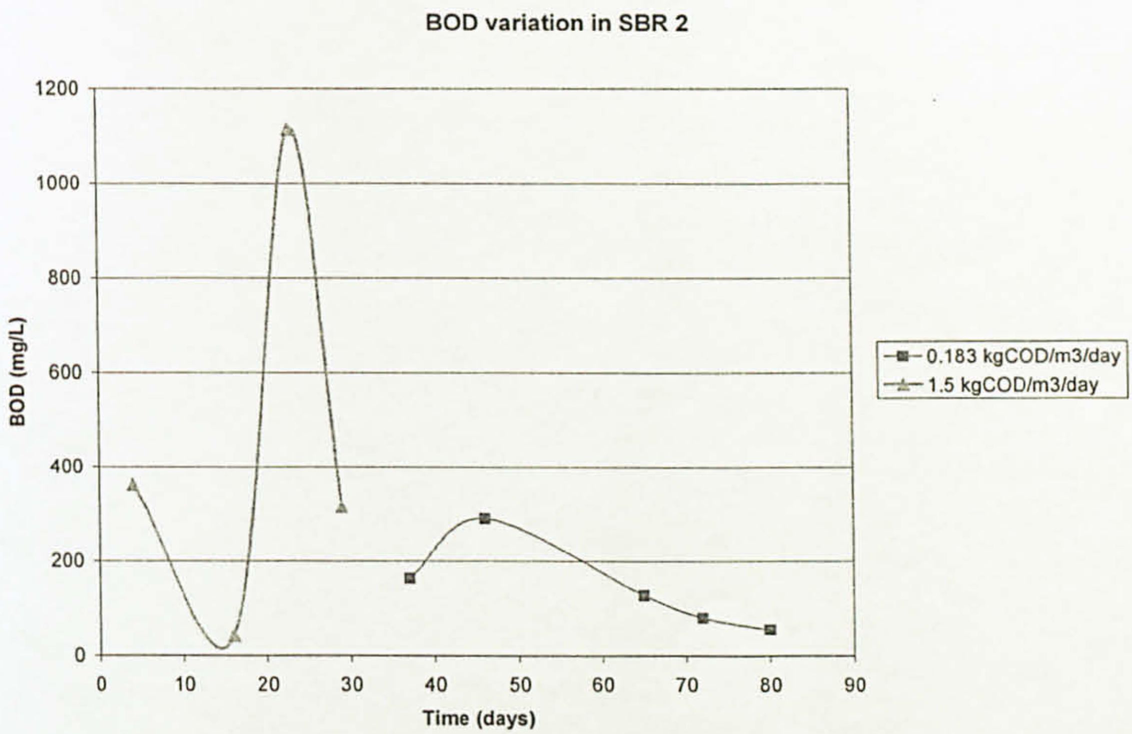


Figure 4.4: BOD variation in SBR 2 at varying organic loading rates

Stable conditions, for the purpose of this study, can be said to have been achieved when there was less than 10% variation in the effluent parameters. Therefore, the stable conditions for the reactors can be determined from the removal efficiency graphs for COD, BOD and sulphide (see figures 4.5, 4.6 and 4.9). SBR 1 achieved stable conditions after 30 days of operation, when the organic loading rate was reduced from 0.7 kg COD/m^3/day to 0.35 kg COD/m^3/day. SBR 2 took longer to achieve stable conditions due to the high organic load of 1.5 kg COD/m^3/day that was used in the first 30 days, thus stable conditions were only achieved after 55 days of operation (25 days after the organic loading rate was reduced to 0.183 kg COD/m^3/day).

COD and BOD removal efficiency of 40% and 72% respectively, were achieved for the highest organic loading rate of 1.5 kg COD/m^3/day in SBR 2. The lower organic loading rates of 0.35 kg COD/m^3/day and 0.183 kg COD/m^3/day achieved COD removal efficiencies of 96% and 95% respectively and BOD removal efficiencies of 98% and 95% respectively. The higher organic loading rate in SBR 1 achieved COD and BOD removal efficiencies of 94% and 82% respectively.

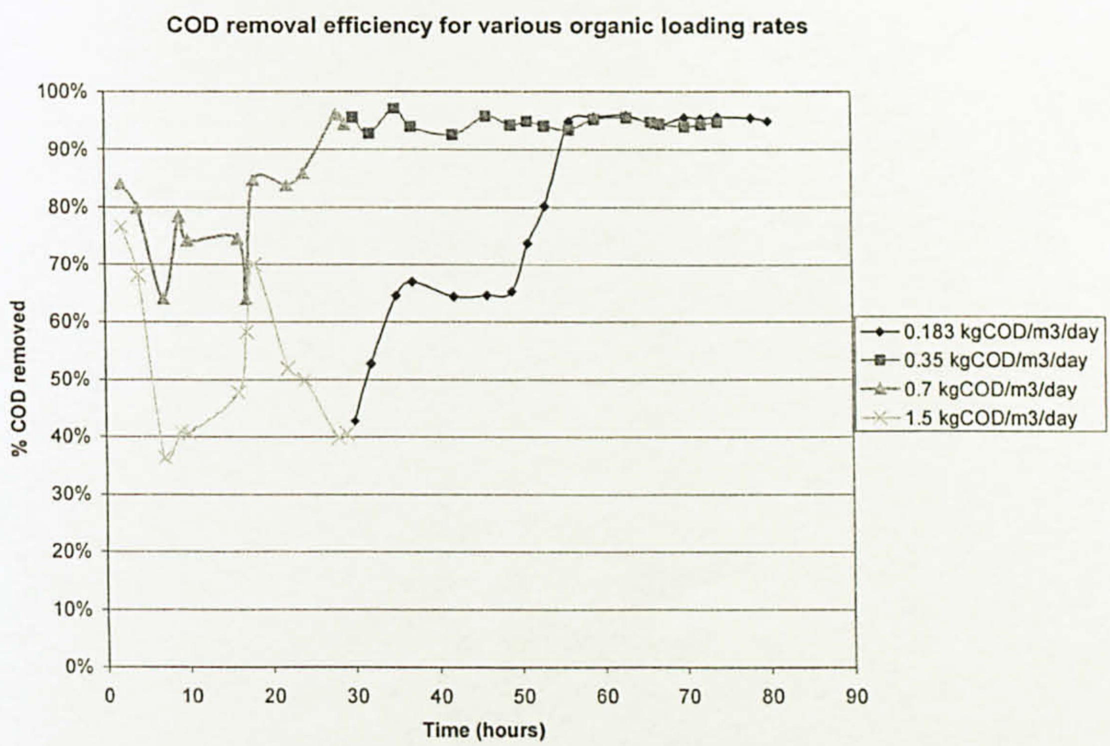


Figure 4.5: COD removal efficiency at varying organic loading rates

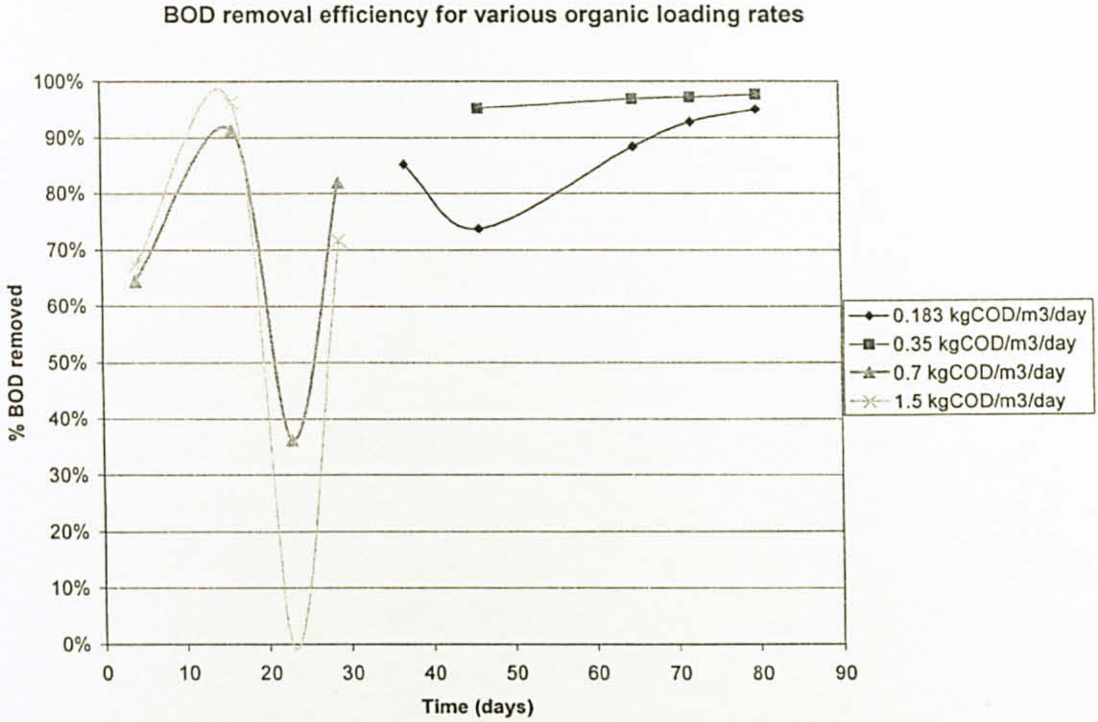


Figure 4.6: BOD removal efficiency at varying organic loading rates

The influent feed for both reactors had a sulphide concentration 2.14 mg/L after a 1:10 dilution. The dilution was done in order to prevent shock loading due to the high COD concentration present in the PDH wastewater (refer to table 3.1). The sulphide concentration was increased to 12 mg/L on day 70 by feeding a 10 mg/L sodium sulphide solution in both reactors. Only 54% sulphide was removed for the highest organic loading rate of 1.5 kgCOD/m^3/day. Sulphide removal of 82% and 97% was achieved for 0.7 kgCOD/m^3/day and 0.35 kgCOD/m^3/day respectively. The highest sulphide removal efficiency 98% was achieved with the lowest organic loading rate of 0.183 kgCOD/m^3/day during stable conditions, as shown in figure 4.1.9. The increased sulphide concentration was not significant to inhibit the SBR performance. The sulphide concentration was reduced to less than 0.5 mg/L within 28 days in SBR 1 and 53 days in SBR 2 (23 days after the organic loading rate was reduced from 1.5 kgCOD/m^3/day to 0.183 kgCOD/m^3/day), thus meeting the EQA limit for sulphide.

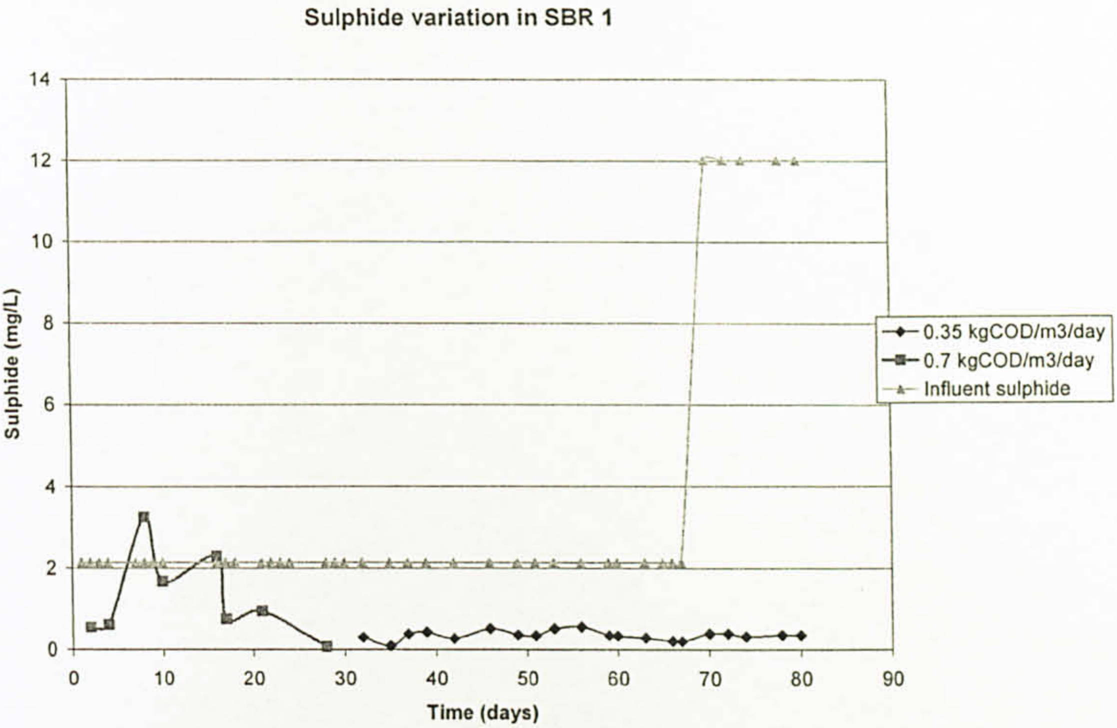


Figure 4.7: **Sulphide variation in SBR 1 at varying organic loading rates**

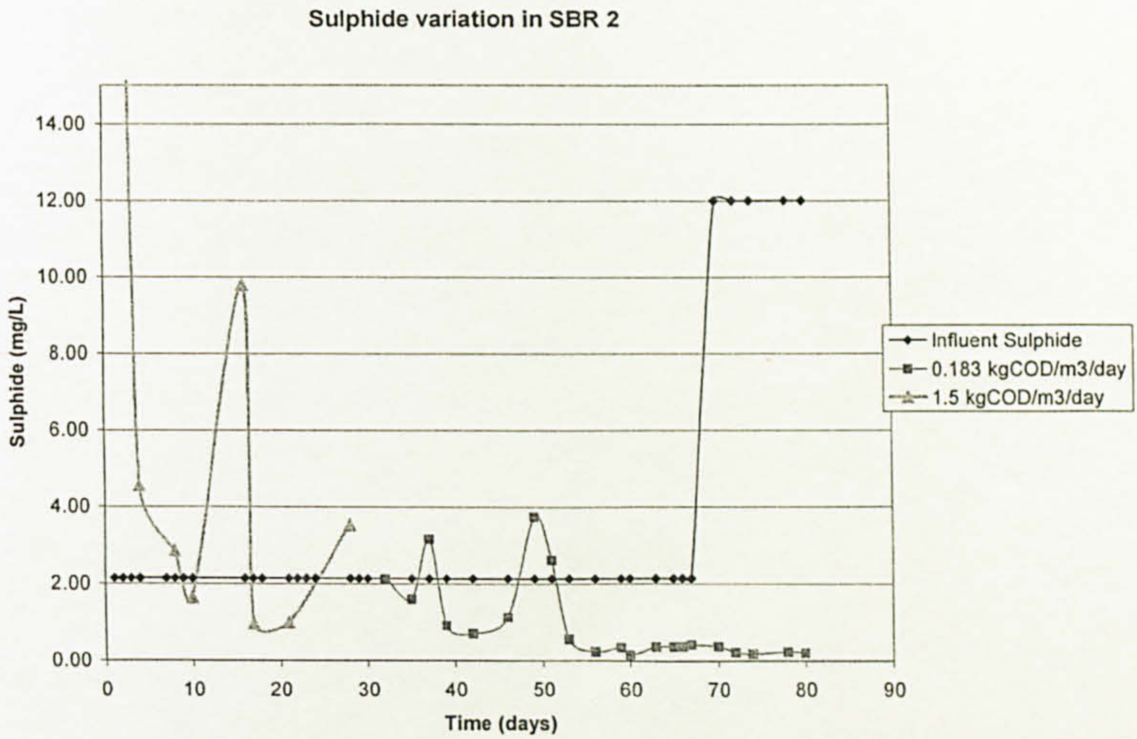


Figure 4.8: **Sulphide variation in SBR 2 at varying organic loading rates**

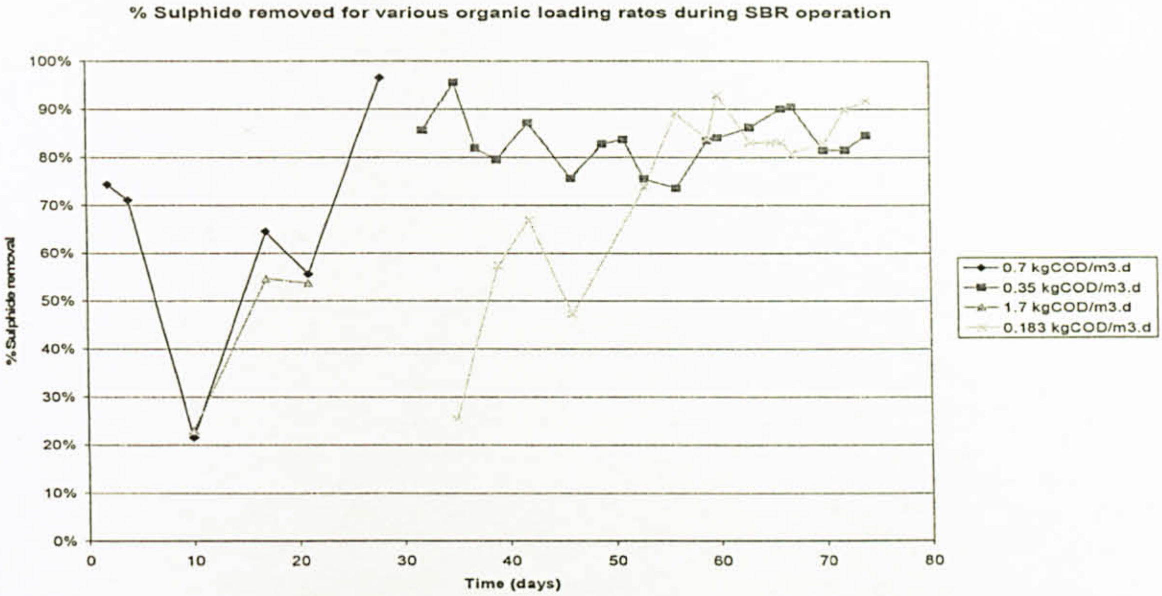
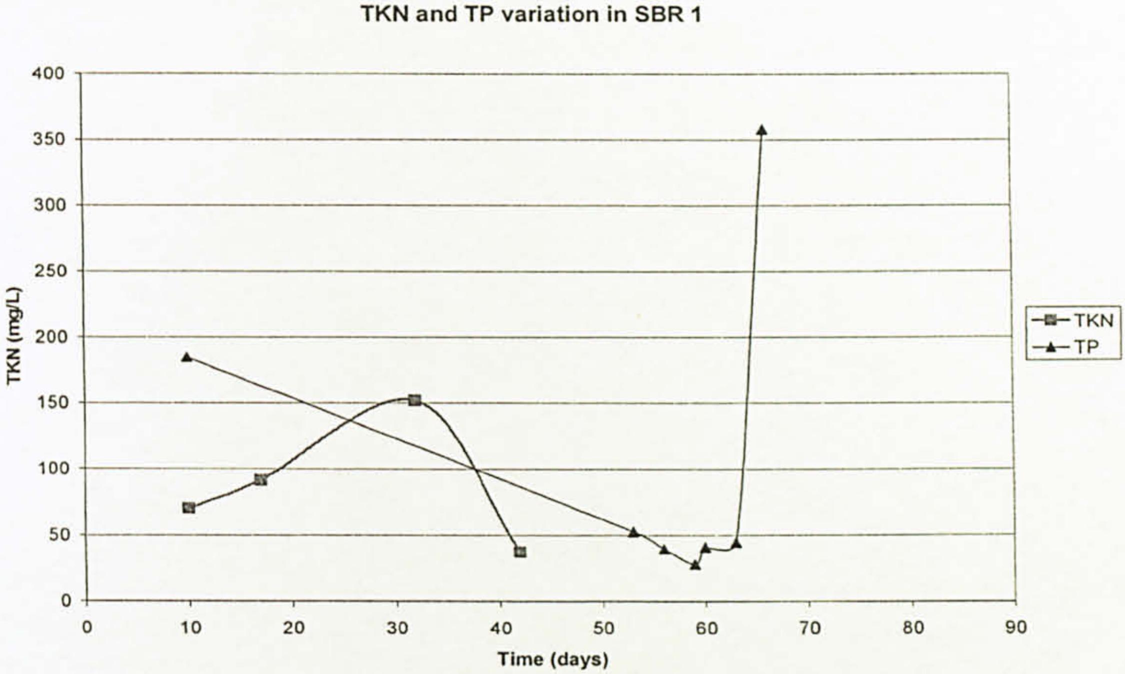


Figure 4.9: Sulphide removal efficiency for varying organic loading rates

Long SRTs normally stimulate endogenous respiration, the result of which would be the release of nitrogen and phosphorus (Klimiuk and Kulikowska, 2005). Total Kjedhal Nitrogen is the sum of ammonia nitrogen and organic nitrogen, where 60% of the TKN value is ammonia nitrogen.

The TKN measured in the effluent of SBR 1, as shown in figure 4.10, increased within the first 30 days, before stable conditions were reached, after which it decreased. Thus indicating that the organic nitrogen was being utilized by the microorganisms to degrade the organic matter and the nitrifying bacteria (nitrosomonas and nitrobacter) had sufficient time to grow in the reactor and thus oxidize ammonia nitrogen to nitrate. Phosphorus is also an important nutrient required by the microorganisms to degrade organic matter. The total phosphorus concentrations decreased in SBR 1 as it was utilized by the microorganisms during the reaction phase, the concentration increased after 63 days of operation as some endogenous respiration may have occurred during this period, releasing some phosphorus.

Figure 4.11 shows the variation in TKN and TP concentrations in SBR 2. The TKN concentration decreased for the first 30 days, after which it increased due to the change in the organic loading rate which may have caused endogenous respiration to occur. Once stable conditions were achieved (55 days), the concentration decreased again as the microorganisms acclimatized to the new organic load. Similarly the total phosphorus concentration decreased during steady conditions.



<u>Figure 4.10</u>: TKN and TP variation in SBR 1 during operation

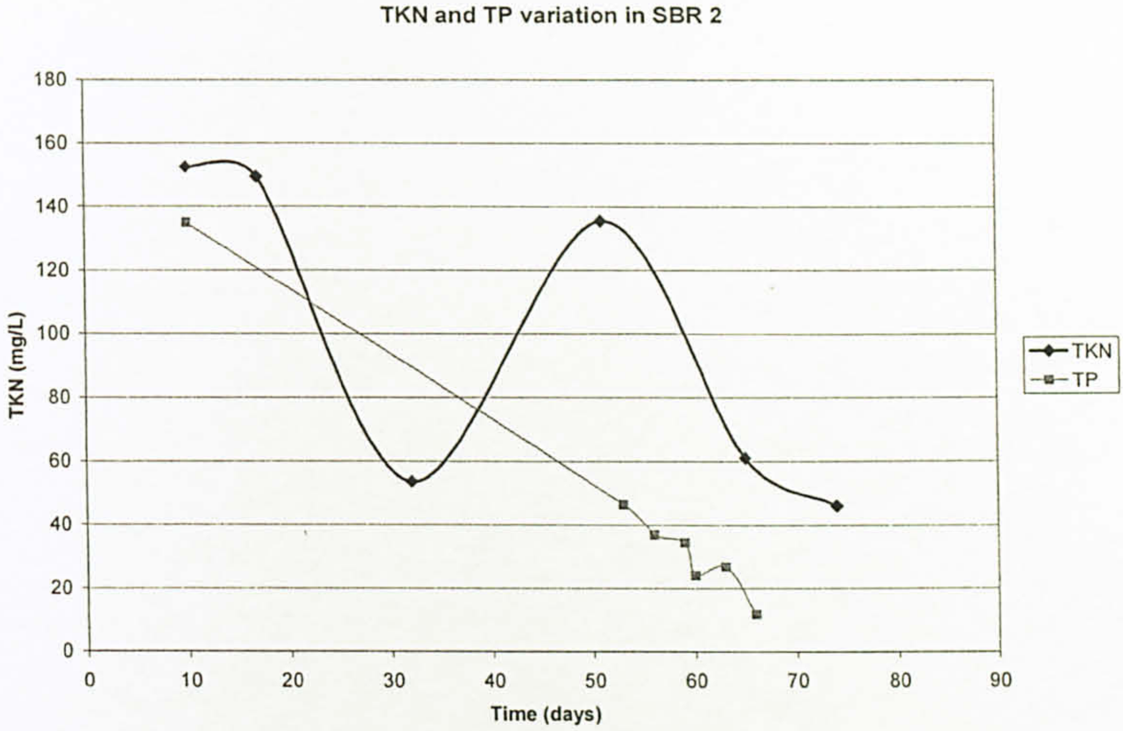


Figure 4.11: TKN and TP variation in SBR 2 during operation

The reactors were fed with 910 mg/L of sulphate (after 1:10 dilution). Aerobic conditions facilitate sulphide oxidation to sulphate, however sulphates cannot be reduced to sulphides in an aerobic system, unless in an anoxic/aerobic environment. As a result the sulphate concentration is still relatively high in both reactors. There is no significant difference between the four organic loading rates in terms of sulphate removal (see Figures 4.12 and 4.13).

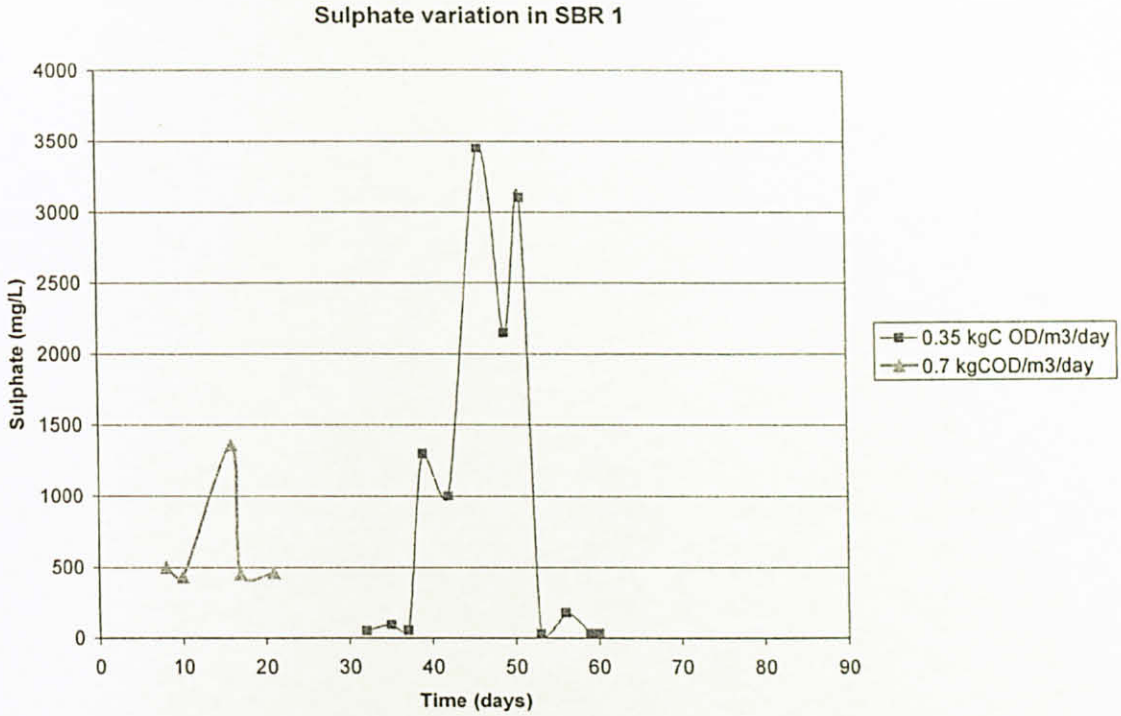


Figure 4.12: Sulphate variation in SBR 1 during operation

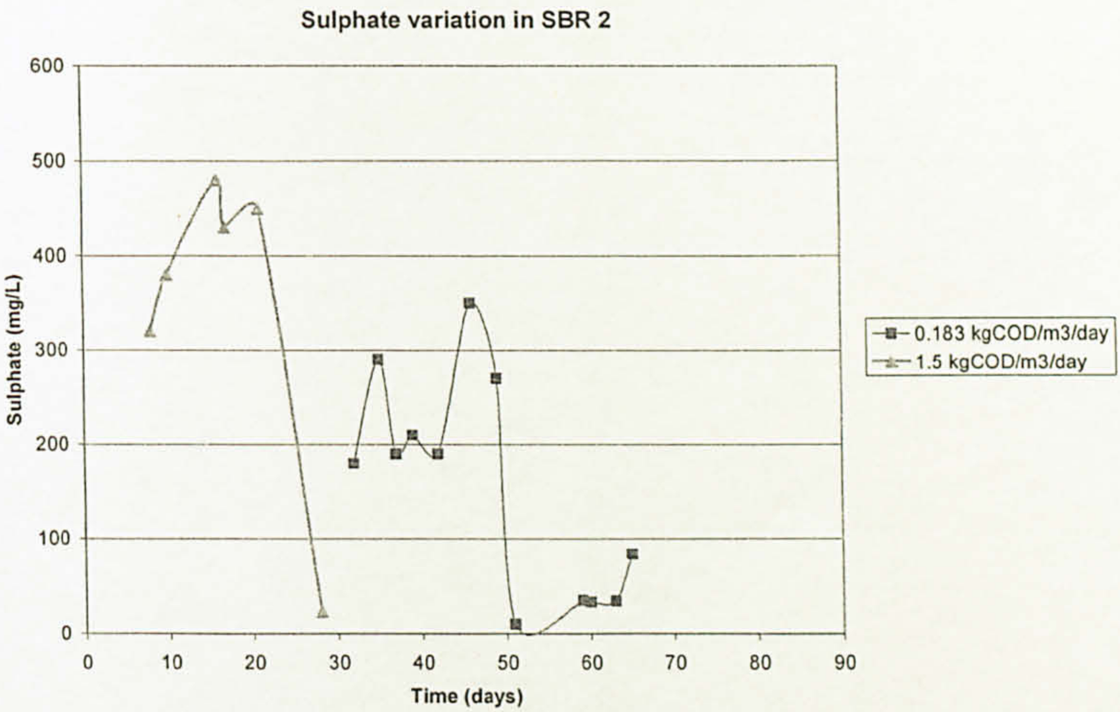


Figure 4.13: Sulphate variation in SBR 2 during operation

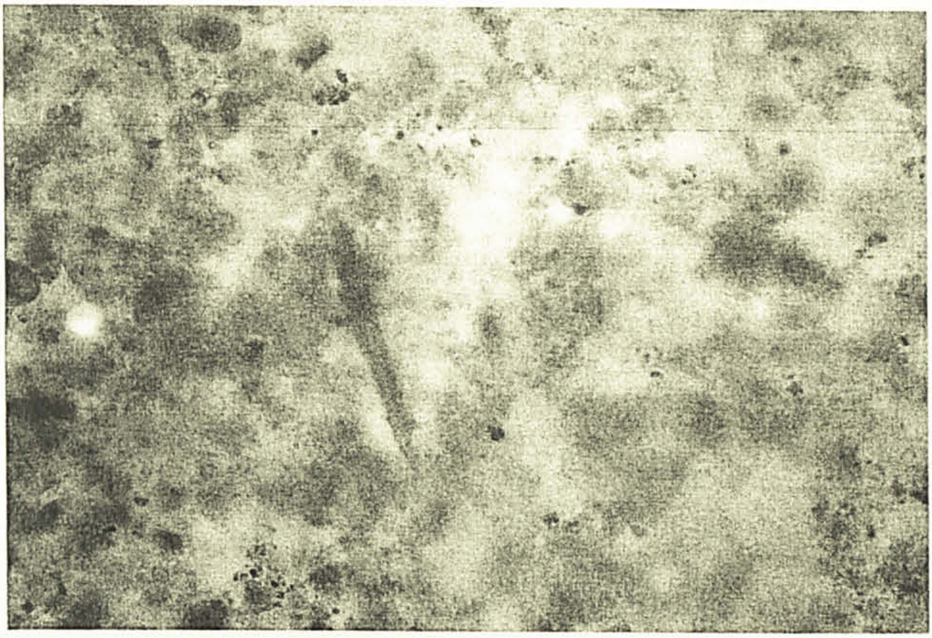


Figure 4.14: Scanning Electron Micrograph (SEM) of suspended biofilm in SBR 2

The sulphate removal in SBR 2 may be attributed to the prevailing anoxic zone in the internal layers of the suspended biofilm as shown in Figure 4.14 and the induced anoxic conditions during the SBR operation. Therefore, it can be assumed that the biofilm floc in SBR 2 are much larger than in SBR 1, thus explaining why the sulphate concentrations in SBR 2 are much lower than SBR 1 and the sulphide concentrations much higher.

The results indicate that a higher organic loading rate and subsequently shorter Hydraulic Retention Time (HRT) inhibit SBR performance. Table 4.1 is a summary of the SBR performance at the various organic loading rates. The best SBR performance is achieved at lower organic loading rates, where 0.35 kgCOD/m^3/day and 0.183 kgCOD/m^3/day yielded the best results.

Table 4.1: Summary of SBR performance at various organic loading rates

Organic loading rate ($kgCOD/m^3/day$)	% COD removed	% BOD removed	% Sulphide removed
1.5	40	72	54
0.7	94	82	82
0.35	96	98	97
0.183	95	95	98

It is evident from the data, that an increase in the organic load inhibits the SBR performance; this is due to the high concentration of toxic and inhibitory substances present in the PDH wastewater.

4.2 Process monitoring

In order to understand the ongoing biochemical process during SBR operation, the process was monitored by determining the VSS and TSS concentrations as well as sludge volume and F/M ratio.

The food to microorganisms ratio (F/M) is commonly used to characterize process designs. The optimum F/M ratio for a good system is typically between 0.4 and 0.5. The variation of F/M ratio during SBR operation is presented in Table 4.2. The F/M ratio was 0.29 during steady state operation for 0.7 $kgCOD/m^3/day$. The F/M ratios for 0.35 $kgCOD/m^3/day$ and 0.183 $kgCOD/m^3/day$ were 0.15 and 0.08 respectively. The F/M ratio for 1.5 $kgCOD/m^3/day$ was quite high at 0.86, indicating process inhibition due to high substrate loading containing toxic substances.

Table 4.2: Hydraulic Retention Time and F/M ratio for various organic loading rates

Organic loading rate ($kgCOD/m^3/day$)	HRT (days)	F/M ratio (as COD)
1.5	5	0.86
0.7	10	0.28
0.35	20	0.15
0.183	40	0.08

The sludge volume is important in assessing the stability of the sludge in an aerobic suspended growth system (Rao et al., 2005). The sludge volume decreased from 2 L to 0.5 L in SBR 1 and from 2 L to 1 L in SBR 2 within the first three days of SBR operation. This was due to the toxic nature of the influent wastewater, despite the 1:10 dilution. However, after stable conditions had been achieved, the sludge volume remained constant, after more sludge was added to both reactors to increase the volume back to the original 2 L.

The target VSS concentration to be maintained in both reactors was 4 000 mg/L. The VSS concentration in SBR 1 was in the range of 3862-5108 mg/L and 4400-5265 mg/L in SBR 2. Figures 4.15 and 4.16 show an initial decrease in the VSS and TSS during the first 15 days of SBR operation, this is due to the toxicity of the wastewater which killed some microorganisms initially. The VSS and TSS concentrations began to increase after 15 days as the biomass was slowly acclimatizing to the new substrate, thus they were able to multiply. Since the organic loading rate was reduced from 0.7 $kgCOD/m^3/day$ to 0.35 $kgCOD/m^3/day$ in SBR 1 and from 1.5 $kgCOD/m^3/day$ to 0.183 $kgCOD/m^3/day$ in SBR 2, it meant there was less food available for the microorganisms, therefore some endogenous respiration occurred. The concentrations then increase again once the microorganisms have acclimatized.

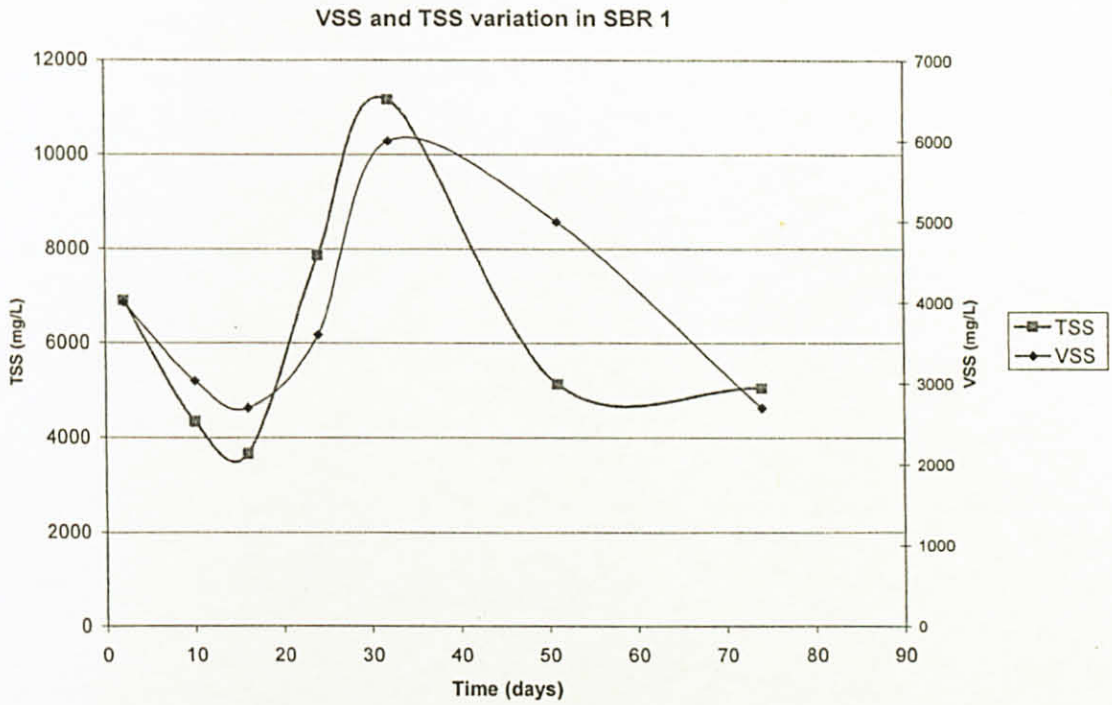


Figure 4.15: VSS and TSS variation in SBR 1 during operation

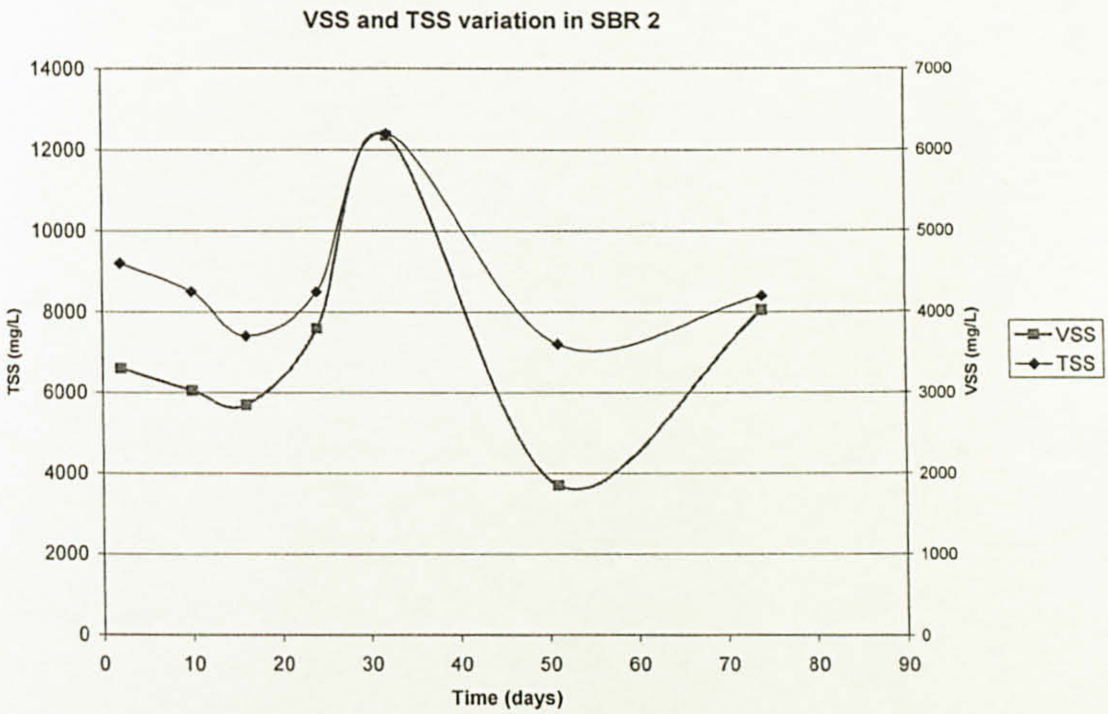


Figure 4.16: VSS and TSS variation in SBR 2 during operation

Biomass consists mainly of organic material; therefore, an increase in biomass can be measured by VSS or by particulate COD (total COD minus soluble COD). At stable conditions, a test was conducted where a sample of 0.5 mL of suspended biomass was collected hourly from each reactor for the first 12 hours of the reaction phase. Samples of supernatant from each reactor were also collected hourly after 5 minutes of settling.

The SCOD and VSS (by particulate COD) for each sample were measured using the reactor digestion method. In biological treatment process, cell growth (biomass production) occurs concurrently with the oxidation of organic or inorganic compounds. Figures 4.17 and 4.18 show this correlation, when the COD concentration increases the VSS concentration decreases and conversely when the COD concentration decreases so the VSS concentration increases. Therefore indicating new cells are produced when the organic substrate (COD) is utilized.

Biomass yield (Y) is typically defined as a ratio of the amount of biomass produced to the amount of substrate consumed;

$$Y = \frac{biomass \quad produced\,(g)}{substrate \quad utilized\,(g)}$$

There is a 2 hour lag phase in SBR 1 as shown in Figure 4.17, even after 8 hours the substrate has not been completely depleted as the VSS continues to increase. SBR 2 has a lower organic loading rate than SBR 1, meaning less organic substrate is available for the biomass. Figure 4.2.4 indicates an exponential decline in VSS concentration as the substrate appears to be depleted after 5 hours, commencing the death phase.

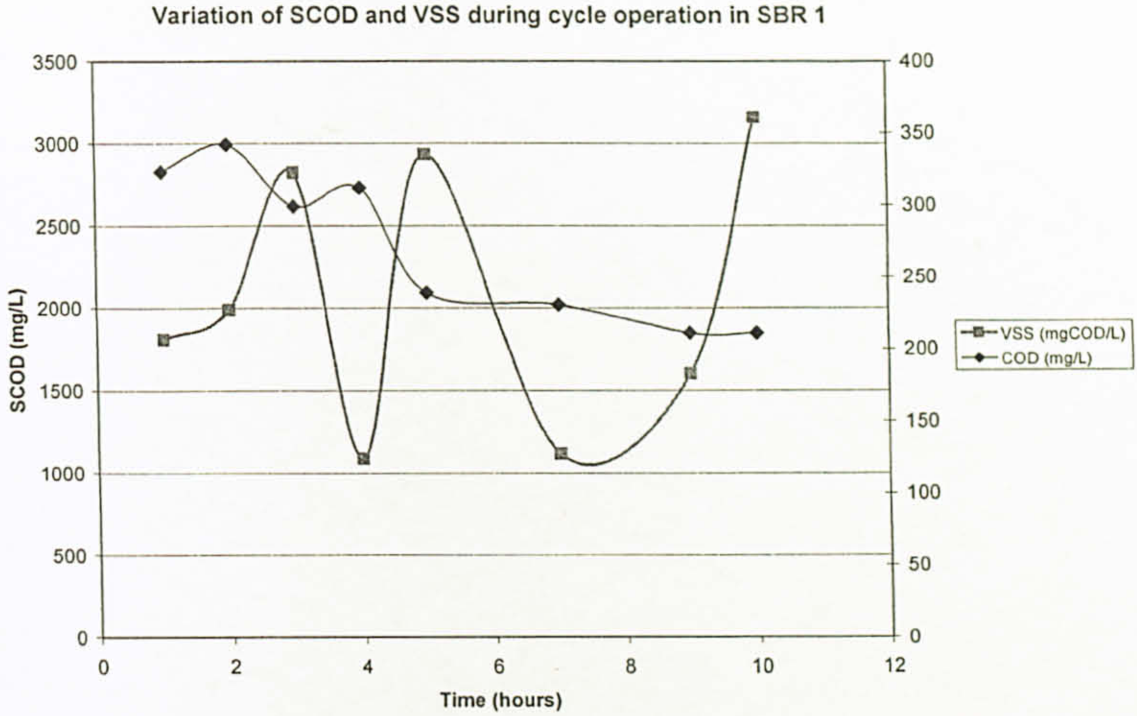


Figure 4.17: VSS and TSS variation in SBR 2 during reaction phase

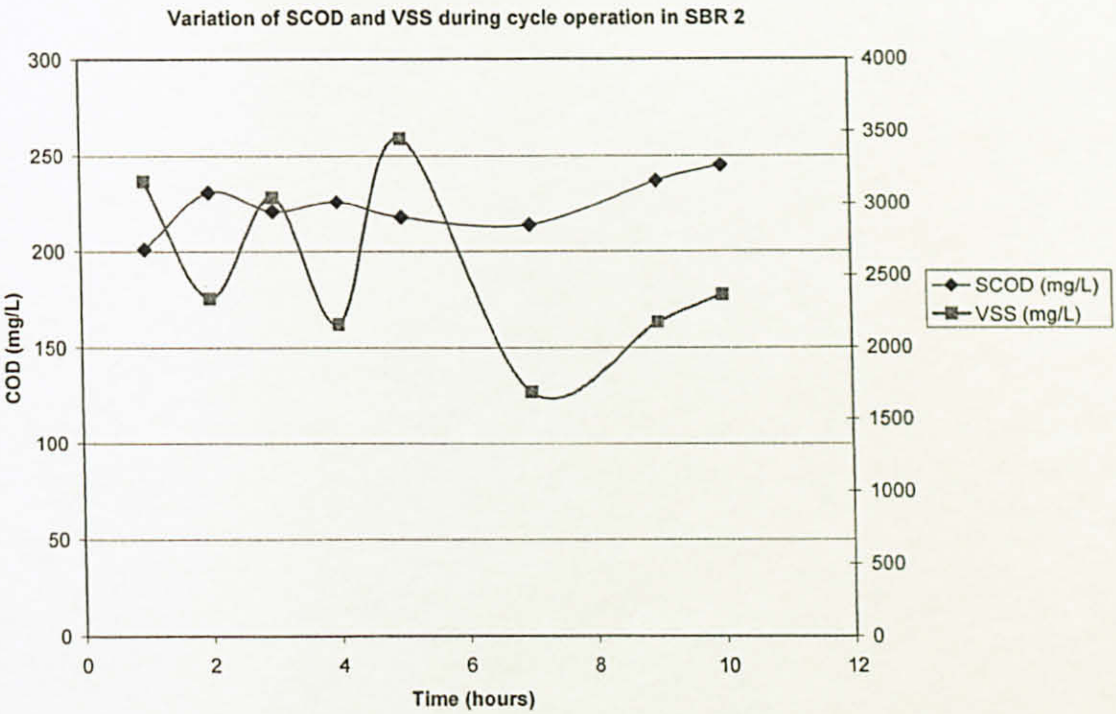


Figure 4.18: VSS and TSS variation in SBR 2 during reaction phase

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The SBR system was successful in treating the PDH wastewater. The performance of the SBR is dependant on the organic loading rate and subsequent HRT. A high organic loading rate inhibited the SBR performance (1.7 $kgCOD/m^3/day$). There is not much difference in the SBR efficiency for the lower organic loading rate of 0.35 $kgCOD/m^3/day$ and 0.183 $kgCOD/m^3/day$, however the former is preferred as it would be less costly to operate. A longer HRT seemed to improve the SBR performance. A high organic loading rate also required a longer acclimatization time; 55 days in SBR 2 compared to 30 days in SBR 1. Therefore, the optimum operating conditions for the SBR would be using a 0.35 $kgCOD/m^3/day$ organic loading rate with a subsequent HRT of 20 days and a 24 hour cycle period, where COD, BOD and sulphide removal efficiencies of up to 96%, 98% and 97% respectively, can be achieved.

It is recommended for future research that the sulphide concentration be increased significantly to determine its effect on the SBR performance. A longer settling period should be used in the cycle period in order to further reduce the BOD and COD concentrations to meet the EQA limits before the effluent is discharged into the river. In order to obtain a deeper understanding of SBR operation, it is recommended that SBR kinetics be explored and investigated in more detail. This will provide a clear indication of which parameters have the most significant influence SBR performance. Heavy metals concentrations should be measured and monitored.

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APPENDIX A1

APPENDIX A

THIRD SCHEDULE

ENVIRONMENTAL QUALITY ACT 1974

ENVIRONMENTAL QUALITY (SEWAGE AND INDUSTRIAL EFFLUENTS) REGULATIONS 1979

(REGULATIONS 8(1), 8(2), 8(3))

PARAMETER LIMITS OF EFFLUENTS OF STANDARDS A AND B

Parameter		Unit	Standard	
			A	B
(i)	Temperature	°C	40	40
(ii)	pH value	-	6.0 - 9.0	5.5 - 9.0
(iii)	BOD at 20°C	mg/ l	20	50
(iv)	COD	mg/ l	50	100
(v)	Suspended Solids	mg/ l	50	100
(vi)	Mercury	mg/ l	0.005	0.05
(vii)	Cadmium	mg/ l	0.01	0.02
(viii)	Chromium, Hexavalent	mg/ l	0.05	0.05
(ix)	Arsenic	mg/ l	0.05	0.10
(x)	Cyanide	mg/ l	0.05	0.10
(xi)	Lead	mg/ l	0.10	0.5
(xii)	Chromium Trivalent	mg/ l	0.20	1.0
(xiii)	Copper	mg/ l	0.20	1.0
(xiv)	Manganese	mg/ l	0.20	1.0
(xv)	Nickel	mg/ l	0.20	1.0
(xvi)	Tin	mg/ l	0.20	1.0
(xvii)	Zinc	mg/ l	2.0	2.0
(xviii)	Boron	mg/ l	1.0	4.0
(xix)	Iron (Fe)	mg/ l	1.0	5.0
(xx)	Phenol	mg/ l	0.001	1.0
(xxi)	Free Chlorine	mg/ l	1.0	2.0
(xxii)	Sulphide	mg/ l	0.50	0.50
(xxiii)	Oil and Grease	mg/ l	Not Detectable	10.0

APPENDIX A2

MONITORED PARAMETERS IN SBR NO. 1															
Date	Days	pH	BOD (mg/L)	COD (mg/L)	Sulphide (mg/L)	Sulphate (mg/L)	VSS (mg/L)	TSS (mg/L)	TKN (mg/L)	Total P (mg/L)	Nitrate (mg/L)	% COD removal	% BOD removal	% sulphide removed	% sulphate removed
02/02/2010	1														
03/02/2010	2			1162	0.55		4000	6900				84%		74%	
04/02/2010	3	8.28													
05/02/2010	4	8.8	394	1468	0.62							80%		71%	
08/02/2010	7			2627								64%	64%		
09/02/2010	8	10.87			3.26	500					0.1			-52%	45%
10/02/2010	9			1580								78%			
11/02/2010	10			1890	1.68	430	3033	4333	70	185		74%		21%	53%
17/02/2010	16		97	1865	2.30	1360	2700	3667				74%		-7%	-49%
18/02/2010	17			2623	0.76	450			92			64%	13%	54%	51%
19/02/2010	18			1117								85%			
22/02/2010	21				0.95	460								56%	49%
23/02/2010	22			1185								84%			
24/02/2010	23		706										36%		
25/02/2010	24			1025			3600	7850				86%			
01/03/2010	28			289	0.073							96%		97%	
02/03/2010	29			413								94%			
03/03/2010	30			328								96%			
05/03/2010	32			529	0.307	51	6000	11167	152			93%		86%	94%
08/03/2010	35			214	0.095	94						97%		96%	90%
10/03/2010	37		6	444	0.389	53						94%		82%	94%
12/03/2010	39				0.438	1300							99%	80%	-43%
15/03/2010	42			543	0.275	1000			37.36			93%		87%	-10%
19/03/2010	46		53	315	0.521	3450						96%		76%	-279%
22/03/2010	49			428	0.37	2150						94%	95%	83%	-136%
24/03/2010	51			378	0.35	3100	5000.00	5133.33				95%		84%	-241%
26/03/2010	53			438	0.523	29.9				52.8		94%		75%	
29/03/2010	56			487	0.567	180.9				39.7		93%		74%	
01/04/2010	59			357	0.354	33				26.02		95%		83%	96%
02/04/2010	60				0.341	32.4				41.1				84%	
05/04/2010	63			335	0.295					44.7		95%		86%	
07/04/2010	65		34										97%		
08/04/2010	66			392	0.215					[redacted]		95%		90%	
09/04/2010	67			413	0.205							94%		90%	
12/04/2010	70			448	0.399							94%		81%	
14/04/2010	72		[redacted]	423	0.397							94%		81%	
16/04/2010	74			391	0.33		2700.00	5050				95%		85%	
20/04/2010	78			391	0.366										
22/04/2010	80		[redacted]	328	0.366										

SBR OPERATING PARAMETERS		
Organic loading rate (kg COD/m^3 day)	0.7	0.35
Hydraulic Retention Time (days)	10	20
Required VSS (mg/L)	4000	4000
Reaction time (hours)	23	47

MONITORED PARAMETERS IN SBR NO. 2

Date	Days	pH	BOD (mg/L)	COD (mg/L)	Sulphide (mg/L)	Sulphate (mg/L)	VSS (mg/L)	TSS (mg/L)	TKN (mg/L)	Total P (mg/L)	Nitrate (mg/L)	% COD removal	% BOD removal	% Sulphide removed	% Sulphate removed
02/02/2010	1														
03/02/2010	2			1720	33.8		4600	6600				76%		-1479%	
04/02/2010	3	8.76													
05/02/2010	4	9.26	362	2340	4.55							68%	67%	-113%	
08/02/2010	7			4653								36%			
09/02/2010	8				2.86	320					-1.2			-34%	65%
10/02/2010	9			4330								41%			
11/02/2010	10			4347	1.65	380	4250	6050	152			41%		23%	58%
17/02/2010	16		42	3817	9.80	480	3700	5700				48%	96%	-358%	47%
18/02/2010	17			3060	0.97	430			149			58%		55%	53%
19/02/2010	18			2197								70%			
22/02/2010	21				0.99	450								54%	51%
23/02/2010	22			3517								52%			
24/02/2010	23		1114										-1%		
25/02/2010	24			3663			4250	7600				50%			
01/03/2010	28			4403	3.53	23						40%		-65%	97%
02/03/2010	29			4350								40%			
03/03/2010	30			4187								43%			
05/03/2010	32			3460	2.13	180	6200	12350	54			53%			80%
08/03/2010	35			2590	1.6	290						65%		25%	68%
10/03/2010	37		164	2417	3.16	190						67%	85%	-48%	79%
12/03/2010	39				0.913	210								57%	
15/03/2010	42			2600	0.71	190						64%		67%	
19/03/2010	46		290	2587	1.13	350						65%	74%	47%	
22/03/2010	49			2540	3.74	270						65%		-75%	
24/03/2010	51			1925	2.62	10	3800.00	3700	135.43			74%		-22%	
26/03/2010	53			1450	0.56					46.4		80%		74%	
29/03/2010	56			387	0.234					36.9		95%		89%	
01/04/2010	59			329	0.346	34.66				34.4		95%		84%	
02/04/2010	60				0.151	32.7				24.1				93%	
05/04/2010	63			309	0.364	34.1				26.9		96%		83%	
07/04/2010	65		128		0.364	83.5							88%	83%	
08/04/2010	66			412	0.365					11.8		94%		83%	
09/04/2010	67			431	0.413							94%		81%	
12/04/2010	70			332	0.367							95%		83%	
14/04/2010	72		[redacted]	347	0.217							95%	90%	90%	
16/04/2010	74			325	0.176		4200.00	8050				96%		92%	
20/04/2010	78			340	0.231							95%		89%	
22/04/2010	80		[redacted]	378	0.196							95%	92%	91%	

SBR OPERATING PARAMETERS

Organic loading rate (kg COD/m³·day)	1.5	0.183
Hydraulic Retention Time (days)	10	40
Required VSS (mg/L)	4000	4000
Reaction time (hours)	23	47

Time	hours	SCOD (mg/L)		VSS (mg/L)	
		SBR1	SBR2	SBR 1	SBR2
10:30	1	323	201	1809.6	3156.8
11:30	2	342	231	1988.8	2339.2
12:30	3	299	221	2820.8	3044.8
13:30	4	312	226	1088	2158.4
14:30	5	239	218	2932.8	3452.8
16:30	7	231	214	1116.8	1689.6
18:30	9	211	237	1601.6	2174.4
19:30	10	211	245	3156.8	2366.4

Biomass Yield, Y = $mgVSS / mgbsCOD = 0.4$

COD of biomass = $gCOD / gVSS = 1.42$