

RUBBER MILL WASTEWATER TREATMENT USING SEQUENCE BATCH REACTOR IN AEROBIC CONDITION

By

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FINAL YEAR RESEARCH PROJECT REPORT

Submitted to the Civil engineering Programme in Partial Fulfillment of the Requirements for the Degree Bachelor of Engineering (Hons) (Civil Engineering)

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CERTIFICATION OF APPROVAL

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> > June 2010

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.

Ceasar Bidal Clement Peter

ABSTRACT

A sequencing batch reactor (SBR) has certain advantages over conventional activated sludge processes (ASP) for the treatment of Rubber mill wastewater. The performance of a sequencing batch reactor in treating rubber mill wastewater effluents was investigated with a suspended biomass configuration and operating under aerobic conditions. Two reactors were used in this study with varying organic loading rates (OLR) and Hydraulic retention time (HRT). A total sequence of 24 h (15 min: filling phase: 23 h: reaction phase (aeration with recirculation); 30 min: setting; and 15 min: withdrawal) was employed and studied with various organic loading rates (0.047 kg COD/m³/day and 0.0933 kg COD/m³/day for reactor 1) and (0.1399 kg COD/m³/day and 0.1866 kg COD/m³/day for reactor 2). The SBR performance was assessed by means of Chemical oxygen demand (COD), Biochemical oxygen demand (BOD), Zinc, Nitrogen removal and operational parameters such as pH, sludge volume (SV), suspended solids (SS) and volatile suspended solids (VSS), which were monitored during the reactors operation. The SBR showed relatively more efficient performance in treating the rubber wastewater about 81.24% and 74.81% COD respectively was removed and 91% and 90% BOD respectively was removed. A final zinc concentration of 0.4 mg/L and 0.98 mg/L were achieved in reactor 1 and 2 respectively.

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LIST OF ABBREVIATIONS

COD	Chemical Oxygen demand
BOD	Biochemical Oxygen demand
Zn	Zinc
VSS	Volatile suspended solids
TSS	Total suspended solids
HRT	Hydraulic retention time
OLR	Organic loading rate
MLVSS	Mix liquor Volatile suspended solids
MLSS	Mix liquor Suspended solids

CHAPTER 1

INTRODUCTION

1.1. Background study

Natural rubber is an elastic hydrocarbon polymer which is a yellowish and amorphous material obtained from milky sap or latex of various tropical plants especially the rubber tree (Hevea Brasiliensis). Rubber industry plays a major role as the contributor to many developing countries' economy. Today, Malaysia is the fourth biggest producer of natural rubber in the world after Thailand, Indonesia and India, the fifth-largest rubber consumer and among the world's largest exporters of rubber products (Vijayaraghavan et al., 2007). The production of natural rubber (dry and latex) in Malaysia was approximately 1.12 million tones in 2007 (Malaysian Rubber Board, 2008). The Malaysian rubber-based products manufacturing industry has established itself as a global supplier, specifically for latex-based products such as gloves, catheters and latex threads. Rubber processing industry produces wastewater as a by-product which contains numerous substances such as rubber hydrocarbon, proteins, minerals, non-rubber hydrocarbons, carbohydrates and any chemicals that might have been added (Asia and Akporhonor, 2007). Wastewater from rubber glove particularly, produces high amount of zinc which can cause pollution if discharged straight into the surface water (Shyan, 2008). Recent methods applied for rubber wastewater treatment are anaerobiccum-facultative lagoon system, anaerobic-cum-aerated lagoon system, aerated lagoon and oxidation ditch system (Industrial Processes & The Environment, 1999). However, most glove factories specifically use chemical treatment methods which involve high amount of chemicals, which is costly and need high maintenance.

1.2. Problem Statement

The Conventional rubber wastewater treatment plants usually comprise a series of big anaerobic ponds followed by oxidation ponds. This type of treatment plant requires large area. The EQA regulation limits for COB and BOD of treated latex wastewater according to the third schedule are 400 mg/L and 100 mg/L respectively (EQA 1974 Act 127). The BOD and COD are at times much higher than discharged limits which would pollute the rivers when accidentally or intentionally discharged. The characteristic rotten-egg odor of hydrogen sulfide and the mercaptans from anaerobic ponds annoys the inhabitants who live close to the factory or even many kilometers away from the factory if they were in the wind direction. In order to meet the regulation requirement concerning environmental control, many factories have been investigating a lot on finding a suitable treating system. Currently, some systems are still on the trial and some factories have been closed or fined due to non-compliance with discharge limits.

Malaysian Rubber Board (2008) stated that, there were about 362 active rubber processing factories in Malaysia in 2007, which of course, produced large quantities of high strength wastewater. The environmental quality regulations for natural rubber industry were described under Environmental Quality Act (EQA 1974 Act 127). Environmental Quality (Prescribed Premises) (Raw Natural Rubber) Regulations 1978 describes the parameter limits of effluent discharge from concentrated latex production and its associated products. The effluent discharge limits are presented in Table 1.1.

Parameter	Unit	Parameter Limits (Third Schedule)
Biochemical Oxygen Demand (BOD); 3-day, 30°C	mg/L	100(50*)
Chemical Oxygen Demand (COD)	mg/L	400
Total Solids	mg/L	-
Suspended Solids	mg/L	150(100*)
Ammoniacal-nitrogen	mg/L	300
Total Nitrogen	mg/L	300
рН		6-9

Table 1.1Effluent discharge limits for concentrated latex productswastewater (Environmental Quality Act, 1978)

*This additional limit is the arithmetic mean value determined on the basis of a minimum of four samples taken at least once a week for four weeks consecutively.

The characteristics of wastewater from Masif Latex process plant are shown in Table 1.2. Wastewater produced by a glove factory has passed through leaching process and tanks washing. Leaching process is a process of immersing the latex-coated formers into a bath or spray of water, to wash out excess additives which have been added during compounding and dipping stage, resulting in highly concentrated wastewater. Based on the Table, the effluent contains high organic load (COD and BOD) which would contribute to environmental pollution if discharged directly into surface waters. The effluent also contains high suspended solids which could cause difficulty in disposal. The high concentration of ammonium-nitrogen in the effluent may cause excessive algae growth, thus lead to eutrophication in rivers and streams. Besides, if the water is used for water supply, it will affect the economy and health as nitrate can cause methemoglobinemia in infants. Also, the high ammonia concentration could affect life of aquatic organisms (Asia and Akporhonor, 2007; Rungruang and Babel, 2008).

Moreover, zinc also is found widely in glove factory wastewater as it is used as a catalyst during manufacture and as a heat disperser in the final product (Bhowmick, 1994). Consequently, it will affect the environment as zinc-polluted sludge will be deposited on the banks and increases the acidity of water. It will also affect human health as it can cause stomach cramps, skin irritations, vomiting, nausea and anemia. Thus, an efficient and practical treatment must be applied to the effluent before being discharged to the environment.

Parameter	Value
Phosphorus, Total	1.26 mg/L
Zinc	23 mg/L
Nitrate	117 mg/L
Nitrite	650 mg/L
Nitrogen Ammonia	6.6 mg/L
Sulphate	69 mg/L
Sulphide	530 mirco g/L
TSS	191 mg/L
COD	933 mg/L
рН	6.4
BOD	542 mg/L

Table 1.2 Influent characteristics of the wastewater

1.3. Objective

The objective of carrying out this project is to determine the appropriate parameters i.e. organic loading rate (OLR) and Hydraulic retention time (HRT) for treating rubber mill wastewater using a sequencing batch reactor (SBR) in aerobic condition, so that the supernatant can be disposed off according to the discharge limit specified in the environmental quality regulations for natural rubber industry under Environmental Quality Act (EQA 1974 Act 127) without any danger to human health or unacceptable damage to the natural environment.

1.4. Scope of Study

The nature of this project requires a thorough understanding of environmental engineering, the effect of industrial waste on both human being and the environment. An understanding of the performance of a sequencing batch reactor and the analysis of the wastewater parameters is required. Hence considerable amount of time should be spent on acquiring this knowledge from relevant sources, books, internet, journals etc.

The scope of the study covered the characterization of rubber factory wastewater and monitoring of SBR performance base on pH, COD, BOD, Total Suspended Solid (TSS), turbidity, color, zinc, ammonium-nitrogen, nitrate, and phosphate using Sequence batch reactor in aerobic condition.

CHAPTER 2 LITERATURE REVIEW

This chapter contains a brief review on sequencing Batch reactor (SBR) which covers the operation of the reactor and sequence involved in the process. And an overview of some of the treatment methods used for rubber factory wastewater.

2.1 Sequence Batch reactor

The Sequencing Batch Reactor (SBR) is an activated sludge process designed to operate under non-steady state conditions. An SBR operates in a true batch mode with aeration and sludge settlement both occurring in the same tank. The major differences between SBR and conventional continuous-flow, activated sludge system is that the SBR tank carries out the functions of equalization, aeration and sedimentation in a time sequence rather than in the conventional space sequence of continuous-flow systems. In addition, the SBR system can be designed with the ability to treat a wide range of influent volumes whereas the continuous system is based upon a fixed influent flowrate. Thus, there is a degree of flexibility associated with working in a time rather than in a space sequence.

2.1.1 Operation of the reactor

Normally the process follows the basic steps of; FILL, AERATE, SETTLE, DECANT an IDLE. The actual cycle time will vary with the effluent results desired. If only BOD reduction is desired, a cycle time as 3 hours may be used. If further treatment, to obtain nitrification / denitrification is required, the cycle time can be extended to accommodate the process requirements. The AERATE phase in the SBR system is typically time/level controlled and can be adjusted depending on the required removal efficiency. The AERATE phase is followed by the SETTLING PHASE. The settling represents the quiescent phase during which no aeration or mixing occurs and is also time/level controlled. The last step is the DECANT step representing the discharge of clarified effluent controlled by level in the reactor.

Aeration phase: Depending on capacity

Settling phase: Normally 30 to 60 minutes

Decant phase level within 30 min: Reduction from maximum to minimum

Table 2.1: Cycle period and phase details of reactor during sequence (typical Values)

Phase	Cycle Period	Air supply	Condition
Filling (min)	15	Off	Anoxic
Reaction with recirculation (h)	23	On	Aerobic
Settling (min)	30	Off	Anoxic
Withdrawal (min)	15	Off	Anoxic

2.1.2 Mix fill

During this period, the SBR basin, which contains acclimated microorganisms (activated sludge), is filled and mixed in the absence of aeration. Raw wastewater concentration in the reactor increases due to non-aeration. Oxygen present from the previous cycle in the form of dissolved oxygen and oxidized nitrogen, and from the influent wastewater in the form of nitrates and nitrites is quickly consumed by the heterotrophs in the presence of high substrate concentration. As MIX FILL continues under anoxic conditions, phosphorus-accumulating microorganisms and denitrifying microorganisms compete for substrate until oxidized nitrogen is eliminated. With both oxygen and oxidized nitrogen eliminated, MIX FILL continues under anaerobic conditions.

2.1.3 React fill

During this period, aeration begins while continuing MIX FILL. As an aerobic condition is developed, the phosphorus accumulating microorganisms use intracellular storage products for growth. During aerobic growth, the stored intracellular organics provide energy to take up extracellular phosphorus and store it as intracellular phosphorus. The microorganisms take up three to four times as much phosphorus than that taken up for growth in the Conventional Activated Sludge Extended Aeration Process. At the end of this phase, inflow is discontinued.

2.1.4 React

During REACT, wastewater flow is diverted to the other SBR reactors in multiple tank configurations while aeration and mixing continues. Reactions for substrate removal initiated during FILL are completed during REACT. Aerobic autotrophs and heterotrophs use residual substrate so that after SETTLE, a treated supernatant liquid exists. The treatment is controlled by air, either on or off, to produce anaerobic, anoxic or aerobic conditions. Controlling the time of mixing and/or aeration produces the degree of treatment required. The on/off cycling of air and mixers provides nitrification, denitrification and phosphorus removal. The REACT period is especially important in handling industrial and other hard-to-treat wastewaters.

2.1.5 Settle

After REACT, mixing and aeration are terminated and the Mixed Liquor Suspended Solids are allowed to SETTLE under perfect quiescent conditions. It is important to ensure that the SETTLE period does not extend beyond the point when anaerobic conditions develop, or phosphorus will be released back into the solution.

2.1.6 Decant and idle

The purpose of the DECANT sequence is to remove treated clarified effluent from the reactor without drawing floating scum or disturbing the settled sludge blanket. Excess waste activated sludge (WAS) is also removed from the SBR during the DECANT phase. Phosphorus incorporated into the sludge is removed from the system with the waste activated sludge. In a multiple tank SBR facility, IDLE time may be possible awaiting the next batch of influent. The IDLE period occurs when actual flows are less than design flows. Adequate IDLE time should be designed into the sequence when phosphorus removal is required since it will provide added flexibility in the event that a longer period is required for any of the above phases.

2.2 Overview of Rubber Wastewater Treatment Methods

Various studies have been conducted to treat wastewater from rubber factory. Thonglimp et al. (2005) studied the effect of F/M ratio, HRT, sulfate and calcium concentration on the removal of BOD and COD on the treatment of industrial latex wastewater by activated sludge system. The reactor volume was 7 Liters. The various values of these studied parameters are shown in Table 2.2.

Table 2.2: Effect of F/M ratio, HRT, sulfate and calcium concentration on the BOD5 and COD removal efficiencies

F/M,day ⁻¹	0.2, 0.3, 0.4, 0.5, 0.6
HRT, hr	4,6,8,10
Sulfate, mg/l	1688, 2000, 3000, 5000, 6500

Effect of F/M ratio:

Five reactors with different F/M ratio as shown in Table 2.2 were parallel operated at the same HRT of 4 hrs, sulfate and calcium concentration of 1,688 and 888 mg/l respectively. The F/M ratio that gave highest removal efficiency at steady state was recorded.

The results from F/M ratio study showed that at the organic loading rate (OLR) of 1.18 kg BOD5/m3.d and HRT of 4 hours the suitable F/M was 0.4 day⁻¹ and the BOD₅ and COD removal efficiencies were highest at 92.2 and 57.5 % respectively.

Effect of HRT:

Three reactors were operated in parallel at the HRT of 6, 8 and 10 days respectively. Each reactor was operated by following the same procedure and also the same sulfate and calcium concentration 1,688 and 888 mg/l respectively. The HRT that gave the highest removal efficiency at steady state was also recorded.

In the HRT study, the HRT was varied from 6, 8 and 10 hours which corresponded to the OLR of 1.15, 1.28, and 1.25 kg BOD_5/m^3d . It was found from the experiment that the removal efficiency increased with HRT. The BOD_5 and COD removal efficiency for various HRT and F/M are shown in Fig.2.1.



Fig.2.1. Effect of HRT on removal efficiency. (Source: Thonglimp et al. 2005)

Effect of sulfate and calcium concentration:

The sulfate concentration of 2,000, 3,000, 4,000 and 6,500 mg/l and the calcium concentration of 1,000, 2,000, 3,000, 4,000 and 6,000 mg/l were parallel studied in four and five reactors respectively with the selected F/M ratio and HRT value from 0.2, 0.3, 0.4, 0.5, 0.6 And 4, 6, 8, 10 hr

The effect of sulfate and calcium concentration was studied at the F/M ratio of 0.4 day⁻¹ and HRT of 15 hours.

The conclusion from SBR study is as follows:

- The experiments were performed with organic loading rate (OLR) varied from 0.9-1.28 kg BOD₅/m³ d.
- 2. The suitable F/M ratio, HRT, sulfate and calcium concentration were 0.4 day⁻¹, 12 hours, 1,688 mg/l and 888 mg/l respectively gave the BOD₅ and COD removal efficiency of 98.6 and 89.3 % respectively. The average effluent BOD₅ value from 9 steady cycles was 7.24 mg/l. It was indicated that this treatment system was suitable for latex wastewater.
- Extension in the Hydraulic retention time (HRT) from 12 to 24 hours didn't have any significance in the BOD₅ removal efficiency but the COD removal efficiency increased from 89.3 % to 92.8 %.
- 4. The sulfate concentration has a lot of effect on BOD₅ and COD removal efficiency. When the sulfate concentration was 6,500 mg/l, the BOD₅ and COD removal efficiency were decreased to 74.9 and 52.1 % respectively.

A study on Treatment of complex chemical wastewater in a sequencing batch reactor (SBR) with an aerobic suspended growth configuration was conducted by Mohan et al. (2003).

SBR was operated in sequencing batch mode with a total 24 h cycle period with an organic loading rate of 0.8 kg COD/m³/day to assess the suitability of the reactor for

treating the complex chemical wastewater under study. Initially after the start up of the reactor (15 days), the reactor was operated with an organic loading rate of 0.8 kg COD/ m^3 /day and the reactor performance was assessed by monitoring carbon removal (COD and BOD) during the sequence (cycle) operation and also throughout the reactor operation.

The variation of COD and BOD removal with the function of the cycle period is depicted in Fig.2.2. Sixty four percent COD removal was observed at an organic loading rate of 0.8 kg COD/ m^3 /day. The COD removal rate was slow (23%) during the initial phase of sequence operation (up to 10 h). With an increase of sequence time a relatively rapid removal was noticed after 10 h and approached 64% at the end of the reaction phase (23.3 h). The initial low COD removal may be due to the relatively high concentration gradient of the substrate (Mohan et al. 2003). With an increase in sequence time, the native suspended biofilm might have become acclimatized to the new substrate (system) conditions facilitating rapid removal of the organic substrate through mineralization.



Fig. 2.2: COD and BOD variation during SBR cycle operation. (Source: Mohan et al. 2003).

The BOD profile during the sequence operation (reaction phase) showed comparably the same pattern as the COD profile. BOD removal of 69% was observed after the reactor attained stability. It can be concluded from the reactor performance data obtained that SBR showed relatively better performance with respect to COD removal when compared to the conventional ASP system (Mohan et al., 2003). The SBR was operated at various organic loading rates (0.8 kg COD/ m^3 /day; 1.7 kg COD/ m^3 /day; and 3.5 kg COD/ m^3 /day).

With continued operation, the reactor showed enhanced performance with respect to COD and BOD removal and attained stable conditions within 3 days after feeding and remained more or less constant thereafter. About 66% of COD removal and 92% of BOD removal was observed during stabilized operation of the reactor. On day 21 after of startup, the reactor was fed with an organic loading rate of 1.7 kg COD/m3/day. Immediately after increase in the organic loading rate, the reactor showed an increase in the outlet COD and BOD levels and approached 47% COD removal and 72% BOD removal within 4 days. On day 28 after startup, the reactor was fed at an organic loading rate of 3.5 kg COD/ m³/day and reactor had a performance with 35% BOD removal and 57% COD removal. Consolidated data of SBR performance at various organic loading rates are presented in Table 2.3.

Organic loading rate (kg COD/m ³ /day)	Percent COD removal	Percent BOD removal	Time to achieve stable performance (days)	Percent sulphate removal	F/M ratio (as BOD) range
0.8	66.4	92.2	4	7.8	0.24-0.29
1.7	47.1	72.7	5	8.3	0.44-0.38
3.5	25.4	57.0	7	8.8	0.94-1.10

Table 2.3: Performance of SBR at various organic loading rates (Mohan et al., 2003)

It is evident from the data, that with increase in organic load, the COD removal rate was reduced. COD removal of 47% was achieved at 1.7 kg COD/m3/day. On increasing the organic loading rate to 3.5 kg COD/ m^3 /day, the COD and BOD removal rates were inhibited markedly. To achieve stable performance (with respect to carbon removal), the reactor required 4 days at 0.8 kg COD/ m^3 /day and 5 days for 1.7 kg COD/ m^3 /day. About 7 days were required to achieve stable performance at an organic loading rate of 3.5 kg COD/ m^3 / day. Sulphate reduction of about 8% was recorded at all the studied organic loading rates. The relatively poor performance of the SBR at higher organic load can be attributed to the presence of high substrate gradients with relatively high concentration of the toxic and inhibitory substances in the wastewater (Mohan et al., 2003).

CHAPTER 3

MATERIALS AND METHODS

3.1 Chemicals and Reagents

Chemicals and reagents that would be used in the study are presented in Table 3.1 below:-

 Table 3.1
 List of chemicals and reagents

Table 3.1 List of ch Chemical/Reagent	Purpose of Use
Distilled water	Solution preparation
Chromic acid	COD test
Mercuric sulfate	
Ferroin indicator	
Pottasium dichromate solution	
Sulfuric acid solution	Alkalinity test
	COD test
	 pH adjustment
Sodium hydroxide solution	pH adjustment
	Total Phosphorus test
Sodium bicarbonate solution	For bicarbonate alkalinity
ZincoVer 5 Reagent Powder Pillow	Zinc test
 Cyclohexanone 	2 Zine test
Mineral stabilizer	Ammonium-nitrogen test
	• Annionium-introgen test
Polyvinyl Alcohol Dispersing	
Agents	
Nessler reagent	
• NitraVer® 5 Nitrate Reagent	Nitrate test
Powder Pillow	
PhosVer 3 Powder Pillow	Total Phosphorus test
Acid Hydrolyzable Test Vial	
Potassium Persulfate Powder Pillow	

3.2 Tools and Equipment

Tools and equipment that will be used in this study are represented in Table 3.2:-Table 3.2 List of tools and equipment

Table 3.2 List of tools and e	
Tools/Equipment	Purpose of Use
Heating block	• COD
COD Vials	
• BOD bottle, volume 300mL	• BOD
• BOD cap	
 DO probe equipped with stirring mechanism 	
• pH meter	• pH
	Alkalinity
• Turbidimeter	Turbidity
• Spectrophotometer	Ammonium-Nitrogen
• Sample cells	Nitrate
	 Phosphorus
	• COD
• Filter paper Whatman GF/C (47mm)	 TSS test
• Drying Oven (105°C) and (550 °C)	VSS
Dessicator unit	
• Filter holder	
• Filtering flask	
• Tweezers	
• W8 Armfield parallel anaerobic digester unit	Anaerobic treatment
(UASB)	
Single channel Masterflex® Pump	
• Glassware	Wastewater
	characterization
	Anaerobic treatment

3.3 Research Methodology



Figure 3.1: Experimental methodology

3.3.1 Seed Sludge Preparation

The seed sludge with mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS), was taken from the Sewage Treatment Plant (STP) of Universiti Teknologi PETRONAS (UTP), Perak and was grown in the lab for a period of 3 months till a thick sludge with a concentration of 9600 mg/L was achieved.

3.3.2 Sample collection

The Wastewater sample was obtained from Masif rubber glove factory, Perak which had passed through leaching process and tanks washing. The sample taken is preserved in a cold room, but above freezing point in order to prevent the wastewater from undergoing biodegradation due to microbial action.

3.3.3 Wastewater characterization

Tests conducted to determine the characteristics of the sample include pH, COD, BOD₅, and TSS, alkalinity, ammonium-nitrogen, phosphate, zinc, turbidity and color (Appendix 3). Analysis is conducted to determine the applicability of aerobic treatment to rubber factory wastewater.

3.3.3.1 pH

pH value of the influent and effluent were monitored throughout the process.

3.3.3.2 Chemical Oxygen Demand (COD)

COD test is carried throughout the experiment to monitor the treatment process. High Range (1-1500 mg/L) COD vials are used. The vials are heated in the heating block with temperature of 150°C for 2 hours then COD is measured using spectrophotometer.

3.3.3.3 Biological Oxygen Demand (BOD₅)

BOD test is also carried throughout the experiment to monitor the treatment process. The modified wrinkle method is used to determine the BOD throughout the experiment.

30 mL sample and 1 mL seed will be poured into 300 mL BOD bottle. The bottle is then filled with dilution water saturated in oxygen and containing the nutrients required for biological growth. Before the bottle is stoppered, the oxygen concentration in the bottle is measured. After the bottle is incubated for 5 days at 20°C, the dissolved oxygen concentration is measured again. The BOD of the sample is the difference in the dissolve oxygen concentration values divided by the decimal fraction of sample used.

3.3.3.4 Total Suspended Solids (TSS)

50 mL samples with different dilutions will be filtered using Whatman glass fiber filter. The filter paper will then be dried at temperature of 103°C for 1 hour. TSS of the sample is the difference in the weight of the pan and filter paper before and after filtering values divided by the volume of the sample.

Zinc is measured using USEPA Zincon Method where 20 mL of sample will be added with ZincoVer5 Reagent Powder Pillow and 0.5 mL cyclohexanone. After 3 minutes reaction, zinc concentration in the sample is then measured using spectrophotometer.

3.3.3.6 Ammonium-nitrogen

Nessler Method is employed here to measure Ammonium-nitrogen where 25 mL of sample will be added with three drops of Mineral Stabilizer and Polyvinyl Alcohol Dispersing Agent and 1.0 mL of Nessler Reagent. After one minute reaction, Ammonium-nitrogen concentration in the sample will be measured using spectrophotometer.

3.3.4 Experimental (Aerobic Treatment)

3.3.4.1 SBR configuration and operation

A sequencing batch reactor of Plexiglas material having a total working volume of 5 L capacity is used for the experiment. The reactor is been operated in suspended growth configuration in sequencing batch mode at a constant temperature of 26-28° C (Mohan et al. 2003). The cycle period employed in this experiment is shown in the table 3.3.

Phase	Cycle Period	Air supply	Condition
Filling (min)	15	Off	Anoxic
Reaction with recirculation (h)	23	On	Aerobic
Settling (min)	30	Off	Anoxic
Withdrawal (min)	15	Off	Anoxic

Table 3.3: Cycle period and phase details of reactors during sequence

The organic loading rate was varied from $(0.0933 \text{Kg COD/m}^3/\text{d.}$ to $0.04665 \text{ Kg COD/m}^3/\text{d})$ in reactor and $(0.1866 \text{ Kg COD/m}^3/\text{d.}$ to $0.13995 \text{ Kg COD/m}^3/\text{d})$ in the reactor 2. HRT (10 and 20 day) in reactor 1, and (5 and 7 days).

The sequence of the SBR operation is controlled by pre-programmed timers (feeding, aeration, recycling and withdrawal).

The supernatant withdrawal operation is done with the help of an ordinary manual pump. Air is supplied by means of diffused aerators.



Fig: 3.2: schematic set up of the reactors (SBR)

3.3.5 Analytical procedures

The performance of SBR with the latex wastewater is being assessed by monitoring carbon removal (COD) throughout the reactor operation and during the cycle period. In addition, pH, BOD, Nitrates, Zinc, and Ammonia-nitrogen is also been determined during sequence operation to assess the performance of the SBR. The analytical procedures for monitoring the above parameters are adopted from the procedure outline in Standard Methods. Volatile suspended solids (VSS) and suspended solids (SS) are also monitored throughout the study to assess the viability of the suspended biomass during SBR operation with the rubber waste effluents.

3.3.6. Preliminary treatment

3.3.6.1 Zinc removal

Wastewater from the rubber processing is acidic in nature with pH in the range of 3.8 to 6.2 and containing high concentrations of COD, BOD, Total-N and zinc. The high BOD/COD ratio of the wastewater (0.58) indicates that the rubber wastewater is biodegradable and can be treated effectively by an anaerobic digestion process commonly employed in this industry. However, because the wastewater contained zinc concentrations of 23 mg/L, which could inhibit the digestion process, it was pretreated by chemical precipitation/flocculation. A treatment process using a combination of Ferric Chloride and Alum at concentrations of 30mg/L, respectively, was used. The optimum settling time was 60 min, whereas the optimum flocculation time was 20 min, and a speed of 20 rpm. The Zinc concentration was reduced from 23mg/L to 6.1 mg/L.

CHAPTER 4

RESULTS AND DISCUSSION

Two reactors are being used in this study. The SBR reactors operates in sequencing batch mode with a total 24 h cycle period, MLVSS concentration 9600 mg/L, organic loading rate of 0.0933 kg COD/m³/day, 0.1866 kg COD/m³/day, and HRT of 10 days and 5 days respectively to assess the suitability of the reactors for treating the rubber wastewater under study.

For the period of 30 days, the reactors were operated with an organic loading rate of 0.0933 kg COD/ m³/day and 0.1866 kg COD/ m³/day, and was reduced to 0.046 kg COD/ m³/day and $0.1399 \text{ kg COD/ m}^3/\text{day for a period of 20 days.}$

The reactors performance was assessed by monitoring carbon removal (COD and BOD), Nitrogen removal, and Zinc removal during the sequence (cycle) operation and also throughout the reactor operation.

4.1 COD and BOD removal

The variation of COD removal with the function of the cycle period is depicted in Figures (4.1 to 4.3). 81.24 % COD removal was observed in reactor 1 at an organic loading rate of 0.0467 kg COD/ m³/day, while 74.81% removal was observed in reactor 2 at an organic loading rate of 0.1399 kg COD/ m³/day. The COD removal rate was slow for both reactors 45.2% and 38.4% respectively during the initial phase of sequence operation up to 3 days as seen in Figure 4.3.



Figure 4.1: COD variation in Reactor 1



Figure 4.2: COD variation in Reactor 2



Figure 4.3: COD removal efficiency in the reactors

With an increase of sequence time a relatively rapid COD removal was noticed after the first 3 days and reached 63% and 60% respectively at the end of 30 days. The initial low COD removal was due to the relatively high concentration gradient of the substrate. With an increase in sequence time, the native suspended biomass became acclimatized to the new substrate (system) conditions facilitating rapid removal of the organic substrate.

The BOD profile during the sequence operation showed a good pattern compared to the COD profile as shown in Figure 4.6. BOD removal of 93.73% for reactor 1, and 91.67% for reactor 2 was observed after the reactor attained stability. There was a drop in the BOD removal efficiency due to 5 days Chinese New Year holidays where the lab was not accessible, as seen in Figure 4.6 the removal efficiency dropped to 85.97% in reactor 1. But for reactor 2, there was no drop because the organic loading rate was high, thus there was enough food for the bacteria to feed on.



Figure 4.4: BOD Variation in reactor 1



Figure 4.5: BOD Variation in Reactor 2



Figure 4.6: BOD removal efficiency in the reactors

4.2 Nitrogen removal

The two most widely used methods for removing nitrogen from wastewater which are physical and biological, are applied in this project. The settling process (physical) is used to remove organic nitrogen bound in suspended solids. While solids removal can remove some nutrients, it cannot remove most of the nutrients including the large fraction of nitrogen that is soluble (Van Horn *et al.* 1994). This leaves biological treatment as the next choice in nitrogen removal

The three major biological processes directly involved with biological nitrogen removal in wastewater treatment viz., ammonification, nitrification, and denitrification were involved in the process.

Ammonification occurs when organic nitrogen is converted to ammonia. As seen in Figure 4.2: there is an increase in the concentration of ammonia nitrogen in both reactors from initially low concentration of 3.76 mg/L and 2.88 mg/L to high as 10.8 mg/L and 9.1 mg/L respectively. This mechanism ultimately allows organic nitrogen to be removed from wastewaters through hydrolysis to amino acids, which are broken down to produce ammonium or directly incorporated into biosynthetic pathways in support of bacterial growth (David P. Whichard, 2001). The Nitrogen as ammonia can be assimilated by bacteria to form cellular mass.


Figure 4.7: Nitrogen ammonia variation in the reactors

The ammonification process is then followed by nitrification process. Ammonium nitrogen is oxidized to nitrite by ammonia oxidizing bacteria (AOB) and then to nitrate by nitrite oxidizing bacteria (NOB). Many AOBs and NOBs are autotrophic, although heterotrophic bacteria are known to function as nitrifiers (Painter, 1977). In both reactors, the nitrite concentration was undetectable.

Very little nitrite exists in a system at any one time because the conversion of ammonium to nitrite by AOBs is generally the rate-limiting step (Antoniou *et al.*, 1990). Consequently, nitrate oxidation follows quickly. The nitrate formed can then be used as a nitrogen source or as an electron acceptor.

During the settling period anoxic condition is developed where the oxygen concentration in the wastewater becomes low enough that the bacteria begin to utilize nitrate as an electron acceptor under anoxic conditions. Nitrate is reduced by heterotrophic bacteria to the intermediate nitrite and then to nitrogen gas. The nitrogen is then able to leave the wastewater as inert nitrogen gas. As seen in Figure 4.10: there is significant removal of the nitrate in both reactors; 90.31% and 88.88% respectively.



Figure 4.8: Nitrate Variation in Reactor 1



Figure 4.9: Nitrate Variation in Reactor 2



Figure 4.10: Nitrate removal efficiency in the Reactors

4.3 Zinc removal

The influent Zinc concentration is rather low 6.1 mg/L, and a high removal efficiency of 92% and 73% respectively was observed in the first 3 days. But with time, there was a buildup of Zinc in both the reactors as seen in Figure 4.11 and Figure 4.12. The buildups lead to decrease in the removal efficiency to 58% and 46% respectively. And this increase in concentration caused toxic condition in the reactor and reduction in the biomass concentration, and increase in COD. But after the 17th day, the Zinc in the influent was removed prior to feeding the reactors which in turn increase the removal efficiency to 93.44% and 83.93% respectively as seen in Figure 4.13.



Figure 4.11: Zinc variation in the Reactor 1



Figure 4.12: Zinc Variation in Reactor 2



Figure 4.13: Zinc removal efficiency in the Reactors

4.4 Process monitoring and reactors Kinetics

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 was at 2L for both reactors, but it decreased from 2 L to 1.5 L in reactor 1 and from 2 L to 1 L in reactor 2 within the first 10 days of reactors operation. This was due to the toxic nature of the influent wastewater. However, after stable conditions had been achieved, and the bacteria got acclimatized to the substrate, 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 reactor 1 was in the range of 7863-9600 mg/L and 6554-9231 mg/L in reactor 2. Figures 4.4.1 and 4.4.2 show an initial decrease in the VSS and TSS during the first 10 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.



Figure 4.14: VSS and TSS variation in the Reactor 1 during operation



Figure 4.15: VSS and TSS variation in reactor 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 4.4.3 and 4.4.4 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;

$$Y = \frac{biomassproduced(g)}{substrate _utilized(g)}$$



Figure 4.16: VSS and SCOD variation in SBR 1 during operation



Figure 4.17: VSS and SCOD variation in SBR 2 during operation

CHAPTER 5

CONCLUSION

The SBRs showed good performance in treating the rubber wastewater using aerobic respiration. It is evident from the results that, the reactors need short period for startup and stabilization of reactor was achieved within 2–5 days. The performance of SBR is dependent on Hydraulic retention time (HRT) and organic loading rate (OLR) as seen in the COD and BOD removal. Reactor 1 with a loading rate of 0.0933 kg COD/m³ /day and 0.0467 kg COD/ m³/day showed relatively high performance with hydraulic retention time of 20 days compared to Reactor 2 of a loading rate of 0.1866 kg COD/ m³/day and 0.1399 kg COD/ m³/day and hydraulic retention time of 7days.

The high concentration of the biomass 9600 mg/L in the reactors has a positive effect on the removal efficiency of both the COD and BOD as evident in the values achieved.

Though there was a buildup in the Zinc concentration for some days, the removal efficiency was not affected much. The COD removal efficiencies of 81.24% and 74.81% respectively are achieved and a BOD of 93.73% and 91.69% are achieved.

The nitrogen removal showed good performance with nitrate having removal efficiency of 90.31% and 88.88% respectively.

Therefore based on the results, the optimum Organic loading rate (OLR) of 0.0467 kg COD/ m^3 /day would be appropriate with a subsequent hydraulic retention time (HRT) of 20 days and 24 hour cycle period, where COD, BOD, Zinc, and nitrogen removal efficiencies of 81.24%, 93.73 %, 93.4, and 90.31 % respectively, can be achieved.

It is evident from the results that the discharge limit for Latex wastewater in Malaysian standard is met. As the COD, BOD, Zinc, and nitrogen final concentration of 175mg/L, 34mg/L,0.4mg/L, and 11.34 mg/L respectively, are within the limits of 400mg/L, 100 mg/L, 2mg/L, and 300mg/L for COD, BOD, Zinc, and nitrogen respectively.

CHAPTER 6

PROJECT COST

Though the project was experimental, its cost was not that high because most of the equipment, chemicals, reagents, and materials are provided in the lab and the cost is covered by the department.

Below are the description and cost of the materials which are not provided in the lab and they aided in the completion of the project.

1.0.Materials

No,	Description	Purpose	Quantity	Price (RM)
1	Diffuser	Aeration	4	4
2	Hand pump	Decanting	1	10
3	Tube	Aeration	2 meters	2
4	Pet food	Culturing bacteria	6 canes	36.4
5	Aquarium compressor	Aeration	2	31
	Total A	mount		83.4

2.0.Electricity

The electricity supply during the project duration is provided in the Laboratory and consumption cost is covered by the department.

Below is the detail description of the electricity consumption of the aerating compressor.

2.1. Culturing of bacteria

The air compressor (aquarium pump) operates at 0.027 amperes and 115 volts.

Wattage = 0.027 amps x 115 volts = 3.2 watt.

2

Therefore the electricity consumption for the 3 months of culturing the bacteria is.

Time (hours) = 3months x 30days x 24 hours = 2160 hours

Electricity consumption (kWh) = $(3.2 \text{ watt } \times 2160 \text{ hours}) / 1000 = 6.912 \text{ kilo watt-hour (kWh)}$

2.2. Aerating the Reactors

Aeration time (hours) = 2months x 30day x 24 hours = 1440 hours

Electricity consumption (kWh) = $(3.2 \text{ watt } \times 1440 \text{ hours}) / 1000 = 4.608 \text{ kilo watt- hour (kWh)}$

Since two reactor are used in the experiment, therefore the electricity consumption =

 $2 \times 4.608 \text{ kWh} = 9.216 \text{ Kwh}$

3.0.Reactor Fabrication

A sequencing batch reactor of Plexiglas material having a total working volume of 5 L capacity is used for the experiment. The two reactor of 5L capacity each was fabricated by previous Final year students. The cost per one reactor is approximately RM 100.

4.0.Car rental

Due to unavailability of a car by the author, the author was renting a car to facilitate the project. Rental cost per hour = RM 10 Fuel price per liter = RM 1.8 Fuel quantity used per rent = 3 liters Hours rented = 8 hours Total Cost = $\{(10) + (1.8 \text{ x3})\} \times 8 = \underline{RM 123.2}$

The ranges of construction costs for a complete, installed SBR wastewater treatment system varies according to the type of wastewater handling facilities and the differences in newly constructed plants versus systems that use existing plant facilities. As such, in some cases these estimates include other processes required in an SBR wastewater treatment plant.

There is typically an economy of scale associated with construction costs for wastewater treatment, meaning that larger treatment plants can usually be constructed at a lower cost per gallon than smaller systems. The use of common wall construction for larger treatment systems, which can be used for square or rectangular SBR reactors, results in this economy of scale.

Operations and Maintenance (O&M) costs associated with an SBR system may be similar to a conventional activated sludge system. Typical cost items associated with wastewater treatment systems include labor, overhead, supplies, maintenance, operating administration, utilities, chemicals, safety and training, laboratory testing, and solids handling.

Labor and maintenance requirements may be reduced in SBRs because clarifiers, clarification equipment, and RAS pumps may not be necessary.

On the other hand, the maintenance requirements for the automatic valves and switches that control the sequencing may be more intensive than for a conventional activated sludge system. O&M costs are site specific and may range from \$800 to \$2,000 dollars per million gallons treated.

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APPENDIX

- Appendix 1 Gantt chart
- Appendix 2 Effluent Analysis of the reactor
- Appendix 3 Influent Characteristics
- Appendix 4 Scanned electron micrograph of suspended Biofilm in the reactor
- Appendix 5 Reaction, decanting, and analyzing process

GANTT CHART

	July 2009	August 2009	September 2009	October 2009	November 2009	December 2009	January 2010	February 2010	March 2010	April 2010	May 2010
Literature Review											
Culturing Bacteria											
Wastewater characterization											
Setup of the reactors											
Experiment and Analysis											
Dissertation writing											

Effluent Analysis of reactor 1

				COL) (mg/L)	BOD	(mg/L)	Zinc	(mg/L)	Ammo	nia (mg/L)	Nitrate	e (mg/L)	
Date	Days	OLR (Kg COD/m ³ .d)	HRT (D)	Eff. COD	% removal	Eff. BOD	% removal	Eff. Zinc	% removal	Eff. Amm	% removal	Eff. Nitrate	% removal	Remarks
3/2/10	1	0.0933	10	511	45.23			0.75	87.7	3.76	43.03			
4/2/10	2	0.0933	10	444	52.41			0.46	92.46				1.0	
5/2/10	3	0.0933	10	441	52.73	105	80.63			4.5	31.82			
8/2/10	6	0.0933	10	266	71.49			1.9	68.85			17.5	85.04	
9/2/10	7	0.0933	10	381	59.16									
10/2/10	8	0.0933	10	255	72.67	88	83.76			6.2	6.06			
11/2/10	9	0.0933	10	303	67.52			0.35	94.26			30	74.35	
12/2/10	10	0.0933	10	427	54.23			1.33	78.2	9.85	-49.24	21.5	81.62	
17/2/10	15	0.0933	10	269	71.17	56	89.66	1.65	72.62	3.15	52.27	14.9	87.26	CNY break
18/2/10	16	0.0933	10	380	59.27			0.2	96.72	10.8	-63.64	39	66.66	
19/2/10	17	0.0933	10	365	60.88			2.55	58.2	7.2	-9.09	25	78.63	
22/2/10	20	0.0933	10	399	57.23			0.8	86.89	4.15	37.12	37.5	67.95	
23/2/10	21	0.0933	10	443	52.52	49	90.95							
24/2/10	22	0.0933	10	363	61.09			0.05	99.18	9.15	-38.64	36.5	68.80	
25/2/10	23	0.0933	10	390	58.20			0.4	93.44	6.75	-2.27	49	58.12	
1/3/10	27	0.0933	10	424	54.56	76	85.97			5.65	14.39	45.5	61.11	Eid Maulid
2/3/10	28	0.0933	10	465	50.16									
3/3/10	29	0.0933	10	404	56.69									
4/3/10	30	0.0933	10	342	63.34			1.15	81.15	7.3	-10.61	20	82.91	
5/3/10	31	0.04665	20	330	64.63	63	88.37							
8/3/10	34	0.04665	20	210	77.49			0.7	88.5	5.7	13.64	27.5	76.49	
9/3/10	35	0.04665	20	174	81.35									

10/3/10	36	0.04665	20	143	84.67			0.45	92.6	3.1	53.03	25.5	78.21	
11/3/10	37	0.04665	20	183	80.39									
12/3/10	38	0.04665	20	183	80.39	38	92.98	0.32	94.75	4.03	38.94	22.5	80.77	
15/3/10	41	0.04665	20	175	81.24			0.30	95.08	3.55	46.21	23.5	79.71	
16/3/10	42	0.04665	20	181	80.60									
17/3/10	43	0.04665	20	177	81.03			0.46	92.45	3.84	24.24	14	88.03	
18/3/10	44	0.04665	20	172	81.56									
19/3/10	45	0.04665	20	175	81.24	34	93.73					10.5	91.03	
22/3/10	48	0.04665	20	180	80.71			0.48	92.13	3.5	46.97			
23/3/10	49	0.04665	20	176	81.14									
24/3/10	50	0.04665	20	174	81.35			0.40	93.44	3.65	44.69	11.34	90.31	
25/3/10	51	0.04665	20	175	81.24									

Influent Characteristics

COD= 933 mg/L

BOD= 542 mg/L

Zinc= 6.1 mg/L

Ammonia= 6.6 mg/L

Nitrate= 117 mg/L

N.B

CNY: Chinese New Year

Effluent Analysis of reactor 2

Date	Days	OLR	HRT	COL	D (mg/L)	BOD) (mg/L)	Zinc	(mg/L)	Ammo	nia (mg/L)	Nitrate	e (mg/L)	
Date	Days	(Kg COD/m ³ .d)	(D)	Eff. COD	% removal	Eff. BOD	% removal	Eff. Zinc	% removal	Eff. Amm	% removal	Eff. Nitrate	% removal	Remarks
3/2/10	1	0.1866	5	574	38.48			1.08	82.29	2.88	56.36			
4/2/10	2	0.1866	5	545	41.59			1.6	73.77					
5/2/10	3	0.1866	5	465	50.16	114	78.97			3.43	48.03			
8/2/10	6	0.1866	5	480	48.55			2.95	51.64		10.00	40.5	65.38	
9/2/10	7	0.1866	5	387	58.52									
10/2/10	8	0.1866	5	333	64.31	75	86.16			4.62	30.00			
11/2/10	9	0.1866	5	352	62.27			2.4	60.65		50.00	22.5	80.77	
12/2/10	10	0.1866	5	480	48.55			1.54	74.75	7.0	-6.06	43.5	62.82	*****
17/2/10	15	0.1866	5	298	68.06	64	88.19	2.54	58.36	6.1	7.58	28.6	75.55	CNY break
18/2/10	16	0.1866	5	470	49.62			3.25	46.72	7.35	-11.36	20.5	82.47	Citr Dicuk
19/2/10	17	0.1866	5	357	61.74			2.05	66.39	4.1	37.88	37.5	67.95	
22/2/10	20	0.1866	5	385	58.74			0.35	94.26	4.3	34.85	36.5	68.8	
23/2/10	21	0.1866	5	315	66.24	53	90.22							
24/2/10	22	0.1866	5	311	66.67			0.55	90.98	7.6	-15.15	21	82.95	
25/2/10	23	0.1866	5	464	50.27			0.25	95.9	5.25	20.45	35.5	69.66	
1/3/10	27	0.1866	5	271	70.95	50	90.77			4.1	37.88	22	81.19	Eid Maulid
2/3/10	28	0.1866	5	337	63.88									
3/3/10	29	0.1866	5	490	47.48									
4/3/10	30	0.1866	5	370	60.34			0.85	86.06	9.1	-37.88	15	87.18	
5/3/10	31	0.13995	7	310	66.77	49	90.96							
8/3/10	34	0.13995	7	280	69.99			1.6	73.77	4.62	30.00	14.5	87.6	
9/3/10	35	0.13995	7	265	71.60									
10/3/10	36	0.13995	7	240	74.28			1.8	70.49	4.51	31.67	26	77.77	
11/3/10	37	0.13995	7	283	69.67									

12/3/10	38	0.13995	7	288	69.13	51	90.59	1.88	69.18	3.01	54.39	12	89.74	
15/3/10	41	0.13995	7	298	68.06			1.74	71.47	2.81	57.42	20.5	82.48	
16/3/10	42	0.13995	7	277	70.31									
17/3/10	43	0.13995	7	254	72.78					2.83	57.12	15	87.18	
18/3/10	44	0.13995	7	239	74.38									
19/3/10	45	0.13995	7	229	75.46	48	91.69	1.05	82.78	2.5	62.12	13	88.88	
22/3/10	48	0.13995	7	238	74.49			1.12	81.64	2.6	60.61	14	88	
23/3/10	49	0.13995	7	237	75.59									
24/3/10	50	0.13995	7	238	74.49			0.98	83.93	2.53	61.67	13	88.88	
25/3/10	51	0.13995	7	235	74.81									

Influent Characteristics

COD= 933 mg/L

BOD= 542 mg/L

Zinc= 6.1 mg/L

Ammonia= 6.6 mg/L

Nitrate= 117 mg/L

N.B

CNY: Chinese New Year

Influent characteristics

Value					
1.26 mg/L					
23 mg/L					
117 mg/L					
650 mg/L					
6.6 mg/L 69 mg/L					
191 mg/L					
933 mg/L					
6.4					
542 mg/L					



Figure: Scanning electron micrograph (SEM) of suspended biofilm in Reactor 1



Figure: Scanning electron micrograph (SEM) of suspended biofilm in Reactor 2



Figure 3.3: Reaction process



Figure 3.3: Decanting



Figure 3.3: Effluent for analysis



Figure 3.3: COD reactors