

CERTIFICATION OF APPROVAL

Treatment of Petroleum Refinery Wastewater using Anaerobic Filter

by

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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 and persons.


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ABSTRACT

Treatment of wastewater is done to avoid water pollution of the water bodies in the world. As water is essential to living creatures, the water bodies such as river and sea should be preserved from any form of pollution. In treating wastewater, the influent will undergoes physical treatment, chemical treatment and biological treatment before it exits the wastewater treatment plant. There are two types of biological treatment process which vary in term of capabilities and economic consideration. These are aerobic treatment process and anaerobic process. The former is commonly used in treating petroleum refinery wastewater. The objective of the study is to determine the efficiency of anaerobic filter in treating petroleum refinery wastewater and determining the effect of operating conditions using anaerobic filter. The sample that is used as the influent for the anaerobic filter is from the effluent of the chemical treatment process taken from PETRONAS PENAPISAN Melaka Sdn. Bhd. (PPMSB) wastewater treatment plant. The anaerobic filter will work at mesophilic condition at a temperature of 35°C. The influent and the effluent of the anaerobic filter are studied. Parameter such as the pH value, chemical oxygen demand (COD), volatile fatty acids (VFA), methane production and alkalinity were studied. The efficiency of using an anaerobic filter were studied based on the COD removal efficiency with respect to the hydraulic retention time (HRT). The removal efficiency of COD using an anaerobic filter can reach up to more than 70% at a HRT of 4 days. The volume of methane gas produced is 100-200cm³. As a conclusion, the study shows that the removal of COD up to more than 70% can be achieved and methane gas are produced using petroleum refinery wastewater as the influent of the anaerobic filter. The best HRT for treating petroleum refinery wastewater is 4 days.

1. Laboratory Test and Analysis

1.1 Environmental Parameters and Sampling

1.1.1 Alkalinity Measurement

1.1.2 pH Measurement

1.1.3 Chemical Oxygen Demand (COD)

1.1.4 Volatile Fatty Acids (VFA)

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CHAPTER 1

INTRODUCTION

1.1 Background

Wastewater treatment process is a necessary process that all wastewater must undergo before discharge into the environment. A wastewater treatment plant can basically have three treatment processes depending on the wastewater to be treated. The three processes consist of the physical unit operation, the chemical unit processes and the biological treatment. The physical unit operation is to remove solid particles from the influent that enter the treatment plant. Chemical unit process is done to remove chemical materials such as organic compounds, phosphorus, heavy metals, etc. Biological treatment is done to remove any organic constituents and compounds found inside the influent. Anaerobic process is categorized as a biological treatment process. It is a process in which microorganisms break biodegradable materials that can be found in the influent in the absence of oxygen (Metcalf & Eddy, 2004).

Anaerobic treatment process can play an important role in a wastewater treatment process and it can contribute methane gas as a source of energy. In using an anaerobic treatment process such as using an anaerobic filter, the efficiency of the wastewater treatment plant can be increased (Metcalf & Eddy, 2004).

A study will be done on the wastewater at PETRONAS PENAPISAN Melaka Sdn. Bhd. (PPMSB) in Melaka, Malaysia. Currently PPMSB petroleum refinery in Melaka is using the conventional activated sludge system for their biological treatment process. The activated sludge system is an aerobic biological treatment process that uses oxygen to treat the wastewater influent. The study will be conducted on a sample of PPMSB petroleum refinery wastewater to test whether an anaerobic filter can treat it efficiently. The evaluation of the anaerobic filter performance will be done based on the standards

and guidelines for wastewater effluent. Table 1.1 shows the criteria that must be met by the effluent from PPMSB sewage treatment plant. PPMSB follows standard B.

Table 1.1 Malaysian Sewage and Industrial Effluent Regulation 1978

Parameter	Unit	Standard	
		A	B
Temperature	C	40	40
pH Value		6.0 - 9.0	5.5 - 9.0
BOD ₅ at 20°C	mg/L	20	50
COD	mg/L	50	100
Suspended Solids	mg/L	50	100
Mercury	mg/L	0.005	0.005
Cadmium	mg/L	0.01	0.02
Chromium, Hexavalent	mg/L	0.05	0.05
Arsenic	mg/L	0.05	0.10
Cyanide	mg/L	0.05	0.10
Lead	mg/L	0.10	0.5
Chromium, Trivalent	mg/L	0.20	1.0
Copper	mg/L	0.20	1.0
Manganese	mg/L	0.20	1.0
Nickel	mg/L	0.20	1.0
Tin	mg/L	0.20	1.0
Zinc	mg/L	1.0	1.0
Boron	mg/L	1.0	4.0
Iron (Fe)	mg/L	1.0	5.0
Phenol	mg/L	0.001	1.0
Free Chlorine	mg/L	1.0	2.0
Sulphide	mg/L	0.50	0.50
Oil and Grease	mg/L	Not Detectable	10.0

Source: ENVIRONMENTAL QUALITY ACT 1974 (ENVIRONMENTAL QUALITY (SEWAGE AND INDUSTRIAL EFFLUENTS) REGULATIONS 1978 [Regulation 8 (1), 8 (2), 8 (3)] PARAMETER LIMITS OF EFFLUENT OF STANDARDS A AND B

1.2 Problem Statement

Pollution is an undesirable effect to the environment that is caused by human activities intentionally or unintentionally and has become a major topic that can be heard everyday in many parts of the world. There are many types of pollution that can occur such as air pollution, noise pollution, water pollution and etc. The effluent exiting a wastewater treatment plant has potential to pollute the surrounding environment if the quality of it does not meet certain required standards. Petroleum refinery wastewater has potential of having xenobiotic branched chain fatty acids (BCFAs) that is harmful to the environment. Conventional aerobic effluent treatment facilities have problem to remove xenobiotic BCFAs that are found in the environment (Chua et al., 1996). For Malaysia, the effluent that exits a wastewater treatment plant must have the desired quality as shown in Table 1.1 which is based on the Malaysian environmental quality act 1978 for sewage and industrial effluent.

The usage of anaerobic process is proposed in this project because of the advantages it has over the usage of an aerobic process. Some of the advantages is the anaerobic process required less nutrients to feed the microorganism that reside inside the filter if compared to aerobic process. The nutrients required are 5 to 20 times less than using aerobic process. Most of the organic compound that is initially available inside the influent is acclimatized giving low organic compound for the effluent. Air pollution due to the usage of aerobic process is also eliminated using anaerobic process. (Metcalf & Eddy, 2004).

1.3 Objectives

The objectives of this study are:

- I. To determine the efficiency of anaerobic filter in treating petroleum refinery wastewater
- II. To determine the effect of operating conditions using an anaerobic filter

1.4 Scope of Study

CHAPTER 1

This study will be focus on the PPMSB wastewater characteristics after it undergoes anaerobic filter treatment. In this research, the influent and the effluent of the anaerobic filter will be tested whether to check its efficiency. Laboratory experiments are conducted to check on certain parameter of the influent and effluent of the anaerobic filter. The experiments that are conducted are on the Chemical Oxygen Demand (COD), pH value, Alkalinity, Volatile Fatty Acids and Methane production. The efficiency of using the anaerobic filter will be compare with the result of using conventional system that already exist at PPMSB wastewater treatment plant which is the activated sludge system.

to be evaluated are shown in Table 2.1. Figure 2.1 shows the anaerobic decomposition system (López et al. 2004, 2006).

Table 2.1 Factors to be considered when choosing anaerobic treatment process

• Flow and loading variables	• Solid retention time
• Organic composition and temperature	• Expected methane gas production
• Nature of nonbiodegradable organic material	• Treatment efficiency needed
• Suspended solids	• Sulfide production
• Nutrients	• Anaerobic toxicity
• Inorganic and organic solids concentrations	• Liquid-Solid separation

CHAPTER 2

LITERATURE REVIEW

2.1 Anaerobic Process

Anaerobic process is a treatment process in which microorganisms breaks biodegradable materials that can be found in the influent in the absence of oxygen. In consideration to use anaerobic treatment process, important factors and the wastewater characteristics will need to be evaluated and considered. The factors and wastewater characteristics that need to be evaluated are shown in Table 2.1. Figure 2.1 shows the anaerobic decomposition process (Metcalf & Eddy, 2004).

Table 2.1 Factors to be considered when choosing anaerobic treatment process

• Flow and loading variations	• Solid retention time
• Organic concentration and temperature	• Expected methane gas production
• Fraction of nondissolved organic material	• Treatment efficiency needed
• Wastewater alkalinity	• Sulfide production
• Nutrients	• Ammonia toxicity
• Inorganic and organic toxic compounds	• Liquid-Solid separation

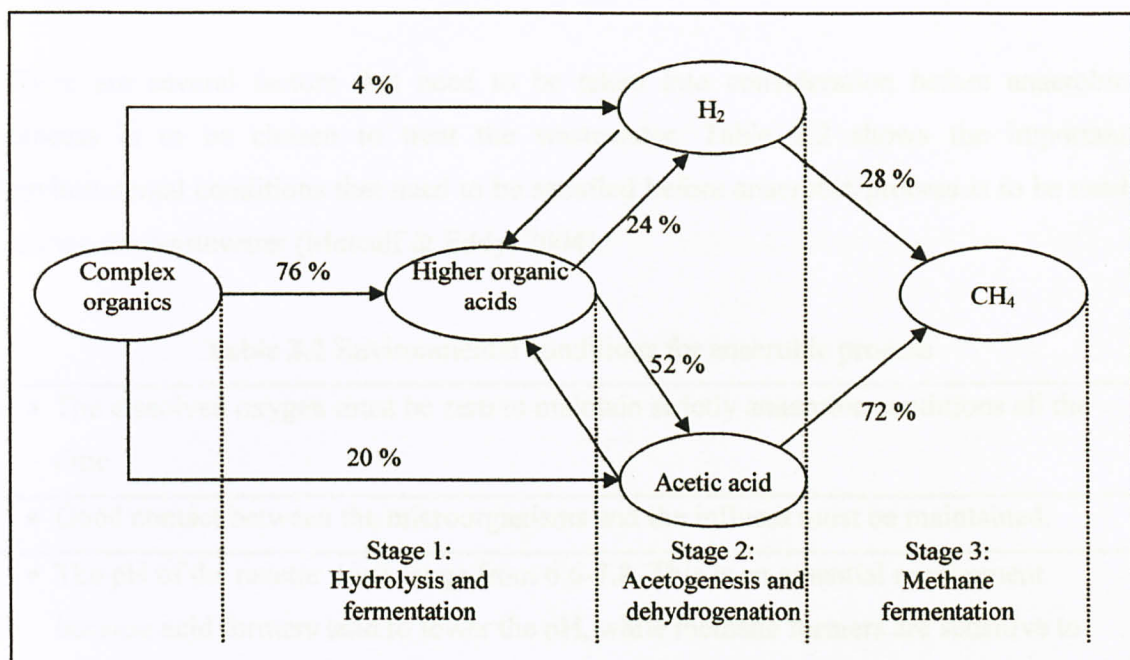


Figure 2.1 Simplified schematic, basic steps and energy flow in the anaerobic decomposition process (Metcalf & Eddy, 2004).

The influent flow and organic load that has a wide variation can cause unbalance effect to the anaerobic process. A fast influent flow might not give the anaerobic filter the time to treat the influent and low organic load might have insufficient food for the microorganism inside the anaerobic reactor. An unbalance between acid fermentation and methanogenesis can occur due to the wide variation. In meeting the peak flow and loading conditions, the flow must be maintained throughout the process. The Chemical Oxygen Demand (COD) concentrations shall be between 1500 to 2000mg/L to ensure a good anaerobic environment inside the anaerobic filter. For a concentration of COD below 1300mg/L, aerobic treatment process is more preferred. This is for the optimal biological reaction rates and stable treatment. The fraction of suspended organic material will determine the type of anaerobic reactor to be used. A range from 2000 to 4000mg/L of alkalinity is required to maintain the pH environment inside the reactor near neutral. Sufficient nutrient is important to ensure proper biomass growth. Chronic toxicity should also be avoided for the biomass growth. The solid retention time is one of the important characteristics in anaerobic process. 20 days is needed generally for effective treatment at 30°C (Metcalf & Eddy, 2004).

Environmental Conditions for Anaerobic Process

There are several factors that need to be taken into consideration before anaerobic process is to be chosen to treat the wastewater. Table 2.2 shows the important environmental conditions that need to be satisfied before anaerobic process is to be used to treat the wastewater (Metcalf & Eddy, 2004).

Table 2.2 Environmental conditions for anaerobic process

<ul style="list-style-type: none"> • The dissolved oxygen must be zero to maintain strictly anaerobic conditions all the time
<ul style="list-style-type: none"> • Good contact between the microorganisms and the influent must be maintained.
<ul style="list-style-type: none"> • The pH of the reactor must range from 6.6-7.8. This is an essential requirement because acid formers tend to lower the pH, while methane formers are sensitive to pH. If pH drops below 6.2, methane formation essentially ceases and more acid accumulates, thus bringing the digestion process to a standstill.
<ul style="list-style-type: none"> • The alkalinity of the digester fluid should range from 1000 to 5000mg/L, and volatile fatty acid should remain below 250mg/L.
<ul style="list-style-type: none"> • The optimum temperature in the mesophilic range should be 30-38⁰C (85-100⁰F) and in the thermophilic range should be 49-57⁰C (120-135⁰F).
<ul style="list-style-type: none"> • Nutrients such as nitrogen and phosphorus should be present in sufficient amounts to ensure proper growth of microorganisms.
<ul style="list-style-type: none"> • The anaerobic process has a relatively slow growth rate. The cellular growth is low, resulting in small quantity of solids production.

2.2 Advantages and Disadvantages of Anaerobic Process

Anaerobic process has their distinctive advantages and disadvantages over aerobic process for biological treatment in treating wastewater. The advantages and disadvantages of using anaerobic filter are shown in Table 2.4. (Metcalf & Eddy, 2004)

Table 2.3 Advantages and Disadvantages of Anaerobic Filter

ADVANTAGES	
<ul style="list-style-type: none">• Less energy required• Less nutrients required, 5 to twenty times lesser• Methane production, a potential energy source• Volumetric organic loading rate is five to ten times higher, thus reduction of installation space requirements• With acclimation most organic compounds can be transformed• Rapid response to substrate addition after long periods without feeding• Off-gases, volatile organic compound (VOCs), and odorous compounds causing air pollution are eliminated• Refractory biomass is ten times less• Anaerobic biomass can be preserved for a long time without feed, thus better seasonal treatment	
DISADVANTAGES	
<ul style="list-style-type: none">• Longer start-up time to develop necessary biomass inventory• May require alkalinity and/or specific ion addition• May require further treatment with an aerobic treatment process to meet discharge requirements• Biological nitrogen and phosphorus removal is not possible• Much more sensitive to the adverse effect of lower temperatures on reaction rates• May be more susceptible to upsets due to toxic substances• Potential for production of odors and corrosive gases	

Anaerobic process when compared to aerobic system has shown to be a viable alternative for treating medium to high strength wastes. The old concept that shows anaerobic process to be slower than the aerobic process is not always true as been found in recent research (Metcalf & Eddy, 2004).

According to Tay & Zhang (2000), anaerobic process primary disadvantage is that it is difficult to maintain the stability of the anaerobic process. The process is sensitive to the change in environmental and operation conditions. Such disturbance in the process will cause the microbial inside to fail in treating the influent. The main cause of instability of the process is from the hydraulic, organic and toxic overloading. The usage of anaerobic process to treat wastewater in the industry is dependent upon the stability of the system (Tay & Zhang, 2000).

2.3 Anaerobic Filter

Anaerobic filter is an anaerobic process that can be used in a Sewage Treatment Plant. It is categorized as an attached growth anaerobic process. There are three types of upflow attached growth process which is the upflow packed-bed reactor, anaerobic expanded-bed reactor and fluidized-bed anaerobic reactor (Metcalf & Eddy 2004). Based on the anaerobic filter operational temperature, anaerobic filter that operates at a temperature of 35°C are call mesophilic while the anaerobic filter that operates at a higher temperature which is about 55°C are call thermophilic (Yilmaz et al.2006). According to Tay & Zhang (2000), anaerobic filter subjected to various disturbance under mesophilic condition have a strong ability to resist organic, hydraulic toxic shocks.

There are many factors that can affect anaerobic filter efficiency. The media surface texture and porosity has their effect on the performance of the anaerobic filter. A media with an open-pored surface texture can have up to 78% COD removal efficiency that is due to its higher retention of attached biofilm. The media with larger porosity also has a high removal efficiency that is 77% while the media with smooth surface and low porosity has a much lower efficiency at 57%. (Show & Tay 1998)

According to Bodkhe (2008), he conducted an experiment to determine the optimum hydraulic retention time (HRT) for an anaerobic filter using municipal wastewater. The physico-chemical characteristics of the municipal wastewater used for the experiment are as shown in Table 2.5 (Bodkhe, 2008).

Table 2.4 Physico-chemical characteristics of the municipal wastewater

Parameter	Concentration
Temperature (°C)	Winter 10 - 30 Summer 20 - 42
pH	7.5 - 8.2
Alkalinity (mg/L as CaCO ₃)	230 - 300
SS (mg/L)	300 - 450
VSS (mg/L)	240 - 382
BOD (mg/L)	200 - 300
COD (mg/L)	350 - 450
COD:N:P ratio	100:10:1.3
Total Kjeldhal nitrogen (mg/L)	30 - 45
Total Phosphorus (mg/L)	5-6
Sulphate as S (mg/L)	60 - 100
Total sulphide (mg/L)	2 - 6
Oil and grease (mg/L)	15 - 20
Phenol (µg/L)	30 - 40

Source: Development of an improved anaerobic filter for municipal wastewater treatment (Bodkhe, 2008)

The optimum time for the hydraulic retention time (HRT) for the anaerobic filter using municipal wastewater with the characteristic in Table 2.5 was found to be 12 hours. A reduction of 91% and 89% of BOD and COD concentration was achieved at HRT 12 hours. The concentration of BOD and COD at 12 hours HRT is 28mg/L and 41mg/L. HRT of higher than 12 hours gives high reduction in organic pollutant and generation of

biogas while HRT lower than 12 hours deteriorate the quality of the effluent (Bodkhe, 2008).

After the influent is treated, suspended biomasses that are left at the interstitial void spaces of the biofilm indicate about 56-58% methane are produce by the suspended biomass. The methane gas 56% is made by the attached bio-film that is operated at 12 and 16g COD/l/d (Show & Tay, 1998).

Comparing anaerobic filter with anaerobic fluidized bed reactor (AFBR) and upflow anaerobic sludge blanket (UASB), anaerobic filter gives the lowest gas production and effluent quality. It has been determined that for treating synthetic wastewater with high rate organic loading influent, the COD removal efficiency can reach up to 90.25% with a gas production of 13.31L/day at steady state. The steady state is dependent to the influent COD and organic loading rate (OLR). For the shock loading tolerances, anaerobic filter has the lowest tolerance compared to AFBR and UASB. Nevertheless, despite having the lowest tolerance to shock loading, anaerobic filter has the fastest recovery from shock loading. In order to have a higher resistance to shock loading, a longer HRT is advised (Tay & Zhang, 2000).

A study on the bacterial population inside pharmaceutical wastewater using anaerobic filter found that anaerobic filter was able to remove xenobiotic branched chain fatty acids (BCFAs) that are persistent in on-side aerobic effluent treatment facilities. Xenobiotic that are persistent to degradation in the environment for example is polyaromatic hydrocarbons that can be found in crude oil (Chua et al.,1996).

There are 3 main species of microorganisms that contribute to the formation of methane that are found inside an anaerobic filter. The microorganisms are *Syntrophomonas* spp., *Methanothrix* spp. and H_2 -utilizing *Methanococcus* spp. *Syntrophomonas* spp. oxidize butanoic acid found inside the wastewater to ethanoic acid. The ethanoic acid will then be decarboxylated by *Methanothrix* spp. to methane (CH_4) and carbon dioxide (CO_2). *Methanococcus* will utilize H_2 on CO_2 to CH_4 and thus increase the concentration of

methane. The theoretical value of methane concentration is 68.75% in biogas (Chua et al., 1996).

2.4 Petroleum Refinery Wastewater Characteristics

A petroleum refining process is the basic job being done at a petroleum refinery. Petroleum refining process is a series of separation and treatment process of crude oil into their wanted product such as gasoline, gas oil, kerosene and jet fuel. Large quantities of water will be use during the refining process for the purpose of cooling systems, desalting water, stripping steam and for flushing during maintenance and shut down plant. There is also wastewater that enters the wastewater treatment plant from other source in the petroleum refinery plant that is from the surface runoff and the sanitary wastewater (Zarooni & Elshorbagy, 2005).

The wastewater characteristic of the wastewater from a petroleum refinery is found to have a high content of BOD and COD. It has also showed to have high concentrations of polyaromatic hydrocarbon (PAHs) and phenolic compounds that enters the major wastewater streams which is the oily water separation unit effluent and in caustic water stream. Some of the streams that was analyse also contain polychlorinated biphenyls (PCBs). The highest levels of pollutant as mentioned above are found in caustic water and due to this, before the wastewater effluent are being disposed into the sea, dilution of the wastewater with process cooling water is being done. Table 2.6 shows the water quality of Al Ruwais petroleum refinery wastewater (Zarooni & Elshorbagy, 2005).

Table 2.5 Water quality index of Al Ruwais petroleum refinery wastewater

Index	Concentration range
Oil level, mg/L	3000
SS, mg/L	> 100
Phenols Level, mg/L	20 - 2000
BOD ₅ , mg/L	150 - 350
COD, mg/L	300 - 800

Source: Characterization and assessment of Al Ruwais refinery wastewater (Zarooni & Elshorbagy, 2005)

The wastewater that are being produced by the petroleum refinery have also a high level of oil, SS (Total Suspended Solid), sulphide, reductive substances and salinity, etc. The characteristic of the oily wastewater are dependable on the type of oil being extracted and process. The subsequent preliminary treatment and the oil/water separation process is a complex multiphase system. The system produce high level of oil, SS (Total Suspended Solid), reductive substances, salts, and bacteria, etc. that is difficult to be disposed of. Table 2.7 shows a petroleum refinery wastewater quality at Daqing oilfield (Qiao et al., 2008).

Oil refinery wastewater are classify as heavy pollutant to soil and the surface of water, because it has high concentration of aliphatic and aromatic petroleum hydrocarbon. The COD and the BOD₅ value are 1100mg/L and 220mg/L, respectively. The petroleum wastewater was from Dalian Petroleum Chemical Company in China (Sun et al., 2005). According to Zarooni & Elshorbagy (2005), the concentrations of the wastewater generated are not the same for every refinery. The process in which the crude oil undergoes plays an important role in producing different composition of wastewater characteristics. The wastewater that enters the wastewater treatment plant inside the refinery is collected from the combination process of the spill oil with water (Zarooni & Elshorbagy, 2005).

Table 2.6 Water quality index of a petroleum refinery wastewater

Index	Concentration range
Oil content, mg/L	50 - 200
SS, mg/L	30 - 160
Medium diameter, μm	2.034
Total Fe, mg/L	2 - 8.4
Mn, mg/L	0 - 1.2
COD _{CR} , mg/L	380 - 490
Sulfide, mg/L	40 - 118
pH	8 - 9
Total mineralization, mg/L	2500 - 2900
Sulfate reduction bacteria (SRB), n/ml	2.5×10^5 - 6.0×10^5
Metatrophic bacteria (TGB), n/ml	2.5×10^1 - 2.5×10^2
Iron bacteria (IB), n/ml	1.3×10^0 - 1.3×10^2

Source: Performance characteristics of a hybrid membrane pilot-scale plant for oilfield-produced wastewater (Qiao et al., 2008)

Petroleum refinery wastewater are classify as heavy pollutant to soil and the surface of rivers because it has high concentration of aliphatic and aromatic petroleum hydrocarbon. The COD and the BOD₅ value are 5500mg/L and 220mg/L respectively. The petroleum wastewater was from Dalian Petroleum Chemical Company in China (Sun et al., 2008). According to Zarooni & Elshorbagy (2005), the compositions of the wastewater generated are not the same for every refinery. The process in which the crude oil undergoes plays an important role in producing different composition of wastewater characteristic. The wastewater that enters the wastewater treatment plant inside the refinery is collected from the combination process of the spill oil with water (Zarooni & Elshorbagy, 2005).

2.5 Petroleum Refinery Wastewater Treatment Process

Every oil refinery wastewater is to be treated before it is being disposed to the environment. PETRONAS PENAPISAN Melaka Sdn. Bhd. (PPMSB) is currently using aerobic suspended growth biological treatment processes to treat the oil refinery wastewater. The process also known as the activated sludge process is a common type of wastewater treatment used in Malaysia both for the industries and for municipal wastewater. There are four factors that are common for all activated sludge systems as shown in Table 2.8. Figure 2.2 shows a typical activated sludge process.

Table 2.7 Common factors for all activated sludge system

<ul style="list-style-type: none">• A flocculent slurry of microorganisms (mixed liquor suspended solids [MLSS]) is utilized to remove soluble and particulate organic matter from the influent waste stream
<ul style="list-style-type: none">• Quiescent settling is used to remove the MLSS from the process flow stream, producing an effluent that is low in suspended solids
<ul style="list-style-type: none">• Settled solids are recycled as a concentrated slurry from the clarifier back to the bioreactor
<ul style="list-style-type: none">• Excess solids are wasted to control the SRT to a desired value

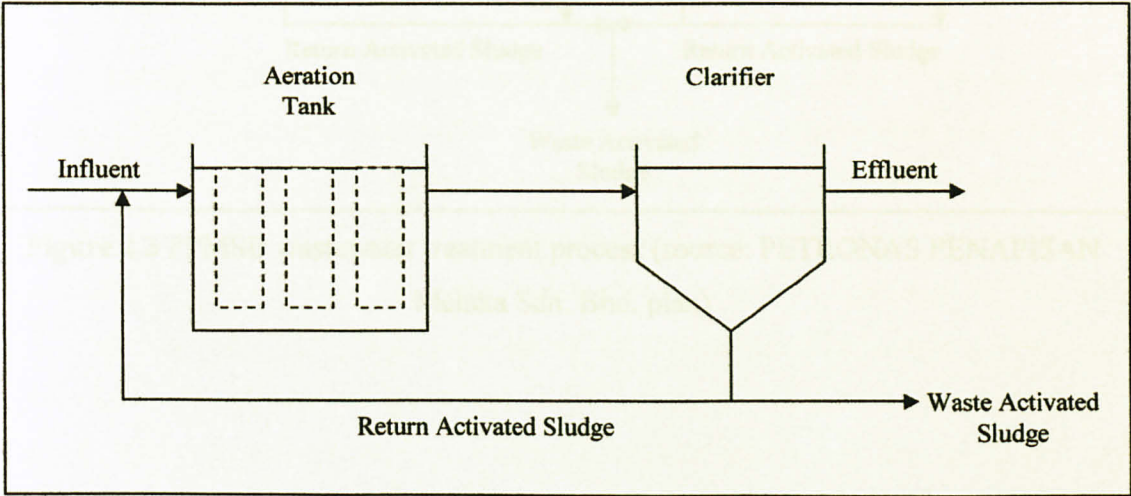


Figure 2.2 Typical activated sludge process model

Aeration tank or aeration basin is an open tank that acts as a medium to aid the transfer of oxygen into the solution inside the tank and in keeping the MLSS in suspension, mixing energy are given from the aeration process. Inside the aeration tank, microorganisms will be mixed with the organic matter that acts as food for them. The microorganisms fed with organic matter and oxygen will then grow and stabilize the organic matter inside the aeration tank. Activated sludge is when the individual organisms create an active mass of microbial floc. Two major types of aeration systems can be found in sewage treatment plants that are known as diffused aeration and mechanical aeration. For diffused aeration, air is supplied into the tank by nozzles that are fixed at the bottom of the tank. Mechanical aeration uses the air from the atmosphere by using a motor fixed with a propeller at the end. By stirring the slurry inside the tank using the motors, oxygen is able to enter and activated sludge process can be done (Qasim, 1999). Figure 2.3 shows a typical biological treatment process to treat petroleum refinery wastewater in PETRONAS PENAPISAN Melaka Sdn. Bhd. (PPMSB).

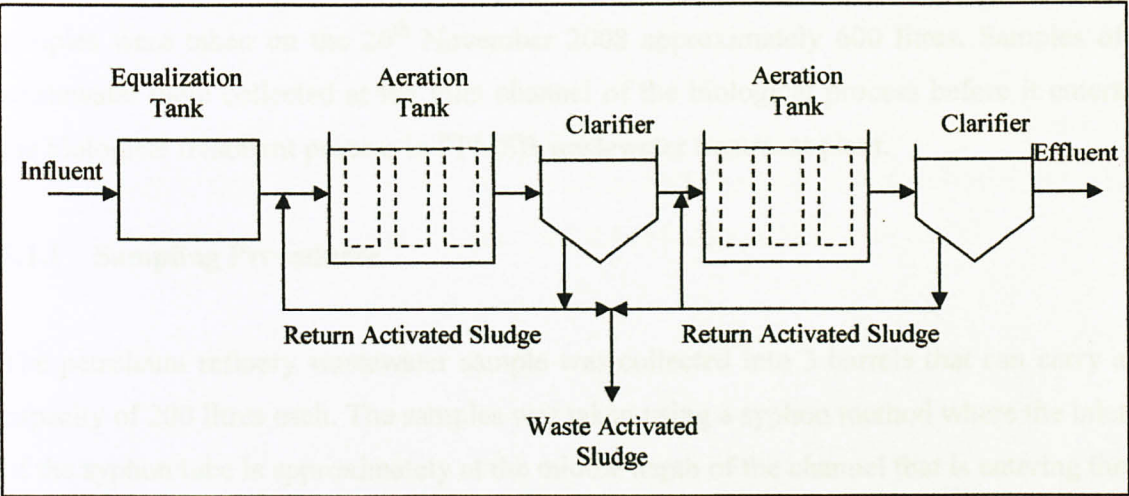


Figure 2.3 PPMSB wastewater treatment process (source: PETRONAS PENAPISAN Melaka Sdn. Bhd. plan)

CHAPTER 3

METHODOLOGY

3.1 Wastewater Sampling

PETRONAS PENAPISAN Melaka Sdn. Bhd. (PPMSB) wastewater treatment plant is situated inside PPMSB oil refinery. The wastewater that enters the wastewater treatment plant comes from the wastewater that is used for the oil refinery process such as for the cooling systems, desalting water, stripping steam and for flushing during maintenance and plant shutdown. Wastewater from the sanitary system does not enter PPMSB wastewater treatment plant but goes to a sewage treatment plant outside of PPMSB oil refinery plant.

The wastewater sample was taken from PPMSB Wastewater Treatment Plant. The samples were taken on the 26th November 2008 approximately 600 litres. Samples of wastewater were collected at the inlet channel of the biological process before it enters the biological treatment process in PPMSB wastewater treatment plant.

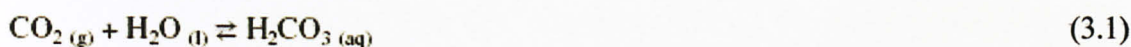
3.1.1 Sampling Procedures

The petroleum refinery wastewater sample was collected into 3 barrels that can carry a capacity of 200 litres each. The samples was taken using a syphon method where the inlet of the syphon tube is approximately at the middle depth of the channel that is entering the activated sludge system in the wastewater treatment plant. The barrel containing the wastewater sample was then sealed and transported to Universiti Teknologi PETRONAS (UTP) civil engineering environmental laboratory for analysis. The sample reached UTP within 24 hours and was then placed inside the laboratory cold storage room to avoid the sample from deteriorating. Analysis of the wastewater sample was then conducted and the sample is then use as the influent for the upflow anaerobic filter.

3.2 Upflow Anaerobic Filter

The anaerobic filter that is used to conduct the anaerobic process as another mean of biological process in treating petroleum refinery wastewater is a mini reactor that is place inside Universiti Teknologi PETRONAS civil engineering environmental engineering laboratory. The reactor is cylindrical in shape with a dimension of 0.25m height, 0.15m diameter and a volume of 5 litres. To create an anaerobic filter, 210 filters media with a diameter of 0.025m are place inside the reactor. A volume of 2 litres biomass is initially inside the reactor before the filters media are inserted into the reactor. The anaerobic filter is operated under mesophilic environment that is the temperature inside the anaerobic filter will be 35⁰C.

A methane collection tank is available beside the reactor for collecting the methane gas. The dimension of the methane collection tank is 0.25m of height, 0.15m diameter and a volume of 5 litres. According to Tay (2000), the main gas compositions that are produced by an anaerobic filter are carbon dioxide (CO₂) and methane. The methane collection tank is filled with sodium hydroxide (NaOH) with a concentration of 5% to absorb CO₂ and only let methane gas accumulate inside the collection tank (Isa et al., 1993). According to Chang (2005) NaOH is hygroscopic and readily absorbs CO₂ in the air. Equation 3.1 and equation 3.2 shows the chemical reaction of CO₂ with NaOH.



A bucket will be placed for the influent and the effluent each. An automatic stirrer is place at the influent bucket to stir the influent and to avoid the biomass to settle at one place. The bucket for the effluent is placed at the outlet of the anaerobic filter to gather the amount of effluent sample exiting the anaerobic filter. A water pump is also being use to pump the influent from the influent bucket into the anaerobic filter. The pump speed is calibrated to give the appropriate flow rate into the anaerobic filter. Figure 3.1 shows the

picture of the anaerobic digester that is use for this project while Figure 3.2 shows the flow diagram of the anaerobic filter treatment process.

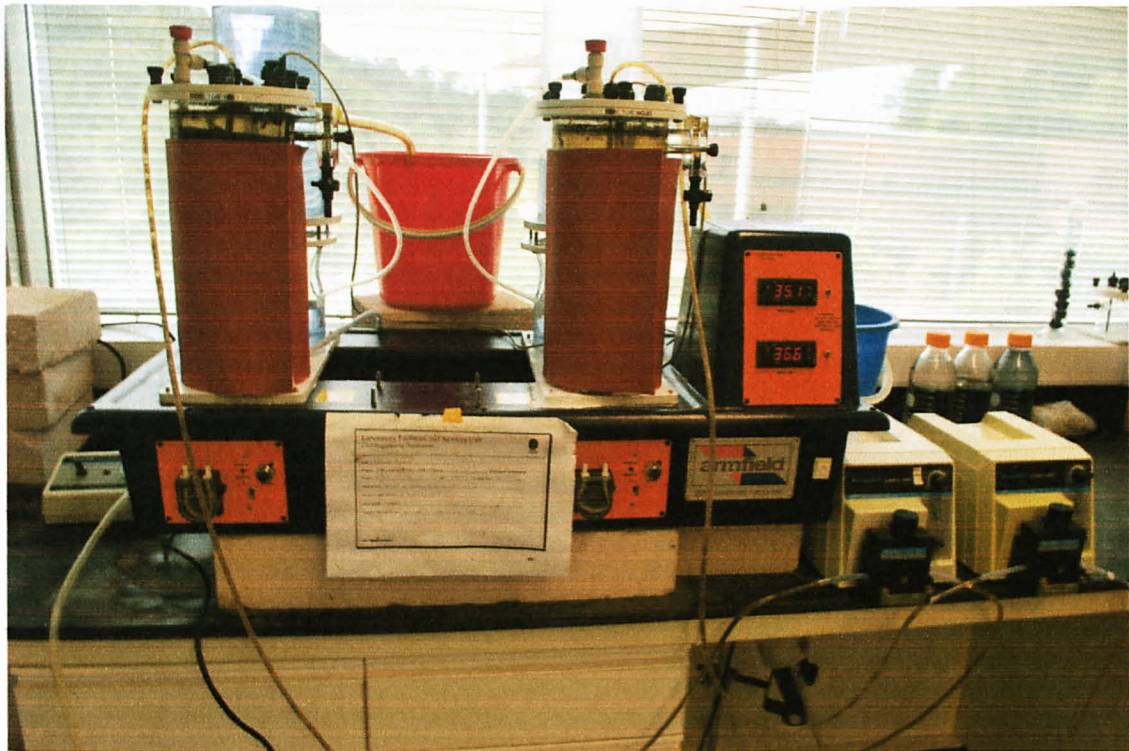


Figure 3.1 Armfield W8 Anaerobic Reactor

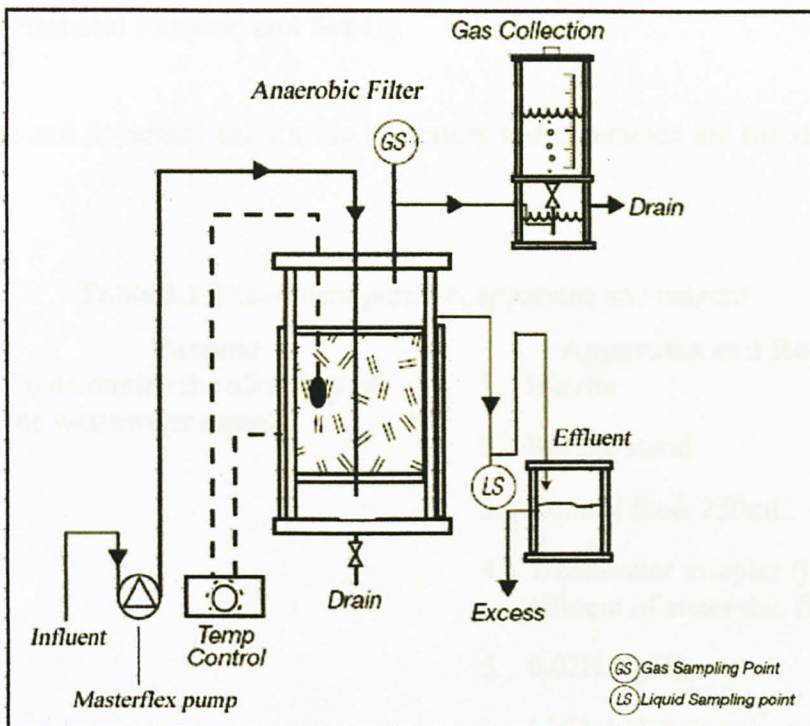


Figure 3.2 Flow diagram of anaerobic filter treatment process

3.3 Laboratory Test And Analysis

To evaluate the performance of the anaerobic filter, laboratory tests are conducted with certain parameters that are relevant in determining the efficiency of using an anaerobic filter. The laboratory tests that are conducted are alkalinity test, Chemical Oxygen Demand (COD) test, pH measurement test and Volatile Fatty Acid (VFA) test. The samples that are used for the laboratory test are from the anaerobic filter influent and effluent. All the laboratory tests conducted are based on the methods recommended in the DR2800 Spectrophotometer Procedures Handbook by Hach Company and the Standard Methods for the Examination of Water and Wastewater published by American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF). Methane production for the anaerobic filter is also recorded from the methane collection tank.

3.4 Experimental Purpose and Set-Up

The purposes and apparatus use for the laboratory test conducted are listed in Table 3.1 below.

Table 3.1 Experiment purpose, apparatus and reagent

Test	Purpose	Apparatus and Reagent
Alkalinity	To determine the alkalinity of the wastewater samples	<ol style="list-style-type: none">1. Burette2. Burette stand3. Conical flask 250mL4. Wastewater samples (influent and effluent of anaerobic filter)5. 0.02N H₂SO₄6. Methyl Orange7. Phenolphthalein
pH	To determine the pH of wastewater samples either it is acid, neutral or alkali	<ol style="list-style-type: none">1. pH meter2. Beaker3. Wastewater samples (influent and effluent of anaerobic filter)
Chemical Oxygen Demand (COD)	To measure the COD equivalent of the organic material in wastewater that can be oxidized chemically using dichromate in acid solution	<ol style="list-style-type: none">1. Reactor – set at 105⁰C2. Pipette3. COD test tube containing potassium dichromate solution4. Wastewater samples (influent and effluent of anaerobic filter)
Volatile Fatty Acids (VFA)	To detect the amount of carbon of more than 6 chains such as oil that is available inside the wastewater	<ol style="list-style-type: none">1. Centrifuge item set2. 10 mL graduated cylinder3. Ethylene Glycol4. Ferric Chloride – Sulphuric Acid solution

- | | |
|--|--|
| | <ol style="list-style-type: none"> 5. Hydroxylamine Hydrochloride solution 6. Pipet 2 mL 7. Pipet, volumetric, Class A, 0.50 mL 8. Pipet, volumetric, Class A, 10 mL 9. Sample cells, 10-20-25 mL 10. Sample cells, 1-inch square glass 11. Sodium Hydroxide Standard solution, 4.5N 12. Sulphuric Acid Standard solution, 19.2N 13. Water bath and rack 14. Deionized water 15. Wastewater samples (influent and effluent of anaerobic filter) |
|--|--|

Source: *Standard Methods for the Examination of Water & Wastewater* and *DR 2800 Spectrophotometer Procedures Handbook*

3.4.1 Alkalinity Measurement

Procedure:

1. 50.0mL aliquot of the sample is taken and is titrate using 0.02N H_2SO_4 with phenolphthalein as indicator (colour changes from pink to colourless) for sample with $\text{pH} > 8.3$. The result gives phenolphthalein alkalinity.
2. Methyl orange is then added into the same aliquot and is then further titrate with 0.02N H_2SO_4 (colour changes from yellow-orange to red). The result gives total alkalinity.
3. The phenolphthalein alkalinity and total alkalinity of the sample is recorded.

		5. Hydroxylamine Hydrochloride solution 6. Pipet 2 mL 7. Pipet, volumetric, Class A, 0.50 mL 8. Pipet, volumetric, Class A, 10 mL 9. Sample cells, 10-20-25 mL 10. Sample cells, 1-inch square glass 11. Sodium Hydroxide Standard solution, 4.5N 12. Sulphuric Acid Standard solution, 19.2N 13. Water bath and rack 14. Deionized water 15. Wastewater samples (influent and effluent of anaerobic filter)
--	--	--

Source: *Standard Methods for the Examination of Water & Wastewater* and *DR 2800 Spectrophotometer Procedures Handbook*

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3. The phenolphthalein alkalinity and total alkalinity of the sample is recorded.

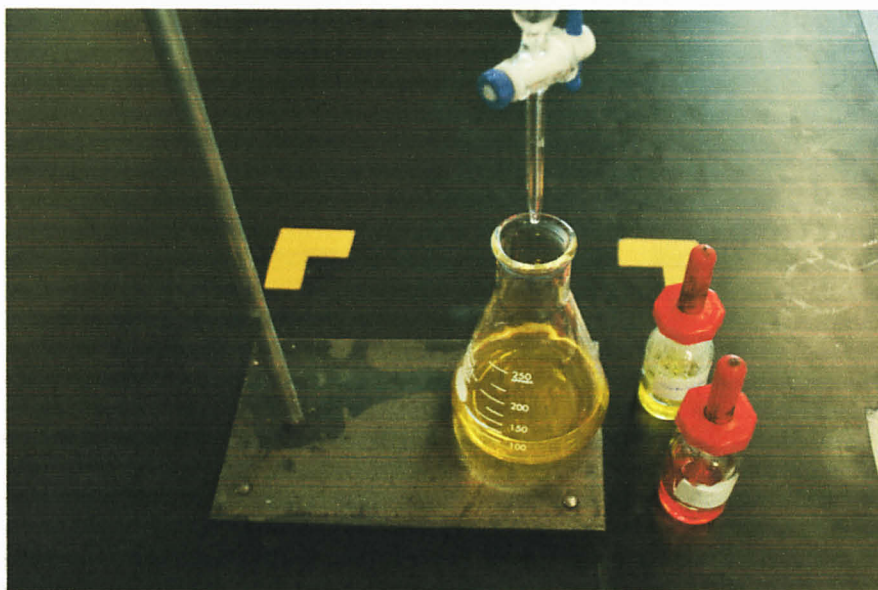


Figure 3.3 Apparatus and reagent for alkalinity test

3.4.2 pH Measurement

Procedure:

1. The Dispenser Button is pressed once.
2. The end of the electrode is inspected for the presence of gel. The Dispenser Button is pressed again if the gel is not oozing.
3. The electrode is placed in the sample and the entire sensing end should submerge and there are no air bubbles under the electrode.
4. The pH value is recorded when the display is stable.
5. The electrode is rinsed thoroughly with deionized water and blot dry.



Figure 3.4 pH meter

3.4.3 Chemical Oxygen Demand (COD)

Procedures:

1. Measured 2mL of wastewater influent sample and is poured into a test tube containing potassium dichromate.
2. The test tube is shaken properly until heat is produced indicating an exothermic process.
3. This procedure is repeated by other groups for other samples (effluent and blank).
4. All the test tubes together with a blank as an indicator were then put into the reactor and left for 2 hours.
5. Three reading are taken down and the average of those reading is calculated.



Figure 3.5 COD test tube and DR 2800 spectrophotometer

3.4.4 Volatile Fatty Acids (VFA)

Procedures:

1. Test for the volatile acids is selected from DR 2800 spectrophotometer.
2. A blank sample is prepared by using a pipet to take 0.5 mL of deionized water into a dry 25-mL sample cell.
3. 25 mL of the sample is filtered using the centrifuge equipment.
4. The sample to be tested is then prepared by taking 0.5 mL of the supernatant using a pipet into a second dry 25-mL sample cell.
5. 1.5 mL of ethylene glycol is pipet into each sample cell and is swirl to mix.
6. 0.2 mL of 19.2N sulphuric acid standard solution is pipet into each cell and is swirl to mix.
7. The cells are then inserted into a boiling water bath for three minutes.
8. The solutions are then taken out from the water bath and are cool to 25°C (until the cell feel cold) with running tap water.
9. 0.5 mL of hydroxylamine hydrochloride solution is pipet using pipet filler into each cell and is swirl to mix.

10. 2.0 mL of 4.5N sodium hydroxide standard solution is pipet using a pipet filler into each cell and is swirl to mix.
11. 10 mL of ferric chloride acid solution is added to each cell and is swirl to mix.
12. 10 mL of deionized water is added to each cell and the cell is cap and invert to mix.
13. 10 mL of the blank solution is transferred from the round 25 mL cell to a clean dry square sample cell.
14. 10 mL of the sample solution is then transferred from the round 25 mL cell to a clean dry square sample cell.
15. A three minutes reaction will begin
16. The sample cell is blotted dry and the blank is inserted immediately into the cell holder with the fill line facing right. The spectrophotometer is then zero and the display will show 0 mg/L HOAC
17. The prepared sample cell is wiped and inserted into the cell holder with the fill line facing right. The reading of the sample is then read.
18. The result is recorded in mg/L HOAC.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 pH value Test

The results for the pH test will be divided into 3 sections which are for 5 days Hydraulic Retention Time (HRT), 4 days HRT and 3 days HRT. Figure 4.1 shows a graph on the pH result for the whole project HRT.

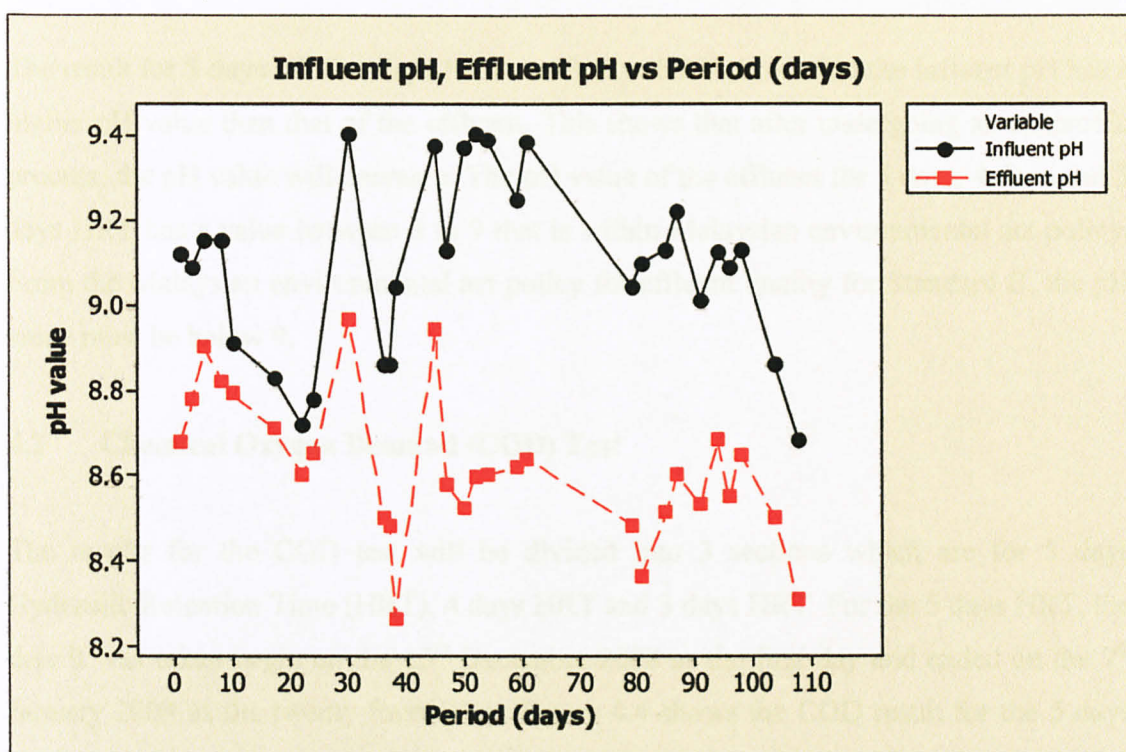


Figure 4.1 Influent pH, Effluent pH vs Period (days)

For the 5 days HRT the period is from day 1 until day 24, the date it was taken begin on the 15th December 2008 as the first day and ended on the 7th January. For the 4 days HRT the period is from day 30 until the day 61, the date it was taken begin on the 13th January 2009 as the first day and ended on the 13th February 2009. For the 3 days HRT the period

is from day 79 until the day 108, the date it was taken begin on the 3rd March 2009 as the first day and ended on the 30th March 2009 as the twenty eight day.

According to Chang (2005), pH value is the measurement of relative activity of hydrogen ions in solution and is use to measure the acidity or the basicity of a solution. The pH value is an important parameter that needs to be monitored especially the pH value of the effluent. The pH of the influent is also important because it is associated with the suitability of the environment in which anaerobic process can take place. The pH value should be within 8 to 10 to allow proper growth of microbes in the anaerobic filter (Show & Tay, 1998).

The result for 5 days HRT, 4 days HRT and 3 days HRT shows that the influent pH has a higher pH value than that of the effluent. This shows that after undergoing an anaerobic process, the pH value will decrease. The pH value of the effluent for 5 days, 4 days and 3 days HRT has a value between 8 to 9 that is within Malaysian environmental act policy. From the Malaysian environmental act policy for effluent quality for Standard B, the pH value must be below 9.

4.2 Chemical Oxygen Demand (COD) Test

The results for the COD test will be divided into 3 sections which are for 5 days Hydraulic Retention Time (HRT), 4 days HRT and 3 days HRT. For the 5 days HRT, the date it was taken begin on the 15th December 2008 as the first day and ended on the 7th January 2009 as the twenty fourth day. Figure 4.4 shows the COD result for the 5 days HRT.

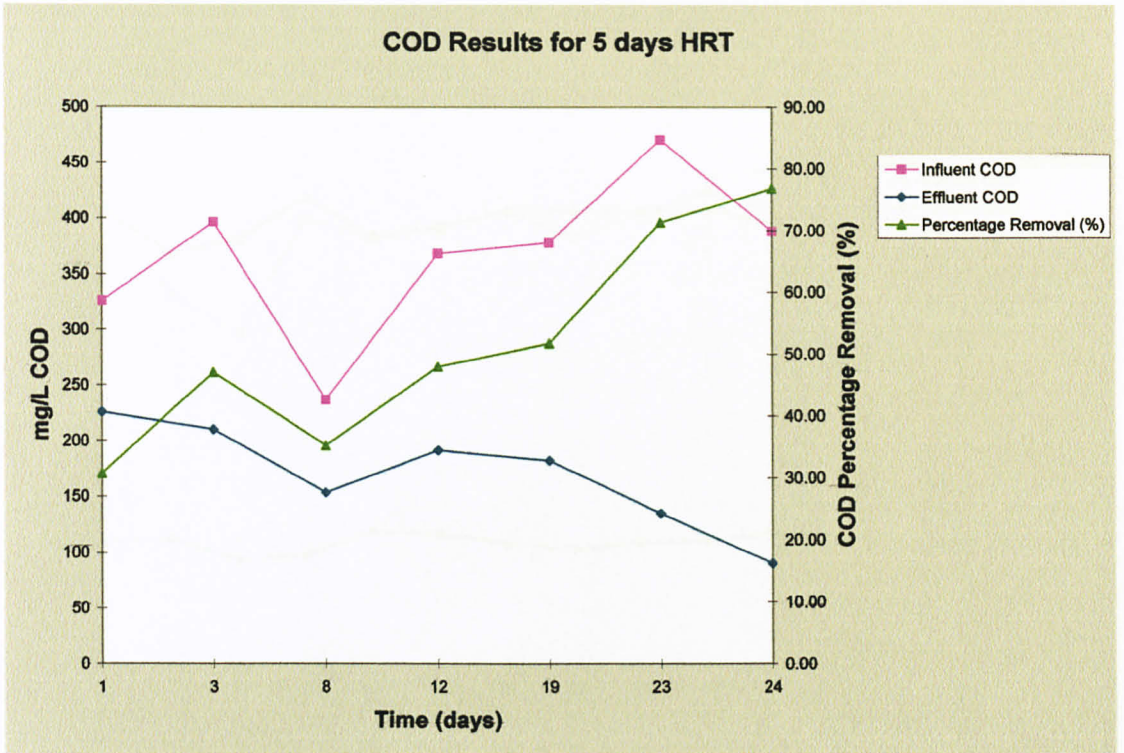


Figure 4.2 COD results for 5 days HRT

Figure 4.5 shows the COD results for the 4 days HRT. the date it was taken begin on the 13th January 2009 as the first day and ended on the 13th February 2009 as the thirty second day.

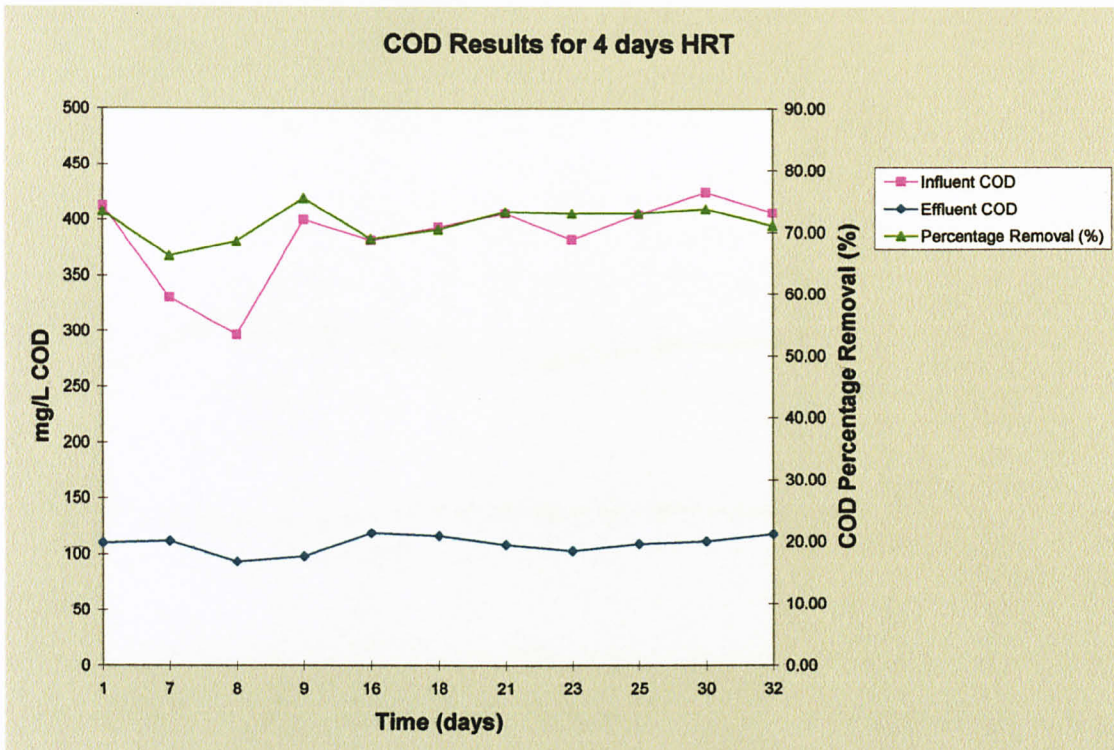


Figure 4.3 COD results for 4 days HRT

Figure 4.6 shows the COD results for the 3 days HRT. the date it was taken begin on the 3rd March 2009 as the first day and ended on the 20th March 2009 as the eighteenth day.

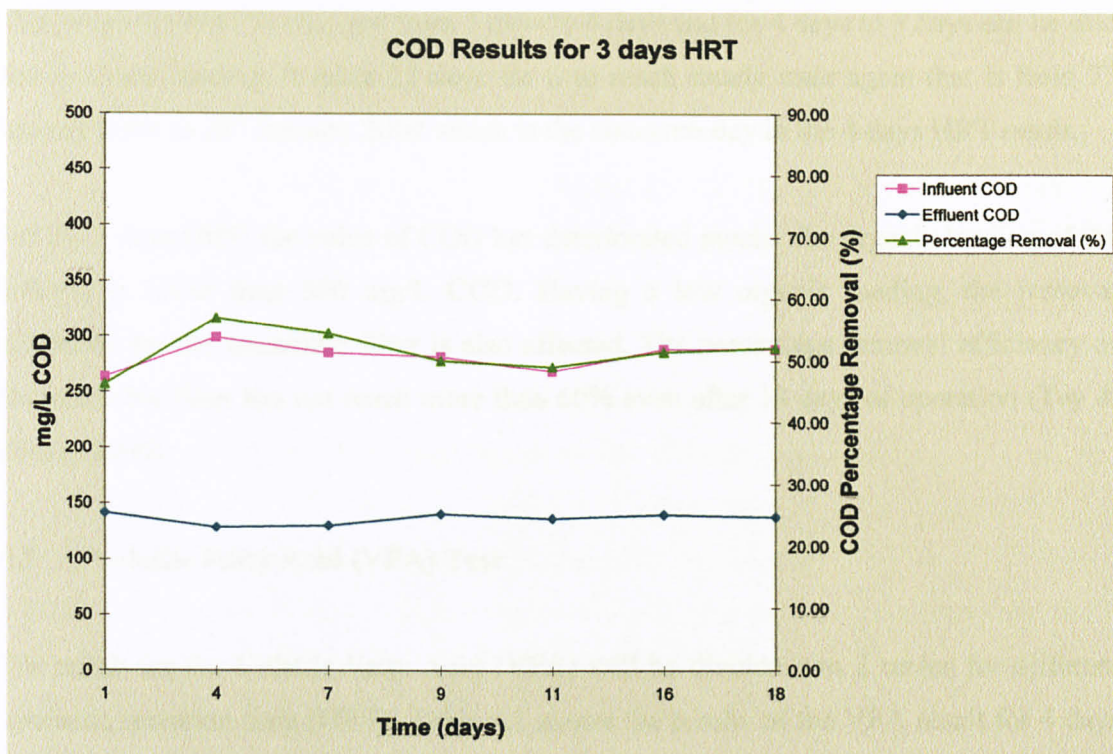


Figure 4.4 COD results for 3 days HRT

In Figure 4.4, the COD removal efficiency shows a good progress after the anaerobic had just started. After 23 days, the COD removal efficiency is more than 70%. After 25 days operating with a Hydraulic Retention Time (HRT) of 5 days, the HRT is change to 4 days. Figure 4.5 shows the COD removal efficiency for a HRT of 4 days. For the first week, the COD level drops due to the change of HRT from 5 days to 4 days. The methanogen and the biomass have not been stabilized. On the 16th day, the COD removal efficiency suddenly drop maybe due to the change of influent from the first barrel of 200 litres of petroleum refinery wastewater to the 2nd barrel and the 3rd barrel of 200 litres of petroleum refinery wastewater that has been sealed before this. For the 3 days HRT, it seems that the wastewater sample to be tested has deteriorated itself due to the cold storage room not functioning well because of certain breakdown for the room system.

According to Tay & Zhang (2000), Anaerobic filter is said to have the lowest tolerance of shock loading if compared to upflow anaerobic sludge blanket (UASB) and anaerobic fluidized bed reactor (AFBR). The change in the removal efficiency of the anaerobic

filter when the HRT is changed from 5 days to 4 days and for 4 days to 3 days can be said due to shock loading. It takes 22 days for it to reach steady state again that is from 7th January 2009 to 28th January 2009 which is the sixteenth day in the 4 days HRT result.

For the 3 days HRT, the value of COD has deteriorated much. The organic loading of the influent is lower than 300 mg/L COD. Having a low organic loading, the removal efficiency for the anaerobic filter is also affected. The percentage removal efficiency of the anaerobic filter has not reach more than 60% even after 18 days of operation (Tay & Zhang, 2000).

4.3 Volatile Fatty Acid (VFA) Test

The result for the Volatile Fatty Acid (VFA) will be divided into 2 tables for different hydraulic retention time (HRT). Table 4.1 shows the results of the VFA result for 4 days HRT and Table 4.2 shows the VFA results for 3 days HRT.

Table 4.1 VFA result for 4 days HRT

Period (days)	Date	Influent VFA (mg/ L HOAC)	Effluent VFA (mg/ L HOAC)
1	30/1/2009	9.3	11
12	10/2/2009	20	33
14	12/2/2009	24	18

Table 4.2 VFA result for 3 days HRT

Period (days)	Date	Influent VFA (mg/ L HOAC)	Effluent VFA (mg/ L HOAC)
1	10/3/2009	26	19
2	12/3/2009	26	19
7	17/3/2009	24	20

The VFA test was conducted to the influent wastewater entering the anaerobic filter and also to the effluent that exits the anaerobic filter. According to Chang (2005), VFA test are conducted to determine the amount of carbon of more than 6 chains that can be detected inside a sample. Such complicated carbon chains are from petroleum product and thus it is a test to detect the amount of oil inside the petroleum refinery wastewater.

As can be seen in Table 4.1 and Table 4.2, the VFA value is very low. This is to be expected. According to Metcalf & Eddy (2004), wastewater undergoes chemical treatment process before it goes to the biological treatment process. The purpose of chemical treatment process is to remove chemical substances such as excess oil that can be found inside the wastewater.

4.4 Methane Gas Production Results

Methane gas production is recorded based on the methane gas collector that is situated beside the anaerobic filter reactor. Figure 4.7 shows the result of the methane gas production for 4 days hydraulic retention time (HRT) that starts from the 23rd January 2009 to 11th February 2009. While Figure 4.8 shows the methane gas production for 3 days HRT that starts from the 3rd March 2009 to 30th March 2009.

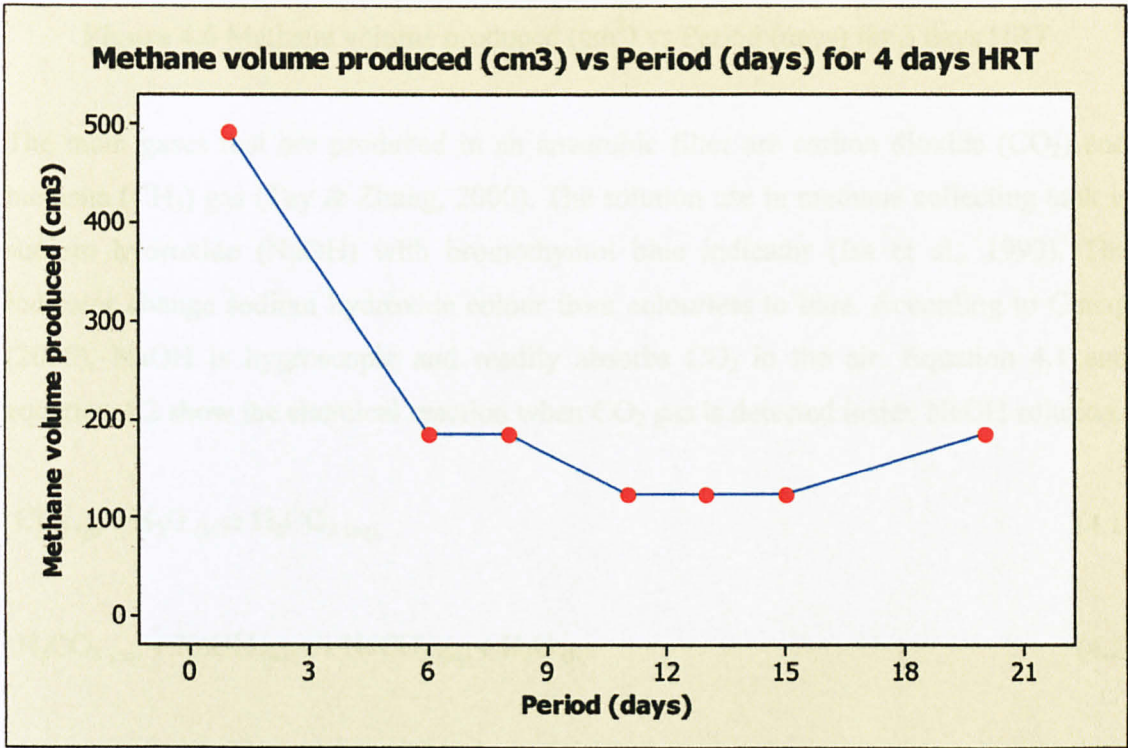


Figure 4.5 Methane volume produced (cm³) vs Period (days) for 4 days HRT

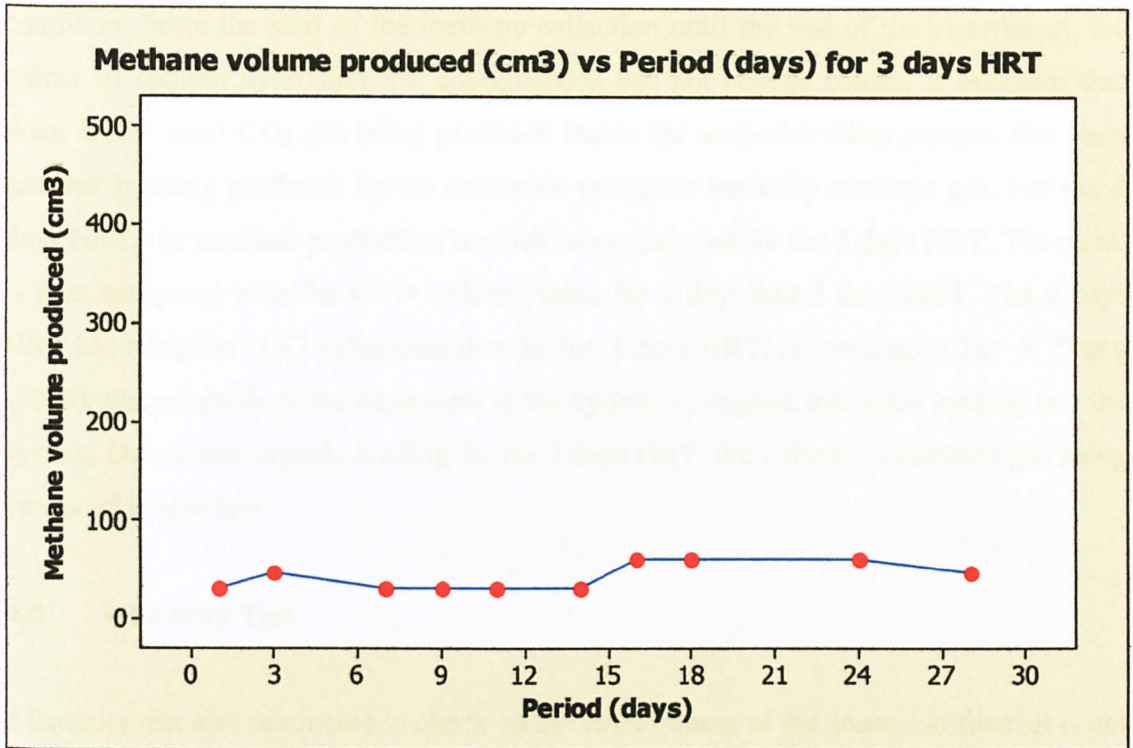


Figure 4.6 Methane volume produced (cm³) vs Period (days) for 3 days HRT

The main gases that are produced in an anaerobic filter are carbon dioxide (CO₂) and methane (CH₃) gas (Tay & Zhang, 2000). The solution use in methane collecting tank is sodium hydroxide (NaOH) with bromothymol blue indicator (Isa et al., 1993). The indicator change sodium hydroxide colour from colourless to blue. According to Chang (2005), NaOH is hygroscopic and readily absorbs CO₂ in the air. Equation 4.1 and equation 4.2 show the chemical reaction when CO₂ gas is detected inside NaOH solution.



When CO₂ react with water (H₂O), carbonate acid (H₂CO₃) an acidic aqueous solution is made. Bromothymol blue indicator will change colour from blue to yellow in acidic

condition. From the start of the methane collection until the end of the experiment, the colour of sodium hydroxide 5% concentration has not change colour. It indicates that there is not much CO₂ gas being produced inside the anaerobic filter reactor. The main gas that is being produced by the anaerobic reactor is basically methane gas. For the 4 days HRT, the methane production is much more than that for the 3 days HRT. The result is then compared with the COD influent value for 4 days and 3 days HRT. The 4 days HRT has a higher COD value than that for the 3 days HRT. According to Tay & Zhang (2000), the gas produce are dependent to the hydraulic, organic and toxic loading into the system. Due to low organic loading for the 3 days HRT, the volume of methane gas being produced is also low.

4.5 Alkalinity Test

Alkalinity test was conducted to check on the environment of the anaerobic filter. It is not advisable to run an anaerobic process with a low alkalinity level. A constant observation of the alkalinity is needed to make sure that the environment of the filter reactor is appropriate for the methanogenesis bacteria to live. (Metcalf & Eddy, 2004)

Figure 4.9 shows the influent and the effluent alkalinity (mg/L CaCO₃) with respect to period in days. The period is taken from the start of the anaerobic filter to the end of its operation.

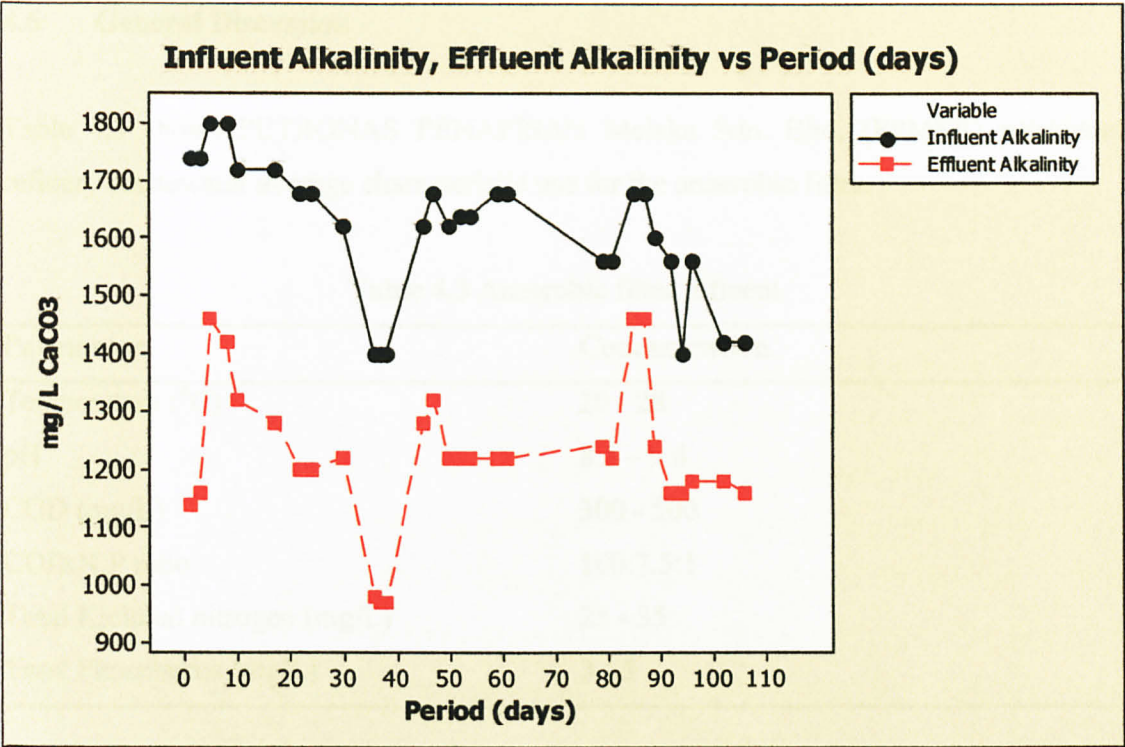


Figure 4.7 Influent Alkalinity (mg/L CaCO₃), Effluent Alkalinity (mg/L CaCO₃) vs Period (days)

The alkalinity of the sample wastewater without adding sodium bicarbonate is 400 – 500 mg/L CaCO₃. According to Metcalf & Eddy (2004), the best condition inside an anaerobic reactor is 1000 – 5000 mg/L CaCO₃. In order to maintain a good environment for the anaerobic process to occur, the influent is to have an alkalinity value of 1000 – 5000 mg/L CaCO₃.

4.6 General Discussion

Table 4.3 shows PETRONAS PENAPISAN Melaka Sdn. Bhd. (PPMSB) petroleum refinery wastewater average characteristic use for the anaerobic filter.

Table 4.3 Anaerobic filter influent

Parameter	Concentration
Temperature (°C)	20 - 28
pH	8.5 – 9.4
COD (mg/L)	300 - 500
COD:N:P ratio	100:7.5:1
Total Kjeldhal nitrogen (mg/L)	25 - 35
Total Phosphorus (mg/L)	3 - 5

From the result of the methane gas production, methane gas is being produced using petroleum refinery wastewater. If methane gas is being produced, there is high probability that methanogen are inside the anaerobic filter. The 3 main methanogen are *Syntrophomonas* spp., *Methanothrix* spp. and H₂-utilizing *Methanococcus* spp. *Syntrophomonas* spp. oxidize butanoic acid to ethanoic acid and *Methanothrix* spp. decarboxylated ethanoic acid to carbon dioxide (CO₂) and methane (CH₄). *Methanococcus* spp. will then reduce CO₂ to CH₄ and thus increase the concentration of methane in the biogas (Chua et al., 1996).

As bromothymol blue indicator that is use with sodium hydroxide (NaOH) with concentration of 5% inside the biogas collection tank did not change colour, it can be an indicator that *Methanococcus* spp. is inside the anaerobic filter. A test such as scanning electron microscope (SEM) should be conducted on the biomass to confirm the type of methanogen inhabiting inside the anaerobic filter.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

An anaerobic filter has a Chemical Oxygen Demand (COD) removal efficiency of more than 70% when the anaerobic filter has stabilized. The COD value using an anaerobic filter is below 100 mg/L COD when the removal efficiency is more than 75%. A COD value of below 100mg/L COD is important to comply with the Malaysian Environmental Quality Act 1974 Regulation 1978. The hydraulic retention time (HRT) based on this experiment can be said to be 4 days based on the COD removal efficiency. The pH value of treating petroleum refinery wastewater using an anaerobic filter is from 8 to 9. A range of 8 to 9 for the pH value complies with Malaysian Environmental Quality Act 1974 Regulation 1978 for industrial effluent. Anaerobic filter using petroleum refinery wastewater produces methane gas. The volatile fatty acids (VFA) for the influent and the effluent exiting the anaerobic filter for this project are very low. The amount of carbon chain found inside the sample is very little. The methane production for this project is quite low. The amount of gases being produced is dependent to the amount of organic, hydraulic and toxic loading to the anaerobic filter (Tay & Zhang 2000).

5.2 Recommendation

In making sure that the possible error that can occur is minimize, some recommendations to the study is proposed. It is important that the result of the study is as accurate as possible so that it can become a future guidance to further study the usage of using an anaerobic filter to treat wastewater. The recommendations for the study are:

1. The wastewater sample should be taken frequently from the petroleum refinery wastewater treatment plant because certain parameter may vary according to what it is being use, especially during the oil refinery plant shutdown when a lot of water is being use to clean the refinery equipment.

2. Laboratory tests should be conducted immediately after the sample is obtained to avoid some parameter to deteriorate with time.
3. Transporting the wastewater to be used to conduct the experiment should be well planned, the usage of a cold storage vehicle is important if the laboratory to conduct the experiment is far to avoid deterioration of the sample.

APPENDICES

APPENDIX I : Case Study

APPENDIX II : PETRONAS PENAPISAN Melaka run, effluent and treated water quality

APPENDIX III : PETRONAS PENAPISAN Melaka effluent treating tank

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APPENDIX VII : pH Results

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APPENDICES

APPENDIX I : Gantt Chart

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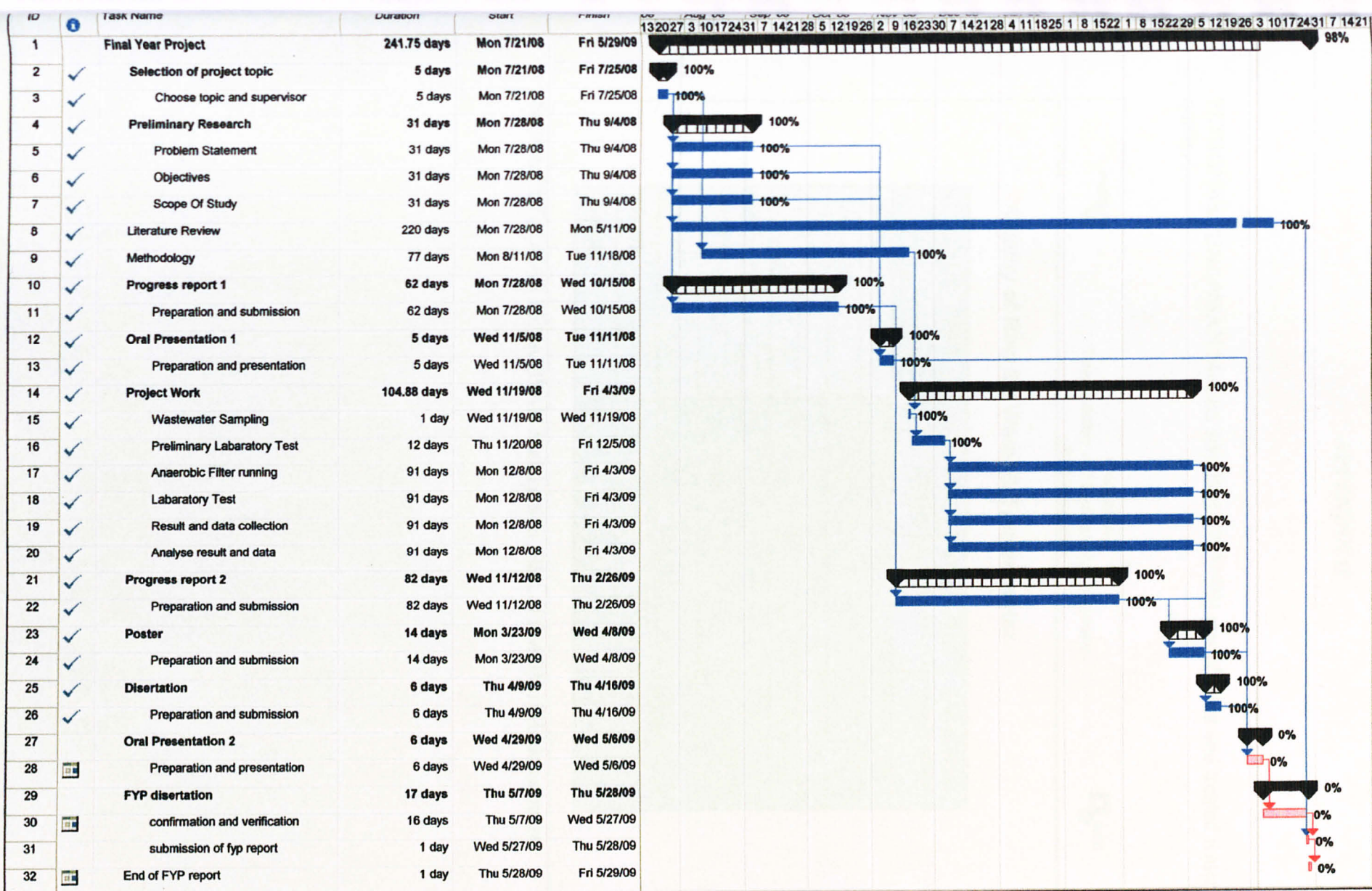
APPENDIX IV : Masterflex 4 phase water pump flow rate vs pump scale

APPENDIX V : Alkalinity Results

APPENDIX VI: Chemical Oxygen Demand (COD) Results



APPENDIX VII : pH Results

APPENDIX VIII : Methane Production Results



APPENDIX II

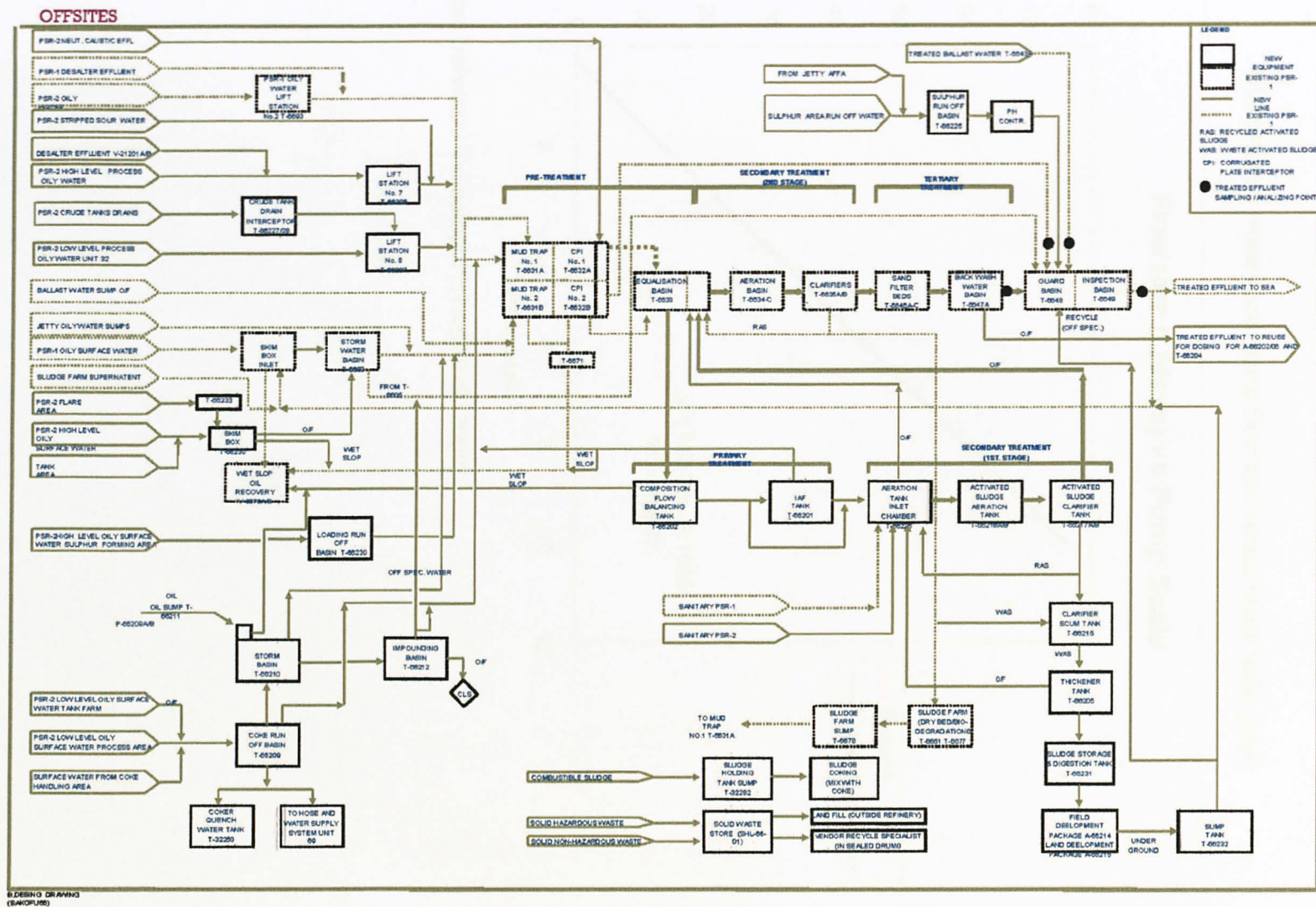
PETRONAS PENAPISAN Melaka Sdn. Bhd. (PPMSB) raw effluent and treated water quality:

<div>PPMSB/MRC Health, Safety and Environment Department ETS Awareness</div>			
● Quality of Raw Eff Water & Treated water			
	<i>Oily Water (Average)</i>	<i>Oily Surface Water(Average)</i>	<i>Treated Water (DOE Spec)</i>
<i>pH</i>	7.5	7	5.5 - 9
<i>Temp o C</i>	38	25	40
<i>BOD mg/l</i>	232	10	50
<i>COD mg/l</i>	613	20	100 max
<i>S.Solids mg/l</i>	162	20	100 max
<i>Oil & Grease mg/l</i>	350	50	10 max
<i>Chloride</i>	500	-	-
<i>Phenol</i>	10	-	1 max
<i>Sulphide</i>	15	-	0.5

Source: PETRONAS PENAPISAN Melaka Sdn. Bhd. (PPMSB) HSE department

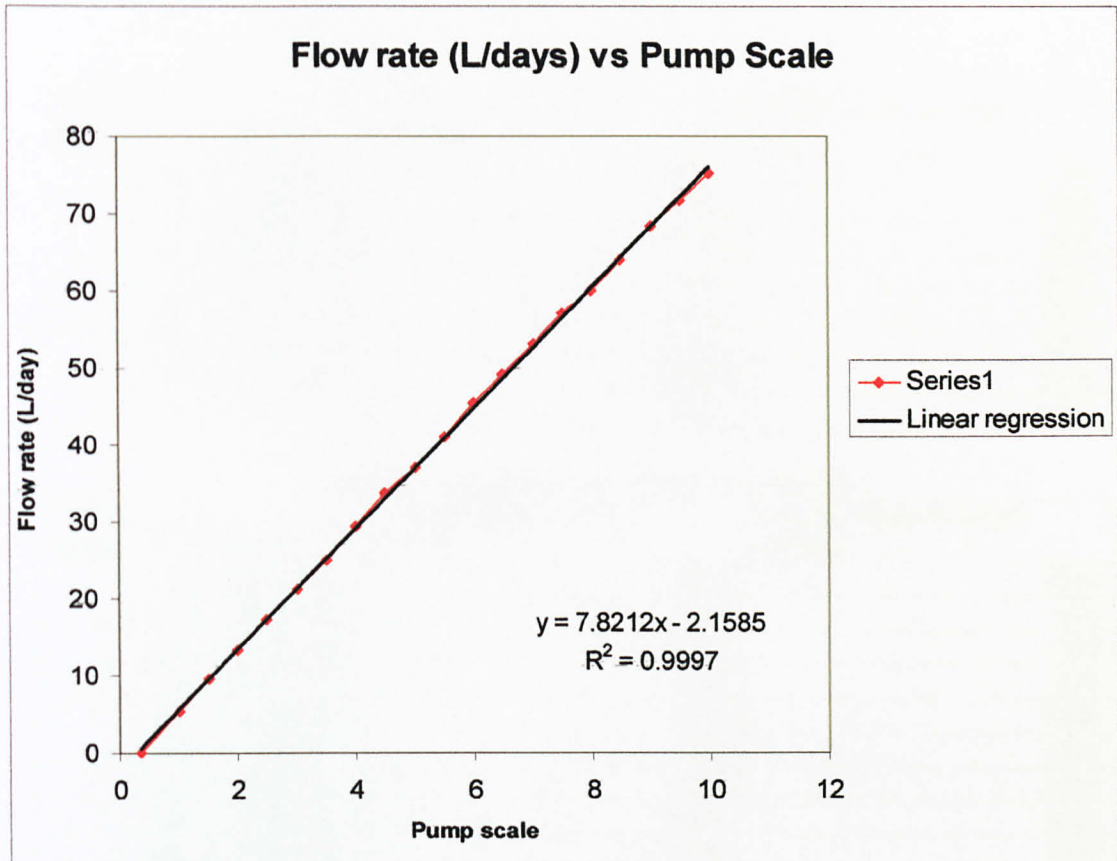
APPENDIX III

● EFFLUENT TREATING UNIT (UNIT 66) - SIMPLIFIED BLOCK FLOW DIAGRAM



APPENDIX IV

Masterflex 4 phase water pump flow rate versus pump scale graph



Source: Universiti Teknologi PETRONAS (2009)

APPENDIX V

Alkalinity Results

Table V.1 Alkalinity results for 5 days HRT

Period (days)	Date	Influent Alkalinity(mg/L CaCO ₃)	Effluent Alkalinity (mg/L CaCO ₃)
1	15/12/2008	1740	1140
3	17/12/2008	1740	1160
5	19/12/2008	1800	1460
8	22/12/2008	1800	1420
10	24/12/2008	1720	1320
17	31/12/2009	1720	1280
22	5/1/2009	1680	1200
24	7/1/2009	1680	1200

Table V.2 Alkalinity results for 4 days HRT

Period (days)	Date	Influent Alkalinity(mg/L CaCO ₃)	Effluent Alkalinity (mg/L CaCO ₃)
1	13/1/2009	1620	1220
7	19/1/2009	1400	980
8	20/1/2009	1400	970
9	21/1/2009	1400	970
16	28/1/2009	1620	1280
18	30/1/2009	1680	1320
21	2/2/2009	1620	1220
23	4/2/2009	1640	1220
25	6/2/2009	1640	1220
30	11/2/2009	1680	1220
32	13/2/2009	1680	1220

Table V.3 Alkalinity results for 3 days HRT

Period (days)	Date	Influent Alkalinity(mg/L CaCO ₃)	Effluent Alkalinity (mg/L CaCO ₃)
1	3/3/2009	1560	1240
3	5/3/2009	1560	1220
7	9/3/2009	1680	1460
9	11/3/2009	1680	1460
11	13/3/2009	1600	1240
14	16/3/2009	1560	1160
16	18/3/2009	1400	1160
18	20/3/2009	1560	1180
26	26/3/2009	1420	1180
30	30/3/2009	1420	1160

APPENDIX VI

Chemical Oxygen Demand (COD) Results

Table VI.1 COD results for 5 days HRT

Period(days)	Date	Influent COD (mg/L COD)	Effluent COD (mg/L COD)	Percentage Removal (%)
1	15/12/2008	325.67	225.67	30.71
3	17/12/2008	396.67	210	47.06
8	22/12/2008	236.67	153.33	35.21
12	26/12/2008	368.33	191.67	47.96
19	2/1/2009	378	182.33	51.76
23	6/1/2009	470.67	135	71.32
24	7/1/2009	388.33	90	76.82

Table VI.2 COD results for 4 days HRT

Period (days)	Date	Influent COD (mg/L COD)	Effluent COD (mg/L COD)	Percentage Removal (%)
1	13/1/2009	413	110	73.37
7	19/1/2009	330	111.7	66.15
8	20/1/2009	296.7	93.3	68.55
9	21/1/2009	400	98	75.50
16	28/1/2009	381.67	118.67	68.91
18	30/1/2009	393.33	116.33	70.42
21	2/2/2009	405.67	108.33	73.30
23	4/2/2009	382.5	103	73.07
25	6/2/2009	405	109	73.09
30	11/2/2009	425	111.33	73.80
32	13/2/2009	406.67	117.67	71.06

Table VI.3 COD results for 3 days HRT

Period (days)	Date	Influent COD (mg/L COD)	Effluent COD (mg/L COD)	Percentage Removal (%)
1	3/3/2009	263.33	141.67	46.20
4	6/3/2009	298.67	128.67	56.92
7	9/3/2009	285	130	54.39
9	11/3/2009	281.67	140.67	50.06
11	13/3/2009	268.33	136.67	49.07
16	18/3/2009	288.33	140	51.44
18	20/3/2009	288.33	138	52.14

APPENDIX VII

pH Results

Table VII.1 pH results for 5 days HRT

Period (days)	Date	Influent pH	Effluent pH
1	15/12/2008	9.12	8.68
3	17/12/2008	9.09	8.78
5	19/12/2008	9.15	8.9
8	22/12/2008	9.15	8.82
10	24/12/2008	8.91	8.79
17	31/12/2008	8.83	8.71
22	5/1/2009	8.72	8.6
24	7/1/2009	8.78	8.65

Table VII.2 pH results for 4 days HRT

Period (days)	Date	Influent pH	Effluent pH
1	13/1/2009	9.4	8.964
7	19/1/2009	8.86	8.499
8	20/1/2009	8.86	8.484
9	21/1/2009	9.04	8.266
16	28/1/2009	9.373	8.94
18	30/1/2009	9.13	8.577
21	2/2/2009	9.371	8.522
23	4/2/2009	9.402	8.598
25	6/2/2009	9.388	8.602
30	11/2/2009	9.248	8.62
32	13/2/2009	9.384	8.638

Table VII.3 pH results for 3 days HRT

Period (days)	Date	Influent pH	Effluent pH
1	3/3/2009	9.04	8.484
3	5/3/2009	9.098	8.364
7	9/3/2009	9.13	8.513
9	11/3/2009	9.221	8.602
11	13/3/2009	9.011	8.531
14	16/3/2009	9.122	8.681
16	18/3/2009	9.089	8.549
18	20/3/2009	9.128	8.648
26	26/3/2009	8.862	8.499
30	30/3/2009	8.684	8.308

APPENDIX VIII

Methane Production Results

Table VIII.1 Methane production results for 4 days HRT

Period (days)	Date	Methane Production (cm3)
1	23/1/2009	492.6
6	28/1/2009	184.73
8	30/1/2009	184.73
11	2/2/2009	123.15
13	4/2/2009	123.15
15	6/2/2009	123.15
20	11/2/2009	184.73

Table VII.2 Methane production results for 3 days HRT

Period (days)	Date	Methane Production (cm3)
1	3/3/2009	30.79
3	5/3/2009	46.18
7	9/3/2009	30.79
9	11/3/2009	30.79
11	13/3/2009	30.79
14	16/3/2009	30.79
16	18/3/2009	61.58
18	20/3/2009	61.58
24	26/3/2009	61.58
28	30/3/2009	46.18