TREATMENT OF PETROLEUM REFINERY WASTEWATER USING UPFLOW ANAEROBIC SLUDGE BLANKET (UASB) REACTOR

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Treatment of Petroleum Refinery Wastewater using Upflow Anaerobic Sludge Blanket (UASB) Reactor

By

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Dissertation submitted in partial fulfillment of
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CERTIFICATION OF APPROVAL

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Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS
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June 2009

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.

Amro Ahmad Ali Abdallah

Abstract

The project is to study the treatment of petroleum refinery's wastewater using up-flow anaerobic sludge blanket, and the experiment was carried out in a laboratory scale upflow anaerobic sludge blanket reactor (UASB) with a volume of 5 liters. The study of removal efficiency of COD and alkalinity has been studied in addition to the volatile fatty acid (VFA) and methane gas collection.

In this study the UASB was used for treating wastewater from a petroleum refinery, where the current system used at the refinery is activated sludge system. The UASB was able to achieve an average of 70% removal of COD with an effluent concentration of 90 mg/l, 30% removal of alkalinity, whereas the influent concentration of COD is average of 450 mg/l.

The experiment was conducted under different hydraulic retention times (HRT), starting with 5 days hydraulic retention time, and then changed to 4 days HRT to check the removal efficiencies under different condition. At 4 days HRT the highest removal efficiency for the COD was obtained and the reactor had acted significantly.

Finally the HRT was changed into 3 days HRT, and more test results were conducted for more analysis and investigation.

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In the name of Allah, the Most Gracious and the Most Merciful

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CHAPTER 1

Introduction

1.1 Background of study:

Wastewater treatment is very important currently, and must be carried out by for any industry that has water to discharge, In Malaysia there are two petroleum refineries one is located at the north east of peninsula Malaysia at Terengganu and the other is in Melaka where the wastewater for the study was taken from. The refining process need a huge amount of water for its processes, as a result of the process a large amount of the water used need to be discharged. Therefore there is need to construct a wastewater treatment plant that is able to treat the wastewater discharged from the refinery to a quality as a recommended by the Department of Environment and finally release to the nearest water shed (the ocean) while considering the high efficiency in removal with low cost basis.

This study focuses on treating petroleum refinery wastewater (sour water) using upflow anaerobic sludge blanket (UASB) reactor. The UASB is an anaerobic reactor, which means the reactor would work and microorganisms will metabolize organic matter in the absence of oxygen.

The reasons of using UASB (Speece, 1996) are its low energy requirements, and unlike the conventional processes of treatment, UASB doesn't require any mechanical aerator. Also the UASB reactor uses small area to setup which is 5 to 10 times less area required than the conventional aerobic digesters. In addition to that the UASB system is very simple and at its best operation conditions it could maintain a high removal efficiency of COD. And finally and the most important is UASB produces biogas (methane gas) which can be used as a bio fuel for power generation.

The only problem is that the UASB require a long start up time to operate but this start up time can be reduced if acclimatized sludge is used.

1.2 Problem statement

Oil and gas industries are facing many challenges and difficulties to meet the environmental regulation, as a huge amount of wastewater is used for cooling the systems and distilling and also during flushing during maintenance and shutting down which need to be discharged later (al Zarooni and Elshorbagy, 2005). As a general rule, approximately 3.5–5m^3 of wastewater are generated per ton of crude oil processed when cooling water is recycled (Dold, 1989).

The treatment of a petroleum refinery wastewater using upflow anaerobic sludge blanket reactor (UASB), and discharge it after treatment are in accordance to the Department of Environment (DOE) Malaysia standards for effluent discharge.

1.3 Scope of the work

The study will cover the following topics:

1. A lab scale UASB with a total volume of 5 liters will be set up with the wastewater brought from the refinery and stored at the lab.
2. Sampling and lab tests will focus on the COD removal efficiency, alkalinity, volatile fatty acids and the amount of biogas produced.
3. The experiment will run at the Methophilic condition with a temperature of 35 °C.

1.4 Objectives:

The main objective of this study is to treat Petroleum refinery wastewater using upflow anaerobic sludge blanket (UASB) reactor, and to compare its effectiveness with aerobic treatment methods, which is currently being used at the refinery.

The effluent characteristics were studied under different hydraulic retention time (HRT) conditions.

CHAPTER 2

LITERATURE REVIEW

2.1 Refinery processes

Petroleum refining involves the distillation of crude oil into final useful products such as gasoline, gas oil; kerosene and jet fuel (Al Zarooni and Elshorbagy, 2005). The refined products are produced after a series of separation and treatment processes. After initial crude desalting and fractionation, several treatment and conversion processes are employed to reach the final blending stocks. Examples of some conversion processes include thermal and catalytic cracking, steam and catalytic reforming, Isomerization, alkylation and lube oil units. Treatment processes on the other hand include naphtha and gas oil desulphurization, sour water strippers and catalyst regeneration units (W. Soko, 2003); (Al Zarooni and Elshorbagy, 2005).

2.2 Effluent Standards:

Large quantities of wastewater are discharged after refining and separation processes have taken place. This wastewater must be treated and then discharged in an appropriate way and follow the quality standards for effluent wastewater that is given by the Department of Environment, Malaysia.

Table 2.1 shows the effluent characteristic's standard .This study will follow standard B due to the direct discharge into the marine outfall.

Table 2.1: Effluent quality standard, Department of Environment (DOE), Malaysia

Parameter	Unites	Standard A	Standard B
pH		6 to 9	5.5 to 9
BOD5	mg/l	20	50
COD	mg/l	50	100
Suspended Solids	mg/l	50	100
Phenol	mg/l	0.001	1
Oil & Grease	mg/l	Not detectable	10
Mercury	mg/l	0.005	0.05
Cadmium	mg/l	0.01	0.02
Arsenic	mg/l	0.05	0.1
Cyanide	mg/l	0.05	0.1
Lead	mg/l	0.1	0.5
Copper	mg/l	0.2	1.0
Manganese	mg/l	0.2	1.0
Nickel	mg/l	0.2	1.0
Tin	mg/l	0.2	1.0
Iron	mg/l	1	5
Sulfide	mg/l	0.5	0.5

The refining processes use large amount of water, especially for cooling systems, desalting water, stripping steam, and water used for flushing during maintenance and shutdown (Dold 1989). In addition, surface water runoff and sanitary wastewaters are accounted in the wastewater system. The quantity of wastewater generated and their characteristics depend on the process itself. As a general rule, approximately 3.5–5 m^3 of wastewater are generated per tonne of crude oil processed when cooling water is recycled (Dold 1989).

The amount of discharged water from the refinery processes is relatively high and should be treated properly.

2.3 Refinery wastewater characteristics

The refinery wastewater has different pollutants; the most important pollutants are suspended solids, COD, Phenol, ammonia, oil & grease, and heavy metals.

The wastewater treatment plant at the refinery is an aerobic one, however there are some same steps to be included if anaerobic treatment would be implemented such as oil skimming and also the CPI tank.

The environmental quality laboratory tests that normally conducted at the refinery are:

1. Chemical oxygen demand (COD)
2. Phenol
3. Ammonia
4. Oil and grease

The management at PETRONAS refinery in Melaka has provided us with some valuable information and papers such us the wastewater characteristics, table 2.2 below show the information provided:

Table 2.2: Sour Water Characteristics (source: Petronas refinery, HSE department)

Parameter	Range
COD (mg/L)	400–600
BOD_5 (mg/L)	232-250
Phenol (mg/L)	10-20
TSS (mg/L)	70-100
pH	7.5–8.2
Sulfide (mg/L)	15
Oil & Grease (mg/L)	350

Other studies about the wastewater characteristics from the refinery discharge (Coelho et al., 2006) is shown in Table 2.3

Table 2.3: Refinery Wastewater Characteristics (Coelho et al, 2006)

Parameter	Average
COD (mg/l)	850–1020
DOC (mg/l)	300–440
BOD5 (mg/l)	570
Phenol (mg/l)	98–128
Ammonia (mg/l)	5.1–21.1
TSS (mg/l)	Not detected
VSS (mg/l)	Not detected
Turbidity (NTU)	22-52
Sulfide (mg/l)	15-23
oil & grease (mg/l)	12.7

2.4 Refinery Wastewater Treatment current system (Activated Sludge Process)

The Petronas refinery in Melaka is currently using the activated sludge process, which is a process that depends on applying oxygen by some mechanical aerators, this oxygen is required for respiration by the microorganisms which allow it to develop and could degrade other pollutants (Metcalf & eddy, 2005).

The refinery wastewater plant at Melaka has the following treatment steps:

2.4.1 Screens:

The screens are used to remove objects with diameter of more than 1 inch, and these screens are cleaned manually

2.4.2 Corrugated Plate Interceptor (CPI) tank

CPI tank is a device designed to separate gross amounts of oil and suspended solids from the wastewater influent (al Zarooni and Elshorbagy, 2005), it works with stocks gravity law, this device is very important because it send the supernatant oil to reprocess at the refinery using oil skimmer.

2.4.3 Equalization tank

This small tank is used for the oil floating on the top of the water to be skimmed off. This also the tank where the oily water and the oily surface water mixed.

2.4.4 Aeration tank (1)

The aeration tank is huge tank with large water volume, accompanied by mechanical aerator, so that the wastewater can be aerated. The oxygen molecules will be increased in the water for the microorganisms to develop.

2.4.5 Clarifier (1)

This represents the sedimentation tank at the system, the main purpose it to collect the floating sludge at the top and remove it, and then will be sent to the sludge thickeners for disposing, the sludge age for the clarifier is 3 days, this clarifier is used to reduce the COD from 700 mg/L to 200-300 mg/L

2.4.6 Aeration Tank (2)

The aeration tank for the second stage treatment, was aimed to reduce the COD removal to further extent, the wastewater was aerated and then released into the secondary clarifier.

2.4.7 Clarifier (2)

This clarifier is to reduce the COD from 300mg/L to less than 100 mg/L

2.4.8 Evaporation and settling bonds

These bonds are used to retain the water from the clarifier to be discharged to the sea. At this point the effluent lab testing are carried out, if the effluent pollutants meet the standards, then it will be discharged at the sea (1.8 Km far from the shore), if the tests doesn't meet the standards, then the water should be pumped to be recycled again.

Figure 2.1 below give the framework for the aerobic process that is implemented at the Petronas refinery.

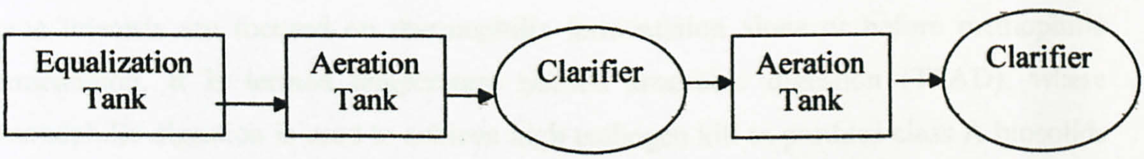

Figure 2.1: flow chart of the Activated sludge system at the refinery

2.5 Advantages of anaerobic digestion:

There are several advantages of anaerobic digestion (Metcalf and Eddy, 2005), compared to the treatment using aerobic digestion.
Some of these advantages are stated below:

1. pollutant are transformed into methane (fuel gas), and carbon dioxide
2. lower biomass growth compared to aerobic process
3. fewer nutrients required
4. lower energy consumption

5. low volume and space demand
6. with acclimation most organic compound can be transformed

2.6 Anaerobic Digestion

Anaerobic digestion is a series of processes in which microorganisms break down biodegradable material in the absence of oxygen.

It include anaerobic suspended growth, upflow and down flow anaerobic attached growth, fluidized bed attached growth, upflow anaerobic sludge blanket and anaerobic lagoons, anaerobic treatment also effectively removes organic matter at low temperatures as reviewed by (Lettinga, 2001).

Anaerobic fermentation and oxidation processes are used for the treatment of waste sludge and also high strength organic wastes.

Although most fermentation processes are done in methophilic condition (30° - 35° C), some interests are focused on thermophilic fermentation alone or before methophilic fermentation. It is termed temperature phased anaerobic digestion (TPAD), where thermophilic digestion is used to achieve high pathogen kill to produce class A biosolids (Tchobanoglous et al., 2003).

(Leal, 2004) presented that the anaerobic digestion process in four major steps:

- **Hydrolysis:**

  The complex organic matter is decomposed into simple soluble organic particles and water is used to split the chemical bonds between the substances.

- **Fermentation (Acido-genesis):**

This process is very popular because it's mainly the process of the chemical decomposition of carbohydrates by bacteria, yeasts, or molds in the absence of oxygen.

- **Aceto-genesis:**

The fermentation products are converted into acetate, hydrogen and carbon dioxide by what are known as acetogenic bacteria, here is where the volatile fatty acids have been produced.

- **Methano-genesis:**

The last step of the anaerobic digestion is methane gas production, which is formed from acetate and hydrogen/carbon dioxide by methanogenic bacteria.

Figure 2.2 show the anaerobic digestion process, and also shows at what step the volatile fatty Acids VFA where produced.

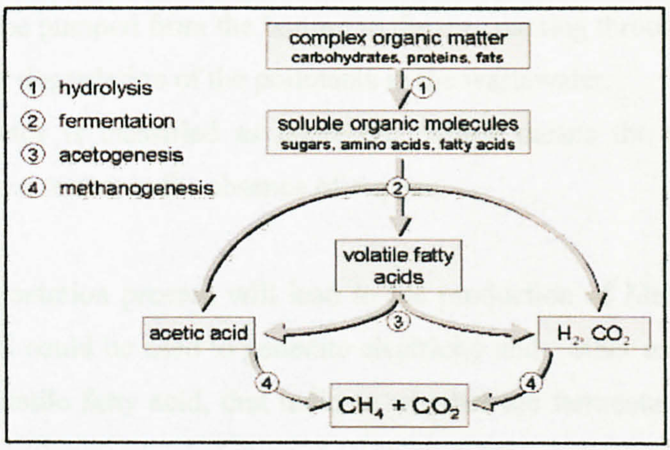

Figure 2.2: Path of Anaerobic Digestion

2.7 Up-flow Anaerobic Sludge Blanket (UASB):

The UASB reactor (figure 2.3) was used for the first time in the Netherlands by Lettinga and his coworkers- Wageningen University (Lettinga and Vinken, 1980). It was later used to treat beet sugar, corn and potato starch (Metcalf and Eddy, 2005).

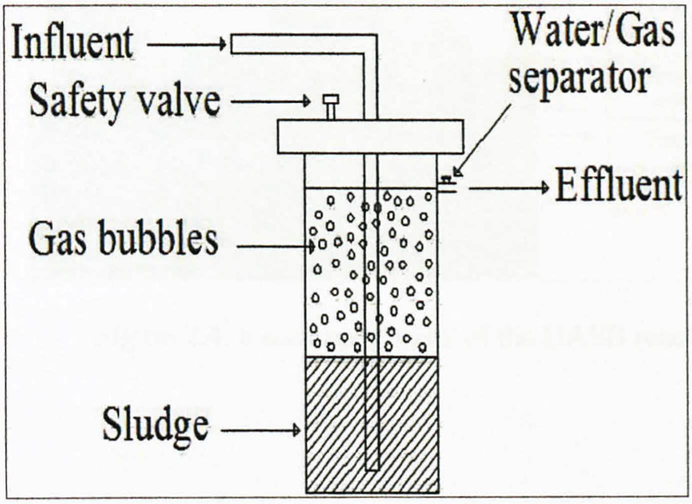

Figure 2.3: The Upflow Anaerobic Sludge Blanket (UASB) reactor

The UASB is the main reactor for the experiment; it is called up-flow because the wastewater will be pumped from the bottom to the top, passing through sludge bed which is responsible for degradation of the pollutants in the wastewater.
The UASB reactor is classified as anaerobic, which means the microorganism will metabolize organic matter in the absence of oxygen.

The fermentation process will lead to the production of Methane (bio-fuel) and CO_2, the bio-fuel could be used to generate electricity and other uses. Another product would be the volatile fatty acid, that indicate whether the fermentation process is good enough or not.

The reason of pumping the wastewater in upflow is to help the bio-fuel and CO_2 flow with effluent wastewater, which makes it easy to capture and store.

Figure 2.4 below shows the lab scale Upflow Anaerobic Sludge Blanket (UASB) reactor and also the necessary devices and equipment that were used during the experiment.

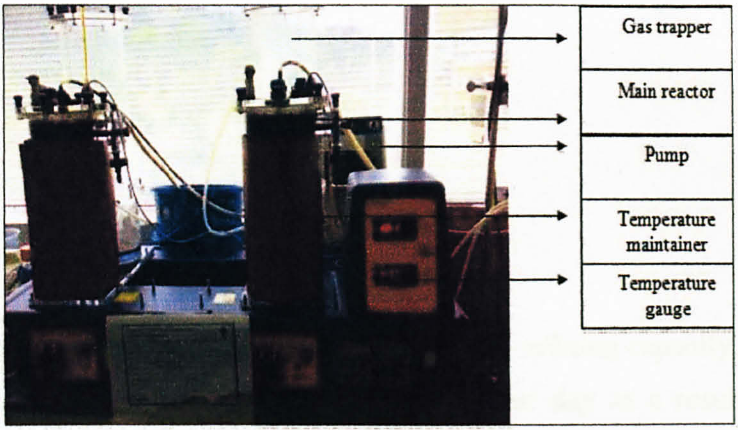

Figure 2.4: a schematic view of the UASB reactor

CHAPTER 3

METHODOLOGY

3.1 Sample collection

The PETRONAS refinery in Melaka has a huge refining capacity, with the overall processing capacity is 250,000 barrels of crude oil per day as a result the discharged wastewater (sour water) is to be very high.

A trip to the refinery was made to view the implemented system and also to observe what are the other techniques used in treating refinery wastewater (the corrugated plates interceptor (CPI) and oil skimmer).The trip was very lucrative in term of knowledge and clarified a lot of information about sour water treatment.

A sample of the wastewater was obtained to check the initial concentration of COD and also the alkalinity as well as other characteristics.

Another site visit to the refinery was performed to collect the influent wastewater. The staff at the treatment plant was very helpful, and they provided all the support needed, the raw wastewater collected after the Corrugated Plate Interceptor tank (CPI). The CPI tank separate the oil from the water and where the oil is sent back to recycled.

The refinery wastewater used for this study was brought from the second visit and after that the experimental work was started.

3.2 Characterization of the oil refinery wastewater:

The characteristics of the petroleum refinery raw wastewater such as pH, chemical oxygen demand (COD), alkalinity, and the volatile fatty acid (VFA) were all checked using the HACH standard methods for analyzing water and wastewater. Three barrels of raw wastewater were collected from the oil refinery; the total volume was about 1 m^3 and was kept in the cold storage room at the environmental laboratory. Some initial test was conducted to compare the characteristics of the collected wastewater to the results obtained from the refinery's Health, Safety and Environment Department

3.3 Experimental research:

The experimental procedures for the UASB reactor is almost like all the anaerobic reactors, where it uses the fermentation process of the sour water (the petroleum refinery wastewater). The raw wastewater undergoes anaerobic digestion process where it was hydrolyzed; the acidogenesis will take place followed by the methogenesis.
The UASB reactor has a sludge accumulated at the bottom of the reactor to degrade the organic matter in the wastewater. The reactor was operated at a temperature of (35-37 $^\circ$C) with different hydraulic retention time (HRT).

3.4 Operational framework:

Figure 3.1 describes the experimental flow starting from the initial stage where the design and preparation of the UASB reactor. A trip was conducted to Melaka to collect the end of pipe effluent from the PETRONAS refinery where a total volume of 1 m^3 was brought for testing and a small sample from the raw before the physical separation to check the characteristics of the wastewater, the sample was stored at the cold storage room at the environmental engineering lab at 4^0 temperature. This specific temperature ensured that the raw wastewater wouldn't freeze and as a result the characteristics will not change.

The reactor was operated at different HRT (5, 4 and 3 days), and sometimes different concentration.

The influent flow rate was calculated based on the respective HRT.

Organic removal such as COD, alkalinity, pH and VFA were analyzed on a regular basis as possible

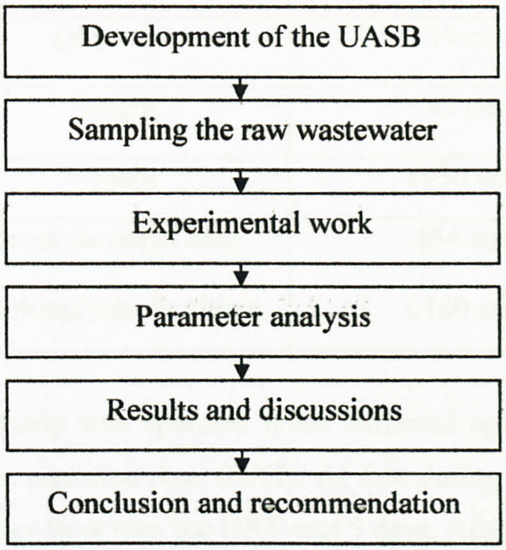

Figure 3.1: Framework of the whole treatment process

3.5 Upflow anaerobic sludge blanket reactor setup:

The UASB reactor that has been used has the cylindrical column shape, all the dimensions has been measured to determine the overall volume and the working volume. The working volume is the overall volume subtracted by the sludge volume, where the sludge in the reactor is approximately 2.2 liters. The dimensions of the lab scale reactor are given at table 3.1

The gas collector was installed to calculate the methane gas production, but no gas-solid separator was installed due to the size of the reactor.

The reactor was connected to one pump only where it pumped the influent from its respective tank, and for the effluent it was discharged with no pump. A proper pipe lines has been used and no leakage has been confirmed before the experiments where conducted and the reactor was operated, below is the dimensions of the reactor

Table 3.1: The dimensions of the UASB reactor

parameter	Value
Diameter	14 cm
Length	45 cm
Volume	6930 cm^3
Cross sectional area	154 cm^2
Working/liquid volume	6160 cm^2

The influent pump was operated under different speed and different flow rate based on the hydraulic retention time (HRT). At first during the acclimatization process the pump was at 1 L/day flow rate, the HRT was 5 days, After reaching a stable result the HRT was changed to 4 days, so the pump was operated at 1.25 L/day and finally for more convincing result the HRT was changed into 3 days with a respective flow rate of 1.33 L/day. Figure 3.2 below shows a schematic view of the experiment setup.

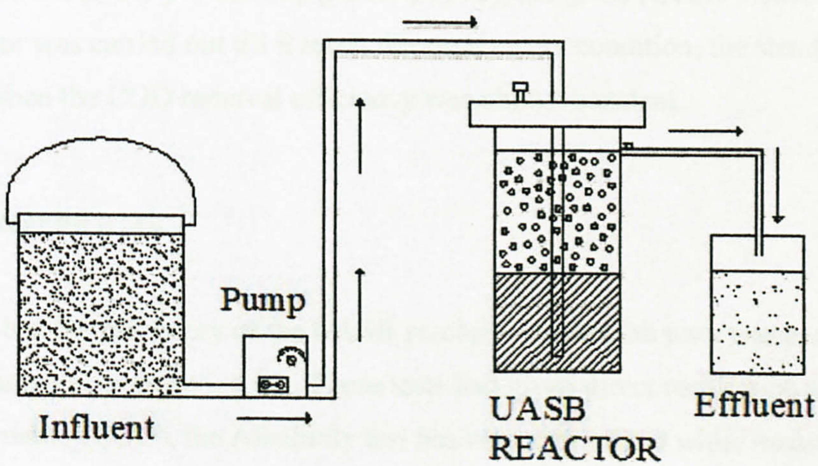

Figure 3.2: UASB experiment setup

The wastewater that is used in the reactor as stated earlier is the petroleum refinery wastewater. This water from its characteristic is considered to be low in strength, because of the low chemical oxygen demand (COD), that is ranged from 300-600 mg/l.

(Metcalf and Eddy, 2005) stated that, through time the reactor will sour, and the pH will drop, so the wastewater will become acidic, and for that reason sodium bicarbonate (Na_2CO_3) was added every time at the influent tank, the rate was to add 2 gram of (Na_2CO_3) to one liter of the raw wastewater was added. And from that the influent pH was raised.

That is because if the pH wasn't maintained from the acidic condition, it certainly will damage the sludge and the microorganism in the reactor for that reason the alkalinity test and the pH was carried out.

The reactor was running daily, at the first 3 days, the reactor heater was working however there was no feeding, and this was to ensure that the microorganism could acclimatize to the temperature that has been used (35 ° C), after that feeding was started, and several lab test as COD, pH and alkalinity was carried simultaneously. More details about the result will be discussed at the result and discussion section.
All the necessary tests was followed using HACH standard method by keeping in consideration the safety precautions (APHA, 1998), using the HACH manual, the startup of the reactor was carried out till it reach the steady state condition, the steady state is known as when the COD removal efficiency was almost constant.

3.6 Experimental work

To test the efficiency of the UASB reactor, several lab tests was conducted at the Environmental engineering lab. These tests had given direct result such as the amount of organic matter (COD), the Alkalinity test has been carried out while measuring the

pH^+, and the volatile fatty acid (VFA) was conducted from time to time to ensure the methane gas production.

3.7 Operational conditions

While conducting the experiments several conditions were kept in mind, as these conditions had a direct effect on the result and the reactor efficiency

3.7.1 Hydraulic retention time (HRT)

The hydraulic retention time is a measure of the average length of time that a soluble compound remains in a constructed reactor. Previous studies had used different HRT such as 12,18 and 24 but it mainly depends on the wastewater concentration or strength. To calculate the hydraulic retention time the following formula shall be used

$$\text{HRT (hours)} = V/Q$$

Where:

V=Reactor volume (active volume)

Q=Volume per hour (discharge of influent)

In the implemented UASB reactor the initial retention time was 5 days which was used even after the acclimatization process become stable, later it was changed into 4 days till today. The future plan in to apply 3 days retention time.

3.7.2 Organic Loading rate (OLR)

Organic loading rate (OLR) range from 3.2 to 32 kg.COD/m^3 can be used for anaerobic treatment (Speece, 1996) so it depends on the water characteristic and the

UASB conditions, in this case the initial concentration of the wastewater was 0.1 kg.COD/m^3, that was for the initial OLR, and later it was changed to 0.125 kg.COD/m^3. To calculate the OLR:

OLR= (Flow Rate (Q) x COD concentration) / Working Volume (V)

3.7.3 Temperature :

Temperature plays a very important role in the operation parameters during processing the experiment. There are 2 types of temperature that bacteria can grow at and fermentation can take place:

1. Methophilic: where the temperature is (35°-37° C).
2. Thermophilic: where the temperature is 50° C or higher

Previous studies have been conducted for different temperature. Table 3.2 below gives the range of temperature. In the current experiment the temperature used would be 35° C which known as methophilic condition.

Table 3.2: The temperature effect on the volumetric loading (Tchobanoglous, 2003)

	Volumetric loading, kg sCOD/m^3.d			
	VFA wastewater		Non VFA wastewater	
Temperature, °C	Range	Typical	Range	Typical
15	2-4	3	2-3	2
20	4-6	5	2-4	3
25	6-12	6	4-8	4
30	10-18	12	8-12	10
35	15-24	18	12-18	14
40	20-32	25	15-24	18

* Average sludge concentration is 25 g/L.

3.8 Alkalinity test

Alkalinity is defined as the ability of a water to neutralize acid or to absorb hydrogen ions. In general it is the sum of all acid neutralizing bases in the water. There are many factors contribute to alkalinity including the type of dissolved inorganic and organic compounds in the wastewater and also the amount of suspended organic matters.

The alkalinity is maintained in wastewater so it helps to resist changes in pH caused by the addition of acids, due to fermentation (Metcalf and Eddy, 2005). If the alkalinity within the treatment system is insufficient, the pH will decrease to the point which toxic to the system's microbial population (Metcalf and Eddy, 2005)
The Alkalinity was tested on regular basis at all the HRT.

The alkalinity test was carried regularly, with the pH test, because both tests are related, the alkalinity is used to resist the changes in pH by the addition of sodium bicarbonate.
Sodium bicarbonate was added with a ratio of 1 liter of wastewater: 2 gram of bicarbonate. This is to ensure that the alkalinity would be on the range of 1500 to 2000 mg/l $CaCO_3$ so that when the changes in pH happened, the alkalinity can resist.
The alkalinity test was carried since the start-up process, and was conducted during 4 and 3 days HRT.

3.9 Dilution Factor

The dilution factor is the ratio of the volume of water to the initial sample of refinery wastewater that will be used, while using the HACH standard method of testing. two types of vials can be used for the COD test, the first one is for low range COD where it can only measure COD till 150 mg/l, the other one was high range vials, and it can read till 1500 mg/l .However the high range were not available at the time the reactor start, so had to carry out the test where the samples were diluted. First DF of 1:10 was used, later for accuracy 1:5 take place.

The initial COD concentration was 600, Therefore if low range vials was used with out dilution, wrong or over range answer would be given, but when dilution factor 1:5 is used the result would be around 120 mg/l which apparently on the range of the low range COD vials.

3.10 **Gas collection:**

Methane gas at standard temperature and pressure (20^0 C and 1 atm) has a lower heating value 35800 KJ/m^3.The methane gas produced is 65% of the total gas, the rest is CO_2.

The methane gas was collected using a 5% of sodium hydroxide (NaOH) solution, when the gas produced by the UASB reactor, the gas bubble is moved into the gas trapper and then the NaOH will be displaced as the amount of methane gas produced, CO_2 will be absorbed by NaOH (Isa et al., 1993).

The digester gas (Methane gas) can be used in cogeneration, cogeneration is a system that produce electricity and produce another form of energy (usually steam or hot water) (Metcalf and Eddy, 2005).

Figure 3.3 shows the gas trapping process and the liquid displacement involved.

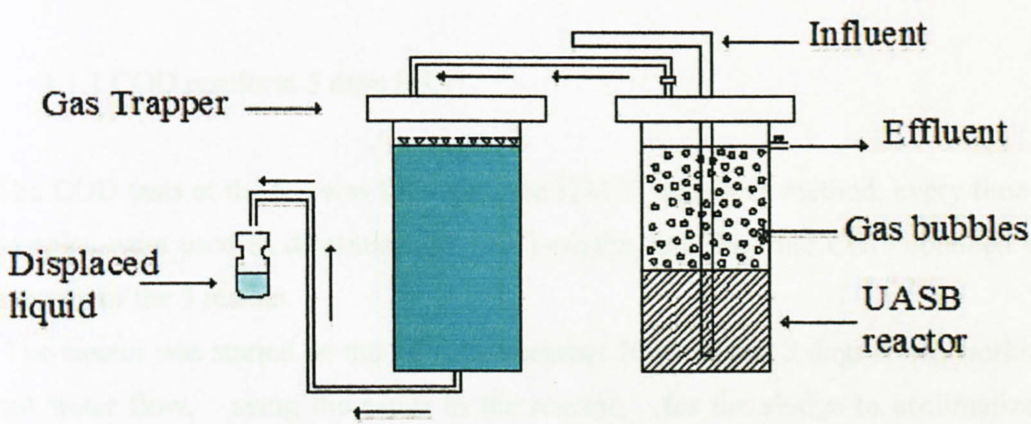

Figure 3.3: Schematic flow for the methane gas, and the gas trapper.

CHAPTER 4

RESULTS AND DISCUSSIONS

The lab experiments were conducted at different hydraulic retention time (HRT). During the startup of the reactor it was 5 days, and when the result of the COD was stable it was changed to 4 days where the best results were obtained and finally to 3 days for overall analysis. Given below are the results of the experiments and will be discussed in details.

4.1 Analysis of the COD result:

The COD test is an experimental test that measures the quantity of organic pollutants than can be removed in chemical oxidation, by adding strong acids. Its unit is in mg/l. (Metcalf and Eddy, 2005).

4.1.1 COD results at 5 days HRT:

The COD tests at the lab was following the HACH standards method, every time 3 vials samples were used to determine the COD results, and the final COD obtained was the average of the 3 results.

The reactor was started on the 11th of December 2008, at first 3 days it was working with out water flow, using the water in the reactor, for the sludge to acclimatize to the methophilic condition, and for the sludge to settle at the bed.

On the 15th of December the COD experiment was conducted for the first time for both influent and effluent, the HRT was set to be 5 days, and so the flow of waster was 1 L/day.

The 5 days HRT was used all over the acclimation process, which was lasted for 17 days, after that experiment continues till stable results were reached.

The time of the whole study was 3 month, so it was decided that the each month a different HRT will be tried.

The results were taken on regular bases till the end of the period of 5 days HRT which was on the 7th of January 2009. Figure 4.1 shows the result of the influent and effluent of the COD concentration under the 5 days HRT.

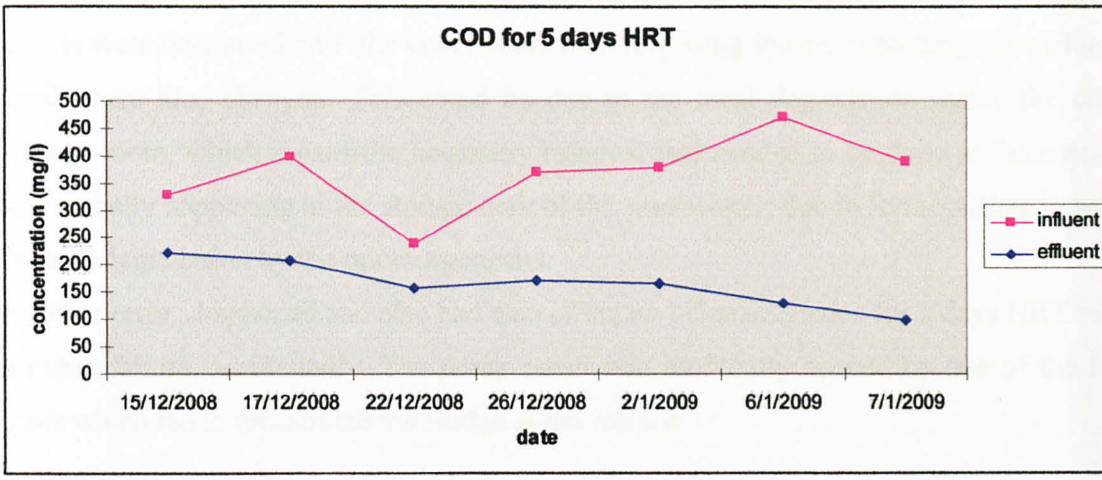

Figure 4.1: COD concentration at 5 days HRT

4.1.2 COD results at 4 days HRT:

After the 5 days HRT period was over, the experiment was continued to invistigate different HRTs.

The HRT 5 days was stopped on the 7th of January, then the HRT was changed into 4 days, and as a result the flow rate was changed to 1.25 L/day. At first the effluent concentration has increased, normally if the discharge increased, that means the more the organic matter will be passing by the system, which means it needs more effort for the microorganism to start degrading as before.

Figure 4.2 gives an overall idea of the concentration obtained at 4 days HRT as well as the minimum effluent concentration achieved.

The minimum concentration achieved was 93.3 mg/l, further on the results were stable at a concentration below 100 mg/l (the minimum requirement for the COD effluent given by the DOE, Malaysia) till the 13th of February 2009; the HRT was then changed to 3 days.

During the 3 days HRT, there was a failure in the cold storage room's cooling system, due to this failure the refrigerating system was not working. As a result, the wastewater characteristics s changed .It can be seen from the graph of figure 4.2 that influent results were decreased and the concentration were getting lower, resulting the effluent result were also changed. This could be due to the local degradation inside the cold storage room, which means the necessary removal that needed to be done at the reactor was actually happening at the storage tank of the wastewater; due to fermentation as well as local degradation by the microorganisms.

Another error happened and also had also effect on t characteristics for 3 days HRT was a Pump failure, accidentally. The pump cover was accidently opened by one of the lab users which led to unstabilize the sludge at the reactor.

It took one week to ensure the recaptured the sludge from the inlet tank and then pumped it back to the reactor as well as 3 more days for settlement of the sludge.

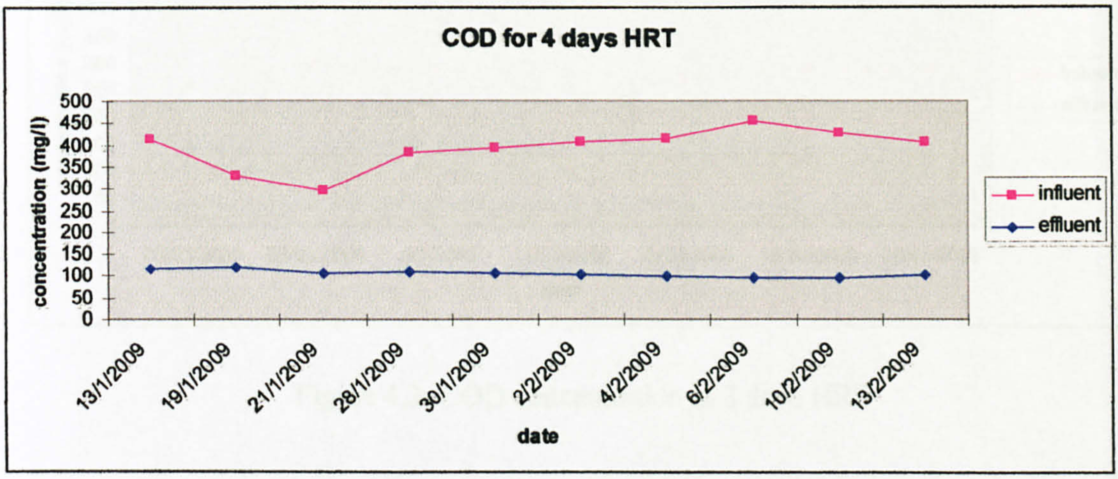

Figure 4.2: COD concentration at 4 days HRT

4.1.3 COD results at 3 days HRT:

The 3 days HRT is the last HRT used for this study, the pump was adjusted for 1.33 L/day flow rate, figure 4.3 shows the influent and effluent COD's concentration, the influent's concentration is lower than the average values obtained at 5 and 4 days HRTs. That is because of the failure of the cooling system at the cold storage room at the laboratory.

Also the effluent concentration is higher; this could be due to the following reasons:

1. changing the flow rate of the pumps
2. local degradation at the cold storage room due to system failure
3. the misplacement of the Pump cover that let to unstable sludge

Figure 4.3 below shows the concentration of the COD for the influent and the effluent as well as the starting date of 3 days HRT and the end date of it.

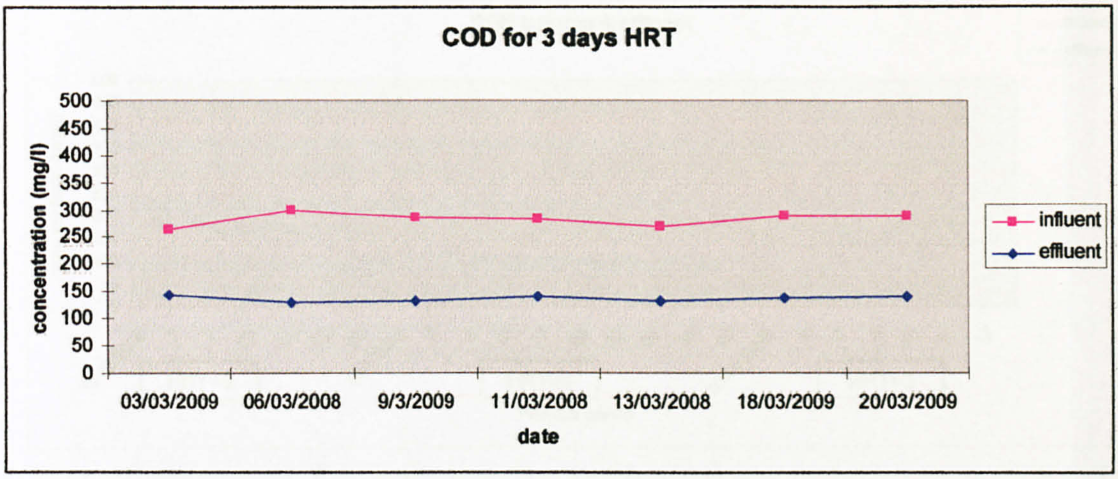

Figure 4.3: COD concentration at 3 days HRT

4.1.4 Over all COD concentration and removal efficiency:

The UASB reactor has shown a great effectiveness in COD removal, while running the experiment, the best removal efficiencies results as well as the best effluent's concentration were obtained during the 4 days HRT, it was because the steady period of 4 days HRT and the long duration of implementing 1.25 L/day flow rate.

If the 5 days HRT was continued much longer it might have given better results, but due to the time constraints the HRT was changed into 4 days.

The maximum removal efficiency obtained was 79% and the relative concentration of effluent was 93.3 mg/l, which meet the Department of Environment (DOE) Malaysia standard B criteria

Figure 4.4 show the overall concentration, and figure 4.5 shows the overall removal efficiency at different HRT.

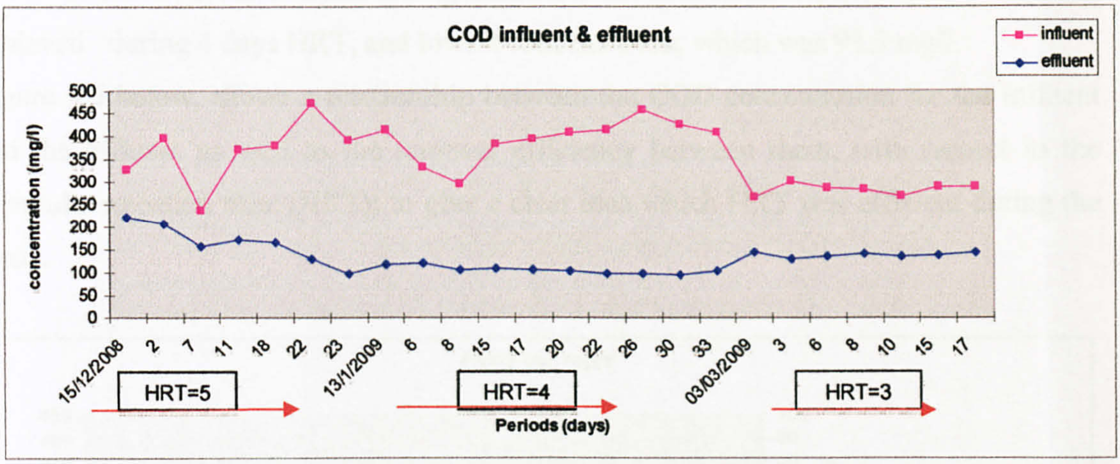

Figure 4.4: The overall COD concentration for 5, 4 and 3 days HRT

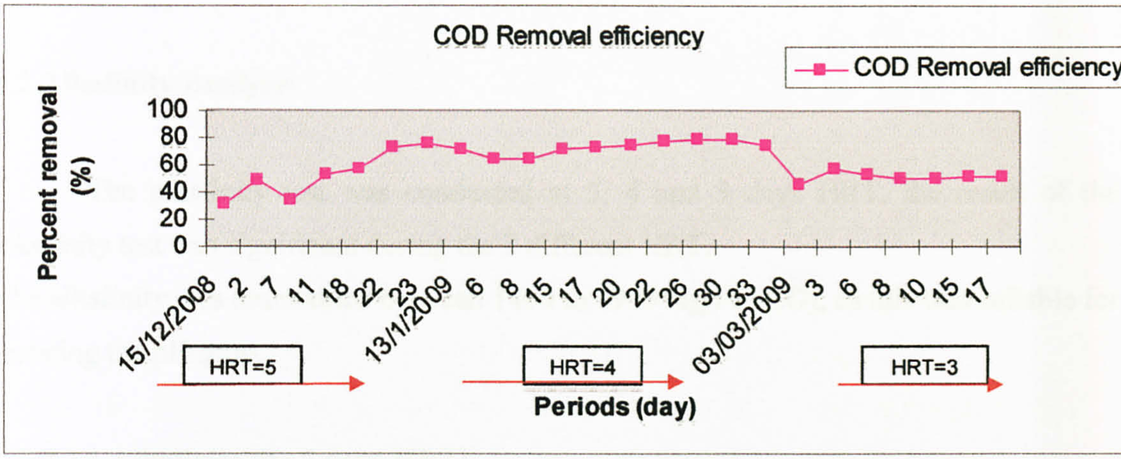

Figure 4.5: The overall COD removal efficiency for 5, 4 and 3 days HRT

4.1.5 COD removal with different HRT:

The experiment was conducted under 3 different hydraulic retention times. This is to investigate the optimum removal efficiency as well as lowest effluent concentration that could be achieved.

From the COD analysis during each HRT it was found that, the best removal was achieved during 4 days HRT, and lowest concentration, which was 93.3 mg/l.

Figure 4.6 below, shows a relationship between the COD concentration for the influent and the effluent as well as the removal efficiency between them, with respect to the hydraulic retention time (HRT); to give a clear idea which HRT was efficient during the study.

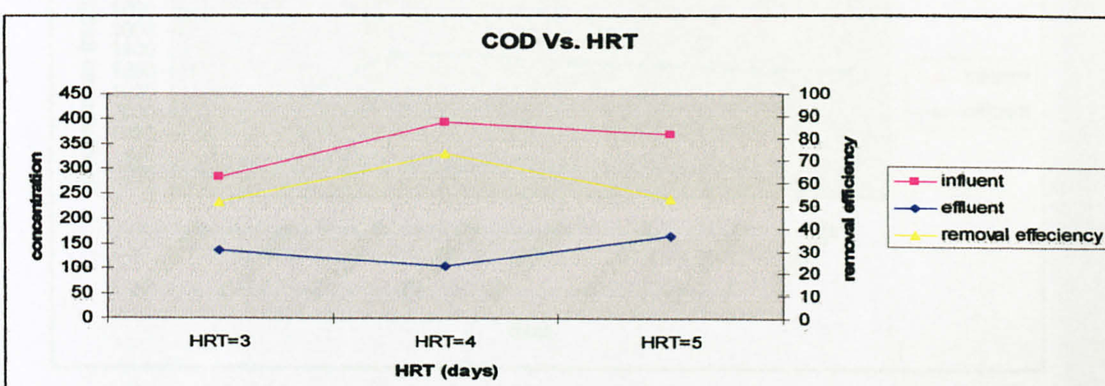

Figure 4.6: Relationship between the COD and different HRTs

4.2 Alkalinity Analysis

The alkalinity test was conducted at 5, 4 and 3 days HRT, the result of the alkalinity test was significant during the 3 different HRT.

The alkalinity was maintained between 1400 to 1900 mg/l $CaCO_3$, as this was suitable for resisting the pH drop.

4.2.1 Alkalinity for 5 days HRT:

The alkalinity during 5 days was assured that the alkalinity was maintained above the ideal range, it was almost stable between 1700 to 1800 mg/l $CaCO_3$.

It was found that the first 2 effluent results was low compared to the rest of the results, due to the recently started reactor. During the acclimation process the reactor was left open for 3 days without wastewater flowing in; to insure settlement of the sludge particles and also the microorganism can adapt to the new temperature.

That caused the sludge to sour and become more acidic, so when the water flow, the alkalinity was reduced to a great extent, but through time the sludge adapt again.

Figure 4.7 below shows the alkalinity test during 5 days HRT, with its respective concentration.

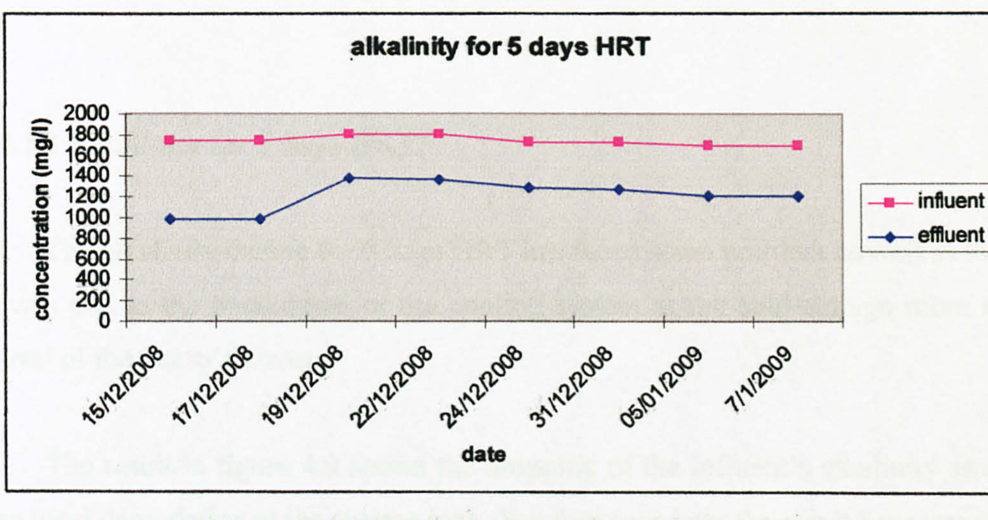

Figure 4.7: The alkalinity results for 5 days HRT

4.2.2 Alkalinity for 4 days HRT:

The alkalinity test was carried during the 4 days HRT, with the results were acceptable except the first 3 results.
The reason for this was the changing of the hydraulic retention time (HRT) from 5 days to 4 days. After few days the result were returned to its planned range.
Figure 4.8 below shows the concentration of the alkalinity for the influent and effluent during the 4 days HRT.

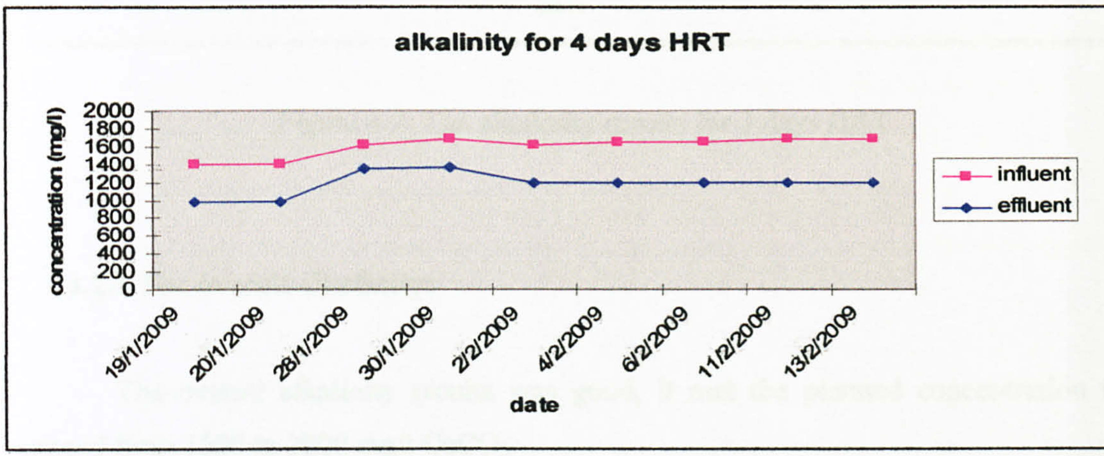

Figure 4.8: The alkalinity results for 4 days HRT

4.2.3 Alkalinity for 3 days HRT:

The alkalinity during the 3 days HRT has faced some problem as well as the COD that was due to the breakdown of the cooling system at the cold storage room and the removal of the pump's cover.

The result in figure 4.9 shows the dropping of the influent's alkalinity as a result of the local degradation at the storage tank. But few days later the result becomes stable.

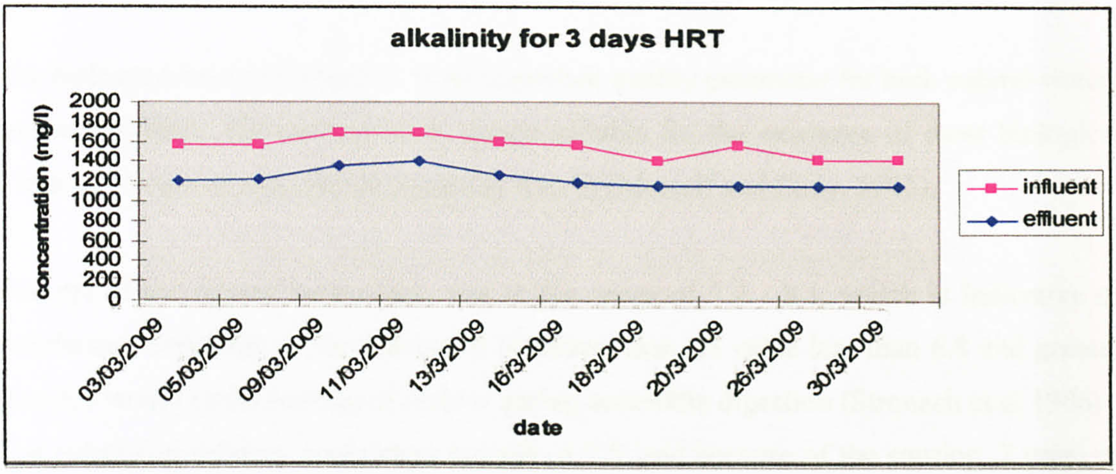

Figure 4.9: The alkalinity results for 3 days HRT

4.2.4 The overall alkalinity:

The overall alkalinity results was good, it met the planned concentration that ranged from 1500 to 2000 mg/l $CaCO_3$.

The alkalinity has setup an n environment for the microorganism to grow at and to degrade efficiently the pollutant at the wastewater.

Figure 4.10 below shows the overall alkalinity at 3 different HRT (5, 4 and 3 days)

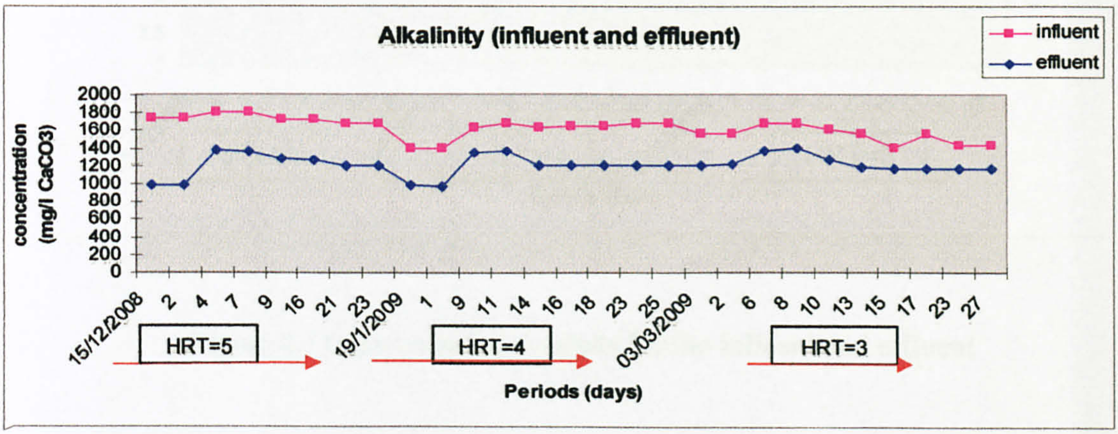

Figure 4.10: The overall alkalinity results for 5, 4 and days HRT

4.3 pH analysis:

The hydrogen-ion concentration is an important quality parameter for both natural waters and wastewaters, the concentration range suitable for the existence of most biological life is quite narrow and critical (typically 6 to 9) (Metcalf and Eddy, 2005).

The pH of the treated wastewater was in the range of 7.4 - 8.1, which is indicative of satisfactory condition of the reactor. It is known that pH value less than 6.8 and greater than 8.3 would cause souring of reactor during anaerobic digestion (Stronach et al 1986) The petroleum refinery wastewater has pH of 7.5, and because of the souring, 2 gram of sodium bicarbonate was added for 1 liter of the wastewater, that lead to the increasing of pH, figure 4.11 shows the influent and effluent pH results, the pH for influent is after the addition of sodium bicarbonate, for that reason it ranged between (8.5-11).
The pH test was held concurrently with the alkalinity test, because the two tests are related.

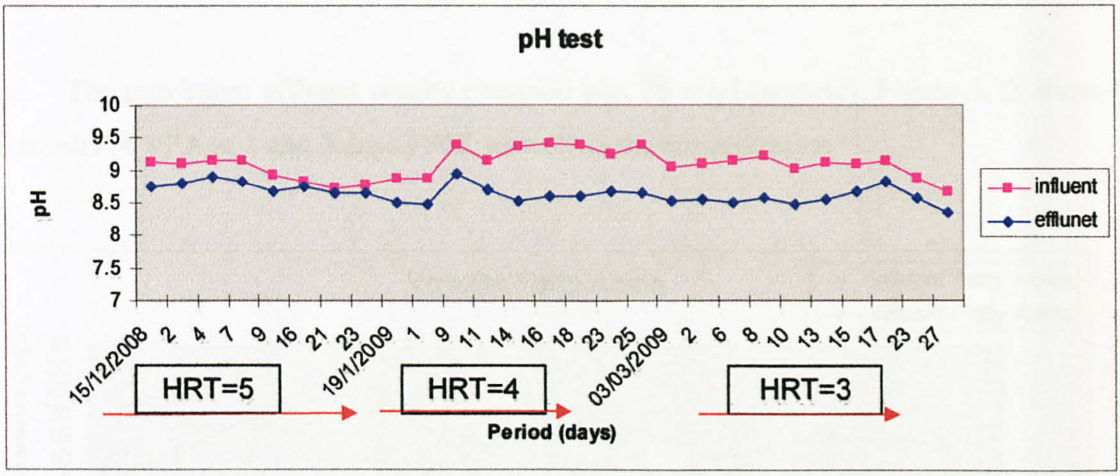

Figure 4.11: the overall pH results for the influent and effluent

4.4 Volatile Fatty Acids (VFA) analysis:

There are three major groups of bacteria that function in anaerobic digestion. The first group hydrolyzes large soluble and not soluble organic compounds such as proteins, fats and oils (grease), and carbohydrates, producing smaller water-soluble compounds. These are then degraded by acid-forming bacteria, producing simple volatile organic acids (primarily acetic acid) (Donavan, 2002).

The volatile fatty acid (VFA) test was conducted to check the effectiveness of the fermentation process, as well as to check the production of the biogas, the test was carried frequently.

The VFA test was carried during the 4 days HRT and continuedto 3 days. This is because during the 5 days HRT the gas production was very low, whereas the COD removal was considerably high, so from there on the volatile fatty acid test was held and the result were taken.

The Petroleum refinery has low protein content, because high protein wastewater converts into volatile fatty acid and ammonia (Natpinit, 2004), that's why the VFA results are not very high.

The maximum effluent results obtained was 26 mg/l (acetate), Figure 4.12 show the results of VFA at 4 and 3 days HRT, as well as the concentration.

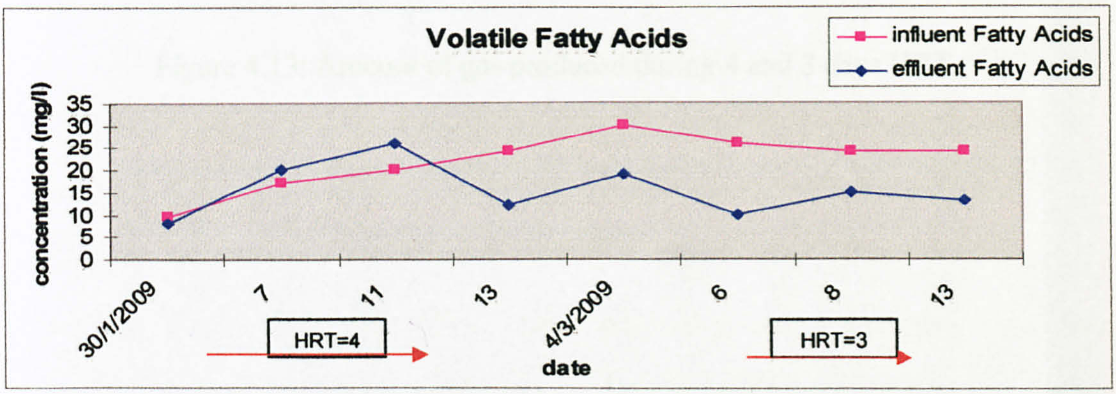

Figure 4.12: Volatile Fatty Acids results for 3 and 4 days HRT

4.5 Gas collection analysis:

The biogas was collected at 4 days HRT and onward, during the acclimatization process the methane gas was significant, but due to a leakage from the UASB reactor, the results during 5 days HRT wasn't accurate so it was neglected.

The methane gas was trapped using a liquid form of sodium hydroxide (NaOH), when the gas produced by the UASB reactor, the gas bubble is moved into the gas trapper and then it displace the liquid, the displaced liquid is representing the produced gas by the reactor.

Figure 4.13 below shows the volume of the gas that has been produced during 4 and 3 days HRT.

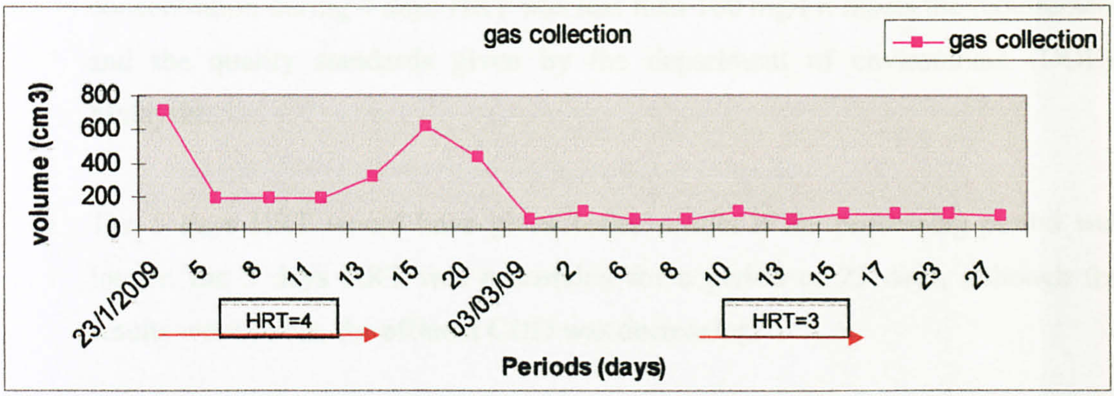

Figure 4.13: Amount of gas produced during 4 and 3 days HRT.

CHAPTER 5

Conclusion and recommendation

5.1 Conclusion:

From the study, the conclusions are as follow:

- For the COD tests, the highest removal efficiency obtained was during the 4 days HRT, with a removal efficiency of 79%, where as the lowest COD effluent concentration was 93.3 mg/l.

- The effluent concentration obtained is very significant, the majority of the effluent concentration during 4 days HRT was less than 100 mg/l it meets the requirement and the quality standards given by the department of environment (DOE), Malaysia.

- The 5 days HRT would have given better results if the processing period was longer, the 5 days HRT was processing for a period of 23 days, although the results were stable, the effluent COD was decreasing.

- An alkalinity test has shown that the environment inside the reactor was good for the microorganisms to grow and to achieve significant removal. The alkalinity concentration was kept on a range of 1500 to 2000 mg/l $CaCO_3$ as recommended by previous studies.

- The volatile fatty acid (VFA) was conducted to ensure that the fermentation process is proceeding effectively, the results obtained are good, although the VFA effluent was low (15-25 mg/l acetate), but that show the efficiency of the fermentation process, the VFA is high if and only if the wastewater contains high proteins.

- The Methane gas produced by the reactor was acceptable, the maximum production was during the 4 days HRT, the total volume of the gas produced during 4 days HRT was 2618.16 cm^3, and the total production for 3 days HRT was 818.89 cm^3.

- The overall results of the UASB reactor was very significant, specially for the COD, but due to the failure of the cooling system at the cold storage room and also the pump failure, the results for 3 days HRT wasn't good enough.

5.2 Recommendations:

- For the UASB reactor, further treatment is required for achieving higher removal efficiency for COD, as well as treating the nitrogen and phosphorous, because anaerobic digesters are not efficient for treating them.

- The temperature used was (35 $^\circ$ C), which is under the mesophilic condition; a study should be done to check the effect of the treatment under the thermophilic condition (55 $^\circ$ C).

- More hydraulics retention time should be tested, for checking good treatment at different conditions, because neither 5, 4 or 3 days are effective for a real UASB reactor specially if the influent flow is huge (e.g. 250 m^3/day).

- Regarding the refinery wastewater, oil and grease test must carried out regularly, because the petroleum refinery wastewater contains around 12.7 mg/l, and the standards given by the DOE, Malaysia regulate a minimum discharge of 10 mg/l for standard (B).

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Appendix A

Table A.1 COD results at 5 days HRT

		influent					effluent				
date	1	2	3	average		1	2	3	average		%
15/12/2008	370	275	332	325.6667		212	196	256	221.3333		32.03685
17/12/2008	430	360	400	396.6667		194	185	240	206.3333		47.98319
22/12/2008	240	270	200	236.6667		180	90	200	156.6667		33.80282
26/12/2008	350	357	398	368.3333		150	180	185	171.6667		53.39367
2/1/2009	364	377	393	378		157	163	174	164.6667		56.43739
6/1/2009	480	472	460	470.6667		105	120	160	128.3333		72.73371
7/1/2009	370	355	440	388.3333		90	110	90	96.66667		75.1073

Table A.2 COD results at 4 days HRT

		influent					effluent				
Date	1	2	3	average		1	2	3	average		%
13/1/2009	370	470	400	413.3333		117	117	117	117		71.69355
19/1/2009	340	320	330	330		119	118	119	118.6667		64.0404
21/1/2009	310	280	290	293.3333		103	105	108	105.3333		64.09091
28/1/2009	400	390	355	381.6667		113	105	107	108.3333		71.61572
30/1/2009	415	390	375	393.3333		106	107	104	105.6667		73.13559
2/2/2009	400	410	405	405.67		105	100	102	102.67		74.69125
4/2/2009	425	400	410	411.6667		97	95	98	96.66667		76.51822
6/2/2009	455	450	460	455		99	94	95	96		78.9011
10/2/2009	400	450	425	425		93	92	95	93.33333		78.03922
13/2/2009	405	410	405	406.6667		103	105	97	101.6667		75

Table A.3 COD results at 3 days HRT

		influent					effluent				
date	1	2	3	average		1	2	3	average		%
03/03/2009	260	250	280	263.3333		132	150	142	141.3333		46.32911
06/03/2008	269	372	255	298.6667		130	129	128	129		56.80804
9/3/2009	280	290	285	285		130	132	135	132.3333		53.56725
11/03/2008	265	275	305	281.6667		139	141	137	139		50.65089
13/03/2008	265	255	285	268.3333		134	132	132	132.6667		50.55901
18/03/2009	280	300	285	288.3333		143	135	136	138		52.13873
20/03/2009	310	270	285	288.3333		146	135	142	141		51.09827

Table A.4 Alkalinity results for 5 days HRT

Date	Influent pH	Effluent pH	pH different	Influent Alkalinity(mg/L CaCO3)	Effluent Alkalinity (mg/L CaCO3)	Alkalinity Removal	Removal Efficiency
15/12/2008	11.12	10.74	0.38	1740	980	760	43.68
17/12/2008	11.09	10.8	0.29	1740	980	760	43.68
19/12/2008	11.15	10.9	0.25	1800	1380	420	23.33
22/12/2008	11.15	10.83	0.32	1800	1360	440	24.44
24/12/2008	10.91	10.68	0.23	1720	1280	440	25.58
31/12/2008	10.83	10.75	0.08	1720	1260	460	26.74
05/01/2009	10.72	10.65	0.07	1680	1200	480	28.57
7/1/2009	10.78	10.65	0.13	1680	1200	480	28.57

Table A.5 Alkalinity results for 4 days HRT

Date	Influent pH	Effluent pH	pH different	Influent Alkalinity(mg/L CaCO3)	Effluent Alkalinity (mg/L CaCO3)	Alkalinity Removal	Removal Efficiency
19/1/2009	8.86	8.5	0.36	1400	980	420	30.00
20/1/2009	8.86	8.48	0.38	1400	970	430	30.71
28/1/2009	9.373	8.953	0.42	1620	1340	280	17.28
30/1/2009	9.13	8.686	0.444	1680	1360	320	19.05
2/2/2009	9.371	8.531	0.84	1620	1200	420	25.93
4/2/2009	9.402	8.602	0.8	1640	1200	440	26.83
6/2/2009	9.388	8.61	0.778	1640	1200	440	26.83
11/2/2009	9.248	8.668	0.58	1680	1200	480	28.57
13/2/2009	9.384	8.645	0.739	1680	1200	480	28.57

Table A.6 Alkalinity results for 3 days HRT

Date	Influent pH	Effluent pH	pH different	Influent Alkalinity(mg/L CaCO3)	Effluent Alkalinity (mg/L CaCO3)	Alkalinity Removal	Removal Efficiency
03/03/2009	9.04	8.533	0.507	1560	1200	360	23.08
05/03/2009	9.098	8.547	0.551	1560	1220	340	21.79
09/03/2009	9.13	8.502	0.628	1680	1360	320	19.05
11/03/2009	9.221	8.578	0.643	1680	1400	280	16.67
13/3/2009	9.011	8.484	0.527	1600	1260	340	21.25
16/3/2009	9.122	8.544	0.578	1560	1180	380	24.36
18/3/2009	9.089	8.668	0.421	1400	1160	240	17.14
20/3/2009	9.128	8.815	0.313	1560	1160	400	25.64
26/3/2009	8.862	8.563	0.299	1420	1160	260	18.31
30/3/2009	8.684	8.346	0.338	1420	1160	260	18.31

Table A.7 Gas collected during 4 days HRT

Date	Cm^3
23/1/2009	709.31
28/1/2009	184.73
30/1/2009	184.73
02/02/2009	184.73
04/02/2009	307.88
06/02/2009	615.75
11/02/2009	431.03

Table A.8 Gas collected during 3 days HRT

Date	Cm^3
03/03/09	61.58
05/03/09	107.76
09/03/09	61.58
11/03/09	61.58
13/3/2009	107.76
16/3/2009	61.58
18/3/2009	92.36
20/3/2009	92.36
26/3/2009	92.36
30/3/2009	79.97

Table A.9 Volatile Fatty Acids for 4 and 3 days HRT

HRT=3days	Influent	Effluent
4/3/2009	30	19
10/03/2009	26	10
12/03/2009	24	15
17/3/2009	24	13
HRT=4days		
30/1/2009	9.3	8
6/2/2009	17	20
10/2/2009	20	26
12/2/2009	24	12