Anaerobic Treatment of Petroleum Refinery Wastewater Using UASB Reactor: Kinetic Analysis

by

Mohamad Pirdaus Bin Mat Isa

Dissertation submitted in partial fulfillment of

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Supervised by: AP Dr. Mohamed Hasnain Isa

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CERTIFICATION OF APPROVAL

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Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

SEPTEMBER 2011

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 the original work contained herein have not been undertaken or done by unspecified sources or persons.

MOHAMAD PIRDAUS BIN MAT ISA

ABSTRACT

Petroleum refineries are complex plants, and the combination and sequence of processes is usually very specific to the characteristics of the raw materials (crude oil) and the products. This industry generates wastewater effluent containing oil, ammonia, sulphides, chlorides, phenols and other hydrocarbons. The most important pollutants are organics, oils, suspended solids and other toxic materials referred to as priority pollutants which be considered hazardous. Accidental discharges of large quantities of pollutants can occur as a result of abnormal operation in a refinery and potentially pose a major local environmental hazard. Previous studies have shown the reasonable performance of biological systems in refinery wastewater treatment. Thus, in this study an Upflow Anaerobic Sludge Blanket (UASB) was studied for treatment of wastewater from PETRONAS Penapisan Terengganu Sdn. Bhd. (PPTSB) at Kerteh, Terengganu. There are two reactors; A and B with total effective volume of 2.4 L for each reactor which were setup in parallel. Wastewater was continuously fed into the UASB reactors using a variable-speed peristaltic pump and seeded with the anaerobic sludge from a local Palm Oil Mill Effluent (POME) anaerobic treatment plant. The steady state performance was evaluated under flowrate is 1.4 L/d and hydraulic retention time of 1.7 days. Both reactors were operated with different Volumetric Organic Loading Rate (VOLR) which was four in total in order to determine the optimum empirical parameters that lead to most efficient anaerobic treatment of petroleum refinery wastewater. Therefore, the kinetic analysis was used to analyze all the data gained from all the experiments conducted. The results show that the kinetic constant, K of Chemical Oxygen Demand (COD) data is 2.18 d^{-1}. From the simulation, this research also found out that kinetic analysis give significant contribution.

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ABBREVIATIONS & NOMENCLATURES

BOD_5	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
DOE	Department of Environment
EQA	Environmental Quality Acts
K	Kinetic Constant
MLVSS	Mixed Liquor Volatile Suspended Solids
OLR	Organic Loading Rate
POME	Palm Oil Mill Effluent
TSS	Total Suspended Solids
UASB	Upflow Anaerobic Sludge Blanket
AFBR	Anaerobic Fixed Bed Reactor

CHAPTER 1
INTRODUCTION

1.1 Background of Study

Oil and gas industry is one of the most important contributors to Malaysia's economy. Malaysia has the 25th largest oil reserves and the 14th largest gas reserves in the world. The total reserves are of the order of 18.82 billion barrels oil equivalent (boe), with a crude production rate of 600 thousand barrels per day. The average natural gas production stands at approximately 5.7 billion standard cubic feet per day. Malaysia has 494,183 km^2 of acreage available for oil and gas exploration, with 337,167 km^2 in the offshore continental shelf area, and 63,968 km^2 in deepwater [1]. Therefore, action needs to be taken in order to guarantee the sustainable development in oil production.

The petroleum industry is organized into four broad sectors: exploration and production of crude oil and natural gas; transport; refining; and marketing and distribution [2]. In this research, only petroleum refining sector is considered. Refineries can be categorized into four different types depending on their complexity [3]:

- **Type I** - Simple (non-conversion) refinery: composed of crude oil distillation; reforming; treatment of distillate products, including desulphurization and/or other quality improvement processes (i.e. isomerisation or speciality manufacturing).
- **Type II** - Type I plus catalytic cracking and/or thermal cracking and/or hydrocracking.
- **Type III** - Type II plus steam cracking and/or lubricant production within the refinery fence.
- **Type IV** - Refineries not in above categories, e.g. those producing only bitumen, lubes, etc. which import their feedstocks from other sources.

Petroleum refineries use relatively large amount of water during the refining process, especially for cooling systems. Surface water runoff and sanitary wastewaters are also generated. The refining process configuration will determine the quantity of wastewater produced and their characteristics. The volume of water produced by a given production facility may vary considerably and has ranged from 500 to 600,000 barrels per day (bbl/day) [4].

Due to the ineffectiveness of purification systems, wastewater discharges may become seriously dangerous, leading to the accumulation of toxic products in the receiving environment with potentially serious consequences on the ecosystem [5]. The toxicity of oil refinery effluent is dependent on a number of factors. The volume, quality, salinity and variability of the discharge, the siting of the outfall, the physical and chemical conditions of the discharge area, the proximity of other effluents and pollutants and the biological condition of the discharge area [6].

As not all refineries have the same processes, the effluents that are produced will have different chemical compositions depending on the type of treatment they receive. Petroleum refinery wastewaters are made up of many different chemicals which include oil and grease, phenols (creosols and xylenols), sulphides, ammonia, suspended solids, cyanides, nitrogen compounds and heavy metals like chromium, iron, nickel, copper, molybdenum, selenium, vanadium and zinc [7].

Anaerobic treatment is a viable method for treating the petroleum refinery wastewater. Anaerobic decomposition of organic matter occurs in the absence of oxygen [8]. Anaerobic treatment processes are well known as efficient methods to degrade strong wastewaters. Due to recent advances in treatment technology and knowledge of process microbiology, application of anaerobic treatment is now extensive for treatment of dilute industrial wastewaters as well [9]. Thus, one of the most preferred technologies is Upflow Anaerobic Sludge Blanket (UASB), normally referred to as UASB reactor which is one of the high-rate anaerobic systems. The reactor efficiency of treating petroleum refinery wastewater at various organic loading rates was studied and its performance was assessed by monitoring pH, dissolved chemical oxygen demand (COD), biogas production and composition. [10].

Based on the experimental data, a kinetic model will be developed. The kinetic parameters will be evaluated, which represented the behavior of UASB reactor very well and obtain the optimum performance design of anaerobic treatment system of petroleum refinery wastewater [8].

1.2 Problem Statement

During the production of oil and gas, large amounts of water are brought to the surface and must be disposed of in an environmentally friendly manner. This is an especially difficult problem in offshore production facilities where space is a major constraint [4]. The areas around oil refinery outfalls all show a similar response to the refinery effluent, whether it is a rocky shore, soft sediment or the water column. The area around the discharge is often found to have a low diversity and abundance of fauna due to the inability of many species to survive in such close proximity to the effluent [6].

Refinery wastewater contains hazardous components that are hard to degrade. As a general guide, approximately 3.5 to 5 cubic meters (m^3) of wastewater per ton of crude are generated. Refineries generate polluted wastewaters, containing biochemical oxygen demand (BOD) and chemical oxygen demand (COD) levels of approximately 150 to 250 milligrams per liter (mg/l) and 300 to 600 mg/l, respectively; phenol levels of 20 to 200 mg/l; oil levels of 100 to 300 mg/l in desalter water and up to 5,000 mg/l in tank bottoms; benzene levels of 1 to 100 mg/l; benzo(a)pyrene levels of less than 1 to 100 mg/l; heavy metals levels of 0.1 to 100 mg/l for chrome and 0.2 to 10 mg/l for lead; and other pollutants. Refineries also generate solid wastes and sludges (ranging from 3 to 5 kg per ton of crude processed), 80% of which may be considered hazardous because of the presence of toxic organics and heavy metals [2].

Petroleum refinery wastewater has been identified to be one of the major sources of water pollution due to its high BOD and COD concentrations. In particular, the discharge of high COD wastewater will contribute to the increment of oxygen demand in the river, causing shortage of oxygen supply and even death to the aquatic life [11].

Therefore, there is an urgent need to find an efficient and practical approach to preserve the environment while maintaining the sustainability of the economy. The development of effective and simple methods for treatment of industrial wastewater is a challenging task to environmental engineers and scientists. Considering the high organic character of petroleum refinery wastewater, anaerobic process is the most suitable approach for its treatment. Despite the promising results on the anaerobic degradation of the petroleum products, however, documentation of the anaerobic treatment of petroleum refinery wastewater is very limited. There are several studies on refinery wastewater treatment which have been carried out using various high rate anaerobic reactors such as anaerobic filter (AF), fluidized bed reactor (FBR), immobilized cell reactor (ICR), up-flow anaerobic sludge blanket (UASB) reactor, anaerobic hybrid digester, membrane anaerobic system (MAS), and modified anaerobic baffled reactor (ABR) [12].

1.3 Objectives

1. To evaluate the treatment of petroleum refinery wastewater by using up-flow anaerobic sludge blanket reactor (UASB).
2. To analyze the kinetics of UASB treating petroleum refinery wastewater.

1.4 Scope of Study

The main scopes of study for this project period will be UASB reactor start-up process, operation under various organic loading rate (OLR), seed sludge acclimatization, wastewater characterization and last but not least kinetic analysis.

1.4.1 Wastewater Characterization

The characteristics of wastewater are determined in terms of flow conditions and chemical quality. The wastewater characteristic data include minimum, average and maximum sustained maximum flows and chemical parameters such as BOD_5, total suspended solids, pH, ammonia and total nitrogen, phosphorus, and toxic chemical [8]. The sample of petroleum refinery wastewater use for this project is taken from PETRONAS Penapisan Terengganu Sdn. Bhd. (PPTSB).

1.4.2 UASB Reactor Start-up

The influent is introduced at the bottom of the reactor. The flow moves upward through a sludge blanket composed of biologically formed granules [8]. The sludge samples used in this project was obtained from the treated Palm Oil Mill Effluent (POME) anaerobic treatment plant that practices anaerobic pond system to treat its wastewater. The seed sludge was allowed to acclimatize before the feeding started. The acclimatization period of the microorganisms in the digester is one of the main factors of the UASB start-up process period [8]. It is essential to understand that the main goal of the start-up in fact is to accumulate quickly as possible a proper sludge bed or blanket [11].

1.4.3 Operation under Various Organic Loading Rate.

For this project, there are four different organic loadings (A1, A2, B1, B2) be tested in the UASB reactor in operation of anaerobic treatment of petroleum refinery wastewater. The organic loading rate varied at determined values according to the plan of the project (refer Table 3.1) by diluted the refinery wastewater before fed in to the reactor.

1.4.4 Kinetic Analysis

Based on the experimental data obtained, the kinetic analysis is apply to determine the optimum empirical parameter which is kinetic constant, K that lead to most efficient anaerobic treatment of petroleum refinery wastewater using UASB reactor.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter provides a brief review on the common concepts of anaerobic wastewater treatment processes. The review covers the petroleum refinery wastewater characteristic, mechanism of anaerobic process, a high rate anaerobic treatment process which is UASB, and options to remove petroleum refinery wastewater solids and oil & grease as pretreatment process. Finally, basic knowledge for the kinetic modeling addressed in this study by model development in anaerobic wastewater treatment process will be provided.

2.2 Petroleum Refinery Wastewater

Oil consists of five types of components, saturated non-cyclic hydrocarbons (paraffins), cyclic hydrocarbons (cycloalkanes), olefinic hydrocarbons (alkenes), aromatics and non-hydrocarbons (sulphur compounds, nitrogen-oxygen compounds and heavy metals). Refinery effluents tend to have fewer of the lighter hydrocarbons than crude oil but more polycyclic aromatics and aliphatics which tend to be more toxic and more persistent in the environment but are anaerobically biodegradable [6,13]. The volume of water produced by a given production facility may vary considerably and has ranged from 500 to 600,000 bbl/day [14].

It is possible to detect two big effects that oil refinery effluent has on the environment. Firstly, the areas around oil refinery outfalls all show a similar response to the refinery effluent, whether it is a rocky shore, soft sediment or the water column [6]. The area around the discharge is often found to have a low diversity and abundance of fauna due to the inability of many species to survive in such close proximity to the effluent caused by toxicity of the effluent. Secondly, there is an enrichment effect which can be distinguished as a peak in the abundance of biomass [15]. The toxicity effect is caused by high concentrations of organic, high concentrations of organic compounds and/or high concentrations of the inorganic compounds such as phenol in the refinery wastes. Meanwhile, the oil and other organic chemicals such as ammonia in the refinery effluent cause the organic enrichment effect [6].

Discharge from an offsite wastewater treatment plant should meet applicable pretreatment requirements. The emissions levels presented in Table 2.1 should be achieved [16].

Table 2.1: Effluents from the Petroleum Industry.

Parameter	**Maximum value (mg/L)**
pH	6 - 9
BOD	30
COD	150
TSS	30
Oil and grease	10
Chromium	
Hexavalent	0.1
Total	0.5
Lead	0.1
Phenol	0.5
Benzene	0.05
Benzo(a)pyrene	0.05
Sulfide	1
Nitrogen (total)[a]	10
Temperature increase	≤3°C

a. the maximum effluent concentration of nitrogen (total) may be up to 40 mg/l in processes that include hydrogenation.

2.3 Anaerobic Treatment

Anaerobic treatment of wastewater can be traced from the beginning of wastewater treatment itself. Anaerobic processes have been used for the treatment of concentrated domestic and industrial wastewater for well over a century. The steep increase in energy prices in the 1970s reduced the attractiveness of aerobic methods, contributing to redirecting research efforts towards energy-saving alternatives like anaerobic treatment. On the other hand, anaerobic bacteria can tolerate a wide variety of toxicants [17]. Acetate and related low molecular weight organic compounds are readily biodegraded under anaerobic conditions by a variety of microorganisms [4].

Generally, anaerobic treatment offers the following advantages [4, 8]:

- *High efficiency.* Good removal efficiency can be achieved in the system, even at high loading rates and low temperatures.
- *Simplicity.* The construction and operation of these reactors is relatively simple.
- *Flexibility.* Anaerobic treatment can easily be applied on either a very large or a very small scale.
- *Low space requirements.* When volumetric organic loading rates high are accommodated, the area required for the reactor is small.
- *Low energy consumption.* As far as no heating of the influent is needed to reach the working temperature and all plant operations can be done by gravity, the energy consumption of the reactor is almost negligible. Moreover, energy is produced during the process in the form of methane.
- *Low sludge production.* The sludge production is low, when compared to aerobic methods, due to the slow growth rates of anaerobic bacteria. The sludge is well stabilized for final disposal and has good dewatering characteristics. It can be preserved for long periods of time without a significant reduction of activity, allowing its use as inoculum for the start-up of new reactors.
- *Low nutrients and chemicals requirement.* In the case of petroleum refinery wastewater, an adequate and stable pH can be maintained with lesser addition

of chemicals. Macronutrients (nitrogen and phosphorus) and micronutrients are also available in petroleum refinery wastewater.

- *Low air pollution.* Off-gases, volatile organic compounds (VOCs), and odorous compounds causing air pollution are eliminated.

Anaerobic decomposition of organic matter occurs in the absence of oxygen [5]. The anaerobic breakdown of organic matter is carried out in an airtight reactor. A multitude of microbial species executes a complex process in a series of interdependent steps [8]:

1. The complex organic compounds (protein, are carbohydrates, lipids) hydrolyzed to simpler organics (amino acids, sugar, peptides)
2. These organics are fermented to volatile acids by *acidogenesis*; the most common acid of anaerobic decomposition is the acetic acid. The groups of microorganisms that bring about these conversions is facultative and obligate anaerobic bacteria, collectively called *acidogens* or *acid formers*. Little change occurs in the total amount of organic material although some lowering pH results.
3. Finally, gasification or conversion of acetic acid (72%) and hydrogen (28%) into methane and carbon dioxide. The microorganisms responsible for this conversion are strict anaerobes and are called methanogens.

Previously, perceived drawbacks of anaerobic treatment systems such as high susceptibility of microbes (in particular methanogens) to a variety of xenobiotic compounds, low stability of the process and long start-up period, could be attributed to lack of knowledge of the basic principles of the process. As a matter of fact, the anaerobic digestion process is highly stable, provided the system is operated in proper conditions. It may be needed that optimum operational conditions to be determined for each particular type of wastewater and more importantly, the process must be sufficiently understood by engineers and operators [12]. Thus, it is very important to investigate the controlling parameters in order to treat the petroleum refinery wastewater by anaerobic treatment process effectively.

Like any process, anaerobic process has limitations and the choice of any process for a given wastewater is often influenced by specific conditions [11]. The anaerobic process is complex, and many rate-limiting reactions occur. Environmental conditions satisfactory to both acid formers and methane bacteria are essential. The important environmental conditions are listed below [8]:

1. The dissolved oxygen must be zero to maintain strictly anaerobic conditions all the time.
2. Good contact between the microorganisms and the influent must be maintained.
3. The pH of the reactor must range form 6.6-7.8. This is an essential requirement because acid formers tend to lower the pH, while methane formers sensitive to pH. If pH drops below 6.2, methane formation essentially ceases and more acid accumulation, thus bringing the digestion process to a standstill.
4. The alkalinity of the digester fluid should range from 1000-5000 mg/L, and volatile fatty acid should remain below 250 mg/L.
5. The optimum temperature in the mesophilic range should be 30-38°C (85-100°F) and in the thermophilic range should be 49-57°C (120-135°F).
6. Nutrients such as nitrogen and phosphorus should be present in sufficient amounts to ensure proper growth of microorganisms.
7. The anaerobic process has a relatively slow growth rate. The cellular growth is low, resulting in a small quantity of solids production.

2.4 Upflow Anaerobic Sludge Blanket (UASB) Reactor

UASB reactor is a high rate treatment system. The term 'high-rate' was once used for the later designs of sewage sludge digesters, but it is now widely used to refer to anaerobic treatment systems meeting at least the following two conditions: (a) high retention of viable sludge under high loading conditions, and (b) proper contact between incoming wastewater and retained sludge. Anaerobic treatment in high-rate reactors is increasingly recognized as the core method of an advanced technology for environmental protection and resource preservation, and it represents, combined with other proper methods, a sustainable and appropriate wastewater treatment system for developing countries [17]. High-rate anaerobic reactors have the following [18] advantages over their suspended growth counterparts:

- operate at high solids retention times and very low hydraulic retention times
- the design is simple;
- characterized by efficient heat and mass transfer;
- require small volumes;
- robust to disturbances;
- biogas generation secures good mixing characteristics.

In the UASB reactor the microorganisms are kept in the reactor due to the production of the highly flocculated, well settling, compact methanogenic sludge granules which develop, resulting in very high biomass content which characterized as well-performing. UASB Reactors, especially feasible for treating soluble containing low or easily hydrolysable solids in wastewater [10, 18]. The factors that influence the formation of granules are [18]:

- Digester startup conditions
- Degree of acclimation to the fed wastewater
- Hydraulic loading
- Organic loading
- Biogas production per unit volume
- Concentration of inhibitors
- Availability of nutrients
- Cation concentration, especially Ca^{2+} and Mg^{2+}
- Concentration and type of suspended solids contained in the wastewater.

The success of the UASB concept relies on the establishment of a dense sludge bed in the bottom of the reactor, in which all biological processes take place. This sludge bed is basically formed by accumulation of incoming suspended solids and bacterial growth. In upflow anaerobic systems, and under certain conditions, it was also observed that bacteria can naturally aggregate in flocs and granules. These dense aggregates have good settling properties and are not susceptible to wash-out from the system under practical reactor conditions [19]. Natural turbulence caused by the infiuent flow and the biogas production provides good wastewater-biomass contact in UASB systems [16].

In one of the few studies, Hovious, et al. [20] found that an anaerobic lagoon was able to remove 53% of the COD from a petroleum refinery wastewater. However, the treatment of undiluted wastewater of a used oil refinery in anaerobic packed bed reactor was not satisfactory. It was reported that acidogenesis bacteria were active while methanogenesis ones were not. But with dilution of the wastewater to one third (total organic carbon (TOC) of 1270 mg/L) 52.67% TOC removal was achieved at an organic loading rate of 1.4 kgCOD/m^3 and an HRT of 3.0 days. In general, anaerobic treatments have been demonstrated to be feasible for pre-treatment of high-strength and dilute complex wastewaters [21]. Table 2.2 [22] below show the performances of UASB reactor compare to Anaerobic Fixed Bed Reactor (AFBR).

Table 2.2: Performance of UASB and AFBR in treating municipal wastewater

Table 1. Summary of Results of AFBR and UASB

	AFBR			UASB		
Parameter	No. obs.	Mean	Std. dev.	No. obs.	Mean	Std. dev.
Influent TSS (mg/L)	82	144	44	40	189	69
Mixed effluent TSS (mg/L)	83	98	35	40	144	74
Settled effluent TSS (mg/L)	83	55	27	42	57	24
Influent VSS (mg/L)	70	126	34	41	162	36
Mixed effluent VSS (mg/L)	70	87	28	42	125	61
Settled effluent VSS (mg/L)	70	47	16	42	50	22
Influent TCOD (mg/L)	82	301	80	40	341	85
Mixed effluent TCOD (mg/L)	83	237	69	42	273	124
Settled effluent TCOD (mg/L)	83	165	68	42	162	70
Fraction of TSS degraded		0.32[a]			0.36[a]	
Fraction of TSS removed after settling		0.60[a]			0.78[a]	
TSS degradation rate (kg/m^3 day)		0.16			0.38	
TSS accumulation rate (kg/m^3 day)		0.17			0.05	
Fraction of VSS degraded		0.32[a]			0.37[a]	
Fraction of VSS removed after settling		0.65[a]			0.69[a]	
Fraction of TCOD degraded		0.22[a]			0.34[a]	
Fraction of TCOD removed after settling		0.43[a]			0.50[a]	
Organic loading (kg TCOD/m^3 day)		3.2			5.5	
Temperature range (°C)		17–28			15–30.5	
Mean temperature (°C)		23.7			20	
Volume of gas, mL CH_4/L sewage at 25°C (1 atm)		20.4			27.7	
Biogas composition (% methane)		54			60	

[a]Calculated by doing a linear regression of all observations, forced through the origin, between effluent and influent water quality parameter.

2.5 Kinetic Analysis.

Modeling of the anaerobic processes is an interesting exercise for design, prediction and control purposes. The Monod model is efficiently applicable for the description of organic matter removal during anaerobic digestion. Under these conditions, at low effluent substrate concentration, which is correlated to high reactor performance, the kinetics is first-order. The first-order model is popular, simple and has been successfully applied both for wastewater and solid waste treatment processes. The first-order kinetic constant, K, is related both to waste water type (pre-acidified or not, complex or soluble) and operational conditions (biomass concentration, temperature, pH, etc) [23].For this project, the kinetic constant was determined at four different organic loading be apply in the anaerobic treatment process using UASB reactor.

CHAPTER 3

METHODOLOGY

3.1 Project Activities

The project is divided into two phases, namely FYP I and FYP II. In FYP I, activities and tasks such as research-based study and information gathering covered all the scope of study for the project, begin with problems towards the environment until treatments carried out in dealing with petroleum refinery wastewater, and have been accomplished. Laboratory experiments were started before the final exam. These experiments particularly aimed to examine and determine the characteristics of the samples. This allows more time for improvement and modification as the project moves on into the second phase.

In FYP II, which is the current state, experiments have resumed accordingly, based on the progress in FYP I. The UASB reactor start operated in treating the petroleum refinery wastewater for four different organic loading (A1, A2, B1, B2). The monitoring work and tests required were conducted properly in order to obtain all necessary data to be further study in kinetic analysis. The project process flow is depicted in Figure 3.1.

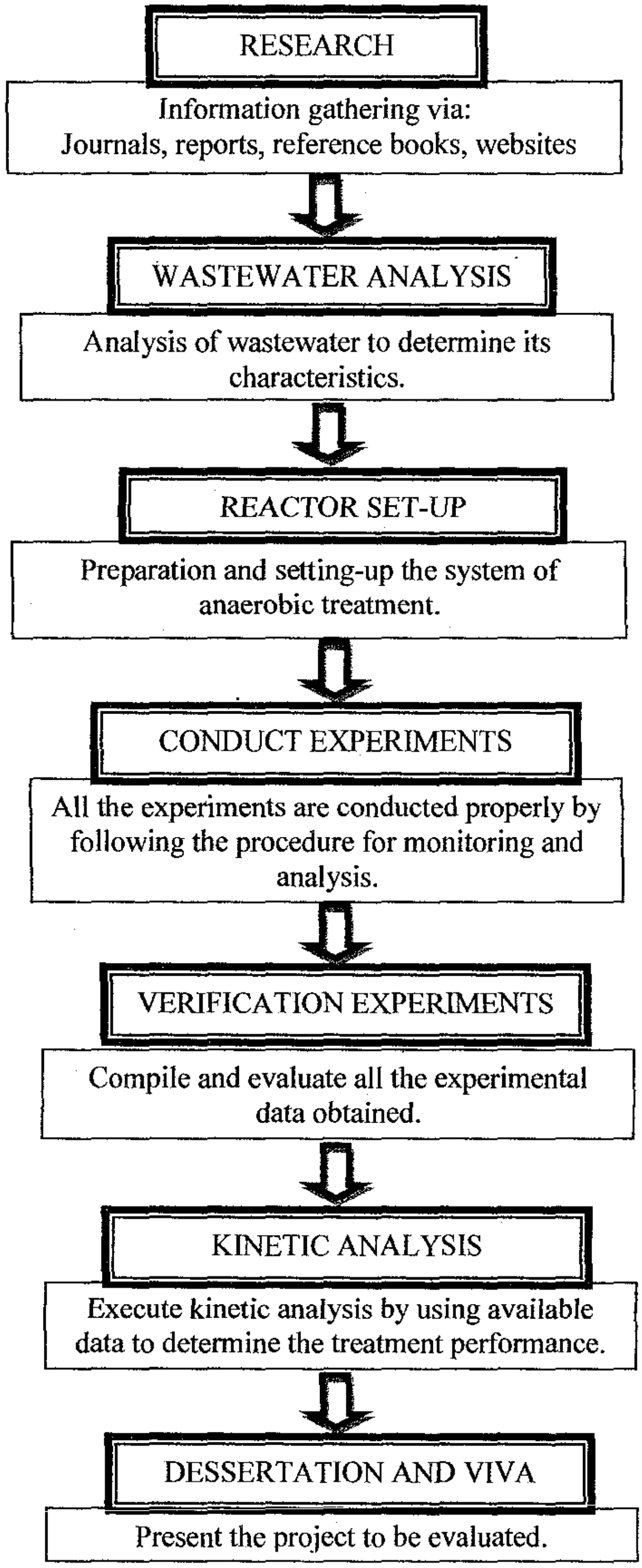

Figure 3.1: Project Process Flow

3.2 Wastewater Preparation.

The petroleum refinery wastewater was obtained from PETRONAS Penapisan Terengganu Sdn. Bhd. which contains high chemical oxygen demand (COD) of 7896 mg/L. Meanwhile, the sludge was brought from a local Palm Oil Mill Effluent (POME) anaerobic treatment plant. The wastewater was stored in cold storage room at 4°C until required. This storage had no observable effect on the composition. The pH was never adjusted and no chemicals were added to the wastewater during storage.

The refinery wastewater was prepared as influent by diluting to the desired organic loading rate which will be tested as a method for reducing the instability and low efficiency problems caused by its high organic content, especially for high-rate anaerobic systems. Then, sodium bicarbonate will be added in the wastewater .This has been done to maintain the alkalinity and the pH of the wastewater to achieve the required condition in anaerobic system.

3.3 Experimental Set-up

The UASB reactor has been design based on the requirement and the feasibility of the project. The water height of the UASB reactor is 340 mm. The reactor has a 94 mm of diameter, and a total effective volume of 2.4 L. The experimental setup of the UASB reactor is shown in Figure 3.2.

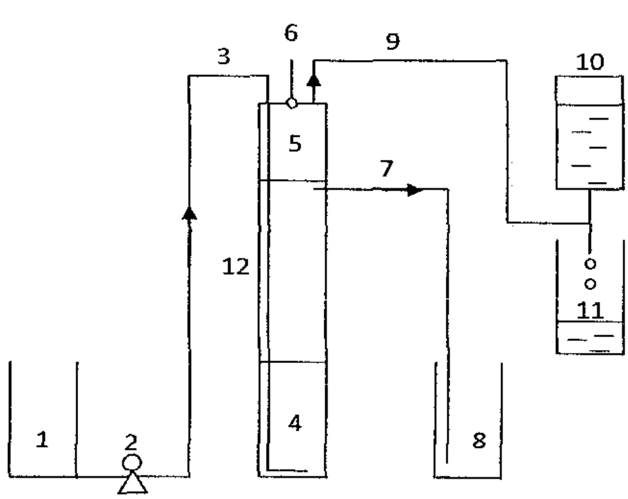

Figure 3.2: Schematic diagram of experimental set-up of the UASB reactor.

Referring to the Figure 3.2, the system was represented by:

1. Influent holding tank
2. Peristaltic pump
3. Influent line
4. Sludge zone
5. Gas zone
6. Sampling point
7. Effluent line
8. Effluent holding tank
9. Gas line
10. Gas collection system by water displacement
11. Water tank
12. UASB reactor

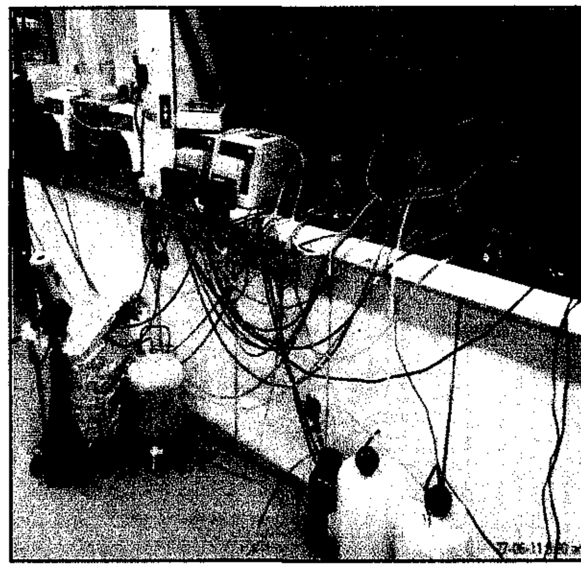

Figure 3.3: Experimental UASB set-up

In order to shorten the duration of the experiments, two UASB reactors were setup in parallel (A and B) and operated at the mesophilic temperature range (35°C) throughout the period of the experiments. Wastewater was continuously fed into the UASB reactor using a variable-speed peristaltic pump. The operation condition was optimized. Tables 3.1 below show the variable organic loading rate apply in the project. The values of organic loading rate determination were based on the time frame of the project and the wastewater characteristic.

REACTOR	OLR	ORGANIC LOADING RATE , mg COD/l	VOLUMETRIC ORGANIC LOADING RATE , mg COD /m^3/ d
A	A1	1000	0.583
	A2	1500	0.875
B	B1	2000	1.167
	B2	4000	2.333

Table 3.1: Organic loading rates (OLR) apply in the UASB reactors.

After the start-up stage had been completed, the steady-state operation was conducted. The steady-state performance was evaluated under flowrate is 1.4 L/d and hydraulic retention time of 1.7 days. At given loading rate, the bioreactor was continuously operated until steady-state condition was achieved (predicted in two weeks), when parameters like effluent COD, VSS and gas production rate in bioreactor became constant. Then samples were collected and subjected to the analysis of the following parameters, i.e. feed and effluent COD, effluent total alkalinity; effluent total volatile fatty acid, effluent suspended solids and volatile suspended solids, reactor pH, gas production and composition were measured according to standard methods [3].Organic loading was changed when steady state was achieved.

The first COD loadings batch which are 1000 mg/L (A1) for Reactor A and 2000 mg/L (B1) in reactor B have starts be operated on 20 August 2011 and done on 10 October 2011. Meanwhile, the second COD loadings batch which is 1500 mg/L (A2) for Reactor A and 4000 mg/L (B2) in reactor B has been start on 31 October 2011 and done on 14 December 2011.

3.4 Analytical Methods

There will be total of 12 test days on the wastewater for every month of the experiment as each week is three days of experiment will be done. The period of the anaerobic treatment using UASB in this project can be divided to two phases; sludge acclimatization and wastewater test which can be summarize in Figure 3.4.

OLR	DETAIL / WEEK	1	2	3	4	5	6	7	8	9	10	11	12	13
A1&B1	Sludge Acclimatization	3[b]	3	3										
	Wastewater Test				3	3	3	3						
A2&B2	Sludge Acclimatization								3	3	3			
	Wastewater Test											3	3	3

b - three days of experiment will be conducted.

Figure 3.4: Gantt chart of the anaerobic treatment stages.

The tests were conducted during sludge acclimatization stage to monitor the progress of the reactor process until start-up of the reactor is finished. Then, the second phase test which is after the reactors were stabled is conducted to obtain all the data for analysis.

3.4.1 Experiments

The experiments that will be conducted in every month to find the characterization of the wastewater are as following:

1.) pH

pH is a numerical expression of the intensity of acidity or basicity of the water sample. A pH value of 7.0 is considered neutral, or neither acid nor basic. A pH less than 7.0 denotes acidity, with the intensity of acidity increasing as the numbers decrease. Number between 7.0 and 14.0 denote as basicity, with intensity increasing as the numbers increase. pH of the wastewater sample was determined using HACH pH meter.

2.) Alkalinity

The alkalinity of water is its quantitative capacity to neutralize a strong acid to a designated pH. The determination of alkalinity levels at various points in a treatment plant aids understanding and interpretation of the treatment process and management of digesters and biological nutrient removal. The experiment is by using titration of 0.1N sulfuric acid (H_2SO_4) with the water sample.

The calculation for alkalinity, as mg $CaCO_3$/L

$$= \frac{(\text{Total mL } H_2SO_4 \text{ titrant used}) \times \text{Normality of } H_2SO_4 \times 50\,000}{\text{mL sample}}$$

3.) Total Suspended Solids (TSS)

Total suspended solids (TSS) are a portion of the Total Solids (TS) retained on a filter disc with a specified pore size, measured after being dried at a specified temperature.TSS was determined by filtering 50 mL of the wastewater samples using a 47 mm filter disc. The filter paper was then dried in a drying oven of 105°C for 1 hour. After the filter paper was cooled off in a desiccator, the filter paper was weighed to determine the suspended solid of wastewater. The TSS was determined by the following formula:

$$TSS,\ mg/L = \frac{(W1-W2)}{\text{Volume of sample, L}}$$

Where;

W1 = mass of residue + filter paper + glass fiber disk (mg)

W2 = W1 after ignition (mg)

4.) Mixed Liquor Volatile Suspended Solids (MLVSS)

Suspended matter in activated-sludge mixed liquor and return sludge can be used to determine process status, estimate the quantity of biomass, and evaluate the results of process adjustments. To measured volatile solids, ignite the sample with glass-fiber disk and filter paper at 550°C for 20 minutes in a muffle furnace. Cool in desiccators to balance temperature and weigh. The value of MLVSS is determined using following equations:

$$MLVSS,\ mg/L = \frac{(W2-W3)}{\text{Volume of sample, L}}$$

Where;

W2 = mass of residue + filter paper + glass fiber disk (mg)

W3 = W2 after ignition (mg)

5.) Chemical Oxygen Demand (COD)

The COD determination measures the oxygen equivalent of that portion of organic matter in sample that can be oxidized by a strong chemical oxidizing agent. The COD can be determined faster than BOD (3 hours instead of 5 days) and can, therefore, be used to estimate reactor performance more rapidly. Place tubes and in block digester preheated to 150°C and reflux for 2 hours. Cool to room temperature and place vessels in test tube track. After cooling process completed, the COD of the wastewater sample was determined using HACH spectrophotometer (DR2800, USA) as shown in Figure 3.6 based on the APHA method.

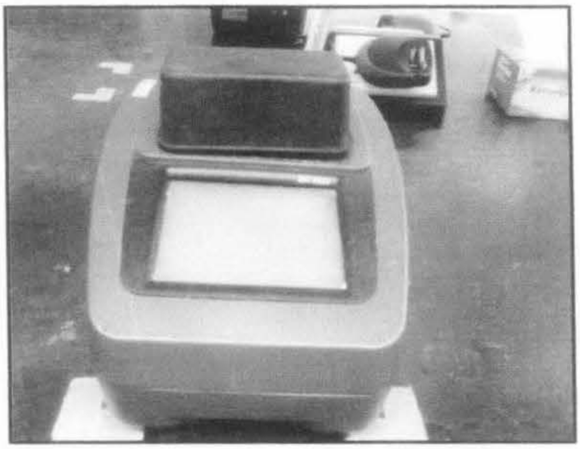

Figure 3.6: HACH spectrophotometer

6.) Biochemical Oxygen Demand (BOD_5)

This test determines the amount of organic material in wastewater by measuring the oxygen consumed by microorganisms in biodegrading organic constituents of the waste. The test consists of measuring DO before and after a 5-days incubation period of the sample at 20°C to determine the amount of oxygen used biochemically. The test is carried out with seeding. The initial and final dissolved oxygen (DO) were measured using DO meter (YSI 5000, USA) as shown in Figure 3.7 below.

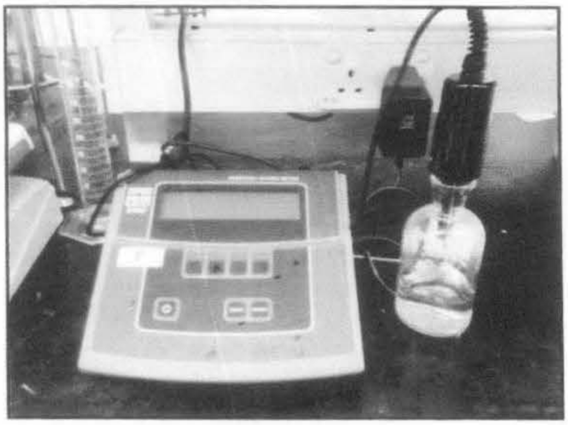

Figure 3.7: DO meter.

The value of BOD is determined using following equations:

- To determine the BOD value without seed correction:

$$= \frac{(Initial\ dissolved\ O_2) - (Final\ dissolved\ O_2) - (Blank\ correction\ )}{Sample\ size\ /\ 300}$$

- To determine the BOD value with seed correction and blank correction:

$$= \frac{(Initial\ dissolved\ O_2) - (Final\ dissolved\ O_2) - (Seed\ \&\ Blank\ correction\ )}{Sample\ size\ /\ 300}$$

7.) Oil and Grease

The partition is applied by gravimetric method involves extraction of dissolved or emulsified oil and grease from wastewater by using an extracting solvent. The common solvents used aren-hexane, methyl-tert-butyl ether (MTBE), and trichlorotrifluoroethane. Oil and grease has the natural tendency to float on the water surface under quiescent conditions, as the density of oil and grease is usually less than one.

Figure 3.8: Oil and Grease Analyzer.

3.5 Kinetic Analysis.

From the research [24], found that it was the best for this project to use first-order of kinetic analysis. The theory of application was as following:

1.) Determination of kinetic constant

The first-order kinetics is represented by the following equation:

$$R_{RS} = \frac{dS}{dt} = K.S_e \tag{3.1}$$

Where:

R_{RS} = volumetric substrate removal rate (kgCOD m^3/d), K = first-order kinetic constant (d^{-1}), Se =effluent substrate concentration (kgCOD/ m^3).

Using equation (3.1) it is possible to determine the kinetic constant, K, as shown below:

$$K = \frac{R_{RS}}{S_e} = \frac{(S_0 - S_e)}{m} \cdot \frac{1}{S_e} = \frac{(S_0 - S_e).Q}{V.S_e} \tag{3.2}$$

Where:

So = influent substrate concentration (kgCOD m^{-3}), τ = hydraulic retention time (d), V = reactor volume (m^3), Q = wastewater flowrate (m^3/d).

In practice, the kinetic constant, K, is derived from the slope of the line of R_{RS} versus Se using experimental data from different steady-state conditions.

In the analysis of the project, the kinetic constant, K were determined from COD and also oil and grease data.

2.) Process simulation

In full scale anaerobic digesters, the volumetric COD loading rate is determined by the raw wastewater COD concentration (kg /m^3) and the hydraulic retention time (d) or wastewater flowrate (m^3/d). After determining the kinetic constant K, using experimental data at different organic loading rates, the reactor effluent COD (S_e) and COD removal (U_S). The same approach is applied for oil and grease. The data can be calculated as follows:

$$S_0 = \frac{S_0 Q}{Q + KV} \tag{3.3}$$

$$U_s = \frac{Km}{1 + Km} \tag{3.4}$$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Wastewater Characterization

Before the petroleum refinery wastewater from PETRONAS Penapisan Terengganu Sdn. Bhd. (PPTSB) is fed in the reactor, the wastewater sample was analyzed to identify its characteristics by conducting experiments mentioned in the previous section. Table 4.1 shows the characteristics of the refinery wastewater sample. Obviously, the petroleum refinery wastewater contain high amount of COD and BOD that was 7896 mg/L and 3378 mg/L, respectively. This wastewater has exceeded the standard of effluent discharged from petroleum industry set by DOE. Hence, it is not suitable to be discharged into any water body without proper treatment. Such discharge will bring adverse effect on the ecosystem by reducing dissolved oxygen content in the water, thus resulting in oxygen deficiency in the aquatic life.

Table 4.1: Characteristics of refinery wastewater sample

Parameter	Average concentration
pH	8.48
COD (mg/L)	7896
BOD (mg/L)	3378
Total Phosphorus (mg/L)	10.2
Nitrate (mg/L)	2.23
Ammonia (mg/L)	13.5
Total Alkalinity (mg/L)	990
Oil & Grease (ppm)	382

4.2 Summary of Tests.

With the characteristics beforehand, anaerobic treatment using UASB reactor were performed in order to reduce the COD, BOD and oil and grease of the sample. There were four different organic loading rates being carried out for preliminary analysis. The test was carried out by varying a single factor while keeping all other factors fixed as a specific set of conditions. In the Table 4.2 below show summarize of the results from tests conducted for all different organic loadings.

Table 4.2: Summary of tests conducted.

		Reactor A		Reactor B	
	COD Load, mg/l	1000	1500	2000	4000
	OLR, $kg/m^3/d$	0.583	0.875	1.167	2.333
Parameters	**Units**	A1	A2	B1	B2
COD i	mg/L	1014	1444	1993	4002
COD e	mg/L	261	316	558	883
BOD_5 i	mg/L	665	1204	1095	1608
BOD_5 e	mg/L	161	209	538	668
Oil & Grease i	ppm	198	204	243	256
Oil & Grease e	ppm	186	176	227	220
MLSS e	mg/L	10456	12336	15971	24352
MLVSS e	mg/L	7892	9402	10900	18464
Ammonia-N i	mg/L	2.66	1.37	4.38	4.3
Ammonia-N e	mg/L	2.97	1.15	2.85	2.32
Nitrate-N i	mg/L	2.38	2.93	4.43	5.02
Nitrate-N e	mg/L	2.57	2.95	4.05	4.63
pH i	-	8.98	6.83	8.98	7.1
pH e	-	8.51	8.05	8.05	8.02

* i – influent; e – effluent

Concentrated on the research have done on this project, the sludge acclimatization period took about three weeks for the system to be stable.

4.2.1 Chemical Oxygen Demand (COD)

The COD concentration varies from the day 4 of the first loading (A1 and B1) period. However, the variations not too far as time move on until at day 44 the COD concentration start to maintain at the same level. Same goes to for the second load (A2 and B2) which stabled after 22 days the loads are fed in the reactors. The unstable period data is the times of sludge acclimatization take place.

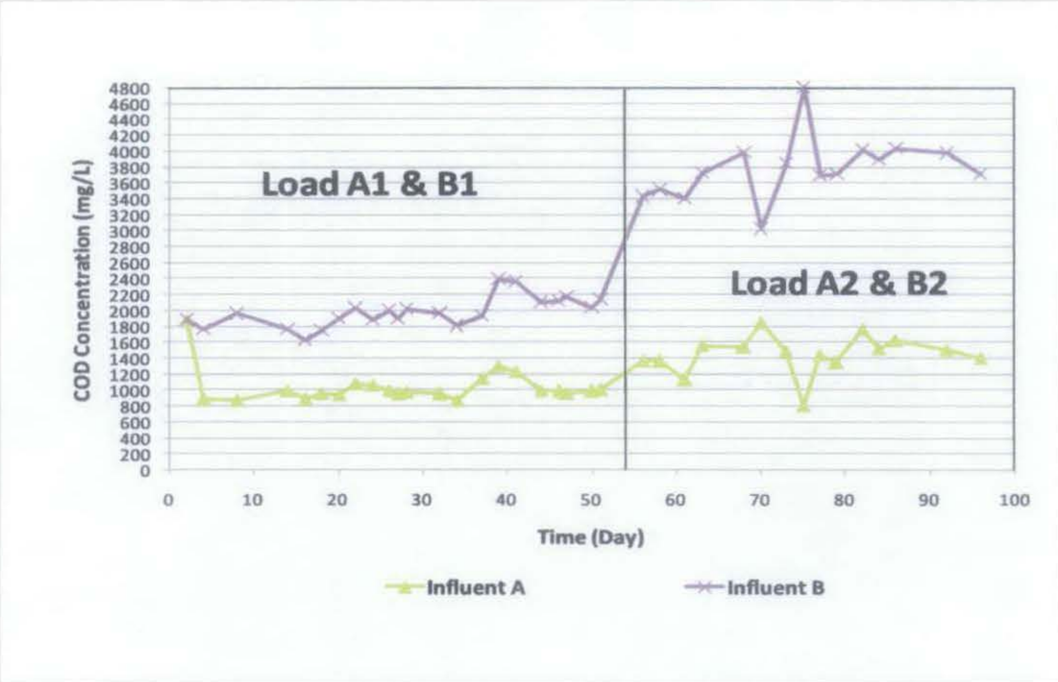

Figure 4.1: Graph of COD Concentration (Influent) versus Time.

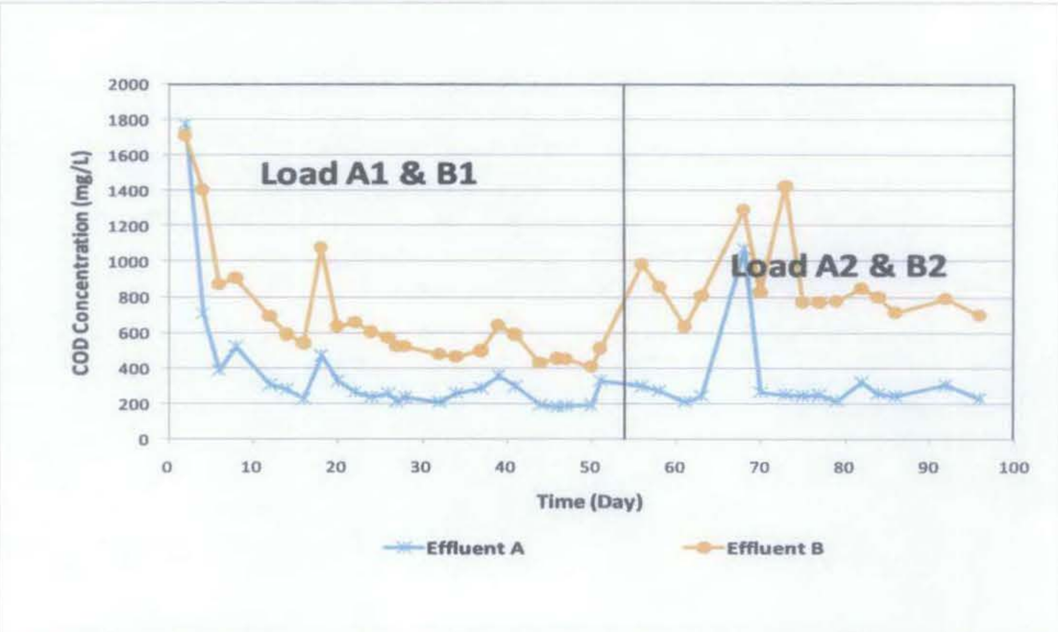

Figure 4.2: Graph of COD Concentration (Effluent) versus Time.

From Figure 4.1, show the average first loading (A1 and B1) of the influent were achieved for 1014 mg/L and 1444 mg/L. Meanwhile, for load A2 and B2 average values were 1993 mg/L and 4002 mg/L. These results indicated the experimental be monitored properly as the data almost same with the organic loading have decided for this project.

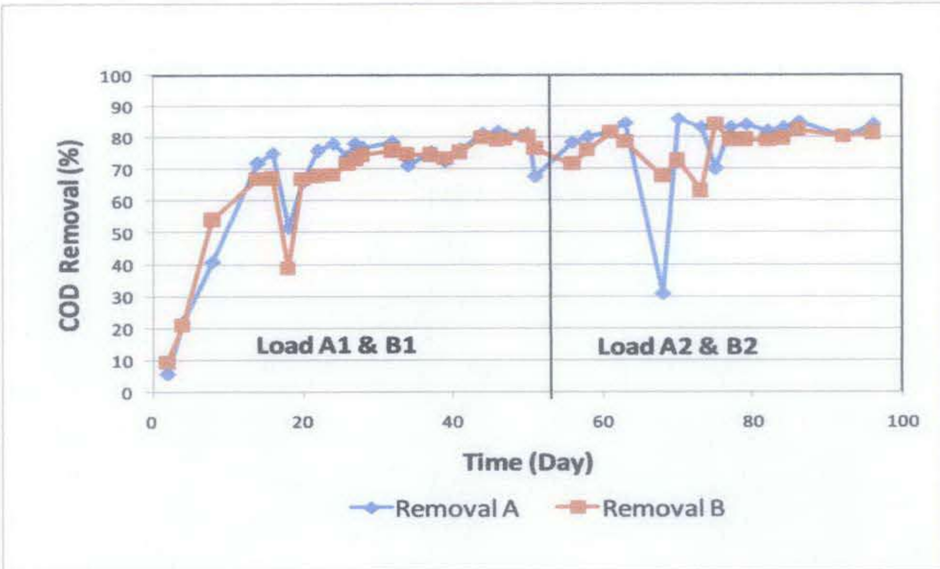

Figure 4.3: Graph of COD Removal Efficiency versus Time.

From Figure 4.2, COD removals at the start-up for both reactor (A and B) varied in the range of about 5-80%. However, increase in influent COD concentrations caused an increase in the effluent COD, resulting in relatively low COD removals. Within the first week of operation, the COD removal efficiency increased up to about 85 %, and then the efficiency not much change along stable reactor period. The optimum COD removal efficiency was achieved by load A1 with average 78.35%.

4.2.2 Biological Oxygen Demand (BOD_5)

As the system for reactor A and reactor B start to stabilize, the BOD_5 tests were conducted to monitor the process happening in the both reactors. It has shown the oxygen used up by microorganism during the oxidation of organic matter in the reactor quite high.

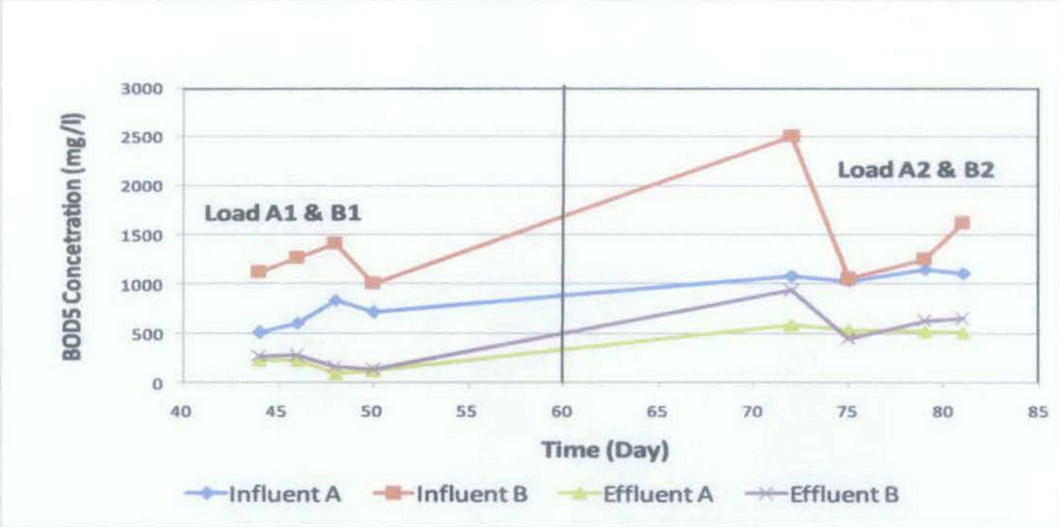

Figure 4.4: Graph of BOD_5 versus Time.

Figure 4.5: Graph of BOD_5 Removal Efficiency versus Time.

According to the results, it can be seen that the first organic loading (A1 & B1) showed good results with BOD removal at 73.48% and 82.56% and second organic loading (A2 & B2) obtained BOD removal for 50.81% and 57.31%. Thus, OLR B1 is the optimum organic load for the reactor is operated if only based on the BOD removal.

4.2.3 Oil & Grease

Oil and grease concentration was tested in this project due to higher amount in the petroleum refinery wastewater sample. This incentive was to evaluate how efficient the anaerobic treatment by using UASB reactor as not many studied done was found.

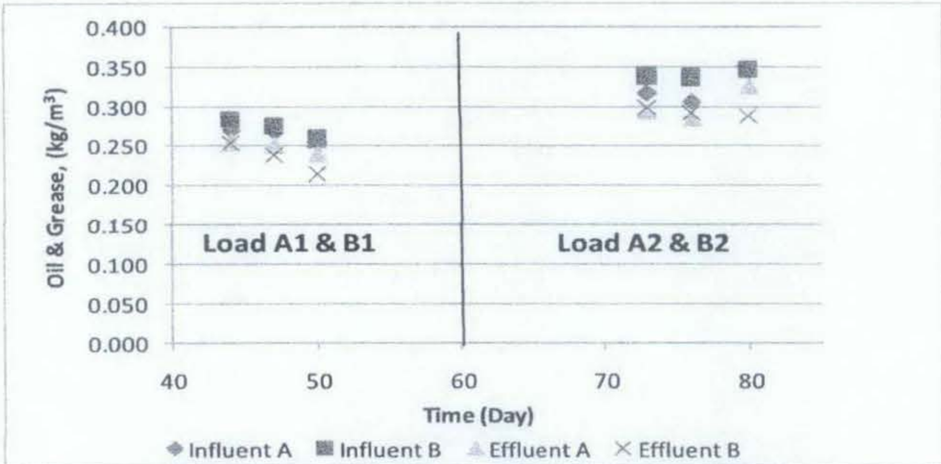

Figure 4.6: Graph of Oil and Grease versus Time

Figure 4.7: Graph of Oil and Grease Removal Efficiency versus Time

The data were taken during reactor in stable state. From the Figure 4.5, the range of oil and grease concentration is 0.24-0.35 kg/m^3. However, it still show the reactors able to remove oil and grease in the wastewater sample as can see in the Figure 4.6.

4.2.4 Ammonia & Nitrate

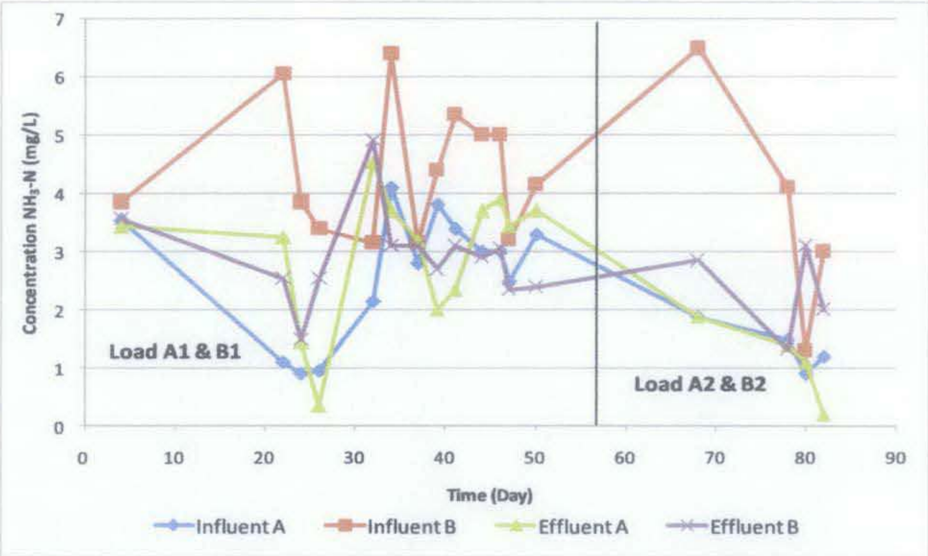

Figure 4.8: Graph of Ammonia Concentration versus Time

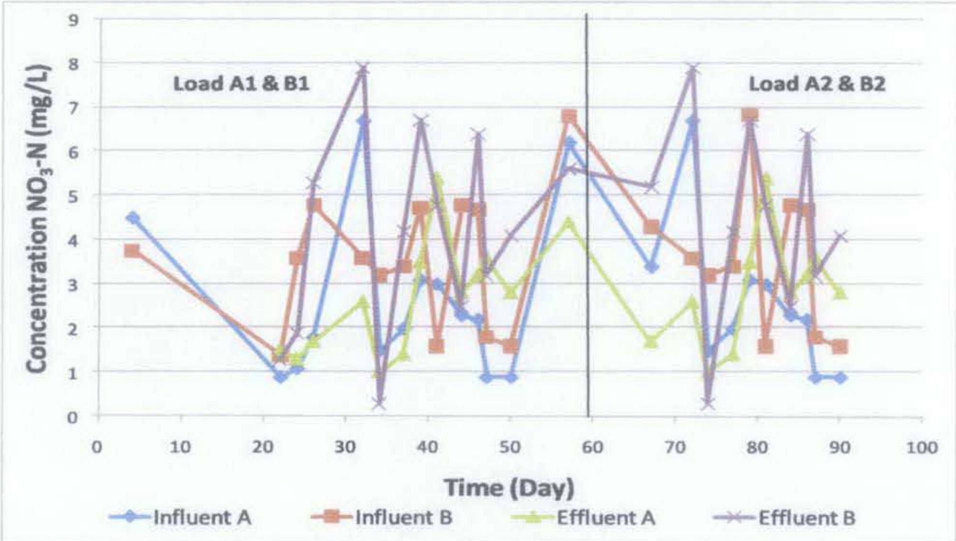

Figure 4.9: Graph of Nitrate Concentration versus Time.

Nutrients such as nitrogen and ammonia should be present in sufficient amounts to ensure proper growth of microorganisms. From the Figure 4.7 and Figure 4.8, the concentration of ammonia and nitrate in the reactor A is lower compared to reactor B due to the COD concentration of influent for reactor A is lower compared to influent in the reactor B. However, after the anaerobic process happened, the concentration of ammonia and nitrate in reactor B drop much more than reactor A about 5%. Perhaps, there were more bacteria in the reactor B compared to reactor A.

4.2.5 pH

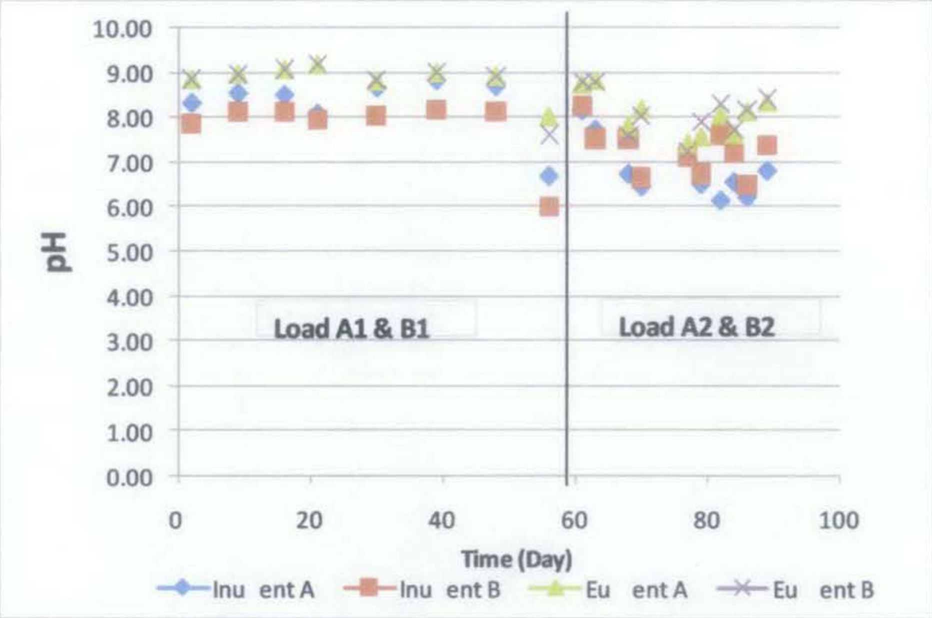

Figure 4.10: Graph of pH versus Time.

The pH of the reactor must range form 6.0-9.5. This is an essential requirement because acid formers tend to lower the pH, while methane formers sensitive to pH. If pH drops below 6.0, methane formation essentially ceases and more acid accumulation, thus bringing the digestion process to a standstill. From the results, it show the system successfully be operated under the allowable control parameters operation range.

4.3 Kinetic Analysis

By refer to the Section 3.5: Kinetic Analysis, the data of COD was analyzed to obtain the kinetic analysis, K. Then, the estimated data are presented to show the optimum parameter for the UASB reactor can perform in petroleum refinery wastewater treatment.

4.3.1 Chemical Oxygen Demand (COD)

Using an Equation 3.1 and 3.2, the volumetric substrate removal rate, R_{RS} is calculated for all organic loads (**Appendix 2**). The data is shown in the Table 4.3 below.

Table 4.3: Volumetric COD removal rate, R_{RS}.

OLR	Se ,kg/m3	RRS ,kg/m3/d
A1	0.229	0.434
A2	0.226	0.646
B1	0.486	0.848
B2	0.673	1.592

Then, by using average experimental data from different steady-state conditions (organic loading), the kinetic constant, K is derived from the slope of the line of R_{RS} versus Se as shown in Figure 4.10.

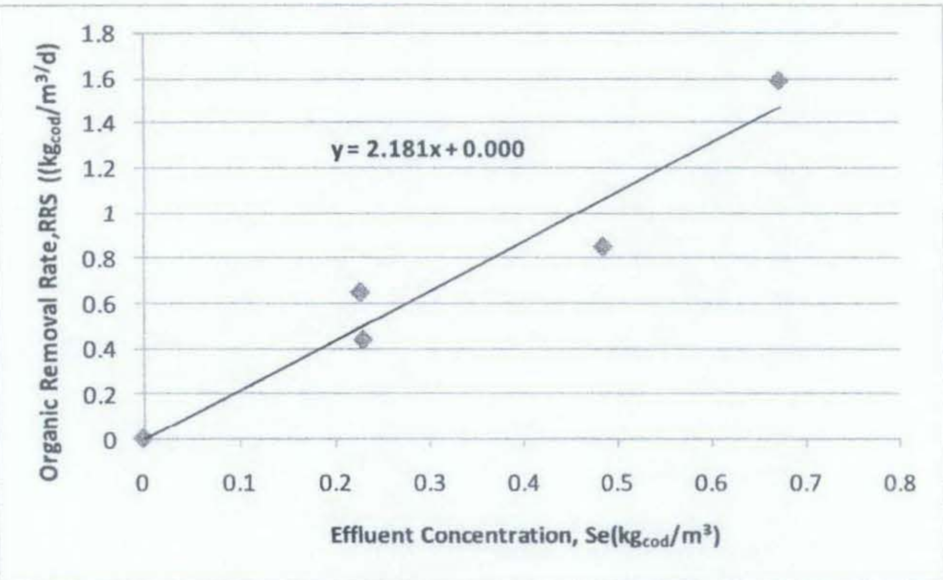

Figure 4.11: Graph of Organic Removal Rate versus Effluent Concentration.

Thus, from the slope of the graph, obtained the kinetic analysis, K is equal to **2.18 d^{-1}**. This value is significantly in the range of 0.9-4.7 d^{-1}. [25] It shown that the UASB reactor in this project operated well in treating the refinery wastewater but not performed higher than researches have been done before.

4.4 Simulation

Simulation are conducted by using the kinetic constant, K get from the kinetic analysis, both of the K values which were from COD and oil and grease data. These will show how accurate the estimation data with the measured data if the same UASB reactor and other related parameters were applied. In this section, Equation 3.3 and 3.4 are applied.

4.4.1 Chemical Oxygen Demand (COD)

All the data analysis was attached in **Appendix 3.**

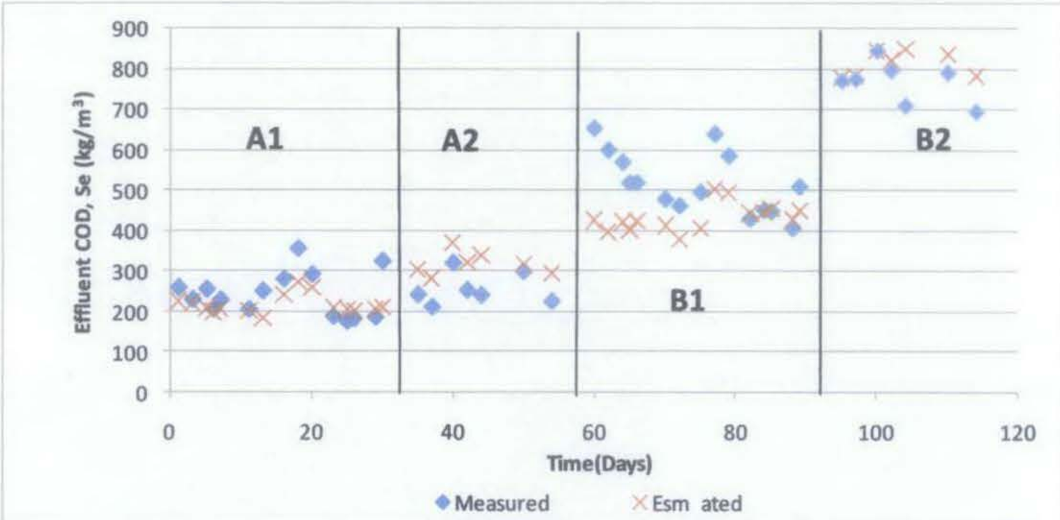

Figure 4.12: Graph of Effluent COD versus Time.

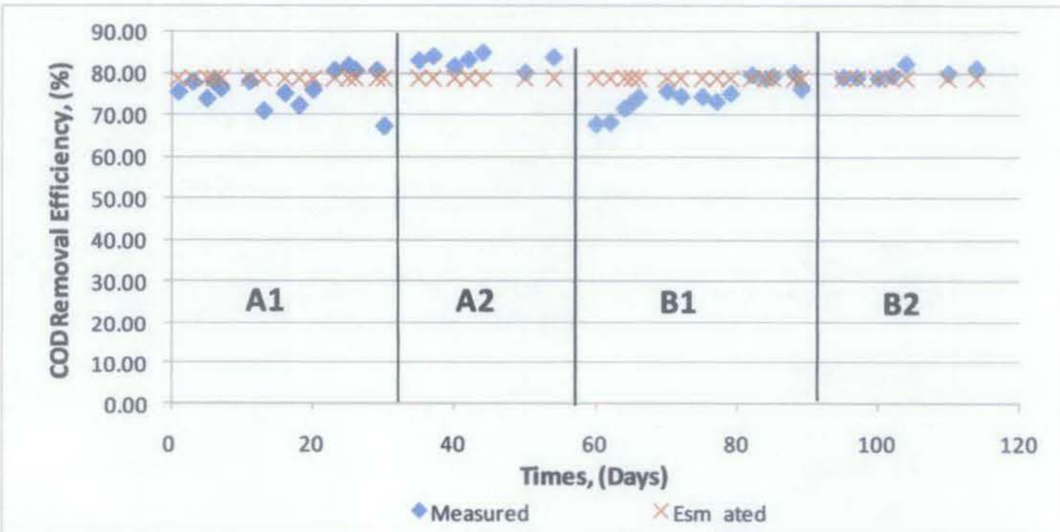

Figure 4.13: Graph of COD Removal Efficiency versus Time.

From Figure 4.12 and 4.13, it shows the data from estimation are not much different from the measured (experimental) data. Thus, the kinetic analysis, K equal to 2.18 d^{-1} is acceptable and rational to be applied in full scale.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The outcomes of this project indicate that anaerobic treatment of petroleum refinery wastewater using UASB reactor has the potential to be applied as since it is efficient, controllable and predictable. Removal efficiency up to 79% can be achieved for COD, while 83% and 17% can be achieved for BOD_5 and oil and grease respectively, at conditions of pH 6 to 9, with four different organic loads (A1, B1, A2, and B2) which is 1014 mg/l, 1444 mg/l, 1993 mg/l and 4002 mg/l. Thus, the UASB reactor performed well in treated the petroleum refinery wastewater. The data and interactions of the influencing factors which is COD was analyzed in kinetic analysis and obtained the kinetic constant is 2.18 d^{-1}.The measured data of the project be compared and evaluated with estimation data using the simulation equation in the kinetic analysis. It turned out very well which the comparison of the pattern and value of the measured data and estimation almost the same. Thus, first-order kinetic model was found to be suitable for representation of substrate removal data. Prediction of UASB reactor operation was possible. The main objectives of this project were achieved successfully.

5.2 RECOMMENDATION

Based on the results of the project, the following recommendations can be considered:

i. Study on other operational conditions that can influence the performance of the reactor such as temperature, biomass concentration, flow rate, etc. or the coupling of any two treatments methods e.g. anaerobic followed by anoxic .
ii. Study on other kinetic analysis like Stover–Kincannon model which has high potential for analysis of the data from anaerobic treatment in order to identified the accurate optimum parameter of the reactor performance.

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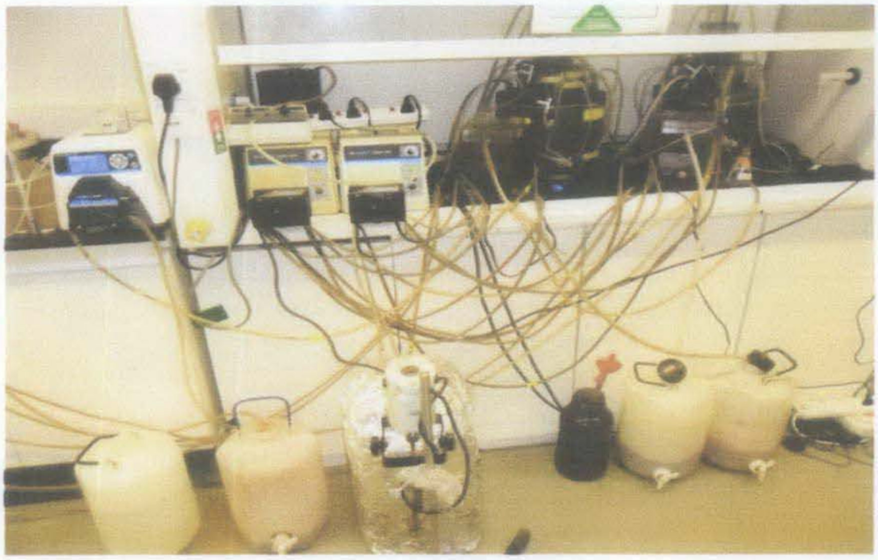
APPENDIX 1 – Project Photos

Collecting anaerobic sludge from POME.



UASB Reactor

COD Test

APPENDIX 2 – Spreadsheets of Kinetic Analysis: COD

A1			A2			B1			B2		
So, kg/m3	Se ,kg/m3	RRS,kg/m3/d	So, kg/m3	Se ,kg/m3	RRS,kg/m3/d	So, kg/m3	Se ,kg/m3	RRS,kg/m3/d	So, kg/m3	Se ,kg/m3	RRS,kg/m3/d
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.984	0.179	0.474	1.343	0.214	0.664	2.039	0.406	0.961	3.715	0.696	1.776
0.963	0.186	0.457	1.408	0.228	0.694	2.107	0.429	0.987	4.035	0.710	1.956
0.982	0.189	0.466	1.620	0.243	0.810	2.168	0.448	1.012	3.690	0.771	1.717
0.992	0.191	0.471	1.440	0.244	0.703	2.117	0.451	0.980	3.710	0.775	1.726
0.950	0.208	0.437	1.523	0.255	0.746	1.805	0.461	0.791	3.975	0.792	1.873
0.949	0.209	0.436	1.508	0.301	0.710	1.961	0.478	0.872	3.895	0.797	1.822
0.981	0.231	0.441	1.758	0.322	0.844	1.929	0.495	0.843	4.015	0.845	1.865
1.057	0.232	0.485				2.138	0.509	0.958			
0.876	0.254	0.366				1.901	0.519	0.813			
0.991	0.258	0.431				2.015	0.519	0.880			
1.074	0.262	0.478				2.001	0.571	0.842			
1.143	0.283	0.506				2.357	0.587	1.041			
1.231	0.294	0.551				1.883	0.601	0.754			
1.005	0.327	0.399				2.391	0.641	1.029			
1.297	0.358	0.553				**2.025**	0.655	0.806			
Average	0.229	0.434	**Average**	0.226	0.646	**Average**	0.486	0.848	**Average**	0.673	1.592

APPENDIX 3 – Spreadsheets of Simulation: COD

A1						A2					
Days	So Measured, kg/m3	Se Measured,kg/m3	Se Estimated ,kg/m3	COD Removal Measured	COD Removal Estimated	Days	So Measured, kg/m3	Se Measured ,kg/m3	Se Estimated, kg/m3	COD Removal Measured	COD Removal Estimated
1	1074	262	227	75.63	78.90	35	1440	244	304	83.03	78.90
2						36					
3	1057	232	223	78.01	78.90	37	1343	214	283	84.08	78.90
4						38					
5	991	258	209	73.97	78.90	39					
6	949	209	200	78.02	78.90	40	1758	322	371	81.68	78.90
7	981	231	207	76.41	78.90	41					
8						42	1523	255	321	83.25	78.90
9						43					
10						44	1620	243	342	85.00	78.90
11	950	208	201	78.11	78.90	45					
12						46					
13	876	254	185	71.03	78.90	47					
14						48					
15						49					
16	1143	283	241	75.28	78.90	50	1507.5	301	318	80.03	78.90
17						51					
18	1297	358	274	72.42	78.90	52					
19						53					
20	1231	294	260	76.11	78.90	54	1408	228	297	83.80	78.90
21											
22											
23	992	191	209	80.71	78.90						
24											
25	984	179	208	81.85	78.90						
26	963	186	203	80.69	78.90						
27											
28											
29	982	189	207	80.75	78.90						
30	1005	327	212	67.45	78.90						

B1					
Days	So Measured, kg/m3	Se ,kg/m3	Se Estimated, kg/m3	COD Removal Measured	COD Removal Estimated
60	2025	655	427	67.65	78.90
61					
62	1883	601	397	68.08	78.90
63					
64	2001	571	422	71.49	78.90
65	1901	519	401	72.72	78.90
66	2015	519	425	74.22	78.90
67					
68					
69					
70	1961	478	414	75.61	78.90
71					
72	1805	461	381	74.45	78.90
73					
74					
75	1929	495	407	74.33	78.90
76					
77	2391	641	504	73.17	78.90
78					
79	2357	587	497	75.11	78.90
80					
81					
82	2107	429	445	79.66	78.90
83					
84	2117	451	447	78.70	78.90
85	2168	448	457	79.35	78.90
86					
87					
88	2039	406	430	80.10	78.90
89	2138	509	451	76.18	78.90

B2					
Days	So Measured, kg/m3	Se Measured ,kg/m3	Se Estimated, kg/m3	COD Removal Measured	COD Removal Estimated
95	3690	771	779	79.11	78.90
96					
97	3710	775	783	79.10	78.90
98					
99					
100	4015	845	847	78.95	78.90
101					
102	3895	797	822	79.54	78.90
103					
104	4035	710	851	82.40	78.90
105					
106					
107					
108					
109					
110	3975	791.5	839	80.09	78.90
111					
112					
113					
114	3715	696	784	81.28	78.90