# Biological Treatment of Refinery Wastewater Using Sequencing Batch Reactor (SBR) System

by

Fadiyatul Nabilah binti Abu Bakar

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Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

Civil Engineering Programme

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Approved by,

_________________________________

(Dr. Amirhossein Malakahmad)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

September 2013

# 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 references and acknowledgements, and the original work contained herein have not been undertaken or done by unspecified source or persons. I also certify that all information sources or literature included in the study are indicated in this report.

……………………………………………..

FADIYATUL NABILAH BINTI ABU BAKAR

# ABSTRACT

This study will determine the overall performance of biological treatment using sequencing batch reactor (SBR) system in treated refinery wastewater. The sample is obtained from Petronas Penapisan Kerteh Sdn Bhd meanwhile sludge sample is obtained from Ethylene Malaysia Sdn Bhd sewerage treatment plant. This experiment is conducted by using a system named Sequencing Batch Reactor. A reactor; with working volume of 2.0L are filled with required volume of refinery wastewater. It is operated with Cycle Time (CT) of 8 hours where 3 cycles per day with Hydraulic Retention Time (HRT) of 24 hours. The cycle time consist of feeding (10 minutes), reacting (240 minutes), settling (120 minutes), decanting (15 minutes) and idling (90 minutes). The SBR shows a good performance in reduction of Chemical Oxygen Demand, Nitrate and Phosphate. The study reveals that the COD removal efficiency is ranging from 70 to 89.9%. Nitrate and Phosphate concentration exist provide nutrient for the microorganism to degrade the organic matter and for its growth. It shows that SBR is applicable in treating refinery wastewater.

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All praises to Allah, the Most Gracious and the Most Merciful for His will upon the completion of my Final Year Project (FYP) and for giving me the strength to successfully perform throughout this journey. I can proudly say that I have taken efforts in this subject; however I still believe it would not have been possible without the continuous and kind support of many individuals. With this given opportunity, I would like to extend my sincere and humble gratitude to all of them.

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# CHAPTER 1

# INTRODUCTION

## 1.1. Background of Study

Petroleum refinery industry has converted crude oil into about 2500 refined products such as liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, lubricating oils and feedstock for the petrochemical industry (Benyahia *et al.).* During the refining process, a huge amount of wastewater are produced approximately 0.4-1.6 times the volume of the processed oil (Mizzouri & Shaaban, 2013). This wastewater comprises of different toxic substances and heavy metals which resulting in serious environmental consequences and damage to the equipment as well as ecosystem due to its disposal into environmental (Wake, 2005).

Existence of excessive effluent limits especially toxic and heavy metals in refinery wastewater will causes a major public health threat, especially to the populations that rely heavily on fish and marine mammals as part of their diet. Meanwhile, with regards to environmental aspect, excessive nitrate and phosphorus release to water bodies may causes overstimulation growth of aquatic plants and algae. It used up dissolved oxygen as they decompose and block the light to deeper water, resulting in eutrophication. Due to eutrophication, scums of algae produces on the water surface. It causes deprivation of oxygen where the fish and the lake itself may die.

Typically, a physical and chemical treatment is used in treating refinery wastewater as it provides high performance in operation. But, the treatment is very high in cost. Meanwhile, a conventional continuous flow activated sludge process operates with aeration vessels and second clarifier. With that, sludge is returned back from secondary clarifier to the aeration vessel. On the other hand, by implementing SBR, it operates without the secondary clarifier and hence no sludge is returned from the latter (Jern, 2006). Thus, SBR is suitable for high treated wastewater such as industrial wastewater due to its simple but efficient operation.

Sequencing Batch Reactor (SBR) is one of a biological treatment methods for wastewater; an alternative to conventional biological wastewater treatment system. It is widely used in an industrial application to treat the wastewater. Sequencing Batch Reactor is operated in five steps, which are carried out periodically as follows: fill, react (aeration), settle (sedimentation/clarification), draw (decant), and idle (Metcalf & Eddy, 2003).

## 1.2. Problem Statement

### 1.2.1 Problem Identification

The refining process in PETRONAS Penapisan Terengganu Sdn Bhd, Kerteh, Terengganu consist of 4 unit of processes which are:

a) desalter unit
b) water sewer unit
c) process water boot unit
d) mericon unit.

These unit comprise of different strength in its chemical oxygen demand concentration and hazardous pollutants such as mercury. In the promotion of environmentally sound and sustainable development, the wastewater need to be treated properly and comply with the standard limits that has been set up by Department of Environment and Environmental Quality Act 1974.

Although physical and chemical treatments are capable in handling industrial wastewater as it provides high performance efficiency in its operation, it clearly shown that the cost of the operation is very high. Thus, this research will focus on determination of performance of biological treatment using Sequencing Batch Reactor (SBR) system. Experiment will be conducted to measure its overall performances of the system. It is hope that the reactor will perform well and benefit the industry as the system provides various advantages including cost-efficient, easy and simple in its operation.

**Table 1.1:** Parameter Effluent Limits of Standards A and B under Environmental Quality Act 1974

| Parameter | | Standard | |
|---|---|---|---|
| | **Unit** | **A** | **B** |
| Temperature | ºC | 40 | 40 |
| pH value | - | 6.0-9.0 | 5.5-9.0 |
| $BOD_5$ at 20ºC* | mg/l | 20 | 50 |
| COD | mg/l | 50 | 100 |
| Suspended Solids | mg/l | 50 | 100 |
| Mercury | mg/l | 0.01 | 0.05 |
| Cadmium | mg/l | 0.01 | 0.02 |
| Chromium, Hexavalent | mg/l | 0.05 | 0.05 |
| Arsenic | mg/l | 0.05 | 0.10 |
| Cyanide | mg/l | 0.05 | 0.10 |
| Lead | mg/l | 0.10 | 0.50 |
| Chromium, Trivalent | mg/l | 0.20 | 1.00 |
| Copper | mg/l | 0.20 | 1.00 |
| Manganese | mg/l | 0.20 | 1.00 |
| Nickel | mg/l | 0.20 | 1.00 |
| Tin | mg/l | 0.20 | 1.00 |
| Zinc | mg/l | 2.00 | 2.00 |
| Boron | mg/l | 1.00 | 4.00 |
| Iron (Fe) | mg/l | 1.00 | 5.00 |
| Phenol | mg/l | 0.00 | 1.00 |
| Free Chlorine | mg/l | 1.00 | 2.00 |
| Sulphide | mg/l | 0.50 | 0.50 |
| Oil and Grease | mg/l | Not Detectable | 10 |

*$BOD_5$; 5 days at 20 ºC

(Source: Schedule Standard of Environmental Quality Act, 1974)

Parameter limits of effluent of Standard A and B is presented in **Table 1.1** as referred to the Environmental Quality (Sewage and Industrial Effluent Regulation, 1979), classified under Third Schedule of Environmental Quality Act 1974. In this study, the effluent limit for COD in Standard A and B is 50 mg/L and 100 mg/L respectively.

### 1.2.2 Significant of the Project

According to PETRONAS Sustainability Report 2011, wastewater management for oil & gas industry is very important to ensure the aim towards sustainability is successful. Therefore, the high removal efficiency in industrial wastewater treatment is strictly recommended as well as in compliance with Environmental Quality Act 1974. In addition, health & safety, equipment and environmental impact could be improved through the high removal efficiency in the wastewater treatment.

## 1.3. Objective and Scope of Study

### 1.3.1. Objectives

The aim of the study is to determine the biological treatment of refinery wastewater using Sequencing Batch Reactor (SBR) system. Therefore, this objective must be achieved:

- To determine removal efficiency of COD, nitrate and phosphate using the SBR system
- To analyse the overall performance of SBR system

### 1.3.2. Scope of Study

This study is basically based on laboratory work. There are three main elements in this scope of study:

a) Gathering of information from Petronas Penapisan Terengganu Sdn Bhd, Kerteh, Terengganu.The sample is obtained from wastewater treatment plant of Petronas Penapisan Terengganu Sdn Bhd (PPTSB), Terengganu. Meanwhile, the sludge is obtained from wastewater treatment plant of Ethylene Malaysia Sdn Bhd, Terengganu.

b) Data analysis and experimental work. Experimental work is operated by using SBR system located at Environmental Laboratory of Civil Engineering Department, Universiti Teknologi Petronas. All the data obtained is then being analysed based on the main objective of the study

c) Analysis of result of experiment. The result is presented in graph and table in order to make a comparison for each analysis. Thus, identification of the result will show the successful of experiment.

## 1.4. The Relevancy of the Project

SBR is one of a biological treatment that can be used in the treatment of refinery wastewater. It is relevant in this study as SBRs can be matched with the shift nature of factory operation easily than continuous flow systems. Besides that, compared to physical and chemical methods which is costly in term of chemicals, equipment and excessive amount of sludge production, biological treatment method gives benefits in many ways such as environmental friendly operations, simple and cheap (Ishak *et al*., 2012)

## 1.5. Feasibility of the Project

### a) Scope Feasibility

The laboratory equipment to conduct the experiment is available in Environmental Laboratory located at Block 13, Civil Engineering Department of Universiti Teknologi Petronas. Apart from that, the sample of wastewater and sludge is obtained from Petronas Penapisan Terengganu Sdn Bhd (PPTSB) and Ethylene Malaysia Sdn Bhd located at Kerteh, Terengganu.

### b) Time Feasibility

The project requires experimental work and data analysis. Thus, to ensure that the project is achievable within the time frame, preliminary experiment will be conducted in Week 14.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 OVERVIEW OF REFINERY WATER AND WASTEWATER

Benyahia (n.d) states that petroleum refinery industry has converted crude oil into about 2500 refined products such as liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, lubricating oils and feedstock for the petrochemical industry. Based on the above statement, petroleum refineries are complex systems of multiple operations that depend on the type of crude refined and the desired products. Hence, it can be a large consumer of water, in which the amount of wastewater is estimated approximately 0.4–1.6 times the volume of the processed oil depending on the size, crude, products and complexity of operations (Coelho *et al.*, 2006).

As the refining process require a huge amount of water, the water to the refinery can be obtained from various type of source of water including surfaced water, purchased water where it is supplied from municipality, and water from the crude itself. Although the amount of water in the refinery can be continually recycled, some of it may losses to the atmosphere, including steam losses and cooling tower evaporation and drift. Sometimes, the small amount of water can also leave together with the refined products. Hence, in order to optimize the performance of water and wastewater treatment system in the refinery, it is recommended in understanding the water processes inside the refinery itself. **Figure 2.1** shows the typical flow of water balance for a refining process.

Wastewater is generated in a refinery that has been contact with hydrocarbons. It includes the water that is rejected from the boiler feed water pre-treatment processes or even during regenerations. Besides, the water that comes from cooling tower can also be considered as wastewater. The contaminated wastewater is typically treated at either a wastewater treatment plant, pre-treated by local publicly owned treatment works or third-party treatment facility. Meanwhile, wastewater that has a minimal contamination or has not been contact with hydrocarbon will be recycled and reuse in a refining process.

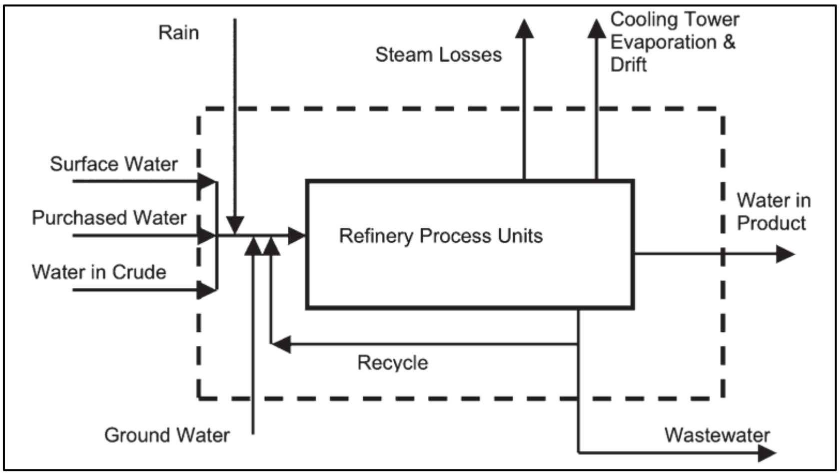



**Figure 2.1:** Typical Water Balance in a Refinery

## 2.2 TYPE OF WASTEWATER TREATMENT

Various treatment systems have been analysed and studied in order to replace the conventional treatment of wastewater. **Table 2.1** shows various treatments from various sources.

There are various treatments available to treat wastewater which is mentioned as below;

a) Physical Treatment
b) Chemical Treatment
c) Biological Treatment

Each treatment provides its own advantages as well as disadvantages. Physical treatment and chemical treatment can achieve very high removal efficiency in the treatment and almost provide no pollution to an environment at all. However, these treatments are complicated in term of providing the apparatus and tools as it is high in cost. Thus, it is not economical to provide these treatments in the industry. With regards to operation of system, biological treatment provides simplicity in its operation. Besides that, it is economical as the space needed for the operation is small and requires no input energy. There are two type of biological treatment which is aerobic and anaerobic treatment. Anaerobic treatment is quite simple as nutrient does not have to be added in the treatment compared to aerobic treatment.

**Table 2.1:** Treatment System in Various Industry

| Source | Rastegar et al.,2011 | Cyr et al., 2002 | Nanseu-Njiki et al., 2008 | Kagaya et al.,2009 |
|---|---|---|---|---|
| **Type of wastewater** | Petroleum Refinery | Pharmaceutical | - | General |
| **Treatment System** | UASB Reactor (Biological Treatment) | Granular Activated Carbon (Chemical Treatment) | Electrocoagulation (Physical Treatment) | Polythiomides (Chemical Treatment) |
| **Specifications** | 10cm diameter,80cm height,6.28L volume | - | 3cm electrodes, | In powder form |
| **COD concentrations** | 500-1200 mg/L | 3755 µg/L | 378 mg/L | 2.1 mg/L |
| **Removal Efficiency (%)** | 81 | 35-99 | 99.95 | 98.6 |
| **Advantages** | • Economize space utilization<br>• Require no external input of energy<br>• Nutrient requirement are less compared to aerobic treatment | • Enhances the adsorption of the wastewater constituent | • Decontamination of effluent containing heavy metal other than mercury can led to removal efficiency almost 100%.<br>• No affect to any side pollution | • Can be used for the removal of Hg under acidic condition |
| **Disadvantages** | • Efficiency of COD removal depends on shape of model<br>• Unable to estimate interrelated effluent parameters except mass balance | • A source of food for bacteria<br>• Can cause human disease due to growth of bacteria<br>• Silver is not a great disinfectant as it protect on the first month of operation only. | • Removal efficiency of mercury is undefined.<br>• High-cost | • Additional cost on powders |

## 2.3 TREATMENT OF REFINERY WASTEWATER

The conventional method of treating refinery wastewater is based on physicochemical, mechanical method and further biological treatment in the integrated activated-sludge treatment unit (El-Naas, Alhaija, & Al-zuhair, 2014). The first step in a typical petroleum refinery wastewater treatment plant is a primary treatment where the combination of physical and physicochemical separation processes is done to remove the free oil, suspended solids and colloidal materials. However, these processes are unable to remove emulsified or dissolved oil, which are removed in the secondary treatment; biological treatment. **Figure 2.2** illustrates the typical conventional operation of industrial wastewater treatment.

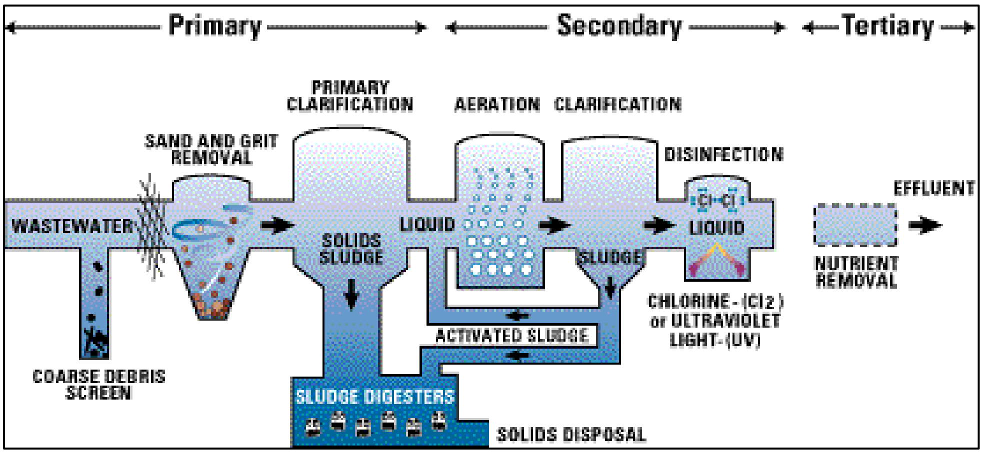



**Figure 2.2**: Conventional operation of refinery wastewater treatment

Activated-sludge process is the most commonly used in industrial biological treatment due to its applicability in treating wastewater with high content of organic matter such as oil refineries, fertilizer industry and chemical manufacturing facilities. In this process, naturally occurring microorganisms feed on the dissolved organics in the wastewater, and convert them to water, carbon dioxide and nitrogen gas, which can be safely released into the atmosphere by referring the standard limits of the parameter effluents listed by Department of Environment.

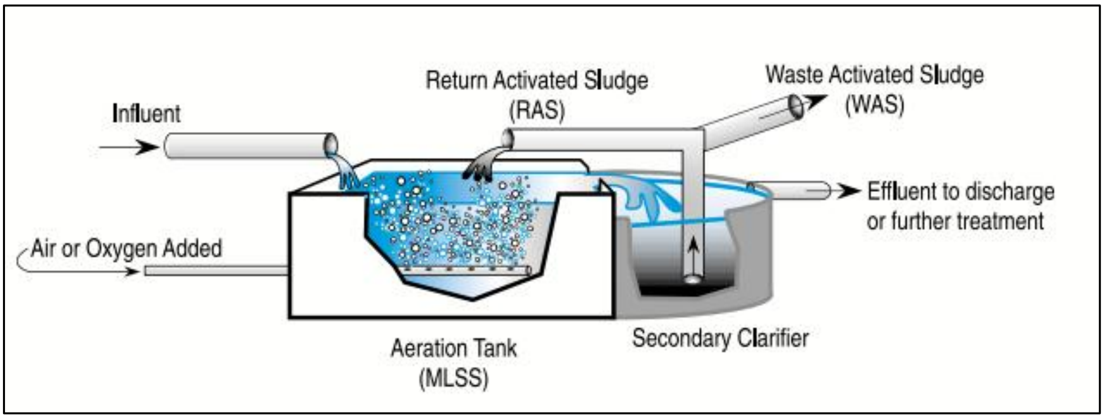



**Figure 2.3**: Activated Sludge Process

**Figure 2.3** shows the basic activated sludge process which consists of several interrelated components, namely; aeration tank and clarifier tank. Biological reaction occurs at aeration tank where aeration source is used to provide oxygen and mixing, while clarifier tank is where the solids settle and are separated from treated wastewater. In the means of collecting settled sediments, there are two type of component which are Return Activated Sludge (RAS) and Waste Activated Sludge (WAS). The function of RAS is to return solids to the aeration tank meanwhile WAS is implied to remove excessive solid from the process.

During the activated sludge process, the aerobic bacteria thrive as they travel through the aeration tank. They will multiply rapidly with enough food and oxygen. The organisms will then settle to the bottom of the clarifier tank, separating from the clearer water, while the sludge is pumped back to the aeration tank where it is mixed with the incoming wastewater or removed from the system as excess, a process called wasting (National Small Flows Clearinghouse, 2003). The effluent that has achieve the standard limit will then discharge or else will undergo further treatment.

Although it can operate at the loading rates as high as 1.2 kg BOD $m^{-3}$ day$^{-}$1 (Thompson *et al.*, 2001) activated sludge process particularly prone to bulking problem. Bulking causes the poor settleability of sludge, resulting in poor effluent quality. Sludge bulking is conventionally controlled by the addition of chemicals such as chlorine, hydrogen peroxide and lime to maximize settleability of sludge. However, it is costly and only offer a short-term solution as the bulking will resume when chemical additions are stopped. Therefore, recently, the implementation of SBR and membrane bioreactor has been considered in treating petroleum refinery wastewater due to its cost-efficiency and simplicity in operation. Several studies on SBR system is explained in next sub-section.

## 2.4 APPLICATION OF SEQUENCING BATCH REACTOR IN REFINERY WASTEWATER

There are also various studies on the application of biological treatment in industrial wastewater as it is simple and cheap in cost. Moreover, it provides an environmental friendly operation to the system. **Table 2.2** summarizes the findings of biological treatment application on various wastewater treatments. Each study carries different scale of reactors, experimental setup and parameters which results in different finding. Though, it is observed that the COD removal efficiency is very high for treated wastewater and eventually proves biological treatment suitable for high-strength wastewater like industrial wastewater (Jamhari, 2011).

**Table 2.2:** Application of Biological Treatment in Various Wastewater Treatments

| Source | Rastegar *et al.*,2011 | Malakahmad *et al.*, 2011 | Sirianuntapiboon & Hongsrisuwan, 2007 | Chan, Chong & Law, 2010 |
|---|---|---|---|---|
| Type of wastewater | Petroleum Refinery | Synthetic Petrochemical | Industrial Estate | POME |
| Treatment System | UASB Reactor | SBR | SBR | SBR |
| Specifications | 10cm diameter,80cm height,6.28L volume | 25cm diameter, 60cm height, 24L volume | Made up of 5mm acrylic plastic, 18cm diameter, 40cm height, 7.5L volume | 2L beaker |
| Hydraulic Retention Time, d | 120 | 15 | 3 | - |
| Cycle time,hr | - | - | 1 | 22 |
| COD concentrations | 500-1200 mg/L | - | 197± 3.3 mg/L | - |
| F/M Ratio | - | - | 0.074 | - |
| Organic Loading Rate (kg/m3/day) | 0.4 | - | - | 1.8-4.2 |
| Removal Efficiency | 81% | 80% COD | 77± 2 COD | 96% COD |
| Biogas Production rate | >0.54 L biogas/L feed | - | - | - |
| SVI (ml/g) | - | 58 | - | 65± 35 |
| Contact time | - | 8 | - | - |

A sequencing batch reactor (SBR) is a fill-and-draw semi-batch biological treatment alternative that employs aeration, sedimentation and clarification in a single reactor. The unit processes of aeration and sedimentation are common to both the SBR and activated sludge systems. However, the unit operations in activated sludge systems take place in different basins, while SBR operation take place in a sequential order in a common basin. Although still practiced in some refineries, SBR technology is increasingly uncommon and has limited application in refinery wastewater treatment (Verkantesh, 2010).

Sequencing batch reactor (SBR) is an attractive alternative to any other methods in refinery wastewater due to its simplicity and flexibility; need less space, can handle wide fluctuations in waste loads and adaptability to various application and condition. It consist of four to five stages of operation; fill, react, settle, draw, and idle as shown in **Figure 2.4** ( Barber *et al*., 2008).

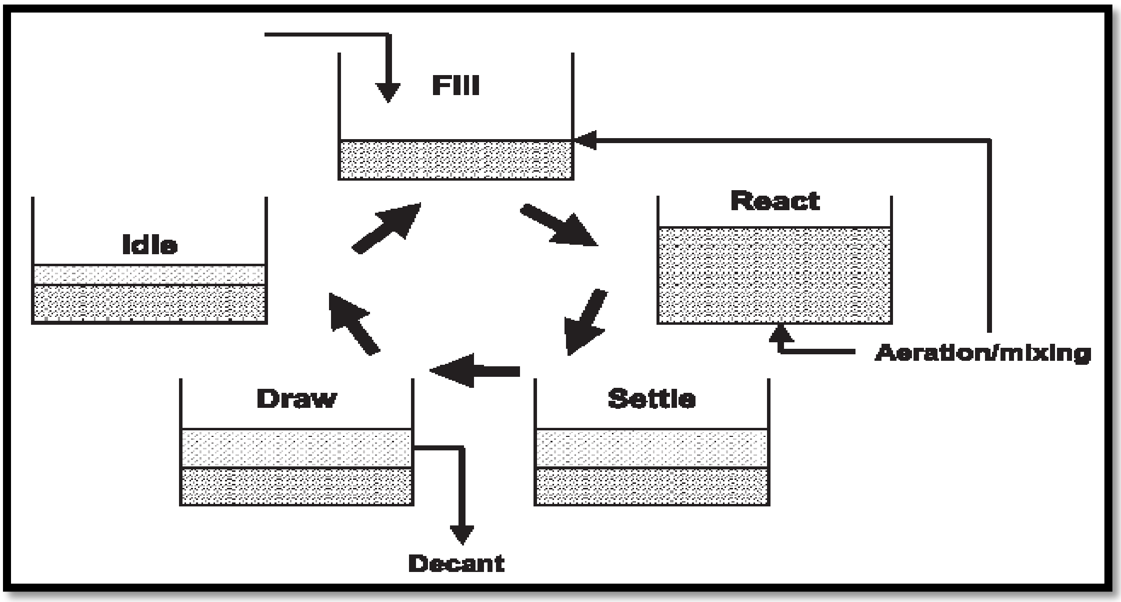



**Figure 2.4:** Illustration of the steps in SBR operations.

(Source: http://web.deu.edu.tr/atiksu/toprak/ani4093.html)

The reaction starts during fill and begin to decline to the discharge concentration during react (Jern, 2006). During the fill stage, part of liquid volume of the reactor is replaced with fresh wastewater. This is sometimes referred to as semi-batch operation. Treatment takes place during the react stage which consist of three different condition; aerobic, anaerobic or a combination of aerobic, anoxic and anaerobic condition. The condition is decided depending on the goal of the system design. After react, mixed liquor suspended solids (MLSS) are allowed to separate by sedimentation during settle period and the treated effluent is withdrawn during draw stage. The time between the end of draw and beginning is termed as idle (Malakahmad *et al*, 2011). Clarified wastewater is removed from the reactor in the decant stage and the cycle is repeated. Often, 24 hours is convenience for the treatment per cycle. **Table 2.3** shows the general duration for each step in a cycle.

**Table 2.3:** General operational duration of SBR system

| **Parameters** | Duration, h |
|---|---|
| **Cycle time** | 6-12 |
| **Fill (25%)** | 1.5 |
| **React (35%)** | 2.1 |
| **Settle (20%)** | 1.2 |
| **Draw (15%)** | 0.5-2.0 |
| **Idle (5%)** | 0-0.3 |

(Source: Jern, 2006)

Typically, sequencing batch reactor (SBR) is used for effluent treatability studies, including solids, carbon and biogas balances to determine the purification (COD/BOD). Besides that, it may be used to determine the optimum operating temperatures, feed rates and ratios. It can also be used to observe the effect of pH and influent nutrient concentration, process stability studies and determination of controlling kinetics.

# CHAPTER 3

# METHODOLOGY

Generally, research methodology refers to a set of procedures used to conduct a research project. In this study, the methodology include:

- Research Methodology
- Project Activities
- Key Milestone
- Gantt Chart
- Tools

## 3.1 RESEARCH METHODOLOGY

### 3.1.1 Sample and Characterization

The wastewater sample used throughout this study is collected from final discharge point of Petronas Penapisan Terengganu Sdn Bhd (PPTSB), Kerteh, Terengganu. Meanwhile, the aerobic sludge sample is collected from Sewerage Treatment Plant (STP) of Etylene Malaysia Sdn Bhd,Terengganu. The wastewater characterization is carried out based on data Standard Methods for Examination of Water and Wastewater (APHA, 1992) and summarized as in **Table 3.1**.

**Table 3.1:** Characteristics of Refinery Wastewater and Sludge Collected From Sewerage Treatment Plant

| Refinery Wastewater | Sludge |
|---|---|
| Parameters | |
| ❖ pH<br>❖ Chemical Oxygen Demand (COD)<br>❖ Biochemical Oxygen Demand (BOD)<br>❖ Mercury Concentration<br>❖ Nitrogen | ❖ Mixed Liquor Suspended Solid (MLSS)<br>❖ Mixed Liquor Volatile Suspended Solids (MLVSS)<br>❖ Sludge Volume Index (SVI)<br>❖ Food over Biomass (F/M Ratio)<br>❖ Hydraulic Retention Time (HRT) |

### 3.1.2 SBR Setup

The sequencing batch reactor comprises of 6 identical reactors with a working volume of at least 2 litres each using one panel. Each reactor can be operated independently of the other. Each reactor can be able to operate in different feeding, aeration, settling, decanting, and idling times. It is designed to have complete monitoring facilities including temperature, pH, dissolved oxygen and influent rate controller that can undergo operations up to two weeks. The system consists of:

a) Reactors
b) Reactor packing
c) Temperature control
d) Feed pumps
e) Air compressor
f) Influent and Effluent tanks
g) Gas collection system
h) Controlling and data acquisition workstation
i) Software

**Figure 3.1 and 3.2** illustrates part of equipment that will be used throughout the experiment.

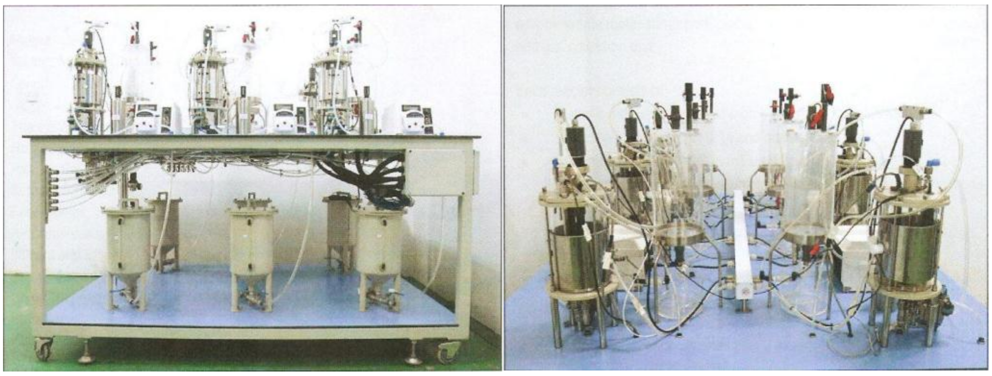
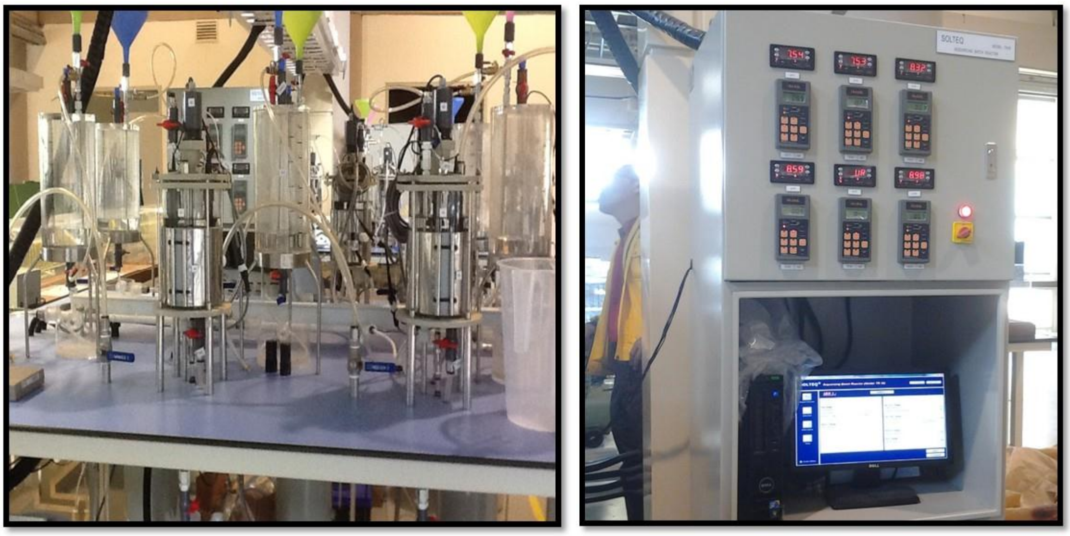


**Figure 3.1:** SBR Equipment



**(a)** **(b)**

**Figure 3.2:** Gas Collection System (a) and SOLDAS Software (b)

## 3.2 EXPERIMENTAL PROCEDURES

### 3.2.1 SBR Operation

A reactor with working volume of 2.0L was filled with required volume of refinery wastewater. Meanwhile, a sludge tanks in the system was filled with waste sludge. The reactor was operated with Cycle Time (CT) of 8 hours where 3 cycles per day with Hydraulic Retention Time (HRT) of 24 hours. The cycle time consist of feeding (15 minutes), reacting (4 hours), settling (120 minutes), decanting (15 minutes) and idling (1.5 hour). The reactor was operated under room temperature with the pH maintained between pH of 6 to 8.

Feeding and decanting volume, V = 0.4L

Feeding and decanting period, t = 10 minutes

Feeding and decanting rate, Q = 0.4/10

= 0.04 L/min

= 40 mL/min

Total volume = 1.8 L

Cycle Time = 6 hours/cycle

HRT = 24 hours

The influent is fed into the reactor using a feed pump with a speed up to 300 rpm. Then, reaction phase takes place with a total reaction time of 4 h. After 4h, the mixing stops to allow for settling of about 120 minutes and the clarified supernatant was discharged from the SBR to the treated wastewater tank. Subsequently, the reactor was filled again for the next cycle after 1.5 hour of idle period (for sludge wasting). The processes were repeated until stable results are obtained.

### 3.2.2 Reactor Performance

The SBR was operated with constant aeration time and influent feed volume at different MLVSS Concentration, dissolved oxygen (DO) concentration, organic loading rates (OLR) and food to microorganism (F/M) ratios. According to Chan et.al (2010), the attainment of the steady state conditions is ascertained when reactor performance remained constant for at least three consecutive measurements. The performance of SBR is evaluated on the basis of COD, BOD and TSS removal as well as sludge volume index (SVI) (Chan, Chong, & Law, 2010). **Figure 3.3** shows the schematic diagram of experimental setup of the reactor.

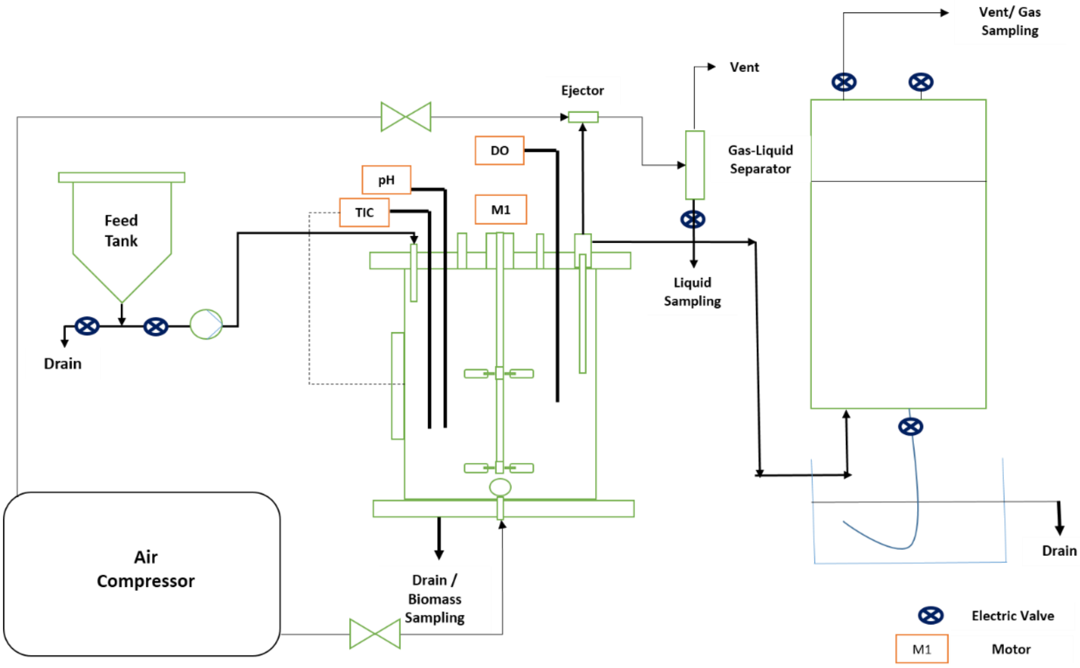



**Figure 3.3:** Schematic Diagram of Experimental Setup

### 3.2.3 Effluent Parameters Measurement

The determinations of effluent parameters listed out as follow were determined in accordance with Standard Methods for Examination of Water and Wastewater (Malakahmad *et al*, 2011):

a) pH
b) Chemical Oxygen Demand (COD)
c) Biochemical Oxygen Demand (BOD)
d) Mixed Liquor Suspended Solid (MLSS)
e) Mixed Liquor Volatile Suspended Solid (MLVSS)
f) Total Suspended Solid (TSS)
g) Sludge Volume Index (SVI)

The details explanations of each parameter are defined as follow:

**Chemical Oxygen Demand Determination**

Chemical oxygen demand was conducted using spectrophotometry method. It can be defined as the oxygen requirement for both organics and non-organics content in wastewater to be oxidized. Effluent sample is diluted in factor of 1:10 in a volumetric flask. Three diluted effluent sample from SBR operation was filled into vials in order to increase precision of the results. Then, it was mixed before being inserted into the reactor at temperature of 150 °C for 120 minutes. After that, the samples were cooled down to room temperature. Then, the blank sample (distilled water) was inserted into the spectrophotometer slot. It was used to set the ZERO reading in the spectrophotometer to calibrate it. The following samples were wiped clean and inserted into the spectrophotometer to get the COD reading (mg/L). It is calculated as:

$$Final\ COD = \frac{COD\ reading}{Dilution\ Factor}$$

COD reading: Based on reading in spectrophotometer

Dilution factor: 1:10

**Biochemical Oxygen Demand Determination**

The BOD test is used to measure waste loads to treatment plants, determine plant efficiency (in terms of BOD removal), and control plant processes. It is also used to determine the effects of discharges on receiving waters. The amount of time required to obtain the result is 5 days. A sample was pipetted into a BOD bottle containing aerated dilution water. The DO content was determined and recorded and the bottle is incubated in the dark for five days at 20°C. At the end of five days, the final DO content is determined and the difference between the final DO reading and the initial DO reading is calculated. The decrease in DO is corrected for sample dilution, and represents the biochemical oxygen demand of the sample.

To determine the value of the BOD in mg/L, use the following formula:

BOD, mg/L = [(Initial DO - Final DO) x 300]/mL sample

**Sludge Volume Index (SVI)**

The sludge from the reactor was tested for every two days. 10 mL of MLSS (sludge) was settled for 30 minutes in a 10mL of graduated cylinder. The SVI was analysed by measuring the volume occupied by the settlement. It is calculated as follow:

$$SVI = \frac{Volume\ occupied}{MLSS} \left(\frac{mg}{L}\right)$$

**MLSS and MLVSS Determination**

MLSS and MLVSS are both used as measures of microorganism in sludge waste system. MLSS determination procedure are quite similar as the determination of total suspended solids (TSS). Glass micro-fibre filter was used to avoid from burning during MLVSS determination afterwards. The sample was passed through the filter pad and dried at 105 °C for one hour. Before that, the weight of the sample was weighed which is known as W1. Meanwhile, W2 was measured as weight of the filter disk, dried sample and aluminium foil. In order to get the determination of MLVSS, the filter disk in MLSS determination is burned at 550 °C for 15 minutes in the furnace. After 20 minutes, filter disks were stabilized inside the desiccator. W3 was measured as the weight of filter, aluminium disk and dried samples after burned at 550 °C.

$$MLSS = \frac{W2 - W1}{Vol.of\ diluted\ sample\ x\ dilution\ factor}(\frac{mg}{L})$$

$$MLVSS = \frac{W3 - W1}{Vol.of\ diluted\ sample\ x\ dilution\ factor}(\frac{mg}{L})$$

**<u>Total Suspended Solid Determination</u>**

Total Suspended Solids is determined by filtering the samples through glass fiber filter which is known as Whatman grade GF/A. The residues were retained on the filter and dried to constant weight at 103-105ºC. It is calculated as follow:

Total Suspended Solids, mg/L = (A-B) x 1,000/C

Where: A = weight of filter and dish + residue in mg

B = weight of filter and dish in mg

C = volume of sample filtered in mL

**<u>Nitrate Determination</u>**

To test for nitrate, Cadmium Reduction Method (Method 8039) was used. Preparation of sample was done by filling the sample cell with 10mL of sample. After that contentof one NitraVer 5 Nitrate Reagent was added, shake for one-minute, and left for five minute reaction period. An amber color will develop if nitrate was present. Content of nitrate can then be measure after the instrument was zero using the blank. Blank was prepared by filling the sample cell with 10mL of similar sample.

**<u>Total Phosphorus Determination (TP)</u>**

PhosVer 3 with Acid Persulfate Digestion Method (Standard Method 8190) is used to determine the concentration of total phosphorus in the treated wastewater. Preparation of sample was done by adding 5mL of sample into the vial together with Potassium Persulfate powder pillow. Then, it was mixed and digest for 30 minutes at

150°C. Once it is cooled, 2 mL (1.54N NaOH) was added into the vials. The vials were wiped and set into ZERO (As control). After that, PhosVer 3 powder pillow was added into the vials and mixed for 2 minutes. The determination of total phosphorus was analysed within 2 to 8 minutes after mixing.

**Removal Efficiency**

On the other hand, removal efficiency is calculated as following:

$$Removal\ efficiency = \frac{C_i - C_f}{C_i} x\ 100\%$$

Where;

$C_i$ = initial concentration (influent)

$C_f$ = final concentration (effluent)

### 3.3 Project Activities

The steps from understanding the project until analysing results of mercury removal efficiency are summarized as below in **Figure 3.4**:

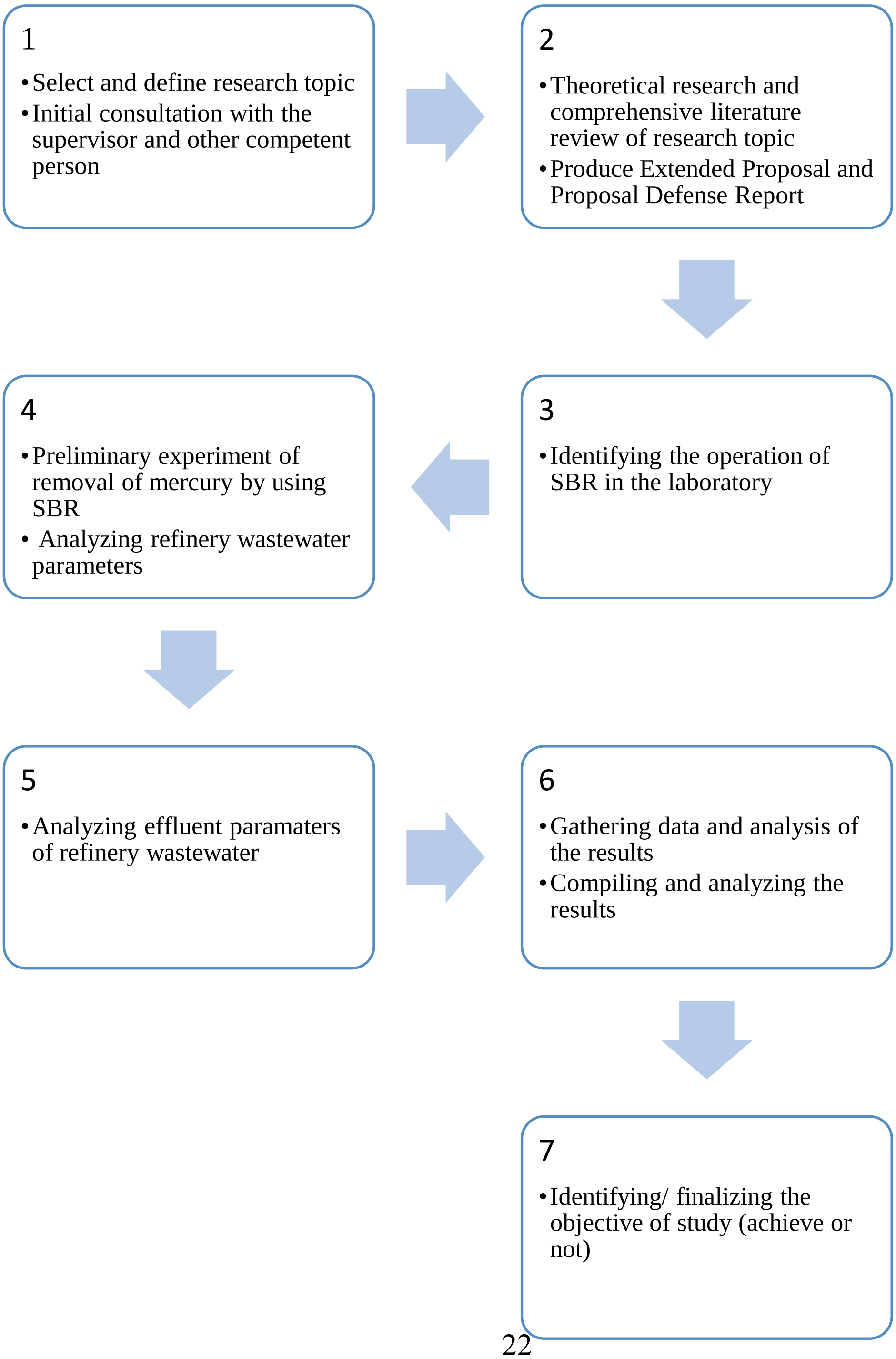


**Figure 3.4:** Project Activities

## 3.4 Key Milestone

Key milestone that needs to be achieved in this study is presented in **Table 3.2**.

**Table 3.2:** Timeline of FYP I and FYP II

| Phase | FYP 1 | | | | | | | | | | | | | | FYP 2 | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Week | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| Topic Selection | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Preliminary Research Work | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Extended Proposal Submission | | | | | | ● | | | | | | | | | | | | | | | | | | | | | | | |
| Proposal Defence | | | | | | | | | ● | | | | | | | | | | | | | | | | | | | | |
| Research and Analysis of Biological Treatment Method | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Submission of Interim Draft Report | | | | | | | | | | | | | ● | | | | | | | | | | | | | | | | |
| Submission of Interim Report | | | | | | | | | | | | | | ● | | | | | | | | | | | | | | | |
| Preliminary Experiment on Mercury Removal | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Submission of Progress Report | | | | | | | | | | | | | | | | | | | | | | ● | | | | | | | |
| Collection And Analysis of Data And Results | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Pre-SEDEX | | | | | | | | | | | | | | | | | | | | | | | | | ● | | | | |
| Submission of Draft Report | | | | | | | | | | | | | | | | | | | | | | | | | | ● | | | |
| Submission of Dissertation (Soft Bound) | | | | | | | | | | | | | | | | | | | | | | | | | | | ● | | |
| Submission of Technical Paper | | | | | | | | | | | | | | | | | | | | | | | | | | | ● | | |
| Oral Presentation | | | | | | | | | | | | | | | | | | | | | | | | | | | | ● | |
| Submission of Dissertation (Hard Bound) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | ● |

● Key Milestone in FYP I and FYP II

The project is divided into two segment, known as Final Year Project I (FYP I) and Final Year Project II (FYP II). It is carried out in 29 weeks; 14 weeks and 15 weeks per semester respectively.

### 3.5 Tools

The tools needed in this study are as below:

a. Sequencing Batch Reactor

b. Laboratory Apparatus

c. Microsoft Office Excel

Sequencing Batch Reactor (SBR) is used as a system for removal of mercury. Hence, existing SBR in the laboratory will be used to conduct the experiment. The samples is collected from Petronas Carigali Kerteh, Terengganu. The operation of SBR is mentioned as in Section 3.1: Research methodology.

The facilities and apparatus are provided in Environmental Laboratory of Civil Engineering Department in Universiti Teknologi Petronas. The apparatus will be used to measure effluent parameters of the refinery waste water in order to get precise outcome.

Microsoft Office Excel is used to ease the presentation of analysis of data and results. It is also used to monitor progress of experiment data.

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 EXPERIMENTAL RESULTS

### 4.1.1 Characterization of Samples

The experiment was done in two parts where the characterization of sample has been done before the operation of Sequencing Batch Reactor (SBR). Firstly, the experiment was done by analysing four different samples from Petronas Penapisan Terengganu Sdn Bhd (PPTSB). The samples consist of:

- Mericon Unit
- Desalter Unit
- Process Water Boot
- Water Sewer Unit

The characterization of these samples was conducted in order to select the sample with medium strength of Chemical Oxygen Demand (COD) concentration to be used for the main objective of this study which is determination of performance of biological treatment by using Sequencing Batch Reactor (SBR) system.

Based on the analysis that has been done, **Table 4.1** tabulates the details of processes of four samples and other parameters.

**Table 4.1:** Characterization of Samples

| Type of sample | COD (mg/L) | $NO_3^-$ | Hg (mg/L) | pH |
|---|---|---|---|---|
| Mericon Unit | 7385 | 595.7 | 1.31 | 10.02 |
| Process Water Boot | 797 | 0.8 | 16 | 7.52 |
| Desalter Unit | 710 | 5.2 | - | 8.45 |
| Water Sewer Unit | 73 | - | - | - |

Thus, based on tabulated analysis, the sample from process water boot unit has been chosen with the initial concentration of chemical oxygen demand of 797 mg/L. **Table 4.2** shows the parameters that have been analysed for operation of sequencing batch reactor (SBR).

**Table 4.2:** Characterization of Sample from Process Water Boot Unit

| Parameters | Wastewater and sludge characteristics |
|---|---|
| Chemical Oxygen Demand (COD) | 797 |
| Biological Oxygen Demand ($BOD_5$) | 199.2 |
| $BOD_5$/COD | 0.29 |
| pH | 7.39 |
| Nitrate | 1.9 |
| Phosphate | 4.44 |
| Mercury | 16 |
| Mixed Liquor Suspended Solid (MLSS) | 3840 |
| Mixed Liquor Volatile Suspended Solid (MLVSS) | 3555 |
| Sludge Volume Index (SVI) | 250 |

### 4.1.2 Operation of SBR

The reactor has been operated for 29 days. COD, nitrate, phosphate and pH measurement are conducted every day at the end of third cycle, while MLSS, MLVSS and SVI test are conducted for every two days interval. Appendix A summarizes the effluent parameters data for the reactor.

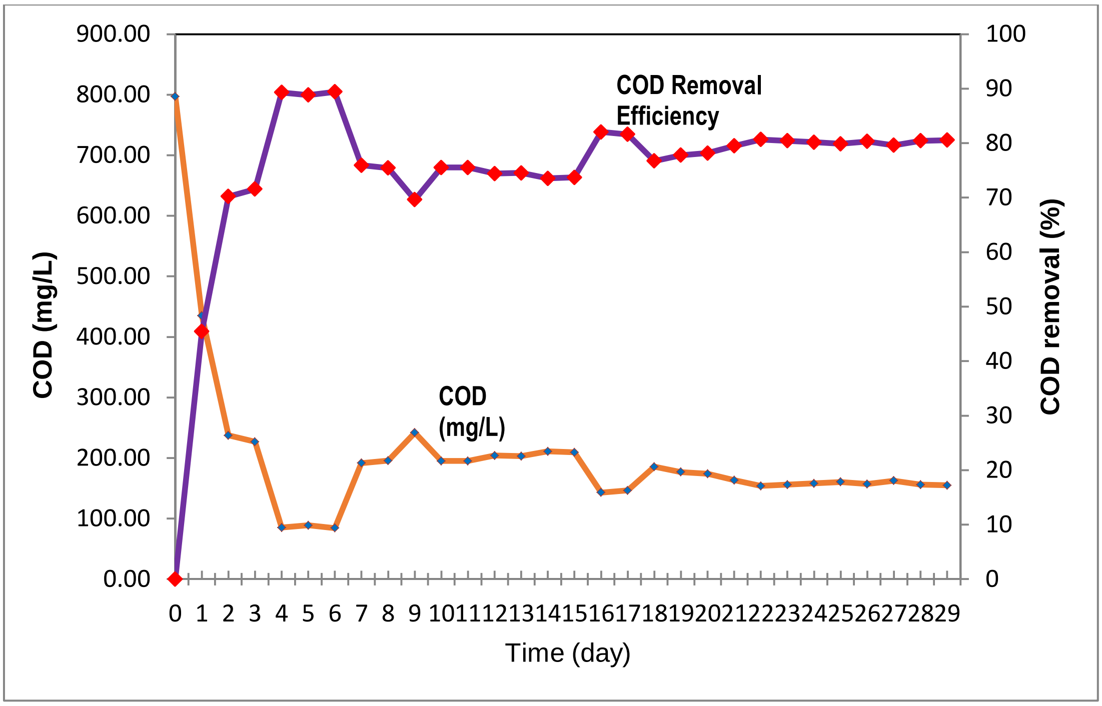



**Figure 4.1:** COD Removal Efficiency

**Figure 4.1** shows the COD removal efficiency of the sequencing batch reactor. It can be seen that the COD is reduced about 45.4% in Day 1 where the initial concentration is 797 mg/L and keep reducing until Day 6 of about 89%. However, as illustrated in above figure, the performance is fluctuated from Day 7 to Day 12. This might happened due to acclimatization towards the surrounding of the reactor. From the result obtained, the reactor is not stable yet and expected to be stable after Day 15. Typically, stable condition or steady state can be said to have been achieved when there is less than 10% variation in the effluent parameters. Apart from that, the COD concentration is not stable may be due to the concentration of MLSS is mixed up with the treated wastewater, resulting in increment of COD concentration. However, on Day 18, it is started to stable and reduced to 150 mg/L until Day 29. It shows that it has achieved its steady state on Day 18 onwards.

**Figure 4.2** on the other hand shows the nitrate concentration throughout the operation of the reactor. As illustrated in the figure below, the nitrate was reduced from 1.9 mg/L to 0.1 mg/L on the first day of the treatment. Denitrification may occurred during the fill period where MLSS and influent wastewater is contacted with each other. Besides, this is the period where the biomass in the reactor is acclimatized to its new surroundings. However, from Day 2 to 29, the concentration of nitrate increasing due to nitrification process that occurred during the treatment. It is indicating that the organic nitrogen has been fully utilized by the microorganisms to degrade the organic matter and nitrifying bacteria, resulting in growth of microorganism. Apart from that, it helps to improve the removal efficiency of the other effluent parameters.

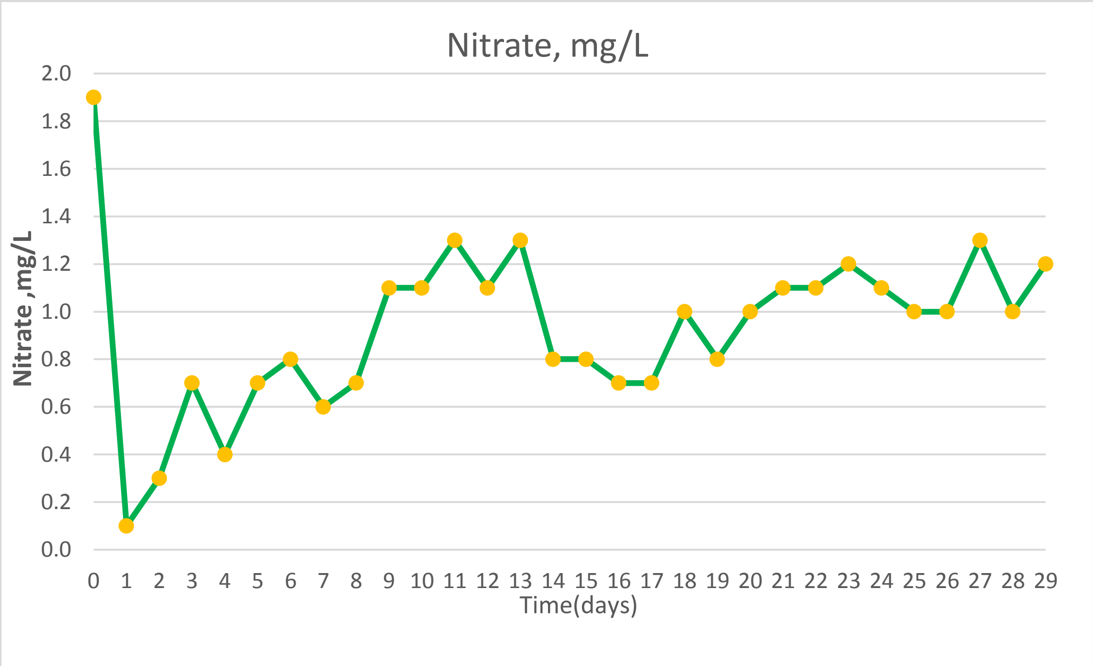



**Figure 4.2:** Effluent nitrate concentration in 29 days

Phosphorus is also an important nutrient required by microorganism to degrade organic matter. **Figure 4.3** illustrates the reduction of total phosphorus concentration from Day 1 to Day 29. As the concentration decreased, it can be proved that it was utilized by microorganisms during the reaction phase. It can be seen that the reduction is about 90%.

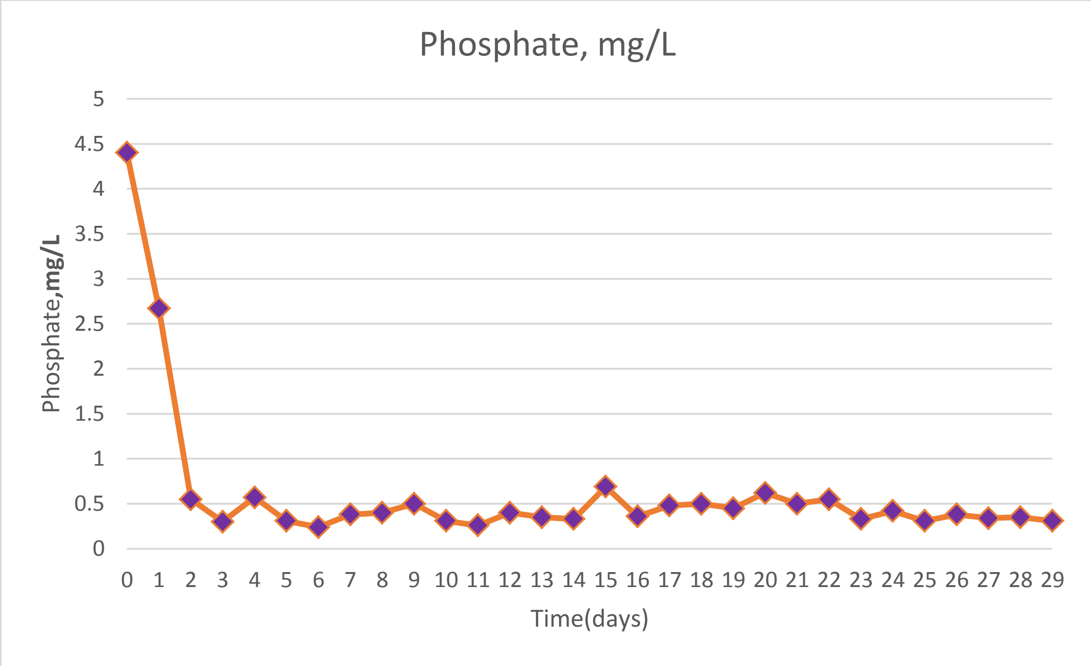



**Figure 4.3:** Effluent Phosphate concentration

### 4.1.3 Microorganism monitoring

In order to ensure a good performance of sequencing batch reactor performance, the determination of F/M ratio, MLSS and MLVSS concentration as well as sludge volume is observed.

Food to microorganism ratio, (F/M) is commonly used to characterize the process design. The typical value of F/M in sequencing batch reactor is ranged between 0.04 to 0.10 kg BOD/ kg MLVSS.d (Metcalf & Eddy, 2003). In this process design the F/M ratio is 0.056.

MLVSS : 3555 g/m$^3$ X 0.002 m$^3$ = 7.11 g

* 1 gram = 1 mL

Thus, the volume of sludge to be added in the reactor;

Volume = 2000/ 7.11 = 281. 3 mL

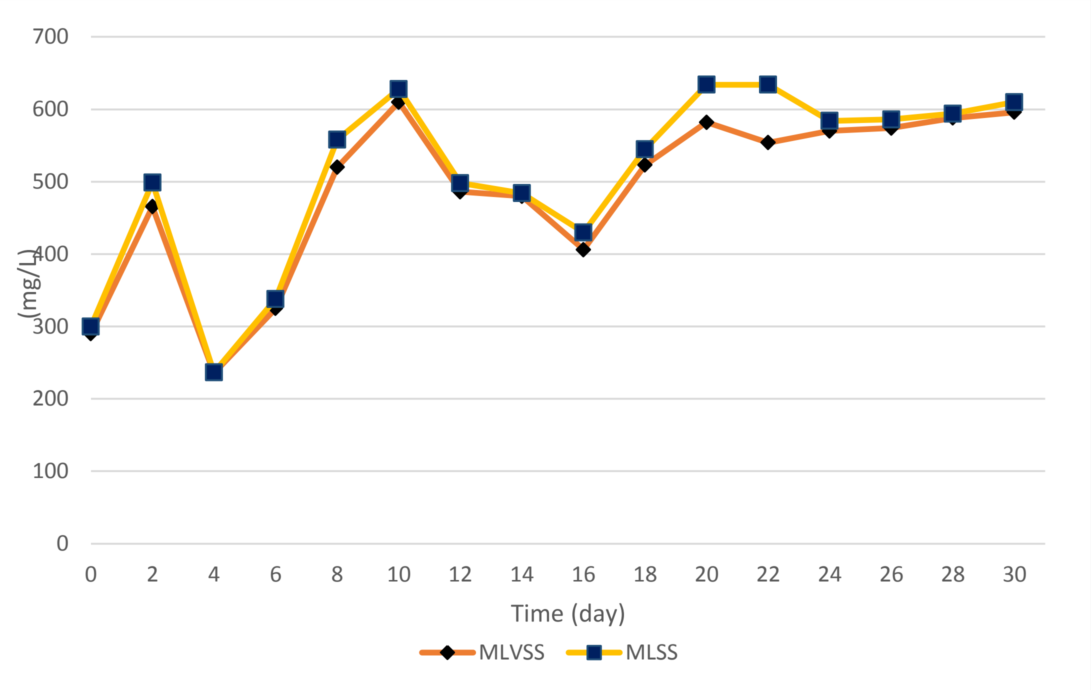



**Figure 4.4:** Mixed Liquor Suspended Solid (MLSS) and Mixed Liquor Volatile Suspended Solids (MLVSS) Concentration

**Figure 4.4** the Mixed Liquor Suspended Solid (MLSS) and Mixed Liquor Volatile Suspended Solids (MLVSS) concentration in the sequencing batch reactor. MLSS is the measure of suspended solids in the operating treatment process. Based on the result obtained, MLSS concentration is increased from 300 mg/L (initial concentration) to 499 mg/L after the 3 cycle of the SBR. However, it is decreased again. It is assumed with two factors, due to the condition of wastewater; toxic as well as due to excess sludge being wasted. Compared to both parameters, the VSS and TSS concentration began to increase as the biomass was slowly acclimatizing to new substrate, thus they were able to multiply and grow further. However, they have not reach stable condition yet. MLVSS represents the microorganism growth inside the biological system. As referred to calculation that has been made, the ratio of MLVSS and MLSS (volatile fraction) is coincides with the typical values given by Metcalf and Eddy which is 0.85. An adequate MLVSS concentration should be maintained to ensure biomass concentration is enough for biological reaction to take place, hence, the process is not overloaded (Malakahmad *et al.*,2011).

**Figure 4.5 shows the variation in sludge volume index.** Sludge Volume Index **(SVI)** is a very important indicator to determine the rate of desludging on how much sludge is to be returned to the aeration basin and how much to take it out from the system. This measurement is important to maintain the sufficient concentration of activated sludge in the system SVI< 150 mL/L is often considered as good settling sludge (Parker *et al.*). In this study, the slduge exhibited good settling sludge properties. In the startup phase, it denotes 130 mL/L as shown in Figure 4.5 and decreasing to 40 mL/L at the end of 29 days.

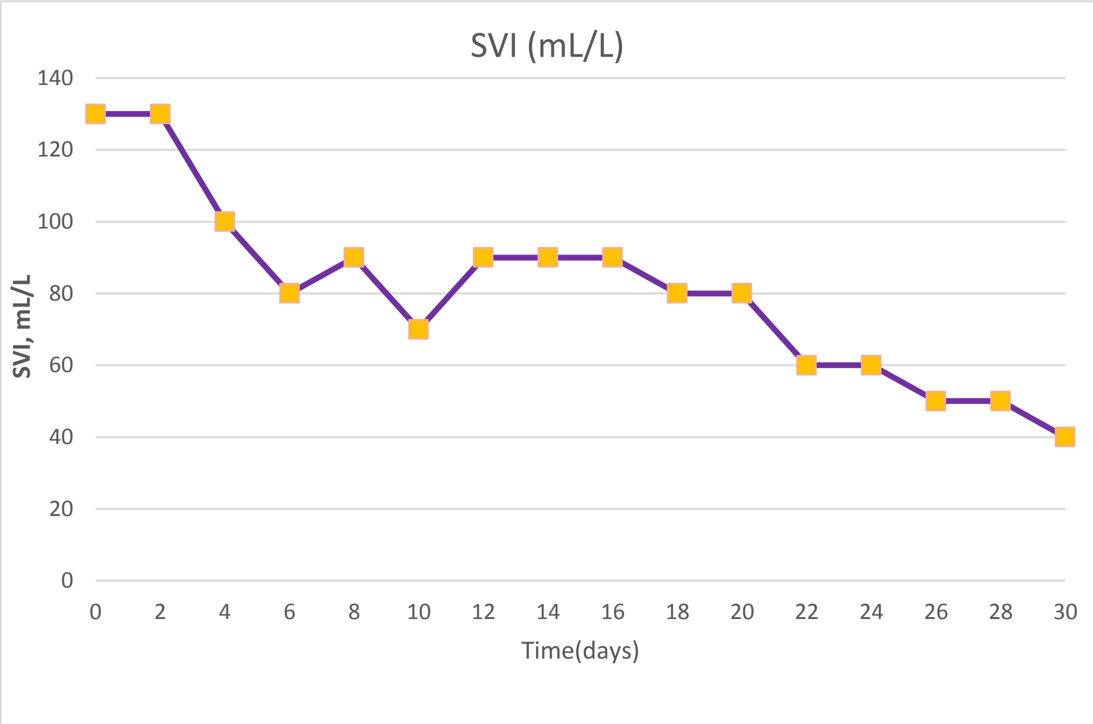



**Figure 4.5:** Sludge Volume Index (SVI)

# CHAPTER 5

# CONCLUSION AND RECOMMENDATION

In conclusion, Sequencing Batch Reactor (SBR) is applicable to treat refinery wastewater such as the wastewater from Petronas Penapisan Terengganu Sdn Bhd. The SBR shows a good performance in reduction of Chemical Oxygen Demand, Nitrate and Phosphate. The study reveals that the COD removal efficiency is ranging from 70 to 89.9%. Nitrate and Phosphate concentration exist provide nutrient for the microorganism to degrade the organic matter and for its growth.

However, further improvement and modification could be done to prove the performance efficiency of SBR. It is recommended that the future study will analyse the high strength of wastewater concentration using SBR system. Besides, further analysis should be done in removal of heavy metal in the refinery wastewater, so that it meets the requirement of Environmental Quality Act 1974 before the treated wastewater being discharged. Therefore, the implication towards hazardous heavy metal can be avoided.

## REFERENCES


Barber, J., Driscoll, T., Chandran, K., & Constable, S. (2008). *Industrial Wastewater Management, Treatment, and Disposal.* Alenxandria, Virginia: McGraw Hill.

Benyahia, F., Abdulkarim, M., Embaby, A., & Rao, M. (n.d.). Refinery Wastewater Treatment: A true Technological Challenge. *College of Engineering*, 186-189.

Chan, Y. J., Chong, M. F., & Law, C. L. (2010). Biological treatment of anaerobically digested palm oil mill effluent (POME) using a Lab-Scale Sequencing Batch Reactor (SBR). *Journal of Environmental Management*, 1738-1746.

Chan, Y., Chong, M., & Law, C. (2010). Biological treatment of anaerobically digested palm oil mill effluent (POME) using a Lab-scale Sequencing Batch Reactor (SBR). *Journal of Environmental Management*, 1738-1746.

Clearinghouse, N. S. (2003). National Small Flows Clearinghouse.

Coelho, A., Castro, A. V., Dezotti, M., & Sant' Anna, J. G. (2006). Treatment of petroleum refinery sourwater by advanced oxidation processes. *Journal of Hazardous Materials, B137*, 178-184.

El-Naas, M. H., Alhaija, M. A., & Al-zuhair, S. (2014). Evaluation of a three-step process for the treatment of petroleum refinery wastewater. *Journal of Environmental Chemical Engineering*, 56-62.

Hargeen, L. (2003). *Mercury on the Environment A Primer.* Toronto: Pollution Probe.

Ishak, S., Malakahmad, A., & Isa, M. (2012). Refinery wastewater biological treatment: A short review. *Journal of Scientific and Industrial Research, 71*, 251-256.

Jamhari, S. (2011). *Combined ASBR and Adsorbent For Biological Treatment of Diluted POME.* Universiti Teknologi Petronas.

Jern, N. (2006). Biological Treatment. In N. Jern, *Industrial Wastewater Treatment* (pp. 97-98). Singapore: Imperial College Press.

Kagaya, S., Miyazaki, H., Ito, M., Tohda , K., & Kanbara, T. (2010). Selective removal of mercury (II) from wastewater using polythiomides. *Journal of Hazardous Materials, 175*, 1113-1115.

Malakahmad, A., Hasani, A., Eisakhani, M., & Isa, M. (2011). Sequencing Batch Reactor (SBR) for the Removal of Hg and Cd from synthetic petrochemical factory wastewater. *Journal of Hazardous Materials, 191*, 118-125.

Metcalf & Eddy. (2003). *Wastewater Engineering Treatment and Reuse* (4th ed.).

Mizzouri, N. S., & Shaaban, M. G. (2013). Individual of combined effect of organic, toxic and hydraulic shocks on sequencing batch reactor in treating petroleum refinery wastewater. *Journal of Hazardous Materials*, 333-344.

*Nitrogen and Water*. (20 December, 2013). Retrieved 15 January, 2014, from The USGS Water Science School: http://ga.water.usgs.gov/edu/nitrogen.html

Ong, S. A., Lim, P. E., Seng, C. E., Hirata, M., & Hano, T. (January, 2005). Effects of Cu(II) and Cd(II) on the performance of sequencing batch reactor treatment system. *Process Biochemistry, 40*(1), 453-460.

Operating & Experimental Manual of Sequencing Batch Reactor (Model TR38). (n.d.). SOLTEQ.

Parker, D., Appleton, R., Bratby, J., & Melcer, H. (n.d.). Anoxic or Anaerobic Selectors: Which is Better? Retrieved 16 January, 2014, from http://www.rmwea.org/tech_papers/secondary_treatment/RMWEA%20Anoxci%20vs.%20Anaerobic%20Selectors.pdf

Peavy, H. S., Rowe, D., & Tchobanoglous, G. (1985). Environmental Engineering. In H. Peavy, D. Rowe, & G. Tchobanoglous, *Environmental Engineering.* Mc-Graw-Hill Book Co.

(2010). *Petroleum refining water/wastewater use and management.* United Kingdom: IPIECA. Retrieved 16 January, 2014, from http://www.perf.org/images/IPIECA_Refining_Water_mgt.pdf

Rastegar, S., Mousavi, S., Shaojaosadati, S., & Sheibani, S. (2011). Optimization of petroleum refinery effluent treatment in a UASB reactor using response surface methodology. *Journal of Hazardous Materials, 197*, 26-32.

Rodriguez, O., Padilla, I., Tayibi, H., & Lopez-Delgado, A. (2012). Concerns on liquid mercury and mercury-containing wastes: A review of the treatment technologies for the safe storage. *Journal of Environmental Management*, 197-205.

Shariati, S. R., Bonakdarpour, B., Zare, N., & Ashtiani, F. Z. (September, 2011). The effect of hydraulic retention time on the performance and fouling characteristics of membrane sequencing batch reactors used for the treatment of synthetic petroleum refinery wastewater. *Bioresource Technology, 102*(17), 7692-7699.

Sirianuntapiboon, S., & Hongsrisuwan, T. (27 June, 2007). Removal of Zn2+ and Cu2+ by a sequencing batch reactor (SBR) system. *Bioresource Technology*, 808-818. Retrieved from Thomasnet.com.

Sirianuntapiboon, S., & Hongsrisuwan, T. (2007). Removal of Zn2+ and Cu2+ by sequencing batch reactor (SBR) system. *Bioresource Technology*, 808-818.

Thompson, G., Swain, J., Kay, M., & Forster, C. F. (2001). The treatment of pulp and paper mill effluent: a review. *Bioresource Technology*, 275-286.

Wake, H. (2005). Oil refineries: a review of their ecological impacts on the aquatic environment. *Estuarine, Coastal and Shelf Science, 62*, 131-140.

# APPENDIX A1

| Date | Days | pH | COD (mg/L) | | | MLSS | MLVSS | Nitrate (mg/L) | Phosphate (mg/L) | Mercury | SVI (mL/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | COD | COD Removal (%) | COD(out) | | | | | | |
| 5/12/2013 | 0 | 7.52 | 797.00 | 0.00 | 0.00 | 300 | 290 | 1.9 | 4.4 | 16 | 130 |
| 6/12/2013 | 1 | 6.81 | 435.00 | 45.42 | 362.00 | 499 | 465.5 | 0.1 | 2.67 | | |
| 7/12/2013 | 2 | 6.98 | 237.30 | 70.23 | 559.70 | | | 0.3 | 0.55 | | |
| 8/12/2013 | 3 | 7.08 | 226.70 | 71.56 | 570.30 | 236.5 | 235.5 | 0.7 | 0.3 | | 100 |
| 9/12/2013 | 4 | 7.56 | 85.30 | 89.30 | 711.70 | | | 0.4 | 0.57 | | |
| 10/12/2013 | 5 | 7.48 | 89.00 | 88.83 | 708.00 | 338 | 325 | 0.7 | 0.31 | | 80 |
| 11/12/2013 | 6 | 7.30 | 84.30 | 89.42 | 712.70 | | | 0.8 | 0.24 | | |
| 12/12/2013 | 7 | 7.33 | 191.67 | 75.95 | 605.33 | 558 | 520 | 0.6 | 0.38 | | 90 |
| 13/12/2013 | 8 | 7.54 | 195.67 | 75.45 | 601.33 | | | 0.7 | 0.4 | | |
| 14/12/2013 | 9 | 7.49 | 242.00 | 69.64 | 555.00 | 628 | 610 | 1.1 | 0.5 | | 70 |
| 15/12/2013 | 10 | 7.80 | 195.00 | 75.53 | 602.00 | | | 1.1 | 0.31 | | |
| 16/12/2013 | 11 | 7.56 | 195.00 | 75.53 | 602.00 | 498 | 486 | 1.3 | 0.26 | | 90 |
| 17/12/2013 | 12 | 7.52 | 204.00 | 74.40 | 593.00 | | | 1.1 | 0.4 | | |
| 18/12/2013 | 13 | 7.59 | 203.00 | 74.53 | 594.00 | 484 | 480 | 1.3 | 0.35 | | 90 |
| 19/12/2013 | 14 | 7.61 | 211.00 | 73.53 | 586.00 | | | 0.8 | 0.33 | | |
| 20/12/2013 | 15 | 7.46 | 209.50 | 73.71 | 587.50 | 430 | 406 | 0.8 | 0.69 | | 90 |
| 21/12/2013 | 16 | 7.48 | 143.00 | 82.06 | 654.00 | | | 0.7 | 0.36 | | |
| 22/12/2013 | 17 | 7.44 | 146.50 | 81.62 | 650.50 | 1756 | 1652 | 0.7 | 0.48 | | 140 |
| 23/12/2013 | 18 | 7.47 | 185.50 | 76.73 | 611.50 | | | 1 | 0.5 | | |
| 24/12/2013 | 19 | 7.50 | 177.00 | 77.79 | 620.00 | 634 | 554 | 0.8 | 0.45 | | 120 |

**APPENDIX A2**

| | COD (mg/L) | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Day | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
| 1 | 435 | 239 | 228 | 83 | 90 | 82 | 193 | 192 | 883 | 194 | 194 | 204 | 203 | 218 | 209 | 146 | 142 | 186 | 180 |
| 2 | 435 | 239 | 226 | 93 | 91 | 87 | 194 | 200 | 267 | 309 | 194 | 204 | 203 | 204 | 210 | 140 | 151 | 185 | 174 |
| 3 | 435 | 234 | 226 | 90 | 87 | 84 | 188 | 195 | 217 | 196 | 197 | 204 | | | | | | | |
| Mean (mg/L) | 435.00 | 237.33 | 226.67 | 88.67 | 89.33 | 84.33 | 191.67 | 195.67 | 242.00 | 195.00 | 195.00 | 204.00 | 203.00 | 211.00 | 209.50 | 143.00 | 146.50 | 185.50 | 177.00 |
| Standard Deviation (±) | 0.00 | 2.89 | 1.15 | 5.13 | 2.08 | 2.52 | 3.21 | 4.04 | 35.36 | 1.41 | 1.73 | 0.00 | 0.00 | 9.90 | 0.71 | 4.24 | 6.36 | 0.71 | 4.24 |