

CHARACTERIZATION AND KINETIC  
STUDY OF ACTIVATED SLUDGE PROCESS  
IN PALM OIL MILL EFFLUENT (POME)  
TREATMENT

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DOCTOR OF PHILOSOPHY

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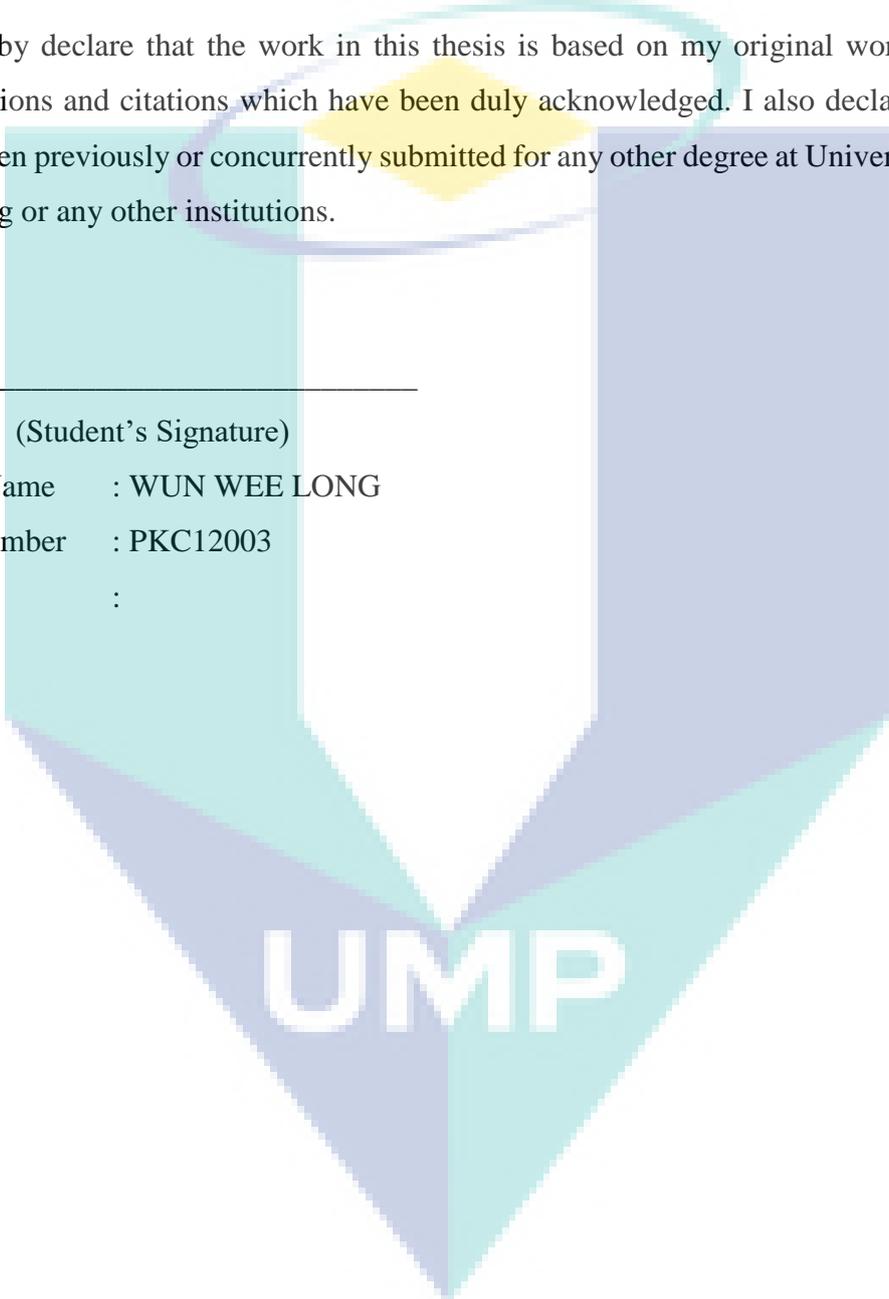
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TREATMENT

WUN WEE LONG

Thesis submitted in fulfillment of the requirements  
for the award of the degree of  
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## ABSTRAK

Sejak beberapa dekad yang lalu, effluen kilang kelapa sawit (*POME*) merupakan salah satu isu utama alam sekitar di negara kita. Disebabkan piawai pelepasan yang ketat, banyak kilang kelapa sawit tidak dapat mematuhi piawai yang tertakluk dalam undang-undang alam sekitar. Oleh itu, sistem penggilapan rawatan *POME* telah dikembangkan dan dilaksanakan untuk meningkatkan prestasi proses rawatan biologi selepas rawatan sistem kolam. Walaupun demikian, proses rawatan biologi masih tidak dapat mencapai piawai pelepasan yang ditetapkan mungkin disebabkan reka bentuk sistem rawatan *POME* yang tidak sesuai. Bagi mencari punca kegagalan rawatan *POME* dalam pematuhan piawai pelepasan yang tertakluk dalam undang-undang, ciri-ciri *POME* and kajian kinetik rawatan *POME* telah dijalankan untuk memperolehi maklumat yang sesuai dalam rekaan bentuk sistem rawatan *POME*. Dalam kajian ini, penentuan komposisi fizikal telah dijalankan melalui proses pengeringan dan penyalaan, manakala analisis penagihan saiz zarah (*PSD*) dijalankan melalui proses penapisan dengan menggunakan kertas turas saiz liang yang berbeza seperti 2  $\mu\text{m}$ , 5  $\mu\text{m}$ , 10  $\mu\text{m}$ , 20  $\mu\text{m}$ , 50  $\mu\text{m}$  and 100  $\mu\text{m}$ . Daripada keputusan kajian ini, sebanyak 46% pepejal tetap keseluruhan (*TFS*) didapati terkandung dalam pepejal keseluruhan (*TS*) dan sebanyak 63% pepejal keseluruhan terdiri daripada zarah-zarah pepejal dengan saiz 20-50  $\mu\text{m}$  dan 50-100  $\mu\text{m}$ . Selain itu, komposisi kimia utama dalam *POME* adalah keperluan oksigen biokimia (*BOD*) dan keperluan oksigen kimia (*COD*). Oleh itu, keperluan oksigen biokimia muktamad ( $L_0$ ) telah diramalkan melalui kaedah kajian kinetik *BOD* seperti *Least Square Method*, *Fujimoto Method*, *Thomas Graphical Method*, *Log Different Method* and *Method of Moment* dengan menggunakan keputusan *BOD* 7-hari anaerobik terawat *POME*. Manakala, penentuan pecahan *COD* anaerobik terawat *POME* seperti keperluan oksigen kimia bioterurai (*bcOD*) dan keperluan oksigen kimia bioterurai mudah larut (*srbCOD*) juga telah dijalankan serentak dengan kajian kinetik proses enapcemar teraktif dalam rawatan *POME*. Daripada kajian tersebut, didapati  $L_0$ , *bcOD* dan *srbCOD* masing-masing dalam kepekatan 1,139 mg/L, 1,235 mg/L and 719 mg/L. Bagi menyiasat kesan-kesan keadaan operasi dalam kajian rawatan *POME* dengan menggunakan enapcemar teraktif, keadaan operasi seperti *pH* awal *POME*, masa pengekalan hidraulik (*HRT*), kadar muatan organik (*OLR*), pepejal terampai mudah meruap dalam campuran keras (*MLVSS*), masa pengekalan pepejal (*SRT*) dan kepekatan gula sebagai sumber karbon luaran telah dipilih dalam kajian ini. Kecekapan enapcemar teraktif dalam rawatan anaerobik terawat *POME* telah dinilai di bawah keadaan aerobik berdasarkan nisbah makanan dan mikroorganisma (*F/M ratio*) dalam 0.3 kg *BOD*/kg *MLVSS*/hari dan didapati keadaan operasi terbaik masing-masing adalah pada nilai  $6.5 \pm 0.1$ , 48 jam, 0.31 g *BOD*<sub>3</sub>/L.hari,  $2000 \pm 200$  mg/L, 10 hari and 50 mg/L dengan kecekapan penyingkiran *COD* dan *BOD* masing-masing sehingga 62 - 68% dan 60 - 65%. Dengan menggunakan nilai ciri-ciri *POME* dan keadaan operasi optimum, kajian kinetik rawatan *POME* dijalankan untuk memperolehi parameter kinetic. Dalam kajian ini, parameter kinetik bagi asas *COD* dan *BOD* telah didapati, di mana pekali hasil maksimum ( $Y$ ), pekali pereputan dalam ( $k_d$ ), kadar penggunaan substrat spesifik maksimum ( $k$ ) dan pemalar-halaju-separuh ( $K_s$ ) yang didapati pada nilai masing-masing 0.2369 mg *VSS*/mg *COD*, 0.1060 hari<sup>-1</sup>, 2.2717 hari<sup>-1</sup> and 758.7705 mg/L bagi asas *COD*, manakala nilai parameter kinetik untuk asas *BOD* masing-masing ialah 0.6718 mg *VSS*/mg *BOD*<sub>3</sub>, 0.0658 hari<sup>-1</sup>, 1.4136 hari<sup>-1</sup> and 556.1526 mg/L. Akhirnya, nilai-nilai yang diperolehi digunakan dalam mereka sistem rawatan *POME* dan membuat perbandingan dengan sistem rawatan *POME* yang direka dengan merujuk kepada nilai-nilai piawai yang dicadangkan oleh Jabatan Alam Sekitar yang diperolehi daripada loji rawatan air kumbahan.

## ABSTRACT

Due to the more stringent discharge standard of the environmental regulation, many palm oil mills are struggled to meet the compliance. Thus, the polishing treatment plant for palm oil mill effluent (POME) discharge are developed and implemented to enhance the biological treatment process after the conventional ponding system. Nevertheless, the biological treatment process yet to achieve the required discharge standard due to the inappropriate system design. Thus, characterization of POME and kinetic study of POME treatment was conducted to obtain the appropriate information for the POME treatment system design. In this study, physical composition determination was carried out through the drying and ignition process of anaerobic treated POME sample for solids contents analysis and particle size distribution (PSD) analysis was conducted via filtration process by using different pore size of filter paper (namely 2  $\mu\text{m}$ , 5  $\mu\text{m}$ , 10  $\mu\text{m}$ , 20  $\mu\text{m}$ , 50  $\mu\text{m}$  and 100  $\mu\text{m}$ ). There was about 46% of total fixed solids (TFS) had been found in total solids (TS) of POME and 63% of TS was contributed by solids particle with particle size of 20-50  $\mu\text{m}$  and 50-100  $\mu\text{m}$ . Besides, major contribution of chemical constituent in POME were biochemical oxygen demand (BOD) and chemical oxygen demand (COD). Hence, ultimate biochemical oxygen demand ( $L_0$ ) was estimated through BOD kinetic study methods, namely Least Square Method, Fujimoto Method, Thomas Graphical Method, Log Different Method and Method of Moment after conducting the 7-days BOD testing of anaerobic treated POME sample. While COD fractional of POME, namely biodegradable COD (bCOD) and soluble readily biodegradable (srbcOD) were determined concurrent with the kinetic study of activated sludge process in POME treatment. From the study, uBOD, bCOD and srbcOD was found at 1,139 mg/L, 1,235 mg/L and 719 mg/L, respectively. In order to investigate the effect of operating conditions on POME treatment using activated sludge, the selected operating conditions in this study were initial pH, hydraulic retention time (HRT), organic loading rate (OLR), initial mixed liquor volatile suspended solids (MLVSS), solid retention time (SRT), and molasses concentration added as a carbon source. The efficiency of activated sludge was evaluated by treating the anaerobic treated POME under aerobic conditions based on the Food to Microorganism (F/M) ratio of 0.3 kg BOD/kg MLVSS.day. The best operating condition for initial pH, HRT, OLR, initial MLVSS, SRT, and molasses concentration were found to be  $6.5 \pm 0.1$ , 48 hours, 0.31 g BOD<sub>3</sub>/L.day,  $2000 \pm 200$  mg/L, 10 days and 50 mg/L, respectively at the removal of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in POME ranging from 62 - 68% and 60 - 65% respectively. By using the result of characterization and optimum operating condition of POME treatment, kinetic study of POME treatment by activated sludge system were carried out to obtain the kinetic parameters for the POME treatment. From this kinetic study, the kinetic parameters for COD and BOD basis had been determined for maximum yields coefficient ( $Y$ ), endogenous decay coefficient ( $k_d$ ), maximum specific substrate utilization rate ( $k$ ) and half-velocity constant ( $K_s$ ) at 0.2369 mg VSS/mg COD, 0.1060 day<sup>-1</sup>, 2.2717 day<sup>-1</sup> and 758.7705 mg/L for COD basis whilst the kinetic parameters value for BOD basis were 0.6718 mg VSS/mg BOD<sub>3</sub>, 0.0658 day<sup>-1</sup>, 1.4136 day<sup>-1</sup> and 556.1526 mg/L, respectively. These kinetics parameters were important in designing the POME treatment system that is able to meet the standard as the design using DOE default value has been shown to under-design and failure to meet the required standard.

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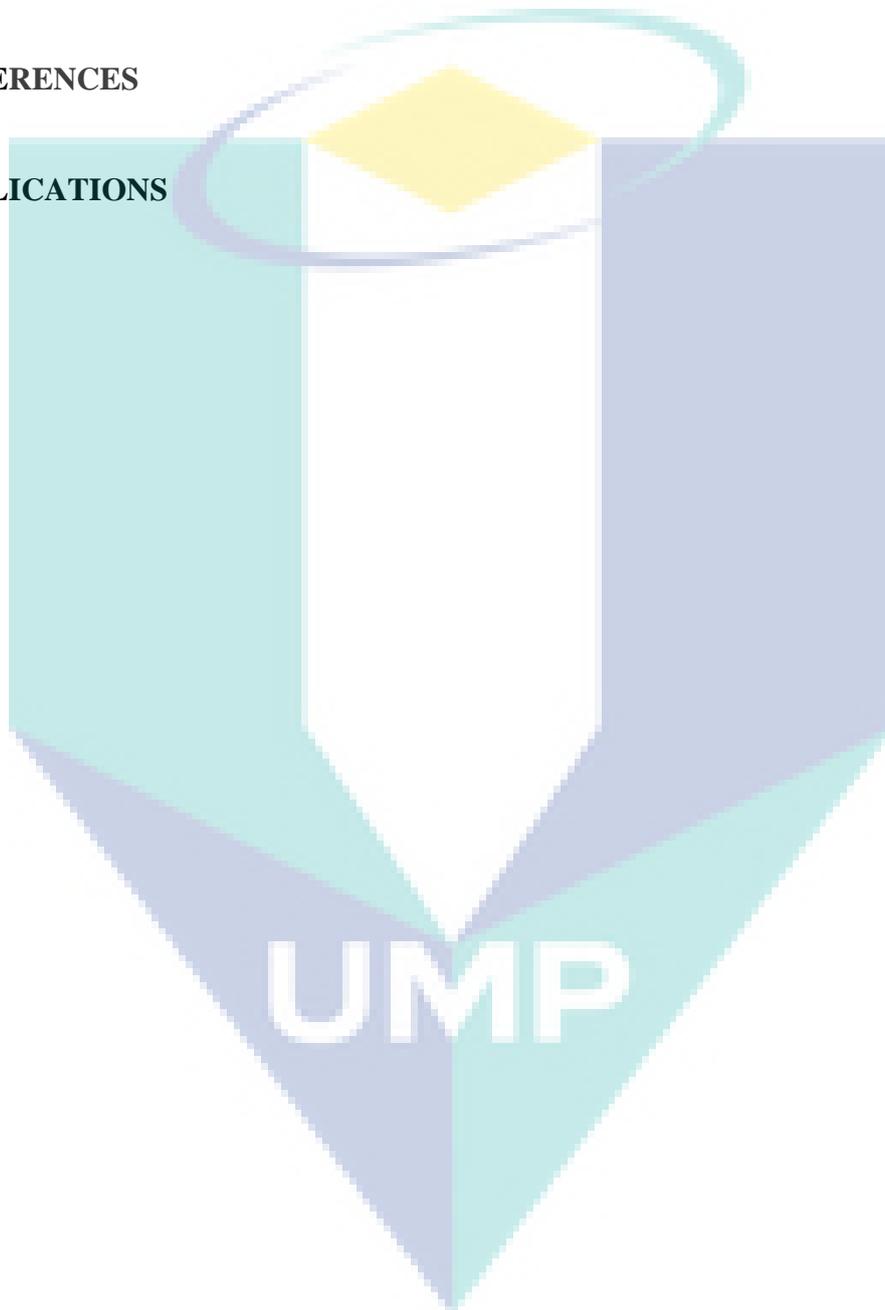
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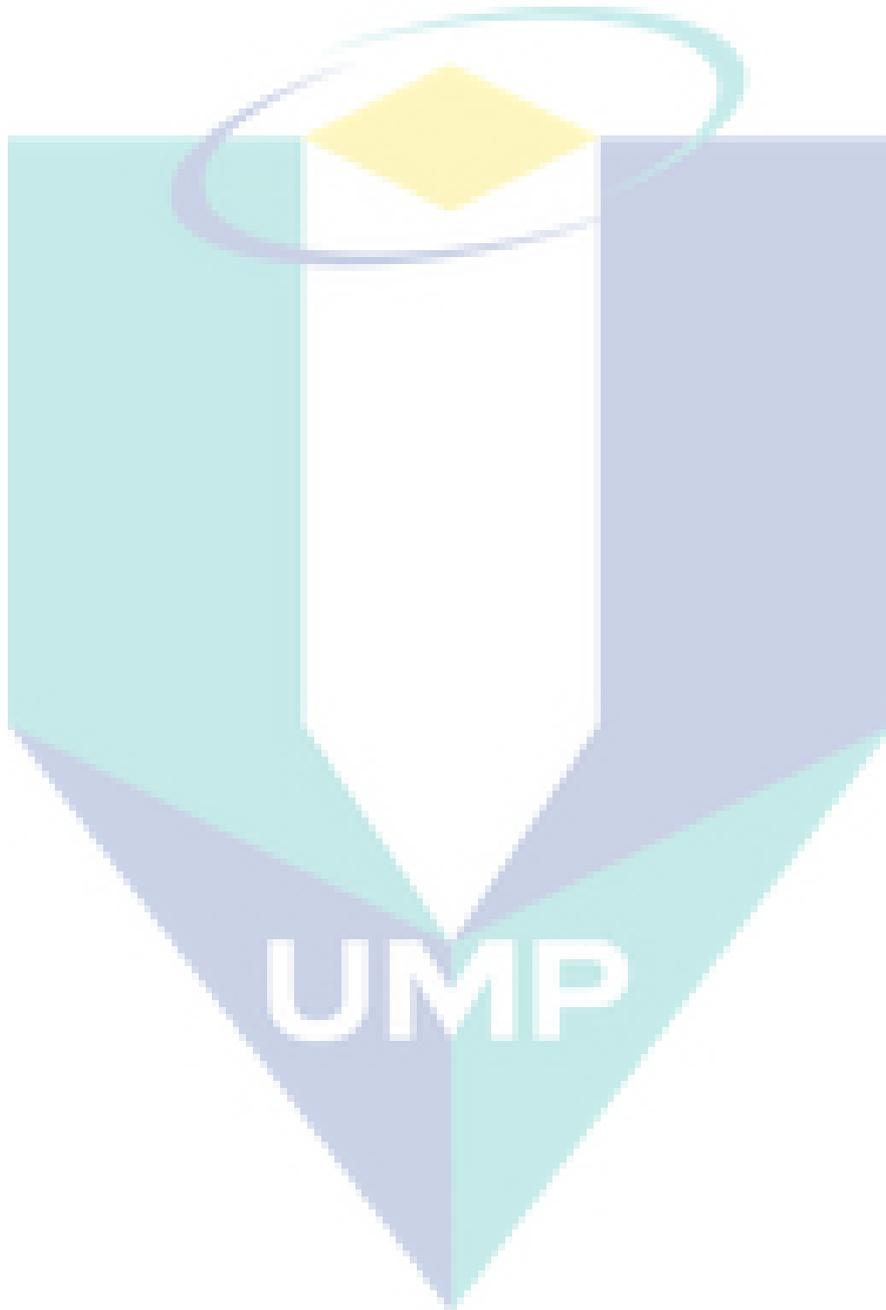
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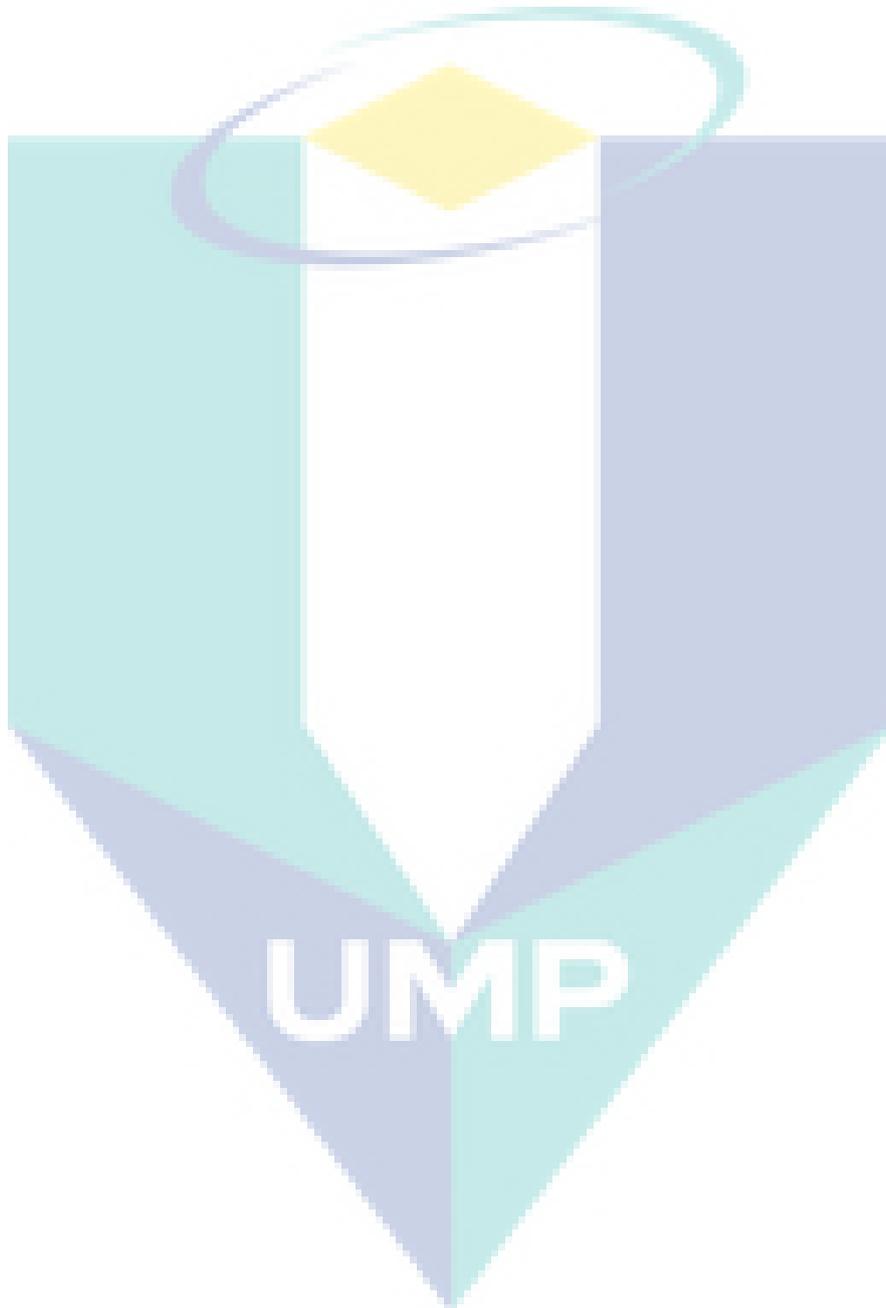
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UMP

## LIST OF SYMBOLS

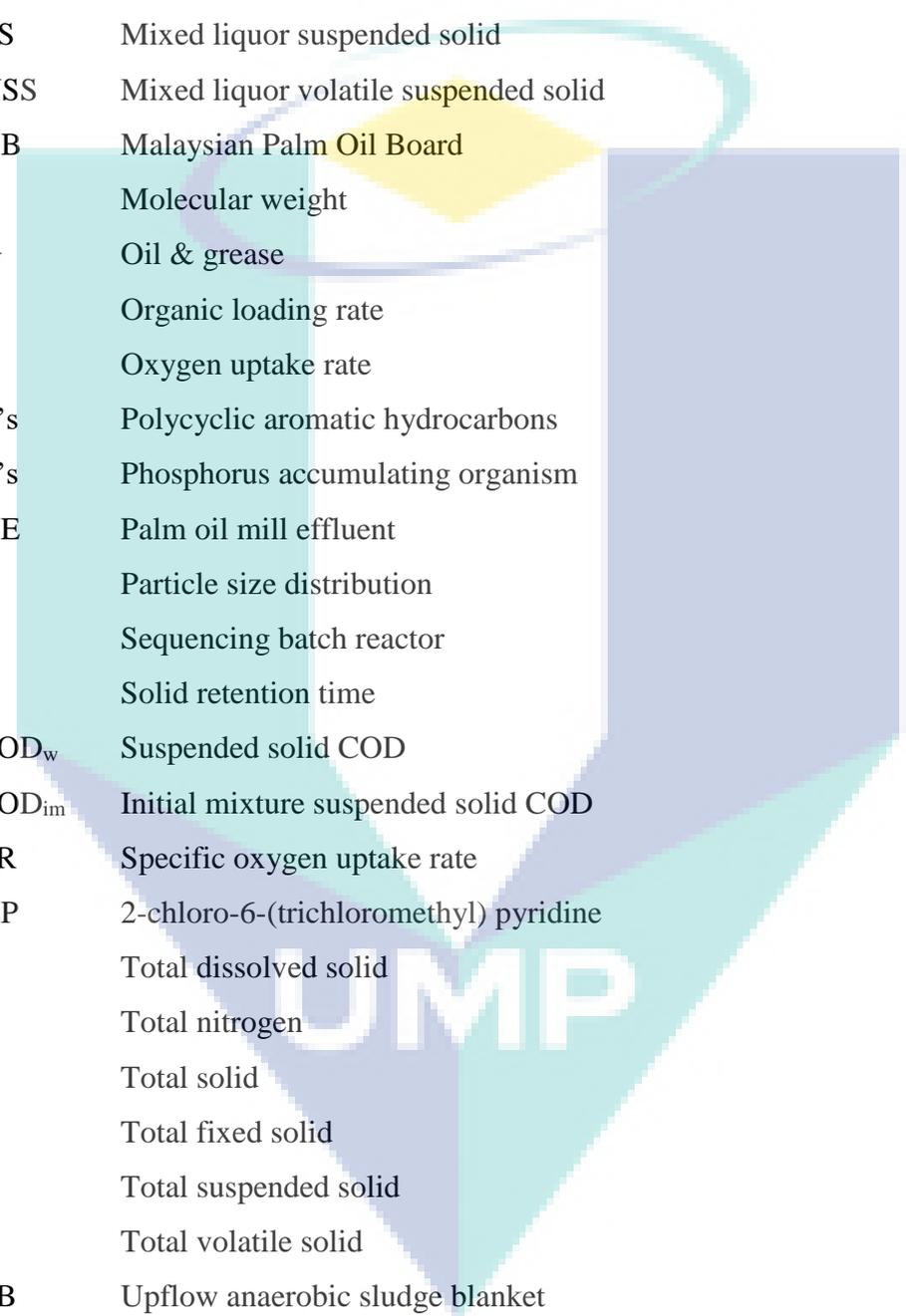
$f_b$	Biodegradable fraction of VSS
$k$	Maximum specific substrate utilization rate ( $\text{day}^{-1}$ )
$k_d$	Endogenous decay coefficient ( $\text{day}^{-1}$ )
$K_s$	Half-velocity constant (mg/L of BOD) or (mg/L of COD)
$k_1$	Reaction rate constant (1/day)
$L_0$	Ultimate carbonaceous BOD (mg/L)
$L_r$	BOD remaining after time, $t$ (mg/L)
$m$	Number of data point minus one
$n$	No of days of incubation for the serial BOD test
$Q_i$	Flowrate of influent (L/day)
$Q_e$	Flowrate of effluent (L/day) or ( $Q_i - Q_w$ )
$Q_w$	Flowrate of wasted sludge (L/day)
$r_g$	Net rate of biomass production (mg VSS/L.day)
$r_{su}$	substrate utilization rate (mg/L.day)
$S_e$	Soluble substrate concentration in the effluent (mg/L)
$S_i$	Soluble substrate concentration in the influent (mg/L)
$S_{eBOD}$	Reciprocal substrate of BOD concentration (L/mg of BOD)
$S_{eCOD}$	Reciprocal substrate of COD concentration, (L/mg of COD)
$t$	Time (day)
$U$	Specific substrate utilization rate ( $\text{day}^{-1}$ )
$U_{BOD}$	Specific substrate utilization rate of BOD ( $\text{day}^{-1}$ )
$U_{COD}$	Specific substrate utilization rate of COD ( $\text{day}^{-1}$ )
$V_d$	Volume of aeration tank (L) calculated by using DOE formula
$V_p$	Volume of aeration tank (L) calculated by using industry formula
$V_r$	Volume of aeration tank (L)
$X$	Biomass concentration in the aeration tank (mg VSS/L)
$X_i$	Biomass concentration in the influent (mg VSS/L)
$X_e$	Biomass concentration in the effluent (mg VSS/L)
$X_w$	Biomass concentration in the wasted sludge (mg VSS /L)
$Y$	Yield coefficient (mg VSS/mg BOD) or (mg VSS/mg COD)
$y$	BOD exerted at time $t$ (mg/L)
$y'$	Rate of change of BOD (mg/L.day)

$y_e$	Estimated BOD (mg/L)
$y_o$	Observed BOD (mg/L)
$\theta$	Hydraulic retention time (day)
$\theta_c$	Solids retention time (days)
$1/\theta_c$	Specific growth rate ( $\text{day}^{-1}$ )



## LIST OF ABBREVIATIONS

ABSR	Anaerobic bench scale reactor
ASBR	Anaerobic sequencing batch reactor
ASM1	Activated sludge model 1
ASM2	Activated sludge model 2
ASM2d	Activated sludge model 2d
ASM3	Activated sludge model 3
AN	Ammoniacal nitrogen
BOD	Biochemical oxygen demand
BOD <sub>3</sub>	Biochemical oxygen demand – 3 days, 30°C
BOD <sub>5</sub>	Biochemical oxygen demand – 5 days, 20°C
cBOD	Carbonaceous biochemical oxygen demand
nBOD	Nitrogenous biochemical oxygen demand
uBOD	Ultimate biochemical oxygen demand
COD	Chemical oxygen demand
bCOD	biodegradable chemical oxygen demand
nbCOD	Nonbiodegradable chemical oxygen demand
pnbCOD	Particulate nonbiodegradable COD
psbCOD	Particulate slowly biodegradable chemical oxygen demand
srbCOD	Soluble readily biodegradable chemical oxygen demand
snbCOD	Soluble nonbiodegradable chemical oxygen demand
tCOD	Total chemical oxygen demand
T <sub>b</sub> OD	Total biological demand
COD <sub>it</sub>	Initial total COD
COD <sub>is</sub>	Initial soluble COD
COD <sub>ism</sub>	Initial mixture soluble COD
COD <sub>itm</sub>	Initial mixture total COD
COD <sub>mb</sub>	Mixture biomass COD
COD <sub>ipm</sub>	Initial POME COD in mixture
COD <sub>fpm</sub>	Final POME COD in mixture
DO	Dissolved oxygen
DOE	Department of Environment
FFB	Fresh fruit bunch



FDS	Fixed dissolved solid
FSS	Fixed suspended solid
F/M Ratio	Food to Microorganism Ratio
HRT	Hydraulic retention time
IAAB	Integrated anaerobic-aerobic bioreactor
MLSS	Mixed liquor suspended solid
MLVSS	Mixed liquor volatile suspended solid
MPOB	Malaysian Palm Oil Board
MW	Molecular weight
O&G	Oil & grease
OLR	Organic loading rate
OUR	Oxygen uptake rate
PAH's	Polycyclic aromatic hydrocarbons
PAO's	Phosphorus accumulating organism
POME	Palm oil mill effluent
PSD	Particle size distribution
SBR	Sequencing batch reactor
SRT	Solid retention time
SS COD <sub>w</sub>	Suspended solid COD
SS COD <sub>im</sub>	Initial mixture suspended solid COD
SOUR	Specific oxygen uptake rate
TCMP	2-chloro-6-(trichloromethyl) pyridine
TDS	Total dissolved solid
TN	Total nitrogen
TS	Total solid
TFS	Total fixed solid
TSS	Total suspended solid
TVS	Total volatile solid
UASB	Upflow anaerobic sludge blanket
VDS	Volatile dissolve solid
VSS	Volatile suspended solid

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UMP

## CHAPTER 1

### BACKGROUND OF STUDY

#### 1.1 Introduction

Over the last few decades, water pollution become a critical and serious problem not only in other regions of the world (Sadoff et al. 2015), but also in Malaysia (Afroz & Rahman, 2017). The increasing of the water pollution problem mainly due to the urban growth (Liyanage & Yamada, 2017), manufacturing activities (Wu et al. 2018) and agro-based industries (Evans et al. 2018). In Malaysia, palm oil industry is one of the most rapidly expanding industries and very important agricultural based industries for the past decades, which produced a huge amount of waste water called palm oil mill effluent (POME). When all the untreated POME discharged into the water bodies, it may have a deleterious environmental impact especially to the aquatic life (Azmi and Yunos, 2014).

Furthermore, discharge of dark brownish coloured of POME which probably from the polymerization of tannins and low molecular weight phenolic compound (Limkhuansuwan & Chaiprasert, 2010) into the river will inhibit the growth of aqua organism by reducing the penetration of sunlight and affecting the photosynthetic activity (Neoh et al. 2012). In addition, the presence of lignin, tannin, humic acids, carotene and other organic matter in POME, which are recalcitrant to the biological degradation process and cause the pollution to the river body if discharge without treatment (Ho et al. 1984).

## 1.2 Problem Statement

Due to the rapid expansion of palm oil industry and public awareness on the environmental pollution, DOE is implemented more stringent regulation, where the BOD<sub>3</sub> discharge standard limit has been reduced from 100 mg/L to 20 mg/L (Zainal et al. 2017). Nevertheless, many palm oil mills are still struggling to comply with the discharge standard of 100 mg/L of BOD<sub>3</sub>.

In order to comply with the DOE discharge standard, other technologies or systems had been used in conjunction with the conventional ponding treatment system, especially the activated sludge system that is considered as low operating cost, simple and ease of handling (Liew et al., 2015). Prior to POME treatment system calculation and design, characteristic of raw POME will be analysed according to the Environmental Quality Act, 1974, Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulation 1977 (Malaysia, 2017). However, the BOD<sub>3</sub> result was used for the design calculation, which was not represent the total BOD or ultimate BOD (uBOD) in POME. Thus, through this study, the ultimate BOD or total BOD can be obtained and used for the POME treatment system design.

Simultaneously, the COD test is used to measure the total organic in POME, which includes the biodegradable and non-biodegradable matter, but in actual biological process of POME treatment, only the biodegradable matter can be digested biologically by microorganism. Hence, by conducting the COD fractional study in this study, level of biodegradation by microorganism in POME treatment can be determined.

In addition, there are no further analysis on other physical composition of POME, such as solid content and particle size, which might affect the POME treatment performance in terms of organic loading rate which contributed by the particulate suspended solid. Through the characterization study of physical composition in POME, solid content and particle size distribution can be determined for solid removal system development.

Even though many palm oil mills had used the activated sludge system in treating POME after conventional ponding system, they are still struggling to comply the

discharge standard stipulated under the Environmental Quality Act, 1974, Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulation 1977 (Malaysia, 2017). This might due to the inefficient of operation control in activated sludge system. Therefore, investigation of operation control in this study is to examine the effect of control parameters according to the DOE performance monitoring guidance document (DOE, 2010b).

In practical, the activated sludge system is designed and calculated based on the kinetic parameters that had been widely used by default. These values are mainly obtained from the municipal wastewater treatment plant, which did not represent the true conditions in the POME. Thus, through the kinetic study of POME treatment by activated sludge process in this study, kinetic parameters can be determined and used for the activated sludge system design for POME treatment.

This study is designed to assess the hypothesis that prior to POME treatment system design, thorough characteristic of POME as well as determination of the kinetic parameters which is more relevance to POME, are required.

### **1.3 Objectives of Study**

Specifically, the objectives of this study were summarized in Figure 1.1 with the details of the target for each objective.

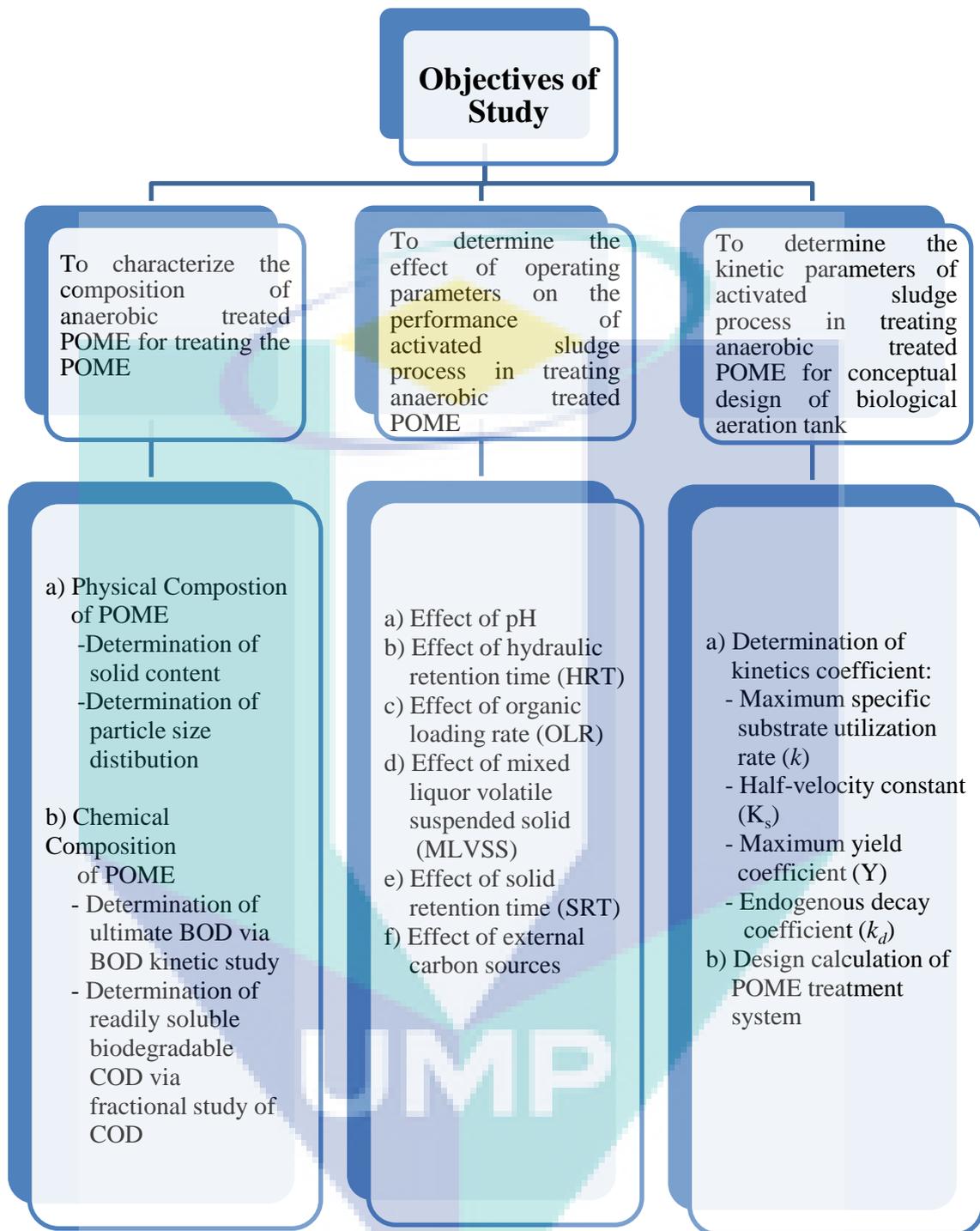


Figure 1.1 Objective of study with description of target objective

#### 1.4 Scope of Study

A study of POME treatment by activated sludge process can be very wide and the biodegradation process is very depending on the behaviour of the microorganism in the activated sludge as well as the characteristic of POME. Different type of POME sample

will give a different type of biodegradation performance result. In this study, the POME sample was collected from an anaerobic pond at Kilang Sawit Neram, Kemaman, Terengganu for the composition and kinetic parameters studies, while the activated sludge sample was collected from Cargill Palm Oil Refinery, Gebeng, Kuantan, Pahang for the biodegradation performance study.

Even though batch reactor can be used for the nitrogen removal via nitrification and denitrification process, this study only emphasizes on the biodegradation of organic matter, mainly BOD and COD by using activated sludge in a batch reactor. The results obtained from this study is only applicable to the prevailing condition and the fine-tuning need to be done when it is applied to the actual field condition.

In this experiment, composition of POME such as solid contents, particle size distribution, organic content (COD and BOD<sub>3</sub>) and nitrogen compound (TN and AN) had been examined prior to performance study of activated sludge in treating POME. In order to study deeply on the organic content in POME, kinetic study of BOD and fractional of COD had been conducted. Then, the performance of POME treatment by activated sludge process had been carried out by manipulating the operating parameters for activated sludge process such as initial pH of POME, hydraulic retention time (HRT), organic loading rate (OLR), initial mixed liquor volatile suspended solids (MLVSS), solid retention time (SRT) and molasses concentration as external carbon source. After that, the kinetic analysis on the POME treatment by activated sludge treatment system has been carried out. Finally, the design calculation comparison of aeration tank volume by using default value and experimental value obtained from this study had been done.

The comprehensive study of POME treatment performance would require considerable study period, but due to restriction of time and resources, the study only focus on anaerobic treated POME sample from the anaerobic pond.

### **1.5 Significance of the Study**

It is significant to get a better understanding of the composition of POME especially the dissolved organic matter, which will contribute to the BOD and COD concentrations in POME. Generally, the BOD<sub>3</sub> and total COD testing were conducted for

POME sample and the result obtained was used for the activated sludge treatment system design. In fact, there are high concentration of dissolved organic matter in POME that are not easily degraded by the activated sludge treatment system (Wang and Chen, 2018). Hence, the determination of ultimate BOD and readily biodegradable COD value is important to establish a sound scientific basis for future activated sludge system design.

As a rule of thumb, the activated sludge treatment system that use to treat the POME is designed based on the empirical method using default values. This approach is considered not appropriate as the default values are not representing the actual value in POME. This will certainly affect the data interpretation and resulting in the rigidity of optimization process. Thus, by conducting the kinetic study in POME treatment, it will help to get more representative kinetic parameters value and provide accuracy data for system design, especially the activate sludge system.

Besides, the study of particle size distribution in POME also contribute to the understanding of solids variability that is present in POME. In practical, solids problem always is another intangible problem that occurred in POME ponding system, which are settled down in each pond when POME flow through the ponding system. Solids sedimentation will cause the sludge accumulation and directly reduce the hydraulic retention time in POME ponding system. Simultaneously, it affects the biodegradable process and the treatment performance. By understanding the particle size distribution in POME, pre-treatment technologies or system can be implemented to remove the excessive solid content prior to biological treatment process and aids in the final compliance of the discharge effluent.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Introduction

For the purpose of this study, there are several technical scientific literatures need to be reviewed including the study of POME characteristic, optimum of activate sludge operating parameters and the kinetic study of activated sludge process. However, most of the literatures only reported on the chemical's composition in POME such as COD and BOD. No physical composition was reported, especially the total solid content that is also one of the organic matters contributing to POME. Secondly, although many researchers had reported the operating parameters of activate sludge process in treating POME, the parameters were not completely studied according to DOE guidance documents (DOE, 2010a and DOE, 2010b). Thirdly, most of the kinetic parameters in POME treatment were determined in COD basis, but COD is not a discharge parameter that need to be complied according to DOE discharge standard requirement. Thus, through this study, the lacking information from the past studied such as physical composition of POME, all the important operating parameters in control of the activated sludge process, and the determination of kinetic parameters in BOD basis are obtained and used in a right approached for POME treatment.

#### 2.2 Palm Oil Industry

Palm oil, as vegetable oil, is extracted from the mesocarp of the fruit of oil palms, while palm kernel oil is extracted from the kernel of the oil palm. Palm oil is widely used in food products, such as cooking oil, shortenings, margarine, and biofuel, whereas palm kernel oil is used as a raw ingredient of consumer products, including soaps, cosmetics, candles, and detergents.

### **2.2.1 History of Oil Palm in Malaysia**

The introduction of the oil palm industry in Malaysia as a commercial plant was started in 1917 at the Tennamaram Estate in Selangor. The oil palm (*Elaeis guineensis*) is indigenous to West Africa and it was planted in Singapore Botanic Garden in the 1870s after Malaya received its first batch of oil palm from the Royal Botanic Gardens in Kew, England. After independence in 1957, to improve to the quality of live in rural area, the government established the Federal Land Development Authority (FELDA) to introduced the large-scale oil palm planting where it was expanded from 55,000 hectares in 1960 to 5.74 million hectares in 2016 and the production of palm oil was growing tremendously from less than 100,000 tonnes in 1960 to about 17.32 million tonnes in 2016 (NST Online, 2017).

Besides FELDA, the Malaysian government expanded the land settlement programmes by the introduction of Federal Land Consolidation and Rehabilitation Authority (FELCRA) and Rubber Industry Small-holders' Development Authority (RISDA). Moreover, through continuous support by the government, the rapid expansion of oil palm cultivated areas also has been impelled in independent smallholders and private estates nationwide.

### **2.2.2 Supply and Demand for Palm Oil and Its Related Issues**

Over the last few decades, Malaysian palm oil industry was basically export-oriented where most of the palm oil product was export to difference country in the world (Ming and Chandramohan, 2002) especially crude palm oil (CPO) and crude palm kernel oil (CPKO) which had contributed a huge amount of revenue for Malaysia as shown in Table 2.1. Malaysian exports of CPO and CPKO witnessed a significant growth of 25.3% and 17.2% from 2,709,398 tonnes and 285,702 tonnes in 2017 to 3,394,522 tonnes and 334,736 tonnes in 2018, respectively. However, in term of revenue, the CPO only shown a small increment of 1.3% from RM 7,719.45 million in 2017 to RM 7,822.19 million in 2018, while CPKO shown a significant reduction of 15.2% from 1,507.19 million in 2017 to RM 1,278.08 million in 2018. This is because the yearly average price of CPO and CPKO had significant decreasing of 20.1% and 31.3%, from RM 2,797.79/tonnes and RM 5,353.79/tonnes in 2017 to RM 2,235.13/tonnes and RM 3,679.79/tonnes in 2018,

respectively. The price trends of palm oil are affected by global oils and fats demand, where the price and production of competing vegetable oil such as soybean oil, corn oil, sunflower oil and rapeseed oil also affected the palm oil price globally (Ali, 2019).

Table 2.1 Summary of supply and demand for palm oil in 2017 and 2018

Descriptions	2017	2018	Difference
Crude Palm Oil (CPO) <sup>(a)</sup>			
Export (tonnes)	2,709,398	3,394,522	685,124
Export Revenue (RM Million)	7,719.45	7,822.19	102.74
Crude Palm Kernel Oil (CPKO) <sup>(a)</sup>			
Export (tonnes)	285,702	334,746	49,044
Export Revenues (RM Million)	1,507.19	1,278.08	-229.11
Yearly Average Price (RM/tonnes) <sup>(b)</sup>			
CPO	2,797.79	2,235.13	-563
CPKO	5,353.79	3,679.79	-1,674

Sources: <sup>(a)</sup>MPOB (2018a), <sup>(b)</sup>MPOB (2018b)

Initially, the export of palm oil products was dominated by developed countries such as the United State of America and European countries. However, for the past few decades, Malaysia had expanded its export market to more than 200 countries worldwide. Nevertheless, Malaysia is still depending on few selected markets as a major export destination such as China, India, Pakistan, Europe, and South East Asia (SEA) countries (Nambiappan et al., 2018). As shown in Figure 2.1, in 2017, the export of palm oil product to China and Europe had reached 1,859,748 tonnes and 1,911,800 tonnes, respectively. This export volume had shown an increasing of 3.1% and 4.2% in 2018, which was reported at 1,917,288 tonnes and 1,991,548 tonnes, respectively. The increasing in palm oil product imports by China because of the trade tension between the United State and China in the middle of 2018, which caused the export reducing of soybean from the United States (Zakariah, 2019). While Europe increased the import of palm oil for its biofuel program implementation in the EU's new renewable energy guidelines, which will take effect in 2020 (Clarke, 2019).

Meanwhile, the export of palm oil products to India and Pakistan in 2017 had reached 2,514,008 tonnes and 1,161,278 tonnes, respectively, but in 2018, the export volume had shown a reduction of 19.3% and 12.4% to 2,028,297 tonnes and 1,016,977 tonnes, respectively. A significant reduction of export to India and Pakistan due to the

competition from Indonesia where their palm oil products are sold at a lower price than Malaysia since 2008 (Rifin, 2010). Nevertheless, the export to SEA had rose for 19.5% from 1,632,973 tonnes in 2017 to 1,952,139 tonnes in 2018 due to rapidly-growing population of SEA (OECD, 2019).

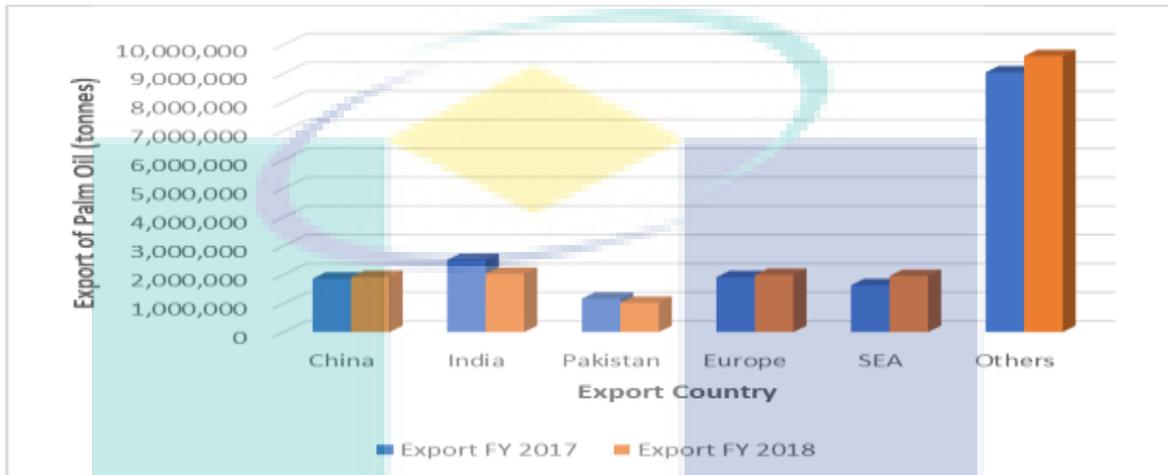


Figure 2.1 Export of palm oil product by destination in 2017 and 2018

Source: MPOB (2018c)

### 2.2.3 Production of Palm Oil

The production of palm oil is affected by Fresh Fruit Bunch (FFB) yield performance. Traditionally, the oil palm started producing FFB after three years of planting and reaching its maximum yield at the age of 12 to 15 years (Nambiappan, 2018). As shown in Table 2.2, total FFB processed has reached 101,022,441 tonnes in 2017, with production of CPO and CPKO at 19,919,331 tonnes and 2,280,913 tonnes, respectively. However, the total processed FFB fell by 3.2% in 2018 ended up at 97,803,919 tonnes, with CPO production of 19,516,141 tonnes which showed a reduction of 2.0% as compared to 2017. Nevertheless, production of CPKO had shown a rose by 0.8% with a total production of 2,299,985 tonnes in 2018.

The FFB yield performance is very depending on weather. As the oil palm being a rain-fed crop, its yield is influenced by the rainfall distribution, which can be divided into two conditions, namely El Nino or hot weather conditions and La Nina or monsoon. Hot weather conditions during El Nino could result in less rainfall and have a stress effect on oil palm eventually could bring down the yield of FFB production, whereas during La

Nina, the heavy rainfall could bring floods that would disrupt the harvesting and the collection of fruits process causing a low FFB production (Rahman et al., 2013).

Table 2.2 Palm oil production in Malaysian Oil Palm Industry in 2017 and 2018

Descriptions	2017	2018	Difference
Fresh Fruit Bunch (FFB) <sup>(d)</sup> FFB Processed (tonnes)	101,022,441	97,803,919	-3,218,522
Crude Palm Oil (CPO) <sup>(e)</sup> Production (tonnes)	19,919,331	19,516,141	-403,190
Crude Palm Kernel Oil (CPKO) <sup>(f)</sup> Production (tonnes)	2,280,913	2,299,985	19,072

Sources: <sup>(d)</sup>MPOB (2018d), <sup>(e)</sup>MPOB (2018e), <sup>(f)</sup>MPOB (2018f)

#### 2.2.4 Waste Generated from Palm Oil Production

According to the statistic of Malaysian Palm Oil Board (MPOB) in year 2018 (MPOB, 2018g), a total of 451 palm oil mills in Malaysia have produced about 97.80 million tonne of Fresh Fruit Bunch (FFB). Yacob et al. (2005) estimated that approximately 0.50 - 0.75 tonnes of Palm Oil Mill Effluent (POME) was discharged for every tonne of FFB from mill. Thus, total POME discharged to the river in year 2018 was estimated in the range of 48.90 – 73.35 million tonnes. The raw POME which is generated by Palm Oil Mill is hot, acidic (pH between 4.0 to 5.0) and brownish colloidal suspension containing high concentration of organic matter, i.e. COD (50,000 mg/L), BOD (25,000 mg/L), total solids (40,500 mg/L) and oil & grease (4,000 mg/L) (Alhaji, 2016).

#### 2.2.5 Characterization and Regulation on POME

Raw POME is a thick brownish colloidal mixture of 95-95% water, 0.6%-0.7% oil and 4%-5% total solids with 2%-4% suspended solids (Ma, 1999), which are produced mainly from sterilizer condensate, separator sludge and hydrocyclone wastewater in a ratio of 9:15:1, respectively (Wu et al, 2010). The average physical and chemical characteristic of raw POME from other studies are described in Table 2.3, where total solids and total suspended solids in POME were reported at 40,500 – 100,000 mg/L and 13,650 – 50,000 mg/L, respectively (Tabassum et al., 2015; Alhaji et al., 2016). However, there was no total solids content has been reported by Loh et al. (2013) and Poh and

Chong (2014) in their raw POME characteristic study. Since the solid content especially total suspended solid is frequently considered as contributing to BOD concentration in the POME, thus it is crucial and vital to perform solid content characteristic study in raw POME in order to develop a pre-treatment system for solid removal in POME prior to the treatment of biological process. In this case, once the solid content in POME is removed, the organic loading rate of POME can also be reduced, eventually it can reduce the BOD concentration as well as total suspended solid in the final discharge (Liew et al., 2015).

Chemical characteristic of POME such as pH, COD, BOD<sub>3</sub>, oil and grease and ammoniacal nitrogen were found at the values of 4.3 – 4.7, 23,080 - 76,988 mg/L, 14,500 – 27,600 mg/L, 4,000 – 5,006 mg/L and 35 mg/L, respectively. These data show that the concentration of raw POME is much higher than the discharge standard limit that is set by DOE, especially BOD<sub>3</sub> discharge limit of 20 mg/L in the year 2020 as shown in Table 2.3.

Table 2.3 Characteristic of raw POME from other studies

Parameters	Loh et al. (2013)	Poh & Chong (2014)	Tabassum et al. (2015)	Alhaji et al. (2016)	DOE Discharge Standard for year 2020
pH	4.5 ± 1.19	4.7 ± 0.19	4.3	4.7	5.0 - 9.0
COD (mg/L)	76,896 ± 119	32,580 ± 9,500	75,000	50,000	NA
BOD <sub>3</sub> (mg/L)	27,500 ± 100	17,000 ± 2,500	27,000	25,000	20
TS (mg/L)	NA	NA	100,000	40,5000	-
TSS (mg/L)	27,000 ± 82	15,000 ± 1,350	50,000	18,000	200
O & G (mg/L)	NA	6,100 ± 1,094	NA	4,000	5
AN (mg/L)	NA	NA	NA	35	20

Nevertheless, due to the requirement for all the palm oil mill to have a proper biogas plant (Loh et al, 2017), raw POME will have to pass through a closed digestion anaerobic treatment prior to further biological treatment process such as conventional ponding system. In this case, anaerobic treatment can reduce the organic loading in raw POME through the decomposition of high organic matter in POME to produce the biogas consisting of methane, carbon dioxide, nitrogen, hydrogen and hydrogen sulfide (Basri et al., 2010). Despite to that, system improvement of POME treatment can be done after the

anaerobic treatment or biogas plant system in palm oil mill. Thus, in this study, the POME sample had been collected after the anaerobic process which is anaerobic treated POME.

In some studies, researchers also used anaerobic treatment POME as the substrate for their further biological treatment process such as the aerobic process by using activated sludge. As shown in Table 2.4, Vijayaraghavan et al. (2007) had successfully proved that by using anaerobic treated POME as a substrate, the reduction of COD and BOD<sub>5</sub> of 98% and 93%, respectively had been achieved at a HRT of 60 hours. However, in this study, there was no TSS removal efficiency being reported, which was one of the important DOE regulatory discharge parameters. Meanwhile, Chan et al. (2010a) reported that removal efficiencies of COD, BOD<sub>3</sub> and TSS were 96%, 98% and 99%, respectively by using sequencing batch reactor at an optimum operation range of 17,500 -20,000 mg/L, 0.17-0.40 BOD<sub>3</sub>/L.day, and 2.5 – 4.6 g TSS/L.day for MLVSS, OLR and SLR, respectively. Even though the excellent performance of POME treatment had been reported in this study, the concentration of MLSS and MLVSS were controlled at 12,000 – 24,650 mg/L and 9,600 – 19,765 mg/L, respectively, which was not practical in actual operation of POME treatment.

Table 2.4 Characteristic of anaerobic treated POME from other studies

Parameters	Vijayaraghavan et al. (2007)	Chan et al. (2010)	Tabassum et al. (2015)
pH	7.8	7.4	7.0
COD (mg/L)	3,908	13,650	4,500
BOD <sub>3</sub> (mg/L)	1,720 <sup>(a)</sup>	1,355	-
TS (mg/L)	-	19,370	22,600
TSS (mg/L)	512	12,750	13,840
TVS (mg/L)	-	-	14,300
TDS (mg/L)	-	-	8,760
TN (mg/L)	134	320	-
AN (mg/L)	36	-	-
O & G (mg/L)	8,020	-	-

<sup>(a)</sup> BOD<sub>5</sub> analysis was conducted in this study.

In the other POME treatment study, Tabassum et al. (2015) described that after aerobic treatment, the COD, BOD<sub>3</sub> and TSS were found at a value of 1,100 mg/L, <20 mg/L and 191 mg/L, respectively with the anaerobic treated POME as a substrate, but they never discussed thoroughly on the POME treatment control and operating condition,

which plays a very important role in the POME treatment performance efficiency.

Even though many literatures showed the total solids and total suspended solids content in raw POME, the information for the solids characteristic study of anaerobic treated POME is still scarce. Tabassum et al. (2015) had reported that total solids content in anaerobic treated POME consist of 61% total suspended solids and 39% total volatile solids. In fact, the total suspended solids had been removed during sedimentation process in conventional ponding system, while the remaining total volatile solids can be digested biologically. However, solids characteristic study is not determined during the raw wastewater characterization, but COD and BOD are typically used to quantify the organic matter in wastewater practically. Most of the time, wastewater characterization is based on the wastewater degradation kinetics in biological assay but not based on physical particles solids evaluation (Sophonsiri and Morgenroth, 2004). As a result, fluctuation of solid concentration in raw wastewater always cause uncontrollable organic loading rate in wastewater treatment plant and eventually affect the performance of wastewater treatment plant. Thus, solid removal shall be considered as a pre-treatment of wastewater treatment plant especially in industry effluent treatment system.

Particle size distribution (PSD) also play a very important role in physical composition of wastewater. It can provide information regarding the types of suspended solid in the wastewater, which eventually affects the quality of wastewater (Garcia-Mesa et al., 2010). Since PSD contains in wastewater, it can be used to correlate with other wastewater composition parameters, such as COD, TSS, color and turbidity (Chavez et al., 2004). In fact, PSD in wastewater can be classified into four operation categories based on the particle size as shown in Table 2.5 (Levine et al., 1991).

Table 2.5 Categorization of particles in different types of particles size

Type of Particles	Particles Size
Soluble Particles	< 0.001 $\mu\text{m}$
Colloidal Particles	0.001 – 1 $\mu\text{m}$
Supracolloidal Particles	1 - 100 $\mu\text{m}$
Settleable Particles	> 100 $\mu\text{m}$

According to Levine et al. (1991), colloidal particles are easier to be degraded in aerobic condition as compared to supracolloidal particles. After biodegradation process, the organic matter in POME will be reduced, and the remaining organic matter composes of soluble particles. Marquet et al. (1999) had found that there was a correlation between the organic matter expressed in BOD and COD with the particle size in wastewater, where the removal efficiency of BOD and COD will be increased when the bigger size particles were being removed.

Generally, organic matter compounds in POME is measured via two parameters, namely BOD and COD. BOD is a standard empirical test to determine the oxygen demand of microbes during degradation of organic matter over a given time periods, usually 5 days in incubation at 20°C. However, for POME sample in Malaysia, the incubation at 30°C for 3 days will be used (Malaysia, 2017). While for COD test, it is a measurement of the oxygen concentration required by oxidizing agent, such as potassium dichromate, to oxidize all the biodegradable and nonbiodegradable organic material (Park et al., 1997). Due to the ease of operation, COD test always been selected for organic matter content determination; however, COD result does not provide the information of the actual biodegradable organic matter in POME that can be digested by microorganism. Thus, BOD test is still a main testing analysis for the organic matter determination and it can be conducted simultaneously with COD test.

Most of the POME treatment literature only reported the value of BOD and COD that were obtained from the analysis, but they never describe the BOD/COD ratio, which is an indicator of the biodegradability level of POME. Samudro and Mangkoedilhardjo (2010) had conducted the BOD/COD ratio study by using landfill leachate sample and classified the BOD/COD ratio into three zone, namely toxic zone, biodegradable zone and acceptable or stable zone. In toxic zone, the BOD/COD ratio of less than 0.10 indicated that there was a high portion of hard-biodegradable BOD present in the landfill leachate sample, which is contributed by humic and fulvic acid. When the BOD/COD ratio is between 0.10 to 1.00, it falls into the biodegradable zone, where the organic matter can be decomposed by microbes naturally or by man-made treatment system. While in the acceptable or stable zone, BOD/COD ratio is between 0.10 to 1.00, where the organic matter can be decomposed and disposed safely to the environment without significant effect on the quality of environment. By knowing the zone of BOD/COD ratio,

appropriate wastewater treatment system can be proposed and designed to achieve the safe levels of organic matter discharge as well as compliance of regulatory discharge standard. Nevertheless, the study of BOD/COD ratio for POME is scarce in the literature, hence more study of BOD/COD ratio needs to be conducted for POME in order to obtain an accurate BOD/COD ratio result.

Besides the organic matters, nitrogen compound especially AN also has been found in all POME conventional ponding system, such as anaerobic pond, facultative pond, aerobic pond and settling tank at 103.47 mg/L, 184.58 mg/L, 163.17 mg/L and 159.50 mg/L, respectively. Even though AN content in POME is always being analysed, there was no AN removal system developed and reported in the literature for POME treatment. AN in POME does not give a serious impact to the environment like those in sewage wastewater which will cause eutrophication to the water body (Chibuogwu et al., 2011). Nevertheless, the nitrogen compound, especially AN, will contribute to the BOD level in POME as nitrogenous BOD (nBOD) and the removal of AN will reduce the BOD level in wastewater (Haider and Ali, 2010). Therefore, to remove the AN, nitrification process in POME may be necessary. In this process, all the AN will be converted into nitrate via nitrite that can be absorbed by most plants as nutrient (Onyia et al., 2001).

## **2.3 Treatment Technology for POME**

Rapid expansion of palm oil has produced large amount of palm oil mill effluent (POME) from palm oil milling process. POME is considered as one of the major pollutant sources that affect the environmental balance. Thus, it is crucial and needed to treat the POME by using the conventional and advance POME treatment technology to comply the DOE discharge regulatory standard.

### **2.3.1 Conventional Method**

Traditionally, more than 85% of the palm oil mills have adopted the ponding system (Ma and Ong, 1985), which consist of cooling pond, anaerobic pond, facultative pond and aerobic pond (Zainal et al., 2017) as shown in Figure 2.2.

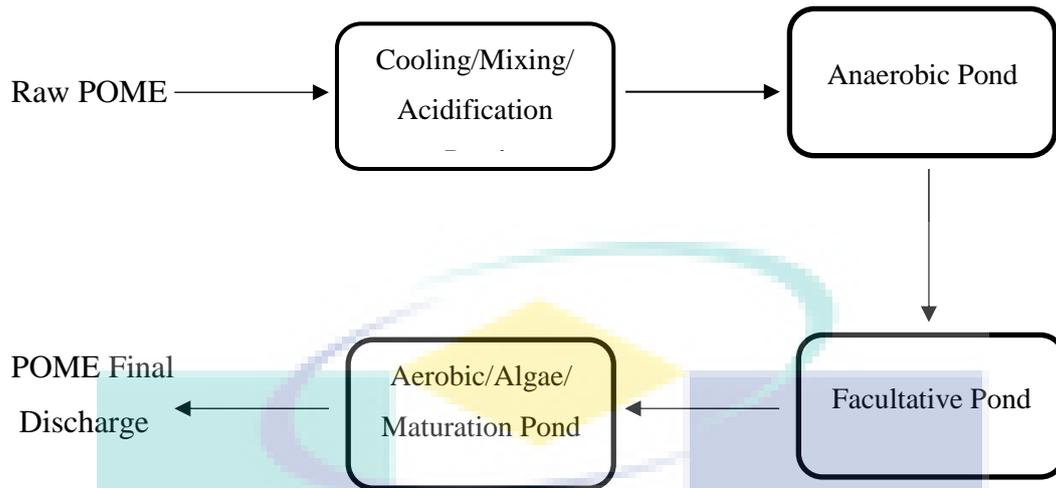


Figure 2.2 Conventional ponding treatment system of POME (Zainal et al., 2017)

The purpose of cooling and mixing pond is to cool down the raw POME and stabilize the pH prior to further biological treatment process such as anaerobic treatment process. Anaerobic pond is used to digest the POME with high concentration of solids (Hojjat et al., 2009) and organic matter (Perez et al., 2001). Facultative and aerobic ponds, on the other hand, serve to reduce the remaining organic content in the POME in order to comply with the regulatory discharge limit before discharging to the water bodies (Zainal et al., 2010). Conventionally, the hydraulic retention time for anaerobic pond, facultative pond and aerobic pond are 45 days, 16 days and 20 days, respectively (Ma and Ong, 1985). Even though POME gone through a long period of biological treatment process in the ponding system, it was not able to meet the discharge standard of 50 mg/L of BOD (Chin et al., 1996). The advantage of the conventional ponding system is most of the solids can be sedimented at bottom of the pond, directly remove most of the biodegradable organic matter such as COD and BOD, but the non-biodegradable organic matter cannot be removed and eventually remain in final discharge of POME, which also a weakness of conventional ponding system in palm oil mill.

### 2.3.2 Advance Treatment of POME

Therefore, in order to comply with the regulatory discharge standard, new advance treatment methods have been studied and developed for the POME treatment by several researchers as shown in Table 2.6. Despite the methods are still in laboratory-

scale study, they have shown a good potential compared to conventional method. Furthermore, there was about 90% of publication about POME has been published for the past few years were discussing about alternative treatment technology for POME (Iskandar et al., 2018).

Table 2.6 POME advance treatment methods from other studies

Methods POME treatment	Performance of treatment			References
	% of BOD removal	% of COD removal	% of TSS removal	
Anaerobic digester tank	-	80.7	-	Yacob et al. (2005)
Upflow anaerobic sludge blanket (UASB)	90.0	88.0	-	Poh & Chong (2014)
Anaerobic bench scale reactor (ABSR)	-	83.2	-	Teng et al. (2013)
Anaerobic baffled reactor (ABR)	-	83.0	-	Malakahmad et al. (2014)
Integrated anaerobic-aerobic bioreactor (IAAB)	98.0	99.0	96.0	Chan et al. (2012)
Aerobic system	82.0	89.0	-	Vijayaraghavan et al. (2007)
	98.0	96.0	99.0	Chan et al. (2010a)
	87.0	86.0	89.0	Chan et al. (2011)
Trickling filter system	-	88.0	-	Gobi et al., 2011
	90.0	90.0	-	Abdullah et al. (2004)
Rotating biological contactor	91.0	88.0	89.0	Najafpour et al. (2005)

Table 2.6 Continued.

Methods POME treatment	Performance of treatment			References
	% of BOD removal	% of COD removal	% of TSS removal	
Coagulation-flocculation	-	52.4	84.9	Huzira et al. (2019)
Electro-coagulation	-	98.0	99.7	Bashir et al. (2017)
Magnetic field	-	98.9	98.5	Mohammed et al. (2014)
Fenton oxidation	-	75.0	-	Taha and Ibrahim (2014)
Activated carbon adsorption	-	89.6	-	Adeleke et al. (2017)

From the Table 2.6, the advance treatment of anaerobic system had shown the good removal of BOD and COD up to 90% and 88%, respectively (Poh & Chong, 2014). However, the efficiency of removal yet to achieve the DOE regulatory discharge standard. Hence, the aerobic treatment followed by anaerobic treatment was developed and shown the removal of BOD, COD and TSS up to 98%, 99% and 96%, respectively (Chan et, 2012). In order to enhance the performance of aerobic system, trickling filter system (Abdullah et al, 2004) and rotating biological contactor (Najafpour, et al., 2005) were developed and shown the removal of BOD and COD of 90% and 90%, respectively for trickling filter system while rotating biological contactor shown the removal of 91%, 88% and 89% for BOD, COD and TSS, respectively. Even though, both of advance aerobic treatment system had shown a good removal of organic matter, it is not widely used in palm oil mill due to high cost of construction and operation. Meanwhile, some researchers used coagulant-flocculant (Huzira et al, 2019) and electro-coagulation (Bashir et al., 2017) for precipitation process, but the application of these two methods are not popular in palm oil mill because the precipitation process only able to remove the solids and organic matter such as COD still remain in POME and discharge to water body. Due to the stringent of environmental law and regulation, advanced oxidation process had been studied to removal the non-biodegradable matter such magnetic field (Mohammed et al., 2014) and fenton oxidation (Taha and Ibrahim, 2014), but because the high cost of construction, so is it not practical if apply in palm oil mill. Simultaneously, in order to

removal the non-biodegradable matter in POME, some researchers also proposed to use activated carbon in adsorption process, but because of the high volume of POME discharge from palm oil mill, it is impossible to capture all the non-biodegradable matter via adsorption process, moreover, after the exhaustion of activated carbon, new batch of activated carbon need to be replaced which might incur high operation cost. Thus, as conclusion, POME treatment system with combination of advanced anaerobic and aerobic system still are the cheaper, economic and practicability to fulfill the requirement of DOE regulatory discharge standard.

### **2.3.3 Current Issued in POME Treatment**

Even though many studies had successfully shown the great performance of the POME treatment, in practical, most of the palm oil miller still unable to meet the proposed stringent BOD regulatory discharge standard of 20 mg/L that will be imposed by DOE in year 2020 (Tabassum, et al., 2015; Liew, et al., 2015). This is because most of the study only focus on the strength and normal application of the treatment system which had widely used in other wastewater with high biodegradable matter. In fact, POME is an organic waste with recalcitrant organic compounds which is obstinate for treatment and it is different from other wastewater as it contains high concentration of non-biodegradable matter such as lignin, phenolic compound (Mohammed and Chong, 2014), polycyclic aromatic hydrocarbon such as naphthalene, fluorene, phenanthrene, fluoranthene and pyrene (Rasdy, et al., 2008). These compounds are not easily degrading biologically by microorganism and bacteria.

In practical, the POME system, especially the aerobic system with activated sludge process, is designed by using empirical analysis of total BOD or total COD, which are default values taken from municipal wastewater. As a consequent, the activated sludge process that design for POME treatment fails to achieve the performance and result required. Hence, POME treatment especially in biological process need to be thoroughly studied in order to develop the most appropriate system or method for the pollutant removal.

## 2.4 Activated Sludge Process

Activated sludge process is the most widely used biological treatment process in municipal wastewater and industrial wastewater. In this process, organic matter will be converted to energy, carbon dioxide and new bacteria cells by microbes in the aeration tank. Even though activated sludge process is an old technology for biological wastewater treatment, new technology had been developed to be adapted with the activated sludge process such as membrane bioreactor, biofilm reactor, moving bed bioreactors etc.

Initially, activated sludge process was developed through modelling the process for the design and operation in wastewater treatment plant. The Activated Sludge Model No.1 (ASM1) was developed for organic matter removal and nitrogen removal process in year 1987. The ASM1 was well accepted and widely used in municipal wastewater as a basis for further model development. In year 1995, Activated Sludge Model No.2 (ASM2) was published for advanced nitrogen removal and biological phosphorus removal. However, due to the scarcity of information in correlation between denitrification and biological phosphorus removal, Activated Sludge Model No.2d (ASM2d) was expanded in year 1999 to include the denitrifying activity of the phosphorus accumulating organism (PAO's). The models were grown more complex and in year 1998, Activated Sludge Model No.3 (ASM3) was developed to study the internal storage compound in activated sludge process, which play a very important role in the metabolism of the organism in activated sludge (Henze et al., 2000).

Despite the widespread use of the activated sludge systems, activated sludge model had been modified to improve the quality of discharge wastewater (Song et al., 2012). However, most of the parameters estimation for activated sludge modelling is based on municipal sewage, and POME had never been thoroughly studied from an ASM modelling perspective either in system design or system operation. In fact, most of the parameters value for activate sludge modelling are default value from municipal sewage studies (Damyanti et al., 2010). Hence, the researcher also used the default value for the POME treatment by activated sludge process study (Vijayaraghavan et al., 2007; Chan et al., 2010a).

In practical, there are always a mismatch between the theoretical design prediction and real industry process due to the parameters uncertainties, neglected model dynamic and disturbance (Hreiz et al., 2015a). Thus, for the theoretical activated sludge system that was designed by using default parameters values, the optimization of operation needs to be done to solve the gap problem between theoretical design and real process behaviour. In this matter, the performance of activated sludge system will be studied via some important parameters such as initial pH of wastewater, HRT, OLR, MLVSS, SRT and external carbon sources based on the real industrial condition.

#### **2.4.1 Principles of Activated Sludge Treatment**

The basic principle of activated sludge processes is using microorganisms to metabolizing soluble organic material producing a purified effluent. A basic activated sludge process is depicted in Figure 2.3, where the wastewater is transferred into an aeration tank to develop biological flocs after biodegradation process of organic matter by microorganism. The mixture of wastewater and activated sludge in the aeration tank is called mixed liquor where the biological mass (biomass) in mixed liquor is called mixed liquor suspended solids (MLSS) or mixed liquor volatile suspended solids (MLVSS). MLSS are made up of organic and inorganic solids, while MLVSS are organic solid which also known as volatile solid matter that consists of living and non-living organics.

In practical, it is difficult to measure living organic matter in activated sludge, thus MLVSS is measured to estimate the quantity of living organic matter. After a certain reaction time, the mixed liquor is transferred to secondary clarifier for the suspended solids settlement by gravity, where the supernatant is discharged as final effluent and settled activated sludge is discharged as wasted activated sludge (WAS). However, in order to maintain a high population of microorganism in aeration tank, some of the concentrated biologically settled activated sludge is recycled back to aeration tank as return activated sludge (RAS).

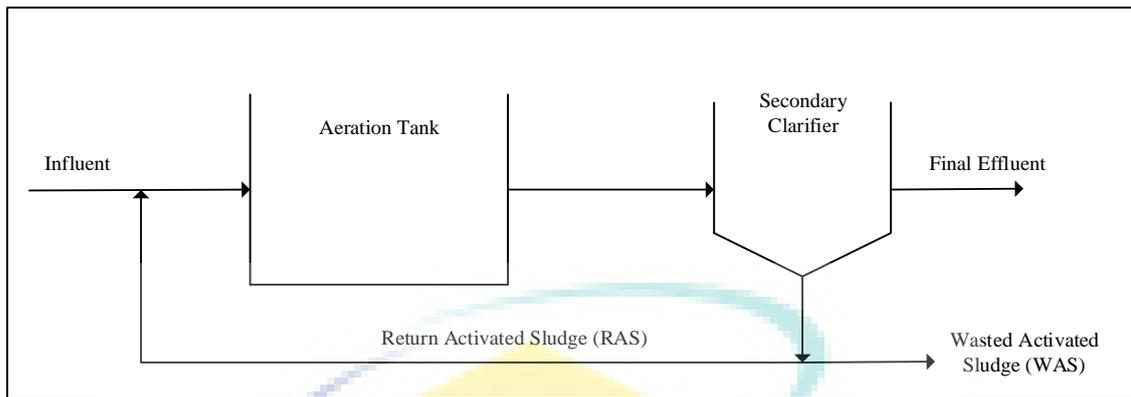


Figure 2.3 Schematic flow diagram of activated sludge process

## 2.4.2 Factors Affecting Activated Sludge

In activated sludge process, there are number of factors that can affect overall efficiency of the process to remove the organic matter in wastewater such as design of system and operating control. Once the design is fixed and system is constructed, this factor which invariably affected the activated sludge process performance cannot be changed. Nevertheless, there are other factors affecting the efficiency of activated sludge process can be controlled, such as PH, HRT, OLR, MLVSS concentration, SRT and external carbon sources.

### 2.4.2.1 Effect of pH

pH is one of the very important control parameters in biological treatment process especially for microbial growth in activated sludge system. The optimum biological activity for microorganism in wastewater treatment process is in the pH range of 6.5 to 8.5 (DOE, 2010b). In the previous study of POME treatment, Vijayaraghavan et al. (2007) had reported that by maintaining the pH in activated sludge reactor at  $7.0 \pm 0.2$  during acclimatization operation, the MLSS was found to increase from 2,370 mg/L to  $3,900 \pm 200$  mg/L with a POME feeding of 5,000 mg/L COD at HRT of 1.5 days. Chan et al. (2010) also reported that the MLVSS in activated sludge reactor was demonstrated a steady rise from 4,300 to 11,700 mg/L by adjusting the reactor pH to 7.4 with OLR of 1.17 – 2.39 g COD/L.day for HRT of 20 hours. Thus, the optimum pH for the activated sludge process can be controlled at range of 6.5 to 8.5.

#### **2.4.2.2 Effect of Hydraulic Retention Time (HRT)**

HRT is another important control parameter in activate sludge system where it exerts a profound influence on the contact time of the influent in the reactor (Pan et al., 2004). For the activated sludge system design, HRT value need to fulfil the criteria that is stated in the DOE guidance document (DOE, 2010a), where HRT for a conventional activated sludge system and an extended aeration activated sludge system are 6-8 hours and 18-36 hours, respectively. Literature for POME treatment with activated sludge process by using anaerobic treated POME showed that a HRT of 60 hours can give a COD removal efficiency up to 98% from initial COD of 3,908 mg/L reduced to 78 mg/L. (Vijayaraghavan et al., 2007). Study of POME treatment in a sequencing batch reactor with HRT of 20 hours also had reported a removal of COD and BOD up to 96% and 98% from 17,050 mg/L and 1,400 mg/L reduced to 735 mg/L and 38 mg/L, respectively. (Chan et al., 2010a). Contradictory, a similar study of POME by using sequencing batch reactor which conducted by Chou, et al. (2016) showed a COD removal efficiency up to 92.9% from 12,620 mg/L to 824 mg/L with HRT of 7.2 days (~172.8 hours). Hence, the HRT that can be used for POME treatment by activated sludge process is at a range of 20 hours to 60 hours, which is more practical in POME industry instead of 7.2 days.

#### **2.4.2.3 Effect of Organic Loading Rate (OLR)**

Organic loading rate is a measurement of the mass of substrate usually represented by BOD or COD applied to the aeration tank volume per day. It is intended to measure the amount of organic load that is able to be treated by the system. OLR is important to determine if this system is suitable to be used as a polishing plant and capable to treat the incoming waste up to the desired standard. By maximising OLR, size of the aeration tank and the oxygen consumption can be minimized in the operation cost perspective (Dionisi and Rasheed, 2018). As mentioned in DOE guidance document, for conventional aeration activated sludge system and extended activated sludge system design, design value for OLR need to be controlled within 0.3 – 0.6 kg BOD/(m<sup>3</sup>.day) and 0.1 – 0.4 kg BOD/(m<sup>3</sup>.day), respectively (DOE, 2010a). In the POME treatment by activated sludge process, controlling the OLR at 1.8 kg COD/m<sup>3</sup>.day and 0.17 – 0.40 kg BOD/m<sup>3</sup>.day can achieve a COD and BOD removal up to 95% and 98% respectively (Chan et al., 2010a). Moreover, Chan et al. (2011) also reported that in thermophilic aerobic treatment of

anaerobically digested POME, removal efficiencies of COD and BOD were 86.3% and 87.0%, respectively with OLR of 2.5 kg COD/m<sup>3</sup>.day. However, it is possible to operate the activated sludge system in POME treatment at higher OLR of 6.0 kg COD/m<sup>3</sup>.day and successfully removed the COD up 90% (Gobi et al., 2011). Therefore, the OLR for the activated sludge process in treating POME can be controlled at range of 0.20 – 0.40 kg BOD/m<sup>3</sup>.day by diluting the anaerobic treatment POME sample into different concentration.

#### **2.4.2.4 Effect of Mixed Liquor Volatile Suspended Solid (MLVSS)**

In the measurement of microorganism concentration in an activated sludge system, analysis of MLSS and MLVSS are carried out. MLSS is a mixed liquor that consist of volatile suspended solids and inert solids, while MLVSS mostly consist of volatile solids concentration in mixed liquor that approximately equal to the amount of microorganisms in wastewater (Tchobanoglous et al., 2004). In DOE guidance document for the activated sludge system design, MLSS concentration need to be controlled within 1,500 – 3,000 mg/L and 3,500 – 6,000 mg/L for conventional activated sludge system and extended activated sludge system, respectively (DOE, 2010a). Due to the quicker of testing, some activated sludge process in treating POME is using MLSS instead of MLVSS to represent the biomass in mixed liquor. COD removal efficiency could be up to 83% by using MLSS concentration of 3,900 ± 200 mg/L as fixed biomass in mixed liquor (Vijayaraghavan et al. 2007). COD and BOD removal efficiency had found increased with MLSS concentration control at 18,000 – 30,000 mg/L and at optimum condition with MLSS concentration of 27,000 mg/L, COD and BOD had shown the removal efficiency at 86.3% and 87.0%, respectively (Chan, et al., 2011). Nevertheless, in order to get more precise and accurate data, Chan et al. (2010a) used the MLVSS concentration for the POME treatment study, where the removal of COD and BOD were 96% and 98%, respectively when the MLVSS concentration was controlled at the optimum condition of 17,500 – 20,000 mg/L. However, in industry practice, it is hardly to maintain the MLVSS in aeration tank more than 10,000 mg/L, thus the MLVSS concentration can be controlled at 2,800 – 4,800 mg/L, where 80% of MLSS concentration that recommended by DOE (2010a).

#### **2.4.2.5 Effect of Solid Retention Time (SRT)**

Solid retention time is the sludge age, or in other words, the amount of time the sludge remains in the reactor before it is being used as the inoculum. It determines the maturity of the sludge and the amount of active microorganism that has adapted to the environment. SRT of activated sludge process need to follow the DOE design guidance document where the default value of SRT need to be within 5-10 days and 15-35 days for a conventional activated sludge system and an extended activated sludge system, respectively (DOE, 2010a). Generally, for an efficient sedimentation of activated sludge in secondary clarifier, biomass requires SRT of 3-4 days for sludge settlement (Hreiz et al. 2015). Besides, to get the optimal operating condition in activated sludge process, the SRT should be controlled at 5-3 days (Descoins et al., 2012) and 4-30 days (Hreiz et al., 2015b). Conversely, poor settlement of activated sludge will occur if the SRT is too long period due to the growth of filamentous bacteria. Hence, El-Shorbagy et al. (2011) suggested that the SRT should be controlled at 4 -27 days to obtain the optimal activated sludge condition. Due to insufficient of literature regarding the effect of SRT for POME treatment by using activated sludge process, further investigation should be carried out to get the optimum value of SRT in the POME treatment.

#### **2.4.2.6 Effect of External Carbon Source**

Wastewater with high concentration of nonbiodegradable organic matter are hard-to-treat by the microorganism in an activated sludge system due to the highly stable molecular structures of nonbiodegradable organic matter. As a result, microorganism need to acquire a degradation capability to break down the nonbiodegradable matter via biodegradation process (Builtron et al., 1988), which may need a large amount of energy for the microorganism to metabolize the nonbiodegradable compound in organic matter (Chong et a., 2010). By supplementing some optimal amount of substrate at 50 mg/L as external carbon sources, microorganism in the activate sludge can gain extra energy to metabolize the nonbiodegradable organic matter in wastewater (Nguyen and Chong, 2015).

## 2.5 Kinetic Study of BOD

Biochemical oxygen demand (BOD) of wastewater can be classified into three oxidation processes as following (Ramalho, 1977):

1. Degradation of organic matter (carbonaceous demand) by aerobic organisms;
2. Oxidation of nitrogenous compound (nitrification) by specific bacteria (e.g., *Nitrosomonas* and *Nitrobacter*);
3. Oxidation of chemical reducing compounds, e.g., ferrous ion ( $\text{Fe}^{2+}$ ), sulfites ( $\text{SO}_3^{2-}$ ), and sulfide ( $\text{S}^{2-}$ ).

Carbonaceous oxygen demand (cBOD) is the oxygen consumed during the oxidation of carbonaceous compound by microorganism, which always occur in the first stage of decomposition in BOD test. While nitrogenous oxygen demand (nBOD) is the oxygen consumed during oxidation of nitrogenous compound (mainly ammonia,  $\text{NH}_3$ ) to nitrate with nitrite being an unstable intermediate compound, and it always occur in the second stage of decomposition in BOD test. nBOD generally start after 6 days, but sometimes if the ammonia, nitrite or nitrifying bacteria present in wastewater, the nitrification process can occur less than 5 days. Thus, in order to eliminate the interference of nitrogenous demand during carbonaceous demand measurement, inhibitory chemicals such as 2-chloro-6-(trichloromethyl) pyridine (TCMP) will be added for cBOD test.

In brief, the  $\text{BOD}_5$  test was carried out by diluting the wastewater sample with nutrient-containing water, the initial dissolved oxygen concentration was then determined. After 5 days incubation at  $20^\circ\text{C}$ , the final dissolved oxygen concentration was measured, and the difference in dissolved oxygen concentration will be calculated to obtain the 5-day BOD value. The amount of oxygen that has been consumed mainly is for the respiration and metabolism of microorganism. During the 5-days test, only some portion of organic matter will be degraded, and the microorganism may need several weeks or longer time to break down the biodegradable matter completely. Furthermore, the 5-days test does not provide the necessary information to predict and assessing the impact of wastewater which flow to the water bodies such as rivers and lakes. In order to oxidize total organic matter and all forms of nitrogen by microorganism, it usually takes about 60 to 90 days (Shun, 2014), which is known as ultimate BOD ( $L_0$ ).

In fact, it is very difficult to estimate the exact value of ultimate BOD and in practical, to incubate the wastewater sample for a long period of time not only will affect the feasibility of testing, but also the accuracy of testing result. The time needed to reach the ultimate BOD is depending on the following factors (Ghangrekar, n.d.):

a) Wastewater Characteristics

Wastewater with different biodegradable properties will have different biodegradable rate. For example, POME is relatively slow degraded due to the polycyclic aromatic hydrocarbons (PAH's) content (Rasdy et al., 2008) as compared to the municipal wastewater with a high content of readily biodegradable organic matter (Wentzel et al., 1999).

b) Nutrients utilization capability of microorganism

Every microorganism has differences in its ability to utilize the organic matter in the wastewater. According to Ohimain et al. (2013), the microorganism that had been found predominant in POME were *Micrococcus* species and *Staphylococcus aureus*. However, for the BOD testing, the microbial inoculum being widely used is typically a mixed culture from domestic wastewater treatment plant activated sludge (Paixao et al, 2000). As a result, the BOD result that being produced from the laboratory may not represent the actual biodegradable process in POME.

c) Temperature

The activity of microorganism and biochemical reaction are very depending on the temperature. Chan et al. (2010b) had reported that POME treated under mesophilic (28°C) condition will produce the highest effluent quality. Furthermore, in practical, all the POME was treated in conventional ponding system with country average temperature of 28°C, but the BOD testing was carried out in the laboratory was set at 20°C. Therefore, the BOD result that was obtained in the laboratory could not represent the actual biodegradable process in the POME. Due to the temperature effect, BOD test for POME has been amended by the government, where all samples are incubated for 3-days at 30°C (Malaysia, 1977).

Generally, the rate of BOD oxidation is proportional to the organic matter remaining at any time,  $t$ . The BOD kinetic reaction can be estimated by referring to the first-order kinetic equation as follow (Tchobanoglous and Stensel, 2004):

$$\frac{dL_r}{dt} = -k_1 L_r \quad 2.1$$

Where  $L_r$  = BOD remaining after time  $t$  (days), mg/L

$k_1$  = Rate constant, 1/day

$t$  = time, day

Integrating the Eq.2.1 at time  $t = 0$  and  $t = t$  yields

$$y = L_0 e^{-k_1 t} \quad 2.2$$

Therefore, when the  $L$  exerted up to  $t$  time ( $y$ ), the equation was corrected as below:

$$\begin{aligned} y &= L_0 - L_r \\ &= L_0 - L_0 e^{-k_1 t} \\ &= L_0 (1 - e^{-k_1 t}) \end{aligned} \quad 2.3$$

Where  $L_0$  = Ultimate carbonaceous BOD, mg/L

Many researchers have studied and developed different methods and formulas to evaluate the kinetic parameters such as rate constant, ( $k_1$ ) and ultimate BOD ( $L_0$ ). Then, the results of the serial BOD test were used to evaluate BOD kinetic parameters by different methods. In this study, there are five different methods of BOD kinetic study were selected, namely Least Square Method, Fujimoto Method, Thomas Graphical Method, Log Different Method and Method of Moment.

### 2.5.1 Least Square Method

As quoted by Shun (2014), the Least Square Method used to estimate the numerical values of the parameters to fit the first order reaction of BOD is defined as follow:

$$\frac{dy}{dt} = k_1 (L_0 - y) \quad 2.4$$

Where  $k_1$  = first order reaction constant, 1/day

$L_0$  = Ultimate BOD, mg/L

$y$  = BOD exerted at time  $t$ , mg/L

The differential Eq. 2.4 is linear between  $\frac{dy}{dt}$  and  $y$ . Let  $y' = \frac{dy}{dt}$  (rate of change of BOD) and  $m =$  number of data point minus one. Hence, two normal equations for finding  $k_1$  and  $L_0$  can be written as

$$ma + b\sum y - \sum y' = 0 \quad 2.5$$

and

$$a\sum y + b\sum y^2 - \sum yy' = 0 \quad 2.6$$

Solving Eq. 2.5 and Eq. 2.6, a relation between  $a$  and  $b$  with  $L_0$  and  $k_1$  can be found as follows:

$$k_1 = -b \quad 2.7$$

and

$$L_0 = -\frac{a}{b} \quad 2.8$$

Thus, the values of  $y'$ ,  $y'y$  and  $y^2$  for the 7 days' incubation BOD values were first calculated. Then, the summation of  $y$ ,  $y^2$ ,  $y'$  and  $y'y$  was determined. These values were then substituted into Eq. 2.5 and Eq. 2.6 to compute the values of  $a$  and  $b$ . Finally,  $k_1$  and  $L_0$  could be estimated with Eq. 2.7 and Eq. 2.8. The limitation of this method is minimum of six observations data ( $n > 6$ ) for  $y$  is required.

### 2.5.2 Fujimoto Method

The Fujimoto Method is an arithmetic plot of  $BOD_{t+1}$  versus  $BOD_t$  for 7 days' incubation as quoted by Tchobanoglous and Stensel (2004). The value gained at the intersection point of the plot with a line of slope 1 corresponds to the ultimate BOD ( $L_0$ ). Once the value of  $L_0$  has been determined, the rate of constant,  $k_1$  can be calculated from the Eq. 2.3.

$$y = L_0(1 - e^{-k_1 t}) \quad 2.3$$

The method assumed that the BOD oxidation occurred linearly, but in fact it is a non-linear regression method that used the  $L_0$  and  $k_1$  determination. Hence, the result may not represent the actual value of  $L_0$  and  $k_1$ .

### 2.5.3 Thomas Graphical Method

As quoted by Gray (2004), Thomas Graphical Method is an approximate method, which is using graphical methods such as non-linear fitting and linear fitting of modified expression of BOD equation as following:

$$\left(\frac{t}{y}\right)^{1/3} = \frac{1}{(2.3k_1)^{1/3}} + \frac{k_1^{2/3}}{3.43L_0^{1/3}} \cdot t \quad 2.9$$

Where  $y$  = BOD exerted in time  $t$ , mg/L  
 $k_1$  = Reaction rate constant (base log10)  
 $L_0$  = Ultimate BOD, mg/L

The rate constant  $k$  and the ultimate BOD ( $L_0$ ) are calculated from the straight line with  $(t/y)^{1/3}$  plotted as a function of time,  $t$ , where the slope  $k_1^{2/3}/(3.43L_0)^{1/3}$  and the intercept  $(2.3k_1)^{-1/3}$  could be used to calculate the values of  $k_1$  and  $L_0$ . The method assumed that the reaction rate of breakdown is at first rapid when the organic matter is high in concentration, and the reactions will be progressively slow down as the organic matter is utilized.

### 2.5.4 Log Different Method

Another two methods that being quoted by Ramalho (1977) were Log Different Method and Method of Moment which are used to determine the reaction rate constant ( $k_1$ ) and ultimate BOD ( $L_0$ ) based on the first order reaction. The Log Different Method is based on the following equation:

$$y = L_0(1 - 10^{-k_1 t})$$

$$\frac{dy}{dt} = L_0(-10^{k_1 t})(\ln 10)(-k_1) = 2.303 L_0 \cdot k_1 \cdot 10^{-k_1 t}$$

$$\log\left(\frac{dy}{dt}\right) = \log(2.303L_0 \cdot k_1) - k_1 t \quad 2.10$$

Plot  $\log (dy/dt)$  versus time,  $t$ , on semilog graph paper, where the  $t$  value corresponding to the middle of each interval (Mid-interval value of  $t$ ). Value  $k_I$  and  $L_0$  can be estimated from the plot as follows:

$$k_1 = - (\text{Slope})$$

$$L_0 = 10^{\text{Intercept}} / (2.303k_1)$$

The constraints of this method are some data seem to be in error during the construction of plot  $y$  against  $t$  in the Cartesian coordinate paper, this data need to be discarded in order to get a reasonable plot for estimation of the value of  $k_1$  and  $L_0$ .

### 2.5.5 Method of Moment

In the Method of Moments, Moore's diagram must first be prepared. Moore's diagram is actually a nomograph which displaying the relationship between  $k_I$ ,  $\Sigma y/L_0$ , and  $\Sigma y/\Sigma yt$ . It is constructed using the equations below:

$$\frac{\Sigma y}{L_0} = n - \left[ \frac{10^{-k_1}(10^{-nk_1} - 1)}{(10^{-k_1} - 1)} \right] \quad 2.11$$

$$\frac{\Sigma y}{\Sigma yt} = \frac{n - \left[ \frac{10^{-k_1}(10^{-nk_1} - 1)}{(10^{-k_1} - 1)} \right]}{\sum_{i=1}^{i=n} i - \sum_{i=1}^{i=n} i \times 10^{-ik_1}} \quad 2.12$$

Where  $\Sigma y$  = sum of BOD

$\Sigma yt$  = sum of BOD value multiply with the incubation time

$n$  = no of days of incubation for the serial BOD test

$k_I$  = BOD rate constant

After that,  $\Sigma y$  and  $\Sigma yt$  were calculated for the system studied using the series of BOD measurements for 7-days. Then, the value of  $\Sigma y/\Sigma yt$  for the system was computed. With this value, value of  $k_I$  can be read through the plot of  $\Sigma y/\Sigma yt$  versus  $k_I$  in the nomograph while the value of  $\Sigma y/L_0$  can be determined from the plot of  $\Sigma y/L_0$  versus  $k_I$  using the same  $k_I$  value obtained.  $L_0$  was then calculated from this value. The constraints of this method is BOD measurements must be a series of regularly space time intervals, where calculation of the sum of BOD values,  $\Sigma y$  accumulated of time intervals and the

sum of the product of time and observed BOD values,  $\Sigma yt$  accumulated to the end of a series need to carried out.

## 2.6 Fractional Studies of Chemical Oxygen Demand (COD)

In practical, the concentration of organic matter in wastewater is measured by BOD and COD for system design and operation, especially in the biological treatment process. Both BOD and COD tests are used to determine the carbonaceous energy content of wastewater by measuring its oxygen demand (Ekama et al., 1984). However, BOD test only able to measure the biochemical degradation of organic matter or “carbonaceous oxygen demand” of the sample, which will underestimate the energy in terms of oxygen demand in wastewater sample. Whilst COD test oxidizes both biologically degradable and nonbiodegradable organic matter lead to the overestimation of energy measurement (Park et al. 1997). Hence, to estimate the more representable design parameter value for organic matter in COD basis, it is necessary to determine the various fractions of the COD in the influent. These fractions are able to describe the behaviour of influent more accurately.

Figure 2.4 shows the fractional of COD in wastewater which initially presented by Ekama et al. (2014) and has been modified by Tchobanoglous and Stensel (2004). Typically, the COD test that is conducted in the wastewater analysis is total COD (tCOD), which consist of two major portions of COD, namely biodegradable COD (bCOD) and nonbiodegradable (nbCOD). The bCOD is then divided into soluble readily biodegradable COD (srbCOD) and particulate slowly biodegradable COD (psbCOD). srbCOD will be degraded biologically by microorganism in activated sludge, while psbCOD will be broken down into simple molecules before taken up by microorganism for digestion. On the other hand, nbCOD is also divided into soluble nonbiodegradable COD (snbCOD) and particulate nonbiodegradable COD (pnbCOD). In this case, snbCOD will go through the biological treatment process and is discharged with the effluent; concurrently, pnbCOD will enmesh into the activated sludge as biomass (Park et al. 1997).

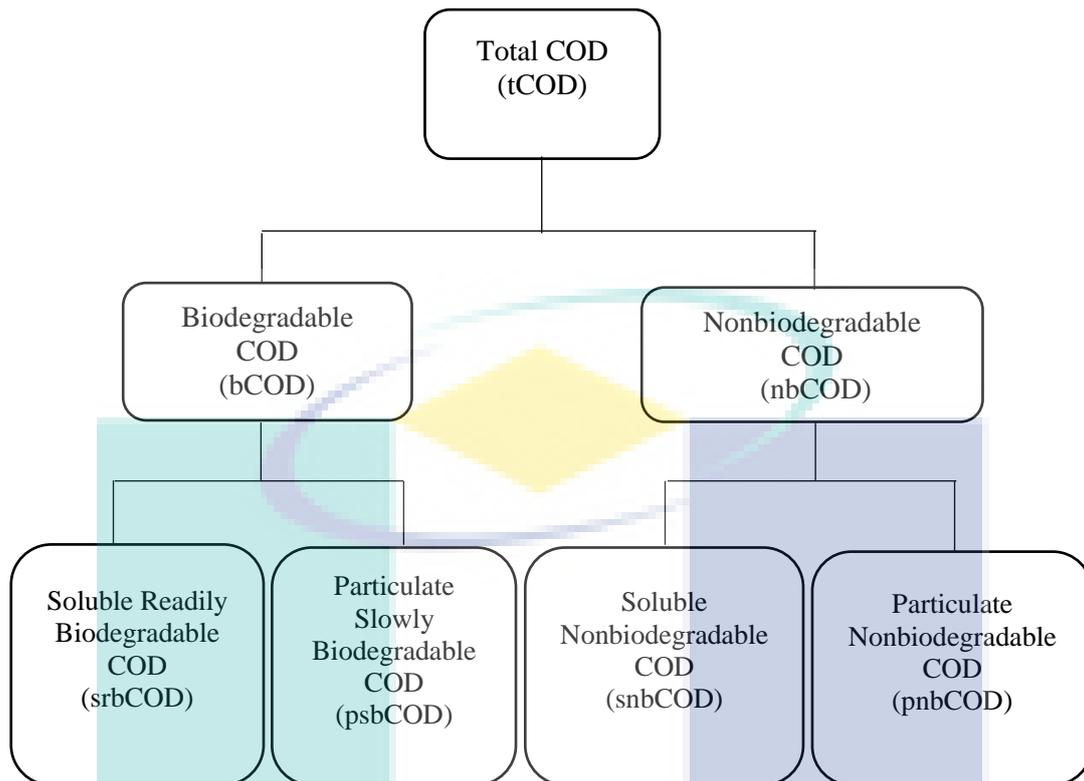


Figure 2.4 Fractionation of COD in wastewater (Tchobanoglous and Stensel, 2004)

Biodegradable chemicals oxygen demand (bCOD) can be determined by using total biological demand ( $T_bOD$ ) concept, where all the particulate organic materials will be hydrolyzed completely after 24 hours of biological oxidation process (Park et al. 1997; Mullis and Schodder, 1971; Hiser and Bush, 1964). In other words,  $T_bOD$  is conceptually equal to the biodegradable COD, which is contributed by the soluble readily biodegradable COD (srbCOD) and particulate slowly biodegradable COD (psbCOD) (Park et al. 1997).

Mamais et al (1993) had developed a rapid physical-chemical method that is widely used in determining the readily biodegradable COD (rbCOD) and nonbiodegradable soluble COD (nbsCOD) in wastewater. This method requires the application of flocculation, precipitation and filtration of wastewater sample to separate the truly soluble COD in the wastewater sample. It is based on the assumption that suspended solids and colloidal material can be removed by the flocculation process with zinc hydroxide to both wastewater sample and settled supernatant sample after treated by activated sludge process. The COD measured in supernatant sample is the soluble COD,

which equal to the nonbiodegradable soluble COD (nbsCOD), as the readily biodegradable COD (rbCOD) has been removed in the activated sludge process.

## 2.7 Kinetic Study of Activated Sludge Process

In the past, the biological wastewater treatments plant was designed based on the empirical parameters which developed by observation and experience such as aeration detention time, hydraulic retention time and organic loading rate. However, over the last decades, the design of biological wastewater treatment plant was based on biological kinetic equations which have been developed according to the concepts of microbial growth kinetics. The behavior and performance of microorganism in the activated sludge process are observed and the kinetic coefficient for substrate utilization and biomass growth were determined. The kinetic coefficient values represent the net effect of microbial kinetics during simultaneous degradation of organic matter in wastewater (Tchobanoglous and Stensel 2004).

The common kinetics coefficient value such as maximum specific substrate utilization rate ( $k$ ), half-velocity constant ( $K_s$ ), maximum yield coefficient ( $Y$ ) and endogenous decay coefficient ( $k_d$ ) can be obtained through the biomass mass balance of the activated sludge process as shown in Figure 2.5. These kinetic coefficient values are required in the activated sludge process design.

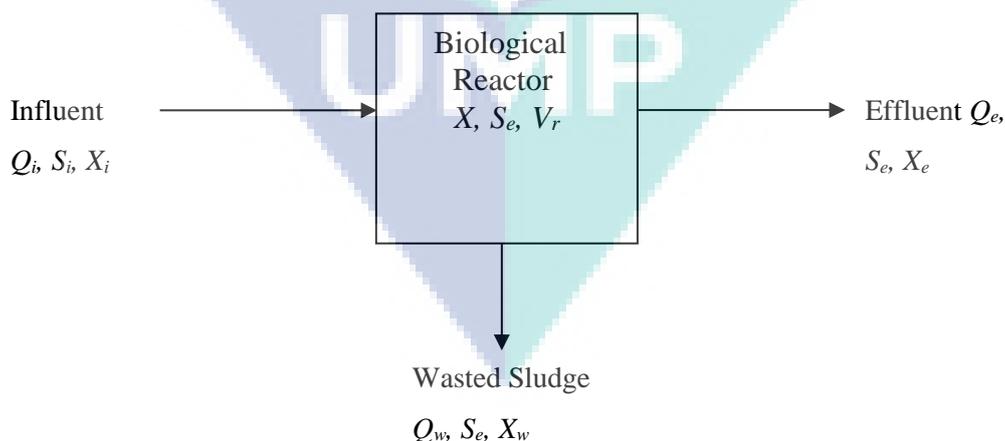


Figure 2.5 Schematic diagram of the activated sludge process in a batch system

Where:

- $Q_i$  = flowrate of influent (L/day)  
 $S_i$  = soluble substrate concentration in the influent (mg/L)  
 $X_i$  = biomass concentration in the influent (mg VSS/L)  
 $X$  = biomass concentration in the aeration tank (mg VSS/L)  
 $V_r$  = volume of aeration tank (L)  
 $Q_e$  = flowrate of effluent (L/day) or  $(Q_i - Q_w)$   
 $S_e$  = soluble substrate concentration in the effluent (mg/L)  
 $X_e$  = biomass concentration in the effluent (mg VSS/L)  
 $Q_w$  = flowrate of wasted sludge (L/day)  
 $X_w$  = biomass concentration in the wasted sludge (mg VSS/L)

In a word statement, the mass balance can be expressed as follows:

Rate of accumulation of microorganism within the system boundary	=	Rate of Flow of microorganism into the system boundary	-	Rate of flow of microorganism out of the system boundary	+	Net growth of microorganism within the boundary
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In symbolic representation:

$$\frac{dX}{dt} V_r = Q_i X_i - [Q_e X_e + Q_w X_w] + r_g V_r \quad 2.13$$

$$\frac{dX}{dt} V_r = Q_i X_i - [(Q_i - Q_w) X_e + Q_w X_w] + r_g V_r \quad 2.14$$

Where:

- $\frac{dX}{dt}$  = rate of change of biomass concentration in the reactor (mg VSS/L.day)  
 $r_g$  = net rate of biomass production (mg VSS/L.day)

At the steady state condition, the rate of change of biomass concentration in the reactor will become constant ( $dX/dt = 0$ ). Assuming that the concentration of biomass in the influent ( $X_i$ ) can be neglected; thus, Eq. 2.14 can be simplified as:

$$(Q_i - Q_w)X_e + Q_wX_w = r_g V_r \quad 2.15$$

Net rate of biomass production ( $r_g$ ) is the resultant of biomass growth and biomass decay that occur at the same time. Since biomass growth rate is proportional to the utilization rate of substrate while biomass decay is proportional to the biomass present,  $r_g$  can be written as:

$$r_g = -Yr_{su} - k_d X \quad 2.16$$

Where,

$Y$  = Yield coefficient (mg VSS/mg BOD)

$r_{su}$  = Substrate utilization rate (mg/L.day)

$k_d$  = Endogenous decay coefficient ( $\text{day}^{-1}$ )

Substituting Eq. 2.16 into Eq. 2.15,

$$(Q_i - Q_w)X_e + Q_wX_w = -(Yr_{su} + k_d X)V_r \quad 2.17$$

$$\frac{(Q_i - Q_w)X_e + Q_wX_w}{V_r X} = -Y \frac{r_{su}}{X} - k_d \quad 2.18$$

The left-hand side of Eq. 2.18 is the reciprocal of Solids Retention Time ( $\theta_c$ ) also known as specific microorganism growth rate as given below:

$$\frac{1}{\theta_c} = -Y \frac{r_{su}}{X} - k_d \quad 2.19$$

Where

$$\theta_c = \frac{V_r X}{(Q_i - Q_w)X_e + Q_w X_w} \quad 2.20$$

The substrate utilization rate can be computed from the following equation:

$$-r_{su} = \frac{Q_i}{V_r} (S_i - S_e) \quad 2.21$$

At the same time, soluble substrate concentration also had been utilized as following equation:

$$-r_{su} = \frac{kXS_e}{K_s+S_e} \quad 2.22$$

where  $k$  = Specific substrate utilization rate ( $\text{day}^{-1}$ )

$K_s$  = Half-velocity constant (mg/L of BOD)

Substituting Eq. 2.21 and Eq.2.22 into Eq. 2.19 separately yields

$$\frac{1}{\theta_c} = Y \frac{Q_i(S_i-S_e)}{XV_r} - k_d \quad 2.23$$

and

$$\frac{1}{\theta_c} = Y \frac{kXS_e}{K_s+S_e} - k_d \quad 2.24$$

In Eq.2.19, the term  $(-r_{su}/X)$  also known as the specific substrate utilization rate,

$U$ . Thus,

$$U = \frac{r_{su}}{X} = \frac{Q_i(S_i-S_e)}{V_r X} = \frac{S_i-S_e}{\theta X} \quad 2.25$$

and

$$U = \frac{r_{su}}{X} = \frac{kS_e}{(K_s+S_e)} \quad 2.26$$

Where  $U$  = Specific substrate utilization rate ( $\text{day}^{-1}$ )

$\theta = V_r/Q_i$  = Hydraulic retention time, day

Substituting Eq. 2.25 into Eq. 2.23 yields

$$\frac{1}{\theta_c} = YU - k_d \quad 2.27$$

Combine Eq.2.25 and Eq.2.26 yields

$$U = \frac{S_i-S_e}{\theta X} = \frac{kS_e}{(K_s+S_e)} \quad 2.28$$

The inverse of Eq.2.28 can be written as

$$\frac{1}{U} = \frac{\theta X}{S_i-S_e} = \frac{K_s+S_e}{kS_e} \quad 2.29$$

$$\frac{1}{U} = \frac{K_s}{kS_e} + \frac{1}{k} \quad 2.30$$

In practice, the maximum yields coefficient ( $Y$ ) and endogenous decay coefficient ( $k_d$ ) are commonly used for activated sludge process design and control, especially for aeration tank volume design calculation as in Eq. 2.23 above.

$$V_r = \frac{\theta_c Q_i Y (S_i - S_e)}{X(1 + K_d \theta_c)} \quad 2.31$$

Even though maximum specific substrate utilization rate ( $k$ ) and half-velocity constant ( $K_s$ ) not directly used for activated sludge process design and control, both of the values can be used to determine the substrate concentration in effluent ( $S_e$ ) from the following equation (Shun, 2014):

$$S_e = \frac{K_s(1 + \theta_c k_d)}{\theta_c(Yk - k_d) - 1} \quad 2.32$$

As mentioned in DOE guidance document, for conventional aeration activated sludge system design, default value for yield coefficient ( $Y$ ) and decay coefficient ( $k_d$ ) are 0.4 – 0.8 kg VSS/kg BOD<sub>5</sub> and 0.03 – 0.15 day<sup>-1</sup> respectively. Meanwhile, default value for yield coefficient ( $Y$ ) and decay coefficient ( $k_d$ ) are 0.1 – 0.3 kg VSS/kg BOD<sub>5</sub> and 0.03 – 0.15 day<sup>-1</sup> respectively for extended aeration activated sludge system design (DOE, 2010a).

In determination of kinetic parameters in the activated sludge process of domestic wastewater, Najafpour et al. (2007) had reported that the decay coefficient ( $k_d$ ), maximum specific substrate utilization rate ( $k$ ) and half-velocity constant ( $K_s$ ) were determined to be 0.06 day<sup>-1</sup>, 1.71 day<sup>-1</sup> and 85.5 mg/L, respectively with SRT of 8 days and a COD removal efficiency up to 90%. However, there was no yield coefficient has been reported in this study. In other literatures of municipal wastewater study, the investigation had shown that the yield coefficient ( $Y$ ), decay coefficient ( $k_d$ ), maximum specific substrate utilization rate ( $k$ ) and half-velocity constant ( $K_s$ ) for conventional activated sludge process were in the range of 0.48–0.8 mg VSS/mg sCOD, 0.0189-0.026 day<sup>-1</sup>, 0.95–0.98 day<sup>-1</sup> and 52-71 mg sCOD/L, respectively, and for extended aeration activated sludge system, the yield coefficient ( $Y$ ), decay coefficient ( $k_d$ ), maximum specific substrate utilization rate ( $k$ ) and half-velocity constant ( $K_s$ ) for conventional activated sludge process were in the range of 0.6174–1.2512 mg VSS/mg sCOD, 0.0198-0.0309 day<sup>-1</sup>, 1.96–3.17 day<sup>-1</sup> and 311.7-508 mg sCOD/L, respectively (Mardani et al, 2011).

The kinetic parameters of activated sludge process in treating industrial wastewater such as chrome tannery wastewater were 0.680 mg TSS/mg COD, 0.024 day<sup>-1</sup>

<sup>1</sup>, 0.2 day<sup>-1</sup> and 23.02 mg/L for yield coefficient ( $Y$ ), decay coefficient ( $k_d$ ), maximum specific substrate utilization rate ( $k$ ) and half-velocity constant ( $K_s$ ), respectively (Goswami et al, 2015). Besides, kinetic study of agro based industrial wastewater in the activated sludge process such as POME treatment has also been investigated and reported to be 0.272 mg TSS/mg COD, 0.131 day<sup>-1</sup> and 0.429 g COD/L for yield coefficient ( $Y$ ), decay coefficient ( $k_d$ ), half-velocity constant ( $K_s$ ), respectively by using sequencing batch reactor (Lim and Vadivelu, 2014).

## 2.8 Design of Activated Sludge System

In practical, the wastewater treatment system designer will refer to the DOE design guidance document as a design guideline for the physical chemicals process and the biological process of wastewater treatment plant. However, DOE allowed to use the design value that is less than the default value in the DOE guidance document by submitting the document with relevance document (DOE, 2010a). In wastewater treatment plant, activated sludge process is the most important secondary biological treatment for organic matter removal. Most of the wastewater treatment plant is designed by using the Activated Sludge Model (ASM) which usually employ trial-and-error approach to get a cost-effective treatment for a given wastewater (El-Shorbagy et al., 2011). However, there are some phenomena in mathematical modelling that had been neglected, such as hydrodynamics phenomena, biochemical reactions and their kinetics as well as liquid-solids separation in their settler (Hreiz et al.2015a). Even though many literatures and research papers had documented and published the kinetic study parameters, this is only valid for biological treatment process in treating the municipal wastewater and not applicable for industrial wastewater. Indeed, industrial wastewater has a big difference with the municipal wastewater in terms of quantity and quality, which depends on the type of manufacturing processes.

Due to the differences of the manufacturing processes and activities, the kinetic parameters of industrial wastewater can be determined through experiments or pilot plant studies, subsequently used for the wastewater treatment plant design and operation optimization. The kinetic parameters typically involved in the biological treatment process design are yield coefficient ( $Y$ ), decay coefficient ( $k_d$ ), maximum specific substrate utilization rate ( $k$ ) and half-velocity constant ( $K_s$ ). In wastewater treatment

design based on kinetic approach, the biochemical interactions between the microorganism and the substrate had been well developed and widely accepted in various industrial wastewater treatment plant design.

In practical, the aeration tank of activated sludge process can be designed by using the following equation (Tchobanoglous and Stensel 2004; Davis, 2010; Shun, 2014):

$$\text{Aeration Tank Volume (Industry), } V_p = \frac{\theta_c Q_i Y (S_i - S_e)}{X [1 + k_d - \theta_c]} \quad 2.33$$

Where  $\theta_c$  = Solid Retention Time (day)  
 $Q_i$  = Influent flow rate (m<sup>3</sup>/day)  
 $S_i$  = Substrate concentration (BOD or COD) influent (mg/L)  
 $S_e$  = Substrate concentration (BOD or COD) effluent, (mg/L)  
 $X$  = Concentration of MLVSS in aeration tank (mg/L)  
 $Y$  = Yield coefficient (kg VSS/kg BOD<sub>3</sub> or kg VSS/kg COD)  
 $k_d$  = Decay coefficient (day<sup>-1</sup>)

However, the design calculation for aeration tank volume is different from the DOE design guideline, where the biodegradable fraction of VSS ( $f_b$ ) had been taken into consideration for the aeration tank volume design. Since there is no biodegradable fraction of VSS value available in literature, thus the default value had been used at 0.72 and 0.57 for conventional activated sludge system and extended aeration activated sludge system, respectively (DOE, 2010a) as following equation:

$$\text{Aeration Tank Volume (DOE), } V_d = \frac{\theta_c Q_i Y (S_i - S_e)}{X [1 + k_d f_b \theta_c]} \quad 2.34$$

Where  $f_b$  = Biodegradable fraction of VSS immediately after generation in the system ( $\theta_c=0$ )

$$= \frac{f'_b}{[1 + (1 - f'_b) k_d \theta_c]} \quad 2.35$$

Where  $f'_b$  = Biodegradable fraction of VSS subject to sludge age,  $\theta_c$

## CHAPTER 3

### MATERIALS AND METHODS

#### 3.1 Introduction

This chapter discussed the experimental methodology and analytical procedures that were used throughout in this study by using conventional activated sludge treatment process in palm oil industry. Firstly, the method to determine the physical composition including solids contents and particle size distribution of POME, and chemical composition such as organic content and nitrogen compound in POME was described. Then, procedure used to investigate the effect of important operating parameters for activated sludge process such as initial pH of POME, hydraulic retention time (HRT), organic loading rate (OLR), initial mixed volatile suspended solids (MLVSS), solid retention time (SRT) and molasses concentration as external carbon source was portrayed. In order to determine the total BOD in POME, kinetic study of BOD had been done to gain the ultimate BOD. Besides that, fractional of COD also been conducted to identify the biodegradable COD (bCOD) and soluble readily biodegradable COD (srbcOD) in POME. Next, the process of conducting kinetic analysis on the activated sludge treatment system by using the data obtained was described. Lastly, the steps of comparing the design calculation of aeration tank volume by using default value that recommended by DOE (2010a) and the finding value in this study.

#### 3.2 Characterization of Anaerobic Treated POME

A total of 10 L anaerobic treated POME was collected from Anaerobic Pond 4 in Neram Palm Oil Mill. The sample was stored in the laboratory refrigerator at temperature less than 4°C to maintain the quality of the POME before the experiment. The POME

sample had been analysed for physical composition and chemicals composition. Physical composition including solid content of POME and particle size distribution (PSD) while chemicals composition including pH, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Ammoniacal Nitrogen (AN). Both physical and chemicals composition determination had been conducted in quadruplicate.

### **3.2.1 Physical Composition**

#### **3.2.1.1 Solid Content**

##### **(a) Total Solid (TS)**

Total Solid (TS) was measured as outlined in Standard Methods APHA 2540 B (total solids dried at 103 - 105°C). In short, 100 ml of sample was dried in an oven (ED 56-230V, Binder, Germany) at 105°C for 1 hour. The sample was then transferred into the desiccators to cool off. After cooling down, it was weighed to obtain the mass of TS.

##### **(b) Total Volatile Solid (TVS) and Total Fixed Solid (TFS)**

Total volatile solid (TVS) and total fixed solid (TFS) were measured as outlined in Standard Methods APHA 2540 E (volatile and fixed solids ignited at 550°C). In brief, the residue from total solid test from TS was ignited at 550°C for 20 minutes. After ignition, the remaining residue represent the TFS while the weight lost on ignition is the TVS.

##### **(c) Total Suspended Solid (TSS) and Total Dissolved Solid (TDS)**

Total suspended solid (TSS) were measured as outlined in Standard Methods APHA 2540 D (total suspended solids dried at 103-105°C). Briefly, 100 ml of well mixed sample were filtered by 2.0 µm pore size Whatman GF/C Glass-Fiber filter paper of known weight using a vacuum pump (Gast High-Capacity Vacuum Pump, Cole Parmer, USA). The filtered paper with solids was dried in an oven at 105°C for 1 hour. The weight

of TSS was obtained through drying and weighing process as per described in Section (a). Then, the filtrate was dried at 180°C for 1 hour for the TDS determination.

#### **(d) Volatile Suspended Solid (VSS) and Fixed Suspended Solid (FSS)**

Volatile suspended solid (VSS) were measured as outlined in Standard Methods APHA 2540 E (volatile solid ignited at 550°C). In summary, the remaining suspended solid residue from Section (c) were ignited at 550°C for 20 minutes. The sample was then transferred into the desiccators to cool off and weighed. After ignition, the remaining residue represent the FSS while the weight lost on ignition is the VSS.

#### **(e) Volatile Dissolved Solid (VDS) and Fixed Dissolved Solid (FDS)**

Volatile dissolved solid (VDS) were measured as outlined in Standard Methods APHA 2540 E (volatile solid ignited at 550°C). In summary, the remaining dissolved solid residue from Section (c) were ignited at 550°C for 20 minutes. The sample was then transferred into the desiccators to cool off and weighed. After ignition, the remaining residue represent the FDS while the weight lost on ignition is the VDS.

#### **3.2.1.2 Particle Size Distribution (PSD)**

Particle size distribution (PSD) were measured as outlined in Standard Methods APHA 2540 D (total suspended solids dried at 103-105°C). Briefly, 100 ml of well mixed anaerobic treated POME sample was filtered with 100 µm pore size filter paper by using a vacuum pump (Gast High-Capacity Vacuum Pump, Cole Parmer, USA). The filtered paper with solids was dried in an oven at 105°C for 1 hour. The weight of TSS was obtained as particle size more than 100 µm. On the other hand, the filtrate was collected and filtered with 50 µm followed by 20 µm, 10 µm, 5 µm and 2 µm filter paper continuously. After each drying, the remaining residue represent the size of particle that consisted in anaerobic treated POME by using different pore size of filter paper respectively.

### 3.2.2 Chemical Composition

For the chemical composition determination, all the analytical reagents used were obtained from Hach Company, USA unless otherwise stated. Table 3.1 summarise the type of analyses and their corresponding reagents.

Table 3.1 Analyses used in the project and their corresponding reagents

Analysis	Reagent
BOD	BOD nutrient buffer pillow
Carbonaceous BOD	2-chloro-6-(trichloromethyl) pyridine (TCMP)
COD	COD Digestion reagent vials
TN	Total Nitrogen Persulfate reagent
	Total Nitrogen reagent A powder
	Total Nitrogen reagent B powder
	Total Nitrogen reagent C vial
AN	Ammonia Cyanurate reagent
	Ammonia Salicylate reagent

#### 3.2.2.1 pH

pH was measured by using pH meter (SevenEasy, Mettler Toledo, USA) and was conducted according to Standard Methods APHA 4500-H<sup>+</sup> B.

#### 3.2.2.2 Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand (BOD) was determined according to Standard Methods APHA 5210-B, where all samples were incubated for 3-days at 30°C as stated in the regulation of EQA 1974. In brief, 3 L distilled water was pre-incubated at 20°C before BOD Nutrient Buffer Pillow was added. The mixture was shaken vigorously for 1 minute in order to dissolve the nutrients and saturate the solution with air. With different types of sample, sample size was selected as in Table 3.2. The sample was stirred gently before the suitable volume was withdrawn.

Table 3.2 Sample volume required in BOD measurement

Wastewater Sample	Minimum Sample Volume, mL	Estimated BOD mg/L
Anaerobic Treatment POME	1	600
Supernatant After POME treatment by activated sludge process	6	100

The sample was then added into the BOD bottle and top up to 300 ml with the nutrient buffer prepared earlier. It is important to ensure that the nutrient buffer was allowed to flow down gently from the side of the bottle so as to prevent trapping of air bubble.

During the measurement of initial Dissolved Oxygen (DO), the BOD bottle was inverted carefully to prevent air bubble from becoming trapped. The initial DO concentration was measured in each bottle by using DO meter (ProOBOD, Yellow Spring Instrument, USA). After measurement, the BOD bottle was capped and wrapped with the parafilm. Then, the BOD bottle was incubated at 30°C for three days in incubator (Incubator IF 30, Memmert, Germany) for BOD<sub>3</sub> test. After three days, the final DO of each bottle was measured and calculated as Eq.3.1.

$$BOD_3, \text{ mg/L} = \frac{DO_i - DO_f}{P} \quad 3.1$$

$DO_i$  = DO initial (before incubation)

$DO_f$  = DO final (after 5-day incubation)

$P$  = Dilution factor of POME sample

### 3.2.2.3 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) was measured according to Reactor Digestion Method (Method 8000) at a wavelength of 620 nm (APHA 5220 D). In brief, 2 ml of POME sample was transferred into high range COD Digestion Reagent Vial (COD concentration range within 0 - 1,500 mg/L). After mixing the contents, the vial was heated

in HACH DRB 200 (HACH, USA) Reactor at 150°C for 2 hours. Then, the COD of sample was measured in HACH DR 890 (HACH, USA) Spectrophotometer.

#### **3.2.2.4 Total Nitrogen (TN)**

Total nitrogen (TN) was measured according to TNT Persulfate Digestion Method which referenced in HACH Manual of Analytical Methods for Method 10072. In brief, 0.5 mL of POME sample and deionized water each was transferred into two different vial which filled with Total Nitrogen Persulfate Reagent Powder. Then, both vials were heated in DRB 200 Reactor at 105°C for 30 minutes. After heating, Total Nitrogen Reagent A Powder was added into both vial for 3 minutes reaction, followed by Total Nitrogen Reagent B Powder for two minutes reaction. After reaction, 2 mL of POME sample and deionized water each was transferred into Total Nitrogen Reagent C Vial for five minutes reaction before the Total Nitrogen measurement by HACH DR 890 Spectrophotometer.

#### **3.2.2.5 Ammoniacal Nitrogen (AN)**

Ammoniacal nitrogen (AN) was measured according to Salicylate Method which referenced in HACH Manual of Analytical Methods for Method 8155. In brief, 10 mL of POME sample and deionized water each was transferred into two different sample cells where deionized water was used as blank. First reagent, namely Ammonia Salicylate Reagent powder was added into both sample cell for 3 minutes reaction, then second reagent, namely Ammonia Cyanurate Reagent powder was added into both sample cell for another 15 minutes reaction. After 15 minutes reaction period, both sample cell will be taken for AN analysis by using in HACH DR 890 Spectrophotometer.

#### **3.2.3 Other Measurements**

Beside the physical and chemical composition determination, the performance of activated sludge in treating anaerobic treated POME was also monitored by measuring the DO for the OUR determination.

### **3.2.3.1 Dissolved Oxygen (DO)**

Dissolved oxygen (DO) measurement were done in accordance with the Standard Methods APHA 4500-O G using dissolved oxygen membrane probe (Pro20, Yellow Spring Instrument, USA).

### **3.2.3.2 Oxygen Uptake Rate (OUR)**

Oxygen uptake rate (OUR) was obtained as outlined in Standard Methods APHA 2710 B. In this method, 300 ml of mixed liquor sample from activated sludge reactor was filled into the BOD bottle and immediately inserted with a self-stirring dissolved oxygen probe (ProODO, Yellow Spring Instrument, YSI, USA). After meter reading has stabilized, initial DO was being recorded whilst timing device was started. DO reading was recorded at time intervals of 1 min over a 15 min period. If the initial DO is low ( $\leq 2.00$  mg/L), the test needs to be started with a fresh new sample which having a higher initial DO level. After obtained the DO result for 15 min, the plot of DO against the time was constructed and slope of the plot was OUR value in milligram of oxygen used per liter of mixed liquor per hour ( $\text{mg O}_2/\text{L.hr}$ ).

## **3.3 Characterization of Activated Sludge**

A total of 5 L activated sludge sample were obtained from Cargill Palm Products Sdn. Bhd., Gebeng, Kuantan and straight away send to laboratory for analysis. The activated sludge sample was analysed for its Mixed Liquor Suspended Solids (MLSS) and Mixed Volatile Suspended Solids (MLVSS) content as per description in TSS and VSS, respectively. The reasons of taken the activated sludge from Cargill because the activated sludge was analysed in good condition and can be used in POME treatment study to replace the current activated sludge in polishing plant of Neram Palm Oil Mill, which was found unhealthy in terms of MLSS and MLVSS concentration.

### 3.4 POME Treatment by Activated Sludge Process

In this study, activated sludge sample had been collected and mixed with POME for acclimatization prior to study the performance of POME treatment in different operating parameters.

#### 3.4.1 Acclimatization of Activated Sludge in POME

10 liter activated sludge sample from Cargill Palm Products Sdn Bhd, Gebeng Industrial Estate, Kuantan, Pahang was acclimatized with anaerobic treated POME sample from Neram Palm Oil Mill, Kemaman, Terengganu. Volume of anaerobic treated POME sample was calculated using the F/M ratio formula:

$$F/M \text{ Ratio} = \frac{BOD \text{ of POME (mg/L)} \times \text{Volume of POME (L)}}{MLVSS \text{ of Activated Sludge (mg/L)} \times \text{Volume of Activated Sludge (L)}} \quad 3.2$$

F/M Ratio was fixed at 0.3 kg BOD/kg MLVSS.day according to the recommendation by Department of Environment Malaysia at a value between 0.15 to 0.40 kg BOD/kg MLVSS.day as the design criteria for sequencing batch reactors (Department of Environment Malaysia, 2010).

The mixed solution of activated sludge and anaerobic treated POME sample were placed into 25 L Sequence Batch Reactor (SBR) tank completed with aeration system. The aeration system consists of an aquarium air pump with air flow output of 110 L/min and pressure at 2 MPa (Model RS Electrical RS-17000, China). The initial pH of POME was adjusted to the neutral pH range ( $7.0 \pm 0.1$ ) before adding to the activated sludge. The acclimatizing operation was conducted under batch mode for hydraulic retention time of 24 hr (Department of Environment Malaysia, 2010). After 24 hr, supernatant and activated sludge were taken for the analyses as depicted in Table 3.3. The acclimatization process of activated sludge was conducted for 10 days to each batch of activated sludge.

Table 3.3 Parameters monitored for difference activated sludge sample and supernatant during acclimatization periods

Sample	Mixed Liquor	Settled Activated Sludge	Supernatant
Parameters analysed	MLSS, MLVSS	MLSS, MLVSS	pH, BOD <sub>3</sub> , COD, TSS

### 3.4.2 Effect of Operating Parameters on POME Treatment by Activated Sludge Process

All POME samples were examined for their initial pH, BOD<sub>3</sub>, COD and TSS before each experiment was run. The experiment was carried out in batch mode and all experiment was run in quadruplicate. The range of all operating parameters studied was summarized in Table 3.4

Table 3.4 Range of operating parameters studied in POME treatment

Operating parameters	Experimental range
pH	4.0 ± 0.1 to 10.0 ± 0.1 with interval of pH 0.5 ± 0.1
Hydraulic retention time (HRT)	12 to 72 hrs with an interval of 12 hrs
Organic loading rate (OLR)	0.27 g BOD <sub>3</sub> /L.day to 0.38 g BOD <sub>3</sub> /L.day
Mixed liquor volatile suspended solid (MLVSS)	1,000 ± 100 mg/L to 10,000 ± 1,000 mg/L with an interval of 1,000 ± 100 mg/L
Solid retention time (SRT)	2 days to 20 days with an interval of 2 days
External carbon sources	10 ± 0.5 mg/L to 100 ± 0.5 mg/L with an interval of 10 ± 0.5 mg/L

The effect of operating parameters on POME treatment by activated sludge process was investigated to obtain the optimum condition of operating parameters which can be used to improve the current activated sludge process in treating POME as well as determine the kinetic parameters in the kinetic study of POME treatment by activated sludge process.

#### **3.4.2.1 Effect of pH**

14 sets of 2 L conical flask completed with aeration system (SOBO aquarium air pump with air flow output of 4 L/min and pressure of 2 MPa) were used. 7.0 L of acclimated activated sludge was distributed into all flasks with 0.5 L each. POME with OLR of 0.31 g BOD<sub>3</sub>/L.day (BOD<sub>3</sub> = 650 ± 20 mg/L) and acclimated activated sludge (MLVSS = 2,000 ± 200 mg/L) with SRT of 7 days and molasses concentration at 20 mg/L were placed into conical flask based on the F/M ratio of 0.3 kg BOD/kg MLVSS.day as per Eq. 3.1.

pH in conical flask had been adjusted to 4.0 ± 0.1 to 10.0 ± 0.1 with interval of pH 0.5 ± 0.1 by using hydrochloric acid or sodium hydroxide (0.1 M). The range of pH was selected because the original pH of raw POME was 4.00 and after the biological treatment process, it can be increased to 10.00. So, the effect of pH was conducted with the range of original pH of POME. Aeration had been carried out for 24 hr. Then, 300 mL of mixed liquor sample for each conical flask were taken for Dissolved Oxygen (DO) test. Once DO test were completed, 100 mL of mixed liquor sample were taken for MLSS and MLVSS test. The balance mixed liquor sample were transferred into 250 mL conical flask and let it stand for 1 hr to settle the sludge. The supernatant was then measured for its pH, BOD, COD and TSS values, while the activated sludge were collected for MLSS and MLVSS analysis.

#### **3.4.2.2 Effect of Hydraulic Retention Time (HRT)**

The set up was similar as in Section 3.4.2.1, except that the pH in conical flask was adjusted to 6.5 ± 0.1. A total of 6 sets apparatus were set up based on the F/M ratio of 0.3 kg BOD/kg MLVSS.day with OLR of 0.31 g BOD<sub>3</sub>/L.day with acclimated activated sludge (MLVSS = 2,000 ± 200 mg/L) at SRT of 7 days and molasses concentration at 20 mg/L. The HRT was controlled at ranging from 12 to 72 hr with an interval of 12 hr between flasks. Samples were withdrawn for each HRT and analysed as described in the previous section.

### **3.4.2.3 Effect of Organic Loading Rate (OLR)**

In this study, 9 sets of 0.5 L acclimated activated sludge with MLVSS concentration of  $2,000 \pm 200$  mg/L with SRT of 7 days and molasses concentration at 20 mg/L was used. POME sample with OLR from 0.27 g BOD<sub>3</sub>/L.day to 0.38 g BOD<sub>3</sub>/L.day (BOD<sub>3</sub> at  $500 \pm 50$  mg/L to  $1,000 \pm 100$  mg/L) were prepared by using distilled water to dilute the POME sample at an interval of 100 mg/L. Volume of POME was adjusted so that together with acclimated activated sludge maintaining F/M ratio of 0.3 kg BOD/kg MLVSS.day. Initial pH was adjusted to  $6.5 \pm 0.1$  and the 4 L/min aeration was carried out for 48 hr. Similar analyses were done for the samples in this study.

### **3.4.2.4 Effect of Mixed Liquor Volatile Suspended Solid (MLVSS)**

10 sets of acclimated activated sludge with solid retention time 7 days and MLVSS concentration from  $1,000 \pm 100$  mg/L to  $10,000 \pm 1,000$  mg/L at an interval of  $1,000 \pm 100$  mg/L were prepared from settled activated sludge and added into 2 L conical flask at F/M Ratio = 0.3 kg BOD/kg MLVSS.day. POME sample with OLR of 0.31 g BOD<sub>3</sub>/L.day and molasses concentration at 20 mg/L were used. Initial pH was adjusted to  $6.5 \pm 0.1$  and the 4 L/min aeration was carried out for 48 hr. Samples were withdrawn and analysed as described in the previous section.

### **3.4.2.5 Effect of Solid Retention Time (SRT)**

10 sets of acclimated activated sludge with MLVSS concentration  $2,000 \pm 200$  mg/L were prepared, followed by POME sample with OLR of 0.31 g BOD<sub>3</sub>/L.day and molasses concentration at 20 mg/L where the volume of POME sample was calculated based on F/M ratio of 0.3 kg BOD/kg MLVSS.day. Initial pH was adjusted to  $6.5 \pm 0.1$  and 4 L/min aeration was carried out for 48 hrs with a solid retention time ranging from 2 days to 20 days at an interval of 2 days. Similar analyses were carried as described previously.

### **3.4.2.6 Effect of External Carbon Source**

In this study, 11 sets of acclimated activated sludge with solid retention time 10 days and MLVSS concentration of  $2,000 \pm 200$  mg/L were added into POME sample with OLR of 0.31 g BOD<sub>3</sub>/L.day. The volume of POME sample was calculated based on the F/M ratio of 0.3 kg BOD/kg MLVSS.day. Initial pH was set at  $6.5 \pm 0.1$  with 48 hr aeration at 4 L/min. During the start-up of aeration process, molasses with concentration of  $10 \pm 0.5$  mg/L to  $100 \pm 0.5$  mg/L with an interval of  $10 \pm 0.5$  mg/L were added into the respective flask as external carbon source. Sampling was done at the end of the experiment and analyses were done as per description in the previous section.

### **3.5 BOD Kinetic Study of POME**

The study of BOD kinetic parameter of POME is required to estimate the ultimate BOD of POME ( $L_0$ , mg/L) and its reaction constant rate ( $k$ , 1/day). Since the temperature of the biological treatment process of POME might be different along the process but the temperature of BOD test was conducted where all samples were incubated for 3-days at 30°C according to EQA 1974 (Malaysia, 1977), hence the estimation of BOD kinetic parameters is desired. This is to gain more accurate BOD result that corresponds to the actual process of POME treatment.

#### **3.5.1 BOD Kinetic Parameters Estimation**

Anaerobic treated POME sample had been taken for BOD analysis in triplicate according to the standard procedures in Section 3.1.2.2. The BOD analysis was conducted for BOD-1 day (BOD<sub>1</sub>), BOD-2 day (BOD<sub>2</sub>), BOD-3 day (BOD<sub>3</sub>), BOD-4 day (BOD<sub>4</sub>), BOD-5 day (BOD<sub>5</sub>), BOD-6 day (BOD<sub>6</sub>) and BOD-7 day (BOD<sub>7</sub>) in different BOD bottles. After gained the BOD result, the data had been compounded and used for the kinetic parameters estimation in different of kinetic study method below.

### 3.5.1.1 Least Square Method (Shun, 2014)

Refer to the Least Square Method, the values of  $y'$ ,  $y'y$  and  $y^2$  for the 7 days' incubation BOD values was calculated to solve the Eq. 2.5 and Eq.2.6 to gain the value of  $a$  and  $b$  for further determination of  $L_0$  and  $k_1$  by using Eq.2.7 and Eq.2.8.

$$na + b\Sigma y - \Sigma y' = 0$$

$$a\Sigma y + b\Sigma y^2 - \Sigma yy' = 0$$

$$k_1 = -b$$

$$L_0 = -\frac{a}{b}$$

### 3.5.1.2 Fujimoto Method (Tchobanoglous and Stensel, 2004)

In this method, an arithmetic plot of  $BOD_{t+1}$  versus  $BOD_t$  for 7 days' incubation was constructed. Then, determine the value at the intersection point of the plot with a line of slope 1 which corresponds to the ultimate BOD ( $L_0$ ). After that, the value of reaction rate constant ( $k_1$ ) was determined by using the Eq. 2.3 below:

$$y = L_0(1 - e^{-k_1 t})$$

### 3.5.1.3 Thomas Graphical Method (Gray, 2004)

Refer to the Thomas Graphical Method, the reaction rate constant ( $k_1$ ) and ultimate BOD ( $L_0$ ) can be calculated from plot as the Eq.2.9.

$$\left(\frac{t}{y}\right)^{1/3} = \frac{1}{(2.3k_1)^{1/3}} + \frac{k_1^{2/3}}{3.43L_0^{1/3}} \cdot t$$

### 3.5.1.4 Log Different Method (Ramalho, 1977)

Refer to the Log Different Method, value of reaction rate constant ( $k_1$ ) and ultimate BOD ( $L_0$ ) can be estimated from the plot as the Eq.2.10.

$$\log\left(\frac{dy}{dt}\right) = \log(2.303L_0 \cdot k_1) - k_1 t$$

### 3.5.1.5 Method of Moments (Ramalho, 1977)

In the Method of Moments, firstly, nomograph of Moore's diagram displaying the relationship between  $k_1$ ,  $\Sigma y/L_0$ , and  $\Sigma y/\Sigma y_t$  need to be constructed using the Eq.2.11 below:

$$\frac{\Sigma y}{L_0} = n - [10^{-k_1}(10^{-nk_1} - 1)/(10^{-k_1} - 1)]$$

After that, the values of  $\Sigma y$  and  $\Sigma y_t$  the series of BOD measurements was calculated for 7-days in this study. Then, the value of  $k_1$  can be gained the plot of  $\Sigma y/\Sigma y_t$  versus  $k_1$  in the nomograph while the value of  $\Sigma y/L_0$  can be determined from the plot of  $\Sigma y/L_0$  versus  $k_1$  using the same  $k_1$  value obtained. Finally,  $L_0$  can be determined from this gained  $k_1$  value.

### 3.5.2 Evaluation of Different Kinetic Study Methods

After the value of kinetic study parameters ( $k$  and  $L_0$ ) been found out by using different methods above, plot of observed BOD ( $y_o$ ) and estimated BOD ( $y_e$ ) against time ( $t$ , day) will be constructed for the comparison. Then, the selected kinetic study methods will be evaluated by calculate the sum of the absolute differences between the observed BOD and estimated BOD as following equation:

$$D = \sum_{i=1}^{i=n} \frac{(y_o - y_e)}{y_e} \quad 3.2$$

where  $D$  = sum of the absolute differences between the observed BOD and estimated BOD

$y_o$  = Observed BOD (gained from BOD testing)

$y_e$  = Estimated BOD (gained from the BOD kinetic equation)

$n$  = no of days of incubation for the serial BOD test

### 3.6 Chemical Oxygen Demand (COD) Fractions Studies of POME

Experiment for COD fractions studies was carried out by transferred 5 L of acclimated activated sludge into 14 L aeration tank by fixing the F/M Ratio at 0.3 kg BOD/kg MLVSS.day. The aeration tank was completed with air flow output of 110 L/min and pressure at 2 MPa aquarium air pump as shown in Figure 3.1, which follow the optimized conditions obtained from the experiment in Section 3.4.2. Supernatant of POME was collected after treated by activated sludge process for the COD measurement and its fraction determination (i.e. bCOD, srbCOD, snbCOD, psbCOD and pnbCOD).

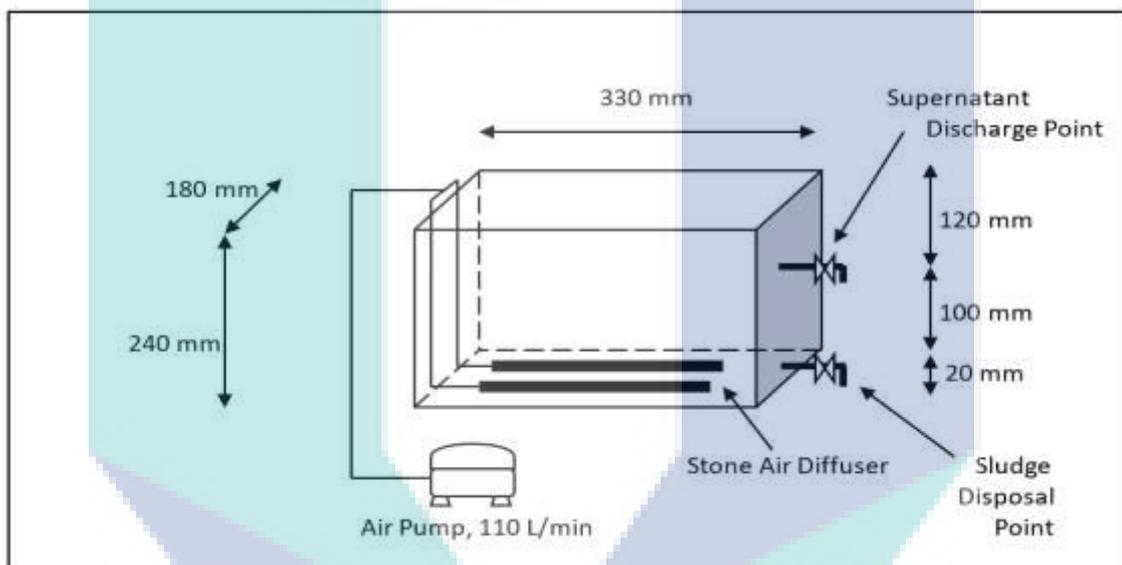


Figure 3.1 Schematic diagram of aeration tank for activated sludge process in POME treatment

#### 3.6.1 Determination of Biodegradable Chemical Oxygen Demand (bCOD)

Experiment to determine the biodegradable chemical oxygen demand, bCOD of POME was carried out by transferring the anaerobic treated POME into the aeration tank which was filled with acclimated activated sludge for the biological oxidation process. In this experiment, COD analysis had been carried out for anaerobic treated POME sample and mixture solution of POME with activated sludge. For the anaerobic treated POME sample, initial total COD ( $COD_{it}$ ) and initial soluble COD of POME ( $COD_{is}$ ) had been done while for the mixture solution of POME with activated sludge, COD analysis had been carried out for initial total COD ( $COD_{itm}$ ), initial soluble COD ( $COD_{ism}$ ) and final

COD of mixture ( $COD_{fpm}$ ). Total COD was measured according to Reactor Digestion Method (Method 8000), while soluble COD was measured by filtering the POME sample through the 0.45  $\mu\text{m}$  filter paper and followed by above COD test method. Then, biodegradable chemical oxygen demand of POME was calculated based on Eq. 3.3 to Eq. 3.8.

$T_bOD$  is the difference between the initial total COD and the final soluble nonbiodegradable COD as follows:

$$T_bOD = bCOD = \text{Initial total COD} - \text{Final soluble nonbiodegradable COD} \quad 3.3$$

The actual  $T_bOD$  value can be obtained through the calculation as followings:

- a) Using the measured initial total COD of POME ( $COD_{it}$ ) and initial soluble COD of POME ( $COD_{is}$ ), the COD of suspended solid of POME ( $COD_w$ ) can be calculated as the following equation:

$$COD_w = COD_{it} - COD_{is} \quad 3.4$$

- b) Using the measured initial total COD of mixture ( $COD_{itm}$ ) and initial soluble COD of mixture ( $COD_{ism}$ ), the COD of suspended solid of mixture ( $COD_{im}$ ) can be calculated as the following equation:

$$COD_{im} = COD_{ism} - COD_{itm} \quad 3.5$$

- c) Using the result of  $COD_w$  and  $COD_{im}$ , the mixture biomass COD ( $COD_{mb}$ ) can be calculated as the following equation:

$$COD_{mb} = COD_{im} - COD_w \quad 3.6$$

- d) The COD of initial mixture of POME ( $COD_{ipm}$ ) was calculated by using the value of  $COD_{itm}$  and  $COD_{mb}$  as following equation:

$$COD_{ipm} = COD_{itm} - COD_{mb} \quad 3.7$$

- e) The COD of final mixture of POME ( $COD_{fpm}$ ) is the measured final soluble COD of the mixture after filtration process.

Therefore, the  $T_bOD$  test can be calculated using the equation:

$$T_bOD \text{ Test} = \text{COD of initial mixture of POME (COD}_{ipm}) - \text{COD of final mixture of POME (COD}_{fpm}) \quad 3.3$$

f) Due to the dilution of POME sample, dilution ratio needs to be adjusted to obtain the POME  $T_bOD$ :

$$\text{POME } T_bOD = T_bOD \text{ Test} \times (\text{Volume of mixture/volume of POME sample}) \quad 3.8$$

### 3.6.2 Determination of Soluble Readily Biodegradable COD (srbCOD) and Soluble Nonbiodegradable COD (snbCOD)

A physical separation method also known as rapid physical-chemical method which developed by Mamais et al. (1993) was used to determine the soluble readily biodegradable COD (srbCOD) and soluble nonbiodegradable COD (snbCOD). This physical separation method was applied to both anaerobic treated POME sample and settled supernatant sample after aeration process of anaerobic treated POME sample with activated sludge. This method assumed that suspended solids and colloidal material is removed effectively by flocculation with zinc hydroxide and followed by filtration with 0.45  $\mu\text{m}$  membrane filter, eventually leaving only the truly soluble organic material.

$$\begin{aligned} \text{Thus, soluble readily biodegradable COD, srbCOD} \\ = (\text{total truly soluble COD of anaerobic treated POME, ttsCOD}) \\ - (\text{soluble nonbiodegradable COD of supernatant, snbCOD}) \quad 3.9 \end{aligned}$$

In brief, 1 mL of zinc sulfate solution (100 g/L) was added to a 100 mL anaerobic treated POME sample and mixed vigorously for 1 min. Then, pH of the mixture was adjusted to about 10.5 with 6 M of NaOH. The sample was gently mixed about 5 to 10 min for floc formation. After that, the sample was settled for 10-20 min. Subsequently, the supernatant was withdrawn and filtered with 0.45  $\mu\text{m}$  membrane filter for COD measurement.

### 3.6.3 Determination of Particulate Slowly Biodegradable COD (psbCOD) and Particulate Nonbiodegradable COD (pnbCOD)

After obtained the result of the biodegradable chemical oxygen demand (bCOD) and soluble readily biodegradable COD (srbCOD), the particulate slowly biodegradable COD (psbCOD) can be calculated using the equation:

$$\begin{aligned} \text{Biodegradable chemical oxygen demand, bCOD} \\ &= \text{Soluble readily biodegradable COD} + \text{particulate slowly biodegradable COD} \\ &= \text{srbCOD} + \text{psbCOD} \end{aligned} \quad 3.10$$

Then, particulate nonbiodegradable COD (pnbCOD) can be calculated as follows:

$$\begin{aligned} \text{Particulate nonbiodegradable COD, pnbCOD} \\ &= \text{initial total COD} - \text{biodegradable chemical oxygen demand} - \text{soluble nonbiodegradable} \\ &\quad \text{chemicals oxygen demand} \\ &= \text{bCOD} - \text{snbCOD} \end{aligned} \quad 3.11$$

### 3.7 Kinetic Study of Activated Sludge Process in POME Treatment

Experiment for kinetic study of activated sludge in POME treatment was carried out by transferring 5 L of acclimated activated sludge into 14 L aeration tank completed with air flow output of 110 L/min and pressure at 2 MPa aquarium air pump, which follow the optimized conditions obtained from the experiment in Section 3.4.2, except the solid retention time. The experiment was carried out with different solid retention time from 10 days to 20 days (DOE, 2010a) with interval of 2 days by adjusting the volume of sludge wasting from the aeration tank according to the Eq.2.20 as following:

$$\theta_c = \frac{V_r X}{(Q_i - Q_w) X_e + Q_w X_w}$$

where  $Q_w$  = Flow of wasted activated sludge (WAS) (L/day)

$X_e$  = TSS of effluent (mg/L)

$X_w$  = TSS of wasted activated sludge (mg/L)

Since the  $X_w \gg X_e$ , thus,

$$\theta_c = \frac{V_r X}{Q_w X_w} \quad 3.12$$

So, the flowrate of wasted sludge (L/day) that need to be removed from the aeration tank for the different solid retention time is

$$Q_w = \frac{V_r X}{\theta_c X_w} \quad 3.13$$

After determination of waste sludge volume, the  $Y$  and  $K_d$  can be determined by using Eq. 2.27 as following:

where

$$\frac{1}{\theta_c} = YU - k_d$$

$$U = \frac{S_i - S_e}{\theta X}$$

A plot of reciprocal of solids retention time,  $1/\theta_c$  ( $\text{day}^{-1}$ ) versus specific substrate utilization rate,  $U$  ( $\text{day}^{-1}$ ) can be constructed using the data obtained from the above experiment to gain the maximum yields coefficient ( $Y$ ) and endogenous decay coefficient ( $k_d$ ) from the gradient and the  $y$ -intercept of the plot, respectively.

Concurrently, maximum specific substrate utilization rate ( $k$ ) and half-velocity constant ( $K_s$ ) can be obtained as Eq. 2.30 as following:

$$\frac{1}{U} = \frac{K_s}{k S_e} + \frac{1}{k}$$

a plot of reciprocal of specific substrate utilization rate,  $1/U$  (day) versus reciprocal effluent  $\text{BOD}_3$ ,  $1/S_e$  (L/mg) can be constructed using the data obtained from above similar experiment and determined the maximum specific substrate utilization rate ( $k$ ) and half-velocity constant ( $K_s$ ) value from the gradient and the  $y$ -intercept of the plot, respectively.

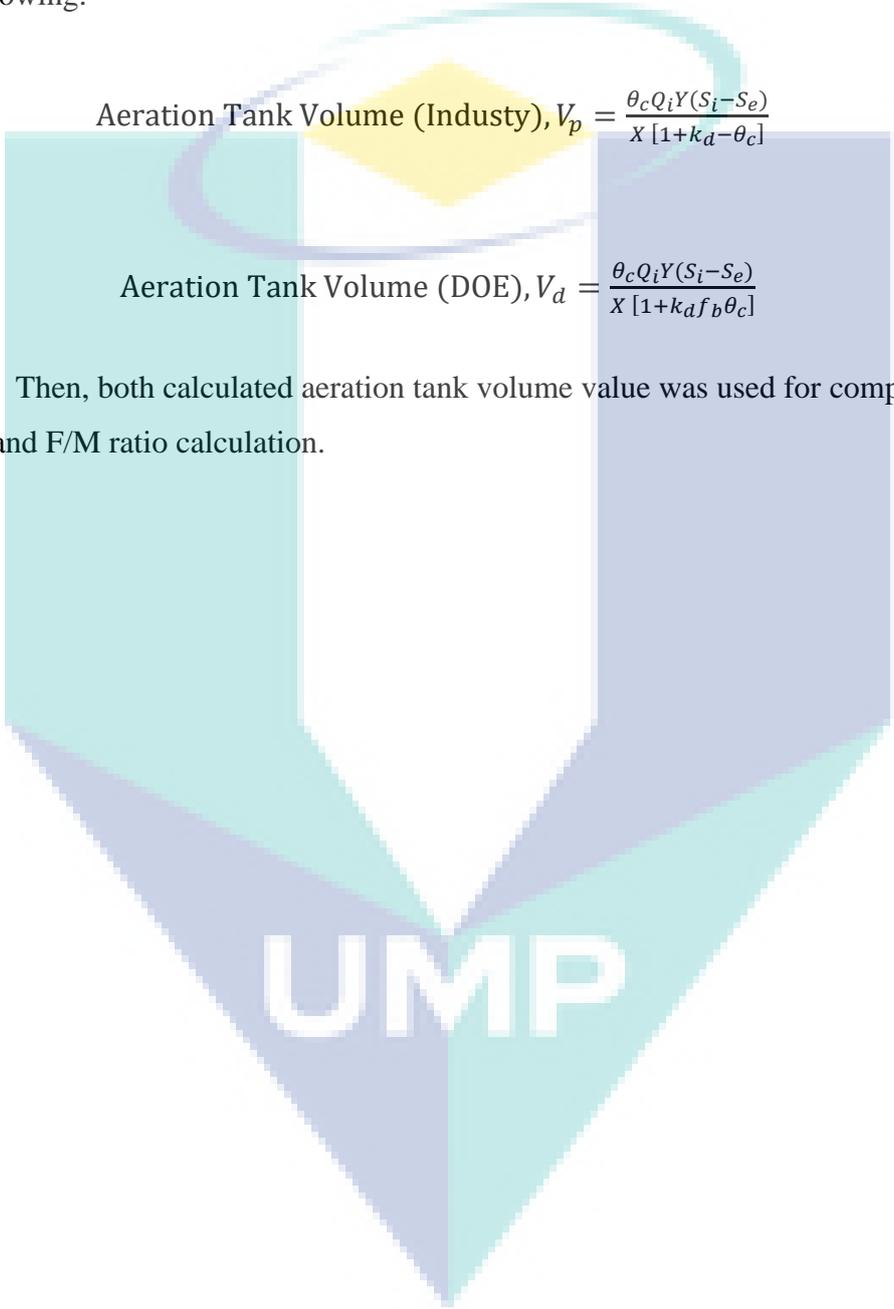
### 3.8 Design Calculation of POME Treatment System

By using the obtained result from above experiment, the volume of aeration tank of activated sludge process in POME treatment system was calculated using the formula by industry and default formula by DOE as shown in Eq.2.33 and Eq. 2.34, respectively as following:

$$\text{Aeration Tank Volume (Industry), } V_p = \frac{\theta_c Q_i Y (S_i - S_e)}{X [1 + k_d - \theta_c]}$$

$$\text{Aeration Tank Volume (DOE), } V_d = \frac{\theta_c Q_i Y (S_i - S_e)}{X [1 + k_d f_b \theta_c]}$$

Then, both calculated aeration tank volume value was used for comparison in HRT and F/M ratio calculation.

The logo for UIMP (Universiti Malaysia Perlis) is a large, downward-pointing arrow shape. It is composed of four triangular sections meeting at a central point. The top-left and bottom-right sections are light blue, while the top-right and bottom-left sections are a slightly darker blue. The letters 'UIMP' are written in a bold, white, sans-serif font across the center of the arrow.

UIMP

## CHAPTER 4

### RESULTS AND DISCUSSION

This chapter discussed the results of the entire research study with the proper discussion and conclusion.

#### 4.1 Characterization of Anaerobic Treated POME

Prior to the study of the POME treatment by activated sludge process, physical and chemical composition of anaerobic treated POME sample was analysed. The physical composition includes solids content of POME and percentage of different size of particle that present in POME sample, while chemical composition of POME such as pH, biochemical oxygen demand-3 days ( $BOD_3$ ), chemical oxygen demand (COD) and ammoniacal nitrogen (AN) were determined according to standard method and HACH method that were stated in Section 3.2.2. Each POME sample was measured four times to gain a mean value. In this case, characterization of raw POME was not conducted because in this study, only anaerobic treatment POME sample will be focused. Furthermore, as stated in regulation of DOE, the raw POME needs to pass through the closed digestion anaerobic treatment to produce biogas (Lot et al, 2017). Thus, it is not necessary to conduct characteristic study of raw POME.

##### 4.1.1 Physical Composition

Anaerobic treated POME had been taken for the physical composition analysis, such as solid contents and particle size distribution prior the biological treatment by activate sludge process.

#### 4.1.1.1 Solid Content of POME

Figure 4.1 shows the solid content in anaerobic treated POME in this study, where the POME sample were analysed for the concentration of different fractions of solid content that present in the sample. The solid content analysis in this study showed that the mean TS concentration was  $29,214 \pm 2,936$  mg/L with  $15,717 \pm 1,682$  mg/L of TVS and  $13,497 \pm 1,882$  mg/L of TFS. TVS normally represent the amount of organic solid in POME After separation by  $2.0 \mu\text{m}$  filter paper, TS was separated into TSS and TDS with concentration of  $25,649 \pm 1,483$  mg/L and  $3,565 \pm 779$  mg/L respectively. In TSS, VSS was found at concentration of  $14,285 \pm 2,087$  mg/L and FSS at concentration of  $11,364 \pm 1,446$  mg/L. However, in TDS, only  $575 \pm 56$  mg/L and  $2,990 \pm 653$  mg/L were found in VDS and FDS respectively. From the particle size distribution (PSD) study conducted, there was about 87.44% of TSS that has a particle size more than  $2 \mu\text{m}$ . This finding shows that by removing the TSS in anaerobic treated POME, the concentration of solid can be reduced and eventually reduce the organic loading rate in POME treatment system.

In the aeration activated sludge system design, the VSS/TSS ratio is very important for the solids production estimation calculation, where the recommended VSS/TSS ratio for municipal waste water treatment plant system was 0.80 - 0.90 (Metcalf & Eddy, 2004), industrial effluent treatment system for conventional activated sludge system and extended aeration activated sludge system were 0.70 – 0.85 and 0.60 – 0.75 (Department of Environment Malaysia, 2010a) respectively.

However, from the result as shown in Figure 4.1, the calculated VSS/TSS ratio was 0.56, and this value was slightly lower than the recommended design value. This indicated that the actual amount of solid production may less than the design amount of solids production, and indirectly might affect the performance of the activated sludge system where the OLR may not match with operated F/M Ratio. In other words, the OLR (measured in BOD/COD) may be higher than the design value and cause incomplete of the organic matter biodegradation process in activated sludge system. This also might be one of the reasons that the existing activated sludge system cannot comply with the final discharge standard consistently. The value of BOD/COD can be calculated after obtain the value BOD and COD from the analysis of wastewater. Thus, beside the wastewater characteristic study, the further calculation of VSS/TSS need to carry out to find the actual

value of VSS/TSS for system design. In this case, if the obtained value is lower than the recommended design value, indicated that the non-volatile matter is high, and pre-treatment is needed before the biological treatment process such as coagulation-flocculation to eliminate the non-volatile matter which is non-biodegradable.

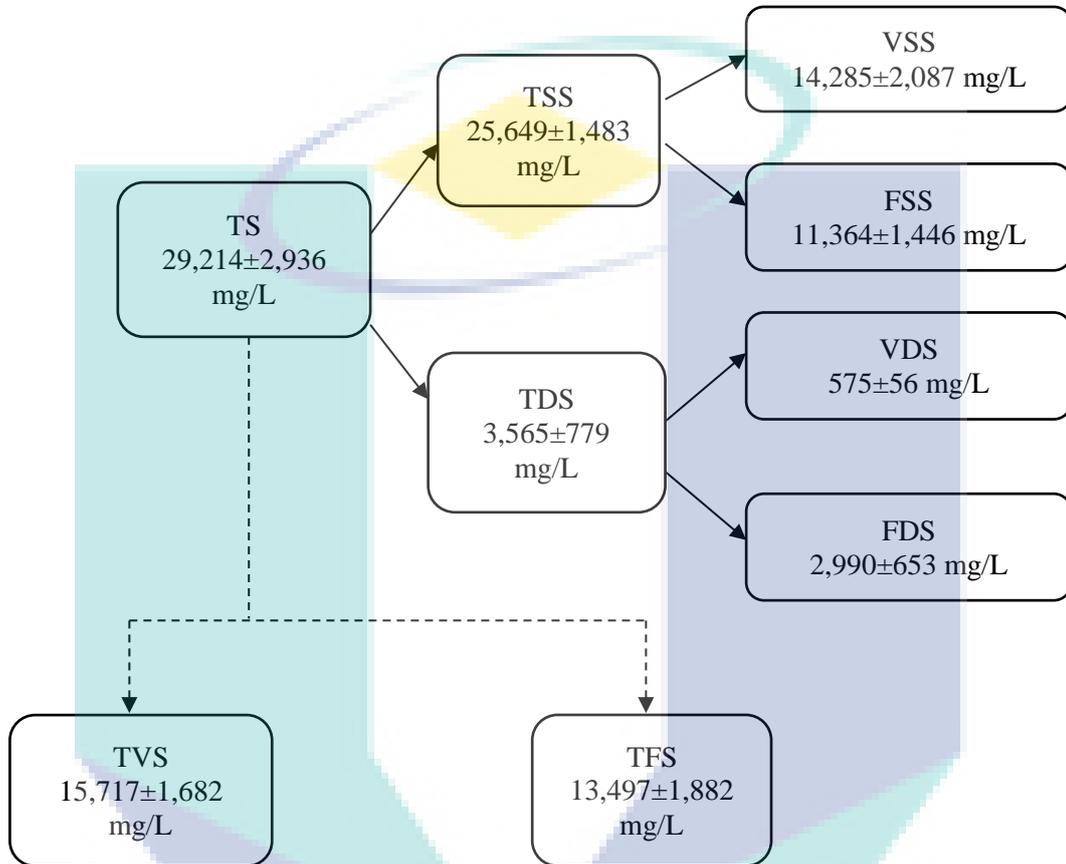


Figure 4.1 Scheme of fractionation of solid content in anaerobic treated POME sample

#### 4.1.1.2 Particle Size Distribution (PSD)

Figure 4.2 shows the particle size distribution of solid present in the anaerobic treated POME sample. The percentage were calculated based on the total weight of 100 g of POME sample. The results show that the highest percentage of solid were 50 - 100  $\mu\text{m}$  of particle size at  $35.18 \pm 0.26\%$  and lowest percentage of solid were 5-10  $\mu\text{m}$  which had found at  $1.48 \pm 0.26\%$ . The solids that less than 2  $\mu\text{m}$  of particle size (also known as total dissolved solids) was found at  $12.58 \pm 0.46\%$ .

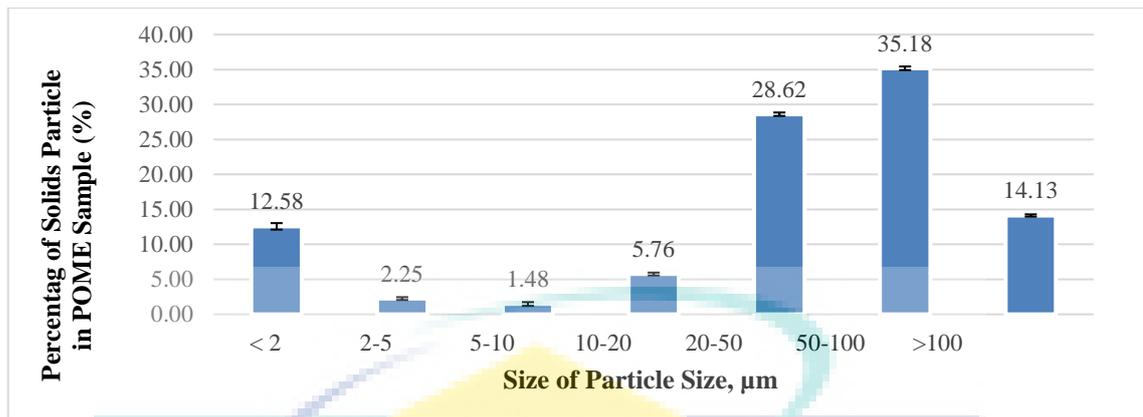


Figure 4.2: Solid particle fractionation of anaerobic treated POME sample

Particle size distribution (PSD) is one of the very important factors for organic matter removal of wastewater evaluation and study (Tran, et al., 2015). Previous studies also reported that the performance of biodegradation process in wastewater was affected by the PSD of wastewater (Karahana et al., 2008; Garcia-Mesa et al., 2010). Most of the organic matter in wastewater had molecular weight more than  $10^3$  amu (atomic mass unit), therefore hydrolysis of molecules in wastewater is required for the biodegradation by bacteria (Sophonsiri and Morgenroth, 2004). For this reason, a better understanding of the PSD of wastewater is needed to ensure the biodegradation process performance can be achieved and complied with the final discharge standard.

In fact, increasing of PSD will lead to increasing of organic matter in wastewater which will increase the chemicals composition especially COD and BOD in waste water (Sophonsiri and Morgenroth, 2004). Thus, particle removal process is crucial and needed in order to reduce the overall amount of organic matter in wastewater. In palm oil industry, some of the palm oil mill had use the filtrations methods, such as bag filtration system, namely Geotube<sup>®</sup> Dewatering Technology where the filter bag was fabricated by high-tenacity polypropylene yarns with pore size distribution 80 -195 µm. From the result shown in Figure 4.2, it is almost 50% of solids with particle size at 50 – 100 µm had been determined in anaerobic treated POME, therefore by using the Geotube<sup>®</sup> Dewatering Technology, 50% of solids particle can be removed and indirectly reduce the organic loading rate.

## 4.1.2 Chemical Composition

Simultaneously, the anaerobic treated POME was also analysed for the chemical composition such as organic matter (namely BOD<sub>3</sub> and COD) and nitrogenous compound (namely TN and AN).

### 4.1.2.1 Composition Analysis of Organic Content

In this study, the mean concentration value of organic content with respect to the concentration of biochemical oxygen demand (BOD<sub>3</sub>) and chemical oxygen demand (COD) in anaerobic treated POME sample were found to have a mean concentration value of  $582 \pm 29$  mg/L and  $2,350 \pm 88$  mg/L respectively. By using the BOD<sub>3</sub> and COD mean concentration value, ratio of BOD<sub>3</sub> and COD were determined as 0.25.

In practical, the organic content of wastewater is normally determined by measurement of COD and BOD<sub>5</sub> (For POME, BOD<sub>3</sub> is measured) during wastewater treatment plant design and operation. However, COD value does not define clearly the information on biodegradable and non-biodegradable compound in wastewater. In fact, BOD<sub>5</sub> value only provide the information for biodegradable compound that can be digested biologically, while chemically biodegraded compound which only can be degraded via chemical oxidation cannot be evaluated by BOD<sub>5</sub> value. Thus, ratio of BOD<sub>5</sub>/COD (BOD<sub>3</sub>/COD for POME) can be used for the biodegradability evaluation of wastewater. In this matter, high ratio of BOD<sub>5</sub>/COD indicated that the wastewater contains high readily biodegradable compound while low ratio of BOD<sub>5</sub>/COD give the indication of high content of slowly biodegradable compound that exist in waste water. In other words, the ratio of BOD<sub>5</sub>/COD is a measurement of organic matter level that can be degraded by microorganism (Mutamim, et al, 2012).

In general, the wastewater with ratio of BOD<sub>5</sub>/COD at between 0.1 to 1.0 could be classified into biodegradable zone where the organic matter can be decomposed by microorganism in nature (Samudro and Mangkoedihardjo, 2010). For the wastewater with the ratio of BOD<sub>5</sub>/COD value of 0.5 or greater, it indicates that the wastewater can be easily degraded by microorganism. If the ratio is below 0.3, the wastewater may consist high content of slowly biodegradable compound (Tchobanoglous and Stensel 2004).

Compared to other industry wastewater study, such as tannery wastewater, ratio of BOD<sub>5</sub>/COD been found at 0.3 due to the high content of organic matter and suspended solids (Durai and Rajasimman, 2011). In addition, the ratio of BOD<sub>5</sub>/COD in range of 0.2-0.3 indicated that the most of organic matter were non-readily biodegradable (Wang et al., 2014).

From this study, the ratio of BOD<sub>3</sub>/COD for POME was found to be 0.25, which is below the ratio of BOD<sub>3</sub>/COD value compared to general wastewater such as sewage wastewater because of the non-readily biodegradable matter in POME especially high content of organic matter and suspended solids. Many researchers had reported that the POME contains high organic matter and suspended solids causing the high level of COD and BOD<sub>3</sub> (Chan et al., 2011; Tabassum et al., 2015; Alhaji et al, 2016; Bashir et al., 2017). In fact, organic matter in POME consisted of both particulate organic matter (POM) and dissolved organic matter (DOM) where both organic matters can be separated by using 0.45 µm filter (Mamais et al., 1993). DOM consists of complex heterogeneous mixture of aliphatic and polycyclic aromatic hydrocarbons (PAHs) compound (Yu et al, 2014).

Study also shown that PAHs had been detected in POME at 100 ppm as a mixture of naphthalene, fluorene, phenanthrene, fluoranthene and pyrene with molecular weight (MW) 128 Da, 166 Da, 178 Da, 202 Da and 202 Da respectively (Rasdy et al., 2008). PAHs with MW more than 300 Da only considered as high MW compound (Pace,1995). Even though PAHs in POME were not classified as high MW compound, the present of PAHs in POME that are biological recalcitrant to environment due to the non-readily biodegradable matter (Wang and Chen, 2018).

#### **4.1.2.2 Composition Analysis of Nitrogenous Compound**

In this study, only carbonaceous compound in POME had been taken into consideration. Thus, only two components in nitrogenous compound of POME were analysed, namely total nitrogen (TN) and ammoniacal nitrogen (AN). Both TN and AN were found at mean concentration value of  $1,182 \pm 41$  mg/L and  $34 \pm 4$  mg/L respectively. According to the Malaysia discharge standard stipulated under the Environmental Quality Act 1974, (Malaysia, 2017), TN and AN in current POME sample were found to exceed

the discharge standard limit of 200 mg/L and 150 mg/L, respectively.

When the wastewater with 80% of nitrogenous compound was discharged to the water body, it will stimulate the algae growth (Huo et al, 2013). Thus, analysis and characterization of nitrogenous compound in wastewater is crucial for the wastewater treatment plant design, operation and optimization, especially in nitrogenous compound removal process (Sheikh et al, 2016). In palm oil industry, most of palm oil mill is using conventional ponding system for POME treatment and only focus in carbonaceous compound removal which represent by BOD<sub>3</sub>. In the nitrogenous compound removal, palm oil mill does not have a proper nitrification-denitrification process, they only recycled the nitrified POME back to the anaerobic pond for denitrification. However, the nitrification process in anaerobic pond does not provide the significant result due to insufficient hydraulic retention time (Onyia et al, 2001). The efficiency of the nitrification-denitrification process could be increased by reducing the biomass in ponding system by filtration system (Mayo and Abbas, 2014). Furthermore, in order to improve the nitrogenous compound removal in POME, evaluation of mass transfer kinetic for nitrogenous compound in POME will enhance the biological process in POME treatment (Fulazzaky et al, 2017).

#### **4.2 Effect of Operating Parameters on the POME Treatment by Activated Sludge Process**

The performance of activated sludge system was examined by referring to the DOE performance monitoring guidance (DOE, 2010b), which include initial pH of POME, hydraulic retention time (HRT), organic loading rate (OLR), initial mixed liquor volatile suspended solids (MLVSS), solid retention time (SRT) and molasses concentration as the external carbon source.

##### **4.2.1 Effect of pH**

First operating parameter investigated in this study is initial pH of POME. pH of anaerobic treated POME seems to increase gradually to alkaline region, around 8.0 to 9.0 after treatment, due to the high content of available phosphate during biodegradation process of POME (Huan, 1987). However, this pH range is not the optimal environmental

pH for the healthy grow of microorganism. Thus, a success treatment of POME required it to have a suitable pH environment for microorganism growth and a final pH that comply with the discharge standard limit set by the DOE at pH 5.5 – 9.0. In this study, HRT was set at 48 hours, SRT was 7 days, MLVSS in the system was  $2,000 \pm 200$  mg/L with OLR of 0.31 g BOD<sub>3</sub>/L.day, molasses concentration of 20 mg/L and the pH was varied from  $4.0 \pm 0.1$  to  $10.0 \pm 0.1$ .

Figure 4.3 shows that when the initial pH of POME is in the acidic region (pH 4.00 – 6.00), the pH attained after treatment is within pH 6.00 to 7.00. Above these initial pH range, there was a drastic increment to the final pH achieved. When the initial pH of POME is above pH 6.50, pH after treatment would be above pH 8 and increased with the increment of initial pH. Hence, the ideal initial pH of POME seems to be pH 4.00 to 6.50.

Conventionally, the initial pH of POME in the acidic region (pH 4.00 – 6.00) usually can be seen in an anaerobic system, where the available phosphorus content will be removed in the anoxic condition (Yamashita and Ikemoto, 2014). Thus, there is no significant increment of POME pH at the end of treatment. However, due to the incomplete phosphorus removal, it might lead to the carryover of remainder phosphorus into the facultative or aerobic system. The carryover phosphorus will be absorbed and precipitated in the soil during biodegradation process of POME and gradually increase the POME pH along the facultative and aerobic system (Okwute & Isu, 2007; Eze et.al, 2013). Since there is no anoxic condition control in the current experiment for the available phosphorus removal, the pH was found increasing gradually from pH 6.20 to pH 8.1 when the initial pH is greater than 6.00 as shown in Figure 4.3. In this case, the optimum pH obtained from this experiment have similar pH range with the optimum pH reported by other aerobic system study where the optimum pH was found to be ranging from 6.50 to 7.50 (Zielinska et al., 2012).

Figure 4.3 also depicts the specific oxygen uptake rate (SOUR) of the microorganism in the POME. Generally, the SOUR achieved by the system was lower than the recommended value provided in the guidance document of the Malaysian Department of Environment. The recommended value of SOUR is 8 - 20 mg O<sub>2</sub>/h.g MLVSS (DOE, 2010b), but at all initial pH of POME, the SOUR value attained was less than 5.00 mg O<sub>2</sub>/h.g MLVSS. The highest SOUR value obtained is at the initial pH of

6.50 (4.33 mg O<sub>2</sub>/h.g MLVSS). In the study of Zielinska et al. (2012), they reported that at pH 6.50 to 7.50, the microbial population had the highest growth rate and the SOUR value obtained indicating that the bacteria are able to grow healthily in the municipal wastewater treatment system. In order to increase the SOUR value, the biomass and solids in aeration tank need to be reduced by increasing the OUR of microorganism.

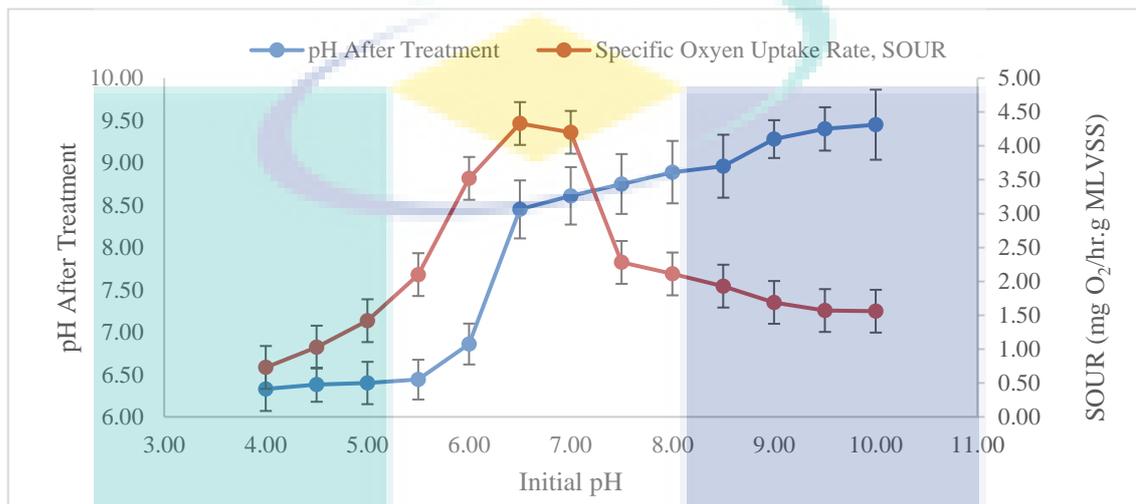


Figure 4.3 Effect of initial pH on the pH after treatment and specific oxygen uptake rate of POME with operating condition: HRT = 48 hours, SRT = 7 days, MLVSS = 2,000 ± 200 mg/L, OLR = 0.31 g BOD<sub>3</sub>/L.day, molasses concentration = 20 mg/L

A good treatment system with an optimum organic removal should attain a MLVSS:MLSS ratio above 0.8 (Harun & Annuar, 2014). Figure 4.4 illustrates that the only system barely achieved 0.8 from graph was the one with initial pH of 7.00. This result disclosed that the conditions of POME are not ideal for the sustaining growth of the microorganism due in which the reason behind required further investigation.

Figure 4.4 shows the percentage reduction of BOD<sub>3</sub> and COD in POME treatment by activated sludge system. Maximum BOD<sub>3</sub> reduction was around 61.61% at initial pH of 7.50 with the final BOD<sub>3</sub> after treatment at a value of ~ 253 mg/L, which does not meet the DOE final discharge standard of 100 mg/L. Maximum COD reduction was at a value of 68.74% which occurred at initial pH of 7.50. Therefore, the ideal initial pH of POME is around pH 6.5 to 7.50, pH 6.50 was chosen as the optimal for the following study because the pH 6.50 to 7.50 is optimum pH for microorganism growth in activated sludge system (Zielinska et al., 2012). The microorganism remains sufficiently active within pH

6.50 – 8.00; outside of this pH range can inhibit or completely stop biological activity (WEF, 2008).

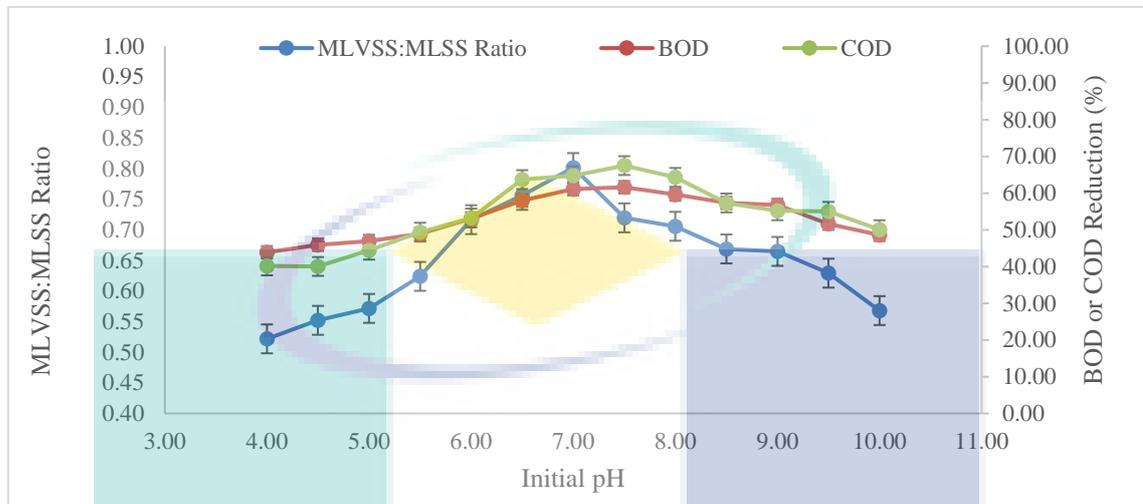


Figure 4.4 Effect of initial pH of POME on MLVSS:MLSS ratio and BOD<sub>3</sub> and COD reduction of POME with operating condition: HRT = 48 hours, SRT = 7 days, MLVSS = 2,000 ± 200 mg/L, OLR = 0.31 g BOD<sub>3</sub>/L.day, molasses concentration = 20 mg/L

#### 4.2.2 Effect of Hydraulic Retention Time (HRT)

Hydraulic retention time is a key parameter to determine the period for the treatment of POME up to the required standard. Too short a period may not enough to enable a complete treatment of the waste, while too long a period is not practical for a high capacity incoming waste like POME. This is mainly due to a big land area would be required for the construction of the plant, which is a significant extra cost to the newly set up plant and a limitation to the existing plant. In this study, the initial pH of the POME was adjusted to 6.5 ± 0.1, SRT was 7 days, MLVSS of the system was at a value of 2,000 ± 200 mg/L with OLR of 0.31 g BOD<sub>3</sub>/L.day, molasses concentration at 20 mg/L and the HRT was varied from 12 h to 144 h.

Figure 4.5 shows that when the HRT was increased from 12 h to 24 h, the pH of POME after treatment increased from 7.33 to 8.30. Above HRT of 24 h, the pH value after treatment increased insignificantly and the value is always less than pH 9.00. It can be seen that the SOUR value was still below the healthy level of 8 mg O<sub>2</sub>/h.g MLVSS irrespective of the HRT period. The maximum SOUR occurred between 48 to 60 h HRT

at a value of  $\sim 4.60 \text{ mg O}_2/\text{h.g MLVSS}$ . Above this HRT, SOUR was constant at a value range of  $3.00 - 4.00 \text{ mg O}_2/\text{h.g MLVSS}$ .

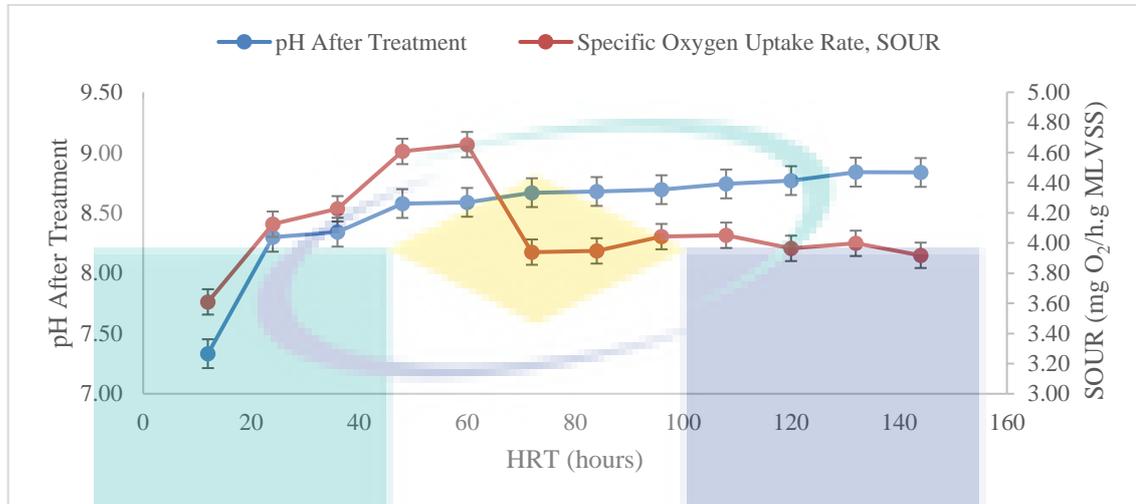


Figure 4.5 Effect of HRT of POME on pH after treatment and specific oxygen uptake rate of POME with operating condition: initial pH of the POME =  $6.5 \pm 0.1$ , SRT = 7 days, MLVSS =  $2,000 \pm 200 \text{ mg/L}$ , OLR =  $0.31 \text{ g BOD}_3/\text{L.day}$ , molasses concentration =  $20 \text{ mg/L}$

Similarly, Figure 4.6 depicts that the ratio of MLVSS:MLSS increased when the HRT was increased and attained a maximum value around 0.78 at HRT between 48 to 60 h. Further increased in the HRT causes a decreased in the MLVSS:MLSS ratio. This may be due to the depletion of nutrients when times prolong that causing the death of some of the microorganism and reduction in OLR (Muda et al., 2011).

As shown in the Figure 4.6, the maximum reduction of  $\text{BOD}_3$  (63.09%) and COD (62.66%) occurred at HRT of 48 hours. Nevertheless, after 48 hours HRT, the plot doesn't show the significant reduction of  $\text{BOD}_3$  and COD. This indicated that most of the readily biodegradable organic matter had been completely digested and remained only the non-biodegradable organic matter in the supernatant. Vijayaraghavan (2007) reported that at 36 hours of HRT, activated sludge process able to achieve 83% of COD removal efficiency for initial COD of POME at  $1,000 \text{ mg/L}$  with MLSS concentration of about  $3,900 \pm 200 \text{ mg/L}$ . The study also showed that aerobic digester could be effective in treating the anaerobically digested POME at HRT up to 7.2 days (Chou et al., 2016). However, it is not practical in operating the aerobic system for POME treatment in longer

HRT and high concentration of MLSS due to the characteristic of POME with high non-biodegradable matter. Thus, the optimal HRT chosen for the following study is 48 hours, in which after 48 hours there is no significant of reduction in COD or BOD as well as increasing of biomass in MLSS and MLVSS.

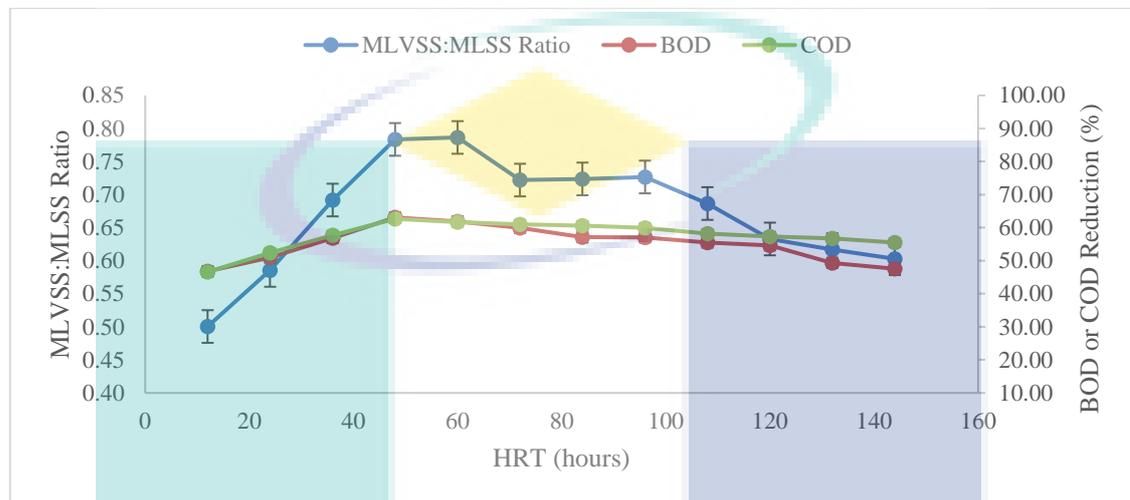


Figure 4.6 Effect of HRT of POME on MLVSS:MLSS ratio and BOD<sub>3</sub> and COD reduction of POME with operating condition: initial pH of the POME = 6.5 ± 0.1, SRT = 7 days, MLVSS = 2,000 ± 200 mg/L, OLR = 0.31 g BOD<sub>3</sub>/L.day, molasses concentration = 20 mg/L

#### 4.2.3 Effect of Organic Loading Rate (OLR)

In this experiment, the OLR was varied between 0.15 g BOD<sub>3</sub>/L.day to 0.38 g BOD<sub>3</sub>/L.day while the initial pH was adjusted to 6.5 ± 0.1, HRT was fixed at 48 h, SRT was 7 days and the MLVSS of the system was at a value of 2,000 ± 200 mg/L and molasses concentration of 20 mg/L.

Figure 4.7 depicts that when the OLR increased from 0.27 g BOD<sub>3</sub>/L.day to 0.38 g BOD<sub>3</sub>/L.day, the pH after treatment increased from 7.29 to 10.59. The pH value was fairly constant between OLR of 0.30 g BOD<sub>3</sub>/L.day to 0.34 g BOD<sub>3</sub>/L.day. Above OLR of 0.35 g BOD<sub>3</sub>/L.day, the pH after treatment increased rapidly when the OLR increased. The pH value exceeded the maximum allowable limit of the standard; hence, this system is not suitable to treat the POME with the incoming organic loading of more than 0.35 g BOD<sub>3</sub>/L.day. The SOUR at all the OLR values was less than 6 mg O<sub>2</sub>/h.g MLVSS. The

maximum SOUR of 5.52 mg O<sub>2</sub>/h.g MLVSS was achieved at OLR value of 0.31 g BOD<sub>3</sub>/L.day. It is obvious that the SOUR of the system was improved as compared to the previous two sections. Nevertheless, it is still below the recommended value of 8 mg O<sub>2</sub>/h.g MLVSS.

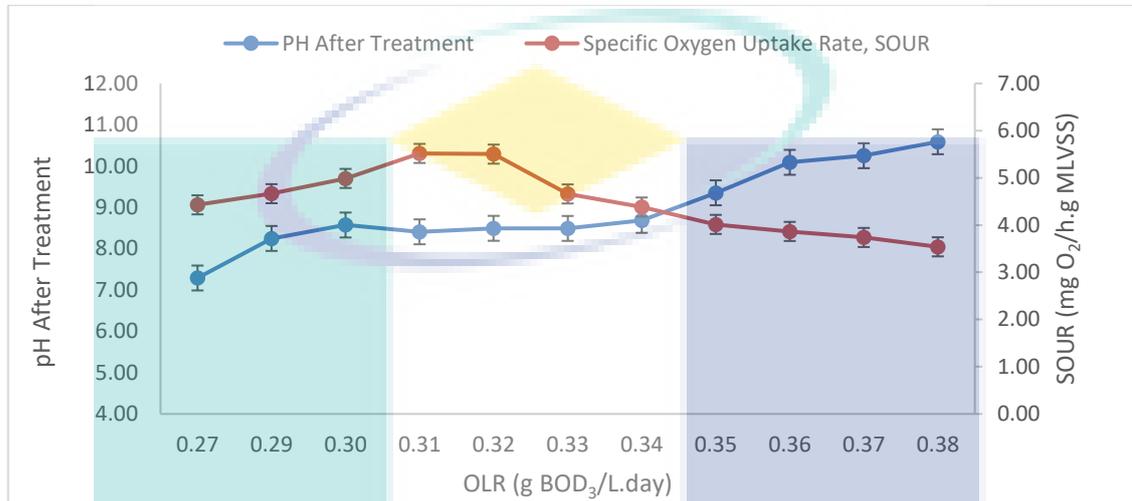


Figure 4.7 Effect of OLR of POME on pH after treatment and specific oxygen uptake rate with operating condition: the initial pH = 6.5 ± 0.1, HRT = 48 h, SRT = 7 days, MLVSS = 2,000 ± 200 mg/L, molasses concentration = 20 mg/L

Figure 4.8 illustrates that when the OLR was increased, the MLVSS: MLSS ratio also increased. A maximum value of 0.8 was attained at OLR value of 0.31 g BOD<sub>3</sub>/L.day. At this value of OLR, percentage reduction of BOD<sub>3</sub> and COD were 61.10% and 63.72%. These were also the maximum reduction that could be achieved in this study. Based on the results obtained in this section, the OLR was fixed at a value of 0.31 g BOD<sub>3</sub>/L.day in the following studies. When the OLR increased, it had depressed the dissolved oxygen in aeration tank, lead to a decreasing of biomass in MLSS and MLVSS. Furthermore, high concentration of OLR also cause the increasing of slowly biodegradable or non-biodegradable organic content. Once the biomass had reduced, the biodegradable process in aeration tank was also being affected and causing incomplete degradation of the biodegradable content. Eventually, the efficiency of BOD and COD removal decreases.

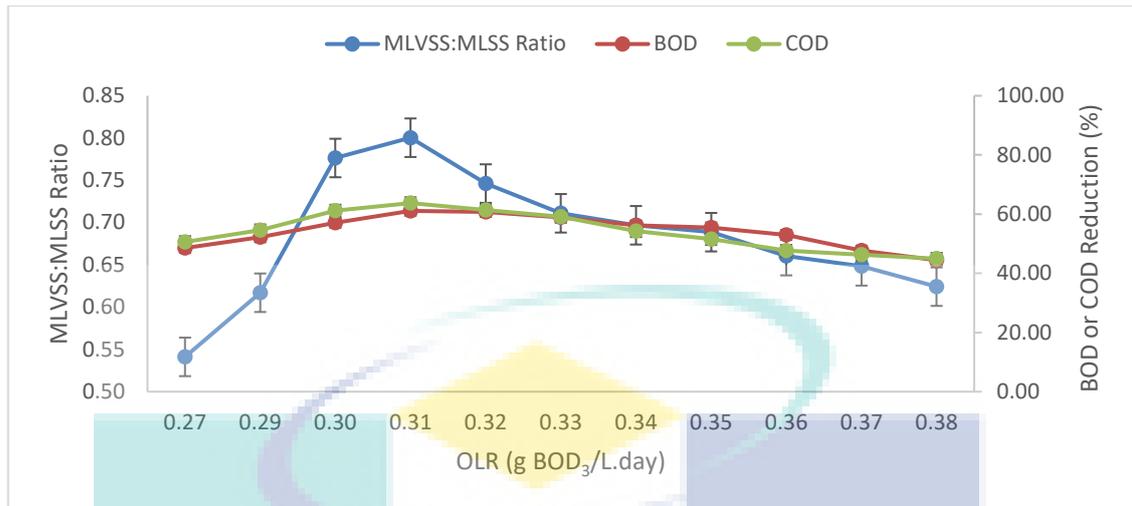


Figure 4.8 Effect of OLR of POME on MLVSS:MLSS ratio and BOD<sub>3</sub> and COD reduction of POME with operating condition: the initial pH = 6.5 ± 0.1, HRT = 48 h, SRT = 7 days, MLVSS = 2,000 ± 200 mg/L, molasses concentration = 20 mg/L

#### 4.2.4 Effect of Mixed Liquor Volatile Suspended Solids (MLVSS)

Mixed liquor volatile suspended solids represent the amount of microorganism available to digest and treat the POME. It is resembling the inoculum size in a fermentation. A sufficient amount of inoculum is required to start a fermentation and digest (or treated) the organic compound in the POME to meet the discharge standard within the HRT. Thus, the MLVSS was varied from 1,000 to 10,000 mg/L at a fixed HRT of 48 h in this study. The pH of the initial POME was adjusted to 6.50 ± 0.1 with the OLR of 0.31 g BOD<sub>3</sub>/L.day, SRT of 7 days and molasses concentration at 20 mg/L.

Illustrated in Figure 4.9 is the pH after treatment. There is an insignificant increased when the initial MLVSS was increased from 2,000 mg/L to 10,000 mg/L. pH after treatment was around 7.29 when initial MLVSS was at a value of 1,000 mg/L, but above this value the pH was above 8.00. Nonetheless, the pH after treatment was still within the standard limit in the range of study. When the initial MLVSS was between 5,000 mg/L to 6,000 mg/L, the SOUR attained for the system was around 5.50 mg O<sub>2</sub>/h.g MLVSS, which is the maximum SOUR that could be achieved by the system within the range of MLVSS. Unfortunately, it is still below the recommended limit.

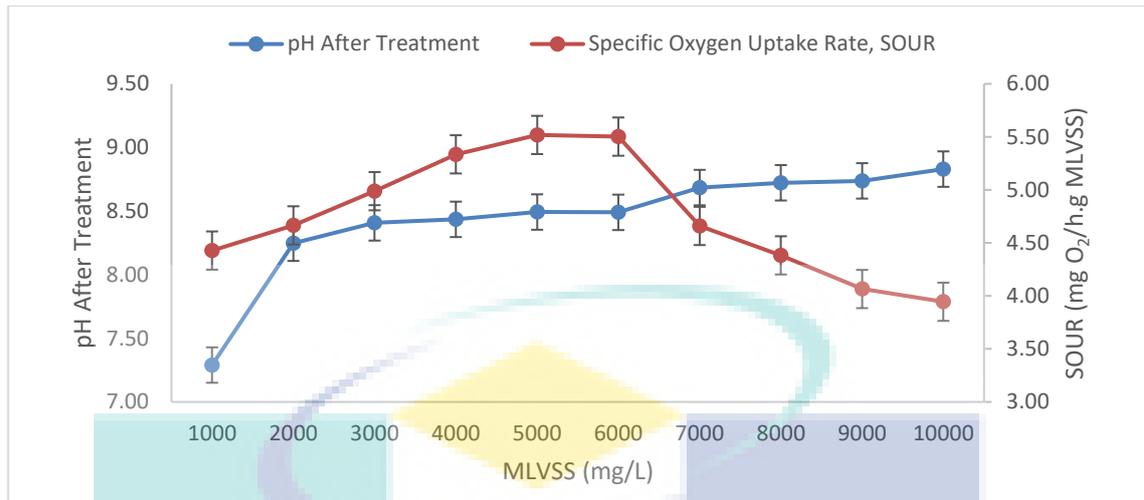


Figure 4.9 Effect of initial MLVSS of POME on pH after treatment and specific oxygen uptake rate with operating condition: the initial pH =  $6.5 \pm 0.1$ , HRT = 48 h, OLR of 0.31 g BOD<sub>3</sub>/L.day, SRT = 7 days, molasses concentration = 20 mg/L

The maximum ratio of MLVSS:MLSS achieved by the system in the range of MLVSS studied was only about 0.8 as depicted in Figure 4.10. This maximum ratio occurred at initial MLVSS value of 5,000 mg/L. Likewise, the maximum BOD<sub>3</sub> reduction (60.74%) and COD reduction (66.65%) also happened at the same MLVSS value (Figure 4.10). Therefore, initial MLVSS value of 5,000 mg/L seems to be an optimal value to initiate the treatment process. The available organic matter in the POME, which is reflected by COD and BOD values, is sufficient for the growing of biomass when MLVSS is ranging from 2,000 – 5,000 mg/L. Nevertheless, when the MLVSS has over the value of 5,000 mg/L, with the same amount food that is provided to the aeration tank, it has become insufficient. This has reduced the amount of MLSS and MLVSS, which was indicated by MLSS:MLVSS ratio value. Once the biomass in MLSS and MLVSS is dropped, the removal efficiency of COD and BOD also affected. It can be explained that the growth of biomass is very depending on F/M ratio where the food supply must be sufficient for the total amount of biomass population as required in F/M ratio.

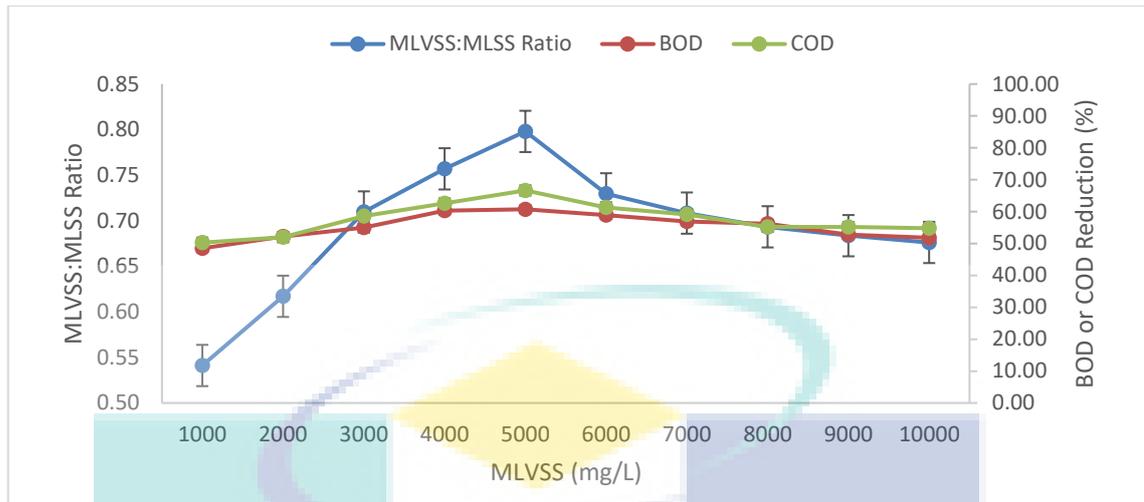


Figure 4.10 Effect of initial MLVSS of POME on MLVSS:MLSS ratio and BOD<sub>3</sub> and COD reduction with operating condition: the initial pH = 6.5 ± 0.1, HRT = 48 h, OLR of 0.31 g BOD<sub>3</sub>/L.day, SRT = 7 days, molasses concentration = 20 mg/L

Practically, it is hard to get initial MLVSS of more than 2,000 mg/L in the existing plant. A concentration step of activated sludge would be required if a higher amount of MLVSS is desired. This would indicate an extra process unit prior to the polishing plant, which also means extra cost and space. Since it is practically not feasible, the following study would still use MLVSS of 2,000 ± 200 mg/L.

#### 4.2.5 Effect of Solid Retention Time (SRT)

The SRT was varied from 2 days to 20 days in this study, where the initial pH of the POME was adjusted to 6.5 ± 0.1 with a MLVSS for the system of 2000 ± 200 mg/L OLR of 0.31 g BOD<sub>3</sub>/L.day and molasses concentration at 20 mg/L. The HRT was fixed at 48 h.

Figure 4.11 depicts that when SRT was increased from 2 days to 6 days, the pH after treatment increased from 7.3 to 8.6 and remained quite constant up to SRT value of 12 days. The pH after treatment increased steadily when SRT was increased above 12 days. Too old a sludge seems to give some negative impact to the system where removal of excessive activated sludge is reduced and cause the increasing of biomass in MLSS and MLVSS, which will lead to insufficient food for bacteria. Usually, this condition can cause foaming in aeration tank and cloudiness of supernatant, eventually the system failed

to comply with the DOE discharge standard (Schuyler, 2010). The maximum SOUR achieved was around 5.5 mg O<sub>2</sub>/h/g MLVSS at SRT of about 10 days. When the SRT is less or more than 10 days, the SOUR values were lower, indicating a non-healthy growth of the microorganism.

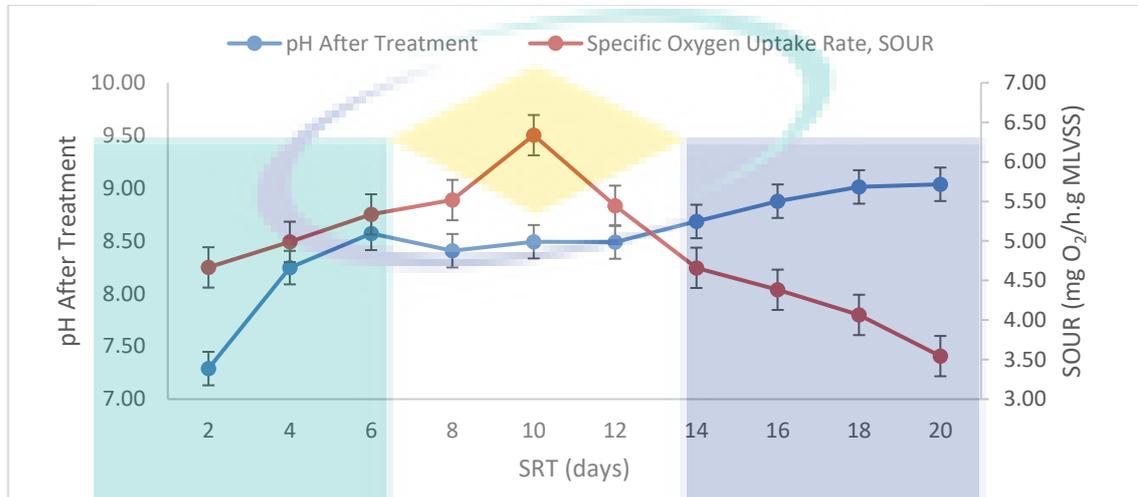


Figure 4.11 Effect of SRT of POME on pH after treatment and specific oxygen uptake rate of POME with operating condition: the initial pH = 6.5 ± 0.1, HRT = 48 h, OLR of 0.31 g BOD<sub>3</sub>/L.day, MLVSS of 2,000 ± 200 mg/L, molasses concentration = 20 mg/L

The maximum ratio of MLVSS:MLSS also took place at SRT of 10 days. The ratio was only around 0.8 (Figure 4.12). After 10 days of HRT, there is insufficient of food that provided to bacteria and cause bacteria death in starving. When the biomass of MLSS and MLVSS are reduced, incomplete biodegradable process is occurred and reduced the COD and BOD removal efficiency. This is in line with the results shown in Figure 4.12, where the maximum BOD<sub>3</sub> reduction was around 60% at SRT of 10 days, while the maximum COD reduction was about 67% at the same SRT value. Even though the overall performance of the system was not entirely efficient, the best SRT within the range of study was still able to be identified, which was 10 days. However, if the HRT too short or sludge too young, the bacteria is not matured enough and could not complete the biodegradable process. As a result, excess organic matter which contribute to COD and BOD will be carried over to the final discharge and exceeded the DOE discharge standard value.

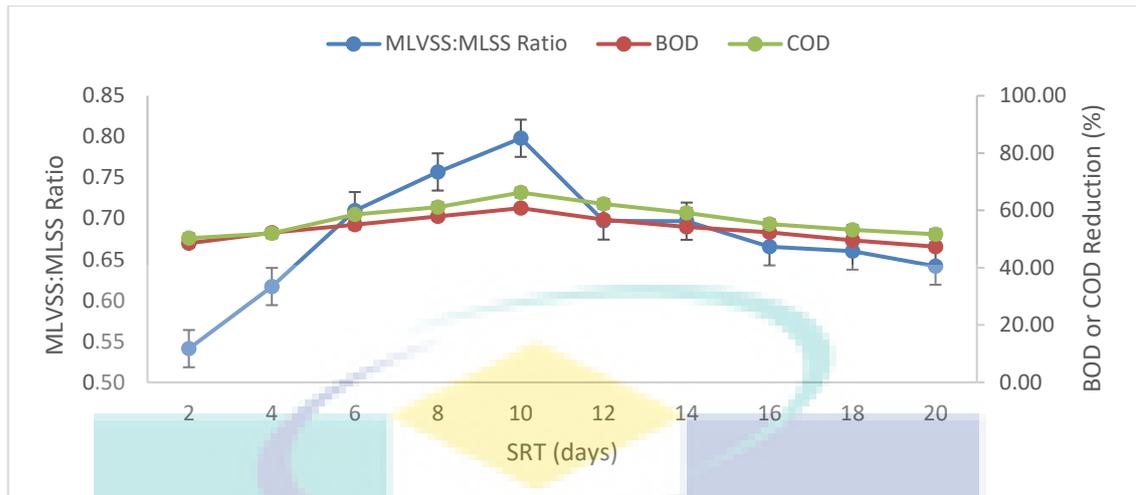


Figure 4.12 Effect of SRT of POME on MLVSS:MLSS ratio and BOD<sub>3</sub> and COD reduction of POME with operating condition: the initial pH = 6.5 ± 0.1, HRT = 48 h, OLR of 0.31 g BOD<sub>3</sub>/L.day, MLVSS of 2,000 ± 200 mg/L, molasses concentration = 20 mg/L

#### 4.2.6 Effect of External Carbon Source

In view of the possible nutrient limitation, this section examined the effect of adding molasses as an external carbon source to the activated sludge system. Molasses was known to be a type of carbon source that is typically supplemented to the fermentation system. As the biological treatment of POME is similar to the fermentation process, molasses was chosen as a carbon source because it is available in large quantity industrially and also cheap in price, which is always a main concern in the industrial perspective. Molasses concentration up to 100 mg/L was supplemented to the POME at the beginning of the reaction in this experiment. Other operating conditions were fixed at the optimal value obtained from the previous sections. That is initial pH of 6.50 ± 0.1 with a MLVSS of the system of 2000 ± 200 mg/L at SRT of 10 days for HRT 48 h and OLR of 0.31 g BOD<sub>3</sub>/L.day.

Figure 4.13 illustrates that addition of molasses did not affect the pH after treatment irrespective of the molasses concentration. This is because pH in the aeration tank is very depending on the phosphorus concentration instead of the concentration of molasses. The pH after treatment is still within the range of standard set by the DOE. When the concentration of molasses added was increased, there was an increment in the SOUR of the system (Figure 4.24). However, at molasses concentration greater than 50

mg/L, the SOUR remained constant at the value of 8.13 mg O<sub>2</sub>/h.g MLVSS due to the growing of biomass in MLSS and MLVSS had reached the maximum limit with constant respiration rate. Since the higher SOUR reflects the healthier is the microorganism, this system is only barely exceeding the minimum requirement of 8 mg O<sub>2</sub>/h.g MLVSS, indicating the vulnerability of the system. In other words, any disturbance would easily upset the system.

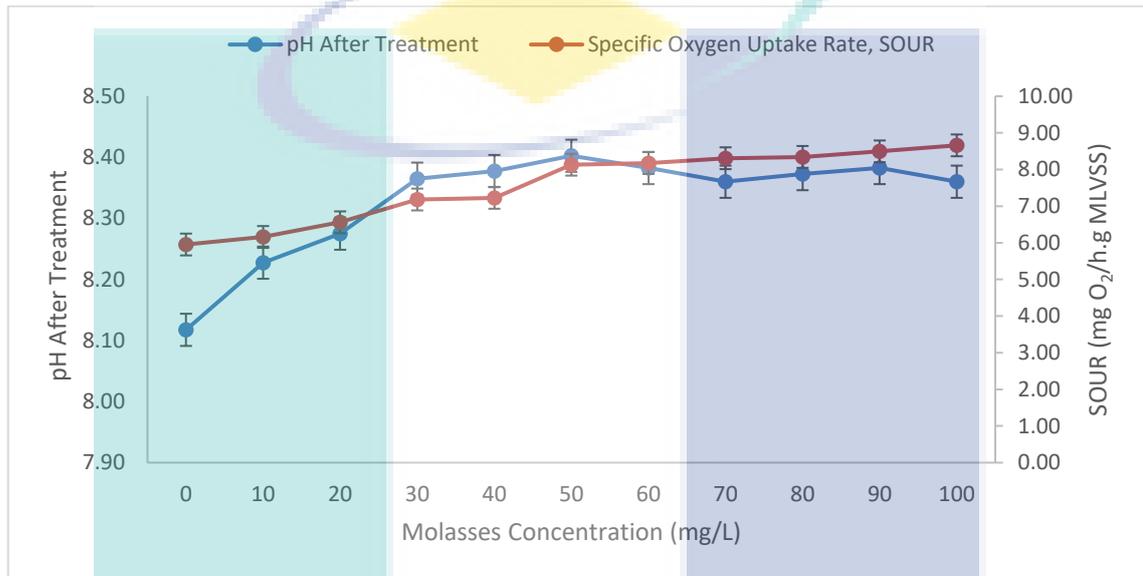


Figure 4.13 Effect of molasses as external carbon source concentration on pH after treatment and specific oxygen uptake rate of POME with operating condition: initial pH =  $6.50 \pm 0.1$ , MLVSS =  $2000 \pm 200$  mg/L, SRT = 10 days, HRT = 48 h, OLR = 0.31 g BOD<sub>3</sub>/L.day

Figure 4.14 shows that once the molasses concentration fed exceeded 50 mg/L, the MLVSS:MLSS ratio would be more than 80. Nevertheless, differences in the ratio was not significant as indicated by the error bar. Correspondingly, the percentage reduction of BOD<sub>3</sub> and COD was not significant with the value of 61 - 69% and 62 - 67%, respectively. This mean that addition of molasses did not aid in the treatment of POME even though it facilitates the healthy grow of the microorganism. Molasses, as a degradable organic component, was only functioned as the food to the microorganism, thus improved the SOUR and support the growth of the microorganism. Other organic components in the POME, however, were non-degradable or slow degradable. As a consequence, there was no further reduction of BOD<sub>3</sub>, or COD could be observed.

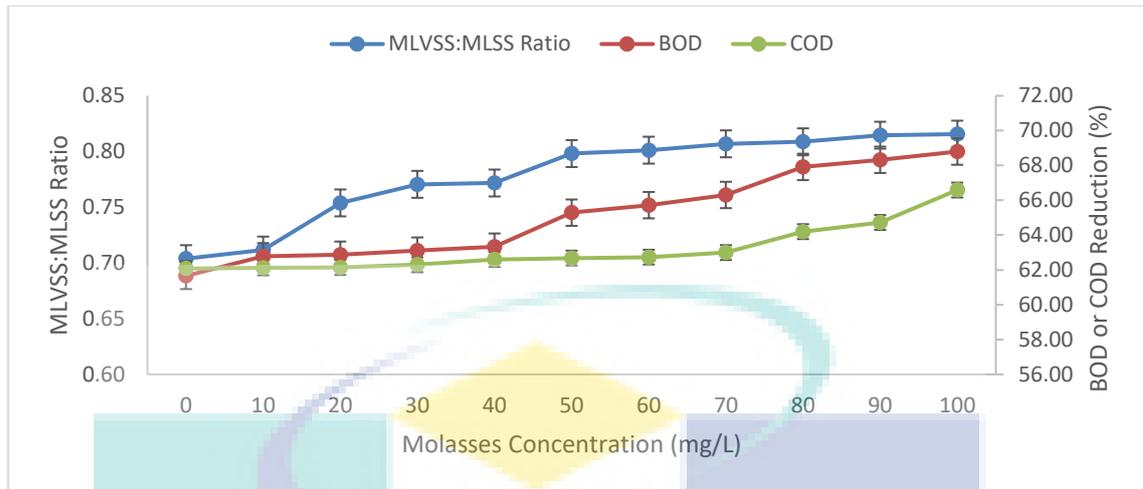


Figure 4.14 Effect of molasses as external carbon source concentration on MLVSS:MLSS ratio and BOD<sub>3</sub> and COD reduction with operating condition: initial pH = 6.50 ± 0.1, MLVSS = 2000 ± 200 mg/L, SRT = 10 days, HRT = 48 h, OLR = 0.31 g BOD<sub>3</sub>/L.day

### 4.3 BOD Kinetic Study of POME

Due to the performance of POME treatment by activated sludge process did not achieved the expected BOD<sub>3</sub> less than 20 mg/L, the BOD kinetic study was conducted to determine the ultimate BOD and reaction rate constant. For this purpose, three samples of BOD were taken during 7-days incubation as shown in Table 4.1.

Table 4.1 BOD result for three samples of POME during 7-days incubation

<i>t</i> (day)	BOD <sub><i>t</i></sub>	Sample 1, (mg/L)	Sample 2, (mg/L)	Sample 3, (mg/L)	Average, (mg/L)
1	BOD <sub>1</sub>	214	207	240	220
2	BOD <sub>2</sub>	459	423	453	445
3	BOD <sub>3</sub>	651	669	663	661
4	BOD <sub>4</sub>	774	750	783	769
5	BOD <sub>5</sub>	801	822	834	819
6	BOD <sub>6</sub>	876	869	897	880
7	BOD <sub>7</sub>	993	987	975	985

\*All BOD is measured in unit of mg/L.

The average BOD result was used for the BOD kinetic parameters estimation in the subsequent subsections by using different methods such as least square method, Fujimoto Method, Thomas graphical method, log different method and method of moment.

### 4.3.1 Least Square Method

According to the least square methods, in order to determine the  $L_0$  and  $k_1$  value, Eq. 2.5 and Eq. 2.6 as following need to be solved:

$$ma + b\Sigma y - \Sigma y' = 0$$

and

$$a\Sigma y + b\Sigma y^2 - \Sigma yy' = 0$$

where  $m$  = number of data point minus one

$y$  = BOD exerted at time  $t$ , mg/L

$y'$  = rate of change of BOD

$$= \frac{dy}{dt}$$

$$= \frac{y_{n+1} - y_{n-1}}{2\Delta t}$$

By using the BOD result in Table 4.1, value for  $n$ ,  $\Sigma y$ ,  $\Sigma y'$ ,  $\Sigma y^2$ ,  $\Sigma yy'$  and  $2\Delta t$  was calculated and shown in Table 4.2.

Table 4.2 Computation table for  $L_0$  and  $k_1$  determination by using least square methods

<b>BOD<sub>t</sub></b>	<b>BOD, y (mg/L)</b>	<b><math>y_{n+1} - y_{n-1}</math></b>	<b><math>2\Delta t</math></b>	<b><math>y'</math></b>	<b><math>y^2</math></b>	<b><math>yy^2</math></b>
BOD <sub>0</sub>	0					
BOD <sub>1</sub>	220	445	2	222.5	48,400	48,950.0
BOD <sub>2</sub>	445	441	2	220.5	198,025	98,122.5
BOD <sub>3</sub>	661	324	2	162.0	436,921	107,082.0
BOD <sub>4</sub>	769	158	2	79.0	591,361	60,751.0
BOD <sub>5</sub>	819	111	2	55.5	670,761	45,454.5
BOD <sub>6</sub>	880	166	2	83.0	774,400	73,040.0
BOD <sub>7</sub>	985					
<b>Sum</b>	<b>3,794<sup>(a)</sup></b>		<b>12</b>	<b>822.5</b>	<b>2,719,868</b>	<b>433,400</b>

<sup>(a)</sup> Value of BOD<sub>7</sub> not included in total and  $n = 6$

After solving the Eq. 2.5 and Eq.2.6, the value of  $L_0$  and  $k_1$  are determined to be:

Ultimate BOD,  $L_0$  = 1,139.58 mg/L

Reaction rate constant,  $k_1$  = 0.270 /day

### 4.3.2 Fujimoto Method

A plot of  $BOD_{t+1}$  versus  $BOD_t$  for 7 days and a plot of the straight line with a slope of 1 had been constructed together as in Figure 4.15.

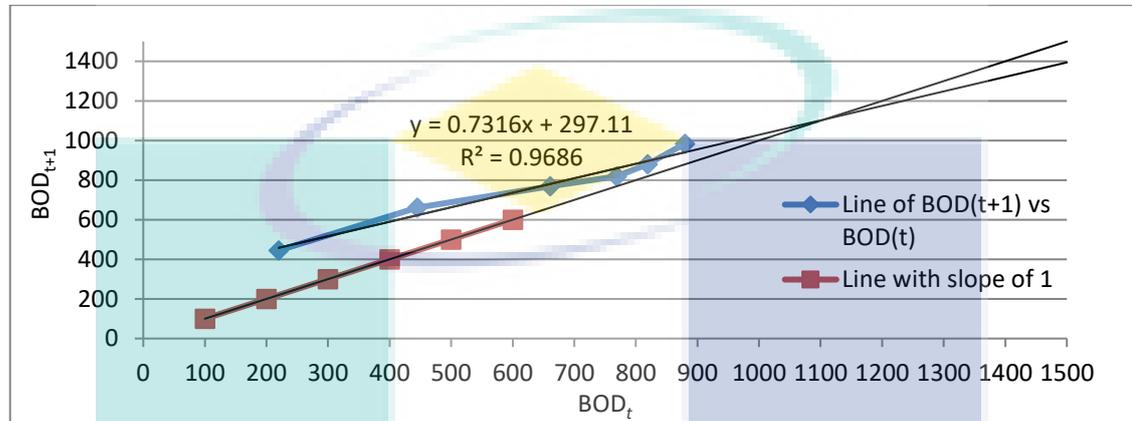


Figure 4.15 Plot of  $BOD_{t+1}$  versus  $BOD_t$  and plot of the straight line with a slope of 1

From the plot in Figure 4.15, the value gained at the intersection point of the 2 plots corresponds to the ultimate BOD,  $L_0 = 1,100.00$  mg/L and reaction rate constant,  $k_1$  gained from the Eq.2.3 where the  $k_1 = 0.034$ /day.

### 4.3.3 Thomas Graphical Method

According to the Thomas method, Eq. 2.9 can be plotted as a straight line with  $(t/y)^{1/3}$  as a function of time,  $t$ :

$$\left(\frac{t}{y}\right)^{1/3} = \frac{1}{(2.3k_1)^{1/3}} + \frac{k_1^{2/3}}{3.43L_0^{1/3}} \cdot t$$

- where  $y$  = BOD exerted in time  $t$ , mg/L  
 $k_1$  = Reaction rate constant (base 10)  
 $L_0$  = Ultimate BOD, mg/L

A plot of  $(t/y)^{1/3}$  as a function of time,  $t$  was then constructed accordingly as shown in Figure 4.16.

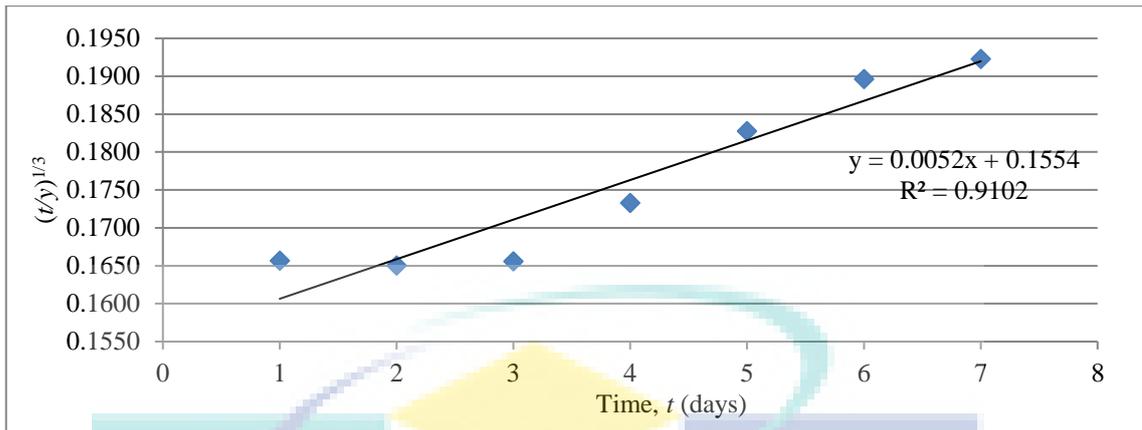


Figure 4.16 Plot of  $(t/y)^{1/3}$  as a function of time,  $t$  (days)

From the plot in Figure 4.16, the ultimate BOD ( $L_0$ ) and reaction rate constant,  $k_1$  and are calculated as following:

$$\begin{aligned} \text{Ultimate BOD, } L_0 &= 1,326.56 \text{ mg/L} \\ \text{Reaction rate constant, } k_1 &= 0.087/\text{day} \end{aligned}$$

#### 4.3.4 Log Different Method

The log different method is based on the Eq. 2.10 as following:

$$\log\left(\frac{dy}{dt}\right) = \log(2.303L_0 \cdot k_1) - k_1 t$$

where the plot of  $\log(dy/dt)$  versus time,  $t$ , day will be plotted on a semilog scale, with the  $t$  value corresponding to the middle of each interval (Mid-interval value of  $t$ ). Value of  $k_1$  and  $L_0$  can be estimated from the plot as follows:

$$\begin{aligned} k_1 &= - (\text{Slope}) \\ L_0 &= 10^{\text{Intercept}} / (2.303k_1) \end{aligned}$$

A plot of  $\log(dy/dt)$  versus time,  $t$ , day had then been constructed as shown in Figure 4.17.

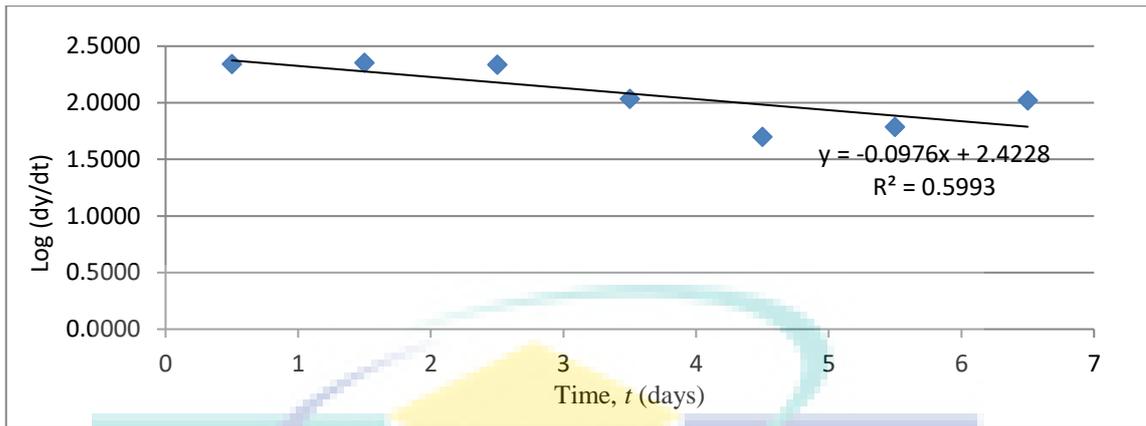


Figure 4.17 Plot of  $\log(dy/dt)$  versus time,  $t$  (days)

From the plot in Figure 4.17, ultimate BOD ( $L_0$ ) and reaction rate constant ( $k_1$ ) are calculated as following:

$$\text{Ultimate BOD, } L_0 = 1,177.62 \text{ mg/L}$$

$$\text{Reaction Rate constant, } k_1 = 0.098/\text{day}$$

#### 4.3.5 Method of Moment

In the Method of Moments, Moore's diagram needs to be prepared for BOD-7 days. Moore's diagram is a nomograph which displaying the relationship between  $k_1$ ,  $\Sigma y/L_0$ , and  $\Sigma y/\Sigma yt$ . It is constructed by using the Eq.211 and Eq.2.12 as following:

$$\frac{\Sigma y}{L_0} = n - \left[ \frac{10^{-k_1}(10^{-nk_1} - 1)}{(10^{-k_1} - 1)} \right]$$

$$\frac{\Sigma y}{\Sigma yt} = \frac{n - \left[ \frac{10^{-k_1}(10^{-nk_1} - 1)}{(10^{-k_1} - 1)} \right]}{\sum_{i=1}^{i=n} i - \sum_{i=1}^{i=n} i \times 10^{-ik_1}}$$

where  $\Sigma y$  = sum of BOD

$\Sigma yt$  = sum of BOD value multiply with the incubation time

$n$  = no of days of incubation for the serial BOD test

$k_1$  = BOD rate constant

$L_0$  = Ultimate BOD

To construct the Moore's diagram for BOD-7 days,  $n = 7$ , Eq. 2.11 will gain Eq.2.13 as following:

$$\frac{\Sigma y}{L_0} = 7 - [10^{-k_1}(10^{-7k_1} - 1)/(10^{-k_1} - 1)]$$

And Eq. 2.12 will yield Eq. 2.14 as following:

$$\frac{\Sigma y}{\Sigma y t} = \frac{7 - [10^{-k_1}(10^{-7k_1} - 1)/(10^{-k_1} - 1)]}{28 - \sum_{i=1}^{i=7} i \times 10^{-ik_1}}$$

where

$$\sum_{i=1}^{i=n} i = \sum_{i=1}^{i=7} i = 1 + 2 + 3 + 4 + 5 + 6 + 7 = 28$$

$$\sum_{i=1}^{i=7} i \times 10^{-ik_1} = (10^{-k_1}) + (2 \times 10^{-2k_1}) + (3 \times 10^{-3k_1}) + (4 \times 10^{-4k_1}) + (5 \times 10^{-5k_1}) + (6 \times 10^{-6k_1}) + (7 \times 10^{-7k_1})$$

A plot of  $\Sigma y/L_0$  and  $\Sigma y/\Sigma y t$  with different  $k_1$  value had been constructed as shown in Figure 4.18.

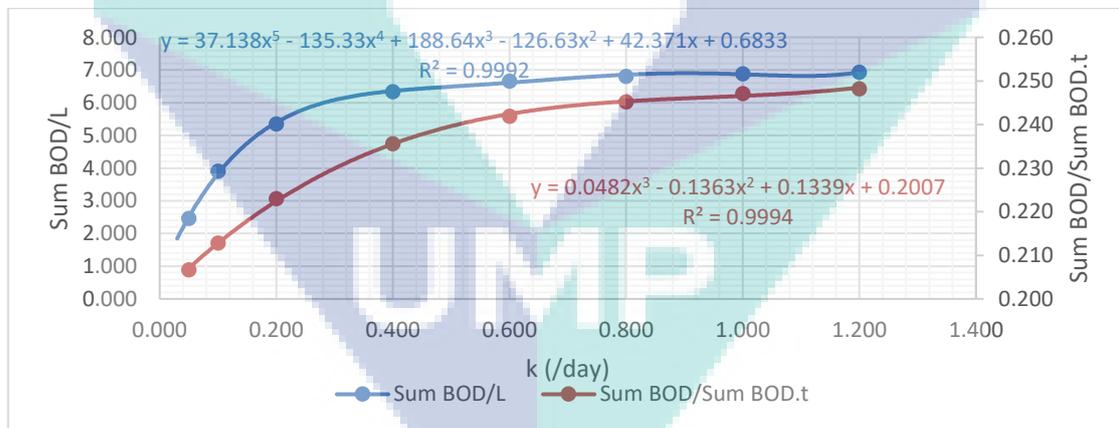


Figure 4.18 Moore's diagram for BOD – 7 days

Then, by refer to the BOD result shown in Table 4.18, the value of  $\Sigma y$  and  $\Sigma y t$  was computed and shown in Table 4.3.

Table 4.3 Computation table for BOD ( $y$ ) and  $yt$  for BOD 7 days

Time, $t$ (days)	BOD $t$	BOD, $y$ (mg/L)	$yt$
1	BOD <sub>1</sub>	220	220
2	BOD <sub>2</sub>	445	890
3	BOD <sub>3</sub>	661	1,983
4	BOD <sub>4</sub>	769	3,076
5	BOD <sub>5</sub>	819	4,095
6	BOD <sub>6</sub>	880	5,280
7	BOD <sub>7</sub>	985	6,895
Sum		$\Sigma y = 4,779$	$\Sigma yt = 22,439$

From Table 4.3,

$$\frac{\Sigma y}{\Sigma yt} = \frac{4,779}{22,439} = 0.213$$

By referring to the line  $\Sigma y/\Sigma yt$  in Figure 4.18, at  $\Sigma y/\Sigma yt = 0.213$ ,  $k_1 = 0.100/\text{day}$ .

From the line  $\Sigma y/L_0$  in Figure 4.30, when  $k_1 = 0.100/\text{day}$ ,  $\Sigma y/L_0 = 3.900$ ,

$$\begin{aligned} \text{Thus, } L_0 &= \frac{\Sigma y}{3.900} = \frac{4,779}{3.900} \\ &= 1,225.38 \text{ mg/L} \end{aligned}$$

#### 4.3.6 Evaluation of BOD kinetic study methods

All the result of kinetic parameters,  $k_1$  and  $L_0$  for five methods above were summarized in Table 4.4. However, the evaluation of each method needs to be carried out to find the most suitable method that can be used for the kinetic parameters estimation, especially for ultimate BOD ( $L_0$ ) that might be used in the POME treatment plant design.

Table 4.4 Summary of BOD kinetic parameters for POME

Methods	Ultimate BOD, $L_0$ (mg/L)	Reaction Rate Constant, $k_1$ (/day)
Least Square Method	1,139.58	0.270
Fujimoto Method	1,100.00	0.034
Thomas Graphical Method	1,326.56	0.087
Log Different Method	1,177.62	0.098
Method of Moment	1,225.38	0.100

All the kinetic parameters for  $L_0$  and  $k_1$  in five methods are fitted into the first order BOD kinetic equation in Eq. 2.3 as following:

$$L_t = L_0(1 - e^{-k_1 t})$$

Where  $L_t$  = BOD at  $t$  time,  $y$  (mg/L)  
 $L_0$  = Ultimate BOD (mg/L)  
 $k_1$  = Reaction rate constant (/day)

A plot of Observed BOD versus Estimated BOD was plotted in Figure 4.19. As can be seen from the plot, there are only one lines that are closed to the line of observed BOD, namely least square method. This indicated that only least square method can be used to estimate the value of reaction rate constants ( $k$ ) and ultimate BOD ( $L_0$ ) where the estimated BOD value almost similar with the observed BOD value from the experiment. Thus, it can be concluded that the  $L_0$  and  $k_1$  for POME were 1,139.38 mg/L and 0.270 day<sup>-1</sup>, respectively.

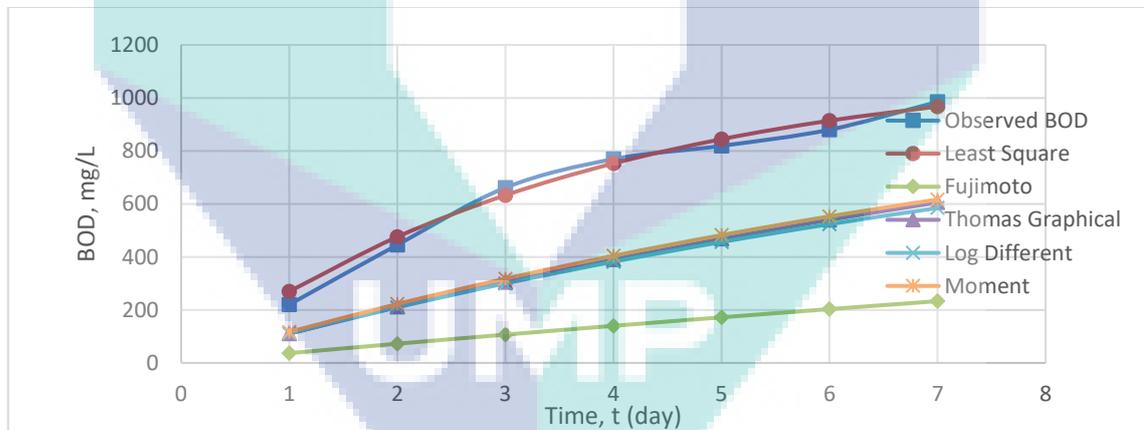


Figure 4.19 Plot of Observed BOD ( $y_o$ ) versus Estimated BOD ( $y_e$ ) value for different kinetic study methods

Besides that, in order to verify the value for  $L_0$  and  $k_1$ , the sum of absolute difference between the observed BOD and estimated BOD had been calculated to determine the sum of absolute difference value for the different kinetic study method and compare with the observed BOD result using Eq. 3.2. and Table 4.10 shows the calculated results.

$$D = \sum_{i=1}^{i=n} \frac{(y_o - y_e)}{y_e}$$

Where D = sum of the absolute differences between the observed BOD and estimated BOD

$y_o$  = Observed BOD (gained from BOD testing)

$y_e$  = Estimated BOD (gained from the BOD kinetic equation)

n = no of days of incubation for the serial BOD test

The sum of absolute differences between the observed BOD and estimated BOD for different kinetic study methods was calculated as shown in Table 4.5. According to Singh (2004), the value of absolute difference for a best method for the BOD kinetic parameters estimation must be less than or equal to 0.35. Thus, there are only least square method that produce the sum of absolute differences less than 0.35 and it can be concluded that the least square method is the most suitable method for the kinetic study of POME where the  $L_0$  and  $k_1$  for POME were 1,139.38 mg/L and 0.270 day<sup>-1</sup>, respectively.

Table 4.5 Sum of absolute differences between the observed BOD and estimated BOD for different kinetic study methods

Least Square	Fujimoto	Thomas Graphical	Log Different	Moment
0.23	30.16	6.24	6.50	5.76

By comparing the result in this study with previous study in other industries, all six methods are not suitable to estimate the value of  $L_0$  and  $k_1$  for distillery and textile industry, due to the high content of non-biodegradable matter in distillery wastewater (Krishnamoorthy et al, 2017) and textile wastewater (Muda, 2011), which are not easily degradable biologically in nature that cause the estimation method cannot be used in their case. However, the BOD kinetic parameters can be determined in dairy wastewater by using Thomas Graphical Method as shown in Table 4.6, which plausible due to high degradable nature of the dairy wastewater.

Table 4.6 Summary of BOD kinetic parameters for other industry (Singh, 2004)

Methods	Sum of absolute differences between the observed BOD and estimated BOD for different kinetic study methods in different industry		
	Distillery	Dairy	Textile
Least Square Method	0.64	0.86	1.37
Fujimoto Method	1.18	0.52	0.69
Thomas Graphical Method	0.47	0.32	0.74
Log Different Method	0.96	2.03	1.74
Method of Moment	0.49	0.38	1.42

#### 4.4 Chemical Oxygen Demand (COD) Fractional Studies of POME

Chemicals Oxygen Demand (COD) Fractional studies of POME had been carried out in batch mode where all the experiments were run in quadruplicate.

##### 4.4.1 Determination of Biodegradable Chemical Oxygen Demand (bCOD)

Biodegradable chemical oxygen demand (bCOD) of POME can be obtained from the experiment where POME sample gone through the biodegradation process in aeration tank by activated sludge. Performance data for the fractional studies of biodegradable COD of POME as shown in Table 4.7. bCOD was determined by using the total biological demand ( $T_bOD$ ) concept where  $T_bOD$  value is conceptually equal to the bCOD (Park et al, 1997) that can be obtained from the value differences between initial mixture of POME COD ( $COD_{ipm}$ ) and final mixture of POME COD ( $COD_{fpm}$ ) as shown in Eq. 3.3. Nevertheless, due to the dilution of POME sample, dilution ratio had been adjusted to obtain the POME  $T_bOD$  as shown in Eq.3.8.

Table 4.7 Performance data for fractional studies of bCOD of POME

Fraction of COD	Experiment of COD Fractional Studies (mg/L)				
	1 <sup>st</sup> Run	2 <sup>nd</sup> Run	3 <sup>rd</sup> Run	4 <sup>th</sup> Run	Mean
Initial total COD of POME (COD <sub>it</sub> )	2,434	2,553	2,510	2,473	2,493
Initial soluble COD of POME (COD <sub>is</sub> )	1,843	1,835	1,836	1,838	1,838
COD of suspended solid of POME (COD <sub>w</sub> )	591	718	674	635	655
Initial total COD of mixture (COD <sub>itm</sub> )	4,742	4,697	4,793	4,703	4,734
Initial soluble COD of mixture (COD <sub>ism</sub> )	712	635	626	694	667
COD of suspended solid of mixture (COD <sub>im</sub> )	4,030	4,062	4,167	4,009	4,067
COD of biomass mixture (COD <sub>mb</sub> )	3,439	3,344	3,493	3,374	3,413
COD of initial mixture of POME (COD <sub>ipm</sub> )	1,303	1,353	1,300	1,329	1,321
COD of final mixture of POME (COD <sub>fpm</sub> )	712	734	742	730	730
Total biological demand (T <sub>b</sub> OD)	591	619	558	599	592
Total biological demand (T <sub>b</sub> OD) of POME	1,233	1,292	1,165	1,250	1,235

Hence, the mean value of biodegradable COD (bCOD) and nonbiodegradable COD (nbCOD) can be obtained from the experiment and calculation as following:

$$\begin{aligned}
 \text{bCOD} &= T_b\text{OD} = 1,235 \text{ mg/L} \\
 \text{nbCOD} &= \text{Total COD} - \text{bCOD} \\
 &= 2,493 - 1,235 \text{ mg/L} \\
 &= 1,258 \text{ mg/L}
 \end{aligned}$$

#### 4.4.2 Determination of Soluble Readily Biodegradable COD (srbCOD) and Soluble Nonbiodegradable COD (snbCOD)

Soluble readily biodegradable COD (srbCOD) dan soluble nonbiodegradable COD (snbCOD) were determined by using physical separation method (Mamais et al, 1993), where the anaerobic treatment POME sample were gone through the coagulation followed by filtration process while the settled supernatant only gone for filtration process. Experiments were ran concurrent with the bCOD determination and performance data had shown in Table 4.8.

Table 4.8 Performance data for fractional studies of srbCOD and snbCOD of POME

Fraction of COD	Experiment of COD Fractional Studies (mg/L)				
	1 <sup>st</sup> Run	2 <sup>nd</sup> Run	3 <sup>rd</sup> Run	4 <sup>th</sup> Run	Mean
Initial total COD of POME (COD <sub>it</sub> )	2,434	2,553	2,510	2,473	2,493
Total truly COD of POME (ttsCOD)	1,364	1,401	1,389	1,378	1,383
Soluble nonbiodegradable COD of POME (snbCOD)	662	678	658	659	664
Soluble readily biodegradable COD of POME (srbCOD)	702	723	731	719	719

As a result, the srbCOD and snbCOD were determined at mean value of 719 mg/L and 664 mg/L, respectively.

#### 4.4.3 Determination of Particulate Slowly Biodegradable COD (psbCOD) and Particulate Nonbiodegradable COD (pnbCOD)

After obtained the value of bCOD, srbCOD and snbCOD, particulate slowly biodegradable COD (psbCOD) and particulate nonbiodegradable COD (pnbCOD) can be calculated by using Eq. 3.10 and Eq. 3.11, respectively as shown in Table 4.9.

Table 4.9 Calculated data for fractional studies of psbCOD and pnbCOD of POME

Fraction of COD	Experiment of COD Fractional Studies (mg/L)				
	1 <sup>st</sup> Run	2 <sup>nd</sup> Run	3 <sup>rd</sup> Run	4 <sup>th</sup> Run	Mean
Initial total COD of POME (COD <sub>it</sub> )	2,434	2,553	2,510	2,473	2,493
Biodegradable COD of POME (bCOD)	1,233	1,292	1,165	1,250	1,235
Soluble readily biodegradable COD of POME (srbCOD)	702	723	731	719	719
Soluble nonbiodegradable COD of POME (snbCOD)	662	678	658	659	664
Particulate slowly biodegradable COD of POME (psbCOD)	531	569	434	531	516
Particulate nonbiodegradable COD of POME (pnbCOD)	539	583	687	564	594

Thus, the psbCOD and pnbCOD were determined at mean value of 516 mg/L and 594 mg/L, respectively.

Figure 4.20 shown the summary of the finding of COD fraction where tCOD was found at 2,493 mg/L in anaerobic treated POME. After the biological oxidation process by activated sludge treatment, POME sample had taken for bCOD and nbCOD determination, which were found at 1,235 mg/L and 1,258 mg/L respectively. Further study on bCOD showed that srbCOD and psbCOD were found at 719 mg/L and 516 mg/L, respectively. Fraction of nbCOD were also being determined concurrently, where snb COD and pnbCOD were found at a value of 664 mg/L and 594 mg/L, respectively. In the COD fractional chart, tCOD comprised about 49.5% of bCOD, which can be biological degraded by bacteria in activated sludge, and the balance of 50.5% is nbCOD that could not be degraded biologically. This fraction is solid particle and need to be removed chemically or mechanically before the biological process, which had been practiced by conventional ponding system via sedimentation process. However, even though, there was about 58.2% of srbCOD was found in bCOD, which can be easily degraded biologically, the balance of 41.8% was psbCOD which are hardly degraded via biological treatment. Thus, determination of the COD fraction is needed to identify the organic matter that present in POME either for biological aeration tank design or process optimization of POME treatment.

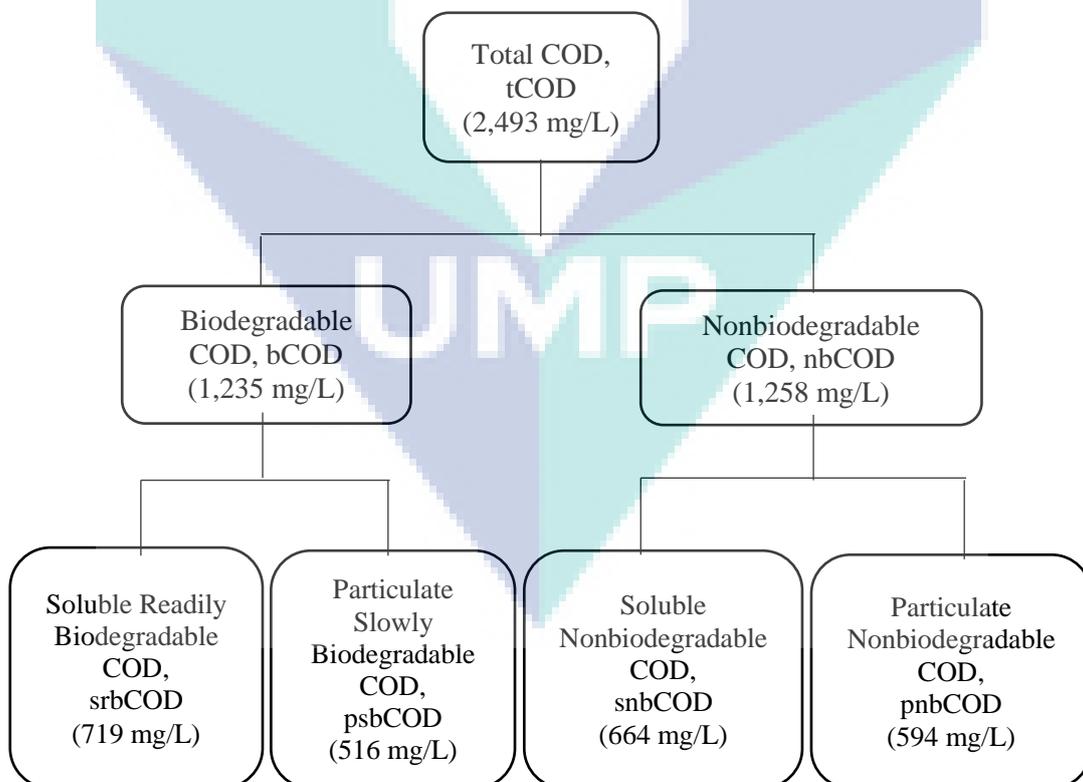


Figure 4.20 Mean concentration value of COD fractional for anaerobic treated POME

#### 4.5 Kinetic Study of Activated Sludge Process in POME Treatment

Kinetic parameter is a basis for design and optimization of POME treatment by activated sludge process. In fact, most of the kinetic parameters value used in design and optimization are considered as default values, which are gained from municipal wastewater. The kinetic parameters for POME treatment have not been thoroughly studied and used in Activated Sludge Models (ASM), either in modelling or design (Damyanti et al., 2010). Thus, the kinetic study of POME treatment by activated sludge system were carried out to gain the kinetic parameters for the POME treatment plant design. In industrial practise, biological methods are invariably employed to remove the contaminant in the POME for the discharge standard compliance.

For the kinetic analysis experiment, the batch study was conducted where performance data were measured and recorded. The performance data including BOD<sub>3</sub> concentration of POME influent and effluent, COD concentration of POME influent and effluent, mixed liquor volatile suspended solids, flow rate of influent and wasted activated sludge as well as volatile suspended solids concentration of wasted activated sludge. Then, the results were compounded for the calculation of specific growth rate, specific substrate utilization rate, reciprocal substrate utilization rate and reciprocal substrate concentration on BOD<sub>3</sub> basis and COD basis for anaerobic treated POME at different solid retention time as shown in Table 4.10 and Table 4.11, respectively.

Table 4.10 Specific growth rate, specific substrate utilization rate, reciprocal substrate utilization rate and reciprocal substrate concentration on BOD<sub>3</sub> basis at different solid retention time for anaerobic treated POME

<b>Solid Retention Time, <math>\theta_c</math> (days)</b>	<b>Specific growth rate, <math>1/\theta_c</math> (days<sup>-1</sup>)</b>	<b>Specific substrate utilization rate, <math>U_{BOD}</math> (days<sup>-1</sup>)</b>	<b>Reciprocal substrate utilization rate, <math>1/U_{BOD}</math> (days)</b>	<b>Reciprocal substrate of BOD concentration, <math>S_{eBOD}</math> (L/mg)</b>
10	0.1000	0.2448	4.08	0.0082
12	0.0833	0.2222	4.50	0.0102
14	0.0714	0.2091	4.78	0.0106
16	0.0625	0.1886	5.30	0.0116
18	0.0556	0.1796	5.57	0.0120
20	0.0500	0.1727	5.79	0.0128

Table 4.11 Specific growth rate, specific substrate utilization rate, reciprocal substrate utilization rate and reciprocal substrate concentration on COD basis at different solid retention time for anaerobic treated POME

Solid Retention Time, $\theta_c$ (days)	Specific growth rate, $1/\theta_c$ (days <sup>-1</sup> )	Specific substrate utilization rate, $U_{COD}$ (days <sup>-1</sup> )	Reciprocal substrate utilization rate, $1/U_{COD}$ (days)	Reciprocal substrate of COD concentration, $S_{eCOD}$ (L/mg)
10	0.1000	0.8738	1.14	0.0022
12	0.0833	0.7826	1.28	0.0024
14	0.0714	0.7586	1.32	0.0026
16	0.0625	0.7045	1.42	0.0029
18	0.0556	0.6955	1.44	0.0031
20	0.0500	0.6548	1.53	0.0032

In order to determine the kinetic study parameters for maximum yields coefficient ( $Y$ ), and endogenous decay coefficient ( $k_d$ ), a plot of reciprocal of solids retention time,  $1/\theta_c$  (day<sup>-1</sup>) versus specific substrate utilization rate,  $U$  (day<sup>-1</sup>) on BOD<sub>3</sub> basis and COD basis were constructed separately as shown in Figure 4.21 by using Eq.2.27.

$$\frac{1}{\theta_c} = YU - k_d$$

where  $U = \frac{S_i - S_e}{\theta X}$

While a plot of reciprocal of specific substrate utilization rate,  $1/U$  (day) versus reciprocal effluent of substrate  $1/S_e$  (L/mg) on BOD<sub>3</sub> basis and COD basis were constructed separately as shown in Figure 4.22 by using the Eq.2.30 to obtain the maximum specific substrate utilization rate ( $k$ ) and half-velocity constant ( $K_s$ ) as following:

$$\frac{1}{U} = \frac{K_s}{kS_e} + \frac{1}{k}$$

From the plot as shown in Figure 4.21 and Figure 4.22, kinetic parameters of POME treatment by activated sludge process for maximum yields coefficient ( $Y$ ), endogenous decay coefficient ( $k_d$ ), maximum specific substrate utilization rate ( $k$ ) and half-velocity constant ( $K_s$ ) for BOD<sub>3</sub> and COD were determined and summarized in Table 4.12.

Determination of kinetic parameters is essential for the aeration activated sludge system design especially the yields coefficient ( $Y$ ) and endogenous decay coefficient ( $k_d$ ). According to DOE (2010a), the recommended of design criteria for extended aeration activated sludge system of  $Y$  and  $k_d$  are 0.1 – 0.3 kg VSS/kg BOD<sub>3</sub> and 0.03 – 0.15 day<sup>-1</sup>. However, in this study, the kinetic parameters of  $Y$  and  $k_d$  were found at 0.6718 kg VSS/kg BOD<sub>3</sub> and 0.0658 day<sup>-1</sup>. The obtained value of  $k_d$  was found within the DOE recommendation value, but the obtained value of  $Y$  was found bigger than the DOE recommendation value. This indicated that the design of the activated sludge system for POME treatment is under capacity if compare to the design value recommended by DOE. This might be one of the reasons that most of POME treatment system does not meet the DOE final discharge standard consistently. On the other hand, the reported  $K_s$  value was 429 mg/L (Lim and Vadivelu, 2014), which is lower than the value of 758.7705 mg/L from this study. The differences of the  $Y$ ,  $k_d$  and  $K_s$  value might due to the growing condition and microbial species involve in the biological process. Thus, more thorough study needs to be done to get more precise values of growth kinetic in POME treatment.

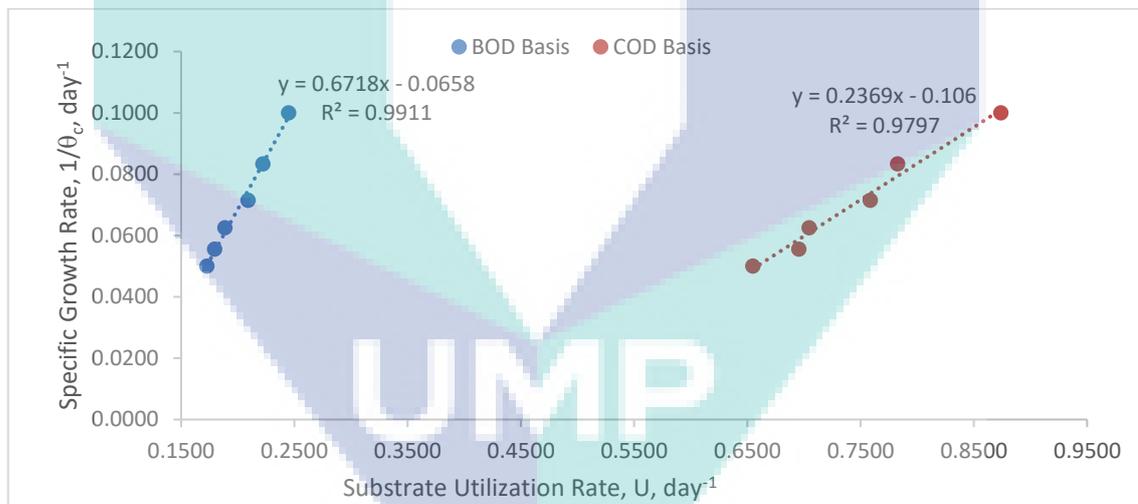


Figure 4.21 Plot of specific growth rate versus substrate utilization rate for maximum yields coefficient ( $Y$ ) and endogenous decay coefficient ( $k_d$ ) determination by using BOD<sub>3</sub> and COD result

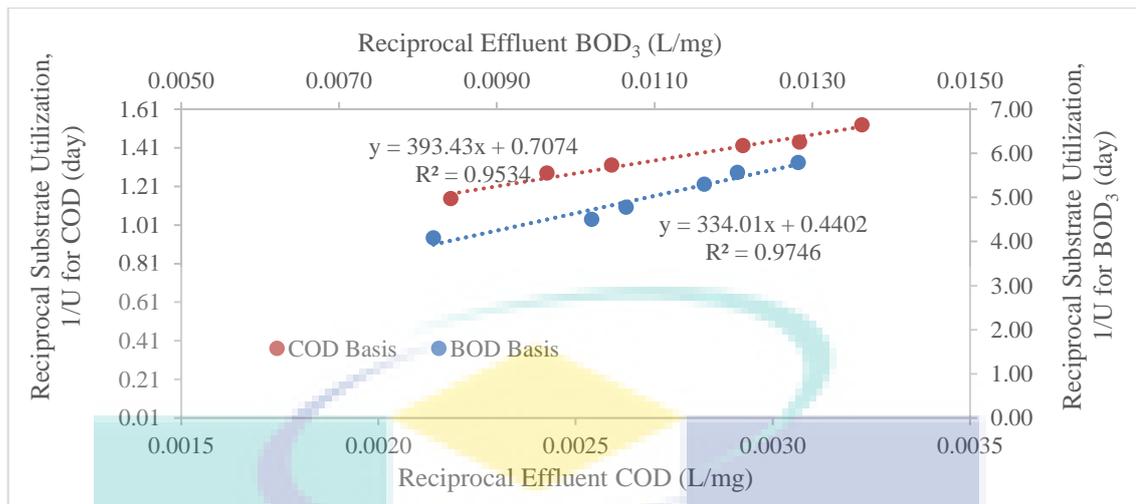


Figure 4.22 Plot of reciprocal substrate utilization versus reciprocal effluent for maximum specific substrate utilization rate ( $k$ ) and half-velocity constant ( $K_s$ ) determination by using  $BOD_3$  and COD result

Table 4.12 Summary of kinetic parameters for the POME treatment by activated sludge process

POME concentration	Kinetic Parameters	Unit	Value
BOD <sub>3</sub>	$Y$	mg VSS/mg BOD <sub>3</sub>	0.6718
	$k_d$	day <sup>-1</sup>	0.0658
	$K_s$	mg/L of BOD <sub>3</sub>	556.1526
	$k$	day <sup>-1</sup>	1.4136
COD	$Y$	mg VSS/mg COD	0.2369
	$k_d$	day <sup>-1</sup>	0.1060
	$K_s$	mg/L of COD	758.7705
	$k$	day <sup>-1</sup>	2.2717

#### 4.6 Design Calculation for POME Treatment Plant

Biological aeration tank is the most important unit operation in the organic matter degradation process, not only economical but also environmentally sustainable in municipal and industrial wastewater treatment (El-Shorbagy et al., 2011). In practical, most of the biological aeration tank was constructed by conceptual design based on the kinetic parameters value from municipal wastewater (Tchobanoglous and Stensel, 2004; Department of Environment Malaysia, 2010a, Shun, 2014). In designing the biological aeration tank, beside the kinetic parameters, influent characteristic such as POME flow

rate and organic matter in POME need to be determined for the volume calculation of the biological aeration tank. In this study, plant design only focusses on the biological aeration tank by using the kinetic parameters obtained from the previous section and the real composition of organic matter obtained from the above experiment as shown in Table 4.13.

Biological aeration tank volume was calculated based on different fraction of BOD and COD, where different authors using different organic matter as basis calculation such as BOD<sub>3</sub> (Peavy et al., 1985, Grady et al., 1999; Qasim, 1999; DOE, 2010a; Karia & Christian, 2013; Shun, 2014), uBOD (WEF, 2010), tCOD (Droste, 1997; Vesilind, 1998; Qasim, 1999), bCOD (Grady et al., 1999; Tchobanoglous & Stensel, 2004; WEF, 2010) and srbCOD (Davis, 2010) by using the aeration tank volume calculation in Eq.2.33.

As shown in Figure 4.23, there are two different organic matter basis, namely BOD and COD with their composition had been used for the biological aeration tank volume calculation. In this case, calculation is based on palm oil mill production capacity with 45 ton/hr for 24 hours operation time per day with POME discharge ratio at 0.65 m<sup>3</sup>/ton of FFB. In the BOD basis, calculation been done by using BOD<sub>3</sub> and uBOD in this study compare with BOD<sub>3</sub> for design calculation based on DOE design criteria. While in COD basis, even though currently there is no discharge standard for COD by regulation, stringent of environmental law and regulation eventually will lead to compliance of the discharge standard for COD. Thus, it is needed to study the COD as design criteria especially for POME. By using default value from DOE design criteria (DOE, 2010a), the biological aeration tank volume was calculated as having a capacity of 917 m<sup>3</sup>. By using BOD<sub>3</sub> result in this study, biological aeration tank volume was calculated to be 1,091 m<sup>3</sup>. This indicates that the conceptual design of aeration tank volume that adopted from DOE design criteria is less than the conceptual design of aeration tank volume from this study which might cause the under capacity of POME treatment system in palm oil industry.

Moreover, in this study, total BOD or ultimate BOD (uBOD) in POME treatment system was also determined and used for the biological aeration tank volume design which was calculated at 1,931 m<sup>3</sup>. It is clearly shown that the biological aeration tank volume is about 2.11 times bigger than the conceptual design calculation from BOD<sub>3</sub>.

However, there was no biological aeration tank has been designed by using uBOD in practical, due to the area restriction and construction cost.

On the other hand, since the COD is not in the DOE discharge standard, so for plant design calculation purpose, the discharge standard value will be taken as similar with the industrial effluent discharge value of Standard A at 80 mg/L (Malaysia, 2017). After calculation, the biological aeration tank volume was found to be 1,262 m<sup>3</sup>. From the result, it can be seen that the conceptual design calculation of biological aeration tank volume for BOD<sub>3</sub> is 1.38 smaller than the biological aeration tank volume that calculated by using tCOD.

Meanwhile, by using bCOD and srbCOD for design calculation, the biological aeration tank volume was calculated to be 604 m<sup>3</sup> and 334 m<sup>3</sup>, respectively. It is much smaller in capacity compared to the conceptual design of biological aeration tank volume, which is calculated by using default value recommended by DOE. However, the design calculation from bCOD and srbCOD is considered as more representative as compared to the design calculation by using tCOD. This is because POME consists of high content of slowly biodegradable compound which is not easily biodegraded by activated sludge process regardless of the biological aeration tank volume. Nevertheless, the slowly biodegradable compound needs to be removed by other treatment processes such as high oxidation process, ion-exchange resin, membrane etc. in the extra step in order to remove all the organic matter completely and eventually comply with DOE discharge standard.

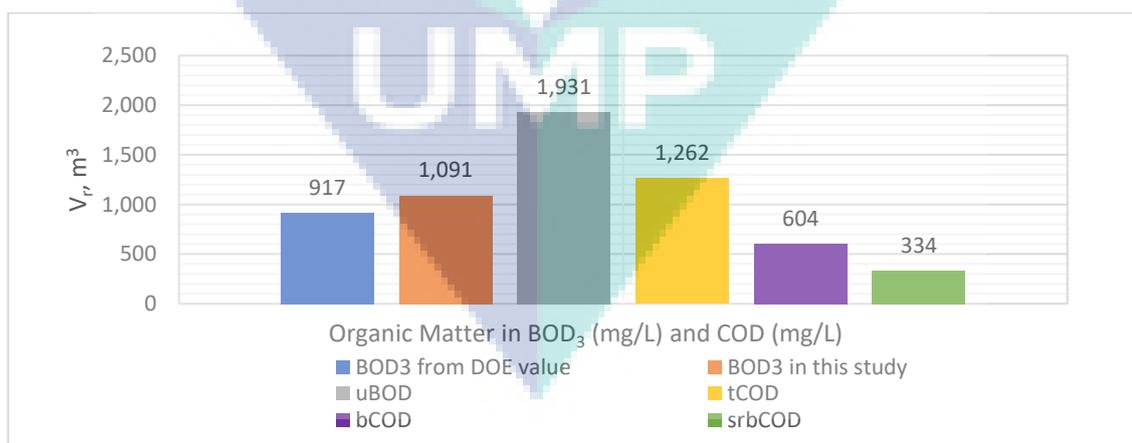


Figure 4.23 Comparison of biological aeration tank volume design calculation based on BOD and COD basis in this study with DOE design criteria

By using the above biological aeration tank volume result, hydraulic retention time had been calculated as shown in Figure 4.24. According to the DOE design guidance document (DOE, 2010a), the HRT for extended aeration tank sludge system need to be designed at range of 18.00 – 36.00 hours. From Figure 4.36, the HRT from the conceptual design of biological aeration tank by using the default value recommended by DOE was found within the design range. Nevertheless, the HRT for biological aeration tank volume calculated using the obtained BOD<sub>3</sub>, uBOD and tCOD had exceeded the design range in the design guidance document, but it was proved that the best performance of POME treatment was found at HRT of 48 hours which had discussed in Section 4.2.2. Hence, the biological aeration tank design using BOD<sub>3</sub> and tCOD can be considered for the DOE submission with the documented evidence from this study.

However, design by using the uBOD result which was found largely oversize from the conceptual design may not be practical due to the cost constraint in palm oil industry, while the design by using srbCOD result was found lower than the design range which is not allowed by DOE unless with the proven evidence. In this study, only the design with the bCOD was found within the HRT design range, but in order to comply with all the stringent regulatory discharge standard, combination with other treatment system need to be implemented to remove the nonbiodegradable COD in POME.

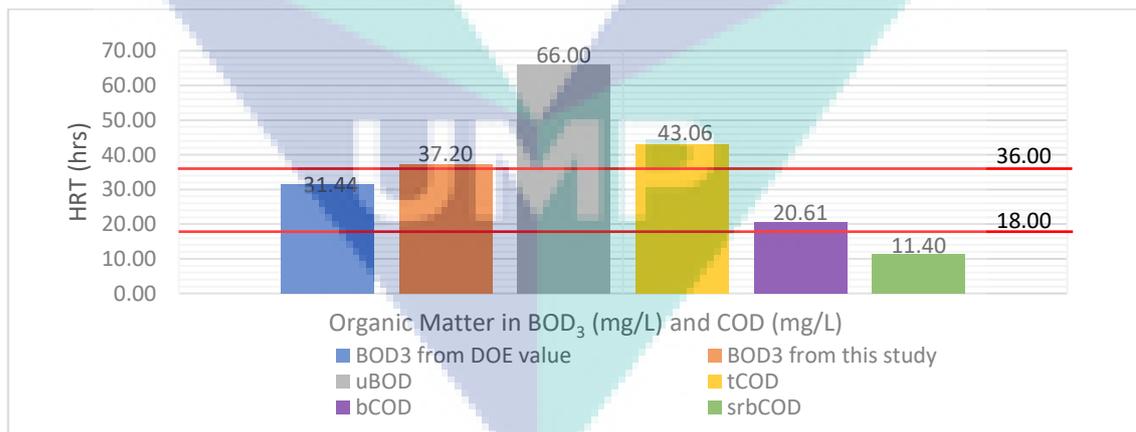


Figure 4.24 Comparison of hydraulic retention time for biological aeration tank volume design calculation based on BOD and COD basis in this study with DOE design criteria.

Similarly, F/M ratio also been calculated by using the obtained biological aeration tank volume result as shown in Figure 4.25. Referring to the DOE design guidance document (DOE, 2010a), the F/M ratio for extended aeration tank sludge system need to

be designed at range of 0.05 – 0.15 kg BOD/(kg MLVSS.day), but in DOE performance monitoring guidance document (DOE, 2010b), F/M ratio is allowed to control at range of 0.15 – 0.70 kg COD/(kg MLVSS. day) or 0.04 – 0.18 kg BOD/(kg MLVSS.day). Even though, the F/M ratio from the conceptual design of biological aeration tank by using the default value recommended by DOE was found slightly over the design range, it still within the F/M ratio range in performance monitoring control range.

However, for others design using the obtained value from this study were found exceed the design range and performance monitoring control range especially design from the tCOD, bCOD and srbCOD. In this case, the design of biological aeration tank with COD result may not be suitable and can be eliminated. Since the F/M ratio from the design that using the BOD<sub>3</sub> and uBOD result were found exceed the design range and performance monitoring control range, but with proper control and monitoring program, the POME treatment may achieve the regulatory discharge standard with combination of other treatment system. As conclusion, the right approach to biological aeration tank design was using the obtained results for BOD<sub>3</sub> including the kinetic parameters, but this only applicable for biodegradable matter in POME. Hence, the nonbiodegradable matter removal by others physical treatment process need to be conducted for the regulatory discharge standard.

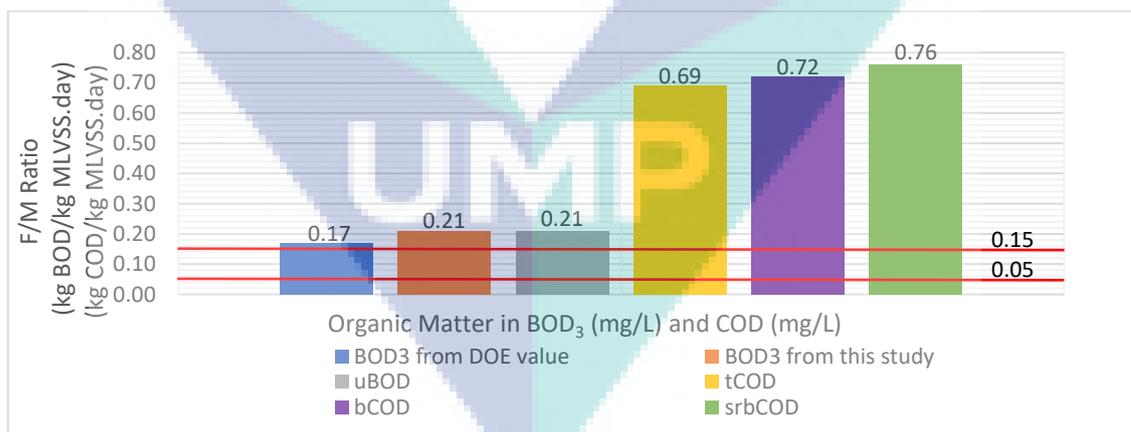


Figure 4.25 Comparison of F/M ratio for biological aeration tank volume design calculation based on BOD and COD basis in this study with DOE design criteria

## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

Generally, in wastewater treatment plant design and operation, characterization study of influent needed to be conducted, therefore the characteristic of POME especially physical and chemical composition had been determined in this research. In physical composition determination, solid contents and particle size distribution had been carried out. From the result obtained, total solid content was found to be 29,214 mg/L in anaerobic treated POME with TVS and TFS content of 15,727 mg/L and 13,497 mg/L, respectively.

The performance studies of POME treatment by activated sludge had been conducted for the effect of operating parameters, namely initial pH of POME, HRT, OLR, initial MLVSS, SRT and molasses concentration as external carbon sources with the optimum condition achieved at  $6.5 \pm 0.1$ , 48 hours,  $0.31 \text{ g BOD}_3/\text{L}\cdot\text{day}$ ,  $2,000 \pm 200 \text{ mg/L}$ , 10 days and 50 mg/L, respectively. However, the reduction of COD and  $\text{BOD}_3$  were found at 62 - 68% and 60 – 64%, respectively.

From the kinetic study experiment, the kinetic parameters for COD and BOD basis had been determined for maximum yields coefficient ( $Y$ ), endogenous decay coefficient ( $k_d$ ), maximum specific substrate utilization rate ( $k$ ) and half-velocity constant ( $K_s$ ) at  $0.2369 \text{ mg VSS/mg COD}$ ,  $0.1060 \text{ day}^{-1}$ ,  $2.2717 \text{ day}^{-1}$  and  $758.7705 \text{ mg/L}$  for COD basis whilst the kinetic parameters value for BOD basis were  $0.6718 \text{ mg VSS/mg BOD}_3$ ,  $0.0658 \text{ day}^{-1}$ ,  $1.4136 \text{ day}^{-1}$  and  $556.1526 \text{ mg/L}$ , respectively.

The main objective of this study is to find the characteristic of anaerobic treated POME and kinetic parameters for the activated sludge system design. Even though many researchers had studied the characteristic of POME, they only focused in chemicals composition such as COD and BOD, no physical composition was reported. In fact, the physical composition especially total solid content in POME contribute a very high concentration of organic matter which cause the high organic loading rate. Thus, the result of physical composition of POME are very useful for the POME pre-treatment prior to biological treatment process.

Furthermore, most of the kinetic parameters in POME treatment were determined in COD basis, but COD is not a discharge parameter that need to be complied according to DOE discharge standard requirement. Hence, kinetic parameters in BOD basis were determined in this study is more appropriate for the calculation of POME treatment system design.

## **5.2 Recommendation**

In order to improve the POME treatment system especially activate sludge process for the desired DOE regulatory discharge standard compliance, several recommendation and suggestion that may provide some useful information for POME treatment in future studies and research.

Firstly, solid particle always be one of the major issues in POME treatment system, by understanding the PSD in POME, more reliable and cost effective of solid removal system need to develop and implement in order to reduce the solid content in POME as well as the organic loading rate into activated sludge process.

Secondly, slowly biodegradable COD and non-biodegradable COD been found in high concentration in POME, which may due to dissolved organic matter (DOM) content. In order to break down the DOM molecules in POME, advance oxidation process followed by activated sludge process may be one of the directions that can be studied and developed.

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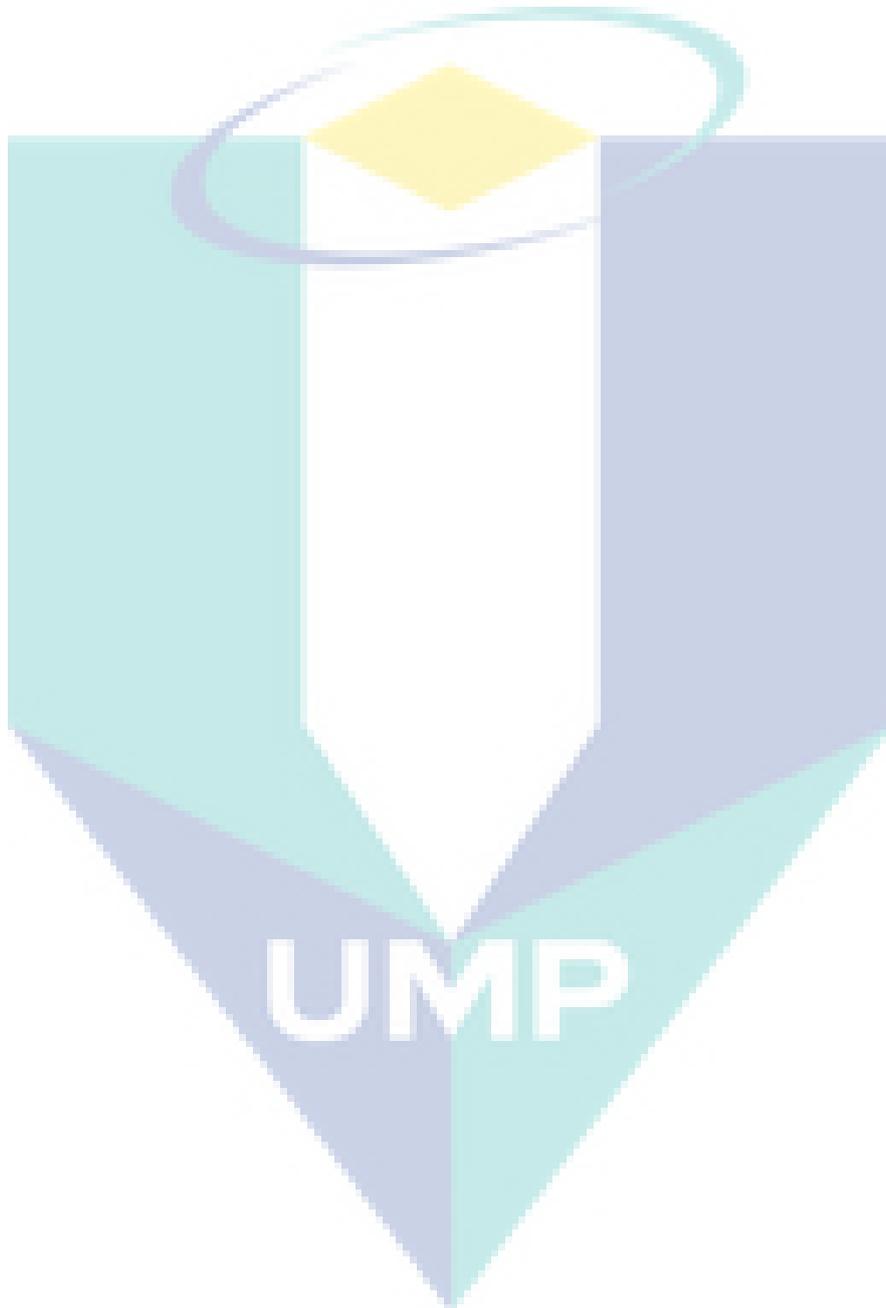
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## APPENDIX A

### RAW DATA FOR CHARACTERIZATION OF ANAEROBIC TREATED POME

Table A.1 Concentration of different solid in POME sample

Fractional of Solid	Concentration of Solid in POME (mg/L)				
	Sample 1	Sample 2	Sample 3	Sample 4	Mean
Total Solid (TS)	23,656	24,767	35,386	33,047	29,214
Total Volatile Solid (TVS)	13,875	13,957	20,756	14,280	15,717
Total Fixed Solid (TFS)	11,456	12,846	18,983	10,703	13,497
Total Suspended Solid (TSS)	22,456	23,985	28,984	27,171	25,649
Total Dissolved Solid (TDS)	2,978	3,056	5,856	2,370	3,565
Volatile Suspended Solid (VSS)	10,153	11,456	18,984	16,547	14,285
Fixed Suspended Solid (FSS)	9,865	10,245	15,687	9,659	11,364
Volatile Dissolved Solid (VDS)	478	504	724	594	575
Fixed Dissolved Solid (FDS)	1,897	1,947	4,587	3,529	2,990

Table A.2 Percentage of different particle size in POME

Size of Particle, $\mu\text{m}$	Percentage of Particle in POME (%)				
	Sample 1	Sample 2	Sample 3	Sample 4	Mean
Less than 2 $\mu\text{m}$	12.12	12.25	13.06	12.88	12.58
2 – 5 $\mu\text{m}$	2.06	2.12	2.50	2.33	2.25
5 -10 $\mu\text{m}$	1.24	1.36	1.85	1.45	1.48
10 – 20 $\mu\text{m}$	5.49	5.76	5.98	5.82	5.76
20 – 50 $\mu\text{m}$	28.33	28.55	28.92	28.66	28.62
50 – 100 $\mu\text{m}$	34.91	35.05	35.50	35.27	35.18
More than 100 $\mu\text{m}$	13.95	14.06	14.34	14.18	14.13

Table A.3 Concentration of chemical composition in POME

Chemical Composition	Concentration (mg/L)				
	Sample 1	Sample 2	Sample 3	Sample 4	Mean
BOD <sub>3</sub>	587	621	718	682	652
COD	2,350	2,269	2,765	2,588	2,493
TN	1,182	1,274	1,376	1,312	1,286
AN	234	249	256	253	248

## APPENDIX B

### RAW DATA FOR EXPERIMENT OF EFFECT OF INITIAL PH ON POME TREATMENT

Table B.1 Raw data for 1<sup>st</sup> run of experiment

<b>Initial pH</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
4.00	6.10	1,537	758	0.55	658	2,587	364	1,587
4.50	6.18	1,930	1,067	1.10	663	2,689	360	1,706
5.00	6.28	2,975	1,576	2.24	670	2,576	338	1,503
5.50	6.31	3,223	1,994	4.06	632	2,367	312	1,208
6.00	6.65	2,929	2,167	7.63	637	2,287	280	1,037
6.50	8.05	3,395	2,558	10.58	658	2,686	255	1,032
7.00	8.12	3,022	2,377	9.37	640	2,587	217	843
7.50	8.35	2,935	2,025	4.43	670	2,743	221	906
8.00	8.42	2,875	1,968	3.96	652	2,597	255	993
8.50	8.52	2,601	1,768	3.42	668	2,365	268	949
9.00	9.09	1,982	1,378	2.33	635	2,746	279	1,212
9.50	9.22	1,829	1,187	1.86	658	2,564	325	1,243
10.00	9.05	1,933	1,079	1.70	663	2,723	334	1,398

Table B.2 Raw data for 2<sup>nd</sup> run of experiment

<b>Initial pH</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
4.00	6.22	1,140	586	0.52	670	2,365	377	1,498
4.50	6.33	1,733	968	1.30	665	2,465	366	1,473
5.00	6.22	2,664	1,376	2.27	635	2,546	333	1,429
5.50	6.29	3,109	1,896	4.84	653	2,465	335	1,252
6.00	6.79	2,958	2,087	7.88	643	2,646	310	1,168
6.50	8.37	3,149	2,389	11.64	635	2,436	269	861
7.00	8.65	2,887	2,268	10.55	648	2,386	249	865
7.50	8.75	2,765	1,978	5.67	657	2,547	266	779
8.00	8.90	2,487	1,785	4.75	669	2,675	258	943
8.50	8.94	2,336	1,648	3.38	648	2,742	242	1,024
9.00	9.20	1,846	1,298	2.57	653	2,465	260	1,019
9.50	9.30	1,732	1,068	1.88	656	2,376	316	1,078
10.00	9.98	1,734	986	1.64	663	2,657	338	1,314

Table B.3 Raw data for 3<sup>rd</sup> run of experiment

<b>Initial pH</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
4.00	6.30	1,476	794	0.46	639	2,287	354	1,286
4.50	6.35	2,107	1,185	1.46	648	2,366	352	1,501
5.00	6.34	2,809	1,586	2.11	657	2,376	369	1,315
5.50	6.38	2,938	1,968	3.86	649	2,467	340	1,146
6.00	6.80	3,021	2,168	7.42	658	2,586	297	1,225
6.50	8.48	3,406	2,675	10.91	637	2,365	261	789
7.00	8.75	2,979	2,398	9.26	658	2,476	271	941
7.50	8.69	2,787	2,189	4.53	648	2,268	250	797
8.00	8.93	2,610	1,896	3.52	663	2,376	274	790
8.50	8.96	2,594	1,796	3.19	648	2,648	292	1,195
9.00	9.21	2,058	1,368	2.26	653	2,476	265	1,150
9.50	9.30	1,786	1,155	1.54	648	2,647	295	1,094
10.00	9.20	1,932	1,078	1.39	659	2,546	354	1,290

Table B.4 Raw data for 4<sup>th</sup> run of experiment

<b>Initial pH</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
4.00	6.70	1,263	685	0.51	658	2,376	378	1,387
4.50	6.66	1,934	1,034	0.55	667	2,437	351	1,297
5.00	6.77	2,380	1,608	2.06	647	2,647	344	1,386
5.50	6.79	3,275	1,957	3.64	658	2,254	338	1,223
6.00	7.21	3,110	2,188	7.38	670	2,376	337	1,194
6.50	8.88	3,708	2,698	11.45	667	2,476	307	944
7.00	8.90	2,972	2,466	10.69	648	2,574	273	881
7.50	9.21	3,169	2,179	4.32	660	2,537	274	793
8.00	9.32	2,830	1,968	3.72	647	2,486	276	898
8.50	9.43	3,108	1,857	3.62	658	2,735	317	1,316
9.00	9.60	2,376	1,416	2.06	638	2,574	310	1,219
9.50	9.78	2,147	1,298	2.11	649	2,646	326	1,182
10.00	9.55	1,969	1,157	2.07	658	2,536	332	1,226

## APPENDIX C

### RAW DATA FOR EXPERIMENT OF EFFECT OF HYDRAULIC RETENTION TIME ON POME TREATMENT

Table C.1 Raw data for 1<sup>st</sup> run of experiment

<b>HRT (days)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
12	7.10	4,789	2,549	9.86	668	2,657	344	1,340
24	8.22	4,335	2,687	11.93	635	2,750	291	1,260
36	8.10	3,941	2,877	12.11	657	2,465	267	1,000
48	8.40	3,853	2,979	14.48	635	2,467	216	842
60	8.65	4,053	3,157	15.22	658	2,376	219	779
72	8.73	4,076	2,867	11.81	670	2,576	243	896
84	8.50	3,674	2,658	11.22	668	2,675	258	945
96	8.40	3,518	2,467	10.36	646	2,576	321	956
108	8.50	3,118	2,168	9.36	648	2,437	250	945
120	8.45	3,317	1,998	8.35	656	2,476	257	968
132	8.82	2,493	1,587	6.70	637	2,657	374	1,054
144	8.85	2,343	1,367	6.12	647	2,647	319	1,103

Table C.2 Raw data for 2<sup>nd</sup> run of experiment

<b>HRT (days)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
12	7.50	4,816	2,478	9.89	657	2,488	337	1,294
24	8.24	4,271	2,577	11.13	648	2,587	300	1,167
36	8.43	3,936	2,768	13.48	657	2,366	263	942
48	8.69	3,620	2,868	13.42	636	2,598	254	921
60	8.73	3,843	3,079	14.93	647	2,486	258	873
72	8.68	3,465	2,757	9.81	668	2,648	242	960
84	8.71	3,423	2,647	9.37	647	2,476	228	903
96	8.77	3,291	2,398	8.75	638	2,687	236	1,006
108	8.83	2,915	2,097	7.23	664	2,377	259	924
120	8.88	2,992	1,905	6.93	647	2,647	256	1,053
132	8.70	2,468	1,489	5.14	670	2,376	276	997
144	8.91	2,066	1,267	4.09	664	2,465	320	1,027

Table C.3 Raw data for 3<sup>rd</sup> run of experiment

<b>HRT (days)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
12	7.32	4,290	2,367	9.30	647	2,376	325	1,223
24	8.40	3,898	2,547	11.00	656	2,437	303	1,125
36	8.39	3,790	2,768	12.12	668	2,476	269	1,006
48	8.63	3,645	2,968	14.16	646	2,576	221	1,104
60	8.74	3,830	3,179	15.55	658	2,647	268	1,079
72	8.58	3,401	2,675	11.29	670	2,487	313	899
84	8.73	3,124	2,489	10.40	665	2,587	240	932
96	8.81	2,845	2,254	9.65	647	2,476	239	920
108	8.79	2,939	2,198	9.54	665	2,487	261	972
120	8.85	2,564	1,895	7.92	647	2,376	257	945
132	8.84	1,933	1,379	5.57	664	2,387	270	870
144	8.78	2,077	1,368	5.91	647	2,768	272	1,101

Table C.4 Raw data for 4<sup>th</sup> run of experiment

<b>HRT (days)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
12	7.41	6,138	2,476	6.56	637	2,548	381	1,520
24	8.33	5,783	2,686	9.19	657	2,658	380	1,416
36	8.44	4,788	2,889	9.97	647	2,686	334	1,293
48	8.59	4,068	3,068	12.64	646	2,387	255	971
60	8.23	4,428	3,257	13.19	664	2,497	256	1,018
72	8.68	4,890	2,945	11.37	670	2,376	275	1,156
84	8.77	4,418	2,656	10.23	647	2,658	322	1,323
96	8.79	3,664	2,507	10.13	657	2,487	320	1,210
108	8.84	3,833	2,236	9.17	647	2,658	306	1,341
120	8.89	3,715	2,056	7.94	637	2,547	326	1,321
132	8.99	3,282	1,685	7.21	646	2,686	385	1,471
144	8.80	2,580	1,436	5.24	667	2,587	366	1,426

## APPENDIX D

### RAW DATA FOR EXPERIMENT OF EFFECT OF ORGANIC LOADING RATE ON POME TREATMENT

Table D.1 Raw data for 1<sup>st</sup> run of experiment

<b>OLR (mg BOD<sub>3</sub>/L. g day)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
0.27	7.32	4,085	2,175	8.98	653	2,576	324	1,291
0.29	8.28	4,189	2,548	10.80	648	2,547	288	1,197
0.30	8.22	3,847	2,957	14.76	659	2,575	261	938
0.31	7.95	4,103	3,256	18.49	670	2,587	232	917
0.32	8.90	4,335	3,189	18.15	668	2,437	233	967
0.33	8.77	4,250	2,968	14.78	647	2,387	243	1,018
0.34	9.03	4,085	2,787	12.15	657	2,574	265	1,115
0.35	9.43	3,720	2,538	11.04	658	2,356	292	1,167
0.36	9.76	3,347	2,287	9.08	664	2,597	329	1,330
0.37	9.86	3,088	2,065	7.99	648	2,538	344	1,331
0.38	10.34	2,583	1,647	6.01	638	2,700	353	1,462

Table D.2 Raw data for 2<sup>nd</sup> run of experiment

<b>OLR (mg BOD<sub>3</sub>/L. g day)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
0.27	7.05	4,083	2,068	9.68	663	2,598	348	1,293
0.29	7.94	4,021	2,466	11.76	659	2,658	328	1,229
0.30	8.55	3,641	2,857	13.91	663	2,437	294	888
0.31	8.79	3,997	3,167	16.37	648	2,548	258	1,011
0.32	8.04	4,259	3,095	15.78	653	2,437	272	896
0.33	8.93	4,069	2,858	13.31	649	2,376	257	938
0.34	8.23	3,536	2,547	10.75	653	2,537	282	1,133
0.35	9.02	3,251	2,254	8.97	637	2,576	271	1,219
0.36	10.43	2,886	2,091	7.63	668	2,498	318	1,324
0.37	10.65	2,738	1,847	7.15	654	2,538	336	1,387
0.38	10.76	2,373	1,537	5.47	643	2,438	362	1,357

Table D.3 Raw data for 3<sup>rd</sup> run of experiment

<b>OLR (mg BOD<sub>3</sub>/L. g day)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
0.27	7.55	3,809	2,146	10.00	639	2,437	341	1,156
0.29	8.44	3,698	2,416	12.06	647	2,586	296	1,167
0.30	8.87	3,726	2,868	15.60	647	2,365	282	962
0.31	8.12	3,944	3,208	19.22	664	2,498	271	910
0.32	8.12	4,182	3,168	18.69	652	2,548	259	1,005
0.33	8.03	4,073	3,004	12.08	648	2,658	288	969
0.34	8.55	4,122	2,895	11.75	653	2,750	303	1,338
0.35	9.84	3,773	2,616	9.31	638	2,576	264	1,248
0.36	10.23	3,685	2,396	9.01	647	2,387	269	1,244
0.37	10.46	3,144	2,106	7.48	664	2,498	347	1,329
0.38	10.48	2,639	1,728	5.82	659	2,598	358	1,409

Table D.4 Raw data for 4<sup>th</sup> run of experiment

<b>OLR (mg BOD<sub>3</sub>/L. g day)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
0.27	7.24	3,580	2,013	8.54	647	2,473	326	1,245
0.29	8.33	4,022	2,386	11.12	654	2,548	336	1,153
0.30	8.65	3,572	2,795	13.00	653	2,546	289	1,359
0.31	8.77	4,009	3,216	16.82	647	2,438	261	818
0.32	8.91	4,194	3,207	17.06	635	2,369	259	916
0.33	8.23	4,443	3,135	15.61	654	2,278	279	1,024
0.34	8.93	4,350	2,968	14.51	659	2,487	299	1,155
0.35	9.12	3,919	2,687	11.20	664	2,598	330	1,261
0.36	9.94	4,145	2,418	9.87	658	2,548	325	1,354
0.37	10.03	3,791	2,198	8.04	648	2,438	340	1,330
0.38	10.77	3,046	1,696	6.07	635	2,538	358	1,425

## APPENDIX E

### RAW DATA FOR EXPERIMENT OF EFFECT OF MIXED LIQUOR VOLATILE SUSPENDED SOLID ON POME TREATMENT

Table E.1 Raw data for 1<sup>st</sup> run of experiment

<b>Initial MLVSS (mg/L)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
1,000	7.32	3,918	2,086	8.62	645	2,657	320	1,420
2,000	8.28	4,907	2,985	12.66	657	2,546	292	1,134
3,000	7.95	4,302	3,145	15.69	664	2,476	263	999
4,000	8.22	4,408	3,365	18.31	635	2,487	220	845
5,000	8.90	4,700	3,686	20.94	658	2,676	229	841
6,000	8.77	5,396	3,768	21.44	637	2,587	239	1,026
7,000	9.03	5,689	3,968	19.76	667	2,648	269	1,130
8,000	9.03	6,266	4,267	18.60	646	2,476	287	1,227
9,000	9.12	6,858	4,687	20.39	670	2,648	332	1,048
10,000	9.01	7,789	5,245	21.61	653	2,704	318	1,154

Table E.2 Raw data for 2<sup>nd</sup> run of experiment

<b>Initial MLVSS (mg/L)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
1,000	7.05	4,257	2,156	10.09	638	2,437	335	1,132
2,000	7.94	4,929	3,023	14.42	664	2,584	330	1,286
3,000	8.79	4,581	3,266	15.91	646	2,347	287	921
4,000	8.55	4,554	3,426	17.06	658	2,647	262	965
5,000	8.04	4,867	3,857	19.94	647	2,587	270	1,026
6,000	8.93	5,561	3,967	20.23	664	2,436	263	896
7,000	8.23	5,616	4,046	18.85	647	2,685	236	1,060
8,000	9.02	6,298	4,367	18.43	653	2,648	259	1,039
9,000	8.84	6,715	4,865	19.36	636	2,547	302	1,137
10,000	9.12	8,237	5,474	22.06	663	2,647	330	1,156

Table E.3 Raw data for 3<sup>rd</sup> run of experiment

<b>Initial MLVSS (mg/L)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
1,000	7.55	3,685	2,076	9.67	648	2,376	346	1,196
2,000	8.44	4,830	3,156	15.75	658	2,658	301	1,261
3,000	8.12	4,736	3,326	18.09	664	2,365	309	839
4,000	8.32	4,402	3,487	20.50	653	2,587	266	1,052
5,000	8.12	4,484	3,647	21.85	668	2,685	265	826
6,000	8.03	4,803	3,757	22.17	645	2,437	287	962
7,000	8.55	5,492	3,857	15.51	634	2,576	294	939
8,000	8.54	6,168	4,276	17.36	654	2,376	270	990
9,000	8.56	7,284	4,736	17.81	647	2,547	269	1,239
10,000	8.54	7,880	5,386	20.84	638	2,750	286	1,223

Table E.4 Raw data for 4<sup>th</sup> run of experiment

<b>Initial MLVSS (mg/L)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
1,000	7.24	3,480	1,957	8.30	648	2,577	327	1,254
2,000	8.33	5,116	3,035	14.14	664	2,658	341	1,338
3,000	8.77	4,702	3,255	15.14	648	2,487	321	1,255
4,000	8.65	4,579	3,297	16.62	653	2,657	284	1,024
5,000	8.91	4,645	3,726	19.49	654	2,476	267	781
6,000	8.23	5,295	3,835	20.40	670	2,355	286	910
7,000	8.93	5,500	3,924	19.54	645	2,584	318	1,162
8,000	8.30	6,353	4,476	21.89	638	2,476	317	1,202
9,000	8.43	6,857	4,638	19.34	664	2,365	334	1,098
10,000	8.65	8,013	5,476	20.59	653	2,658	324	1,323

UMP

## APPENDIX F

### RAW DATA FOR EXPERIMENT OF EFFECT OF SOLID RETENTION TIME ON POME TREATMENT

Table F.1 Raw data for 1<sup>st</sup> run of experiment

<b>SRT (days)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
2	7.32	4,051	2,157	9.15	664	2,657	330	1,420
4	8.28	4,072	2,477	12.36	634	2,546	282	1,134
6	8.22	3,773	2,758	15.00	643	2,498	254	1,008
8	7.95	3,888	2,968	16.86	634	2,436	262	966
10	8.90	4,191	3,287	20.48	658	2,376	229	763
12	8.77	4,332	3,025	16.15	663	2,487	285	904
14	9.03	4,187	2,857	14.23	653	2,685	294	1,145
16	8.56	3,629	2,476	10.80	639	2,437	308	1,208
18	8.92	3,187	2,178	9.47	670	2,657	342	1,258
20	9.13	2,923	1,968	7.83	654	2,648	354	1,251

Table F.2 Raw data for 2<sup>nd</sup> run of experiment

<b>SRT (days)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
2	7.05	4,081	2,067	9.86	658	2,648	345	1,230
4	7.94	3,876	2,377	11.58	648	2,548	322	1,268
6	8.55	3,767	2,686	13.38	659	2,537	292	996
8	8.79	3,812	2,868	14.83	654	2,695	279	982
10	8.04	4,024	3,189	20.95	662	2,358	276	818
12	8.93	4,253	2,987	16.37	638	2,498	272	960
14	8.23	3,867	2,786	12.98	648	2,437	301	962
16	9.02	3,427	2,376	10.03	648	2,487	306	975
18	9.04	3,280	2,376	9.46	653	2,547	324	1,137
20	9.04	3,275	2,176	8.83	664	2,647	350	1,238

Table F.3 Raw data for 3<sup>rd</sup> run of experiment

<b>SRT (days)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
2	7.55	3,930	2,214	11.05	645	2,547	344	1,282
4	8.44	3,898	2,547	13.86	653	2,633	299	1,249
6	8.87	3,927	2,758	16.22	658	2,438	306	865
8	8.12	3,670	2,907	17.41	657	2,587	268	1,052
10	8.12	3,880	3,156	19.66	636	2,424	252	813
12	8.03	3,936	3,079	17.03	654	2,547	291	951
14	8.55	3,785	2,658	10.69	665	2,648	293	965
16	8.98	3,429	2,377	9.65	659	2,695	301	1,123
18	9.10	3,500	2,276	8.56	648	2,438	328	1,186
20	8.95	3,439	2,078	6.32	654	2,575	338	1,271

Table F.4 Raw data for 4<sup>th</sup> run of experiment

<b>SRT (days)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
2	7.24	3,889	2,187	10.19	635	2,548	320	1,240
4	8.33	4,107	2,436	11.33	647	2,655	332	1,337
6	8.65	3,839	2,658	13.40	664	2,483	329	1,253
8	8.77	4,061	2,924	15.29	658	2,566	286	989
10	8.91	3,998	3,207	20.27	643	2,439	262	848
12	8.23	5,164	3,126	16.97	638	2,387	272	923
14	8.93	3,937	2,686	13.38	653	2,548	310	1,146
16	8.95	3,855	2,287	11.18	647	2,647	321	1,285
18	8.99	3,749	2,187	9.12	652	2,648	328	1,230
20	9.03	3,304	2,068	6.41	668	2,538	348	1,264

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## APPENDIX G

### RAW DATA FOR EXPERIMENT OF EFFECT OF EXTERNAL CARBON SOURCES POME TREATMENT

Table G.1 Raw data for 1<sup>st</sup> run of experiment

Molasses Concentration (mg/L)	pH after treatment	MLSS (mg/L)	MLVSS (mg/L)	OUR (mg O <sub>2</sub> /L.h)	BOD Initial (mg/L)	COD Initial (mg/L)	BOD Final (mg/L)	COD Final (mg/L)
0	8.35	2,938	2,067	12.36	654	2,376	241	942
10	7.98	3,238	2,346	14.36	639	2,675	188	900
20	8.21	3,601	2,676	17.31	657	2,586	239	1,041
30	7.94	3,699	2,865	20.37	647	2,598	225	976
40	8.42	3,990	3,046	22.39	665	2,576	232	875
50	8.74	4,063	3,187	25.62	658	2,469	217	979
60	7.89	4,115	3,265	26.32	637	2,587	199	883
70	8.40	4,178	3,298	27.18	648	2,546	217	815
80	8.54	4,249	3,367	28.38	665	2,538	220	897
90	8.21	4,576	3,498	29.91	649	2,573	192	1,018
100	7.85	4,380	3,514	31.59	658	2,695	194	934

Table G.2 Raw data for 2<sup>nd</sup> run of experiment

Molasses Concentration (mg/L)	pH after treatment	MLSS (mg/L)	MLVSS (mg/L)	OUR (mg O <sub>2</sub> /L.h)	BOD Initial (mg/L)	COD Initial (mg/L)	BOD Final (mg/L)	COD Final (mg/L)
0	8.56	2,769	1,979	11.52	649	2,583	233	991
10	8.85	3,243	2,278	13.87	654	2,648	242	1,047
20	8.24	3,385	2,547	16.68	637	2,574	252	1,015
30	8.65	3,498	2,776	19.68	647	2,685	218	979
40	8.06	3,998	3,012	21.51	659	2,587	201	943
50	8.94	3,898	3,089	25.79	647	2,466	261	830
60	8.53	4,059	3,176	26.45	659	2,647	221	1,009
70	8.43	3,967	3,187	26.87	658	2,534	260	971
80	8.33	4,047	3,256	28.19	664	2,443	201	922
90	8.33	4,084	3,367	28.23	654	2,647	230	827
100	9.12	4,185	3,404	28.73	638	2,546	174	831

Table G.3 Raw data for 3<sup>rd</sup> run of experiment

<b>Molasses Concentration (mg/L)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
0	8.03	3,041	2,109	12.72	654	2,487	261	882
10	8.21	3,241	2,316	14.68	648	2,543	258	1,023
20	8.43	3,459	2,675	17.47	665	2,547	226	928
30	8.53	3,657	2,865	20.97	668	2,695	254	1,039
40	7.99	4,106	3,176	22.96	646	2,649	256	1,077
50	8.07	3,944	3,208	26.02	663	2,547	232	928
60	8.67	3,916	3,146	25.92	645	2,588	221	918
70	7.85	3,901	3,177	25.83	658	2,645	200	1,049
80	7.92	3,966	3,266	26.91	645	2,685	211	967
90	8.54	4,117	3,398	28.61	663	2,568	202	928
100	7.83	4,105	3,417	29.18	636	2,668	196	884

Table G.4 Raw data for 4<sup>th</sup> run of experiment

<b>Molasses Concentration (mg/L)</b>	<b>pH after treatment</b>	<b>MLSS (mg/L)</b>	<b>MLVSS (mg/L)</b>	<b>OUR (mg O<sub>2</sub>/L.h)</b>	<b>BOD Initial (mg/L)</b>	<b>COD Initial (mg/L)</b>	<b>BOD Final (mg/L)</b>	<b>COD Final (mg/L)</b>
0	7.53	2,982	2,098	12.55	668	2,543	272	972
10	8.05	3,274	2,307	14.05	651	2,547	242	971
20	8.04	3,559	2,657	17.78	653	2,659	252	887
30	8.54	3,911	2,857	20.60	667	2,446	274	995
40	8.95	3,898	3,105	22.32	658	2,644	271	1,019
50	8.04	3,985	3,197	25.67	645	2,587	197	1,023
60	8.44	3,895	3,215	26.65	638	2,598	243	1,311
70	8.76	4,008	3,288	27.72	653	2,498	205	950
80	8.39	4,070	3,314	26.64	663	2,647	214	903
90	8.45	4,025	3,398	28.34	648	2,533	206	865
100	8.64	4,193	3,414	29.60	647	2,546	241	846

## APPENDIX H

### CALCULATED DATA FOR BOD KINETIC STUDY OF POME

Table H.1 Computation table for  $BOD_{t+1}$  versus  $BOD_t$  value for Fujimoto Method

$BOD_t$	$BOD_t$ (mg/L)	$BOD_{t+1}$ (mg/L)
BOD <sub>1</sub>	220	445
BOD <sub>2</sub>	445	661
BOD <sub>3</sub>	661	769
BOD <sub>4</sub>	769	819
BOD <sub>5</sub>	819	880
BOD <sub>6</sub>	880	985
BOD <sub>7</sub>	985	

Table H.2 Computation table for  $(t/y)^{1/3}$  versus time,  $t$  (day) for Thomas Graphical

Method				
Time, $t$ (day)	$BOD_t$	$BOD, y$ (mg/L)	$\frac{t}{y}$	$\left(\frac{t}{y}\right)^{1/3}$
1	BOD <sub>1</sub>	220	0.0045	0.1657
2	BOD <sub>2</sub>	445	0.0045	0.1650
3	BOD <sub>3</sub>	661	0.0045	0.1656
4	BOD <sub>4</sub>	769	0.0052	0.1733
5	BOD <sub>5</sub>	819	0.0061	0.1828
6	BOD <sub>6</sub>	880	0.0068	0.1896
7	BOD <sub>7</sub>	985	0.0071	0.1923

Table H.3 Computation table for  $\log(dy/dt)$  versus time,  $t$  (day) for Log Different

Method					
Time $t$ , (day)	$BOD_t$	Mid-interval of $t$ , day	$BOD, y$ (mg/L)	$dy/dt$	$\text{Log}(dy/dt)$
1	BOD <sub>1</sub>	0.5	220	220	2.3424
2	BOD <sub>2</sub>	1.5	445	225	2.3522
3	BOD <sub>3</sub>	2.5	661	216	2.3345
4	BOD <sub>4</sub>	3.5	769	108	2.0334
5	BOD <sub>5</sub>	4.5	819	50	1.6990
6	BOD <sub>6</sub>	5.5	880	61	1.7853
7	BOD <sub>7</sub>	6.5	985	105	2.0212

Table H.4 Computation table for  $\sum y/L_0$  and  $\sum y/\sum yt$  with different  $k$  value for Method of Moment

$k$ Value	Sum BOD/ $L_0$ $\sum y/L_0$	Sum BOD/Sum BOD.t $\sum y/\sum yt$
0.05	2.465	0.207
0.10	3.908	0.213
0.20	5.358	0.223
0.40	6.340	0.236
0.60	6.665	0.242
0.80	6.812	0.245
1.00	6.889	0.247
1.20	6.933	0.248

Table H.5 Observed BOD ( $y_o$ ) and Estimated BOD ( $y_e$ ) value for different kinetic study methods in evaluation of BOD kinetic study methods

Time, $t$ (day)	BOD $_t$	Observed BOD, $y_o^{(a)}$ (mg/L)	Estimated BOD, $y_e^{(b)}$ (mg/L) for different kinetic study method				
			Least Square	Fujimoto	Thomas Graphical	Log Different	Moment
1	BOD $_1$	220	269.65	36.77	110.53	109.93	116.61
2	BOD $_2$	445	475.49	72.31	211.86	209.60	222.12
3	BOD $_3$	661	632.63	106.67	304.74	299.97	317.60
4	BOD $_4$	769	752.58	139.87	389.88	381.90	403.98
5	BOD $_5$	819	844.15	171.97	467.92	456.18	482.15
6	BOD $_6$	880	914.06	202.99	539.47	523.53	552.88
7	BOD $_7$	985	967.42	232.98	605.05	584.59	616.87

<sup>(a)</sup> Observed BOD ( $y_o$ ): BOD result gained from the experiment

<sup>(b)</sup> Estimated BOD ( $y_e$ ): BOD value gained when fitted into the first order BOD kinetic equation

**APPENDIX I**  
**RAW DATA FOR AERATION TANK VOLUME OF ACTIVATED SLUDGE**  
**SYSTEM CALCULATION**

Table I.1 Raw data for aeration tank volume of activated sludge calculation using BOD result

Parameters	Design calculation	Design calculation from	
	recommended by DOE	this study	uBOD
	BOD <sub>3</sub>	BOD <sub>3</sub>	
$Q_i$ (m <sup>3</sup> /day) <sup>(1)</sup>	702	702	702
$S_i$ (mg/L)	652	652	1,139
$S_e$ (mg/L) <sup>(2)</sup>	20	20	20
$\theta_c$ (day)	35	10	10
$k_d$ (day <sup>-1</sup> )	0.03	0.0658	0.0658
$Y$ (mg VSS/mg BOD)	0.3	0.6718	0.6718
$X$ (mg/L)	3,000 <sup>(3)</sup>	2,000	2,000
$V_r$ (m <sup>3</sup> )	916.52 <sup>(4)</sup>	1,090.62 <sup>(5)</sup>	1,931.02 <sup>(6)</sup>
$\theta$ (hrs)	31.44 <sup>(7)</sup>	37.20 <sup>(8)</sup>	66.00 <sup>(9)</sup>
F/M Ratio (mg BOD/mg MLVSS)	0.17 <sup>(10)</sup>	0.21 <sup>(11)</sup>	0.21 <sup>(12)</sup>

Notes:

- (1) Palm Oil Mill production capacity: 45 ton/hr for 24 hours operation per day  
POME discharge rate: 0.65 m<sup>3</sup>/ton of FFB  
Thus, daily flow of POME = 45 ton/hr × 0.65 m<sup>3</sup>/ton × 24 hours/day  
= 702 m<sup>3</sup>/day
- (2) New POME discharge standard = 20 mg/L
- (3) DOE design criteria range for MLSS = 3,000 – 6,000 mg/L and VSS/SS range = 0.60 - 0.75,  
Thus, MLVSS,  $X = 0.75 \times \text{MLSS}$   
=  $0.75 \times 3,500$   
= 2,625 mg/L  
For the design calculation,  $X$  shall not smaller than 2,625 mg/L, so,  $X = 3,000$  mg/L been selected.

- (4) Aeration tank volume calculation formula as following:

$$\text{Aeration Tank Volume, } V_r = \frac{\theta_c Q Y (S_i - S_e)}{X [1 + k_d f_b \theta_c]} \quad 2.34$$

$$\text{Biodegradable fraction of VSS, } f_b = \frac{f'_b}{[1 + (1 - f'_b) k_d \theta_c]} \quad 2.35$$

Where  $f'_b = 0.8$  (DOE default value)

Thus,

$$\begin{aligned} \text{Biodegradable fraction of VSS, } f_b &= \frac{0.8}{[1 + (1 - 0.8)0.03 \times 35]} \\ &= 0.6612 \end{aligned}$$

$$\text{Aeration Tank Volume, } V_r = \frac{35 \times 702 \times 0.3(652-20)}{3,000 [1+(0.03 \times 0.6612 \times 35)]}$$

$$= 916.52 \text{ m}^3$$

(5) From section 4.1.1.1 in this study,

$$\text{Biodegradable fraction of VSS, } f_b = \frac{\text{VSS}}{\text{TSS}}$$

$$= \frac{14,285}{25,649}$$

$$= 0.5569$$

Thus,

$$\text{Aeration Tank Volume, } V_r = \frac{10 \times 702 \times 0.6718(652-20)}{2,000 [1+(0.0658 \times 0.5569 \times 10)]}$$

$$= 1,090.62 \text{ m}^3$$

(6) Aeration Tank Volume,  $V_r = \frac{10 \times 702 \times 0.6718(1,139-20)}{2,000 [1+(0.0658 \times 0.5569 \times 10)]}$

$$= 1,931.02 \text{ m}^3$$

(7) Hydraulic Retention Time,  $\theta = \frac{916.52}{702}$

$$= 1.31 \text{ days @ } 31.44 \text{ hours}$$

(8) Hydraulic Retention Time,  $\theta = \frac{1,090.62}{702}$

$$= 1.55 \text{ days @ } 37.20 \text{ hours}$$

(9) Hydraulic Retention Time,  $\theta = \frac{1,931.02}{702}$

$$= 2.75 \text{ days @ } 66.00 \text{ hours}$$

(10) F/M Ratio =  $\frac{Q_i \times S_i}{V_r \times X}$

$$= \frac{702 \times 652}{916.52 \times 3,000}$$

$$= 0.17 \text{ kg BOD/kg MLVSS.day}$$

(11) F/M Ratio =  $\frac{702 \times 652}{1,090.62 \times 2,000}$

$$= 0.21 \text{ kg BOD/kg MLVSS.day}$$

$$(12) \quad F/M \text{ Ratio} = \frac{702 \times 1,139}{1,931.02 \times 2,000}$$

$$= 0.21 \text{ kg BOD/kg MLVSS.day}$$

Table I.2 Raw data for aeration tank volume of activated sludge calculation using COD result

Parameters	Design calculation from this study		
	tCOD	bCOD	srbCOD
$Q_i$ (m <sup>3</sup> /day)	702	702	702
$S_i$ (mg/L)	2,493	1,235	719
$S_e$ (mg/L) <sup>(1)</sup>	80	80	80
$\theta_c$ (day)	10	10	10
$K_d$ (day <sup>-1</sup> )	0.1060	0.1060	0.1060
$Y$ (mg VSS/mg COD)	0.2369	0.2369	0.2369
$X$ (mg/L)	2,000	2,000	2,000
$V_r$ (m <sup>3</sup> )	1,261.67 <sup>(2)</sup>	603.91 <sup>(3)</sup>	334.11 <sup>(4)</sup>
$\theta$ (hrs)	43.20 <sup>(5)</sup>	20.64 <sup>(6)</sup>	11.52 <sup>(7)</sup>
F/M Ratio (mg COD/mg MLVSS)	0.69 <sup>(8)</sup>	0.72 <sup>(9)</sup>	0.76 <sup>(10)</sup>

Note:

(1) Discharge standard A for COD = 80 mg/L

$$(2) \quad \text{Aeration Tank Volume, } V_r = \frac{10 \times 702 \times 0.2369(2,493-80)}{2,000 [1+(0.1060 \times 0.5569 \times 10)]}$$

$$= 1,261.67 \text{ m}^3$$

$$(3) \quad \text{Aeration Tank Volume, } V_r = \frac{10 \times 702 \times 0.2369(1,235-80)}{2,000 [1+(0.1060 \times 0.5569 \times 10)]}$$

$$= 603.91 \text{ m}^3$$

$$(4) \quad \text{Aeration Tank Volume, } V_r = \frac{10 \times 702 \times 0.2369(719-80)}{2,000 [1+(0.1060 \times 0.5569 \times 10)]}$$

$$= 344.11 \text{ m}^3$$

$$(5) \quad \text{Hydraulic Retention Time, } \theta = \frac{1,261.67}{702}$$

$$= 1.80 \text{ days @ } 43.20 \text{ hours}$$

$$(6) \quad \text{Hydraulic Retention Time, } \theta = \frac{603.91}{702}$$

$$= 0.86 \text{ days @ } 20.64 \text{ hours}$$

$$(7) \quad \text{Hydraulic Retention Time, } \theta = \frac{334.11}{702}$$

$$= 0.48 \text{ days @ } 11.52 \text{ hours}$$

$$(8) \quad F/M \text{ Ratio} = \frac{702 \times 2,493}{1,261.67 \times 2,000}$$

$$= 0.69 \text{ kg COD/kg MLVSS.day}$$

$$(9) \quad F/M \text{ Ratio} = \frac{702 \times 1,235}{603.91 \times 2,000}$$

$$= 0.72 \text{ kg COD/kg MLVSS.day}$$

$$(10) \quad F/M \text{ Ratio} = \frac{702 \times 719}{334.11 \times 2,000}$$

$$= 0.76 \text{ kg COD/kg MLVSS.day}$$

Table I.3 Design criteria for Extended Aeration Activated Sludge System (DOE, 2010a)

Design variable	Unit	Design Range
F/M Ratio	kg BOD/ (kg MLVSS.day)	0.05- 0.15
HRT, $\theta$	hours	18 – 36*
MLSS	mg/L	3,500 – 6,000*
Yield coefficient, $Y^*$	kg VSS/kg BOD <sub>5</sub> <sup>(1)</sup>	0.1 – 0.3
Decay coefficient, $k_d^*$	day <sup>-1</sup>	0.03 – 0.15
Sludge age, $\theta_c$	day	15 – 35*
VSS/SS	-	0.60 – 0.75

Note:

\* The design value shall not be smaller than the lower range

(1) BOD<sub>3</sub> result was used for POME biological aeration tank volume design calculation

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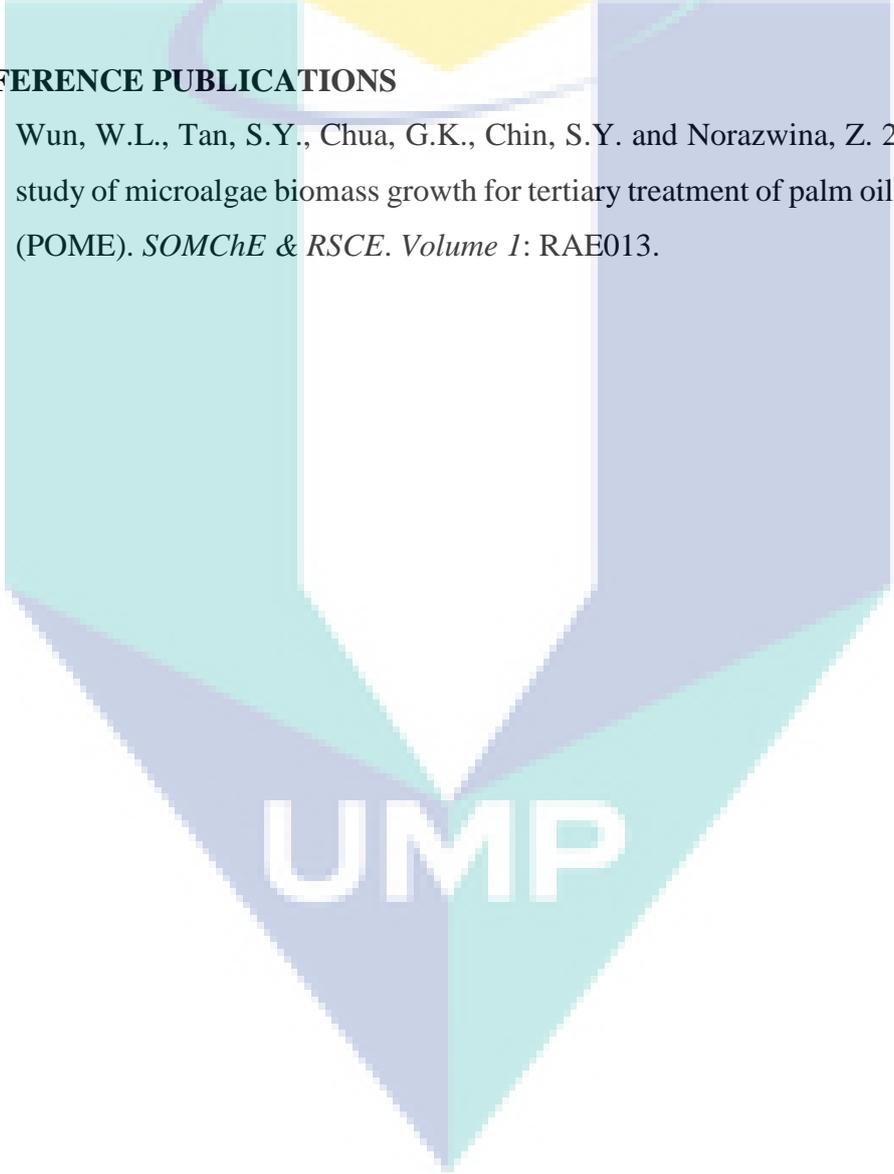
## PUBLICATIONS

### JOURNAL PUBLICATIONS

1. Wun, W.L., Chua, G.K. and Sim, C.Y. 2017. Effect of palm oil mill effluent (POME) treatment by activated sludge. *Journal CleanWAS*. 1(2):06-09.
2. Wun, W.L., Chua, G.K., Chin, S.Y. and Zainol, N. 2019. Kinetic study of palm oil mill effluent (POME) treatment by activated sludge. *Journal of Chemical Engineering and Industrial Biotechnology*. 5: 48-56.

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1. Wun, W.L., Tan, S.Y., Chua, G.K., Chin, S.Y. and Norazwina, Z. 2014. Kinetic study of microalgae biomass growth for tertiary treatment of palm oil mill effluent (POME). *SOMChE & RSCE. Volume 1*: RAE013.



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