Investigate the Relation between Particle Size Distribution (PSD) Using Image Analysis Method and Chemical Oxygen Demand (COD) In POME Sample

by

Anis Afiqah Bt Mohd Fathilah

16912

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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Universiti Teknologi PETRONAS

32610 Bandar Seri Iskandar

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

____

(Dr. Taslima Khanam)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ANIS AFIQAH BT MOHD FATHILAH

ABSTRACT

Palm Oil Mill Effluent ("after this will be mentioned as POME") is generated as by-product during clarification and purification process to produce Crude Palm Oil (CPO). POME is a by-product which contains harmful organic soluble material if released to the environment and; therefore, it need to be treated first before discharged to the environment. Chemical Oxygen Demand ("after this will be mentioned as COD") represents total organic solvent in the wastewater and also amount of oxygen needed by the microorganism to oxidize the organic carbon completely to carbon dioxide, water and ammonia. Particle Size Distribution ("after this will be mentioned as PSD") generally will affect the settling velocity, rate of sedimentation, flocculation, coagulation and absorption of organic compound. Thus, biological degradation rate in term of COD reduction is also influenced by PSD. To observe the particle size, bright field microscopy is used to acquire the image of particle size under light microscopy, and later the image will be analysed using Matlab 7.3 in order to extract all the image parameters needed. Therefore, the main objective of this paper is to evaluate the potential of PSD in the POME influent and effluent, investigate the relation between PSD and COD in order to determine COD for fast assessment for the wastewater fractions in term of biodegradability. In this research, two sample of POME will be obtained which are fresh POME collected from FELCRA Nasaruddin and effluent POME collected from environment analysis laboratory after it undergo wastewater treatment. Next, the COD will be obtained using Reactor Digestion Method-DR5000 according to method proposed by HACH Solution. In order to get the PSD, the image capture under light microscopy and processes using Matlab7.3. By conducting this research, image analysis algorithm can be developed in monitor the particle size, and the relation between PSD and COD can be observed.

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Special thanks to the examiners for the Proposal Defense and Poster Presentation, who were being very supportive and guiding me through my mistakes to make the project even better. Not to forget coordinator for his/her continuous monitoring and guidance also the lab technicians for their assistances.

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TABLE OF CONTENTS

LIST OF ABBREVIATIONS AND NOMENCLATURES

PSD	Particle Size Distribution
COD	Chemical Oxygen Demand
POME	Palm Oil Mill Effluent
RBCOD	Readily Biodegradable Chemical Oxygen Demand
SBCOD	Soluble Biodegradable Chemical Oxygen Demand
ISCOD	Inert Soluble Chemical Oxygen Demand
IPCOD	Inert Particulate Chemical Oxygen Demand
ASM	Activated Sludge Model
OUR	Oxygen Uptake Rate

LIST OF FIGURES

LIST OF TABLES

LIST OF APPENDIX

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The amount of oil palm shelter has increased in the last few years, with a parallel increase in palm oil production. Hence, palm oil waste which is a by-product of the milling process will also increase. The palm oil production process in mills consists of few steps. From Fresh Fruit Bunches (FFB) process of palm oil, it will give different types of residue. Among the waste produced, palm oil mill effluent (POME) is categorized as dangerous waste for the environment if discharged without being treated first. Palm oil mill effluent is a thick brownish liquid that comprises high suspended solids, Oil and Grease, Chemical Oxygen Demand and Biological Oxygen Demand values (P.F.Rupani, 2010).

According to Sawyer (1967), Chemical Oxygen Demand (COD) represents the amount of oxygen necessary to oxidize the organic carbon completely to carbon dioxide, water and ammonia. Major development has been achieved since the introduction of activated sludge model, in which COD was fractioned into four categories according to their biodegradation characteristics and physical state: readily biodegradable COD (RBCOD), slowly biodegradable COD (SBCOD), inert soluble COD (ISCOD), inert particulate COD (IPCOD) (G.A.Ekama, 1986). Recently, the research been directed towards particle size information for an enhanced understanding of COD fractionation and correlated biodegradation patterns (E.Dulekgurgen, 2006). From the previous research, it is found that PSD can only be used as qualitative index on the wastewater biodegradability, and there is no specific relation between PSD and wastewater biodegradability that can be found.

The particle size of the organic matter in the domestic wastewater ranges from nano scale to several millimeters. The small size organic particles usually can be consumed by biomass easily. While the larger particles usually need to be hydrolyzed before it can be used by the biomass (Metcalf, 2002). The PSD of these organics has found to be an important factor affecting the biodegradation process (O.Karahan, 2008). Many studies tried to relate the wastewater PSD by using varies method such as sequential filtration and ultrafiltration (E.Dulekgurgen, 2006;O.Karahan, 2008), particle counters (Dailey), and laser scattering technique (J.Wu C. , 2012) to the biodegradability fractions. By using sequential filtration and ultrafiltration, they successfully divided particle range into particulate (settleable (>10^5 nm) and supracolloidal (10^3 nm -10^5 nm)), soluble range (<2nm) and assume others to be colloidal (2nm-1600nm). For particle counter method, it only measured particulate in filter effluent and laser scattering technique is a straightforward method for measuring the low range of particle size which is between 0.1µm-0.4µm.

From the previous research, many studies try to relate particle size with its biodegradability fractions but unfortunately there is no specific relation between particle size and biodegradability fractions can be found. Researcher also had difficulties to come out with one single definition of size fractions in sequential filtration and ultrafiltration method as there is variation among the exact cut off size given in the studies. By using filtration method, certain operating parameters need to be maintained and the operator must work under the required temperature and pressure. Proper cleaning after filtered each sample need to be done in order to avoid errors in next filtration. In addition to that, measuring particle size using laser scattering technique not preferable as it only measure low range particle size, and measurement for particle size below 0.1μm can be a great uncertainty. Therefore, the author will use and develop image analysis method in this paper work to further investigate relation between PSD and COD fractionation.

1.2 Problem Statement

From the previous research, some studies try to relate particle size with its biodegradability fractions but unfortunately there is no specific relation between particle size and biodegradability fractions. Researcher also had difficulties to come out with one single definition of size fractions in sequential filtration and ultrafiltration method as there is variation among the exact cut off size given in the studies. By using filtration method, certain operating parameters need to be maintained, and the operator must work under the required temperature and pressure. Proper cleaning after filtered each sample need to be done in order to avoid errors in next filtration. In addition to that, measuring particle size using laser scattering technique not preferable as it only measure low range particle size and measurement for particle size below 0.1μm can be a great uncertainty. Therefore, the author will use and develop image analysis method in this paper work to further investigate relation between PSD and COD fractionation.

Earlier, most of the researcher use respirometric analysis where it measured the biological oxygen consumption under experimental condition and it is proof to be useful technique in monitoring activated sludge process. However, this method required complicated activated sludge model in which the involved parameters need to be carefully monitored and most of the wastewater treatment operators do not have the skills and modeling knowledge to carry out the analysis. Therefore, the author has come out with another study to investigate the relation between PSD and COD using the image analysis method parallel with reactor digestion method for better interpretation of biodegradability fractions using wastewater from Palm Oil Mill Effluent (POME).

1.3 Objective

The objectives of this study are:

1) To evaluate the potential of PSD via image analysis method
2) To investigate the relation between PSD and COD in order to determine the COD for the fast assessment for the wastewater fractions in term of biodegradability.

1.4 Scope of Study

The scopes of studies are as following:

1) Monitoring particle size using light microscopy
2) Determined PSD using image analysis algorithm in Matlab
3) Proposed method will be applied to determine COD of Palm Oil Mill Effluent.

CHAPTER 2

LITERATURE REVIEW

2.1 Palm Oil Mill Effluent (POME)

Palm oil industry is one of the major profit earner and largest producer in Malaysia. As demand of palm oil keep increasing from year to year, it is not surprising that very large production of effluent become main source of water pollution in Malaysia. In Malaysia, it is estimated that at least 60 million tonnes of POME was generated in the year 2009 alone (Ng, 2011). Fresh POME is a hot, acidic (pH between 4 and 5), brownish colloidal suspension containing high concentration of organic matter, high amounts of total solids (40,500 mg L^{-1}), oil and grease (4,000 mg L^{-1}), COD (50,000 mg L^{-1}) and BOD (25,000 mg L^{-1}) (Ma, 2000).

2.2 Chemical Oxygen Demand Fractionation and Its Biodegradability

According to Sawyer (1967), COD represents the amount of oxygen necessary to oxidize the organic carbon completely to carbon dioxide, water and ammonia. Nowadays, research effort has been directed towards particle size information for a better understanding COD fractionation and correlated biodegradation patterns (E.Dulekgurgen, 2006).

2.2.1 COD Fractionation and Biodegradability by Respirometry Analysis

Research by (O.Karahan, 2008) had established scientific link between PSD and biodegradability of different COD fractions by using filtration/ultrafiltration, respirometric analysis and model evaluation. Respirometric analysis is one of the methods to determine biological oxygen consumption rate under the certain experimental condition. Respirometry is useful technique for monitoring and controlling the activated sludge process as oxygen consumption is directly associated with the biomass growth and also substrate removal. By interpreting the oxygen uptake rate (OUR) profile; the area under the curve was used for estimation of biodegradable COD. Activated Sludge Model (ASM) or model evaluation widely used previously as a basis for further model development in wastewater treatment plant. ASM1 developed primarily for municipal activated sludge to model and describe the removal of organic carbon compounds and ammonium-N, with facultative consumption of oxygen or nitrate as the electron acceptor (A.Damayanti, 2010). ASM2 develop nitrogen removal processes including biological phosphorus removal processes and lastly ASM3 similar to ASM1 for biological N removal.

PSD profiles were determined in physical separation experiments, using eight membrane discs, each with different pore sizes between 2 and 1600 nm. Biodegradability-related COD fractionation was determined at each size interval by model simulation and calibration of the corresponding oxygen uptake rate (OUR) profile (O.Karahan, 2008). For better interpretation result, the PSD was divided into three groups which is particulate (settle able (>10^5) and supracolloidal (10^3-10^5)), colloidal (2nm-1600nm) and lastly soluble (<2nm). PSD analyses defined COD fingerprint with two significant portions at two ends of size distribution, with 60% of total COD at the particulate range, 25% at the soluble range and the remaining 15% well distributed among the colloidal range (O.Karahan, 2008).

2.2.2 COD Biodegradability Fractionated by Simple Physical-Chemical Analysis

A simple physical-chemical method was developed as an alternative to the respirometry method for determining the wastewater COD fractions in terms of biodegradability. Wastewater was fractionated into soluble (C_S), colloidal (C_C), non-settleable(C_{NS}) and settleable(C_{SS}) particle components by the physical-chemical method (J.Wu G. G., 2014). The COD biodegradability fractions including readily biodegradability COD (RBCOD), slowly biodegradability COD (SBCOD), inert soluble COD (ISCOD) and inert particulate COD (IPCOD) were determined from the respirometry and modeling method (J.Wu G. G., 2014). The result from the study indicates that physical-chemical conversion method can be reliable tool for the fast assessment for the wastewater fractions in terms of biodegradability and conversion matrix was derived to prove this method can produce stable result.

$$\begin{bmatrix} \boldsymbol{RBCOD} \\ \boldsymbol{SBCOD} \\ \boldsymbol{ISCOD} \\ \boldsymbol{IPCOD} \end{bmatrix} = \underbrace{\begin{bmatrix} \mathbf{0.21} & \mathbf{0.20} & \mathbf{0.19} & \mathbf{0.89} \\ \mathbf{0.11} & \mathbf{0.41} & \mathbf{0.62} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0.11} \\ \mathbf{0.68} & \mathbf{0.39} & \mathbf{0.19} & \mathbf{0} \end{bmatrix}}_{\text{Conversion matrix}} \begin{bmatrix} \boldsymbol{CSS} \\ \boldsymbol{CNS} \\ \boldsymbol{CC} \\ \boldsymbol{CS} \end{bmatrix} \pm \begin{bmatrix} \mathbf{19} \\ \mathbf{15} \\ \mathbf{5} \\ \mathbf{51} \end{bmatrix}$$

FIGURE 1. Conversion Matrix

2.3 Particle Size Distribution

It is important to know how particle size will affect the rate of biodegradability in wastewater because size of particle will influence the settling velocity of particle. Theoretically, larger particle will settle down easily as it is denser than small particle but it will also depend on the shape, roundness and density of the particle. Besides that, concentrations of adsorbed metals also depend on the particle size. From previous research, it was highlighted that PSD will affect the rate of sedimentation, flocculation, filtration, mass transfer, adsorption, diffusion and also biochemical reaction. Therefore, characterization of the size distribution of the contaminants in wastewater is important for developing a more fundamental understanding of the complex interaction that occur in the unit operations and treatment processes. Size distribution analyses of wastewater are also valuable for developing improved techniques for process selection and evaluation (A.D.Levine G. T., 1985). Furthermore, the biological degradation rate in terms of COD reduction is influenced by particle size distribution (A.D.Levine G. , 1991). Many studies tried to relate the wastewater PSD by measured by sequential filtrations (E.Dulekgurgen, 2006) ultrafiltration (O.Karahan, 2008), particle counters (Dailey), or laser scattering technique (J.Wu C. , 2012) to the biodegradability fractions.

2.4 Image Processing and Analysis

Originally, image analysis been used to characterize the morphology species such as filamentous bacteria and fungi. After that, (K.Grijspeerdt, 1997) found that low magnification microscopy (50x or 100x) of fixed or unstained slides together with image analysis become common to measure the shape and size of activated sludge flocs. Image analysis method more simple and can be categorized as non-laborious task. Furthermore, the application of automated techniques makes the measurement more reproducible and clearer, especially in the comparison to the traditional microscopic observations (E.L.Bizukojc, 2005). According to E.L.Bizukojc (2005) also, the automated image analysis procedures aim at quantification of the size and shape of activated sludge flocs Lately, by attaching the microscope to programmed image analysis software it become possible for faster evaluation of the activated sludge properties. A basic image processing procedure can be done by the example from (D.P. Mesquita, 2009), which start from image acquisition, background correction, image pre-processing and segmentation.

2.5 Image Analysis Techniques

According to JC (1990), there are four steps of image analysis procedure: sample and slide preparation, imaging and grabbing, image processing, and image analysis. Firstly, a slide or sample should be prepared and after that image is gained using optical, bright-field, confocal laser scanning or fluorescence microscope. After that, the images are captured by means of CCD cameras and kept on optical or magnetic data carriers with the use of relevant software (E.L.Bizukojc, 2005). In this study, the author use Matlab 7.3 to further analyze the image of particle size. According to E.L.Bizukojc (2005), image processing is a set of operations which are used to convert an image in order to allow measurement of the observed object and it will also enhanced the quality of an image by reducing noise, improving objects and identifying their edges. Next, the processed images are then separated and as a result a binary image is obtained before size of the objects and others parameters are measured.

Key point in using image analysis procedure is that an adequate number of images should be captured. According to K.Grijspeerdt (1997), minimum 150 objects which correspond to 10 images analyzed to obtain statically relevant result. However, according to da Motta.N (2001), maximum 70 images need to be captured as this number sufficient to obtained steady results. Later, (E.L.Bizukojc M. , 2005) confirmed that 40 image analysis was enough to gain stable result.

2.6 Fenton Process

According to S. Dogruel (2009) , Fenton’s reagent process, known as advanced oxidation process, involving catalytic decomposition Fe^{2+} to Fe^{3+} and H_2O_2 under acidic condition; pH around 2-5. The equation for Fenton’s reagent is as below:

$$Fe^{2+} + H_20_2 \rightarrow Fe^{3+} + OH^- + \bullet OH \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+ \quad (2)$$

One of the advantages of Fenton’s reagent treatment was easy to handle, and prove to be effective in term of removal rate and lower operating expenses in the industrial wastewater.

Research conducted by S. Dogruel (2009), they found that Fenton’s reagent was more remarkable in the soluble size range and it can only be useful as one of the option for preliminary treatment that involved series of filtration, oxidation and biological treatment steps.

CHAPTER 3

METHODOLOGY

3.1 Materials

3.1.1 Biomass Sampling

There will be two POME sampling to be analyzed which is influent and effluent palm oil mill.

1. Influent: Fresh POME collected from FELCRA Nasaruddin, Bota Perak at the fourth holding tank before discharged to the drain. It is to mention that the effluent of POME wastewater treatment at FELCRA Nasaruddin, Bota will be used as influent in this project.
2. Effluent: Sample will be taken after undergo Fenton Reagent treatment process. Fenton Reagent process used to oxidize contaminants of wastewater by using mixture of ferrous ion and hydrogen peroxide.

3.2 Method

3.2.1 Preparing the sample

The POME samples both raw and treated are allowed to be settled down for 45 minutes in order to separate the upper and lower layer. After that, it will be tested under light microscopy for particle size distribution and COD testing.

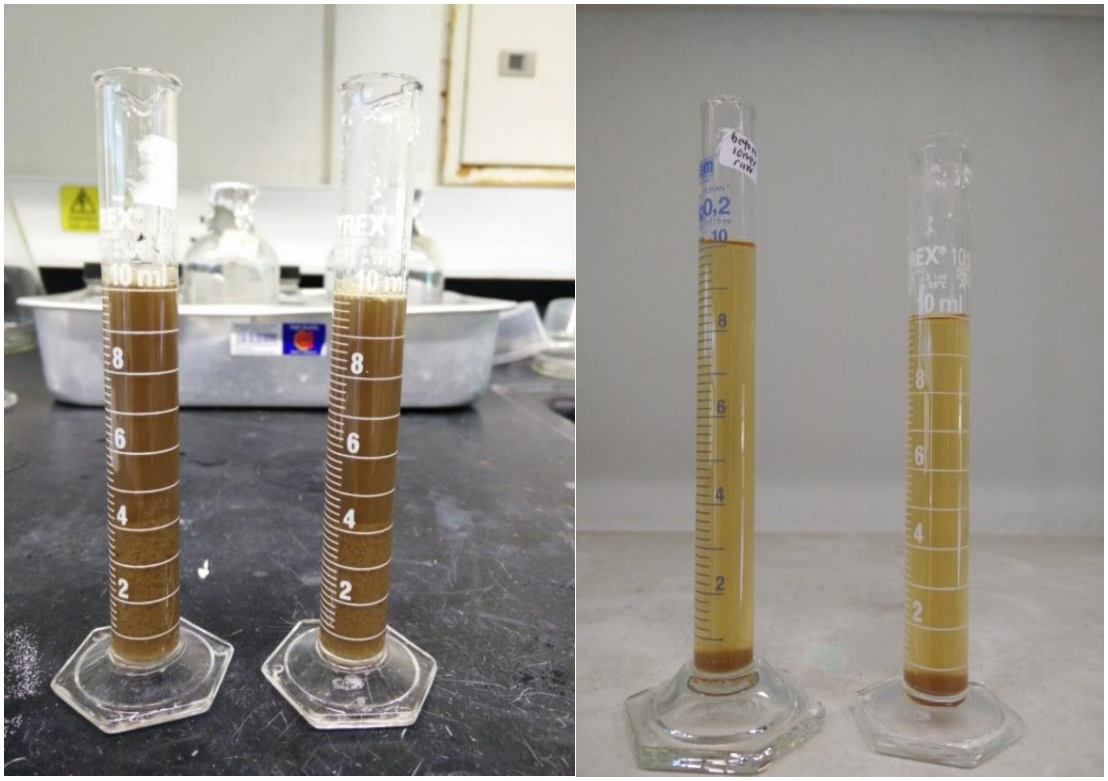

FIGURE 2. Sample Preparation

3.2.2 Measuring Chemical Oxygen Demand (COD)

COD measurement will be carried out by using spectrophotometer DRB200 and 5000-Reactor Digested Method according to Standard Method provided by HACH. The reactor digestion solution containing sulfuric acid, potassium dichromate, mercuric sulfate, silver sulfate and chromic acid will be mixed with 2 mL of the sample before heating for 2 hours at 120°C. After that, the sample will be left to cool down to room temperature before determination of COD value using 5000-spectrophotometer.

FIGURE 3. DRB200 Spectrophotometer

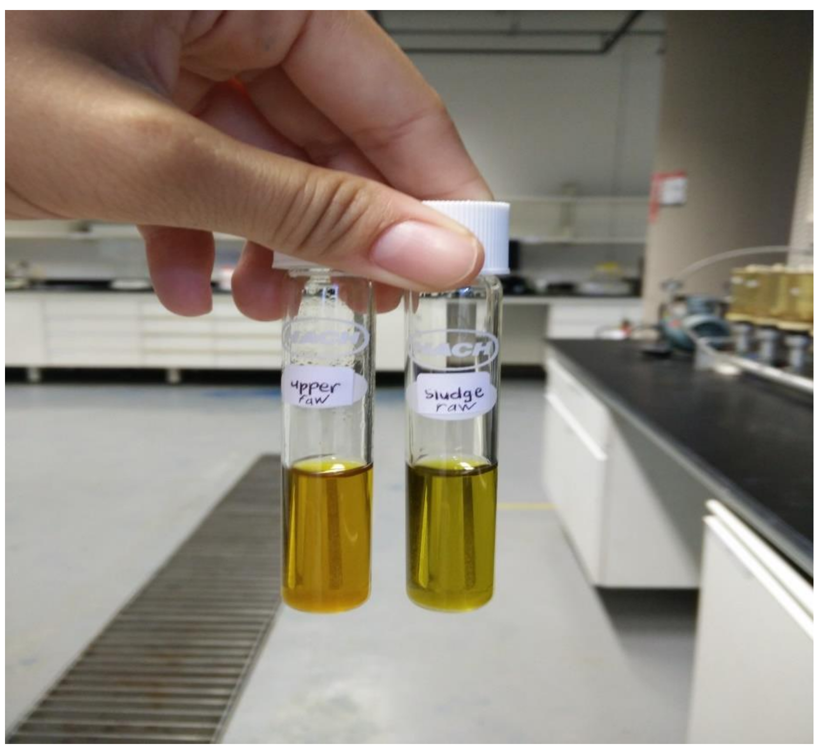

FIGURE 4. Reagent and sample for COD determination

3.2.3 Bright field image acquisition

Microscopy connected to the PC or known as automated image analysis aim at quantification of shape and size of the activated sludge flocs. This method do not allow for detailed identification of bacterial or microorganism and also visualization inside the flocs. Below are the steps to acquire the bright field image:

1. A recalibrated micropipette will be used to transfer sample on the microscope slide.
2. Each sample taken will be set to 10µL covered with 20mm x 20mm cover slip and total three slides per sample will be analyses in order to get accurate result.
3. Using light microscopy (MEIJI Microscopy MX 4300L), the segregates on the slides were then captured.
4. Image will be captured in the upper, middle, bottom of the slide in order to increase the accuracy of the result later.

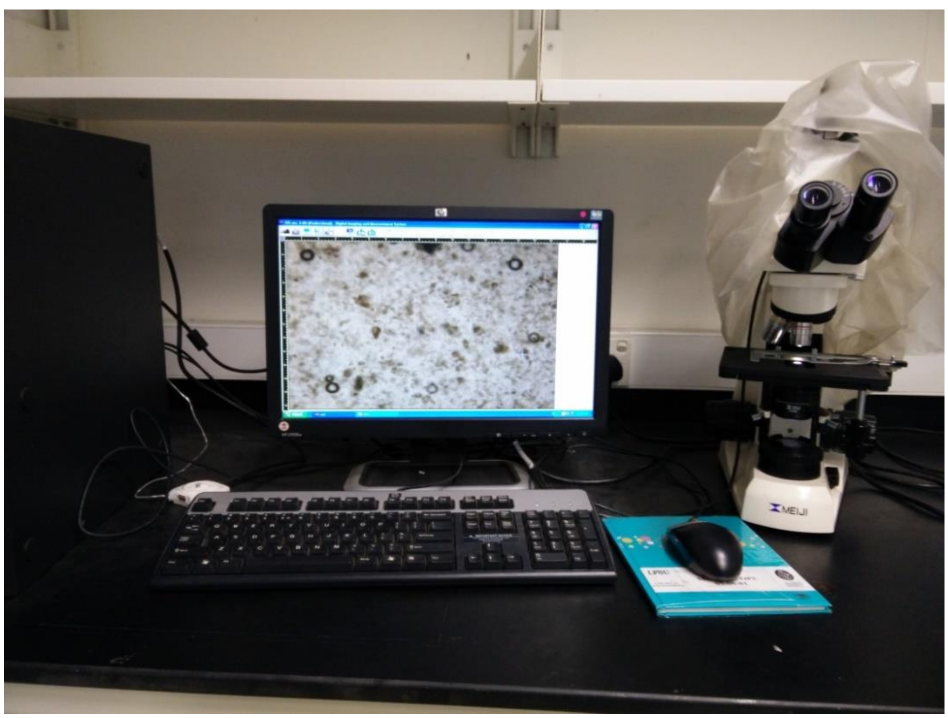

FIGURE 5. MEIJI MX4300L Light Microscopy

3.2.4 Image Analysis Processing

The image analysis analyzed in Matlab 7.3 and will be used in order to identify the size of the particle in the wastewater sludge. The image processing procedures are as below:

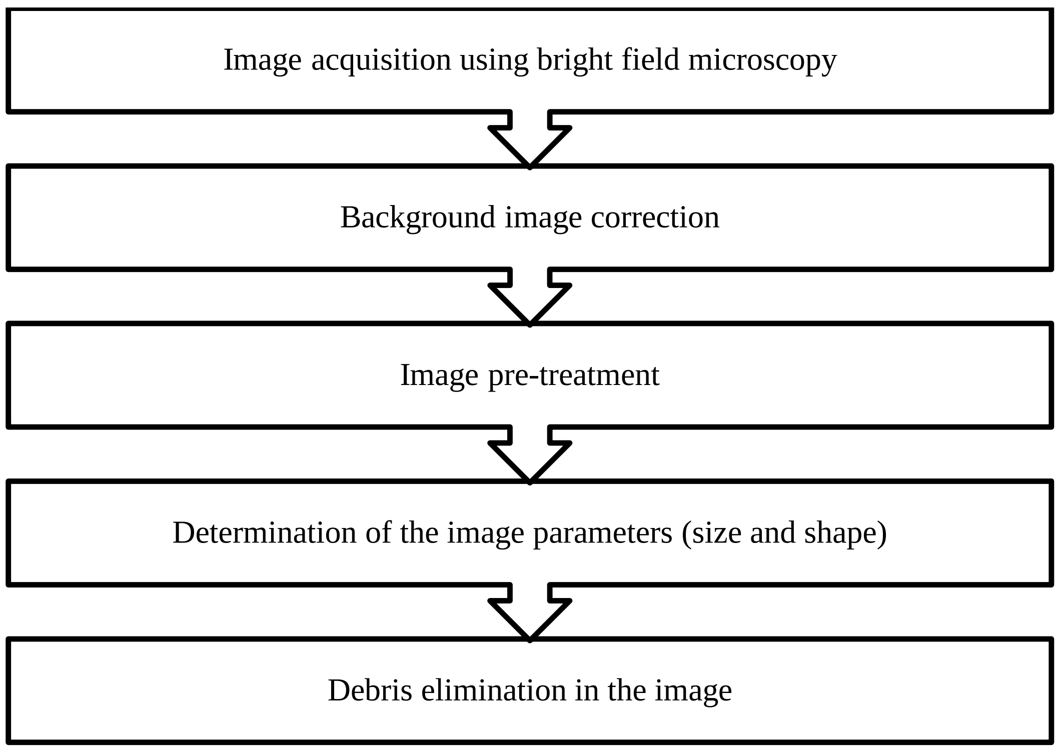

FIGURE 6. Procedures of the image processing

3.3 Process Flow of the Study

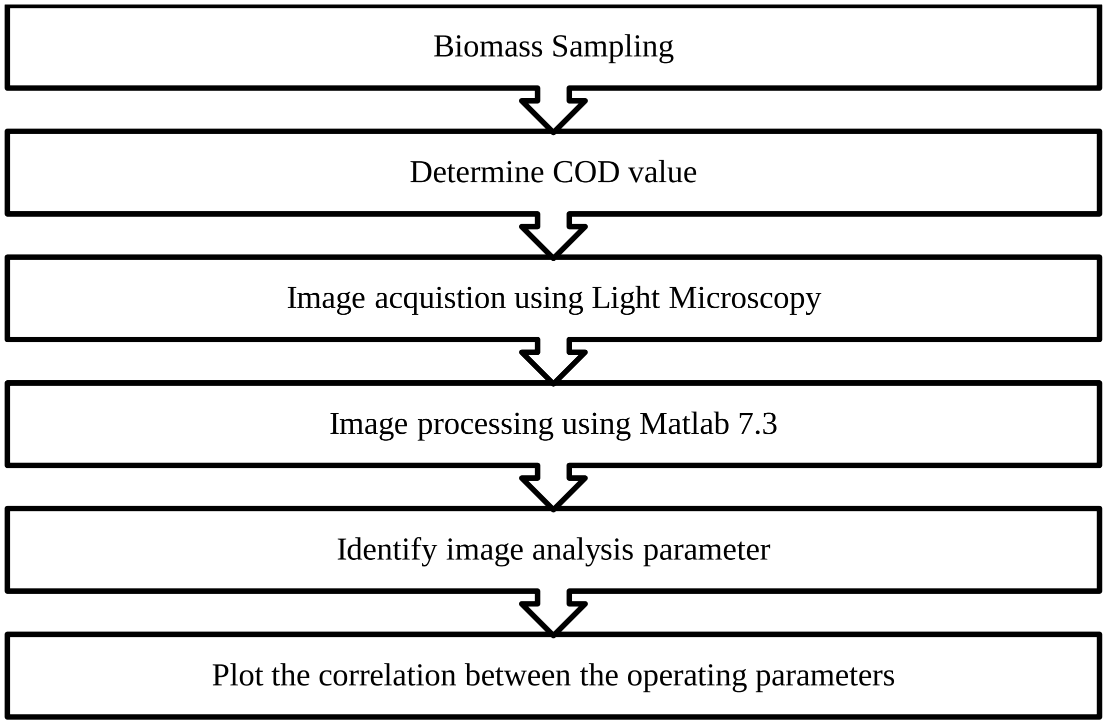

FIGURE 7. Process flow of the study

3.4 Project Key Milestone

TABLE 1 Project key milestone for FYPI

Week	Description
Week 1- Week 3 **Title Selection And Allocation**	Students are required to select the project titles given by the coordinator
Week 3 **First Meeting With The Supervisor**	Student is required to meet their supervisor in order to get the main ideas about the project. Project started with reading the articles, journals and any materials related to the study.
Week 4 – Week 8 **Extended Proposal Preparation**	Student starts to prepare for their extended proposal which consists of introduction, literature review and methodology. Students are required to come out with review from previous research that related to the project. In addition, student is also required to briefly explain the methodology that will be used for the project.
Week 9 **Proposal Defense Presentation**	Student is required to prepare presentation slide contains summary of their extended proposal to be present in front of the examiner
Week 9 – Week 13 **Preparation For The Interim Report**	This time, abstract and current progress report is added to the report. The student will also modify their report based on the feedback from the proposal defense presentation in order to improve their research.
Week 14 **Submission Of The Interim Report**	Student is required to send their final interim report to the supervisor and coordinator.

TABLE 2. Project key milestone for FYPII

Week	Description
Week 1- Week 7 **Experimental Activities**	Students are required to conduct their experimental activities in order to get the ideas and required results referring to their research paper with the guideline from their respective supervisor.
Week 3 – Week 7 **Progress Report Preparation**	Student starts to prepare for their progress report includes summary of project progress and expected result. The student will modify the previous interim report according to the comments given by their respective supervisor.
Week 8 **Progress Report Submission**	Student is obligatory to submit their progress report to the supervisor during week 8.
Week 11 **Pre-Sedex**	Student is required to develop a poster for a short presentation to report on their project progress to panel of internal examiner.
Week 13 **Technical Paper Submission**	Student is required to submit complete technical paper according to the previous sample of technical paper provided by the coordinator.
Week 15 **Dissertation Report Submission**	Student is required to submit their complete dissertation to respective supervisor. Supervisor will examine the report and make comments if any changes needed.

3.5 Project Timeline

3.5.1 Gantt Chart for Final Year Project I

TABLE 3. Gantt chart for FYP1

No	Detail / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Title selection and supervisor allocation	■													
2	Understanding the project		■	■											
3	Identifying the objectives and scope of study			■											
4	Conducting preliminary studies on the project				■	■									
5	Finding inventories data				■	■									
6	Preparation of extended proposal					■	■	■							
7	Submission of extended proposal								■						
8	Proposal defense									■					
9	Continuation of project work										■	■	■	■	■
10	Preparation of interim report											■	■	■	
11	Submission of interim report														■

3.5.2 Gantt Chart for Final Year Project II

TABLE 4 Gantt chart for FYPII

No	Detail / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Collection of influent and effluent sample	■													
2	Image analysis using light microscopy		■	■											
3	Image analysis using Matlab			■	■										
4	Submission of progress report							■							
5	COD testing						■	■							
6	Analysis of data						■	■	■	■	■	■	■		
7	Report completion												■		
8	Pre-SEDEX										■				
9	Submission of Draft Final Report											■	■		
10	Submission of technical report												■	■	
11	Viva													■	
12	Submission of Dissertation (hard bound)														■

CHAPTER 4

RESULTS AND DISCUSSION

By using the Matlab 7.3, the image analysis algorithm is conducted using the images each from upper and lower layer of influent and effluent sample of POME. In the Matlab, threshold value was set to 85 and commands are given to remove the dark particles, remove the small blobs and blobs touching the edge. The total particle number, maximum size and minimum size of the particle are obtained. All the data are gathered below:-

4.1 Preparing the Sample

The POME samples both influent and effluent, are allowed to be settled down for 45 minutes in order to separate the upper and lower layer. After that, it will be tested under light microscopy for particle size distribution and COD testing.

TABLE 5. Amount of influent and effluent after 45 minutes settling

	Influent	Effluent
Obtained (mL)	20	150
Upper (mL)	12	148
Lower (mL)	8	2

4.2 Particle Size Distribution

4.2.1 Influent

The image are captured using the light microscopy (MEIJI Microscopy MX 4300L)

Upper Layer

From 13 images captured, Matlab identified total of 49 individual particles for the upper layer of influent.

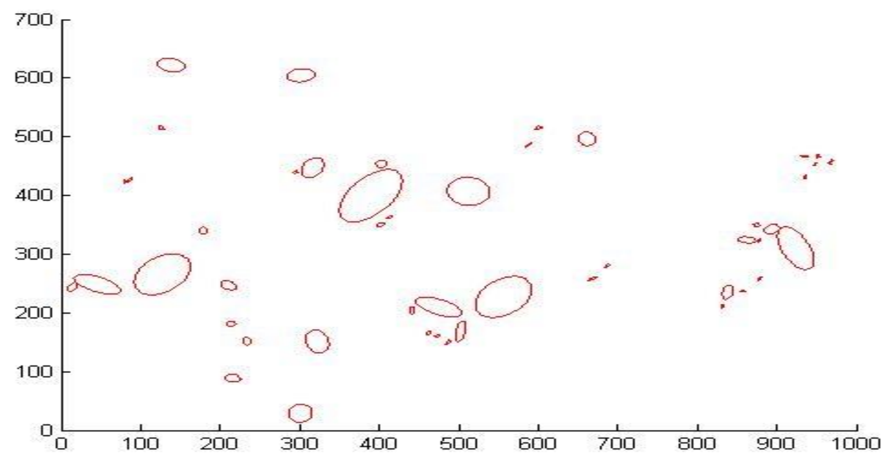

FIGURE 8. Influent Upper Layer Particle Identified Using Matlab

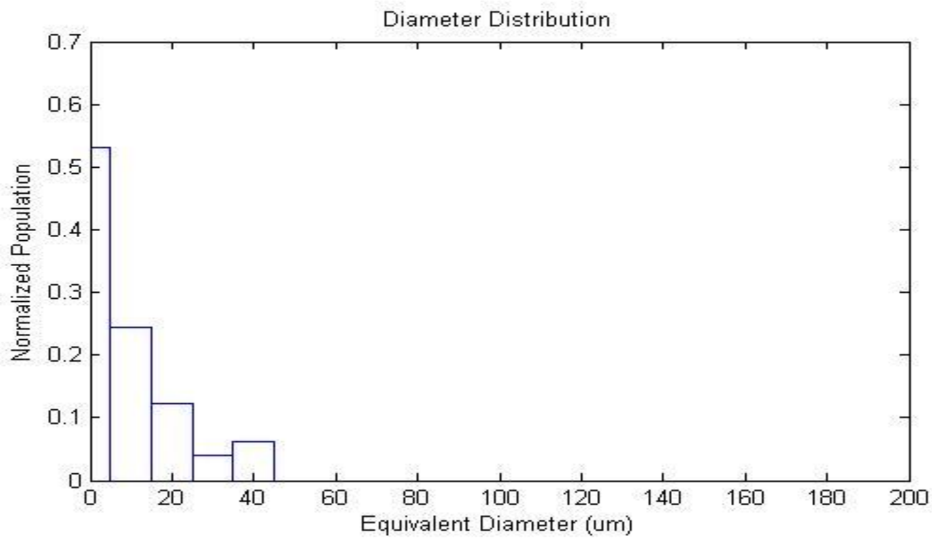

FIGURE 9. Diameter Distribution for Influent Upper Layer

Lower Layer

From 7 images captured, Matlab identified total of 21 individual particles for the lower layer of influent.

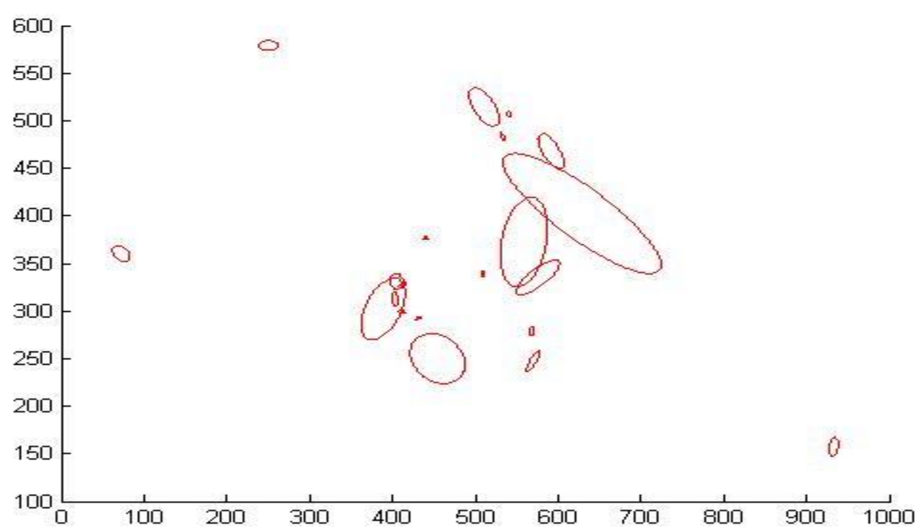

FIGURE 10 Influent Lower Layer Particle Identified Using Matlab

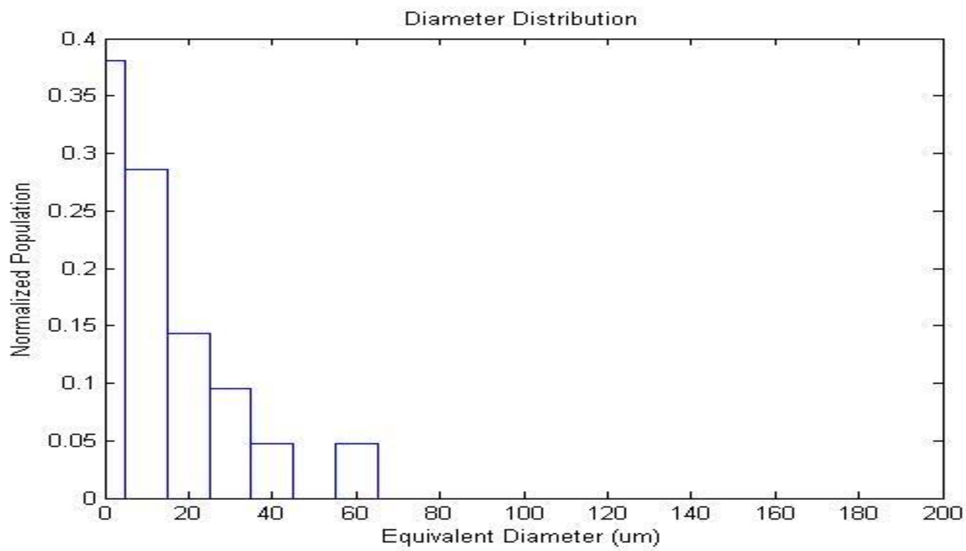

FIGURE 11. Diameter Distribution for Influent Lower Layer

From the result obtained for upper layer of influent, as shown in Figure 8, there is 49 particles identified, and the maximum equivalent diameter is 42.3238 μm while the average equivalent diameter is 5.9526 um.

On the other hand, the result obtained for lower layer of influent, as shown in Figure 10, there is 21 particles identified and the maximum equivalent diameter is 63.5689 um while the average equivalent diameter is 13.6703 um.

As can be seen in Figure 9 and Figure 11, both upper and lower layers of influent are having highest population of particle having diameter between 0 – 5 um which is 0.53 and 0.38. However, by comparing upper and lower layer of influent population, lower layer has bigger equivalent diameter which is 0.05 population of particle having diameter of 55 – 65 um.

Since the POME sample left to settle down for about 45 minutes, all bigger particles with higher density will settle down at the bottom of the measuring cylinder.

This will explain why the average equivalent diameter in the lower layer is bigger than in upper layer of influent and it can be concluded that lower layer of influent has bigger diameter size than upper layer of influent.

4.2.2 Effluent

Upper Layer

From 11 images captured, Matlab identified total of 509 individual particles for the upper layer of effluent.

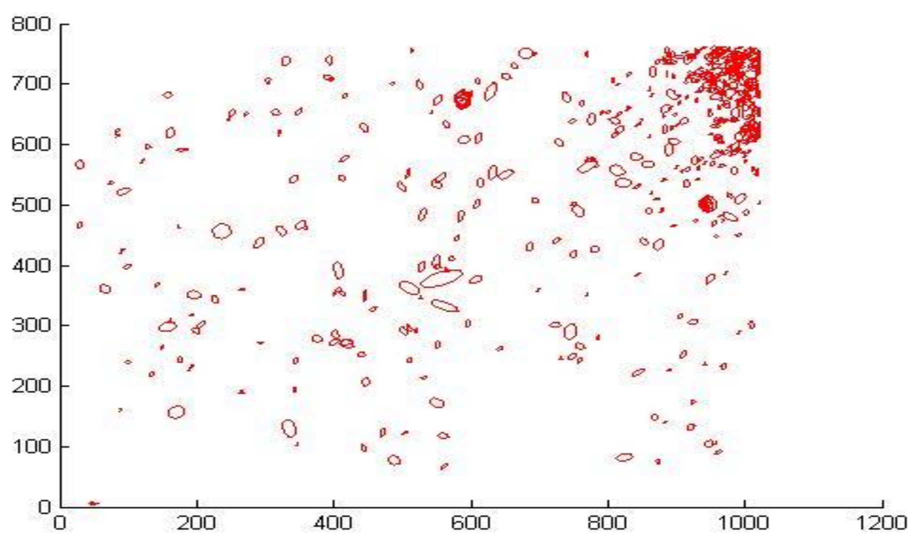

FIGURE 12. Effluent Upper Layer Particle Identified Using Matlab

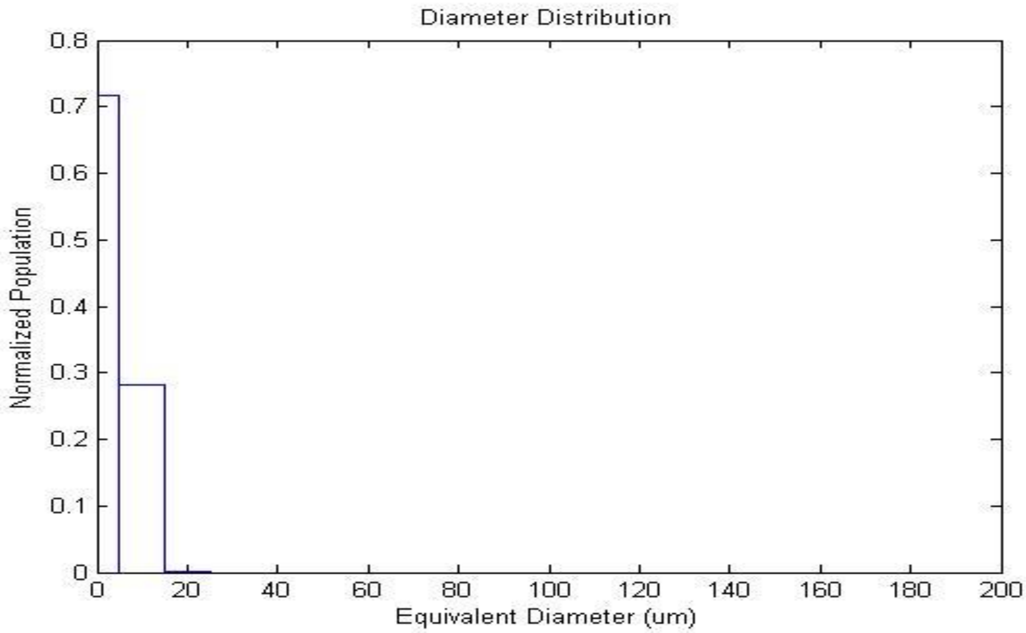

FIGURE 13. Diameter Distribution for Effluent Upper Layer

Lower Layer

From 8 images captured, Matlab identified total of 409 individual particles for lower layer of effluent.

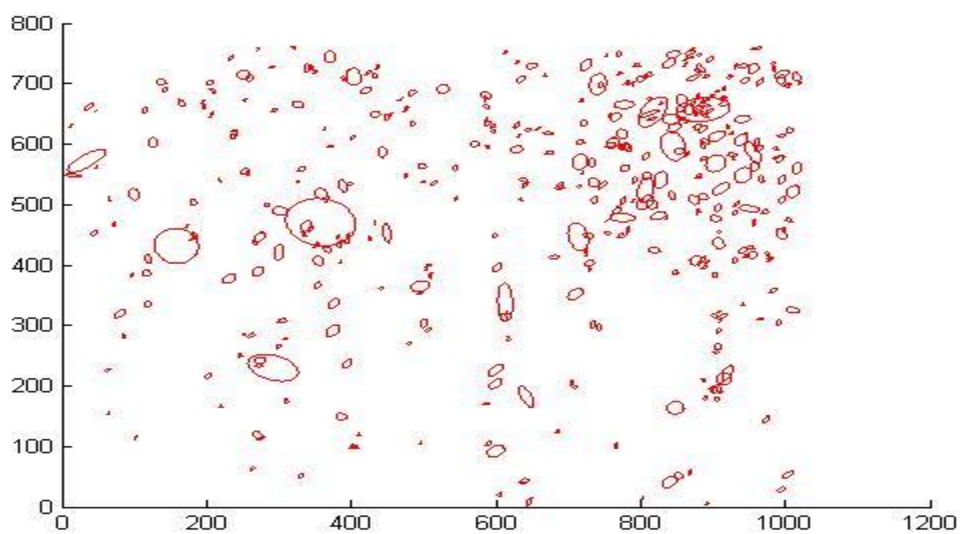

FIGURE 14. Effluent Lower Layer Particle Identified Using Matlab

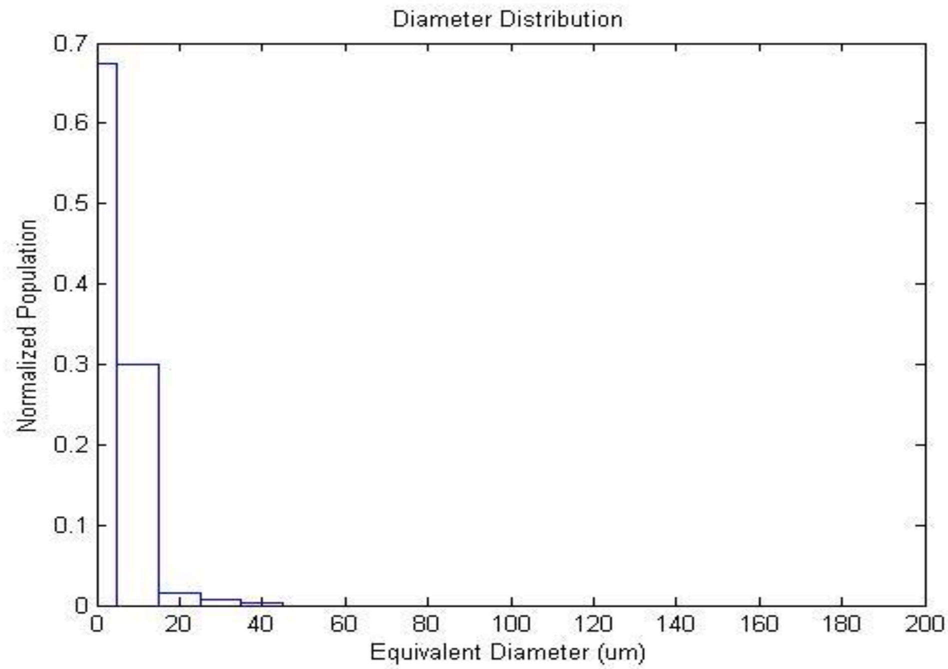

FIGURE 15. Diameter Distribution for Effluent Lower Layer

From the result obtained for upper layer of effluent, as shown in Figure 12, there is 509 particles identified, and the maximum equivalent diameter is 18.4711 um while the average equivalent diameter is 4.2601 um.

On the other hand, the results obtained for lower layer of effluent as shown in Figure 14, there is 409 particles identified, and the maximum equivalent diameter is 40.002 um while the average equivalent diameter is 5.0261 um.

Theoretically, the effluent should contain high distribution of smaller particle size than the influent. For the upper layer of effluent, for equivalent diameter of 0 – 5 um is about 0.71 of population, and the lower layer of influent around 0.67 of population. By comparing the population of upper and lower layer of effluent and influent, it shows that effluent has bigger population of particle size between 0 – 5 um.

By comparing the particle size distribution at the influent and effluent it can be seen that influent have bigger particle size up to 65 um while effluent only have particle size up to 40 um only. It is to mention that the effluent samples are taken at the fourth holding tank before it was discharged to the drain. After that the sample will undergo another treatment which is Fenton Reagent process treatment to further treat the wastewater and it is used as the effluent sample. Therefore, Fenton Reagent process treatment had successfully managed to reduce the bigger particle size of POME.

Next, the discussion will be on the Chemical Oxygen Demand (COD) for the upper and lower layer of influent and effluent.

4.3 Chemical Oxygen Demand

Chemical oxygen demand is the amount of oxygen necessary to oxidize the organic carbon completely to carbon dioxide, water and ammonia. In this project, COD measurement will be carried out by using spectrophotometer DRB200 and 5000-Reactor Digested Method according to Standard Method provided by HACH.

The result is in mg/L defined as the amount of oxygen in milligrams consumed per liter of sample under the standard conditions procedure. The sample is heated for 2 hours with the reagent inside it which is sulfuric acid and potassium dichromate, known as strong oxidizing agent. The oxidizable organic compounds react; hence, reducing the dichromate ion, $Cr_2O_7^{2-}$ to green chromic ion Cr^{3+}. The reagent used in this project is high range (20-1,500 mg/L), and the amount of Cr^{3+} produced is measured. The COD reagent also contains mercury to complex chloride interferences and silver ions as catalyst.

4.3.1 Influent

TABLE 6. Influent COD (Before Fenton Reagent Process)

	COD (mg/l)		
	1st reading	2nd reading	Average
Total	11,560	11,770	11,665
Upper layer	11,750	12,990	12,370
Lower layer	13,350	14,860	14,105

According to the literature, influent POME range between 15,000 – 50,000 mg/L for the total solid of 40,500 mg/L. However, in this project the POME sample collected at the fourth holding tank, and it undergo further treatment which is Fenton Reagent process and this explain why COD value is lower than the range from literature.

As shown in Table 6, total COD for influent and effluent are lower than COD at the lower layer and upper layer. This is because after the POME been left to 45 minutes settling time, all the bigger particle have settle down due to its higher density while the smaller particle will be in the upper layer of POME.

In term of particle size distribution population, for the upper layer of influent about 0.53 of particle contains 0 – 5 um and COD obtained for this layer is 12,370 mg/L. The rest significant population are 0.25 from particle size range from 5 – 15 um and 0.12 from particle size 15 – 25 um.

In the other hand, for the lower layer of influent, 0.38 of particle contains 0 – 5 um and COD obtained for this layer is 14,105 mg/L. The rest significant populations are 0.29 from particle range 5 – 15 um and 0.14 from particle size 15 – 25 um. In addition, it also have 0.05 population of maximum equivalent diameter range from 55 – 65 um compared to the upper layer of influent which have 0.06 population of maximum equivalent diameter size from particle range 35 – 45 um. Therefore, it can be concluded that, the higher particle size distribution, the higher the COD contents.

4.3.2 Effluent

TABLE 7. Effluent COD (After Fenton Reagent Process)

	COD (mg/l)		
	1st reading	2nd reading	Average
Total	773	852	813
Upper layer	941	889	915
Lower layer	2,540	2,830	2,685

For the upper layer of effluent, 0.71 of particle contains size range of 0 – 5 um, and COD obtained is 915 mg/L. The maximum size range in the upper layer of effluent is 15 – 25 um and contains about 0.002 from the total population.

Next, for the lower layer of effluent, 0.67 of particle contains size range of 0 – 5 um, and COD obtained is 2,685 mg/L. the maximum size range in the lower layer of effluent is 35 – 40 um and contains about 0.005 form the total population.

By comparing the population size in the influent and effluent, both upper and lower layer effluent has higher population contribution of smaller particle size. This shows that Fenton Process had successfully managed to eliminate bigger size of segregates in the POME.

4.4 Overall Summary Data

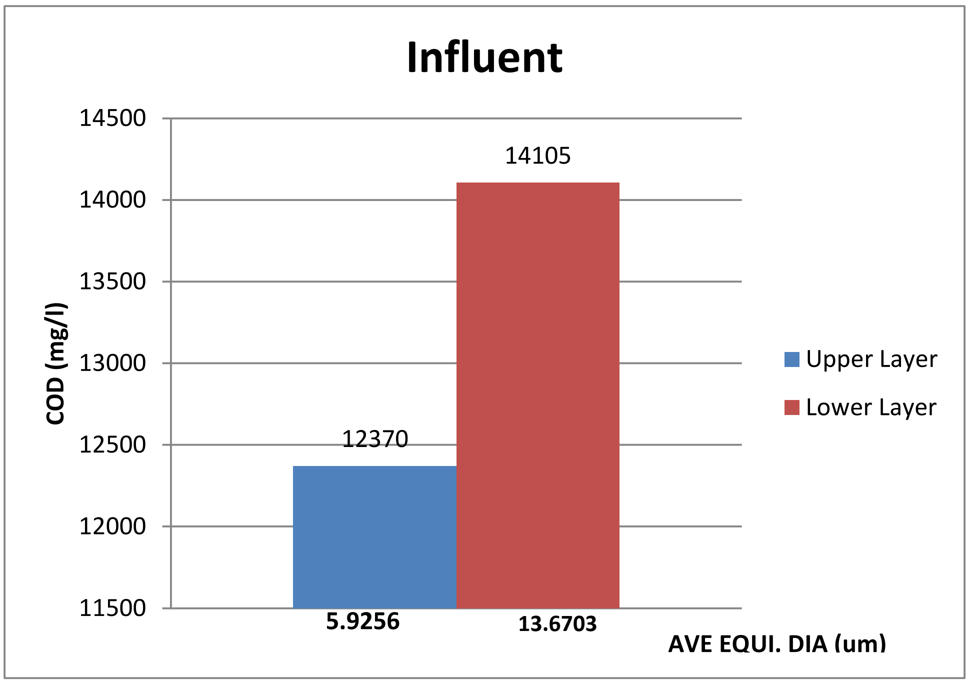

FIGURE 16. Impact of Fenton Reagent treatment on Influent POME

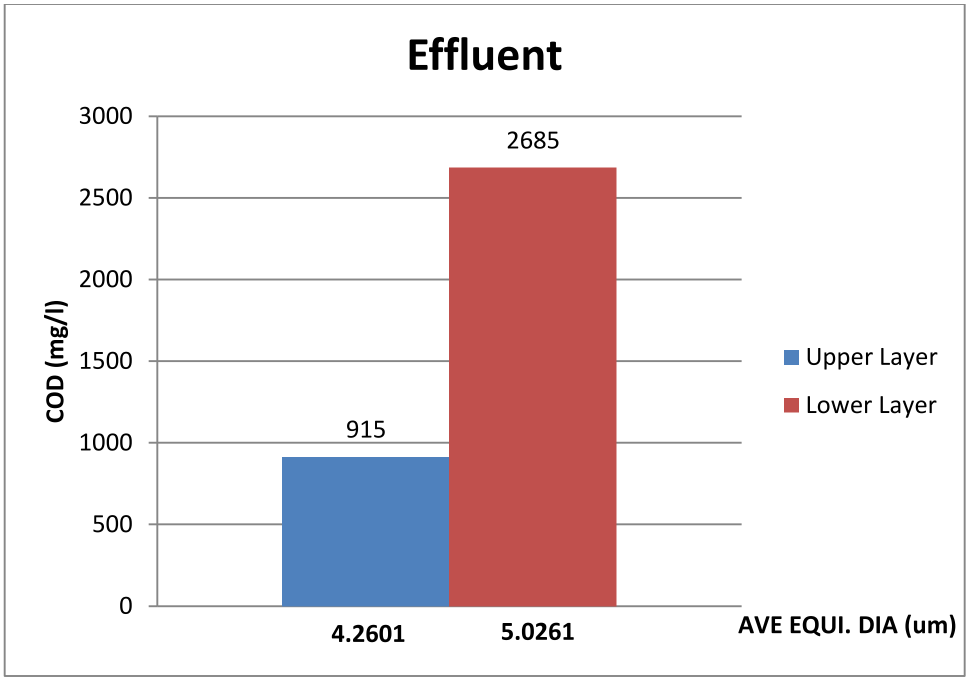

FIGURE 17. Impact of Fenton Reagent treatment on Effluent POME

TABLE 8. Summary Data of Experimental Result

	Particle Size Distribution						Chemical Oxygen Demand (mg/L)	
	Influent			Effluent				
	Total particle number	Max. Equivalent Diameter (um)	Average Equivalent Diameter (um)	Total particle number	Max. Equivalent Diameter (um)	Average Equivalent Diameter (um)	Influent	Effluent
Upper	49	42.3238	5.9526	509	18.4711	4.2601	12,370	915
Lower	21	63.5689	13.6703	409	40.002	5.0261	14,105	2,685

Conventional characterization of the effluent shows that the on-site biological treatment as referring to the Figure 20 and Figure 21, the Fenton Treatment process had a total COD removal efficiency of 93% and this figure shows that Fenton process managed to reduce the level of pollution in the POME.

COD removal efficiency = $\frac{COD_{influent} - COD_{effluent}}{COD_{influent}}$ x 100%

COD removal efficiency = $\frac{11{,}665 - 813}{11{,}665}$ x 100%

COD removal efficiency = 93%

CHAPTER 5

CONCLUSION AND RECOMMENDATION

By conducting this study, image analysis method can be used to monitor the Particle Size Distribution (PSD) in Palm Oil Mill Effluent (POME). Besides that, POME can also be thoroughly studies as previous research used tannery, textile and domestic wastewater to come out with PSD and COD fraction related to its biodegradability. In this project, particle size distribution was observed under light microscopy with COD testing for the purpose of exploring meaningful correlation between physical characterization and its organic constituents. As a result, COD for the upper layer influent and effluent is lower than COD for the lower layer influent and effluent as bigger particle can be observed at the lower layer. In the other hand, particle size distribution also give out proportional result which is bigger particle observed at the lower layer up to 65 um when observed under the light microscopy. As conclusion, this study is important since it provided the opportunity to investigate the relation of PSD by using image analysis method and others standard parameters of POME sample. On the other hand, by knowing how particle size affect the parameters of wastewater treatment plant, such as COD, the operators can estimate the efficiency of their wastewater treatment plant based on COD at influent and effluent.

As for recommendation, this study can be improved with better equipment such as new technology for the light microscopy in order to get clearer image for the particle size distribution. Next, different POME samples which undergo various treatment processes can be included in the observation in order to generate better relation between particle size and COD.

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APPENDIX

Appendix I – Equivalent Diameter for Upper Layer of Influent

RAW UPPER																									
Image 1		Image 2		Image 3		Image 4		Image 5		Image 6		Image 7		Image 8		Image 9		Image 10		Image 11		Image 12		Image 13	
1	42.3238	1	9.3818	1	3.43	1	16.6733	1	9.4742	1	5.2394	1	4.0152	1	14.5072	1	4.5733	1	4.2267	1	2.0874	1	3.025	1	4.3786
2	5.7924	2	16.1016	2	3.3005	2	15.168	2	19.3242	2	18.9485	2	18.5886			2	6.0499	2	3.3005	2	3.6155	2	29.3727	2	3.5548
		3	8.5304	3	3.3005			3	11.641	3	39.1469	3	39.258			3	12.4022			3	3.2338	3	2.8006		
		4	3.9052	4	2.7217					4	25.3689									4	5.2394	4	9.1466		
		5	2.0874	5	3.4929															5	2.9521	5	2.1893		
		6	10.1836																	6	2.6404	6	3.0962		
																				7	2.4699				
																				8	3.6155				
																				9	2.1893				
																				10	2.1893				

Appendix II – Equivalent Diameter for Lower Layer of Influent

RAW LOWER													
Image 1		Image 2		Image 3		Image 4		Image 5		Image 6		Image 7	
1	7.3209	1	9.4972	1	2.8773	1	63.5689	1	41.3342	1	3.43	1	30.8911
2	8.9541	2	5.6784	2	7.6412					2	16.6994		
3	33.6587	3	2.38	3	3.3659					3	3.0962		
4	8.2711	4	2.7217							4	2.4699		
		5	2.1893							5	15.579		
										6	15.4526		

Appendix III – Equivalent Diameter for Upper Layer of Effluent

TREATED UPPER																					
Image 1		Image 2		Image 3		Image 4		Image 5		Image 6		Image 7		Image 8		Image 9		Image 10		Image 11	
1	5.6784	1	2.6404	1	2.1893	1	7.4682	1	5.6784	1	3.43	1	2.38	1	11.6784	1	2.6404	1	2.2867	1	3.9052
2	6.7317	2	4.2267	2	2.0874	2	2.0874	2	4.0691	2	3.6753	2	3.9052	2	2.4699	2	2.9521	2	2.5566	2	2.0874
3	3.1657	3	5.5621	3	2.38	3	2.38	3	5.8671	3	2.6404	3	5.9775	3	9.3586	3	13.6882	3	7.4973	3	3.9606
4	4.7601	4	10.8867	4	2.5566	4	5.1976	4	3.4929	4	2.38	4	2.1893	4	4.4281	4	4.2779	4	2.1893	4	5.0703
5	2.1893	5	4.4281	5	2.0874	5	2.8006	5	7.7825	5	2.9521	5	5.6011	5	5.7546	5	4.1749	5	3.7341	5	6.157
6	5.4433	6	2.7217	6	6.3658	6	2.8773	6	7.6412	6	12.1179	6	4.2779	6	8.8562	6	7.2611	6	7.7825	6	2.2867
7	4.0691	7	2.4699	7	5.4832	7	5.5621	7	2.6404	7	4.3786	7	5.4433	7	4.0691	7	8.8069	7	4.8507	7	6.0858
8	5.4433	8	18.4711	8	5.1976	8	5.1131	8	4.9837	8	6.6993	8	2.9521	8	6.86	8	6.0858	8	7.6127	8	6.0499
9	2.4699	9	11.7713	9	3.6753	9	9.679	9	5.1976	9	4.2267	9	6.8281	9	3.43	9	5.1131	9	7.017	9	5.7924
10	6.5012	10	2.38	10	5.6399	10	4.5254	10	3.1657	10	2.1893	10	8.5813	10	4.477	10	5.3219	10	5.3627	10	8.3236
11	4.3286	11	7.439	11	7.8104	11	3.2338	11	4.8056	11	8.5559	11	5.6011	11	7.3209	11	11.7898	11	5.9409	11	4.4281
12	10.0327	12	4.6207	12	2.5566	12	3.3659	12	2.7217	12	4.1749	12	4.0152	12	9.6339	12	3.43	12	3.1657	12	4.9837
13	5.6399	13	4.3786	13	4.477	13	2.1893	13	7.3209	13	2.0874	13	6.7962	13	10.4162	13	3.4929	13	13.4797	13	3.5548
14	5.3219	14	5.6399	14	2.8773	14	2.8006	14	12.7658			14	4.477	14	6.9859	14	2.8773	14	2.0874	14	6.5347
15	9.405	15	6.5347	15	2.1893	15	4.2779	15	2.38			15	4.477	15	9.6112	15	2.6404	15	6.297	15	2.38
16	2.8773	16	8.0576			16	5.1131	16	3.43			16	10.6028	16	8.6572	16	5.0272	16	2.8006	16	6.8917
17	4.5254	17	2.2867			17	4.6676	17	11.8818			17	2.1893	17	3.025	17	3.025	17	2.38	17	11.6784
18	8.2182	18	3.43			18	3.2338	18	6.1215			18	3.9052	18	2.5566	18	2.6404	18	4.0691	18	8.5048

19	2.4699	19	2.2867			19	6.3315	19	3.6753			19	2.0874	19	3.43	19	3.6753	19	5.9041	19	2.4699
20	3.9052	20	2.2867			20	3.9606	20	3.7341			20	2.8006	20	7.2911	20	4.7601	20	2.9521	20	7.4973
21	2.1893	21	2.4699			21	10.2263	21	8.1115			21	2.7217	21	4.7601	21	3.025	21	2.9521	21	9.4972
22	4.5254	22	2.2867			22	2.2867	22	4.8954			22	3.3659	22	4.5254	22	5.8299	22	10.4371	22	6.7317
23	6.1215	23	6.6339			23	2.9521	23	2.0874			23	2.9521	23	2.0874	23	3.3005	23	3.6155	23	7.4682
24	2.0874	24	11.1242			24	4.0152	24	2.6404			24	2.0874	24	4.6676	24	2.1893	24	6.9232	24	4.477
25	2.5566	25	2.0874			25	5.4433	25	2.38					25	2.2867	25	2.38	25	7.0788	25	2.4699
26	2.0874	26	4.1749			26	2.2867	26	6.8281					26	2.0874	26	2.8006	26	3.6155	26	3.3005
27	2.7217	27	2.4699			27	3.2338	27	3.025					27	3.4929	27	3.6753	27	4.0152	27	6.0858
28	3.3005	28	6.5012			28	3.3659	28	5.9041					28	2.7217	28	2.8006	28	3.6155	28	2.6404
29	2.0874	29	3.43			29	2.2867	29	2.0874					29	10.8666	29	5.4032	29	3.6155	29	2.0874
30	2.8006	30	2.1893			30	2.9521	30	2.1893					30	2.8006	30	3.6155	30	2.38	30	3.0962
		31	2.8773			31	2.1893	31	3.792					31	5.8671	31	3.849	31	3.9052	31	4.477
		32	2.6404			32	2.2867	32	6.297					32	2.1893	32	2.6404	32	2.5566	32	2.0874
						33	2.5566	33	2.5566					33	2.0874	33	4.2267	33	6.8917	33	3.2338
						34	4.2267	34	2.5566					34	2.7217	34	3.9606	34	2.7217	34	8.7073
						35	5.7924	35	2.6404					35	2.1893	35	3.9052	35	3.849	35	2.0874
						36	2.2867	36	3.4929							36	2.38	36	2.6404	36	2.2867
						37	2.38	37	8.8808							37	3.7341	37	2.1893	37	2.2867
						38	2.4699	38	3.7341							38	2.6404	38	8.1383	38	2.2867
						39	5.5621	39	2.38									39	2.2867	39	2.1893
						40	3.3005	40	3.792									40	7.6127	40	2.5566
						41	2.0874	41	2.6404									41	3.6753	41	5.5621

						42	3.025	42	2.1893									42	2.0874	42	2.8006
						43	2.0874	43	3.2338									43	2.38	43	3.849
						44	2.0874	44	2.8006									44	6.8917	44	2.8006
						45	2.6404	45	3.4929									45	5.4032	45	2.6404
						46	8.6067	46	3.9052									46	2.2867	46	2.0874
						47	2.8773	47	4.0691									47	6.1923	47	3.0962
						48	7.3506	48	2.4699									48	2.6404	48	2.0874
						49	2.7217	49	7.4973									49	4.2779	49	2.0874
						50	2.2867	50	2.8006									50	2.1893	50	10.1407
						51	2.0874	51	5.0703									51	2.1893	51	3.025
						52	2.4699	52	2.2867									52	2.6404	52	9.6112
						53	2.0874	53	2.4699									53	3.7341	53	6.0138
						54	2.2867	54	2.0874									54	3.1657	54	8.2182
						55	2.0874	55	3.9052									55	2.1893	55	4.1223
						56	2.8006	56	2.9521									56	2.0874	56	5.1131
								57	4.3286									57	2.4699	57	2.9521
								58	2.9521									58	2.1893	58	5.4832
								59	2.6404									59	2.7217	59	2.1893
								60	2.7217									60	3.4929	60	3.025
								61	2.5566									61	7.017	61	2.6404
								62	5.2808									62	7.0788	62	2.0874
								63	2.0874									63	3.3005	63	3.6155
								64	2.2867									64	3.3659	64	2.7217

								65	2.6404									65	2.8773	65	5.1131
								66	4.1749									66	4.6676	66	2.1893
								67	3.025									67	2.2867	67	2.6404
								68	4.2267									68	2.1893	68	2.4699
								69	2.6404									69	3.025	69	3.4929
								70	4.2779									70	2.1893	70	3.0962
								71	2.8006									71	2.5566	71	2.38
								72	2.5566									72	4.5733	72	2.2867
								73	4.9397									73	8.7572	73	3.6753
								74	2.9521									74	2.8006	74	5.4832
								75	2.2867									75	3.792	75	2.9521
								76	3.7341									76	12.0818	76	2.1893
								77	3.849									77	4.7141	77	4.8507
								78	2.9521									78	4.8954	78	5.4832
								79	3.849									79	2.8006	79	5.6784
								80	3.7341									80	5.0272	80	2.4699
																		81	5.0272	81	2.2867
																		82	3.6753	82	2.38
																		83	2.8006	83	6.297
																		84	4.4281	84	2.2867
																		85	2.9521	85	2.8006
																		86	2.5566	86	4.477
																		87	2.0874	87	2.2867

																88	2.0874	88	2.8773
																89	2.0874	89	2.1893
																90	2.7217	90	2.5566
																91	2.1893	91	3.7341
																		92	2.8773
																		93	2.6404
																		94	2.5566
																		95	2.9521

Appendix IV – Equivalent Diameter for Lower Layer of Effluent

TREATED LOWER															
Image 1		Image 2		Image 3		Image 4		Image 5		Image 6		Image 7		Image 8	
1	3.9606	1	2.0874	1	5.8671	1	2.0874	1	5.0272	1	18.8794	1	2.2867	1	2.38
2	2.0874	2	2.38	2	3.7341	2	4.2779	2	4.7601	2	3.7341	2	3.7341	2	6.1215
3	2.6404	3	2.0874	3	2.9521	3	2.4699	3	9.0509	3	3.0962	3	2.1893	3	4.8954
4	2.1893	4	12.3494	4	2.6404	4	4.477	4	10.4996	4	4.2267	4	3.2338	4	2.4699
5	2.6404	5	5.1976	5	2.8006	5	2.0874	5	5.5621	5	5.1976	5	2.38	5	6.86
6	4.6207	6	2.5566	6	4.9837	6	3.43	6	40.0002	6	2.8006	6	4.5254	6	4.7601
7	2.38	7	8.8808	7	2.0874	7	3.9606	7	6.764	7	2.8773	7	3.5548	7	4.0691
8	2.7217	8	11.0061	8	2.7217	8	7.3209	8	5.4032	8	9.1704	8	2.4699	8	6.4339
9	2.1893	9	2.0874	9	2.0874	9	5.5228	9	3.025	9	3.43	9	3.3005	9	10.6438
10	2.4699	10	5.0272	10	3.9606	10	5.6784	10	8.3497	10	2.38	10	3.43	10	8.1916
11	3.849	11	4.6676	11	7.048	11	5.7924	11	2.0874	11	6.8917	11	11.2023	11	4.0691
12	2.5566	12	3.5548	12	2.5566	12	2.1893	12	2.6404	12	4.3786	12	3.0962	12	8.5813
13	2.1893	13	3.6155	13	4.5733	13	3.1657	13	4.0152	13	6.0499	13	2.4699	13	4.3286
14	4.7141	14	2.2867	14	5.5228	14	6.0499	14	2.9521	14	2.1893	14	5.1131	14	4.0691
15	2.7217	15	2.7217	15	10.6233	15	3.6753	15	2.1893	15	3.4929	15	2.0874	15	2.6404
16	2.0874	16	2.5566	16	2.0874	16	9.7239	16	12.7828	16	4.4281	16	3.43	16	8.2711
17	5.6784	17	9.3119	17	2.8773	17	2.6404	17	2.6404	17	2.1893	17	2.5566	17	3.025
18	3.6155	18	10.3111	18	3.43	18	3.6753	18	2.2867	18	4.3286	18	3.4929	18	3.4929

19	19.143	19	3.1657	19	2.0874	19	5.6784	19	2.7217	19	2.2867	19	4.2267	19	12.0818
20	8.7323	20	2.2867	20	6.3315	20	10.2475	20	12.314	20	2.9521	20	2.9521	20	4.4281
21	3.6155	21	5.6011	21	4.477	21	7.866	21	20.2599	21	9.3119	21	2.2867	21	7.017
22	2.38	22	2.0874	22	2.4699	22	5.8671	22	2.1893	22	5.9409	22	12.9689	22	6.2274
23	5.5228	23	2.5566	23	4.2267	23	2.38	23	4.2779			23	2.0874	23	2.38
24	2.0874	24	2.8006	24	2.7217	24	6.9546	24	4.9837			24	5.3627		
25	2.38	25	2.1893	25	2.8773	25	3.4929	25	4.3786			25	2.1893		
26	2.6404	26	7.6412	26	2.0874	26	2.0874					26	9.405		
27	4.0691	27	5.0703	27	2.0874	27	7.9487					27	11.2991		
28	2.1893	28	3.3659	28	2.8006	28	3.5548					28	8.165		
29	4.0152	29	2.8006	29	2.6404	29	4.0691					29	4.8954		
30	2.38	30	7.2911	30	4.1223	30	5.8671					30	6.8281		
31	2.0874	31	6.0499	31	3.3659	31	3.1657					31	15.993		
32	3.849	32	4.2779	32	2.38	32	5.0703					32	5.5621		
33	2.0874	33	4.7141	33	3.43	33	3.3659					33	22.5886		
34	2.38	34	4.3286	34	4.1223	34	9.2178					34	8.3236		
35	3.6155	35	3.3659	35	4.8507	35	7.8104					35	5.1976		
36	4.8056	36	2.0874	36	3.792	36	3.3005					36	6.4677		
37	11.1242	37	3.0962	37	18.0897	37	7.976					37	27.7635		
38	3.9052	38	8.6823	38	5.8671	38	10.7051					38	4.3286		
39	2.6404	39	2.8006	39	4.6676	39	3.025					39	2.7217		
40	2.4699	40	2.1893	40	4.2779	40	2.2867					40	2.2867		
41	2.4699	41	2.0874	41	4.477	41	3.2338					41	2.38		

42	5.3627	42	2.38	42	3.1657	42	5.6399					42	2.2867		
43	6.9859	43	7.4096	43	2.1893	43	5.0703					43	2.38		
44	2.1893	44	3.0962	44	2.1893	44	5.8299					44	2.4699		
45	2.8006	45	2.4699	45	5.2394	45	3.43					45	3.792		
46	2.5566	46	6.5012	46	3.025	46	9.7463					46	2.38		
47	7.3506	47	2.8773	47	3.1657	47	6.9232					47	14.5971		
48	3.1657	48	4.9397	48	7.1401	48	6.3999					48	3.1657		
49	2.6404	49	4.1749	49	4.0152	49	3.6155					49	4.2267		
50	4.9397	50	3.792	50	4.5254	50	3.849					50	2.0874		
51	2.2867	51	3.1657	51	9.1466	51	3.3005					51	2.0874		
52	3.43	52	2.6404	52	6.4677	52	6.5679					52	3.9052		
53	9.3586	53	2.0874	53	4.9837	53	10.8265					53	9.1466		
54	3.3005	54	2.1893	54	6.8917	54	12.7145								
55	2.7217	55	4.6207	55	4.1223	55	8.8069								
56	5.6399	56	2.4699	56	2.4699	56	2.2867								
57	6.1923	57	3.0962	57	2.8773	57	9.7909								
58	3.025	58	8.632	58	9.265	58	8.4017								
59	9.543	59	4.7141	59	4.2779	59	4.3786								
60	4.0152	60	3.849			60	2.8006								
61	2.1893	61	4.477			61	8.5813								
62	3.0962	62	5.9775			62	2.6404								
63	3.9606	63	3.025			63	3.7341								
64	2.5566	64	3.7341			64	2.0874								

65	2.38	65	5.9041												
66	2.1893	66	2.1893												
67	2.9521	67	7.1401												
68	2.8006	68	6.5347												
69	5.8671	69	5.6784												
70	2.1893	70	5.3219												
71	5.4832	71	34.3316												
72	2.1893	72	30.515												
73	7.6127	73	2.7217												
74	4.8954	74	3.9606												
75	14.7456	75	7.017												
76	2.1893	76	3.7341												
77	8.1115	77	6.8917												
78	5.2394	78	2.8773												
79	2.9521	79	4.8507												
80	3.2338	80	2.7217												
81	2.9521														
82	3.3005														
83	2.2867														