Faculty of Resource Science and Technology

REMOVAL OF RESIDUAL OIL IN PALM OIL MILL EFFLUENT (POME) BY USING MIXTURE OF NON-IONIC AND ANIONIC SURFACTANT

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This Final Year Project is submitted in partial fulfillment of the Degree of Bachelor of Science with Honors

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DECLARATION

I hereby declare that no portion of work referred to in this dissertation has been submitted in support of an application for another degree of qualification to this or any other university or institution of higher learning.

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List of Abbreviations

Brij 30	Poly(oxyethylene)(4) lauryl ether
cm^{-1}	Percentimeter
˚C	Degree celcius
CMC	Critical Micelle Concentration
FTIR	Fourier Transform IR Spectroscopy
GE-460	Glycolic acid ethoxylate lauryl ethers
g/mL	Gram per mililiter
Hr	Hour
H_2S	Hydrogen sulphide
IFT	Interfacial tension
L	Liter
mg/L	Miligram per liter
mins	Minutes
m^3	Meter cubic
nm	Nanometer
ppm	Part per million
rpm	Revolutions per minute
surfactant	Surface active agent
wt%	Weight percent
%	Percent

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REMOVAL OF RESIDUAL OIL IN PALM OIL MILL EFFLUENT (POME) BY USING MIXTURE OF NON-IONIC AND ANIONIC SURFACTANTS

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ABSTRACT

Palm oil mill effluent (POME) is oily waste water produced from palm oil extraction process. Discharging POME to the river will deplete the amount of dissolved oxygen in the river and endanger the aquatic life. Therefore, the residual oil and grease in POME must be removed before being discharged to the river. In this study, the residual oil was removed by using the mixture of anionic (GE-460) and non-ionic (Brij-30) surfactants. *n*-hexane is used as solvent in oil extraction process for comparison. Five experimental parameters were studied to obtain the optimum oil and grease removal in POME. Parameters studied were concentration of surfactant, ratio of the mixture of surfactant, mixing time, mixing speed, mixing time and pH value. The results showed that the optimum conditions for the removal of residual oil in POME are 0.0004 M of GE-460 and 0.00001 M Brij, mixture of surfactants with ratio of 1:1, mixing time of 30 minutes at 180 rpm mixing speed and pH 5. The average value for the extracted oil under the optimum condition was 1250 mg/L. For qualitative analysis of oil and grease, the bonding in extracted oil and grease can be analysed by using infrared spectrophotometry (FTIR). The FTIR graph detected a bonding at 2930 cm^{-1} that showed the presence of CH_2, a common characteristic of oil and non polar part of surfactant. Bond at 3400 cm^{-1} showed the presence of O-H, C-O at 1163-1099 cm^{-1} and 1637 cm^{-1} for carbonyl group.

Keywords: Palm oil mill effluent, residual oil, anionic (GE-460), non-ionic (Brij-30), solvent extraction

ABSTRAK

Air sisa kilang kelapa sawit (POME) merupakan sisa air berminyak yang terhasil semasa proses mengekstrak minyak kelapa sawit. Pembuangan POME ke dalam sungai akan mengurangkan jumlah oksigen terlarut di dalam sungai dan membahayakan hidupan akuatik. Oleh itu, minyak sisa dan gris di dalam POME harus disingkirkan sebelum POME dialirkan ke dalam sungai. Dalam kajian ini, minyak sisa dibuang dengan mengunakan campuran surfaktan anionik (GE-460) dan surfaktan bukan ionik (Brij-30). n-heksana digunakan sebagai pelarut dalam proses pengekstrakan minyak untuk perbandingan. Terdapat lima parameter yang dikaji untuk menyingkirkan minyak dan gris di dalam POME yang optimum. Parameter yang dikaji ialah kepekatan surfaktan, nisbah campuran surfaktan, masa proses untuk pencampuran, kadar kelajuan proses pencampuran dan nilai pH. Hasil kajian menunjukkan bahawa keadaan optimum untuk pembuangan minyak sisa dalam POME ialah dengan mengunakan 0.0004 M GE-460 dan 0.00001 M Brij 30 , campuran surfaktan dengan nisbah 1:1, masa pencampuran selama 30 minit dengan kadar kelajuan pencampuran 180 rpm dan pH 5. Nilai purata bagi minyak yang dibuang dalam keadaan optimum adalah 1250 mg/L. untuk menganalisis kualiti minyak sisa dan gris, spektroskopi inframerah (FTIR) telah digunakan untuk menganalisis ikatan di dalam sisa minyak dan gris yang diekstrak. Graf FTIR telah mengesan ikatan pada 2930 cm^{-1} *yang menunjukkan kehadiran* CH_2, *iaitu ciri-ciri umum untuk minyak sisa dan gris dan surfaktan. Ikatan pada 3400* cm^{-1} *menunjukkan kehadiran O-H, C-O pada 1163-1099* cm^{-1} *dan 1637* cm^{-1} *untuk kumpulan karbonil.*

Kata kunci: Air sisa kilang kelapa sawit, sisa minyak, anionik (GE-460), bukan ionik (Brij 30), pelarut pengekstrakan

1.0 INTRODUCTION

Palm oil is an important agriculture based industry for Malaysia due to its tropical climate. Oil palm industry has been recognized for its contributions towards economic growth and rapid development. However, it also contributed to environmental pollution due to the production of huge quantities of by-products such as solid biomass and palm oil mill effluent (POME) from the oil extraction. Discharging the effluent to the river will lead to water pollution (Rupani *et al*., 2010).

Palm oil mill effluent (POME) is oily waste water produced from the oil extraction process. During oil extraction, large amount of water is consumed. To produce 1 tonne of crude oil, 5-7.5 tonnes of water are needed. From that amount of water more than half of the amount will become palm oil mill effluent (POME) at the end of the process (Ahmad *et al*., 2004).

According to Thani *et al*., (1999) excessive quantity of untreated POME will deplete the water-body of its oxygen and thus will endanger the aquatic life. Residual oil in POME must be removed because the presence of oil and grease in water can affect water treatment process especially in the biological treatment stages. Besides that, the residual oil must be removed to meet specific standard of allowable limit water discharge set by the Malaysian Department of Environment (DOE) (Ahmad *et al*., 2004). Department of Environment has set a maximum limit of 50 mg / L for residual oil (Thani *et al*., 1999). Therefore, POME requires an effective treatment before being discharged. The standard discharge for POME can be referred to table 1.1.

Table 1.1 Standard Discharges of palm oil mill effluent (POME)

PARAMETER		PARAMETER LIMITS FOR CRUDE PALM OIL MILLS	REMARKS
Biochemical Oxygen Demand (BOD; 3-Day, 30°C)	mg/L	100	
Chemical Oxygen Demand (COD)	mg/L	*	
Total Solids	mg/L	*	
Suspended Solids	mg/L	400	
Oil and Grease	mg/L	50	
Ammoniacal Nitrogen	mg/L	150	Value of filtered sample
Total Nitrogen	mg/L	200	Value of filtered sample
pH	-	5 - 9	
Temperature	°C	45	

According to Ahmad *et al.*, (2004) untreated POME contains about 4000-6000 mg/L of oil and grease. Oil droplet in POME is divided into two phase. The oil are suspended in POME as an emulsion or floating as oil droplets on the upper layer of the suspension. Residual oil in POME can be removed by using surfactant. Surfactant is a long organic molecule that consists of hydrophilic head and hydrophobic tail. Surfactant stabilized the emulsion of oil in water. Stabilized emulsion of oil in water is known as micelles. The stabilized droplets then can be separated from water (Sethupathi, 2004). In this study, the residual oil was removed by using the mixture of anionic (GE-460) and non-ionic (Brij-30) surfactants.

The objectives of this study are:

1. To remove the residual oil by using the mixture of non-ionic and anionic surfactants.
2. To study how several parameters such as surfactants dosage, mixing time, mixing speed, sedimentation time, pH value and ratio of the mixture of the surfactants will affect the removal of the residual oil.
3. To determine the optimum condition for removal of residual oil in POME.

2.0 LITERATURE REVIEW

2.1 Palm oil mill effluent (POME)

POME is a combination of wastewater generated from three principal sources which is sterilizer condensate (36%), clarification wastewater (60%) and hydro-cyclone wastewater (4%). Average of 0.9 – 1.5 m^3 of POME is generated for each ton of crude palm oil produced (Wu and Mohammad, 2007). According to Ahmad *et al*., (2004), to produce 1 tonne of crude oil, 5-7.5 tonnes of water is needed. From that amount of water more than half of the amount will become palm oil mill effluent (POME) at the end of the process. POME is an oily and thick brownish liquid that is discharged at temperature in the range of 80 to 90 ˚C during the palm oil extraction process. It consists of 95-96% water, 0.6-0.7% oil and grease and 4-5% total solids. Typical characteristics of POME can be referred to Table 2.1 (Thani *et al.,* 1999).

Table 2.1 Characteristics of palm oil mill effluent (POME)

PARAMETER*				
GENERAL PARAMETERS			**METAL & OTHER CONSTITUENTS**	
	MEAN	**RANGE**		
pH	4.2	3.4 – 5.2		
Oil & Grease (O&G)	6,000	150 – 18, 000		
Biochemical Oxygen Demand (BOD, 3-day, 30°C)	25,000	10,000 – 44,000	Phosphorus Potassium	180 2,270
Chemical Oxygen Demand (COD)	50,000	16,000 – 100,000	Magnesium Calcium	615 440
Total Solids (TS)	40,500	11,500 – 79,000	Boron	7.6
Suspended Solids (SS)	18,000	5,000 – 54,000	Iron Manganese	47 2.0
Total Volatile Solids (TVS)	34,000	9,000 – 72,000	Copper Zinc	0.9 2.3
Ammoniacal Nitrogen (AN)	35	4 – 80		
Total Nitrogen (TN)	750	80 – 1,400		

**All parameters units in mg/L except pH*

Other than oil and grease, POME composition also includes dissolved constituent such as high concentration of protein, carbohydrate, nitrogenous compounds, lipids and minerals. There are no chemical added during the palm oil extraction process. Therefore, POME is considered as non-toxic wastewater (Rupani *et al.*, 2010).

However, according to Thani *et al*., (1999) excessive quantity of untreated POME will deplete the water-body of its oxygen and thus will endanger the aquatic life. Residual oil in POME must be removed because the presence of oil and grease in water can affect water treatment process especially in the biological treatment stages Besides that, the residual oil must be removed to meet specific standard of allowable limit water discharge set by the Malaysian Department of Environment (DOE) (Ahmad *et al*., 2004).

2.2 Environmental Quality Regulation

In 1978, the enactment of the environmental Quality Regulations detailing POME discharge standard was made by our government. Initially, the allowable concentration of oil and grease parameter of the untreated POME is 150 ppm. Later, the allowable concentration is reduced to 75 ppm and nowadays, the allowable concentration for oil and grease is 50 ppm (MPOB, 2012). The effluent discharge standards for crude palm oil mills are presented in Table 2.2.

Table 2.2 Effluent discharge standards for crude palm oil mills (Environmental Quality Act 1974)

Parameter	Unit	Parameter Units (second schedule)
Biochemical Oxygen Demand BOD	mg/L	100
Chemical Oxygen Demand (COD)	mg/L	*
Total Solids	mg/L	*
Suspended Solids	mg/L	400
Oil and Grease	mg/L	50
Ammoniacal Nitrogen	mg/L	150
Total Nitrogen	mg/L	200
pH	-	5-9
Temperature	°C	45

2.3 Surfactant

According to Idris and Awang (2007), surfactant monomer is composed of a non polar (lypophile) portion and polar (hydrophile) portion. Surfactants are classified depending on the polar moieties. Anionic surfactants are the most commonly used surfactants. These surfactants are stable, cheap and resistant to retention. Non-ionic surfactants do not ionize in aqueous because their hydrophilic group is a non- dissociate type. Therefore, the surfactants cannot form ionic bond. However, when dissolve in aqueous solutions, these surfactants exhibit surfactant properties by electro negativity contrast between their constituents.

According to Sethupathi (2004), aqueous solubility of hydrophobic compound can be increased by using surfactants. Under proper conditions, the affinity of hydrophobic cores of micelles will increase. Therefore, hydrophobic solutes tend to stay in the micelle. This important property of surfactant makes it solubilize considerable amounts of palm oils and triglycerides in oil-containing micelles effectively. Surfactant lowers the interfacial tension (IFT) between aqueous extracting systems. When a water sample contains sufficient amount of oil, the oil will form a distinctive monomolecular layer on the surface of water. Therefore, the mixture of oil and water will form two immiscible layers.

The critical micelles concentration (CMC) is a concentration of surfactant where almost all additional surfactant added to the system goes into the micelles. CMC is a characteristic that is very important for a surfactant. Interfacial tension (IFT) is strongly changed with the concentration of surfactant before it reaches CMC. After it reaches CMC, surfactant changes their physical properties of formation, become organized and aggregate to form micelle (Sethupathi, 2004).

Surfactant creates a gap between the oil and the water. The polar part of the surfactant will reside in the water layer meanwhile non polar part will dissolved in the oil. Micelles is a stable emulsion of water in oil or oil in water that formed by surfactant micelles (Sethupathi, 2004). Figure 2.1 shows the formation of stable emulsion of water in oil or oil in water.

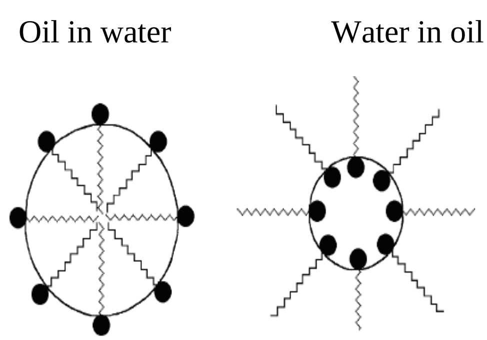


Figure 2.1 Surfactant stabilized micelles

2.3.1 Poly(oxyethylene)(4) lauryl ether

The commercial name for Poly(oxyethylene)(4) lauryl ether is Brij-30. Brij-30 is a non-ionic surfactant. Brij-30 has a hydrophilic head which will attach to the surrounding aqueous system and a lipophile long chain that will attaches to the target. This surfactant is colourless to yellow oily liquid and have pleasant odour (MSDS, 2010). CMC for Brij 30 is in the range of 7-14.52 mg/L (Chan and You, 2010). Table 2.3 shows the properties of Brij-30 and Figure 2.2 shows the molecular structure for Brij-30.

Table 2.3 Properties of Brij-30

Molecular formula	$C_{12}H_{25}(OCH_2CH_2)_4O$
Melting point	1.67 ˚C
Density	0.95 g/ml
Molecular weight	362.56 g/ml

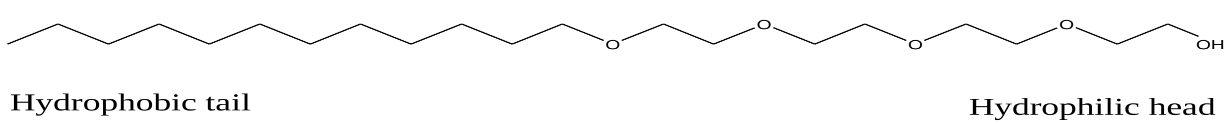


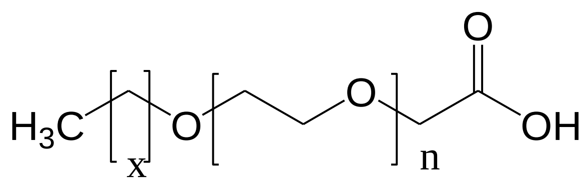
Figure 2.2 Molecular structure for Brij-30.

2.3.2 Glycolic acid ethoxylate lauryl ethers

GE-460 is a commercial name for glycolic acid ethoxylate lauryl ethers. GE-460 is an anionic surfactant. The molecular structure for GE-460 is $CH_3\ (CH_2)_{11\text{-}13}O\ (CH_2CH_2O)_{4.5}CH_2COOH$ (Chan and You, 2010). Table 2.4 shows the properties of GE-460 and Figure 2.3 shows the molecular structure for GE-460.

Table 2.4 Properties of GE-460

Molecular Formula	$CH_3(CH_2)_{11\text{-}13}O(CH_2CH_2O)_{4.5}CH_2COOH$
Molecular Weight	460
CMC (mg/L)	130
Micellar size (nm)	7.6



Hydrophopic tail Hydrophilic head

x= 11-13

Figure 2.3 Molecular structure of GE-460

2.4 Residual oil

Any types of oil consist of fatty acids as the main constituents. Fatty acid is a weak acid. The molecular structure of fatty acid consists of a long-chain aliphatic hydrocarbon with a carboxylate group on one end. Oleic, linoleic and palmitic are naturally occurring fatty acids. It is soluble in organic solvents such as methylene chloride, ether, or alcohols and poorly soluble in the very non-polar organic solvents like hexane (Sethupathi, 2004). The extract of POME oil droplets consists of 84 wt% neutral lipids and 16 wt% of complex lipids. The neutral lipid consists of 83% triglycerides, 0.3% diglycerides, 0.5% monoglycerides and 0.2%

free fatty acids (Ahmad *et al*., 2004). Table 2.5 showes the fatty acid components of palm oil (Lim *et al.*, 2005).

Table 2.5 Fatty acid components of Palm Oil

Common name	Systematic name	Percentage of total weight
Lauric	n-dodecanoic	<1
Myristic	n-tetradecanoic	1-6
Palmitic	n-hexadecanoic	32-47
Stearic	n-octadecanoic	1-6
Arachidic	n-eicosanoic	<1
Palmitoleic	n-hexadec-9-enoic	<1
Oleic	n-octadec-9-enoic	40-52
Gadoleic	n-eicos-9-enoic	<1
Linoleic	n-octadec-9,12-dienoic	5-7

2.5 Emulsion

An emulsion is defined as a system in which one liquid is dispersed in the form of droplets. Agitation energy must be reduced in order to produce a certain droplet size. Therefore, a suitable surfactant can be added to the system to reduce the agitation energy. According to Sethupathi (2004), stabilized emulsions are very difficult to be separated and difficult to remove by physical separation. In oily waste water systems, the system is favourable for emulsification of oil in water when the interfacial tension of the oil and the sludge is thermodinamically low.

2.6 Removal of residual oil from palm oil mill effluent (POME)

Previous study by Sethupathi in 2004 used chitosan to remove oil and grease from palm oil mill effluent (POME). Chitosan is a biodegradable of chitin obtain from the shrimp shell wrap. The research was carried out using different parameters. The studied parameter were effect of weight dosage, initial concentration, sedimentation time and mixing time, mixing rate, pH and temperature on the yield of extraction. According to the study, the optimum condition for removal of residual oil was obtained by using 0.5g/L of powdered chitosan with sedimentation time of 30 minutes, mixing time of 30 minutes, mixing speed of 100 rpm, pH 4.0 - 5.0 and at a temperature in the range of 50-70°C. The study shows that Chitosan powder is better for removal of residual oil compared to chitosan flake.

Another study by Ahmad *et al*., (2004), using rubber powder to remove the residual oil from POME. Synthetic rubber powder was used as a material in their study. In this study, the experiment was conducted using a jar test apparatus. The removal process was carried out under several parameters such as adsorbent dosage, mixing speed, mixing time and pH. They found that almost 88% removal of residual oil was obtained using an adsorbent dosage of 30 mg dm^{-3}, and mixing speed of 150 rpm for 3 hr and pH value at neutral condition.

2.7 Analysis of oil and grease

According to Stenstrom *et al.,* (1986), the earliest method used to analyze oil and grease is Hazen’s Method. In Hazen’s Method, hydrochloric acid is used as a solvent for the removal of residual oil. First, 500 mL of oily waste water will be evaporated until the volume of the sample reduced to 50 mL. Next, hydrochloric acid will be added to neutralized the sample.

Then, the oily wastewater was evaporated once again in pre-weighed container to determine residue.

Later, oil and grease analysis was develop and modified. The solvent used for extraction was modified since there were lots of new commercial solvent produced by chemist. According to Saxena *et al.,* (2011), *n*-hexane is the preferred solvent throughout the world because it is easy to find *n*-hexane. Besides that, it has high extraction efficiency compare to other solvent

Nowadays, the development of technology facilitate the analysis of oil and grease that the extracted oil and grease in the solvent can be measured by infrared spectrophotometry. The qualitative analysis of oil and grease by using infrared spectrophotometry is possible due to common characteristic of oil and grease. Oil and grease contain CH_2 in their molecular structure. Therefore, infrared spectrophotometry will showed a light absorption at 2930 cm^{-1}.

2.8 *n*- Hexane

Maria *et al.,* (2008) stated that *n*-hexane is a polar solvent. It is suitable for free fatty acids extraction because readily dissolved in organic material such as oil and grease. Besides that, extraction using solvent has several advantages. It gives higher yield and less turbid oil. *n*-hexane is more suitable to extract free fatty acids compare to ethanol. According to Saxena *et al.,* (2011), commercial technique that commonly used to recover oil from oil seed is solvent extraction.

Nowadays, *n*-hexane is the most preferred solvent used in oil extraction process due to its efficiency and availability. *n*-hexane is a selective solvent and can extract the oil and grease from the materials without affecting other compound (Anderson, 2011).

The molecular formula for *n*-hexane is C_6H_{14}. It is colourless and in the form of liquid. *n*-hexane is stable at room temperature and pressure. *n*-hexane is soluble in alcohol, ether, chloroform, acetone and other organic solvents (MSDS, 2000). Table 2.6 shows the physical and chemical properties of *n*-hexane.

Table 2.6 Physical and chemical properties of *n*-hexane.

Molecular weight	86.18
Boiling point	156 F (69 ˚C)
Freezing point	-139 F (-95 ˚C)
pH	Neutral
Volatility	100 %
Odor threshold	64-244 ppm

3.0 MATERIALS AND METHODS

3.1 Sample Collection

Samples of palm oil mill effluent (POME) were collected from Felcra Jaya palm oil mill in Kota Samarahan.

3.2 Material

Brij 30, GE-460, acetone and *n*-hexane with purity of 96% were supplied by Sigma-Aldrich. 99% Potassium bromide (KBr) powder for FTIR pellet, ascorbic acid powder with purity of 99% and sodium hydroxide pellet with purity of 99% for pH adjustment were supplied by Merck. All solutions were prepared with distilled water.

3.3 Quantitative analysis of extracted oil and grease by using solvent extraction

The amount of residual oil was measured by using oil and grease method. This method was recommended by APHA Standard Method of Examination of Water and Wastewater (1992). The experiment was conducted by using organic solvent, *n*-hexane. The mixture of POME and *n*-hexane was transferred to a separating funnel. The mixture was shaken for 2 minutes and left to allow further separation to occur. Then the extracted oil was drained into the pre-weighed petri dish. The extraction process was repeated with another 20 mL of hexane. To remove any oil left on the funnel walls, the funnel walls was rinsed with *n*-hexane.

Excess n-hexane and water content in the extract oil was removed by using water bath. After the distillation, a petri dish and the remaining contents was dried in dessicator for 24 hours. The drying and cooling steps were repeated until the weight become constant