CHARACTERIZATION OF CLAY AND KAPOK AS OIL SORBENTS

by

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Dissertation submitted in partial fulfillment of

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

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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 person.

Nur Amira bt Jumat

ABSTRACT

Clay such as bentonite, montmorillonite and sepiolite have high sorption properties, surface area, porosity and cation exchange capacity which make them potential materials as oil and heavy metals adsorbent. Ceiba pentadra (L.) Gaertn. or locally known as kapok has large and non-collapsing hollow lumens that enable oil sorption. Kapok also exhibits excellent hydrophobic-oleophilic characteristic.The objectives of this study were to investigate the efficiency of clay and kapok for Palm oil mill effluent (POME) sorption and to analyze the characteristics of clay and kapok since POME contains about 4000-6000 mg/L of oil and grease that must be reduced to 50 mg/l of DOE permissible limit before it can be discharged into waterways. Several methods are used for characterization such as Fourier Transform Infrared Spectrophotometer (FTIR) and Thermogravimetric analysis (TGA). Montmorillonite clay and kapok were packed in the column at different packing density until they were saturated and achieved complete sorption of POME. POME dripped from column was analyzed for its oil and grease content and compared with the raw POME. After sorption analysis was done, clay and kapok were dried and characterized by using FTIR and TGA. Higher packing density showed lower sorption capacity of POME because sorbent material was less loosely packed. Kapok at 0.10 g/cm^3 showed the highest sorption capacity of POME and percentage of oil removed as compared to clay and double packing sorbents of treated clay with sulfuric acid and kapok. Based on the FTIR and TGA, the increment in transmittance percentage showed the occurrence of oil sorption in clay and kapok. Therefore, clay and kapok have shown great potential as oil sorbent in terms of its high sorption capability.

Keywords: clay, sorption, montmorillonite, kapok, hydrophobic-oleophilic, POME, FTIR, TGA

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ABBREVIATIONS AND NOMENCLATURE

DSC	Digital Scanning Calorimetry
FTIR	Fourier Transform Infrared Spectrophotometer
POME	Palm Oil Mill Effluent
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscopy

CHAPTER 1

INTRODUCTION

1.1 Background of study

Wastes from heavy hydrocarbons such as lubricant oil, crude oil and oily wastewater such as palm oil mill effluent (POME) pose serious threats to the environment. Lubricant oil wastes are produced from machineries in plants or factories and vehicles, containing high values of ash, carbon residue, asphaltenic materials, metals, water and other toxic chemicals (Nabil *et al*, 2010). Oily wastewater can be toxic and hazardous to microorganisms responsible for degradation in conventional sewage processes, making pretreatment before disposal is vital.

Oil palm industry forms the economic backbone of Malaysia and ranks second after Indonesia as the largest producer in the world. The growing demand has led to an increase in amount of palm oil production with increasing wastes generated. The liquid waste from palm oil mill is known as palm oil mill effluent (POME). Based on calculation from MPOB's Malaysian Oil Palm Statistics (2009), the amount of POME for 2011 is postulated to be nearly 60 million tonnes and the figures are expected to rise every year (Ng *et al*, 2010). Palm oil-processing mills in Malaysia discharge the large volume of oily wastewater from the mixture of their sterilizer condensate, separator sludge and hydrocyclone wastewater at the ratio of 9:15:1. About 50% of water used in the extraction of palm oil will result in POME, while other 50% will be lost as steam (Ahmad *et al*, 2008).

applications are as drilling fluids, foundary bond, paint and absorbents. Clay minerals are able to remove heavy metals from wastewater such as plumbum, zinc and nickel (Ayari *et al*, 2005), and proved to be a good oil sorbent material in removing oily wastewater (Rajakovic *et al* , 2006) and waste lubricant oil (Nabil *et al*, 2010). In addition, it has large surface area and high cation exchange capacity gives added advantage as an adsorbent. Kapok or Ceiba pentandra (L.) Gaertn is cultivated in Southeast Asia, Malaysia, Sri Lanka, other parts of East Asia and Africa. Kapok fibers from Philippines have been investigated for their ability to remove diesel, hydraulic oil and diesel-water mixture in batch and continuous system (Hori *et al*, 2000). Kapok has hydrophobic-oleophilic characteristic which attributes to the good oil sorption.

1.2 Problem statement

Palm oil mill effluent (POME) contains about 4000-6000 mg/L of oil and grease that must be reduced to 50 mg/l of DOE permissible limit before it can be discharged into river or canal. Emulsified oil droplets are the most difficult part to be disposed of as they are sheltered from spontaneous coalescence into larger flocks, making oil separation by simple gravity a difficult and time consuming process (Ahmad *et al*, 2005). Adsorption by natural sorbent materials to remove the residual oil from POME is an attractive process due to abundant natural sorbent as low cost material. Clay and kapok are environmentally friendly and have great potential to remove residual oil from POME efficiently.

1.3 Objectives and scope of study

The objectives of this study are:

1. To investigate clay and kapok for the base study on their capabilities as POME sorbent material

2. To study the optimization of POME sorption by packed column reactor
3. To characterize clay by using several techniques such as Fourier Transform Infrared Spectrophotometer, and Thermogravimetric Analysis

The scope of study includes the experimental works on clay and kapok using batch system, characterization of clay and kapok before and after sorption of POME and conducting analysis on the oil and grease content of POME.

are sodium montmorillonite, calcium montmorillonite, saponite, nontronite and hectorite (Murray, 2007). Most smectites are now referred to as bentonites or montmorillonite. Montmorillonite is a very soft phyllosilicate group of minerals that form in microscopic crystal. The basic structural unit is a layer consisting of two inward-pointing tetrahedral sheets with a central alumina octahedral sheet. The layers are continuous in the a and b directions, but the bonds between layers are weak and have excellent cleavage, allowing water and other molecules to enter between the layers causing expansion in the c direction (Grim, 1962). Specifically indicates a high alumina end member of the montmorillonite group with some slight replacement of Al_{3+} by Mg_{2+} and substantially no replacement of Si_{4+} by Al_{3+} (Grim, 1962). The chemical formula for montmorillonite is $(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2{\cdot}n(H_2O)$ or chemically known as hydrated sodium calcium aluminium magnesium silicate hydroxide.

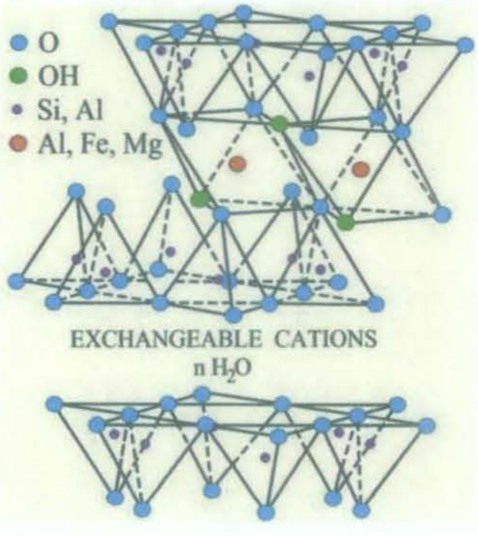

Figure 1: Structure of montmorillonite

(Source: Grim, 1962)

Bentonite is composed mostly of montmorillonite with minor concentrations of quartz mainly. There are different types of bentonite, such as potassium (K), sodium (Na), calcium (Ca), and aluminum (Al) (Murray, 2007). They have high sorptive capacity, high viscosity, high swelling capacity, high layer charge, high plasticity, and high surface area, thixotropic, high cation exchange capacity and very low permeability (Murray, 2007). Their absorption capacity is as much as 8 times greater than other clays. (Kennedy, 1990). Figure 2 shows the scanning electron micrograph of sodium montmorillonite.

Figure 2: SEM of Sodium Montmorillonite

(Source: Murray, 2007)

2.1.2 Sepiolite

Sepiolite is a clay mineral that has complex magnesium silicate. It is a natural hydrous magnesium silicate structurally consists of two sheets of SiO_4 tetrahedron bonded via oxygen atoms to a central sheet of octahedrally arranged magnesium atoms with chemical formula $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$. Sepiolite has internal channels called "zeolitic channels" which run the length of its structure and open via pores of varying shapes and dimensions at the surface. Along the edges of the tetrahedral sheets are silanol (SiOH) groups which can readily hydrogen bond with water and other polar molecules while the magnesium layer also provides adsorption sites.

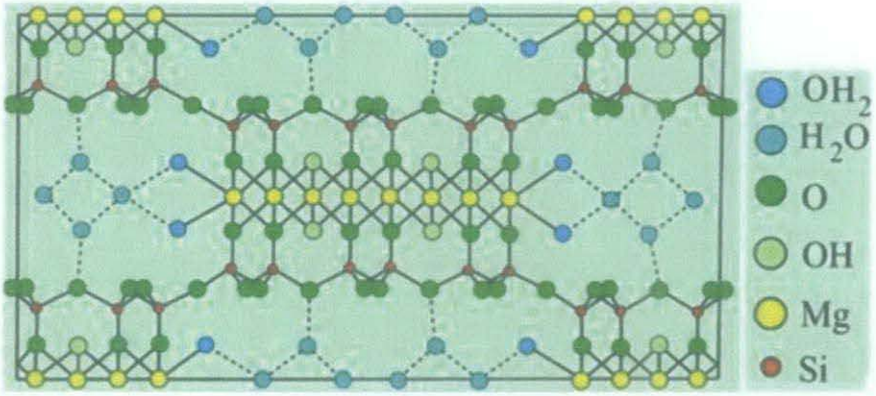

Figure 3: Structure of sepiolite

(Source: Grim, 1962)

Some of the properties and abilities of sepiolite are moderate layer charge, medium base exchange capacity, high surface area, high sorptive capacity and high viscosity (Murray, 2007).

Figure 4: SEM of sepiolite

(Source: Murray, 2007)

2.1.2 Kaolinite

Kaolinite is a common phyllosilicate minerals, also known as aluminium silicate hydroxide, $Al_2Si_2O_5(OH)_4$. Kaolinite is named for its locality, Kao-Ling, Jianxi in China. It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral (Deer *et al*, 1992). The silicate sheets (Si_2O_5) are tightly bonded to gibbsite layers, aluminum oxide/hydroxide layers, $Al_2(OH)_4$ with only weak bonding existing between these silicate/gibbsite paired layers

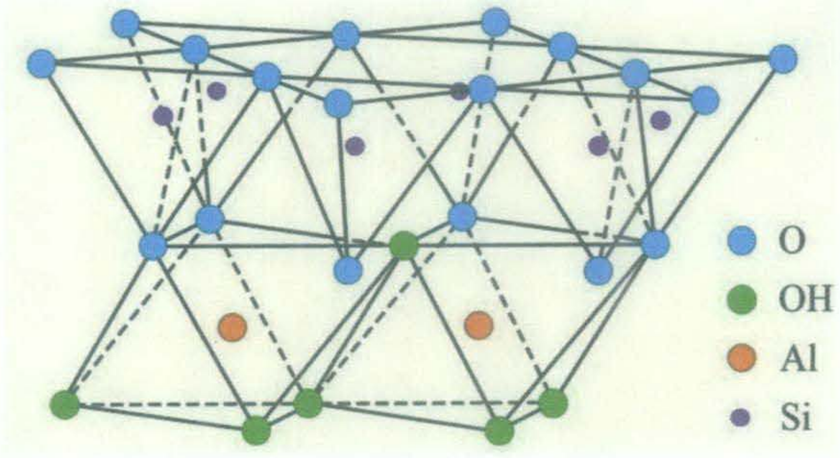

Figure 5: Structure of kaolinite

(Source: Grim, 1962)

Kaolinite shares the same chemistry but different in structure with dickite, nacrite and halloysite. Some of the physical characterictics of kaolinite are minimal charge on the layer, very low cation exchange capacity, low surface area and low absorption capacity (Murray, 2007). Thus, kaolinite is not the right candidate for efficient oil removal as compared to montmorillonite, bentonite and sepiolite and it is more suitable to be used in the production of ceramics and porcelain. Figure 6 shows the scanning electron micrograph of kaolinite.

Figure 6: SEM of kaolinite

(Source: Murray, 2007)

2.2 Applications

Clays have found applications in industries such as processes, agriculture, construction and engineering. In recent years, clays have been explored as adsorbent in removing oil and heavy metals.

2.2.1 Oil removal

Bentonite shows lower residual oil adsorption based on the effect of adsorbent dosage as compared to activated carbon (Ahmad *et al*, 2005). The process can be aided with commercial coagulant to enhance the oil removal efficiency (Qiu et al, 1995). However, bentonite shows a good adsorption of residual oil even after prolonged mixing time suggesting that strong bonding of residual oil onto its surface as well diffusion of oil into their particles is important (Ahmad *et al*, 2005). In addition, bentonite shows effective oil removal at low pH or at strong acid regent and has the ability to act as a binder, assist

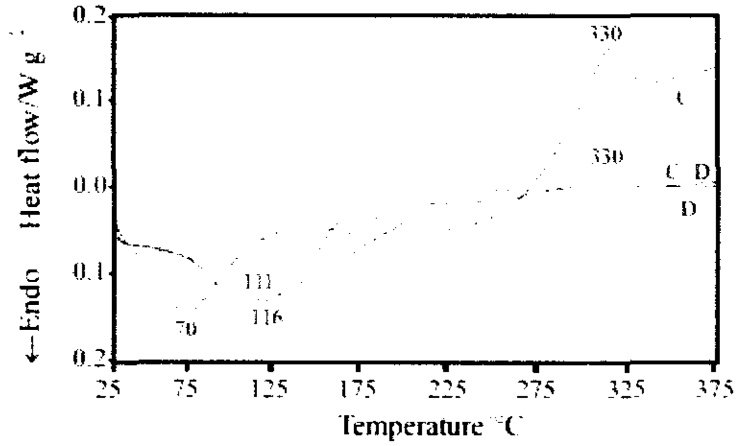

Figure 7: DSC analysis for diesel (D), organo-clay (C), and organo-clay with diesel (C-D) (Carmody *et al*, 2008)

2.2.2 Heavy metals removal

Bentonite has been tested in the sorption of heavy metals (Pb, Zn & Ni) from wastewater. The result from the study shows that Pb is sorbed highest followed by Zn and Cd. Only the amount of Pb sorption remained higher then the Cation Exchange Capacity (CEC) of the clay fraction due to its bivalent form (Ayari *et al*, 2005). Phosphatic clay is effective in adsorbing Pb, Cd and Zn. The sorption behaviors of Cd (24.5 mg/g) and Zn (25.1 mg/g) are similar; however they are different with Pb (37.2 mg/g) that has the highest amount sorbed (Singh *et al*, 2001).

2.3 Mode of operation

2.3.1 Batch

In a batch tank study, wool based sorbent is compared with sepiolite, and the result has shown the higher oil sorption capacity of wool fibers as compared to sepiolite

(Rajakovic *et al*, 2006). This could be due to the form of oil present in water, plus the characteristic of wool with its lumen network that may act as effective sponge to sorb oil.

2.3.2 Continuous, packed bed column

For continuous process, sepiolite has shown a higher sorption capacity as compared to wool-based sorbent (Rajakovic *et al*, 2006). The experiments suggest that in the dynamic condition, the more rigid sepiolite and the volume of oily wastewater can affect oil removal (Rajakovic *et al*, 2006). Increase in volume of effluent up to 1000 cm^3 has caused 22% decrease in sorption capacity of sepiolite (Rajakovic *et al*, 2006).

Packing material can be random and structured. It is used to improve the separation in the distillation column and offers lower pressure drop. Ceramic random packing from China clay material is commercially produced by Jintai Group. It is suitable for higher temperature, lower temperature and more resistant to all types of acid. An experiment on biodegradation of individual dinitrotoluenes by a defined mixed culture in packed bed reactors containing fire clay as packing material has been reported (Paca *et al*, 2009).

2.4 Kapok as a natural oil sorbent

2.4.1 Kapok

Kapok or kekabu fiber or Ceiba pentadra (L.) *Gaertn.* belongs to the *Bombaceae* family and planted traditionally in village area. The fibers are lighter than cotton, yellowish brown in color, more buoyant than cork, water repellent and resistance to rot. Individual fibres are 0.8-3.2 cm long, averaging 1.8 cm in length, with diameter of 30 to 36 µm (Kapok, 2002).

Figure 8: Kapok seed and tree

When the kapok fiber is placed on the water surface, it floats on the surface, causing slight water surface depression due to the inability to penetrate into the fiber. The delay in water wetting is important for an oil sorbent material because it may encounter water before oil during the process (Lim & Huang, 2005).The fiber is used as stuffing material in mattresses and pillows as well as in textile industry. The seeds produce oil that is processed for soap manufacturing and the residue used as fertilizer.

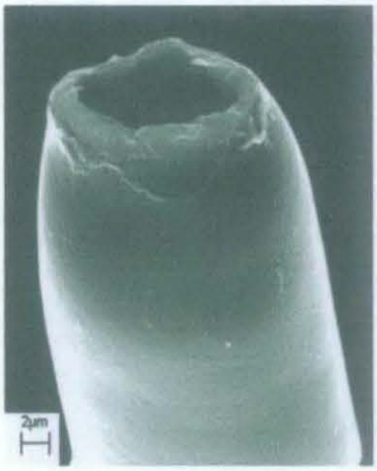

Figure 9: SEM image of kapok fiber

(Source: Abdullah *et al*, 2010)

Kapok exhibits hollow tubular structures (or lumen) with an average external diameter of 21.5 ± 6.5 µm (Abdullah et al, 2010). This is not much different as compared to the kapok originated from Thailand with average external diameter of 16.5 ± 2.4 µm (Lim & Huang, 2007).

2.4.2 Application of kapok as oil sorbent material

Kapok fibers from Philippines have successfully removed diesel, hydraulic oil and diesel water mixture in batch and continuous process. Kapok fiber is significantly hydrophobic and does not wet with water in the absence of organic solvents such as ethanol and acetone (Hori *et al*, 2000). Kapok has been reported to effectively achieve the oily water separation under different packing densities and flow rates where the oil and water movement are influenced by the affinity of liquid to kapok fibers (Anisa Ur Rahmah & Abdullah, 2011).

Hydrophobic waxy coating on the kapok surface makes the sorption capacity even higher and increases the kapok sorptivity (Anisa Ur Rahmah, 2009). Kapok has been shown to be stable for prolonged use even after fifteen cycles of reuse, with only 30% diesel oil sorption capacity reduction (Abdullah et al, 2010). Kapok does not need chemical pretreatment to enhance oil absorbency due to its high selectivity for various oils and excellent water repellent (Lim & Huang, 2007). In addition, it is observed that a significant amount of oil is diffused in the hollow tubes of kapok which suggesting that water cannot penetrate the tube because of its high surface tension (Hori, 2000). Hence, the hydrophobic-oleophilic characteristic of kapok contributes to its high oil sorption capacity.

2.5 Oil recovery from POME

POME contains vitamins and antioxidants such as carotenoids and the oil recovered can be used for biodiesel production. The methane emission can be captured through the utilization of green technologies to produce biogas, which is a form of renewable energy (Ng *et al*, 2010). Therefore, if the residual oil from POME adsorbed by sorbent materials can be recovered, it can be used as a cost-effective feedstock for biofuel to generate electricity. The highest value of oil and grease that could be recovered from POME are 3280 mg/L and 1710 mg/L by using *n*-hexane and petroleum ether, respectively in a single batch extraction (Ahmad *et al*, 2008). The initial concentration of oil and grease in POME is 4610 mg/L which means that 71% and 37% of oil and grease can be recovered by using *n*-hexane and petroleum ether, respectively. However, the concentration of carotene obtained from POME is small as compared to the concentrated carotene obtained in CPO (Ahmad *et al*, 2008).

CHAPTER 3

METHODOLOGY

3.1 Sorption experiment

3.1.1 Experimental materials and methods

The type of clay used in this study was montmorillonite supplied from R&M Chemicals, Essex, U.K. The clay was in a powder form and brown in color with wet sieve of 0.2%. Kapok was purchased from Bota, Perak. The kapok fibers were dry, light, fluffy and pale yellow in appearance. Palm oil mill effluent is obtained from Palm Oil Mill FELCRA Bhd in Bota, Perak at a temperature ranging from 80-90°C but it may vary from day to day depending on the factory conditions.

The chemical used for treating the clay was sulphuric acid (H_2SO_4). The apparatus used in the experiments were 20 ml syringe, beaker, measuring flask, filter paper, separatory funnel, cylinder, test tubes, Erlenmeyer flask, and retort stand.

3.1.2 Experimental setup

Oil sorption was investigated in the batch system. A syringe was used as a packed-bed column reactor. Filter paper was inserted into the syringe to separate small particles such as clay powder and kapok fiber from the POME dripped into beaker. The retort stand was used to give support for the packed column and small beaker used to collect POME dripped after the oil sorption completed.

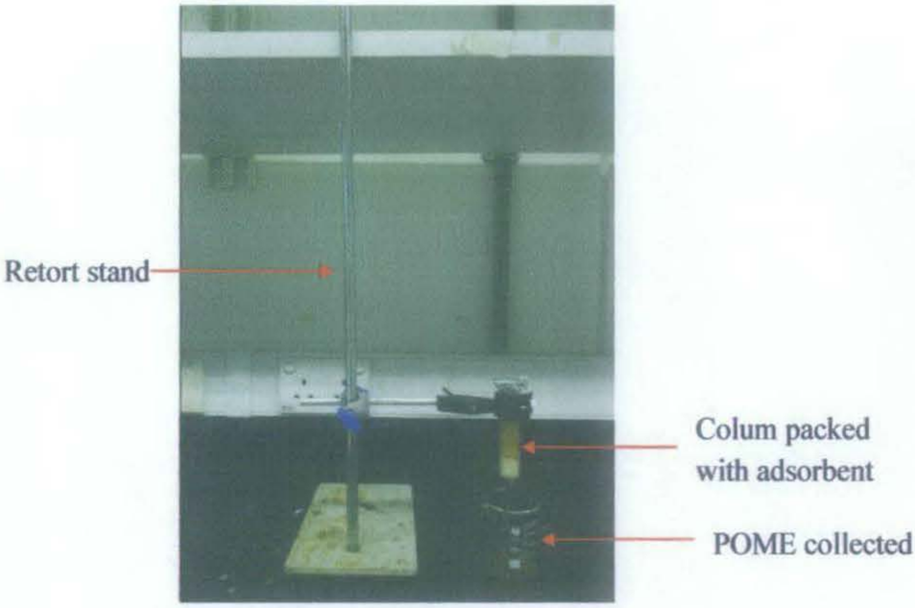

Figure 10: Experimental setup of oil sorption

3.1.3 Experimental procedure

Fresh POME was sedimented for 2 hours to separate sand and solid particles and the supernatant was analyzed. Different adsorbents were packed in different column at different packing density. Raw clay, raw kapok and the double packing of clay and kapok were packed in the column at different packing density as shown in Table 2. Initial weight of the column and weight before and after 15 ml POME was added were recorded. The packed column was left in room temperature for a complete adsorption.

To treat clay, 50 ml of 5% H_2SO_4 was prepared in a beaker. 5 g clay powder was added in each beaker and stirred by using magnetite stirrer for 24 hours. After stirring for 24 hours, the solution was filtered for 1 hour to separate water and unreacted chemicals. Then, it was dried at 60°C in drying oven for 24 hours. Dried treated clay was grinded before it was packed in each column. To compare the effectiveness of double packing, clay treated with H_2SO_4 and raw kapok were packed at different packing density as shown in Table 2 and added with 15 ml POME. Next, the experiment was repeated for 1 month POME by using raw clay, raw kapok, clay/kapok and clay- H_2SO_4 to observe the difference of 1 month POME content with the fresh POME.

Table 3: Experimental parameters

Adsorbent	Packing density (g/cm^3)
Clay	0.90, 1.20, 1.50
Kapok	0.10, 0.11, 0.13
Clay/kapok	0.86, 0.82, 0.56
Clay- H_2SO_4 /kapok	0.86, 0.82, 0.56
Treated clay (H_2SO_4, HCl, NaOH)	1.13, 1.09, 1.08

3.2 Analysis of Palm Oil Mill Effluent (POME)

Oil and grease analyzer used was InfraCal TOG Model HATR-T2. Samples of POME from before and after sorption were analyzed for its oil and grease content. Since most of samples have pH oh more than 5, the samples were first adjusted to pH less than 2 with sulfuric acid. Hexane was used as solvent to extract the oil from water at 1:10 ratio of solvent to sample. Hexane was added into bottles containing POME and shake vigorously for 2 minutes for complete mixing. After the two layers separated, 50 µl was extracted from the upper layer using a syringe and deposited in the center of the sample crystal. Oil concentration displayed was recorded.

Figure 11: Oil and grease analyzer

3.3 Characterization of clay and kapok fiber

Clay and kapok fiber were characterized by using Fourier Transform Infrared Spectrophotometers (FTIR) to identify the functional group and Thermogravimetric Analysis (TGA) to measure the weight loss as a function of temperature or time.

3.3.1 Fourier Transform Infrared Spectrophotometers (FTIR)

FTIR was used to identify the functional group in raw clay, raw kapok, clay- H_2SO_4 samples. Adsorption band was recorded and analyzed as it represents the characteristic of functional group of compound. Infrared spectrum of clay and kapok were analyzed by using Spectrum One FTIR (Perkin Elmer, USA). 2 mg sample was mixed with 200 mg of KBr and compressed into pellet by using a hydraulic pump.

Figure 12: Fourier Transform Infrared Spectra (FTIR)

3.3.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (Perkin Elmer) measures the amount and rate of change in the weight of material as a function of temperature or time. The technique characterizes materials that exhibit weight loss or gain due to decomposition, dehydration or oxidation

TGA of samples were obtained at a heating rate of 2°C min^{-1} and resolution 6.0°C from room temperature to 900°C in a high purity of flowing nitrogen atmosphere of 80 mL min^{-1}.

Figure 13: Thermogravimetric Analyzer

3.4 Gantt chart

Table 4: Gantt chart for FYP 2

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	Oil sorption experiment	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥						
2.	Submission of progress report								●						
3.	Characterization of sorbent materials and analysis of POME								🟥	🟥	🟥				
5.	Pre-EDX												●		
6.	Submission of draft report												●		
7.	Submission of dissertation (soft bound)													●	
8.	Submission of technical paper													●	
9.	Oral presentation														●
10.	Submission of project dissertation (hard bound)														●

● Milestone

🟥 Process

CHAPTER 4

RESULT AND DISCUSSION

4.1 Effect of packing density on POME sorption capacity

Two parameters studied to evaluate the performance of sorbent materials were packing density and POME lifetime. 24 samples for fresh and 1 month old POME were packed in different packing density but, only 16 samples had reached the complete sorption of POME. Clay packed with kapok at density of 0.56, 0.82 and 0.86 g/cm^3 and treated clay with sulfuric acid packed with kapok at 0.82 g/cm^3 had not achieved complete sorption. Complete POME sorption was obtained when the sorbent materials had reached saturation point where POME started to drip from column.

After few days sorbed with POME, the height of clay in the column increased indicating adsorption occurrence and the color changed from light brown to dark brown. The color of kapok changed from transparent white into yellowish suggesting the POME entrapment inside the kapok structure.

4.1.1 Fresh POME

At 0.10 g/cm^{3,} kapok showed highest sorption capacity of POME, 98% as compared to the 0.11 and 0.13 g/cm^3 while clay showed highest sorption capacity at 0.90 g/cm^3. Treated clay with sulfuric acid packed together with kapok (clay-H_2SO_4/kapok) showed the highest sorption capacity at 0.56g/ cm^3. Kapok showed highest sorption capacity of POME as compared to clay and clay-H_2SO_4/kapok. The similarity between these adsorbents is the higher the packing density, the lower the POME sorption will be.

Although the amount of POME sorbed per unit mass decreases with increasing density, the mass and volume sorbed POME for each different packing density is not significantly different for clay but it is significantly different for kapok and clay-H_2SO_4/kapok (Figure 14).

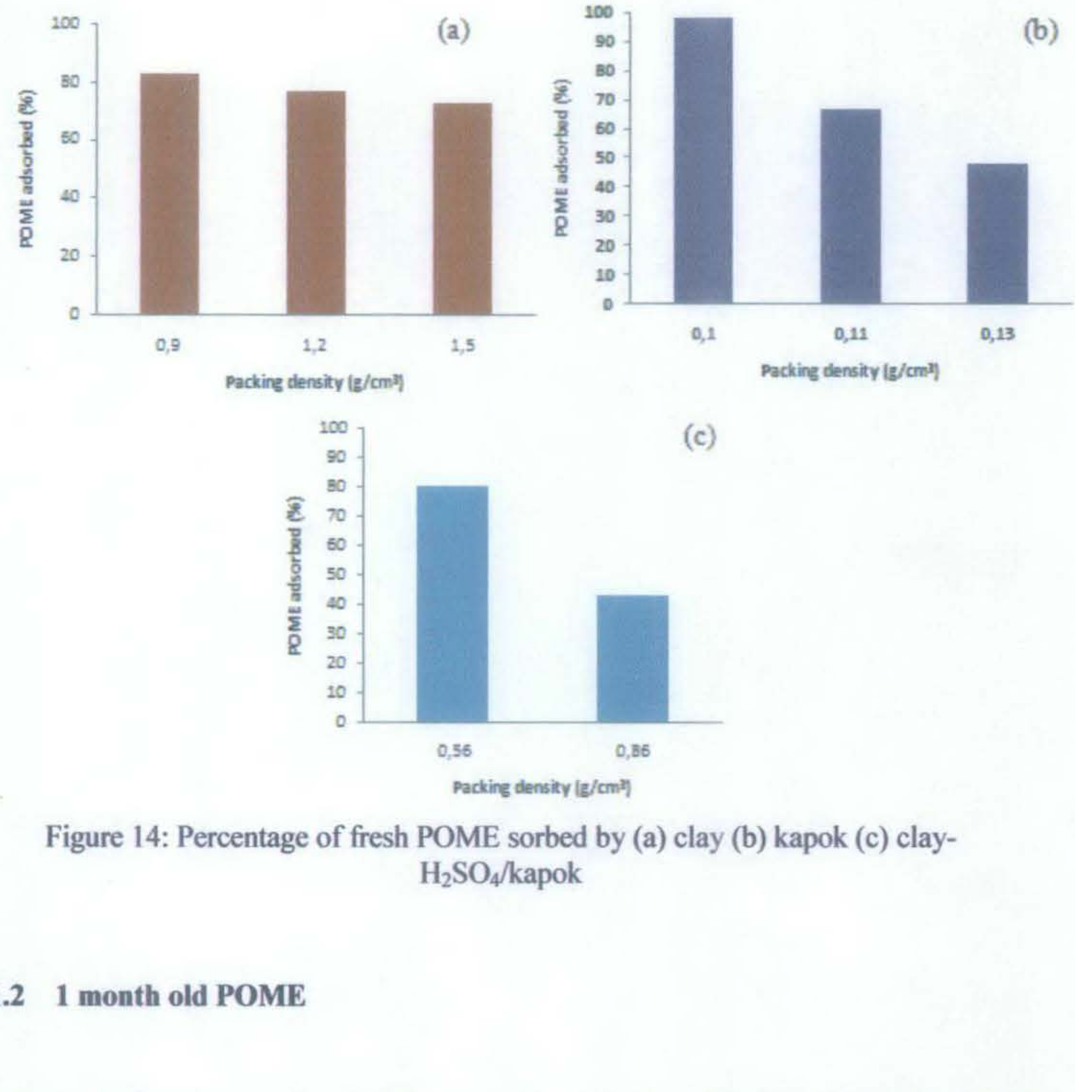

Figure 14: Percentage of fresh POME sorbed by (a) clay (b) kapok (c) clay-H_2SO_4/kapok

4.1.2 1 month old POME

At 0.10 g/cm^3, kapok showed highest sorption capacity of POME, 97%, while clay showed highest sorption capacity at 0.90 g/cm^3 and clay-H_2SO_4/kapok showed the highest sorption capacity at 0.56g/ cm^3. Kapok showed highest sorption capacity of POME as compared to clay and clay-H_2SO_4/kapok. Only clay has increment in the sorption capacity of POME from 82% (fresh POME) to 90% (1 month old POME) as compared to kapok and clay-H_2SO_4/kapok (figure 15). However, the duration of POME stored in ambient temperature does not have significant difference since the fresh and 1 month old POME were taken at different day resulting in different content of POME that varies each day depending on the discharge conditions.

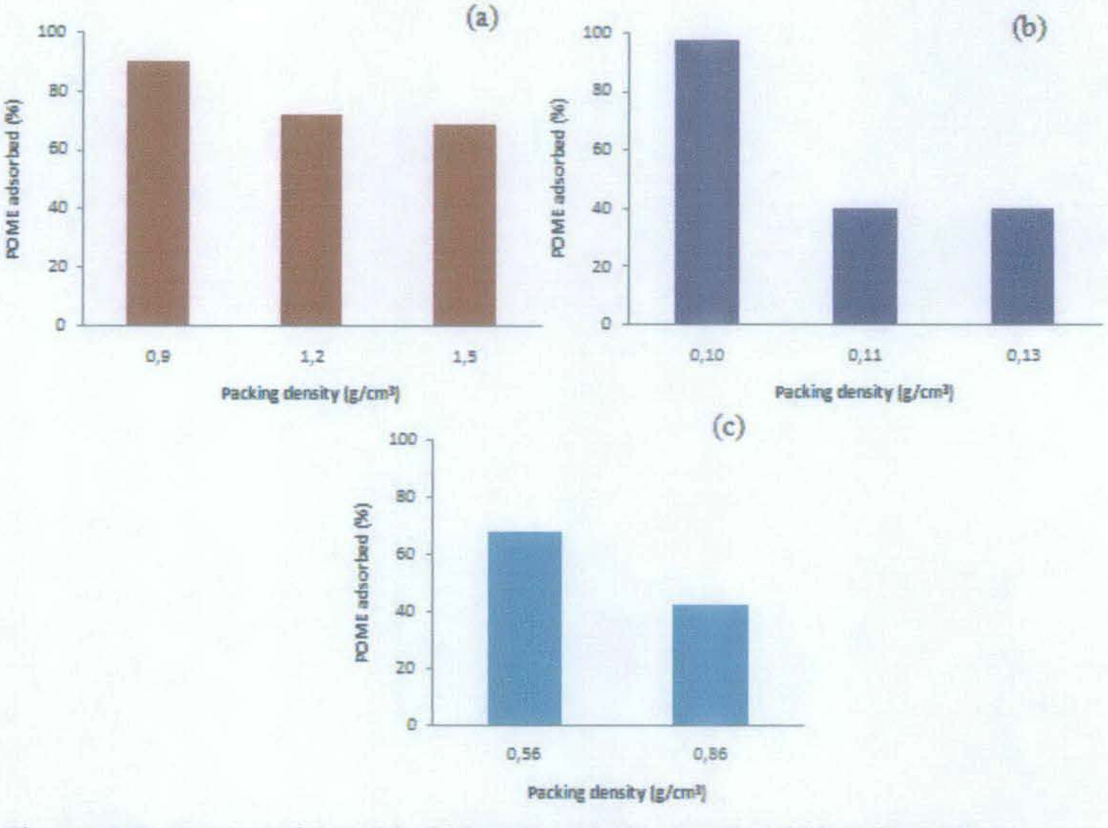

Figure 15: Percentage of 1 month old POME sorbed by (a) clay (b) kapok (c) clay-H_2SO_4/kapok

For both fresh POME and 1 month, the sorption capacity of POME increases with decreasing packing density. It seems that the lower the packing density, the more loosely packed it becomes, the easier the POME can sorb through. Higher packing density can cause compactness since the mass of sorbent material increases as well. The other possible reason for lower sorption capacity is the method of packing the sorbent materials in the column during the experiment since it was packed manually.

Kapok showed the highest sorption capacity of fresh and 1 month old POME as compared to other sorbent materials due to its hollow lumen network with the inter fiber pores located in the kapok microstructure (Abdullah *et al*, 2010). Clay showed to be a better sorbent material than the double packing sorbent materials but less better performance as compared to kapok. Clay has high surface area and exchange capacities that attributes to the high sorption capacity. However, since POME contains mostly water than oil, clay could be sorbing water as well unlike kapok that has hydrophobic-oleophilic characteristic.

4.1.3 Effect of double packing on POME sorption capacity

The possible reason clay packed with kapok at density of 0.56, 0.82 and 0.86 g/cm^3 and treated clay with sulfuric acid packed with kapok at 0.82 g/cm^3 had not achieved complete sorption was due to the compactness. POME may not be able to penetrate into the structure of clay and kapok since it was too compact. However, after treating the clay with sulfuric acid, the sorption rate increased and POME was allowed to penetrate into the kapok and clay until it was saturated.

As the pure clay is more crystalline, acid treatment can alter the crystallinity and interlayer structure to produce more amorphous clay and N_2 adsorption/desorption analysis indicates that with acid treatment, the surface area and pore volume are increased (Panda *et al*, 2010). This can be the possible reason of double packing sorbent materials; clay-H_2SO_4/kapok can achieve complete POME sorption and saturation point as compared to untreated clay/kapok. Sulfuric acid treatment with clay had increased the surface area, pore volume and produced more amorphous clay which allows the POME to sorb through even in the double packing of sorbent materials.

4.2 Oil and grease content in POME

The amount of oil removed by sorbent materials can be obtained by determining the oil and grease content of raw POME and compared it with the POME dripped from column. From figure 16 and 17, kapok at 0.10 g/cm^3 removed the highest amount of oil and grease as compared to clay and clay-H_2SO_4/kapok. From figure 14 and 15, kapok showed the highest sorption capacity of POME therefore, it removed the highest amount of oil content in POME. However, the amount of oil removed by kapok at 0.11 g/cm^3 was higher than clay at packing density of 0.90 g/cm^3 although the sorption capacity of kapok at 0.11 g/cm^3 was lower than clay at 0.90 g/cm^3. Thus, it appears that the sorption capacity is not the solely parameter in determining the efficiency of oil removed but the types of sorbent materials used has significant effect as well.

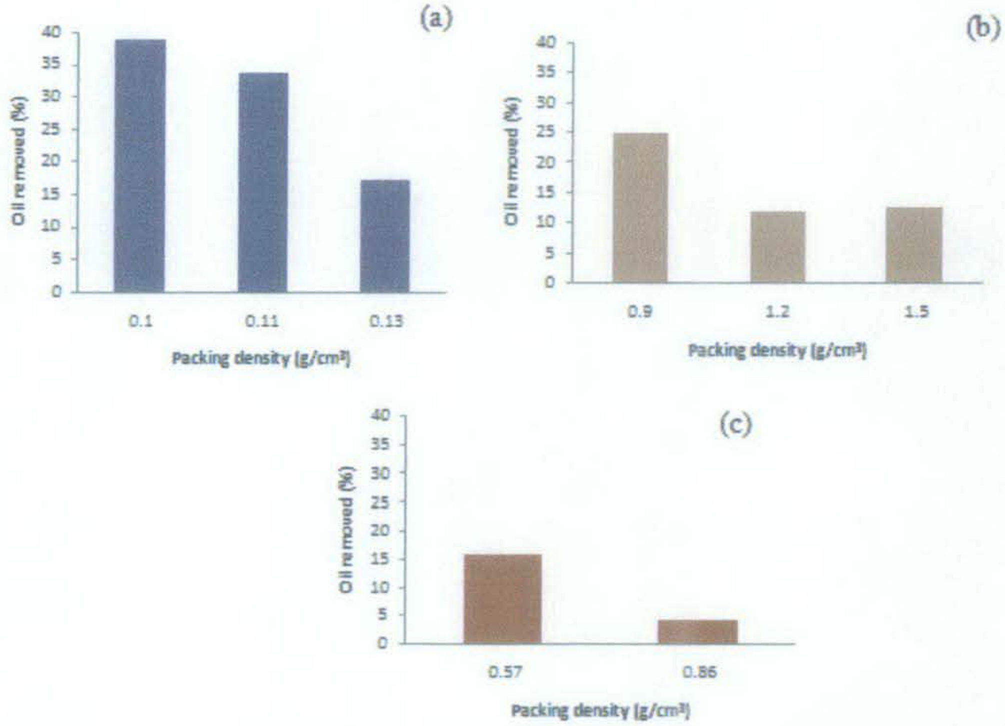

Figure 16: Percentage of oil removed from fresh POME by (a) kapok (b) clay (c) clay-H_2SO_4/kapok

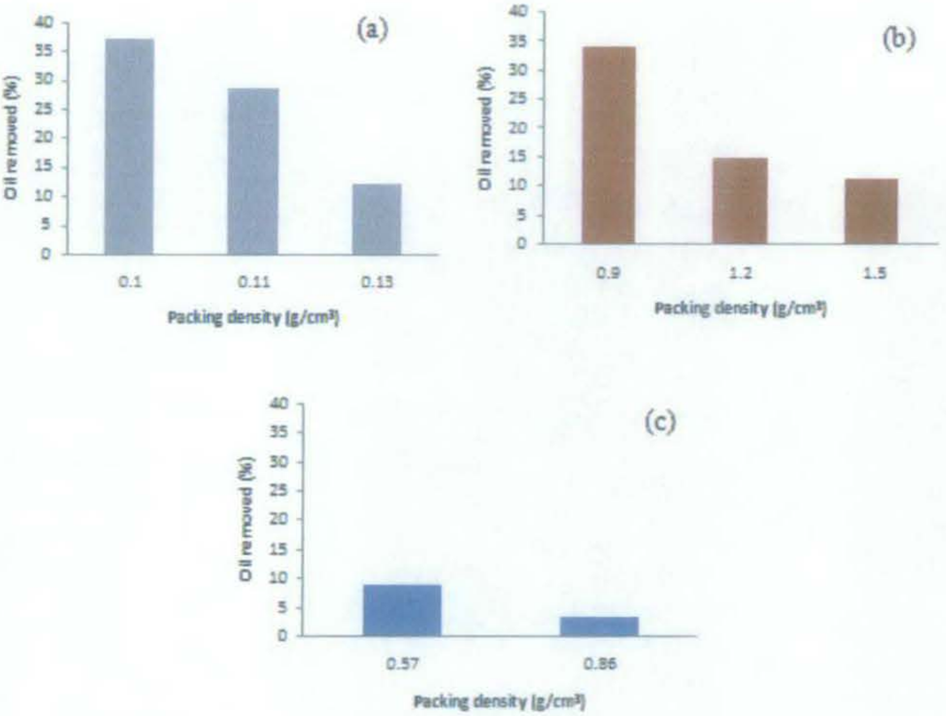

Figure 17: Percentage of oil removed from fresh POME by (a) kapok (b) clay (c) clay-H_2SO_4/kapok

High amount of oil removed using kapok can be a result of hydrophobic waxy coating on the kapok surface. Waxy surface coatings prevent water to sorb through it and increase the efficiency of oil sorbed. Within loosely-packed kapok, the oil is mainly entrapped inside the kapok fiber pores resulting in the higher amount of oil sorbed (Abdullah, 2010). Unlike kapok that has hydrophobic-oleophilic characteristic, the sorption capability of clay mainly comes from its high surface area. The selectivity of oil in water cannot be determined since clay does not exhibit hydrophobic characteristic. Since POME contains mostly water than oil, so clay could sorb more water and became saturated leaving the oil dripping from column.

4.3 Characterization of clay and kapok

4.3.1 Fourier Transform Infrared Spectrophotometers (FTIR)

Functional group analyses of sorbent materials before and after sorption of POME were carried out by radiating the sample that was mixed with KBr pellet with infrared light. Infrared radiation is absorbed by organic molecule and used it as energy for molecular vibration. The absorption occurs when the infrared energy radiant matches the vibration energy (Anisa Ur Rahmah, 2009). The spectrophotometer records the transmittance of a sample for wavelengths within region of the electromagnetic spectrum. The infrared spectrum is a plot of percentage transmittance against wavelength number (cm^{-1}). The percentange of transmittance is the ratio between final and initial intensity.

The FTIR spectra as shown in Figure 18 indicates all the components of raw clay, clay after sorption and treated clay with sulfuric acid after sorption. The adsorption bands at 3430-1635 cm^{-1} correspond to OH frequencies for the water molecule adsorbed on the clay surface. The (Si-O) bands were strongly evident in the silicate structure and can be recognized in the infrared spectrum by the very strong absorption bands in the 1100-1000 cm^{-1} region (Ayari *et al*, 2005). The infrared absorbency at 918-914 cm^{-1} indicates the presence of dioctahedral smectite with [Al, Al-OH] stretching bands (Ayari *et al*, 2005). Bands at 798-538 cm^{-1} can be assigned to [Si-O] and [Si-O-Al].

The significant difference between samples after sorption of POME with the raw clay is that the absorption bands at 2918 (b) and 2924 cm^{-1} (c) which confirm the CH_2 and CH_3 stretching that can be associated with the presence of fatty acids (Anisa Ur Rahmah, 2009). This has proven the occurrence of oil sorption inside clay structure.

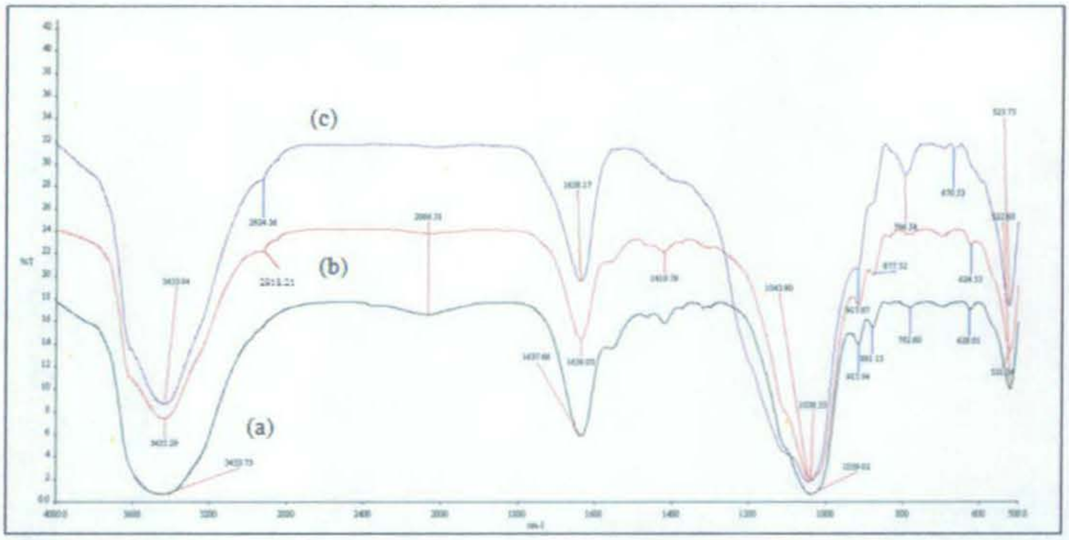

Figure 18: FTIR spectrum of (a) raw clay (b) untreated clay after POME sorption (c) H_2SO_4 treated clay after POME sorption

The FTIR spectra as shown in Figure 19 indicate kapok as a lignocellulosic material with hydrophobic waxy coating similar to previous study (Anisa Ur Rahmah, 2009). At 2920-2912 cm^{-1} region, a well pronounce trough was observed which corresponds to the CH_2 and CH_3 stretching that associated with the presence of plant wax. The bands around 1735 and 1250 cm^{-1} were due to the presence of carbonyl group in the ester bonds which associated with the presence of plant wax (Lim & Huang, 2007). Adsorption bands around 1161 and 898 cm^{-1} correspond to the presence of cellulose and hemicelluloses. Around 1050 cm^{-}1, C-O stretching band corresponds to the presence of cellulose, hemicelluloses and lignin.

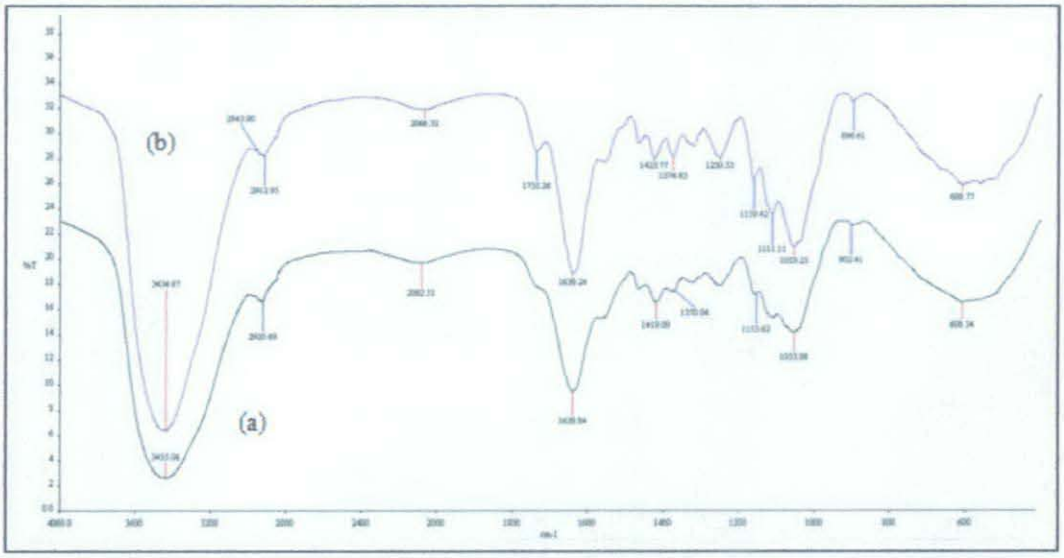

Figure 19: FTIR spectrum of (a) Raw kapok (b) after POME sorption

4.3.2 Thermogravimetric Analysis (TGA)

Measurements of changes in raw clay, clay, clay-H_2SO_4 and kapok after POME sorption, mass with temperature are made using a thermobalance or thermogravimetric analyzer. A themobalance is a combination of a suitable electronic microbalance with a furnace, a temperature programmer and computer for control that allows the sample to be simultaneously weighed and heated or cooled in a controlled manner, and the mass, time and temperature data to be captured (Brown, 2001). TG curve is usually plotted as the mass percent against temperature or time.

TGA curves from Fig 20 for raw clay and clay after sorption indicate the first weight loss occurred at 30-100°C. These transformations were due to the removal of adsorbed and interlayer water from the clay mineral (Ayari *et al*, 2005). Further weight loss could be due to the removal of water decomposition from the clay mineral. There is not much difference between these curves. TGA curve of clay-H_2SO_4 shows a slight difference in the percentage of weight loss. It shows the less percentage weight loss of water as compared to clay and clay after sorption curves. The other possible thermal processes for these curves are thermal reaction of organic material (200-500°C), dehydroxylation or evolution of water from hydroxyls belonging to the clay layers and transformation of the clay into crystalline phase (>500°C) (Carmody *et al*, 2008).

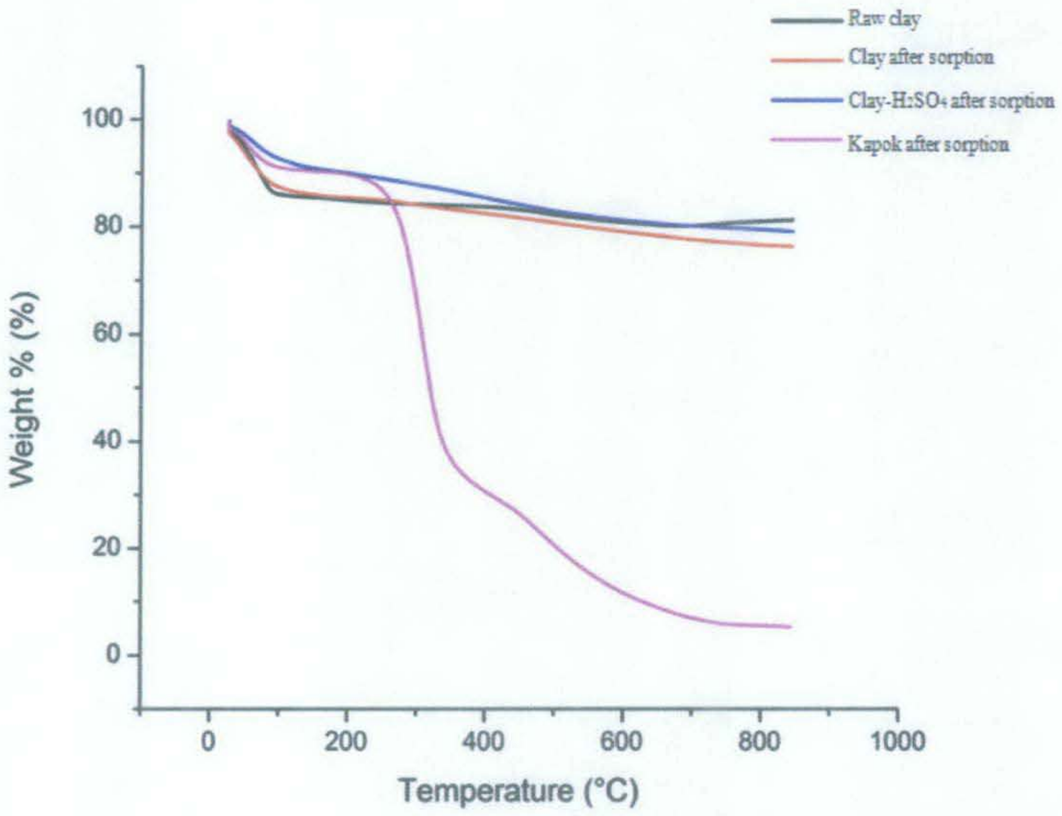

Figure 20: TGA curves of different sorbent materials

Based on Figure 20, kapok thermal analysis represented multi-stage decomposition and different curve obtained as compared to clay because it is a lignocellulosic material. Curve at 30 to 100°C were due to water removal from kapok fiber. Hemicellulose started its decomposition easily with the weight loss happened at 220 - 315°C. Weight loss from 315 to 400 °C could be attributed to cellulose. Lignin is the most difficult to decompose and its decomposition occurred slowly under the ambient temperature to 900°C (Yang *et al*, 2007).

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The potential of montmorillonite clay and Kapok or *Ceiba pentadra* (L.) Gaertn. as Palm oil mill effluent (POME) sorbent materials have been investigated based on the packing density optimization and characterization of clay and kapok. The performance of clay, kapok, and treated clay with sulfuric acid were investigated using single packing and double packing of sorbents in fresh and 1 month old POME.

Kapok has the highest sorption capacity at 0.10 g/cm^3, clay at 0.90 g/cm^3 and clay-H_2SO_4/kapok at 0.56 g/cm^2. It is observed that as the packing density increases, the sorption capacity decreases. Higher packing density is less loosely-packed thus the harder the POME can sorb through. Kapok has the highest sorption capacity followed by clay and clay-H_2SO_4/kapok. Kapok at 0.10 g/cm^3 has removed the highest amount of oil and grease content in fresh and 1 month old POME, 39% and 37% respectively. However, it appears that clay at 0.9 g/cm^3 has lower percentage of oil removed as compared to kapok at 0.11 g/cm^3 although it sorbs higher POME. This is because kapok exhibits hydrophobic-oleophilic (water repellent-oil attractant) characteristics while clay has only high surface area as a factor of sorption capacity.

Infrared spectrum shows that clay has silicate and alumina structure. Absorption band around 2918 cm^{-1} is observed only in clay and clay-H_2SO_4 samples that can be associated with fatty acid contents. This has proven the occurrence of oil sorption in clay. Infrared spectrum of kapok shows that kapok is a lignocellulosic material with hydrophobic waxy coating.. TGA curves of clay shows the weight loss of clay mostly due to water removal from clay minerals. TGA curve for kapok on the other hand shows the decomposition of water, hemicellulose, cellulose and lignin.

5.2 Recommendations

For future development and improvement of this study, experimental works in batch system can be conducted in larger size of column so that more analyses can be done. The performance of clay and kapok as oil sorbents can also be investigated in continuous system to get various results and to conduct comparative study of sorbent materials performance between batch and continuous system. Oil recovery of sorbent materials after the sorption can be investigated further when the large size of column is used because small size of column limits the amount of POME that can be sorbed thus reducing the efficiency of oil recovery.

This study has proven the performance of clay and kapok as natural oil sorbent material in a batch system but the condition for large scale application of clay and kapok need to be investigated further. These include the study on engineering parameter such as column height, column diameter, temperature and pressure to achieve optimum condition for pilot plant scale.

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