



Physicochemical and sorption characteristics of Malaysian *Ceiba pentandra* (L.) Gaertn. as a natural oil sorbent

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ABSTRACT

Ceiba pentandra (L.) Gaertn (kapok) is a natural sorbent that exhibits excellent hydrophobic–oleophilic characteristics. The effect of packing density, the oil types and solvent treatment on the sorption characteristics of kapok was studied in a batch system. Oil sorption capacity, retention capacity, entrapment stability and kapok reusability were evaluated. Based on SEM and FTIR analyses, kapok fiber was shown to be a lignocellulosic material with hydrophobic waxy coating over the hollow structures. Higher packing density at 0.08 g/ml showed lower sorption capacity, but higher percentage of dynamic oil retention, with only 1% of oil drained out from the test cell. Kapok remained stable after fifteen cycles of reuse with only 30% of sorption capacity reduction. The oil entrapment stability at 0.08 g/ml packing was high with more than 90% of diesel and used engine oil retained after horizontal shaking. After 8 h of chloroform and alkali treatment, 2.1% and 26.3% reduction in sorption capacity were observed, respectively, as compared to the raw kapok. The rigid hollow structure was reduced to flattened-like structure after alkali treatment, though no major structural difference was observed after chloroform treatment. Malaysian kapok has shown great potential as an effective natural oil sorbent, owing to high sorption and retention capacity, structural stability and high reusability.

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1. Introduction

The world is facing a great risk from petroleum product contamination in the environment. With approximately 10 million tons of petroleum products and derivatives being used daily worldwide, the risks are even greater during transportation, transfer and storage. Between 1974 and 1994, there are 175 major oil spills worldwide [1]. The cost just to cleanup the contaminated site may go as high as \$20–\$200 per litre in USA and Canada, depending on the location and type of oil spilled. Integrated strategies must be worked out to reduce social, economic and environmental impact from oil spills. The use of sorbent materials for oil removal is attractive principally due to its ability to transform oil contaminant in the liquid phase into solid or semi solid phase. Other considerations include the availability of the material, the economics, high oil sorption rate and sorption capacity, low water pickup rate, high oil retention capacity during transfer, high recovery of the sorbed oil through simple method, good reusability, and excellent physical and chemical resistance against deformation, photo-degradation and chemical attacks [2,3].

Oil sorbent materials can be classified into organic, inorganic and synthetic organic products [4,5]. Organic sorbents include

straw, corn cob, wood fiber, sawdust, cotton fiber, kapok fiber, wool fiber, kenaf fiber, *Salvinia* sp., rice husk, coconut husk, cattail fiber and bagasse [2,3–15]. The mineral inorganic products include perlite, graphite, vermiculite, zeolites, bentonites, organo clay, fly ash, sand and diatomite [16–23]. From environmental engineering point of view, natural sorbent materials are attractive because of the possibility of sorbent collection, complete oil removal from the spill site, easy disposal with the least environmental hazard, more economical than most synthetic sorbents, and possible co-application with other strategy such as the application of microbial consortium for oil spill remediation. Based on the oil uptake of between 30 and 40 g oil/g fiber, natural sorbents such as cotton, wool, milkweed and kapok show better performance than most other sorbent materials. Only exfoliated graphite (83 g oil/g fiber) and polyurethane foam (100 g oil/g fiber) register higher oil uptake than natural sorbents [4,19]. The hydrophobic–oleophilic properties of oil sorbent are determined by factors such as the chemical constituent of the sorbent, the amount of the surface wax, the physical configuration of the fiber such as the hollow lumen, the twists and the crimps, and the surface roughness and its porosity [24,25].

Ceiba pentandra (L.) Gaertn. or locally known as *kekabu* or kapok, is cultivated in Southeast Asia, Malaysia, Sri Lanka, other parts of East Asia and Africa. The fibers are lustrous, yellowish-brown in color, light, inelastic and brittle. In Malaysia, kapok fiber has been used mainly as a stuffing material for beds and pillows. Kapok fibers originated from Philippines have been investigated for their

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properties and performance as oil sorbent for diesel, hydraulic oil, engine oil and diesel–water mixture in batch and continuous systems [5,14,15]. Kapok fiber treated with alkali has been reported for use as composite reinforcement material [26,27]. There has yet to be any report on the use of Malaysian kapok for oil removal, on the stability of oil entrapment during rigorous shaking, and on the oil sorption capacity after alkali treatment.

In this study, the physicochemical and oil sorption characteristics of Malaysian kapok were investigated. Several parameters such as the packing density and the types of oil were studied in a batch system. The oil sorption capacity, the percentage of dynamic oil retention, the oil entrapment stability, and kapok reusability were evaluated. The effects of chloroform and alkali treatment on the hydrophobic–oleophilic properties and the stability of hollow structures were investigated to assess the role of waxy layer on the kapok surface during oil sorption processes.

2. Materials and methods

2.1. Materials

Kapok fiber used in this study was originated from Bota Kanan Village, Perak, Malaysia. Visible dusts and lumps were removed from the raw fibers. To ensure the freshness of the raw materials, no further treatment was carried out.

Diesel oil (Petronas D2, Petronas Sdn Bhd.), new engine oil (Petronas Synthium, Petronas Sdn Bhd.) and used engine oil collected from the local automobile workshop, were used as the experimental oils. Diesel oil was dyed using Oil red O (Sigma–Aldrich, Germany) and used without further purification. Diesel represents low-viscosity, less volatile oil and has better compositional uniformity, which minimizes transient change in its chemical and physical characteristics during experiments. New engine oil and used engine oil represent medium and heavy hydrocarbons. For solvent treatment, chloroform (Systherm, UK) and NaOH (R&N Chemicals, USA) were used.

2.2. Characterization of kapok fiber and experimental oils

Kapok morphology was analyzed by Scanning Electron Microscopy (SEM, LEO 1430P VPSEM) and Optical Microscopy (Nikon Eclipse ME 600, Japan). For SEM analyses, the samples were mounted on round stainless steel sample holders with double-sided conductive adhesive tapes. The samples were sputter-coated with gold using a sputter coater (Polaron SC 764) to provide conductive coating that enhances the images under SEM. SEM images were examined using accelerating voltage at 15 kV. The diameter of kapok fiber was measured using a measuring tool bar as made available in the SEM computer program package.

The density of kapok fiber was measured by Ultrapycnometer 1000 (Quantochrome, USA). Around 0.5 g of kapok was placed inside the sample cell. Nitrogen was used as the purging gas using a flow mode. Twenty runs were carried out for each density measurement.

Infrared spectrum of raw kapok was analyzed using Spectrum One FTIR (PerkinElmer, USA). Kapok fiber of 2 mg weight was mixed with 200 mg of KBr and compressed into a pellet by using a hydraulic pump. Two scans were carried out at 500 until 3000 cm^{-1} wavelength, at a resolution of 4 cm^{-1} .

Interactions between solid and liquid were characterized based on contact angle and surface tension. Static and dynamic contact angle and the surface tension between extracted kapok walls and the experimental oils, were measured using Interfacial Tension, IFT 700 (Vinci Technologies, France). The instrument is equipped with charge-coupled device (CCD) camera to capture image and video

of the solid–liquid interface. The contact angle was determined by processing the video frames captured during the measurement. The value of surface tension was calculated from the drop shape of the image recorded by CCD camera, using Laplace equation as shown below:

$$\Delta p = \frac{2\gamma}{r} \cos \theta \quad (1)$$

where Δp is the pressure difference between gas and liquid phase (bar), γ is the surface tension (MN/m), θ is the contact angle ($^\circ$), and r is the droplet radius (mm)

For both contact angle and surface tension measurement, 1 g of fiber was soaked inside 100 ml of chloroform for 4 h. The fibers were separated from the liquid by vacuum suction filtration. The remaining liquid was left evaporated from the surface of the test plate inside the viewing cell chamber of IFT 700. One drop of oil was placed on the kapok surface by using a hand pump filling system. The measurement was started immediately after the oil drop was captured by the CCD camera.

Density measurement of experimental oils was carried out using DMA 5000 Density Meter (Anton Paar, Austria). Viscosity of new and used engine oil was measured using CAP 2000+ Viscometer (Brookfield Engineering Laboratories, Inc., USA). The viscosity of diesel oil was measured using Cannon-Fenske Routine type for transparent liquid (No. 100/N856, Cannon Instrument Co., USA). The temperature was maintained at 25 $^\circ\text{C}$, during viscosity measurement, using a water bath (Labline, USA).

2.3. Oil sorption and dynamic oil retention capacity

The procedure for determining oil sorption capacity generally followed the method F726-99 (ASTM, 1998c) [28]. Loosed-form kapok was packed inside 87.5 cm^3 wire-mesh basket and immersed inside an oil bath until it reached the equilibrium stage. Several packing densities were tested: 0.02, 0.04, 0.06 and 0.08 g/ml. The test cells were soaked inside a 500 ml beaker glass (Pyrex, Germany) filled with 400 ml of experimental oil, for 30 min in diesel oil, 60 min in fresh engine oil and 90 min in used engine oil. The difference in duration reflected the speed at which the oil penetration reached equilibrium stage. The oil-saturated test cells were then lifted and the oil was left dripping out from the test cell above the oil baths. The transient weight of oil bath was recorded using a balance for each minute of dripping for 30 min. The experimental procedure was carried out in 3 replications and the results were calculated based on mean values. The oil sorption capacity was calculated as shown in Eq. (2).

$$\text{oil sorption capacity} = \frac{S_i - S_F}{S_A} \quad (2)$$

where S_i is the weight of the oil before sorption inside the oil bath (g), S_F is the weight of oil inside the beaker at 1 min dripping (g), and S_A is the dry weight of kapok (g)

The percentage of dynamic oil retention capacity was calculated as follows:

$$\text{percentage of dynamic oil retention capacity} = \frac{W_t}{W_{t=1}} \times 100\% \quad (3)$$

where $W_{t=1}$ is the weight of oil bath (g) at 1 min dripping, $W_{t=i}$ is the weight of oil bath (g) at t min dripping, $i = 2, 3, 4, \dots$

To study the effect of packing density on the saturation time and the bed height difference, a column was fabricated from a plastic syringe of 35 ml volume. Kapok was packed in a 20 ml working volume of the designated column to give packing densities of 0.02, 0.04, 0.06 and 0.08 g/ml. Experimental oil of 20 ml volume was poured into the column until saturation. The saturation point was noted from the appearance of the first oil droplet from the column tip. The saturation time is calculated from the time the oil

was poured into the column until the saturation point. The bed height difference was measured from the initial bed height until the height after which no remaining oil was observed dripping out of the column.

2.4. Oil entrapment stability

To check the stability of oil entrapment inside the kapok assembly after oil sorption, an external force in the form of horizontal shaking was applied. Only kapok that have been soaked inside diesel and used engine oils were investigated. The oils were chosen due to their significant differences in viscosity. After 30 min of allowing the oil dripping out, the kapok-filled wire-mesh basket at each packing density was placed inside a horizontal shaker at 150 rpm for 30 min. Weight difference of the test cell was recorded.

2.5. Reusability of kapok

Kapok reusability was tested using a 250 ml graduated glass column packed with kapok at 0.04 g/cm^3 in 100 ml working volume. Diesel oil of 100 ml volume, was poured into the column until saturation point. Free dripping of oil was allowed for 15 min before a pressure difference was applied via a vacuum pump (BUCHI Vacuum Controller V-800) at 525 mbar every 10 min interval, for 3 times. Upon completing each desorption process, the test cell was weighed to monitor the oil sorption capacity and the packing height. The saturation time for each of the cycle was noted when the first oil droplet appeared from the test cell. The bed height difference was also observed after each sorption–desorption cycle.

2.6. The effect of solvent treatment

Kapok of 5 g weight was added into either 200 ml of chloroform or 125 ml of 1% (w/w) NaOH at pH 13. The duration of soxhlet extraction for both chloroform and alkali treatment under reflux were 4 and 8 h. After alkalization, washing with water was applied to remove any waxy debris from the fiber.

Extracted liquid and kapok was separated by filtration using vacuum suction (BUCHI, Germany) for 10 min. Kapok was then dried inside drying oven (Memmert, Germany) at 60°C for 24 h. After drying as a result of alkalization, the kapok fiber became pulp-like and hardened. The dried material was grounded using a blender to form the fine fibers. The powder form was used for the determination of oil sorption and retention capacity. Infrared spectrum of raw and solvent-treated kapok was analyzed using Spectrum One FTIR (PerkinElmer, USA). Two scans were carried out at 400 until 3000 cm^{-1} wavelength, at resolution of 4 cm^{-1} . The oil sorption capacity and percentage of dynamic oil retention of extracted kapok were determined as described earlier, using a packing density of 0.04 g/ml and diesel as the experimental oil.

3. Results and discussions

3.1. Characterization of kapok and oil properties

Kapok microstructures as analyzed by SEM (Fig. 1) exhibit hollow tubular structures (or lumen) with an average external diameter of $21.5 \pm 6.5 \mu\text{m}$. This was not significantly different from kapok originated from Thailand which record the average external diameter of $16.5 \pm 2.4 \mu\text{m}$ [5]. OM image (data not shown) showed transparent channel of kapok. Raw kapok fibers showed smooth surfaces, with the density of 1.3 g/cm^3 . Clusters of kapok fiber exhibited rod-like structures with consistent fineness, which correlated well to the configuration of each fiber.

The infrared spectrum of raw kapok is shown in Fig. 2. At 2918 cm^{-1} , a well-pronounced trough was observed which corre-

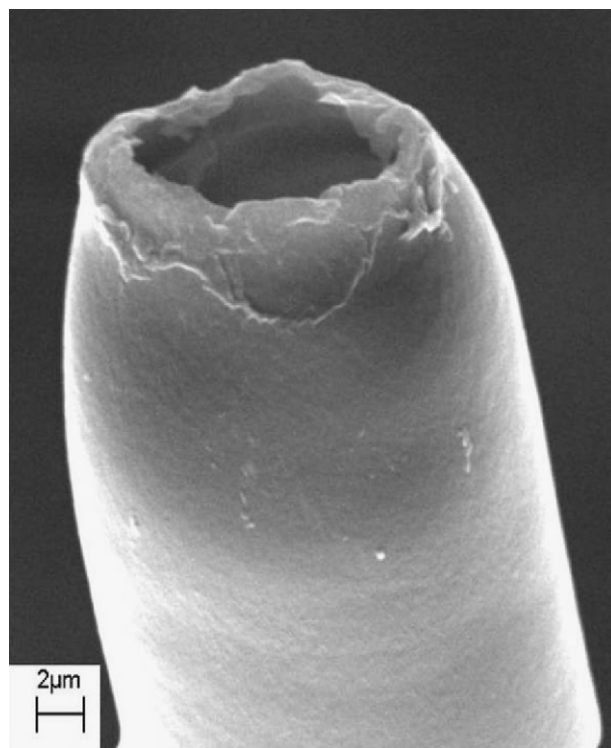


Fig. 1. SEM images of kapok fiber.

sponds to the asymmetric and symmetric aliphatic CH_2 and CH_3 stretching. This can be associated with the presence of plant wax, which generally consists of *n*-alkanes, smaller portion of alcohols, fatty acids, aldehydes, ketones and *n*-alkyl esters [15,29]. The bands around 1736 , and 1242 cm^{-1} are due to the presence of carbonyl group ($\text{C}=\text{O}$) in the ester bonds [15]. The $\text{C}=\text{O}$ stretching vibrations are believed to be associated with the aliphatic aldehydes, esters and ketones of kapok wax. The band around 1510 cm^{-1} corresponds to $\text{C}-\text{O}$ stretching in lignin, while the band at 1050 cm^{-1} is within the region of carbohydrate or polysaccharides. An infrared spectrum pattern of cotton shows similar spectrum to our study with the band at 2891 cm^{-1} being suggested due to the CH stretching of CH_2 and CH_3 , the bands at 1745 and 1234 cm^{-1} , respectively, being attributed to the presence of carbonyl $\text{C}=\text{O}$ stretching of ester and $\text{C}-\text{O}$ stretching of acetyl group associated with the presence of plant wax, and the band at 1017 cm^{-1} for $\text{C}-\text{O}$ stretching being associated with the presence of cellulose, hemicellulose and lignin [30].

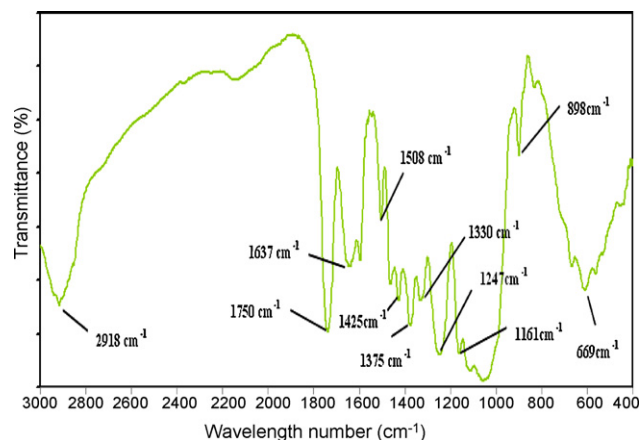


Fig. 2. FTIR spectrum of raw kapok.

Table 1
The physical properties of experimental oil.

Experimental liquid	Density at 25 °C (g/cm ³)	Viscosity at 25 °C (cP)	Surface tension (MN/m)	Contact angle (°)
Water	1.001	0.8	66.0	102.0
Diesel	0.839	6.5	12.8	24.9
New engine oil	0.865	165.7	23.5	21.4
Used engine oil	0.883	260.8	19.3	36.8

The FTIR spectra (Fig. 2) indicate all the components of Malaysian kapok as a lignocellulosic material, with hydrophobic waxy coating, similar to that reported previously [5,10,15]. The chemical composition of kapok harvested from the Phillipines and Southern Vietnam, analyzed on the basis of dry fiber, suggest not only high amount of acetyl group content (13%), but also the presence of cellulose (35%), xylan (22%) and lignin (21.5%) [10].

Table 1 shows the experimental oil characteristics based on density, viscosity, surface tension and contact angle. The oil density and viscosity could influence the oil sorption and draining rate and sorption capacity of the sorbent. Solid–liquid phase interactions between sorbents and experimental oils were quantified based on contact angle. Sensile drops technique was applied for the contact angle determination. Liquid forms a droplet on the surface of the sorbent, and is not considered a wetting liquid when the $\theta > 90^\circ$. At $\theta < 90^\circ$, a liquid tends to spread onto the surface of the sorbent and serves as the wetting liquid. All the three experimental oils can be classified as the wetting liquid for the kapok sorbent as $\theta < 90^\circ$. Water on the other hand showed high surface tension at 66 MN/m with $\theta > 90^\circ$. Surface tension is the resultant intermolecular force when one fluid exerts on another surface or liquid. Low value of surface tension suggests that oil could penetrate the kapok tubular structure and remain trapped within the solid sorbent. The presence of wax together with the high buoyancy of the fiber which is due to the air entrapment inside the tubular structure, could have been the main reason for hydrophobic and oleophilic nature of kapok.

3.2. Oil sorption experiments

3.2.1. Oil sorption capacity

The capacity of kapok to sorb and retain the absorbed oil during field application, transfer and handling operation is important parameters for sorbent evaluation. Transparent channels were observed under OM before the oil sorption inside kapok assembly. After 2 weeks with oil sorbed, and then allowed to drip out, the color and physical appearance of kapok fiber changed into yellowish-brown with the used engine oil. However, the kapok tubular structure appeared to remain intact as confirmed by OM and SEM observation. The color change suggests the penetration and oil entrapment inside the hollow structure. This network of hollow structures could have provided, not only ample interspatial area for oil to be retained and trapped within the kapok assembly as similarly being suggested for Milkweed floss [24], but also the architecture for uniform distribution of absorbed oil within the kapok assembly.

Table 2
Oil sorption capacities of kapok at various packing densities for different experimental oils.

Packing density (g/ml)	Oil sorption capacity (g oil/g sorbent)		
	Diesel oil	Used engine oil	New engine oil
0.02	36.7	50.8	47.4
0.04	20.8	25.4	25.1
0.06	13.9	16.8	15.9
0.08	10.8	12.2	12.1

Table 2 shows the oil sorption capacity of kapok at various packing density. At 0.02 g/cm³, kapok showed highest sorption capacity for engine and used engine oil, and the lowest capacity for diesel. The higher sorption capacity of oils than diesel is a result of engine oil being heavier than diesel within the same unit volume. With two- and three-fold increase in packing density, the oil capacity was reduced proportionally. The order of increasing oil sorption capacity has been attributed to packing density [5]. However, we have found that the mass (65–90 g) and volume (80–100 ml) of sorbed oil, regardless of oil types, were actually not significantly different for each different packing density. There appears to be a maximum capacity in which kapok fiber can trap oil within its structure. It could be that the higher the packing density, and the less loosely packed it becomes, the harder the oil can sorb through. It suggests for the availability of penetrable lumen network with the inter-fiber pores located in the kapok microstructure, for kapok to be effective as oil sorbent. In addition, with four-fold increase in packing density, the void fraction (percentage ratio of kapok fiber volume to wire-mesh basket volume, at specific packing density) was not increased linearly, but rather reduced by 6% (data not shown). The void fraction of 98.5% at 0.02 g/ml may be mainly as a consequence of inter-fiber pores, while the void fraction at 0.08 g/ml may instead be contributed more by the presence of hollow structure, due to a more compact architecture.

High sorption capacity of kapok is also a result of hydrophobic waxy coating on the kapok surface. At the initial stage of oil sorption onto the kapok surface, the hydrophobic interactions and the Van der Waals forces could play important role between the experimental oils and waxy surface coating [24]. Chemical compatibility between oil and kapok surface wax leads to minimum surface tension and contact angle for minimum energy barrier for oil to penetrate the fiber tubular structure. After minimum energy barrier is overcome, void fraction availability or the presence of effective space inside the kapok assembly would predominantly affect the sorption capacity of the fiber at specified packing density. Higher amount of effective space will increase the oil sorption capacity which is achievable at low packing density.

3.2.2. Dynamic oil retention and entrapment stability

The dynamic oil retention of kapok at various packing density over time interval was measured by allowing the oil to drip from the test cell for a specified duration. The amount of oil retained between 96% and 99% (Fig. 3a) suggests that, despite its lower viscosity, diesel was not readily dripped out at any packing density as compared to new and used engine oil. With new and used engine oil (Fig. 3b and c), only 78% of the oil remained at 0.02 g/ml density, whilst more than 90% of oil was retained at 0.08 g/ml. When an external force was applied in the form of horizontal shaking, 66% of diesel and 82% of used engine oil were retained at 0.02 g/ml (data not shown), and more than 90% oil remained stable within the entrapment at 0.04–0.08 g/ml. Apart from sorption and retention capacity, saturation time and bed height drop are two other important parameters to evaluate the effect of packing density on kapok performance. The saturation time (data not shown) increased from around 1000 s (heavy oils) at 0.02 g/ml to 7500 s (used engine oil) at 0.08 g/ml. The saturation time remained below 200 s for diesel at all packing. The bed height drop increased only slightly, as the

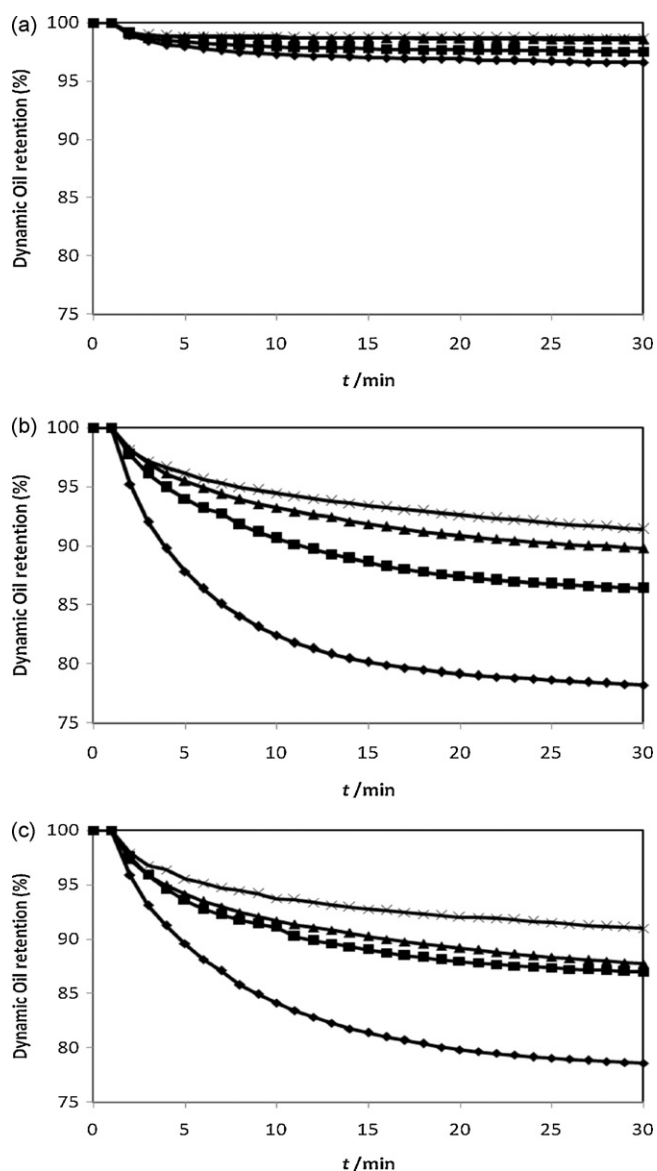


Fig. 3. Percentage of dynamic oil retention of (a) diesel oil, (b) new engine oil, and (c) used engine oil at packing density of (◆) 0.02 g/ml, (■) 0.04 g/ml, (▲) 0.06 g/ml, and (×) 0.08 g/ml.

packing density and oil viscosity increased (data not shown). At 0.02 g/ml, 15% of bed height drop was observed with both new and used engine oil. However no significant bed height drop was observed at 0.04 g/ml packing density.

The draining process happens due to instantaneous dripping of oil from kapok assemblies in the wire-mesh test cell, and the oil draining out from the extra-lumen liquids. The draining occurs as the capillary pressure is insufficient to hold the weight of the oils. Capillary pressure is a function of surface tension, capillary diameter and contact angle between solid and liquid interfaces. The capillary pressures together with the hollow lumen network, inter-fiber distances and liquid bridges between the fibers play important roles in the holding up of oil within the unstructured fibers assembly [12]. Loosely packed kapok potentially allows higher percentage of oil dripping out due to the high hollow lumen network with larger inter-fiber distances that destabilize the liquid bridges between the fibers. The liquid–liquid bridges are the predominant forces that hold up the oil within the assembly, as the oil is mainly entrapped inside the kapok fiber pores. With packed-

assembly, the stabilization force comes from the capillary pressure inside the tubular structure. Most heavy oils trapped inside the inter-fiber pores are stabilized by liquid bridges, developed within the structures. The dripping out of oil is further assisted by its heavy nature, although the viscosity is higher than diesel. In contrast, with the lowest viscosity, diesel drains out at a faster rate. This helps the system to reach equilibrium sooner with the tendency for diesel to remain within the kapok assembly.

In densely packed kapok, the significant reduction of oil flow was mainly due to the constriction of channel flow sizes, resulting in longer saturation time. The rate of oil penetration into a capillary movement is inversely proportional to the oil viscosity. The high viscosity of engine oils actually reduced the rate of absorption within the internal capillary movement [24]. This resulted in longer saturation time. When external force is applied in the form of horizontal shaking, it could easily destabilize the liquid bridges between fibers, thus reducing the capability of kapok assembly to retain the oil. The inter-fiber liquid bridges are sufficient enough to hold up the sorbed oil within its structure, hence increasing the kapok assembly resistance against external forces from the horizontal shaker. Similarly, the low percentage of bed height drop was primarily due to a more packed-density and the reduced amount of inter-fiber pores, thus limiting the space for reduction of kapok packing height.

The Van der Waals forces and hydrophobic interactions coupled with the availability of void fraction and the oleophilicity of kapok fibers, are all the contributing factors in this oil–kapok fibers complex interaction. The stability of the liquid bridges formed at the contact area between wax fibers and the oils, within the range of the stabilization capability of the liquid bridges, is attributable to the natural compatibility between wax surface and the oil. When the capillary pressure becomes the predominant force that holds up the oil within the kapok assembly, the liquid hold up capacity affected by the capillary pressure is more stable than the liquid bridges. Based on this consideration, 0.04 g/ml packing density may be suitable for sorbent development as it ensures stable oil entrapment inside the kapok assembly. In the field application, this means ease of handling and transportation of the sorbed material for further treatment.

3.2.3. Reusability of kapok fiber

Kapok reusability experiment evaluates kapok durability over prolonged usage, without significant reduction in performance due to tearing, crushing or any mechanical deformation [5]. In this study, diesel oil and 0.04 g/ml packing density were chosen as experimental conditions. Fig. 4a shows that the capacity was 17 g oil/g sorbent in the first cycle and dropped to 13 g oil/g sorbent in the second cycle, with 77% of oil recovered from the test cell. From the second cycle until the fifteenth cycle, no significant changes in the sorption capacity were observed. The conserved structure could be the reason behind the excellent oil sorption capacity of kapok. The significant reduction in the second cycle however has also been reported by others [5]. This sudden drop from the first and the second cycle could be due to irreversible deformation as 20–23% oil remained trapped inside kapok lumens after desorption in the first cycle. The continuous deformation due to this remaining oil in the kapok assembly, affected the capacity of kapok to absorb more oil in the subsequent cycle [5,24]. The inter-fiber distance could have been contracted after the sorbed oil being drained out. Full recovery of the effective pore may not be achieved once the test cell was soaked inside the oil bath. This effective pore reduction coincides with the packing height reduction after oil desorption (Fig. 4b). After fifteen cycles, the bed height was reduced by almost 25%. The saturation time of the test cell dropped from 160 s to approximately 90 s after the second cycle, and remained constant until the fifteenth cycle (Fig. 4c). The fast saturation time (80–160 s) was a

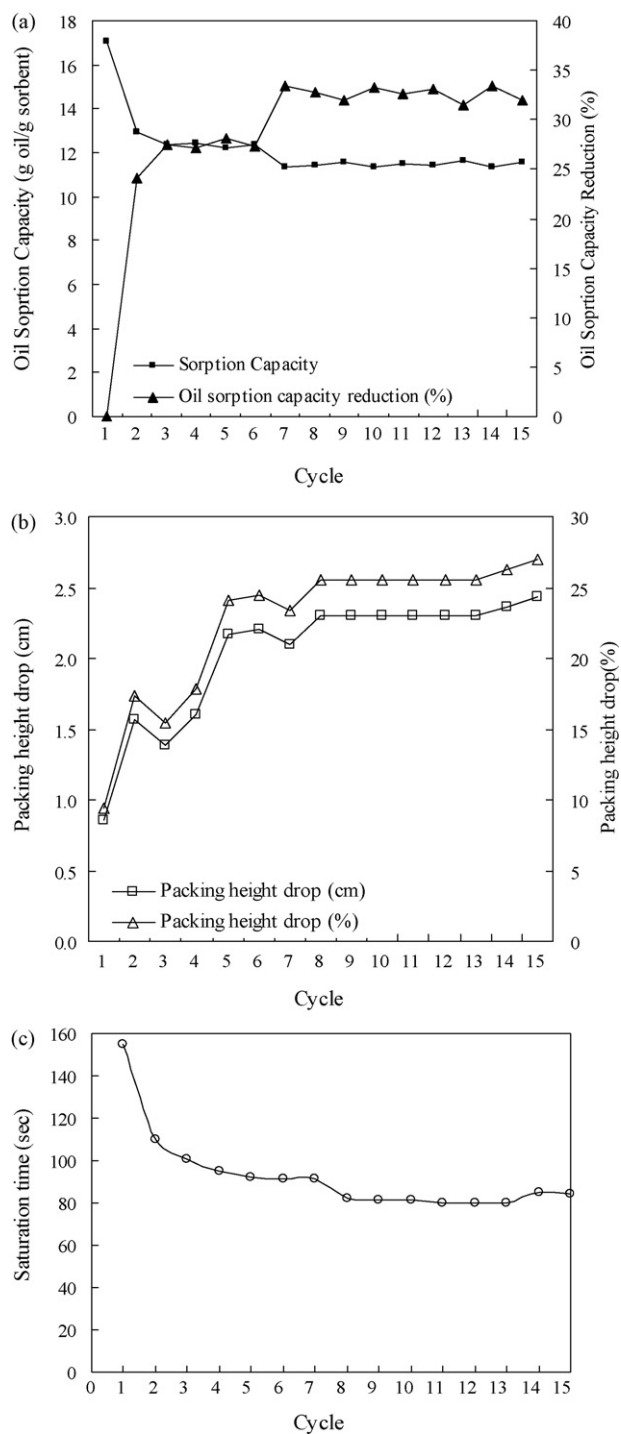


Fig. 4. The sorption characteristics of kapok fiber during fifteen sorption-desorption cycles in terms of (a) oil sorption capacity reduction, (b) packing height drop, and (c) saturation time cycles.

result of diesel having all the properties to penetrate easily into the fiber microstructure. For comparison, the saturation time for new and used engine oils at 0.04 g/cm^3 , were between 2000 and 4000 s (data not shown).

Reusability of natural fiber has been investigated by centrifugation at 3000 rpm [5], and by mechanical pressing with two roller at 50 psi [24]. In our study, the sorbed oil inside kapok assembly was recovered using vacuum pump at 525 mbar. Higher energy may be needed to draw out the oil entrapped inside kapok hollow structure instead of just from the inter-fiber pores. The oil entrapment inside

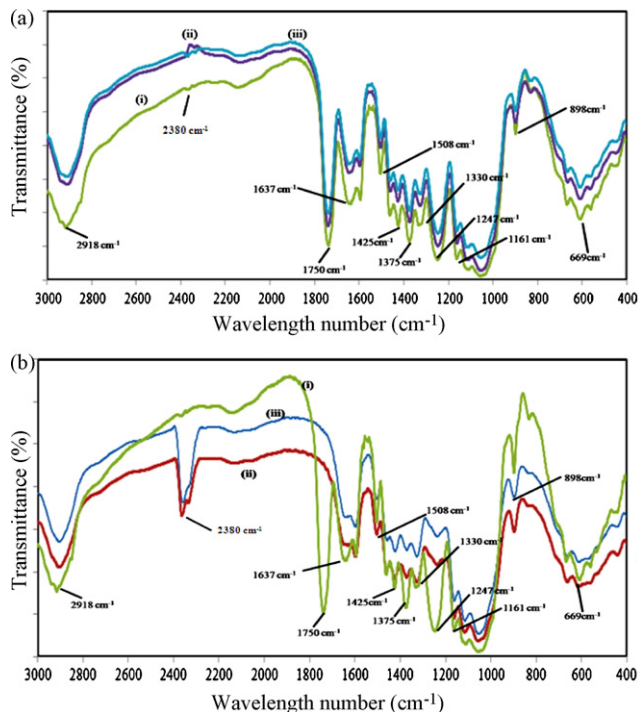


Fig. 5. (a) FTIR spectrum of (i) untreated kapok, (ii) after 4 h, and (iii) 8 h of chloroform treatment. (b) FTIR spectrum of (i) untreated kapok, (ii) after 4 h, and (iii) 8 h of alkali treatment.

kapok hollow structure is more stable than inter-fiber pores. Unrecovered oil trapped inside kapok lumens reduce the oil sorption capacity, thus reducing the capacity for oil uptake in the second cycle. In a study with cotton fiber, more than 90% of oil is recovered using the squeezed-roller at its maximum pressure, and after the second cycle, 84% of oil sorption capacity is still achievable [24]. The disadvantage of this pressed method nevertheless is the disruption of initially naturally occurring fiber network which reduces the possibility for continued use in the longer cycles.

3.3. The effect of solvent treatment

3.3.1. Infrared spectra

Chloroform was chosen as one of the extracting solvent due to its hydrophobicity, similar to the kapok waxy surface. Chloroform regeneration is likely to occur inside the soxhlet chamber, allowing for a continued extraction of kapok wax surface. Alkali treatment was carried out by boiling the kapok fiber inside the reflux apparatus. Fig. 5a shows the FTIR spectrum of untreated and treated kapok using chloroform. A well-pronounced trough at 2918 cm^{-1} which is associated with the presence of plant wax was increased significantly with chloroform extraction. The transmittance trough at 1425 and 1375 cm^{-1} , corresponding to the presence of wax surface, also showed increasing values. The transmittance increment was similarly observed for band positioned around 1750 and 1250 cm^{-1} correlating to the presence of carbonyl group (C=O) in the ester bonds. These increments suggest the possibility of wax removal from the kapok surface. The difference between 4 and 8 h extraction was not significant with only slightly higher percentage of wax removal in the latter. Others have reported that kapok immersed in chloroform after 1 h had absorbance value reduced at similar band positions as in our study, to indicate wax removal [15].

Fig. 5b shows the infrared spectrum of alkali-treated kapok. The profile was different from the chloroform-treated profile where there are significant increments or reductions in transmittance as compared to untreated profile. With NaOH treatment, the hydro-

Table 3
Oil sorption capacity of chloroform and alkali-treated kapok at 0.04 g/ml packing density.

Untreated	Oil sorption capacity (g oil/g fiber)			
	Chloroform-treated		Alkali-treated	
	4 h	8 h	4 h	8 h
20.8	20.5	20.4	17.7	15.4

gen bonding inside kapok fiber is possibly reduced via the hydroxyl group reduction. This can be observed from the transmittance increment of $-\text{OH}$ bands at 3361 cm^{-1} . The hydroxyl groups facilitate the hydrogen bonding with the carboxyl groups, such as fatty acids on the surface of the natural fiber. Similar to chloroform-treated kapok, transmittance increments around 2918, 1750 and 1250 cm^{-1} are attributed to the wax removal. However, the effect at 1750 cm^{-1} corresponding to the presence of the carbonyl group ($\text{C}=\text{O}$) in the ester bonds was most significant where no sharp transmittance trough was observed after 4 and 8 h alkali treatment. This phenomenon is termed “deesterification” [27]. Transmittance increment at 1651 cm^{-1} suggests greater water removal, and at around 1604 cm^{-1} implies the removal of unsaturated carbon chain ($\text{C}=\text{C}$ stretching) inside the traces of oil. Comparing between Fig. 5a and b, other than the peak at 1750 cm^{-1} flattened out, the disappearance of sharp transmittance trough around 1247 cm^{-1} can also be observed which indicates the removal of $\text{C}-\text{O}$ stretching of acetyl group [26]. In addition, new troughs were observed at 2380 cm^{-1} and the greater separation between untreated and alkali-treated kapok at 898 cm^{-1} . The latter suggests the increased removal of β -glucosidic linkage between sugar units in hemicelluloses and celluloses [27,30].

3.3.2. Kapok microstructures and morphology

Based on SEM analysis (Fig. 6b), chloroform-treated kapok was not physically significantly different from the untreated one. Although the silky appearance of chloroform-treated kapok was reduced while some parts of the fiber were flattened, the buoyancy and fluffiness was retained. The overall tubular structure remained intact with scattered white spots observed on the kapok surface which may indicate the lesser extent of wax removal. Other study has similarly reported this reduction of silky cluster of kapok after only 1 h chloroform treatment [15]. With alkali treatment (Fig. 6c), there was a total disappearance of air entrapment inside kapok fiber and the structure became completely flattened, similar to a flat ribbon-like structure with increased density. The silky and smooth structure had also changed into hardened structure and the color changed to dark from originally fluffy white. This could be due to excessive removal of hemicellulose and lignin [5].

3.3.3. Oil sorption and retention capacity

As shown in Table 3, no significant difference in oil sorption capacity was observed between chloroform-extracted and untreated kapok. On the other hand, the oil sorption capacities of alkali-treated kapok were reduced by 14.9% and 26.3% after 4 and 8 h treatments, respectively, with the oil sorption capacity after 8 h treatment 11.4% lower than the former. Fig. 7 shows that after chloroform treatment, the oil retention capacity was increased slightly by 2% and 1.5% after 4 and 8 h extraction, respectively. For alkali treatment, the oil retention capacity for 4 h treatment was not significantly different from untreated kapok, but was much reduced after 8 h treatment. Other study on the use of kapok for oily water mixture separation, has reported the reduction of oil and water retention capacity by 48.9% and 9.1%, respectively [15].

The physicochemical characteristics of kapok fibers such as the amount of surface wax, molecular arrangement, physical configu-

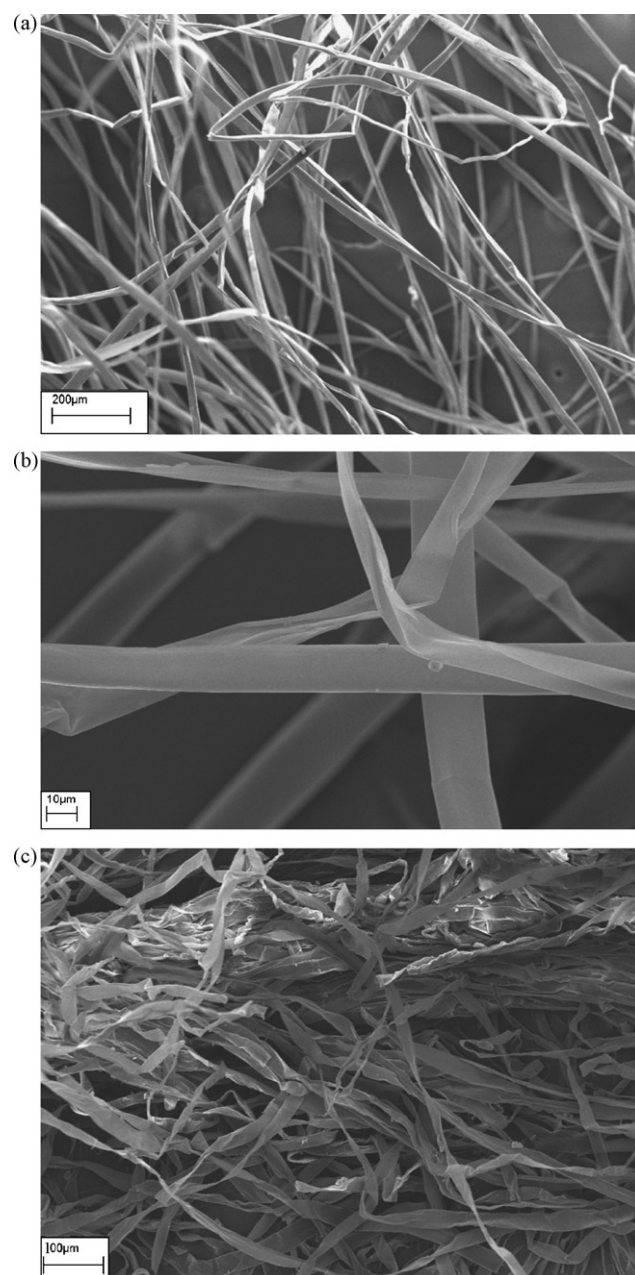


Fig. 6. SEM image of (a) untreated, (b) chloroform-treated and (c) alkali-treated kapok.

ration of fiber such as the hollow lumen, the twists and the crimps, the surface roughness, porosity and fineness could affect the oil sorption and retention capacity of sorbent. It appears that waxy content is not a primary factor affecting the oil sorption and retention capacity. As long as the tubular and hollow structure of kapok remained intact and conserved, high oil uptake and retention could still be achieved. It has been suggested that although viscose rayon (VR) is a hydrophilic polymer, the presence of physical configurations such as the twist and the crimp, provide sufficient space for oil entrapment and the sorption capacity as high as 19 g oil/g fiber [24]. With alkali treatment, the whole kapok structure could have been disrupted and higher amount of wax may have also been removed. With more compact density, the air entrapment inside kapok structure was significantly decreased. The flattened structure also did not provide ample interstitial volume for oil entrapment.

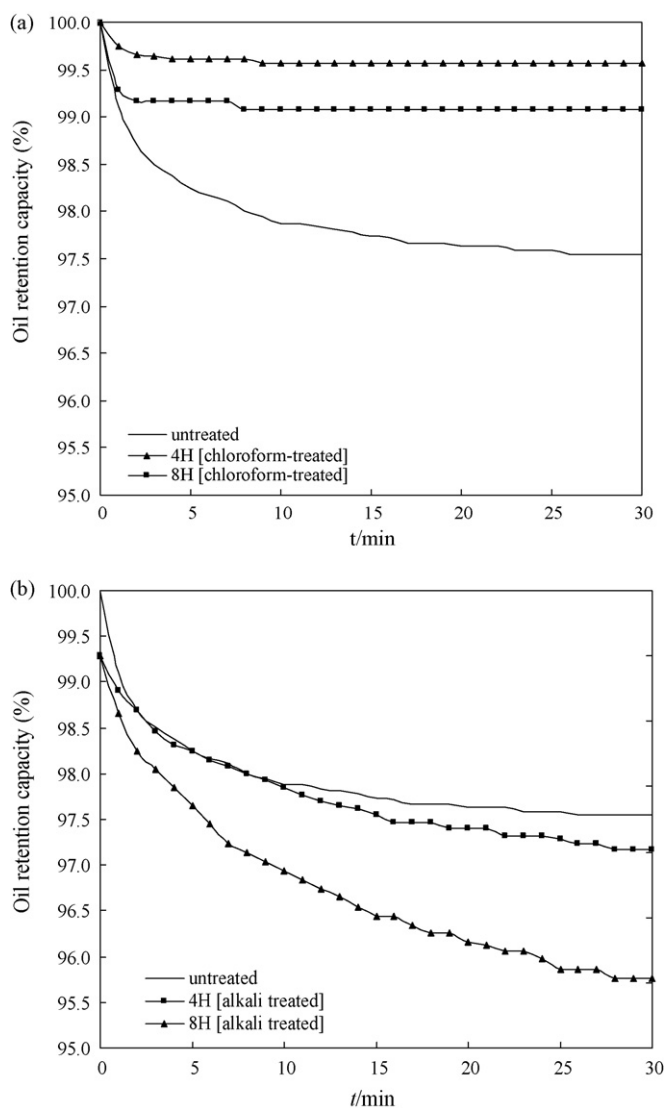


Fig. 7. Oil retention profile of kapok after (a) chloroform and (b) alkali treatment.

Plant wax determines the plant wettability, optical appearance, water repellency and the solubility among organics and polar solvents. Wax content of kapok (about 3%) which is also higher than cotton (0.4–0.8%), and high acetyl content (13%) may be responsible for its high hydrophobicity [24]. With reduction of meager amount of surface wax, the slightly increased retention capacity in chloroform treatment confirm our earlier suggestion that wax is not the only factor governing the draining out of extra-lumen liquids. However, as the presence of surface wax caused the tubular structure to provide sufficient capillary pressure that can hold up the absorbed oil, significant removal as in alkali-treated kapok, could have reduced capillary pressure inside the tubular structure and hence the retention capacity.

Generally, natural fibers are chemically treated using NaOH to remove the lignin-containing component, such as pectin, waxy substances and oil layer that cover the external surface of fiber cell wall. This treatment removes the fibrils and produces rough surface plant fibers [27]. Cellulose structure changes upon NaOH treatment, commonly known as mercerization or alkalization. Chemical treatment to modify the surface properties of natural fibers could improve the desired properties such as to produce fiber with better mechanical properties for the polymer reinforcement material [26,27].

4. Conclusions

C. pentandra (L.) Gaertn (kapok) as a natural sorbent exhibited high hydrophobic–oleophilic characteristics, which were attributable to its waxy surfaces and hollow lumens as confirmed by SEM and OM observations and infrared spectrum. Kapok exhibited stability for prolonged use, with higher saturation time and low bed height reduction at higher packing density and higher oil viscosities. Even after fifteen cycles of reuse, only 30% of oil sorption capacity reduction was observed, using diesel at 0.04 g/cm³ packing density. More than 90% of diesel and used engine oil were retained inside the assembly after a horizontal shaking. The infrared spectra of chloroform and alkali-treated kapok suggests the wax removal from the kapok surface. Therefore, the removal of wax together with the collapse of rigid, hollow structure could reduce the oil sorption capability though these may increase kapok hydrophilicity. The overall sorption characteristics of kapok imply that Malaysian kapok is a potential lignocellulosic material for oil removal with high oil sorption and retention characteristics and stable for prolonged use.

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