Ali, N., El-Harbawi, M., Jabal, A.A. and Yin, C-Y. (2012) ***Characteristics and oil sorption effectiveness of kapok fibre, sugarcane bagasse and rice husks: Oil removal suitability matrix.*** **Environmental Technology, 33 (4). pp. 481-486.**

Characteristics and oil sorption effectiveness of kapok fiber, sugarcane bagasse and rice husks: Oil removal suitability matrix†

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†Experimental studies presented in this article were conducted at Universiti Teknologi PETRONAS

Abstract

The characteristics and water/oil sorption effectiveness of kapok fiber, sugarcane bagasse and rice husks have been compared. The three biomass types are subjected to field-emission scanning electron microscopy-energy dispersive x-ray spectroscopy while the surface tension analyses for liquid-air and oil-water systems have also been conducted. Both kapok fiber and sugarcane bagasse exhibit excellent oil sorption capabilities for diesel, crude, new engine and used engine oils since all their oil sorption capacities exceed 10 g/g. Synthetic sorbent exhibits oil sorption capacities comparable to sugarcane bagasse while rice husks exhibit the lowest oil sorption capacities among all the sorbents. Kapok fiber shows overwhelmingly high oil-to-water sorption (O/W) ratios ranging from 19.35 to 201.53 while sugarcane bagasse, rice husks and synthetic sorbent have significantly lower O/W ratios (0.76 to 2.69). This suggests that kapok fiber is a highly-effectual oil sorbent even in well-mixed oil-water media. An oil sorbent suitability matrix has been proposed to aid relevant stakeholders for evaluation of customized oil removal usage of the natural sorbents.

Keywords: Kapok fiber; sugarcane bagasse; rice husk; oil sorption

Introduction

Rapid global industrialization coupled by consumer need for energy resources have driven huge demand for fossil fuel for both industrial and end-user markets. This presents an environmental drawback in terms of possible oil spill contamination that may arise during sea transportation of petroleum products. There have been numerous cases highlighted in the mass media involving various offshore operations and tankers accidentally spilling petroleum products or derivatives into the open sea; one of the most frequently referenced being the infamous 1989 Exxon Valdez oil spill at Prince William Sound, Alaska. Presently, the much-highlighted *Deepwater Horizon* (BP) oil spill that occurs in the Gulf of Mexico in April 2010 is now considered as one of the largest offshore oil spill in United States history. The pressures exerted by the United States government as well as the public on the accountable oil and gas conglomerate have provided a significant impetus to compel other oil and gas industrial stakeholders to search for effective oil spill management and remediation strategies.

In most cases, cost-effective sorbents are typically utilized to remove oil spills. Such sorbents can be classified as either inorganic mineral, organic synthetic or organic vegetable products [1,2]. Examples of mineral products include clayey materials and graphite while synthetic products are sorbents made of polypropylene and polyurethane foam. The usage of natural organic-based sorbents derived from plant sources represents a vital development in sustainable environmental technology since it emphasizes on the biodegradability, reusability and cost-effectiveness aspects. There have been numerous reported studies involving usage of natural plant-based sorbents for sorption of oil such as bark [3], kenaf [4], kapok [5], milkweeds [4], rice husks [6] and sugarcane bagasse [7]. Many of these natural sorbents exhibit comparable or even higher oil sorption capacities than synthetic sorbents, but they also sorb water as well, rendering reduced oil sorption capacities. This presents a disadvantage when used in marine environments [8]. As such, it is highly desirable to ensure that the natural sorbent is highly hydrophobic or lipophilic so that high oil selectivity over water can be maintained. In this regards, it has been well-established that kapok fiber is an excellent natural oil sorbent through comprehensive studies conducted by several research groups [5,9,10]. Lim and Huang [5] suggest that its superior oil removal capability is attributed to its waxy fiber surface and large lumen that promote internal capillary oil movement. In the absence of kapok fiber, however, other natural sorbents should also be considered. While the oil sorption capacities of the latter are lower than the former, we surmise that given the right conditions, other natural sorbents can also be fully optimized for the purpose of oil removal from oil-water medium. As such, a direct comparison of the characteristics and oil sorption effectiveness of natural sorbents with regards to different oil types will greatly facilitate the end-user in evaluating the suitability of each sorbent for specific oil removal tasks.

The aim of this study is to compare the characteristics and water/oil sorption effectiveness of kapok fiber, sugarcane bagasse and rice husks so that each biomass can be tailored for either water or oil sorption applications. We evaluate four oil types for this study, namely, diesel, crude, new engine and used engine oils so that our findings can have diverse implications and may aid future research in this regards. We propose an oil sorbent suitability matrix subsequent to analyses of our findings to aid relevant stakeholders in deciding the customized usage of such natural sorbents. We use the term 'sorbent' throughout the paper rather than 'absorbent' or 'adsorbent' since we deem that there is always possibility of existence of both specific mechanisms when it comes to sorption of oil or water using biomass. In chemical-based processes, absorption is taken to mean the uptake of bulk fluid into the overall matrix of the sorbent while adsorption refers to physico-chemical 'attachment' of fluid molecules on the micro/nano-sized porous surfaces of the biomass. There are many instances of misuse of the terms 'adsorbent' and 'absorbent' in the open literature and hence we prefer to avoid such misuse by utilizing a more generic term in this paper.

Materials and methods

Collection, preparation and characterization of kapok fiber, sugarcane bagasse and rice husks samples

Raw kapok fiber, sugarcane bagasse and rice husks were obtained from agricultural village settlements in the state of Perak, Malaysia. All visible foreign impurities found in the samples were manually removed before experimentation. The hard external sugarcane layer was removed from its stalk and the resultant bagasse was washed with water to remove foreign materials. It was then dried in sunlight to remove moisture. The bagasse was subsequently grounded to sizes less than 4 mm. A synthetic sorbent made of inert polypropylene and polyester fibers was also included in the study so that a direct comparison between the oil sorption effectiveness of commercial sorbent with that of natural biomass can be made. Figure 1 shows all the natural and synthetic sorbents used in the study. Field emission scanning electron microscopy (FESEM)

(Zeiss Supra 55 PP) together with energy dispersive x-ray (EDX) spectroscopy (Oxford INCA) were used to analyze the biomass' surface morphologies and elemental compositions, respectively. The average densities of the natural sorbents were determined using Quantachrome Ultrapycnometer 1000 where 10 analysis runs per sorbent were performed.

Determination of liquid properties

Densities of liquids were determined using Anton Paar DMA 35N Density Meter. The surface tension data for liquid-air and oil-water were determined using Interfacial Tension Meter, IFT 700 (Vinci Technologies, France) via the established pendant drop method. In this method, a liquid drop is produced from the end of a capillary needle and put in contact with either air or liquid at a specified temperature. The shape of the liquid drop was recorded using a camera and subsequently a software (Drop Analysis System) analyzed and calculated the surface tension of the drop.

Water and oil sorption experiments

The water and oil sorption capacities of the biomass were determined using a standard method (F726-99) stipulated by the American Society for Testing and Materials (ASTM) [11]. According to this method, commercial sorbents in the form of rolls, films, sheets, pads, blankets or webs are categorized as Type I sorbents while kapok fiber, sugarcane bagasse and rice husks are categorized as Type II sorbents since the latter are unconsolidated and particulate-based. Diesel oil (PETRONAS Dynamic Diesel), crude oil (Tapis crude oil), new engine oil (PETRONAS Mach 5 SL 10W-30) and used engine oil were employed to evaluate the oil sorption capacity of the biomass. The sorption capacity was expressed as gram of liquid absorbed per gram of dry sorbent (g/g).

Results and discussion

Characteristics of kapok fiber, sugarcane bagasse and rice husks

Figure 2 shows the micrographs of kapok fiber, sugarcane bagasse and rice husks. With the exception of sugarcane bagasse which is subjected to minor size reduction, the kapok fiber and rice husks are relatively unprocessed. Therefore, the micrographs illustrate the microstructures of the biomass which closely mirror their as-received bulk condition. This is important in the context of their utilization as oil sorbents since it is cost-effective to use them in their current form without incurring significant processing cost.

Kapok fiber has a microstructure which is distinct from the other biomass in which hollow tubular structures (or lumen) can be clearly seen. The diameters of the lumen are determined to be approximately within the 5 – 10 μm range which are smaller than the lumen diameters range (19 – 12 μm) reported by Lim and Huang [5]. The sugarcane bagasse exterior appears to be rough while the surface morphology of rice husks exhibits extended and interconnected dome-shaped regions, an observation previously reported by Markovska and Lyubchev [12].

Table 1 shows the elemental compositions (detected via EDX) and average densities of kapok fiber, sugarcane bagasse and rice husks. Both kapok fiber and sugarcane bagasse contain carbon percentages higher than 50% and this provides an initial indication of their high lignocellulosic content. The high percentage of silica (> 20%) detected in rice husks is due to the presence of opaline silica (plant-based hydrated amorphous form of silica) found predominantly in the outer epidermis of rice husks [13,14].

Properties of liquids

Table 2 shows the liquid densities as well as liquid-air and oil-water surface tension data at 25°C. The liquid densities and liquid-air surface tension data are consistent with findings reported by Lim and Huang [5]. The oil-air surface tension values for all four oil types are very similar to one another while water-air surface tension is significantly higher (68.5 MN/m). There is a possibility that such high water-air surface tension may, to an extent, inhibit penetration of water into the internal hollow biomass structures due to presence of pore air [5]. This implies that adhesion forces between water molecules at the water-air interface are considerably higher than that of oil molecules at the oil-air interface, rendering the relative inability of water molecules to 'wet' the pore air.

Water and oil sorption capacities

Figure 3 shows the water and oil sorption capacities of kapok fiber, sugarcane bagasse, rice husks and synthetic sorbent. It is observed that more than 50% of rice husks have sunk to the bottom of the container during the water sorption experiment. According to the ASTM F 726-99 standard, rice husk is considered to have failed this test since the percentage of settled (sunk) sorbent is more than 10%. This observation is consistent with the density of rice husks showed in Table 1 which is higher than water density. The synthetic sorbent has the highest water sorption capacity while it is conversely true for kapok fiber. In this case, the observed relative hydrophobicity of kapok fiber and hydrophilicity of synthetic sorbent are apparent. The sugarcane bagasse appears to exhibit comparable water sorbing capability since its water sorption capacity is more than 5 g/g. The high water sorption capacity of the bagasse is also reported by Said et al. [7] where they found that it ranges from 400 to 700 % water absorptivity. Therefore, it is envisioned that the bagasse can be applied as an inexpensive bulk water removal material.

The usage of the four oil types is justifiable since they represent two broad classifications of oil which are relevant in the context of our study, namely, light- (e.g. crude oil) and heavy-weight (engine oil) oils. As such, it is believed that our study can provide findings which have universal applicability. Crude oil contains low-boiling fractions that evaporate swiftly after a spill and often before substantial cleanup operations can commence [15]. Such evaporative tendency is reflected by its relatively low density compared to engine oils. Both kapok fiber and sugarcane bagasse exhibit excellent oil sorption capabilities for all oil types since all their oil sorption capacities exceed 10 g/g. However, kapok fiber is evidently a more superior oil sorbent compared to sugarcane bagasse especially in terms of sorption of engine oils where the new engine oil sorption capacity is 200% more than for sugarcane bagasse. Synthetic sorbent exhibits oil sorption capacities comparable to sugarcane bagasse while rice husks exhibit the lowest oil sorption capacities among all the sorbents. Therefore, rice husks may be unsuitable as sorbent material for both water and oil, though it can still be used as a decent sorbent for engine oils since its sorption capacities for such oils are higher than 5 g/g. An apparent trend can be observed from Figure 3; all sorbents have substantially higher new and used engine oils sorption capacities compared to diesel or crude oil. This phenomenon is also observed by Lim and Huang [5] in which they postulate that the higher viscosity of engine oil is responsible for its higher sorption in kapok fiber. Table 3 compares the oil sorption capacities of biomass in this study with other sorbents. It is obvious that kapok, sugarcane bagasse and rick husks afford superior oil sorption capacities compared to other reported media such as vermiculite and peat.

Figure 4 shows the oil-to-water (O/W) sorbency ratios (oil sorption capacity/water sorption capacity) of kapok fiber, sugarcane bagasse, rice husks and synthetic sorbent. The result affords quantification on the relative oil/water selectivity of the sorbents whereby high O/W ratio indicates that the sorbent has high affinity for oil and *vice versa*. Quite clearly, kapok fiber exhibits overwhelmingly high O/W ratios ranging from 19.35 to 201.53 while sugarcane bagasse, rice husks and synthetic sorbent have considerably lower O/W ratios (0.76 to 2.69). This implies that kapok fiber can be effectively used as an oil sorbent even in the presence of significant amount of water. For rice husks and synthetic sorbent which exhibit O/W ratios lower than 1 for diesel and crude oils, the presence of water may complicate the oil sorption process since water may also interfere by saturating the sorbents before its intended oil sorption usage can be fully realized.

For the convenience of relevant stakeholders, a suitability matrix for usage of kapok fiber, sugarcane bagasse, rice husks and synthetic sorbent for oil removal has been constructed (Table 4). To the best of our knowledge, such matrix has not been previously created by any research groups. This matrix is constructed based on the perceived oil sorption suitability *vis-à-vis* the potential interference caused by concurrent water sorption. In highly-agitated oil spill waters (which may be due to wave action and strong ocean current), sorbents that show good water sorption capacities are not effective oil sorbents due to the aforesaid reason. Nonetheless, such sorbents may be relatively effective for removal of oil from clearly stratified oil/water layers in still seawaters. In any case, the best biomass sorbent for oil removal is kapok fiber due to its exceptionally superior oil sorption capacity. However, the other biomass may be suitable in certain circumstances (based on the suitability matrix) should the fiber be unavailable for oil removal.

Conclusions

Kapok fiber and sugarcane bagasse exhibit superior oil sorption capabilities for all four oil types since all their oil sorption capacities exceed 10 g/g while rice husks exhibit the lowest oil sorption capacities among all the sorbents. Kapok fiber shows overwhelmingly high O/W ratios (19.35-201.53) while sugarcane bagasse, rice husks and synthetic sorbent have significantly lower O/W ratios (0.76-2.69). The oil sorbent suitability matrix can be utilized by pertinent stakeholders for rapid evaluation of oil removal usage of the natural sorbents. The method used for creation of suitability matrix can also be tailored for future studies involving other natural sorbents.

Acknowledgements

The authors gratefully acknowledge Universiti Teknologi PETRONAS for providing the necessary funding for completion of this study.

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Table 1

Elemental compositions and average densities of kapok fiber, sugarcane bagasse and rice husks.

	C (%)	O (%)	Si (%)	Average density (g/cm^3)
Kapok fiber	53.79	46.21	-	0.7358
Sugarcane bagasse	50.92	49.08	-	0.9866
Rice husks	24.01	51.03	24.94	1.1575

Table 2

Properties of liquids at 25°C.

	Density at 25°C (g/cm^3)	Liquid-air surface tension at 25°C (MN/m)	Oil-water surface tension at 25°C (MN/m)
Water	1.00	68.50	-
Diesel oil	0.83	26.77	18.85
Crude oil	0.84	27.72	15.35
New engine oil	0.85	28.25	17.60
Used engine oil	0.93	27.35	7.52

Table 3

Comparison of oil sorption capacities of biomass in this study with other sorbents.

Sorbent	Type of oil	Sorption capacity (g/g)	Reference
Canadian peat	Standard mineral oil	7.85	[16]
Walnut shell	Standard mineral oil	0.30	[17]
Walnut shell	Canola oil	0.51	[17]
Vermiculite	Standard mineral oil	2.53	[18]
Vermiculite	Canola oil	2.57	[18]
Kapok fiber	Diesel oil	19.35	This study
Sugarcane bagasse	Diesel oil	10.51	This study
Rice husks	Diesel oil	2.60	This study

Table 4

Suitability matrix for usage of kapok fiber, sugarcane bagasse, rice husks and synthetic sorbent for oil removal.

	Kapok fiber	Sugarcane bagasse	Rice husks	Synthetic sorbent
Removal of diesel or crude oil from oil-water mixture	• Highly recommended.	• Moderately suitable. • Reduced capacity due to water sorption.	• Not suitable. • O/W ratio < 1.	• Not suitable. • O/W ratio < 1.
Removal of engine oil from oil-water mixture	• Highly recommended.	• Moderately suitable. • Reduced capacity due to water sorption.	• Moderately suitable. • Reduced capacity due to water sorption.	• Moderately suitable. • Reduced capacity due to water sorption.
Removal of diesel or crude oil from clearly stratified oil/water layers	• Highly recommended.	• Suitable for relatively stagnant oil layer.	• Not suitable. • Diesel/crude oil sorption capacity < 5 g/g.	• Suitable for relatively stagnant oil layer.
Removal of engine oil from clearly stratified oil/water layers	• Highly recommended.	• Very suitable for relatively stagnant oil layer. • O/W ratio > 2. • Engine oil sorption capacity > 10 g/g.	• Suitable for relatively stagnant oil layer.	• Suitable for relatively stagnant oil layer.

Figure Captions

Figure 1. Kapok fiber, sugarcane bagasse, rice husks and polypropylene.

Figure 2. Micrographs of (a) kapok fiber, (b) sugarcane bagasse; and (c) rice husks.

Figure 3. Water and oil sorption capacities of kapok fiber, sugarcane bagasse, rice husks and synthetic sorbent.

Figure 4. Oil-to-water sorbency ratios of kapok fiber, sugarcane bagasse, rice husks and synthetic sorbent.

Figure 1. Kapok fiber, sugarcane bagasse, rice husks and polypropylene.

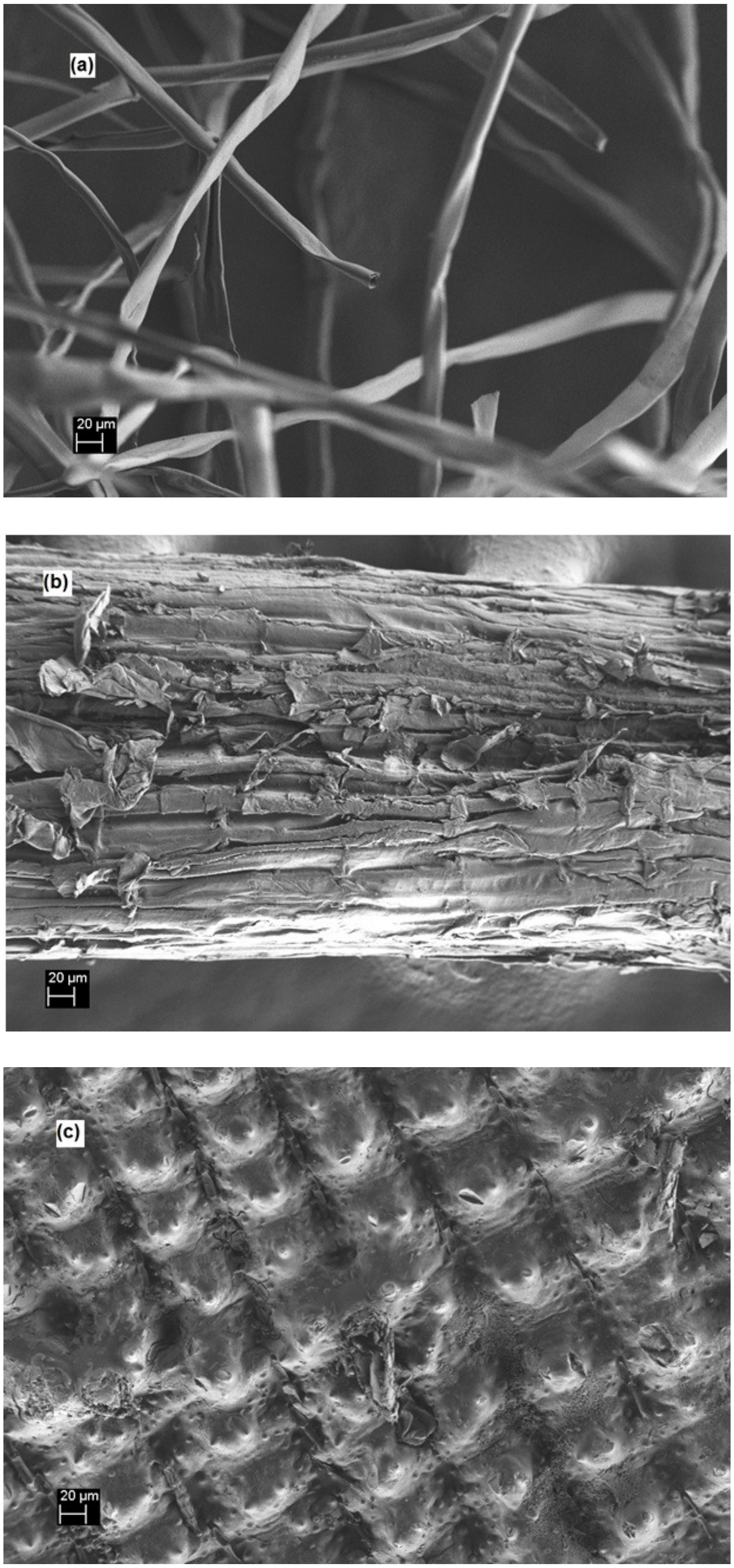
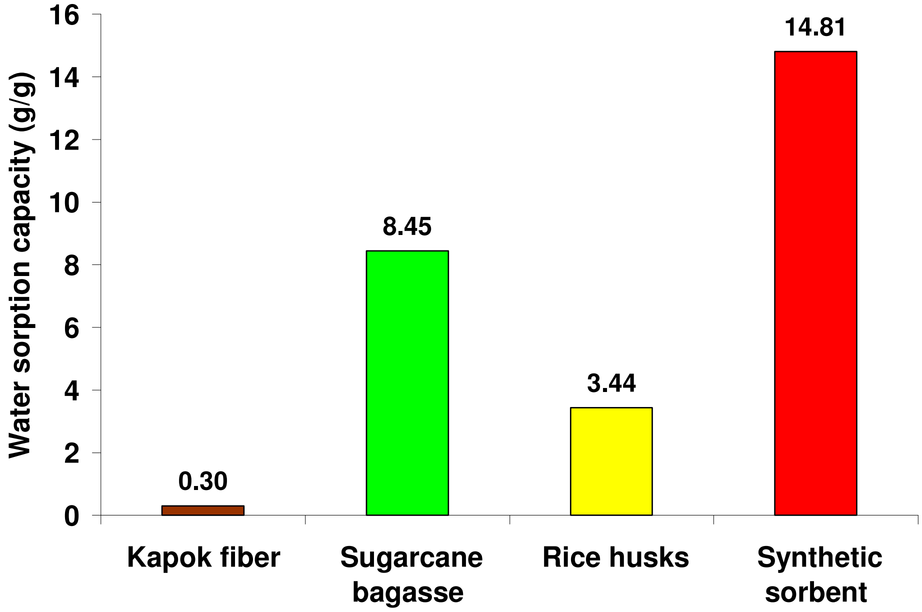
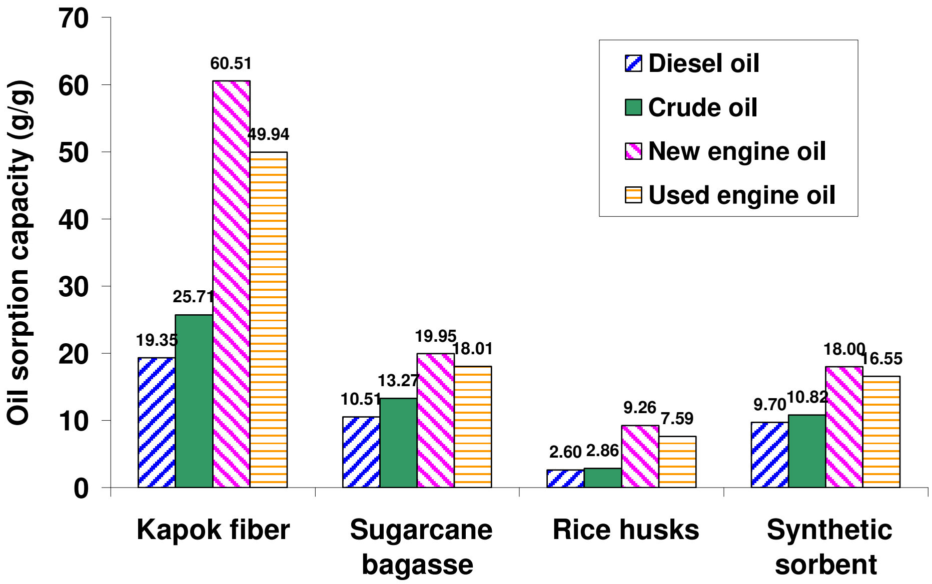


Figure 2. Micrographs of (a) kapok fiber, (b) sugarcane bagasse; and (c) rice husks.





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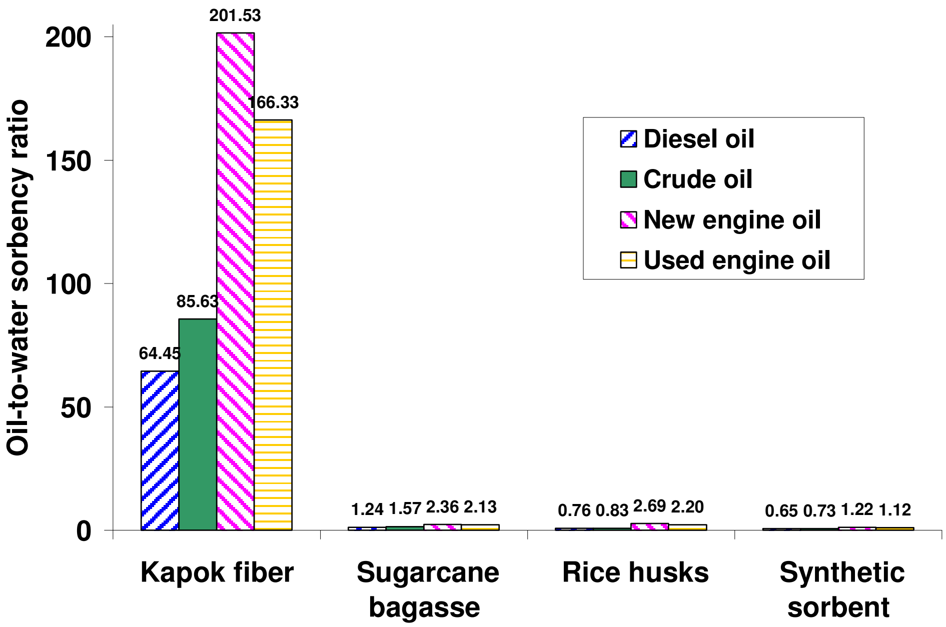

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