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Fabrication and Characterization of Modified ZnO- Kapok Fiber for Separating Surfactant-Free Oil-in-Water Emulsions

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Abstract. Natural sorbents have several benefits, including high sorption capacity, superior biodegradability, and low cost. Kapok is one of the natural fibers that can be used as absorbent material. These distinctive qualities give kapok fibers greater oil sorption capacity than other oil sorbents currently on the market. However, it is difficult to hold oil properly due to its waxy coating and smooth fiber surface. Thus, in this study, the rough surface fiber has been coated using ZnO via the hydrothermal method. Considering that ZnO is instinctually hydrophilic, this modification of the fiber compounds increases the adsorption of oil in fiber. The surface morphology interaction has been proven with an experiment using a scanning electron microscope (SEM) for morphology investigation, Fourier-transform infrared spectroscopy (FTIR) for identifying organic or inorganic materials, and physical interaction (contact angle analysis). The results obtained display a significant difference between modified kapok fiber with ZnO and raw kapok fiber. The FTIR analysis shows that the modified kapok exhibits the peak's level of intensity at 3268.88 cm^{-1} (stretching vibration peak of surface –OH decreases obviously as compared with that of raw kapok fiber, an absorption peak (symmetric stretching vibration of Zn–O–Zn) is observed at 652.28 cm^{-1}. These results suggested that the whole sum of –OH was diminished, and hydrophobic ZnO nanoparticles were developed on the kapok fiber's surface. A surface morphology analysis using SEM shows that ZnO particles are present on the kapok fiber surface while comparing it to the raw kapok. Modified kapok shows a higher contact angle (138°) compared to raw kapok (125.5°). This can conclude that the kapok fiber modification was successfully achieved using the hydrothermal method.

INTRODUCTION

The inclusion of oil in an aquatic system can have disastrous effects on the oceanic ecosystem. An assortment of techniques has been introduced to eliminate oil from harmful areas, such as in-situ burning [1], biodepolluting [2], and the use of absorbing materials [3]. Because of their superior performance, materials with unique wettability characteristics, such as those that are hydrophobic/oleophilic or hydrophilic/underwater superoleophobic, have

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recently attracted the attention of various researchers for the separation of oil/water mixtures [4,5]. The sorbents will absorb or ingest the oil from the outer layer of the sullied water, prompting the recuperation of oil. Until now, the sorbent utilized in mechanical extraction incorporate mineral-based sorbents [6], synthetic or organic polymers [5], $CaCO_3$ powder [7], cellulose aerogels [8], and natural sorbents [9] have been created and utilized as oil sorbents.

The use of natural sorbents offers a few benefits, like a high sorption limit, incredible biodegradability, and minimal expense. The fibers are for the most part grouped into two significant classes, which are synthetic fiber and natural fiber [10]. Regular filaments can be developed from plant strands, for example, sisal, hemp, bamboo, coir, flax, kenaf, jute, ramie, oil palm, pineapple, banana, and kapok. Natural fibers are recyclable, biodegradable, and beneficial to the environment. They are also used in high-end vehicle industries for interiors, panel lining, soundproofing, and other applications [11]. Kapok fiber (*Ceiba pentandra L. Gaertn*.), a silky lignocellulose fiber with a microtubular structure, is a promising biomaterial for adsorption [12]. It has a high lignin concentration, which makes them hydrophobic. In comparison to cotton, which contains at least 90 percent cellulose, kapok fiber contains 64 percent cellulose, 13 percent lignin, and 23 percent a mixture of hemicelluloses, pectin, and wax that coats the individual fibers [13]. In contrast to other plant fibers, kapok has a greater surface area due to its hollow lumen, which has a diameter of about 10–20 μm in diameter and a wall thickness of 1–2 μm. These interesting qualities such as high hollowness and natural hydrophobic properties, furnish kapok fibers with a superb oil sorption capability than current oil sorbents [14,15]. Nevertheless, the smooth fiber's surface caused by its waxy layer makes it tough to properly hold oil [16].

Kapok fiber's hydrophobicity and maximum oil sorption limit can be additionally improved by surface alteration. It could be much powerful and affordable as natural sorbent materials. Among various materials utilized for the alteration of kapok fibers, zinc oxide (ZnO) nanostructure offers a high surface region, amazing compound steadiness, and low poisonousness [17]. The ZnO nanoparticles are chosen as a coating material because of minimal expense, more extensive band hole (3.37 eV), enormous binding energy (60 meV), numerous dynamic destinations, greater surface reactivity, and naturally steady [18,19]. A superhydrophobic material is considered to have a water contact point greater than 150° and a sliding point under 5° [20].

Therefore, in this work, the rough surface-modified kapok fiber with ZnO was studied. By boosting the rowdiness of the material's surface and raising the weak surface energy on the surface of the materials, it is possible to physically and chemically alter the absorbent's surface to create superhydrophobic/superoleophobic materials.

MATERIAL AND METHODS

Materials

In this paper, kapok fibers have been utilized as main material, which has been collected from local sources. The raw fibers were cleaned of any visible lumps and dust. There was no additional processing performed to preserve the raw components fresh. ZnO nanoparticles using the Brand: Sigma Aldrich (<100 nm particle size) in dispersion form with 1.7 g/mL ± 0.1 g/mL at 25 the °C, the concentration of 20 wt.% in H_2O and a pH of 7.5 ± 1.5 were used as a coating on the kapok fiber surface.

Preparation for Zinc oxide (ZnO) coating

The solution with 5 ml solution of ZnO nanoparticles (<100 nm particle size) in dispersion form with 1.7 g/mL ± 0.1 g/mL at 25°C, concentration 20 wt.% in H_2O, and a pH of 7.5 ± 1.5 was prepared in the beaker. Kapok fiber was weighted to $1.0 \pm 0.01\ gram$. ZnO nanoparticles were then transferred into a steel autoclave and a clean kapok fiber was dipped into the solution. The steel autoclave was transferred into a heating and drying oven at 100 °C for 4 hours for a hydrothermal reaction between kapok fiber and ZnO nanoparticles. After that, the sample was cooled down to room temperature before the sample was taken out.

Characterization of raw and modified kapok fiber

Scanning Electron Microscopy (SEM with Energy Dispersive X-Ray Analysis (EDX)) (Oxford Instruments) was operated to investigate the morphology of the kapok. The samples were attached to rectangular stainless steel sample holders using conductive double-sided sticky tape for SEM analysis. To create a conductive coating that improves the

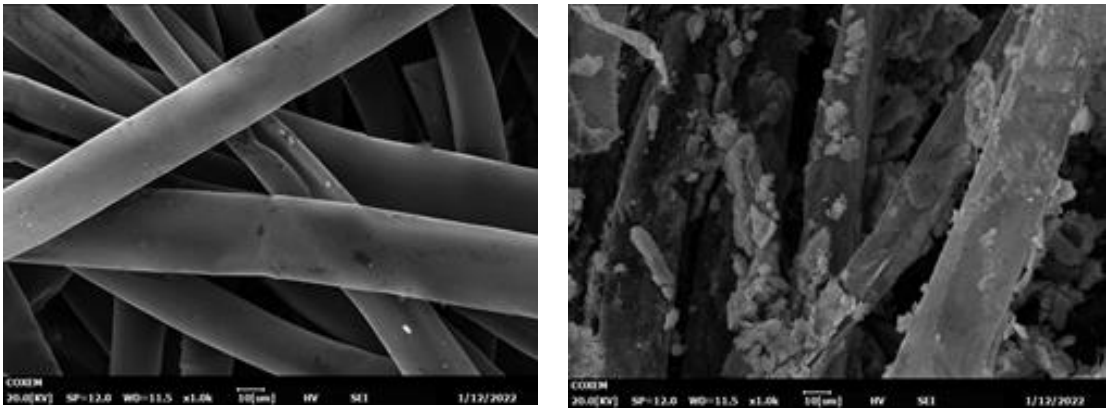
micrographs under SEM, the samples were sputter-coated with gold using a sputter coater. Using an accelerating voltage of 20 kV, the surface morphology was evaluated using SEM.

The contact angles were used to classify the interactions between solids and liquids. The contact testing was done using a contact angle machine (VCA Optima). To flatten the sample surfaces, the sample was squeezed with a glass film for a few days. As soon as the sample is positioned, a droplet of water was positioned on the sample surface. The VCA Optima used a high-resolution camera and advanced computer technology to take a static or moving image of the droplet and identify tangent lines as the foundation for measuring contact angles. A syringe, used either manually or mechanically, makes it simple to dispense test liquid. Line drawing errors were eliminated by computerized operations, and dynamic images were captured for analysis that must be done quickly.

The infrared spectrum of raw and modified kapok was analyzed using Fourier Transform Infrared Spectroscopy, FTIR (Agilent Technologies). The preparation of the test samples for FTIR analysis was done by cutting a piece of raw and modified kapok fiber (loose form) and using it as a sample. The sample was put inside an FTIR spectrometer, which then fired IR beams at it to quantify the quantity of each frequency and the beam the sample absorbed. However, the sample must be thin enough to allow the infrared light to pass through. Two different scans were carried out at 4000 and 650 cm^{-1} wavelengths, at a resolution of 8 cm^{-1}.

RESULT AND DISCUSSION

The micrograph of SEM analysis for raw and modified kapok fibre was displayed in Fig. 1. Fig. 1(a) shows that the surface of raw kapok fiber is silky and smooth due to the layer of wax on its surface. The lignin component is responsible for kapok fiber hydrophobicity. While modified kapok fiber has a rough surface due to the ZnO coating on the kapok surface as in Fig 1(b). The raw kapok has a smooth fiber surface, which may be pertaining to the existence of natural wax, lignin, and hemicellulose [21]. The inclusion of ZnO nanoparticles increased the kapok fiber surface roughness. Surface roughness is a critical factor for improving the oil sorption capability of kapok fiber [14]. The rod-like morphologies and uniform fineness that were present in kapok fiber clusters were closely tied to the individual fiber's arrangement.



(a) (b)

Figure 1. SEM morphology of (a) raw kapok, (b) modified kapok with ZnO

Elemental composition via EDX analysis for raw and modified kapok was shown in Table 1 and Table 2. The C and O atoms made up the sample's outermost layer in both cases. According to C.S. Quek, kapok fiber contains 0.338% N, 45.2% C, 6.26% H, 0.105% S, and 48.1% O as its constituents. It has the same chemical structure as cellulose, which has the formula $(C_6H_{10}O_5)n$. This is the reason why the fiber surface has a high content of C and O atoms and also reveals that the major component of kapok fibre is cellulose [22]. The O% atomic percentage for modified kapok fiber decreased compared to the raw kapok after hydrothermal treatment from 45.68% to 30.87% because of the kapok fiber's surface groups and the oxygen-containing groups of ZnO interaction as supported by FTIR results [23].

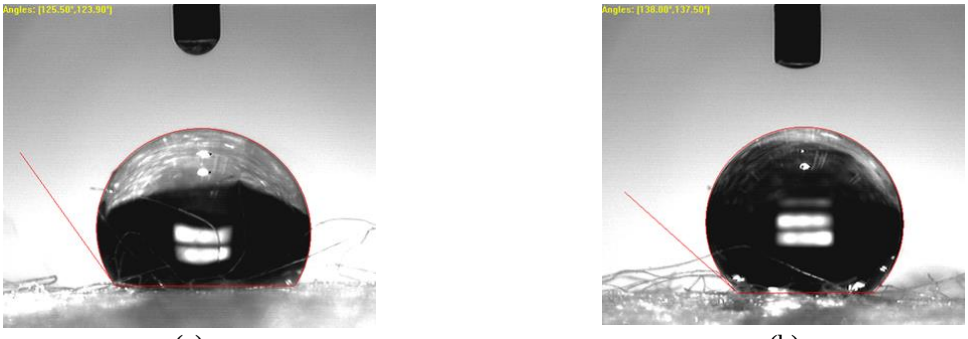
TABLE 1. Elemental composition of raw kapok

Spectrum 1				
Element	**Line Type**	**Weight (%)**	**Weight (%) sigma**	**Atomic (%)**
C	K series	46.42	1.10	53.98
O	K series	52.32	1.08	45.68
Cu	K series	0.82	0.21	0.18
K	K series	0.44	0.07	0.16
Total		100.00		100.00

TABLE 2. Elemental composition of modified kapok

Spectrum 1				
Element	**Line Type**	**Weight (%)**	**Weight (%) sigma**	**Atomic (%)**
C	K series	30.08	0.85	52.46
O	K series	23.58	0.57	30.87
Zn	K series	43.10	0.71	13.81
Ca	K series	0.23	0.06	0.12
Na	K series	3.01	0.57	2.74
Total		100.00		100.00

The water contact angle for raw kapok fiber was observed at 125.50° as displayed in Fig. 2(a) indicating that raw kapok fiber was originally a material that has low wettability pertaining to the existence of wax, it's silky and smooth surface. In the study carried out by J. Wang [24], the contact angle of raw kapok fiber was 116°. Regardless, the contact angle for raw kapok may differ depending on the country of origin [25]. As for the modified kapok fiber, the contact angle was observed at 138.00° as displayed in Fig.2(b). The surface roughness is one of the factors that influence the contact angle of the substrate [26]. This comparison shows that the modified kapok with ZnO has a higher contact angle compared to the raw kapok due to the difference in their surface roughness.



(a) (b)

FIGURE 2. Contact angle (a) raw kapok (b) modified kapok

Fig. 3 shows the FTIR spectra for raw and modified kapok with ZnO. Based on the analysis, the O-H bond and C-O bond are usually found in both raw and modified kapok. However, the band intensity of the peak for modified kapok observed at 3268.88 cm^{-1} (Surface -OH vibration peak stretching) reduces substantially in comparison to that of raw

kapok fiber, suggesting an interaction between the surface groups of kapok fiber and the oxygen-containing groups of ZnO. The FTIR band around 3268.88 cm^{-1} decreased after kapok fiber underwent a hydrothermal process. It could be explained by the hydroxyl groups being reduced by the high-temperature dehydration procedure [23]. A peak of absorption (symmetric Zn-O-Zn stretching vibration) is observed at 652.28 cm^{-1}. The substantial absorption bands corresponding to the stretching vibrations of CH_2 and CH_3 that are asymmetric and symmetric occur at 1420.12 and 1375.39 cm^{-1}. These alterations suggest that the sum amount of –OH was decreased, and hydrophobic ZnO nanoparticles were developed on the surface of the kapok fiber [24].

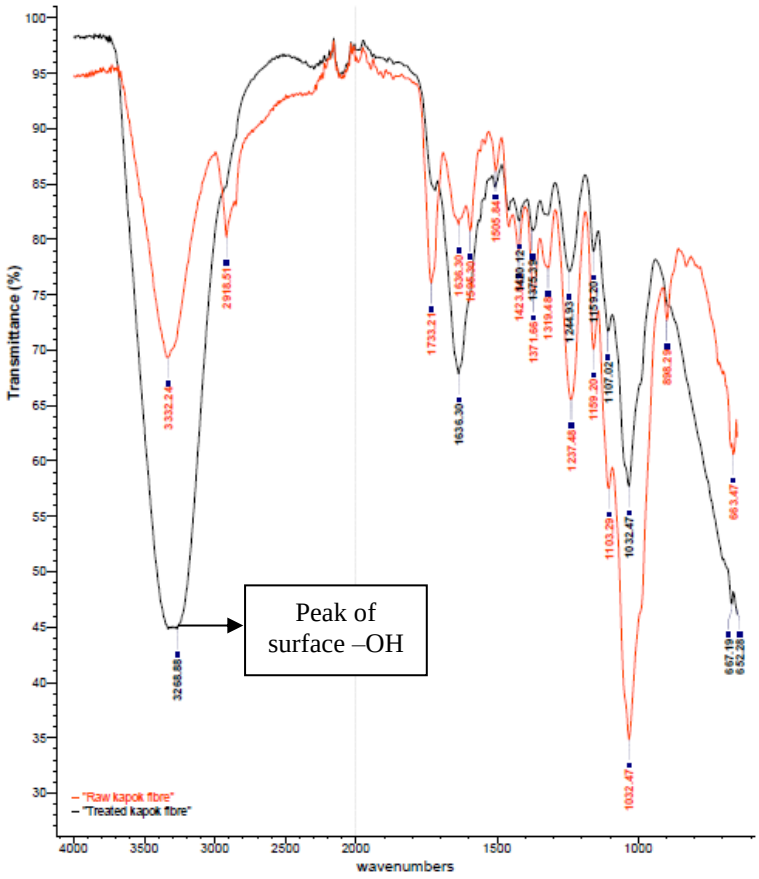


FIGURE 3. FTIR spectra for raw and modified kapok

CONCLUSION

According to the analysis using SEM-EDX, FTIR spectrum, and contact angle measurements, kapok is a natural sorbent that possesses excellent hydrophobic-oleophilic qualities that are due to its waxy surfaces and hollow lumens. Furthermore, the modified kapok fiber surface had a higher water contact angle than the raw kapok because their surfaces became rough pertaining to the existence of ZnO on the modified kapok fiber surface, supported by the characterization results using SEM-EDX, FTIR spectrum, and contact angle analysis.

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