Kapok fibre as potential oil-absorbing material: Modification mechanism and performance evaluation

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Abstract. Kapok fibre has gained considerable attention as a potential oil-absorbing material due to its lipophilicity, hydrophobicity, and configuration of its central lumen which is the key component of its high oil absorption capacity. However, the weak structural integrity of the fibre greatly retards its application. This study aims to develop a reinforcement method for kapok (Ceiba pentandra) fibre to enhance its reusability and oil recovery. Oil-sorption capacities of several modified kapok fibres have been evaluated to resolve the oil-polluted water issues.

Oxidation using sodium chlorite (NaClO₂) followed by sol-gel coating with tetraethylorthosilicate (TEOS) and sponge formation via freeze-drying method successfully enhance the structural integrity of the fibre without significantly reduce its hydrophobicity. Further coating the sponge with dodecyltrimethoxysilane (DTMS) using the chemical vapor disposition method results in superhydrophobic fibre. The best performance achieves an oil-sorption capacity of 48.6 g-oil/g-fibre and can maintain 62.6% of its oil-sorption capacity even after ten reuse cycles.

1. Introduction
Kapok fibre is a natural cellulosic fibre that is light (low density), hydrophobic, and oleophilic. Unlike other fibre, kapok has a lumen (air cavity) in the middle of its waxy fibre wall is the key to its high oil absorption capacity and good buoyancy [1]. Kapok fibres are characterized by having a high level of acetyl groups (13.0%), which make them superhydrophobic and do not get wet with water [2].

Pristine kapok has shown relatively stable performance in reclaiming oil from oil-in-water emulsion as it shows little change in morphology after being used as an oil absorbent. It also selectively absorbs oil from water or seawater with an oil intake of 40 g/g fibre [2]. Kapok fibre has shown high oil-to-water sorption (O/W) ratios, up to more than 200 times [3]. In kapok fibre, there is two-steps oil sorption mechanism: (i) oil is absorbed by utilizing the similarity of hydrophobic properties and van der Waals forces between oil and waxy layer on the wall surface of kapok while water is rejected; (ii) the absorbed oil then passes through the fibre cellulosic wall and enter the lumen by utilizing the capillarity effect. The oil sorption capacity and oil retention of kapok fibre are highly dependent on the oleophilic fibre wall and the physical properties of the oil (e.g., density, viscosity, surface tension, as well as contact angle with kapok surface) [4]. Furthermore, Abdullah et al. have found out that the kapok fibre can
maintain its ability to absorb oil up to 15 cycles with a capacity reduction of only 30% compared to the new kapok fibre [5].

Although detected as a good oil absorbent, the utilization of kapok fibre in the field is still underdeveloped due to the challenges in modulation and reusability. The short length and waxy smooth surface of kapok fibre cause poor inter-fibre cohesion; the wax content on the fibre surface allows the oil to diffuse in the lumen but hardly holds the oil not to diffuse out of the lumen (low retention) [6]. Therefore, surface modification on kapok fibres has to be done to enhance their inter-fibre cohesion as well as oil retention. The aim of this study is to evaluate several surface modification methods for removing the wax on the kapok fibre surface reinforcing its structural integrity as well as oil sorption capacity and recovery without losing its affinity to oil and water repellency.

2. Materials and Methods
Kapok fibre was purchased from a farmer in Kadipaten Village, Tasikmalaya Regency, Indonesia. Sodium chlorite (NaClO₂), Acetic acid (CH₃COOH), ammonium hydroxide solution (NH₃·H₂O), n-hexane, methanol, ethanol, and cooking oil were purchased from local suppliers. Tetraethyloxosilicate (TEOS) was purchased from Merck & Co., while dodecyltrimethoxysilane (DTMS) and sodium dodecylbenzene sulfonate (SDBS) were purchased from Shandong Bovi Energy Technology Co., China.

Super-hydrophobic kapok fibre was prepared by a sol-gel silanation technique adapted from Wang et al. [7]. The fibre was separated from seeds and cleaned from dust by aeration before pretreated using NaClO₂ in a glass reactor (equipped with overhead stirrer and condenser) under acid condition (pH 4.5, temperature 80°C, stirring rate 400 rpm) to eliminate the waxy layer from the kapok surface exposing the hydroxyl group on the cellulosic material. The concentration of NaClO₂ was varied from 0.25%, 0.5%, 3%, 4%, and 5% to give the optimum oil sorption capacity vs. weight loss [8]. The effect of concentration variations from 0.5 to 3 %-w have been reported previously and are not reconsidered in this study.

The pretreated fibres were mixed with TEOS (4%-w) and surfactant SDBS (1.2 mmol/L) at room temperature for 20 minutes with slow addition of NH₃·H₂O (1.8%-w) to perform a homogeneous sol-gel reaction on the kapok surface. The resulting fibre was then washed with methanol and dried in a vacuum oven. The hydrophilized TEOS coated fibre was freeze-dried prior to the hydrolyzation with dodecyltrimethoxysilane (DTMS) via chemical vapor deposition in oven preset at 120°C for an hour to form a superhydrophobic layer. Variations of pretreatments and coating methods were conducted to gain optimum results.

The chemisorption of the TEOS and DTMS on the kapok fibre was characterized using attenuated total reflectance Fourier transform infrared (FTIR ATR, Bruker) and compared to the spectra of pristine kapok fibre summarized in Table 1. The hydrophobicity of the pristine and modified kapok fibre was determined by water contact angle measurements. Oil was recovered from the fibre without severe disruption of the appearance of the fibre. The oil sorption capacities, intakes and recovery of pristine and modified kapok fibre were analyzed and presented in gram oil per gram dried kapok. The sorption/desorption cycle was repeated ten times to evaluate the recyclability of the fibre.

| Wavenumbers (cm⁻¹) | Assignment |
|-------------------|------------|
| 3419              | Non-free O-H stretching |
| 2929 and 2850     | Asymmetric and symmetric C-H stretching in CH₂ and CH₃ |
| 1741              | C=O stretching of ketones, carboxylic and ester groups in lignin; acetyl ester in xylan |
| 1504 and 1602     | Aromatic ring C-C skeletal stretching |
| 1375              | C-H bending |
| 1245              | C-O bending |
| 1065              | C-C stretching |
3. Results and Discussion

Hydroxyl groups on cellulosic fibre are important for the purpose of modification [10]. Therefore, the purpose of pretreatment is to distort the waxy layer, exposing the hydroxyl groups on the wall surface of kapok fibre to be chemically bonded with silica precursors at TEOS coating stage without damaging the wall structure that may result in the reduction the oil sorption capacity. Figure 1 shows the visible appearance (A) as well as O-H stretching FTIR spectra (B) of pristine and pretreated kapok fibre of different concentrations of NaClO₂. The increasing concentration of NaClO₂ enhances the whiteness and compactness of kapok fibre, as well as the hydroxyl group concentrations on the fibre surface. However, severe weight loss of the treated fibre may indicate wall structure damage. Therefore, further assessment of oil sorption capacity has to be done to determine the optimum NaClO₂ concentration for pretreatment process.

![Figure 1. Kapok fibre before and after pretreatment using different concentration of NaClO₂](image)

Oil sorption capacity of the NaClO₂-oxidized fibres have been measured and results are shown in Figure 2. Compared to the pristine kapok, the oxidized kapok loses its oil sorption capability indicating the reduction of the surface wax content. The oil sorption capacity of the fibre was first increased with the increment concentration of NaClO₂ to 0.5%-w but gets decreased afterward. Thus, kapok fibre pretreated with NaClO₂ concentration of 0.5%-w is chosen to be further studied.

![Figure 2. Oil absorption capacity of Kapok fibre after pretreatment with different concentration of NaClO₂](image)
Table 2 summarizes the variations of the modification process conducted in this study. With average fibre length of 1.8 cm [6], kapok fibre is poorly modulated; therefore, coating is an effective way to reinforce the cellulosic fibres and enhance their inter-fibre cohesion. The kapok fibre is coated with organosilane DTMS with or without TEOS as the precursor. To retain their structural integrity, the coated kapok fibres have been soaked and stirred in water with different weight ratios (0.2 and 0.6 %-w) then freeze-dried. Strand scission was done prior to the freeze-drying process to promote a homogeneous fibre dispersion in water.

Table 2. Variations of modification processes on kapok fibre samples

| Code  | Variations                                                                 |
|-------|---------------------------------------------------------------------------|
| Var.0 | Raw kapok fibre                                                           |
| Var.1 | Kapok fibre sponge after NaClO2-pretreatment, TEOS coating, strand scission, freeze-dried with fibre to water concentration 0.6 %-w, followed by DTMS coating |
| Var.2 | Kapok fibre sponge after NaClO2-pretreatment, TEOS coating, strand scission, and freeze-dried with fibre to water concentration 0.2 %-w, followed by DTMS coating |
| Var.3 | Kapok fibre sponge after NaClO2-pretreatment, TEOS coating, freeze-dried with fibre to water concentration 0.6 %-%w (without strand scission), followed by DTMS coating |
| Var.4 | Kapok fibre sponge after NaClO2-pretreatment, freeze-dried with fibre to water concentration 0.6 %-%w (without strand scission), followed by DTMS coating |

The FTIR spectra of the pristine and modified kapok fibre have been recorded to assess the success of each modification process. Figure 3 shows the FTIR spectra of pristine and modified kapok fibre as indicated on the graph. TEOS coating reduces the intensity of the hydroxyl group (at 3342 nm⁻¹) but brings up the Si-O-Si spectra (at 1051 nm⁻¹); while DTMS coating increases the intensity of spectra at 2923 and 2856 that belong to -CH₂ and -CH₃, respectively [8].

![Figure 3. FTIR Spectra of pristine and modified kapok fibres](image)

Figure 4 shows the water contact angle (WCA) on pristine and modified kapok fibres. Chemical modification using TEOS and DTMS does not significantly affect the WCA. Freeze-dried modified kapok fibres, however, show higher WCA compared to those without structural integrity enhancement. Superhydrophobic kapok sponges (WCA = 152.3 ± 3.5) could be achieved after NaClO2-pretreatment,
TEOS coating, freeze-drying with fibre to water concentration 0.6 % w (without strand scission), then followed by DTMS coating.

![Figure 4](image.png)

**Figure 4.** Water contact angle of raw kapok fibre, NaClO₂-pretreated, DTMS coated, and TEOS-DTMS coated samples, respectively

Reusability analyses have been carried out to test the structural integrity enhancement of the sponge during ten times recycle. Figure 5 shows the oil sorption capacity of pristine kapok fibres vs. modified sponges. The pristine kapok loses 55% oil sorption capacity at the 4th cycle and could only retain 29.8% of its oil sorption capacity at the end cycle. The pristine kapok fibres tend to crumble and hard to be recovered as a whole. Most modified sponges have better reusability than the pristine kapok.

Var. 2 (strand scission, 0.2 % w fibre in water) shows the highest oil sorption capacity at the first cycle due to the highest pore volume; although the sponge is not crumbled, it directly loses its integrity in the second cycle. Comparing Var. 1 and Var. 3, strand scissions enhance the air cavities inside the sponge that can be substituted with oil. In terms of their structural integrities throughout the cycles, the sponge without strand scission shows slightly better reusability compared with that with strand scission.

The effect of TEOS as a precursor for DTMS coating can be analyzed from the comparison of Var.3 and Var.4. Overall, the addition of TEOS results in a better reusable sponge. TEOS itself enhances the hydrophilicity of the kapok fibre, making the fibre suspension more homogeneous for the freeze-drying process. A homogeneous fibre suspension causes the fibres to intertwine and results in stronger structural integrity of the sponge. Var.3, therefore, is the best variation with oil-sorption capacity of 48.6 g-oil/g-fibre and oil-sorption retention of 62.6% even after ten reuse cycles.
4. Conclusion
Kapok fibre sponge shows the optimum oil sorption capacity after oxidation using 0.5 %-w sodium chlorite (NaClO₂) solution followed by sol-gel coating with tetraethyloctosilicate (TEOS) and sponge formation via freeze-drying method successfully enhance the structural integrity of the fibre without significantly reducing its hydrophobicity. Further coating the sponge with organosilane such as dodecyltrimethoxysilane (DTMS) using the chemical vapor disposition method recovers the superhydrophobicity of the fibre. The best performance achieves an oil-sorption capacity of 48.6 g-oil/g-fibre and can maintain 62.6% of its oil-sorption capacity even after ten reuse cycles.

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