Comparative study of acid-treated and alkali-treated carbonised Kapok–fibres for oil/water absorption system

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Abstract. Kapok predominantly utilized as an adsorbent in removing wastewater such as dye, oil and heavy metals. However, a comparative study between acid-treated and alkali-treated carbonized Kapok fibers has not been carried out in detail. In this study, as-made Kapok fibers were carbonized and subsequently undergo acid (HCL) and alkali (NaOH) treatment. The resultant treated Kapok fibers were characterized using Fourier transform infrared (FTIR) spectroscopy, Elemental Analyzer (EA) and Thermogravimetric Analysis (TGA). As-made carbonized Kapok fibers were tested with oil/water absorption model system. A reduction of band intensity at 1740 cm⁻¹ and 1245 cm⁻¹ occurred for NaOH treated sample compared with HCL. The composition of carbon in Kapok fiber increased after carbonization treatment using NaOH (62.42%) and HCL (66.15%) compared with untreated (0.17%). For oil/water absorption system, the result indicated that HCL-treated Kapok fibre was the highest absorption on 28.10 gg⁻¹ diesel, 27.28 gg⁻¹ petrol and 39.84 gg⁻¹ for used vegetable oil respectively in comparison with NaOH-treated and as-made carbonized Kapor fibers. In conclusion, modification of the surface of carbonized Kapok fibers could significantly alter its textural properties which could enhance its oil absorptive behavior.
1. Introduction
Apparently, one of the attractive and viable natural fibers, Kapok has found significant interest in environmental engineering application such as oil absorbency [1]. Kapok fiber possesses unique physical properties such as the fluffy texture and high spongy [2].

One of the strategies to realize this via carbonisation of Kapok, has proven to make a huge improvement on its oleophilic properties. However, high amount of energy was consumed during the carbonisation process. Indeed, the process is not economical but from a precise environment viewpoint, the carbonised Kapok provides benefits economically and socially. Kapok fibers were treated with two chemical solutions which is hydrochloric acid and sodium hydroxide before it will be burn in a furnace. The purpose of this treatment was to remove the wax and impurities that surrounded Kapok surface for oil sorption capacity improvement. Previous study showed that the comparison of this two solution (is hydrochloric acid and sodium hydroxide) not mentioned clearly. So, the efficiency of this both solutions was investigated in this study.

The main purpose of this study to evaluate the physical properties of Kapok as carbonized fibres after treated with sodium hydroxide solution and hydrochloric acid solution. The physical experiments such as Fourier Transform Infrared Spectra (FTIR), Thermographic Analysis (TGA) and Elemental Analyzer (EA) were employed to characterise both raw and treated Kapok fibres. All result show that, the carbonised Kapok after treated using these solutions can enhance the ability of oil sorption in water system and its physical properties become better compared with untreated Kapok.

2. Materials and Method
2.1 Carbonised Kapok preparation
Kapok fibres were treated using sodium hydroxide and hydrochloric acid solution as pretreatment. This process removed lignin, wax and impurities on the surface of fibres. The Kapok fibres were soaked in 0.5 M of sodium hydroxide solution for 24 hours. After that, the sample was soaked again in 0.5 M hydrochloric acid solution for 30 minutes. The samples were rinsed with deionized water after the process completed and dried in oven at 60°C for one hour. The treated samples of Kapok were carbonized in a furnace at 450°C for three hours.

2.2 Characterization of as-made and treated Kapok fibers
2.2.1 Fourier Transform Infrared (FTIR) spectroscopy
This analysis functions to determine the molecular bonding and functional group in polymer materials. This is because the polymer molecules contained different vibration frequencies. The samples recorded on FTIR that has presence of functional groups in polymer (Perkin Elmer, Optima 8000, USA) in the range 4000-650 cm⁻¹. FTIR analysis were performed in room temperature.

2.2.2 Thermographic analysis (TGA)
By using Perkin Elmer Simultaneous Thermal Analyzer (TGA 8000), TGA was evaluated from 30°C to 750°C at 10°C/min at nitrogen atmosphere.

2.2.3 Elemental analyzer (EA)
This analysis functions to determine the element content in Kapok fiber which is carbon, hydrogen, nitrogen, oxygen and sulphur. All of the elements were analyzed by elemental analyzer (Perkin Elmer, 2400 Series II, US).

3. Result and Discussion
3.1 FTIR analysis
FTIR analysis (Figure 1) is a tool for identification of functional group. The most important feature of these spectrums is the broad band centred at 3410 cm⁻¹ assigned to non-free O-H stretching vibration, the strong peak around 2914 cm⁻¹ assigned to asymmetric and symmetric stretching vibration in CH₂ and CH₃ (Lim and Huang, 2007). The absorption peak at 1740 cm⁻¹ was due to C=O
stretching vibration of ketones, carboxylic groups and esters in lignin [3]. By comparing the spectra of untreated and treated Kapok fiber, the following findings were obtained. The increased of absorption bands at 3410 cm$^{-1}$ can be observed for all treated samples, implying the increment of cellulose hydroxyl groups in fiber walls [4]. A remarkable reduction of band intensity at 1740 cm$^{-1}$ and 1245 cm$^{-1}$ occurs for NaOH treated sample, suggesting that strong alkali can result in significant deesterification of Kapok fiber [5].

3.2 EA analysis

The EA analysis (Table 1) was conducted to detect the presence of Carbon, Hydrogen, Nitrogen and Sulphur. Based on the table above, the percentage of carbon in NaOH and HCl sample shows the highest percentage compared to the others. This may due to its carbonized properties that were obtained from the carbonization process which performed at 450ºC. Next, Hydrogen and Nitrogen compound were also found the highest at NaOH and HCl samples. Moreover, based on the analysis, hydrogen and nitrogen are found abundantly in NaOH treated Kapok. Increase amount of hydrogen and nitrogen helped increasing sorption of oil.

| Sample   | Carbon   | Hydrogen | Nitrogen |
|----------|----------|----------|----------|
| NaOH     | 62.42%   | 8.18%    | 0.79%    |
| HCl      | 66.15%   | 7.97%    | 0.69%    |
| Untreated| 0.17%    | 0.23%    | 0.57%    |

3.3 TGA Analysis

TGA analysis was performed to study the physical properties of a substance as a function of temperature whilst the substance is subjected to a controlled temperature programme. The analysis was used to accurately identify the decomposition temperatures of the components in three types of Kapok which are NaOH-treated Kapok, HCl-treated Kapok and untreated Kapok. The results obtained from the TGA were clearly presented in Figure 2 (a-c) for all three samples. The results clearly presented that all samples were not thermally stable as the weight percent reduce as the temperature rise up to 750ºC.

In general, from the TGA curves in figure, all samples suffered an initial weight loss in the range of 39.24 ºC to 108 ºC. The weight loss at this stage was due to the evaporation of moisture content or any other volatile compounds within the samples [6]. Based on the TGA curves in Figure 2 (c), a major decomposition occurred in temperature range of 237.74ºC to 366.5 ºC which is ascribed to the
dehydration, dissociation of lignocelluloses and residual. In the third region which is from 358ºC to 661ºC where a weight loss was due to the degradation of cellulose and lignin content. Meanwhile, the presence of carbon has been detected in the range of 500ºC to 750ºC prior to the formation of ashes. The weight of the substance could not decrease to zero mainly because of the incomplete combustion due to the absence of oxygen.

![Figure 2. TGA analysis on (a) carbonized chemical modified Kapok with NaOH, (b) carbonized chemical modified Kapok with HCl and (c) as-made untreated Kapok](image)

3.4 Removal of oil in oil/water system using carbonised Kapok and raw Kapok

Removal of oil from oil/water system was performed by pouring an oil layer on water surface in a beaker. The samples were in contact with various types of oil which were diesel, petrol, used vegetable oil and lubricant oil. Three types of oil were placed in a beaker filled water respectively as shown in Figure 5 (A1-A3 (petrol), B1-B3 (diesel) and C1-C3 (used vegetable oils)). Carbonised kapok fibres were then placed in the beaker with oil layer as shown in the same plate. The samples were left for 10 minutes with data was recorded every two minutes interval. After ten minutes, samples were taken out from the beaker and weighed to determine the mass after oil absorption.

From the data recorded, it can be seen that Kapok fibre that had undergoing further enhancement showed a positive result to act as a natural sorbent (Figure 3). Particularly, carbonised samples of Kapok fibre had reached high reading after two minutes of sorption of oil in water. From the graph in Figure 3 and 4, oil absorbency of Kapok fibre after extending time to ten minutes nearly reached equilibrium which proved that Kapok fibre can absorb oil in such fast rate and hold much oil without releasing it back to the mixture. Large hollow lumen that HCL-treated Kapok fibre had contributed to such positive result besides waxy surface on Kapok fibre allow it to not sink in water. Eventually, it shows that Kapok fibre can become a better option to act as a natural sorbent.

Afterwards, the data after ten minutes for HCL-treated Kapok fibre was recorded which is 28.10 g·g⁻¹ for diesel while 27.28 g·g⁻¹ was recorded for petrol and 39.84 g·g⁻¹ was recorded for used vegetable oil.
oil. From Figure 4, untreated Kapok reached 23.24 g·g⁻¹ for diesel, 21.09 g·g⁻¹ for petrol, 28.86 g·g⁻¹ for used vegetable oil and 26.53 g·g⁻¹ for lubricant oil. It also can be seen from the graph that oil sorption capacity for both samples in various types of oil nearly reached equilibrium. There was also slight increment in oil sorption capacity when extending contact time of chemically modified carbonized Kapok fibre on different types of oil. This is due to effective interstice structure among interconnected single fibre and low minimum surface energy on fibre surface that enhance sorption rate of Kapok fibre [7] [8]. In a nutshell, chemically modified carbonized Kapok fibre potentially act as an effective natural sorbent and demonstrated ability in cleanup of spilled oil in water environment.

Figure 3. Removal of oil in the oil/water system for treated Kapok

Figure 4. Removal of oil in the oil/water system for untreated Kapok
Figure 5. Pictures for the clean-up of petrol (A1-A3), diesel (B1-B3) and used vegetable oil (C1-C3) from water by treated Kapok fibre

4. Conclusions
Carbonised Kapok fibre was prepared using sodium hydroxide and hydrochloride acid. The result of this study showed the hydrochloric acid treatment gave better sorbent properties of carbonised Kapok fibre compared with sodium hydroxide treatment. The carbonised Kapok fibre via hydrochloric acid treatment also showed a good oil waste sorbent in water system compared with untreated Kapok and carbonised Kapok fibre via sodium hydroxide treatment.

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