Oil spill removal using kenaf core fibers as biosorbent material

P Siwayanan¹,*, D G Ramachandran², R Jamaluddin³ and S Ahmad³

¹ School of Energy and Chemical Engineering, Xiamen University Malaysia, 43900 Sepang, Selangor, Malaysia & College of Chemistry and Chemical Engineering Xiamen University, Xiamen 361005, China
² Chemical Engineering Department, UniversitiTeknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
³ Group Components Automotive Sdn. Bhd., 40460 Shah Alam, Selangor, Malaysia

* parthiban.siwayanan@xmu.edu.my

Abstract. Offshore crude oil exploration has led to oil spillage in the sea and causes an enormous negative impact on the surrounding environment, animals and human beings. In this paper, studies have been carried out to utilize Malaysian grown Kenaf core fibers as biosorbent material to clean-up the spilled oil from the sea. Kenaf fibers have natural oleophilic characteristics and therefore would be suitable to be used as biosorbent material. Studies were conducted to understand the surface characteristics, to evaluate the absorption capacity under simulated sea conditions and to determine oil/seawater sorption characteristics of Malaysia grown Kenaf core fibers. The crude oil/seawater absorption capacity study has indicated that both 20 mesh and 40 mesh Kenaf fibers can absorb 4 times its original weight in crude oil upon short contact time with crude oil/seawater. This study also reveals that the Kenaf fibers tend to absorb seawater upon prolonged contact with crude oil/seawater. Based on the separate crude oil and seawater sorption tests, both 20 mesh and 40 mesh Kenaf core fibers were found to have the ability to absorb 5-6 times and 1-6 times of its original weight in crude oil and seawater respectively, depending on the contact time.

1. Introduction

Oil exploration has been a significant contributor to a country’s economy because the resulting petroleum products can be used to produce a multitude of applications and generate high income [1]. However, such exploration has its drawback where it could lead to oil spillage in the ocean and polluting the sea. Oil is a toxic organic waste that can cause harm to the surrounding environment particularly on aquatic organisms, plant, animal and human being [2, 3]. Oils found in contaminated seawater include fats, lubricants, cutting liquids, heavy hydrocarbons such as tars, grease, crude oils, diesel oil, and light hydrocarbons such as kerosene, jet fuel and gasoline [4]. Factors that cause an oil spill in the ocean include human errors, equipment failure, natural disasters or deliberate acts [5, 6]. Since most of the oil spill incident takes place in the middle of the ocean, the spilled oil could not be recovered and cleaned up immediately. Thus, the spilled oil will spread out over the sea surface within a short time. Due to the density differences between oil and water, oil could not be dissolved or decomposed in water and this will cause the oil to float on the seawater [6]. As a result, all the organisms that are living in the surrounding area will be affected and also could harm their lives. There are many recorded oil spill incidents that caused loss of human’s life, sea creatures life and many other impacts to the environment [5].
During an oil spill, oil spill response team is responsible for removing the spilled oil in the sea. Many techniques are available commercially to expedite the removal process. These include biodegradation, chemical dispersants, in situ-burning, boomers and skimmers, vacuuming and oil sorbent [3, 7, 8]. In line with the global green development, many researchers have shown their immense interest in using natural organic materials as one of the methods to remove oil spill [9]. This development has led enormous research and development towards natural organic oil absorbent simply because of its advantages in terms of availability, easy operation process, low cost and biodegradable characteristics [2, 7, 10]. In the current market, there are many natural organic absorbents available for oil removal and these include peat moss, sawdust, cotton, kapok and others [1, 8, 11]. However, this paper will only focus on Malaysia Kenaf core fibers and their application as an oil absorbent.

The fast-growing Kenaf, which scientifically known as *Hibiscus cannabinus L.*, is a fibrous plant that has the potential to be explored in a multiple of applications such as making ropes, paper, mattress, automotive products and others [12, 13, 14]. With natural oleophilic characteristics, Kenaf is known to have a significant tendency to attract oil [15]. Kenaf is a short-lived perennial herbaceous fiber plant that made up of two different types of fibers, which classified as core and bast. In Kenaf stalk, the outer layer or the phloem is referred to as bast, which contains 25% - 40% of the stalk dry weight. The inner woody layer or the xylem is known as the core, which holds 60% - 75% of the stalk dry weight. Kenaf plant can grow at a fast rate and will require 4 - 5 months to reach a maximum height of 4.5 m. This woody base plant can survive in any climate with a minimal amount of water, fertilizers and pesticides. Kenaf also has the ability to yield 600 - 10,000 kg of dry fiber per acre, which is about 3 - 5 times greater than the yield of southern pine trees, where it requires up to 7 years to reach the optimal harvest size [14, 16, 17]. Kenaf is also claimed as one of the most sustainable fiber plants in the world due to its growth rate and ability to replenish the environment [18, 19, 20].

Generally, an oil sorbent material can remove the oil from a surface by two mechanisms, which include adsorption or absorption. Adsorption is a process by creating an adherence of oil to the respected sorbent materials by considering the viscosity of the oil. However, absorption process will give more importance on the capillary attraction where the oil particles will fill up the pores within the sorbent material and uptake into the material due to its capillary force [1, 21]. This paper will highlight the absorption process since the focus of the research is on to the use of Kenaf core fibers as oil absorbent. Natural Kenaf core fibers are covered with a layer of waxy substances, which allows them to have high buoyancy forces and also to absorb the oil easily from the surface of the water [17, 22].

The best characteristic to determine the effectiveness of an oil absorbent is its hydrophobic-oleophilic tendency. This characteristic, typically allows the absorbents to absorb oil and not water from the sea. However, Kenaf core fibers are not 100% hydrophobic materials where there are possibilities for the fibers to absorb water when they are in contact with water [14, 19, 22, 23, 24]. Kenaf core fibers comprise 87.40% of hole-cellulose, 49% of alpha-cellulose and 19.2% of lignin. The cellulose content of the fiber will be easily attracted to the water molecules; therefore, when the fibers are immersed in water, the fibers will start to swell. However, there are some contents of lignin as well, which inhibit the water absorption in the fiber matrix. In alkaline or seawater, the electrostatic interaction will be more electronegative, and due to that, the moistures can penetrate completely and swell the fibers with a high concentration of positive charge. Besides that, the interaction between the carboxyl group of the Kenaf core fibers cellulose chain and the hydroxyl group of the seawater also leads the hydroxide ions to be absorbed into the fibers, which then causes the swelling effect [14].

2. Material and methods

2.1 Materials

Kenaf core fibers, which used in the experimental work, were obtained in two different mesh sizes (20 mesh and 40 mesh) from National Kenaf and Tobacco Board of Malaysia. Other materials, such
as crude oil was obtained from Petronas Refinery, Melaka while seawater was collected from Lumut, Perak.

2.2 Crude Oil/Seawater Absorption Capacity Test
This test was performed using a modified funnel under a simulated oceanic condition. The test setup is shown in Figure 1. The modified funnel was initially filled up with 500 mL of seawater and then followed by the addition of 10 g of crude oil. The test was conducted using 2.5 g, 3.0 g and 3.5 g of both 20 mesh and 40 mesh Kenaf core fibers. The Kenaf core fibers were evenly sprinkled using a metal sieve onto the surface of the seawater that covered with a layer of crude oil. The effect of contact time (1 min, 3 min and 5 min) against absorption of crude oil was studied. The percentage of crude oil absorbed by Kenaf core fibers was determined using the following equations:

\[
\text{Percentage of crude oil absorbed} = \frac{M_o}{M_f} \times 100\% \quad (1)
\]

\[
\text{Percentage of seawater absorbed} = \left( \frac{M_f - M_i - M_o}{M_f} \right) \times 100\% \quad (2)
\]

where, \(M_o\): mass of crude oil, \(M_i\): initial mass of Kenaf core fibers, \(M_f\): final mass of Kenaf core fibers.

![Figure 1. Setup for crude oil/seawater absorption capacity test.](image)

2.3 Crude Oil Sorption Test
This test, which illustrated in Figure 2, was conducted by immersing 2.5 g, 3.0 g and 3.5 g of Kenaf core fibers into a modified container (holder) containing an excess amount of crude oil without the presence of seawater. The effect of contact time (1 min, 3 min and 5 min) against absorption of crude oil was studied. The percentage of crude oil absorbed by Kenaf core fibers were calculated using the following equation:

\[
\text{Percentage of crude oil absorbed} = \frac{M_f - M_i}{M_{fI}} \times 100\% \quad (3)
\]

where, \(M_i\): initial mass of Kenaf core fibers, \(M_{fI}\): final mass of Kenaf core fibers and crude oil absorbed.

![Figure 2. Oil sorption test setup.](image)
2.4 Seawater Sorption Test
This test, as illustrated in Figure 3, was conducted by immersing 2.5 g, 3.0 g and 3.5 g of Kenaf core fibers into a container containing seawater without any addition of crude oil. The effect of contact time (1 min, 3 min and 5 min) against absorption of seawater was studied. The percentage of seawater absorbed by Kenaf core fibers were calculated using the following equation:

\[
\text{Percentage of seawater absorbed (\%) = \left( \frac{M_f - M_i}{M_f} \right) \times 100\%}
\]

where, \( M_i \): initial mass of Kenaf core fibers, \( M_f \): final mass of Kenaf core fibers and seawater absorbed.

![Figure 3. Seawater sorption test setup.](image)

2.5 Scanning Electron Microscopy Analysis
The surface characteristics of the Kenaf core fibers samples was observed using Evo LS 15, Zeiss scanning electron microscope (SEM). SEM was operated under vacuum at 20kV and the images were taken using 100 and 300 times magnification. These micrographs were used to observe the surface morphology of Kenaf core fibers before and after oil absorption.

3. Results and Discussion

3.1 Crude Oil/Seawater Absorption Capacity Study
Figure 4 and 5 display the crude oil and seawater absorbed by 20 mesh and 40 mesh Kenaf core fibers respectively against the contact time. These results indicate the absorption capacity and selectivity of the Kenaf core fibers towards the crude oil and seawater. Although the particle size of 20 mesh and 40 mesh fibers are different, the behavior towards the oil and water were almost the same. In this test, the mass of crude oil was fixed while the mass of Kenaf core fibers was manipulated. Generally, the oil absorbent tends to absorb up to 15 times its weight in oil. Thus, in this absorption capacity study, the test was initiated with the use of 0.5 g Kenaf core fibers in 10 g of crude oil. However, the Kenaf core fibers could not absorb all the crude oil and leaves behind some even after the seawater has been drained out. The same results were demonstrated when using 1.0 g, 1.5 g and 2.0 g of Kenaf core fibers. This test proves that 0.5 g to 2.0 g of Kenaf core fibers could not absorb the entire 10 g of crude oil for both sizes of 20 mesh and 40 mesh. The minimum mass of 2.5 g Kenaf core fibers was therefore required to absorb 10 g of crude oil, which is equivalent to the absorption capacity of 4 times of its weight in oil. Subsequently, the test was continued with a gradual increase of 0.5 g mass of Kenaf core fibers until it reaches 3.5 g.
Figure 4. Crude oil and seawater absorbed using 20 mesh Kenaf core fibers at 1 min, 3 min and 5 min.

Since Kenaf core fibers are not 100% hydrophobic, some amount of seawater will be absorbed as well. Both Figure 4 and Figure 5, clearly indicates that when the contact time is prolonged, more seawater tends to be absorbed. Therefore, the optimum mass ratio obtained for both 20 and 40 mesh Kenaf core fibers was 1:4 (Kenaf core fibers: crude oil) provided the contact time is limited to 1 min. However, by comparing the absorption capacity of 20 mesh and 40 mesh Kenaf core fibers at the given optimum condition, 40 mesh Kenaf core fibers were found to absorb less seawater as compared to 20 mesh Kenaf core fibers.

3.2 Crude Oil Sorption Study

This study was conducted to determine the oleophilicity of Kenaf core fibers and their crude oil absorption capacity by immersing Kenaf core fibers into crude oil without the presence of seawater. The test conditions used in this study were the same as the previous crude oil/seawater absorption capacity test. The test results, which shown in Figure 6, indicates that Kenaf fibers tend to absorb more crude oil with the increase of the mass of fibers and contact time.

Figure 5. Crude oil and seawater absorbed using 40 mesh Kenaf core fibers at 1 min, 3 min and 5 min.

In comparison to the previous test results, more amount of crude oil was observed to be absorbed by Kenaf core fibers. Thus, this test proved that Kenaf core fibers could absorb more than four times...
its weight in oil without the presence of seawater. Besides that, in this oil sorption test, it can be concluded that Kenaf core fibers can absorb about six times of its weight in oil while 20 mesh Kenaf core fibers can absorb more amount of oil as compared to 40 mesh Kenaf core fibers.

![Figure 6](image.png)

**Figure 6.** Percentage of crude oil absorbed using both 20 mesh and 40 mesh Kenaf core fibers at 1 min, 3 min and 5 min.

3.3 Seawater Sorption Study

As mentioned previously, Kenaf core fibers are not 100% hydrophobic and data obtained from the earlier crude oil/seawater absorption capacity study has supported this fact where the presence of seawater was observed in the oil absorbed Kenaf core fibers. Therefore, further seawater sorption test was conducted to study the hydrophilicity of the Kenaf core fibers. This test was conducted on seawater using the same 20 mesh and 40 mesh sizes of Kenaf core fibers with the contact time of 1 min, 3 min and 5 min. In this test, the minimum amount of Kenaf core fibers used was 2.5 g, which follows the minimum amount of fibers used to absorb 10 g of oil in the earlier crude oil/seawater absorption capacity test.

Figure 7 illustrates the absorption of seawater for Kenaf core fibers of 2.5 g, 3 g and 3.5 g. The results have proven that Kenaf core fibers tend to absorb seawater similarly to the characteristics observed in the previous crude oil/seawater absorption capacity study. The results also have indicated that the 20 mesh Kenaf core fibers have relatively higher absorption capacity than 40 mesh Kenaf core fibers. Upon prolonged contact time, Kenaf core fibers of both sizes were likely to absorb more seawater. The seawater sorption occurs mainly because of the cellulose content in Kenaf core fibers. The appropriate contact time for Kenaf core fibers, as observed in this test, was at 1 min while the 40 mesh Kenaf core fibers seemed to be highly suitable as sorbent material as it can absorb less amount of seawater as compared to 20 mesh Kenaf core fibers especially when using more amount of Kenaf core fibers.
Figure 7. Percentage of seawater absorbed using 20 mesh and 40 mesh Kenaf core fibers at 1 min, 3 min and 5 min.

3.4 Analysis using SEM

Further evaluation was carried out using SEM image analysis to study the surface morphology and behavior of Kenaf core fibers before and after oil absorption. The samples collected from crude oil/seawater absorption capacity test were analyzed. Figure 8 and 9 illustrate the changes in the surface structure of the 20 mesh Kenaf core fibers before and after oil absorption. The Kenaf core fibers, as shown in Figure 8, were observed to have inter-fiber pores while in Figure 9, these inter-fiber pores were filled with the crude oil. The same results were obtained for 40 mesh Kenaf core fibers, as shown in Figure 10 and 11. The flow of crude oil into the inter-fiber pores was driven by the capillary pressure. This capillary pressure is the main driving force for the transportation of crude oil into the pores of the Kenaf core fibers [1]. As seen in Figure 9 and 11, for both 20 mesh and 40 mesh, the expansion in the inter-fiber pores and disorientation of the fiber wall were observed. These results indicate the swelling effect of the Kenaf core fibers.

Figure 8. 20 mesh Kenaf core fibers before oil absorption (x 100 and x 300 magnification).
4. Conclusions
In this paper, several studies have been conducted to utilize Malaysia grown Kenaf core fibers as the natural occurring organic absorbent in removing crude oil under simulated oceanic condition. From the crude oil/seawater absorption capacity study, 40 mesh Kenaf core fibers were found to absorb four times of its weight in crude oil. The optimum time to remove the crude oil was within 1 min as fibers upon prolonged contact time likely to absorb more amount of seawater. Based on the crude oil sorption study, more amount of crude oil was observed to be absorbed with the increase of contact time and mass of Kenaf core fibers. Between the two different mesh sizes, 20 mesh Kenaf core fibers were found to absorb more crude oil as compared to 40 mesh Kenaf core fibers. However, in the seawater sorption study, the optimum contact time of the Kenaf core fibers was at 1 min and 40 mesh
Kenaf core fibers seemed to be highly suitable as sorbent material as it can absorb less amount of seawater when compared to 20 mesh Kenaf core fibers. From SEM analysis, Kenaf core fibers with inter-porous structure were observed to have the swelling tendency, which enhances the absorption characteristics. The results obtained from these studies have shown that Malaysian Kenaf core fibers have great potential to be used as oil spill absorbent.

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