Oil Removal From Palm Oil Mill Effluent (POME) by Using Kenaf Core (*Hibiscus Cannabinus*)

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ABSTRACT
Increasing attention on the environmental issue especially the wastewater from the palm oil mill effluent (POME) has become one of the great concern to many researchers. The excessive amount of untreated POME may cause the reduction of oxygen and sunlight in the water, which in turn affects the aquatic life. The availability of the conventional and current treatments such as ponding system will take more retention time and sometimes fails to obey the standard regulation discharge limit set by the Department of Environmental (DOE) Malaysia. Thus, in this research, the adsorption technology was chosen to treat POME due to its effectiveness, low cost with simple treatment operation. The kenaf core (Hibiscus Cannabinus) was proposed as a potential adsorbent to removal the oil from POME due to its abundance availability in Malaysia. The objective of this research was to study the characteristic of raw kenaf core fibre by using FTIR and SEM analysis. The effect of mass of raw kenaf core fibre used in oil removal from POME was also being investigated. IR spectra showed the appearance of ester stretching (at 1753 cm-1) and C-H stretching of alkane at 2922 and 2853 cm-1. These two functional groups are known for their hydrophobicity and expected to capture the oil. The rough surface was observed with the formation of large pores in the raw kenaf core fibre through the SEM images. The rough surface might have increased the adsorption capacity and the existence of pores might have facilitated the oil entrapment. Utilization of 5.0 g of kenaf core fiber resulted to 78.6% of oil removal efficiency. Meanwhile, the maximum adsorption capacity was achieved at 399.0 mg/g by using 1.0 g of raw kenaf core fibre mass. The raw kenaf core fibre is a potential natural adsorbent to remove the oil from POME.

Keywords: *Palm oil mill effluent (POME), oil removal, adsorption, adsorbent, kenaf core*

1. INTRODUCTION

Nowadays, oily wastewater is becoming one of the environmental concerns. It comes from various sources such as the food, cooking oil, vegetable oil, textile and leather industries, metal, oil and gas production, vehicles, domestic sewage and kitchens [1]. The environmental pollution occurs during oil and gas production when the environment is contaminated by the oil through transportation and during the refining process [2, 3]. Normally, the concentration of oily wastewater produced by industrial activities could reach as high as 40,000 mg/l [4]. One of the main sources of industrial oily wastewater in Malaysia is the palm oil mill effluent (POME).

The raw POME is usually a very viscous brown liquid and voluminous colloidal matters, which contains of 95-96% of water, 4-5% of total solids that consists of suspended solid and last but not least around 0.6-0.7% of oil and grease. Normally, the POME will be discharged from the process pipeline at the temperature of 80-90°C and it is acidic [5]. This POME is a mixture of waste collected and discharged from the three main sources such as clarification wastewater (60%), condensate sterilizer (36%) and hydrocyclone wastewater (4%) [6]. Finally, only about 0.9, 1.5 and 0.1 m^3, respectively, from these three sources will be discharged for the handling out of one tonne of CPO [7].

POME wastewater has become one of major problem to the environment that could give the adverse effect to human and aquatic life, generally. Numerous studies have been done in order to overcome the POME problem, but there are still have a few weaknesses that have to be improvised from time to time. The conventional treatment such as ponding system has low operating cost and more convenient. However, this treatment requires a long retention time and large area to treat the POME [8]. Other treatments available are such as micro and ultrafiltration, coagulation, flotation, biological treatment (including pond treatment) and membrane reactor. The technologies are either inefficient, time consuming, high-cost, complex in operation or highly skilled operator needed. Unfortunately, the efficiency of the oil removal is low and need to be improved by using another alternative method such as through the adsorption method. Adsorption is chosen over other method due to its effectiveness and feasibility [9]. Normally, the POME contains nearly 4000 – 8000 mg/L of oil and grease content. Thus, sometimes the ponding treatment fails to treat the POME and produce the effluent that does not obey the Malaysian Department of Environment (DOE) standard [10]. According to the DOE, the maximum allowable limit of oil and grease amount for POME discharge is 50 mg/L. Thus, it is a crucial scenario that all the palm oil milling industries to find an effective treatment on the oil removal of POME before being discharged to the water river.

Recently, due to the concern on the adverse effect on the environmental, a natural adsorbent has been developed in removing the oil from POME. The commercial adsorbent to treat the wastewater such as activated carbon is based on chemical derivatives, thus may affect the environment and aquatic life. Several papers have reported on the types of natural adsorbent used in the oil removal from POME such as chitosan flakes and powder [11], palm shell activated carbon and palm shell activated carbon magnetic composite [12], sago bark and esterified sago bark [9, 13], natural zeolite [14], chitosan in empty fruit bunch (EFB) filter [15] and modified oil palm leave (OPL) and modified oil palm frond (OPF) [16].

Kenaf (*Hibiscus cannabinus L.*) is a fiber plant which originated with roots in ancient Africa. It has been grown for food and fibre for several thousand years. It is a common tropical and subtropical wild plant of Africa and Asia. The plant stem is consists of 65% inner core fiber and 35% outer bast fiber, generating low and high quality of pulp, respectively [17]. The kenaf crop production is rapid as it has high growth rate and low crop rotation. In a period of 4-6 months, the plant can reach a height ranging from 4 to 5.6 m, where the crop is ready to be harvested during that time. Kenaf also has a very good adaptability to development, where it can survives under a variety climatic conditions and soil types [18, 19]. Kenaf is a good source of raw material fiber to be used as pulp, paper and other fiber products [20]. Recent studies have revealed the potential use of kenaf core and bast fibres for adsorption [21, 22], bioremediation enhancement [23] and also for sound absorption and thermal insulation application [24].

In this research, the adsorption process has been proposed to remove the oil from POME. The adsorption treatment has been chosen due to the high oil removal efficiency, low cost and simple operation. In this adsorption process, the raw kenaf core fibre is used as the adsorbent instead of the common adsorbent such as activated carbon, which is more environmental friendly, low cost and easily purchased due to its availability in worldwide. The objectives of this research are to study the characteristic of raw kenaf core fibre as well as to report preliminary study (the effect of mass of raw kenaf core fibre) as adsorbent to remove oil from POME. To date, there is still no research conducted on the raw kenaf core fibre to be used as an oil adsorbent to remove the oil from POME.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Raw Kenaf Core Fibre

Kenaf stalk was obtained from Lembaga Kenaf dan Tembakau Negara (LKTN), Malaysia. Whole stalks of raw kenaf core fibre were chipped into smaller size using a chipper mill. The chipped raw kenaf core fibre was dried in the industrial oven at 60°C for 7 days to ensure all the moisture were removed.

2.1.2. Palm Oil Mill Effluent (POME)

The POME was collected from the drain coming from the Sime Darby East Oil Mill Pulau Carey, before entering the first treatment pond. The effluent temperature was 90°C (raw POME). POME was filtered through a muslin cloth strainer to separate the solid particles of millimetre size. The POME filtrate was analysed for pH, oil and grease content and total solid. The POME sample was stored at 4°C prior to analysis.

2.2 Characteristics of Raw Kenaf Core Fibre

2.2.1. Fourier Transform Infrared (FT-IR) Spectroscopy

Fourier Transform Infrared Spectroscopy, also known as FT-IR analysis or FT-IR Spectroscopy, is an analytical method used to identify organic, inorganic materials (in some cases) and polymeric compound. The model of FTIR used was Spectrum 100 from Perkin-Elmer (M) Sdn. Bhd. The raw kenaf core fibre was tested for FTIR analysis in order to analyze the functional groups exist in the raw kenaf core fibre.

2.2.2. Scanning Electron Microscopy (SEM) Analysis

The surface morphology of the raw kenaf core fibre was analyzed by using SEM analysis. It was done by using the scanning electron microscope. The model of SEM was S-3400N (Hitachi Brand) from Hi-Tech Instrument Sdn. Bhd.

2.2.3. Preparation adsorbent from Raw Kenaf Core Fibre

The surface The chipped raw kenaf core fibre was ground, washed with distilled water and dried in the oven at 60°C fro 24 hours. Then, it was seived by using stainless steeel seive shaker to the size of 2 mm and kept in the desicator untill further use.

2.2.4. Application of Raw Kenaf Core Fibre on POME

The performance of the raw kenaf core fibre was evaluated based on the oil removal efficiency of raw kenaf core fibre from POME. The raw kenaf core fibre was blend with 100 ml of POME for 30 mins at room temperature (210 rpm). Next, the mixture was filtered and the filtrate was collected prior to the oil & grease testing.

2.2.5. Determination of Oil and Grease content in POME

The solution of HCl:water was prepared with the ratio of 1:1 and then about 2 mL of the solution was added into the filtrate to obtain POME at pH ≤ 2. Then, the filtrate was dried in the water bath for 2 hours to remove the water content in the POME and followed by 1 hour of oven drying at 103°C. The cake of POME obtained from drying was then refluxed by using Soxhlet apparatus for 4 hours in order to extract the oil from POME. The extracted oil was then dried in the oven at 103°C for 4 hours to ensure all the hexane were removed. Finally, the extracted oil was cooled down in the desicator for 30 mins prior to weighing. The oil and grease content or concentration can be calculated based on the equation below:

$$Oil \,\&\, Grease \left(\frac{mg}{L}\right) = \frac{\left[(W_f - W_i)\; x\; 1000\frac{mg}{g}\right]}{V} \tag{1}$$

where W_f and W_i are the final and initial weight of flask, respectively (g) and V is the volume of POME (L).

Meanwhile, to calculate the oil removal efficiency, it can be determined based on the equation below:

$$Oil\ removal\ efficiency\ (\%) = \left[\left(\frac{C_o - C}{C_o}\right)\right] x\ 100\% \tag{2}$$

where Co and C are the initial oil and grease concentration (mg/L) in POME and the oil and grease concentration (mg/L) in the filtrate, respectively [12, 13].

3. RESULTS AND DISCUSSION

3.1. Characteristics of Raw Kenaf Core Fibre

3.1.1. Fourier Transform Infrared (FT-IR) Spectroscopy

Analysis of the FT-IR spectrum provide important information about the molecular structure of the functional groups. The trend of the FTIR spectrum for raw kenaf core fibre contains some main peaks which are almost similar to many lignocellulosic plants.

FT-IR spectra in raw kenaf core fibre showed the presence of strong bond at 3370 cm^{-1} due to O-H stretching, C-H stretching of alkane at 2922 and 2853 cm^{-1} , C=C stretching of ketone (2319 cm^{-1}), C=O stretching of ester (1753 cm^{-1}), C=O stretching of conjugate acid (1703 cm^{-1}). Furthermore, the presence of N-H bending of amine (1594 cm^{-1}), C-H bending of alkane (1459 cm^{-1}), O-H bending at bandwidth of 1421, 1373 and 1326 cm^{-1} and C-O stretching at 1240 cm^{-1} were also noticeable in the spectra [25]. Based on the functional groups described, it was found that the presence of ester group was responsible to capture the oil from POME since ester has a hydrophobic properties [13]. Meanwhile, alkane molecules are non-polar (hydrophobic) [26]. The appearance of alkane (C-H stretching) in the IR spectrum indicates that the raw kenaf core fibre has potential to attract oils and helps to remove the oils from POME.

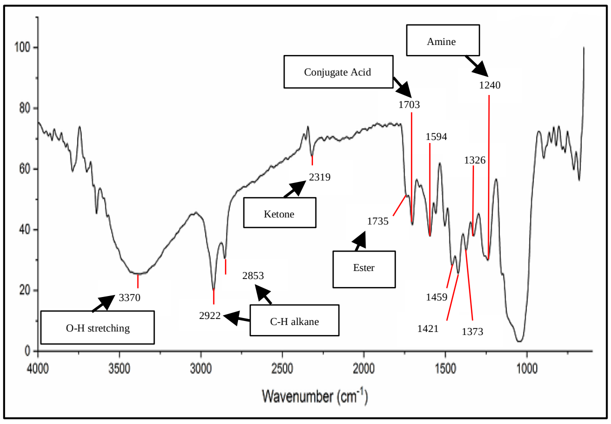

Figure 1 FT-IR spectrum of the raw kenaf core fibre

3.1.2. Scanning Electron Microscopy (SEM) Analysis

SEM is effectively used to study the solid inorganic materials through the microanalysis and failure analysis. Electron microscopy is conducted at high magnifications, produces images with high-resolution and measures very small features and objects accurately.

The surface morphology of raw kenaf core fibre was shown in Figure 2 by using 50x magnification. Based on Figure 2, the random distribution of pores was observed on its surface. However, as the magnification increased up to 100x (Figure 3), the rough surface of raw kenaf core fibre was clearly noticeable. The pores were marked by using arrows. Rough surface morphology and entangle pores structure of sorbent surface are desirable since it linked to high adsorption capacity.

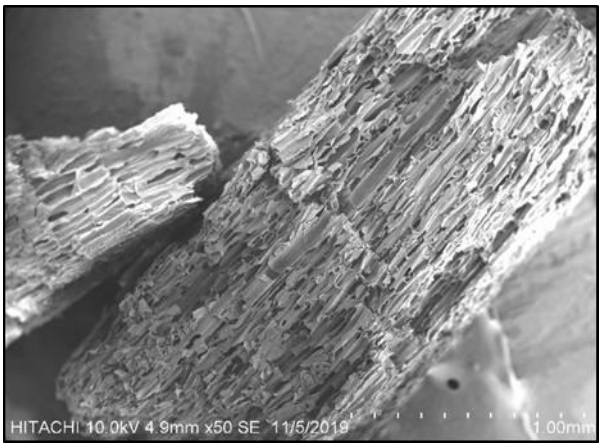

Figure 2 The SEM image of raw kenaf core fibre by using 50x magnification

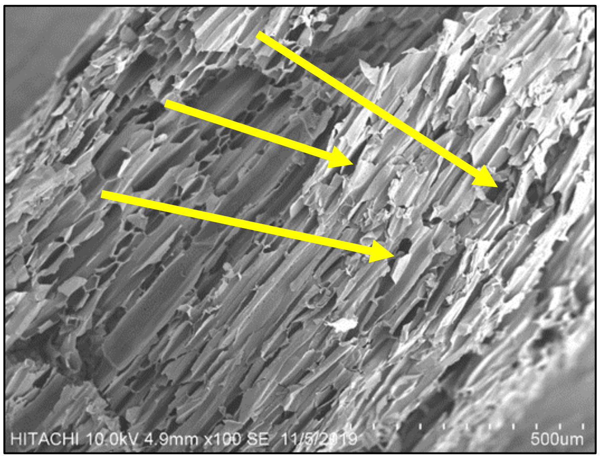

Figure 3 The SEM image of raw kenaf core fibre by using 100x magnification

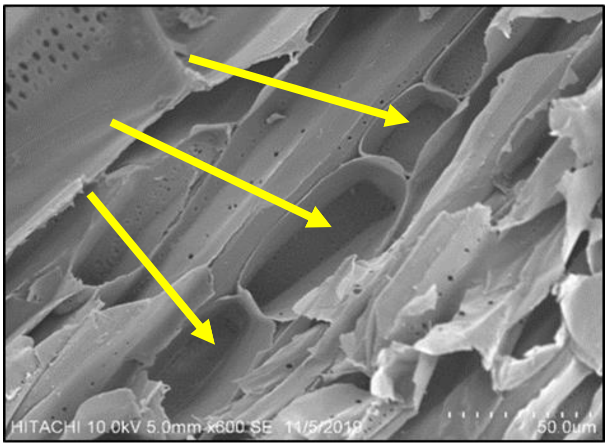

Figure 4 The SEM image of raw kenaf core fibre by using 600x magnification

This is because such a morphology and structure contribute more active sites for oil adsorption rather than smooth surface and increases the adhesion between oil and surface [27, 28].

The larger image of pores was more visible when the magnification was increased to 600x as shown in Figure 4. The arrows shows the most probability location of oil being trapped into the raw kenaf core fibre. The presence of large pores in the raw kenaf core fibre might have facilitated the adsorption of oil towards it, where it captured the oil into the pores.

3.2. Effect of mass of Raw Kenaf Core Fibre towards the Oil Removal Efficiency and Adsorption Capacity

The effect of mass of raw kenaf core fibre used in the oil removal from POME was studied between 1 to 6 g. Based on Figure 5, the oil removal was recorded at 41% when 1 g of raw kenaf core fibre was applied and the percentage of oil removal has been increased continuously as the mass of raw kenaf core fibre increased up to 5 g. The percent of oil removal at 2 g, 3 g, 4 g and 5 g were 48.9%, 63.9%, 75.4% and 78.6%, respectively. The results obtained were slightly higher at each of the mass tested compared to the adsorption of raw sago bark towards the oil from POME [9].

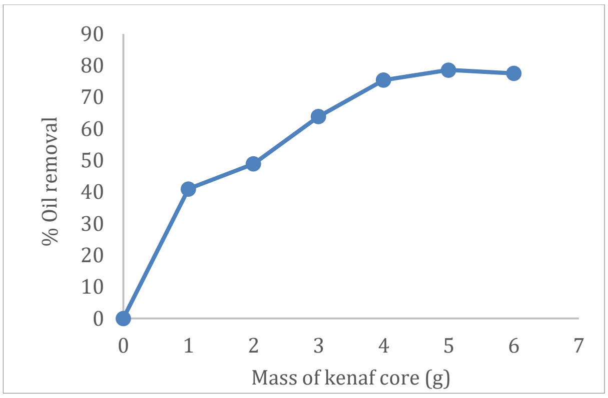

Figure 5 Effect of mass of raw kenaf core fibre in the percentage of oil removal from POME

Sorbent dosage or mass contributes to the increase oil removal efficiency. This phenomenon is correlated with an increase of the binding sites available for adsorption in higher sorbent dosage [11]. Nevertheless, the percentage of oil removal has decreased to 77.5% when the mass increased to 6 g. It showed that the maximum mass of raw kenaf core fibre used in the oil removal from POME was achieved at 5 g with the value of 78.6%. This is due to the saturation effect which can causes a reduction in the efficiency of oil removal when maximum adsorption capacity has been reached [29]. The maximum percentage obtained was higher compared to raw sago bark at similar

dosage of 5 g, which was only 55.5% of oil removal from POME [9].
The effect of mass of raw kenaf core fibre towards the adsorption capacity value is shown in Figure 6. The highest value of adsorption capacity was recorded at 399.0 mg/g by using 1 g of raw kenaf core fibre.

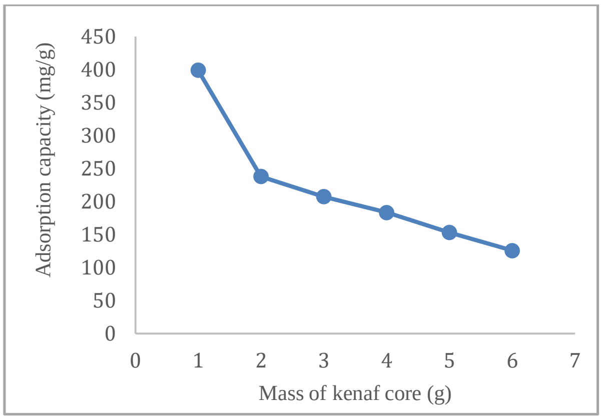

Figure 6 Effect of mass of raw kenaf core fibre in the adsorption capacity value

However, the trend was decreasing as the mass of raw kenaf core fibre increased. The value of adsorption capacity at 2 g, 3 g, 4 g, 5 g and 6 g were 238.0 mg/g, 207.3 mg/g, 183.5 mg/g, 153.0 mg/g and 125.7 mg/g, respectively. The adsorption capacity decreased with an increase in sorbent dosage or mass mostly due to the increased binding sites of unsaturated oil.

4. CONCLUSION

The performance of raw kenaf core fibre as oil adsorbent from POME was investigate in this study. Based on the characteristic testing, the FTIR spectra proved the presence of hydrophobic moieties that facilitated the entrapment of oil on the raw kenaf core fibre. The results obtained was also supported by the SEM image. Rough surface and large pores are important to increase the oil adsorption capacity and oil entrapment in the raw kenaf core fibre, respectively. The effect of mass of raw kenaf core fibre towards the oil adsorption from POME was also being studied. It can be concluded that the mass of raw kenaf core fibre is directly proportional to the percentage oil removal but inversely proportional with the adsorption capacity. This proves that the raw kenaf core fibre can be used as natural potential adsorbent to remove oil from POME. Since this is a preliminary study, the raw kenaf core will be further explored on the effect of pH, time, temperature, initial POME concentration as well as kinetic study.

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