Adsorption of Used Cooking Oil (UCO) by using Raw and Modified Kapok Fibre through Esterification

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Abstract. UCO is one of the domestic wastes in our daily life. Normally, UCO are produced by hawkers, restaurants and household in a large quantity. The UCO usually exist in water mixture and eventually can cause water drainage problem which can lead to the environmental problem. Therefore, in order to overcome this problem, a study was conducted to test the adsorption of RKF and MKF towards the UCO. As for the MKF, the adsorption was tested by using different concentrations of Calcium Oxide (CaO) in percentage during the esterification. The oil removal percentages were calculated for RKF and MKF. Based on the results, it was found that the RKF has adsorbed 25.32g of UCO with a 50.64% of adsorption. As compared to MKF, it was able to increase the hydrophobic properties which resulted more UCO adsorption by 26.78g of UCO with the increment in the adsorption of 53.56% by using CaO of 5 wt% of RKF mass. However, when the percentage of CaO was increased, the UCO adsorption was also increased. The results showed that by using CaO of 10 wt% and 15 wt% of RKF mass, the UCO adsorption was increased to 28.50g (56.84%) and 31.73g (63.46%), respectively. Thus, MKF has higher adsorption of UCO compared to RKF. The highest amount of UCO adsorption has been achieved by using CaO of 15 wt% in the esterification, which was 31.73g corresponded to 63.46%.

1. Introduction
Nowadays, cooking oil has become one of the important element in the food preparation. There are various types of cooking oil such as olive oil, peanut oil, corn oil, coconut oil, canola oil, palm oil, grapeseed oil, avocado oil, sesame oil and etc. Malaysian use 45 million kilograms of cooking oil where each person uses 1.45 kg of cooking oil per month [1]. In Malaysia, most of the oil are derived from the palm oil. In 2008, the production of palm oil was 17.7 million tonnes which has used up about 4.5 million hectares of land in Malaysia. It stated that there was an increasing demand for the palm oil production [2]. Cooking oil usage has led to the arising problem of waste cooking oil which known as the used cooking oil (UCO). UCO could become a serious problem for home plumbing, drainage and wastewater system. Poured UCO down the sink followed by the hot water and soap or through the garbage disposal could cause the UCO to solidify into the thick layers inside the pipelines which will led to the water flow constriction and water backflow. The UCO could also eventually flow into the river and stream, causing environmental problems together with odor pollution. The treatment of the water drainage problem due to the UCO are very expensive. On the other hand, there are some operators reused the cooking oil which can cause health problem [3].

In order to overcome this problem, an alternative method has been chosen instead of the expensive treatment. Natural fiber, which is a renewable source has a good thermal properties, good insulating properties and environmentally friendly [4]. Based on the findings, these properties are present in raw kapok fiber (RKF) which makes it a good source in oil retention. However, natural fiber has low hydrophobicity and low buoyancy. Through numerous studies, the natural adsorption of RKF can be
enhanced by chemical alterations such as acetylation [5]. Modification of the natural fiber could increase the desirable characteristic such as high hydrophobicity, good buoyancy and low cost. Acetylation alters the RKF surface characteristic from smooth into rough surface as the rougher surface enables exposure of larger surface area for adsorption which enables higher interfacial hydrophobicity. Figure 1a shows the ripe kapok pod.

Apart from acetylation, another method of chemical alterations is through the esterification. Esterification is a process where an ester bond is formed by the reaction between carboxylic acid and alcohol. A carboxylic acid is a group that contains –COOH group whereas in ester, the hydrogen in group is replaced by hydrocarbon group [6]. For example, the oil adsorption by using the sawdust and sugarcane as adsorbent, respectively, had been increased by using the esterification modification. The adsorption was increased by the replacement of O-H functional group in the fibers with C=O and C-O group [7]. On the other hand, sago bark (SB) had been used in the removal of oil from palm oil mill effluent (POME). The adsorption was increased by the modification SB into esterified sago bark (ESB). The results showed that ESB has higher oil removal efficiency because the modification gives rougher surface and more exposure of the internal structure with the oil entrapment sites. In addition, calcium oxide (CaO) was used as a catalyst in the esterification. The CaO was able to neutralize the negative zeta potential of oil in POME and resulted in the reduction of electrostatic repulsion that allows more oil droplets coalescence [8].

Since RKF naturally adsorbs oil, conducting chemical alteration through esterification by modifying the RKF into modified kapok fiber (MKF) could enhance the adsorption of oil. Thus, it is expected that the oil adsorption is higher in the MKF compared to RKF. A few samples of MKF were prepared based on different concentration of catalyst, CaO added in the esterification reaction.

2. Experiment

2.1. Esterification of Kapok Fiber
The sample of RKF was purchased. In the esterification, the chemicals involved were stearic acid (SA), Calcium oxide (CaO) and ethyl acetate (EA). 1g of raw kapok fiber (RKF) was weighed and the ratio of SA to kapok fiber was measured at 1:1. Then, CaO of 5 wt% of RKF mass was added. The mixture was mixed in a beaker of 150 ml. Next, 100 ml of EA was added into the mixture and transferred into the round bottomed flask. Lastly, the mixture was set as in Figure 2 (reflux condensing method) with the magnetic stirrer rotating at 150 rpm and temperature of 85 °C [8]. The reflux was operated for 5 hours. The esterification reaction were repeated for CaO of 10 wt% and 15 wt% of RKF mass, respectively.
2.2. Mixture Preparation of the Used Cooking Oil (UCO) and Water

50g of UCO was mixed with 50mL of tap water. The mixture obtained was homogenized for 10 minute by using a magnetic stirrer at 150 rpm.

2.3. Measurement of Oil Adsorption Capacity

1g of dried sample of RKF was weighed to obtain $W_i$ (weight of the initial sorbents). Then, the sample was mixed with the oil and allowed to be immersed in the oil mixture at the room temperature for 30 minutes. Next, the RKF was drained and wiped with filter paper to remove the excess oil from the bottom of the drainer. The oil adsorption capacity of the sample was determined from the calculation based on the equation below:

$$Q = \frac{W_t - W_i - W_w}{W_i} \times 100$$  \hspace{1cm} (1)

Where $Q$ is the oil sorption capacity of the sorbents, calculated as grams of oil per gram of sample. Meanwhile, $W_i$ is the weight of the wet sorbent after draining (g) and $W_w$ is the weight of the water adsorbed in the sorbent (g). The water content was determined by extraction separation method by using n-hexane as the solvent.

3. Results and Discussion

3.1. The Comparison of the Oil Adsorption Capacity between RKF and MKF

RKF naturally has oil adsorption ability due to its hydrophobic surface and huge hollow lumen. In the previous research, RKF was used in the treatment of oil-containing wastewaters [9]. RKF is a type of cellulosic fibre, where its structure consists of hydroxyl group which limits their oil adsorption as it behaves to more hydrophilic [10]. Thus, to enhance the adsorption of RKF, chemical modification was conducted to check whether the UCO adsorption can be enhanced by using esterification method. Figure 1b shows the comparison of the submerged RKF and MKF, respectively, in the water for UCO adsorption test.
Stearic acid is a type of carboxylic acid with a chemical component of $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ that contains carboxyl functional group which is $-\text{COOH}$. Stearic acid was chosen in the esterification due to the reason of having 18 carbon chain, which contribute to the higher hydrophobic properties [11]. From the results, it showed that RKF adsorbed 25.32 g of UCO, gave about 50.64% of adsorption. Next, the MKF by using CaO of 5 wt% of RKF mass was tested in UCO water mixture. Based on Figure 3, the results showed that the MKF adsorbed higher amount of UCO, which contributed 26.78 g (53.56%) as compared to RKF. Thus, it showed that the hydrophobic properties of RKF had been increased due to the chemical alteration by the replacing of O-H group in the RKF with the carbonyl group, C=O and carbon-oxygen bond, C-O after the esterification reaction [7].

3.2. Effect of CaO (wt%) in the UCO Adsorption by using MKF

The MKF was performed by refluxing the RKF with stearic acid (SA), calcium oxide (CaO) as a catalyst and ethyl acetate (EA). The samples were prepared at three different CaO concentrations, namely, 5 wt%, 10 wt% and 15 wt% of RKF mass, respectively. The function of CaO was to allow more chemical alteration on the RKF surface due to the high catalytic activity at mild reaction condition. The advantage of using CaO as a catalyst in this research was due to its long catalyst lifetime and low in cost [12]. Based on Figure 4, the adsorption of UCO increased as the concentration of CaO increased as compared to the RKF. This was supported by the amount of the UCO adsorption by using CaO of 5 wt%, 10 wt% and 15 wt% of RKF mass, which were 26.78g (53.56%), 28.51 g (56.84%) and 31.74g (63.46%), respectively.

Based on the results of esterification reaction, the presence of O-H group in RKF was replaced by the hydrophobic group from SA onto the surface of MKF. Moreover, the increment adsorption of UCO was due to the negative zeta potential in UCO, which was neutralized by the calcium ions of calcium oxide in the MKF. The neutralization of charge resulted in the reduction of electrostatic repulsion and consequently enhanced the UCO droplets coalescence [8]. Thus, the higher concentration of CaO leads to the higher reduction of electrostatic repulsion in MKF, which allowed the adsorption of UCO to increase in the 5 hour time span and caused more available binding site for UCO adsorption.
Figure 4: Comparison of the amount of UCO adsorption using RKF and MKF at 3 different concentrations of CaO

Figure 5 shows that the adsorption of the MKF towards the UCO has been increased with the increasing of amount of concentration of CaO added in the esterification reaction. Therefore, the CaO concentration can affects the conversion of RKF surface to be more hydrophobic and eventually increased the adsorption of UCO.

Figure 5: Comparison of the amount of UCO adsorption by using 3 different concentrations of CaO

4. Conclusion
Study on adsorption capacity shows that the RKF was able to adsorp UCO up to 25.32g with a 50.64% of adsorption. The adsorption was due to kapok fibre surface which has hydrophobic properties. However, chemical alteration by esterification of RKF to convert to MKF was able to increase the hydrophobic-oleophilic properties by replacing more O-H group with C=O and C-O group which resulted more UCO adsorption by MKF up to 26.78g with increment in the adsorption up to 53.56% using CaO of 5 wt% of RKF mass. Meanwhile, by comparing the adsorption of MKF by using different concentrations of CaO, it can be concluded that increasing the CaO concentration has reduced the electrostatic repulsion and increased the UCO adsorption. This was supported by the results obtained by using CaO of 10 wt% and 15 wt% of RKF mass, which were 28.50g (56.84%) and
31.73g (63.46%), respectively. In conclusion, MKF performed better than the RKF in the UCO adsorption. Among the amount of CaO concentrations tested, using the CaO of 15 wt% of RKF mass gave the highest amount of UCO adsorption. For future study, it is recommended to increase the CaO concentration in the process of modifying RKF into MKF in order to maximize the potential of MKF in UCO adsorption.

Acknowledgments
The author would like to acknowledge the Faculty of Chemical Engineering, Universiti Teknologi MARA, Shah Alam for the financial support and lab facilities. A special thanks to my supervisor, Madam Nor Halaliza Alias for giving the support and opportunity during the whole process of doing the research.

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