Removal of Oil and Grease in Wastewater using Palm Kernel Shell Activated Carbon

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Abstract. Oil and grease wastewater is produced from many sources such as industry and municipal. The discharge of oil and grease in wastewater system causes bad effect towards the environment and wastewater system itself. Palm Kernel Shells (PKS), an agricultural waste was chosen to see its ability in removing oil and grease in wastewater. The PKS was carbonized at 400 °C, activated with KOH and carbonized again at 800 °C. The parameter affecting oil and grease removal such as different oil and grease concentration, contact time and flow rate were studied. The oil and grease removal study was conducted by the column adsorption method and followed by the gravimetric method to identify the remaining oil and grease. PKS activated carbon shows maximum removal of 99.89% at flow rate 1mL/min after 6 hours contact time with 5% w/v initial concentration of wastewater. SEM micrograph of PKS activated carbon after adsorption of oil and grease shows that oil and grease has covered the pores of the surface of the PKS activated carbon. Overall, the PKS activated carbon has the ability in removing oil and grease which indicates that PKS can be used as an alternative treatment in removing oil and grease.

1. Introduction
Quality of rivers have deteriorated over the years and evolved into global pollution [1]. Industrial, agricultural, and urban activities are channelling their waste irresponsibly into the streams [2,3,4]. Oil and grease contaminate the wastewater by the sources of crude oil productions, oil refinery, petrochemical industry, metal processing, compressor condensates, lubricants, cooling agents, car washing and also restaurants operations [5]. Waste generated containing oil and grease is generally classified as hazardous pollutants especially when the waste is being flow into aquatic environment. The oil and grease will form a layer on the water surface thus decreases the biological activity of the natural treatment process. Skimming tanks and oil and grease traps in treatment plants are other conventional techniques in removal of oil and grease. These treatments do not seem to be working as they have low efficiency in removing the oil and grease. then increase the cost in maintenance and inspection of the pipes [6]. Activated carbon seems to be the alternative of the high cost conventional techniques in removing oil and grease in wastewater. Activated carbon has the properties of thermo-stability, high performance, high adsorptive effect, large surface area and well-developed structure [7]. Agricultural waste such as banana peel also has been proved to treat oil and grease [8]. Activated carbon prepared from agricultural product such as kenaf core fiber [9], rubberwood sawdust [10], foxtail palm fruit [11] and palm kernel shell [12] will reduce the cost of activated carbon production. In this study, palm kernel shell is chosen as the materials that the activated carbon will be produce from which is produce from the palm oil industry and is considered as an agricultural waste. The palm oil industry in Malaysia
generates large amount of the palm kernel shell [13] and this enable the usage of the activated carbon from palm kernel shell as it is easily to be obtained.

2. Materials and Methods

2.1 Oil and Grease Wastewater Characterization
The oil and grease wastewater samples were collected from fish cracker industry located at Tumpat, Kelantan. The collected wastewater was undergone the gravimetric method analysis to determine the concentration of oil and grease. The wastewater sample was spiked with used cooking oil (1%, 5% and 10%) because the concentration of oil and grease in the wastewater sample was below than the standard discharged which listed under the Environmental Quality Act, 1974.

2.2 Wastewater In-situ Analysis
The parameter of temperature, total dissolved solid, pH, salinity and dissolved oxygen (DO) were analysed in-situ using YSI Multiparameter.

2.3 Preparation of Palm Kernel Shell Activated Carbon
Palm Kernel Shell (PKS) was collected from palm oil plantation mill, Kelantan. The PKS was washed, dried under the sun until fully dried and was crushed into smaller pieces and sieved (2.36 mm). Sieved PKS was placed into crucible and was closed with its lid and wrapped with aluminium foils and placed into muffle furnace and carbonized at 400 °C for 1 hour. 3M of KOH solution was used to soak the carbonized PKS with the ration of 1:1. The mixture of carbonized PKS and KOH solution was placed on a hot plate at the temperature of 80 °C and was continuously stirred for 2 hours. After 2 hours, the PKS and KOH solution mixture was filtered and was dried overnight in oven at 120 °C. The dried sample was cooled at room temperature and was washed until the pH7 was obtained using hot distilled water. After obtaining pH7, the sample was dried in the oven at 120 °C, cooled and stored.

2.4 Column Adsorption Set up
The column adsorption set up consists of retort stand to hold the column in place and a peristaltic pump to control the flow rate of the wastewater. A tube was connected to the source of the wastewater to the column through the peristaltic pump. The height of the PKS activated carbon was kept at constant height of 10 cm throughout the experiment. A set up without the PKS activated carbon present in the column was also conducted as a control.

2.5 Adsorption Analysis

2.5.1 Effect of Different Concentration of Oil and Grease in Different Time
The wastewater was spiked with used cooking oil into 1% w/v, 5% w/v and 10% w/v oil concentration. The spiked wastewater (1% w/v oil concentration) was pumped into the column that was filled with PKS activated carbon. The height of the PKS activated carbon was measured at 10 cm and was kept constant throughout the adsorption process. The wastewater flow rate was kept constant at 1 mL/min and the experiment was run 24 h time. The wastewater that passed through the column was collected at every 2 hours until 24 hours and followed by analysis using gravimetric method. The similar experiment was continued with the different oil and grease concentrations (5% w/v and 10% w/v) respectively.

2.5.2 Effect of Different Flow Rate
The optimum concentration oil and grease wastewater (5% w/v) was pumped into the column that was filled with PKS activated carbon. The flow rate of the oil and grease wastewater was set into 1 mL/min,
3 mL/min and 5 mL/min. The wastewater that flowed through the column was collected and was analysed using gravimetric method.

### 2.6 Gravimetric Method

Concentration of oil and grease before and after treatment was determined using gravimetric method. The wastewater was extracted with n-Hexane. Hydrochloric acid solution (HCl) was added with the ratio of 1:1 to decrease the pH to 2 or less and act as sample preservation. The mass of the round bottom flask was weight immediately using analytic electronic balance. The extraction process was done three times using a separating funnel and n-hexane was used as a solvent. The final extracted solution was undergone distillation process in order to remove the n-hexane from the solution. The solution was oven dried at 105 °C overnight to remove water from the round bottom flask [8]. The residue in the round bottom flask was weighed using analytic electronic balance. To obtain constant weight the round bottom flask was weighed a few times with heating it for 10 minutes in the oven and was left for 30 minutes to cool. The percentage (%) removal of oil and grease in the wastewater will be calculated by the following equation:

\[
\text{Percentage removal of oil (\%) = } \frac{C_i - C_f}{C_i} \times 100
\]

(Equation 1)

Where Ci was represented as the initial reading of the sample, Cf was the final reading of the sample.

### 2.7 Characterization of Activated Carbon using Scanning Electron Microscopy (SEM)

The morphological view of raw PKS, PKS activated carbon before and after treatment were analysed using SEM. Before the samples were characterized, the samples were dried to remove any moisture on the surface of the samples and coated with platinum before analysis.

### 3. Result and Discussion

#### 3.1 In-Situ Analysis of Wastewater

The readings of the in–situ analysis of the wastewater was done by using YSI Multiparameter to obtain the parameter stated in Table 1.

**Table 1.** The in-situ analysis of the wastewater

| Parameter          | Readings |
|--------------------|----------|
| Temperature, °F    | 76.43    |
| Total Dissolved Solid, % | 1.597  |
| Dissolved Oxygen, % | 3.2     |
| pH                 | 5.6      |
| Salinity           | 1.29     |

In comparison to the elements under the discharged standard by the Environmental Quality Act, 1974 the in-situ analysis shows that most of the element passed the discharged standard B. The total dissolved solid was relatively low at 1.597% which passed the standard A discharge which must be less than 50%. pH passed the standard B of discharged standard with the readings of 5.6.

#### 3.2 Adsorption Analysis

**3.2.1 Effect of Different Concentration of Oil and Grease with Different Time**

Figure 1 shows the percentage removal of oil and grease with different initial oil and grease concentration within 24 hours at flow rate 1 mL/min.
Figure 1. Percentage removal of oil and grease, % against time, hour.

For concentration of 1% w/v oil and grease, the highest percentage removal was 99.93% after 20 hours where the oil and grease concentration remain in the wastewater was 4 mg/L. This amount can be directly discharged to the river because it was below Standard B where a maximum of 10 mg/L is allowed. The 20 hours’ time can be said as the optimum time in removing oil and grease for the 1% w/v oil and grease concentration as it shows the highest percentage removal. The optimum contact time for oil and grease removal at 5% w/v oil and grease concentration was at 6 hours’ time as it shows highest percentage removal (99.89%). For 10% w/v oil and grease concentration, the maximum removal was 99.87% after 2 hours contact time but it reduces to 73.04% after 24 hours might be due to saturation level of activated carbon.

It was found that as the contact time was longer, the rate of oil and grease removal also increase. This was due to in the beginning, the present of active sites in activated carbon. So, as the contact time increased, the active sites on the adsorbent were filled with oil molecule. However, with the increase of contact time, the adsorption sites start to reduce due to oil molecules begin to fill the adsorption site [14]. This is when a second phase start, the slow phase adsorption where adsorption still occurs but at slow adsorption [15].

3.2.2 Effect of Different Flow Rate.
Oil and grease removal with different flow rate was shown in Figure 2. Experiments were conducted for maximum 6 hours contact time at 5% w/v.

Figure 2. Percentage removal of 5% oil and grease concentration with different flow rate.

From Figure 2, it shows that column flow rate of 1 mL/min show the highest removal among other flow rate. The highest percentage removal is at 6 hours with 99.89%.
Flow rate of 1 mL/min show the highest percentage removal compared to 3 mL/min and 5 mL/min which can be seen clearly from Figure 2. Oil and grease removal are more efficient at slower flow rate in comparison with the higher flow rate [16].

3.3 Characterization of PKS Activated Carbon using Scanning Electron Microscopy (SEM)

The raw PKS, activated PKS before and after treatment were analysed using SEM to see the surface morphology. The Figure 3 shows the surface of the raw PKS sample has no visible pores on its surface. The raw PKS show smooth with some rugged surface presence [17].

Figure 3. The SEM image of raw PKS (5000x magnification)

Figure 4 show the PKS activated carbon that has been carbonized at high temperature and activated using KOH as the activation agent. The SEM image show the surface of the activated PKS has numbers of pores. The pores are irregular in shaped and some pores are unusually large [18]. The surface also shows burn out pores with tunnel or honeycomb like structure [19]. These pores are likely to be appeared by the carbonization and activation process that the raw PKS undergoes. The carbonization at high temperature and activation using KOH leads to the pores structure to be present at the surface of the PKS activated carbon. The well-developed porous structure with the regular pores size shows the activation has taken place

Figure 4: The SEM image of activated PKS (5000x magnification)

Figure 5 show the PKS activated carbon that has been used for the removal of oil and grease. The figure shows the pore which seems to be the oil and grease has covered the pores on the surface of the PKS activated carbon. It shows the adsorption of the oil and grease onto the surface of the PKS activated carbon surfaces.
4. Conclusion
This study shows that the PKS activated carbon in the column have capability in removing the oil and grease in the wastewater. PKS activated carbon shows maximum removal of 99.89% at flow rate 1 mL/min after 6 hours contact time with 5% initial concentration of wastewater.

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