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Removal of Emulsified Oil in Wastewater by Corn Cob Carbon

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Abstract. Oil pollution is a serious environmental concern which is caused by rapid industrial development around the world. In this study, corn cob carbon was used as a natural adsorbent for emulsified oil wastewater remediation. Three parameters that were studied include contact time, dosage of corn cob carbon and concentration of emulsified oil wastewater. The physical and chemical structures of raw and corn cob carbon were characterized. The corn cob carbon showed good efficiency in emulsified oil removal with a percentage of 96% at 2 hours contact time, 1 g of corn cob carbon and 5% of emulsified oil wastewater concentration. The apparent porosity of corn cob carbon was the reason for the sinking of emulsified oil particles absorbed on the surface of corn cob carbon. TGA shown 3.60% and 58.17% of mass loss within the first and second thermal decomposition, respectively. The functional groups of corn cob samples are C-H, -C≡C-, C=C, -C-H and C-O. SEM analysis showed that pores were found in the corn cob carbon and a layer of oil was present on its surface after the adsorption process. Therefore, corn cob carbon could be considered as an alternative to remove emulsified oil in wastewater due to its good adsorption capacity and low secondary pollution.

1. Introduction

Improper discharge of oil during various stages of its production, transportation and utilization from domestic or industrial effluent cause oil pollution. The high organic and inorganic content present in the effluent of oil pollution lead to serious environmental effects, posing as a threat towards aquatic and terrestrial life [1]. According to the Fifth Schedule paragraph 11(1)(a) under the Environmental Quality (Industrial Effluents) Regulations 2009, the acceptable condition for Standard A and B are 1.0 mg/L and 10 mg/L respectively. Therefore, treatment for oil pollution from industrial effluent is essential prior to its disposal. Moreover, among the existing methods for oil removal, adsorption showed greater performance through low-cost adsorbing materials such as biomass [2].

Agricultural wastes have been converted and value-added to act as natural sorbents [3,4]. A natural adsorbent is cheap, environmentally friendly and can be conducted easily such as corn cob carbon. It is lightweight, non-allergic, non-toxic, biodegradable and odourless. The high buoyancy and developed pores of corn cob contributes to its recent utilisation as an oil sorbent [5]. Corn cob carbon that goes through adsorption process causes oil particles to adhere on its surface. The high viscosity of oil leads to the formation of a thick layer on the surface of sorbents. Therefore, it is deemed as a simple alternative solution for small food factories for the treatment of oil wastewater.

2. **Materials and Methods**

2.1 Materials

The emulsified oil wastewater was obtained from a fish cracker factory at Kelantan, Malaysia and characterized through in-situ analysis and ex-situ analysis. The wastewater stock solution was diluted to several concentrations: 5%, 10%, 15%, 20% and 30% by using a blender (Model ELB-A1812G (SS)). N-hexane (95% pure, Bendosen) was used as a solvent in this experiment. Corn cob was acquired from local stalls.

2.2 Preparation of Corn Cob Carbon

Raw corn cobs (RCC) were rinsed with distilled water to remove any impurities. They were then oven-dried at 50 °C for 24 hours. After that, they were cut into small pieces and blended by using a blender into a maximum size of 2.18 mm. The raw corn cobs were carbonized by using a furnace at 450 °C for 2 hours. Later, they were rinsed thoroughly and oven-dried at 105 °C overnight. The corn cob carbon was placed in a sealed bag and stored in a desiccator for further experiments.

2.3 Batch Adsorption

The experiment was conducted in a 250 ml conical flask with 100 ml emulsified oil wastewater solution using corn cob carbon. The concentrations of emulsified oil wastewater solution that were prepared include 30%, 20%, 15%, 10% and 5%. These concentrations were treated separately with 1 g, 2 g and 3 g of corn cob carbon in the orbital shaker (Model SI-300/300R/600/600R, JIEO TECH, Korea) at various contact time: 1 hour, 2 hours, 4 hours, 8 hours, 16 hours and 24 hours. After that, the corn cob carbon was filtered out from the conical flask using filter papers. The amount of oil before and after the experiment was determined by the gravimetric method. All adsorption experiments were performed in duplicates and the average values obtained were used for data analysis. A control removal without the usage of corn cob carbon was prepared for every parameter to calculate the percentage of removal by using filter paper. The sample removal is known as the removal of emulsified oil wastewater with the use of corn cob carbon.

After that, the filtrate was analysed for oil concentration using gravimetric method with oil extraction solvent, n-hexane. The adsorption uptake of emulsified oil adsorbed (q_t, mg/g) was calculated in Eq. 1:

$$q_t = \frac{C_o - C_i}{m} V \quad (1)$$

Where C_0 and C_i (mg/L) were initial and final emulsified oil mass concentration, V (L) was the volume of the wastewater sample and m (g) was the mass of corn cob carbon used.

2.4 Gravimetric method

Gravimetric method is an analytical method to measure mass or change in mass. It is one of the few definitive techniques that require values to be in SI unit [6]. Through gravimetric method, the remaining filtered wastewater was extracted by n-hexane. Hydrochloric acid solution (HCl) was added at a ratio of 1:1 as a sample preservation step to decrease the sample pH to 2. The remaining emulsified oil wastewater after filtration was extracted by using n-hexane. Then, extraction was carried out four times in the separatory funnel. After the extraction process, the residual oil was collected in the round-bottom flask and underwent distillation to remove the n-hexane. The sample was oven dried at 105 °C overnight to evaporate excess water from sample. Then, the sample was weighed by using analytic electronic balance. The empty round-bottom flask must be weighed to calculate the amount of residual oil.

2.5 Determination of emulsified oil removal

The percentage of oil removal by corn cob carbon was calculated by using Eq. 2.

$$Percentage\ oil\ removal\ (\%) = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

C_i represented the initial concentration of the sample while C_f was the final concentration of the sample.

2.6 Characterization of Corn Cob
The raw corn cob, corn cob carbon before and after adsorption were characterized in terms of their physical and chemical structures through thermogravimetric analysis (TGA), Fourier Transform Infrared Spectrometer (FTIR) and Scanning Electron Microscope (SEM). The corn cob carbon after adsorption was oven-dried overnight at 105 °C for the characterization analysis. All the corn cob samples were prepared in powder form for the FTIR characterization process. For TGA and SEM, all the characterized samples were prepared in their original form.

3. Result and Discussion

3.1 Wastewater Sample Analysis
Table 1 described the physical and chemical parameters for the wastewater. The BOD, pH and ammoniacal nitrogen were normal since the parameters did not exceed the limits established by DOE. Dissolved oxygen recorded was also good and did not cause any harmful effect to the water body. There are three parameters that exceeded the threshold critically which were COD, suspended solids and Oil and Grease (O&G). Suspended solids recorded 327 mg/l compared to 100 mg/l limit allowed by DOE. COD and O&G recorded values of 3415 mg/l and 3383 mg/l compared to the 100 mg/l and 10 mg/l DOE limits, respectively. The high levels of O&G content was a result of the cooking oil used during the boiling process which in turn led to a high level of COD [7].

Table 1. Wastewater analysis

| Physio-chemical Parameter	Average Reading	EQR (Industrial Effluents) Standard B
pH Value	9	5.5-9
BOD_5 (mg/L)	37	40
COD (mg/L)	3415	200
Suspended Solid (mg/L)	327	100
Dissolved oxygen (%)	17.75	-
Ammonical Nitrogen (mg/L)	15	20
Oil and Grease (mg/L)	3383	10

The water samples containing high suspended solids, BOD and ammoniacal nitrogen content were classified as Class V water which is high polluted water with no other utilization.

3.2 Characterization of Corn Cob Carbon
TGA analysis, scanning electron microscopy and Fourier Transform Infrared (FTIR) were applied to determine the surface morphology as well as structures of the carbon. Figure 1 displayed the TGA profile of the raw corn cob between 0-1000°C in nitrogen atmosphere.

The raw corn cob underwent three stages of thermal decomposition. Firstly, 3.598% of the mass was lost within 30 °C to 150 °C moisture loss at this stage [8]. Secondly, a significant mass was lost at 58.174% from 180 °C to 550 °C due to the degradation of raw corn cob and distillation of oleophilic material [5]. Moreover, the sudden increase in mass loss was due to the release of volatile components such as CO, CO_2 and other hydrocarbons [9]. Lastly, there were mass losses after 550 °C. The main thermal decomposition of the raw corn cob was because of its intrinsic hemicellulose, cellulose and lignin. The pyrolysis temperature of hemicellulose is 200-280 °C, cellulose at 280-380 °C and lignin at 380-500 °C [10]. Ceylan and Topgyu [11] supported this finding and stated that pyrolysis of biomass occurred in three stages which include dehydration, thermal decomposition of main components and steady decomposition of lignin. The first stage takes place at a temperature below 122 °C mainly involved moisture removal. The thermal decomposition at temperature between 122 °C to 550 °C

involved a high amount of volatile formation. Finally, the decomposition of tar occurred at a temperature higher than the second stage.
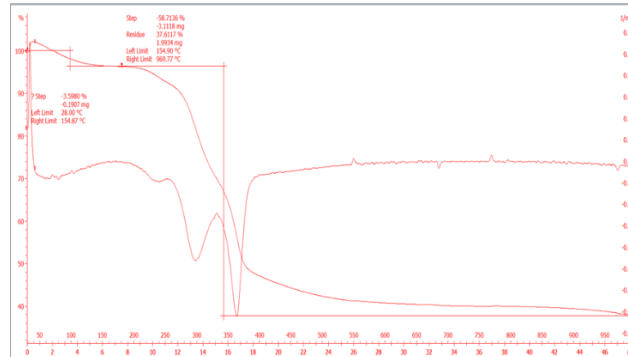

Figure 1. TGA curve of raw corn cob

Figure 2, 3 and 4 showed the surface morphological structure of raw corn cob, corn cob carbon before and after adsorption of emulsified oil. The SEM analysis of corn cob samples was conducted at accelerating voltage of 10 kV and 1500x magnification. In Figure 2 there were irregularities and no pores observed on the raw corn cob surface. In Figure 3 some pores existed after formation of corn cob carbon. These results were supported by Ismail [12] who stated that the raw corn cob has no pores and displayed cellular texture with improper pore structure. The formation of some pores can be developed and further enhanced during pyrolysis. Kumar [13] claimed that pyrolysis of carbon released volatile materials, consequently creating holes and porous structure on the carbon. Thus, this porous structure contributes to extra adsorption sites for adsorbates of interest. After the adsorption process, a sticky layer can be observed on the corn cob carbon surface as presented in Figure 4. Porosity was apparent in corn cob carbon due to the sinking of emulsified oil particles absorbed by the biological absorbent [14].
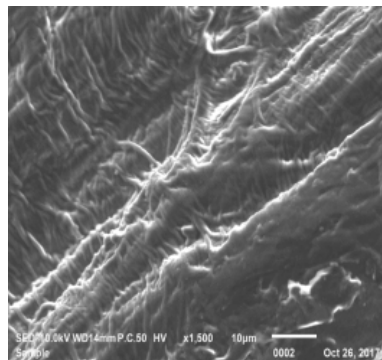
Figure 2. Surface morphological structure of raw corn cob
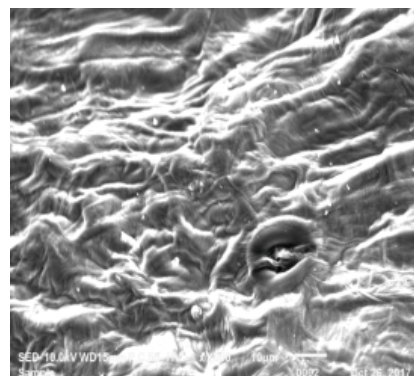
Figure 3. Surface morphological structure of corn cob carbon before adsorption
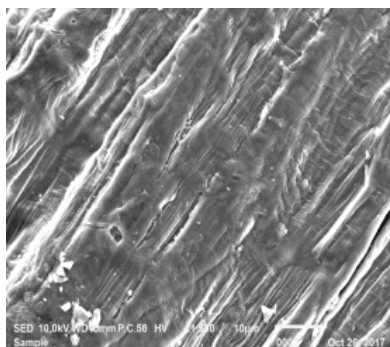
Figure 4. Surface morphological structure of corn cob carbon after adsorption

The descriptions of the chemical structures of corn cob carbon before and after adsorption verified the possible functional groups in its binding mechanism. The functional data were tabulated in Table 2.

Table 2. Functional groups in corn cob samples.

| Functional Group	Corn Cob Carbon Before Adsorption (cm^{-1})	Corn Cob Carbon After Adsorption (cm^{-1})
Alcohol (O-H)	3323	3338
Stretching Alkane (C-H)	2916	2915
Alkyne (-C≡C-)	2116	2118
Aromatic (C=C)	1578	1581
Alcohol (C-O)	1120	-
Acid Anhydrides (C-O)	1120	1170
Alkyl Halide (C-Cl)	745	743
Alkyl Halide (C-Br)	574	592

Firstly, comparisons on the spectra were made for corn cob carbon before and after the adsorption process. FTIR spectra of carbonized corn cob before and after adsorption were similar but with several band shifts. Shift of bands in the functional groups showed that they were involved in the adsorption process [15]. Absorption peaks at 3323 cm^{-1} in carbon before adsorption and it shifts to 3338 cm^{-1} after the adsorption indicated the presence of the O-H group [16]. Minor peak shifts from 2916 cm^{-1} to 2915 cm^{-1} indicated the stretching of C-H group in the carbon [17]. Peaks at 1578 cm^{-1} shifted to 1581 cm^{-1} corresponded to the existence of aromatic C=C group. Absorption peaks at 1120 cm^{-1} for alcohol C-O group lost its intensity after the adsorption process. Acid anhydrides were determined by peaks at 1120 cm^{-1} that shifted to 1170 cm^{-1}. Peaks at 745 cm^{-1} shifted to 743 cm^{-1} and 574 cm^{-1} to 592 cm^{-1} indicated alkyl halide C-Cl and C-Br functional groups, respectively.

Bansal & Goyal [18] reported surface acidity that is influenced by the presence of carbonyl functional group were responsible in determining adsorption capacity of oils or referred to as natural organic matter (NOM). High presence of carbon-oxygen functional group led to the increase in surface hydrophilic condition which makes adsorption of lipids unfavourable. Thus, by decreasing the amount of carbon-oxygen functional group and increasing the hydrophobic state on the carbon surface helps in adsorption capacity of the NOM.

3.3 Batch Adsorption Experiment

3.3.1 Effect of different concentrations of oil wastewater
Figure 5 showed the percentage of emulsified oil removal using different concentrations of emulsified oil wastewater.
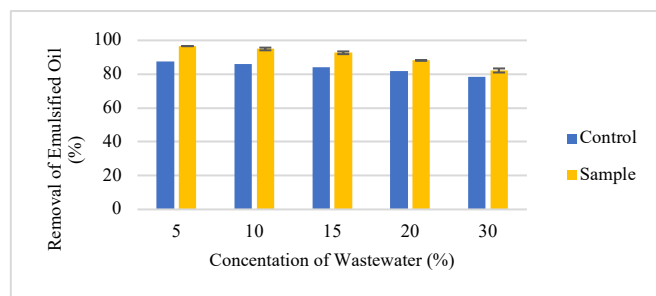
Figure 5. Comparison between the emulsified oil removal of control and sample experiment in different concentrations of wastewater

The percentage of emulsified oil removal declined slightly due to the increase in emulsified oil wastewater concentration from 5% to 30%. The removal percentage for control experiment dropped from 87% to 78% while the removal for sample experiment declined from 96% to 82%. The reason for the reduction in oil removal is because of the saturation of active sites by the adsorbates at higher concentration onto the adsorbents surface. In addition, a prominent decreasing trend was observed in Figure 6 which justified the decrease in oil adsorption uptake with increasing initial concentration of emulsified oil wastewater. This finding was in line with a study by Olufemi [19] which also reported a reduction of emulsified oil uptake via adsorption with higher concentration of emulsified oil wastewater due to fewer adsorption sites at higher oil concentration.
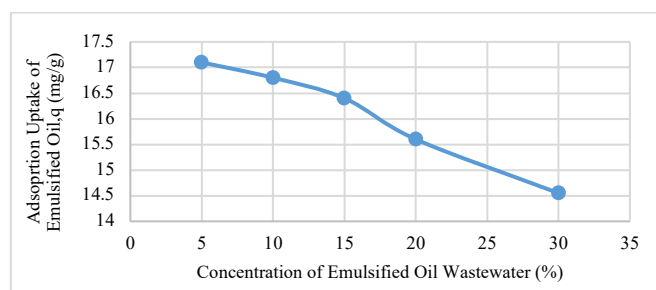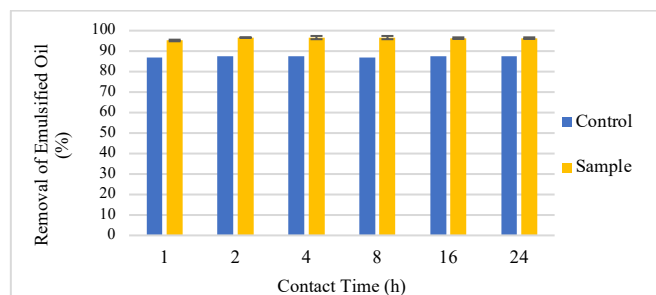

Figure 6. Adsorption uptake of emulsified oil by varying different concentrations of emulsified oil wastewater

The high emulsified oil wastewater concentration caused rapid saturation and adhesion on the surface of the corn cob carbon. A large amount of unattached emulsified oil were still available in the wastewater [20]. When the active surface area decreased, the binding sites of corn cob carbon were occupied quickly due to the increasing amount of oil adsorbed per unit weight of corn cob carbon [21]. The adsorbed oil clogged the pores near the outer surface of the corn cob carbon therefore the remaining oil could not diffuse into the sites deep within the interior surface [22].
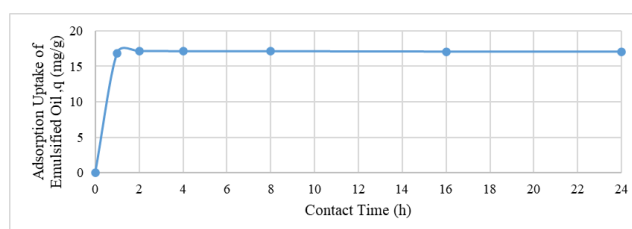
3.3.2 Effect of different contact time
Figure 7 showed the percentage of emulsified oil removal with different contact time. The control experiment was conducted without corn cob carbon and recorded 87% removal in every contact time. The highest percentage removal with the carbon was 96% after 2 hours contact time. Therefore, it can

be represented as 6 mg/L of emulsified oil remaining and considered as permissible compared to the Standard B which is 10 mg/L. Therefore, 2 hours contact time was selected for the next experiments.

Figure 7. Comparison between emulsified oil removal of control and sample experiment by different contact time
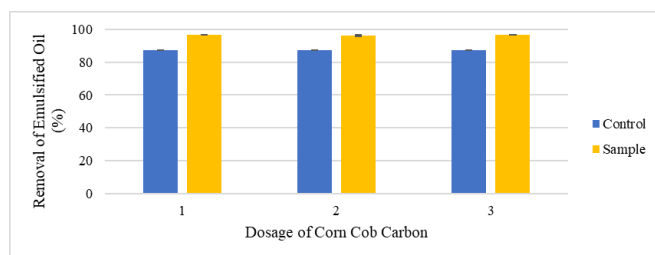

Figure 8. Adsorption uptake of emulsified oil by different contact time

The percentage of sample removal increased with time before reaching a plateau. Figure 8 showed that the adsorption uptake of emulsified oil increased from 16.9 mg/g to 17.1 mg/g when contact time increased and reached equilibrium after 2 hours. The adsorption remained constant due to the emulsification of oil particle saturated on the carbon surface. The adsorption and desorption process on the carbon surface reached equilibrium after it was saturated [7]. The result obtained agreed with works by Husin [23] who stated that the amount of oil adsorbed per unit mass of carbon increased at lower times before reaching a plateau. The existence of the bare surface contributed to the initial high rate of oil uptake. Moreover, the increase in the amount of oil adsorbed resulted in the decrease of available adsorption sites. The remaining adsorption uptake of emulsified oil became asymptotic to the time axis after a definite interval of time and no further adsorption took place in the batch experiment. Another finding by Ahmad Samsuir [24] reported lower oil reduction at longer contact time. The study reported 62% oil removal achieved in 1 hour compared to half of the removal recorded in 24 hours. The study proved that oil adsorption required a shorter time for efficient removal.

3.3.3 Effect of different dosages
Figure 9 showed the percentage of emulsified oil removal with different dosages of corn cob carbon. The control experiment showed 87% removal of emulsified oil wastewater while the sample experiment showed 96% removal for all dosages of corn cob carbon. When the carbon dosage increased, the percentage removal should increase due to the more available binding sites for adsorption [25]. However, the result was insignificant because the percentage of sample removal remained constant. It might be contaminated with dust or ash contained in corn cob carbon or the content of 5% emulsified oil wastewater was not dissolved evenly during the batch adsorption preparation. Therefore, 1 g of corn cob carbon was used for the next parameter experiments.

Figure 9. Comparison between the emulsified oil removal of control and sample experiments using different dosages of corn cob carbon

Figure 10 showed the adsorption uptake of emulsified oil (mg/g) from the sample experiment with different dosages (g) of corn cob carbon.
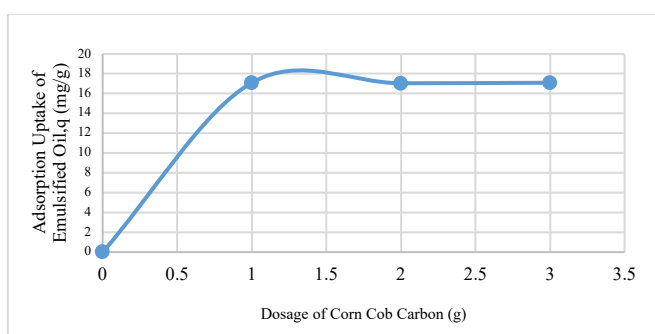
Figure 10. Adsorption uptake of emulsified oil with different dosages of corn cob carbon

The result showed 17.1 mg/g uptake of emulsified oil from 100 mL of wastewater for all carbon dosages. Ruiz [26] reported an increase in emulsified oil removal as the corn cob carbon mass increased. Inversely, the adsorption capacity expressed as equilibrium adsorbent phase concentration decreased as carbon mass used increased. There are more sites for emulsified oil to be adsorbed with increased dosage of carbon. Therefore, the competition for bonding sites between molecules of emulsified oil decreased when dosage of carbon increased [27]. However, in this study, the amount of adsorption did not increase with the increased carbon dosage.

4. Conclusion
In this study, the corn cob carbon showed good efficiency in emulsified oil removal with a percentage of 96% at 2 hours contact time, 1 g of corn cob carbon and 5% of emulsified oil wastewater concentration. Therefore, corn cob carbon can act as the natural adsorbent and played an effective role in the emulsified oil removal process.

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