Environmentally Friendly Recovery and Characterization of Waste Lubricating Oil using acid with Spent Bleaching Earth

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In this study, the properties of waste lubricating oil (WLO) were investigated upon the regeneration of spent bleaching earth (SBE). Acid treatment to recover WLO to its base oil form and remove contaminants was carried out using glacial acetic acid. The characterization of the recovered WLO samples was conducted on water content, sludge formation, absorbance, and presence of the functional groups in the WLO samples by using Fourier-transform infrared spectroscopy (FTIR). The results of the water content level showed positive in five different samples of WLO and its removal percentage was within the range of 3.63% to 11.01%. After the acetic acid treatment, the mass of sludge produced for 10 mL of WLO was within the range of 0.13 g to 0.89 g. The characterization of the regenerated SBE was done using oil removal analysis, scanning electron microscope (SEM), and Fourier-transform infrared spectroscopy (FTIR). Number of cycles in solvent extraction and regeneration heat treatment temperature on the regeneration of SBE were studied and tested to recover WLO. In addition, the response surface methodology (RSM) was used to obtain optimum values of number of cycles, regeneration temperature of SBE, and amount of SBE solid loading required for better adsorption efficiency. From the results, it was found that the optimized set of parameters were 8 cycles in Soxhlet extraction, 400^{o}C of SBE heat treatment process, and 40 g of SBE loading in 10 mL of WLO.

Key words: Spent bleaching earth; waste lubricating oil; heat regeneration process; number of cycles; solid loading; pore size

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Lubricating oil derived from oil trade is employed to shield rubbing surfaces and promote easier motion of connected elements [1]. The usage of a lubricating oil after a certain time period reduces efficiency due to the different unwanted components that contain filings, metal powder, other oils, and additives as well. The oxidation of lubricating oil produces waste lubricating oil (WLO) that has darker color, acid value which increases the precipitate, bad odor, oil sludge, and water content [2]. Due to the internal combustion of the engine, most contaminants are generated containing phenolic compounds, aldehydes, acidic compounds, additives, metals, varnish, gums, and other asphaltic compounds [3]. Massive amounts of ash content, carbon residue, asphaltenic materials, metals, water, and other dirty materials were also identified in WLO [4-6]. The problematic issue that arises due to the usage of oil is the poor disposal of WLO that is produced from engines and machinery. Various environmental problems can arise if the waste is not disposed [7].

Due to the increasing necessity for environmental protection, the disposal of WLO has become very vital. The common disposal practice of WLO is to obtain the energy by burning. Numerous methods that exist to recover WLO include heating and filtration, reusing by acid-clay treatment [1,5,7], solvent extraction [3,8], solvent extraction followed by adsorption [9-11], treatment with adsorbent, continuous elusion technique, distillation, distillation/clay, activated charcoal/clay treatment and many more [8-12]. Environmental concerns are related to each one of these techniques. The acid-clay method is the best method to recycle WLO [1]. The results showed that base oil from the acid-clay method contains the lowest water content compared to other refining methods. However, there is also a disadvantage because this process generates three types of waste products, which are acid tar, asphalt residual, and spent clay. Although the acid-clay method is widely used, it does have certain limitations. In conventional acid-clay treatments, two main problems typically arise, which are production of acidic sludge and highly expensive adsorbents such as activated carbon (AC), kaolin, alumina, silica gels, etc. Shakirullah *et al.* [13] showed that the existing acid-clay treatment techniques for recovery are tedious, require endless chemicals, and give low yield. The challenges and inadequacies of the current acid-clay strategy were overcome by the new

modified acid treatment. The treatment using clay or adsorbent can be improved by the addition of catalysts [14].

Adsorption is a process whereby an adsorbent is used to adsorb the unwanted contaminants from the used oil to improve the properties [15-21]. Adsorbents are used to adsorb contaminants such as color pigments, trace metals, oxygen, sulfur, chlorine, and nitrogen [22-25]. Spent bleaching earth (SBE) from the palm oil industry is used to adsorb the unwanted color pigment and undesirable residues from crude palm oil [26,27]. Palm oil refineries produce the largest amount of SBE in landfills that causes serious environmental issues that need to be taken into consideration [26]. Disposal of SBE at dumpsites can cause environmental issues as the leaching of the residual fat by rain may pollute ground water, as well as a potential fire hazard [26]. The bulky nature, high residual oil content, and increasing global production of SBE, a clay waste material from edible oil processing industries poses major disposal problems [28-31]. Consequently, its regeneration and reuse have produced substantial interest among researchers. Heat treatment, solvent cleansing, and chemical treatment using acids and salt solutions have been used in SBE regeneration for adsorption of various adsorbates [32-35].

In this study, used materials were reused to reduce waste disposal in landfills. Hence, the aim of this study was to utilize SBE as an adsorbent to recover WLO. This study also focused on investigating the regeneration parameters of SBE via response surface methodology (RSM) and identifying the performance of SBE on recovering WLO. This study also measured the ability of SBE to reclaim the color of the recovered oil and optimized the number of cycles in solvent extraction of SBE, the temperature in heat regeneration of SBE, and the SBE solid loading in WLO. Characterization of SBE involving solvent extraction and heat regeneration treatment was done by scanning electron microscope (SEM) and Fourier-transform infrared spectroscopy (FTIR) analyses.

MATERIALS AND METHODOLOGY

Materials

WLO was collected from a local car service center and SBE was obtained from a local palm oil refinery. The WLO samples underwent acid treatment followed by treatment with an adsorbent. Glacial acetic acid and n-hexane were purchased from Sigma Aldrich.

Experimental Factor

There are various factors that affect the reclamation of WLO. The dosage of adsorbent and temperature affect the bleaching efficiency of WLO. Besides, the temperature of the reaction also affects the bleaching efficiency. Other factors also affect the recovery of WLO, such as pore size of an adsorbent. The temperature of the acid treatment was kept in the range of 30°C to 50°C to avoid the effect of glacial acetic acid oxidation of the oil at higher temperatures.

Regeneration of SBE

In order to regenerate SBE, two steps are needed, which are solvent extraction and followed by heat treatment. A sample of 10 g of SBE was placed into a thimble and covered with gauze at the top layer. Hexane was filled into a round bottomed flask and extraction was carried out for 2, 5, and 8 cycles. Then, SBE underwent heat treatment at elevated temperatures. In the heat treatment process, 2 g of SBE was put in a furnace and heated at temperatures from 200°C, 300°C, and 400°C for 1 h. After heating, SBE was cooled to room temperature before being taken out from the furnace as regenerated SBE (RSBE) [26].

Acid-clay Treatment

WLO was filtered to remove unwanted solid particles present in the oil. Then, the oil was subjected to the dehydration process to remove the presence of water in the oil at a temperature of 250°C in an oven for 1 h. Once the oil had reached room temperature, 0.8 g of glacial acetic acid was added into 10 g of WLO. The mixture was then heated and stirred at room temperature and left for 24 h for settling the sludge. In the last stage, the mixture was subjected to centrifugation to separate base oil from sludge for 1 h. After acid treatment, clay treatment was conducted and RSBE was used to treat the base oil. About 4 g of RSBE was added in 1 mL of base oil. The mixture of base oil and sludge was heated up to 250°C and centrifuged for about 1 h. After centrifugation, the oil was then filtered to obtain the final oil and analyzed. Various tests were conducted to study the efficiency of the acid-clay treatment and the properties of the recovered oil.

Characterization of WLO

WLO was compared with the final base oil obtained from the treatment process. The density of lubricating oil is influenced by the aromatic components in WLO. The specific gravity of WLO was determined by calculating the ratio of the mass of volume of substance to the mass of the same volume of water. A higher value of specific gravity indicates that the engine oil was contaminated by metals and oxidized products [36]. The water content in WLO was calculated due to absorption directly from the air. This test was conducted by weighing 100 mL of WLO using an electronic balance and then heated at an elevated temperature. After cooling to room temperature, the 100 mL oil was weighed again to determine the weight of oil after dehydration. Water content removal percentage was calculated using equation (1):

$$Water\ content\ \ removal\ (\%) = \frac{Mass\ of\ oil\ (initial) - Mass\ of\ oil\ (final)}{Mass\ of\ oil\ (initial)} x\ 100 \quad (1)$$

The absorbance of the treated WLO was also measured. The UV-Vis was used to determine the intensity of dark color in the oil samples. As the dark color of a treated engine oil reduces, the absorbance of the treated engine oil becomes lower**.** Then the molecular compounds that were present in the used and VMO were determined via FTIR that focused on the unwanted components such as aldehyde, methane, carbonyl compounds, and carboxylic acid.

Characterization of SBE

After the regeneration of SBE, the oil removal was calculated. It was conducted by weighing 20 g of SBE after the solvent extraction. SBE was set to the heat regeneration process. After heat regeneration of SBE, the hot solid was left to cool down to room temperature before taking the weight of SBE after heat regeneration. Oil removal percentage from RSBE was calculated using equation (2) [27]:

$$\boldsymbol{Oil\ removal}\ (\%) = \frac{\boldsymbol{W_{SBE} - W_{RSBE}}}{\boldsymbol{W_{SBE}}} \boldsymbol{x\ 100 - \omega}\% \quad (2)$$

Where, W_{SBE}, W_{RSBE}, and ω are weight of SBE, RSBE, and moisture content of virgin bleaching earth (VBE), respectively.

FTIR was conducted on SBE and RSBE to identify and compare different functional groups present such as carboxylic acid, C-H carbonaceous chains, oil and free fatty acids, and ester carbonyl in the clay before and after regeneration [28]. The pore sizes of SBE and RSBE were measured using SEM.

Response Surface Methodology (RSM) Modeling

RSM model was analyzed on three parameters, which were SBE regeneration temperature, number of cycles in Soxhlet extraction, and SBE loading. In the RSM software, central composite design (CCD) was used as the model to obtain the set of experiments. Three parameters with two responses were conducted on the CCD model. The SBE regeneration temperature was set from 200ºC to 400ºC, the range on the number of cycles in Soxhlet extraction was set from 2 cycles to 8 cycles, and the SBE solid loading in WLO was from 10 g to 40 g for every 10 mL of WLO [36]. On the other hand, the responses that were included in the CCD model were absorbance and the intensity of the aldehyde component from FTIR analysis. In the CCD model, the central point was set at 5 and the alpha value selected was face centered, which was 1. Then, a set of 20 experiments with different parameter values were selected as the actual design experiments. Thus, after conducting the experiments, the values of the responses were inserted in the CCD model. Table 1 shows the data of the RSM model.

Table 1. Details of the RSM model

File version	11.0.3.0
Study type	Response surface
Subtype	Randomized
Runs	20
Blocks	No blocks
Design type	Central composite
Design model	Quadratic
Build time (ms)	1.0

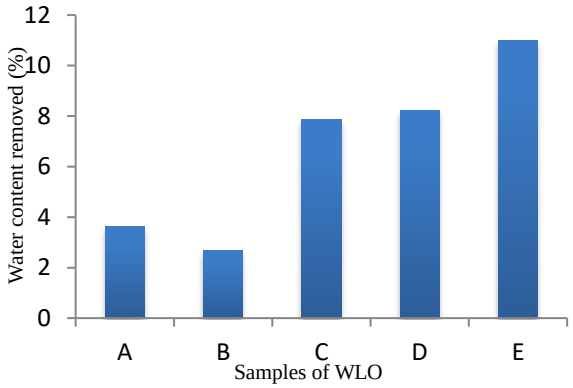


Figure 1. Water content removal of WLO samples

RESULTS AND DISCUSSION

Water Content

Water content in WLO is one of the contaminants referred to as chemical contamination. The presence of water in engine oil (EO) is due to the moisture absorption from the air [36]. Figure 1 shows the results for the water content removed. It can be seen that all the WLO samples contained water. Five samples of WLO were calculated on the presence of water content and all samples showed positive results. The water content removal percentage was within the range from 3.63% to 11.01%, as shown in Figure 1.

Sludge Formation

Poly-condensation and polymerization reactions of WLO result from long molecular weight products that are no longer soluble in the hydrocarbon [36]. The resulting precipitate is called sludge. Figure 2 shows that after the acetic acid-treatment of WLO, the mass of sludge produced for 10 mL of WLO was within the range from 0.13 g to 0.89 g. The results obtained almost satisfied the review provided by Hamawand *et al.* [36].

Density of WLO

The density of motor oil depends on the oil composition, whereby a highly aromatic compounds oil will have a higher specific density compared to the highly saturated compounds in oil that results in lower specific gravity. Table 2 shows the density and API value of the WLO samples.

As shown in Table 2, the density of all the WLO samples was higher than the virgin motor oil (VMO). The higher density of the WLO was due to the solids that were present in the WLO. The density of the WLO increased due to the metal contamination and oxidation products that were formed while the engine oil was in use [36].

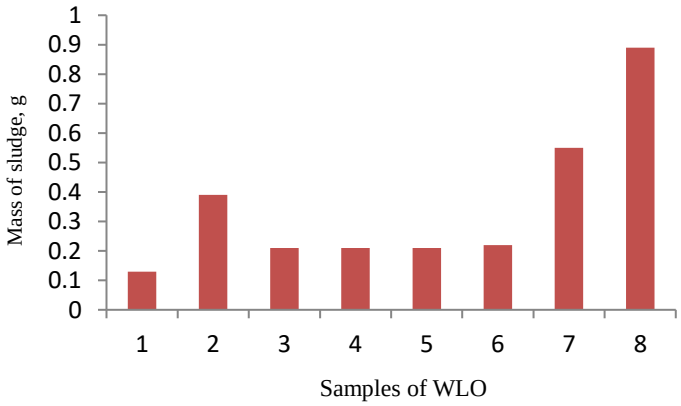


Figure 2. Mass of sludge produced

Table 2. Density and API values of WLO samples

Sample	Sample conditions	Density (g/mL)	API
	VMO	0.53	133.98
	WLO	0.82	41.48
A	2 cycles 200°C 10 g	0.71	67.00
B	2 cycles 200°C 40 g	0.64	89.60
C	2 cycles 300°C 25 g	0.75	57.92
D	2 cycles 400°C 10 g	0.71	67.80
E	2 cycles 400°C 40 g	0.33	94.90
F	5 cycles 200°C 25 g	0.73	61.54
G	5 cycles 300°C 25 g	0.75	56.33
H	5 cycles 300°C 25 g	0.74	59.72
I	5 cycles 300°C 25 g	0.71	68.64
J	5 cycles 300°C 25 g	0.69	73.87
K	5 cycles 300°C 25 g	0.79	46.94
L	5 cycles 300°C 25 g	0.61	79.38
M	5 cycles 300°C 10 g	0.71	67.80
N	5 cycles 300°C 40 g	0.73	61.54
O	5 cycles 400°C 25 g	0.74	59.72
P	8 cycles 200°C 10 g	0.82	41.06
Q	8 cycles 200°C 40 g	0.82	42.76
R	8 cycles 300°C 25 g	0.76	54.68
S	8 cycles 400°C 10 g	0.70	70.64
T	8 cycles 400°C 40 g	0.64	89.59

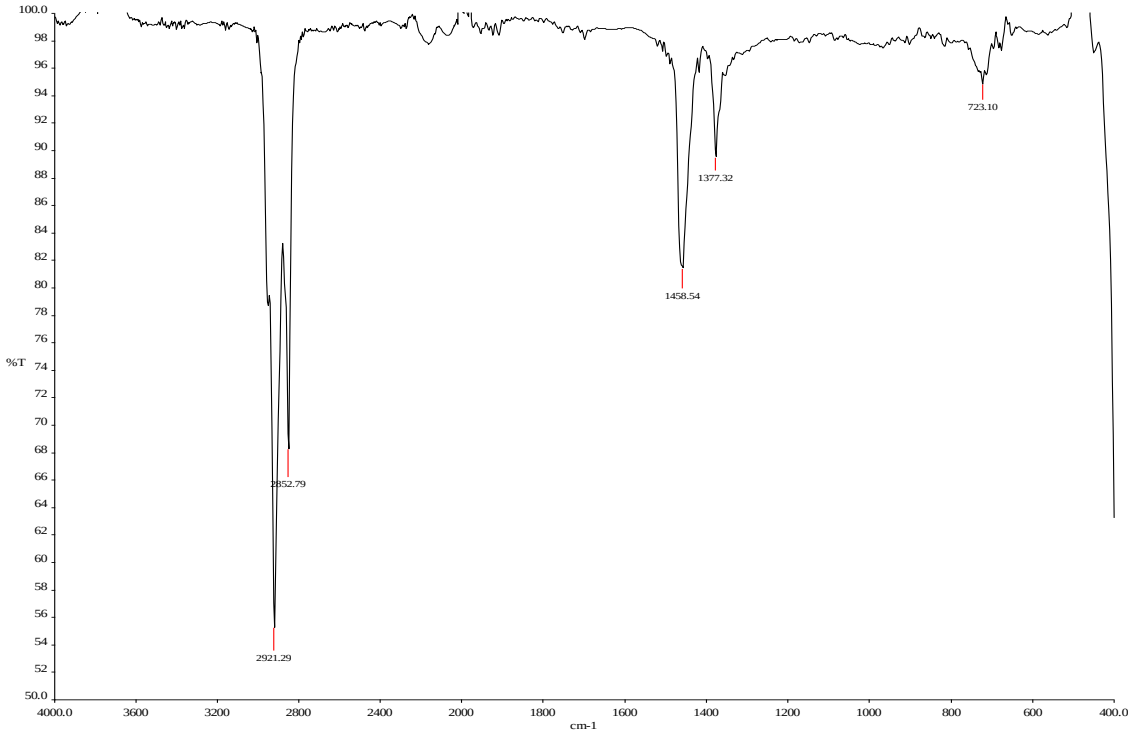


Figure 3. FTIR analysis of VMO

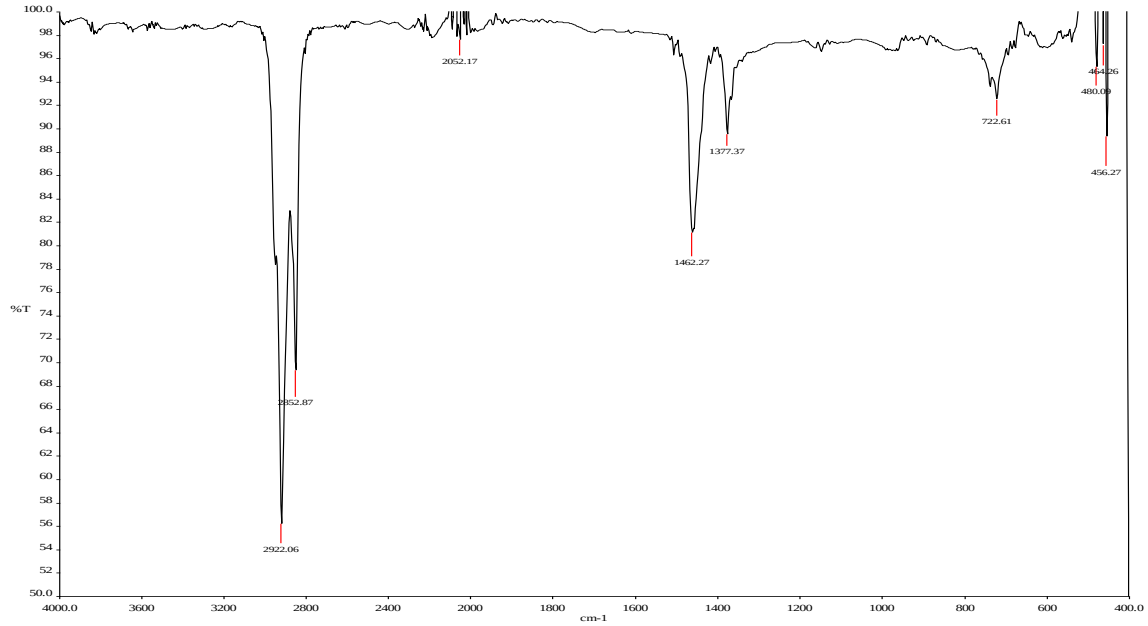


Figure 4. FTIR analysis of WLO

FTIR Analysis on WLO

The components of WLO were identified by FTIR, such as alkanes, alkenes, aldehydes, CH_3, carbonyl compounds, and carboxylic acids. Figures 3 and 4 show the results of the FTIR analysis of VMO and WLO, respectively.

In VMO, alkanes were detected at the wavelengths of 2921 cm^{-1} and 1459 cm^{-1}, alkenes at 723 cm^{-1}, CH_3 at 1377 cm^{-1}, and aldehyde at 2853 cm^{-1}, whereas carbonyl compounds and carboxylic acids were

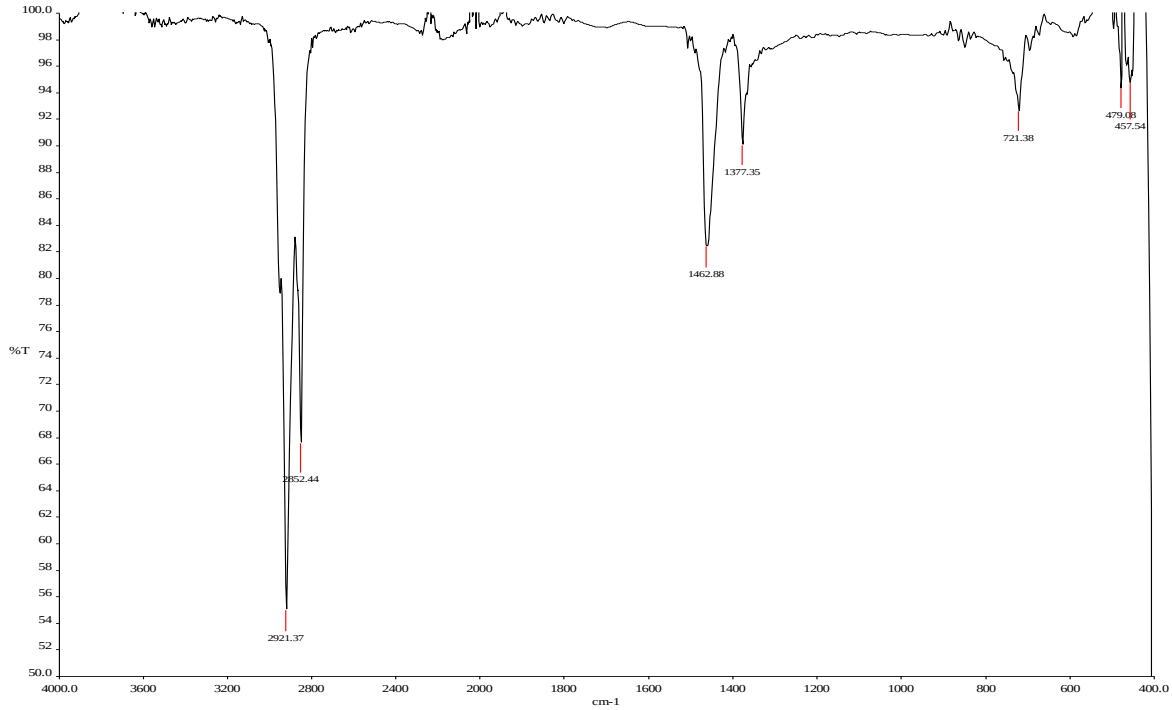


Figure 5. FTIR analysis of sample T

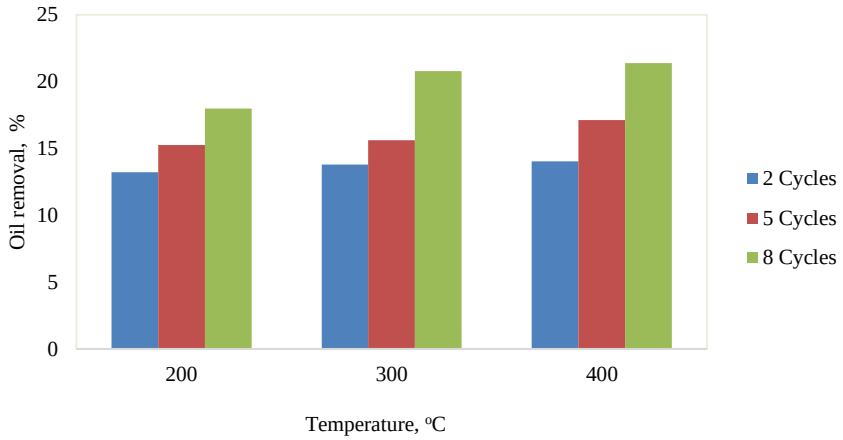


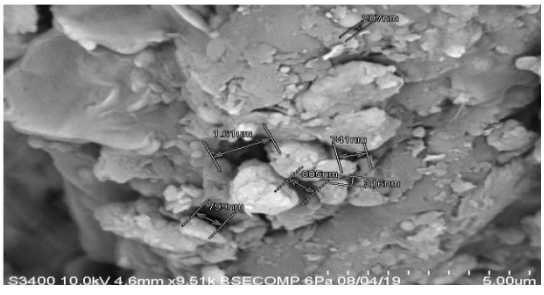
Figure 6. Oil removal from SBE at 2 cycles, 5 cycles, and 8 cycles

undetected (UD). In WLO, alkanes were detected at the wavelengths of 2922 cm^{-1} and 1462 cm^{-1}, alkenes at 723 cm^{-1}, aldehyde at 2853 cm^{-1}, CH_3 at 1377 cm^{-1}, carboxylic acid at 2052 cm^{-1}, and carbonyl compounds was UD. All the samples from samples A to T did not exhibit the presence of carboxylic acids, where the acetic acid-clay method improved the properties of WLO by removing carboxylic acids that were originally present in WLO. After the acid-clay recovery process, in all samples, aldehyde was found. Thus, acetic acid recovery process does not help in the removal of aldehyde component from processed WLO. Figure 5 shows the FTIR analysis of sample T and it can be seen that carboxylic acids had being removed.

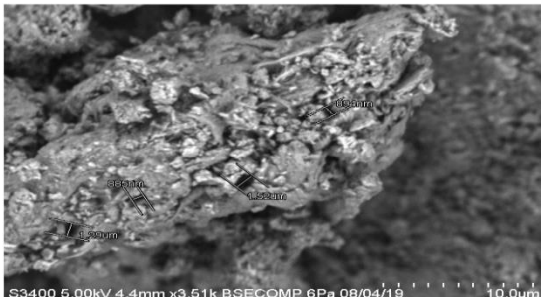
Oil Removal Analysis from SBE

It was identified that after the solvent extraction and heat regeneration processes, there was the presence of oil in the SBE sample. Figure 6 shows the oil removal from SBE at different cycles.

Figure 6 shows that the percentage of oil removal from SBE increased as the temperature of the heat regeneration process increased. It can be seen that the oil removal from SBE at 200ºC was 13.22%, at 300ºC was 13.80%, and at 400ºC was 14.04%. Figure 6 also shows that the oil removal percentage from SBE increased linearly as the number of cycle's regeneration temperature increased. In the 5 cycles solvent extraction, the percentage of oil removal increased as the regeneration temperature increased as well. Figure 6 also illustrates the oil removal percentage from SBE in the 8 cycles solvent extraction process. It can be seen that the oil removal from SBE was 18.00%, 20.80% and 21.40% at 200ºC, 300ºC, and 400ºC, respectively. The oil removal percentage from SBE in 8 cycles increased as the temperature of the heat regeneration process increased.



(a)



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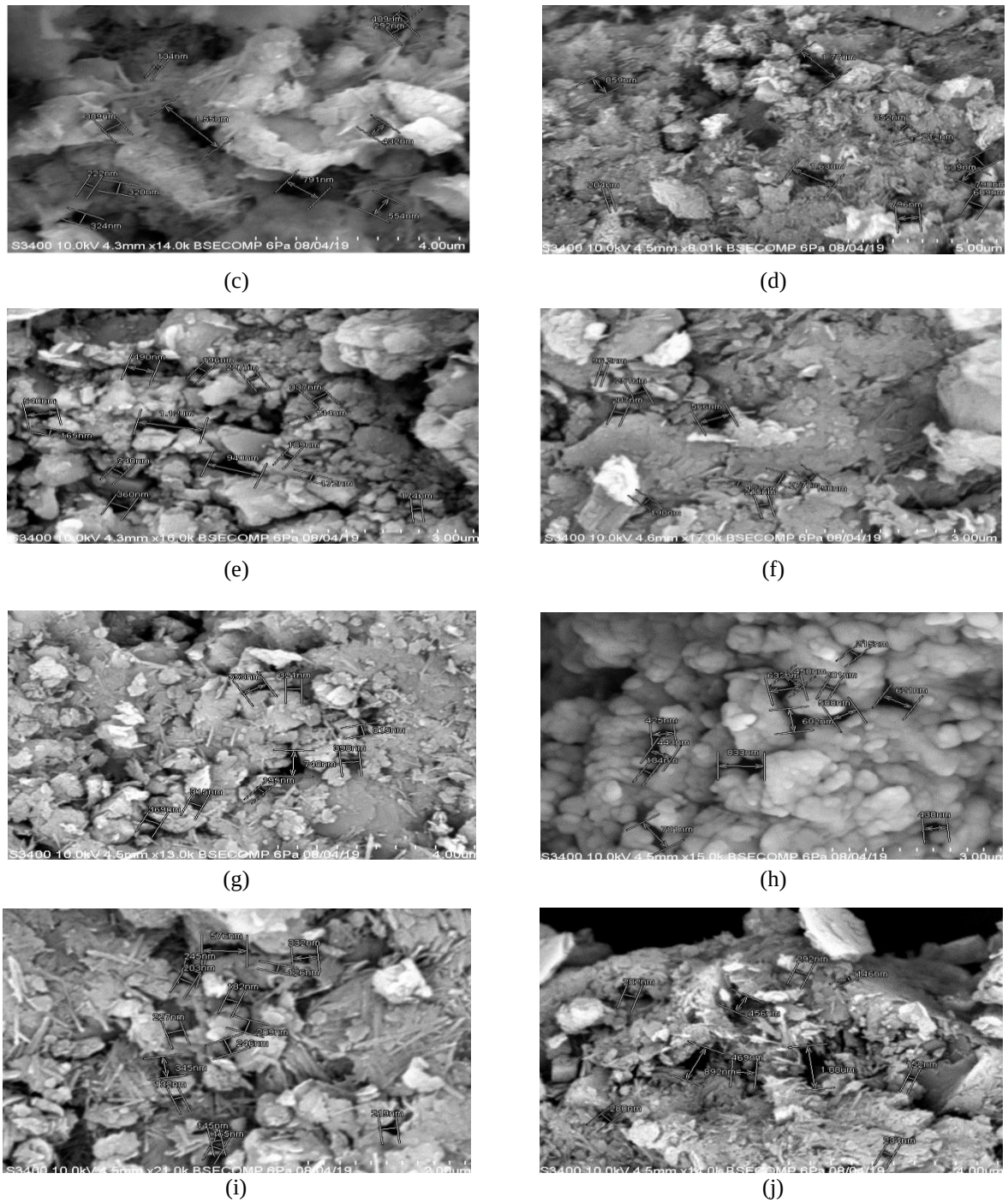

(c) (d)

(e) (f)

(g) (h)

(i) (j)

Figure 7. SEM images of (a) NSBE, (b) 2 cycles 200ºC RSBE, (c) 2 cycles 300ºC RSBE, (d) 2 cycles 400ºC RSBE, (e) 5 cycles 200ºC RSBE, (f) 5 cycles 300ºC RSBE, (g) 5 cycles 400ºC RSBE, (h) 8 cycles 200ºC RSBE, (i) 8 cycles 300ºC RSBE, and (j) 8 cycles 400ºC RSBE

Scanning Electron Microscope (SEM) on RSBE

The structural properties of SBE play a vital role in the efficiency of adsorbing pollutants [37]. Figure 7 shows SEM images of new SBE (NSBE) and RSBE samples of different cycles at different temperatures.

Table 3 shows the pore size analysis of RSBE.

Table 3. Pore size analysis of RSBE

Sample	Pore size
NSBE	316 nm
2 cycles 200ºC RSBE	322 nm
2 cycles 300ºC RSBE	352 nm
2 cycles 400ºC RSBE	489 nm
5 cycles 200ºC RSBE	540 nm
5 cycles 300ºC RSBE	566 nm
5 cycles 400ºC RSBE	576 nm
8 cycles 200ºC RSBE	632 nm
8 cycles 300ºC RSBE	748 nm
8 cycles 400ºC RSBE	892 nm

Table 4. List of components found in the samples of SBE

Sample	Wavenumber (cm^{-1})			
	O-H carboxylic acid	C-H carbonaceous chains of oil and free fatty acids	Ester carbonyl	Si-O
NSBE	3586	2919, 2851	1742	1003
2 cycles 200ºC RSBE	3694	2924. 2853	1743	997
2 cycles 300ºC RSBE	3615	UD	UD	1010
2 cycles 400ºC RSBE	UD	UD	UD	1010
5 cycles 200ºC RSBE	3620	2924	UD	1001
5 cycles 300ºC RSBE	3625	UD	UD	1007
5 cycles 400ºC RSBE	3403	UD	UD	UD
8 cycles 200ºC RSBE	UD	2922	UD	1004
8 cycles 300ºC RSBE	UD	UD	UD	1008
8 cycles 400ºC RSBE	UD	UD	UD	1007

It can be seen that the pore size of the respective RSBE samples increased after regeneration. SBE is of a smaller pore size compared to the other RSBE. Sabour and Shahi [27] reported that thermal treatment on SBE helped to show improvement in the pore size and surface area of regenerated SBE.

FTIR Analysis on RSBE

Majid and Mat [28] reported that the components present in SBE and RSBE are almost the same. They also mentioned that the absence of bonds of residual oil indicates the de-oiling and regeneration process eliminates the oil residue adsorbed in the pores of SBE. Table 4 shows the list of components found in SBE.

The FTIR spectra of 3350-3550 cm^{-1} indicated the presence of stretching vibrations of O-H of carboxylic acid [28]. Moreover, the presence of Si-O stretching was indicated by the band near 980-1010 cm^{-1}. Certain SBE samples exhibited bands at 2850-2930 cm^{-1}, which indicated the presence of stretching vibrations of C-H carbonaceous chains of oil and free fatty acids. On the other hand, a band at 1730 cm^{-1} was also observed indicating the ester carbonyl of residual oil. The untreated SBE contained carboxylic acid, Si-O, C-H carbonaceous chains of oil and free fatty acids, and also the ester carbonyl of residual oil. RSBE samples of 2 cycles, with heat regeneration at 200ºC and 300ºC, indicated the presence of O-H carboxylic acid groups. For 2 cycles RSBE at 200ºC, there was the presence of C-H carbonaceous chains of oil and free fatty acids and ester carbonyl which were UD in RSBE at 300ºC and 400ºC. Si-O was present in all 2 cycles RSBE samples. Moreover, RSBE at 5 cycles, at all heat regeneration temperatures, indicated the presence of O-H carboxylic acid and the absence of ester carbonyl. C-H carbonaceous chains of oil and free fatty acids were only present in RSBE of 5 cycles at 200ºC. Si-O was present in all RSBE samples upon regeneration at different temperatures of 8 cycles. Ester carbonyl and O-H carboxylic acid were UD in all 8 cycles RSBE. Whereas, C-H carbonaceous chains of oil and free fatty acids were found in RSBE of 8 cycles at 200ºC, but UD at regeneration temperatures of 300ºC and 400ºC.

Kheang *et al*. [38] reported that neither natural bleaching earth (NBE), SBE or RSBE contains Si. This clearly shows that all the RSBE samples contained Si-O, indicating that the samples were bleaching earth.

Optimization of Experimental Design by using RSM

In this study, three factors were taken into consideration, which were temperature of SBE regeneration, number of cycles in Soxhlet extraction of SBE, and SBE loading in WLO. On the other hand, the responses examined were the absorbance of the recovered WLO and the intensity of the aldehyde component present in the recovered WLO. Table 5 shows the list of parameters of the experiment that were studied. According to Wafti *et al.* [26], SBE needs to be heated to the temperature ranging from 400ºC to 1000ºC. However, in this RSM model, the temperature range from 200ºC to 400ºC was selected as the design parameter. On the other hand, solvent extraction needed to be conducted for 8 h, which was approximately 8 cycles in the Soxhlet extraction. Thus, in the RSM model, the range used was 2 to 8 cycles. The solid loading range was from 25 g to 40 g of SBE, for 10 mL of WLO. UV-Vis was measured on WLO to identify the light absorbance at different wavelengths.

Regression Equation using CCD Model

From the ANOVA analysis, the reduced 2FI model was used to handle any constraints that occur in the mixture design. 2FI model is a sequential sum of squares in two factor interactions. On the other hand, CCD was used as the model to have sets of 20 runs of experiments to identify the significant results from the set of experiments. The actual response on the absorbance of the recovered WLO is expressed in equation 3:

$$\text{Absorbance of the recovered WLO} = 3.53838 - 0.001574A + 0.063588B - 0.006485C - 0.006485AB - 6.10833E - 6AC \quad (3)$$

Table 5. Sets of experiments in RSM model

Run	Factor 1: A	Factor 2: B	Factor 3: C	Response 1 Absorbance of the recovered WLO	Response 2 Intensity of the aldehyde component
1	300	5	25	2.5427	30.0
2	300	5	10	3.1044	29.5
3	200	2	40	3.0298	31.0
4	300	8	25	3.0172	29.5
5	300	5	25	2.5346	33.5
6	300	5	25	2.5241	30.0
7	400	5	25	2.4403	30.5
8	200	8	10	3.1064	29.5
9	200	8	40	3.0244	30.0
10	300	5	25	2.5721	30.0
11	300	2	25	2.8950	30.5
12	300	5	25	2.5421	30.5
13	200	2	10	3.2064	30.0
14	200	5	25	3.1264	31.0
15	400	2	10	2.7560	29.5
16	400	8	10	2.3172	30.0
17	400	8	40	2.1744	30.5
18	300	5	25	2.5247	29.5
19	300	5	40	2.4473	28.5
20	400	2	40	2.5669	30.5

Table 6. ANOVA analysis of variance

Source of variation	Sum of squares	*df*	Mean square	F-value	p-value Prob >F	
Model	1.34	5	0.2675	7.46	0.0013	Significant
A	1.05	1	1.05	29.25	<0.0001	
B	0.0663	1	0.0663	1.85	0.1953	
C	0.1557	1	0.1557	4.34	0.0560	
AB	0.0659	1	0.0659	1.84	0.1968	
AC	0.0007	1	0.0007	0.0187	0.8931	
Residual	0.5020	14	0.0359			
Cor Total	1.84	19				

Where, A is SBE regeneration temperature, B is the number cycles in Soxhlet extraction, C is the SBE solid loading in WLO, AB is SBE regeneration temperature number of cycles in Soxhlet extraction, and AC is SBE regeneration temperature SBE solid loading in WLO.

Statistical Analysis of the Design Model

The statistical analysis of the experiments depended on the ANOVA data. It was analyzed by the p-value, R^2, and adjusted R^2, as shown in Table 6.

Table 6 indicates the model F-value of 7.46, which implies that the model was significant. The p-value of the model indicated that there was only a chance of 0.13% that an F-value could occur largely due to disturbance. On the other hand, the p-value was less than 0.05, which indicated that the model terms were significant. The larger the F-value and the lower the p-value imply that the model is significant [39]. Thus, factor A indicated a larger F-value of 29.25 and a smaller p-value of less than 0.0001 that had greater effects on the adsorption of recovered WLO. In terms of the interaction between factors, AB and AC, AB was more significant as the F and p-values were significant.

Table 7 illustrates the fit statistics of ANOVA model in RSM. The R^2 value of this model indicated how perfect the model estimated the experimental data points. Therefore, this model could estimate the experimental data point up to 72.71%. On the other hand, the amount of variation about mean explained by the model was measured by adjusted R^2, which was 0.6296. The predicted R^2 value of 0.5098 was in reasonable agreement with the adjusted R^2 of 0.6296, with a difference of less than 0.2. This is because, based on the study conducted by Behera *et al.* [39], the predicted R^2 value obtained from the equation should be near to the R^2. R^2 value from this model was 0.7271 and the predicted R^2 value was 0.5098. This implies that the experimental data for the absorbance of the recovered WLO fitted well with the predicted value of the model. Besides, the lower standard deviation, 0.1894 portrayed that a good model that gave a good value between the predicted and actual values of the response, which was the absorbance.

Table 7. Fit statistics of ANOVA model

Statistics	Values
Standard deviation	0.1894
Mean	2.72
C.V.%	6.96
R^2	0.7271
Adjusted R^2	0.6296
Predicted R^2	0.5098
Adeq. precision	10.4007

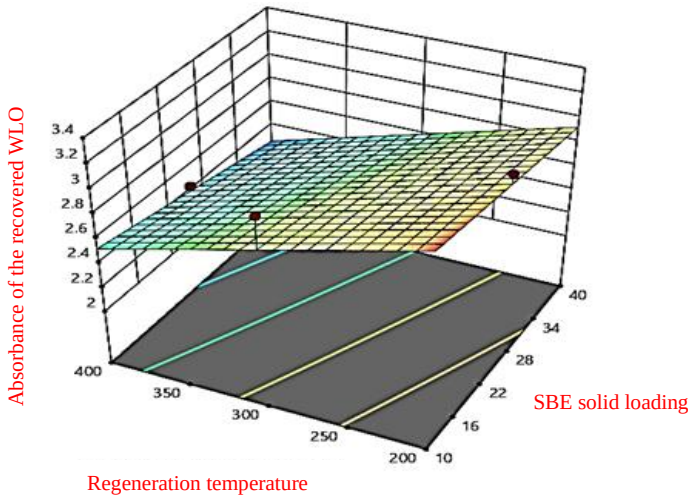

Figure 8. 3D illustration of adsorption between components

3D-Model of Interactions between Factors

Figure 8 shows the 3D linear RSM model. It illustrates the factors that affected the absorbance of the recovered WLO. By taking SBE solid loading as the constant at the middle level, the relation between SBE solid loading and heat regeneration temperature of SBE was studied. For the number cycle as the middle level constant, as heat regeneration temperature increased on SBE, the absorbance of the recovered WLO decreased. Besides, as the SBE solid loading increased, a decrease in the absorbance value of the recovered WLO was observed. This shows that as the mass of adsorbent increases, the higher the adsorption process.

Optimization on the Absorbance of the Recovered WLO

Table 8 shows the numerical method which was conducted to determine optimum operating parameters where the minimized absorbance value needed to be obtained**.** The minimized value of the absorbance was achieved at 400^{o}C with the number of 8 cycles and SBE solid loading to 10 mL of WLO of 40 g. The minimized value of absorbance was achieved at 2.093. Based on Hussain and Karmakar [40], as the concentration of EO decreases, the absorbance decreases and indicates that the oil is less deteriorated. Thus, the low absorbance value of WLO showed the least contaminated oil, where the dark color pigment was impregnated on the surface of the RSBE.

Optimization Experimental Design by using RSM of Intensity of the Aldehyde Component

In this study, the intensity of aldehyde component was taken as the reference to study the effect of SBE regeneration temperature, number of SBE Soxhlet extraction, and SBE solid loading in WLO on the removal of aldehyde component from WLO. Besides, compared to other components present in the FTIR analysis, aldehyde was used for analysis purpose as it showed better results in intensity change compared to the other components. Table 9 shows that no factors were analyzed with respect to the FTIR analysis.

Table 8. Results on the optimization in recovered WLO absorbance

Type of components	Goal to achieve	Value of optimisation
Heat regeneration of SBE (^{o}C)	In range	400
Number of cycles	In range	8
SBE solid loading (g)	In range	40
Absorbance	Minimize	2.093
Desirability	1.000	

Table 9. ANOVA analysis on the FTIR response in RSM

Source of variation	Sum of squares	*df*	Mean square	F-value	p-value Prob >F	
Model	0.0	0		0.2499	0.9817	Not significant
Residual	18.20	19	0.9579			

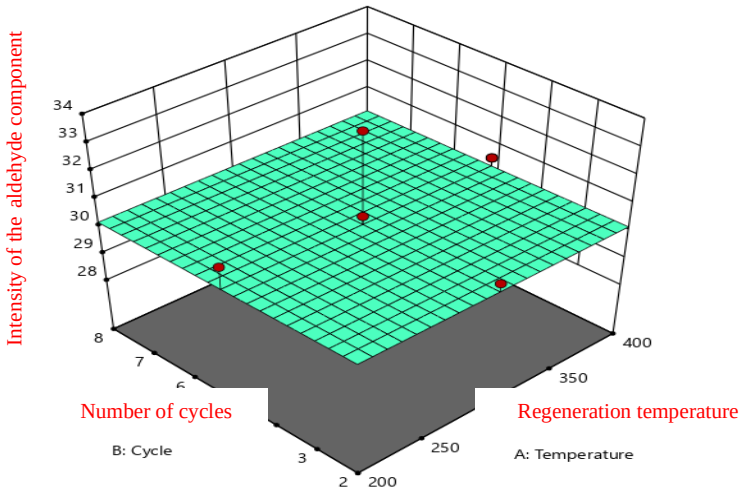

Figure 9. 3D model illustration of between components

ANOVA analysis showed that there was no significant model terms present in RSM model. The F-value was too small, which was 0.2499, and a higher p-value indicated that the model was not significant.

Thus, the FTIR analysis was not affected by any of the factors. This is because the aldehyde intensity changes in the FTIR analysis was approximately the same as other samples. Figure 9 shows a flat plane where the model is not significant. This is because all the factors in the model did not influence the aldehyde intensity present in the FTIR analysis. In this study, the FTIR analysis on aldehyde composition did not provide a significant model from RSM analysis. According to Hamawand *et al.* [36], acid-clay recycling method was effective in removing unwanted components from WLO. However, the FTIR analysis on the recovered WLO did not show a large difference in aldehyde composition. Therefore, the FTIR intensity analysis is not an appropriate parameter to be used in RSM model, as the results from FTIR were not significant and did not vary as well.

CONCLUSION

In conclusion, acid-clay method was found to improve the properties and color of WLO. The results of the water content level showed positive content in five different samples of WLO and its removal percentage was within the range of 3.63% to 11.01%. After the acetic acid-treatment, the mass of sludge produced for 10 mL of WLO was within the range of 0.13 g to 0.89 g. The contaminants in WLO could be removed via the acid-clay method. Adsorption of the reclaimed oil was low compared to WLO. The lowest absorbance value, 2.093 of recovered WLO was obtained by considering three operating parameters. Moreover, based on the RSM 2FI model, analysis on absorbance response showed that a minimum absorbance value was obtained with SBE heat regeneration at 400°C, 8 number of cycles in Soxhlet extraction, and 40 g of SBE solid loading with a desirability of 1. On the other hand, the analysis on intensity of aldehyde component did not show any optimized value, thus the model found to be non-significant.

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