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Adsorptive Desulfurization of Model Fuel by Modified Activated Carbon

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The purpose of this study was to identify the effect of modified activated carbon (MAC) on the adsorption isotherms and kinetics of dibenzothiophene (DBT) removal in a model fuel. In this study the commercial activated carbon (AC) was modified by chemical treatment with nitric acid (HNO_3) followed by adsorption experiments with different concentrations and contact times. The MAC was characterized using Fourier-transform infrared spectroscopy (FTIR) to identify changes in the MAC functional groups. A broad and intense peak at 3471.53 cm^{-1} for MAC was detected which indicates the stretching vibration of the O–H bond. After adsorption, the solution was analysed using ultraviolet-visible (UV-vis) light spectroscopy. In this study, the amount of DBT adsorbed by the MAC was in the range of 46.8% to 68.3%. Equilibrium isotherm data were analyzed according to Langmuir and Freundlich isotherm models. Pseudo first-order and pseudo second-order kinetic models were used to test the adsorption kinetics. The adsorption capacity and the rate of adsorption for DBT was found to be 1.54 mg/g and 0.74, respectively. Kinetic studies indicated that the sorption of DBT followed the pseudo first-order kinetic model with a correlation coefficient of 0.9912.

Key words: Desulfurization; adsorption; activated carbon; isotherms; kinetics

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Daily life now depends on a continuous energy supply. Nearly 82% of global energy is derived from fossil fuels [1]. Climate change and global environmental pollution are the results of the usage of fossil fuels as well as other human activities. Sulfur is one of the elements that can be found in fuel, but its presence makes fuel less efficient and harmful to both the engine and the environment [2]. Examples of sulfur containing compounds (SCC) found in crude oils are 4,6-dimethyldibenzothiophene (4,6-DMDBT), dibenzothiophene (DBT) and benzothiophene (BT) [3]. Attention has been given to the environment as new regulations have been initiated requiring low sulfur compounds in hydrocarbon-based fuels. There is no specific effective method or strategy to reduce air pollution without reducing the sulfur content to very low levels. Thus, due to the harmful effects of SCC, the desulfurization of crude oil plays an important role in refining processes.

During combustion, SCC converts to sulphur oxides (SO_x) which are known as the main source of air pollution [4]. Acid rain triggers ozone layer degradation which leads to various types of diseases such as respiratory tract disease. SCC in fuel needs to be reduced to at least 10 ppm or even lower, compared to the current regulatory limit of 500 ppm [5]. The Occupational Safety and Health Administration (OSHA) has introduced new regulations to reduce the amount of sulfur to 10 ppm to 50 ppm.

There are many methods and technologies to remove SCC from fuel. Various conventional approaches of desulfurization for improving the removal efficiency of SCC have been developed. The most common desulfurization method in the oil and gas industry is catalytic hydrodesulfurization (HDS) [6]. However, HDS technology that can reduce the sulphur content to less than 10 ppm is difficult and very costly. Some alternative technologies have been developed to reduce or remove SCC from fuel by oxidation, extraction, adsorption and biodesulfurization [6-11]. It was found that adsorption is the most effective method of SCC removal in fuels after HDS treatment, and using this technique, ultra-low sulphur content in fuel can be achieved [12-17].

Activated carbon (AC) can be produced in a wide range of production processes and derived from many different sources. The raw materials used for the production of AC, activation process used to activate the carbon, and the parameters chosen for the process determines both the chemical and physical properties and also the performance of the AC. AC's porous structure allows it to adsorb materials from both liquid and gas phases [18-20]. Modifying AC will result in a greater adsorption capacity of SCC in the fuel [21-23]. In order to improve adsorption capacity of AC, several treatment methods have been developed such as impregnation treatment, basic treatment, acid treatment and plasma treatment. The surface modification can be done by oxidation using oxidizing agents such as nitric acid (HNO_3), hydrochloric acid (HCl) and sulfuric acid (H_2SO_4). These oxidizing agents can change the AC functional groups by introducing new acidic functional groups on the activated carbon [24]. According to Deng *et. al.* [8], AC modified by acid treatment is better at removing benzothiophene from model fuel than AC modified by basic treatment. Gawande and Kaware [25] stated that acid activated bentonite showed the highest efficiency for the removal of sulphur compared to unmodified AC. *Previous research has* also shown that *AC* modified and treated through chemical activation helps to increase surface adsorption and removal capacity [26,27].

In this study the commercial AC was modified by chemical treatment with HNO_3 [24]. The parameters of interest were the concentration of the chemical used for modification and the amount of dibenzothiophene (DBT) absorbed from the model fuel. The selected parameters for this study included the concentration of adsorbent (20, 40, 60, 80 and 100 ppm) and contact time (15, 30, 45 and 60 min) to evaluate the adsorption capacity of DBT from the fuel.

MATERIALS AND METHODOLOGY

Materials

HNO_3 (purity, 68%), n-heptane, DBT (purity, 99%) were purchased from Rinitek Sdn Bhd (Kota Kinabalu, Malaysia). The AC (NORIT) was purchased from Sigma-Aldrich, which consists of coconut shell in powder form with ~100 mesh particle size. It is made from charcoal of the hard-shell of the coconut which has some inherent properties such as high micro-porosity, high density, low attrition loss, intrinsic hardness, low ash content, etc.

Stock Solution Preparation

1000 ppm stock solution was prepared for DBT for adsorbate as a model fuel where this adsorbate was dissolved in n-heptane [16,28]. Combined solutions with same concentrations were prepared by successive dilution and mixing of the three solutions based on the following equation:

$$M_1V_1 = M_2V_2 \tag{1}$$

where M_1 is the initial molarity, V_1 is the initial volume, M_2 the molarity and V_2 the volume.

Preparation of Modified Activated Carbon (MAC)

Commercial AC was treated by mixing it with HNO_3. 30 ml of 20% of HNO_3 solution was transferred into a flask containing 10g of AC. By determining the concentration percentage of HNO_3 and weight of MAC, the ratio of impregnation, X_p can be calculated by using equation 2 [29]:

$$X_p = \frac{Weight\ of\ the\ HNO_3}{Weight\ of\ the\ MAC} \tag{2}$$

The flask was sealed using foil and a few small holes were punched on the top of the foil to allow vapour to evaporate. The mixture was left for 3 days in the sonicator bath to ensure full dissolution. The mixture was then filtered and the filtrate was transferred to a crucible to obtain its weight. The crucible was weighed first before use to avoid any errors in calculation. The product was then subjected to further drying in an oven at 120ºC for 24 h.

Adsorption Experiment

For the adsorption experiment, different concentrations of the model fuel (20, 40, 60, 80 and 100 ppm) were placed in beakers, each with 50 ml of a solution with same adsorbent dose (0.5g), and magnetically stirred for 60 min. The adsorption temperature was maintained at 25ºC and the stirrer was set to a speed of 120 rpm. Data was taken at 15, 30, 45 and 60 min. After adsorption, the solid and solution were separated using a syringe. The solution was filtered and then analyzed using an ultraviolet-visible (UV-vis) spectrophotometer (UNICO UV-4802) and the concentration of the adsorbed DBT concentration was determined. The amount of adsorption at equilibrium (q_e) (mg/g) was calculated using equation 3:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{3}$$

where C_o and C_e are the initial and equilibrium adsorbate concentration (mg/l), V is the volume of the solution (l) and W is the weight of MAC used (g).

Analysis of Data

Fourier-transform infrared spectroscopy (FTIR) (Perkin Elmer) was used for the functional group identification of unmodified AC and MAC. The residual concentration of DBT in the model fuel was analysed using a UV-vis spectrophotometer at a wavelength of 324 nm. The residual concentration of DBT in the model fuel was calculated from the absorbance used by the calibration curve.

Adsorption Isotherm and Kinetics

Two models (Langmuir and Freundlich isotherm models) were used to study the interaction between the molecules of the adsorbate and the surface of the adsorbent. Langmuir model theory is based on an assumption that the monolayer is formed on the absorbent surface, so one molecule of an adsorbate can only be absorbed in one site on the surface of an adsorbent and its molecular forces decrease with an increase in distance [30]. On the other hand the Freundlich isotherm model makes an assumption that the enthalpy of adsorption doesn't depend on the amount absorbed. Based on heterogeneous surfaces, the equation that defines Freundlich can be obtained by making an assumption that a logarithmic decrease in the enthalpy of adsorption will result in an increase in the fraction of occupied sites [30]. An adsorption kinetic study was performed to determine the efficiency of the adsorption process. Kinetic models are used to investigate the experimental data and to determine the adsorption mechanism. For this study, pseudo first-order and pseudo second-order models were applied.

RESULTS AND DISCUSSION

Fourier-transform infrared spectroscopy (FTIR) analysis on unmodified AC and MAC

Both unmodified AC and MAC were characterized using FTIR. Figure 1 shows the FTIR spectra for both samples. Based on the FTIR spectral analysis, the functional groups found on MAC are similar with AC. However, a number of small peaks were detected at 3800-3700 cm^{-1} which indicate O-H stretching vibrations of hydroxyl functional groups. This might be due to the acidic treatment which reduces the hydroxide groups and produces more acidic groups on the surface of MAC [31]. The presence of C=C bonds in both spectra were indicated by the peaks at 2186.47 cm^{-1} and 2174.67 respectively. In unmodified AC, CH_2 was represented by a peak at 1035.82 cm^{-1}. The intense peak at1562.38 cm^{-1} in MAC showed that nitrogen was successfully introduced into the AC. This is also supported by the presence of a peak at 2152.58 cm^{-1} which is assigned to the N_2O gas released [24].

Adsorption Isotherm Study

The prepared MAC was used in the adsorption of SCC in order to estimate the applicability of these materials in adsorptive desulfurization. To thoroughly understand the adsorptive desulfurization of DBT in n-heptane using MAC, adsorptive isotherms and kinetics were obtained. Table 1 shows the DBT data concentration in the adsorption experiments.

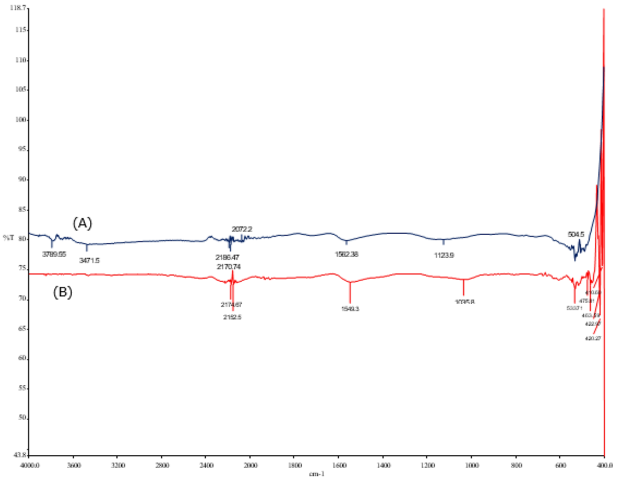

Figure 1. FTIR spectra of MAC (A) and unmodified AC (B) samples

Table 1. DBT data concentration in adsorption experiments

C_0 (mg/l)	C_e (mg/l)	q_e (mg/g)	C_e/q_e (g/l)	R_L
20	6.35	1.17	5.45	0.006
40	12.54	2.75	4.57	0.031
60	21.09	3.89	5.42	0.021
80	34.20	4.58	7.47	0.016
100	53.20	4.68	11.37	0.013

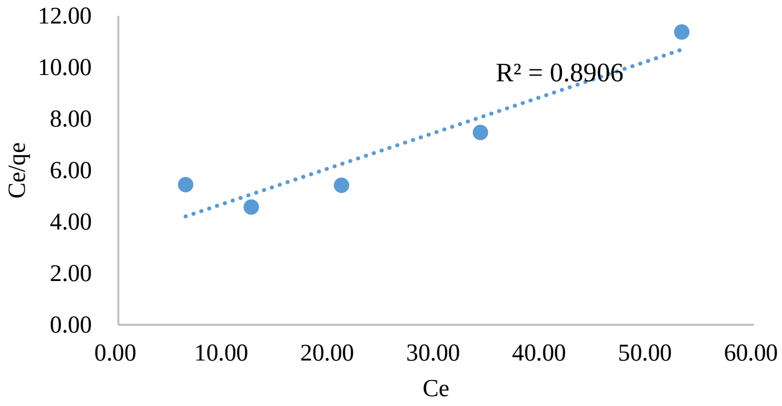

Figure 3. Langmuir isotherm for DBT

The data in Table 1 shows that the adsorption of DBT using MAC was effective and successful. The data also shows that as the concentration increases, the amount of adsorption at equilibrium increases rapidly and then starts to slow down. This is because adsorption decreases with increasing initial concentration of DBT in the n-heptane solution. This can be interpreted by the decrease in density of adsorption sites to total sulfur species with increasing initial concentration.

Langmuir Isotherm

The Langmuir isotherm is shown in Figure 3. The values used to plot the Langmuir graph can be obtained by calculating C_e and q_e. Equation 4 is the linear equation from the Langmuir isotherm and was used to determine the adsorption capacity (Q_o) and Langmuir constant(K_L). The separation factor (R_L) was calculated using equation 5 [32,33].

$$\frac{C_e}{q_e} = \frac{1}{Q_o}\frac{1}{K_L} + \frac{1}{Q_o}(C_e) \qquad (4)$$

$$R_L = \frac{1}{1+K_L C_o} \qquad (5)$$

From this study, the value for Q_0 was found to be 1.54 mg/g, which is the adsorption capacity of DBT. The value for K_L was 0.74 which is the rate of adsorption. In this study, the amount of DBT adsorbed by MAC was in the range of 46.8% to 68.3%. The isotherm was found to be linear over the entire concentration range, with a good linear correlation coefficient. Based on Table 1, the R_L value is between 0 and 1, which means adsorption of DBT is favourable [34].

Freundlich Isotherm

For the Freundlich isotherm, it is assumed that the adsorption intensity or surface heterogeneity energy for which the energy term in the Langmuir equation varies as a function of surface coverage [35]. Table 2 shows the DBT data concentration for the Freundlich isotherm.

Table 2. DBT data concentration for Freundlich isotherm

C_e (mg/L)	q_e (mg/g)	lnC_e	lnq_e
6.35	1.17	1.85	0.15
12.54	2.75	2.53	1.01
21.09	3.89	3.05	1.36
34.20	4.58	3.53	1.52
53.20	4.68	3.97	1.54

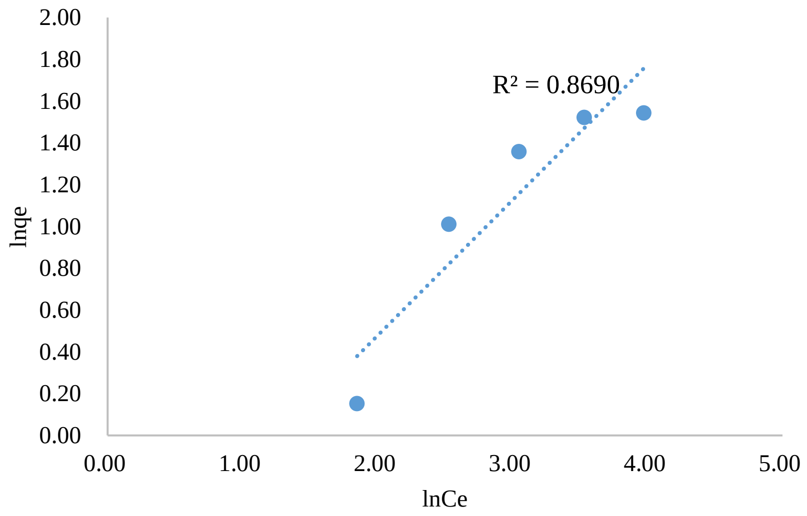

Figure 4. Freundlich isotherm for DBT

Figure 4 shows the Freundlich isotherm for DBT.

The K_f value in the Freundlich isotherm indicates the intensity of the adsorption, for which the value obtained was 0.4410. In addition, the heterogeneity factor, n, was found to be 1.5425. From these results, the Langmuir isotherm model was found to be more suitable than the Freundlich isotherm model since the correlation coefficient of the Langmuir model (R^2 = 0.8906) was higher than Freundlich model (R^2 = 0.8690). These results indicate the Langmuir equation is more applicable than the Freundlich equation. The validity of the Langmuir equation indicates a monolayer adsorption of DBT on the specific homogeneous sites of MAC [31,36].

Adsorption Kinetics Studies

Adsorption kinetics are almost similar to the adsorption isotherm as both the equation and experiment are quite similar. In the adsorption isotherm, the amount of DBT adsorbed was calculated by obtaining the value of q_e (mg/g) while in adsorption kinetics, the amount of DBT adsorbed was calculated at a predetermined time q_t (mg/g) (Equation 6) [33]:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (6)$$

where, C_t is the concentration of DBT at a predetermined time (mg/l). The kinetic data was interpreted using two kinetic models, pseudo first-order and pseudo second-order. The q_t value was the same as for the adsorption isotherm, 1.17 mg/g. This experiment was done using a 20 mg/l initial concentration in 60 min for 15 min intervals. Table 3 shows the adsorption kinetic data for DBT.

Table 3. Adsorption kinetic data for DBT

t (min)	C_0 (mg/l)	C_t (mg/l)	q_t (mg/g)	ln $(q_e - q_t)$	t/q_t	$t^{1/2}$
0	20	20.00	0.00	0.16	-	0.00
15	20	16.15	0.39	-0.25	38.46	3.87
30	20	12.73	0.73	-0.82	41.10	5.48
45	20	7.61	1.24	-	36.29	6.71
60	20	6.35	1.37	-	43.80	7.75

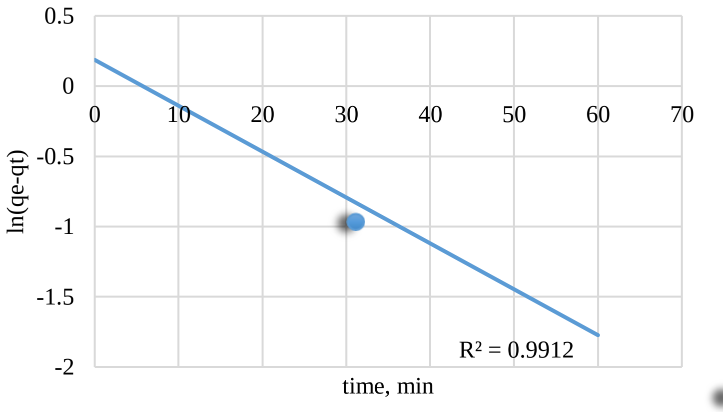

Figure 5. Pseudo first-order plot for DBT

Table 4 shows the pseudo first-order model data for DBT.

Table 4. Pseudo first-order model for DBT

C_0 (mg/l)	q_e (mg/g)	k_1 (h^{-1})	Calculated lnq_e	Experiment lnq_e	R^2
20	1.17	-0.0327	0.157	0.187	0.9912

The adsorption rate constant was determined using a pseudo first-order (Lagergren) equation (Equation 7) [37]:

$$ln(q_e - q_t) = lnq_e - k_1 t \qquad (7)$$

where q_e (mg/g) is the adsorption uptake at equilibrium, q_t (mg/g) is the amount of sulfur adsorbed on the adsorbent at time t and k_1 (h^{-1}) is the rate constant. Figure 5 shows the pseudo first-order plot for DBT.

As shown in Figure 5, the R^2 value for pseudo first-order is 0.9912 which can be said to be linear with a good correlation coefficient, which means this adsorption kinetic experiment fits with Langerdren's equation. Other than that, both calculated and experimental values of $\ln q_e$ do not differ much. Hence, it could be concluded that Langergren's first-order plot does fit very well with the experimental kinetic data. Since the adsorption processes followed the pseudo-first order equation, it therefore suggests that the adsorption can be described by a simple chemical interaction between the DBT molecules and the functional elements on the surface of the MAC.

The pseudo second-order equation is derived from the adsorption equilibrium using equation 7:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \qquad (8)$$

where, t here is a predetermined time and k_2 is the rate constant of second-order adsorption (g/mg.h) while q_e (mg/g) is the adsorption uptake at equilibrium, q_t (mg/g) is the amount of DBT adsorbed on the adsorbent at time t. Figure 6 shows the pseudo second-order plot for DBT.

From Figure 6, it is clear that the pseudo second-order kinetic model is not suitable for this kinetic experiment as the R^2 value is 0.1979. It was also found that the calculated and experimental value of q_e were hugely different (Table 5).

Pseudo first-order and pseudo second-order models for DBT adsorption were compared for their adsorption rate constants, R^2 values and the differences between the experimental and calculated q_e values at different initial concentrations. By comparing the Figures 5 and 6, it was observed that the correlation coefficients (R^2) for the pseudo-first-order model are closer to unity, and hence are a better fit. Overall, the adsorption kinetics of DBT are better represented by the pseudo first-order kinetic model.

Comparison of Results from Different Studies

Table 6 shows the literature values of previous studies for adsorptive desulfurization of fuel for comparison.

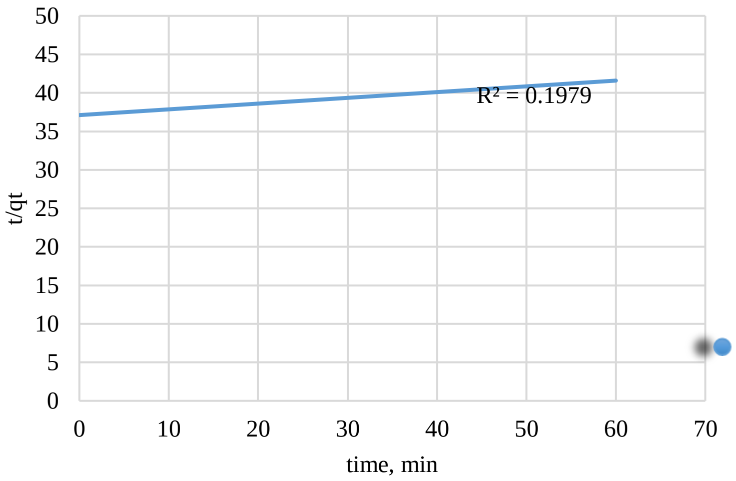

Figure 6. Pseudo second-order plot for DBT

Table 5 shows the pseudo second-order model data for DBT.

Table 5. Pseudo second-order model data for DBT

C_0 (mg/l)	q_e (mg/g)	$1/q_e$	Experiment q_e	R^2
20	1.17	0.0747	13.38	0.1979

Table 6. Previous studies for adsorptive desulfurization of fuel

Reference	Compounds	Fuel	Method	Results
[6]	DBT	*n*-heptane	Removal of DBT from model oil by silver nanoparticles modified AC prepared from brewer's spent grains using wet impregnation (WI) method.	The AgNPs^{kp}/AC and AgNPs^{cw}/AC exhibit higher adsorption capacities for DBT with maximum values of 25.7 and 29.8 mg $_{DBT}$/g$_{Ads}$ at 25 °C respectively, than ACB with 13.9 mg $_{DBT}$/g$_{Ads.}$
[12]	Sulfur	Diesel fuel	Desulfurization of diesel fuel by two types of commercially available adsorbents, one AC (Norit SXRO PLUS) and one zeolite (AXENS MSE 13X), was studied.	AC Norit SXRO PLUS showed the best results regarding sorption capacity in both time and initial sulfur concentration. The lowest total sulfur content achieved was of 8.8 mg kg^{-1} at the sorption capacity of 0.1018 mg g^{-1}.
[38]	DBT	*n*-octane	The removal of DBT from *n*-octane was performed using an adsorption process with sewage sludge-derived AC (S-ACs) at ambient conditions.	The S-AC prepared by KOH-activation exhibited the highest adsorption capacity with up to 14.12 mg/g or around 70.6% DBT removal

[39]	DBT, BT and thiophene	Hexane (85%) and toluene (15%)	Waste tire-derived AC was used for adsorptive desulfurization	The adsorption of DBT, BT and thiophene by the AC-HNO_3 90 °C were higher than that of the raw AC by about 2.2, 3.4 and 3.8 times respectively.
This study	DBT	n-heptane	Adsorptive desulfurization by commercial AC which was undergone modifications through HNO_3	DBT adsorbed by the MAC was in the range of 46.8% to 68.3%. and found that as the concentration of absorbent increased, the percentage of DBT removal decreased

CONCLUSION

Based on FTIR spectral analysis, the functional groups found in MAC are similar to those in AC. However, a number of small peaks were detected at in the range of 3800-3700 cm^{-1}, which indicate O-H stretching vibrations of hydroxyl functional groups. Even though the functional groups found were similar, it has been proved that MAC can increase the adsorption of DBT from model fuel compared to unmodified AC. As the concentration of absorbent increased, the percentage of DBT removal decreased. This was because low concentrations of adsorbent contain a lower amount of SCC than the more concentrated adsorbent. In this study, the amount of DBT adsorbed by the MAC was in the range of 46.8% to 68.3%. Further, the adsorption was found to obey the Langmuir isotherm model instead of the Freundlich isotherm model. The adsorptive capacity and the rate of adsorption for DBT was found to be 1.54 mg/g and 0.74, respectively. Kinetic studies indicated that the sorption of DBT tended to follow the pseudo first-order kinetic model with a correlation coefficient value of 0.9912.

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