

## Desulfurization Performance of Iron Glycerol Activated Carbon

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Adsorptive desulfurization was proposed in this work as an alternative technique for removing sulfur from model diesel. It has emerged as a potentially economically feasible and effective alternative to meet the strict environmental standards for sulfur levels in diesel. The synthesis of activated carbon was derived from glycerin pitch and acted as an adsorbent. The resulting activated carbon was undergone a crucial step, polymerization with sulphuric acid before being thermochemically treated with iron nitrate ( $\text{FeNO}_3$ ) at 700 °C in  $\text{N}_2$  atmosphere. The surface properties and functionalities of activated carbon were revealed by Brunauer-Emmett-Teller (BET) analysis, field emission scanning electron microscopy with energy dispersive X-ray spectroscopy (FESEM-EDX), and Fourier transform infrared spectroscopy (FTIR). Further, the adsorption capacity was studied systematically by analyzing the effects of calcination temperature, contact time, adsorbent dosage, and temperature, under optimum conditions of calcination temperature 700 °C, 30 min contact time, 30 °C temperature, and 0.1 g dosage. 78.65% of dibenzothiophene (DBT) was removed and this result showed glycerin pitch as potential material for the adsorptive desulfurization process.

**Key words:** Desulfurization; activated carbon; dibenzothiophene; model diesel

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Petroleum consists of heteroatoms such as metals, sulfur, nitrogen, and oxygen as well as carbon and hydrogen. By all heteroatom, sulfur is the most prevalent element with 0.03 to 6 wt % in natural gas and crude oils. Crude oil has been refined to produce usable products such as diesel, gasoline, and various other forms of petrochemicals. These mixtures are classified based on the boiling ranges during the acquisition of the different extracts [1]. Nitrogen and sulfur compounds in fossil-based fuels are the most harmful scavengers to the environment and human health [2]. Sulfur compounds are suggested to be removed in the refining process since they lead to corrosion issues in pipelines, pumping equipment, and refining equipment as well as the deactivation of the catalyst used in the processing of crude oil. From a green perspective, the residual sulfur in fuels may result in the release of hazardous gases that combine with water to produce acid rain may bring harmful effects on flora and fauna, soil acidification, and corrosion of buildings [3]. Thus, the control of sulfur content in fuels is becoming increasingly strict around the world. Concern forced government authorities to establish limits on sulfur content in fuels to ultra-low levels [4].

In a petroleum refinery, desulfurization is an essential procedure for crude oil to meet global trends

toward cleaner fuel. Several research organizations worldwide are actively investigating the removal of sulfur compounds from fossil fuels to fulfill environmental laws. However, there is no inclusive approach to classifying desulfurization [5]. The adsorptive desulfurization performance relies mainly on the adsorbent's ideal characteristics, which are high surface area and pore volume, high surface-active sites, and good structural strength and stability [6]. In contrast to conventional methods, the advantage of adsorptive desulfurization is as an efficient and cost-effective method to remove organosulfur compounds from diesel fuel due to its low-energy consumption [7]. Activated carbon has better adsorptive capacity and selectivity for organosulfur compound removal than other adsorbents due to hydrogen bonding interactions involving their surface functional groups [8].

Over the last few years, the green technology concept has been stimulated to encourage the utilization of waste by modifying its physical state to a higher-value product. Activated carbon derived from organic waste has the potential to be competitive and outperform commercial carbons. Activated carbon synthesis from bio-wastes is commonly environmentally friendly, renewable, and easily obtainable [9]. Activated carbons are unique materials having amorphous graphite-like structures, a wide surface area,

and various pore structures. The properties of activated carbon can be modified depending on the application by modifying the synthesis and activation strategies [10]. Therefore, the raw materials chosen must be in a high carbon content, high volatile content, low ash, and low cost [11]. Glycerin pitch, a byproduct of the biodiesel manufacturing process, may be used for the transformation of activated carbon. The production of waste glycerin has increase due to the rising demand for biodiesel [12]. The development of value-added goods like activated carbon from crude glycerin would have minimized waste management and brought a positive environmental impact. Payne *et al.*, [13] for instance discovered that activated carbon-supported iron had been employed as sorbents to remove pollutants broadly. Iron is a promising desulfurization candidate because of its low cost, ease of recycling, and strong adsorptive performance [14].

This study is to develop new activated carbon derived from the glycerin pitch with iron nitrate as an activating agent. The prepared activated carbon was evaluated in the removal of DBT, under an optimum condition of calcination temperature 700 °C, 30 min contact time, and at room temperature with the amount of 0.1 g of activated carbon. The goal of this study is to synthesize iron-impregnated glycerol activated carbon to be utilized as a promising adsorbent for the desulfurization process to produce commercial green diesel.

## MATERIALS AND METHODS

### Materials

Dibenzothiophene (DBT, 97%) was purchased from Across Organics. Iron (III) nitrate ( $\text{Fe}(\text{NO}_3)_2$ ), hydrochloric acid (HCl) (37%), *n*-octane (99%), and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were obtained from Quality Reagent Chemical. Glycerin pitch was obtained from Oleo Palm Industry (Malaysia).

### Preparation of Activated Carbon

First, of foremost, glycerol activated carbon (AC) was prepared by preparing 1:4, glycerol waste: sulfuric acid in a 500 mL beaker followed by carbonization at 180 °C with constant stirring at 300 rpm until a black viscous mass formed. The glycerol polymer was filtered and washed with distilled water until achieved a neutral pH. The dried glycerol polymers undergo the wet impregnation method by mixing with a 40% iron nitrate ( $\text{FeNO}_3$ ), solution. The activation of iron-impregnated glycerol activated carbon (AC-Fe) occurred by using a furnace in the presence of nitrogen gas at the temperature of 700 °C for 2 hr. At room temperature, the obtained materials were washed with 1 M HCl solution. The acid was then washed away with distilled water until it reached a neutral pH and then allowed to dry at room temperature overnight. Later, AC-Fe was calcined for 2 hr at 400, 500, and 700 °C in a furnace in nitrogen atmosphere.

### Adsorption Desulfurization of Model Fuels

Model diesel fuel was made by dissolving dibenzothiophene (DBT) in *n*-octane with a sulfur concentration of 50 ppm. The proposed adsorption desulfurization tests were conducted when 0.1 g glycerol activated carbon and 8 mL model diesel fuel were added to a 50 mL round bottom flask. The mixture was treated until the reaction was completed. The treated oil was then further analysed using UV-Vis spectroscopy to determine the amount of residue sulphur. The optimum condition for the desulfurization process: 700 °C, time 30 min, at room temperature, and 0.1 g dosage.

### Characterization

Various characterization methods were used to characterize the activated carbon. A Fourier transform infrared (FT-IR) (Perkin Elmer Spectrum 2000) spectrophotometer was used to investigate the surface functionalities of the adsorbents. The spectra were between 500 and 4000  $\text{cm}^{-1}$ . Scanning electron microscopy Quanta FEG-650 with EDX analyzer was used to examine the surface morphology of the activated carbon. The activated carbon homogeneity, crystalline shape, and particle size can all be determined using FESEM examination. EDX was used to determine the elemental composition. The surface texture and porosity of the adsorbents were studied by Brunauer-Emmett-Teller (BET) Micromeritics ASAP 20120 adsorption analyzer with evacuation temperature at 90 °C for 1 hr. The analyte was determined by using Shimadzu UV-Vis spectrophotometer at the maximum wavelength ( $\lambda_{\text{max}}$ ) 325 nm.

## RESULTS AND DISCUSSION

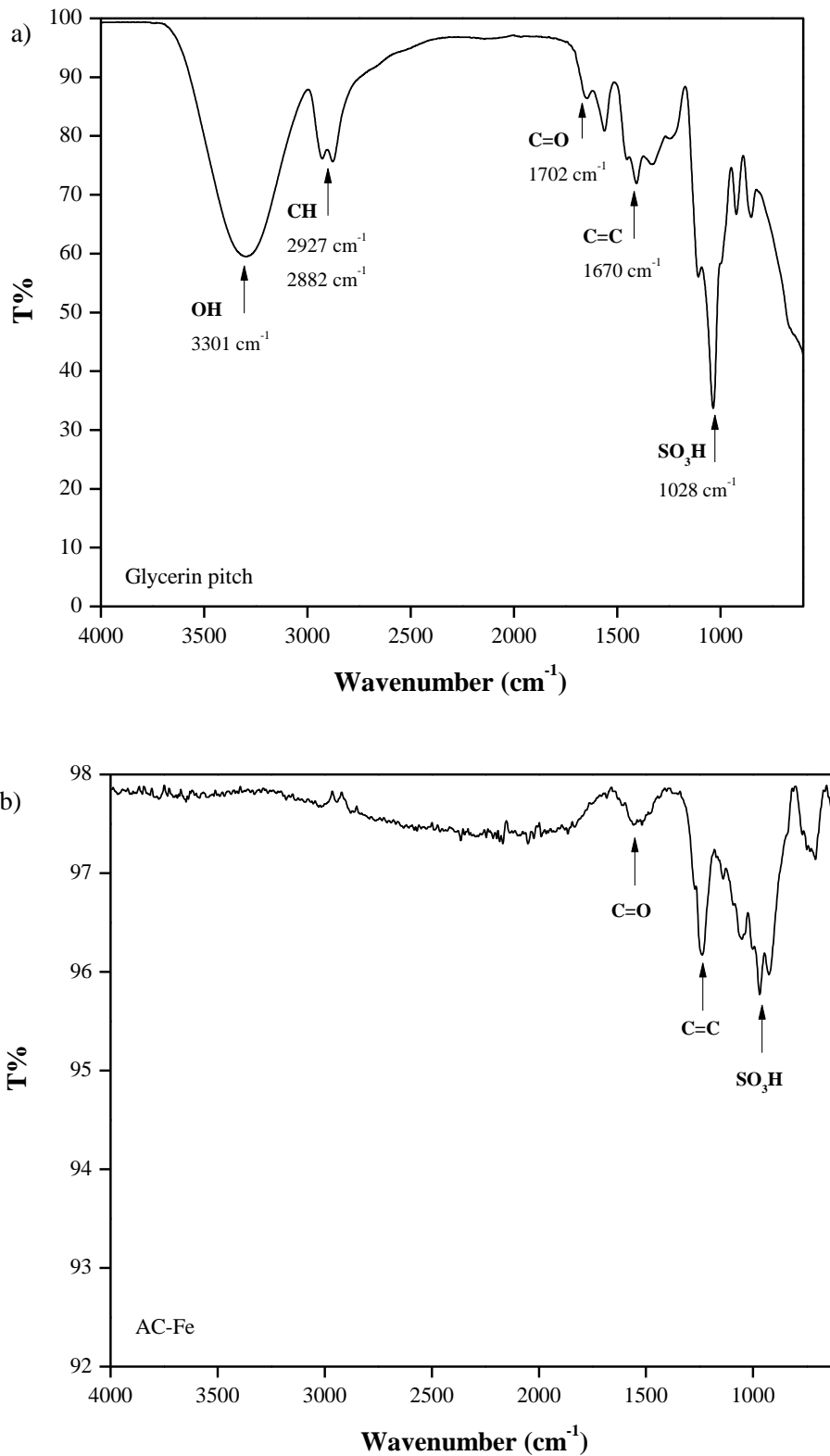
### Characterization of Activated Carbon

#### FTIR Analysis

The synthesized activated carbons were further characterized using FTIR analysis to determine the functional group as shown in Figure 1. The glycerin pitch possessed a broad band at 3301  $\text{cm}^{-1}$  which consigned to hydroxyl group (O-H) stretching vibration. The medium bands that appeared at about 2927 and 2882  $\text{cm}^{-1}$  were attributed to stretching vibrations of C-H group. However, the O-H and C-H group start to diminish when undergoing carbonization due to the loss of chemisorbed water and hydroxylic groups in the process to form activated carbons. The other medium intensity band located at 1702  $\text{cm}^{-1}$  and 1670  $\text{cm}^{-1}$  was assigned to C=O and C=C groups, respectively. The carbonyl peak was a composite peak due to -CHO and -COOH [15]. The intensity peak of -SO<sub>3</sub>H at 1028  $\text{cm}^{-1}$  started to decrease when underwent thermal

treatment at 700 °C resulted in partial decomposition of  $-\text{SO}_3\text{H}$  due to the dehydroxylation of the adjacent sulphonyl groups [16]. The FTIR

measurements proved that the activated carbon was primarily made of carbon and oxygen, with a trace amount of residual sulfur.



**Figure 1.** FTIR spectra of a) glycerin pitch and b) AC-Fe.

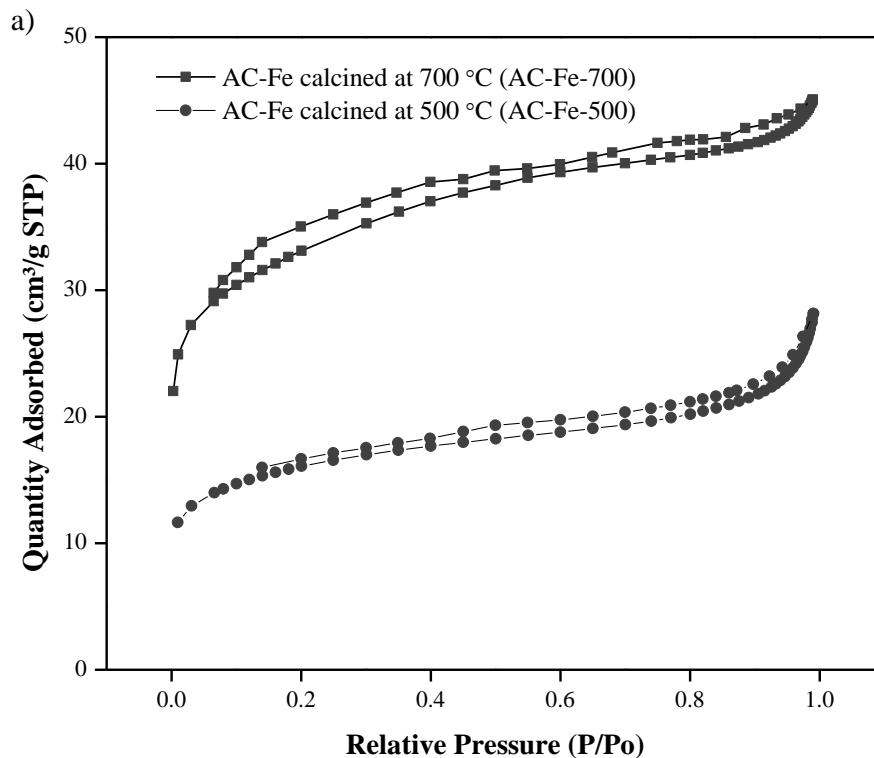
### BET Analysis

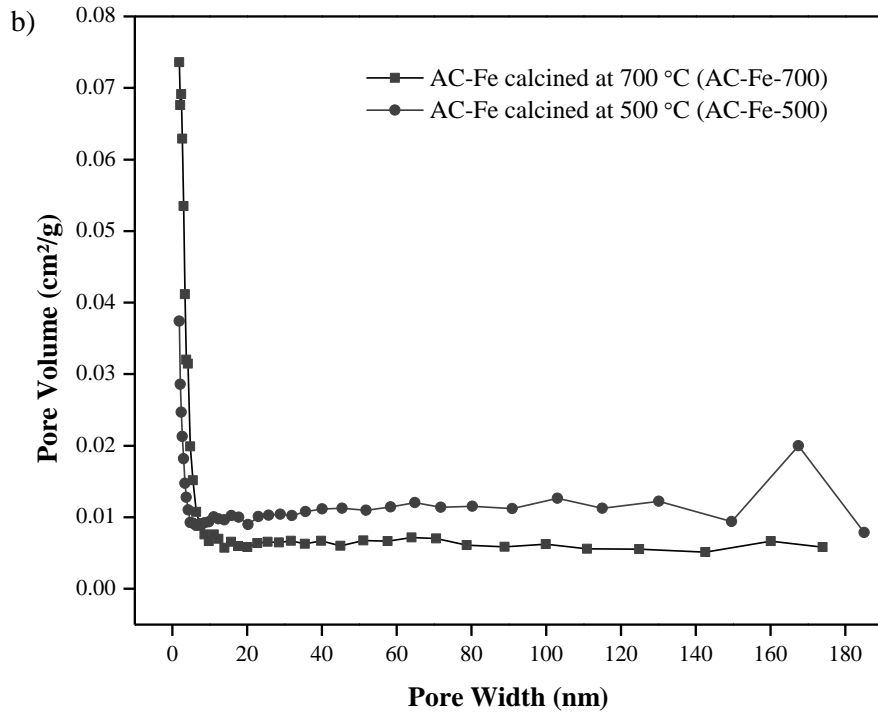
The activated carbons were measured by the nitrogen adsorption-desorption method and the results are unveiled in Figure 2. Table 1 summarizes the BET surface area, pore volume, and pore size of AC-Fe calcined at different calcination temperatures. The surface area of AC-Fe calcined at 700 °C (AC-Fe 700) demonstrated a high surface area of 120.29 m<sup>2</sup>/g as compared to the AC-Fe calcined at 500°C (AC-Fe 500) (58.52 m<sup>2</sup>/g) which could be attributed to the impact of calcination temperature. The observed trend verifies that the irons were correctly put onto the activated carbon support. As activated carbon was exposed to a higher temperature, the solvent and volatile compounds trapped within the pores were evacuated more successfully [17]. More active sites formed during high calcination give a better adsorption performance [18]. The reduction in the surface area might imply that

some metals obstruct the pores, causing a reduction in pore volume [19]. Considering that the molecular size of DBT was 0.80 nm [20] and the activated carbons have a pore diameter in a range of 2 nm, it was considered appropriate for the removal of the DBT molecule due to their comparable molecular sizes to that of smaller pore sizes. Thus, AC-Fe calcined at 700 °C was a proper material to be used for the desulfurization of DBT molecule. The adsorption isotherms of AC-Fe exhibit Type H2 isotherm classification. A hysteresis loop involved pores nature gradually filling up to a relative pressure of 0.8. The presence of low micropores and mesopores in the samples can be seen at low nitrogen as depicted in Figure 2(a) [21]. Such H2 type materials were known to have complicated pore structures that were typically made up of linked networks of pores with various sizes and shapes. It appears that the activated carbon was mesoporous in this way [10].

**Table 1.** Physical properties of activated carbons.

Adsorbent	S <sub>BET</sub> (m <sup>2</sup> /g)	Average Pore Volume (cm <sup>3</sup> /g)	Average Pore Size (nm)
AC-Fe 700	120.29	0.0686	2.2841
AC-Fe 500	58.52	0.0411	2.8129



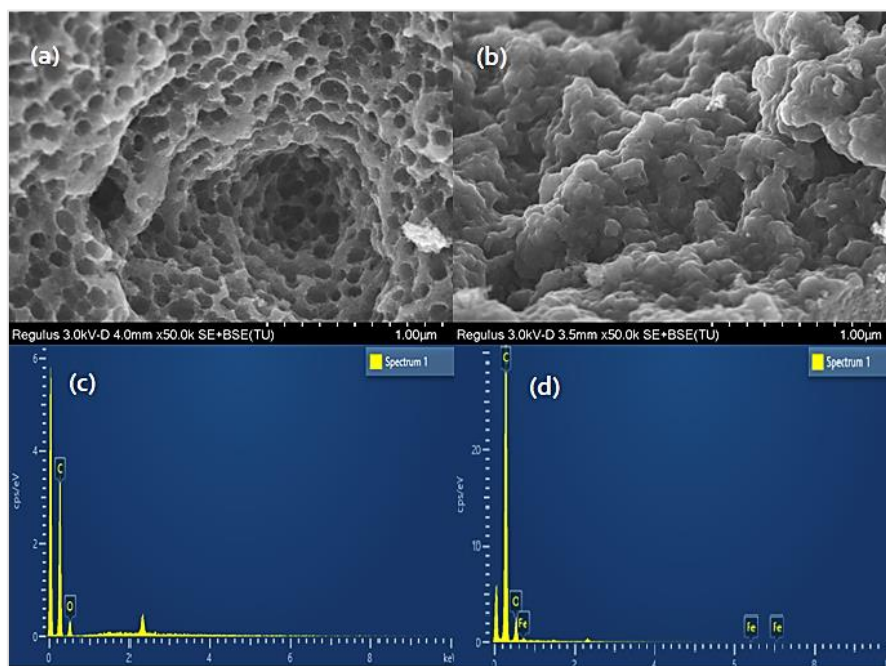


**Figure 2.** a) N<sub>2</sub> adsorption/desorption isotherm, b) pore size distribution of AC-Fe 700 and AC-Fe 500.

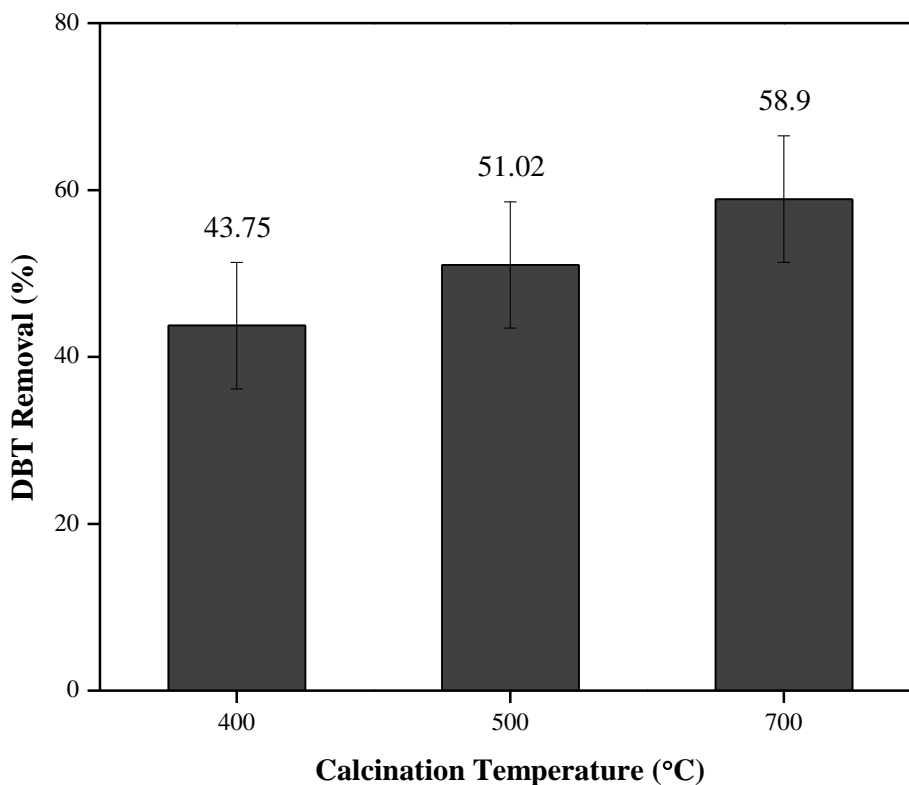
### FESEM-EDX Analysis

The surface morphology and elemental distribution of AC and AC-Fe were observed by FESEM-EDX analysis at 50,000x magnification respectively. The surface morphology of the AC displayed huge open pores and uneven clusters of smooth-surfaced. Carbon (72.88%) and oxygen (8.24%) were the sole atom discovered on the AC surface, according to the EDX

analysis. The iron metal activation process modified the porosity of activated carbon surface [22]. The increased porosity development in the activated sample AC-Fe was visible in the FESEM images (Figure 3). The AC-Fe had a rough morphology with diverse deep hollow shapes and sizes [23]. Through EDX analysis, Fe (1.80%) was distinctly discovered from AC-Fe. This indicates that iron metal was successfully impregnated on the surface of the activated carbon.



**Figure 3.** FESEM analysis of a) untreated AC, b) AC-Fe at 50 000x magnification and EDX spectra of c) AC, (d) AC-Fe.



**Figure 4.** DBT removal by AC-Fe as a function of calcination temperature. Reaction conditions: T = 30 °C, time = 30 min, dosage = 0.1 g.

### Adsorption Desulfurization

Screening tests using model diesel fuel containing DBT that involve several parameters have been investigated to find the best condition and potential of iron-loaded activated carbon for adsorption desulfurization.

### Effect of Calcination Temperature

The influence of calcination temperature on activated carbon was investigated in a range of 400 to 700 °C. Subtle variations in the properties of the activated carbons were observed in Figure 4. The results showed that the AC-Fe calcined at 700 °C was more effective in the desulfurization of DBT than the other activated carbon calcined at different temperatures. The calcination process played an important role in the structural evolution of pore sizes of adsorbent [24]. When the calcination temperature of activated carbon rises, it was consistent with the BET surface area and pore volume. A considerable reduction in particle size was found, resulting in an increase in surface area and a synergistic impact due to the presence of the common interface between activated carbon and iron.

### Effect of Contact Time

The impact of contact time for DBT adsorption over AC-Fe with the calcination temperature of 700 °C,

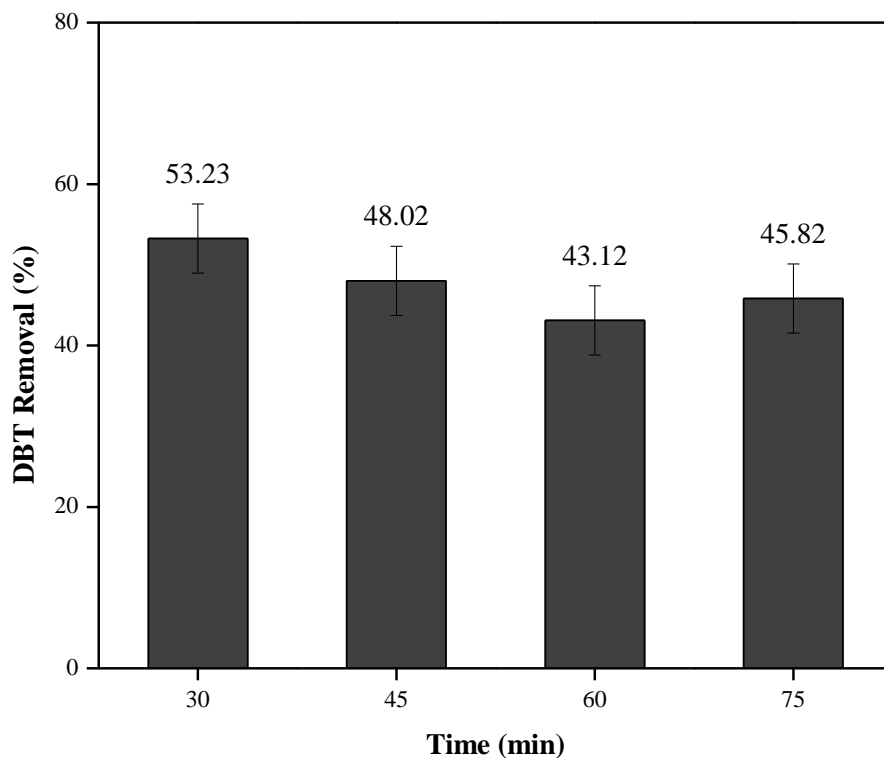
which was the highest quality activated carbon for the DBT adsorption, was explored in time minutes of 30, 45, 60, and 75 were shown in Figure 5. It appears that DBT removal decreased slowly as the contact time increased. A prolonged reaction time resulted in a decrease in the removal of sulfur may be due to a decreased in the number of adsorption sites on the surface of the adsorbent. Whereas the available adsorption sites on the surface of the adsorbent have been fully occupied with the DBT molecules or the evaporation of model fuel with time increasing [25]. The DBT removal slightly increased at a stamped time of 75 minutes may because there were unoccupied activated carbon sites left during desulfurization. Anyhow, 30 minutes was chosen as an ideal contact time for desulfurization.

### Effect of Temperature

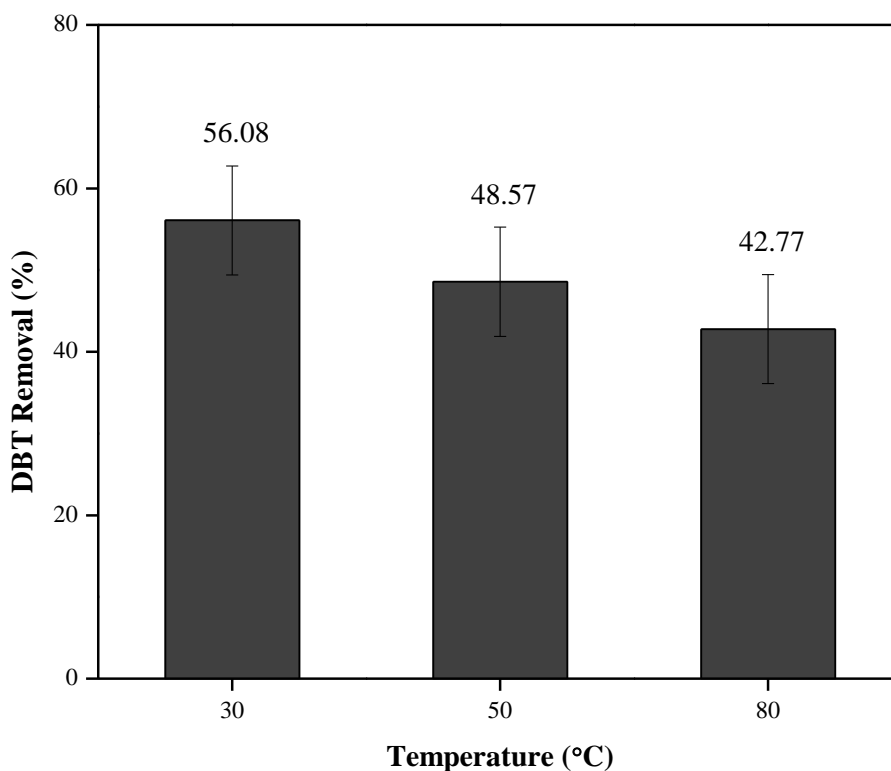
The effects of temperature for DBT removal were tested over a temperature range of 30 to 80 °C. Figure 6 revealed that DBT removal increased with increasing temperature, with maximal adsorption at 30 °C. Further increase in temperature resulted in a declined DBT removal. The percent of DBT removal at 30, 50, and 80 °C, was 56.08, 48.57, and 42.77%, respectively. The maximum desulfurization occurs at an ambient temperature of 30 °C, whereas DBT adsorption decreases with rising temperature, causing a reduction in desulfurization. In addition, a

higher temperature causes an increase in the molecular kinetic energy, which in turn reduces the attractive forces that exist between the adsorbent

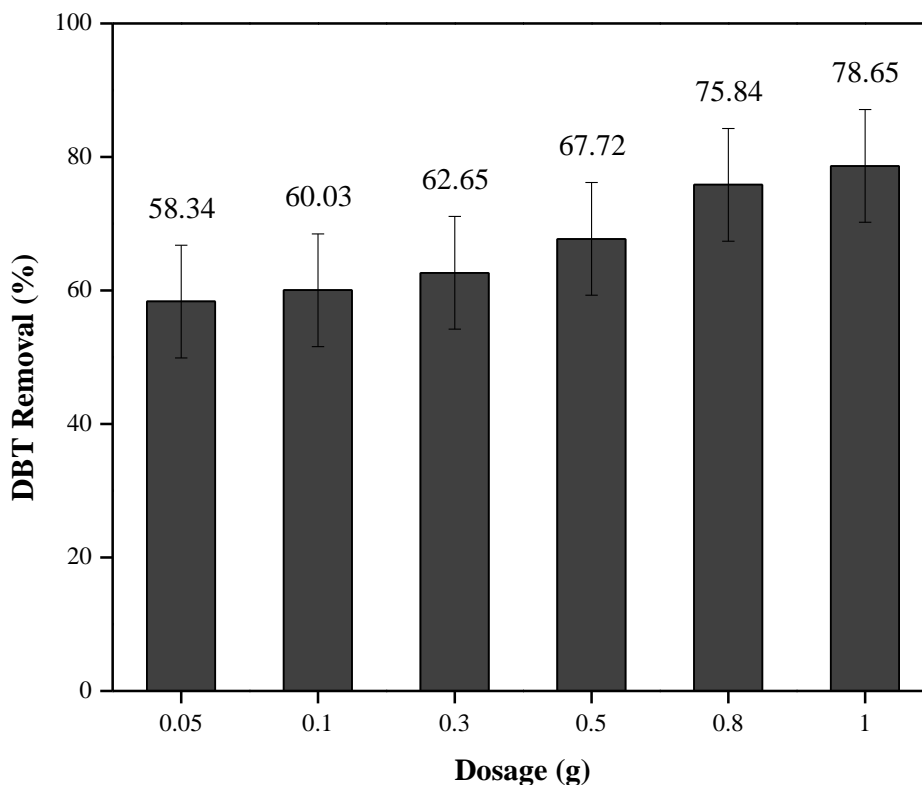
surface and the DBT molecules. This results in a lower rate of DBT removal when the temperature increased [26].



**Figure 5.** DBT removal by AC-Fe as a function of contact time. Reaction conditions: calcination temperature = 700 °C, T = 30 °C, dosage = 0.1 g.



**Figure 6.** DBT removal by AC-Fe as a function of temperature. Reaction conditions: calcination temperature = 700 °C, time = 30 min, dosage = 0.1 g.



**Figure 7.** DBT removal as a function of AC-Fe dosage. Reaction conditions: calcination temperature = 700 °C, T = 30 °C, time = 30 min.

### Effect of Dosage

The percentage of DBT extraction was analyzed as a function of the AC-Fe masses in the range of 0.05 g to 1.00 g for a better understanding of the impact of dosage on the adsorptive desulfurization process. Figure 7 summarizes that the percentage of DBT adsorbed increases with increasing the dosage of iron-impregnated AC from 58.34% to 78.65%. These results were reasonable since the number of active sites increases with increasing the adsorbent mass, resulting in better adsorption performance [27].

### CONCLUSION

The adsorptive desulfurization (ADS) process was applied in this study using different calcination temperatures, contact times, dosages, and temperatures with the help of glycerol activated carbon. The results demonstrated that the desulfurization of DBT was effectively accomplished by wetness impregnation with iron nitrate under very mild conditions. The successful evaluation of the experimental data was confirmed by the textural characterization performed using FTIR, BET, and FESEM-EDX. Based on this study, AC-Fe derived from glycerin pitch successfully achieved 78.65% of desulfurization of DBT under calcination temperature 700 °C, 30 min contact time, 30 °C, and with 1.0 g

dosage. It potential to be used as an adsorbent in desulfurization to achieve ultra-low-sulfur diesel with promising practical applications involving the process of fuel oil due to its cost-effectiveness, low-energy consumption, mild conditions, and high efficiency.

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