

## ADSORPTION DESULFURIZATION OF SIMULATED DIESEL FUEL USING GRAPHENE OXIDE

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**Abstract.** Graphene oxide (GO) was synthesized from graphite powder by the improved Hammers method and used for the adsorption of organosulfur compound (dibenzothiophene, DBT) from model diesel fuel. FT-IR spectroscopy, X-ray diffraction, SEM, EDX, and BET were used to characterize the GO. Several factors, such as solution pH, initial DBT concentration, adsorption contact time, adsorption temperature, and adsorbent dosage were used to test the DBT removal efficiency. The results show that the maximum removal was 96.4 % at pH = 5, initial solution concentration of 200 ppm, adsorption time of 45 min, temperature of 45 °C and adsorbent dosage of 0.4 g/25 mL.

**Keywords:** adsorption desulfurization, dibenzothiophene, graphene oxide.

### 1. Introduction

The production of fuel oil with free sulfur content (10–15 ppm) under USEPA guidelines has been a major problem for most countries using the desulfurization process<sup>1</sup>. Although the hydrodesulfurization (HDS) method is widely used to remove sulfur compounds from diesel fuel, it is still less effective for persistent sulfur compounds such as benzothiophene (BT) and its derivatives, which are highly resistant to thermal decomposition in the refinery<sup>2,3</sup>.

Over the past few decades, various technologies have been developed for sulfur removal: oxidative desulfurization (ODS), adsorption desulfurization (ADS), biodesulfurization (BDS), and extractive desulfurization (EDS) methods<sup>4</sup>. In the oxidative desulfurization (ODS) process, sulfur compounds are converted to sulfoxides and sulfones using appropriate oxidizing agents under mild

conditions<sup>5, 6</sup>, whereas the adsorption desulfurization (ADS) process removes sulfur from oil fractions by adsorption on high surface area adsorbents<sup>7</sup>. In the biodesulfurization (BDS) method, bacteria are used as catalysts to remove organosulfur compounds from oil fractions without breaking the hydrocarbon chains<sup>8</sup>. Appropriate solvents are used in the process of extractive desulfurization (EDS) to remove more soluble organic sulfur compounds from fuels. This process is carried out under mild operating conditions<sup>9</sup>. The relatively low cost, environmental friendliness, and ease of operation make adsorption a widely used method among these methods<sup>10</sup>.

Graphene is a one-atom-thick carbon (sp<sup>2</sup>) with a two-dimensional (2D) layer. Excellent electrical, thermal and mechanical stability, in addition to a high specific surface area, are the main properties that make it an excellent adsorbent in industry<sup>11</sup>. Graphene oxide has the potential to be used as an adsorbent due to its non-specificity. Recently, many carbon-based materials, such as carbon nanotubes (CNTs) and graphene oxides (GOs), have been used in adsorption compared to zeolites and metal oxides<sup>12,13</sup>.

In this work, graphene oxide was synthesized from natural graphite powder using an improved Hammers procedure. The graphene oxide was analyzed using FTIR, XRD, SEM, EDX, and BET. The effect of various factors, such as solution pH, initial DBT concentration, contact time, temperature, and adsorbent dosage on the adsorption efficiency was investigated.

### 2. Experimental

#### 2.1. Materials

Natural graphite powder (< 20 μm) was supplied from Sigma Aldrich. All chemical reagents used in this research, 98 % sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), 85 % phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), potassium permanganate (KMnO<sub>4</sub>), 30 % hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), 36 % hydrochloric acid (HCl), and absolute ethanol were purchased from Sigma Aldrich.

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## 2.2. Preparation of Adsorbent

Graphene oxide (GO) has been synthesized from graphite powder by chemical oxidation using the improved Hummers method<sup>14</sup>. Firstly, 9/1 volume of concentrated H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> were mixed and stirred for 15 min at 0–5 °C. 3.0 g of graphite powder and 18 g of KMnO<sub>4</sub> were added to the solution under continuous stirring. Then the solution was heated at 35 °C for 4 h under stirring. 250 mL of deionized water (DW) was added gradually to raise the temperature of the solution to 95 °C and kept for 15 min. Then, 30 % H<sub>2</sub>O<sub>2</sub> (5 mL) was added to reduce the residual oxidants. The solution was centrifuged at 4000 rpm, washed with deionized water several times, washed with 5% HCl, and finally dried at 70 °C all night.

## 2.3. Batch Adsorption Experiments

The removal efficiency of DBT from simulated diesel fuel was studied in a batch adsorption system with a speed of 300 rpm. 0.1M HCl was added dropwise to the solution to adjust the pH at the range of 4–7. DBT was dissolved in 25 mL of n-hexane as a stock solution with an initial concentration of 200–500 ppm. All adsorption experiments were performed at temperatures of 25–55 °C, contact time of 15–60 min, and adsorbent dosage of 0.1–0.4 g. After completing each run, the sample was centrifuged to separate the sorbent, and finally, the sample was analyzed to determine the percentage of sulfur remaining. The removal of sulfur components was obtained using the equation

$$\% \text{ Removal} = \frac{C_0 - C_f}{C_0} \cdot 100,$$

where  $C_0$  represents the initial sulfur content (ppm), and  $C_f$  represents final sulfur concentration (ppm).

## 3. Results and Discussion

### 3.1. Adsorbent Characterization

FTIR spectroscopy was used to examine the bond stretch interaction in the graphene oxide as shown in Fig. 1. The stretching of C=C, C=O, and –OH groups are observed at 1620 cm<sup>-1</sup>, 1735 cm<sup>-1</sup>, and 3433 cm<sup>-1</sup>, respectively. This indicates that oxygen functional groups were introduced between the graphene oxide layers during the oxidation<sup>15, 16</sup>.

The X-ray diffraction pattern for GO powder is shown in Fig. 2. A sharp peak was observed at  $2\theta = 12.26^\circ$  with a d-space distance of 0.79 nm<sup>17</sup>. The results showed that the regular crystalline pattern of graphite was damaged, and oxygen functional groups appeared in the

GO structure, which is similar to the value reported in the literature<sup>18</sup>.

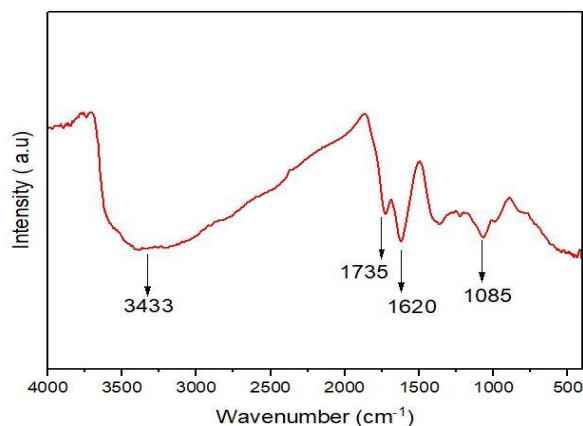


Fig. 1. FT-IR spectrum of graphene oxide

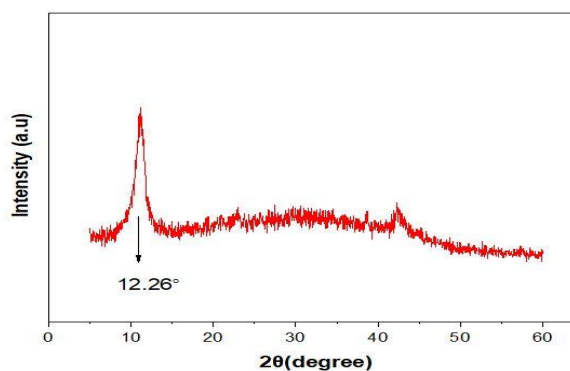


Fig. 2. XRD pattern of graphene oxide

The SEM image of GO is shown in Fig. 3. The surface morphology of GO showed a folded and wrinkled curtain sheet. This morphology indicates that graphite was well-exfoliated during the oxidation process<sup>19</sup>.

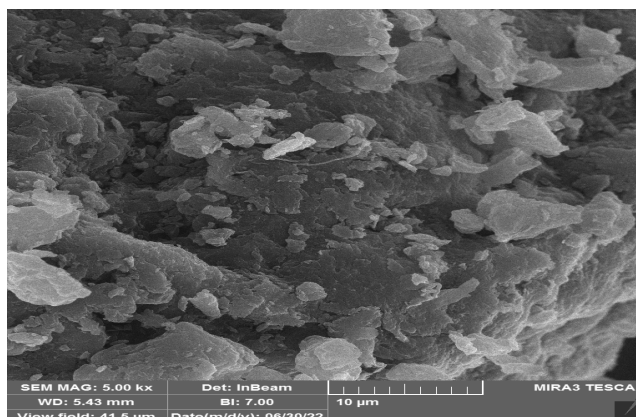


Fig. 3. SEM image of graphene oxide

The chemical composition of graphene oxide was determined by EDX spectroscopy as shown in Fig. 4. It was observed that GO consists of carbon and oxygen with a ratio of 1:1, and some impurities of less than 7 % are derived from graphite<sup>20</sup>.

The surface area ( $S_{BET}$ ) volume of the pore ( $V_p$ ) and diameter of the pore ( $D_p$ ) of GO were calculated using the Brunauer Emmett and Teller BET (ISO-9277-2010) method. The values are summarized in Table 1.

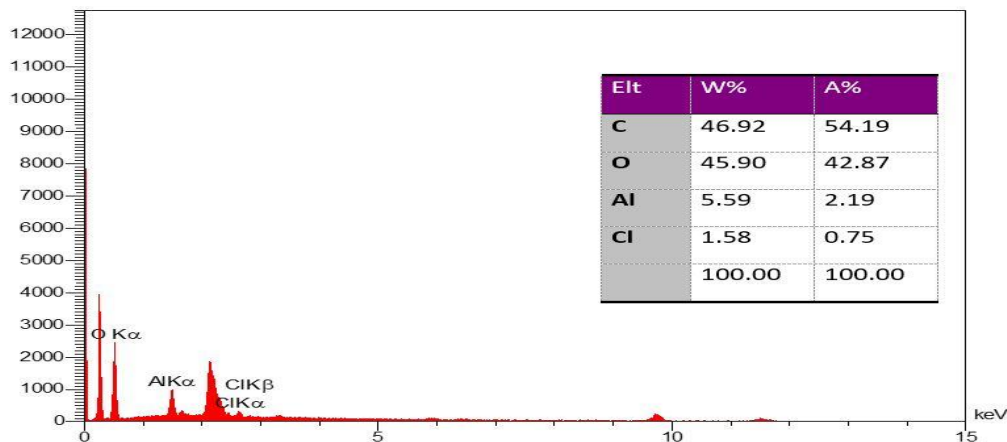


Fig. 4. EDX spectrum of graphene oxide

Table 1. Structure properties of Graphene oxide

	Surface Area ( $S_{BET}$ ), $m^2 / g$	Volume of the pore ( $V_p$ ), $cm^3 / g$	Diameter of the pore ( $D_p$ ), nm
Graphene oxide	29.80	0.18	4.36

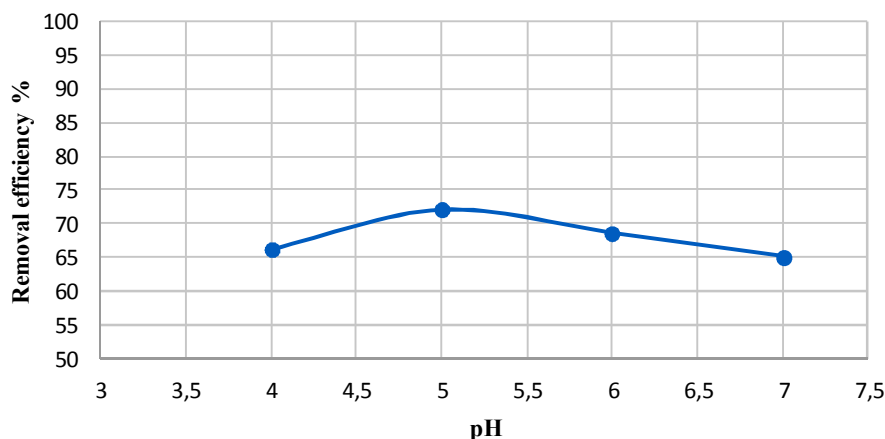


Fig. 5. pH effect on removal efficiency [Temp = 25 °C, contact time = 15 min, DBT concentration = 300 ppm, and adsorbent dosage = 0.2 g]

## 3.2. Adsorption Performance

The influence of several operating conditions, for example, initial pH, DBT concentration, contact time, temperature, and adsorbent dosage on the efficiency of adsorption DBT has been investigated using graphene oxide as an adsorbent. 25 mL of simulated diesel fuel was used for the experimental batch.

### 3.2.1. Effect of Initial pH

The effect of initial pH on the removal efficiency of DBT was studied at pH = 4, 5, 6, and 7 under other constant conditions (temperature 25 °C, contact time 15 min, DBT concentration 300 ppm, and adsorbent dosage 0.2 g). The results are shown in Fig. 5. The maximum removal was found to be 72.1 % at pH = 5. The increase

in the pH value decreased percentage removal, so the pH value of 5 was selected as the optimal one<sup>21</sup>.

### 3.2.2. Effect of Initial Concentration of DBT

The effect of different initial concentrations of DBT on the removal efficiency was investigated at 200, 300, 400, and 500 ppm (Fig. 6). In brief, the removal efficiency dropped dramatically with the rising concentration of DBT<sup>22</sup>. The optimal value for DBT removal was 75 % with the DBT initial concentration of 200 ppm.

### 3.2.3. Contact Time Effect

The effect of contact time (from 15 to 60 min) on the DBT adsorption (200 ppm) was investigated at pH = 5, and a temperature of 25 °C. It was shown that the rate of DBT removal increased slightly from 75.8 % to 82.9 % with the increase in time<sup>23, 24</sup> and the adsorp-

tion / desorption equilibrium was reached at about 45 min (Fig. 7).

### 3.2.4. Temperature Effect (Fig. 8)

The temperature effect was examined at 25, 35, 45, and 55 °C and the results can be seen in Fig. 8. It was noticed that the percentage of DBT removal increased gradually to 89.5 % when the temperature was raised from 25 to 45 °C<sup>25, 26</sup>.

### 3.2.5. Adsorbent Dosage Effect

Fig. 9 shows the effect of adsorbent dosage on the adsorption of the DBT. The study was carried out at the dosage of 0.1–0.4 g, a temperature of 45 °C, the equilibrium time of 45 min, and pH of 5.0. The efficiency of DBT removal increased dramatically with increasing dosage of adsorbent. The maximum removal of DBT was 96.5 % at adsorbent dosage of 0.4 g<sup>27, 28</sup>.

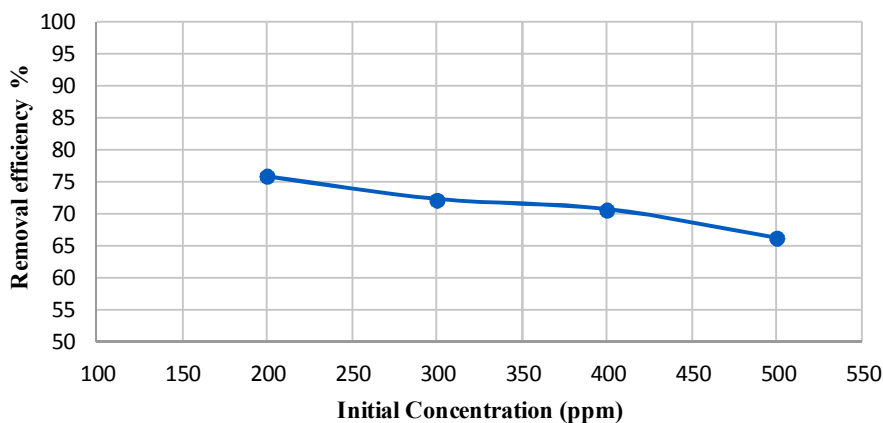


Fig. 6. Effect of DBT concentration on removal efficiency [pH = 5, Temp = 25 °C, contact time = 15 min, and adsorbent dosage = 0.2 g]

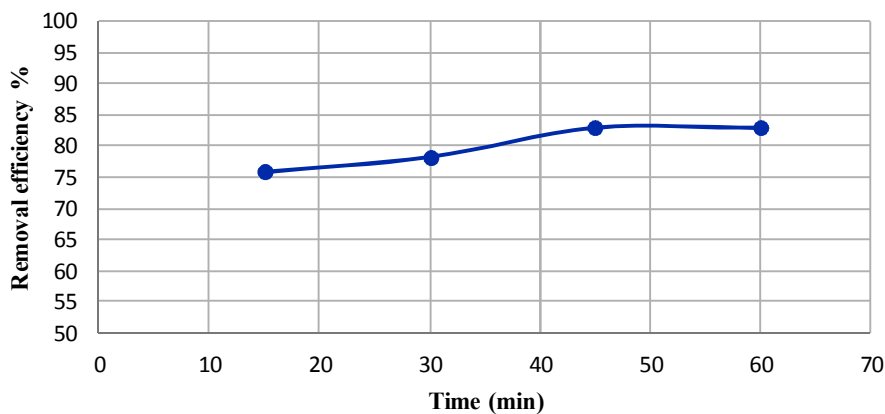


Fig. 7. Contact time influence on removal efficiency [pH = 5, DBT concentration = 300 ppm, Temp = 25 °C, and adsorbent dosage = 0.2 g]

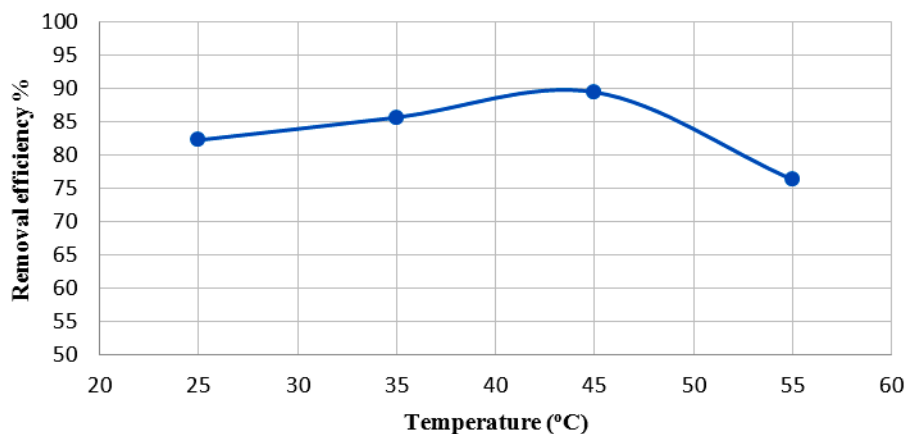


Fig. 8. Effect of temperature on removal efficiency [pH = 5, DBT concentration = 300 ppm, contact time = 45 min and adsorbent dosage = 0.2 g]

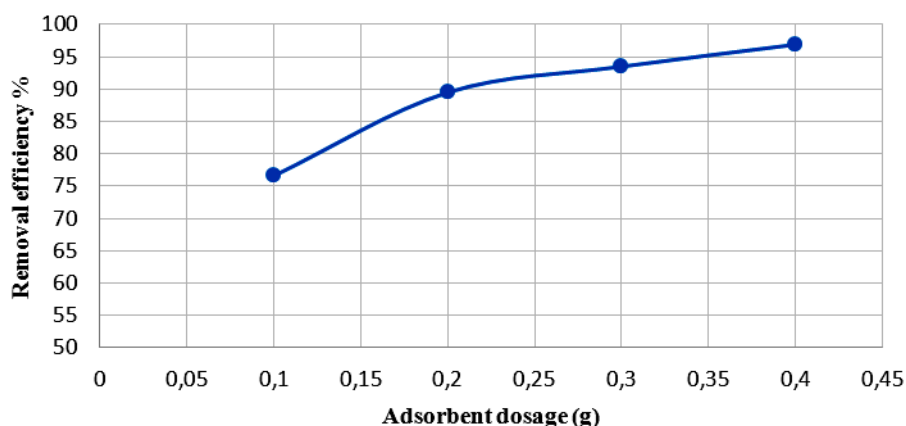


Fig. 9. Adsorbent dosage effect on removal efficiency of DBT [pH = 5, DBT concentration = 300 ppm, contact time = 45 min and temperature = 45 °C]

## 4. Conclusions

Carbon materials such as graphene oxide were prepared using an improved Hummers method. Introducing oxygen functional groups on the GO surface could increase the d-space between layers to 0.38 nm. The efficiency of graphene oxide for DBT adsorption was investigated under a wide range of conditions, for example, initial pH, DBT concentration, contact time, temperature, and adsorbent dosage. The results showed that maximum removal was 96.5 % under the following conditions (pH = 5, the concentration of DBT = 200 ppm, contact time = 45 min, temperature = 45 °C, and adsorbent dosage = 0.4 g).

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## АДСОРБЦІЙНЕ ЗНЕСІРЧЕННЯ ІМІТОВАНОГО ДИЗЕЛЬНОГО ПАЛИВА З ВИКОРИСТАННЯМ ОКСИДУ ГРАФЕНУ

**Анотація.** Оксид графену (ОГ) синтезовано із графітового порошку за вдосконаленим методом Хаммерса і використано для адсорбції сіркоорганічної сполуки (добензотіофену, ДБТ) із модельного дизельного палива. Для характеристики ОГ використано ІЧ-спектроскопію, рентгенівську дифракцію, СЕМ, метод енергодисперсійної рентгенівської спектроскопії (EDX) та BET. Для перевірки ефективності вилучення ДБТ досліджено декілька факторів, таких як рН розчину, початкова концентрація ДБТ, час контакту адсорбції, температура адсорбції та дозування адсорбенту. Результати показують, що максимальне вилучення становило 96,4 % за рН = 5, початкової концентрації розчину 200 м. ч., часу адсорбції 45 хв, температури 45°C і дозування адсорбенту 0,4 г/25 мл.

**Ключові слова:** адсорбційна десульфуризація, добензотіофен, оксид графену.