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Research Article

ZnO-Activated Carbon Blended as a Catalyst for Oxidative Desulfurization of Dibenzothiophene

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Abstract

The problem of sulfur content in heavy oil is a challenge for researchers to meet the needs of environmentally friendly fuels. The catalyst preparation plays an important role in the desulfurization process. The synthesis of ZnO-activated carbon as a catalyst and its activity in oxidative desulfurization (ODS) reaction has been successfully carried out. In this work, the ZnO and activated carbon (AC) were blended by a solid-solid reaction. The ZnO, AC, and ZnO-AC were then characterized using acidity test with pyridine vapor adsorption, Fourier Transform Infra-Red (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX), and Surface Area Analyzer (SAA). ODS of dibenzothiophene (DBT) reaction was performed by using H_2O_2 under variation of the reaction time (30, 60, 120, and 150 min) for the ZnO-AC catalyst. The efficiency of ODS-DBT was analyzed by a UV-Visible spectrophotometer. The XRD analysis result showed that ZnO-AC blended displays new crystal peaks of Zn in the AC diffractogram. The surface area (734.351 m^2/g) and acidity (4.8780 mmol/g) of ZnO-AC were higher than ZnO and AC themselves. ZnO-AC produced the highest efficiency of ODS-DBT which was 93.83% in the reaction time of 120 min. Therefore, the simple procedure of this physical blending was proved effective to homogenize between ZnO and AC into ZnO-AC so that it has good physicochemical properties as an ODS-DBT catalyst.

Keywords: Oxidative Desulfurization; Dibenzothiophene; ZnO; Activated Carbon; Physical Blending

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1. Introduction

As for 2040, International Energy Agency reported that energy and fossil fuel demands would still increase around 30% [1]. The strict regulation towards sulfur content that cannot exceed more than 15 ppm is one of the greatest difficulties in fulfilling the world demands on petroleum oil [1,2]. Hydrodesulfurization (HDS) has received great attention for the past years, this reaction involved the usage of hydrogen gas as well as high temperature and pressure [3]. Major drawbacks of this reaction are the relatively high cost of HDS due to the high usage of hydrogen and heat [4]. Another alternative for the sulfur removal process has been proposed, such as oxidative desulfurization, ultrasound-

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assisted oxidative desulfurization, extractive desulfurization, adsorptive desulfurization, biodesulfurization, and so on [3–6].

The oxidative desulfurization (ODS) technique has also gained large interest as an alternative to HDS due to its comparatively low cost, mild condition, and simplicity [1–4]. In ODS reaction, there are two steps involved in the process: the conversion of sulfur-containing compounds into their respective sulfoxides and sulfones, followed by extraction of these compounds using extractant [3]. The oxidation process required oxidants, such as H_2O_2 which is considered an environmentally friendly and green oxidant, and acid catalyst [6].

Several solid catalysts had been examined for ODS reaction including heteropoly acid, either alone or supported [7], and metal oxides, *i.e.* oxides of (Mo, Mn, Sn, Fe, Co, Zn) metals [8]. However, most of it either concerned complicated and multistep synthesis techniques or unrecyclable. The latest literature survey shows that ZnO was reported for adsorptive desulfurization [9] and ZnO was able to remove the sulfur content without changing the main hydrocarbon structure where non-sulfur-containing crude fuel oil mass remains unchanged. Another study stated that the increment of the catalytic activity of ZnO can be corresponded to a lower band gap value (3.35 eV) compared to 3.65 eV for $Zn_5(OH)_8Cl_2 \cdot H_2O$, which would increase the absorption capacity of higher wavelength radiation [10]. A novel percent of nano-catalyst with 18% zinc oxide (ZnO) was an active component over nano-alumina for sulfur removal from kerosene fuel by air (oxidative desulfurization (ODS) method) [11]. Riad and Mikhail showed that Zn-incorporated hydroxyapatite catalysts were investigated towards oxidative desulfurization of light gas oil with a total sulfur content of 1281.8 ppm. The maximum observed sulfur removal reached 89.7% using zinc catalysts prepared via the ion exchange technique [12].

Currently, activated carbon (AC) has been found in an increasing number of catalytic reactions. It is used as either the support for the active phases or as the catalyst itself, because of its physical performance and surface functional groups, which contain oxygen [13]. For this reason, AC is selected as the support material for ZnO due to its effectiveness as a heterogeneous catalyst in H_2O_2 decomposition to form hydroxyl radicals which is a powerful oxidant [14]. In the ODS process, the hydroxyl radicals reacted with organic acids to form peracids and oxidized the organosulfur compounds to their corresponding sulfoxides and sulfones.

Several studies on the synthesis of ZnO-AC have been carried out previously. Swat *et al.* synthesized AC/ZnO as adsorbent through thermal co-precipitation for desulfurization of model diesel fuels (MDFs) at ambient temperature [15]. Meanwhile, Ahmed Zeki *et al.* produced ZnO/AC composites also through thermal co-precipitation as a catalyst for ODS-DBT [16]. Khlaif *et al.* made ZnO Nanoparticles Loaded AC as an adsorbent in adsorptive desulfurization in crude oil through an impregnation process using an ultrasonic device [17]. As far as the authors know, no one has ever synthesized ZnO-AC through the physical mixing of both materials as a catalyst for ODS-DBT. This method is considered easier, simpler, and more applicable than the previously proposed method.

Therefore, in this research, a cost-effective catalytic oxidative desulfurization process was developed by preparing ZnO-AC as a catalyst with a physical blending method together with hydrogen peroxide as oxidant and acetonitrile as an extraction solvent to produce a lower sulfur concentration.

2. Materials and Methods

2.1 Materials

Zinc oxide (ZnO) and activated carbon (AC) were used for the catalyst preparation. The model fuel was made of n-hexane and dibenzothiophene. Hydrogen peroxide 30% (w/w) was used as an oxidizing agent and acetonitrile was used as solvent extractant. All the materials were supplied by Merck.

2.2 Preparation and Characterization of ZnO-AC

ZnO was blended with activated carbon (AC) with a weight ratio of 1:9, it was crushed and sifted through 100 mesh. The ZnO-AC catalyst was then calcined at 500 °C for 5 h with an N_2 gas of 20 mL/min. All catalysts (ZnO, AC, and ZnO-AC) were analyzed by X-Ray Diffractometer (Philips X'Pert MPD), Surface Area Analyzer (SAA, JW-BK112 Surface Area and Mesopore Size Analyzer), acidity test using pyridine gas as an adsorbate, and Fourier-Transform Infrared Spectrometer (FT-IR, Shimadzu IRPrestige-21). ZnO-AC was analyzed by Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX, Hitachi SU 3500).

2.3 Acidity Test

The acidity of ZnO, AC, and ZnO-AC was tested using a gravimetric method of pyridine vapor adsorption. All of the samples were dried overnight at 105 °C until their mass was constant. This was done to release the vapor traps beneath the catalyst. The acidity value was calculated using Equation (1):

$$Acidity\left(\frac{mmol}{g}\right) = \frac{(W_2 - W_1)\times 1000}{(W_1 - W_0)\times MW\ of\ pyridine} \quad (1)$$

where W_0 is mass of empty porcelain crucible (g), W_1 is mass of porcelain crucible containing catalyst after oven (g), W_2 is mass of porcelain crucible after adsorption (g), and *MW* of pyridine is 79.1 g/mol.

2.5 Catalytic Performance in ODS-DBT

The model compound dibenzothiophene (DBT) was dissolved into n-hexane to make a 500 ppm stock solution. The oxidative desulfurization experiment was performed in a three-necked 500 mL round-bottomed flask equipped with a condenser fitted with a magnetic stirrer and immersed in an oil bath controlled by a thermometer. The mixture of the dibenzothiophene (20 mL) and the catalyst (0.1 g) was then introduced and heated under vigorous stirring. Once the temperature was attained at 60 °C, 0.1 mL of 30% aqueous solution of H_2O_2 as oxidant was introduced for 2 h under stirring. The oxidized DBT solution was then transferred to a separating funnel followed by the addition of extraction solvent (acetonitrile) and extracted with the volume ratio of the total solvent to oxidized ODS solution was 1:1. The amount of the remaining DBT in n-hexane was measured using a UV-Vis spectrophotometer at the wavelength of 235 nm to determine the efficiency of DBT removal. The removal percentage of DBT is calculated based on equation (2).

$$(\%) = \frac{C_0 - C_t}{C_0}\times 100 \quad (2)$$

where C_0 is the DBT initial concentration in the stock solution and C_t is the DBT concentration of the oxidized DBT solution in the n-hexane layer after reaction time (*t*).

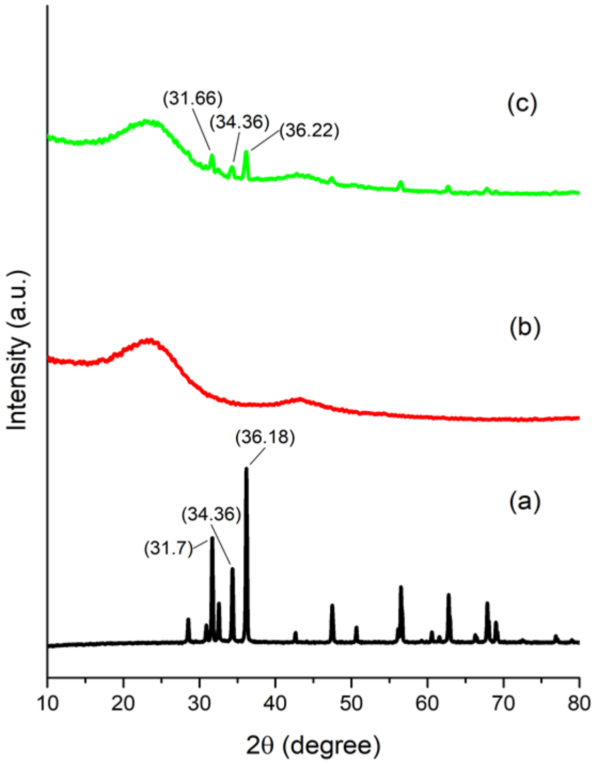

Figure 1. X-ray diffractogram of (a) ZnO, (b) AC, and (c) ZnO-AC.

3. Results and Discussions

3.1 Catalyst Characterization

The XRD patterns of ZnO, AC, and ZnO-AC samples were recorded at 2θ between 10° to 80°. The Cu Kα radiation operates at 40 kV and 30 mA with λ= 1.54 Å. Figure 1 shows the XRD patterns of ZnO, AC, and ZnO-AC. In Figures 1(a), the three main diffraction peaks were observed at 31.7° (hkl plane of 100), 34.5° (hkl plane 002), and 36° (hkl plane of 101) that correspond to the wurtzite structure of ZnO with diffraction data also showed good agreement with JCPDS Data Card No: 36-1451 [19]. For Figure 1(b) and (c), the diffraction profiles exhibited broad peaks at 2θ around 24° and 42° was assigned to the reflection from (002) and (100) planes, respectively [18]. The ZnO structure does change after blended with 90 wt% AC suggesting the blending process was successful. It can be seen that the blending ZnO with AC could increase the crystallinity of AC. This proves that blending ZnO with AC can remove the amorphous phase of AC so that the crystal character is purer. Scherrer's formula [20] was used to calculate the crystallite size of the ZnO,

Table 1. Properties of the ZnO, AC, and ZnO-AC.

Catalysts	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)	Crystallite Size (nm)	Acidity (mmol/g)
ZnO	7.38	0.029	7.798	39.295	1.9083
AC	695.971	0.334	5.199	-	3.9355
ZnO-AC	734.351	0.382	5.313	-	4.8780

AC, and ZnO-AC which was observed in Table 1.

The surface area and porosity properties of ZnO, AC, and ZnO-AC were also shown in Table 1. The ZnO-AC sample possesses an average (BJH) pore size of 5.313 nm, which corresponds rather well to the pore size of the initial AC used as a support material. According to the BET evaluation, ZnO-AC has a higher surface area of 734.351 m^2/g compared to ZnO and AC themselves. It can be seen that AC blending with 10 wt% of ZnO does not block the AC pores, instead, it increased the porosity of AC as a support material. This positive contribution of ZnO dispersion was quite astonishing for physical blending, where no solvent was involved during the blending method, however AC was still able to disperse ZnO in a homogenous manner. The good dispersion of ZnO across the AC support would ultimately affect its performance in ODS reaction, as this reaction required a catalyst with a high surface area.

Pore characteristics of the ZnO, AC, and ZnO-AC were determined by N_2 adsorption-desorption measurement as illustrated in Figure 2. ZnO was found to be of Type III in nature as per the IUPAC classification that describes adsorption on macroporous adsorbents with weak adsorbate-adsorbent interactions [21]. The typical IV (a) curve accompanied with an H3 type hysteresis loop was observed in the isotherms of AC and ZnO-AC, indicating the predominance of mesopores [22]. The presence

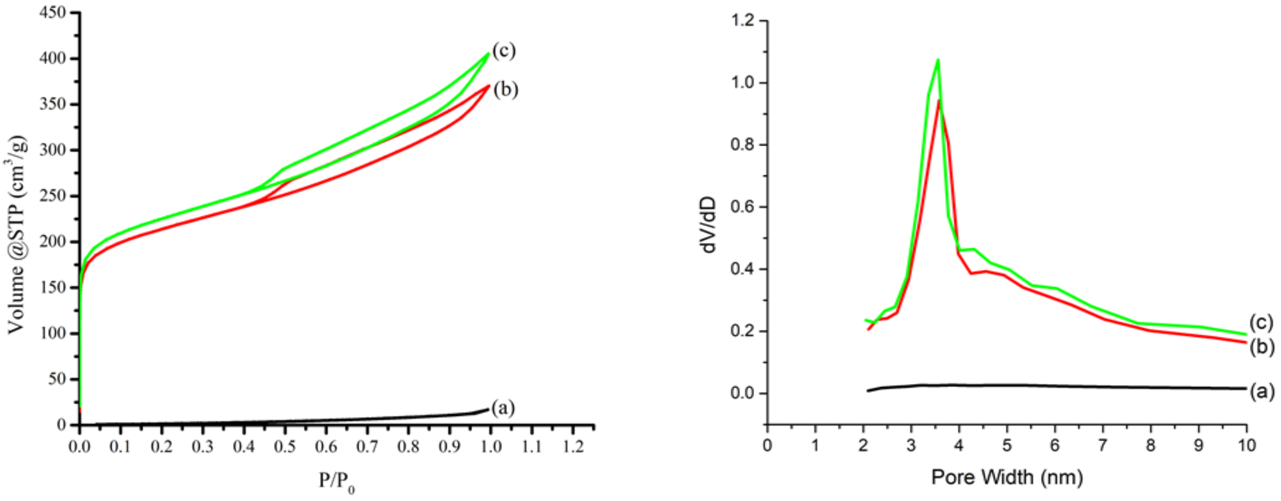

Figure 2. N_2 adsorption-desorption isotherm (left side) and Pore size distribution (right side) of (a) ZnO, (b) AC, and (c) ZnO-AC.

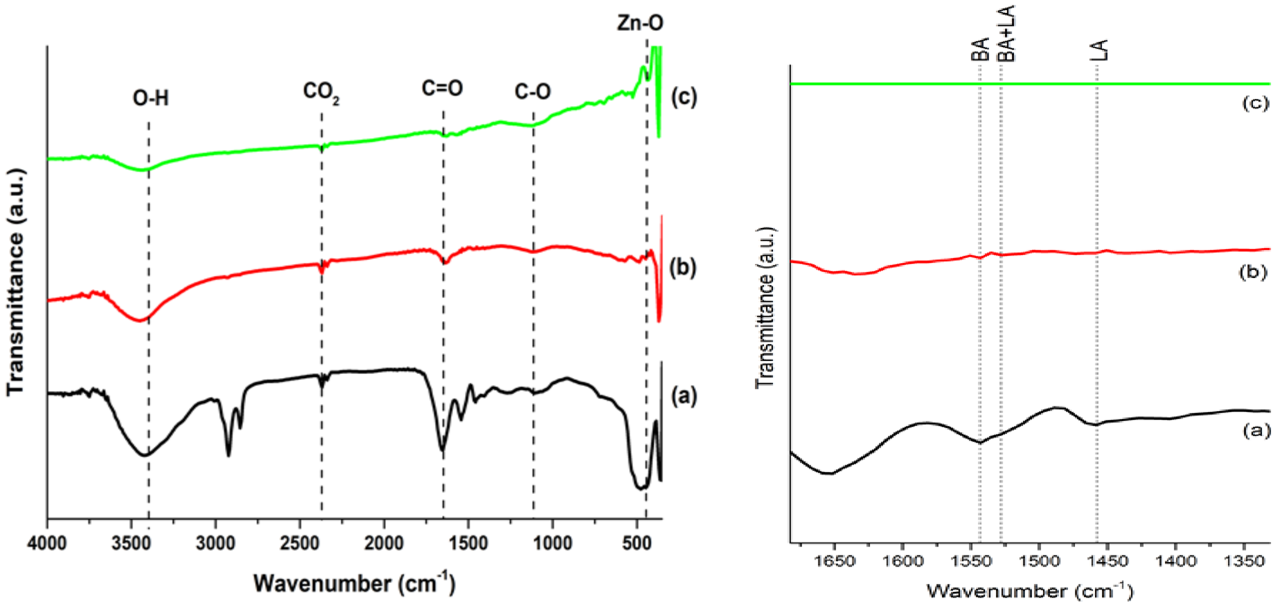

Figure 3. FTIR spectra after pyridine adsorption of (a) ZnO, (b) AC, and (c) ZnO-AC in normal size (left side) and enlarged size (right side).

of mesopores in the ZnO, AC, and ZnO-AC was also indicated by the pore size distribution as depicted in Figure 2.

The acidity value of the catalysts was determined gravimetrically using pyridine vapor, which is shown in Table 1. As the ZnO blended into AC, its acidity increased. These properties could be owed to the good dispersion of ZnO across AC, which was mentioned earlier in the porosity properties section. The amount of acid sites is crucial in ODS as the catalyst serves as a polyacid. In ODS, acid sites of catalysts are required for DBT conversion into sulfoxides and sulfones. The Brønsted and Lewis acid sites of each catalyst could be seen in Figure 3 in an enlarged size. The vibration band appearing at 1550 cm^{-1} is assigned to Brønsted (B) acid sites, whereas the vibration band at 1450 cm^{-1} is attributed exclusively to Lewis (L) acid sites. The band observed at 1525 cm^{-1} is due to both Brønsted and Lewis (B+L) acidic sites [23]. The figure also shows an absorption band at about 3400 cm^{-1} which refers to the stretching vibration of the O−H bond originating from water molecules adsorbed on the sample surface. The peak of stretching C=O between 1600–1700 cm^{-1} and stretching of C−O asymmetry between 1200–1300 cm^{-1} were also evident. The band observed at about 2300 cm^{-1} is associated with a C=O stretching mode which may be due to CO_2 absorption from water. The absorption band observed at 420–430 cm^{-1} is associated with the characteristic vibrational mode of the Zn-O bond. The results of this study are following previous research [24].

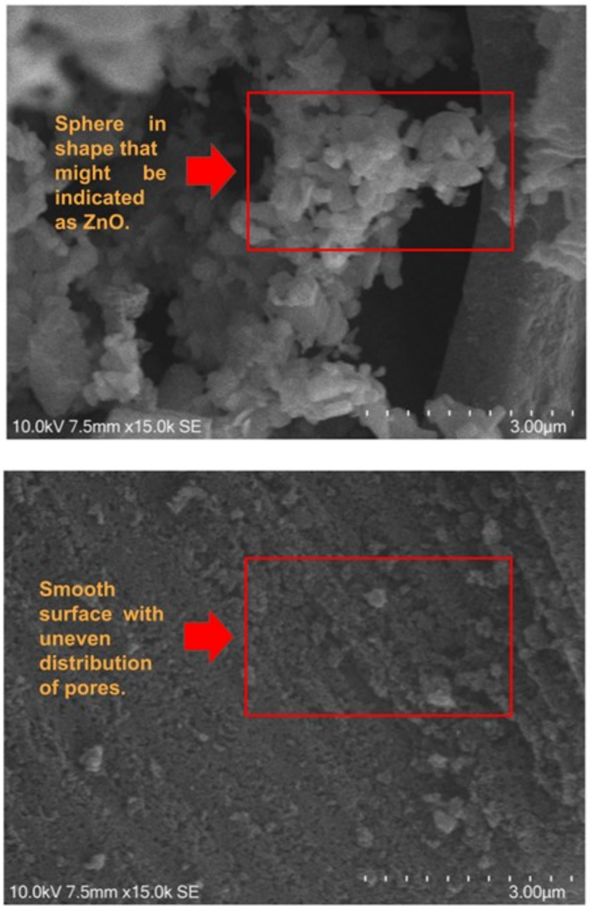

Figure 4. SEM micrographs of ZnO-AC.

The surface morphology of ZnO-AC is illustrated in Figure 4. The SEM micrograph showed a smooth surface with uneven distribution of pores. It was also shown some sphere in shape that might be indicated as ZnO. SEM image shows ZnO particles were spherical and agglomerated. Meanwhile, the morphology of AC exhibited fiber-like and porous with plenty of grain boundaries. The pores were indicating the availability of catalytic sites for desulfurization to take place [25]. Energy dispersive X-ray (EDX) analysis was also conducted on the ZnO-AC sample. The blending ZnO with AC was succeeded indicated by the amount of Zn (13 wt%), O (4 wt%), and C (83 wt%) presence in the sample. Based on these results, this material does not contain any impurities.

3.2 Oxidative Desulfurization of Dibenzothiophene

The remaining dibenzothiophene (DBT) concentration was determined by a UV-Vis spectrophotometer. The absorption at 235 nm was used to monitor the DBT concentration as the maximum absorbance in this molecule due to its chromophore functional group. The efficiency of ODS-DBT in percentage is shown in Table 2. A synergistic effect between ZnO and AC was observed in improving the efficiency of ODS-DBT, in which both single ZnO and AC gave lower efficiency of ODS-DBT. The efficiency of ODS-DBT was found to increase by blending ZnO with AC and it is believed due to the good dispersity of the combined ZnO-AC catalyst, as this was also confirmed by its higher surface area and acidity. Besides, the efficiency of ZnO-AC is further improved by the adsorptive capability of ZnO and AC themselves that assist in increasing the possible contact between DBT with catalyst active sites. Indeed, the introduction of ZnO to AC contributes to

Table 2. Catalytic ODS performance of ZnO, AC, and ZnO-AC catalysts.

Catalyst	The efficiency of ODS-DBT (%)
ZnO	71.04
AC	91.26
ZnO-AC	93.83

the increment of the contact surface area of the catalyst, which subsequently increasing the sulfur removal efficiency. Although in this case, it does not have a significant effect because its weight percentage is small compared to AC, which is 1:9. Compared to the literature, the results of previous studies revealed that ZnO-AC was able to remove sulfur up to about 85% [15] and 75% [17]. Thus, it can be concluded that the ZnO-AC catalyst that we prepared through the physical blending technique is so potent that it provides a desulfurization efficiency of more than 90%.

The catalytic data in Figure 5 clearly show that the DBT removal efficiency increases with an increment of reaction time. However, insignificant sulfur removal was witnessed after 120 min of reaction time exceeding to longest tested time; 150 min. It is anticipated that at prolong reaction time of more than 120 min, it does not have much effect on the proportion of desulfurization due to the degradation of most oxidants. Quantitative analysis through titration method discovered that most of H_2O_2 were utilized after reaction, either through selective utilization or unselective utilization due to (i) decomposition to oxygen and water, (ii) hydrogenation to water, and (iii) direct non-selective formation of water [26].

4. Conclusions

The physical blending technique proved to be effective for the synthesis of ZnO-AC. This is evidenced by the specific surface area and acidity of ZnO-AC which are higher than ZnO and AC, which indicates the homogeneity of the distribution of ZnO nanoparticles on the AC surface. With these characteristics, this catalyst can produce of DBT removal of 93.83% with an ODS reaction time of 120 minutes.

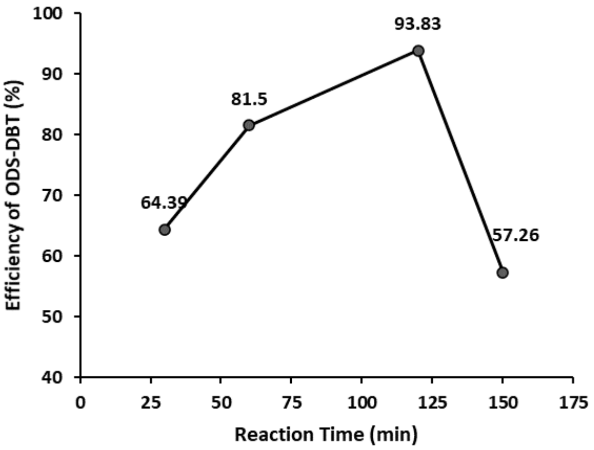

Figure 5. Effect of reaction time on ODS-DBT of ZnO-AC catalyst.

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