

# **Evaluation the performance of the tin (IV) oxide (SnO<sub>2</sub>) in the removal of sulfur compounds via oxidative-extractive desulfurization process for production an eco-friendly fuel**

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## **Abstract**

Catalysts play a vital role in petroleum and chemical reactions. Intensified concerns for cleaner air with strict environmental regulations on sulfur content in addition to meet economic requirements have generated significant interests for the development of more efficient and innovative oxidative catalysts recently. In this study, a novel homemade nano catalyst (manganese oxide (MnO<sub>2</sub>) over tin (IV) oxide (SnO<sub>2</sub>)) was used for the first time as an effective catalyst in removing dibenzothiophene (DBT) from kerosene fuel using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as oxidant in catalytic oxidative-extractive desulfurization process (OEDS). The catalyst was prepared by impregnation method with various amount of MnO<sub>2</sub> loaded on SnO<sub>2</sub>. The oxidation step was carried out at different operating parameters such as reaction temperature and reaction time in batch reactor. The extractive desulfurization step was performed by using acetonitrile as solvent under several operating conditions (agitation speed and mixing time). The activity of MnO<sub>2</sub>/SnO<sub>2</sub> catalyst in removing various sulfur compounds from kerosene fuel at the best operating conditions was investigated in this work. The results of the catalyst characterization proved that a high dispersion of MnO<sub>2</sub> over the SnO<sub>2</sub> was obtained. The experiments showed that the highest DBT and various sulfur compounds removal efficiency from kerosene fuel under the best

operating conditions (oxidation: 5% MnO<sub>2</sub>/SnO<sub>2</sub>, reaction temperature of 75 °C, and reaction time of 100 min, extraction: acetonitrile, agitation speed of 900 rpm, and mixing time of 30 min) via the catalytic oxidative-extractive desulfurization process was 92.4% and 91.2%, respectively. Also, the MnO<sub>2</sub>/SnO<sub>2</sub> catalyst activity was studied after six consecutive oxidation cycles at the best operating conditions, and the catalyst prove satisfactory stability in terms of sulfur compounds removal. After that, the spent catalyst were regenerated by utilizing different solvents (methanol, ethanol and iso-octane), and the experimental data explained that iso-octane achieved highest regeneration efficiency.

**Key words:** Nano-catalyst; tin (IV) oxide; manganese oxide; oxidative- extractive desulfurization.

## 1. Introduction

Organic sulfur compounds found in fuel such as dibenzothiophene (DBT), benzothiophene (BT), thiophene (Th) and their derivatives can cause significant environmentally, healthy, and industrial problems [1-3]. Therefore, severe environmental regulations have been imposed in the petroleum refinery to minimize the level of sulfur compound in fuel in order to treat the problem that caused by sulfur found in fuels [2]. Presently, hydrodesulfurization (HDS) is widely utilized for the removal of organic sulfur compounds from fuels. This process operates in the presence of a catalyst at elevated operating condition (such as reaction temperature) where hydrogen is employed to transform organic sulfur compounds into H<sub>2</sub>S and the corresponding hydrocarbon [4-8]. However, this technique is efficient to eliminate aliphatic organosulfur compounds but less effective for removing aromatic sulfur compounds such as Th, DBT, and their alkylated derivatives [9, 10]. Therefore, several alternative techniques such as biodesulfurization (BDS), adsorptive desulfurization (ADS), oxidative desulfurization (ODS) and ionic liquids desulfurization (ILD) have been studied by some scholars in recent years [5, 11, 12]. ODS is a highly promising technique for eliminating refractory aromatic sulfur compounds like Th and DBT, which are difficult to be reduced by HDS [8]. Also, it is oxidized organosulfur compounds under mild operating conditions (low temperature and at atmospheric pressure) and without utilizing of hydrogen [14, 15]. In this operation, sulfur compounds are oxidized by utilizing an oxidant in the existence of an appropriate catalyst to produce sulfoxides and sulfones, which have various physical, thermal properties and high polarity, therefore can be easily separated from the

fuel by employing precipitation, extraction, or adsorption [11, 16, 17]. Extractive desulfurization (EDS) has given good results toward eliminating the refractory sulfur containing compounds from liquid fuels. Moreover, EDS is operated in moderate operating conditions, which leads to reduced consumption of energy [18]. The solubility of the refractory sulfur compound in the extractive solvents is the key to the removal of sulfur compounds by utilizing extraction process. The refractory sulfur compounds are extracted into solvent because they have higher solubility in the extractive solvent in the comparison to hydrocarbon compounds. Solvents widely utilized in EDS process include acetonitrile, methanol, dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), and lactones [14]. Nanomaterials have appeared as sustainable alternates to traditional materials as strong high surface area heterogeneous catalysts and catalysts supports [17]. They are composed of small particles with a diameter  $< 100$  nm [20]. The significantly different properties of nanomaterials from conventional materials are owing to two main factors: raised relative surface area, and quantum impacts. These factors can promote characteristics like strength, reactivity and electrical properties [21]. Tin (IV) oxide nanoparticles are an important class of semiconducting crystalline nanomaterials that are widely employed in various fields, such as photo-catalysis, microelectronics, imaging science, nonlinear optics, photoelectron-chemistry, and electrooptic owing to their mechanical and chemical stability [21, 22]. Tin (IV) oxide nanoparticles are exploited more effectively as a catalyst and as a carrier in supported catalysts because of the faster transition of the oxide ions within nanoparticles of the tin (IV) oxide to raise the surface to volume ratio [23]. Also, tin (IV) oxide is found to be an active and versatile catalytic material due to its attractive properties such as redox and acid-base [24]. Manganese oxides are considered as significant materials owing to their extensive usage in industrial applications such as ion exchange, molecular adsorption, high-density magnetic storage media, electrochemical materials, catalysts and solar energy transformation [25]. Manganese oxide ( $\text{MnO}_2$ ) nanoparticles display elevated adsorption capability owing to their polymorphic structure and high BET surface area [26]. In this study, oxidative desulfurization process was implemented in a batch reactor in the presence of novel homemade catalyst with different operating conditions (time and temperature) under atmospheric pressure. After that, the oxidized sulfur compounds were removed in extractive desulfurization process by utilizing acetonitrile as extractive solvent.

The novelty of this work is to produce a novel nano-catalyst for the removal of sulfur compounds in the oxidative-extractive desulfurization (OEDS) operation, which comprise of MnO<sub>2</sub> as active metal and SnO<sub>2</sub> as support. This study is the first to evaluate the performance of tin (IV) oxide (SnO<sub>2</sub>) in an oxidative desulfurization process. To the best of our knowledge, the using of MnO<sub>2</sub>/SnO<sub>2</sub> nano-catalyst in ODS-EDS process has not been investigated in the past as catalyst for ODS-EDS process. Also, the OEDS process is carried out by using kerosene fraction as feedstock with initial sulfur compound (400 ppm DBT) in a batch reactor utilizing the H<sub>2</sub>O<sub>2</sub> as an oxidant and acetonitrile as solvent. In addition, the performance of MnO<sub>2</sub>/SnO<sub>2</sub> catalyst in eliminating different sulfur compounds from kerosene under the best operating conditions was studied in this work. The spent MnO<sub>2</sub>/SnO<sub>2</sub> catalyst turned into regenerated through solvent extractive regeneration (SER) process by employing different solvents (methanol, ethanol, acetonitrile, and isooctane).

## 2. Experimental Work

### 2.1 Chemical materials and fuel

#### 2.1.1 Oil feedstock

Hydrotreated Kerosene obtained from North Refinery Company/ Iraq is applied as liquid feedstock for ODS-EDS process. The physical characteristics of the Hydrated Kerosene are illustrated in Table 1.

**Table 1: Characteristics of kerosene feedstock.**

Physical property	Values	Physical property	Values
Specific gravity at 15.5 °C	0.7845	Distillation	(°C)
API gravity	48.8	Initial boiling point	160
Total Sulfur Content (ppm)	10	(°C)	
Flash Point, (°C)	52	50%	194
H <sub>2</sub> S ppm	Nil	90%	235
		Final boiling point	255
		(°C)	

Sample kerosene feedstock is prepared by adding DBT (obtained from Sigma Aldrich with purity ~98%) for hydration of kerosene at concentration of 400 ppm to evaluate the activity for ODS-EDS reaction in the presence of the novel prepared catalysts.

### 2.1.2 Catalyst preparation materials

The materials utilized for the preparation of catalyst are illustrated in Table 2.

**Table 2: Chemicals and materials utilized for generation of catalysts.**

<b>Chemicals</b>	<b>Formula</b>	<b>Molecular Weight g/mole</b>	<b>Purity %</b>	<b>Supplier</b>
Manganese (II) chloride	MnCl <sub>2</sub> .4H <sub>2</sub> O	197.91	98	Thomas Baker
Tin (II) oxide	SnO <sub>2</sub>	134.71	97	Sigma Aldrich

### 2.1.3. Oxidant

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is employed as an oxidant in ODS reaction. This oxidizing agent was obtained from Merck Millipore Company, Germany. The properties of the oxidant utilized are illustrated in Table A.

### 2.1.4 Solvent for EDS process

The solvent utilized in EDS reaction is acetonitrile. This solvent was provided from Sigma-Aldrich Company. The properties of the solvent are summarized in Table B.

### 2.1.5 Solvents for SER process

Methanol, ethanol and iso-octane have been employed as for the solvent extractive regeneration (SER) process of MnO<sub>2</sub>/SnO<sub>2</sub> catalyst. Table C explained the properties of these solvents.

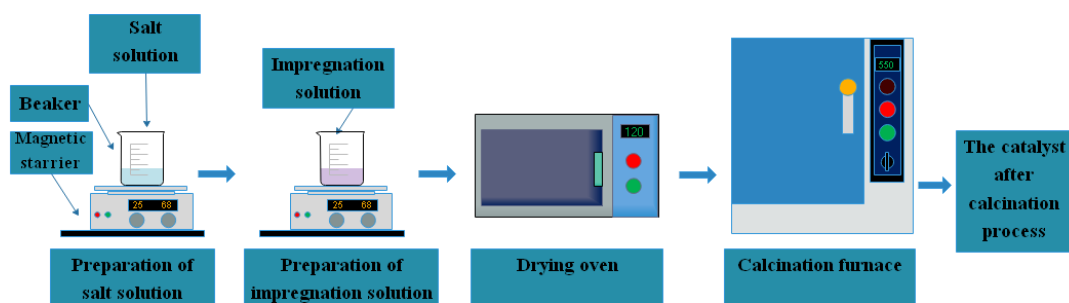
## 2.2 Catalyst preparation and characterization

### 2.2.1 Preparation of MnO<sub>2</sub>/ SnO<sub>2</sub> catalyst

The nano-catalyst (MnO<sub>2</sub>/ SnO<sub>2</sub>) is generated by employing the impregnation method. The Nona-catalyst is produced by the following steps:

- 1- Preparing the salt solution by dissolving 0.9 g of manganese (II) chloride in 45 mL of deionized water, then the mixture is mixed via magnetic stirrer for 1 hour at 25°C.
- 2- The impregnated solution is formed by progressively adding 5 g of the tin (IV) oxide nanoparticles to the salt solution with mixing by utilizing magnetic stirrer for one hr until the totally impregnated of solution is achieved.
- 3- The solution is dried via putting it in an oven at 120°C overnight.
- 4- Finally, the calcination step is implemented by elevating the temperature of furnace to 400°C for 2 hours and then to 550 °C for 3 hours.

The stages of catalyst preparation are presented in Figure.1.



**Figure 1: The stages of catalyst generation operation.**

### 2.2.2 Characterization of MnO<sub>2</sub>/ SnO<sub>2</sub> catalyst

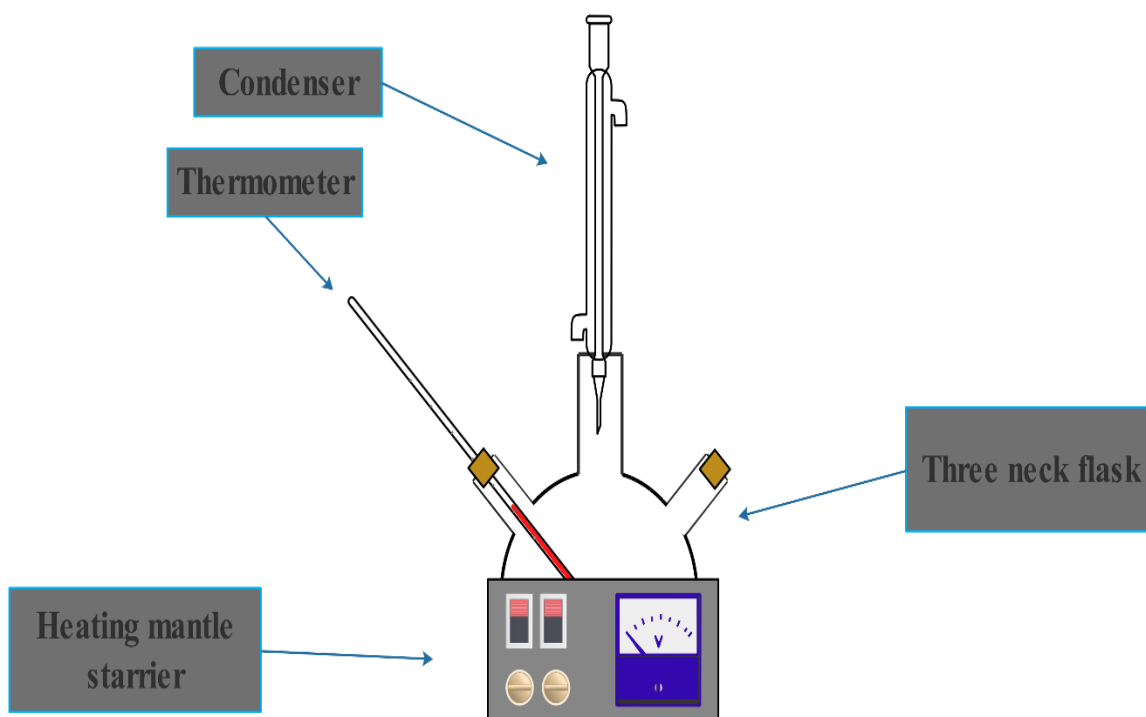
Structural phase of the prepared MnO<sub>2</sub>/ SnO<sub>2</sub> was tested by employing powder X-ray diffraction (XRD) (SHIMADZU, Japan) utilizing CuK $\alpha$  radiation Nickel filter with wave length ( $\lambda = 1.5406 \text{ \AA}$ ) and the data are recorded for 2 theta range from 5-60 degree at scanning speed of 5 degree / min. Fourier transform infrared (FTIR) was tested for prepared catalyst (SHIMADZU, Japan). The surface morphology of synthesized nano MnO<sub>2</sub>/ SnO<sub>2</sub>

catalyst was tested by using scanning electron microscopy (SEM) (Zeiss-EM10C-100 KV). Surface area and pore volume (textural analysis) were analyzed via Brunauer–Emmett–Teller (BET) type (Micromeritics, USA).

## 2.3 Oxidative-extractive desulfurization process

### 2.3.1 Batch oxidative desulfurization process

Three-neck flask of 500 mL is utilized to perform the ODS reaction. The middle neck is connected to a vertical condenser in order to prevent the vaporization of kerosene. The second neck is employed to know the reaction temperature by connecting a thermometer to the feedstock inside the flask. The third neck is used to add an oxidizing agent ( $H_2O_2$ ) at the beginning of the reaction as well as to withdraw the sample when the reaction is complete. The heating mantle stirrer is used to heat and mix of the reaction in the batch reactor. The operation diagram and experimental device of ODS is shown in Figure 2.



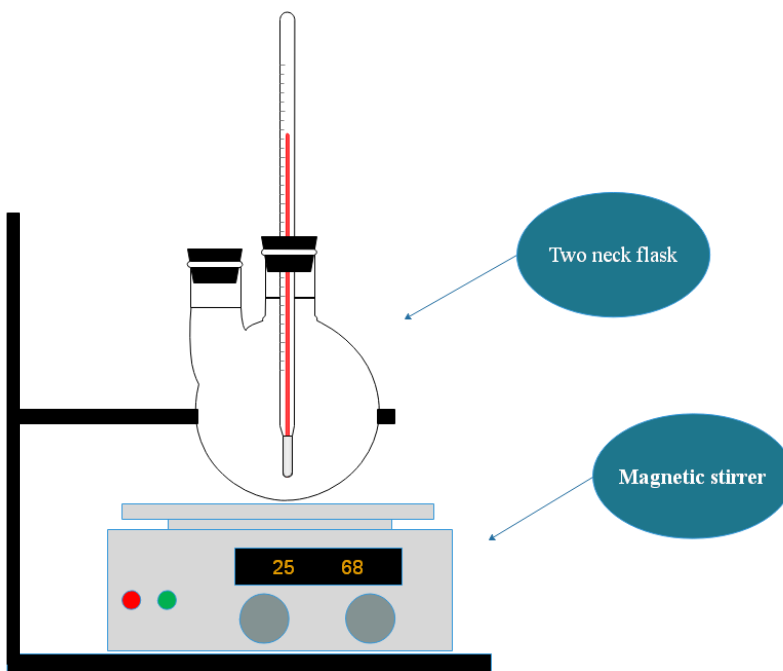
**Figure 2: Operation schema of ODS system.**

A solution of DBT dissolved in hydrotreated kerosene was utilized as feedstock with the initial sulfur concentration of 400 ppm. The oxidative desulfurization reaction was implemented by adding the prepared catalyst (0.9 g) and feedstock (90 mL) into the three-necked flask. Then, the flask was heated by using heating mantle stirrer. When the wanted temperature is arrived, 30 mL of the oxidant is added to the flask. On the completion of the oxidation reaction, the product was cooled and centrifuged to separate

oil phase, aqueous phase, and catalyst. After that, the fuel was processed into extraction process. The spent catalyst was regenerated and employed in new oxidation experiments.

### 2.3.2 Extractive desulfurization process

The extraction reaction is implemented in two-neck flask of 250 mL. The middle neck is employed to determine the reaction temperature by placing a thermometer to the mixture inside the flask. The mixing process of the extractive solvent and the oil feedstock is carried out by employing the magnetic stirrer. The experimental device of EDS is illustrated in Figure 3.





### Figure 3: Operation schema of EDS system.

The mixture of oil phase and the aqueous phase produced from ODS reaction was separated by using a 250 mL separation funnel. The oil phase was washed with deionized water at 100°C to eliminate the traces of the catalyst from the oil phase. Subsequently, 50 mL of the washed organic phase and 50 mL of solvent (acetonitrile) were inducted into the two-neck flask. The phases were mixed by using the magnetic stirrer. The produced mixture was placed in separation funnels and left overnight. Finally, the solvent phase was separated from the oil phase and their weights were measured.

The oxidative-extractive desulfurization process was achieved using the same experimental procedure for investigating the activity of MnO<sub>2</sub>/SnO<sub>2</sub> catalyst in removing various sulfur compounds from non-hydrated kerosene (obtained from North Refinery Company/ Iraq, specific gravity of 0.786, total sulfur compounds of 3200 ppm, ASTM distillation 140-240 °C at the best operating conditions.

#### 2.3.3 Operating conditions

The operating conditions utilized in ODS and EDS processes were presented in Tables 3 and 4.

**Table 3: The operating condition of ODS process.**

Operating conditions	Values
Type of catalyst	SnO <sub>2</sub> , 1% MnO <sub>2</sub> / SnO <sub>2</sub> , 5% MnO <sub>2</sub> / SnO <sub>2</sub>
Reaction temperature	30°C, 45°C, 60°C, 75°C
Batch time	25min, 50min, 75min, 100min
Oil/H <sub>2</sub> O <sub>2</sub>	30
Pressure	1 atm

**Table 4: The operating condition of EDS process.**

Operating conditions	Values
Reaction temperature	Ambient temperature

Batch time	10min, 20min, 30min
Stirrer speed	300rpm, 600rpm, 900rpm
Oil/Solvent	1
Pressure	1 atm

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## 2.4 Regeneration of the spent catalyst

The activity of MnO<sub>2</sub>/SnO<sub>2</sub> catalyst was investigated after six oxidation cycles at the best conditions that achieved higher removal of DBT from kerosene fuel. After the completion of the oxidation process, the final product was cooled and centrifuged to separate oil phase, aqueous phase, and catalyst. After that, the spent catalyst was regenerated by utilizing batch solvent extractive regeneration (SER) system. In a (SER), DBT compounds are eliminated by treating the spent catalyst with iso-octane, ethanol and methanol. About 10 mL of the solvent was used to shake the suspension for (60 min) at 60 °C for each gram of spent catalyst. After that, the washed catalyst was filtered and putted in an oven in order to dry at 110 °C for 6 h.

## 2.5 Analysis of kerosene fuel samples

The sulfur contents of the feedstock of kerosene and the treated samples were tested using X-ray fluorescence (EDXRF) (RX-360SH, Tanaka Scientific, Ltd, Japan) apparatus according to ISO 9454 and ASTM D4294-03. The sulfur removal efficiency was determined by equation 1.

$$X_s = \frac{C_{S\ in} - C_{S\ out}}{C_{S\ in}} \times 100 \dots \dots \dots (1)$$

## 3. Results and Discussion

### 3.1 Catalyst characterization

#### 3.1.1 Surface area and pore volume analysis

The results of pore dimensions and surface area of the prepared catalysts are illustrated in Table 5. It is clear from the table that that after the loading process of manganese oxide over tin (IV) oxide, the pore volume and the surface area was reduced remarkably owing to the occupancy of the areas by manganese oxide within the samples.

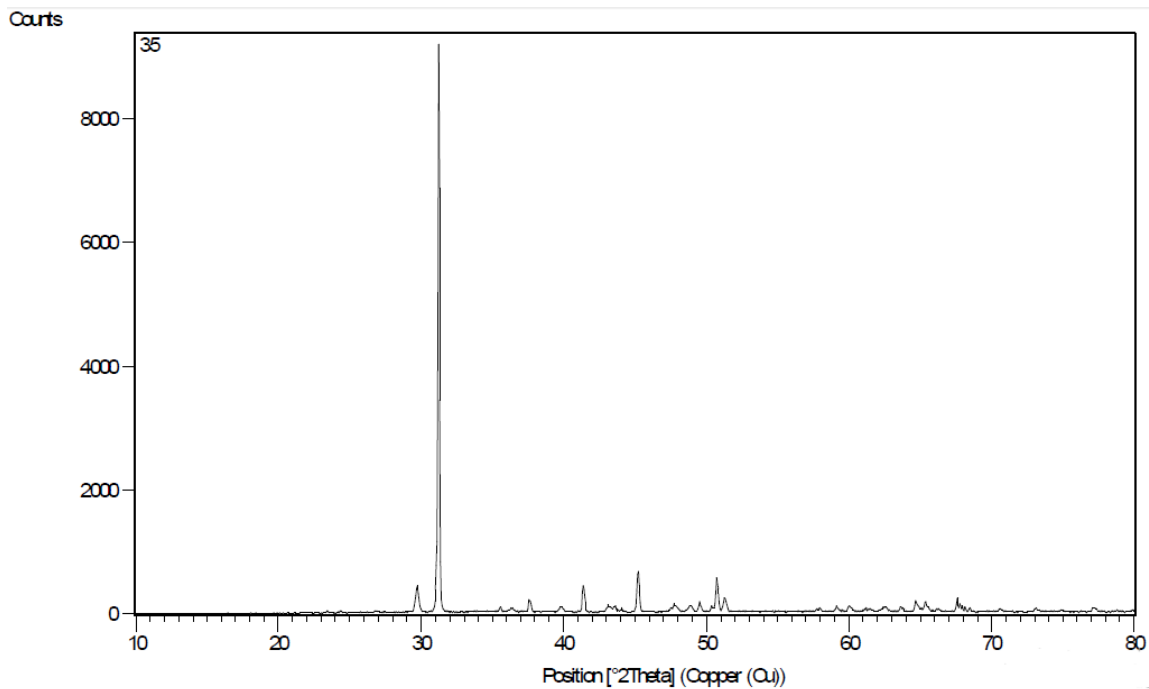
**Table 5: summary of surface area, pore volume and pore size of the prepared catalysts.**

<b>Sample</b>	<b>Surface area (m<sup>2</sup>/g)</b>	<b>Pore volume (cm<sup>3</sup>/g)</b>	<b>Pore size (nm)</b>
SnO <sub>2</sub>	8.1888	0.024919	12.17252
1% MnO <sub>2</sub> / SnO <sub>2</sub>	7.6911	0.024518	12.75151
5% MnO <sub>2</sub> / SnO <sub>2</sub>	3.9796	0.006907	6.94276

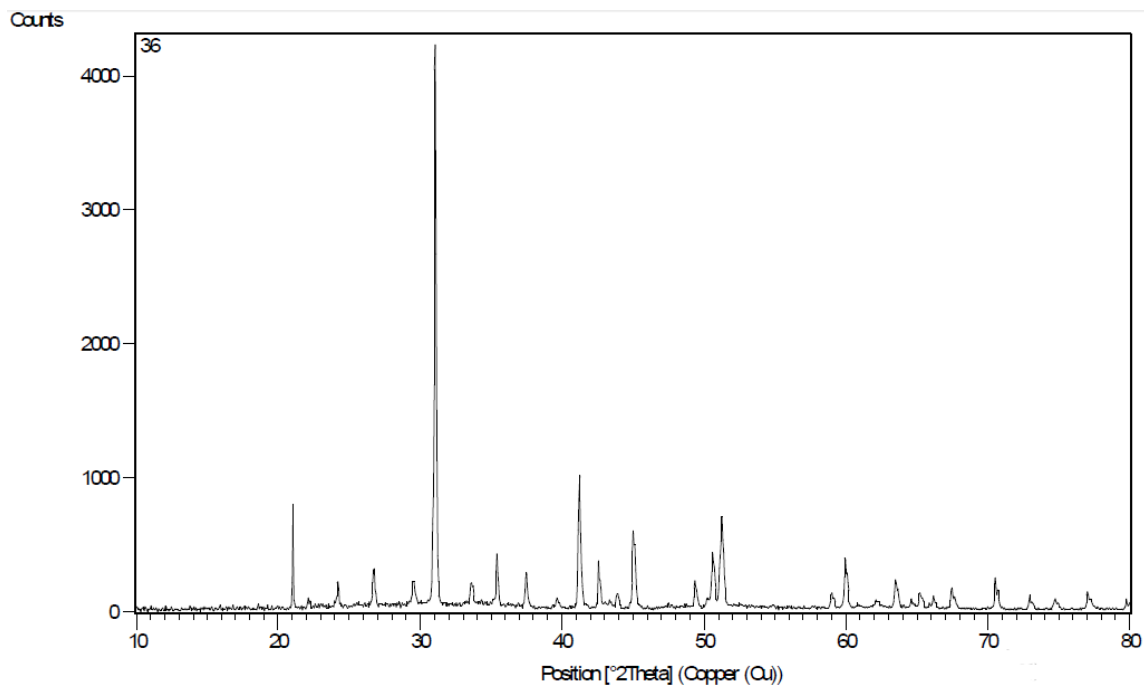
N<sub>2</sub> adsorption & desorption isotherm and BJH cumulative adsorption pore volume distribution for the prepared catalysts are shown in Figures A - F.

### **3.1.2 X-ray diffraction (XRD)**

The XRD patterns of the prepared catalysts after loading 1% and 5% of MnO<sub>2</sub> over SnO<sub>2</sub> are illustrated in Figures 10 and 11. As presented in Figures, after loading of MnO<sub>2</sub> over SnO<sub>2</sub>, the diffraction peaks occurred at 2θ angles around (41°, 45°, 51° and 60°), which correspond to the diffractions of MnO<sub>2</sub> [27]. Also, after increasing the amount of MnO<sub>2</sub> to 5%, the diffraction peaks of SnO<sub>2</sub> declined while the peaks intensity of MnO<sub>2</sub> elevated as illustrated in the Figures 4 and 5. This behavior indicates that there is a high dispersion of the MnO<sub>2</sub> over SnO<sub>2</sub> support.



**Figure 4: XRD patterns for the prepared catalyst (1% MnO<sub>2</sub>/ SnO<sub>2</sub>).**



**Figure 5: XRD patterns for the prepared catalyst (5% MnO<sub>2</sub>/ SnO<sub>2</sub>).**

### 3.1.3 Fourier transform infrared (FTIR)

The FTIR spectra of the prepared catalysts are displayed in Figure 6. As shown, the absorption bands at around 500 to 650  $\text{cm}^{-1}$  can be correlated the stretching vibration of Sn–O and the O–Sn–O bending vibration, respectively [28]. The peaks about at  $\sim 3400 \text{ cm}^{-1}$ ,  $\sim 1600 \text{ cm}^{-1}$  and  $\sim 1070 \text{ cm}^{-1}$  are due to stretching vibrations of Sn–OH groups and owing to O–H stretching vibrations of the physically adsorbed water molecules from the environment by SnO<sub>2</sub>, and which may present in the surface of the SnO<sub>2</sub> [29, 30]. The peaks at  $\sim 2920$ ,  $\sim 2850$ , and  $\sim 1430 \text{ cm}^{-1}$  were corresponding to C–H stretching and bending vibrations [31].

After loading of MnO<sub>2</sub> over SnO<sub>2</sub>. The broad absorption peak from 500 to 900  $\text{cm}^{-1}$  has increased with increased the amount of the loading of MnO<sub>2</sub> due to the antisymmetric stretching mode of (Sn, Mn)-O bands and Mn-O vibration mode [32, 33]. Also, with raising the amount of MnO<sub>2</sub> content over SnO<sub>2</sub>, the peak at  $\sim 1400 \text{ cm}^{-1}$  has increased due to O–H bending vibrations combined with Mn atoms. Such behaviors denotes that there is a high dispersion of the MnO<sub>2</sub> over SnO<sub>2</sub>.

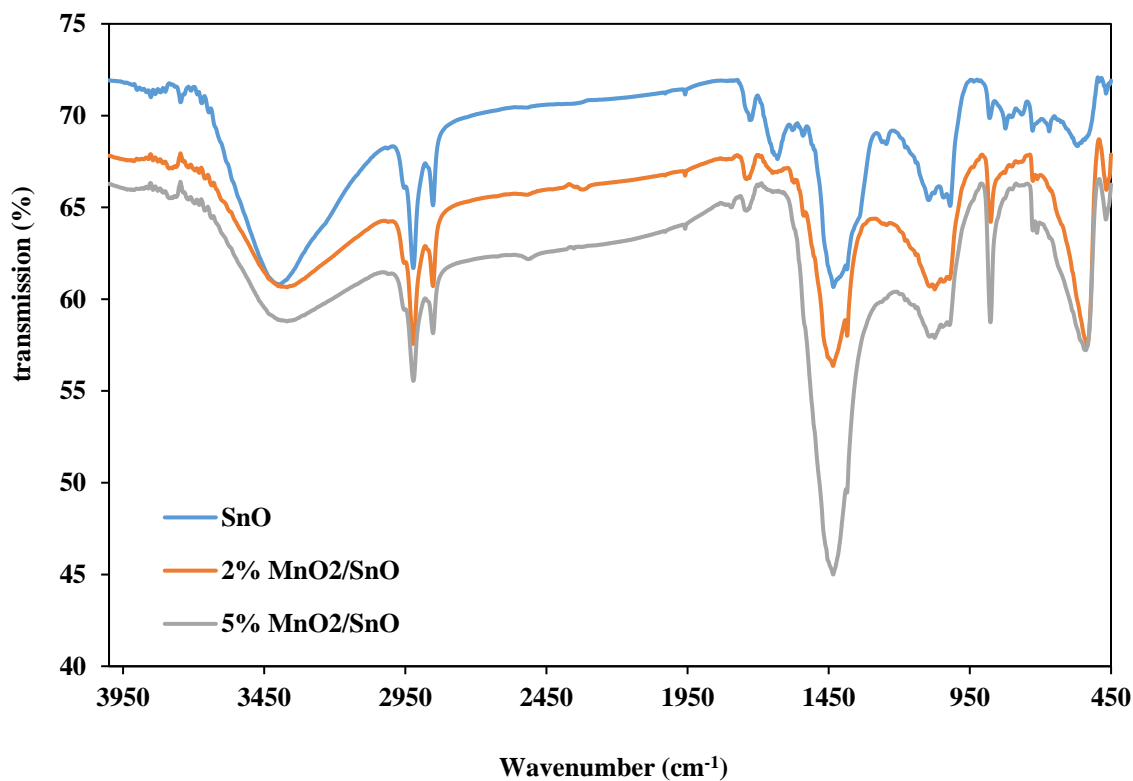
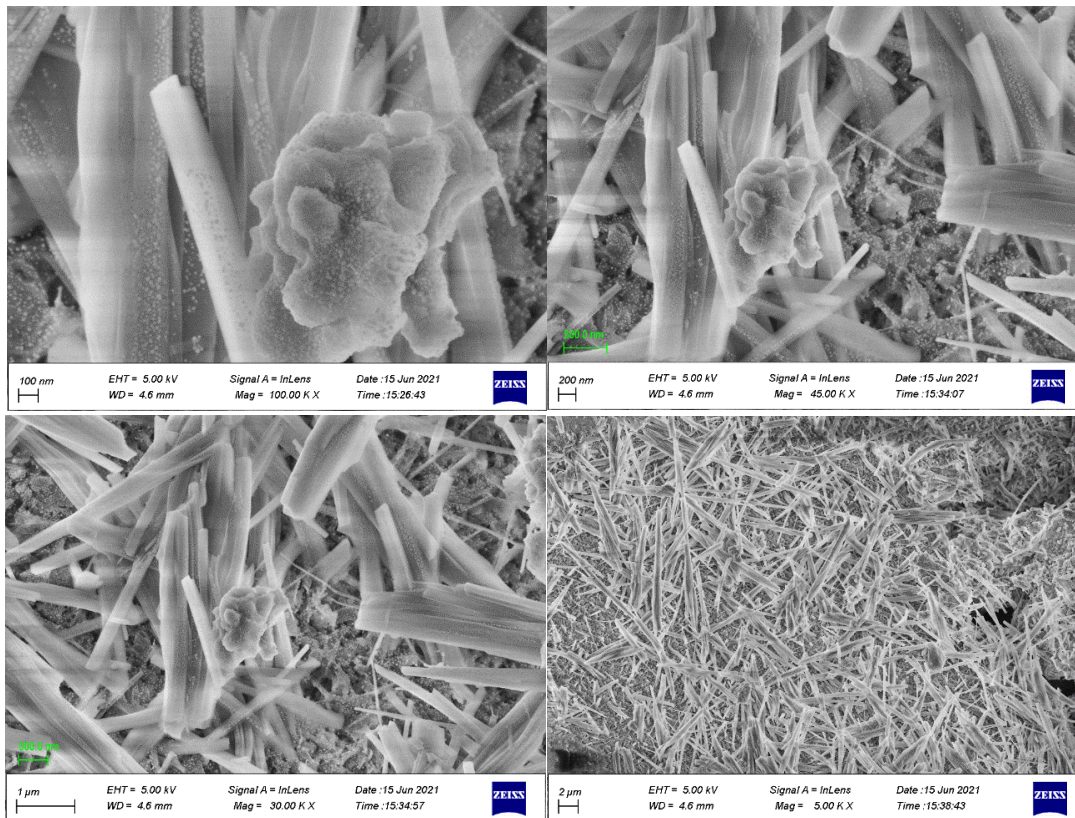


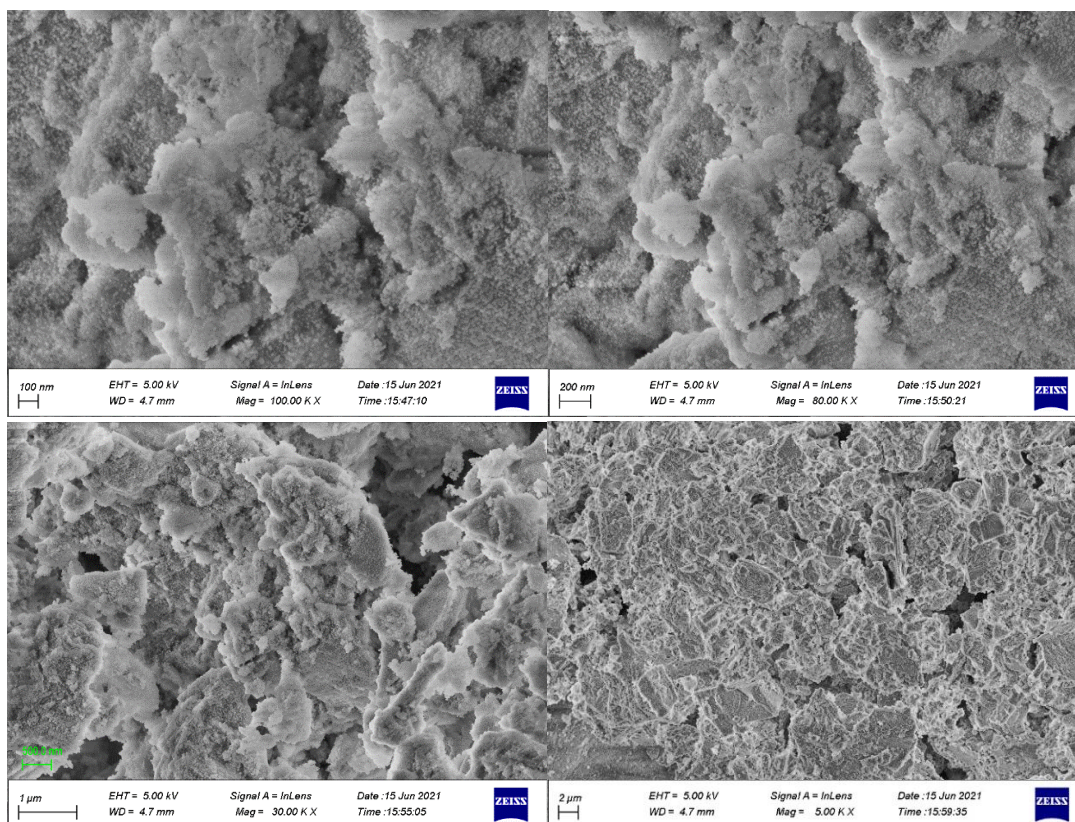
Figure 6: FTIR for prepared catalysts.

### 3.1.4 Scanning Electron Microscopy (SEM)

The morphology of the prepared catalysts was examined by utilizing scanning electron microscopy (SEM). The images of the prepared catalysts surface are illustrated in Figures 7 and 8. The SEM images do not show the precise distribution of metal particles, but the bright spots in the image may indicate the presence of heavier elements over the surface of SnO<sub>2</sub>. These results indicate that there is good distribution of MnO<sub>2</sub> over SnO<sub>2</sub>.



**Figure 7: SEM for the prepared catalyst (1% MnO<sub>2</sub>/ SnO<sub>2</sub>).**



**Figure 8: SEM for the prepared catalyst (5% MnO<sub>2</sub>/ SnO<sub>2</sub>).**

### 3.2 Oxidative-Extractive desulfurization results

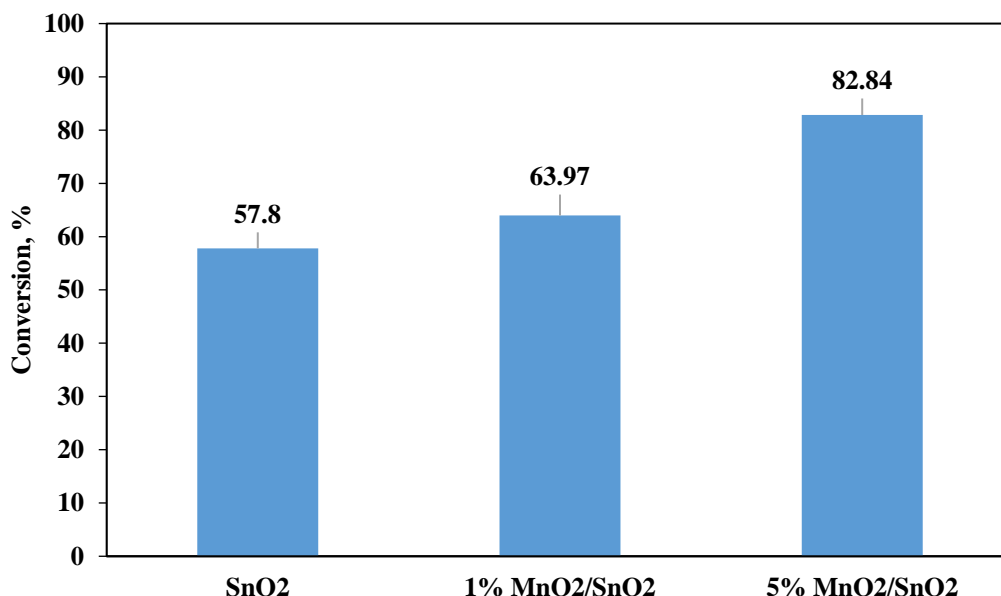
The removal of sulfur compounds is carried out by using the oxidative-extractive desulfurization process. The results of sulfur removal by ODS-EDS process are evaluated by employing X-ray fluorescence following the ASTM D4294 method.

#### 3.2.1 ODS results

ODS reaction is performed in a batch reactor by using kerosene as an oil feedstock and H<sub>2</sub>O<sub>2</sub> as an oxidant. The activity of ODS reaction is investigated in the presence of the prepared novel catalyst and under various operation conditions such as reaction temperature and batch time.

### 3.2.1.1 Impact of MnO<sub>2</sub> loaded over the catalyst support

The influence of the loading amount of MnO<sub>2</sub> on the activity of oxidative desulfurization operation has investigated via loading various quantities of MnO<sub>2</sub> over the catalyst support. Three catalysts were prepared containing various quantities of MnO<sub>2</sub> (0%, 1% and 5%). Figure 9 illustrate the effect of amount of loading MnO<sub>2</sub> on the sulfur removal efficiency. As presented in this Figure. The removal of sulfur compounds before the loading of MnO<sub>2</sub> was 57.8%. It is due to the use of H<sub>2</sub>O<sub>2</sub>, which is considered a strong oxidizer as well as there may be a slight role for tin (IV) oxide in activating the reaction. The activity of ODS reaction increases with the increasing quantity of MnO<sub>2</sub> loaded over the catalyst support. It is due to the availability of active sites that lead to increases of the oxidation reaction activity. Also, MnO<sub>2</sub> has high adsorption capacity toward sulfur compounds [34].



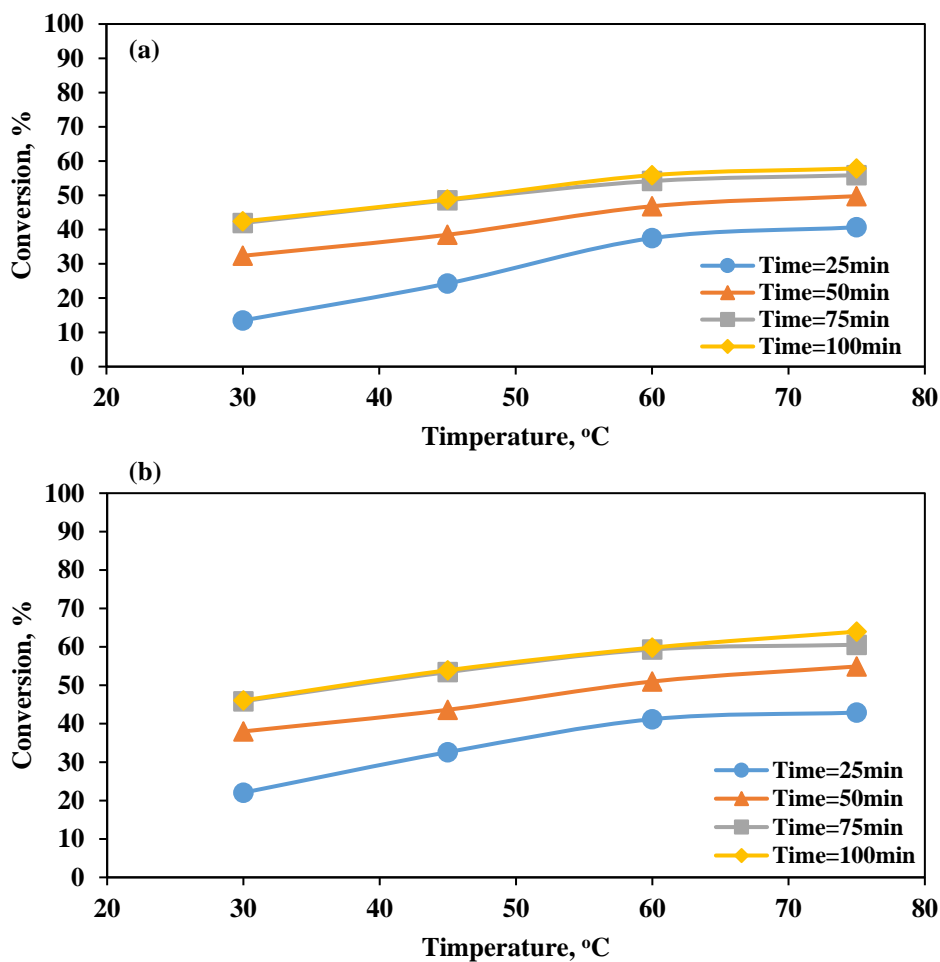
**Figure 9: the effect of amount of loading MnO<sub>2</sub> on the sulfur removal efficiency in ODS reaction.**

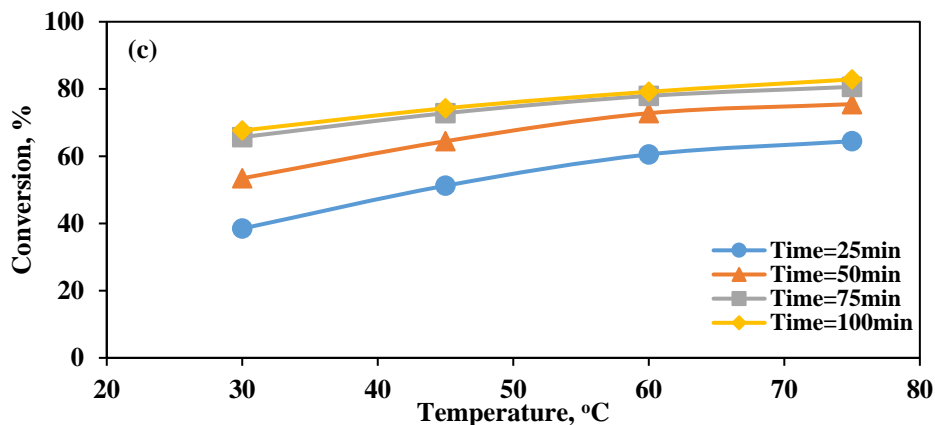
### 3.2.1.2 Impact of reaction temperature on the ODS activity

The reaction temperature is the most important parameter of the oxidative desulfurization process. The impact of reaction temperature on the removal rate of DBT was investigated and the results are illustrated in Figure 10. For all prepared catalysts, it was observed that the conversion of DBT increases with increasing temperature from 30 °C to 60 °C due to



faster movement of the molecules, the rising of the collision between sulfur compounds and the oxidizing agent, and the removal of strongly adsorbed sulfones from the surface of catalyst. When the reaction temperature was 75 °C, the conversion of DBT attained the maximum of 57.8%, 63.97% and 82.84% after 100 min in the presence of SnO<sub>2</sub>, 1%MnO<sub>2</sub>/SnO<sub>2</sub> and 5%MnO<sub>2</sub>/SnO<sub>2</sub>, respectively. However, when the temperature of reaction is increased above 60 °C, the removal rate of sulfur compounds under the same conditions was decreased due to the deficiency of oxidant that is resulted by the thermal decomposition of H<sub>2</sub>O<sub>2</sub> at the higher reaction temperature.

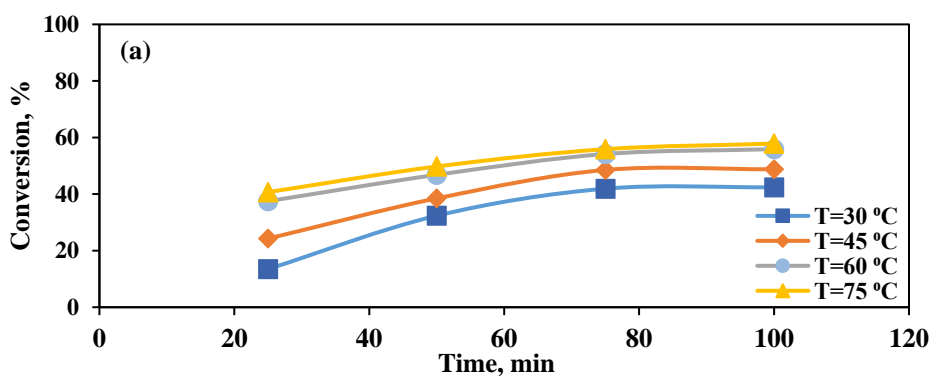


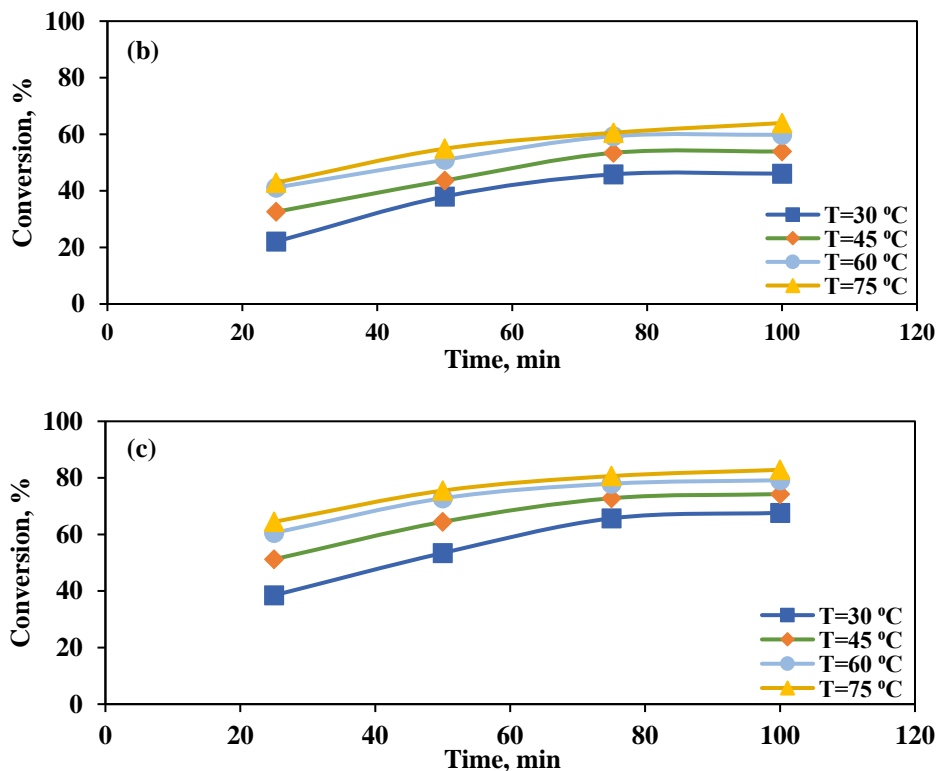


**Figure 10: The effect of reaction temperature on the conversion of sulfur compounds in ODS reaction for (a) SnO<sub>2</sub> (b) 1%MnO<sub>2</sub>/ SnO<sub>2</sub> (c) 5%MnO<sub>2</sub>/ SnO<sub>2</sub>.**

### 3.2.1.3 Impact of batch time on the ODS activity

The influence of batch time on the removal of sulfur compounds is presented in Figure 11. As shown in this Figure, the sulfur removal increased with increasing batch time up to 60 min. Further increase in batch time from 60 min to 75 min had a little impact on the conversion of sulfur compounds because of the decomposition of H<sub>2</sub>O<sub>2</sub> and the deposition of adsorbed oxidized sulfur compounds on the surface of catalyst [36, 37].

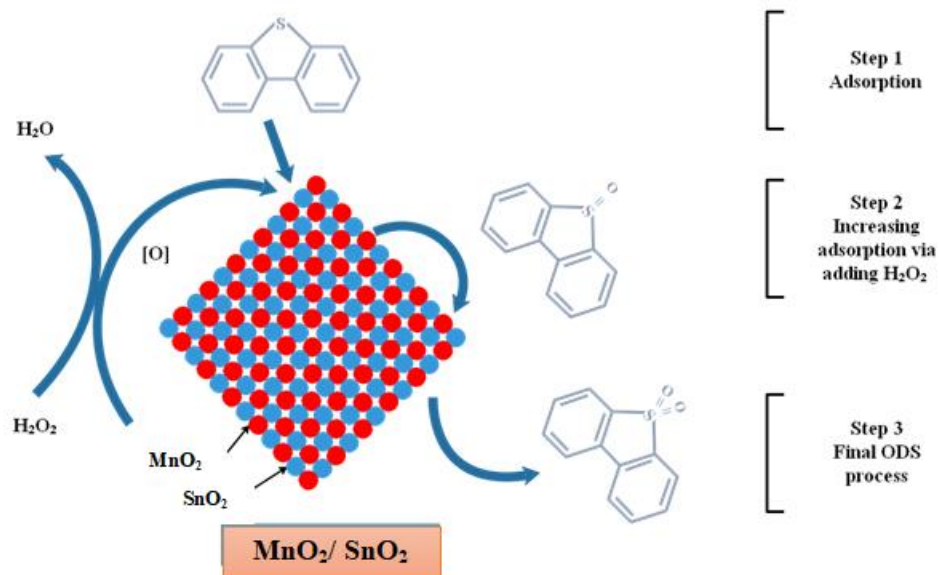




**Figure 11: The effect of batch time on the conversion of sulfur compounds in ODS reaction for (a) SnO<sub>2</sub> (b) 1%MnO<sub>2</sub>/ SnO<sub>2</sub> (c) 5%MnO<sub>2</sub>/ SnO<sub>2</sub>.**

### 3.2.2 Mechanism for ODS Reaction

The mechanism for ODS process using MnO<sub>2</sub>/ SnO<sub>2</sub> catalyst and H<sub>2</sub>O<sub>2</sub> as oxidant summarized in Figure 12. The oxidative desulfurization reactions achieved according to the following consequence steps. In the first step, sulfur (DBT) molecules are absorbed into the pore channel of MnO<sub>2</sub>/ SnO<sub>2</sub> catalyst through adsorption process. After that, the oxygen released from the oxidant (H<sub>2</sub>O<sub>2</sub>) to oxidize the sulfur (DBT) molecules to sulfoxides (DBTO) during the second step. In the final step, the sulfoxides (DBTO) oxidized into sulfones (DBTO<sub>2</sub>), which are more polar than DBT. Sulfoxides and/or sulfones were more polar, more molecular weight, and have higher boiling point than non-oxidized sulfur compounds, which leads to enhance solubility in polar solvents, thus permitting the selective removal of these compounds from fuel by using different methods such as solvent extraction and solid adsorption [4, 8].



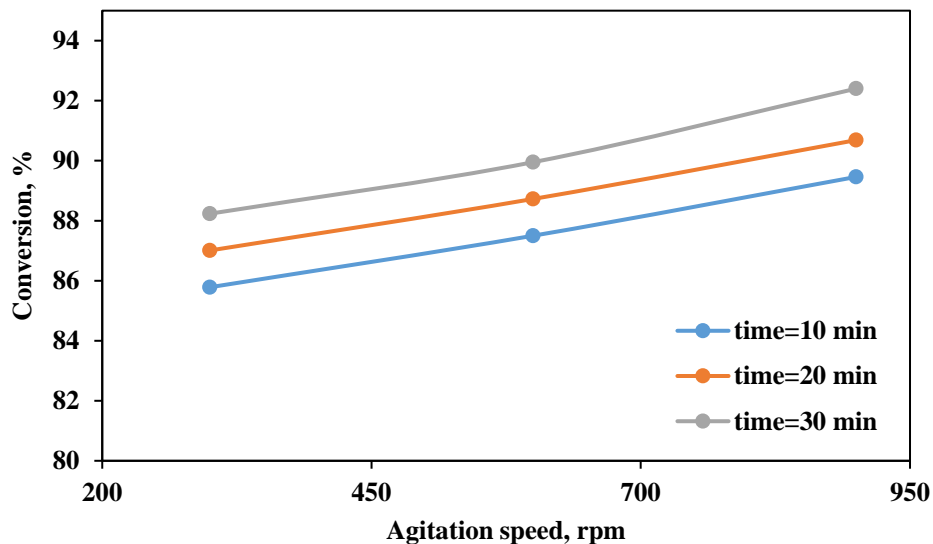
**Figure 12: The Suggested Mechanism for ODS Reaction.**

### 3.2.3 EDS results

After the oxidation step, EDS process is performed to extract the oxidized sulfur compounds by utilizing acetonitrile as solvent under various operating conditions such as agitation speed and batch time.

#### 3.2.3.1 Effect agitation speed on the EDS activity

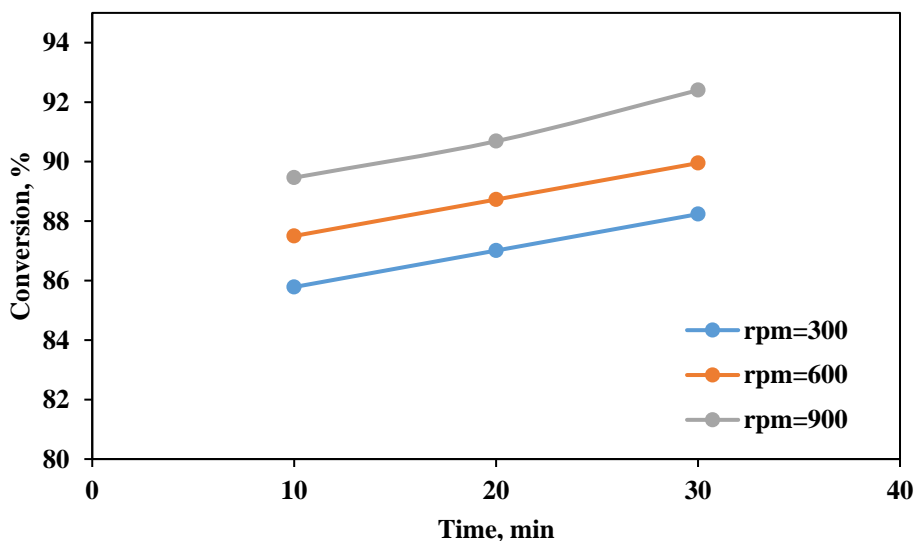
The impact of agitation speed on the extractive desulfurization activity is illustrated in Figure 13. It can be observed that the removal of sulfur compounds improves with increasing speed of mixing. The overall sulfur elimination rate depends on the mass transfer among phases. So, the removal rate of sulfur compounds increases with rising in the mass transfer. Also, extraction rate is affected by agitation speed due to increasing the collisions among the atoms of reactants, which leads to increase the extraction performance [35].



**Figure 18: The effect of agitation speed on the conversion of sulfur compound in EDS process.**

### 3.2.3.2 Effect of mixing time on the EDS activity

The impact of mixing time on the removal of sulfur compounds by extraction process was investigated in 10, 20 and 30 min as presented in Figure 14 at different agitation speed, and it can be observed that the sulfur removal is increasing by increasing the reaction time. This is because increasing the batch time leads to more contact among the reactants and enhancement of extraction performance.



**Figure 14: The effect of batch time on the conversion of sulfur compound in EDS reaction.**

The comparison between the efficiency of the catalyst used in present study and the previous studies is shown in the Table 6 below:

**Table 6: Comparison between the efficiency of the catalyst used in present study and the previous studies.**

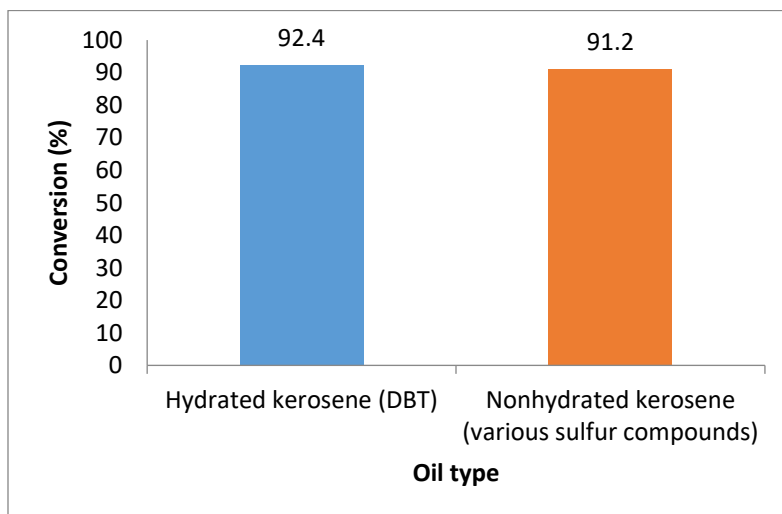
Sulfur model	System, oxidant/ catalyst	Conversion	Reference
DBT	Model diesel, Air/HPW/MOFs	90%	[39]
TH	<i>n</i> -heptane, H <sub>2</sub> O <sub>2</sub> /TiO <sub>2</sub> /ZSM-12	60%	[40]
DBT	Diesel, H <sub>2</sub> O <sub>2</sub> /V/ZSM-5	80%	[41]
DBT	Diesel, H <sub>2</sub> O <sub>2</sub> / Fe <sub>2</sub> O <sub>3</sub> / AC	71%	[42]
DBT	Kerosene, H <sub>2</sub> O <sub>2</sub> / MnO <sub>2</sub> / SnO <sub>2</sub>	92.4%	Present study

As shown in this Table, the prepared catalyst (MnO<sub>2</sub>/SnO<sub>2</sub>) is effective to remove the sulfur compounds via the oxidative-extractive desulfurization process as compared with another catalysts. So, the tin (IV) oxide (SnO<sub>2</sub>) can be confidently used as catalyst support in the oxidative-extractive desulfurization process.

### 3.2.4 Catalyst activity in removing various sulfur compounds via ODS-EDS process

The best operating conditions for the oxidative extractive desulfurization process for removing DBT from hydrated kerosene (initial DBT content of 400 ppm) using 5% MnO<sub>2</sub>/SnO<sub>2</sub> as catalyst, H<sub>2</sub>O<sub>2</sub> as oxidant, and acetonitrile as solvent in batch system were oxidation: reaction temperature of 75 °C, and reaction time of 100 min, extraction: agitation speed of 900 rpm, and mixing time of 30 min. The performance MnO<sub>2</sub>/SnO<sub>2</sub> catalyst in removing of various sulfur compounds from nonhydrated kerosene (initial sulfur content of 3200 ppm) under the best operating conditions was investigated in the present study. Figure 15 showed the experimental results of catalyst activity in removing DBT and

different sulfur compounds from hydrated and nonhydrated kerosene, respectively. From Figures 15, The experimental data proved that the highest DBT and various sulfur compounds removal efficiency from kerosene fuel under the best operating conditions via the catalytic oxidative-extractive desulfurization process was 92.4% and 91.2%, respectively. The reason of this variation in the desulfurization efficiency of both types of kerosene (hydrated and nonhydrated) is due to the fact that hydrated kerosene contains only one type of sulfur compounds but nonhydrated kerosene contains various sulfur compounds like alkylated benzothiophenes (BT), dibenzothiophene (DBT), and alkylated derivatives of DBT. So that, the removal rate of these compounds from nonhydrated kerosene is more complex than the removal of DBT from hydrated kerosene at the best conditions.



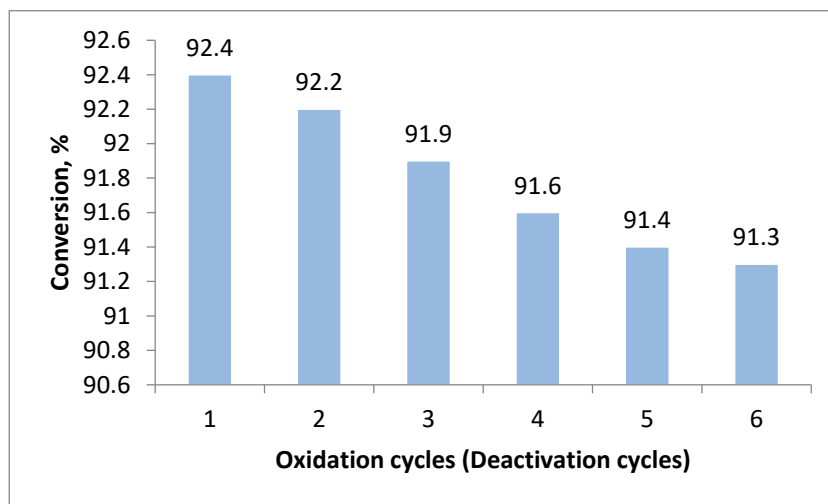
**Figure 15: catalyst activity in removing DBT and different sulfur compounds from kerosene fuel.**

### **3.3 Deactivation and regeneration of the catalyst**

#### **3.3.1 Deactivation study**

In this study, the (MnO<sub>2</sub>/SnO<sub>2</sub>) catalyst efficiency was evaluated after six oxidation cycles at the best operating conditions. The DBT removal efficiency from kerosene fuel after each cycle are illustrated in Figure 16. As shown in Figure, The catalyst attained a peripheral

reduction in overall DBT elimination after six cycles. This behavior indicates the high stability of the used catalyst at the best conditions. The slight reduction in the efficiency of catalyst activity may be owing to the loss of some active sites during the process of recovery.

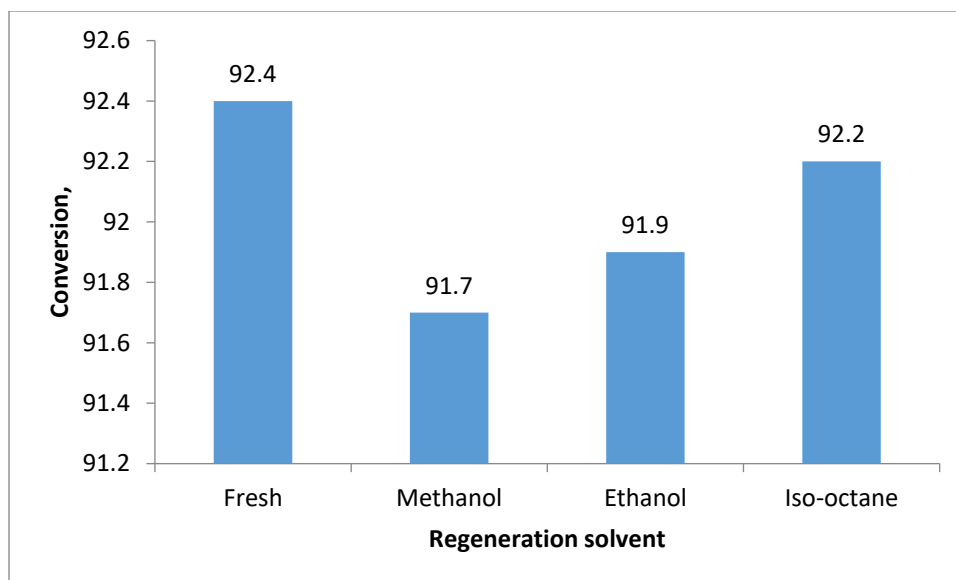


**Figure 16: Recovery performance of ( $\text{MnO}_2/\text{SnO}_2$ ) catalyst in terms of DBT removal efficiency for six consecutive cycles at the best conditions.**

### 3.3.2 Regeneration study

Various solvents were employed to evaluate the solvents activity in solvent extraction regeneration (SER) process of the spent ( $\text{MnO}_2/\text{SnO}_2$ ) catalyst (after six cycles) in terms of DBT compounds removal. Methanol, ethanol and iso-octane are used as regeneration solvents for SER process. Figure 17 showed the DBT removal efficiency of the catalyst after the regeneration process by using various solvents. As shown in Figure, the regeneration performance of the different used solvents decreases according to the following order: iso-octane > ethanol > methanol. So, by utilizing iso-octane as a regeneration solvent, the spent ( $\text{MnO}_2/\text{SnO}_2$ ) catalyst can be excellently regenerate.





**Figure 17: Regeneration performance of (MnO<sub>2</sub>/SnO<sub>2</sub>) catalyst in terms of DBT removal efficiency utilizing various solvents.**

#### 4. Conclusion

In this work, ODS-EDS process was studied to remove the sulfur compounds from kerosene fuel. ODS reaction was implemented in batch reactor using H<sub>2</sub>O<sub>2</sub> as oxidant and in the presence of the novel prepared nano-catalyst (MnO<sub>2</sub>/ SnO<sub>2</sub>). The utilizing of the tin (IV) oxide (SnO<sub>2</sub>) as catalyst or catalyst support in ODS-EDS process has not been studied in the previous works. Characterization of the catalyst, which was prepared by impregnation method, showed that a high distribution of manganese oxide (MnO<sub>2</sub>) over the tin (IV) oxide (SnO<sub>2</sub>) was achieved. Also, the impact of operating condition on removal of sulfur compounds was investigated by applying various operating conditions such as reaction temperature (30, 45, 60 and 75°C) and batch time (25, 50, 75 and 100 min). After that, EDS reaction was conducted by employing acetonitrile as solvent at various operation conditions (agitation speed and batch time). The experimental data explained that the highest DBT and various sulfur compounds removal efficiency from kerosene fuel at the best conditions (oxidation: 5% MnO<sub>2</sub>/SnO<sub>2</sub>, reaction temperature of 75 °C, and reaction time of 100 min, extraction: acetonitrile, agitation speed of 900 rpm, and mixing time of 30 min) via the catalytic oxidative-extractive desulfurization process was 92.4% and 91.2%, respectively. Also, the MnO<sub>2</sub>/SnO<sub>2</sub> catalyst performance was investigated after six

consecutive oxidation cycles at the best conditions, and the catalyst prove satisfactory stability in terms of sulfur compounds removal. After that, the spent catalyst were regenerated by employing various solvents (methanol, ethanol and iso-octane), and the experimental data showed that the regeneration performance of the used solvents decreases according to the following order: iso-octane > ethanol > methanol. Such results gave a good indication for the removal of sulfur compounds and for obtaining an environmentally friendly fuel.

## 5. Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared for affecting the present study.

## 6. Acknowledgement

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## Nomenclatures

<b>Symbol</b>	<b>Definition</b>	<b>Unit</b>
DBT	Dibenzothiophene	( - )
OEDS	oxidative-extractive desulfurization process	( - )
BT	Benzothiophene	( - )
Th	Thiophene	( - )
BDS	Biodesulfurization	( - )
ADS	Adsorptive desulfurization	( - )
ODS	Oxidative desulfurization	( - )
EDS	Extractive desulfurization	( - )

ILD	Ionic liquids desulfurization	(-)
ppm	Part per million	(-)
DMSO	Dimethyl sulfoxide	(-)
DMF	Dimethyl formamide (DMF)	(-)
SER	solvent extractive regeneration process	(-)
XRD	X-ray diffraction test	(-)
SEM	Scanning electron microscopy test	(-)
FTIR	Fourier transform infrared	(-)
BET	Brunauer–Emmett–Teller	(-)

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