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Oxidative desulfurization of model fuel using a NiO-MoO_3 catalyst supported by activated carbon: Optimization study

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ABSTRACT

In this study, oxidative desulfurization of dibenzothiophene (DBT) with an H_2O_2-acetic acid system whereas the catalyst used is molybdenum oxide supported on activated carbon (AC). The effect of loading nickel oxide as a promoter as well as the impact of catalyst dosage and the initial sulfur concentration were investigated. The ranges for these parameters are catalyst dosage (0.5–1.5) g, nickel loading (2–6) wt.% and initial sulfur concentration (400–800) ppm. A Response Surface Methodology (RSM) combined with Box-Behnken design (BBD) was utilized to evaluate the impacts of studied variables; the evaluation consists of the level of order significance of each factor, the interaction effects of parameters was analyzed with Analysis of variance (ANOVA) and determine the optimum conditions for oxidative desulfurization (ODS). Results showed that sulfur removal efficiency from model fuel ranged between 23 and 71%, and these results were fitted with a second-order polynomial model with a high correlation coefficient R^2 (0.9719). The optimal condition for DBT oxidation is 0.5 g. Ni wt. 6% and 700 ppm for catalyst dosage, nickel loading, and initial sulfur concentration respectively.

1. Introduction

The rapid technological development in recent decades has led to an increase in the population in the world, which in turn has caused a noticeable increase in the consumption of fuels such as jet fuel, gas oil, and gasoline, which contain organic sulfur compounds (OSCs).) and are a major cause of air pollution (Choi et al., 2014). These OSCs are found in many forms like sulfides, thiol, and thiophene with their derivatives which may be described as highly harmful to health and the environment via sulfur oxides (SOx) emission during combustion. Moreover, the presence of sulfur in petroleum products also may be causing corrosion of internal combustion engines, poisoning catalytic converters, and causing air pollution, (Alwan et al., 2021). For all mentioned above the sulfur compounds must be removed or eliminated to allowed limits which pay attention to scientists working towards sulfur removal. There are various desulfurization technologies like hydrodesulfurization (HDS), oxidative desulfurization (ODS), extractive desulfurization, and biodesulfurization etc. for production of low-sulfur fuel. HDS is a classical technology used in large-scale processes which desulfurizes different fuels by using hydrogen at high pressure and Ni-Mo or Co-Mo catalyst under elevated temperature, but the HDS has low reactivity towards benzothiophene (BT), dibenzothiophene (DBT), and its alkylated derivatives (Alwan, 2022). There are many disadvantages to using HDS as follows; it requires severe operating conditions such as high reaction temperature (between 300 and 400 °C), hydrogen at high pressure (30–75 bars), the huge amount of catalyst, use of large reactors, and long residence time which causes high operation cost (Choi et al., 2016) .

The ODS technology may be described as a promising technique because it does not need to work at extremely high temperatures, as well as atmospheric pressure is enough to achieve the reaction (Alwan 2021) .The ODS efficiency is a two-step process, first step the sulfur present is oxidized to sulfoxide or suldones in presence of oxidation agent such potassium ferrate, tetra-butyl hydroperoxide, hydrogen peroxide ozone, molecular oxygen, etc., this oxidation reaction is a selective oxidation, it is oxidized OSCs to its sulfur forms without breaking Carbon-carbon bonds. Among these oxidant agents hydrogen peroxide H_2O_2 is preferred due to high oxidation reactivity and it maybe consider as green oxidant (environmentally-friendly) as well as its low cost safety, and high selectivity (Choi et al., 2014). The oxidation of sulfur caused increasing in polarity sulfur containing compounds. Thus, the sulfoxides and sulfones are easily removed from oil phase with polar solvent or adsorbents and this is the second step. (Zhu et al., 2012; Choi et al., 2022). The most common used solvents such as acetonitrile, methanol,

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dimethylsulfoxide (DMSO), acetone and, dimethylformamide (DMF). Using of solvent has many disadvantages; toxicity, disposal, reusability, cost and explosiveness, thus solvent selection may represent challenge for example recovery of DMSO challenge via similar boiling point, while acetonitrile characterized by its high polarity which extract a lots of aromatic, and methanol is a good solvent for sulfones extraction but has density closed to diesel density separation is difficult. The ease of OSCs oxidation depends on electrons densities on sulfur atom. High electron density sulfur atoms are easier to oxidize (Badoga et al., 2018).

The ODS process require to use various transition metal oxides catalyst such as titanium, copper, cobalt, manganese, iron, tungsten, molybdenum, vanadium and so on .The metals oxides catalyst need support (carrier) like alumina .Using of synthesized CoMo/Alumina with different Co/Mo ratio for BT and DBT oxidation on fixed bed reactor was showed 30% removal for BT and 90% removal for DBT, and they reported about that using MoOx catalyst supported on alumni is very active but it has faster deactivation rate (Chica et al., 2006). Titanium oxide nanotubes and H_2O_2 exhibited good activity for DBT oxidation (Lorençon et al., 2014). Tian et al. conducted ODS reaction for removing BT and DBT with H_2O_2 and phosphomolybic acid supported on silica and they get removal efficiency about 99% (Tian et al., 2016). To promote classical molybdenum based catalyst for ODS reaction of DBT at mild operating conditions M. Yaseen et al. used 2 wt.% loading as promoter to classical molybdenum based catalyst in presence of oxidation system consists H_2O_2 and formic acid and (Muhammad et al., 2018). There are many workers interested to use carbon and its allotropes as catalyst support via its high chemical and thermal stability as well as its mechanical strength such as grapheme and carbon nanotubes (Alwan, 2022).

In this study the molybdenum-based catalyst was synthesized by wet impregnation for activated carbon, the molybdenum oxide represented as active phase while nickel oxide is a promoter because the molybdenum base catalyst lost its activity during oxidation desulfurization reaction so the goal for this study is the effect of adding nickel as catalyst promoter as well as to analyze the effect of some other variables on DBT oxidation to remove sulfur from model fuel. The studied variables are catalyst amount, nickel (Ni wt.%) loading, and initial sulfur concentration while the response is the sulfur removal efficiency. The experiments were designed by applied Box-Bohenken experimental design combined with Response Surface Methodology (RSM).

2. Experimental work

Activated carbon AC (568 m^2/g and 0.0062 cm^3/g for specific surface area and pore volume respectively) purchased from the local market was used as catalyst support, ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 6H_2O$ (AHM) with purity 99% (HOPKIN & WILLIAMS), nickel nitrate $Ni(NO_3)_2\cdot 6H_2O$ with purity 99% (CHD Ltd.).

The catalyst was prepared by wet impregnation AC with nickel and molybdenum oxide from their precursor as follows; AHM and $Ni(NO_3)_2\cdot 6H_2O$ are sources for molybdenum oxide and nickel oxide respectively. The molybdenum was loaded 15 wt.%, while the nickel loaded (2, 4, and 6 wt.%) to investigate the impact of nickel content as a catalyst promoter. For impregnation of 10 g from AC, two solutions were prepared as follows; first solution, 2.007 g of AHM salt (as molybdenum oxide source), second solution, 1.0297, 2.0594 and 3.0891 g of nickel nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$) salt (as nickel oxide source) dissolved in distilled water to get loaded nickel percentage 2%, 4%, and 6% where they are symbolized as 2%NiMo/Ac, 4%NiMo/Ac and 6%NiMo/Ac respectively. These two solutions were added, followed loaded on an AC surface by co-impregnation method to precipitate cobalt and molybdenum oxides. The impregnated AC was dried at 110 ºC for two hours and calcination was done at 400 ºC for four.

Table 1
Independent (controllable) variables and their levels.

Variables, Unit	Symbol Coded	Actual	Levels -1	0	1
Catalyst dosage, g.	x_1	X_1	0.5	1.0	1.5
Ni% loaded	x_2	X_2	2	4	6
Sulfur initial concentration ppm	x_3	X_3	400	600	800

Table 2
Box-Behnken design matrixes.

Run	design parameters x_1	x_2	x_3	Run	design parameters x_1	x_2	x_3	Run	design parameters x_1	x_2	x_3
1	1	0	-1	6	0	1	1	11	0	0	0
2	-1	0	1	7	0	-1	-1	12	-1	0	-1
3	1	-1	0	8	0	0	0	13	0	1	0
4	1	1	0	9	0	0	0	14	-1	1	0
5	0	-1	1	10	1	0	1	15	-1	-1	0

2.1. *Using Box-Behnken design with response surface methodology RSM*

RSM is a practical procedure used for evaluating the relation between actual experimental results (response) with studied variables (control variables), and this is usually done by combining RSM with factorial design techniques such as central-composite design CCD and Box-Bohenken design BBD. BBD technique can reduce the required number of experiments without decreasing the accuracy of the optimization in comparison with other factorial design methods (Alwan, 2021). The required experiments number to cover the studied variables system according to using BBD is:

$$N = 2k(k-1) + r \tag{1}$$

Where N is the number of experiments, k is the number of variables, and r is the replicate number of central points (3–6). BBD stated that the levels of the studied variables were adjusted to only three levels (-1.0, 1) with equal values for the interval between each level, thus for three variables with three levels, the number of experiments was 15−18 depending on the number of replicated experiments number (r in the equation). The catalyst dosage, Ni% loaded in catalyst, and initial sulfur concentration is chosen as studied (controlled) variables on DBT conversion (Table 1), the experimental design with using of design expert version 13 as shown in Table 2.

The experiments results for the effects of catalyst dosage (x_1), Ni wt.% loaded on catalyst (x_2) and, sulfur initial concentration (x_3) on oxidative desulfurization were fitted as second-order polynomial, and it can be used to estimate predict values and optimization the system, for three variables where the second-order polynomial represents by equation

$$R\% = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j + \varepsilon \tag{2}$$

Where R% is predicated response, β_0 is the intercept coefficient, β_i is the linear effect (slope) of input variable x_i, β_{ij} is interaction effect of linear by linear between two input variables x_i, and B_{ii} is squared effect.

2.2. *ODS activity investigation*

The model fuel (DBT dissolved in n-heptane) was prepared by using three different DBT concentration (400, 600, and 800 ppm); the DBT concentration prepared according to Box-Behnken design BBD. ODS reaction for DBT was conducted under mixing of model fuel at 50 °C in presence of prepared catalyst and H_2O_2 –CH_3COOH oxidation system, where the ODS reaction was examined under the effect of three independent variables; catalyst dosage, Ni% loaded on the catalyst and, initial sulfur concentration with the range for these studied variables

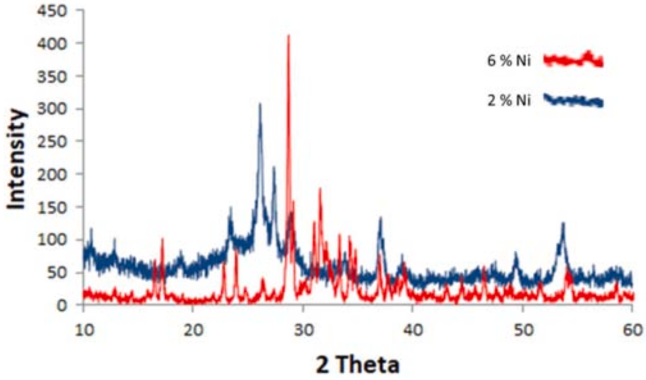


Fig. 1. XRD pattern for 2% NiMo/Ac, and 6% NiMo/Ac catalysts.

which shown in Table 1. The total number of experiments required to cover the three-level for the three-variables system is 15 according to Eq. (1), all experiments were arranged according to Box–Behnken experimental design as shown in Table 2. The oxidation reaction starts by heating 100 ml of model fuel using the magnetic stirrer heater to reach the required temperature (50 °C), 10 ml of hydrogen peroxide, and 5 ml of acetic acid with the needed dosage of catalyst added to model fuel. The reaction stopped after 60 min. Subsequently OSCs were converted into the polar compounds such as sulfoxides and /or sulfones m which separated by using acetonitrile (with 1:1 volume ration) during extraction step. The separation done in separation funnel in which the upper phase was the low sulfur fuel while the below phase was the mixture of oxidative compounds and solvent (acetonitrile).The sulfur content in the final product was measured by X-ray fluorescence (Sulfur Meter model RX-620SA/Tanka Scientific). The DBT conversion (R%) is related with initial sulfur concentration (Si) and final sulfur concentration (So) as in the following equation:

$$DBT\ conversion(R\%) = \frac{Si - So}{Si} \times 100 \tag{3}$$

3. Result and discussion

3.1. Characterization of prepared catalyst

The XRD (Shimadzu Model XRD- 6000 –Japan) patterns for prepared catalysts are shown in Fig. 1, which contains the pattern for 2% NiMo/Ac (blue curve) and 6% NiMo/Ac (red curve). As the result show the peaks around 2θ equal to 28.9 and 28.77 are attributed to graphite (carbon) at 2% NiMo/Ac and, 6% NiMo/Ac respectively (Wang et al., 2015). There are many peaks for molybdenum trioxide MoO_3 at 27.38° at 2%NiMo/Ac, while peaks at 2θ equal to 32.72, and 39.26° at 6% NiMo/Ac (JCPDS No.05–0508), these peaks with sharp shapes indicate that MoO_3 have good crystalline and Juehan noted the result closed to this work results (Alwan 2022), (Jegal et al., 2013) and (Dedual et al., 2014). $NiMoO_4$ phase is diffracted at 2θ equal to 23.46 and 23.94 on 2% NiMo/Ac and,6% NiMo/Ac patterns respectively, according to the

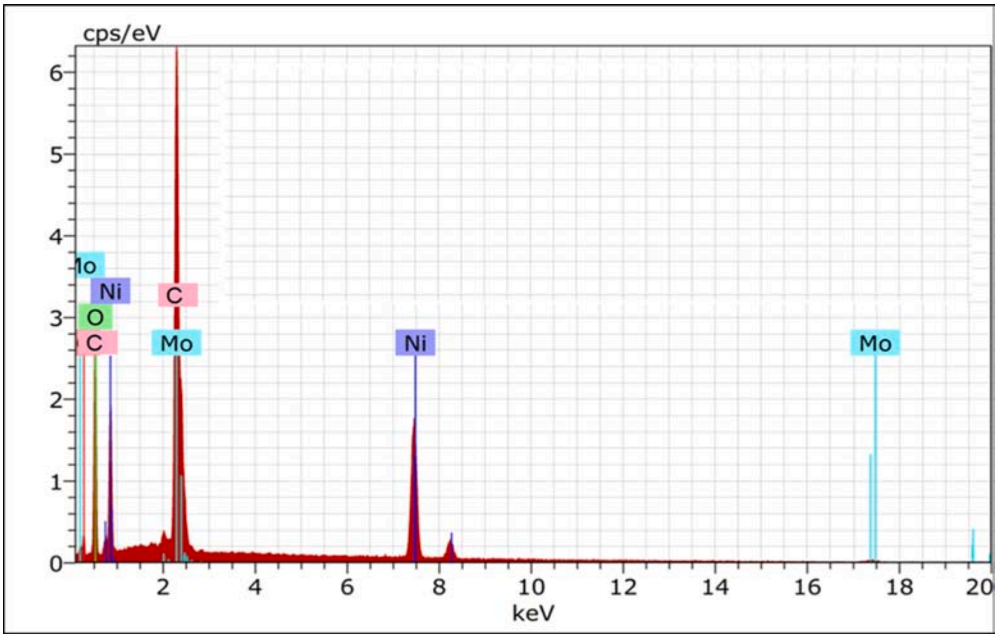


Fig. 2. EDX spectrum for 6% NiMo/Ac catalyst, the analysis confirms the presence of carbon about 82%, nickel 5.7% and molybdenum 14.5%.

Table 3
Experimental (observed) and predicted DBT conversion at different conditions.

Run	Catalyst dosage, g.	Ni% loaded	Sulfur initial concentration ppm	DBT conversion R%	Run	Catalyst dosage, g.	Ni% loaded	Sulfur initial concentration ppm	DBT conversion R%
1	1.5	4	400	0.468	9	1	4	600	0.623
2	0.5	4	800	0.624	10	1.5	4	800	0.571
3	1.5	2	600	0.662	11	1	4	600	0.615
4	1.5	6	600	0.605	12	0.5	4	400	0.230
5	1	2	800	0.629	13	1	6	400	0.240
6	1	6	800	0.710	14	0.5	6	600	0.590
7	1	2	400	0.370	15	0.5	2	600	0.598
8	1	4	600	0.595					

Table 4
ANOVA analysis results for RSM for quadratic model.

Source	DF	Adj. SS	Adj. MS	F-value	*p*-value
Model	9	0.39941	0.04438	16.77	0.003
Linear	3	0.25973	0.086577	32.71	0.001
Catalyst dosage (X_1)	1	0.02135	0.021356	8.07	0.036
Ni% loaded (X_2)	1	0.001617	0.001617	0.61	0.470
Initial sulfur conc. (X_3)	1	0.23675	0.236758	89.45	0.000
Square	3	0.079546	0.026515	10.02	0.015
(Catalyst dosage)^2 (X_1^2)	1	0.000435	0.000435	0.16	0.702
(Ni% loaded)^2 (X_2^2)	1	0.006120	0.006120	2.31	0.702
(Initial sulfur conc.)^2 (X_3^2)	1	0.069720	0.069720	26.34	0.004
2-way Interaction	3	0.060141	0.020047	7.57	0.026
Catalyst dosage* Ni% loaded (X_1X_2)	1	.000584	0.000584	0.22	0.658
Catalyst dosage* Initial sulfur conc.(X_1X_3)	1	0.048400	0.048400	18.29	0.008
Ni% loaded * Initial sulfur conc. (X_2X_3)	1	0.11157	0.11157	4.22	0.095
Error	5	0.013234	0.002647		
Lack –of – Fit	3	0.009093	0.003031	1.46	0.430
Pure Error	2	0.004141			
Total	14	0.412651			

standard card (JCPDS No. 86–0361), and this good agreement with (Ghosh et al., 2013). Furthermore, the nickel oxide exhibited diffraction peaks at 2θ equal about 43.26 and 54.34 which agreed with Dong et al. (Jang and Park, 2012).The presences of dispersion active metallic oxides (nickel and molybdenum) were further confirmed by EDX (BRUKER Model X Flash 6l10 Germany) elemental mapping as shown in Fig. 2.

3.2. Catalyst activity results

Table 3, shows the DBT conversion for all experiments done according to Box –Behnken design BBD. The DBT conversion ranged between 23 and 71% whereas these results fitted with a second-order polynomial (quadratic model), this equation relate between R% as a function for a function of independent variables (catalyst dosage, Ni% loaded and sulfur initial concentration) and as with respect to actual value below:

$$R\% = -1.516 + 0.989X_1 - 0.1557X_2 + 0.00555X_3 - 0.0121X_1X_2 - 0.0011X_1X_3 + 0.00132X_2X_3 - 0.043X_1^2 + 0.01018X_2^2 - 0.000003X_3^2 \quad (4)$$

The analysis variance ANOVA results for the predicated model as seen in Table 4, ANOVA gained by Minitab software version 17. The predicted model shows good fitting for actual data due to the high value of correlation coefficient R^2 (0.9719) and close value for adj. R^2 (0.9213) indicates that the assumed model is reasonably well fitting with actual results. F-value for regression model is 16.77 is greater than tabulated value ($F_{95,\ 5,0,05} = 4.77$). Based on F-value results, the initial sulfur concentration shows the highest effect on DBT conversion (sulfur removal efficiency) followed by catalyst dosage and Ni% loaded as predicated according to their F-values 89.45, 8.07, and 0.61 for initial sulfur concentration, catalyst dosage, and Ni% loaded respectively. The optimum DBT conversion is 75.74% at 0.5 g, 6% and 700 ppm for catalyst dosage, Ni loaded and initial sulfur concentration respectively.

The impact of the studied variable individually and optimization of the studied system were shown in Fig. 3, the DBT conversion increased

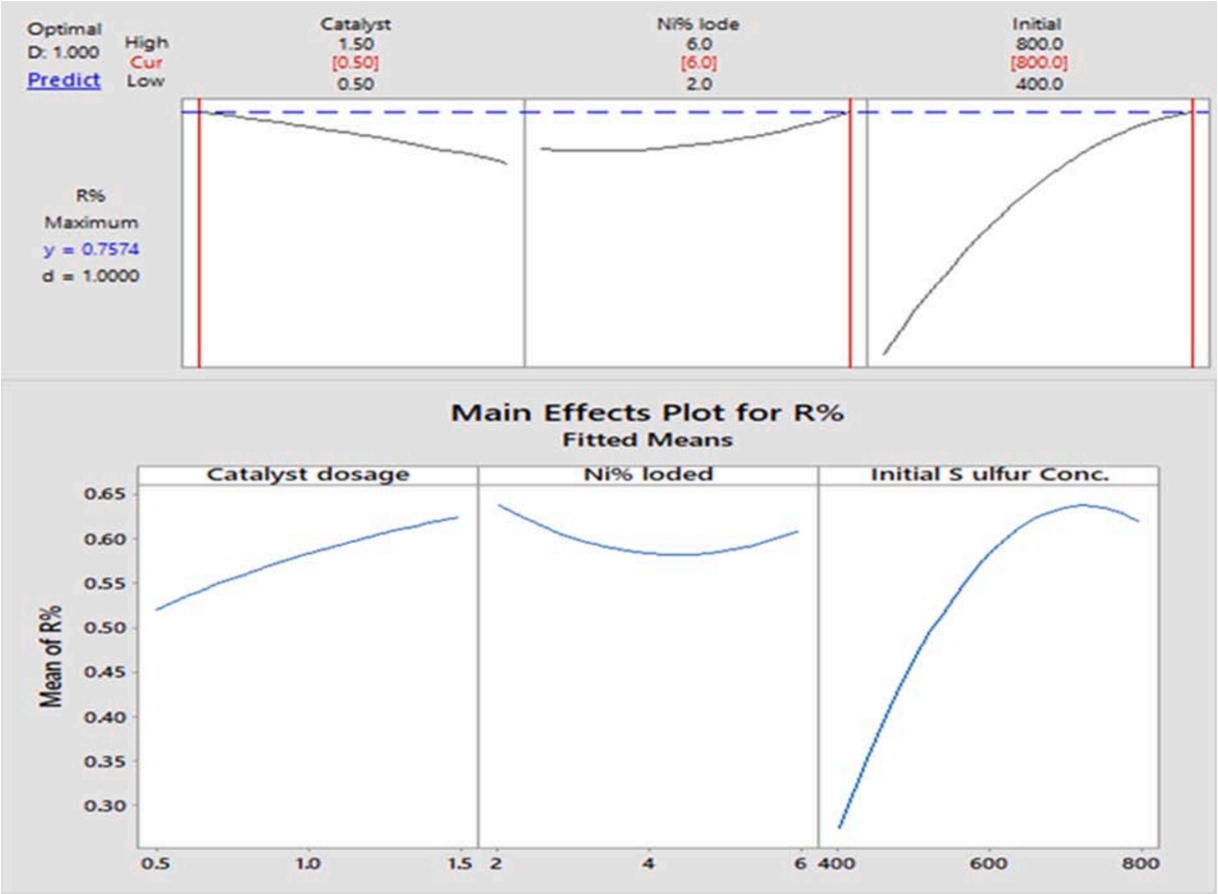


Fig. 3. Effect of studied variables on DBT conversion, the conversion increased with catalyst dosage and initial sulfur concentration, and decreased with Ni loaded increasing (up graph). The optimum DBT conversion is 75.74% at 0.5 g, 6% and 700 ppm for catalyst dosage, Ni loaded and initial sulfur concentration respectively (lower graph).

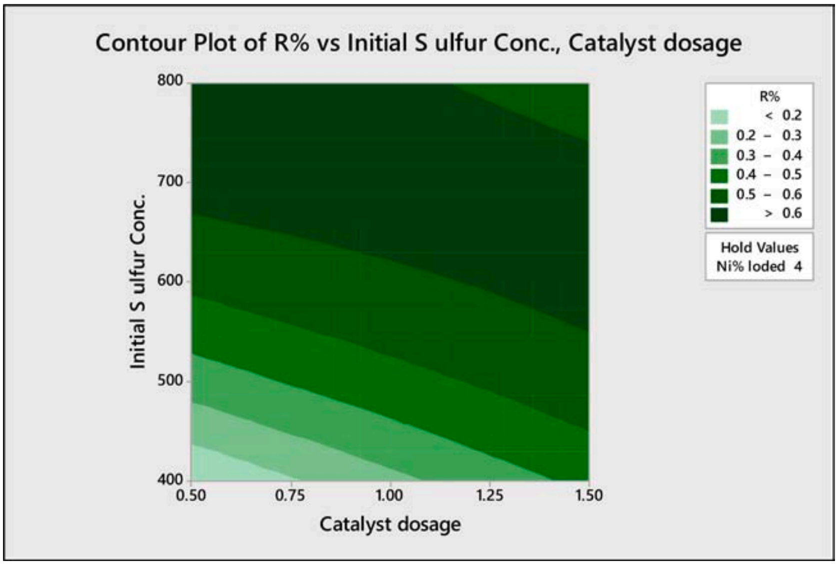


Fig. 4. The interaction effect of initial sulfur concentration and catalyst dosage on DBT conversion while holding Ni% loaded at 4%.

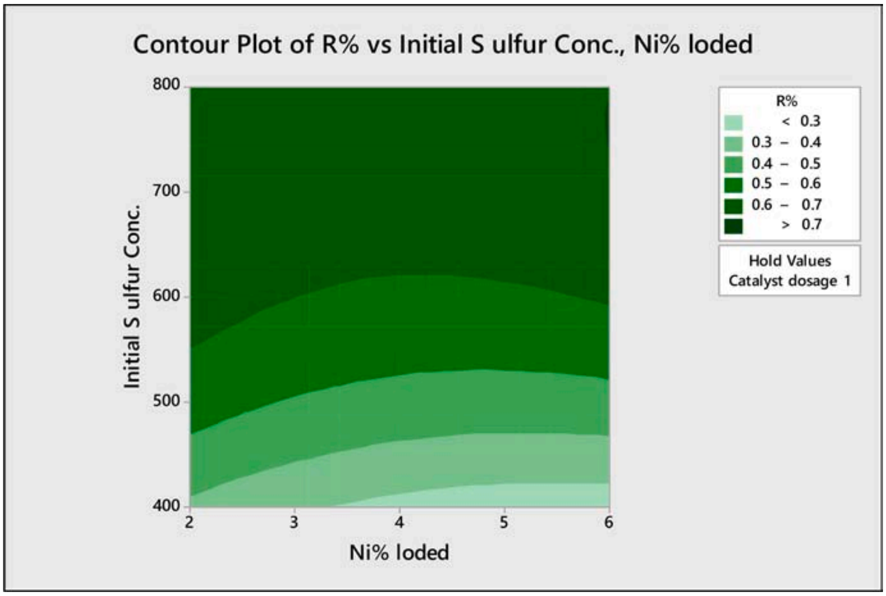


Fig. 5. The interaction effect of initial sulfur concentration and Ni% loaded on DBT conversion while holding catalyst dosage at 1 g.

with an increase in initial sulfur concentration from 200 ppm until reached near 700 ppm, with further increases in initial sulfur concentration the DBT conversion decreased and this may be because of the presence of the limited number of active sites in a fixed amount of catalyst, in which these limited active sites are insufficient for conversion of BDT (Subbaramaiah et al., 2018) . DBT conversion was raised via the increasing of dosage (amount) of catalyst, which increased the amount of catalytic intermediate produced by reaction with oxidant agent (H_2O_2), in another meaning when catalyst amount increased will provide more active sites (providing more chance of surface interaction between DBT molecules and catalyst active phase) that responsible on DBT conversion (Yu and Wang, 2013), (Cheng et al., 2015) and (Chu et al., 2010). The impact of nickel weight percent loaded on DBT conversion was decreased with increasing of nickel weight percentage because increasing of amount of nickel loaded leads to less-active surface species formation which maybe caused blockage of some active cites by Ni species (Kim et al., 1996). Zhang et al. (2008) reported that increasing nickel content led to lower nickel dispersion, Figs. 4–6 show the interaction effect for each pair from studied variables.

3.3. Proposed mechanism

For better understanding the ODS mechanism by H_2O_2/CH_3COOH system in presence of NiO-MoO_3/Ac catalyst, by assuming is the presence of NiO as a catalyst promoter, while the MoO_3 as an active phase, the reaction initiated by MoO_3, involving the hydrolytic cleavage of hydrogen peroxide to produce strong oxidation agents (active hydroxyl radical ($OH^\bullet$) (Ahmad et al., 2021), these active radicals were attack acetic acid to produce peracetic acid, which offers oxygen to DBT to produce DBTO (sulfoxide;contains $S = O$) and with further attack the $DBTO_2$ (sulfones; contains $O = S = O$) was produced (Scheme 1) .

$$DBT \xrightarrow{[o]} DBTO \xrightarrow{[o]} DBTO_2 \quad (5)$$

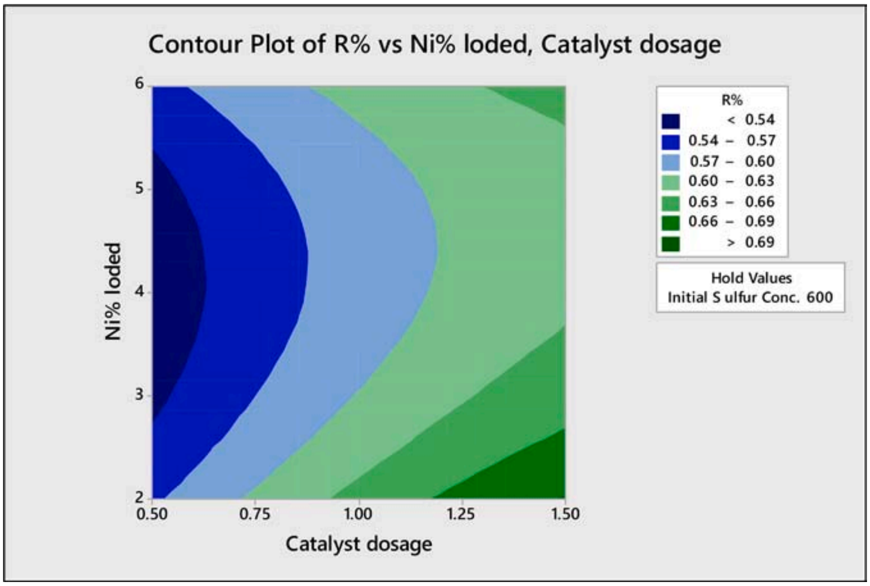
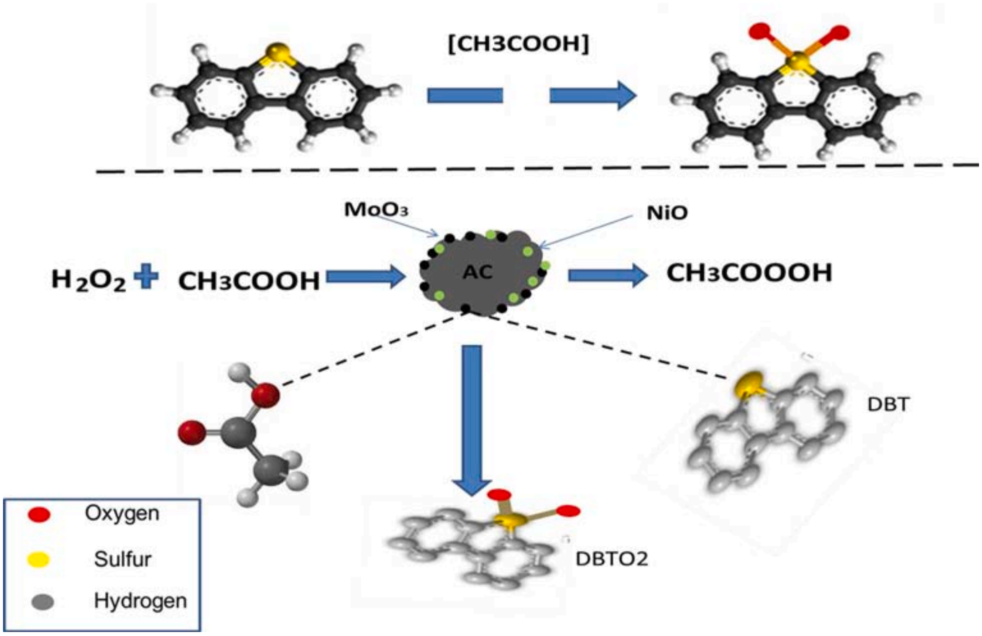


Fig. 6. The interaction effect of catalyst dosage and Ni% loaded on DBT conversion while holding initial sulfur concentration at 600 ppm.



Scheme 1. Mechanism of ODS for DBT with H_2O_2/CH_3COOH oxidation system in presence of NiO-MoO_3/Ac catalyst.

4. Conclusion

In this study, the oxidation reaction ODS for DBT dissolved in n-heptane is done using molybdenum oxide-nickel oxide supported on AC and an H_2O_2 – acetic acid system as an oxidant agent. The study consists of the investigation of the effect of three parameters which are arranged by combined RSM and Box-Behnken design. The studied variables were catalyst dosage, Ni% loaded, and initial sulfur concentration. Results show that DBT conversion (sulfur removal efficiency) ranged between 23 and 71%, and they were fitted with seconds–order polynomial (high correlation coefficient R2 = 0.9719). These results agreed with many previous studies but the most point considered is the use of nickel oxide for enhancement of the molybdenum-based catalysis activity. In contrast, the using nickel oxide caused decreasing in sulfur removal efficiency and which may mean that the deactivation of the catalyst was happen rapidly. The optimum DBT conversion is 75.74% at 0.5 g, 6% and 700 ppm for catalyst dosage, Ni loaded and initial sulfur concentration respectively.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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