

Gasoil Desulfurization by Ozone at High-Entropy Oxide Catalyst: Optimization, Thermodynamic, and Kinetics Investigation

Abstract

Oxidative desulfurisation (ODS) is a promising alternative technology for producing sulfur-free fuel compared to conventional hydrodesulfurisation technology, as the ODS reaction can be performed under moderate operating conditions. This study focuses on investigating the performance of oxidation desulfurisation of Iraqi gas oil using a novel catalyst. High-entropy oxides (HEO) catalysts are prepared by mechanochemical mixing of cobalt, chromium, iron, titanium, and nickel chlorides using a nanoball mill. The HEO catalyst was characterised by X-ray diffraction (XRD), Energy Dispersive Spectroscopy (EDS), and Fourier Transform Infrared Spectroscopy (FTIR). Scanning Electron Microscopy (SEM) was used to investigate the prepared catalyst morphology. Characterisation findings indicate that the prepared catalysts are in the nano to semi-micron range, with different shapes and varying active functional groups. The gasoil ODS performance was investigated by using ozone as the oxidant agent and the impact of catalyst amount (0.5-1 g), temperature (150-200 °C), and the oxidation time (30-60 minutes) on catalytic desulfurisation performance. A Box-Behnken experimental design (BBD) was used to design the experiments. The removal efficiency ranged between 85% and 99%, with an optimum sulfur removal efficiency of 98% achieved

at 0.59 g, 200 °C, and 60 minutes for catalyst dosage, reaction temperature, and oxidation time, respectively. The analysis of variance (ANOVA) revealed that the effects of the studied variables follow the following order: oxidation time, reaction temperature, and catalyst dosage.

A kinetics study shows that the reaction obeys a pseudo 1st order reaction and has a relatively low activation energy (22.033 kJ/mol) due to the presence of a catalyst. Thermodynamically, the reaction is non-spontaneous, as indicated by its positive Gibbs free energy (ΔG), and the reaction rate increases with temperature.

Keywords: dibenzothiophene, high entropy oxide, ozone, oxidation, Box- Behnken experimental design

1. Introduction

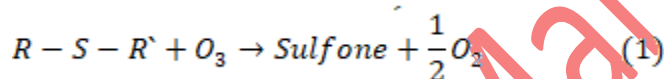
SO_x emissions increase as the consumption of transportation fuel increases due to sulfur organic compounds (SOCs) present in transportation fuel products. These compounds may be associated with fuels in various forms, including sulfide, thiol, mercaptan, disulfide, and thiophene. SOCs present in fuels cause bad consequences such as pollution of the environment and human health (respiratory disease and cancer), corrosion in metallic equipment and buildings, soil eutrophication, and poisoning of valuable catalysts in the upstream unit [1 -2]. On the other hand, the high sulfur concentration fuel increases the cost of refining petroleum fractions [3] for that, there are environmental regulations issued by governments in different countries around the world that limit the sulfur content in

various types of fuels [2], for instance, the Chinese national V standard was enacted in China, which identifies the sulfur content limit not more 10 ppm [4], and the European Union has also executed the Euro VI standard, which specify the sulfur concentration to 10 ppm; thus, it is necessary to produce low-content sulfur fuel with less than 10 ppm, or even free sulfur fuel [5].

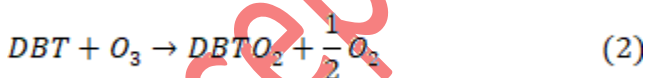
Different techniques have been used for removing sulfur from fuels, such as hydrodesulfurisation (HDS) [5 - 7] adsorptive desulfurisation (ADS) [8 - 10] , bio-desulfurisation [11 - 12] , extraction [13 - 14] , reactive adsorption desulfurization [16] Electrochemical desulfurization technique [17]and oxidative desulfurization (ODS)[16 - 18] . Among these different methods, HDS is considered the most common and significant technique that is used in petroleum refineries. Still, this process does not remove heavy thiophenic derivatives (T) such as benzothiophene, dibenzothiophene, and 4,6-dimethyl dibenzothiophene effectively because of the high electron density on the sulfur atom, which makes HDS inefficient for breaking the carbon-sulfur bonds [21] .The ODS technique may be considered an alternative and promising method for removing thiophenic components because it can be performed under moderate conditions (low pressure and temperature). Its selectivity characterises ODS, which does not require the provision of expensive hydrogen gas for desulfurisation. In this process, the oxidation of SOC_s produces sulfoxides and sulfones, depending on the oxygen availability provided by oxidation agents [20].

There are many oxidants used in the ODS reaction, including hydrogen peroxide [22], molecular oxygen [23], ozone, and organic peroxides. Hydrogen

peroxide (H₂O₂) is widely used as an oxidising agent in the ODS process to reduce the sulfur content associated with the fuel. It was decomposed into water, forming an oil-water biphasic system, which resulted in a lowering of the fuel quality. Therefore, it was necessary to recover it using alternative techniques, such as solvent extraction [24]. Oxygen has significant advantages when used as an oxidising agent due to its low cost, high availability, and relatively safe use [21]. On the other hand, ozone is classified as a very strong oxidation agent due to its high oxidation potential (2.076 V), which is higher than that of H₂O₂ (1.77 V) [25]. Ozone is a very strong oxidant and can be oxidised by OSCs present in fuel as follows:

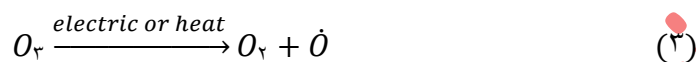


Where R-S-R' is a sulfur compound such as mercaptan, sulfide, thiophene, etc., while sulfone is the oxidised sulfur product; for example, the DBT oxidation can be represented as below [26]:



The proposed mechanism for the ozonation of OSCs (e.g., DBT) involves ozone attacking the sulfur atom to produce the corresponding sulfoxide, which is then further oxidised to produce the corresponding sulfone. The sulfoxide is an intermediate product (R-S-O-R'). In contrast, the sulfone is the more stable product (R-SO₂-R') [27]. Using transition metals as a catalyst enhances the ozone oxidation power for organic compounds. This enhancement results from free radicals produced

by ozone. The free radicals are involved in oxidation reactions and support desulfurization processes for producing sulfoxides and sulfones, due to direct contact between ozone and the fuel [28]. Ozone breaks down through decomposition under the influence of electrical fields, impurities, or heat [29]. In the present case, decomposition was done under heat as follows:



As mentioned above, the catalyst system is required for the ODS reaction, in which there have been many attempts to use different catalyst systems in the ODS reaction, for instance, cerium supported on alumina [30], Fe₂O₃ supported on Graphene oxide [31], MoO₃ supported on carbon nanotubes [32], NiO-MoO₃ supported on activated carbon [33], the hollow PW₁₂ /TiO₂ at MgCO₃ [34], CuO/TiO₂-SiO₂ , and CuO/SiO₂ nano catalysts [35], NiW supported on activated carbon [36], MnO₂-FeO₃ supported on activated carbon [19], polyoxometalates, and metal-organic frameworks [37].

HFO is a novel type of solid crystalline structure that contains five or more metal species that are characterised by their unique physical properties. The configurational disorder and entropy (S) were stabilised, so these types of materials at high temperature show high stability because of the disordered distribution of metal species, and because of entropy contribution, the Gibbs free energy (G) at high temperature is at a more negative value [38], which means materials are stable thermodynamically at high temperature. According to entropy engineering, the

atoms within the HEO crystalline structure are disordered, which confers unforeseen benefits to these atoms, such as various redox behaviours, oxygen vacancies, and cation compositions [36-38]. The non-arranged atoms in the crystalline unit cell, or disorder, prevent lattice defects and cause defect stabilisation [39]. The HEO proved to be an excellent material for various catalytic processes due to the presence of these defects. For instance, a holy HEO catalyst (MgCuZnNiCo)O is a wonderful material for benzyl alcohol oxidation [40]. The improved configurational entropy will lead to an increase in endurance for lattice deformation, allowing for the combination and stability of high-concentration metal cations, which in turn will enhance the activation of oxygen presence in the lattice and the formation of active species [41]. HEO exhibits a variety of effects or high entropy complexes, allowing for the easy control of the chemical states of each species, which can result in either the elements being rich or deficient in electrons [42].

The instability of metal oxides sometimes occurs during the ODS reaction because of organic acidic species in fuels. Consequently, some scientists have found that transition metal nitrides are potentially suitable alternatives to transition metal oxides for catalytic oxidation reactions [40]. They are characterised by having catalytic activities higher than those of transition metal oxides; for instance, the Mo₂N/porous carbon catalyst, which achieved an excellent desulfurisation efficiency compared to the tungsten trioxide/zirconium oxide (WO₃/ZrO₂) catalyst[43]. The surface of HEO or a multi-component structure is unstable due to its high surface energy and large curvature [44]. Scientists have developed a method for controlling

the synthesis of polyhedral catalysts by regulating the supersaturation associated with surface energy during crystal growth. This strategy provides an effective means of controlling the surface structure and shape of nano- and microcrystals, which is necessary for numerous applications [45]. It's supposed that the elements were uniformly distributed and had similar signal intensity for the elements in HEO, in which these elements were arranged in disorder and interacted with each other [46]. Metals are vital for catalytic applications, particularly those involving high-energy polyhedral crystals, such as those found in HEO. Polyhedral HEO is a promising option for superior catalytic reactions, as the different crystal facets are characterised by distinct surface atom arrangements, which provide adsorption/desorption active sites for reactant accessibility and intermediate or product formation, thereby increasing the catalyst activity and selectivity for the reaction. On the one hand, the different faces in polyhedral have remarkably different electronic features [47].

In this paper, a high-entropy oxide, HEO (CoCrFeNiZn)O_x (HEO), was prepared by mechanochemical mixing, where the metal precursors were mixed using a nanoball mill, and finally the catalyst was calcined at 600 °C, 650 °C, and 700 °C. The synthesised HEO catalyst was used for the desulfurisation of gas oil, utilising ozone as the oxidant agent. The oxidation desulfurisation investigation examines the effects of catalyst amount, temperature, and oxidation time on removal efficiency. The study included the estimation of kinetic and thermodynamic parameters (reaction rate constant, activation energy, Gibbs free energy, and entropy change).

2. Experimental method

۲.۱. Feed

Iraqi gas oil was used as a feeds of the ODS reaction . Gas oil was supplied from the atmospheric crude oil distillation column in Al-Najaf refinery (Al-Najaf, Iraq). The gas oil is characterised by its high sulfur content, 1.5 wt% (15,000 ppm), and (0.8406) specific gravity. The initial (IBP) and final (EBP) boiling points are 225 °C and 367.8 °C, respectively. The distillation data for gas oil is presented in Table 1. The other parameters are as follows: viscosity at 40 °C is 3.2 cSt, ash content is 0.002%, cetane index is 56.1, and flash point is 94.5 °C.

Table 1. Temperature-volume profile of the gas oil

Vol. %	۱۰	۲۰	۳۰	۴۰	۵۰	۶۰	۷۰	۸۰	۹۰
Temp (°C)	۲۴۶	۲۵۳.۲	۲۶۰	۲۶۷	۲۷۵.۵	۲۸۵.۳	۲۹۷.۷	۳۱۴.۷	۳۴۱.۲

۲.۲. Chemicals

There are five metal chlorides used; cobalt (II) chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ -Merck 99%), nickel (II) chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -Sigma-Aldrich 98%), chromium (III) chloride ($\text{CrCl}_3 \cdot \text{H}_2\text{O}$ - Alfa Chemika 99%), titanium (ZnCl_2 -Sigma-Aldrich 99%), and iron (III) chloride (FeCl_3 Sigma-Aldrich 99%): Acetonitrile (CH_3CN -Sigma-Aldrich 99.9%), and hydrochloride (HCl -Merck 37%).

۲.۳. Catalyst preparation

The catalyst was prepared by mixing the metal chlorides mechanochemically, each at an equal mole ratio (0.0025 mol), and 0.125 mol of urea. The mixture was

poured into a nano ball mill (NOAH model NQM-o.4) supplied with ceramic balls (7 mm) in diameter. Mixing and grinding were performed at 400 rpm for 2 hours at ambient temperature, during which the five-salt mixture was converted to a paste form, followed by a moisture-removing step by pouring the produced paste into a desiccator, which was kept at 80 °C overnight; then the resultant was transferred to the muffle furnace (JINYU model 1700) to start the calcination step at three different temperatures (600, 650, and 700) °C for three hours [2]. The catalyst was characterised by Fourier Transform Infrared Spectrophotometer (FTIR) and X-ray diffraction (XRD). Surface morphology and texture properties were measured using the BET method.

2.4. ODS reaction and solvent extraction

The ODS reaction was done in a lab-scale reactor (three-neck round-bottom flask, 250 mL). The flask was equipped with three necks; the first one was for introducing ozone, the second was equipped with a condenser for total reflux, and the third one was used for introducing feedstock (gas oil) and inserting the catalyst dosage for each run, as well as for product suction after the run is over. During the experiment, this neck was closed after inserting the thermocouple through it. The total reflux condenser is used to avoid gas oil evaporation. The ozone flow rate is 20 mL/min. The lab-scale experimental rig is shown in **Fig. 1**.

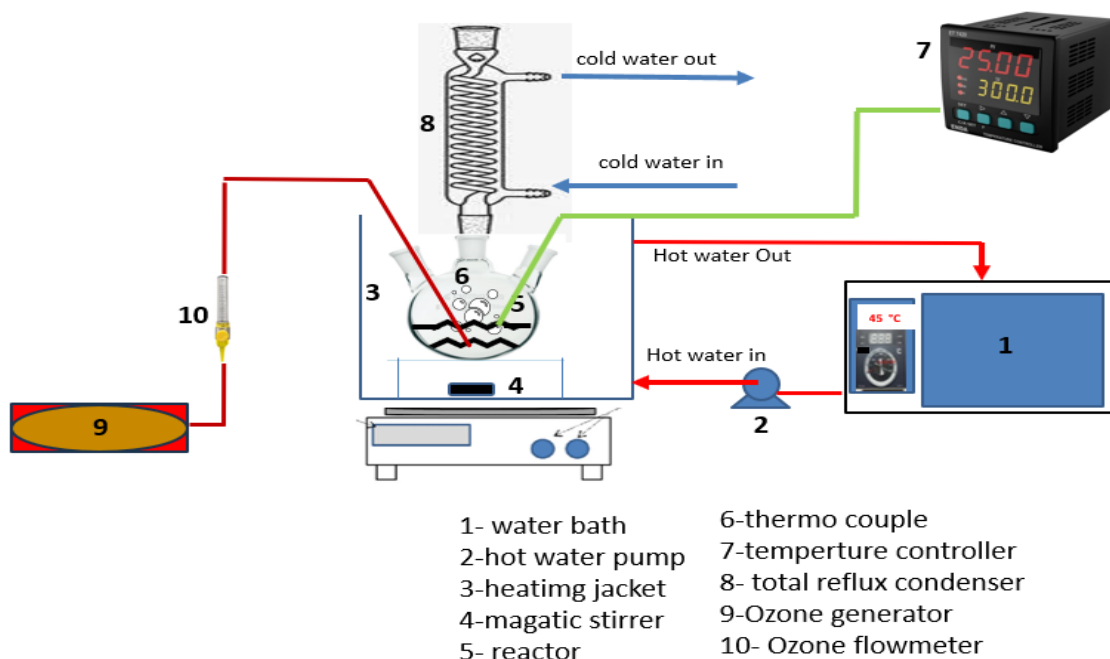


Figure 1- The schematic of the experimental setup for the ODS reaction.

The operating conditions (catalyst dosage, temperature, and reaction time) were adjusted according to the Box-Behnken experimental design BBD, which is illustrated in Table 3. The gas oil was poured into the reactor, and heating was started until the specified temperature was reached. The specified catalyst amount was introduced into the reactor, and ozone feeding commenced, marking the start of the reaction. The reaction was stopped after the specified reaction time had elapsed. The solvent extraction step was done by mixing the ODS reaction product with acetonitrile, and the mixture was shaken well using a shaker (ORBITAL Shaker, Rotator Model VRN-480 from GEMMY Industrial Corp) at 100 rpm for 30 minutes. The mixture was left inside the separation funnel to settle, where there are two layers formed; the over layer consists of sulfones and solvent (oxidation product and

acetonitrile), and the upper layer is composed of low-sulfur fuel. Finally, the removal efficiency (R%) was calculated after measuring the final total sulfur content by an X-ray fluorescence sulfur analyser (SPECTROSCAN SL TU 4276-002-23124704):

$$R\% = \frac{Si - So}{Si} \times 100 \quad (4)$$

Where (Si) is the initial sulfur concentration, and (So) is the final sulfur concentration.

4. Results and discussion

4.1. Catalyst Characterization

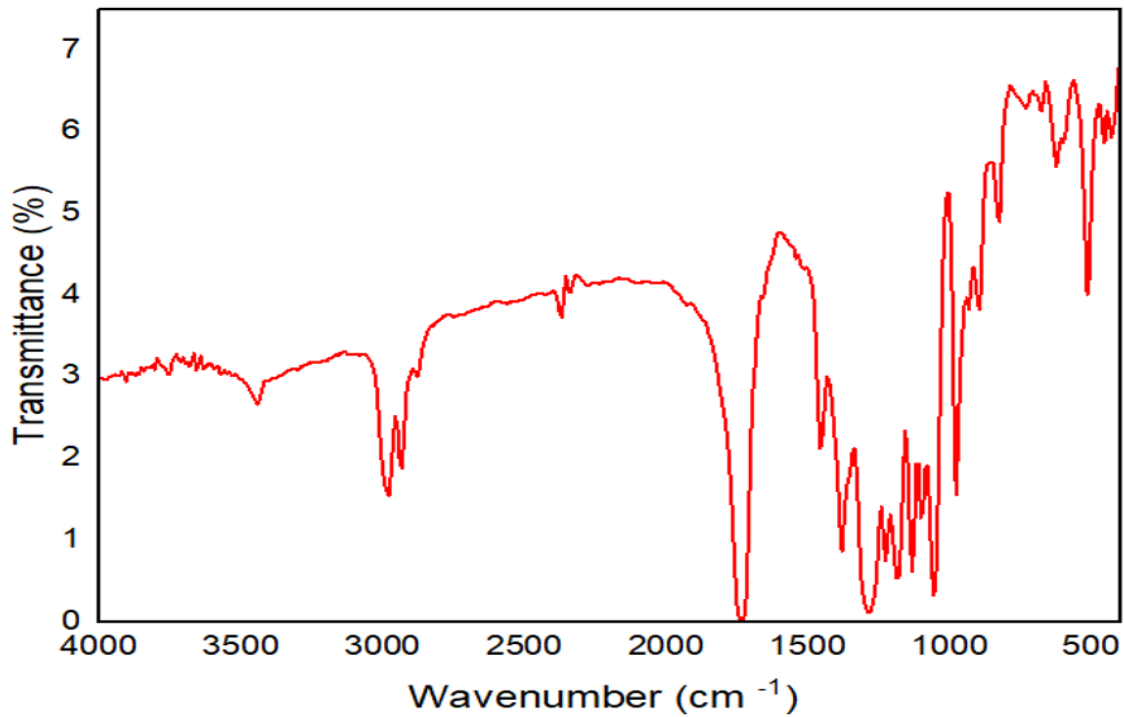


Figure 1- FTIR spectrum for HEO catalyst.

FTIR spectroscopy can be utilized to detect and analyse metal-oxygen vibrations, which are important for characterising metal oxides and other materials. As shown in Fig. 2, the FTIR spectrum of the prepared HEO catalyst exhibits a characteristic set of bands. There is an adsorption band near 3441 cm^{-1} , which is assigned to the O-H stretch vibration, indicating the presence of a hydroxyl group and/or an adsorbed water molecule [48]. The peaks at ≈ 2980 and 2930 cm^{-1} relate to the stretching of C-H vibrations, demonstrating the presence of aliphatic structures. The peak at around 1735 cm^{-1} represents carboxyl groups, such as those found in ketones, aldehydes, and carboxylic acids, for C=O stretching in aromatic rings. The band at 1380 cm^{-1} is attributed to the presence of O-H, which represents a phenolic cluster [48], [49] [50]. There is a band at around 1288 cm^{-1} , which corresponds to the C-O bond. Some peaks appear at $500\text{--}800$, corresponding to metal-oxygen (M-O) vibrations. The characteristic absorption bands in the FTIR spectrum within the $400\text{--}1100\text{ cm}^{-1}$ range, particularly in the $400\text{--}600\text{ cm}^{-1}$ region, are indicative of metal-oxygen bond vibrations. The adsorption band at 570 cm^{-1} , which is assigned to cobalt-oxygen (Co-O), and around 660 cm^{-1} was allocated to the linking vibration of cobalt-oxygen-cobalt (Co-O-Co) [51]. The peaks around 980 cm^{-1} can be attributed to chromyl (Cr=O) vibrations [52], the wide absorption band in the. The range between 700 and 600 cm^{-1} is attributed to the nickel-oxygen (Ni-O) stretch vibration [53]. The zinc oxide group, or zinc-oxygen (Zn-O) vibration band, is located at a wavenumber of approximately 580 cm^{-1} [52]. The iron-oxygen (Fe-O) band vibration can be recognised at a low wavenumber of roughly 500 cm^{-1} [53].

Fig.3 shows XRD patterns of the prepared HEO catalyst. As seen, the pattern reflects the complete incorporation of these five components into a supersaturated solid solution at the selected calcination temperatures (600, 650, and 700 °C). The specific peaks are detected at two θ angles of around 35.6° and 62.2°, relating to the (111) and (220) planes, respectively, indicating the production of cubic cobalt oxide [54]. The peak around 35.64 is attributed to cobalt oxide of face-centred cubic (FCC) structure [55], while the peak at 62.02 ° is indexed (220) perfectly to the face-centred cubic FCC crystal. It can be attributed to the nickel oxide present [52]. In contrast, the sharp peaks at 36.74 and 53.76° correspond to the crystal planes for (110) and (116), respectively, which are attributed to the presence of Cr₂O₃. They have a hexagonal structure, which agrees with the findings of W. G. Adnan et al. [56]. The results reveal that thermal treatment is necessary for the formation of high-entropy metal oxides [57], while the broad peak at approximately 31.3° is characteristic of the zinc oxide (ZnO) structure [42], [58].

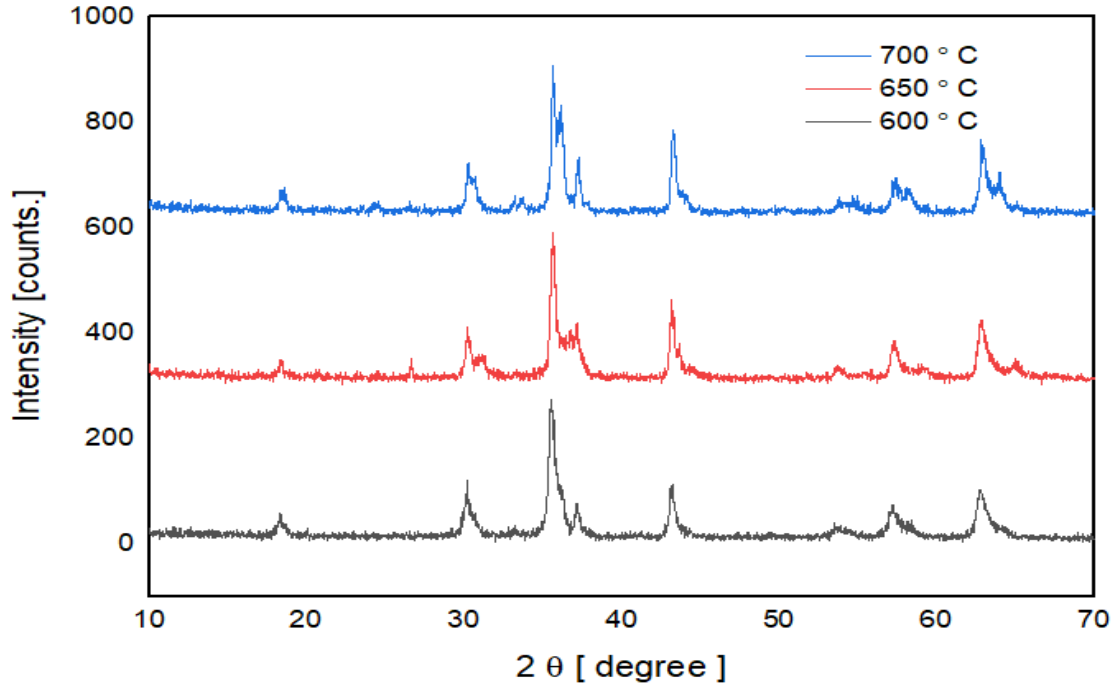


Figure 3- XRD pattern for the HEO catalyst.

The average crystallite size (d_p) of the prepared catalyst particles was estimated from the XRD pattern by applying the famous Scherrer formula given below [59] :

$$d_p = \frac{\kappa \lambda}{\beta \cos(\theta)} \quad (5)$$

Where (λ) is the radiation wavelength of the Cu target ($0.1518 \text{ \AA}$), (κ) is the equipment constant, β (FWHM) is the full width at half maximum, and (θ) is the Bragg's angle of diffraction. The crystallite size depends on various parameters such as peak widening, intensity, dislocation density (δ), sharpness, and material strain (ϵ) [60]. The dislocation density (δ) is defined as the number of dislocation lines per

unit volume, or it refers to defects inside a crystal. The dislocation density is estimated by [61]:

$$\text{dislocation density } (\delta) = \frac{1}{d_p^2} \quad (6)$$

The low value for dislocation density indicates that the materials produced have a high degree of crystallinity (good crystallinity) [58 - 59]. The strain (ϵ) of the films is estimated using the equation [61] :

$$\text{strain } (\epsilon) = \frac{\beta}{4 \cos(\theta)} \quad (7)$$

Table 2 presents the calculated values for crystal size using the Scherrer formula. As seen, the average crystallite size is 5.17 nm, while the 5th, and 6th columns show the dislocation density (δ) and strain (ϵ) respectively.

Table 2. The structural parameters for the prepared HEO catalyst

$2\theta (^{\circ})$	FWHM	d(Å)	Crystal size dp (nm)	Dislocation density (δ) nm ²	strain (ϵ) ×10 ⁻³
18,34	0,252	4,8326	5,80	2,92	60,97
30,22	0,317	2,9048	5,40	3,37	60,00
31,32	0,536	2,8041	2,67	14,08	133,80
35,64	0,441	2,0171	2,01	10,84	141,99
36,74	0,474	2,4441	4,73	4,48	70,48
37,16	0,601	2,4177	7,02	2,03	50,79

43,16	0,303	2,0942	4,41	0,14	80,90
43,64	0,383	2,0723	3,78	7,00	94,30
03,76	0,431	1,7036	18,86	0,28	18,92
07,28	0,463	1,6071	3,30	9,18	108,10
62,86	0,038	1,4772	6,26	2,00	06,90
60,02	0,321	1,4333	1,00	41,00	229,81

The structure and morphology of the surface HEO catalyst were examined by SEM (FEI model QUANTA 450). At the same time, the elemental analysis was done using energy-dispersive spectrometry (EDS) (BRUKER model X Flash 6110) as displayed in **Fig.4**. The SEM images proved that the particles of the prepared catalyst have sizes ranging from nanoparticles to semi-microns with many shapes, including polyhedral, cubic, semi-spherical, and irregular. Some particles have sharp edges with high crystallinity, especially zinc and chromium oxides. The chromium and zinc oxide particles, such as nanoporous grids with narrowing ends, appear to be broadly agglomerated [59]. As seen, the polyhedral particles are not uniform in size; however, it is clear that these polyhedral particles have distinct corners and edges with varying numbers of faces. It can be observed that the catalyst surface features a multi-height stepped surface; these steps are capable of generating active sites, thereby enhancing the catalyst's activity. The SEM analysis also reveals that the catalyst surface displays particle aggregation, regardless of their shape (cubic, semi-spherical, polyhedral, etc.), which is observed in the structure. The aggregated particles are a significant

conformation for metal oxides. The elemental mapping of the prepared catalyst was defined using EDS. The EDS spectra are illustrated in **Fig. 5**. As noted, the figure presents EDS measurements for the five elements, including oxygen, which provides strong evidence of metal oxide formation. It can be recognised that the presence of metals (iron, zinc, nickel, cobalt, and chromium) is used for catalyst synthesis. Still, the weight percentage differs from that planned, indicating the occurrence of undesirable agglomeration somewhere on the catalyst surface, as is evident in the SEM image. Hence, these results confirm the successful deposition of metal onto the catalyst surface. The simple inequality between observed findings and predetermined values was attributed to the fact that the observed results reflect the composition of the prepared catalyst surface, where the oxidation of the surface, contamination, and adsorption of other elements may contribute to this disparity.

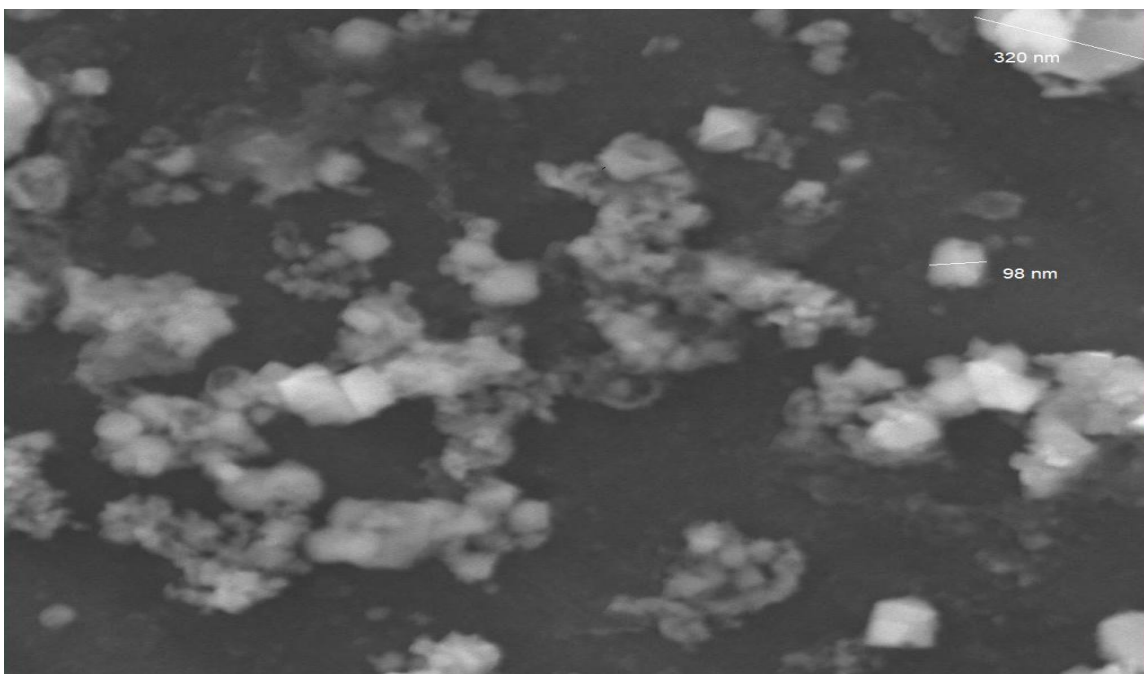


Figure 4- SEM images of the prepared HEO catalyst

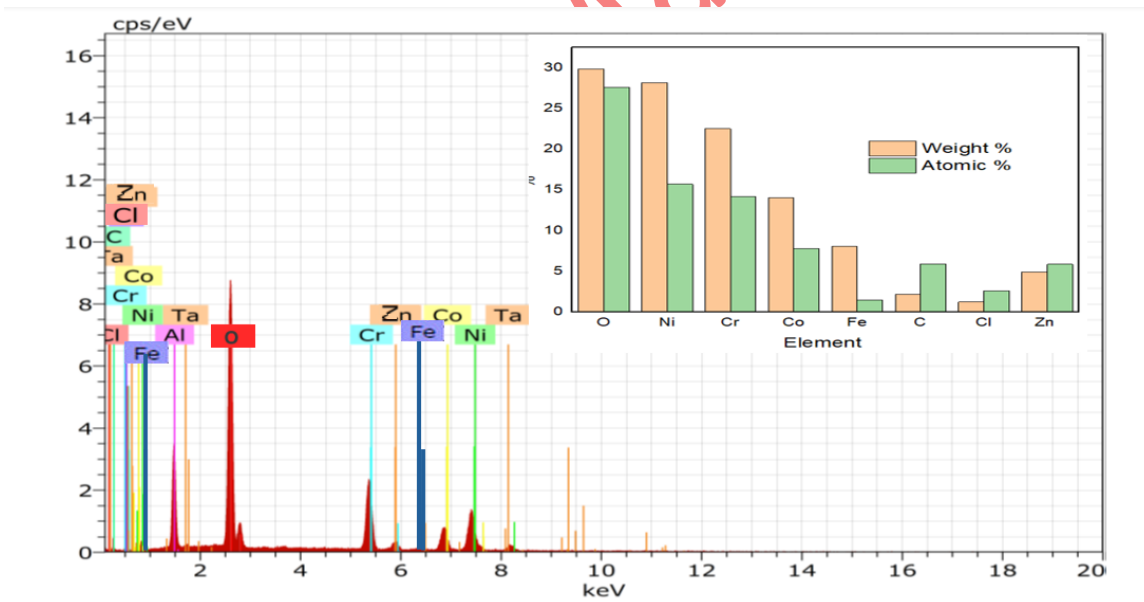


Figure 5- EDS results for the HEO catalyst showing the elemental mapping.

The surface area and pore volume of the synthesised HEO catalyst were obtained through BET surface area analysis. The adsorption and desorption of

nitrogen gas by the HEO catalyst resulted in a type IV isotherm, as shown in **Fig. 6**, **indicating** the mesoporous nature of the HEO catalyst. The obtained texture properties, as determined by BET analysis, include surface area, pore size, and pore volume, which are 33.06 m²/g, 8.515 nm, and 0.07 cm³/g, respectively. A similar examination is conducted for synthesising a hollow Lamellar HEO for the aerobic oxidation of benzyl alcohol. The BET analysis revealed that the BET pore volume and surface area of the holey lamellar HEO catalyst were 0.106 cm³/g and 42 m²/g [40].

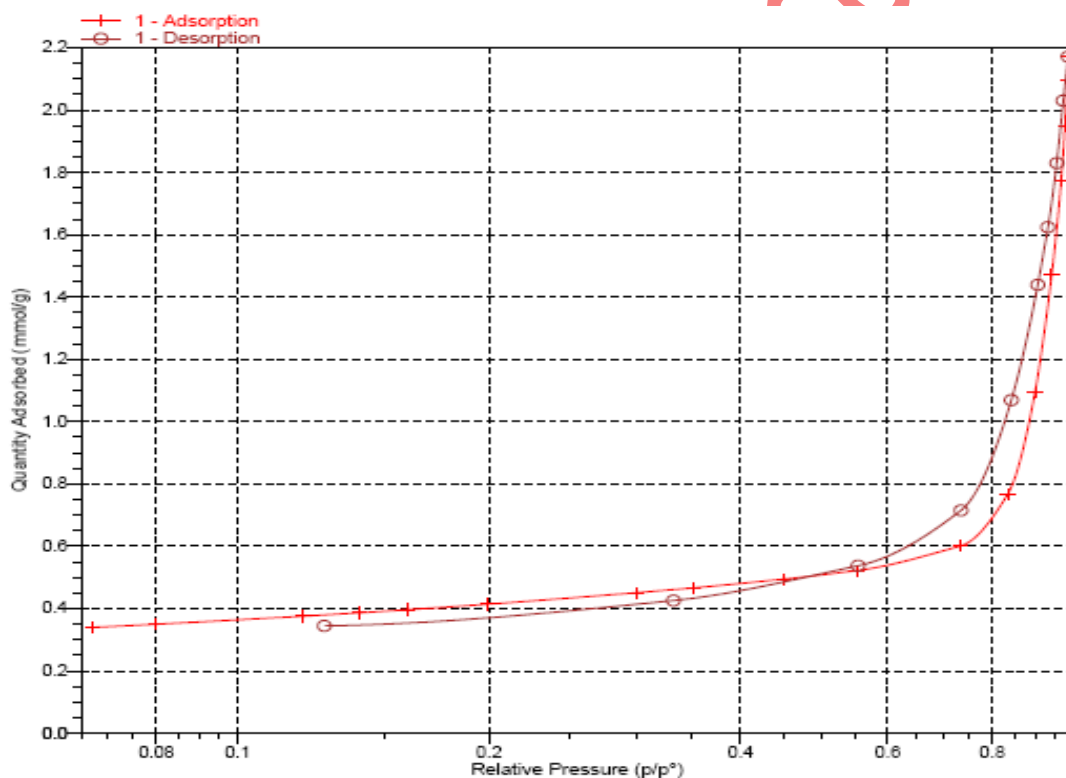


Figure 6: N₂ adsorption–desorption isotherms of synthesised HEO catalyst.

4.2. Performance of catalytic ODS reaction

An experimental design technique was employed to investigate the impact of the studied parameters (catalyst dosage, temperature, and time) on removal efficiency and to optimise the operating conditions. BBD was used here from the available RSM techniques. The application of BBD involved the lowest number of experiments for investigating the impact of each independent variable, which was measured at three levels: low, medium, and high (in terms of coded values -1, 0, and 1). The number of required experiments for applying BBD is:

$$N = 2k(k - 1) + r \quad (8)$$

Where N is the number of runs, k is the number of studied variables, and r is the number of replicates of central points, thus the minimum number of runs is 15 for three replicated runs. The ranges for the chosen variables studied are listed in Table 3. In contrast, Table 4 presents the matrices for BBD in optimising the ODS reaction, examining the impact of catalyst amount (dosage), temperature, and oxidation time on removal efficiency.

Table 3: Experimental design levels of chosen variables studied.

Variables (unit)	Symbol in BBD	levels		
		-1	0	1
Catalyst dosage (g)	x_1	0.5	0.75	1.0
Reaction Temperature (°C)	x_2	100	170	200
Oxidation time (minutes)	x_3	30	40	60

Table 4: Experimental design matrix generated by applying BBD, and experimental responses with real values for the operating conditions for all runs

Run	Coded value			Real value			R%
	Factor 1 x_1 catalyst dosage)	Factor 2 x_2 (reaction Temperature)	Factor 3 x_3 (oxidation time)	Factor 1 x_1 catalyst dosage)	Factor 2 x_2 (reaction Temperature)	Factor 3 x_3 (oxidation time)	
1	-1	-1	0	0,5	100	40	71
2	1	-1	0	1	100	40	77
3	-1	1	0	0,5	200	40	82
4	1	1	0	1	200	40	79
5	-1	0	-1	0,5	170	30	58
6	1	0	-1	1	170	30	68
7	-1	0	1	0,5	170	60	84
8	1	0	1	1	170	60	80
9	0	-1	-1	0,75	100	30	62
10	0	1	-1	0,75	200	30	73
11	0	-1	1	0,75	100	60	76
12	0	1	1	0,75	200	60	99
13	0	0	0	0,75	170	40	70
14	0	0	0	0,75	170	40	71

The RSM can be used to predict a statistical second-order polynomial correlation between the dependent response (sulfur removal efficiency) and the studied variables as follows [64] :

$$R\% = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j + \varepsilon \quad (9)$$

According to the observed experimental results that are listed in Table 2, the equation illustrates the mathematical relationship as follows:

$$R\% = 133 + 90.9x_1 + 1.01x_2 - 0.07x_3 - 22.8x_1^2 + 0.0039x_2^2 + 0.0004x_3^2 + 0.003x_1x_2 - 0.92x_1x_3 + 0.0078x_2x_3 \quad (10)$$

R% is the sulfur-removing efficiency. X₁, B, and C represent catalyst amount, temperature, and oxidation time, respectively. The predicted model has a high correlation factor (R² = 97.01%) and an adjusted R² (adj. R² = 88.03%). The high R² value indicates that the model performs strongly in relation to the experimental data. The adjusted R² gives a more accurate assessment of the model's performance. R² measures how well the model's predicted sulfur removal matches the actual efficiency. These values indicate that the model explains a significant portion of the variance in desulfurization efficiency. This reflects accuracy and robustness in capturing relationships between the studied variables and the response. The similar R² and adjusted R² values further support the reliability of the model, showing that it explains data complexity without overfitting [65]. The optimum ranges for the

variables—catalyst dosage, reaction temperature, and oxidation time—are 0.59 g, 200°C, and 60 minutes, respectively. This results in an optimum sulfur removal efficiency (98%) as shown in **Fig.7**.

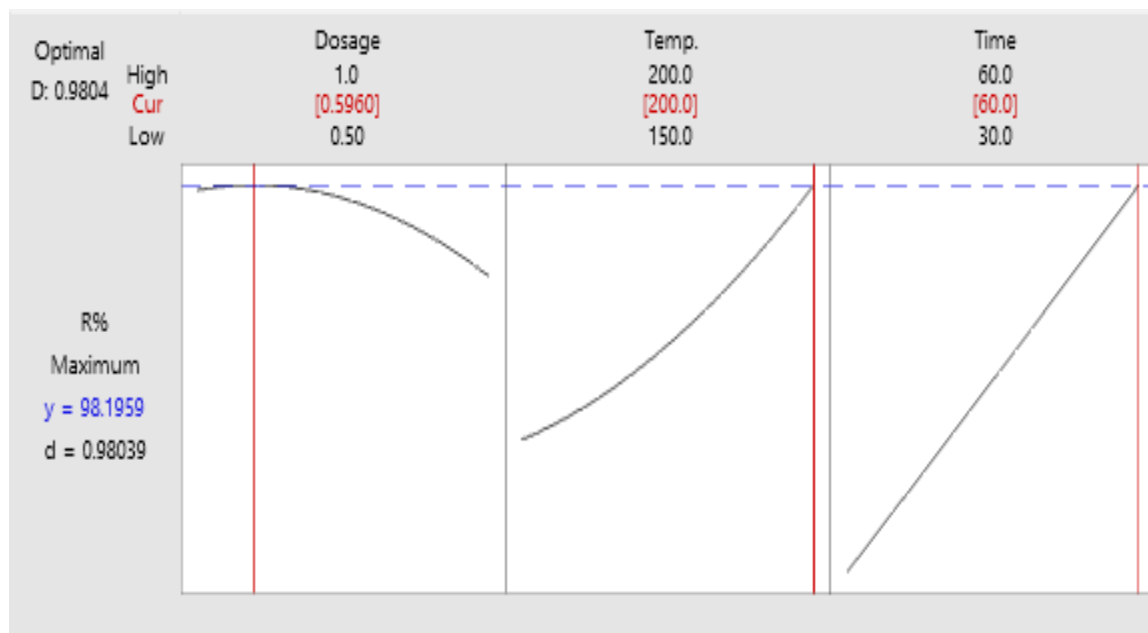


Figure 7- The optimum removal efficiency is 98% at 0.59 g, 200 °C, and 60 minutes for catalyst amount, reaction temperature, and oxidation time, respectively, according to BBD analysis.

The analysis of variance ANOVA results of sulfur removal efficiency are presented in Table 5. According to the ANOVA investigation, the model is accepted based on the F-test (F-value), with an F-value of 10.81, which is greater than the tabulated value ($F_{9,5, 0.05} = 4.77$). The oxidation reaction time has the most significant effect on sulfur removal efficiency, followed by temperature and catalyst amount, as specified by their F-values of 57.47, 29.5, and 0.02, respectively (see Fig. 8).

Table 5: ANOVA results for the second-order polynomial model for sulfur removal efficiency.

Source	Df	Adj SS	Adj MS	F-Value	P-Value
Model	9	1291,04	143,000	10,81	0,038
Linear	3	1104,9	368,960	29	0,01
Dosage	1	0,24	0,236	0,02	0,902
Temp.	1	391,67	391,667	29,0	0,012
Time	1	762,99	762,993	57,47	0,000
Square	3	03,44	1,148	1,34	0,407
Dosage*Dosage	1	16,37	16,374	1,23	0,348
Temp.*Temp.	1	14,10	14,104	1,07	0,378
Time*Time	1	0,02	0,016	0	0,974
2-Way Interaction	3	83,2	27,730	2,09	0,28
Dosage*Temp.	1	0,43	0,433	0,03	0,868
Dosage*Time	1	47,98	47,983	3,61	0,103
Temp.*Time	1	34,79	34,788	2,62	0,204
Error	3	39,83	13,277		
Total	12	1331,37			

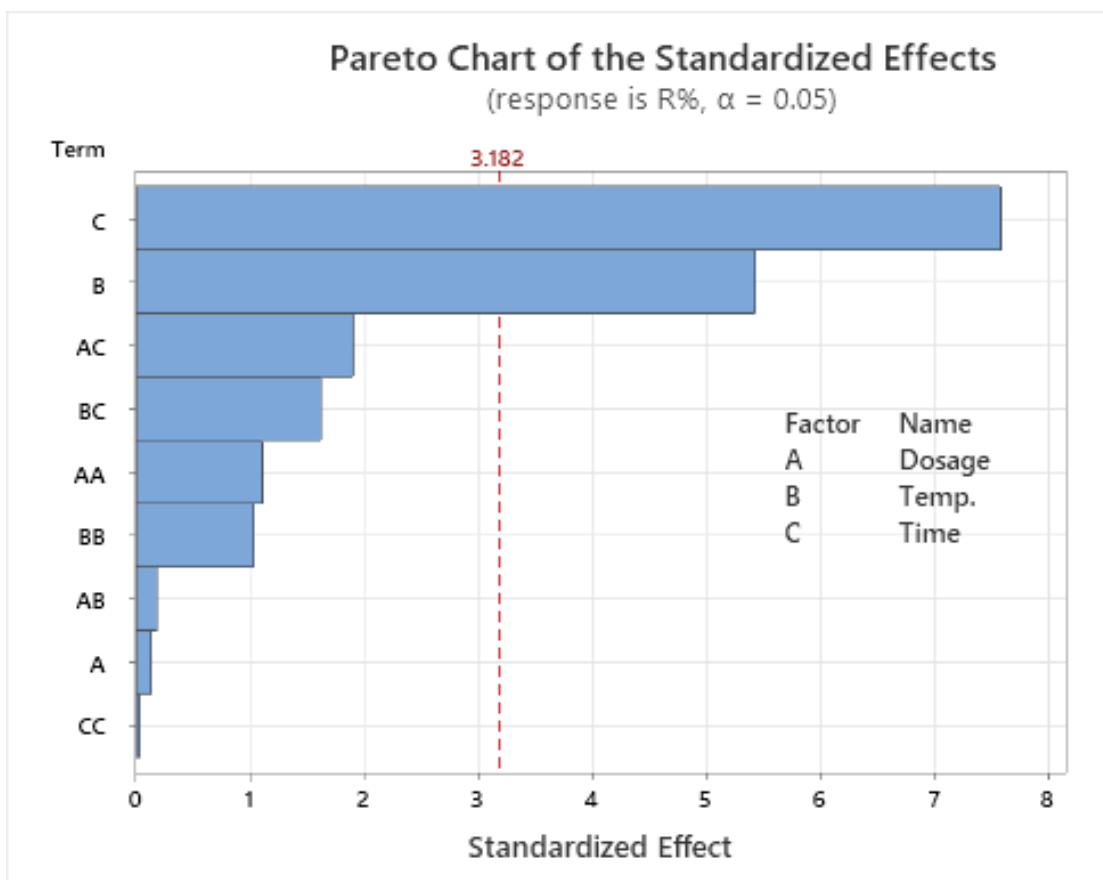


Figure 8- Main effect of studied variables on sulfur removal efficiency by ODS reaction shown by Pareto chart.

4.3. Evaluation of ODS reaction performance

The prepared catalyst activity toward sulfur removal from gas oil by ODS reaction is examined at three operating variables [catalyst dosage (amount), temperature, and oxidation time] as an attempt to clarify the impact of these parameters on sulfur removal, in which the effect of the studied variables on sulfur removal individually was illustrated in **Fig. 9**; the sulfur removal increased with temperature and oxidation reaction time. By the way, the temperature range used

(150-200 °C) needs more investigation because, in this temperature range, ozone decomposes, in which O_3 rapidly breaks down into oxygen and highly reactive atomic oxygen (O), but in the presence of a catalyst, ozone can still serve as a primary oxidant agent with short residence time or strong ozone adsorbed by the catalyst; finally, these will lower the activation energy [66]. At the same time, a decrease was observed as the catalyst dosage increased. As seen, the increase in catalyst amount cause increasing in sulfur removal, and this may be attributed to the abundance of active sites, which provide a good opportunity to reaction to take place [67], the rising in sulfur removal is not continuous with increasing the amount of catalyst, in which the sulfur removal value starts to decrease after it reaches the maximum value, and this may be because of the occurrence of agglomeration between particles via increasing the catalyst amount, which minimizes active sites on the catalyst surface [36, 63 - 64]. The obtained findings confirmed that removal efficiency improved with temperature, indicating that temperature is a significant parameter for enhancing ODS process performance. The increasing of sulfur removal with reaction temperature can be attributed to the raising in temperature is significantly effect on the rate of reaction, as in the Arrhenius equation, and this will enhance the sulfur removal efficiency. From another view, raising the reaction temperature leads raising the number of reactant molecules which having sufficient activation energy so this will improve the oxidation reaction between the reactants [19]. The rising reaction temperature causes an increase in the homogeneity between reactant species. It enhances the dispersion of reactants, allowing them to easily interact with the active

sites within the pores [65]. Furthermore, it influences the density of acid sites within the catalyst structure—a factor dependent on temperature—which ultimately affects the catalyst's properties and enhances the efficiency of the oxidative desulfurization process [63].

The results remarkably confirmed that sulfur removing efficiency is increasing with the reaction time because the increasing reaction time means increasing the contact between reactants species (OSCs in gas oil and ozone) via high interaction between the reactants species and improves sulfur removal, where the ODS reaction needs enough time like any other reaction to increase the conversion and boost the oxidation reaction which expanding the opportunity to reaction to happen, and this is agreed with Mohammed et al. [70] Jarullah et al. [66] noted that, for prolonged reaction times, sulfur removal may decrease due to the depletion of contributing OSCs over time and reach an equilibrium state[71].

Employing RSM analysis can create 2-dimensional contour charts for investigating the interactive effect of each pair of factors on sulfur removal, while keeping the other factor constant. This enables the determination of the impact of catalyst amount, temperature, and reaction time on sulfur removal. **Fig. 10** illustrates the interaction between the operating factors and the dependent response of sulfur removal. As shown, a strong interaction is observed, with a significant deviation between nonparallel curves. The impact of catalyst amount on the other parameters (reaction time and temperature) minimises their trend within the studied range, as

catalyst dosage decreases sulfur removal. In contrast, time and temperature increase it [72] .

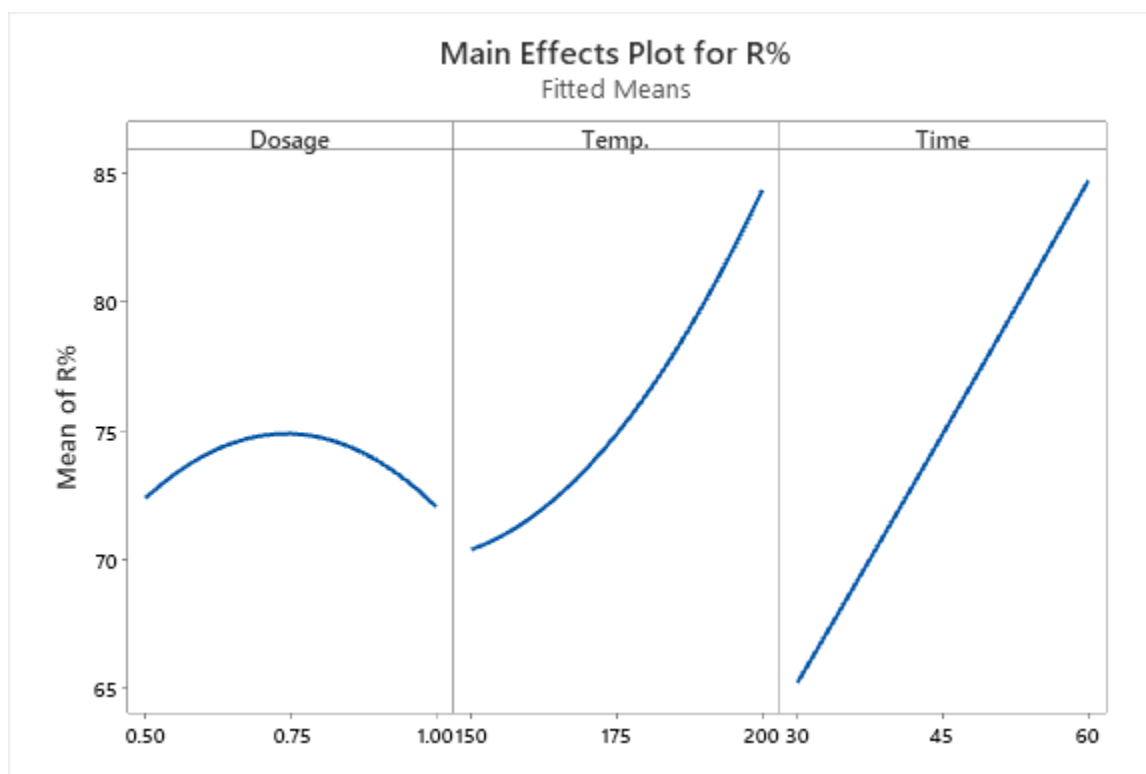


Figure 9- The effect of the studied variables individually on sulfur removal efficiency.

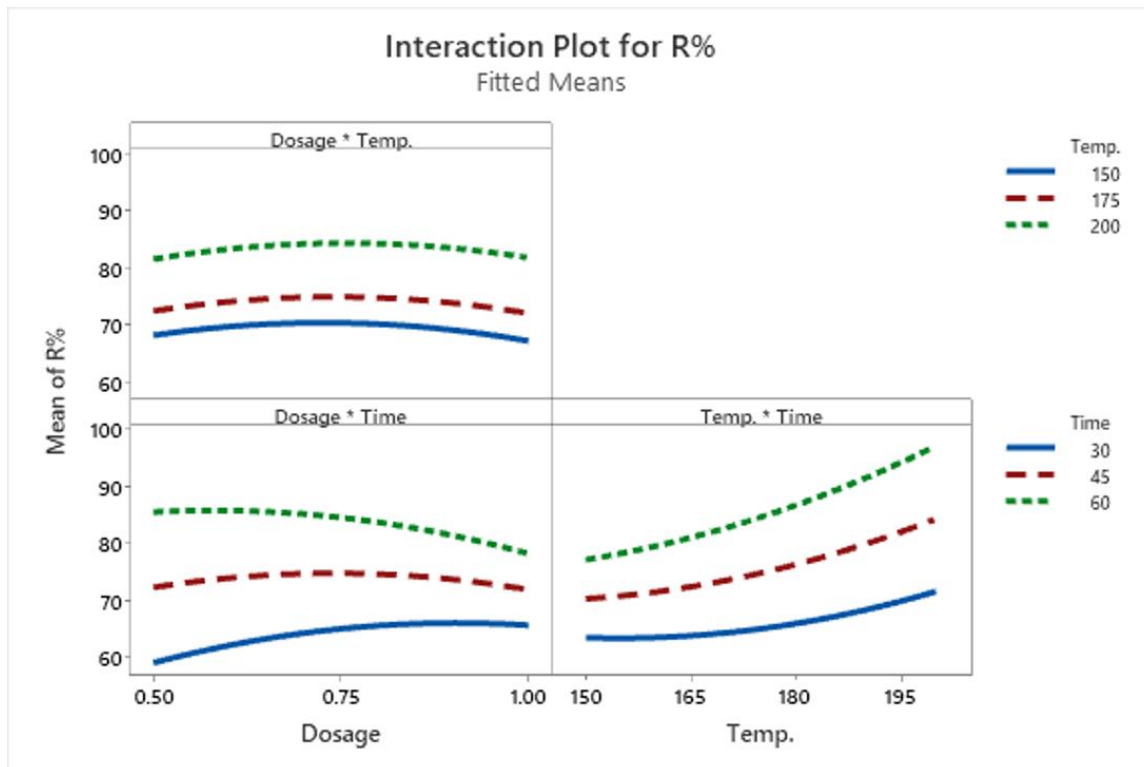


Figure 10- Interaction effect between the operating factors on sulfur removal efficiency.

The mutual influence of the operating parameters on the ODS reaction was examined as follows: **Fig. 11** shows the interactive effect of temperature and reaction time on sulfur removal, where both have an explicit impact on sulfur removal. At 30 minutes, the removal efficiency increased from 60% to approximately 73% at temperatures ranging from 150 - 200 °C. At 60 minutes, the removal efficiency increased approximately from 75% to 93%. As shown, the maximum sulfur removal efficiency is displayed in the upper-right location (violet area), where the removal efficiency increases with increasing time and temperature, as declared above [51],

[55], [73]. The interaction impact of catalyst amount with reaction temperature (Fig.12), and the interaction effect of catalyst dosage with reaction time (Fig.13), as seen from the effect of the catalyst amount, is clearly obvious, even though temperature and time have an encouraging effect on the removal efficiency, in which the efficiency is in the area of 80 – 90% (not more than 90%), and this is because of the fact, as declared above, that the dosage of the catalyst has an effect in reducing the sulfur removal efficiency.

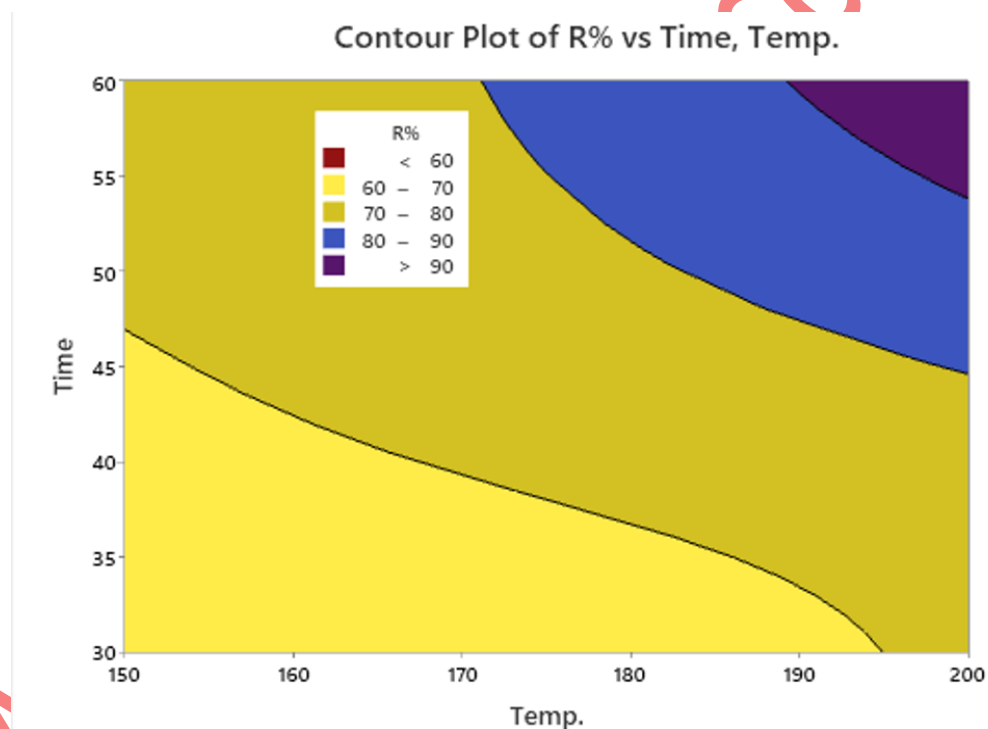


Figure 11: Contour plot showing the interaction effect of reaction temperature and oxidation time on sulfur removal efficiency, while catalyst dosage was kept constant at 0.75 g.

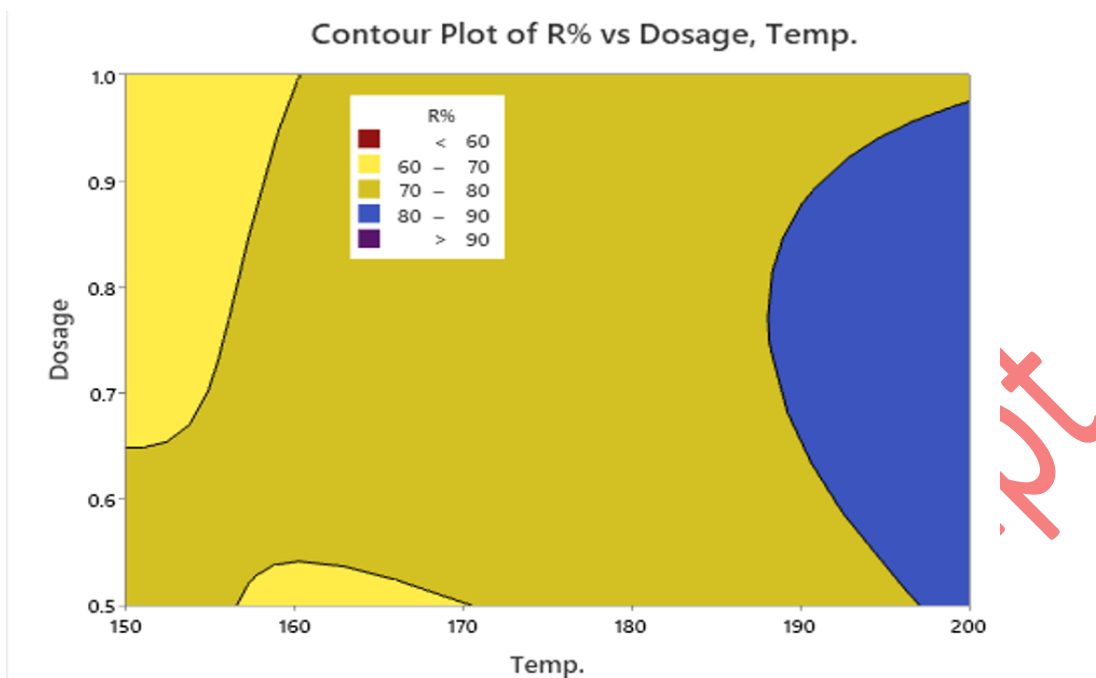


Figure 12- contour plot showing the interaction effect of catalyst dosage with reaction temperature on sulfur removal efficiency, while oxidation time was kept constant at 45 minutes.

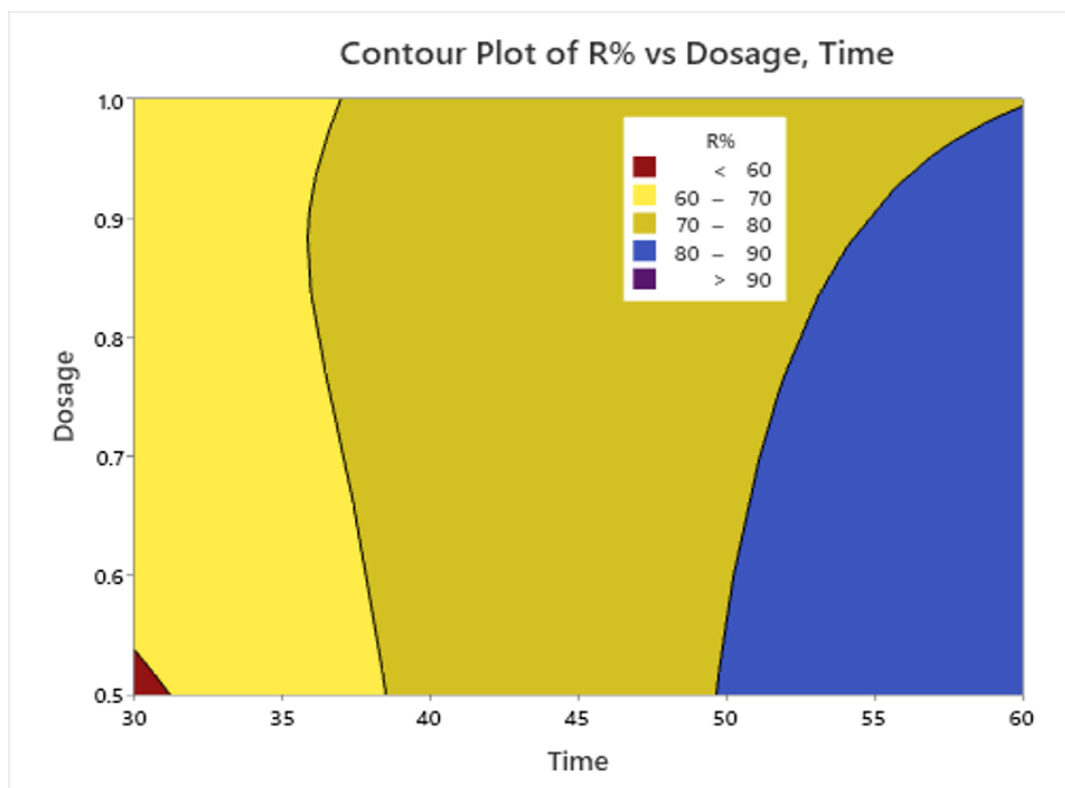


Figure 13- contour plot showing the interaction effect of catalyst dosage and oxidation time on sulfur removal efficiency, while reaction temperature was kept constant at 175 °C.

4.4. Reaction Kinetics and Thermodynamics for ODS reaction calculations

The kinetics study is used to investigate reaction behaviour and determine the reaction time. The kinetics models most widely used are the pseudo-first- and second-order models [74]. For the present work, we assume the OSCs associated with gas oil are DBT, in which the DBT removal by O₃ as follows:

$$-r_{DBT} = \frac{d[DBT]}{dt} = k[C_{DBT}]^n[C_{O_3}]^m \quad (11)$$

Where n and m are the reaction orders with respect to DBT and ozone concentrations, respectively. The solution for the above equation for the pseudo 1st order equation is:

$$-r_{DBT} = \frac{d[DBT]}{dt} = k[C_{DBT}][C_{O_3}] \quad (12)$$

By assuming the ozone amount is in excess, so we can neglect the change in ozone concentration in comparison with the changing in DBT concentration, and the equation will become as follows:

$$\frac{d[C_{DBT}]}{dt} = k[C_{DBT}] \text{ where } k = k[C_{O_3}] \quad (13)$$

The integration of the equation yields the corresponding pseudo-first-order equation.

$$\ln \frac{[C_{DBT}]_0}{[C_{DBT}]_t} = kt \quad (14)$$

Where $[C_{DBT}]_t$ and $[C_{DBT}]_0$ are the final and initial concentration of DBT at final , respectively. By converting equation (14) in terms of conversion (X_A) of DBT :

$$\ln \left(\frac{1}{1 - X_{DBT}} \right) = kt \quad (15)$$

$$\text{Where } X_X = 1 - \frac{[C_{DBT}]_t}{[C_{DBT}]_0} = \frac{[C_{DBT}]_0 - [C_{DBT}]_t}{[C_{DBT}]_0}$$

The solution for pseudo second order is given as:

$$\frac{1}{[C_{DBT}]_t} = \frac{1}{[C_{DBT}]_0} + kt \quad (16)$$

A straight line with high correlation factor slope to unit was gain when plotting $(1/(1-X_{DBT}))$ versus time, as seen in **Fig.14**; therefore, the experimental data well fit the pseudo first order model.

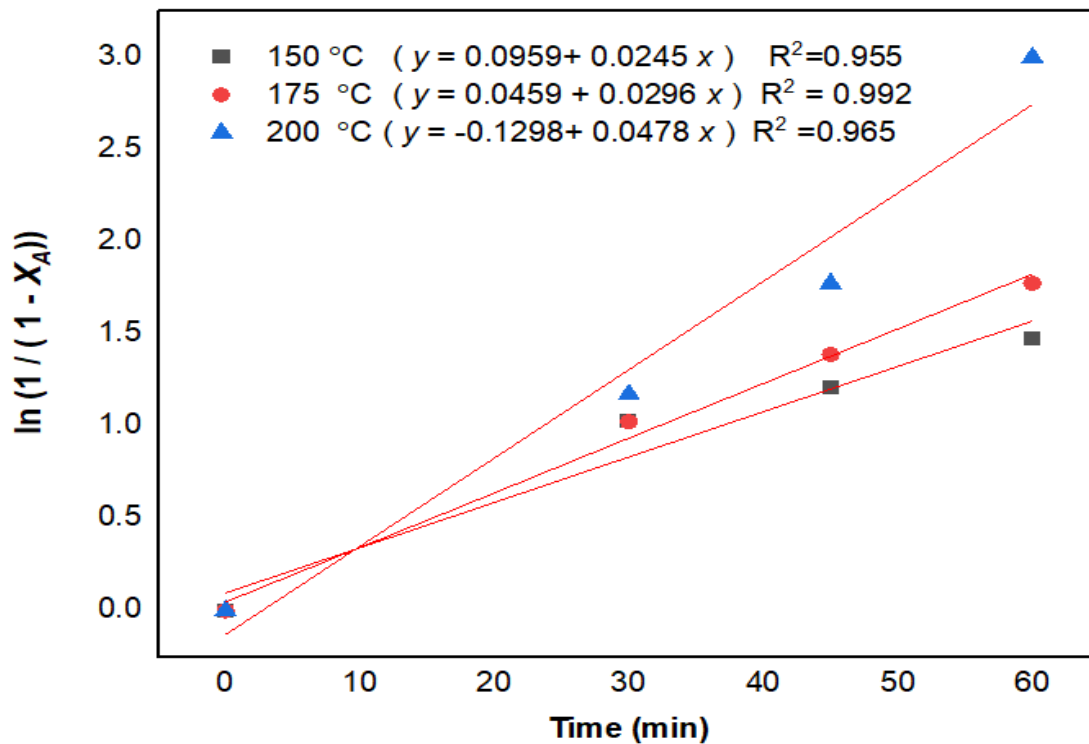


Figure 14- The model of reaction kinetics study by plotting $\ln (1 / (1-X_A))$ vs. time for a pseudo-first-order reaction.

The results analysis according to the Arrhenius equation:

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \quad (17)$$

Where E_a is reaction activation energy (kJ/mol), T is temperature (K), and k_0 is pre-exponential factor (min^{-1}). By linearize equation (17) we get the following:

$$\ln k = \ln k_0 - \frac{E_a}{RT} \quad (18)$$

The plotting of $\ln(k)$ against $1/T$ supposedly yields a straight line, as shown in Fig. 15. The activation energy and pre-exponential factor are estimated by aim of the straight line slope and intercept. They are estimated activation energy and preexponential factors are 22.033 kJ/mol and 12.24 min^{-1} , respectively. The presence of catalyst in the reaction reduces the activation energy for the reaction, making it relatively low [75]. For comparison, the value of the activation energy. Table 6 lists some estimated quantities of activation energy in previous literature, as shown in the Table 6.

Table -6: Activation energy for dibenzothiophene for various catalysts /H₂O₂

Catalyst	Fuel	Activation energy kJ /mol	References
H ₃ PW ₁₂ O ₄₀	Model fuel	40,9	[76]
H ₃ PMo ₁₂ O ₄₀	Model fuel	29,0	[76]
H ₃ SiW ₁₂ O ₄₀	Model fuel	28,3	[76]
HPW/aEVM	Model fuel	30,3	[77]
Fe ₂ O ₃ /Graphene	Gas oil	36,26	[31]
NiFe ₂ O ₄ -PEG	Model fuel	35,86	[78]
Cu/titanium silicate-1	Model fuel	28,67	[79]
MoO ₃ /Carbon nanotube	Model fuel	12,99	[32]

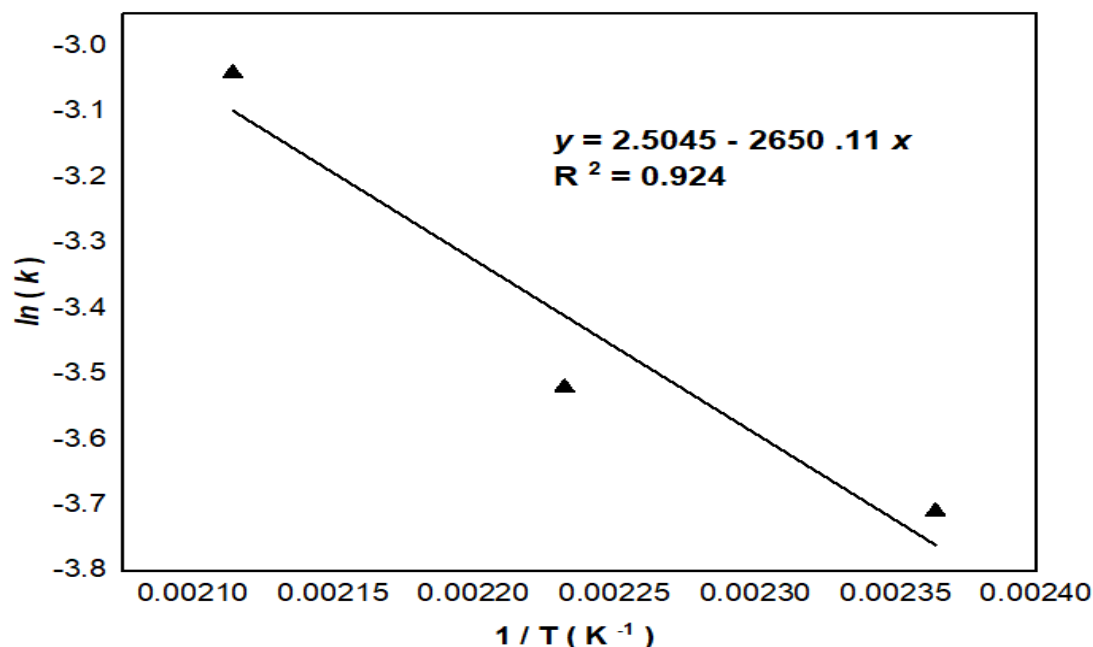


Figure 15- The effect of reaction temperature on reaction rate constant according to the Arrhenius formula.

Thermodynamic parameters were evaluated to determine if complex formation occurred during the reaction; therefore, the Eyring equation was used to obtain thermodynamic parameters for the ODS reaction [78].

$$\ln \frac{k}{T} = -\frac{\Delta H}{RT} + \frac{k_B}{h} + \frac{\Delta S}{R} \quad (19)$$

Where k_B and h are Boltzmann and Planck constants respectively, in which $k_B = 1.3807 \times 10^{-23}$ J/K, and $h = 6.626 \times 10^{-34}$ J.S. A straight line could be obtained when plotting $(\Delta H / RT)$ versus $\ln(k/T)$. The entropy change (ΔS) was determined from

the straight-line intercept, while the enthalpy change (ΔH), and Gibbs free energy change (ΔG) were estimated as follow:

$$\Delta H = E_a - RT \quad (20)$$

$$\Delta G = \Delta H - T\Delta S \quad (21)$$

As observed in **Fig. 16**, the high correlation factor for the plotted straight line ($R^2=0.9997$) was obtained; the intercept = -6.348, therefore, the ΔS is -52.776 (J/mol. K). The Arrhenius and thermodynamic parameters of the ODS at different temperatures are summarised in Table 7.

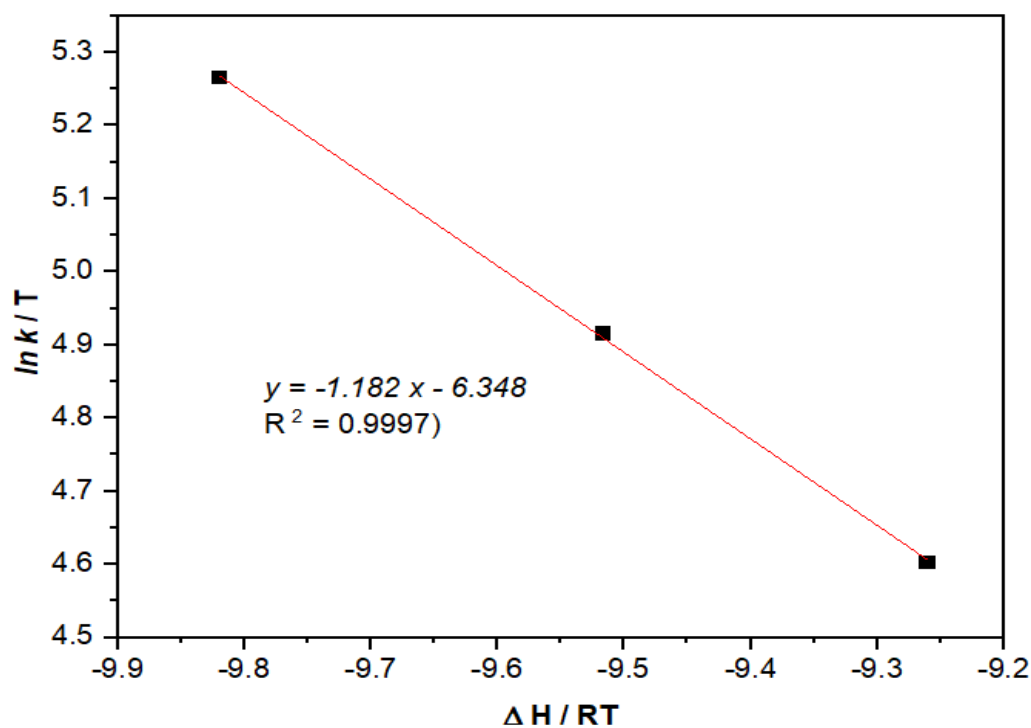


Figure 16- Typical plot used for the estimation of activation entropy for the reaction.

Table 7: Thermodynamic Parameters for ODS reaction

Temperature (K)	k (Arrhenius constant)	ΔH (kJ /mol)	ΔS (J /mol. K)	ΔG (kJ /mol)
323	0.023	18.016	-52.776	30.840
348	0.033	18.308	-52.776	31.902
373	0.040	18.100	-52.776	32.063

The reaction rate constant (k) increases with temperature; the positive Gibbs free energy (ΔG) implies that the ODS reaction is non-spontaneous. Still, the rising ΔG value with temperature means that temperature is improving the reaction. In contrast, a positive value for enthalpy change refers to an endothermic reaction, and a negative entropy change indicates a decrease in randomness or a reduction in stochasticity[78].

4.9. Possible ODS mechanism of the catalyst P-HEO

Ozone (O_3) is described as a very strong oxidant [27], Hanlu Wang et al proposed the mechanism for reaction BT with Ozone included two paths as follows: the first path is formation of the complex ($C_8H_6S-O(I)-O_2$) because of convergence between BT (C_8H_6S) and ozone molecules in which this happened endothermically (6.6 kJ/mol), this complex is overcome energy barrier of (15.2 kJ/mol) where the oxygen atom (I) was attacking sulfur atom to produce a transition state ($C_8H_6S=O(I)-O-O$), finally an exothermic step occurred by broken the (O(I)

-- O-O) bond to result a sulfoxide (C₈H₆SO) and oxygen molecule. There is another ozone molecule that was close to the C₈H₆SO molecule produced to form C₈H₆SO -- O- O-O endothermically, followed by desorption of O₂ to create the final product corresponding to the sulfone C₈H₆SO₂. This mechanism is suggested according to the energy bond length between different atoms. At the same time, the second path is more satisfactory both thermodynamically and kinetically, in which ozone molecules attack unsaturated bonds at the BT ring structure via the Criegee mechanism, in which ozone cleaves the alkene double bond and forms a primary ozonide, and it decomposes into a carbonyl compound and carbonyl oxide [80]. Cunhua Ma et al. [81]. The same mechanism is reported, depending on the IR spectra analysis of ozonation of BT, they proposed that the disappearance the stretching vibration C-S bond presence in BT and appearing stretching vibration bond for O=S=O at wavelength 1283, and 1117 cm⁻¹ and a peak for S=O at 1073⁻¹ and this is a good indication for oxidation of BT to BTO and/or BTO₂.

It can be concluded that, in the presence of the HEO catalyst, the reaction mechanism is summarised as shown in Fig. 17. The catalyst surface adsorbs and transfers more ozone, which can be considered a significant activity sponsor for HEO in the ODS reaction. The ozone decomposes under the effect of heat to produce oxygen molecules and radical oxygen as follows [29]:



The composition of the HEO catalyst consists of multiple metals, so its surface is characterised by high electronegativity [91], which contributes to the synergistic activation of ozone with heat to form radical oxygen that attacks the sulfur atom, forming a sulfoxide after releasing an oxygen molecule. The availability of ozone caused more attack on the sulfur atom to produce an intermediate component that can eject O_2 to form the corresponding sulfone $C_8H_6SO_2$ (DBTO₂).

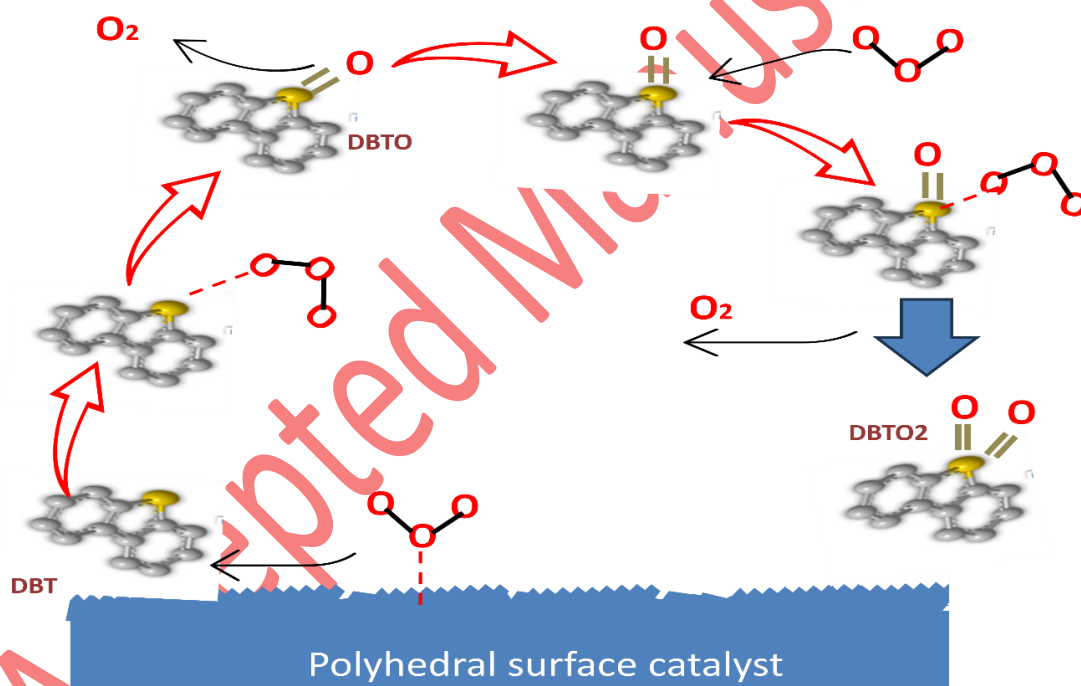


Figure 17- proposed mechanism for ODS reaction at HEO catalyst.

9. Conclusion

The oxidative desulfurisation (ODS) of Iraqi gasoil employing a new high-entropy oxides (HEO) catalyst prepared by mechanochemical mixing of nickel,

chromium, cobalt, titanium, and iron chlorides in a scale reactor. The oxidation reaction is achieved using ozone as the oxidant agent, with catalyst amount, temperature, and oxidation time serving as operational parameters under various operating conditions. The experimental findings have shown that removal efficiency is significantly improved by increasing temperature and oxidation time, while it decreases with increasing catalyst dosage. The optimal removal efficiency was 98% at 0.59 g, 200 °C, and 60 min for catalyst amount, reaction temperature, and oxidation time, respectively. The kinetics and thermodynamics calculations indicate that the ODS reaction follows pseudo-first-order kinetics. The reaction is non-spontaneous and endothermic, where the temperature increases both the reaction rate constant and the Gibbs Free energy. The activation energy is relatively low (22.033 kJ/mol) due to the presence of the catalyst.

Nomenclature

ΔG	Gibbs free energy
ΔH	Change in Enthalpy
ΔS	change in entropy
$d[DBT]$	Change in DBT concentration
dp	Average crystal size
dt	Change in time
E_a	Activation energy
h	Planck constant
k	number of variables
k	Reaction rate constant

k_B	Boltzmann constant
N	Number of experiments
r	replicate the number of central points
R%	Sulfur removal efficiency
$-r_{DBT}$	Rate of reaction
Si	Initial sulfur content
So	Final sulfur content
t	time
T	Temperature (K)
x_1	Catalyst dosage (g)
x_2	Reaction Temperature (°C)
x_3	Oxidation time (minutes)
X_A	Reaction conversion
β	FWHM is the full-width half-maximum
β_0	intercept coefficient
β_i	linear effect coefficient
β_{ii}	squared effect coefficient
β_{ij}	the interaction effect coefficient
δ	dislocation density
ε	materials strain
θ	angle of diffraction
κ	equipment constant
λ	radiation wavelength

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References

- [1] P. Zuo, Y. Liu, J. Jiao, J. Ren, R. Wang, and W. Jiao, "Ultrafine W₂C well-dispersed on N-doped graphene: Extraordinary catalyst for ultrafast oxidative desulfurization of high sulfur liquid fuels," *Appl. Catal. A Gen.*, vol. 743, p. 118791, 2022. <https://doi.org/10.1016/j.apcata.2022.118791>.
- [2] C. Deng *et al.*, "High-entropy oxide stabilized molybdenum oxide via high temperature for deep oxidative desulfurization," *Appl. Mater. Today*, vol. 20, p. 107680, 2022. <https://doi.org/10.1016/j.apmt.2022.107680>.
- [3] S. J. C. Ng and A. E. S. Choi, "Advancements in new desulfurization technology for industry scale applications," *Results in Engineering*, vol. 27, p. 107077, 2020. <https://doi.org/10.1016/j.rineng.2020.107077>.
- [4] H. Lü *et al.*, "Deep catalytic oxidative desulfurization (ODS) of dibenzothiophene (DBT) with oxalate-based deep eutectic solvents (DESs)," *Chemical Communications*, vol. 51, no. 53, pp. 10703–10706, 2015. <https://doi.org/10.1039/c9cc03322a>.
- [5] H. Lin *et al.*, "High-entropy oxide based biomimetic catalysis system enables robust oxidative desulfurization with an excellent regeneration ability," *Sep. Purif. Technol.*, vol. 348, p. 127729, 2024. <https://doi.org/10.1016/j.seppur.2024.127729>.
- [6] H. H. Alwan, A. A. Abd, H. F. Makki, and M. R. Othman, "Optimizing hydrodesulfurization of naphtha using NiMo/graphene catalyst," *Journal of Industrial and Engineering Chemistry*, vol. 130, pp. 539–551, 2024. <https://doi.org/10.1016/j.jiec.2024.01.077>.
- [7] M. K. Prabhu, J. N. Louwen, E. T. C. Vogt, and I. M. N. Groot, "Hydrodesulfurization of methanethiol over Co-promoted MoS₂ model catalysts," *Nat. Commun.*, vol. 10, no. 1, p. 1170, 2024. <https://doi.org/10.1038/s41467-024-01049-7>.
- [8] S. K. Al-Taweel, H. A. Al-Jendeel, and B. A. Al-Tabbakh, "Synthesis of sulfated zirconia-HY zeolite catalysts doped by platinum metal for hydroisomerization reaction," *Journal of Ecological Engineering*, vol. 26, no. 3, 2020. <https://doi.org/10.12911/22998993/199087>.
- [9] S. A. Ganiyu and S. A. Lateef, "Review of adsorptive desulfurization process: Overview of the non-carbonaceous materials, mechanism and synthesis strategies," *Fuel*, vol. 294, no. March 2020, 2021. <https://doi.org/10.1016/j.fuel.2021.120273>.
- [10] Y. Oday and H. A. Al-Jendeel, "Synthesis and Characterization of Acidic Activated Carbon from Corncobs for Adsorption Desulfurization of Simulated Crude Oil," *Journal of*

- [11] A. Qasim and H. H. Alwan, "Enhancement of light Naphtha quality using calcite adsorbent from eggshells by adsorptive desulfurization," *S. Afr. J. Chem. Eng.*, vol. 46, pp. 196–204, Oct. 2023. <https://doi.org/10.1016/j.saice.2023.08.007>.
- [12] F. Liu *et al.*, "Effect of microbial nutrients supply on coal bio-desulfurization," *J. Hazard. Mater.*, vol. 384, p. 121324, 2020. <https://doi.org/10.1016/j.jhazmat.2019.121324>.
- [13] O. I. Dada, L. Yu, S. Neibergs, and S. Chen, "Biodesulfurization: Effective and sustainable technologies for biogas hydrogen sulfide removal," *Renewable and Sustainable Energy Reviews*, vol. 209, p. 110144, 2020. <https://doi.org/10.1016/j.rser.2020.110144>.
- [14] S. Kumar, V. C. Srivastava, and S. M. Nanoti, "Extractive desulfurization of gas oils: a perspective review for use in petroleum refineries," *Separation & Purification Reviews*, vol. 46, no. 4, pp. 319–347, 2017. <https://doi.org/10.1080/104222119.2017.1288733>.
- [15] J. Yan *et al.*, "Extraction desulfurization with mixed solvents of organic solvent + organic solvent or deep eutectic solvent as extractants: Liquid-liquid equilibrium experiments and molecular dynamics simulations," *Fluid Phase Equilib.*, vol. 560, p. 113600, 2023, <https://doi.org/10.1016/j.fluid.2022.113600>.
- [16] J. Xu *et al.*, "Ultra-deep desulfurization via reactive adsorption on peroxophosphomolybdate/agarose hybrids," *Chemosphere*, vol. 111, pp. 731–737, 2014. <https://doi.org/10.1016/j.chemosphere.2014.05.033>.
- [17] I. Mohammed, H. H. Alwan, and A. N. Ghanim, "Using Box-Behnken experimental design for optimization of gas oil desulfurization by electrochemical oxidation technique," in *IOP Conference Series: Materials Science and Engineering*, IOP Publishing Ltd, Nov. 2020. <https://doi.org/10.1088/1757-899X/928/2/022108>.
- [18] A. Haruna, Z. M. A. Merican, and S. G. Musa, "Recent advances in catalytic oxidative desulfurization of fuel oil – A review," *Journal of Industrial and Engineering Chemistry*, vol. 112, pp. 20–36, 2022. <https://doi.org/10.1016/j.jiec.2022.05.023>.
- [19] J. I. Humadi and W. T. Mohammed, "Fast, ultradeep, and continuous desulfurization of heavy gasoil in novel oscillatory basket central baffled reactor using MnO₂-incorporated Fe₃O₄- supported activated carbon catalyst," *Fuel*, vol. 400, Nov. 2020. <https://doi.org/10.1016/j.fuel.2020.130717>.
- [20] W. Zhang, X. Li, H. Wang, Y. Song, S. Zhang, and C. Li, "Deep desulfurization of model oil by photocatalytic air oxidation and adsorption using Ti(1-x)MxO₂ (M=Zr, Ce)," *Korean*

Journal of Chemical Engineering, vol. 34, no. 12, pp. 3132–3141, 2017.

<https://doi.org/10.107/s11814-017-229-4>.

- [21] H. Lü *et al.*, “Deep catalytic oxidative desulfurization (ODS) of dibenzothiophene (DBT) with oxalate-based deep eutectic solvents (DESs),” *Chemical Communications*, vol. 51, no. 53, pp. 10703–10706, 2015. <https://doi.org/10.1039/c5cc03324a>.
- [22] Z. Feng, Y. Zhu, Q. Zhou, Y. Wu, and T. Wu, “Magnetic WO₃/Fe₂O₃ as catalyst for deep oxidative desulfurization of model oil,” *Materials Science and Engineering: B*, vol. 240, pp. 85–91, 2019. <https://doi.org/10.1016/j.mseb.2019.01.009>.
- [23] L. Sun *et al.*, “Aerobic oxidative desulfurization coupling of Co polyanion catalysts and p-TsOH-based deep eutectic solvents through a biomimetic approach,” *Green Chemistry*, vol. 21, no. 10, pp. 2629–2634, 2019. <https://doi.org/10.1039/c9gc02941k>.
- [24] C. Ma, D. Chen, F. Liu, X. Sun, F. Xiao, and B. Dai, “Oxidative desulfurization of a model fuel using ozone oxidation generated by dielectric barrier discharge plasma combined with Co₃O₄/γ-Al₂O₃ catalysis,” *RSC Adv.*, vol. 5, no. 117, pp. 96945–96952, 2015. <https://doi.org/10.1039/c5ra16277v>.
- [25] M. Rodríguez-Peña, J. A. Barrios Pérez, J. Llanos, C. Sáez, M. A. Rodrigo, and C. E. Barrera-Díaz, “New insights about the electrochemical production of ozone,” *Curr. Opin. Electrochem.*, vol. 27, p. 100697, 2021. <https://doi.org/10.1016/j.coelec.2021.100697>.
- [26] J. Wang, D. Zhao, and K. Li, “Oxidative Desulfurization of Dibenzothiophene Using Ozone and Hydrogen Peroxide in Ionic Liquid,” *Energy & Fuels*, vol. 24, no. 4, pp. 2027–2029, Apr. 2010. <https://doi.org/10.1021/ef901324p>.
- [27] H. Wang, R. Zhou, M. Jiang, Z. Lin, and Y. Deng, “Ozonolysis mechanism of heterocyclic organic sulfides: A computational study,” *Comput. Theor. Chem.*, vol. 190, pp. 88–93, 2016. <https://doi.org/10.1016/j.comptc.2016.06.015>.
- [28] A. V Akopyan, D. A. Grigoriev, P. L. Polikarpova, E. A. Eseva, V. V Litvinova, and A. V Anisimov, “Ozone-assisted oxidative desulfurization of light oil fractions,” *Petroleum Chemistry*, vol. 57, no. 10, pp. 904–907, 2017. <https://doi.org/10.1134/S096054411710024>.
- [29] N. M. Abdullah, H. Q. Hussien, and R. R. Jalil, “Heavy Naphtha Desulfurization by Ozone Generated via the DBD Plasma Reactor,” *Iraqi Journal of Chemical and Petroleum Engineering*, vol. 20, no. 2, pp. 131–137. <https://doi.org/10.31699/IJCPE.2024.2.12>.

- [30] S. Jatav and V. C. Srivastava, "Ce/Al₂O₃ as an efficient catalyst for oxidative desulfurization of liquid fuel," *Pet. Sci. Technol.*, vol. 37, no. 7, pp. 733–740, 2019. <https://doi.org/10.1080/10916466.2018.1567323>.
- [31] H. H. Alwan, A. A. Ali, and H. F. Makki, "Optimization of Oxidative Desulfurization Reaction with Fe₂O₃ Catalyst Supported on Graphene Using Box-Behnken Experimental Method," 2020. <https://doi.org/10.9767/bcrec.15.1.7770.175-185>.
- [32] H. H. Alwan, "Oxidative desulfurization of a model fuel using MoO₃ nanoparticles supported on carbon nanotubes catalyst: Examine most significance variables, optimization, kinetics and thermodynamics study," *S. Afr. J. Chem. Eng.*, vol. 4, no. January, pp. 23–29, 2022. <https://doi.org/10.1016/j.sajce.2022.03.002>.
- [33] S. A. Abdulhadi and H. H. Alwan, "Oxidative desulfurization of model fuel using a NiO-MoO₃ catalyst supported by activated carbon: Optimization study," *S. Afr. J. Chem. Eng.*, vol. 4, pp. 19–19, Jan. 2023. <https://doi.org/10.1016/j.sajce.2023.01.001>.
- [34] S. U. Hassan *et al.*, "Investigating catalytic oxidative desulfurization of model fuel using hollow PW₁₂/TiO₂@MgCO₃ and performance optimization via box-behnken design," *Chemosphere*, vol. 339, p. 139662, 2023. <https://doi.org/10.1016/j.chemosphere.2023.139662>.
- [35] H. J. Mohammed, A. T. Jarullah, B. A. Al-Tabbakh, and H. M. Hussein, "Preparation of synthetic composite nano-catalyst for oxidative desulfurization of kerosene," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 45, no. 1, pp. 1672–1680, 2023. <https://doi.org/10.1080/155677.23.2023.2181890>.
- [36] M. AbdulHassan and H. H. Alwan, "Boosting tungsten-based catalyst activity for aerobic oxidative desulfurization of gas oil by cerium," *Results in Engineering*, vol. 23, p. 105007, 2024. <https://doi.org/10.1016/j.rineng.2024.105007>.
- [37] S. J. C. Ng, A. E. S. Choi, N. P. Dugos, and M.-W. Wan, "Driving Sustainable Solutions: Exploring Supported-Polyoxometalate Catalysts for Enhanced Oxidative Desulfurization," *Chem. Eng. Trans.*, vol. 113, pp. 79–84, Nov. 2024. <https://doi.org/10.1016/j.sajce.2024.01.001>.
- [38] H. Chen *et al.*, "Mechanochemical Synthesis of High Entropy Oxide Materials under Ambient Conditions: Dispersion of Catalysts via Entropy Maximization," *ACS Mater. Lett.*, vol. 1, no. 1, pp. 83–88, Jul. 2019. <https://doi.org/10.1021/acsmaterialslett.9b00744>.
- [39] Y. Sun and S. Dai, "High-entropy materials for catalysis: A new frontier," *Sci. Adv.*, vol. 7, no. 20, p. eabg1600, 2021. <https://doi.org/10.1126/sciadv.abg1600>.

- [٤٠] D. Feng *et al.*, "Holey lamellar high-entropy oxide as an ultra-high-activity heterogeneous catalyst for solvent-free aerobic oxidation of benzyl alcohol," *Angewandte Chemie*, vol. ١٣٢, no. ٤٤, pp. ١٩٦٧١–١٩٦٧٧, ٢٠٢٠. <https://doi.org/10.102/anie.2020.4892>.
- [٤١] Y. Sun *et al.*, "Defect engineering of ceria nanocrystals for enhanced catalysis via a high-entropy oxide strategy," *ACS Cent. Sci.*, vol. ٨, no. ٨, pp. ١٠٨١–١٠٩٠, ٢٠٢٢. <https://doi.org/10.1021/acscentsci.2c00340>.
- [٤٢] H. Chen *et al.*, "An ultrastable heterostructured oxide catalyst based on high-entropy materials: A new strategy toward catalyst stabilization via synergistic interfacial interaction," *Appl. Catal. B*, vol. ٢٧٦, p. ١١٩١٥٥, ٢٠٢٠. <https://doi.org/10.1016/j.apcatb.2020.119155>.
- [٤٣] Md. M. H. Mondol, B. N. Bhadra, and S. H. Jung, "Molybdenum nitride@porous carbon, derived from phosphomolybdic acid loaded metal-azolate framework-٦: A highly effective catalyst for oxidative desulfurization," *Appl. Catal. B*, vol. ٢٨٨, p. ١١٩٩٨٨, ٢٠٢١. <https://doi.org/10.1016/j.apcatb.2021.119988>.
- [٤٤] C. Burda, X. Chen, R. Narayanan, and M. A. El-Sayed, "Chemistry and Properties of Nanocrystals of Different Shapes," *Chem. Rev.*, vol. ١٠٥, no. ٤, pp. ١٠٢٥–١١٠٢, Apr. ٢٠٠٥. <https://doi.org/10.1021/cr00063a>.
- [٤٥] H. Lin *et al.*, "Supersaturation-Dependent Surface Structure Evolution: From Ionic, Molecular to Metallic Micro/Nanocrystals," *J. Am. Chem. Soc.*, vol. ١٣٥, no. ٢٥, pp. ٩٣١١–٩٣١٤, Jun. ٢٠١٣. <https://doi.org/10.1021/ja404371k>.
- [٤٦] L. Dong, J. Chen, S. Huang, and S. Xing, "Simultaneously boosting radical and nonradical activation of peroxymonosulfate by ZnNiCoMnAlOx high entropy oxide for rapid degradation of sulfamethoxazole," *Chem. Eng. Sci.*, vol. ٣١٨, p. ١٢٢٢١٤, ٢٠٢٥. <https://doi.org/10.1016/j.ces.2025.122214>.
- [٤٧] J. Zhang, Q. Kuang, Y. Jiang, and Z. Xie, "Engineering high-energy surfaces of noble metal nanocrystals with enhanced catalytic performances," *Nano Today*, vol. ١١, no. ٥, pp. ٦٦١–٦٧٧, ٢٠١٦. <https://doi.org/10.1016/j.nantod.2016.08.012>.
- [٤٨] M. S. Tizo *et al.*, "Efficiency of calcium carbonate from eggshells as an adsorbent for cadmium removal in aqueous solution," *Sustainable Environment Research*, vol. ٢٨, no. ٦, pp. ٣٢٦–٣٣٢, ٢٠١٨. <https://doi.org/10.1016/j.serj.2018.09.002>.
- [٤٩] M. R. F Rahman, "Characterization of Activated Carbon from Granulated Sugar". <https://doi.org/10.52088/ijesty.v5i2.247>.

- [50] F. H. Hussein, A. F. Halbus, A. J. Lafta, and Z. H. Athab, "Preparation and characterization of activated carbon from iraqi khestawy date palm," *J. Chem.*, vol. 2015, 2015. <https://doi.org/10.1155/2015/290748>.
- [51] H. Xu *et al.*, "Preparation method of Co₃O₄ nanoparticles using degreasing cotton and their electrochemical performances in supercapacitors," *J. Nanomater.*, vol. 2014, no. 1, p. 723057, 2014. <https://doi.org/10.1155/2014/723057>.
- [52] C. M. Muiva, T. S. Sathiaraj, and K. Maabong, "Effect of doping concentration on the properties of aluminium doped zinc oxide thin films prepared by spray pyrolysis for transparent electrode applications," *Ceram. Int.*, vol. 37, no. 2, pp. 555–560, 2011. <https://doi.org/10.1016/j.ceramint.2010.09.042>.
- [53] F. Ahangaran, A. Hassanzadeh, and S. Nouri, "Surface modification of Fe₃O₄@ SiO₂ microsphere by silane coupling agent," *Int. Nano Lett.*, vol. 3, pp. 1–5, 2013. <https://doi.org/10.1186/2228-0326-3-23>.
- [54] N. A. Jawad and K. H. Hassan, "Structural characterization of NiO nanoparticles prepared by green chemistry synthesis using arundo donax leaves extract," in *Journal of Physics: Conference Series*, IOP Publishing, 2021, p. 012007. <https://doi.org/10.1088/1742-6596/1818/1/012007>.
- [55] K. Deori and S. Deka, "Morphology oriented surfactant dependent CoO and reaction time dependent Co₃O₄ nanocrystals from single synthesis method and their optical and magnetic properties," *CrystEngComm*, vol. 15, no. 42, pp. 8470–8474, 2013. <https://doi.org/10.1039/c3ce41502c>.
- [56] W. G. Adnan and A. M. Mohammed, "Green synthesis of chromium oxide nanoparticles for anticancer, antioxidant and antibacterial activities," *Inorg. Chem. Commun.*, vol. 109, p. 111683, 2014. <https://doi.org/10.1016/j.inoche.2014.111683>.
- [57] H. Chen *et al.*, "Entropy-stabilized metal oxide solid solutions as CO oxidation catalysts with high-temperature stability," *J. Mater. Chem. A Mater.*, vol. 6, no. 24, pp. 11129–11133, 2018. <https://doi.org/10.1039/c8ta01772g>.
- [58] A. C. Mohan and B. Renjanadevi, "Preparation of zinc oxide nanoparticles and its characterization using scanning electron microscopy (SEM) and X-ray diffraction (XRD)," *Procedia Technology*, vol. 24, pp. 761–766, 2016. <https://doi.org/10.1016/j.protcy.2016.05.078>.
- [59] N. Singh, S. Chand, and M. Taunk, "Facile in-situ synthesis, microstructural, morphological and electrical transport properties of polypyrrole-cuprous iodide hybrid

nanocomposites," *J. Solid State Chem.*, vol. 303, p. 122501, 2021.

<https://doi.org/10.1016/j.jssc.2021.122501>.

- [60] M. Balakrishnan and R. John, "Properties of sol-gel synthesized multiphase TiO₂ (AB)-ZnO (ZW) semiconductor nanostructure: An effective catalyst for methylene blue dye degradation," *Iranian Journal of Catalysis*, vol. 10, no. 1, pp. 1-16, 2020.
- [61] Z. R. Khan, M. Zulfequar, and M. S. Khan, "Optical and structural properties of thermally evaporated cadmium sulphide thin films on silicon (100) wafers," *Materials Science and Engineering: B*, vol. 174, no. 1-3, pp. 145-149, 2010.
<https://doi.org/10.1016/j.mseb.2010.03.007>.
- [62] I. W. Sutapa, A. Wahid Wahab, P. Taba, and N. L. Nafie, "Dislocation, crystallite size distribution and lattice strain of magnesium oxide nanoparticles," in *Journal of Physics: Conference Series*, IOP Publishing, 2018, p. 012021. <https://doi.org/10.1088/1742-6596/979/1/012021>.
- [63] W. Huang, J. Cai, J. Hu, J. Zhu, F. Yang, and X. Bao, "Atomic structures and electronic properties of Cr-doped ZnO() surfaces," *Chinese Journal of Catalysis*, vol. 42, no. 6, pp. 971-979, 2021. [https://doi.org/10.1016/S1872-2067\(21\)63710-X](https://doi.org/10.1016/S1872-2067(21)63710-X).
- [64] M. Alibolandi, J. T. Darian, M. Ghaedian, S. J. Royaei, and A. Shafeghat, "Non-catalytic oxidative desulfurization of gas condensate by ozone and process optimization using response surface methodology," *Korean Journal of Chemical Engineering*, vol. 37, no. 11, pp. 1877-1877, 2020. <https://doi.org/10.1007/s11814-020-0905-1>.
- [65] A. Mishra and B. C. Meikap, "Optimization of process parameters for waste motor oil pyrolysis towards sustainable waste-to-energy utilizing a combinatorial approach of response surface methodology and desirability criteria," *Fuel*, vol. 303, p. 129226, 2023. <https://doi.org/10.1016/j.fuel.2023.129226>.
- [66] X. Li, Z. Wang, B. Chu, J. Ma, and H. He, "Challenges and opportunities of catalytic decomposition of ozone at room temperature," *Fundamental Research*, 2020. <https://doi.org/10.1016/j.fmre.2020.12.001>.
- [67] P. Sikarwar, U. K. A. Kumar, V. Gosu, and V. Subbaramaiah, "Catalytic oxidative desulfurization of DBT using green catalyst (Mo/MCM-41) derived from coal fly ash," *Environ. Chem. Eng.*, vol. 6, no. 2, pp. 1737-1744, 2018. <https://doi.org/10.1016/j.jece.2018.02.021>.
- [68] M. A. Alheety, S. A. Al-Jibori, A. Karadağ, H. Akbaş, and M. H. Ahmed, "A novel synthesis of MnO₂, nanoflowers as an efficient heterogeneous catalyst for oxidative

desulfurization of thiophenes," *Nano-Structures & Nano-Objects*, vol. 20, p. 100392, 2019. <https://doi.org/10.1016/j.nanoso.2019.100392>.

- [19] Y. Shu, J. Bao, S. Yang, X. Duan, and P. Zhang, "Entropy-stabilized metal-CeOx solid solutions for catalytic combustion of volatile organic compounds," *AIChE Journal*, vol. 77, no. 1, p. e17046, 2021. <https://doi.org/10.1002/aic.17046>.
- [20] I. Mohammed, H. H. Alwan, and A. N. Ghanim, "Study reaction kinetics of fuel model desulfurization by electrochemical oxidation technique," *Al-Qadisiyah. J. Eng. Sci.*, vol. 14, pp. 1-5, 2021. <https://doi.org/10.30772/qjes.v14i3.710>.
- [21] H. M. Hmood *et al.*, "Kaoline-based catalyst for a high stability desulfurization of sour heavy naphtha in a three-phase oscillatory baffled reactor," *Particuology*, vol. 48, pp. 249-260, 2024. <https://doi.org/10.1016/j.partic.2023.06.011>.
- [22] F. Y. AlJaberi, "New design of an electrocoagulation reactor to remove pollutants from groundwater: Analysis and optimization using response surface methodology," *S. Afr. J. Chem. Eng.*, vol. 46, pp. 205-216, 2023. <https://doi.org/10.1016/j.sajce.2023.08.008>.
- [23] M. K. Trivedi *et al.*, "Characterization of physical, thermal and structural properties of chromium (VI) oxide powder: Impact of biofield treatment," *Powder Metallurgy & Mining*, vol. 4, no. 1, 2015. <https://doi.org/10.5281/zenodo.116080>.
- [24] A. Sengupta, P. D. Kamble, J. K. Basu, and S. Sengupta, "Kinetic Study and Optimization of Oxidative Desulfurization of Benzothiophene Using Mesoporous Titanium Silicate-1 Catalyst," *Ind. Eng. Chem. Res.*, vol. 51, no. 1, pp. 147-157, Jan. 2012. <https://doi.org/10.1021/ie202401a>.
- [25] Y. Dai, D. Zhao, and Y. Qi, "Sono-desulfurization oxidation reactivities of FCC diesel fuel in metal ion/H₂O₂ systems," *Ultrason. Sonochem.*, vol. 18, no. 1, pp. 264-268, 2011. <https://doi.org/10.1016/j.ultsonch.2010.06.007>.
- [26] A. E. S. Choi, S. Roces, N. Dugos, and M.-W. Wan, "Oxidation by H₂O₂ of benzothiophene and dibenzothiophene over different polyoxometalate catalysts in the frame of ultrasound and mixing assisted oxidative desulfurization," *Fuel*, vol. 180, pp. 127-136, 2016. <https://doi.org/10.1016/j.fuel.2016.04.014>.
- [27] P. Huang, G. Luo, L. Kang, M. Zhu, and B. Dai, "Preparation, characterization and catalytic performance of HPW/aEVM catalyst on oxidative desulfurization," *RSC Adv.*, vol. 9, no. 8, pp. 4681-4687, 2019. <https://doi.org/10.1039/c7ra26087a>.
- [28] F. Vafaei, M. Jahangiri, and M. Salavati-Niasari, "A new phase transfer nanocatalyst NiFe₂O₄-PEG for removal of dibenzothiophene by an ultrasound assisted oxidative

process: Kinetics, thermodynamic study and experimental design," *RSC Adv.*, vol. 11, no. 50, pp. 31448–31459, Sep. 2021. <https://doi.org/10.1039/d1ra06750f>.

- [79] N. Jose, S. Sengupta, and J. K. Basu, "Optimization of oxidative desulfurization of thiophene using Cu/titanium silicate-1 by box-behnken design," *Fuel*, vol. 90, no. 2, pp. 626–632, 2011. <https://doi.org/10.1016/j.fuel.2010.09.026>.
- [80] Z. Hassan, M. Stahlberger, N. Rosenbaum, and S. Bräse, "Criegee Intermediates Beyond Ozonolysis: Synthetic and Mechanistic Insights," *Angew. Chem. Int. Ed.*, vol. 60, no. 28, pp. 15138–15152, Jul. 2021. <https://doi.org/10.1002/anie.202114974>.
- [81] C. Ma *et al.*, "Deep oxidative desulfurization of model fuel using ozone generated by dielectric barrier discharge plasma combined with ionic liquid extraction," *Journal of Industrial and Engineering Chemistry*, vol. 20, no. 5, pp. 2769–2774, 2014. <https://doi.org/10.1016/j.jiec.2013.11.005>.