

Performance Enhancement of Adsorption Desulfurization Process via Different New Nano-Catalysts Using Digital Baffle Batch Reactor and Mathematical Modeling

Amer T. Nawaf^{1,a,*}, Hussein H. Hamed², Shymaa Ali Hameed³, Aysar
T. Jarullah^{3,b}, Layth T. Abdulateef⁴, Iqbal M. Mujtaba^{5,c}

¹Petroleum and Gas Refinery Engineering Department, College of Petroleum Process
Engineering, Tikrit University

³Al-Hawija Technical Institute, Northern Technical University

³Chemical Engineering Department, College of Engineering, Tikrit University

⁴Chemical Engineering, Middle Technical University

⁵Department of Chemical Engineering, Faculty of Engineering & Informatics, University of
Bradford, Bradford BD7 1DP, UK

^a Email: Amer.Talal@tu.edu.iq

^b Email: A.T.Jarullah@tu.edu.iq

^c Email: I.M.Mujtaba@bradford.ac.uk

Abstract

Several new homemade nano-catalysts are prepared here to reduce sulfur compound found in light gas oil (LGO) utilizing the adsorption desulfurization technique. The effect of different support materials (Fe₂O₃, Cr₂O₃ and CdO) having the same particle size (20 nm) on the adsorptive desulfurization performance for loading 5% nickel sulfate (5wt%NiO) as an active component for each catalyst, is studied. Oxidative desulfurization process (ODS) in a novel digital baffle batch reactor (DBBR) is used to evaluate the performance of the catalysts prepared. Moderate operating

conditions are employed for the ODS process. The efficient new nano-catalysts with for the removal of sulfur are found to be 93.4%, 85.6% and 62.1% for NiO/Fe₂O₃, NiO/Cr₂O₃ and NiO/CdO, respectively at 175 °C, 75 min and 2 ml of H₂O₂. The best kinetic model and the half-live period for the nano-catalysts related to the relevant reactions have also been investigated here.

Keyword: Adsorption desulfurization, DBBR, H₂O₂, Nano catalyst, Mathematical model.

1. Introduction

Crude oils or oil fractions are regarded as the main source for energy and transportation fuel and have widely been used for chemical and petrochemical industries. Nowadays, the worlds consumption of energy is 36% whereas 90% of vehicles fuel is provided by petroleum derivatives [1]. For instance, energy consumption in the world for the year 2018 (shown in Figure 1) [2] showed that the petroleum represents the major consumption of the total energy consumption. Petroleum cuts have high sulfur compounds, which are considered one of the main contaminants in the derivatives of petroleum, causing significant amount of air pollution, leading to critical environmental and health impacts [3,4]. Since 1971, the environmental protection agency (EPA) with other protection agencies around the world have proposed new regulations to limit the sulfur content in the derivatives of fuels. Thus, strict legislations for sulfur content have been established with respect to oil products and more restrictions are expected to be more stringent in the future [5].

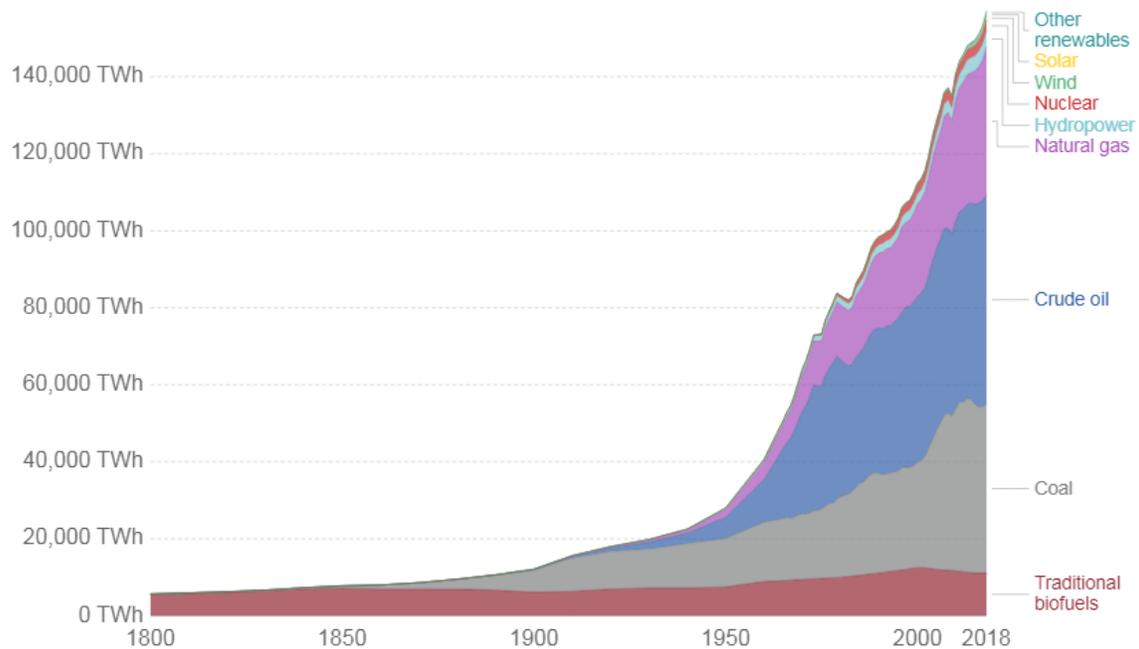


Figure 1: Energy consumption by energy source [2]

Therefore, the main aim of the recently proposed legislations is to reduce and remove all the types of sulfur compounds found in the oil feedstock with respect to transportation fuels [5]. The organosulfur compounds in the diesel fuels produce poisonous sulfur dioxide gases (SO_2) through the oxidation process generated by vehicle engines, which can cause adverse effects on the environment. Light gas oil and heavy gas oil are presently used as the primary energy sources for ships, trains, trucks and some automobiles in addition to the car fuel. Diesel fuel is considered a more attractive fuel than other sources such as gasoline due to the higher compression ratios being used to give higher fuel efficiencies in the engine. Therefore, further use of diesel fuel will require solutions to some major environmental pollution problems [6,7]. So, alternative methods and processes are being developed to find a solution of such problems. Among these technologies, the type of the catalyst being used/developed/modified and the process to be used are important decisions to be made. Sulfur compounds found in petroleum or synthetic oils are generally classified into two types: heterocycles and non-heterocycles. The non-heterocycles includes

thiols, sulfides and disulfides, while the heterocycles are mainly composed of thiophenes with one to several aromatic rings and sulfur contents with alkyl substituent in addition to nitrogen compounds are difficult to remove from fuel [8]. Thiophene compound is difficult to remove by traditional process owing to the high operating conditions required for removing pollutants from diesel fuel [9]. The traditional process of removing sulfur compounds in oil refineries is commonly known as catalytic hydrotreating (HDT) process which converts the sulfur compounds to H₂S and hydrocarbons. However, it renders difficulty to produce an environmentally friendly fuel owing to high resistance of sulfur compounds requiring more active catalysts and large amount of hydrogen under severe reaction conditions and thus more expensive compared to other processes. More recently, the promising technique used for sulfur removal is the oxidative desulfurization process (ODS) due to its low operating cost and safe operating conditions (less than 373 K) and low pressure (1 bar). Also such process uses air as an oxidant instead of using hydrogen. The most significant matter in the oxidative desulfurization process is the selection of right catalyst for the sulfur compounds. Also, in the ODS reactions the most refractory sulfur compounds have high reactivity towards the oxidation reactions. The thiophenes sulfur compounds present in fuels can be easily oxidized into corresponding sulphones and sulphoxides. Also, different types of catalysts and oxidants can be used in this process and then the compounds being formed due to chemical reaction can easily be removed by extraction or adsorption due to their high polarity [10-13]. In this work, different support materials (Fe₂O₃, Cr₂O₃ and CdO) are used to prepare new homemade nano-catalysts via the Incipient Wetness Impregnation (IWI) method with loading of 5 wt% of NiO. Adsorption desulfurization process (ADS) is applied to evaluate the reactivity of the catalyst prepared (NiO/Fe₂O₃, NiO/Cr₂O₃ and NiO/CdO) using novel

digital baffle batch reactor (DBBR). Finally, kinetic model of the Adsorption Desulfurization Process of DBBR has been investigated in the study.

2. Material Used and Experimental Design

2.1 Material Application

- Light gas Oil (LGO)

The light gas oil (LGO) is used in the experiments as oil feedstock that supplied from *Baiji* North refinery (*Salah-AlDeen/Iraq*). The main specifications of LGO are: Specific gravity 0.852, Viscosity 5 cst, Cetane index 53 and Flash point 56 °C.

- Nickel Sulfate (II)

The active material (nickel sulfate (II) = $\text{NiSO}_4(\text{H}_2\text{O})_6$) used in the catalyst preparation was supplied by Sigma Aldrich with purity of 99.7% and dissolved by deionized water.

- Dibenzothiophene (DBT)

Dibenzothiophene (DBT) is the model sulfur compound selected to evaluate the reactivity of the sulfur in the adsorption desulfurization process and has been purchased from Aldrich with purity >98%.

- Support Materials (Fe_2O_3 , Cr_2O_3 and CdO)

Different commercial support materials are used to prepare the homemade nano-catalysts. All these materials (Fe_2O_3 , Cr_2O_3 and CdO) have the same particle size diameter of 20 nm with spherical shape. These materials have obtained from *Alpha Chemika Company*.

- Hydrogen Peroxide (H_2O_2)

Hydrogen peroxide supplied from Aldrich with purity above 99.99% is used as oxidizing agent to oxidize DBT compound to sulfoxide and sulfones.

2.2. Incipient Wetness Impregnation (IWI) Process

Incipient Wetness Impregnation (IWI) [14-16] process has been applied to prepare the new homemade nano-catalysts utilized for ODS reactions. Metal oxide (support) is treated with deionized water for 1 hr and then 5 g of Fe_2O_3 , Cr_2O_3 and CdO are separately putted in an oven for 5 hr at $150\text{ }^\circ\text{C}$ to remove any moisture in the support surface. 0.473 g from nickel sulfate (II) ($\text{NiSO}_4(\text{H}_2\text{O})_6$) is dissolved by deionized water for the purpose of preparing the active material. The amount of the active material (nickel sulfate (II)) is dissolved by 35 ml of deionized water in a beaker (volume equal to 50 ml) having a magnetic stirrer where the solution is filtered without heating to remove any impurities. After that, IWI process is applied by slowly adding the solution containing the active materials to the first support (Fe_2O_3) for 1.5 hr. Calcination process of the product is started by the furnace at $350\text{ }^\circ\text{C}$ to get the first new homemade nano-catalyst ($\text{NiO}/\text{Fe}_2\text{O}_3$). The same procedure is applied to prepare the other nano-catalysts ($\text{NiO}/\text{Cr}_2\text{O}_3$ and NiO/CdO). Figure 2 shows the new nano-catalyst designed of Fe_2O_3 with metal oxide (nickel sulfate (II) ($\text{NiSO}_4(\text{H}_2\text{O})_6$)) by IWI.

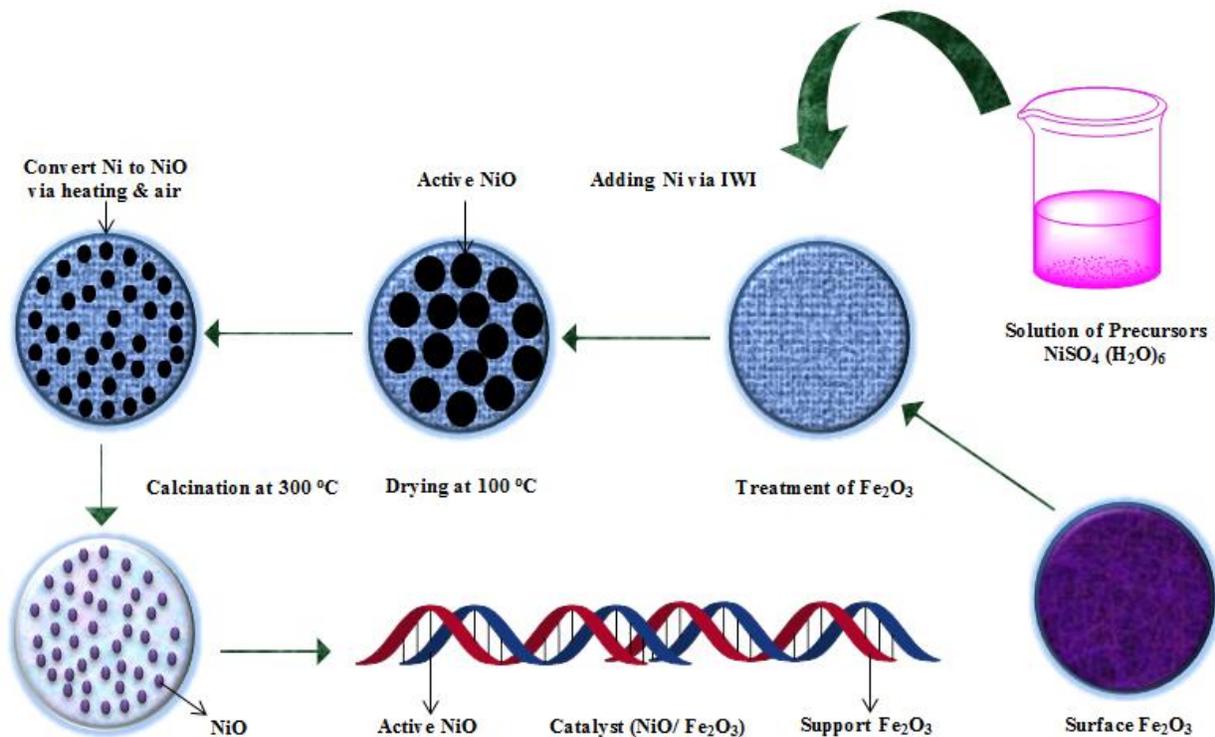


Figure 2: New nano-catalyst designed with metal oxide (NiO) by IWI

2.3 Experimental Procedure

- Digital Baffle Batch Reactor (DBBR)

The DBBR is locally designed to give the best mass transfer through the adsorption desulfurization process (ADS). Such new design has been built at the College of Engineering/Tikrit University-Iraq. The digital baffle batch reactor includes digital mixer, cylinder with a length of 145 mm and the impeller (six flat-blades turbine) with a diameter of 90 mm (the dimension of the impeller were: 5 cm in length and 5 cm in depth). Six flat blades turbine has been designed in a new shape to contain circular holes which are equally distributed over the surface of the metal in a hexagonal manner leading to increase the mixing channels inside the reactor and increasing the conversion process through the path (oil model), catalyst and

oxidant. The reactor with a volume of 200 ml was made from stainless steel consisting of four baffles (high of 20 cm and width of 2.5 cm). Baffles are put in equal dimensions inside the reactor on the surface of the batch reactor (about 38 cm among the baffles) and a protrusion of 2.5 cm is coming out with each baffle. The reactor is insulated by woolen material from the outer circumference and supplied with electrical power with a range of rev/min up to 5000 and can operate at a high temperature (above 1000 °C). Figure 3 illustrates the experimental setup and the specifications of the system are shown in Table 1.

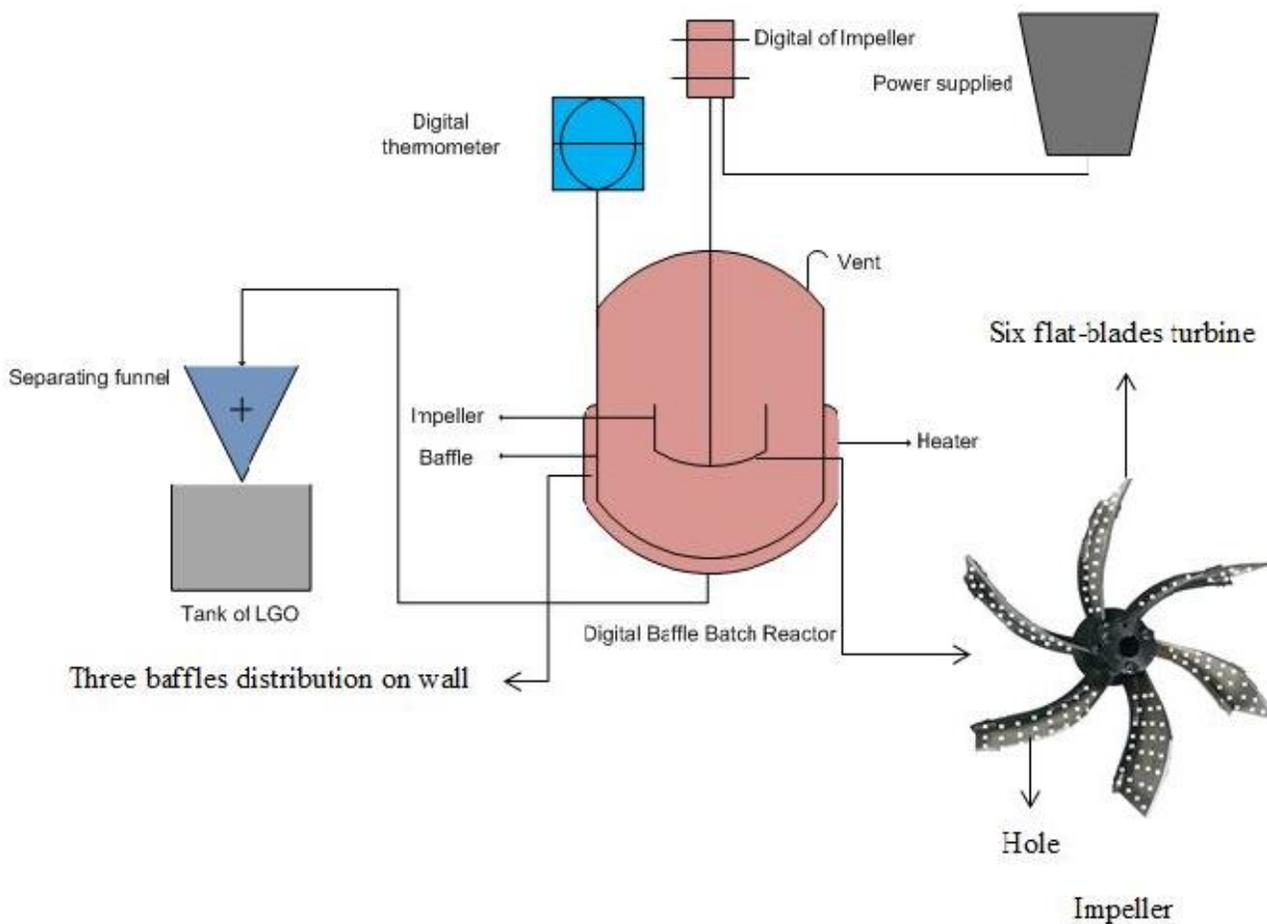


Figure 3: Schematic representation of the experimental DBBR system

Table1: Specification of DBBR system

No.	Description	Specification
1.	Mixing chamber inside diameter (Diameter of cylinder D)	110 mm
2.	Cylinder height (Stainless steel)	145 mm
3.	Impeller type (Stainless steel)	Six flat-blades turbine
4.	Impeller diameter	90 mm
5.	Batch reactor (Stainless steel)	Batch made of glass (200 ml)
6.	Baffle (Stainless steel)	Three distribution on the wall of the batch
7.	Preheater	Electrical heater
8.	Insulated reactor	glass wool

- Adsorption Desulfurization (ADS) Process

The hydrotreated light gas oil (LGO) is used as the oil feedstock to evaluate the catalyst performance supplied from *Baiji North Refinery* located in *Salah-Aldeen/Iraq*. The light gas oil is then injected by DBT as a model sulfur component with a concentration of 850 ppm (represents the initial sulfur content of the untreated LGO). Adsorption desulfurization reactions were carried out in the digital baffle batch reactor (DBBR) using LGO as a feedstock and H₂O₂ as an oxidant. In such process, 150 ml of LGO was charged for each run to carry out the ADS. The amount of H₂O₂ needed for the chemical reactions was (1, 1.5 and 2 ml) at constant pressure at 0.5 bar in all experiments. The catalyst prepared (NiO/Fe₂O₃, NiO/Cr₂O₃ and NiO/CdO) is separately charged into the digital baffle batch reactor containing the light gas oil. Adsorption desulfurization processes are conducted at moderate operating conditions, which are: the reaction time (25-75) min and reaction temperatures (120-160) °C at constant stirring rate of 450 rpm for the purpose of obtaining a good mixing and avoiding segregation (stagnant regions inside the reactor) of both

fluid and catalyst. The gases produced from the ADS are evaporated during the oxidation reactions then condensed through the condensation process attached to the process. The product sulfur concentrations of LGO could be given are analyzed via X-ray diffraction instrument based on ASTM D7039 method (are determined in *Sammraa Power Station Laboratories/Ministry of Electricity-Iraq*).

Note, all analytical techniques that have been utilized for the properties of the feedstock and the products were accurate, fast and repeatable. Product analysis has been repeated twice for each sample at each operating condition to ensure the accuracy of the results. Average results have been taken into accounts for each run with maximum deviation of 1.5 % among all runs.

3. Results and Discussion

3.1 Characterization of the Catalyst Prepared

3.1.1 Surface Area of Nano-Catalyst Prepared

The Brunauer-Emmett-Teller (BET) of the prepared Nano-Catalyst (5%NiO/Fe₂O₃, 5%NiO/Cr₂O₃ and 5%NiO/CdO) was measured by BET method. BET was carried out in Nanotechnology and Advanced Materials Research Center/Iraq. The values of the surface areas for the Nano-catalysts obtained at 24 hr and crystallization temperature of 85 °C using Nano-Catalyst are listed in Table 2. The chemical and physical properties of the prepared Nano-Fe₂O₃, Cr₂O₃ and CdO-supported-catalyst, the specific surface area are important factors affecting the process. Where, loading metal oxides (nickel oxide) on the structure of the surface Nano-zeolite-supported related to the catalyst activity can be obtained. It is noticed that the BET of the prepared

Nano catalyst decreases after loading the metal oxide on the catalyst supported approximately by (5%)NiO/ Nano – support (wt%) compared to that of nickel oxide. Such surface area of the prepared catalyst is still high [16]. The value of surface area presented in Table 2 could be attributed to the deposition of nickel oxide powder in the pores of supported materials causing the blockage and interferes nitrogen diffusion. However, this value is still acceptable for adsorption compared to the surface area of metal oxides on its own. The specific surface area of the designed catalyst still high, the number of effective active site increased leading to increase the adsorption process of the reaction rate.

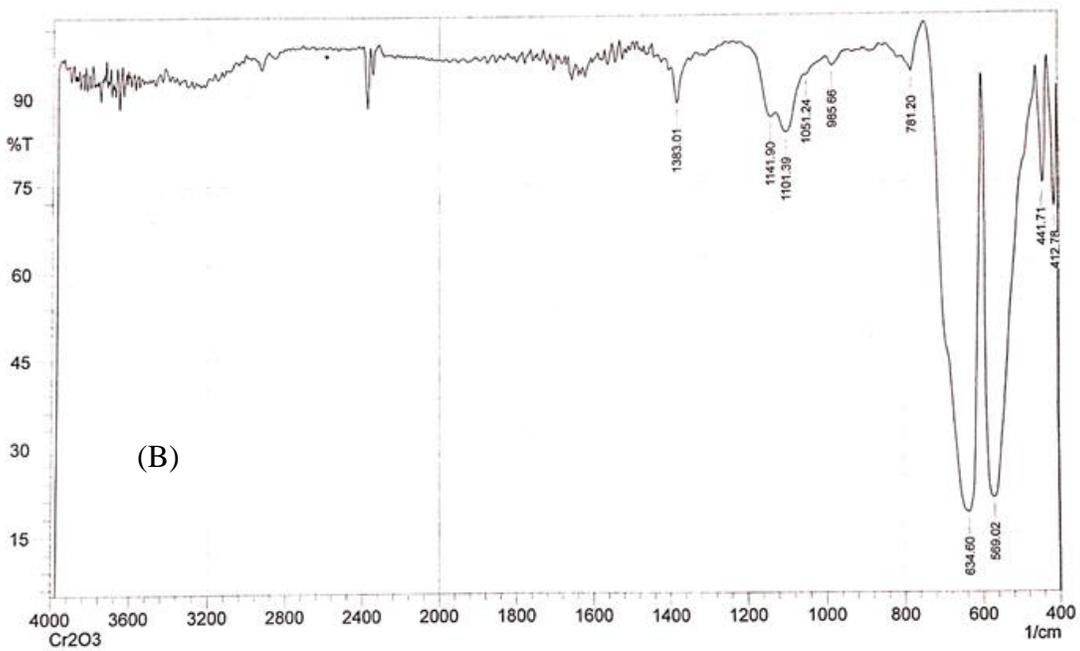
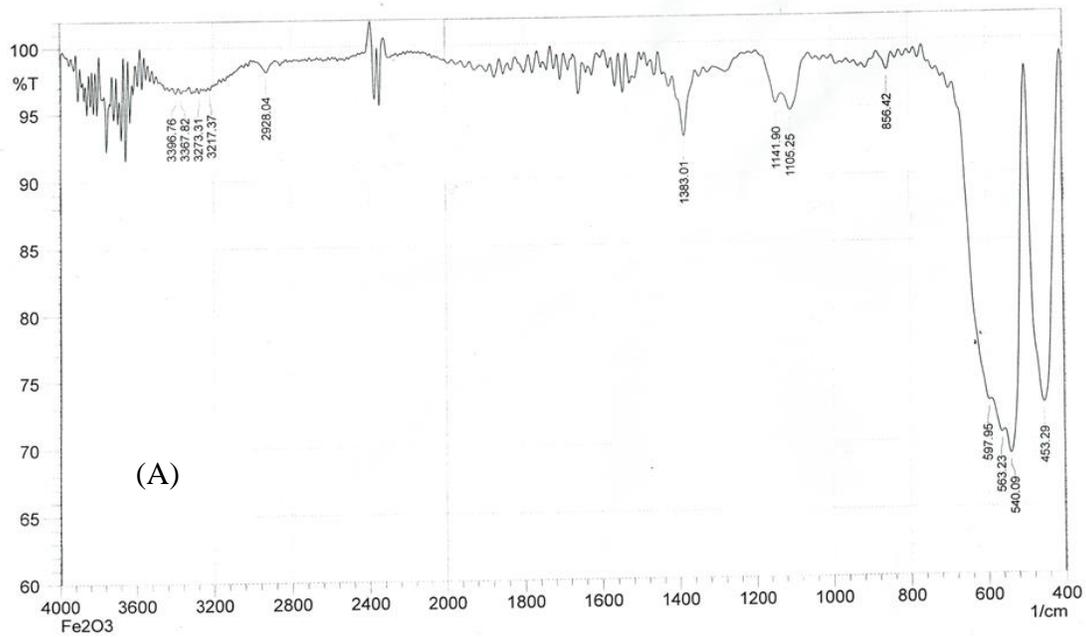
Table 2: Surface area for Nano-catalyst

Catalyst type	Surface area (m ² /g)
NiO/Fe ₂ O ₃	92.23
NiO/Cr ₂ O ₃	74.2
NiO/CdO	64.9

3.1.2 Fourier Transform Infra - Red (FTIR) Spectroscopy

Fourier Transform Infra-Red (FTIR) of the samples was recorded by Nicolet 6700 spectrometer and Model: FTIR 8400S/Shimadzu/Japan applied in Nanotechnology and Advanced Materials Research Center/Iraq. The surface catalyst chemistry involving surface acidity is reported utilizing infrared technique for the deigned new homemade nano-catalysts illustrated in Figure 4 (A) NiO/Fe₂O₃, B) NiO/Cr₂O₃ and C) NiO/CdO). The transmittance was recorded at wavenumber range of 350– 7800 cm⁻¹. The background correction of the spectra was performed by 16 scans with resolution from 0.5 to 16 cm⁻¹ for the background noise correction. FTIR analyses of the

catalyst (5%NiO/Fe₂O₃, 5%NiO/Cr₂O₃ and 5%NiO/CdO) prepared after treatment with the metal oxide were carried out to characterize functional groups on their surfaces and follow any potential structural change due to the treatment with nickel sulfide. FTIR spectra are shown in Fig. 4 (A, B and C). Figure 4 (A) the NiO/Fe₂O₃ catalyst spectrum has several significant absorption peaks recorded in the range of 4000 cm⁻¹ to 400 cm⁻¹. The broad absorption band centered at 3396.76 cm⁻¹ is assigned to O–H stretching vibrations and the band at 1383.01 cm⁻¹ is attributable to H–O–H bonding vibration mode indicating that the presence of traces of water is found in the sample. The broad absorption band in the region 440–600 cm⁻¹ is assigned to Ni–O stretching vibration mode [17-19]. The FTIR spectra of NiO nanoparticles over Cr₂O₃ showed several significant absorption peaks. The broad absorption band in the region of 400–640 cm⁻¹ is assigned to Ni–O stretching vibration mode; the broadness of the absorption band indicates that the NiO powders are nano-crystals as shown in Figure 4 (B). While in the catalyst NiO/CdO was broad absorption band in the region 416.64 cm⁻¹ as shown in the Figure 4 (C).



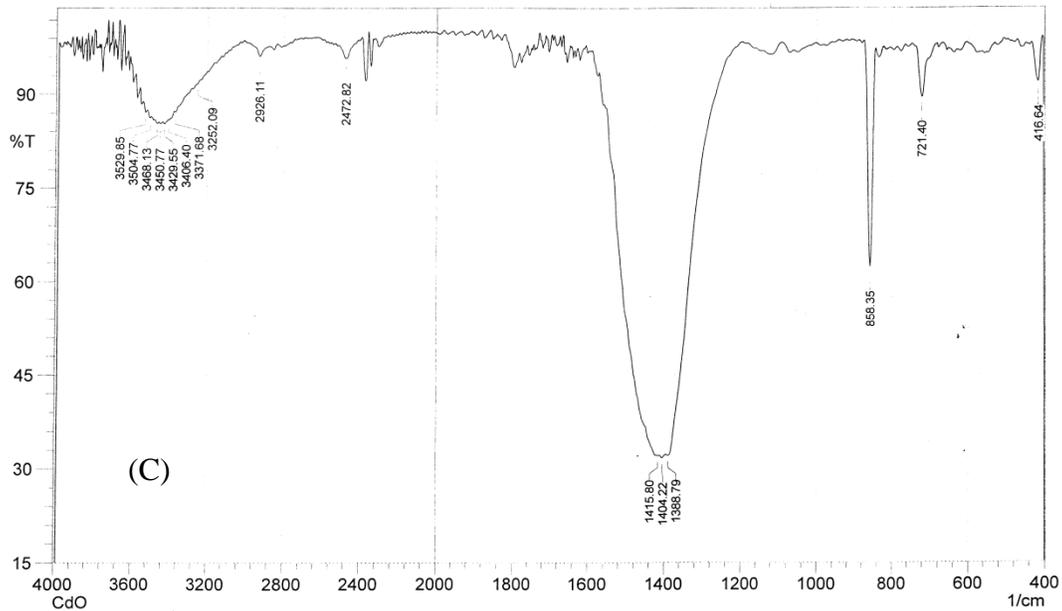


Figure 4: FTIR of the designed Nano-catalysts (A) NiO/Fe₂O₃, (B) NiO/Cr₂O₃ and (C) NiO/CdO

3.2 Influence of Operating Conditions on ADS

3.2.1 Effect of new Catalysts on Adsorption Desulfurization Process

In the experimental work, the best sulfur removal among the designed catalysts (NiO/Fe₂O₃, NiO/Cr₂O₃ and NiO/CdO) was for NiO/Fe₂O₃ as reported in the Figures 5 and 6. Figure 5 shows the influence of catalyst type on ADS at reaction temperature of 160°C and amount of oxidant 2 ml from H₂O₂. The catalyst NiO/Fe₂O₃ has shown high distribution of the active materials based on the support Fe₂O₃ that has high reactivity toward the oxidative desulfurization reactions especially when hydrogen peroxide is used as oxidant. The best sulfur removal (93.4%) of such catalyst has obtained at 160 °C and 2 ml H₂O₂. It is also noticed from Figure 5 that NiO/Cr₂O₃ and NiO/CdO result in lower conversion (85.6% and 62%, respectively) compared to that by NiO/Fe₂O₃ at the same operating conditions. It is due to the fact that Cr₂O₃ and CdO as the

catalyst support, have low surface area and pore volume resulting in low sulfur removal. Figure 6 shows the influence of catalyst type on ADS at reaction temperature of 140°C and oxidant amount of 1.5 ml H₂O₂. The highest amount of the oxidant used (H₂O₂) for all the catalysts is 2 ± 5 ml giving the highest sulfur conversion as shown in the Figure 5. Such behavior is probably attributed to the surface of the catalyst that plays an important role in the removal process toward ADS particularly via using metal oxide (Fe₂O₃) [20] and active materials (NiO).

Comparison of the results in Figure 5 and 6 shows for all catalyst, longer batch time, higher temperature and higher amount of H₂O₂ give better conversion of sulfur and NiO/Fe₂O₃ catalyst performs better than the other two.

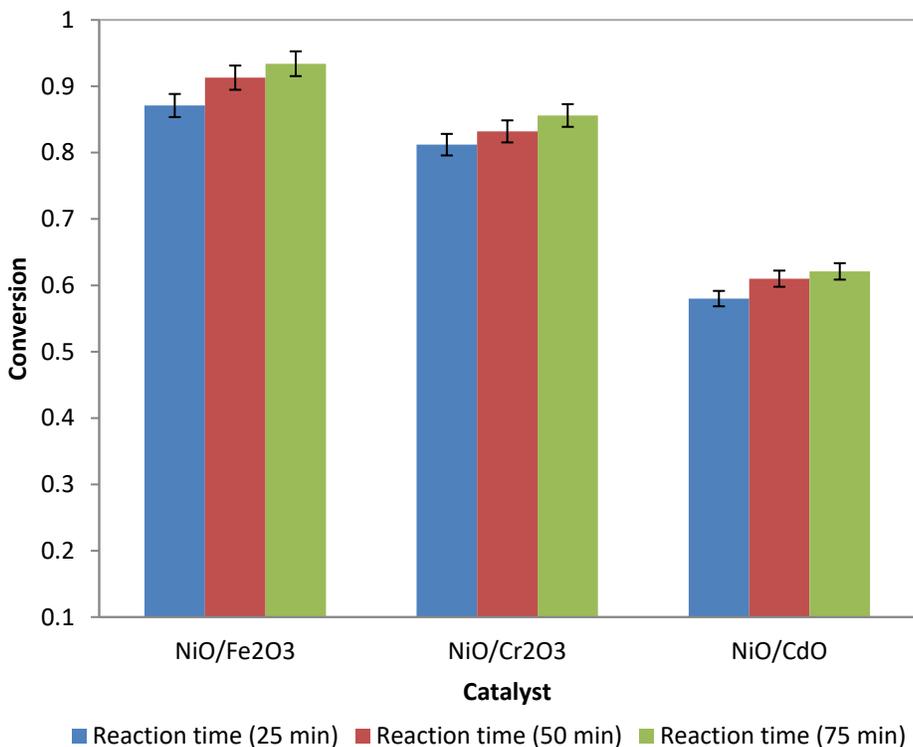


Figure 5: Influence of catalyst type on ADS at reaction temperature of 160°C and amount of oxidant 2 ml of H₂O₂

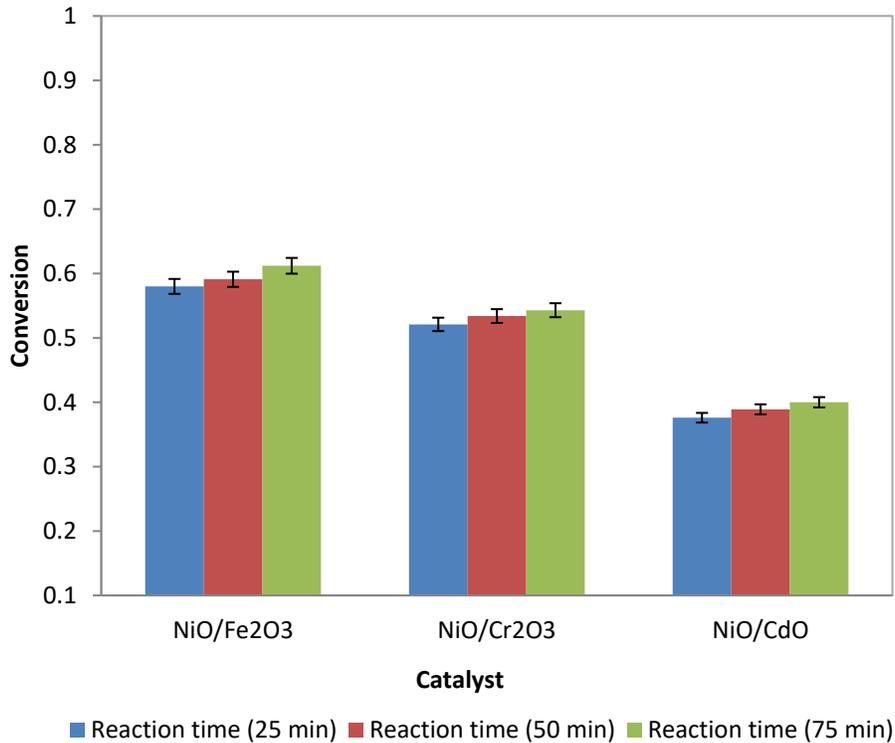


Figure 6: Influence of catalyst type on ADS at reaction temperature of 140°C and oxidant amount of 1.5 ml H₂O₂

3.2.2 Effect of Adsorption Reaction Time on Sulfur Removal

The influences of digital baffle batch reactor (DBBR) time on the conversion of sulfur compound via adsorption desulfurization reaction of the catalysts prepared are shown in Figures 7 - 9 for NiO/Fe₂O₃, NiO/Cr₂O₃ and NiO/CdO, respectively. The batch time considered for adsorption reactions were 25 min, 50 min and 75 min. From the results shown in these Figures, it has been noticed that the sulfur conversion increases with increasing the batch reaction time as increasing the contact time between the catalyst [20,21], hydrogen peroxide (H₂O₂) causing an increase of transfer of oxygen atoms and DBT in the pore site of the catalyst [14]. In Figure 7, the sulfur conversion increases from 87.1% to 93.4 when the reaction time increases from 25 to 75 min at 2

ml of H₂O₂ and 160 °C (temperature of reaction) using NiO/Fe₂O₃ catalyst. Same behaviors have observed in Figures 8 and 9 for NiO/Cr₂O₃ and NiO/CdO, respectively. Where, the conversion of sulfur compound increases from 81.2% to 85.6% NiO/Cr₂O₃ and 58% to 62.1% for NiO/CdO with increasing the batch time from 25 to 75 min at 160 °C and 2 ml of H₂O₂ giving a clear indication that Fe₂O₃ support showed high reactive than other support toward ADS as well as to increase the residence time between the reactants and products.

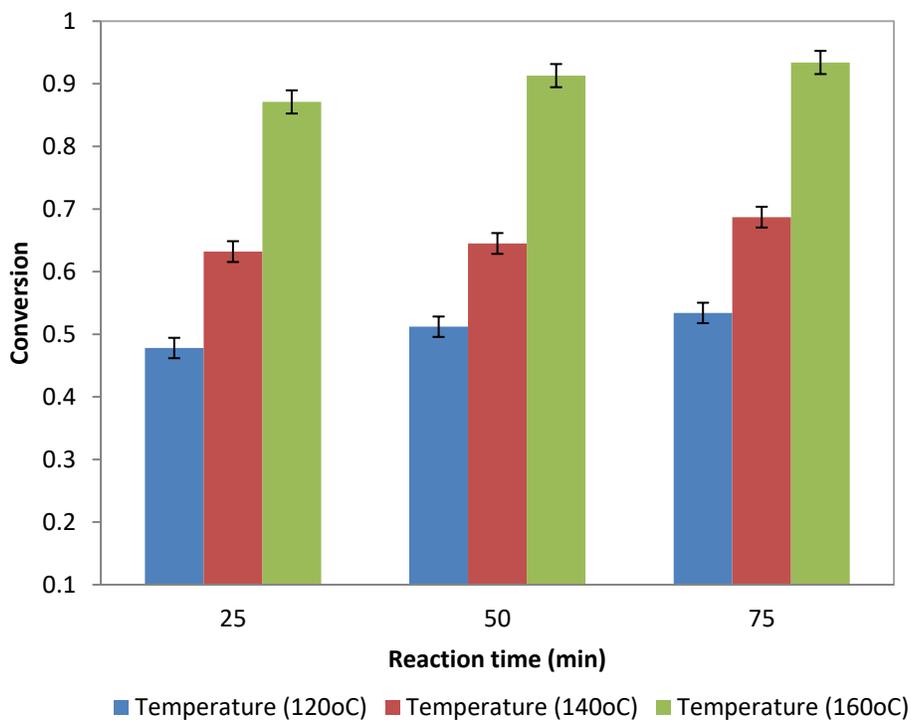


Figure 7: Influence of reaction time of sulfur conversion at H₂O₂ of 2 ml and catalyst weight of 0.5 g using NiO/Fe₂O₃ as a catalyst

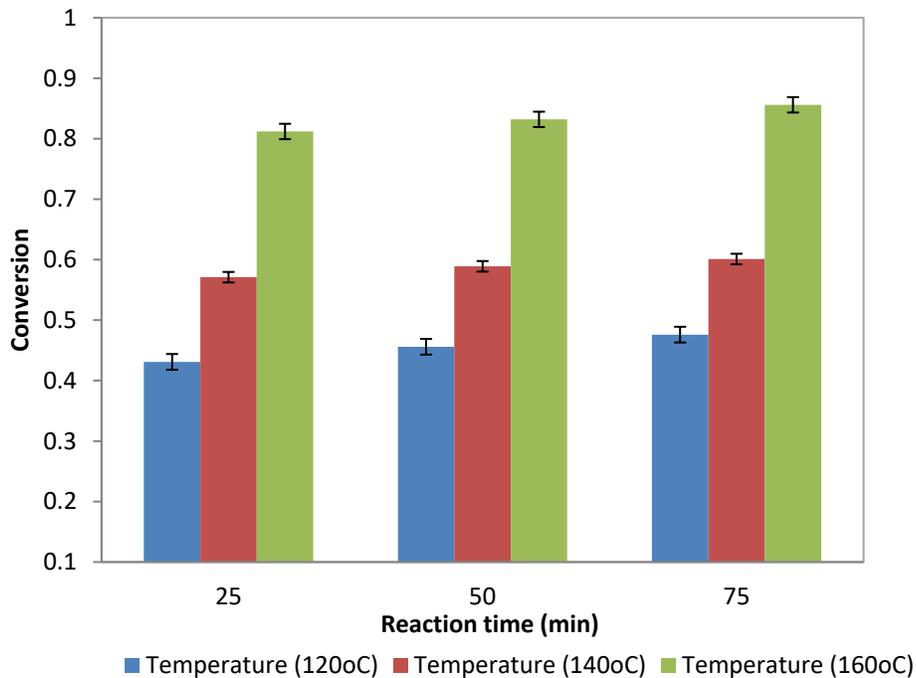


Figure 8: Influence of reaction time of sulfur conversion at H₂O₂ of 2 ml and catalyst weight of 0.5 g using NiO/Cr₂O₃ as a catalyst

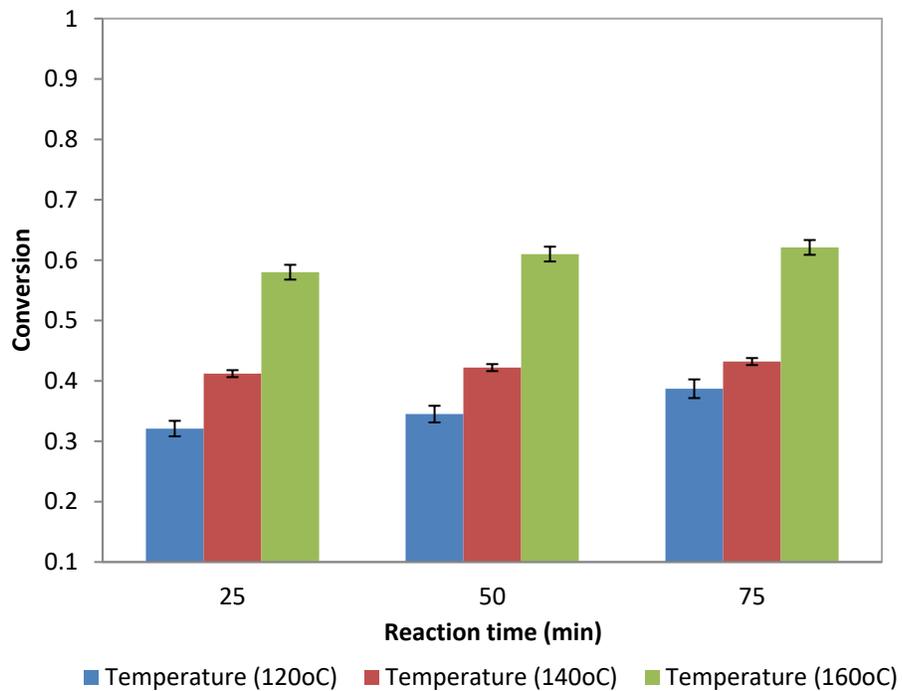


Figure 9: Influence of reaction time of sulfur conversion at H₂O₂ of 2 ml and catalyst weight of 0.5 g using NiO/CdO as a catalyst

3.2.3 Effect of Amount of Oxidant (H_2O_2) on ADS

Adsorption desulfurization process (ADS) is applied to evaluate the reactivity of the catalyst prepared (NiO/Fe_2O_3 , NiO/Cr_2O_3 and NiO/CdO) using novel digital baffle batch reactor (DBBR). Adsorptive desulfurization using porous (Fe_2O_3 , Cr_2O_3 and CdO) materials is based on the ability of a solid sorbent to selectively adsorb organic sulfur compounds from model light gas oil (LGO). In the present study, different sorbents were prepared via Ni loadings onto supports for enhancing LGO fuel by reducing sulfur content. To improve the sorption performance of (NiO/Fe_2O_3 , NiO/Cr_2O_3 and NiO/CdO) for sulfur removal, oxidative desulfurization is carried out in association with adsorptive desulfurization and hydrogen peroxide is used as an oxidizing agent for improving the adsorbent efficiency for sulfur removal. Effect of hydrogen peroxide (H_2O_2) dosages on percent sulfur removal are given in Figures 10, 11 and 12. As can be seen from these Figures, The total sulfur removal has increased in the presence of oxidant as the dosage of H_2O_2 in LGO increased from 1 to 2 ml.

The effect of the oxidizing agent (H_2O_2) on sulfur content with catalyst NiO/Fe_2O_3 utilizing adsorption desulfurization efficiency has shown in Figure 10 at 160 °C reaction temperature. The results showed that the sulfur removal efficiency increased with increasing the amount of oxidant (H_2O_2). Where, increasing such amount from 1 to 2 ml, the sulfur removal has increased from 76.7% to 93.4% using NiO/Fe_2O_3 and from 69.1% to 85.6% employing NiO/Cr_2O_3 as illustrated in the Figure 11 at 160 °C and 75 min for both catalysts. While, no high effect of oxidizing agent for sulfur removal using the catalyst (NiO/CdO) was observed (the sulfur removal was 48.7% to 62.1%) at 160 °C and 75 min as shown in the Figure 12. Increasing of oxidizing agent through ADS process, the concentration rate of sulfur compound has increased leading to increase the sulfur removal. Hydrogen peroxide (H_2O_2) attached as oxidant with the adsorbent showed a

tangible effect related to the sulfur removal using the new homemade nano-catalysts (NiO/Fe₂O₃, Cr₂O₃ and CdO) prepared in this study. Such strong active materials (active compounds) and support can be attracted to the high reaction among the hindered sulfur compounds and H₂O₂ giving high sulfur removal by converting them to sulfones which can easily be adsorbed on the catalysts [14,15].

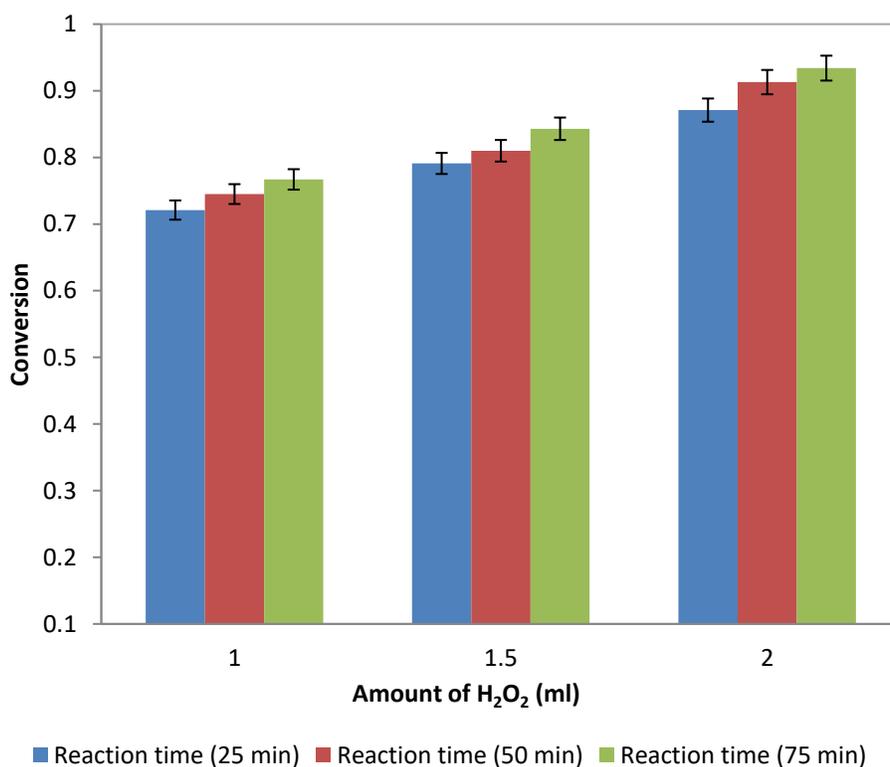


Figure 10: Effect of the amount of oxidant on adsorption desulfurization process ADS using NiO/Fe₂O₃ at reaction temperature of 160°C

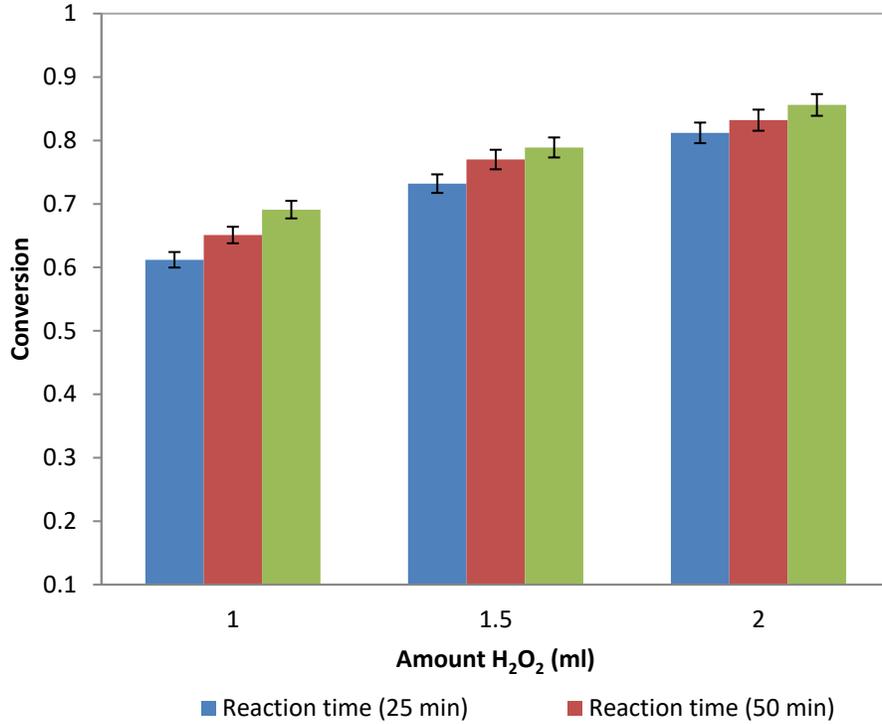


Figure 11: Effect of the amount of oxidant on adsorption desulfurization process ADS using NiO/Cr₂O₃ at reaction temperature of 160°C

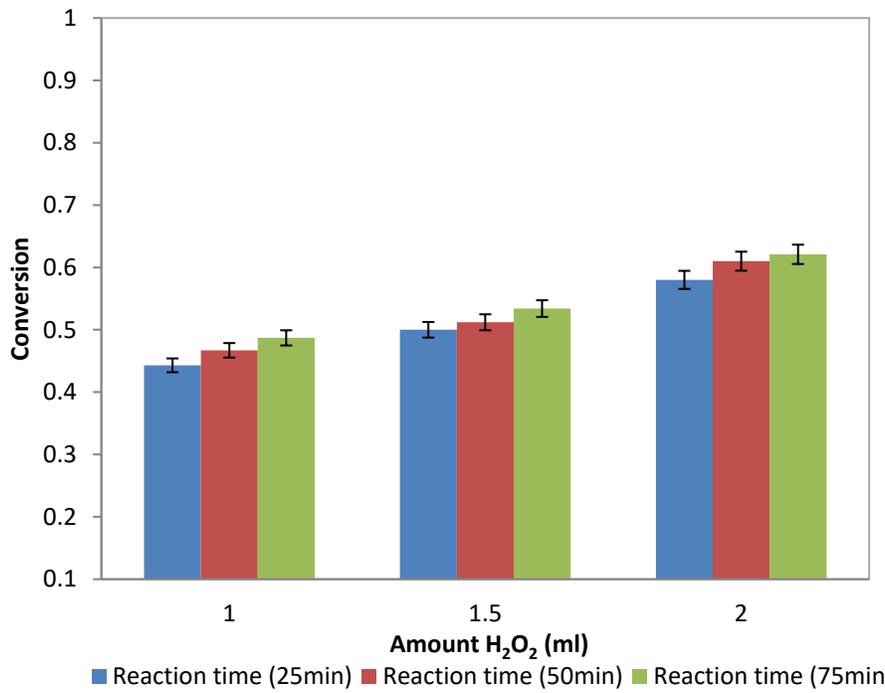


Figure 12: Effect of the amount of oxidant on adsorption desulfurization process ADS using NiO/CdO at reaction temperature of 160°C

3.2.4 Influence of Temperature on Adsorption Desulfurization Process

The impact of reaction temperature on the ADS reactions for sulfur removal (DBT conversion) is studied at 120, 140 and 160 °C utilizing different catalysts as shown in the Figure 13 and 14. From these Figures, it can be observed that the conversion is increased when the reaction temperature is increased [22,23]. Where, Figure 13 shows the effect of reaction temperature on ADS process for sulfur removal at 160°C, 2 ml of H₂O₂ using NiO/Fe₂O₃ and 93.4% of sulfur removal has obtained. As the temperature is increased from 120 °C to 160 °C, the conversion has increased from 42.1% to 84.3%, 73.8% to 78.9% and 29.9% to 53.4% with batch time of 75 min and 1.5 ml from H₂O₂ for NiO/Fe₂O₃, NiO/Cr₂O₃ and NiO/CdO, respectively (as shown in Figure 14). This behavior is due to fact that increasing temperature increases the number of molecules involving in the oxidation reaction by increasing the activation energy and as a result increasing the diffusion inside the pore of molecules of sulfur and oxygen [24]. Figure 15 and 16 illustrate the comparison among the catalysts prepared with respect to the catalyst type and sulfur conversion under the same operating condition of each catalyst and it has been reported that the best new homemade nano-catalyst for sulfur removal is NiO/Fe₂O₃. It is observed that the sulfur removal of DBT increased with increasing the reaction time at different temperatures. However, the temperature had a great influence on DBT removal during different time ranges [25, 26].

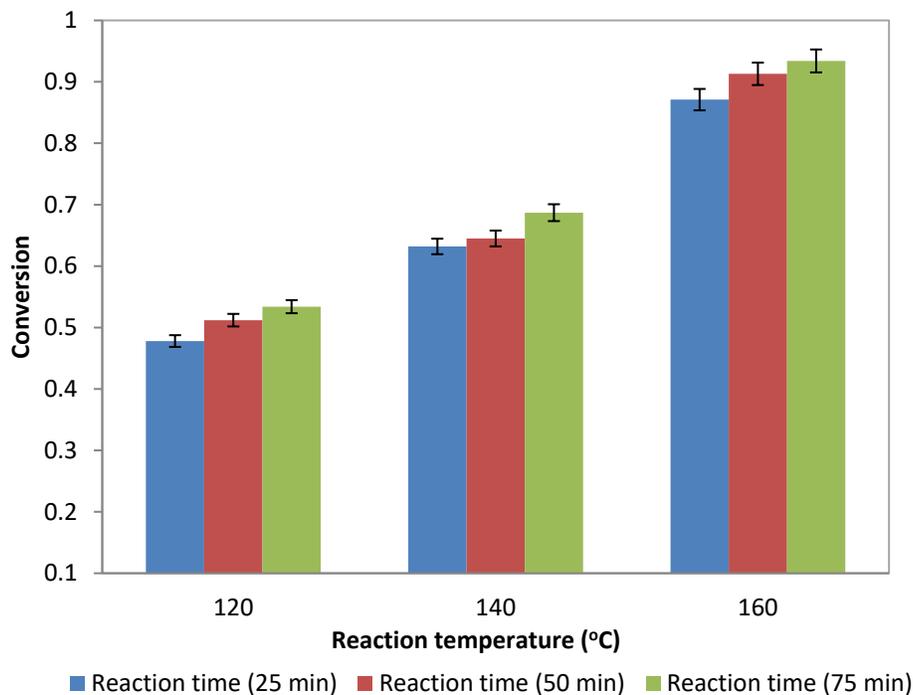


Figure 13: Effect of reaction temperature on ADS using NiO/Fe₂O₃ at 160 °C and 2 ml of H₂O₂

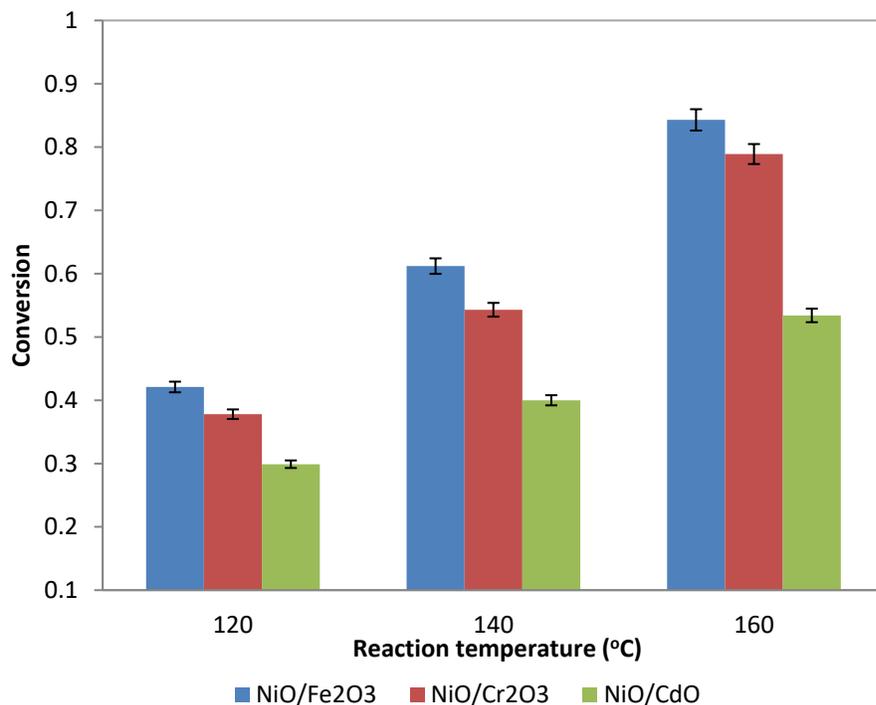


Figure 14: Effect of reaction temperature on ADS for different catalysts at 75min and 1.5 ml of H₂O₂

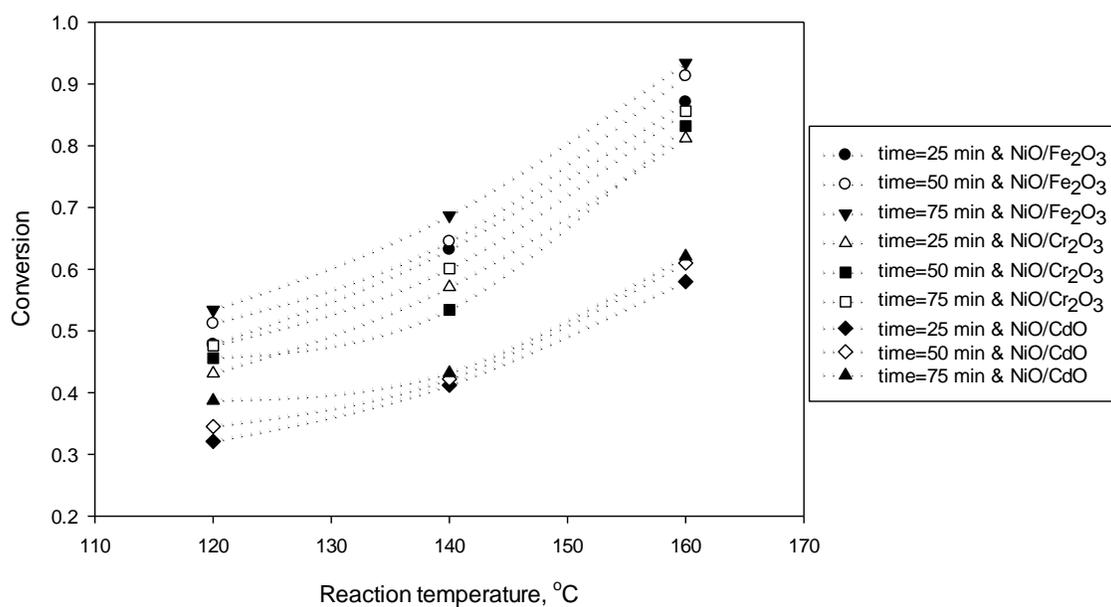


Figure 15: Comparison among the catalysts prepared at 2 ml of H₂O₂ with different reaction temperature and time

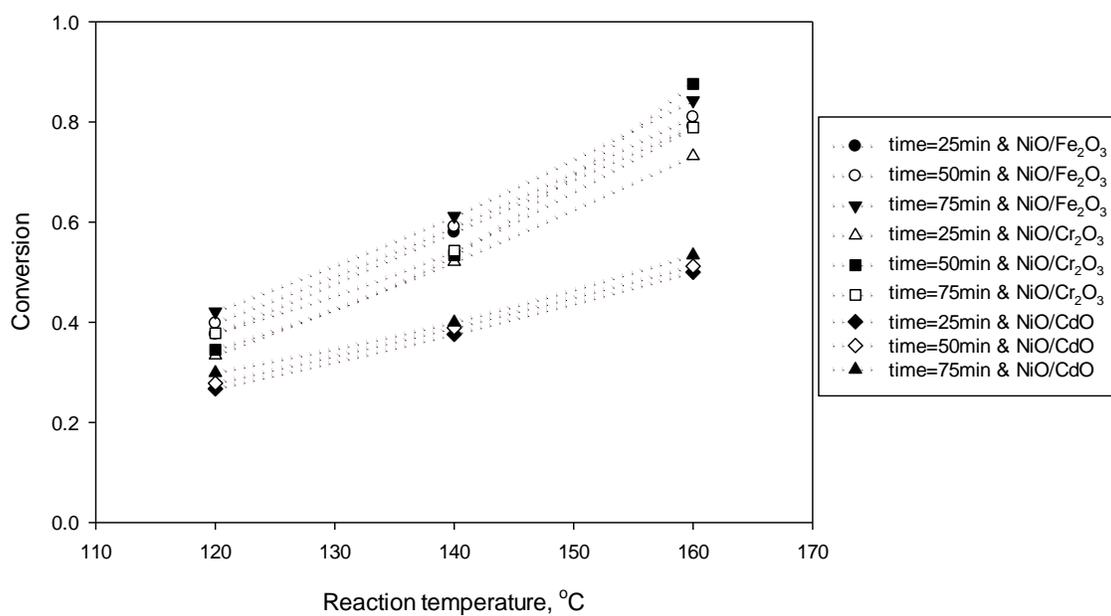


Figure 16: Comparison among the catalysts prepared at 1.5 ml of H₂O₂ with different reaction temperature and time

3.3 The Mechanism Suggested for Oxidative Desulfurization Reaction

The mechanism suggested for the oxidation desulfurization reactions based on nano-catalyst with hydrogen peroxide is described in Figure 17. The chemical reaction is occurred according to the following three steps. In the first step, the dibenzothiophene compounds are absorbed into the pore channel of the nano-catalyst ($\text{NiO}/\text{Fe}_2\text{O}_3$, $\text{NiO}/\text{Cr}_2\text{O}_3$ and NiO/CdO) through adsorption desulfurization process. After that, the active peroxy groups generated by Ni, and the oxygen produced via oxidizing agent (H_2O_2) will be utilized to oxidize the dibenzothiophene to corresponding sulfoxide in the second step. In the third step, sulfoxide (DBTO) generated will be converted to sulfone (DBTO₂).

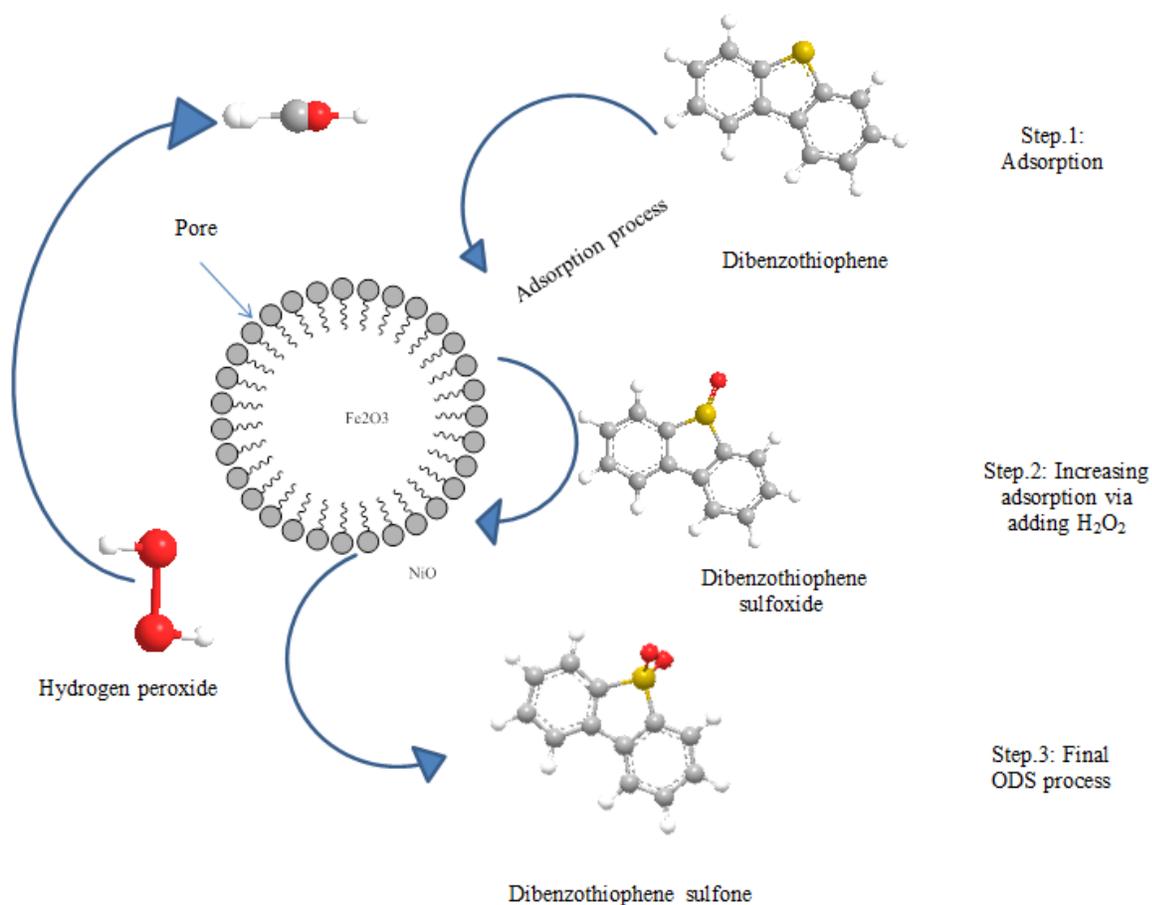


Figure 17: The mechanism of desulfurization process

4. Mathematical Modeling of Adsorption Desulfurization Process (ADS)

4.1 Model Based on Kinetics of ADS

The kinetics model related to the adsorption desulfurization process (ADS) is studied here based on hydrogen peroxide (H₂O₂) as oxidant for all the catalysts prepared (NiO/Fe₂O₃, NiO/Cr₂O₃ and NiO/CdO). Pseudo first and second order kinetics, which are expressed within the kinetic rate equation (described below) to find the best kinetic model through the comparison among correlation coefficients, are modeled here.

Mole balance equation on the digital baffle batch reactor (DBBR) for desulfurization process can be represented as [13,27,28]:

$$[Mole\ in\ DBBR] = [Mole\ out\ DBBR] + [Accumulation] + [Dissappearance\ by\ reaction] \quad (1)$$

The input and output chemical reaction materials (light gas oil, hydrogen peroxide (H₂O₂) and catalyst) for DBBR equal to zero. So,

$$[Mole\ in\ DBBR] = [Mole\ out\ DBBR] = 0 \quad \dots\dots (2)$$

Substitution equation (2) in equation (1), the following equation is obtained:

$$[Accumulation\ of\ reaction] = -[Dissappearance\ by\ reaction] \quad \dots\dots (3)$$

In adsorption desulfurization reaction, the oxidation reaction can find the value of the reaction accumulation and the chemical reaction disappearance, as follows:

$$Dissappearance\ of\ chemical\ reaction = \frac{dN_{DBT}}{dt} \quad \dots\dots (4)$$

$$Accumulation\ of\ reaction = -[R_{DBT}][V_{DBBR}] \quad \dots\dots (5)$$

Where, R_{DBT} represents the reaction rate of adsorption desulfurization process. Substitution, equation 4 and 5 in equation 3, the reaction rate of ADS at constant density is obtained:

$$-\left[\frac{dN_{DBT}}{dt}\right] = -[R_{DBT}][V_{DBBR}] \dots\dots\dots (6)$$

$$-\left[\frac{dC_{DBT}}{dt}\right] = -[R_{DBT}] \dots\dots\dots (7)$$

Pseudo order equation for adsorption desulfurization reaction is represented as follows:

$$-[R_{DBT}] = KC_{H_2O_2}^m C_{DBT}^n \dots\dots\dots (8)$$

The apparent rate constant ($K_{app.}$) can be expressed as [29]:

$$K_{app.} = KC_{H_2O_2}^m \dots\dots\dots (9)$$

For Pseudo first order (n=1) reaction and from equation (9), equation (8) can be rearranged to be:

$$-[R_{DBT}] = K_{app.}C_{DBT} \dots\dots\dots (10)$$

$$-\left[\frac{dC_{DBT}}{dt}\right] = K_{app.}C_{DBT} \dots\dots\dots (11)$$

$$\int_{C_{DBT_0}}^{C_{DBT}} \frac{dC_{DBT}}{C_{DBT}} = K_{app.} \int_0^t dt \dots\dots\dots (12)$$

$$\ln \frac{C_{DBT_0}}{C_{DBT}} = K_{app.}t \dots\dots\dots (13)$$

For Pseudo second order (n=2) reaction, the following reaction rate equation can be obtained

$$-[R_{DBT}] = K_{app}.C_{DBT}^2 \quad \dots\dots\dots (14)$$

$$-[R_{DBT}] = -\frac{dC_{DBT}}{dt} = K_{app}.C_{DBT}^2 \quad \dots\dots\dots (15)$$

$$\int_{C_{DBT_0}}^{C_{DBT}} \frac{dC_{DBT}}{C_{DBT}^2} = K_{app}. \int_0^t dt \quad \dots\dots\dots (16)$$

The final expression for the pseudo second order reaction can be written as:

$$\frac{1}{C_{DBT}} = \frac{1}{C_{DBT_0}} + K_{app}.t \quad \dots\dots\dots (17)$$

4.2 Kinetic Model for Adsorption Desulfurization Reaction

Amount of oxidant (H₂O₂) can effect on sulfur removal found in LGO liquid fuel at different reaction times, reaction temperatures and catalysts. The reaction rate constants based on the pseudo first and second order kinetics model have been estimated at different oxidant amounts and reaction temperatures. The comparison between such two kinetic models (first order and second order) for adsorption desulfurization reaction employing different Nano-catalysts (NiO/Fe₂O₃, NiO/Cr₂O₃ and NiO/CdO) prepared are shown in Table 3–5 for the purpose of giving further insight of the process. Based on the results presented in these Tables, it has been found that the ADS reactions of model fuel LGO employing the prepared all type of Nano-catalysts is followed by the pseudo second order kinetic giving a good fit than pseudo first order kinetics.

Table 3: Kinetic model result for ADS using NiO/Fe₂O₃

Catalyst	Order of chemical reaction	Reaction temperature, °C	Rate constant (min) ⁻¹ Con ¹⁻ⁿ	Amount of oxidant
NiO/Fe ₂ O ₃	First order	120	0.0055	1 ml (H ₂ O ₂)
		140	0.0114	
		160	0.0194	
		120	0.007	1.5 ml (H ₂ O ₂)
		140	0.012	
		160	0.084	
		120	0.0095	2 ml (H ₂ O ₂)
		140	0.0155	
		160	0.036	
	Second order	120	8.116*10 ⁻⁶	1 ml (H ₂ O ₂)
		140	2.13*10 ⁻⁵	
		160	5.163*10 ⁻⁵	
		120	1.14*10 ⁻⁵	1.5 ml (H ₂ O ₂)
		140	2.475*10 ⁻⁵	
		160	8.422*10 ⁻⁵	
		120	1.645*10 ⁻⁵	2 ml (H ₂ O ₂)
		140	3.442*10 ⁻⁵	
		160	2.21*10 ⁻⁴	

Table 4: Kinetic model result for ADS using NiO/Cr₂O₃

Catalyst	Order of chemical reaction	Reaction temperature, °C	Rate constant (min) ⁻¹ Con ¹⁻ⁿ	Amount of oxidant
NiO/Cr ₂ O ₃	First order	120	0.000516	1 ml (H ₂ O ₂)
		140	0.0092	
		160	0.015	
		120	0.017	1.5 ml (H ₂ O ₂)
		140	0.01	
		160	0.02	
		120	0.0086	2 ml (H ₂ O ₂)
		140	0.012	
		160	0.025	
	Second order	120	7.415*10 ⁻⁶	1 ml (H ₂ O ₂)
		140	1.56*10 ⁻⁵	
		160	3.507*10 ⁻⁵	
		120	4.073*10 ⁻⁵	1.5 ml (H ₂ O ₂)
		140	1.863*10 ⁻⁵	
		160	5.865*10 ⁻⁵	
		120	1.424*10 ⁻⁵	2 ml (H ₂ O ₂)
		140	2.362*10 ⁻⁵	
		160	9.325*10 ⁻⁵	

Table 5: Kinetic model result for ADS using NiO/CdO

Catalyst	Order of chemical reaction	Reaction temperature, °C	Rate constant (min) ⁻¹ Con ¹⁻ⁿ	Amount of oxidant
NiO/CdO	First order	120	0.0035	1 ml (H ₂ O ₂)
		140	0.0056	
		160	0.008	
		120	0.0047	1.5 ml (H ₂ O ₂)
		140	0.006	
		160	0.0101	
		120	0.0065	2 ml (H ₂ O ₂)
		140	0.0075	
		160	0.0129	
	Second order	120	4.791*10 ⁻⁶	1 ml (H ₂ O ₂)
		140	8.33*10 ⁻⁶	
		160	1.374*10 ⁻⁵	
		120	6.69*10 ⁻⁶	1.5 ml (H ₂ O ₂)
		140	1.045*10 ⁻⁵	
		160	1.797*10 ⁻⁵	
120		9.903*10 ⁻⁶	2 ml (H ₂ O ₂)	
140		1.193*10 ⁻⁵		
160		2.57*10 ⁻⁵		

4.3 Half-live period for Nano-Catalyst

From Nano-catalysts (NiO/Fe₂O₃, NiO/Cr₂O₃ and NiO/CdO) obtained in this work, the half-live period (t_{1/2}) is also evaluated for each catalyst by using the following equations at 160°C and 2 ml of H₂O₂:

For NiO/Fe₂O₃: $t_{1/2} = \frac{\ln 2}{K} = \frac{0.6931}{0.036} = 19.25 \text{ min}$ (18)

For NiO/Cr₂O₃: $t_{1/2} = \frac{\ln 2}{K} = \frac{0.6931}{0.025} = 27.72 \text{ min}$ (19)

For NiO/CdO: $t_{1/2} = \frac{\ln 2}{K} = \frac{0.6931}{0.0129} = 53.73 \text{ min}$ (20)

The half-live period of DBT adsorption desulfurization process was 19.25, 27.72 and 53.73 min for NiO/Fe₂O₃, NiO/Cr₂O₃ and NiO/CdO, respectively. Mass ratio of model fuel (light gas oil) to

Nano-catalyst was about 150/0.5 for all catalysts prepared separately. Accordingly, it was further considered that the adsorption and diffusion on kinetic model having an effect on DBT conversion through the oxidation reaction. Such effect of adsorption diffusion process was ignored in the public domain.

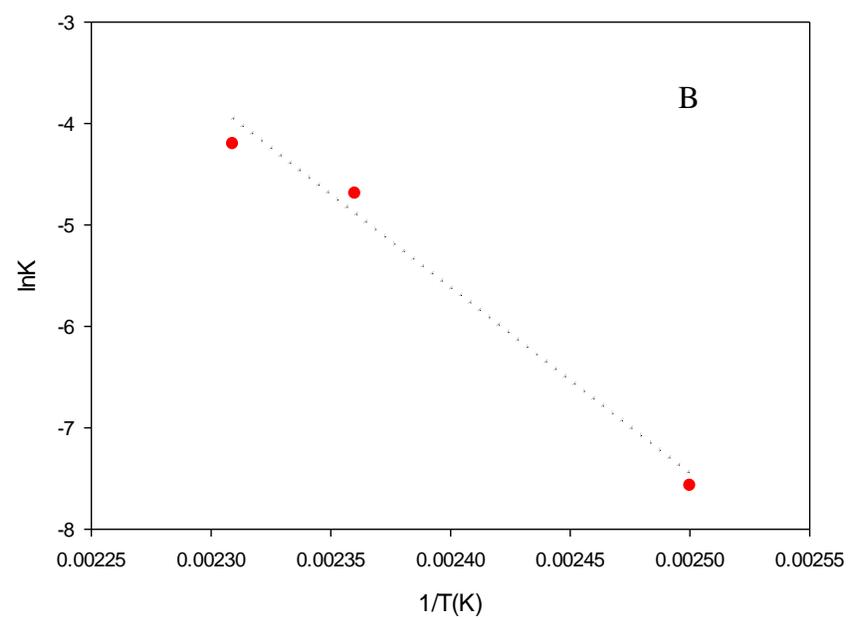
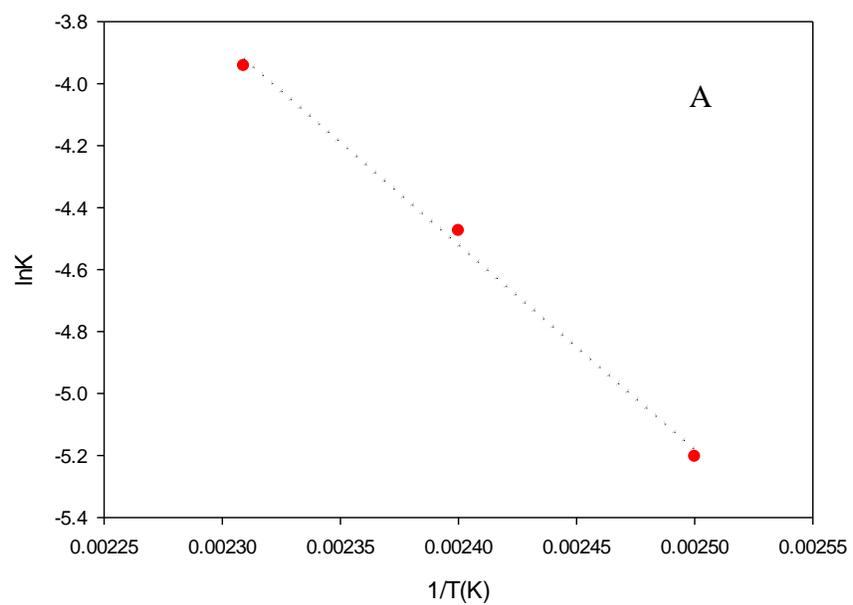
4.4 The Activation Energy for Adsorption Desulfurization Process

The activation energy can be estimated via Arrhenius equation, as follows [30-32]:

$$K = A_o \text{Exp} \left[-\frac{EA}{RT} \right] \dots\dots\dots (21)$$

$$\ln K = \ln A_o - \left[\frac{EA}{RT} \right] \dots\dots\dots (22)$$

A plot of (ln K) against (1/T(K)) [33] will give a straight line with a slope equal to (-EA/R), (R) gas constant and (EA) activation energy is then linearly evaluated as shown in Figure18 A, B, and C for NiO/Fe₂O₃, NiO/Cr₂O₃ and NiO/CdO, respectively. The values of the activation energies for these catalysts of the relevant reactions are 54.983, 151.871 and 36.006 KJ/mole for NiO/Fe₂O₃, NiO/Cr₂O₃ and NiO/CdO, respectively. It is clearly observed based on the results, the low amount of the prepared nano-catalyst (NiO/Fe₂O₃, NiO/Cr₂O₃ and NiO/CdO) gives higher activation energy for such reactions studied here indicating that the new nano-catalyst prepared in this work can be utilized confidently to reactor design, operation and control.



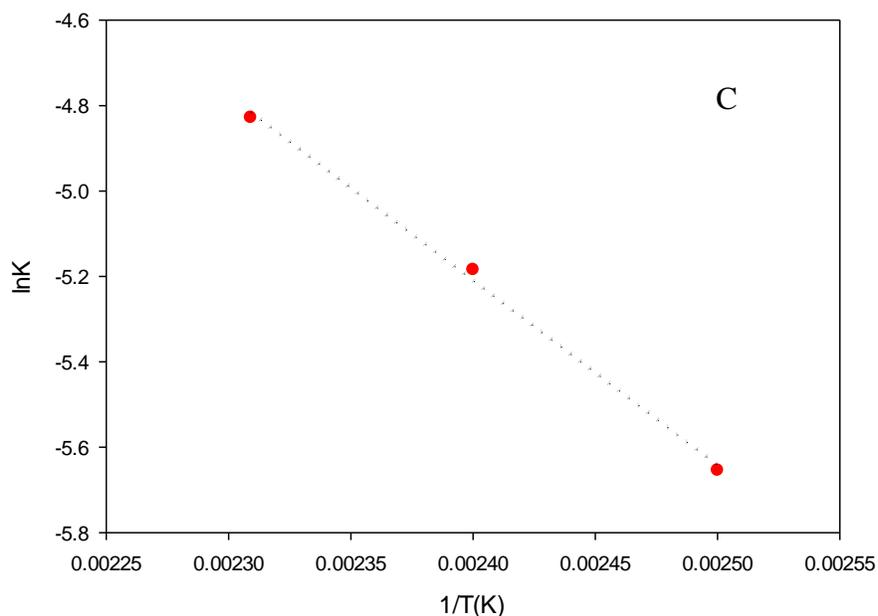


Figure 18: lnK versus 1/K of adsorption desulfurization process for (A) NiO/Fe₂O₃, (B) NiO/Cr₂O₃ and (C) NiO/CdO

5. Comparison results between this study and previous studies

Feedstocks that undergo catalytic refining processes generate products, such as gasoline and diesel with large amounts of sulfur containing organic compounds. The associated organic sulfur compounds exist in several forms such as mercaptans, aliphatic and cyclic thioethers and thiophenes and their derivatives. The products containing sulfur compounds are usually desulfurized through several processes using well-established catalyst systems [34]. There are two approaches used to reduce sulfur level in petroleum refining business, conventional hydrodesulfurization (HDS) and non-hydrodesulfurization (Non-HDS). The comparison results (related to sulfur removal compounds by different methods) and parameters between this study and last studies are shown in the Table 6 and 7.

Table 6: Comparison results between this study and last studies related to sulfur removal compounds by different methods

Process method	Operating conditions	Feedstock	Reactor	Catalyst	Removal	Requirement	References
Desulphurization via Extraction	Ionic liquid /Model diesel 1:3, time 30 min	LGO	Batch	-	82.9%	Solvent : [BMIM][FeCl ₄]	[35]
Hydrodesulfurization	Temp.: 380-450°C Pressure 6 MPa LHSV 1 hr ⁻¹	LGO	Fixed bed reactor	CoMo/Al ₂ O ₃ ,	92%	Excess hydrogen	[36]
Desulphurization by Precipitation	Temp.: 40°C Time: 5 hr	Heavy crude oil	Batch	Fe and H-bentonite	81.4385%	Fe-Bentonite	[37]
Adsorption desulfurization and oxidative desulfurization	Time: 75 min Temp.: 175°C at atmospheric pressure	LGO	Novel reactor (DBBR)	NiO/Fe₂O₃, NiO/Cr₂O₃ NiO/CdO	93.4%, 85.6%, 62.1%	Oxidant (H₂O₂)	This study

Table 7: Comparison parameters between this study and last studies

Parameter	Previous work	This study
Catalyst	Traditional	New
Design reactor	Batch, semi batch and TBR three phase	Novel reactor (DBBR)
Support of catalyst	Traditional (Al ₂ O ₃ , AC, zeolite and other)	New (Fe ₂ O ₃ , Cr ₂ O ₃ and CdO)
Active materials	Pd, Mo, Ag and others	Ni
Oxidant	H ₂ SO ₄ , Air, O ₃ , TBHP and others	H ₂ O ₂
Operating conditions	Severe	Moderate without pressure
Pollution	Pollutes air by H ₂ S	Environmental friendly
Maintenance	High cost	Low cost
catalyst structure	Particle	Nano catalyst
Physical properties	Mostly changed	Fixed
Hydrocarbon fuel	broken	Adding oxygen
Dead zones	Found	Eliminated by the new design

6. Conclusions

A new synthetic nano-catalyst (NiO/Fe₂O₃, NiO/Cr₂O₃ and NiO/CdO) has prepared by IWI method with the same particle sizes for all (20 nm) to improve the adsorption desulfurization process using new design digital baffle batch reactor (DBBR). The adsorption desulfurization process of the adsorbents has strongly dependent on the particle sizes of the support, where the surface of such adsorbents having similar role of the active compounds. NiO/Fe₂O₃ is found very well adsorbent toward sulfur compound with sulfur removal 93.4% at moderate conditions. The Ni/Cr₂O₃ has also shows an excellent desulfurization performance giving sulfur conversion of 85.6%. This interaction of the metal (Ni) with metals oxide (Fe₂O₃, Cr₂O₃ and CdO) could prevent Ni phase from agglomeration and assisting the sulfur atom to transfer from Ni phase to Fe₂O₃, Cr₂O₃ and CdO through the structure within the ADS. Addition of H₂O₂ has significantly improved the sorption performance of (NiO/Fe₂O₃, NiO/Cr₂O₃ and NiO/CdO) and more than 90% sulfur removal could be achieved in the presence of oxidant.

The adsorbent prepared NiO/CdO having lower activation energy (36.006 kJ/mol) than those obtained by NiO/Fe₂O₃ adsorbent (54.83 kJ/mol) and NiO/Cr₂O₃ (151.871KJ/mol). Such observations indicating that the new nano-catalyst prepared in this work can confidently be utilized to reactor design, operation and control. The best kinetics model related to the adsorption desulfurization process (ADS) has also studied here based on hydrogen peroxide (H₂O₂) as oxidant for all the catalysts prepared. Second order kinetics model have been reported for ADS reaction, which can be used to represent the system.

Reference

1. Gruenspecht, H., Selected US energy issues: a view from the Energy Information Administration. 2016.
2. Emeritus. Energy Transitions: Global and National Perspectives (Second expanded and updated edition).
3. Sarda, K.K, Bhandari, A., Pant, K.K., Jain, S. Deep desulfurization of diesel fuel by selective adsorption over Ni/Al₂O₃ and Ni/ZSM-5 extrudates. *Fuel*, 2012, 39: pp. 86-91.
4. Armstrong, S.M., Sankey, B.M., and Voordouw, G. (1997). Evaluation of sulfate reducing bacteria for desulfurizing bitumen or its fractions. *Fuel*, **76**, pp 223.
5. Babich, I.V., and Moulijn, J.A. Science and technology of novel processes for deep desulfurization of oil refinery streams: a review. *Fuel*, 2003, 82: pp. 607–631.
6. Kabe T., Ishihara A., Qian W. Hydrodesulfurization and hydrodenitrogenation, Kodansha Ltd., Tokyo, WILEY-VCH Verlag GmbH, Weinheim, 1999.
7. Nawaf, A.T., Jarullah, A.T., Gheni, S.A., Mujtaba, I.M. Development of kinetic and process models for the oxidative desulfurization of light fuel, using experiments and the parameter estimation technique. *Industrial & Engineering Chemistry Research*, 2015. 54(50): p. 12503-12515.
8. Liu, Y, Gao L, Wen, L and Zong B. Recent Advances in Heavy Oil Hydroprocessing Technologies. *Recent Patents on Chemical Engineering*, 2009, 2: p. 22-36.
9. Ali, M.F., Al-Malki, A., El-Ali, B., Martinie, G., and Siddiqui, M.N. Deep desulphurization of gasoline and diesel fuels using non-hydrogen consuming techniques. *Fuel*, 2006, 85: p.1354-1363.

10. Palaić, N., Setrić- Bionda, K., Margeta, D. and Podolski, Š. Oxidative Desulphurization of Diesel Fuels. *Chemical-biochemical engineering*, 2015, 29(3): p. 323-327.
11. Qian, E.w. Development of novel non-hydrogenation desulfurization process-oxidative desulfurization of distillate. *Journal of the Japan petroleum institute*, 2008, 51(1): p.14-31.
12. Abdulateef, L.T., Nawaf, A.T., Mahmood, Q. A., Dahham, O. S., Noriman, N. Z., Shayfull, Z. Preparation, characterization and application of alumina nanoparticles with multiple active component for oxidation desulfurization. *AIP Conference Proceedings* 2030, 020031 (2018); DOI: 10.1063/1.5066672.
13. Nawaf, A.T., Jarullah, A.T., Abdulateef, L.T. Design of a Synthetic Zinc Oxide Catalyst over Nano-Alumina for Sulfur Removal by Air in a Batch Reactor. *Bulletin of Chemical Reaction Engineering & Catalysis*, 2019. **14**(1): p. 79-92.
14. Sarda, K.K., Bhandari, A., Pant, K.K., Jain, S. Deep desulfurization of diesel fuel by selective adsorption over Ni/Al₂O₃ and Ni/ZSM-5 extrudates. *Fuel*, 2012, 93, p. 86–91.
15. Ugal, J., Jimaa, RB., Al-Jubori, W.M., Abbas, B.F., Al-Jubori, N.M. Oxidative Desulfurization of Hydrotreated Gas Oil using Fe₂O₃ and Palladium Loaded over Activated Carbon as catalyst. *Oriental journal of chemistry*, 2018, 34 (2): p. 1091-1097.
16. Nawaf, A.T., Gheni, S.A., Jarullah, A.T., Mujtaba, I.M. Optimal design of a trickle bed reactor for light fuel oxidative desulfurization based on experiments and modeling. *Energy & Fuels*, 2015, **29**(5): p. 3366-3376.
17. Anandan K., Rajendran V. Morphological and size effects of NiO nanoparticles via solvothermal process and their optical properties. *Mater. Sci. Semicond. Process*, 2011, 14: p. 43.

18. Sheena, P.A., Priyanka, K.P., Sabu, N.A., Sabu, B., Varghese, T., Effect Of Calcination Temperature On The Structural And Optical Properties Of Nickel Oxide Nanoparticles. *nanosystems: physics, chemistry, mathematics*, 2014, 5 (3): P. 441–449.
19. Qiao, H., Wei, Z., Yang, H., Zhu, L., Yan, X. Preparation and Characterization of NiO Nanoparticles by Anodic Arc Plasma Method. *Nanomaterials*, 2009, p.5.
20. Shihab, M.A., Nawaf, A.T., Mohamedali, S.A., Alsalmoney, M. N. Improving Porosity of Activated Carbon Nanotubes via Alkali Agents for the Enhancement of Adsorptive Desulfurization Process. *Materials Science Forum*, 2020, 1002: p. 423-434.
21. Saleh, A.T., Sulaiman, O.K., AL-Hammadi, A.S., Dafalla, H., Danmaliki, I.G. Adsorptive desulfurization of thiophene, ben-zothiophene and dibenzothiophene over activated carbon manganese oxide nanocompo-site: With column system evaluation. *Cleaner Prod*, 2017, 17: p. 959-6526.
22. Nawaf, A.T., Gheni, S.A., Jarullah, A.T., Mujtaba, I.M. Improvement of fuel quality by oxidative desulfurization: Design of synthetic catalyst for the process. *Fuel Processing Technology*, 2015, 138: p. 337–343.
23. Xun, S., Jiang, W., Guo, T., He, M., Ma, R., Zhang, M., Zhu, W., Li, H. Magnetic mesoporous nanospheres supported phosphomolybdate-based ionic liquid for aerobic oxidative desulfurization of fuel. *Journal of colloid and interface science*, 2019, 534:pp. 239-247.
24. Chan, K., Jung, J., Lee, J., Sang, B., Kyungil, C., Sang, H. Hydrodesulphurization of DBT, 4- MDBT, and 4,6-DMDBT on fluorinated CoMoS/Al₂O₃ catalysts. *Appl. Catal. A*, 2000, 200: 233-242.

25. Ding, W., Zhu, W., Xiong, J., Yang, L., Wei, A., Zhang, M., Li, H. Novel heterogeneous iron-based redox ionic liquid supported on SBA-15 for deep oxidative desulfurization of fuels. *Chemical engineering journal*, 2015, 266:pp. 213-221.
26. Wu, P., Wu, Y., Chen, L., He, J., Hua, M., Zhu, F., Chu, X., Xiong, J., He, M., Zhu, W., Li, H, Boosting aerobic oxidative desulfurization performance in fuel oil via strong metal-edge interactions between Pt and h-BN. *Chemical Engineering Journal*, 2020, 380: pp.122526.
27. Levenspiel, O., "Chemical Reaction Engineering", 3rd edition, Department of Chemical Engineering, Oregon State University, John Wiley & Sons, 1999.
28. Ahmed, G.S., Jarullah A. T., Al-Tabbakh, B.A., Mujtaba, I.M. Design of an environmentally friendly reactor for naphtha oxidative desulfurization by air employing a new synthetic nano-catalyst based on experiments and modelling. *Journal of Cleaner Production*, 2020, 257: p. 120436.
29. Jose, N., Sengupta. S., Basu, J.K. Optimization of oxidative desulfurization of thiophene using Cu/titanium silicate-1 by box-behnken design. *Fuel*, 2011, 90: pp.626–632
30. Sampanthar, J.T., Xiao, H., Dou, J., Nah, T.Y., Rong, X., and Kwan, W.P. A novel oxidative desulfurization process to remove refractory sulphur compounds from diesel fuel. *Applied Catalysis B: Environmental*, 2006, 63: pp. 85–93.
31. Sachdeva, T. O., and Pant K. K. Deep desulfurization of diesel via peroxide oxidation using phosphotungstic acid as phase transfer catalyst. *Fuel Processing Technology*, 2011 pp.1-5.
32. Rezvani, M.A., Khandan, S., and Aghmasheh, M. Synthesis and characterization of new nanocomposite TBA-PW11Ni@NiO as an efficient and reusable heterogeneous catalyst in

- oxidative desulfurization of gasoline. Taiwan Institute of chemical engineers, 2017, pp. 1-8.
33. Sachdeva, T. O., Pant, K. K. Deep desulfurization of diesel via peroxide oxidation using phosphotungstic acid as phase transfer catalyst. *Fuel Processing Technology*, 2010, pp.1-5.
34. Chen, B., Huang, C., Zhang, J., Liu, Z. and Li, Y. Desulphurization of gasoline by extraction with new ionic liquids. *Energy Fuels*, 2004, 18, pp. 1862-1864.
35. Gao. H., Xing, J., Li, Y., Li, W., Liu, Q., Liu, H. Desulfurization of Diesel Fuel by Extraction with Lewis-Acidic Ionic Liquid. *Separation Science and Technology*, 2009, 44: 971–982.
36. YU, H., LI, S., JIN, G. hydrodesulfurization and hydrodenitrogenation of diesel distillate from fushun shale oil. *Oil Shale*, 2010, 27(2): pp. 126–134.
37. Al-Bidry, M.A., Azeez, R.A. Removal sulfur components from heavy crude oil by natural clay. *Ain Shams Engineering Journal*, 2020. In press, doi.org/10.1016/j.asej.2020.03.010.