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Oxidative Desulfurization of Petroleum Products Using Decorated Cobalt Oxide on the Surface of Modified Carbon Nanotubes

H. Hassanpour Souderjani, A. Kazemi-Beydokhti *

Department of Chemical Engineering, School of Petroleum and Petrochemical Engineering, Hakim Sabzevari University, Sabzevar, Iran

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ABSTRACT

Due to the dangerous effects of sulfur in hydrocarbon compounds and its impact on environmental health, a new formulation based on surface-modified carbon nanotubes and cobalt oxide has been prepared. Oxidative desulfurization is the main section of this process that is utilized to reduce this impurity. After decorating cobalt oxide on the surface of nanotubes, the TEM images and Thermogravimetric analysis were studied to evaluate the structure of this complex. The results show that the combination of metal oxide and functionalized nanoparticles presents higher efficiency in sulfur removal. In addition, the reaction rate was raised by increasing the number of functional groups on the surface of nanotubes. Then, the influence of temperature, the reaction time and the concentration of the oxidizing agent in the sample was investigated. The results show that the higher temperature and higher number of oxidizing agents could provide higher efficiency in the desulfurization process. Due to the presence of CNTs in the synthesized catalyst, it is possible that sulfur compounds get adsorbed with CNT. By matching the data with the Pseudo first and second-order adsorption kinetics, it was found that the adsorption is done as pseudo-first-order adsorption kinetics. Since the ODS process is performed by a chemical reaction, the kinetics of the reaction were adapted to the first-order equation and the activation energy required for the reaction was calculated. This result can be utilized for the better desulfurization of hydrocarbon fuels for different applications.

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1. Introduction

The use of fossil fuels, which produces a lot of greenhouse gases, is very common in different countries. The sulfur compounds, as the main impurities present in these fuels, cause pollution, acid rain and a large range of

*Corresponding author: a.kazemi@hsu.ac.ir (A. Kazemi Beydokhti)

respiratory diseases. For this reason, extensive research has been carried out on removing the sulfur compounds from hydrocarbon fuels [1-4]. Sulfur compounds are found in crude oil as thiophene and its derivatives. There are varied types of sulfur impurities, with different concentrations, in fossil fuels by increasing the boiling point, the concentration and complexity of sulfur compounds increase [5]. Figure 1 shows the different types of sulfur compounds [6] most of which contain thiophene, benzothiophene (BT) and dibenzothiophene (DBT). These compounds cause many problems for human life and living organisms [7]. In addition, sulfur is the main reason for corrosion in equipment and pipelines, and for the catalyst poisoning in the oil, gas, and petrochemical industries [8, 9]. Therefore, the developed countries have very strict laws for the allowed concentration of sulfur impurities. These values are 10 and 5ppm for the diesel and gasoline respectively [10].

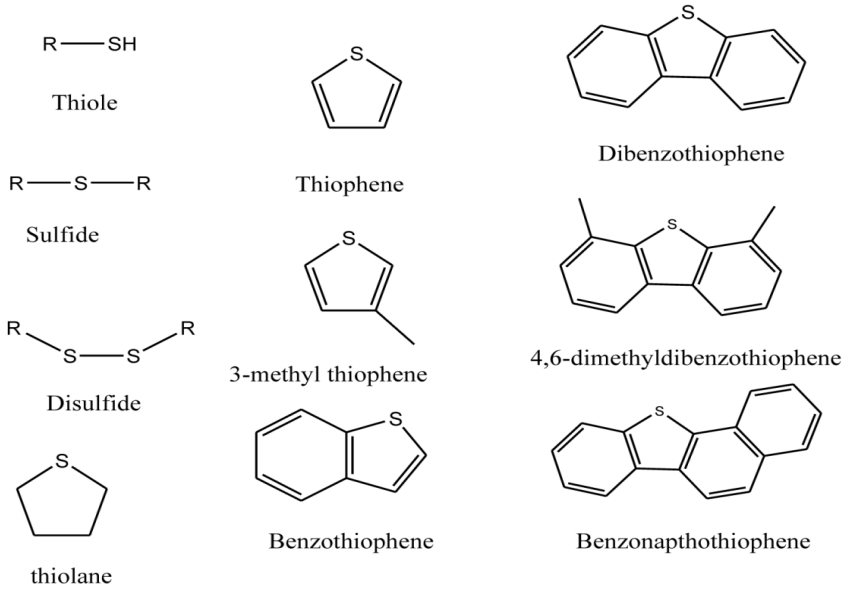

Figure 1. Sulfur compounds in fossil fuels.

There are various methods to remove sulfur from hydrocarbon fuels [5, 11, 12]. One of the conventional methods is desulfurization with hydrogen (HDS) [13]. This method has several disadvantages including the high economic costs, need for special equipment, and harsh operating conditions such as high temperature and pressure [2]. Researchers try to economically find a better way with normal conditions. With oxidative desulfurization (ODS), under normal operating conditions, the maximum removal of sulfur (90 to 99.85 %) from fossil fuels can be achieved [3, 4]. ODS has two main parts: I) The conversion of sulfur compounds to sulfone and sulfoxide by using an oxidizing agent and II) The removal of oxidized compounds using various adsorption or extraction methods. At ODS, the selective oxidant is very important and must have high selectivity of sulfur compounds and the Oxidants should not oxidize aromatic compounds and olefins. The most common oxidant is H_2O_2 or CH_3COOH. Figure 2 shows the oxidation reaction of sulfur compounds in the presence of hydrogen peroxide in the ODS process. The polarity of

sulfur compounds changes with the oxidation of sulfur compounds to sulfoxides and sulfones. Polarity makes it easier to remove sulfur by extraction or adsorption [5]. ODS performs in the presence of heterogeneous catalysts prepared from the oxide-mediated metals of V, W, Mo, Mn, Co, Fe supported on alumina, silica, and titanium [14].

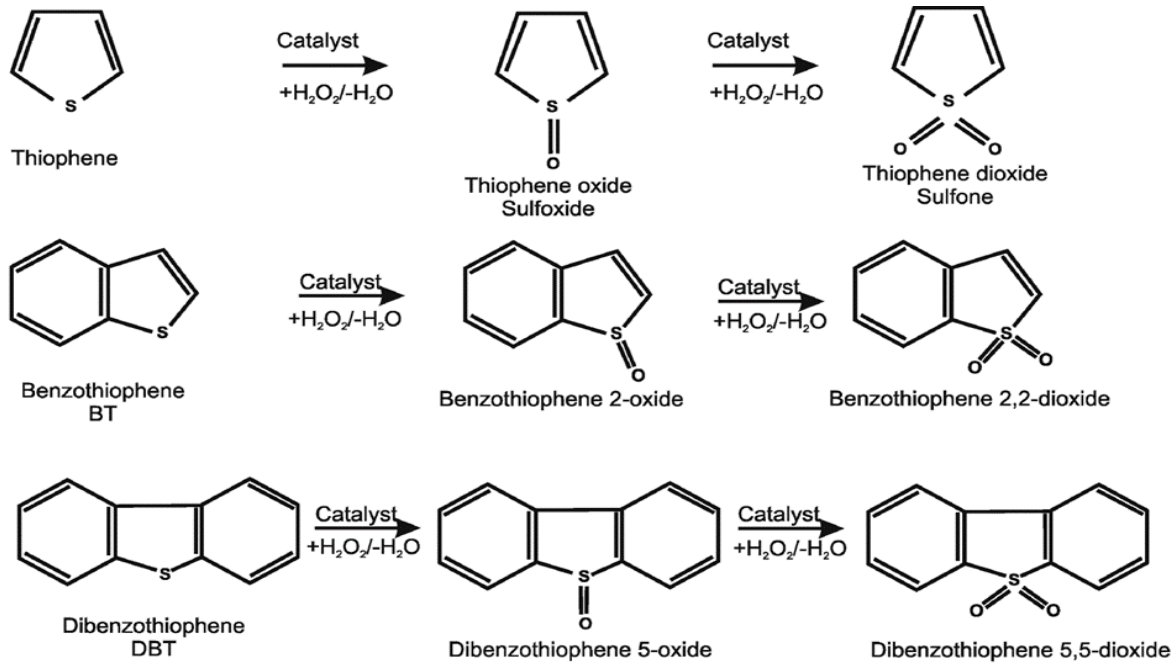

Figure 2. Oxidation reaction of sulfur compounds to sulfoxides and sulfones [5].

Due to the unique electrical, physical, mechanical, and chemical properties of carbon nanotubes (CNTs), various attempts have been made to utilize this nanoparticle in similar processes [15, 16]. Using hybrid materials containing metal oxides and CNTs is one of these techniques. Mohammedi et al. used palladium metal oxide and functionalized CNTs under ambient conditions and could remove 90 % of sulfur in the fuel [3]. In another study, the molybdenum oxide and surface modified CNTs were investigated to evaluate the desulfurization process. They could achieve 98 % of the sulfur removal at 60 °C in their samples [1].

In this study, the use of CNTs is investigated for the removal of sulfur in petroleum products. We tried to remove sulfur oxides or sulfonates in the presence of an oxidizing agent consisting of a combination of functionalized CNTs and cobalt oxide. Due to the decoration of cobalt oxide on the surface of the CNTs, nanoparticle dispersion improves in the MDF. After oxidizing the sulfur in the fuel, the prepared catalyst absorbed the impurities and the sulfur value was measured to demonstrate the quality of the fuel.

2. Material and method

2.1. Material

Multi-walled carbon nanotubes (MWCNT) were purchased from Neutrino Company. Normal heptane, Chloroform, and other solvents were obtained from Rad Kimiagaran Company. In addition, Dibenzothiophene (DBT), Benzothiophene (BT), and cobalt oxide were bought from Sigma-Aldrich.

2.2. Experimental

2.2.1. Preparation of the model diesel fuel (MDF)

Normal heptane was used as the base fluid for all the samples. Besides, BT and DBT were utilized as sulfur impurities with a concentration of 200 ppm.

2.2.2. ODS process of the prepared diesel fuel

The surface modification of carbon nanotubes was performed using the acid treatment. A combination of sulfuric acid and nitric acid (3:2, vol/vol) was applied to decorate carboxyl and hydroxyl groups on the surface of CNTs. Next, Co_2O_3 was decorated on the surface of nanotubes. For that purpose, the surface-modified carbon nanotubes were dispersed in the mixture of cobalt nitrate solution and acetone at a concentration of 0.5 to 1.0 wt %. Then, this suspension has been placed in an ultrasonic water bath for 30 minutes. After filtration, suspended nanoparticles were placed in the oven at 300 °C for 2 hours, and the efficiency of the prepared catalysts in the sulfur removal was examined. Dry samples were characterized by TEM images and TGA analysis. Then, the effects of temperature, the concentration of the oxidant and the contact time were also studied.

2.2.3. Pseudo first and second order adsorption kinetics model

To determine the Pseudo-first-order kinetics of the reaction, the Lagergren equation as in Eq. (1) is used:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

where k_1 (min^{-1}) is the constant of this equation. This first-order differential equation can be solved with these boundary conditions, $q_t = 0$ at $t = 0$ and $q = q_t$ at $t = t$:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

By making a linear relationship between the laboratory data and Eq. (2), using the slope and intercept of the line, the amount of the adsorbed sulfur and the equilibrium constant of the first-order reaction can be obtained respectively.

The Pseudo second-order kinetic model [18] is expressed by Eq. (3):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where the K_2 (g/mg min) is the constant of this equation. By integrating $q_t = 0$ at $t = 0$ and $q = q_t$ at $t = t$ in Eq. (3), Eq. (4) is obtained.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \quad (4)$$

The linear relationship of t/q_t in terms of t can validate the second-order kinetic model of the experimental data. It should be noted that chemical adsorption is the main hypothesis for the rate-limiting step.

2.2.4. Study of the kinetics of the reaction

For a better study of the kinetics of the chemical reaction, ODS synthesis was investigated at different temperatures. Eq. (5) is Pseudo first-order reaction kinetics, and by calculating k in Eq. (5). The activation energy is obtained through Eq. (6).

$$-\ln\left(\frac{C_t}{C_0}\right) = kt \quad (5)$$

$$\ln k = \frac{E_a}{RT} + \ln A \quad (6)$$

3. Results and discussion

3.1. TEM

According to our previous experiments, the surface modification of CNTs is one of the

key points of this research. It is so important to optimize the surface treatment of nanotubes. Due to the degradation rate and structural changes of CNTs in the acid treatment, TEM images were used to track this procedure. Figure 3b shows clearly the cutting sections of CNTs. These sites are rich in hydroxyl and carboxyl functional groups. In addition, carboxyl groups can oxidize the sulfur impurities and can bond to the cobalt oxide. Figure 3a presents the raw CNTs before treatment.

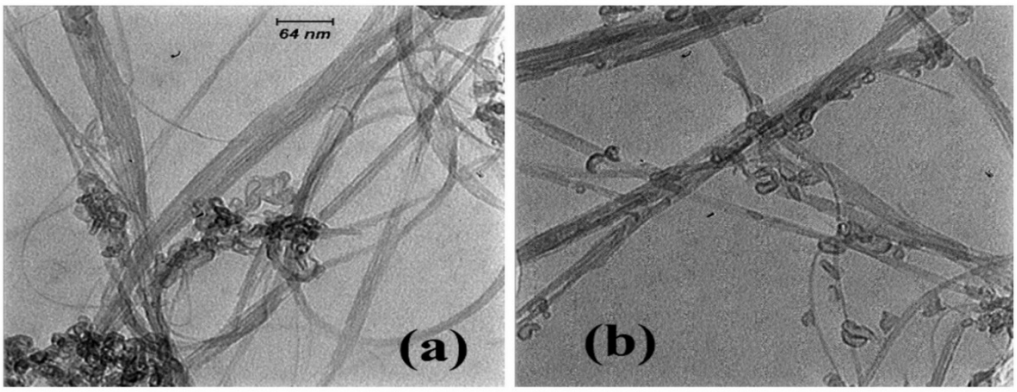

Figure 3. TEM images of (a) pristine CNTs and (b) oxidized CNTs.

3.2. Thermogravimetric analysis (TGA)

Although TEM shows the active sites of functional groups, the quantitative value of these functional groups is still unknown. The thermogravimetric analysis (TGA) helps us to obtain the exact number of carboxyl groups [19]. Three samples of CNTs with different numbers of functional groups were utilized in this research. Figure 4 shows the TGA graphs of these samples. The first one belongs to pristine nanotubes. Sample 1 has the lowest modification (10 %) and the third sample has the largest (25 %) number of functional groups. Sample 2 also shows a 20 % drop in the mass change when it was burned.

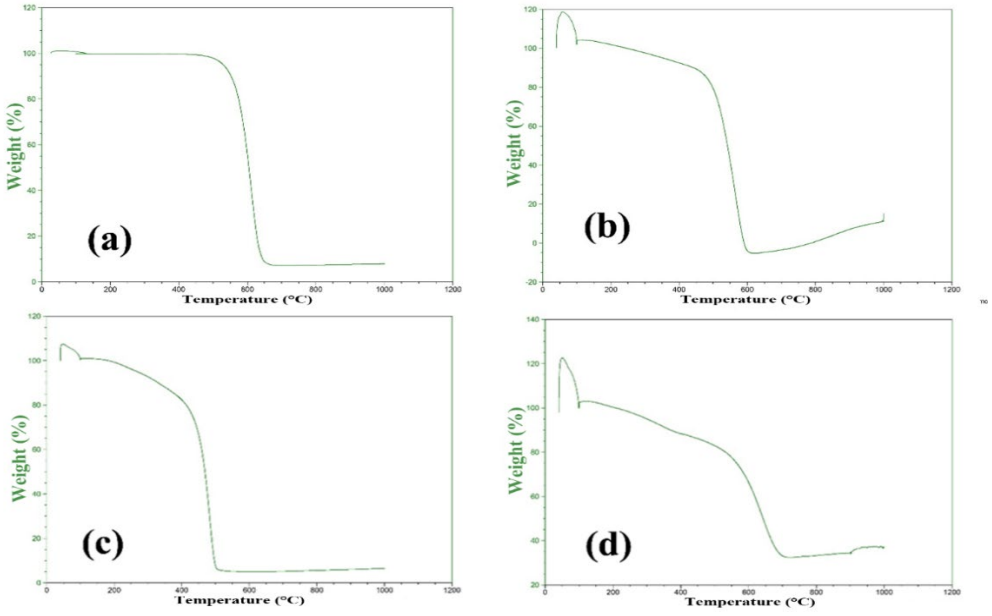

Figure 4. TGA of: a) pristine CNTs and oxidized CNTs with different surface modifications, b) sample 1, c) sample 2, d) sample 3.

3.3. Sulfur removal

In this section, two samples were used to evaluate the capability of the prepared sample in the sulfur removal. The efficiency of the sulfur removal of sample 3 was obtained from Eq. (7). The Co_2O_3 and oxidized CNT/Co_2O_3 catalysts were examined under the same conditions. The synthesized complex could remove 95 % of sulfur while the cobalt oxide could eliminate 80 % of contaminants. This is despite the fact that increasing the number of functional groups on the surface of CNTs can improve this value. It is important that the surface modification should be controlled during this process. Otherwise, the cylindrical shape of nanotubes will get open, and the physical properties of this nano platform will change.

$$\text{Sulfur removal efficiency (\%)} = \left[\frac{C_i - C_f}{C_i}\right] * 100 \qquad (7)$$

where C_i (mg/l) is the initial concentration and the C_f (mg/l) is the final concentration of the aromatic sulfur compound after the ODS treatment.

3.4. Kinetics study

3.4.1. Kinetics of adsorption

The reaction kinetics of the thiophene compounds were investigated in the prepared formulations at 60 °C during the times of 30, 60, 90 and 120 min. Besides, the experimental data were evaluated on two types of first and second-order kinetic models.

To evaluate the Pseudo-first-order kinetic model, ln (q_e-q_t) was plotted in terms of t (min) based on the experimental data (Figure 5-a). These results show that the synthesized nanocatalyst exactly follows the Pseudo-first-order kinetic model and have a correlation coefficient greater than 0.99. The results show that there is a linear relationship between ln (q_e-q_t) and time and the prepared complexes do not follow the Pseudo second-order kinetic model. (Figure 5-b). The obtained equilibrium constants for the first-order kinetic model (K1) show a greater value than the equilibrium constants of the second-order kinetic model (K2), and on the other hand, the experimental data show much greater matching in the first-order equation than the second-order one.

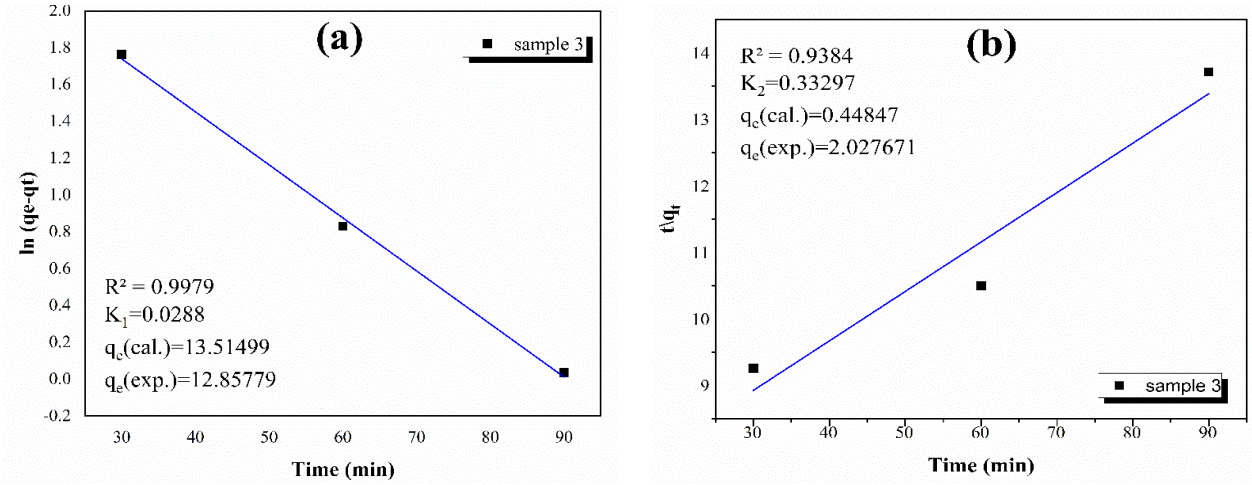

Figure 5. Experimental data with respect to a) Pseudo first-order, b) Pseudo second-order kinetics.

3.4.2. Kinetics of the reaction

Processing the results using Eq. 5 shows a linear relationship between -ln (C_t/C_0) and the reaction time (min) and that the slope

increases by increasing time and temperature. Figure 6 shows that the ODS process follows the Pseudo-first-order kinetics. Therefore, using the results of Figure 6, the reaction activation energy can be calculated.

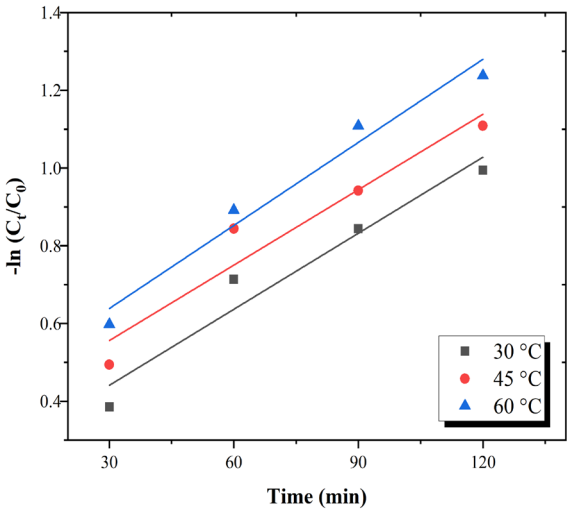

Figure 6. Pseudo-first-order kinetics for the oxidation of sulfur.

By obtaining a linear relation between -ln (k) and 1/T according to Eq. 6, it is obtained the linear equation: y = 292.27x + 4.0757. The correlation coefficient in Figure 7 is 0.9686 and the apparent activation energy is 2429.93 J/mol.

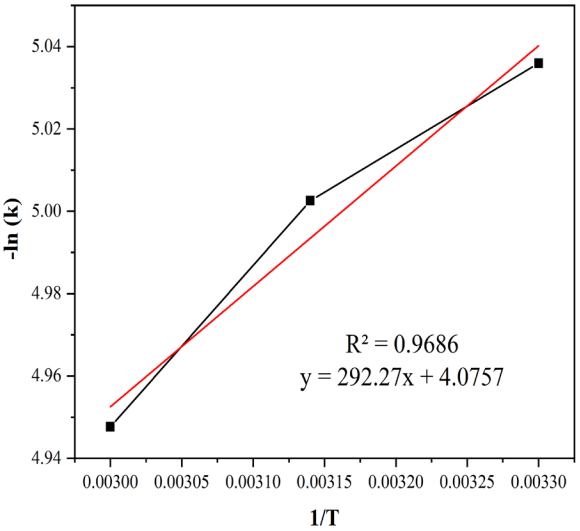

Figure 7. The inverse plot of temperature (1/T) versus root of the reaction rate constant -ln(k).

3.5. Effect of the concentration of the functional group in the desulfurization process

The type and number of functional groups on the surface of CNTs can play key roles in the better desulfurization of hydrocarbon fuels (Figure 8). It is clear that a small amount of the oxidant can remove a significant percentage of sulfur impurities in a way that with the 0.025 (mg/l) of oxidized CNTs, 68 % of sulfur impurities are removed. The best result was produced in 0.1 (mg/l) of functionalized nanotubes.

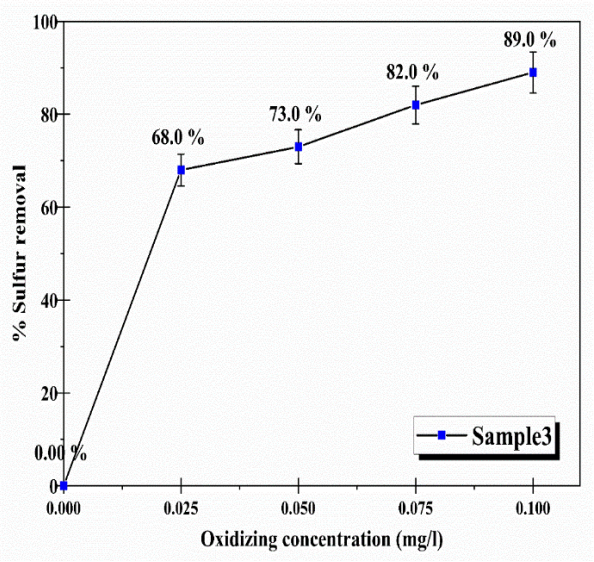

Figure 8. Effect of the concentration of the oxidant in the sulfur removal of the sample 3.

3.6. Effect of temperature and the elapsed time

Temperature and time have a similar effect on the sulfur removal. About 50 % of eliminations occur in the first 30 minutes and after two hours this value increases to 85 % (Figure 9). Temperature can also improve this elimination by more than 25 % when increased from 30 ºC to 60 ºC. However, after 90 min, the absorption rate remained almost constant and did not change much over time.

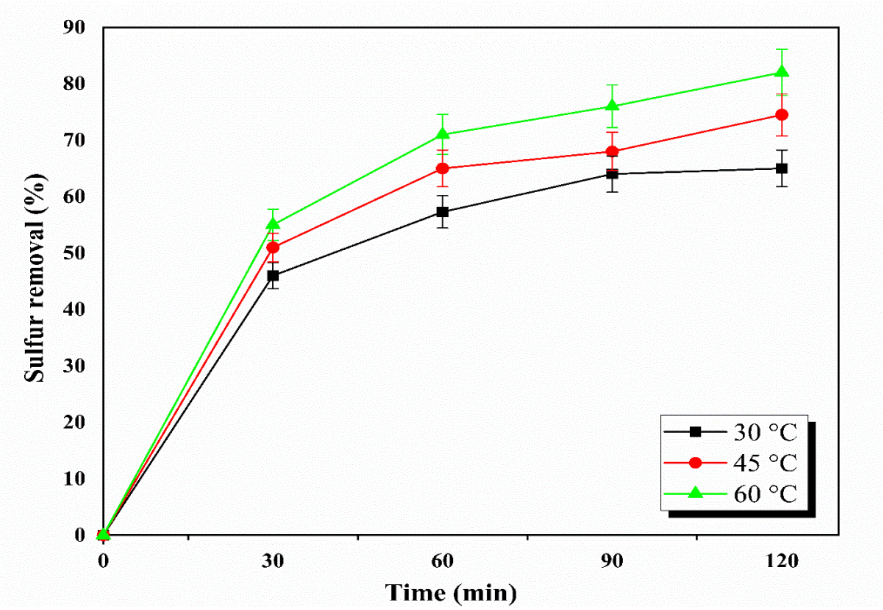

Figure 9. Effect of temperature and time in the sulfur removal of the model fuel.

4. Conclusions

The ability of a new complex based on the surface-modified CNTs and cobalt oxide has been evaluated in this research. This formulation has been used as a new nanocatalyst to remove the sulfur compounds in gas oil and gasoline. TEM images present a clear change in the structure of CNTs and the TGA analysis can measure the number of these functional groups. The result shows that only 0.025 mg/l of the complex could remove 68 % of sulfur impurities and 0.1 mg/l of functionalized nanotubes could eliminate 89 % of sulfur compounds. The elapsed time and temperature of sample fuels could significantly improve this value. More than 25 % increment in the sulfur removal was obtained after increasing the temperature from 30 ºC to 60 ºC in less than two hours. By matching the data with the Pseudo first and second-order adsorption kinetics, it was found that the adsorption was done as Pseudo-first-order adsorption kinetics and also the sulfur removal occurred physically. The ODS process is a chemical reaction and the kinetics of the reaction was adapted to the first order equation. Using this equation, the required activation energy is calculated (2429.93 J/mol). This finding can be more effective in the sulfur removal of hydrocarbons using nanocatalyst in the oil, gas, and petrochemical industries.

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Nomenclature

ADS	Adsorptive Desulfurization.
BT	Benzothiophene.
CNTs	Carbon Nanostructures.
DBT	Dibenzothiophene.
MDF	Model Diesel Fuel.
MWCNT	Multi-Walled Carbon Nanotubes.
ODS	Oxidative Desulfurization.
SWCNT	Single-Walled Carbon Nanotubes.
C	concentration [mg/l].
k	equation constant [L/mg].
q	adsorbent capacity [mg/g].
t	time [min].
T	temperature [°C].

Subscripts

e	equilibrium
f	final
i	initial
m	maximum

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