



Experimental study and evaluation of heavy crude oil desulfurization process using combination of Alkalines Solutions and Catalytic Oxidative

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Abstract

Research on the desulfurization of heavy crude oil will be carried out utilizing Alkalines, Oxidative desulfurization, and a combination of Alkalines and Oxidative desulfurization, among other approaches. In this study, the effects of alkaline solutions with different weights (10–30 gm), temperatures (30–60°C), contact times (30–60 min), and mixing speeds (300–500 rpm) were studied. It was revealed that the removal efficiency of the individual alkaline process was very low. Several tests are carried out to offer a suitable technique for the removal of sulfur from heavy crude oil while considering a variety of procedures. According to the findings of the study, the combination of oxidative and alkaline desulfurization generates the best desulfurization effect, which is around 64.45 %. This is followed by oxidative desulfurization, which produces a 56.54 % desulfurization effect. A study found that alkalines removed the least amount of sulfur (39.52 %) when no oxidative desulfurization was used. It is also being researched the influence of different H₂O₂ concentrations, treatment times, and temperatures on crude oil desulfurization when using a combination of alkaline and oxidative procedures. The results show that when the temperature and H₂O₂ volume ratio increase, the ultimate sulfur removal rate increases, but virtually maintains constant as treatment time increases. These significant findings will pave the way for widespread usage of combination alkaline and oxidative desulfurization procedures.

1. Introduction

The global need for crude oil as an energy source continues to grow as a society and economic development progress, and as a result, the hydrocarbon feedstock produced from known wells is becoming heavier and sourer in composition day by day as the content of organosulfur compounds increases [1, 2, 3]. High sulfur components in crude oil refining are becoming more and more difficult because of strict environmental regulations, also its catalyst deactivation and erosion issues in pipelines and refining equipment [4, 5]. Heavy crude oil has many primary characteristics, the main features of which are its high viscosity, density, acidity, and sulfur content. The quality of crude oil differs because of the differences in geological location of different crude oil reservoirs [3, 6, 7]. When it comes to crude oil contamination, sulfur is by far the most common contaminant, and it may be found both in organic and inorganic forms, as shown by the discovery of many sulfur-containing compounds as shown in Fig. 1 [8].

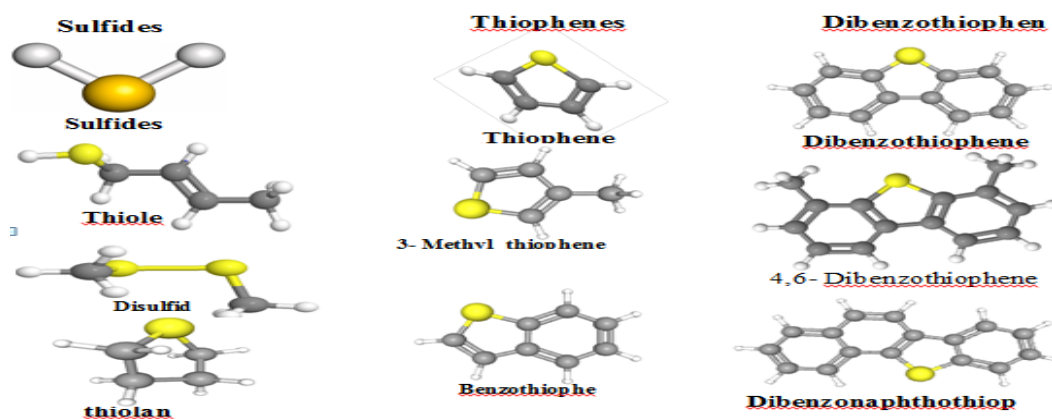


Figure 1. Representative S- compounds present in crude oils

Hydrodesulfurisation (HDS), the most common technique used in industrial treatment to reduce the level of sulfur to a minimum, however high sulfur content leads to an increase in hydrodesulfurization costs, researchers are more and more attracted by the search for an alternative method for eliminating sulfur [9]. Heavy crude oil may be desulfurized by a range of physical, chemical, microbiological processes. Therefore, it is necessary to develop a simple-to-use, effective, and environmentally friendly method for removing the sulfur components from crude oil. Alternatives to the hydrodesulfurization process include desulfurization via oxidative, adsorptive, solvent extraction, chlorinolysis-based, alkylation, supercritical water, radiation-based, and caustic desulfurization [10–13].

Oxidative desulfurization (ODS) is widely recognized as a new and green alternative approach for deep HDS [12] and has received considerable study interest [13-16]. ODS is frequently coupled with other treatments. H_2O_2 [7] and peroxy organic acids [17-19] have been studied. Caustic treatment is a possible low-cost alternative to conventional desulfurization. Using concentrated NaOH or $Ca(OH)_2$ to remove H_2S , methyl, ethyl, propyl mercaptans and thiophenols from acid liquid fuels, the "Caustic" process can also dissolve the C-S bond, but not heavy-mercaptans or ar. The alkali used in the procedure can be recycled [16]. Caustic is used to clean crude oil by combining it with organosulfur compounds to form water-soluble alkali metal ions. Yusra et al. (2020) employed sodium hydroxide to desulfurize crude oil. Heavy crude oil desulfurization efficiency was 56.89 percent [14]. They found that applying a sodium hydroxide solution reduced the sulfur content of kerosene by 60%, diesel oil by 70%, and gasoline by 81.4 percent [20-22]. Butt (2021) studied the effect of desulfurization of coals with $Ca(OH)_2$. The sulfur content of coals has been reduced to less than 66% [23].

The purpose of this study is to determine the best method for treating sulfur-containing heavy crude oil from southern Iraq's Al-Basra Oil Field, including alkaline treatment by NaOH and $Ca(OH)_2$, oxidative desulfurization, and a combination of the two. Determine between sulfur removal and effective parameters. The effects of contact time, mixing rate, and temperature on the efficacy of sulfur removal were investigated. This work will pave the way for the application of oxidative desulfurization using alkali.

2. Materials and methods

2.1. Chemicals

In the experiments, the samples of crude oil were supplied from Middle Refineries Company MRC/Dora Refineries from the strategic line of oil fields in Basra Iraq. The following reagents were used in this study: NaOH (purity $\geq 96\%$), $\text{Ca}(\text{OH})_2$ (purity $\geq 95\%$) and Formic acid (HCOOH) (purity $\geq 95\%$). They were purchased from Sigma-Aldrich. Hydrogen peroxide (H_2O_2) (PubChem, 30% wt). The crude oil samples used in the research were obtained from Middle Refineries Company MRC/Dora Refineries in Baghdad Iraq.

2.2. Analysis method

Heavy crude oil samples were analyzed using an X-ray analyzer manufactured by the Horiba Company in Japan. The technique of "X-ray fluorescence" was used to determine the total sulfur content of a sample. The ASTM D-4294 standard was applied to samples of extremely polluting oil. This unit was supplied with membrane spectroscopy that supports typically the thin film of a carrier material put on the frame.

3. Experimental scenarios and procedures

During the first procedure, a study was carried out to investigate the influence of the alkaline solution ratio on the desulfurization of heavy crude oil with high sulfur content (Iraq). The treatment alkalines technique desulfurization (sodium hydroxide and calcium hydroxide processes) was investigated to determine the influence of reaction duration, reaction temperature, the weight of alkalines, and mixing speed on the outcome. Each experiment generated varied concentrations of alkalines by taking 10, 20, and 30 grams of alkalines and adding a constant quantity of water for each different weight of NaOH or $\text{Ca}(\text{OH})_2$ in a 100 ml flask. After transferring 50 ml of the heavy crude oil samples to the second batch (the autoclaves reactor), an alkaline solution was injected at a preset volume ratio of 1:1 to the autoclaves reactor. We were able to improve the mass transfer rate by mixing the phases for 30 to 60 minutes at mixing speeds of 300 to 500 rpm and temperatures of 30 to 60 C, respectively [14], using a hot plate magnetic stirrer, as shown in Fig.1. Using a funnel was required to separate the solvent and heavy phase from one another. The total sulfur content of sour and treated heavy crude oils was determined using ASTM d-4294 techniques [24]. Middle Refineries Company / Dora Refinery completed the full test, including all testing and analysis.



Fig. 2: Schematic Diagram of the Caustic Method's Experimental Setup

During the second step, an investigation of oxidative desulfurization of the treated oil was conducted. The operation was carried out using amount of H_2O_2 oxidant ranging from 4 to 8 mL, temperatures ranging from 30 to 90 °C, and contract periods ranging from 30 to 90 min. The various amount of H_2O_2 and formic acid (1:1 by volume) were applied to 50 mL of crude oil [25].

Sulfur concentrations were measured using X-ray fluorescence, and sulfur removal was calculated using the following equation [26]:

$$\text{Sulfur removal (\%)} = \left(1 - \frac{C_o}{C_t}\right) \times 100 \quad \dots(1) \quad (1)$$

C_0 (ppm) indicates the sulfur concentration at the start of the reaction; C_t (ppm) represents the sulfur concentration at a certain period after the reaction has started.

4. Results and Discussion

4.1 Analyses of heavy crude oil

The sample of heavy crude oil utilized in this research was examined in the laboratory of the Middle Refineries Company / Dora Refinery. As shown in Table 1. the crude oil used as an API value of 22.79 and specific gravity of 0.9171, indicating that it was classed as heavy crude oil with a sulfur content of 3.7942% weight or 37942 ppm.

Table.1: Detailed examination of heavy crude oil

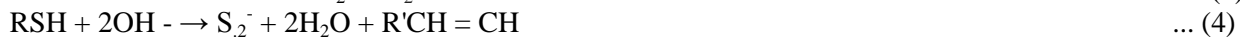
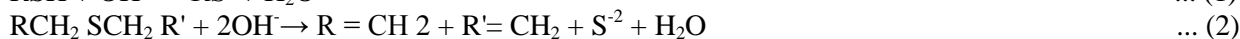
Test	Unit	Results	Test method
API	-----	22.6	ASTM D 5002
Density @ 20/20	gm./cm ³	0.9171	ASTM D 5002
Sp. gravity @ 15.6 °C	-----	0.9171	ASTM D 5002
Sediment	% vol.	0.0114	ASTM D 473
Salt	ppm	31	ASTM D 3230
Water content	% vol.	0.1	ASTM D 4006
Asphaltenes content	% wt.	2.48	JPI- 5S -45 - 95
Pour point	°C	-36	ASTM D 5853
Sulfur	ppm	37900	ASTM D 4294
Sulfur	%	3.79	ASTM D 4294
Ash content	% wt.	0.0120	ASTM D 482
Freezing point	°C	-42	ASTM D 97
DI Hydrogen sulfide H ₂ S (vapor)	ppm	110	-----
Flash point	°C	1150	ASTM D 93
Fire point	°C	138	ASTM D 93
Dynamic viscosity @ 26.7 °C	CP	49.27494	ASTM D 7042
Dynamic viscosity @ 48.9 °C	CP	21.82055	ASTM D 7042
IBP	°C	53	-----

4.2 Alkalines Desulfurization

4.2. 1 Effect of Weight Alkalines on the removal of sulfur

Figures 3 and 4 show the effect of varying the weight of alkalines (NaOH and Ca(OH)₂) on desulfurization. The results clearly show that increasing the caustic NaOH weight to 20 gm and the Ca(OH)₂ weight to 6 gm under the same conditions improves the sulfur removal capability of the treatment alkaline process by 39.52 % and 35.83 %, respectively.

This is because the amount of cations in the sulfur removal solution affects the reaction products produced when OH⁻ attacks sulfur compounds, followed by cation penetration into the reaction sites. When OH⁻ ions penetrate reactive sulfur compounds, they are likely to be followed by smaller ions such as Na⁺ more than larger ions such as Ca⁺⁺. Both cations, however, will penetrate reactive sulfur compounds [17]. Strong bases can neutralize and bring some sulfur compounds into aqueous solution, which is weakly acidic [27].



The milk of lime (Ca(OH)₂). The release of calcium and hydroxyl ions throughout the dissolution process is depicted in equations (5) and (6) [28].



The results clearly show that when the NaOH amount was increased to 30 gm under the same conditions, the sulfur removal capacity of the caustic treatment process did not change significantly. When compared to Ca(OH)₂, the performance of removal will decrease slightly with max weight. The higher the amount of Na⁺ and Ca⁺⁺ in the phase, the greater the pace at which cations seep into crude oil, and the greater the likelihood that it will reach equilibrium quickly enough and then disintegrate into a reverse process [29, 30].

After a more in-depth examination of the data, it becomes clear that while sulfur removal rates are relatively modest at short contact times, they both increase significantly between 30 and 60 min at long residence times of 60 min. In the case of caustic desulfurization, the latter appears to be a satisfactory value.

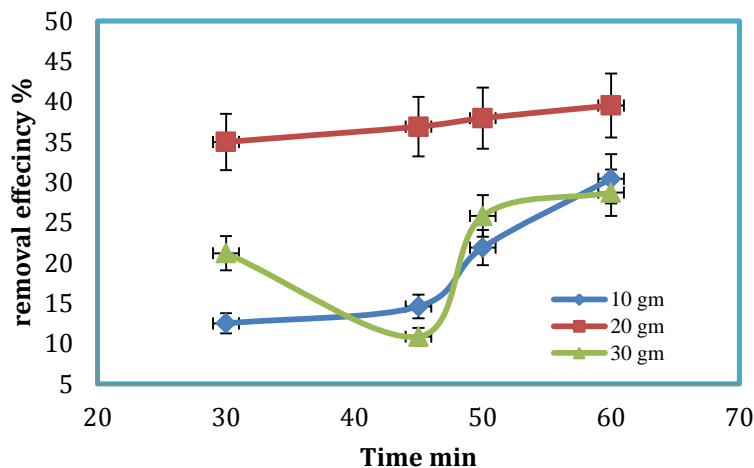


Figure 3: The effect of NaOH weights on removal efficiency of caustic sulfur compounds at (Mixing Temperature = 40 ° c, mixing speed = 400 initial S-concentration = 3790 ppm.).

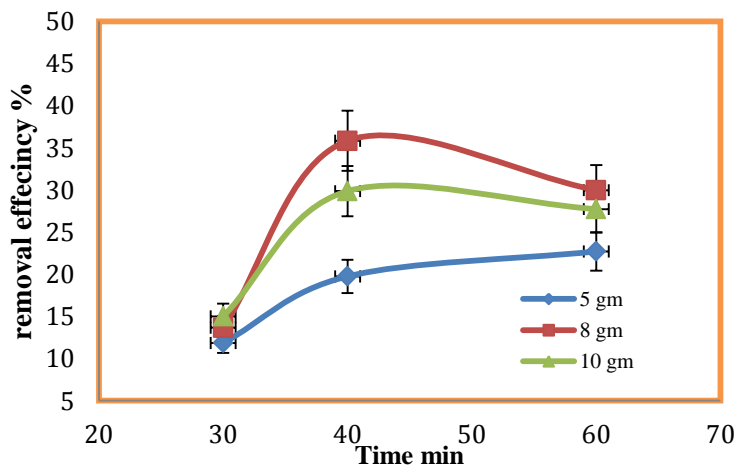


Figure 4: The effect of $\text{Ca}(\text{OH})_2$ weights on removal efficiency of sulfur compounds at (Mixing Temperature = 40°C , mixing speed = 400 initial S-concentration = 3790 ppm.).

4.2.1 Effect of reaction temperature on the removal of sulfur

During the alkaline treatment procedure, the temperature might play a role in deciding the outcome. When the temperature of the alkaline process is raised, the diffusion rate of mass transfer and the speed with which the process reaches equilibrium is increased. The effect of temperature on sulfur removal is depicted in Figs. 5 and 6. These show the combined effect of temperature and contact time variations on sulfur removal while keeping the alkaline weight and mixing speed constant throughout. The treatment of alkaline capability for sulfur removal reduced as the temperature of the reaction mixture increased. This is owing to the fact that the compounds' composition is temperature-sensitive, and they deteriorate at quite high temperatures. This demonstrates that, depending on the substance, there is a preferable temperature [31]. In exothermic processes, the capacity for sulfur removal increases as the temperature of the reaction decreases. In most cases, the caustic of NaOH is exothermic. As a result, increasing the temperature will result in a decrease in removal [32]. Tests with calcium hydroxide revealed that the desulfurization rate did not decrease when the temperature was raised to high levels. In the case of $\text{Ca}(\text{OH})_2$, increasing the temperature causes a change in the reaction rate and, finally, a change in the breakdown of $\text{Ca}(\text{OH})_2$, making the compound extremely soluble in oil; this high volatility is likely the source of the low activity of removal of sulphur [33]. In comparison to $\text{Ca}(\text{OH})_2$, desulfurization of NaOH was more effective at 60°C than at 30°C , or 40°C . This occurs because the contact time between the unreacted sulfur and the NaOH solution increases as the mixing time increases. Similarly, Moaseri et al. [34] reported similar findings. Thus, low temperatures combined with lengthy contact times ensure a uniform distribution of heat in the reaction, demonstrating that sulfur removal rates are slow at short contact times, accelerate between 30 and 60 minutes, and then slow again at long residence times exceeding 60 minutes. This latter figure appears to be adequate for the alkaline desulfurization process.

According to the experimental results, the crucial variable in the alkaline process is the amount of time to mix heavy crude oil. Overall desulfurization performance is minimally affected by the weight of alkaline or mixing temperature.

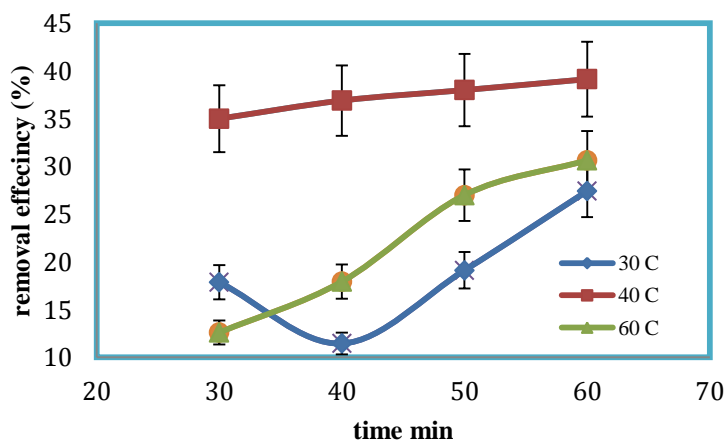


Figure 5: The effect of temperature on removal efficiency of sulfur compounds by NaOH caustic at (NaOH weight= 20, Mixing speeds = 400 rpm, and initial S-concentration = 3790 ppm.).

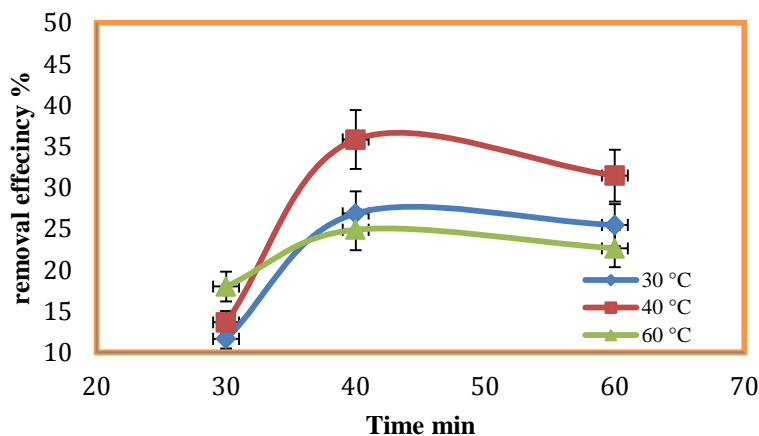


Figure 6: Figure 3: The effect of temperature on removal efficiency of sulfur compounds by Ca(OH)₂ caustic at (Ca(OH)₂ weight= 6, Mixing speeds = 400 rpm, and initial S-concentration = 3790 ppm.).

4.2.2 Effect of mixing Speed on the removal of sulfur

The effect of mixing speed was investigated by altering it between 300 and 500 rpm. As illustrated in Figure 5, the sulfur content decreased as high speed combined with long contact times ensures an even more diffuse were increased within the experimental range, indicating an increase in reaction rate. Furthermore, bases react with the organic acids in crude oil to form anionic surfactants. This is mostly due to increased disturbance, which increases the likelihood of sodium hydroxide and diffusing to reach sulfur compounds found in heavy crude oil, as well as the frequency with which they occur [18].

Even the most effective caustic desulfurization procedure will not be able to achieve an adequate reduction in the quantity of sulfur-containing compounds in the heavy crude oil.

It was only possible to achieve a decrease in the total sulfur content of 42.21% using this method. A caustic process alone would not be a viable option, and efforts should be made to develop more effective procedures.

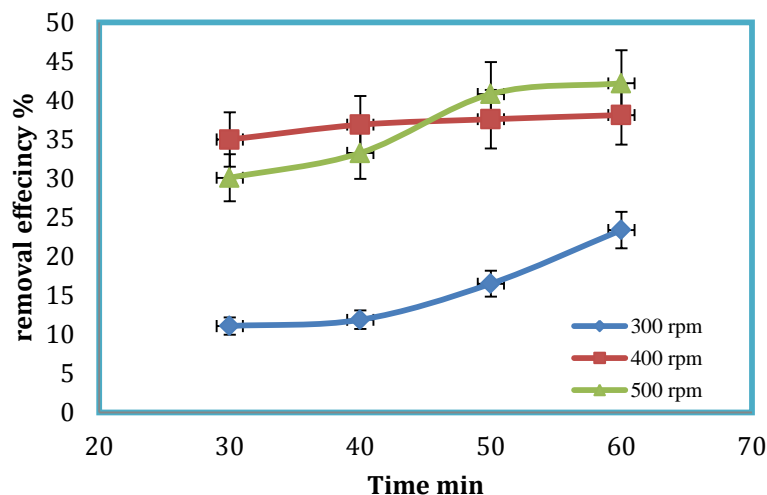


Figure 7: The effect of mixing Speed on removal efficiency of NaOH caustic sulfur compounds at (NaOH weight= 20, Mixing Temperature = 40 ° c, and initial S-concentration = 3790 ppm.).

4.3 Oxidative desulfurization

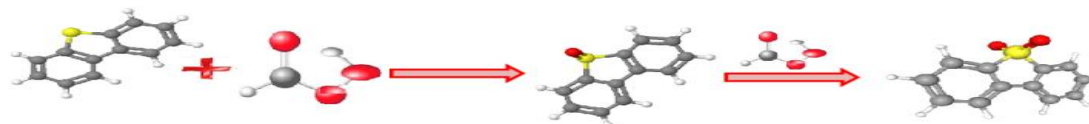
4.3.1 Effect of H₂O₂ amounts on the removal of sulfur

The ODS method can be used to extract sulfur from heavy crude oil by combining H₂O₂-CH₃COOH to yield peroxyformic acid. Investigate the influence of oxidant dose on the oxidative characteristics at temperatures ranging from 30 to 60 degrees Celsius. Using peroxyformic acid, I sulfur is subsequently transformed to sulfoxide and/or sulfone [19,35].

The mechanisms of reaction are listed below. In the first stage, H₂O₂ reacts with formic acid to generate an unstable intermediate molecule that is quickly dehydrated to yield peroxyformic acid [36]:



Peroxyformic acid then oxidizes the sulfide in oil, such as benzothiophene and dibenzothiophene, producing sulfoxide and sulfone [37]:



As illustrated in Fig. 6, the rate of crude oil desulfurization increases in direct proportion to

the amount of oxidant used. The elimination of sulfur from heavy crude oil increased from 38.92 % to 59.76 % as the amount of peroxyformic acid increased from 4 ml to 6 ml. This is because the increasing number of molecules involved in the process increases the likelihood of molecular collisions, which results in a fall in the sulfur mass fraction. Because the desulfurization action is nearing saturation, supplementing it with more oxidants does not necessarily improve its efficacy. Excessive oxidant addition causes the oil to oxidize rapidly, destroying its constituents. All of these findings support the concept that an excessive amount of an oxidant is detrimental to desulfurization [38].

A complex crude oil composition, the presence of more complex components in crude oil, or a higher sulfur concentration in crude oil may all contribute to the issue. The optimal oxidant levels for crude oil are 6mL when considering the desulfurization effect, environmental safety, and economic benefits.

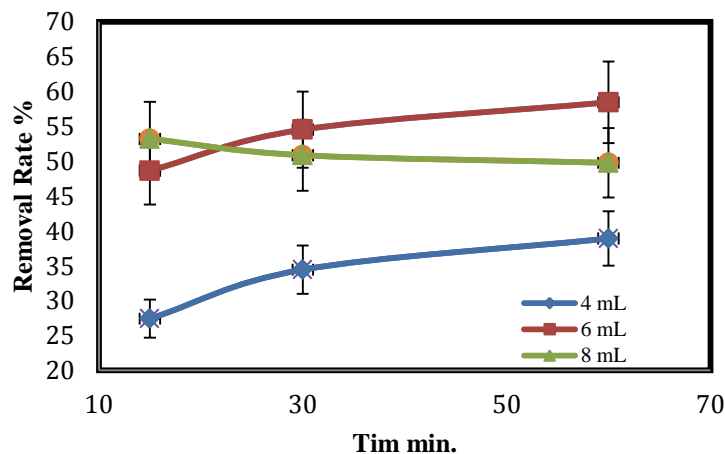


Figure 8: The effect of H₂O₂ dose on removal efficiency of Oxidative sulfur compounds at (Mixing Temperature = 60 °c, mixing speed = 500 and initial S-concentration = 3790 ppm.)

4.3.2 Effect of reaction temperature on removal of sulfur

Because the reaction temperature in the ODS system has a substantial effect on the catalysis of hydrogen peroxide, a range of temperatures was examined while keeping all other experimental parameters constant. Figure 6 plots data for constant oxidizer parameters at three distinct temperatures as a function of time. When the temperature was 30 °C, 60 °C, and 90 °C, the removal of sulfur reached 41.68 percent, 57.54 percent, and 51.67 percent, respectively, in 30 minutes. The reaction equilibrium was also attained in a shorter period when the temperature was raised higher. As a result, increasing the reaction temperature within a specific temperature range was found to be favorable to the sulfur removal process. The results showed that a lower reaction temperature was unsuitable for the oxidation of sulfur, and that the removal of sulfur increased when the reaction temperature was increased. Hydrogen peroxide, on the other hand, decomposes into water and oxygen at elevated reaction temperatures, resulting in a decrease in desulfurization efficiency [39].

The oxidation effect is greatest when the reaction has proceeded to a certain point in time and degree. Excessive mixing makes the breakdown of the oxidizer inefficient, which in the first place damages the growth of the oxidation process. Unlike the previous method of caustic process, reaction time and mixing speed have a significant effect on process efficiency while other variables, such as temperature, only have a little effect on the overall desulfurization rate for crude oil. It may be more advantageous to operate at a temperature (60 °C), with a mixing period of 30 min for crude oil, for reasons of safety, ease of operation, and cost-effectiveness.

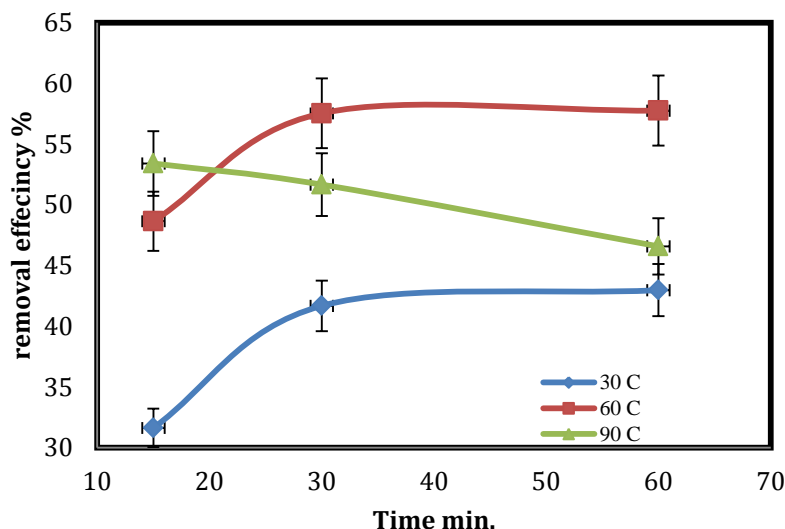


Figure 9: Effect of the reaction temperature on sulfur removal wt% at weights H₂O₂ = 6 gm, Mixing time = 15, 30 and 60 min, mixing speed = 500 initial S-concentration = 3790 ppm.).

4.4 Combined Alkalines and oxidative desulfurization

It was essential to combine the two previous methods to get greater sulfur removal efficiency. A two-stage method consisting of ODS oxidizes via peroxyformic acid oxidizes (first step), followed by a caustic wash was used to remove the ODS according to the first scheme. The processes in the next scheme were carried out in the reverse order of the procedures in the preceding scheme. As demonstrated by the results shown in part A of Table 2, the caustic wash process is not able to achieve a greater reduction in total sulfur content following peroxyformic acid oxidizes treatment because all light sulfur compounds are eliminated during the oxidative step, as demonstrated by the results shown in part B of Table 2. The use of a first caustic wash followed by oxidative desulfurization may result in more sulfur removal on the other hand. Possibly because the removal of light sulfur compounds in the first stage may provide a better opportunity for the oxidative process to extract heavier sulfur compounds from crude oil in the second stage.

TABLE 2: Sulfur compounds were measured in treated crude oil following coupled desulfurization processes.

part	process scheme	experimental conditions				S-Rem. (%)	
		T (°C)	t(min)	Concentration			Sp.(rpm)
				W (gm)	V(mL)		
A	Caustic treatment and oxidative desulfurization	40	50	20	6	500	64.45%
B	oxidative and caustic desulfurization	40	50	20	6	500	38.23%

5. Conclusion

In this study, four-step desulfurization studies on heavy crude oil were carried out and optimized, employing a variety of reagents and reaction conditions. A comparison was made between the desulfurization effects of caustic wash and the effects of the simple oxidation technique on crude oil.

Although the caustic process removed some sulfur due to their low mercaptans and high organic sulfur content, the oxidation process using H₂O₂ as the oxidant provided the most successful and inexpensive method for deep desulfurization, decreasing the total sulfur content to 56.54 wt.%. Combining the two previous procedures of oxidizing with ODS followed by a caustic wash does not result in a

larger decrease of sulfur content because all light sulfur compounds are removed during the oxidative step. On the other hand, it is possible that using a first caustic wash followed by oxidative desulfurization will result in more sulfur removal.

Conflict of Interest: The authors declare that they have no conflict of interest.

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