Desulfurization of AL-Ahdab Crude Oil using Oxidative Processes

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ABSTRACT

Two different oxidative desulfurization strategies based on oxidation/adsorption or oxidation/extraction were evaluated for the desulfurization of AL-Ahdab (AHD) sour crude oil (3.9wt% sulfur content). In the oxidation process, a homogenous oxidizing agent comprising of hydrogen peroxide and formic acid was used. Activated carbons were used as sorbent/catalyst in the oxidation/adsorption process while acetonitrile was used as an extraction solvent in the oxidation/extraction process. For the oxidation/adsorption scheme, the experimental results indicated that the oxidation desulfurization efficiency was enhanced on using activated carbon as catalyst/sorbent. The effects of the operating conditions (contact time, temperature, mixing speed and sorbent dose) on the desulfurization efficiency were examined. The desulfurization efficiency measured at the best operating conditions(optimum conditions): 60°C, 500rpm, 60min contact time and sorbent dose of 0.7g AC/100 ml AHD crude, was 32.8% corresponding to a sulfur content of 2.6 wt%. Applying the same optimum operating conditions and at 3:1 solvent/oil ratio, the oxidation/extraction method gave comparable desulfurization efficiency of 31.5%.

Key words: desulfurization technologies, oxidative desulfurization, adsorption, extraction, activated carbon.

ازالة الكبريت من نفط خام الاحدب بأستخدام عملية الاكسدة

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الخلاصة

في هذا البحث تم تقييم نوعين من عمليات الأكسدة لأزالة مركبات الكبريت من نفط خام الأحدب الحامضي (محتوى كبريتي = 3.9 wt%) وهي العمليات المستندة الى عمليات الأكسدة/الأمتزاز أو الأكسدة/ الأستخلاص. في عملية الأكسدة تم استخدام نظام بيروكسيد الهيدروجين /حامض الفورميك كمادة مؤكسدة. استخدم الكاربون المنشط كعامل مساعد / كمادة مازة في عملية الآكسدة/امتزاز بينما استخدم الأسيتونايترايل كمذيب في عملية الآكسدة/ أستخلاص. دلت النتائج على ان الكاربون المنشط كان له دور كبير في زيادة كفاءة عملية الآكسدة/امتزاز. تم دراسة تأثير المتغيرات العملية (زمن التلامس، درجة الحرارة، سرعة الخلط، وكمية المادة المازة) على كفاءة عملية الأكسدة/ الأمتزاز . كانت كفاءة عملية الأكسدة/ امتزاز في افضل ظروف العمل (60°C، 500rpm، 60min، 0.7g كاربون منشط لكل 100ml من النفط الخام) تقريبا 32.8% (محتوى كبريتي= 2.6wt%) وهي مقاربة لكفاءة عملية الأكسدة/الأستخلاص (31.5%) والتي اجريت تحت نفس الظروف العملية وباستخدام نسبة 3:1 مذيب/نفط خام.

الكلمات الرئيسية: تكنولوجيا عمليات ازالة الكبريت، ازالة الكبريت بطريقة الأكسدة، الأمتزاز، الأستخلاص، الكاربون المنشط.

1. INTRODECTION

A common problem facing refineries around the world is that crude oils are becoming heavier, with higher sulfur contents. This result in higher sulfur levels in both straight-run and secondarily processed fuels. Therefore, it is preferable to reduce the sulfur content of crude oil before the oil is refined.

The current HDS technology cannot be suited for the desulfurization of sour crude oil since it leads to shortened catalyst life and more hydrogen consumption, so the production cost will increase. Studying new desulfurization processes is the key to bring more profit to the oil refining companies. A lot of effective work is being done to reduce or eliminate the pollution resulted from processing of sour crude oils and many new technologies for the desulfurization of crude oil are being studied recently.

,Reda, 2006 used oxidative desulfurization assisted by 35 kHz frequency ultrasonic irradiation to reduce the sulfur content of East Baghdad crude oil. The experimental results revealed that the highest removal efficiency was about 76% at 60^oC, $80W/cm^2$ sonication power intensity applied for 12 minutes.

Torkmani et al., 2008 isolated the first native fungus, identified as Stachybotrys sp. which is able to remove sulfur and nitrogen from heavy crude oil selectively at 30°C. This fungus was able to desulfurize 76% and 64.8% of the sulfur content of Iranian heavy crude oils (Soroush and Kuhemond oil fields) with initial sulfur contents of 5wt% and 7.6wt% in 72 and 144 h, respectively.

Lin et al., 2010 studied the oxidative desulfurization (ODS) of Azeri crude oil under the electric field. The desulfurization process was carried out in the electric desalting unit. The desulfurization rate of crude oil reached about 77 at 115^oC, a desulfurizer dosage of 200μg/g, and a demulsifier dosage of 50μg/g. Also the test results showed that the density and viscosity of crude oil decrease with the removal of sulfur compounds while other basic properties of crude oil are little affected after desulfurization process.

Hammad et al., 2012 treated high sulfur content crude oil feed stream by combined solvent extraction and hydrotreating and provided a treated crude oil product stream of substantially reduced sulfur content and without significant volume loss.

Wang et al., 2013 investigated the simultaneous desulfurization and demetalization of crude oil by electric desalting based on the oxidation of alkyl thiophene and nickel compounds with the compound of Chitosan Schiff Base under the condition of microwave irradiation. By using the optimized conditions for microwave irradiation , up to 56% of sulfur and 82% of nickel removal rates were achieved for model compounds in crude oil samples.

Hosseini and Hamidi, 2014 examined the effect of ultrasonic irradiation on the removal of sulfur from sour crude oil (5.2wt% sulfur) using oxidative method. The results showed a desulfurization efficiency of about 93.2% when ultrasound irradiation was used.

Oxidative desulfurization (ODS), as the name implies, involves a chemical reaction between an oxidant and sulfur that facilitates desulfurization. ODS involves two conceptually different steps. The first step is the sulfur oxidation, which oxidize the organic sulfur compounds to their corresponding sulfoxides, Eq.(1) and sulfones, Eq.(2).

$$R\text{-}S\text{-}R + 1/2\ O_2 \rightarrow R\text{-}(SO)\text{-}R' \qquad (1)$$

$$R\text{-}S\text{-}R' + O_2 \rightarrow R\text{-}(SO_2)\text{-}R' \qquad (2)$$

The sulfoxides and sulfones have two properties that are different from the unoxidized sulfur compounds and that facilitate desulfurization. First they are more polar, which increase selectivity during solvent extraction and adsorption. Second, the C-S bond strength is decreased when the sulfur is oxidized therefore it is easier to remove the oxidized sulfur by thermal decomposition from the unoxidized sulfur compounds. The second step is the sulfur removal, which exploits the properties of the oxidized sulfur to effect their removal by extraction, adsorption, distillation, or decomposition methods.

In the present work the capability of two oxidative desulfurization schemes to desulfurize AL-Ahdab Iraqi crude oil with initial sulfur contents of 3.9wt% was studied. The factors that affect this process such as contact time, temperature, mixing speed and sorbent dose were investigated.

2. MATERIALS AND METHODOLOGY

2.1 Materials

Acetone, acetonitrile and methanol (>99.0% purity) were obtained from Aldrich. Formic acid (>99% purity) and hydrogen peroxide (30 wt%) were obtained from Fluka. Granular activated carbon (AC) was obtained from local markets, the physical specification of the activated carbon, as measured in the laboratories of Petroleum Research and Development Center/Ministry of Oil are summarized in **Table 1.** All the chemicals were used as received without any further treatment. Al-Ahdab (AHD) crude oil (API = 25.8, SG = 0.896, Sulfur content = 3.9 wt%) obtained from Al-Daura refinery was used as a feed stock.

2.2 Method of Analysis:

The total sulfur content of the untreated and treated crude oil samples was determined by SELFA-2800 sulfur in oil analyzer (Horiba, USA). The test method is based on ASTM D-4296. All total sulfur measurements were performed by Central laboratory of AL-Daura Refinery.

The desulfurization efficiency is calculated as the ratio of sulfur removed to that initially present in crude oil, Eq.(3).

$$DE\ \% = \frac{C_o - C}{C_o} \times 100 \qquad (3)$$

2.3 Experimental Procedure

2.3.1 Oxidation/adsorption experiments

In the oxidation/adsorption experimental runs, 100ml of Al-Ahdab crude oil, 3ml hydrogen peroxide, 4ml formic acid, 5ml distilled water, and the required dose of activated carbon (0.2 to 0.7g) was heated to the required temperature (35 to 60 ^{0}C) and stirred at 500 rpm for the required period of time (15 to 60 min). The contents were allowed to cool to room temperature and the reaction mixture is transferred to a vacuum filtration system to separate the activated carbon particles from the reaction mixture for which the sulfur content is measured. A simplified process flow diagram is given in **Fig. 1**.

2.3.2 Oxidation/extraction experiments

In each oxidation experiment, 100 ml of AHD crude oil was mixed with an aqueous solution consisting of 3 ml hydrogen peroxide, 4ml formic acid and 5ml distilled water and introduced into the reactor. The reaction mixture was continuously stirred at 500 rpm and 60^{o}C for 60 min. Afterword stirring for the required contact time, the aqueous and oil phases were decanted in a separation funnel. This oxidized feedstock was used throughout the extraction experiments.

In the extraction run, 20ml of AHD crude oil with an appropriate amount of solvent according to the preset solvent/oil ratio were charged into 500ml three-necked flat-bottomed glass reactor equipped with a condenser and a thermometer. The reactor was then placed in a constant-temperature water bath and the mixture was stirred at 300 rpm for 30 min at 30^oC. The dispersion formed was then allowed to separate in a separation funnel into two distance phases. The aqueous phase was removed and the oil phase (treated crude oil) was analyzed for the total sulfur content measurements. Each experimental run was repeated 2 to 3 times and each data point was determined based on the mean value with slandered deviation of 1-3%. A simplified process flow diagram is given in **Fig. 2**.

3. RESULTS AND DISCUSSION

3.1 Oxidation / Adsorption Desulfurization

Among the several oxidants that have been used in ODS processes, hydrogen peroxide (H_2O_2) is preferentially chosen as the primary oxidant due to its environmentally benign properties as stated by **Javadli and De Klerk, 2012.** However, H_2O_2 needs to be activated in the presence of a catalyst. Among the different oxidation systems, H_2O_2/carboxylic acid especially formic acid has the advantages of reaction simplicity and commercial availability as proposed by **Mamaghani, et al., 2013.**

Activated carbon is a material with well-developed porous structure, large surface area and many surface oxygen-containing functional groups. To elucidate the effect of activated carbon as a catalyst/sorbent on sulfur removal from AHD crude oil the following operating variables were studied.

3.1.1 Effect of catalyst/sorbent dose

The sorbent dosage is an important parameter, since it determines the capacity of a sorbate at a given initial concentration. As shown in **Fig.3** the rate of sulfur removal increases gradually in direct relationship with the increase in catalyst/sorbent dose. This is an expected result because as the amount of sorbent increased, the available surface area increased, thereby exposing more active sites for the binding of sulfur species. Moreover, it was thought that activated carbon catalyzes the decomposition of hydrogen peroxide to produce hydroxyl radicals that act as strong oxidizing agents like perhydroxyl ions (OH^{-2}) that can easily oxidize the refractory sulfur compounds into sulfones as explained by **Zhou et al., 2009.**

On increasing the sorbent dose beyond 0.7g the desulfurization efficiency is almost constant and no more sulfur is further removed from the solution. This implied that there were enough active sites for sulfur compounds oxidation in the case of activated carbon dose amount of 0.7g**.**

3.1.2 Effect of reaction time

The effect of the reaction time is shown in **Figs.4** and **5** for high and low mixing speeds**.** At a contact time of 60 minutes and 500 rpm, the desulfurization efficiency obtained was 32.8%, but to obtain the same desulfurization efficiency at lower speed (200 rpm) it needs mixing time of about two hours. Increasing the mixing time increases the contact time between the unoxidized sulfur and the oxidation system on one hand and between the oxidized sulfur and the sorbent on the other hand. Besides, on increasing the mixing speed fine emulsions are formed between the two immiscible liquids, which is beneficial when working with biphasic systems. When these emulsions are formed, the surface area available for reaction between the two phases is significantly increased, enhancing the mass transfer in the interfacial region, thus increasing the rate of reaction.

Moreover **Fig.5** indicates that no significant change in desulfurization efficiency is obtained beyond 2 hours contact time. This is due to the adsorption of alkyl-substituted sulfoxides and sulfones, produced during the oxidation process on the surface of activated carbon, thus suppressing the adsorption process in accordance of **Campos-Martin et al., 2010.** At this point of time, it is thought that a dynamic equilibrium is reached and the amount of sulfur adsorbed indicates the adsorption capacity.

3.1. 3 Effect of reaction temperature

The effect of temperature on the removal of total sulfur was studied at range of 35-60^{o}C. The results show that temperature has large effect on removal of total sulfur. **Fig.6** indicates clearly a strong dependence of desulfurization efficiency on temperature. The desulfurization efficiency increased from 16.4% to 32.8% by increasing the temperature range from 35 to 60 ˚C.

The main function of oxidants is that they can donate oxygen atoms due to electrophilic addition reaction to the sulfurous compounds present in crude oil to convert them into respective sulfones or sulfoxides. The rate of decomposition of H_2O_2 during oxidative desulfurization is dependent on the temperature and concentration of the peroxide present in the compound. The increase in temperature leads to the increase in the rate of free radical formation and also indicates that there is activation energy for the adsorption process. At low temperature, the adsorption process is basically governed by weak Van der Waals forces; however at higher temperature chemisorption and probably chemical reaction dominate showing an increase in the sorption capacity.

Increasing the reaction temperature beyond 60℃ and operating at mild operating pressure causes the loss of valuable volatile hydrocarbons in crude oil. Moreover, crude oil is very complex mixture that contains alkenes and aromatics, and these compounds can also be oxidized consuming part of the oxidant and degrading the quality of the crude oil. These undesirable oxidation reactions are evident at temperatures of about 80–90^{o}C, For this reason, the reaction has to be conducted at temperatures lower than 80^{o}C and short reaction times as found by **Campos-Martin et al., 2010.** Moreover, **Manatt et al., 2004,** found that when the temperature exceeds 70^{o}F, H_2O_2 rapidly decomposed and reduce the oxidation rate.

3.2 Oxidation/Extraction Desulfurization

The efficiency of extractive desulfurization is limited by the solubility of the organosulfur compounds in the solvent. So, appropriate solvent selection is very important for efficient desulfurization. In the present work, methanol, acetone and acetonitrile were chosen in a pre-screening step as potential solvents. The effect of solvent type and solvent to oil ratio (S/O) on the desulfurization efficiency of AHD crude oil have been investigated to select the most effective solvent and the best (S/O) ratio. The results, as presented in **Fig.7** show that acetonitrile performed the best as an extraction solvent in the desulfurization of AHD crude oil. **Martinie et al., 2010** showed that the sulfur removal ability of acetonitrile is mostly due to its higher polarity as compared with acetone and methanol.

Acetonitrile is used widely as an extractive agent in desulfurization of petroleum fractions due to its high polarity, volatility (having a relatively low boiling point at 355K and can be easily separated by distillation) and its low cost as clarified by **Shiraishi, 2000.**

As can be observed from **Fig.7,** acetonitrile extracting ability increases with increasing its ratio. For acetonitrile, on increasing the solvent/oil ratio from 1:1 to 3:1, the desulfurization efficiency increased from about 10.3% to 28.5%. An increase in the level of desulfurization can be expected by increasing the solvent/oil ratio. However, on the other hand, an increase in the solvent/oil ratio leads to a decrease in the oil recovery. Similar findings were obtained by **Sobati et al., 2010.**

The main problem is related to the presence of two phases: an oil phase with the oxidized polar sulfur compound and a polar solvent which is not soluble in the oil phase. For this reason, there is some mass transfer limitation between the two phases. Accordingly, the increase in solvent/oil ratio facilitates the transfer of oxidized sulfur compounds at the polar-apolar interface, increasing notably the mass transfer across the interphase as explained by **Campos-Martin et al., 2010.**

Using single stage extraction treatment with acetonitrile, **Fig.8** indicates a decrease in the sulfur content of AHD crude from 3.9 wt% to 2.7 wt%, corresponding to a desulfurization efficiency of 31.5 %, while maintaining a high crude oil recovery yield. These findings indicate that oxidation/extraction process is an efficient desulfurization method and comparable with oxidation/adsorption, **Fig.9,** for treating sour crude oil.

4. CONCLUSIONS

1. The oxidation desulfurization efficiency can be enhanced by using activated carbon as a catalyst and sorbent since activated carbon can catalyze the decomposition of hydrogen peroxide to produce hydroxyl radicals that act as strong oxidizing agents.
2. The oxidation desulfurization efficiency increases with increasing; reaction temperature, time and mixing speed. The optimum operating conditions are 60° C, 60 min and 500rpm.
3. The extraction of sulfur compounds from AHD crude oil with acetonitrile shows better performance as compared to acetone and methanol due to its higher polarity.
4. The oxidation desulfurization catalyzed by activated carbon is comparable to oxidation/extraction method. The desulfurization efficiencies of both methods are 32.8 and 31.5% respectively.

ABBREVIATIONS

AC	**Activated carbon**
AHD	Al-Ahdab Crude oil
API	American Petroleum Institute
HDS	Hydrodesulfurization
ODS	Oxidative Desulfurization
OSC	Organosulfur Compounds
SG	specific Gravity

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Table 1. Physical properties of activated carbons.

Test	**Results**
Surface area (m^2/g)	702
Pore volume (cm^3/g)	0.59
Bulk density (g/cm^3)	0.72
Particle density (g/cm^3)	1.91
Particle Size	1mm

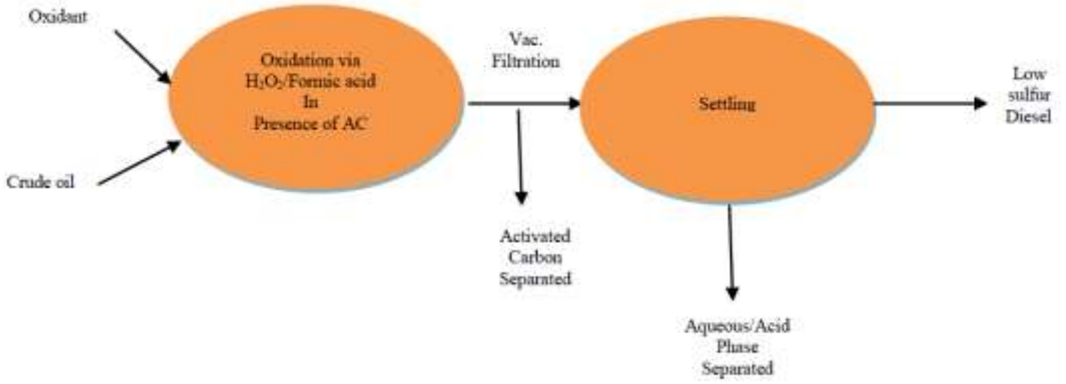

Figure 1. General process flow of diagram for adsorptive desulfurization.

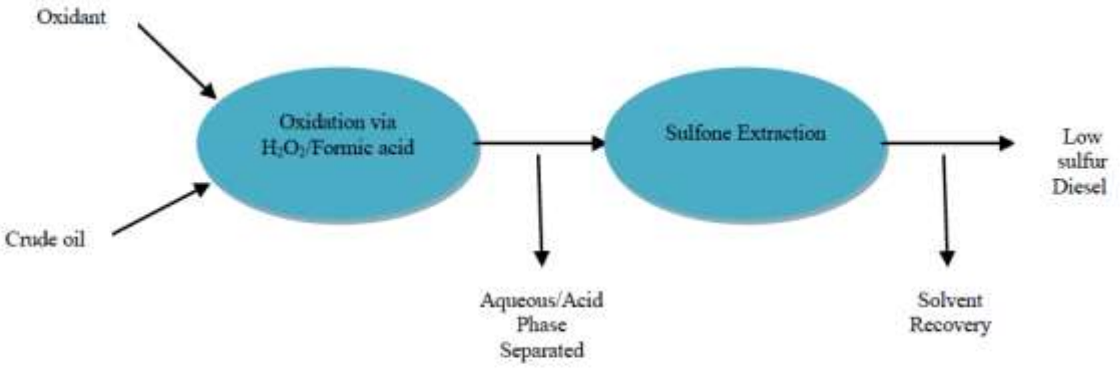

Figure 2. General process flow of diagram for extractive desulfurization.

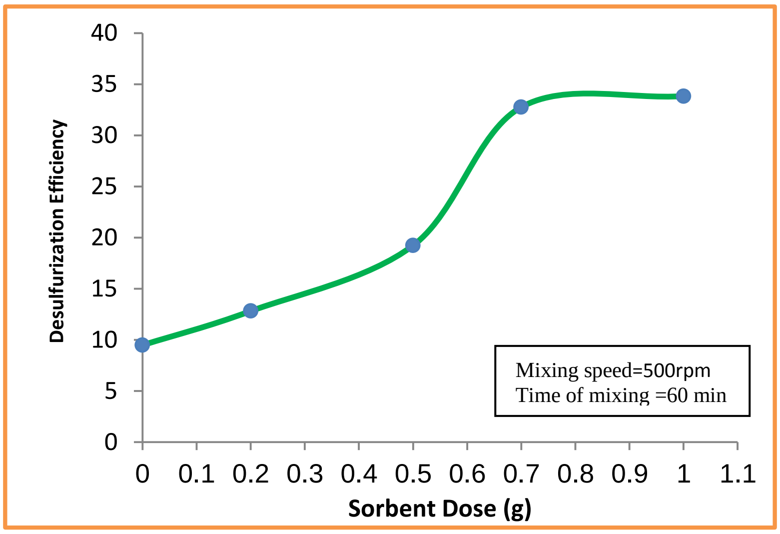

Figure 3. Effect of sorbent dose on the desulfurization efficiency.

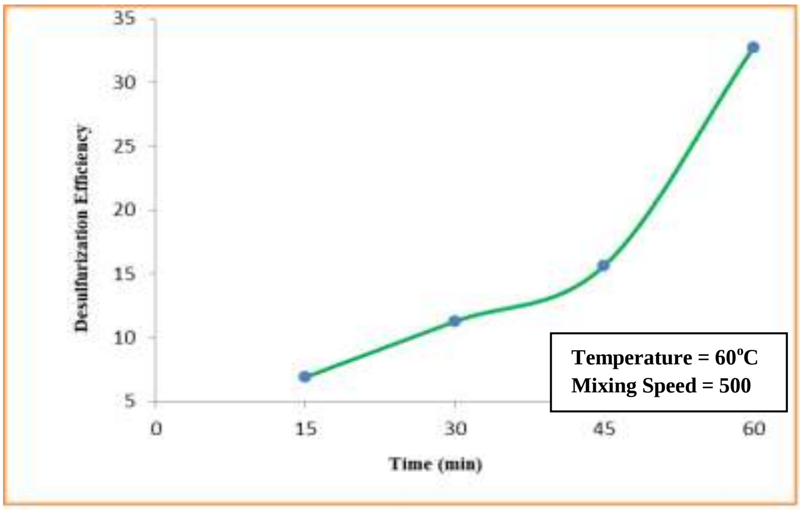

Figure 4. Effect of contact time on the desulfurization efficiency.

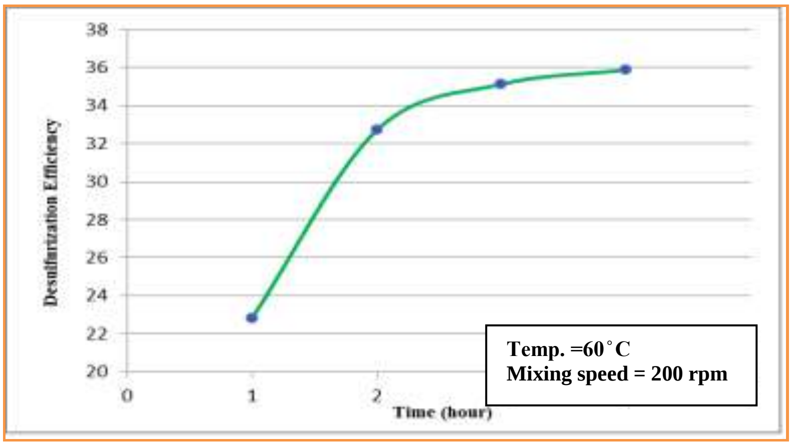

Figure 5. Effect of contact time on the desulfurization efficiency.

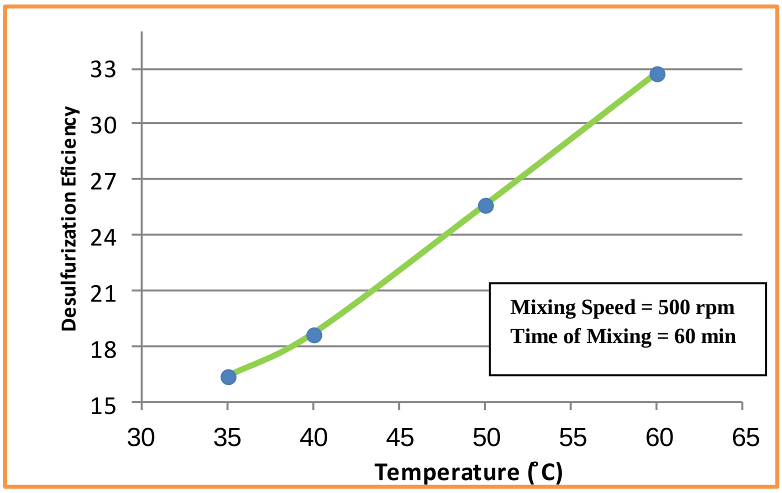

Figure 7. Effect of operating temperature on the desulfurization efficiency.

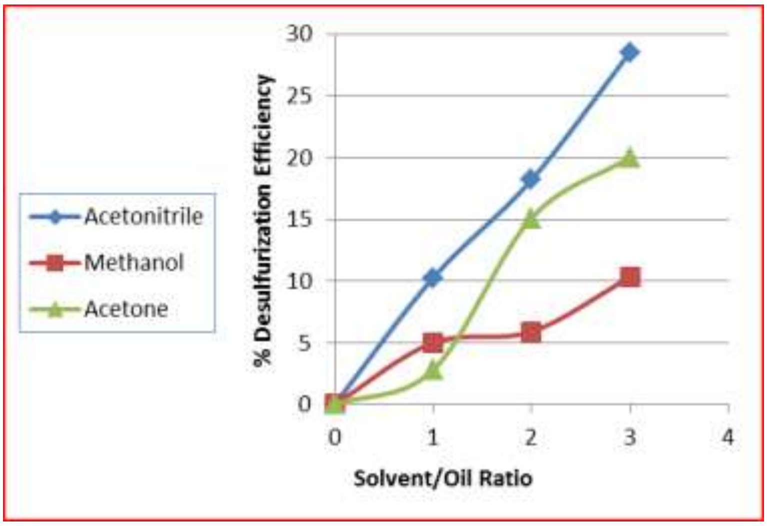

Figure 8. Effect of solvent/oil ratio on desulfurization efficiency.

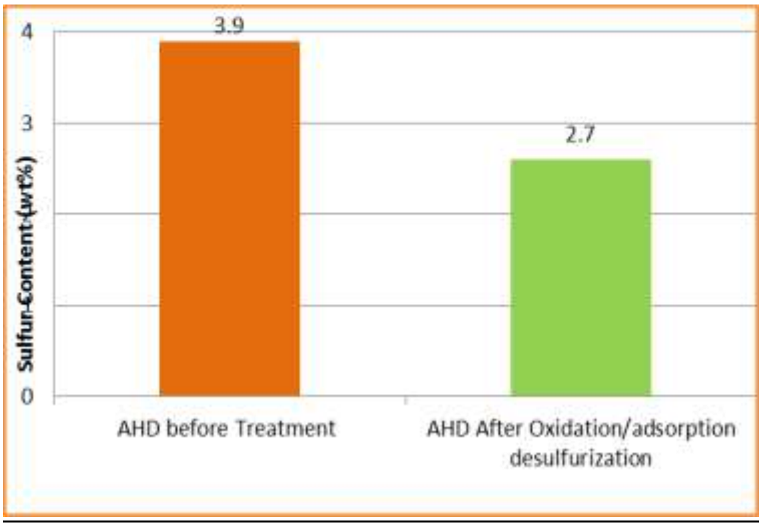

Figure 9. Effect of the oxidation/adsorption treatment on the sulfur content.

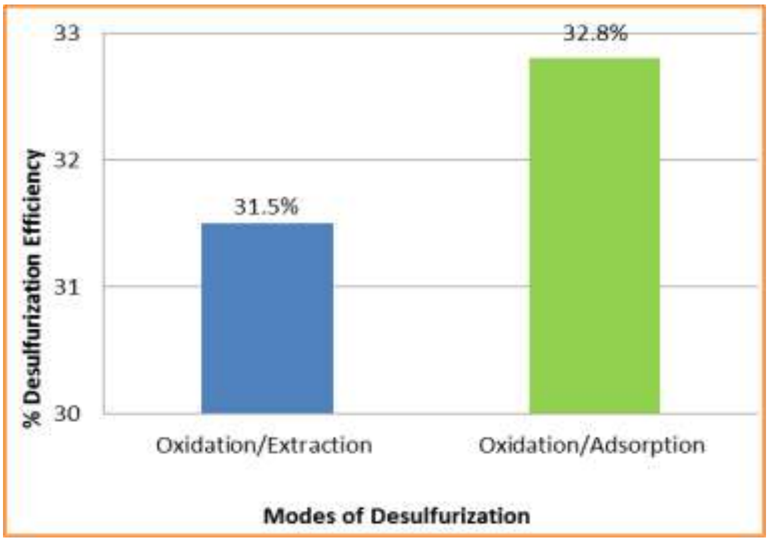

Figure 10. Effect of the oxidative mode on the desulfurization efficiency.