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## **Total Sulfur Determination in AL-Masila (Hadramout –Yemen) Crude Oil after Desulfurization using Oxidative Process**

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### **ABSTRACT**

*Environmental concerns have introduced a need to remove sulfur-containing compounds from oil. As oxidative desulfurization is conducted under very mild reaction conditions, the present research work is aimed at reducing the sulfur content of AL-Masila (Hadramout – Yemen) crude oil (0.402 wt.% sulfur content) prior to processing by subjecting oxidation with hydrogen peroxide in the presence of acetic acid as a catalyst and solvent extraction for which different solvents have been tested including acetonitrile, acetone and ethanol. The measured sulfur content of the crude oil, indicated that acetonitrile has higher ability to extract sulfur compounds (than the other two), at 3:1 solvent/oil ratio. The effects of the operating conditions (contact time, temperature, and mixing speed) on the desulfurization efficiency were investigated. The desulfurization efficiency measured at the optimum conditions: 65 °C, 500 rpm, 60 min and 100 ml AL-Masila crude oil, was 39.7% corresponding to a sulfur content of 0.242 wt.%.*

**Keywords:-***Crude oil, oxidative desulfurization, hydrogen peroxide, solvents*

### **INTRODUCTION**

Oil is the blood of industry and also a principal item reflecting the development level of the national economy [29]. The quality of crude oil depends mainly on the sulfur content and API gravity [12]. A problem which petroleum refineries are facing around the world is that crude oil used as feedstock for refining process is becoming heavier day by day with higher sulfur content [27].

Increasing sulfur compounds in the crude oil also lead to increase the sulfur compounds in its products. Therefore, reducing sulfur compounds from crude oil has become an urgent task to meet clean fuel production needs [1]. Crude oil contains a large variety of sulfur compounds (thiols, sulfides, disulfides and thiophenes), which generate SO<sub>2</sub> and airborne particulate emissions during

combustion [11]. Sulfur compounds can cause several corrosion problems in pipeline, pumping, and refining equipments, as well as premature failure of combustion engines and poisoning of the catalytic converters that are used in automotive engines [2].

Many countries have adopted more stringent environmental regulations to restrict the sulfur level of fuels limiting the sulfur level to less than 10 ppm [20]. Therefore, desulfurization of light oil is extremely important within the petroleum processing industry. Conventional methods for reducing the sulfur content of transportation fuels are hydrodesulfurization (HDS) technology. However, a high temperature, high pressure, and large amount of hydrogen and active catalysts are necessary for HDS [26]. In addition, the investment and operation costs of this method are very

high. To make up for shortages of HDS and obtain cleaner fuels, many non-HDS technologies have been developed in recent decades, such as oxidation [18], adsorption [13], extraction [16], alkylation [28], bio-desulfurization [25], and their combinations.

Among these methods, numerous studies on oxidative desulfurization (ODS) technology have been issued in comparison to traditional hydrogenation technology; oxidative desulfurization technology possesses the advantages of low investment and operation costs, mild reactive conditions, and a simpler technological process. The common oxidants of oxidative desulfurization are H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, and peroxy acid [30]. As oxidative desulfurization is conducted under very mild reaction conditions, much attention has recently been devoted to this process [10]. The ODS invariably involves two different steps - the first being the sulfur oxidation, which changes the nature

of the sulfur compounds, and the second is the removal of sulfur by liquid extraction at the end [17]. In the present research work we have aimed at reducing the sulfur content of AL-Masila (Hadramout – Yemen) crude oil (0.402 wt.% sulfur content) prior to processing by subjecting oxidation with hydrogen peroxide in the presence of acetic acid as catalyst and then using different solvents (acetonitrile, acetone and ethanol) for removing sulfur.

## MATERIAL AND METHODS

### Materials

Acetonitrile (99.8% purity, UK) and acetone (>99.8% purity, UK, HPLC grade) were obtained from Sigma-Aldrich Chemicals; acetic acid (98%, UK) and ethanol (absolute, UK) were obtained from Fisher Scientific; hydrogen peroxide (30% aqueous solution, England) was obtained from BDH. Some chemical and physical properties of AL-Masila crude oil, Hadramout –Yemen, are given in Table 1.

**Table 1:-Some chemical and physical properties of AL-Masila (Hadramout –Ye) crude oil.**

Test description	Test method	Result
Gravity	(D-4052 ASTM, 2019) <sup>1</sup> [5]	33.1
Specific Gravity at 15.5 °C	(D-4052 ASTM, 2019) [5]	0.8599
Vapor Pressure (kPa)	(D-5191 ASTM, 2019) [6]	5.1
Total Sulfur (Wt. %)	(D-4294 ASTM, 2019) [3]	0.4015
Carbon Residue (Wt %)	(D-189 ASTM, 2019) [9]	0.25
Pour Point °C	(D-97 ASTM, 2019) [8]	-11
Kinematic Viscosity at 40°C mm <sup>2</sup> /s	(D-445 ASTM, 2019) [4]	4.897
Water Content (Vol %)	(D-95 ASTM, 2019) [7]	0.05
Element Concentration (ppm) <sup>2</sup>		
Vanadium (V)		25
Nickel (Ni)		13
Lead (Pb)	IP 501(IP, 2019) <sup>3</sup> [14]	NIL
Sodium (Na)		3
Calcium (Ca)		1
Zinc (Zn)		NIL
Iron (Fe)		2
Magnesium (Mg)		1
Copper (Cu)		NIL

<sup>1</sup>ASTM: American Society for Testing and Materials; <sup>2</sup>ppm: part per million; IP: Institute of Petroleum.

## METHOD OF ANALYSIS

The total sulfur content of the untreated and treated petroleum samples decided by SELFA-2800 sulfur-in-oil analyzer (Horiba, USA). The test method is based on ASTM D-4294 [3]. All the experiments of total sulfur measurements were performed at Aden Refinery Company's laboratory.

The concentrations of some elements (Table 1) in the studied crude oil were determined using Inductively Coupled Plasma hyphenated to Optical Emission Spectrometry (ICP-OES) Model Thermo Scientific iCAP 6000 Series, USA at Central Processing Facility Laboratory of AL-Masila Petroleum Exploration and Production Company, Hadramout – Yemen.

## EXPERIMENTAL PROCEDURE

In each oxidation experiment, 100 ml of AL-Masila crude oil was mixed with an aqueous solution consisting of 3 ml hydrogen peroxide, 4 ml acetic acid and 5 ml distilled water and introduced into 500 ml three-necked flat-bottomed glass reactor equipped with a condenser and a thermometer.

The reactor was then placed in a constant-temperature water bath. The reaction mixture was continuously stirred at 500 rpm and 65<sup>o</sup>C for 60 min. In the extraction run, 20 ml of crude oil with an appropriate amount of solvent were decanted in a separation funnel. This oxidized feedstock was used throughout the extraction experiments [15].

The dispersion formed was then allowed to separate in a separation funnel into two distinct phases.

The aqueous phase was removed and the oil phase (treated crude oil) was analyzed

for the total sulfur content. Each experimental run was repeated a minimum of 3 times.

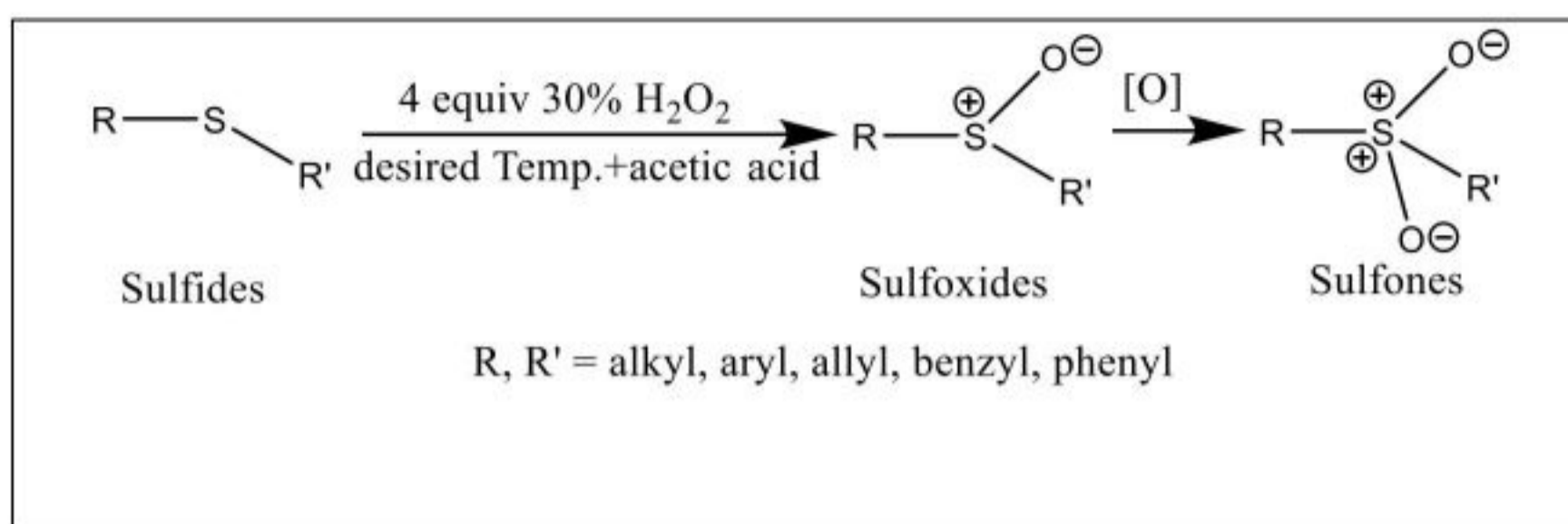
## RESULTS AND DISCUSSION

Due to the very mild operation conditions, the oxidative desulfurization (ODS) technology has been widely recognized as one of the most effective methods. Further, as regards to select a better oxidant (among very many) for ODS, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is the preferred one as the primary oxidant due to its environmentally benign properties [22].

After desulfurization reaction, H<sub>2</sub>O<sub>2</sub> decomposes to H<sub>2</sub>O and O<sub>2</sub>, so there is no secondary pollution, and meanwhile oxygen is a kind of favorable oxidant. Proper catalysts can accelerate reaction and increase oxidation efficiency. The mechanism is considered as: in the reaction system, H<sub>2</sub>O<sub>2</sub> first reacts with acetic acid quickly and generates oxygen atom [O], and then [O] reacts with unoxidized sulfur compounds (sulfides) to form sulfoxides and/or sulfones [30].

The sulfoxides and sulfones have two properties that are different from sulfides and that facilitate desulfurization. First one, is the polarity where they are more polar, causing to increase solvation during extraction and adsorption. Another, the carbon-sulfur bond strength is decreased when the sulfur is oxidized thus, it is easier to eliminate the oxidized sulfur (sulfones then sulfoxides) by thermal decomposition from sulfides. The second step is the sulfur elimination, which exploits the properties of the oxidized sulfur to affect their removal by extraction method.

A general view of a reaction of oxidation of sulfides to sulfoxides and then to sulfones is shown in Scheme 1.

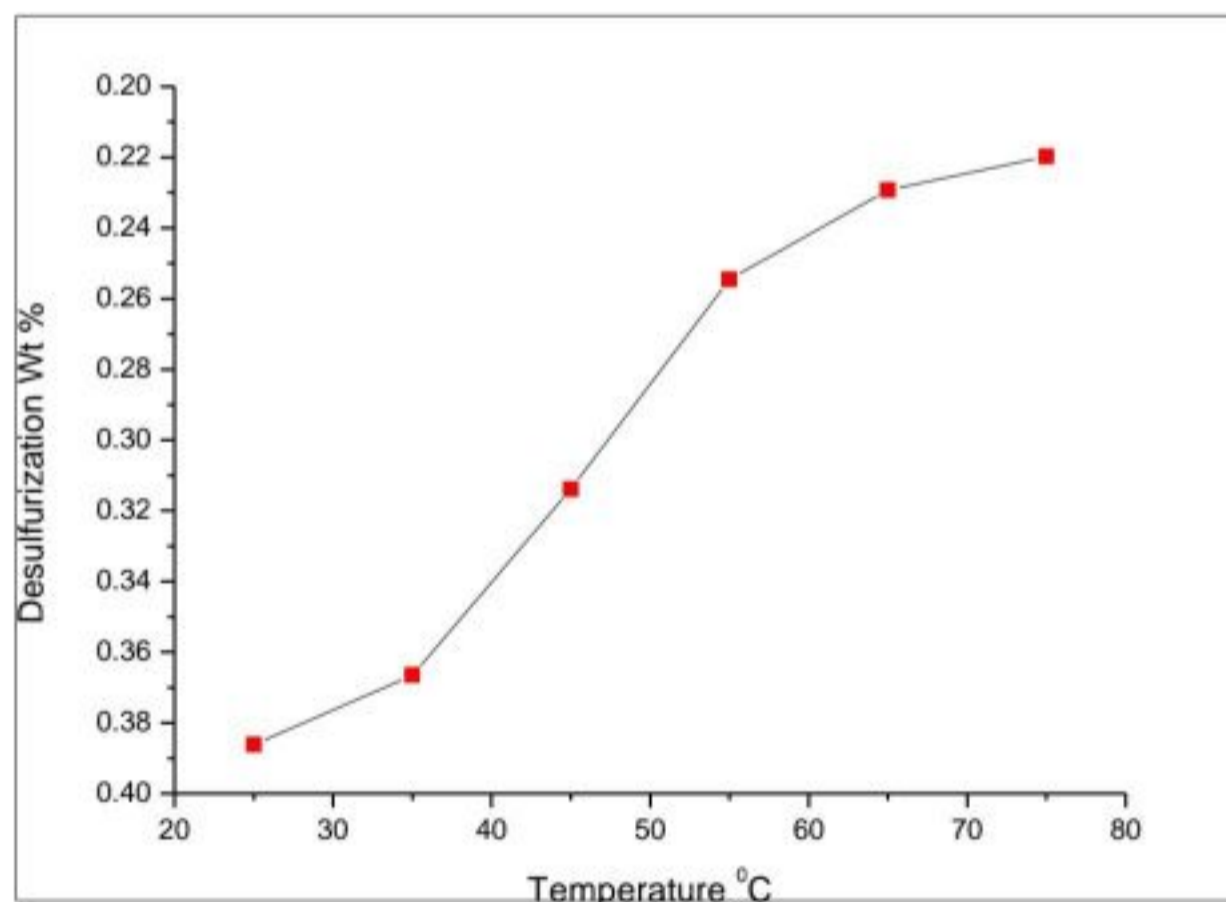


**Scheme 1:** Oxidation of sulfides to the corresponding compounds.

### Effect of Reaction Temperature

The results obtained indicate an enhancement in the efficiency of extractive desulfurization on increasing reaction temperature (Figure 1). However, increasing the reaction temperature beyond 65°C causes the loss of valuable volatile hydrocarbons. Where crude oil is a very complex mixture that contains alkenes and

aromatics, these compounds can also be oxidized consuming part of the oxidant and degrading the quality of the crude oil and fuel [19]. These undesirable oxidation reactions are evident at temperatures of about 80 – 90°C; for this reason, the reaction has to be conducted at temperatures lower than 80 °C and to short reaction times [23].

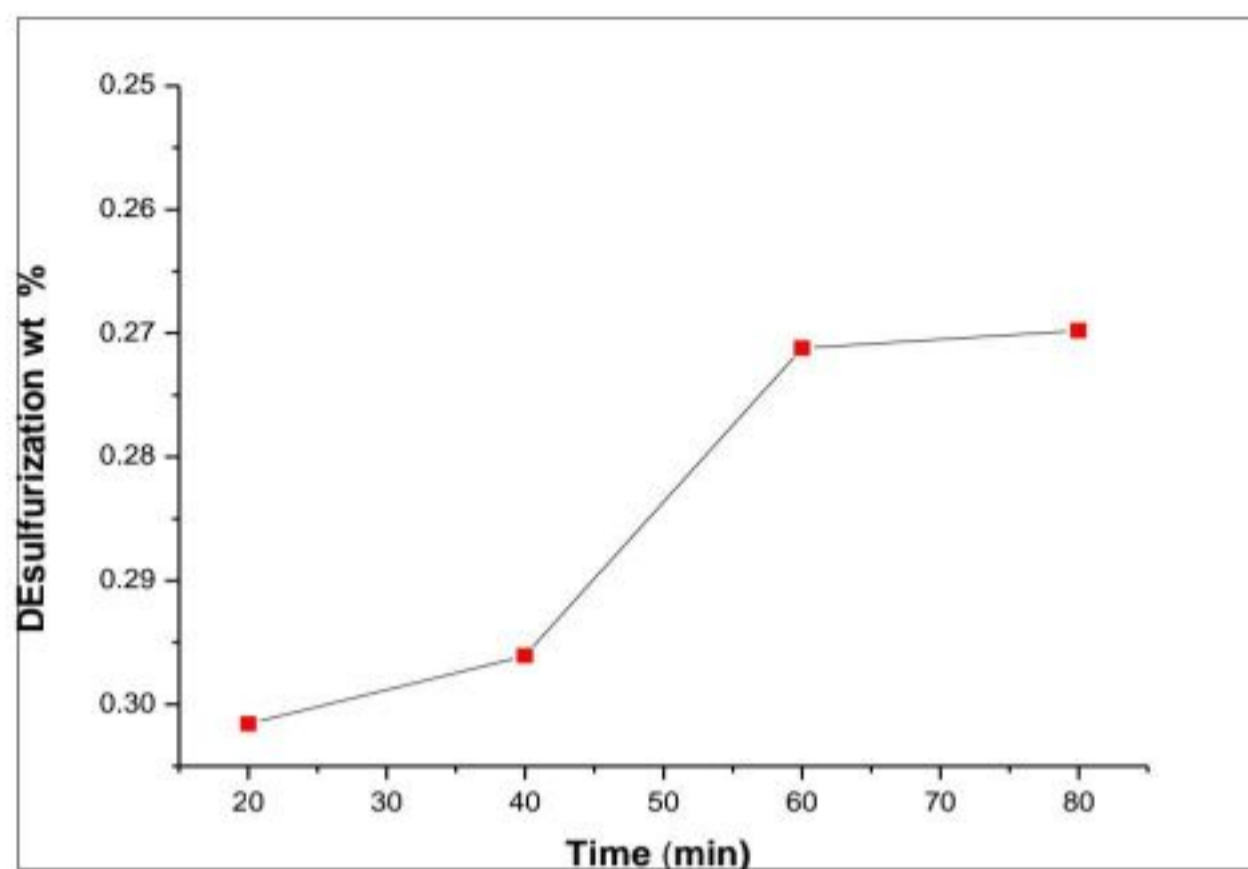


**Fig.1:-**Desulfurization efficiency versus temperature. Experimental conditions: 500 rpm. and 60 min.

### Effect of Reaction Time

The effect of the reaction time is shown in Figure 2. At a contact time of 60 minutes and 500 rpm, the desulfurization efficiency

obtained was 32.4%. Increasing the mixing time increases the contact time between the unoxidized sulfur and the oxidation system.



**Fig.2:-**Desulfurization efficiency versus time of mixing. Experimental conditions: 500 rpm. and 60°C.

### Effect of Solvent Type and Solvent/Oil Ratio

The efficiency of extractive desulfurization is limited by the solubility of the organosulfur compounds in the solvent. So, appropriate solvent selection is extremely important for efficient desulfurization.

The effect of solvent type and solvent to oil ratio (S/O) on the desulfurization efficiency of AL-Masila crude oil using acetonitrile, acetone, and ethanol as solvents has been investigated to select the most effective solvent and the best (S/O) ratio.

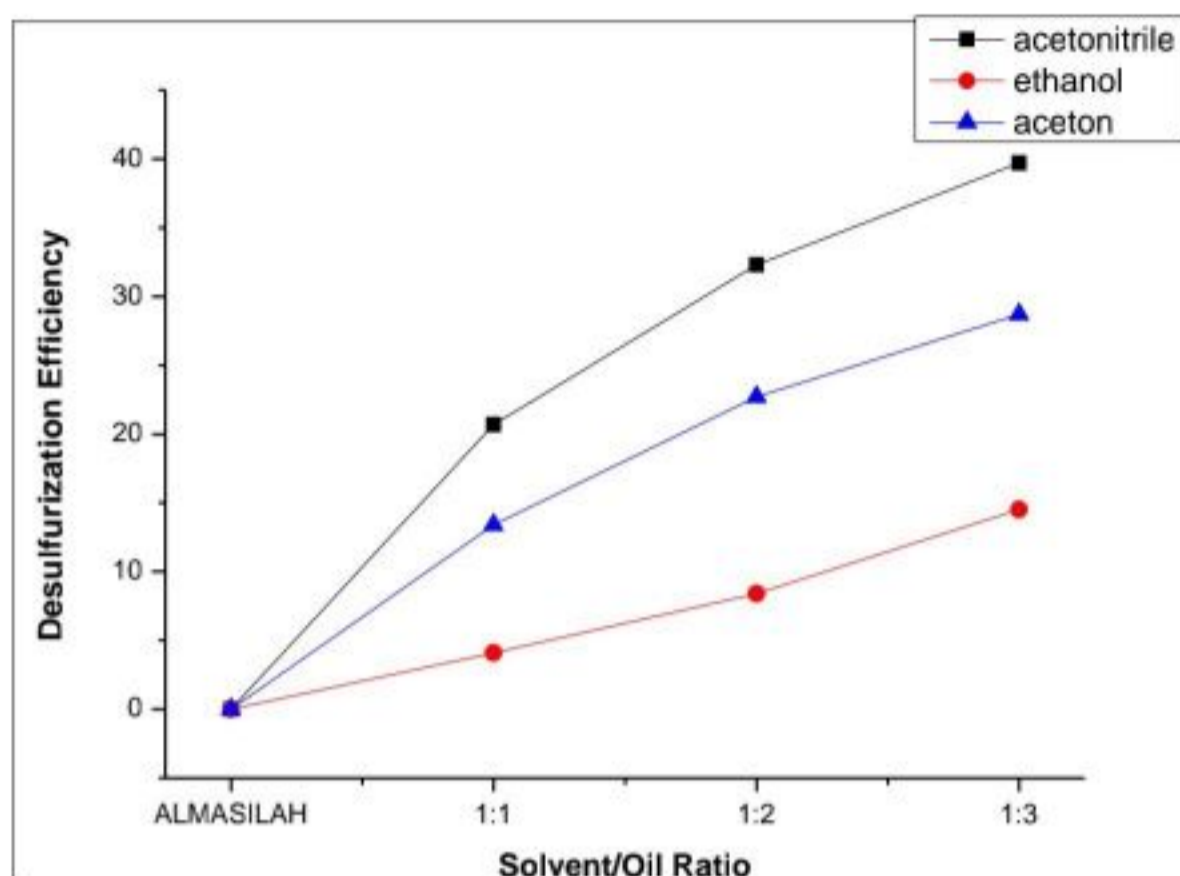
The results are presented in Figure 3, which shows that acetonitrile is the best as an extraction solvent in the desulfurization of AL-Masila crude oil. As can be observed from Figure 3, acetonitrile's extracting ability increases with increasing its ratio. For acetonitrile, on increasing the

solvent/oil ratio: 1:1, 2:1 to 3:1, the desulfurization efficiency increased from about 20.7% to 39.7%.

Acetone showed less effectiveness in sulfur reduction, the desulfurization efficiency for 3:1 solvent/oil ratio was only 28.7%. The lowest performance was obtained with ethanol, the removal efficiency increased from 4.1% to 14.5% by increasing the solvent/oil ratio from 1:1 to 3:1.

The sulfur removal ability of acetonitrile is mostly due to its higher polarity as compared with acetone and ethanol. Hence, acetonitrile was chosen as an extraction solvent and the solvent/oil ratio chosen for further studies is 3:1.

Acetonitrile is used widely as an extractive agent in desulfurization of petroleum fractions due to its high polarity, volatility and its low cost [24].

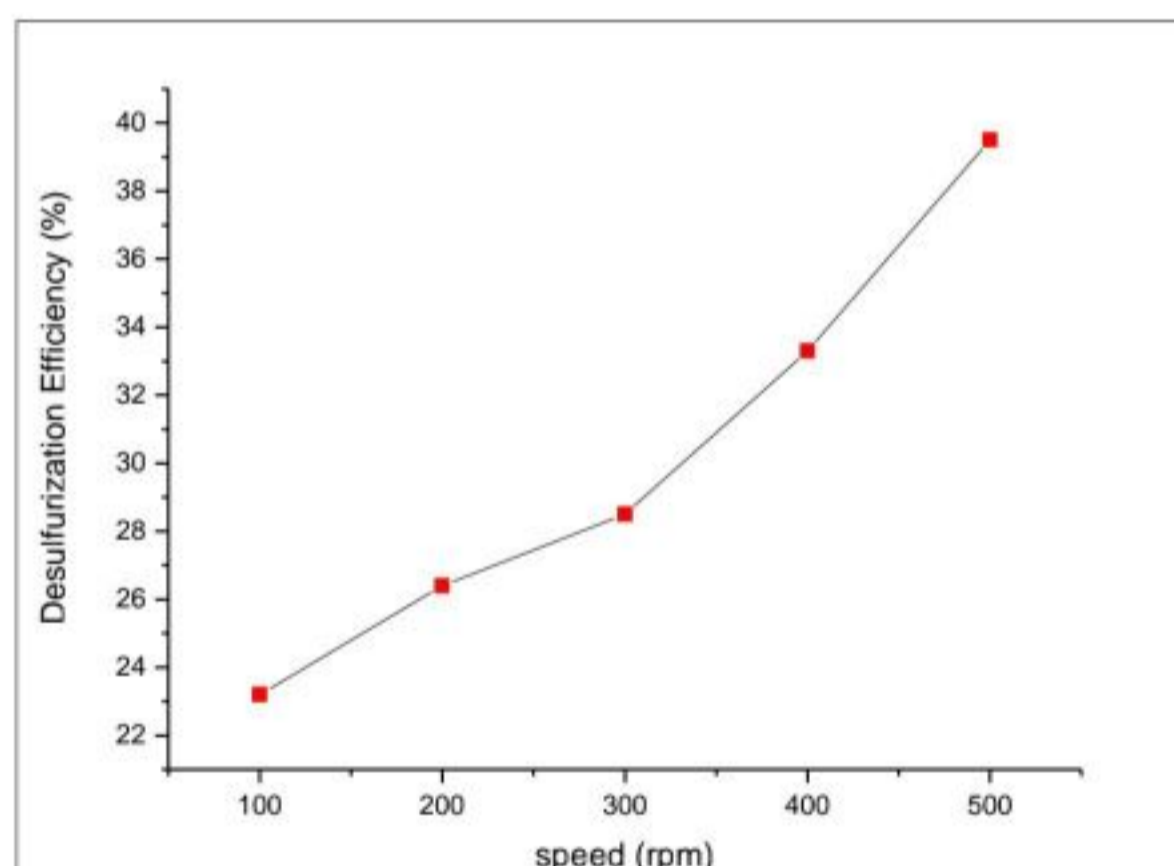


*Fig.3:-Desulfurization efficiency versus solvent/oil ratio.*

### Effect of Stirring Speed

The impact of stirrer speed on the oxidation desulfurization efficiency using

H<sub>2</sub>O<sub>2</sub>-acetic acid system is delineated in Figure 4.



*Fig.4:- Desulfurization efficiency versus mixing speed at temperature 65 °C and 60 min mixing time.*

The trend of the results indicates an increase in the desulfurization efficiency as the mixing speed increases. Moreover, the experimental observations indicated a high tendency for foaming on a further increase in the mixing speed beyond 500

rpm be inferred that 500 rpm is the ideal mixing speed.

At low stirrer speed, the oxidant molecules may have less chance to pass the oil/oxidant interface. By increasing stirrer speed, oxidant has more chance to diffuse across the oil (diffusion control) [21].

## CONCLUSION

Based on the present experimental study and the results obtained from using oxidation desulfurization for the desulfurization of AL-Masila crude oil, the extraction of oxidized sulfur compounds from crude oil with acetonitrile shows better performance as compared to acetone and ethanol due to its higher polarity. The oxidation desulfurization efficiency increases with increasing the reaction temperature, time and mixing speed. The optimum operating conditions are: 65 °C, 60 min and 500 rpm.

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