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SULFUR REMOVAL OF CRUDE OIL USING COMBINATIONS OF OXIDATION–EXTRACTION AND OXIDATION–ADSORPTION SYSTEMS

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Abstract

Sulfur is one of the nonhydrocarbon components available in crude oil and petroleum products. The need for eliminating sulfur compounds has been receiving high attention because of its undesirable attributes. Two different combinations of oxidation/extraction and oxidation/adsorption systems were applied to Baba Kurkur and Sherao crude oils to improve the parameters and the efficiency of desulfurization methods. In the oxidation process, in situ generations of a homogeneous oxidizing agent was obtained by the addition of hydrogen peroxide and acetic acid. To improve the efficiency of simple oxidation desulfurization method, activated carbon was used as an effective adsorbent, and acetone solution was used to extract sulfur compounds present in crude oil. The efficiency of desulfurization method was measured under different operating conditions to the sulfur content up to 2.07 wt%, and the influence of different parameters like; reaction time, temperature, and adsorbent dosage efficiency was studied. At the optimum operating conditions of 65°C, 60 min contact time, and adsorbent dose of 2 gm /100 mL, the sulfur removal was 43%, and at 2:1 solvent/oil ratio, extraction method gave comparable sulfur removal efficiency of 58%.

***Keywords**: Sulfur removal; Extraction; Oxidation; Adsorption; Crude oil.*

1. Introduction

Crude oil is the largest and widely used source of energy in the world. With an increasing demand for crude oil and petroleum products, petroleum refineries, storages, and petroleum fields are being confronted high sulfur content in the feedstock due to the declining supply of crude oil. The dissolved sulfide components in the crude oil, such as hydrogen sulfide, mercaptan, sulfoether, disulfide, and thiophene, can be encountered while well drilling activities. Sulfur can be part of gas deposits in carbonate reservoirs, or it can be the result of operations performed during drilling. Sulfur is the most notorious and undesirable petroleum contaminants and common problem facing personnel; due to the extreme toxicity of sulfur in the gaseous phase; and equipment because of sulfide stress cracking (SSC) phenomena affecting most strength steels.

The sulfides components in the crude oil, directly affecting the safe production and may cause to spread unpleasant odor, poisoning and inactivating the catalysts, and corrode the equipment in the oil exploration and extraction activities, transportation, marketing branch sells and distributes the petroleum products, and oil refining process [1]. Sulfur concentration can range from 0.1 to 8 wt% in the crude oils; moreover, these percents are becoming the gravity of the crude oil heavier with higher sulfur contents; therefore, there is an effect of sulfur concentration in increasing the density of crude and change the quality of crudes. The combustion of sulfur compounds is converted to sulfur oxides (SOx), causing corrosion, acid rains and air pollution, deforestation, water contaminants, smog, global warming, and even polluting the environment [2]. Therefore, identifying new technology of crude oil desulfurization has attracted significant interest. Nowadays, in the petroleum industry, the conventional process of hydrodesulfurization (HDS) is used to remove sulfur from petroleum distillates in which hydrogen gas is used to remove the sulfur contents through the formation of hydrocarbons and H_2S [3].

Eliminate sulfur (S) from crude oil and from petroleum products required high temperatures ranging from 300 to 400°C and high hydrogen pressure ranging from 30 to 130 atmospheres. High temperature and high pressure lead to some problems such as high cost, high energy operating conditions, and tend to remove some compounds such as heteroatomic products and aromatic hydrocarbons. Also, one of the constraints of a HDS process is the difficulty of removing thiophenic, and dibenzothiophene (DBT) compounds because of their steric hindrance [4]. Therefore, development of alternative desulfurization processes like adsorption, oxidation, extraction and bio desulfurization, are required because HDS is too expensive process for costly hydrogen and not efficient. There are a need to have attracted wide attention to the non-hydrogenated desulfurization (NHDS) methods taking into consideration cost, efficiency and meet the environmental regulations and petroleum industry requirements. Adsorption is a process currently used as HDS alternative method for clean fuels. It is often used to remove trace impurities from crude oil.

Adsorption may be physical or chemical; in physical adsorption, ions or molecules transfer process are obtained. The molecules and ions in a free phase bound and accumulate to a surface of the adsorbent substance by intermolecular forces, while in chemical adsorption, interaction between the solid and adsorbed is occurring. The commercial powder activated carbon got the highest sulfur removal efficiency. Oxidative desulfurization (ODS) is a chemical process can remove sulfur compounds from fuel feedstocks significantly. It has received more concern to be an innovative technology for ultra-deep desulfurization because it doesn't require sever conditions of operation, can be used to reduce the cost of operation and no hydrogen is required. Also, the oxidation process can be used to convert thiophene, benzothiophene, dibenzothiophene, and their derivatives into sulfones and sulfoxides. These compounds can be removed from the mixture by extraction, adsorption, distillation, or decomposition. Hydrogen peroxide (H_2O_2) as oxidizing agent which is the most promising oxidation systems in terms of selectivity, product quality, safety, environmental impact, and cost of effectiveness.

Many extraction processes for removing sulfur-containing compounds have been investigated. Based on the literature, it is found that impossible to obtain low sulfur content in the desulfurization process only from the extraction process. In order to obtain a more effective desulfurization process, an extraction process should be combined with hydrotreating or oxidation as a second treatment step. Wang *et al.* [4] used electrochemical catalytic oxidation in fluidized-bed reactor, and the optimal electrochemical desulfurization conditions are studied to achieve deep desulfurization for gasoline. Fabio *et al.* [2] used ultrasound energy to assist the oxidation process in removing sulfur compounds from some petroleum products in a batch laboratory system. The study showed high efficiency for sulfur removal in less severe pressure and temperature conditions when compared to the conventional hydro desulfurization processes. Adeyi *et al.* [5] the authors try to capture sulfur compounds in the crude oil**,** by comparing the desulphurization potentials of two metal oxides using activated manganese dioxide and activated zinc oxide. Activated manganese dioxide appeared to be more efficient during the adsorption compared with activated zinc oxide. Hariz *et al.* [6] investigated the performance of an electrocoagulation process in the removal efficiency of sulfide and organic compounds. The method was found to be highly efficient using two parallel EC units**.** Raja *et al.* [1] studied the desulfurization of crude oil by the oxidation companied extraction method. The study conducted at operating conditions of 30 wt% H_2O_2 and different percentages of acetic acid and showed that the crude oil quality and the structure were not affected after desulfurization by using N-dimethyl formamide as an extraction. Luna, *et al.* [7] evaluated sulfur removal of diesel fuel by using oxidation with high shear mixing condition. The author used alumina and activated carbon as adsorbents to enhance the oxidation method. The effects of adsorbent type, treatment time and dosage percent were studied, and it was concluded that by using the adsorbent material, the oxidation desulfurization efficiency is enhanced. Most of the studies in the open literature dealt with model fuels with low sulfur content rather than real ones. In the present study, we try to desulfurize real Iraqi crudes, which were Baba Kurkur and Sherao with sulfur contents of 1.8 and 2.07wt% respectively using two oxidative desulfurization combinations. The effects of different operating conditions that affect the desulfurization process was also investigated.

2. Experiment

2.1. Chemicals

Acetone, (>99.0% purity) activated carbon, hydrogen peroxide (H_2O_2), and acetic acid was obtained commercially.

2.2. Crude oil

Baba Kurkur and Sherao were the two Iraqi crude oils tested in this study, which contained a different percentage of sulfur. Their physical properties are listed in Table 1. The two samples of crudes were obtained from the gas separation station of Kirkuk field as a feedstock.

Table 1. The physical properties of crude oils used in this work

Physical properties	Baba Kurkur crude oil	Sherao crude oil
	Value	
Pour point (°C)	-30	-27
Red vapor pressure (psi)	10.6	14.0
Specific gravity / density (kg/m^3) at 15.6°C	0.8485/847.9	0.8472/846.9
API gravity	35.3	35.5
Carbone residue (wt %)	Nil	0.8%
H_2S (ppm)	75	50
Salt content (PTB)	Nil	131
Base sediment and water (wt %)	0.03	0.4
Sulfur content (wt %)	2.07	1.83
Asphalt (wt %)	1.33	1.8
Ash (wt %)	0.008	0.017
Viscosity (cSt)	7.2 at 80°F	6.7 at 80 F

2.3. Experimental procedure

2.3.1. Oxidation/extraction of crude oil

All the oxidation experiments of crude oil were performed in the batch process mode. The reactor used for the treatment studies consists of a glass cylinder of 250 mL capacity, and a magnetic stirrer with a hot plate. The mixture of acetic acid and H_2O_2 was combined directly into the reactors' Pyrex glass, which contains 100 mL of crude oil using a high speed magnetic stirrer for oxidizing the sulfur compounds. The required amount of H_2O_2 and acetic acid were mixed to prepare the peracetic acid at selected temperatures and different reaction times. All the oxidative desulfurization experiments were operated at atmospheric pressure. After oxidation process, the extractant was added to the oxidation reaction system at 65°C for 20 min. Thereafter, the mixture was cooled to room temperature, and solvent (acetone) was separated from the oil using a glass separator funnel for the solvent extraction step. Figure 1 shows the process flow diagram of oxidation/extraction desulfurization.

2.3.2. Oxidation/adsorption of crude oil

The same glass reactor equipment was used in the oxidation/adsorption experiments. The first step of the work was to study the effect of the amount of oxidation solution using an excess amount of 30wt % of H_2O_2-acetic acid to 100 mL feedstocks. Then, the mixture was combined in the reactor with the required dose of activated carbon. The speed of agitation was maintained at 500 RPM, and the effect of reaction temperature was studied at temperature range from 35 to 75°C for treatment time of 20 to 70 min. At the end of the process, the resulting emulsion was allowed to cool to room conditions, and the treated mixture is separated by transferring it to a centrifugal system in order to produce an effective separation of activated carbon particles from the reaction emulsion. A simplified process flow diagram and experimental conditions are given in Figure 1.

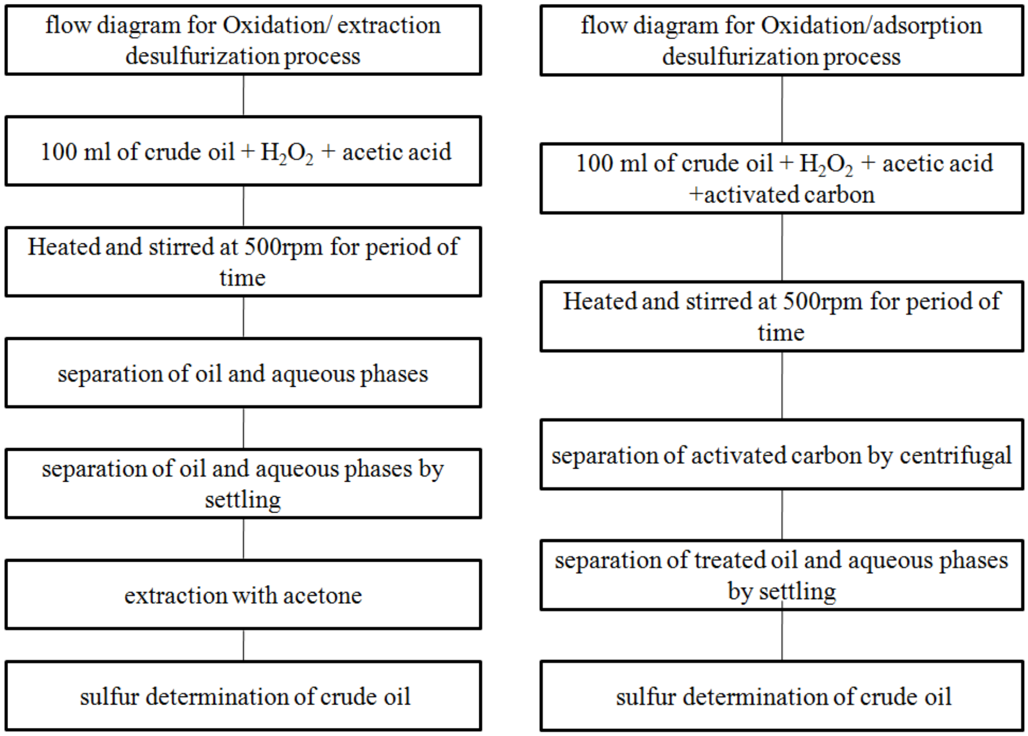

Figure 1. The process flow diagram of oxidation/extraction and oxidation/adsorption desulfurization

2.4. Analysis method

The sulfur content (wt %) of the two samples of crude oil was measured by SELFA-2800 sulfur analyzer manufactured by Horiba, USA, in the central laboratory of AL-Daura Refinery. The desulfurization efficiency is calculated by the following equations as the ratio of sulfur removal;

$$DE\% = \frac{wo-w}{wo} X\ 100\% \quad (1)$$

where, DE% =desulfurization rate; wo=initial sulfur content of crude oil; and w= final sulfur content of treated crude oil.

3. Results and discussion

In this study, the oxidative desulfurization was applied to two types of Iraqi crude oil. This technology one of the alternative methods proposed in the petroleum industry. It consumes fewer amounts of chemicals, required low temperature and pressure as reaction conditions, and the treatment time for desulfurization is less compared with the conventional methods. Among the different oxidation systems that have been used in the oxidative desulfurization process, H_2O_2/acetic acid (ethylenediaminetetraacetic acid) is preferentially chosen because it has the advantages of reaction simplicity which can satisfy the purpose of green chemistry and commercial availability. The reaction mechanism of oxidation desulfurization as follows;

$$H_2 + CH_3COOH \rightarrow H_2O + CH_3COOOH \quad (2)$$

$$CH_3COOOH + S \rightarrow SO + SO_2 + CH_3COOH \quad (3)$$

The organic sulfur is oxidized to sulfoxide and eventually sulfone by acetic acid or acidic medium; hence, the efficiency of sulfones compounds removal and different sulfur containing compounds can be easily separated from the crude oil by solvent extraction and adsorption.

3.1. Oxidation/adsorption desulfurization

In the present work, the desulfurization of crude oil by oxidation was carried out in different conditions. The effect of reaction time, reaction temperature and H_2O_2/ acetic acid ratio were studied. In oxidation system, $H_2O_2$was activated in the presence of acetic acid as a catalyst followed by adsorption to remove organic-bound sulfur from crude fuels. The Oxidation / Adsorption experiment was carried out with activated carbon as an adsorbent. Activated carbon is an effective adsorbent material with a strong physical bond for trapping of impurities, and many surface oxygen-containing functional groups that provide higher yields. The effect of sorbent dosage of activated carbon on desulfurization from Baba Kurkur crude oil was studied in the optimum conditions of oxidation.

The effect of the oxidation time is illustrated in Figure 2. The experiments carried out at a high shear mixing-assisted oxidative of 500 RPM, 65°C temperature, and 2 gm activated carbon adsorbent. It is observed that the desulfurization rate increasing with mixing time due to increase the residence times between the oxidation system and crude oil and between the oxidized sulfur and the adsorbent. The reaction time mechanism may be experimentally ascertained in 60 min as shown in Figure 2. No significant change in the process efficiency was undergoing beyond 60 min of treatment time, which was the optimized reaction time.

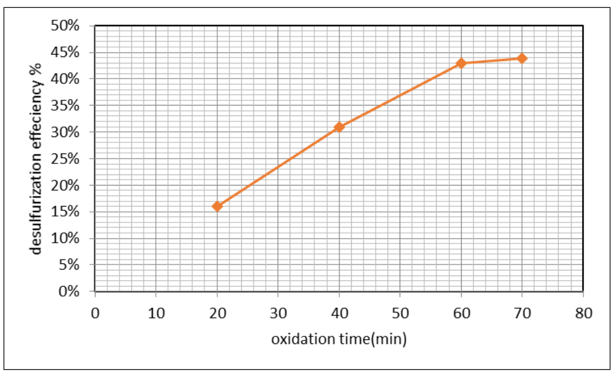

Figure 2. Effect of oxidation time on the desulfurization rate with an operating condition of: 30 wt% H_2O_2/acetic acid, acetic acid/H_2O_2 ratio is 2/1, T= 65°C and with activated carbon 2 gm as an adsorbent

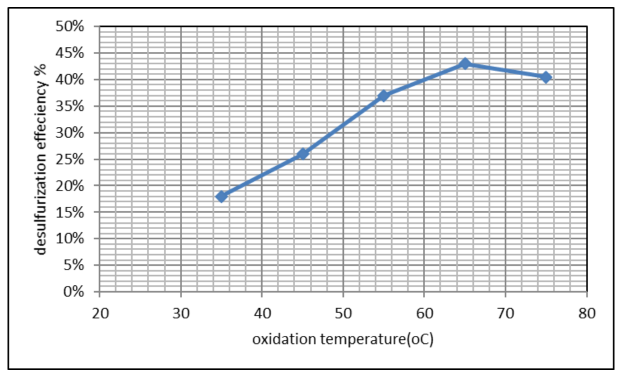

Figure 3. Effect of temperature on the desulfurization rate with an operating condition of: 30 wt% H_2O_2/acetic acid, acetic acid/H_2O_2 ratio is 2/1, treatment time= 60 min and with activated carbon 2 gm as an adsorbent

The effect of temperature on the sulfur removal was advised on a range of 35-75°C, as illustrated in Figure 3. It is indicated a sturdy dependence of the process efficiency on temperature; the reaction proceeds completely with the oxidation temperature increased. At low temperatures, there actions may not have sufficient thermal energy to attain thermodynamic equilibrium, and the adsorption process is generally classified as physisorption, which is governed by weak Van Der Waals forces. The results show that the desulfurization rate decreases with temperature exceed of 65°C; this is may be due to decomposition of oxidant components. Additionally, the quality of oil could be also changed with increasing temperature due to strip of valuable volatile components in crude oil. Also, as the temperature increases the unsaturated components can be oxidized and led to consuming part of the oxidant. Therefore, the 65°C is the optimal oxidation temperature, which has more effect on sulfur removal.

The effect of the acetic acid/H_2O_2 ratio of desulfurization is represented in Figure 4. The desulfurization rate displays an uptrend when the acetic acid/H_2O_2 ratio increases. The desulfurization remains constant as the ratio increase more than two; this is may be excessive acidity, which may weaken the adsorbs ion effect, leading to maintaining the desulfurization rate or reducing it slightly.

Figure 5 presents the effect of activated carbon at varying adsorbent dosages. The figure shows that increasing the adsorbent dosage from 1 to 2 g increased the desulfurization efficiency at a treatment time of 60 min. The slight increase in desulfurization efficiency at an activated carbon dosage greater than 2 gm can be attributed to the decline in the effective sulfur species binding sites onto the prevalence of the adsorbent due to the concentration gradient reduction, resulting in a lower efficiency process.

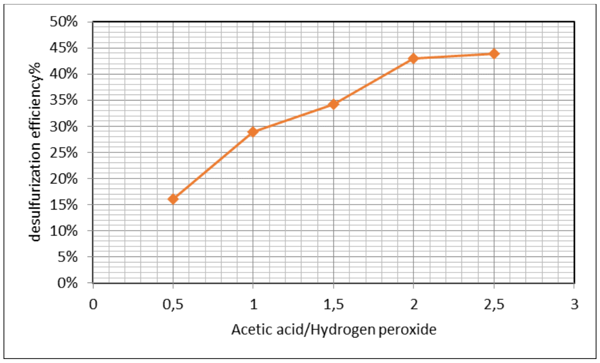

Figure 4. Effect of acetic acid/H_2O_2 ratio on the desulfurization rate with an operating condition of: 30 wt% H_2O_2/acetic acid, T= 65°C, treatment time= 60 min and with activated carbon 2 gm as an adsorbent

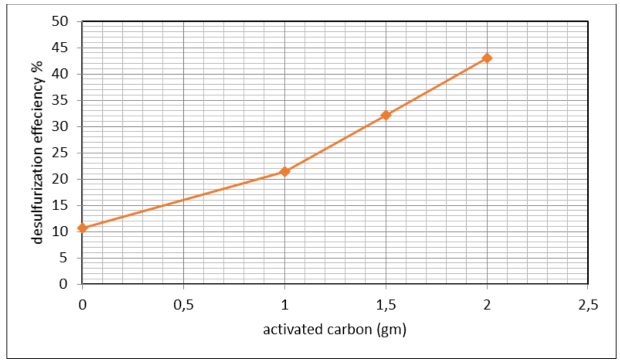

Figure 5. The effect of the adsorbent on the desulfurization rate with an operating condition of: 30 wt% H_2O_2/acetic acid, T= 65°C, treatment time= 60 min and acetic acid/H_2O_2 ratio is 2/1

3.2. Oxidation/extraction desulfurization

Generally, the organosulfur compounds are undesirable, polar, and present in different fractions of crude. Organosulfur compounds are very reactive during thermal reactions and need severe operating conditions to remove it completely. Desulfurization via an extraction process can be applied to eliminate organosulfur compounds from crude oil after oxidation. In the present work, acetone was chosen as potential extraction solvents because of the sulfur compounds have higher solubility in the solvent.

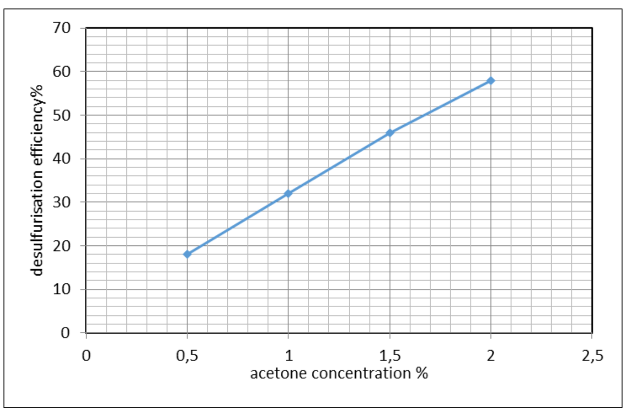

Figure 6. Effect of solvent to oil ratio (S/O) on the desulfurization rate with an operating condition of: 30 wt% H_2O_2–acetic acid, dosage of acetic acid /H_2O_2 ratio is 2/1, T= 65°C, treatment time= 60 min

The effects of solvent to oil volume ratio (S/O) have been investigated on the extraction efficiency of Sherao crude oil at the optimum conditions which have been studied to select the best (S/O) ratio. Figure 6 shows that acetone as an extracting agent is capable of extracting sulfur compounds. The desulfurization efficiency increases with increasing the solvent ratio because the sulfur compounds get oxidized by oxidation process, then increasing the solubility of those compounds in the system by extraction with acetone. It is important to point out that a sulfur removal of 58% efficiently extracted using a solvent (acetone), which was obtained using 2 volume ratio of acetone to oil.

3.3. Effect of desulfurization on fractions yield

The qualitative evaluation of different types and structures of desulfurization is difficult due to the complex composition of crude oil. Hence, to identify what happens to crude oil while desulfurization by oxidative/adsorption, the Iraqi crude oils were treated at the optimal desulfurization conditions. It distilled into four fractions, to study the effect of desulfurization on the yield of each fraction of crude oil also to calculate the desulfurization rate for different fractions as shown in Table 2 and 3. Table 2 shows that oxidative /adsorption desulfurization method not effect the fractions yield of Baba Kurkur crude oil. This indicates that the experimental oxidative systems have an insignificant influence on the crude oil composition of the feedstock, which makes the process to be a promising technology for applications in the future. From the desulfurization rate of different fractions, we can conclude that the heavy fraction crude contains more complicated structures of sulfur compounds than light crude oil. In other word, the heavy fraction contains components with high and strong polarity, which would weaken the sulfur removal effect.

Table 2. The fractions yield before and after desulfurization of Baba Kurkur crude oi

Fractions	Gasoline	Kerosene	Gas oil	Residue
Yield before desulfurization %	34.5	10.5	15	40
Yield after desulfurization %	33.7	9.8	15.7	40.8
Desulfurization rate %	68	51	34	17

Also, the oxidative /extraction desulfurization process effect on the yield of each fraction of Sherao crude oil was studied under solvent (acetone) and an oil volume ratio of 1.5. This process has little more effect on the yield of different fractions; this is may be due to the extra heat required for extraction process as shown in Table 3.

Table 3. The fractions yield before and after desulfurization of Sherao crude oil

Fractions	Gasoline	Kerosene	Gas oil	Residue
Yield before desulfurization %	35	11	14	40
Yield after desulfurization %	33.8	10	15.2	41
Desulfurization rate %	71	45	38	19

4. Conclusions

This study presents the use of adsorption and extraction scheme, combined with hydrogen peroxide and acetic acid for the desulfurization of real crude oil. This process carried out in a batch reactor system. The elimination of sulfur compounds was 58% of Sherao crude oil and 43% of Baba Kurkur crude oil. This may be attributed to the presence of complicated structures of sulfur compounds in heavy fraction crude compared with light crude oil. A high desulfurization rate of real crude oil was achieved at the oxidation temperature of 65°C for a treatment time of 60 min with acetic acid to H_2O_2 ratio of 2:1. The noticeable fractions yield from the crude oil remains almost unaffected after oxidative /adsorption and oxidative /extraction desulfurization of crude oil. This indicates that the experimental oxidative systems have an insignificant influence on the composition of crude oil feedstock, which makes the process to be a promising technology for applications in the future.

References

[1] Raja L. AL-Otaibi D. Xulian HL. Linhua S. Qingyin L. Desulfurization of Saudi Arabian crudes by oxidation–extraction Method, Appl. Petrochem. Res. 2015; 5: 355–362.
[2] Fabio DA. Paola MDA. Cezar BA. Matheus NAG. Elizabeth MM. Mauricio AS. Heloisa MAN. Valderi DL. Erico FMM. Sulfur removal from hydrotreated petroleum fractions using ultrasound-assisted oxidative desulfurization process, Fuel. 2011; 90: 2158–2164.
[3] Rafiee E. Sahraei S. Moradi GR. Extractive oxidative desulfurization of model oil/crude oil using KSF montmorillonite-supported 12-tungstophosphoric acid, Pet. Sci. 2016; 13: 760–769.
[4] Wang W. Wang S. Liu H. Wang Z. Desulfurization of gasoline by a new method of electrochemical catalytic oxidation, Fuel. 2007; 86: 2747–2753.
[5] Adeyi AA. Aberuagba F. Comparative Analysis of Adsorptive Desulphurization of Crude Oil by Manganese Dioxide and Zinc Oxide, Res J Chem Sci. 2012; 2: 14-20.
[6] Hariz IB. Halleb A. Adhoum N. Monser L. Treatment of petroleum refinery sulfidic spent caustic wastes by electrocoagulation, Separation and Purification Technology. 2013; 107: 150–157.
[7] Luna MDGD. Samaniego ML. Ong DC. Wan MW. Lu MC. Kinetics of sulfur removal in high shear mixing-assisted oxidative adsorptive desulfurization of diesel, Journal of Cleaner Production. 2018; 178: 468-475.

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