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Reduction of Sulfur Compounds from Petroleum Fraction Using Oxidation-Adsorption Technique

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Abstract

Oxidation of sulfur compounds in fuel followed by an adsorption process were studied using two modes of operation, batch mode and continuous mode (fixed bed). In batch experiment oxidation process of kerosene with sulfur content 2360 ppm was achieved to study the effect of amount of hydrogen peroxide(2.5, 4, 6 and 10) ml at different temperature(40, 60 and 70)°C. Also the effect of amount acetic acid was studied at the optimal conditions of the oxidation step(4ml H_2O_2 and 60 °C).Besides, the role of acetic acid different temperatures(40, 60, 70) °C and 4ml H_2O_2, effect of reaction time(5, 30, 60, 120, 300) minutes at temperatures(40,60) °C, 4ml H_2O_2 and 1 mlHAC) and effect of reaction temperature were studied.

The results showed that the percentage removal of sulfur compounds increases with the increasing amount of hydrogen peroxide and amount of acetic acid also the percentage removal of sulfur compounds increases by addition acetic acid, reaction time up to 300 minutes and reaction temperature.

In the fixed bed adsorption process, the oxidized kerosene having sulfur content being reduced to 939.28 ppm, was let to flow through a bed of $10Ni/\gamma\text{-}Al_2O_3$. The results showed that a sulfur removal of 95.38 % was obtained. By this the total sulfur removal of 98.38 % was obtained from the two consecutive processes. The resultant fuel had only 43.47 ppm. Also a study of the capability of the same bed to desulfurize raw feed of kerosene of 2360 ppm of sulfur compounds was investigated. 43.3% removal of sulfur compounds was achieved which reflects the catalytic properties of the adsorbent which could act as an oxidative adsorptive material. The results showed that by increasing feed flow rate, the breakthrough curve becomes steeper. Also the maximum removal of sulfur compounds was obtained in the case of bed height 20 cm and flow rate 0.3 l/h.

Key words: Oxidation-Adsorption, Petroleum Fraction, Sulfur Compounds

Introduction

The use of fossil fuels in various sectors for heat and power generation continues to loom up global stability and sustainability, more over sulfur containing compounds present in gasoline and diesel are making extra undesirable effectdue to the emission of toxic gases[1]. In order to protect the human health and reduce the environmental hazards, environmental regulation that tend to limit the sulfur levels to very low levels, have already been introduced in many countries during the last few decades. Also sulfur should be removed from the petroleum fractions as it causes poisoning of catalysts, corrosion of surfaces, and air pollution [2,3].

Nowadays, hydrodesulfurization (HDS) is the main method for the removal of sulfur from petroleum distillates in a refinery. Although HDS can eliminate aliphatic and cycle sulfur containing compounds effectively, it needs high temperature and high hydrogen pressure, which leads to many problems such as high investment, high operating cost and reduction of the catalyst cycle length. Besides, it is difficult for HDS to remove thiopheniccompounds such as dibenzothiophene (DBT) and its derivatives due to their steric hindrance. Therefore, the development of the alternative desulfurization processes like adsorption, oxidation, extraction and biodesulfurization is necessary [4]. Among these methods, Oxidative desulfurization (ODS) has been demonstrated to be a promising method for ultra- deep desulfurization technology because of its mild operation conditions, no hydrogen required and low cost of operation. During the process, the organosulfur compounds are oxidized to their corresponding sulfoxides or sulfones. The process is carried out in the presence of a catalyst and an oxidant agent, and the oxidized sulfur compounds are subsequently removed by extraction, adsorption, distillation, or decomposition [5,6]. Potential oxidative routes to produce ultralow sulfur fuels include the use of various oxidizing agent such as nitric acid, nitrogen oxides, organic hydroperoxides and peroxide. The most promising oxidation systems in the terms of selectivity, product quality, safety, environmental impact and cost of effectiveness are those using hydrogen peroxide as oxidizing agent [7]. Fig.(1) shows simplified network for ODS of DBT(8).

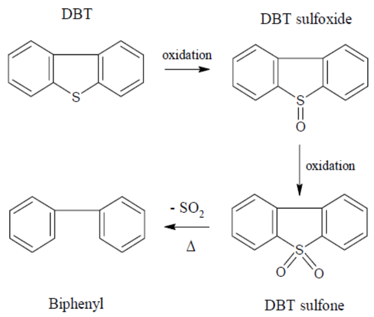

Fig. 1, Simplified network for ODS of DBT.

Adsorption is one of the most promising processes for deep desulfurization of fuel. This process is effective in the selective removal of low concentration materials from liquids. The fuel is brought in contact with a solid adsorbent which selectivity adsorbs sulfur containing compounds [9]. Desulfurization by adsorption depends on the ability of a solid sorbent to selectively adsorb organosulfur compounds from oil [10] on the other hand, adsorptive desulfurization is a new challenge to remove sulfur compounds from the transportation fuels, because adsorption would be accomplished relatively at lower temperature and pressure. Chen et al 2010[11] utilized an UOAD(ultrasound-assisted oxidative desulfurization) for a diesel fuel of, and the study revealed in a 89% reduction producing a fuel containing 800ppm sulfur compounds.

Most of the previous studies dealt with model fuels rather than real ones with low sulfur content of less than 1000 ppm (12). The main objective of this work is to study the oxidative desulfurization as applied to Iraqi kerosene with 2360 ppm sulfur content, followed by the study of the ability of nickel loaded on –Alumina for a further sulfur removal. This study was designed as follows: Batch mode Oxidation using hydrogen peroxide. The effects of the amount of H_2O_2,amount of acetic acid, temperature, addition of acetic acid, and reaction time were studied. 10% Ni/γ-Alumina was prepared by impregnation method and used for treating the oxidized kerosene from the batch step. The effect of flow rate, bed height, and adsorbent loading was studied, also desulfurization of raw kerosene using a bed of Ni/γ Al_2O_3 was studied.

Experimental

Materials

Kerosene, Boiling point 156.2-237.3^{0}C with sulfur content 2360 ppm, density 0.78 g/cm3,was supplied by the Al-Dora Refinery, γ-Alumina (spheres,3mm)supplied by Procatalyse, France. Hydrogen peroxide(50%) from Schralau. Acetic acid(99.5%), Rediel, and $N_2NiO_6.6H_2O$(99.7%), Fisher certified.

Procedure

Oxidation experiments (Batch Mode)

In each experimental run, 100 ml of untreated kerosene was introduced into a three – necked round bottom flask reactor equipped with fractionating column, condenser Fig(3), was stirred continuously at constant mixing speed(500 rpm) and heated to the desired reaction temperature using the magnetic stirrer heater. When the mixture reached the selected reaction temperature, the specified amount of Hydrogen peroxide was aed to the reaction mixture. The reaction time was set to be 300 minutes. Then, the solution was allowed to settle in a 100 ml separating funnel where clear distinguishable phases were obtained. After that sample was withdrawn. Figure (2) shows the two phase separation. In order to study the effect of acetic acid, the specified amount of the acid was added to the reaction mixture after the addition of hydrogen peroxide immediately. This procedure was followed as in Ahmedzeki and Ban 2014[12].

Fig. 2, Two Phase separation

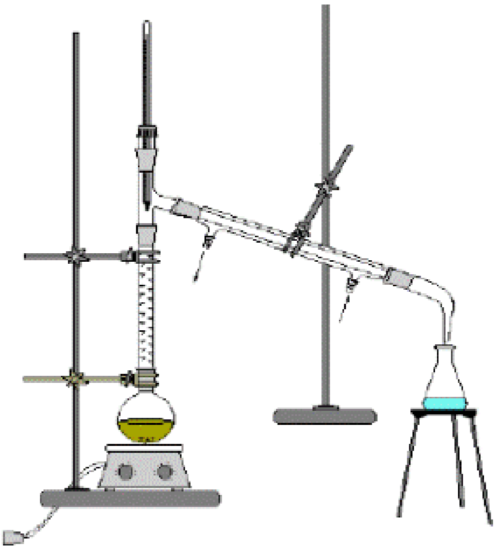

Fig. 3, Oxidation setup

Adsorbent preparation

Nickel loaded on gamma alumina was prepared by the impregnation method. Trials were made to obtain the desired loading percent. It was intended to prepare 10wt% Ni [13]. For this, 50g of γ-Al_2O_3 was soaked in 60wt% $Ni(NO_3)_2.6H_2O$ aqueous solution in 600 ml beaker. The mixture was stirred in a Jar test apparatus for 48 hrs. The next steps were, filtration using Buckner funnel with a vacuum pump, overnight drying in an oven at 110 °C and finally calcination in a programmable electrical furnace at 550°C for 5 hrs. Characterization of the adsorbent was made using XRD, , surface area, and Atomic absorption

Adsorption Experiments (Continuous Mode)

The complementary desulfurization step was carried out in a continuous mode laboratory rig (Fig 4). It consisted of QVF adsorption column 2.54 cm diameter and length of 35 cm. A Gauze plate of fine mesh was placed in the bottom of column to hold the spheres of the adsorbent. Kerosene from the previous step (with the best conditions) was fed to the column in a down flow manner. Flow rate of the entering feed was measured by a rotameter and was distributed by two layers one of ceramic balls and the other of glass beads. The flow rate and bed height were adjusted at the desired value for each run. Samples of the effluent from the adsorption column were analyzed for sulfur content at different time intervals. This test was made in the Al-Dora Refinery by Sulfur content analyzer (Antek). Extra runs were carried out on a fresh feed to investigate the capability of Ni/γ-Al_2O_3 to reduce sulfur content without the oxidation step using hydrogen peroxide.

Fig. 4, Continuous adsorption unit

Results and Discussion

Oxidation Experiments

Effect of Amount of Hydrogen Peroxide

Different amounts of H_2O_2 (2.5, 4, 6, and 10) ml was added to 100 ml of kerosene at differenttemperature (40, 60, and 70)°C at constant stirrer speed of 500 rpm and constant time of 300min.. As shown in Figure (5), the removal efficiency of sulfur compounds was found to increase with increasing amount of H_2O_2 to a certain point. This can be explained that the larger excess of hydrogen peroxide, on the one hand can be attributed to the thermal decomposition during the reaction attributed to the function of the oxidant in converting sulfur compound to sulfoxides and/ or sulfones. On the other hand excess amount is present the thermal decomposition during the reaction would cause a dilution and increase of the aqueous phase by which a decrease in the removal efficiency will occur[14].Another reason is the different types of sulfur compound like sulfides, thiophenes and their derivatives which differ in their reactivity keeping them unconcerned with higher amount of the oxidant. Therefore, from an economic point of view, and reaction rate into consideration, 4 ml H_2O_2 was chosen for further investigation, These results are well agreed with Li et al.,2013[14].It was noticed that at 70 °C and using 10 ml of H_2O_2 an increase in the sulfur removal was obtained. So, it can be concluded that increasing the amount of H_2O_2 along with increasing temperature had more pronounced effect resulting a more sulfur removal to about 65%.

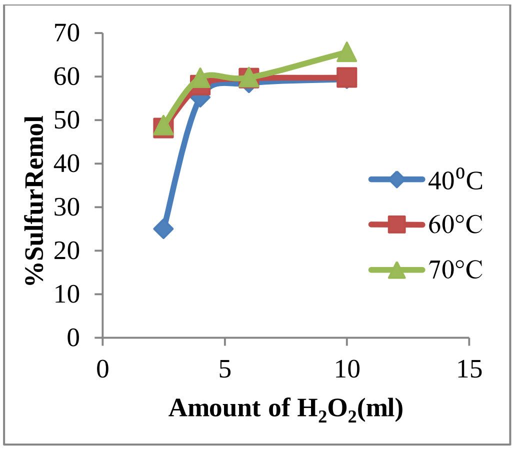

Fig. 5, The effect of amount of H_2O_2 on sulfur removal at different temperatures,500 rpm,300min.

Effect of Reaction Temperature

The effect of reaction temperature on sulfur removal efficiency was investigated for reaction time of 300 minutes at 40°C, 60°C and 70°C using different amount of hydrogen peroxide; (2.5, 4, 6 and 10) ml as shown in Figure (6). The results obtained indicated an enhancement the oxidation of thiophene compounds and it derivatives to sulfoxide and sulfones on increasing reaction temperature from 40°C to 70°C improvement in sulfur removal efficiency. As clear at 40 °C the sulfur removal was lower than those 60 °C and 70°C. The increase in reaction temperature enhances the oxidation of kerosene. This may be related to the decomposition of hydrogen peroxide paralleled with increase in reaction temperature to produce hydroxyl radicals that act as strong oxidizing agent. Therefore, 60°C as chosen as the reaction temperature and the higher temperature had no further beneficial effect on sulfur removal. The same behavior was also, observed by many investigators, like Lanju et al., 2006[15], who studied oxidation of thiophenes by using silica gel in hydrogen peroxide and formic acid system, and found that the sulfur removal rates are improved with the temperature exceeds 50°C while Peng et al., 2007[16] reported that the best results occurred at 70°C because increasing temperature contributed to the acceleration in the reaction speed; Cui et al., 2007[17]; Zhang et al., 2012[18] and Yu and Wang.,2013[19] found the oxidation reaction run efficiently under 60 °C

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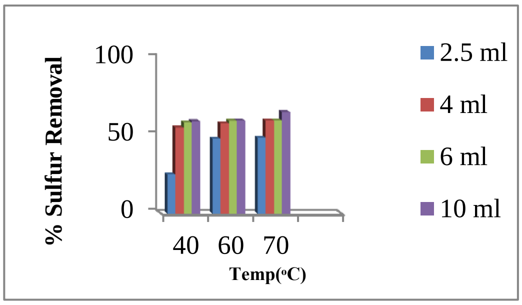

Fig. 6, The effect of reaction temperature on sulfur removal at different amount of H_2O_2 at 300min

Effect of Amount of Acetic Acid

The effect of amount of acetic acid on sulfur removal efficiency at temperature 60°C and 4 ml hydrogen peroxide was studied for the purpose of determining the best amount that will bring a best removal. The results of the dependence acetic acid catalyst oxidant are shown in Figure (7). This Figure represents the plotting of the amount of acetic acid with sulfur removal. The sulfur removal increase with increasing amount of acetic acid. This figure can clearly show that the increase in the sulfur removal is due to peracetic acid forming by acetic acid and hydrogen peroxide.Therefore the oxidation reaction can be promoted by increasing acetic acid concentration. Besides the oxidation rate increases with decreasing pH for example at 6 ml of acetic acid (pH 1.83) sulfur removal was 70% while at 8 ml acetic acid (pH 1.63) sulfur removal increased to 74.19%.

The above results agreed with those obtained by Yu et al., 2005[20] and Dehkordi et al., 2009[21].

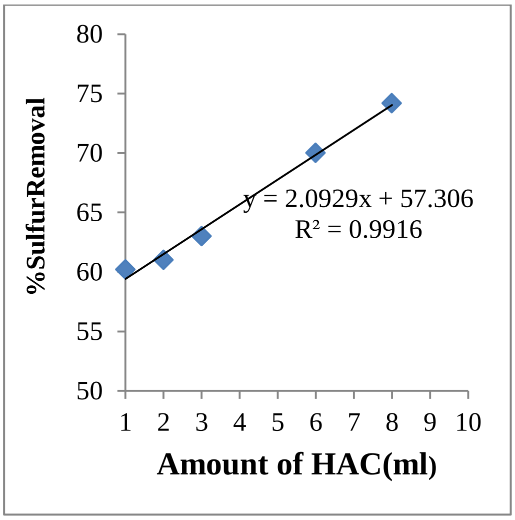

Fig. 7, The effect of amount of acetic acid on sulfur removal, at 60°C and 4 ml H_2O_2

The Role of Acetic Acid in Oxidation Desulfurization

In order to evaluate the improvement obtained by addition acetic acid on removal of organosulfur compounds, applying different temperature (40, 60, and 70)°C, for a constant amount of hydrogen peroxide 4 ml and 1 ml acetic acid was investigated, as shown in Fig. (8) .

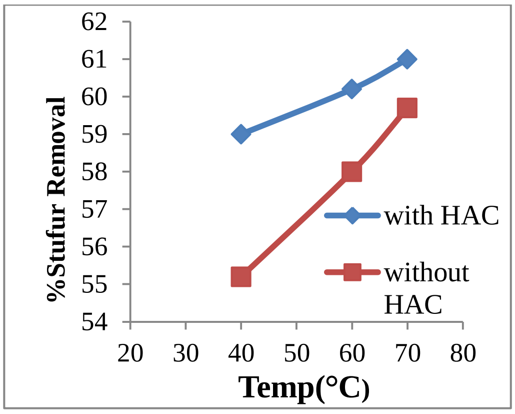

Fig. 8, The effect of addition acetic acid 4 ml H_2O_2, 1 ml HAC

It is obvious that the addition of acetic acid is improving the sulfur removal efficiency. At constant time of 300 minutes and without using acetic acid the sulfur removal obtained was 59.7% at 70ºC but it was 61% with acetic acid at the same temperature. This is explained that the sulfur removal increase by addition acetic acid because acetic acid catalyzes the oxidation reaction of sulfur containing compounds via forming peracetic acetic, which acts as an oxidizing agent giving its oxygen atom to the sulfur-containing compounds present in kerosene. Peracetic acid is formed in situ by acetic acid and hydrogen peroxide, therefor, the oxidation reaction can be promoted by addition acetic acidDehkordi et. al.,2009[21].

It is known that acids cause polarization of the O–O bond in hydrogen peroxide and accelerate the reaction both in the hetero- and homolytic direction due toa decrease in the activation energy of the transitional state. However, crude-cut sulfides can be oxidized into sulfoxides while heating without acids. In this case, initially molecules of hydrogen peroxide and then the acids formed participate in polarization of hydrogen peroxide. The degree of polarity is lower in the first case than in the second case. This is indicated by the low oxidation rate of sulfides in the absence of acids **[**22].

Effect of Reaction Time

Fig. (9) shows sulfur removal as a function of reaction time at operating temperature 40°C and 60ºC, amount of H_2O_2 4 ml and 1 ml acetic acid. The results were improved by increasing time of the reaction. This could be explained by describing interaction of oxidizing agents as time proceeds H_2O_2 and acetic acid can interact with dibenzothiophene to produce sulfones. This reaction like any other reaction needs enough time to complete and promotes as time goes on. Best results were observed at 300 minutes [23]. A similar behavior was obtained byYanxiuet al., 2013[24] forOxidative desulfurization of model sulfur compound by potassium ferrate presence of phosphomolybdic acid catalyst who found that the residual sulfur content decreased with an increasing oxidation time. The reaction was close to equilibrium and the residualsulfur content almost did not change.

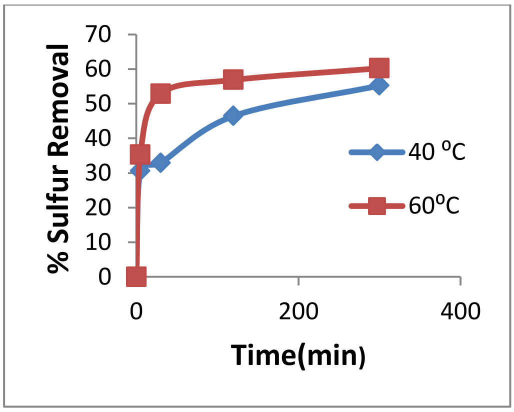

Fig. 9, The effect of reaction time on sulfur removal, amount of H_2O_2= 4 ml, amount of HAC= 1 ml, Temp=40°C and 60°C

Adsorbent Characterization

X-Ray Diffraction (XRD)

X-ray diffraction is one of the oldest and most frequently applied techniques in catalyst characterization. It is used to identify crystalline phase inside catalysts by means of lattice structural parameters, and to obtain an indication of particle size[25].XRD analysis was carried out to identify the phase transformation of Al_2O_3 support. By comparing with standard XRD pattern it is concluded that alumina was of gamma phase.The comparison of lattice spacing between alumina and standard XRD is shown in Table(1). The results showed that the gamma alumina was very near to the standard.

Table (1), comparison of lattice spacing between alumina and standard XRD

Alumina		Standard XRD	
Angle(2-Theta) deg.	D, spacing (Å)	Angle(2-Theta) deg.	D, spacing
19.5143	4.54528	19.450	4.56
31.1419	2.86963	31.936	2.8
37.1027	2.42115	37.603	2.39
39.1761	2.29765	39.491	2.28
45.8365	1.97808	45.862	1.977
59.9244	1.54236	60.897	1.520

Nickel Content and its Effect on Surface area, Pore and Porosity

The surface area, pore volume and porosity of γ-Al_2O_3 and Ni/γ-Al_2O_3 is shown in Table (2).

As observed in Table (2) surface area and pore volume of the sorbent decreased with loading Ni on γ-Al_2O_3 by blocking the active sites. On increasing the nickel content loading total specific surface area of the adsorbent decreased from 203.6 m^2/g (for γ-Al_2O_3) to 174.5391 m^2/g (for Ni/γ-Al_2O_3).

Table (2), Adsorbent Characterization

	Surface area (m^2/g)	Pore volume (cm^3/g)	Porosity (%)
γ-Al_2O_3	203.6	0.561	83.7040
Ni/γ-Al_2O_3	174.5391	0.458	80.6325

The pore volume of sorbent also decreased accordingly as the loading of the metal increased on the support. This is due to the Ni impregnation on the microstructure. These nickel particals are responsible for the adsorption of refractory sulfur compounds. Thus nickel the development of larger Ni particals at higher concentration ($>$ 10%) reduces the active sites per unit mass due to the agglomeration and growth of Ni crystal. Which filled the pores of the support covering its surface.

The desulfurization process strongly depends on the properties of the metal as well as the support materials. Adsorption of sulfur compounds onto γ-Al_2O_3 is a complex process and mainly controlled by both chemical interaction and physical factors. Ni metal sites helps in the removal of the organosulfur compounds having heteroatoms while the acidic parts of support helps in the removal of the substituted sulfur compounds having alkyl hindrance, reported that Ni has a reactive tendency and has been effective metal for removal of refractory sulfur compounds which have no alkyl hindrance. The sulfur removal increased up to 8-10% metal loading and decreasing thereafter.

This can be explained by the fact that Ni has strong molecular orbital that can attract the hindered benzothiophene and other cyclic sulfur compounds which can donate the electron density to the metal and further can make the metal more effective. This is results agreed withSarda et al., 2012[12].

Effect of Operating Conditions

Effect of Flow Rate

The effect of varying the volumetric flow rate (0.3 and 0.6) l/hr on the adsorption sulfur compounds from kerosene is shown by breakthrough curves drawn in Figures(10,11) in term of C/C_o versus time .The adsorbent bed height was fixed at 10 cm or 20 cm and inlet concentration of oxidized kerosene (939.28 mg/l) from the previous oxidation step.

Increasing the flow rate may be expected to make reduction on the thickness of the surface film. Therefore, this will decrease the resistance to mass transfer and increase the mass transfer rate due to easy passage of the adsorbent molecules through the particles and entering easily to the pores, in contrast this will decrease the contact time required between at a high flowrate to reach the desired concentration.

As flow rate increased, the breakthrough curves become steeper and reached the breakthrough quickly. This means that the contact time between kerosene and Ni/γ-Al_2O_3 is minimized, loading to early breakthrough. Increasing the flow rate gave to a shorter time for saturation due to adsorbate concentration, therefore the sulfur compounds do not have sufficient time to diffuse into pores of the adsorbent hence, sulfur removal increases with decreasing flow rate as shown in Figures (12, 13). These results agree with that obtained by Zeinab, 2012[26] and Hamsa, 2013[27].

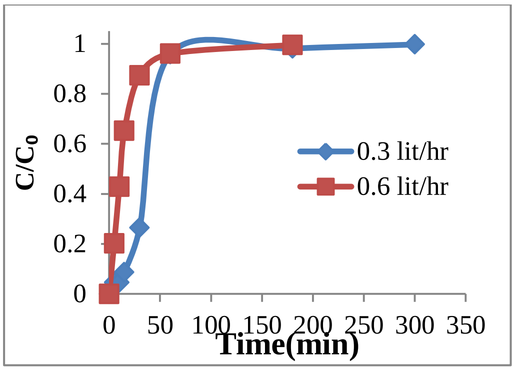

Fig. 10, Breakthrough curves for adsorption sulfur compounds at different flow rate, H=20 cm)

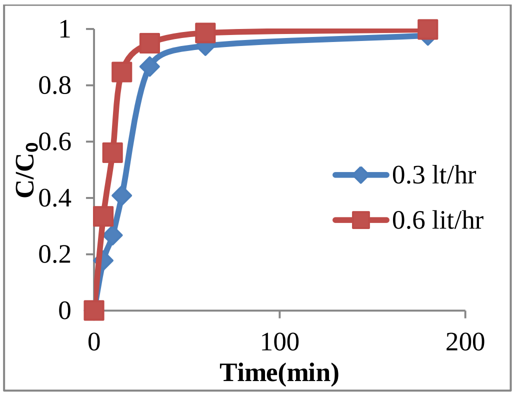

Fig. 11, Breakthrough curves for adsorption sulfur compounds at different flow rates,H=10 cm

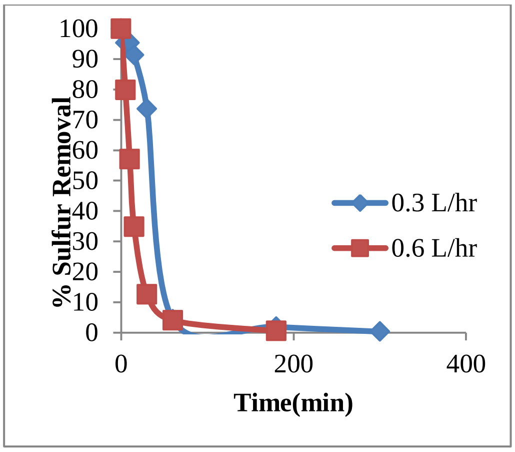

Fig. 12, Sulfur removal efficiency at different flow rates, H=20 cm

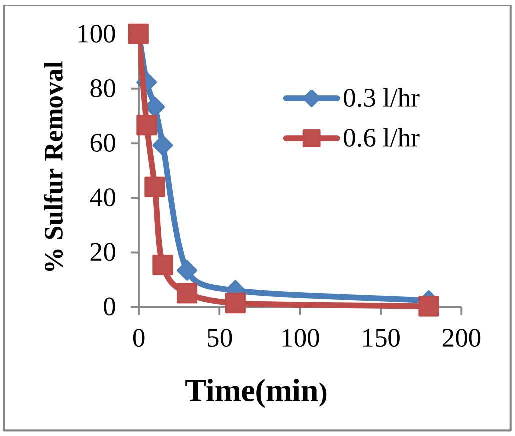

Fig. 13,Sulfur removal efficiency at different flow rates, H=10 cm

Effect of Bed Height

The effect of bed height was investigated for sulfur compounds adsorption onto Ni/γ-Al_2O_3; the experimental breakthrough curves are presented in Fig. (14, 15).

The breakthrough curves were obtained for two bed heights (10 and 20) cm which represented a weight of (43.8 and 87.6) grams respectively. This was studied for two flow rates(0.3 or 0.6) l/hr. It is clear that the increase in bed height increases the breakthrough time also, means an increase in the mass of the adsorbent packed in the column which offers more available adsorption sites for an adsorbate to be adsorbed. This shows that at smaller bed height the effluent adsorbate concentration ratio increased more rapidly than for a higher bed. Furthermore, the bed is saturated in less time for smaller bed height. Therefore, removal efficiency increases with increasing bed height, increasing the sorbent mass increased the corresponding sorption sites and sulfur species get enough time to diffuse into pores of the adsorbent as shown in Figures(16,17). This behavior was in agreement withMohammd, 2004[28] and Hamsa, 2013[27].

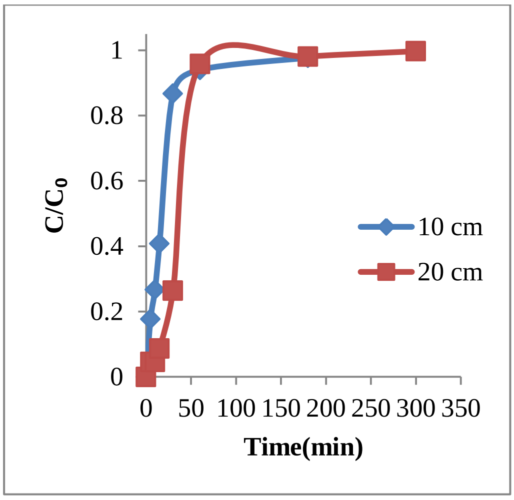

Fig. 14, Breakthrough curves for the adsorption sulfur compounds at different bed height, Q=0.3 l/hr

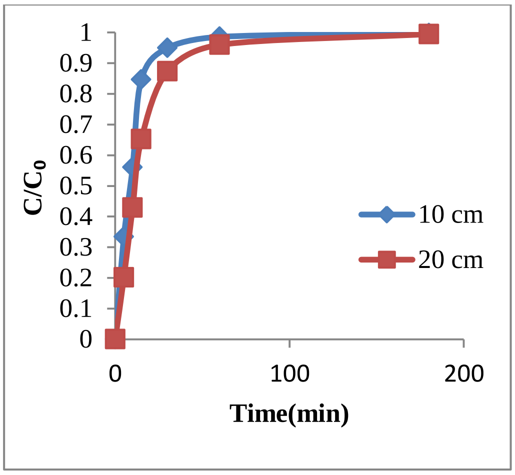

Fig. 15, Breakthrough curves for adsorption sulfur compounds at different bed height, Q=0.6l/hr

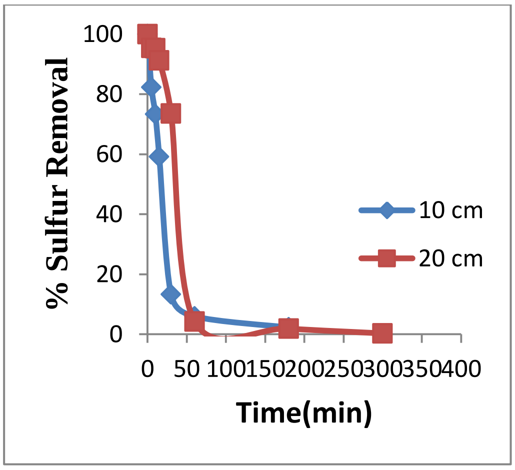

Fig. 16, Sulfur removal efficiency at different bed height, Q=0.3 l/hr

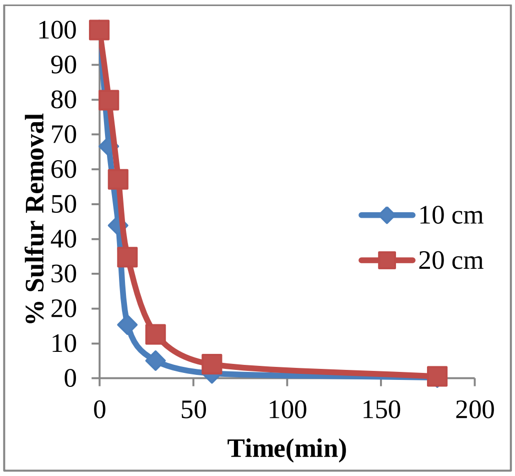

Fig. 17, Sulfur removal efficiency at different bed height, Q=0.6 l/hr

From these results, it is clear that the maximum removal of sulfur compounds was obtained at the bed height 20 cm with flow rate 0.3 l/hr. shown in Figure (12), 95.38% of the sulfur compounds was removed at the first five minutes. Also, it can be seen that after 30 minutes, 73.6% removal was obtained which is good enough to get rid of this amount of the harmful sulfur compounds, so regeneration of the bed at this time is recommended. At this time the bed adsorption capacity was calculated using Equation(1), where it was found equals to 1.182 mg sulfur/g Ni/γ-Al_2O_3[29].

$$q = \frac{V_f}{1000\,.m_{ads}} \int_0^t (C_i - C(t))\,\mathrm{dt} \quad .... (1)$$

q: adsorption capacity(mg Sulfur/g ads)
V_f : feed volumetric flow rate(ml/minute)
m_{ads} : weight of adsorbent(g).
C_i: initial concentration (mg/l).
$C_{(t)}$: concentration at any time (mg/l).
t: time(minute).

Breakthrough Curves with H_2O_2 and without H_2O_2

Fig. (18), shows breakthrough curves for adsorption of sulfur compounds in kerosene with H_2O_2 and without H_2O_2 while Figure(19) shows sulfur removal efficiency as a function of time. These Figures shows sulfur removal increased from 43.3% without H_2O_2 to 95.38% in the presence of H_2O_2. This is due to the fact that H_2O_2 oxidized benzothiophe and its derivatives to sulfoxide and then to corresponding sulfones which can be easily adsorbed on Ni/γ-Al_2O_3. Thus a combination of oxidant and adsorbent is effective because Ni has strong molecular orbital that can attract the hindered sulfur compounds and H_2O_2 can remove the linear and cyclic sulfur compounds by converting them to sulfones which can be adsorbed easily [12]. While adsorption process of kerosene without H_2O_2 can be explained that thiophene has two lone pair of electrons on the sulfur atoms: one pair lies on the six –electron pi system and their lies in the plane of the ring thiophene can act either as an type donor by donating the lone pairs of electrons that lie in the plane of the ring to the adsorbent or as a pi type donor by utilizing the delocalized pi electron of the aromatic ring (pi bond) to form a pi type complex with the metal ions. On the other hand, the sulfur adsorption capacity and selectivity of adsorbent can be further improved by modifying various types of surface active sites for sulfur adsorption, such as Lewis sites, useful functional groups, electronic defect centers, micro-structural defects and so on. According to Lewis acid-base theory, most thiophene sulfur compounds in jet fuels are Lewis base, which are easy to be adsorbed at Lewis acid sites. Hence, materials can be design and select that process strong Lewis acid sites to selectivity adsorb thiophene sulfur compounds with lone pair in jet fuels. The Lewis acid-base adsorption mechanism is interaction between the acid sites on the surface of adsorbent and thiophene derivatives. Additionally, it is known that the sulfur compounds have more affinity to oxidation than their analog hydrocarbon in jet fuels; therefore, perfect redox properties of adsorbent can improve oxidation of sulfur compounds into sulfones and sulfoxides. High conversions of sulfides to sulfones and sulfoxides provide stronger polarities that enhanced selective removal of organic sulfur compounds with solid adsorbent at ambient temperature and atmospheric pressure. As a consequence, perfect redox properties of adsorbent can indirectly increase the sulfur adsorption capacity and selectivity [30].

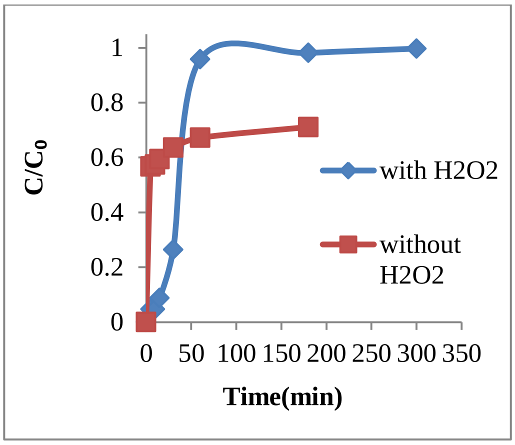

Fig. 18, Experimental breakthrough curves for adsorption sulfur compounds Q= 0.3 l/hr, H=20 cm)

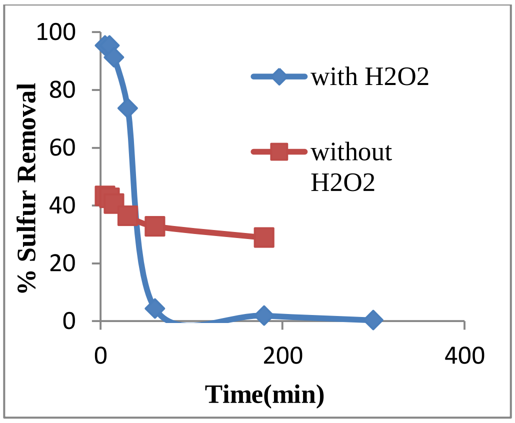

Fig. 19, Sulfur removal efficiency with H_2O_2 and without H_2O_2, Q=0.3 l/hr, H=20 cm

Conclusions

The present study led to the following conclusions:

1- The oxidation of sulfur compounds from kerosene by hydrogen peroxide with acetic acid shows better performance as compared to oxidation without acetic acid. The sulfur removal efficiency of both conditions is 60.2% and 58% respectively.2-Sulfur removal efficiency by oxidation process increases with increasing reaction temperature, amount of hydrogen peroxide and reaction time. The preferable operating conditions are 60^o C, 4 ml $H_2O_2$and 300 minute.

2- Acetic acid was found to act as a catalyst for the oxidation process. It was found that by adding 1ml acetic acid at 4 ml H_2O_2 and reaction temperature 60 °C the removal efficiency was enhanced to 60.2%.

3- The fixed bed adsorption process may be considered as a complementary desulfurization process. It was found that the sulfur removal increases with increasing bed height and decreasing flow rate.

4- The highest sulfur removal efficiency is 95.38%, obtained by treating oxidized kerosene in the presence H_2O_2 by Ni/γ-Al_2O_3 at fixed bed experiment in adsorption process at 20 cm bed height with 0.3 l/hr flow rate to obtain ultra-fine fuel.

5- Maximum sulfur removal efficiency of kerosene without H_2O_2 oxidization step in the Ni/γ-Al_2O_3 fixed bed is 43.3%.

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