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3 **Desulphurization of Tawke diesel fuel by**
4 **ADSORPTION on Na-Y type zeolite, Local Clay and**
5 **Active Carbon**

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11 **ABSTRACT**

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The removal of sulfur compounds from Tawke diesel fuel is processed by the use of granular Na-Y type zeolite, MOR type zeolite, molecular sieve 3A type, local clay and activated charcoal. The results are characterized by sulfur meter to ensure before and after desulfurization. FTIR and GC analysis are also used to enhance the characterization of sulfur removal. it is clear Apparently from our results that the desulfurization by activated charcoal is more efficient than by the clay, zeolite type and almost reach more than 10%.

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14 *Keywords: desulfurization, diesel, adsorbive desulfurization, Na-Y type zeolite, active*
15 *carbon, clay adsorbent*

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17 **1. INTRODUCTION**

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19 Sulfur compounds are undesirable materials in petroleum generally and in diesel
20 especially due to fear of environmental pollution and corrosion of the refinery equipments.
21 Removal of these compounds is of great concern today. During combustion, sulphur
22 compounds are converted mainly to sulphur dioxide (SO₂), which is a major cause of
23 air pollution and acid rains [1, 2]. In order to prevent air pollution caused by exhaust
24 gases, governments of many countries all over the world have assigned sulphur removal
25 from transportation fuels since the last twenty years ago. For example, USA government
26 limits the sulphur maximal content in on-road fuels to 15 ppm [3,4]. Identical or even
27 stronger demands were made for the fuels produced in the European Union as 10 ppm
28 [5]. Demands for clean diesel fuels in Iraq generally and in Kurdistan region especially are
29 high. The removal of organic sulfur compounds from transportation fuels is becoming a more
30 important issue in the recent years not only for environmental regulations but also because
31 of the possibility that these fuels can be re-formed on-board to produce hydrogen-rich gas as
32 a fuel for fuel cells for mobile, portable, and stationary applications. To reform these liquid
33 fuels for fuel cell applications, the sulfur level should be further reduced close to zero ppm
34 because the presence of even traces of sulfur is a poison to the reforming catalysts as well
35 as electrode catalysts[6].

36 Hydrodesulphurization (HDS) is currently being used in the petroleum industry. HDS is the
37 only one widely used industrial technology. This method has some disadvantages due to the
38 expensive catalysts and using valuable hydrogen for this process. HDS also has limited
39 effectiveness on removing thiophenes, benzothiophene, dibenzothiophene and its
40 derivatives from diesel [7,8].

41 Adsorption is the most common HDS alternative method currently used to achieve ultra
42 clean fuels[9]. Adsorption is a mass transfer process wherein molecules in a free phase
43 become bound to a surface by intermolecular forces. It can be done under ambient
44 conditions, such as room temperature and normal pressure. The reaction rate is very high.

Sulfur compounds in diesel can be removed by physical adsorption, chemisorption and π -complexation adsorption. Physisorbed sulfur compounds can be easily removed from adsorbents by heating or decreasing pressure[8]. So, it is easy to regenerate the adsorbents. The zeolite-based adsorbents have been used as promising materials for selectively removing the sulfur derivatives from diesel. Metal ion exchanged Y zeolites showed high selectivity and capacity for sulfur compounds using π -complexation between metal ion and sulfur compounds [10]. The selectivity of the zeolite-based adsorbents varies according to fuel composition such as aromatic and moisture concentrations[11]. Activated charcoal, Clay minerals also were used to remove nitrogen and sulfur compounds, besides their using in petroleum refinery as catalyst for cracking reactions[12].

This paper discusses the non hydrodesulfurization processes, by zeolite, local clay and activated carbon. The development of the mentioned processes is given, along with a discussion of recent studies in this field.

2. MATERIAL AND METHODS

Diesel sample used in this study was obtained by fractional distillation from Tawke crude oil -Zakho KRG-Iraq. Typical physical and chemical properties of diesel fuels that was (are) used are presented in Table 1.

Table 1 Physical and Chemical Properties of Diesel Products

Tests	Diesel Fuel	Method
B.P, °C	185-350	ASTM D86
Density at 15.6°C	0.8334	ASTM D1217
API Gravity at 15.6 °C	38.08	ASTM D 1298
Water content,	133.122	-
Cetane index	56.5	ASTM D976
Diesel index	49.7	Calculate
Cloud Point , °C	-15.5	-
Sulfur content wt%	1.0092	ASTM D4294
Flash Point , °C	84	ASTM D93
Aniline Point , °C	65	ASTM D611
Refractive Index (n) at 25.3 °C	1.462687	ASTM D1218

The adsorbent materials used in this study are commercial activated charcoal p.a., powder from Carl Roth GmbH + Co. KG, (Melting point 3550 °C, Bulk density of 150-250 kg/m³), granular Na-Y type zeolite having SiO₂/Al₂O₃ molar ratio of 5.4, granular MOR type zeolite without binder having SiO₂/Al₂O₃ molar ratio of 9 and molecular sieve 3A type from Sigma-Aldrich. Commercial activated charcoal is used after calcining at 700 °C (40% weight loss) for 4 h. H-form of Y and H-MOR without binder zeolites was prepared by ion exchanging with NH₄NO₃ solution at 70 °C to obtain NH₄-form of zeolite. After ion exchange and then filtered the solution, samples washed with distilled water, dried at 120 °C for 4 h, and then calcined at 550 °C for 4 h to obtain H-form of each Y and MOR type zeolite. The ion exchange process is repeated four times, each time for one hour to complete the required level of ion exchange. Clay is collected from (Zawita), this clay is modified with hydrochloric acid 0.1 N in order to remove the organic materials and increase the adsorption capacity. 100 g of the clay sample was mixed with 500 ml of 0.1 N HCl solution and refluxed for 2 h. The slurry was

then filtered and washed with deionized water then dried in the oven at 120 °C for 6 h. This clay was ground to fine powder and then screened through a 200 micron mesh sieve. Finally the clay sample was activated by heating at 600 °C in the Muffle furnace for 5 h and then stored in a vacuum desiccator.

All adsorbent materials present in this study were used after heating at 600 °C for 2 hours prior using.

2.1. METHOD

Diesel fuel was mixed with 5 % and 10% by mass with both commercial activated charcoal and clay for 1-6 hrs using flask shaker at a rate of 60 round /min at 30 °C and ambient pressure. The resulting solution was filtered to separate the solid adsorbent material from filtrate. The filtrate was analyzed for sulfur content. This step is to choose the proper contact time that gives highest sulfur removal.

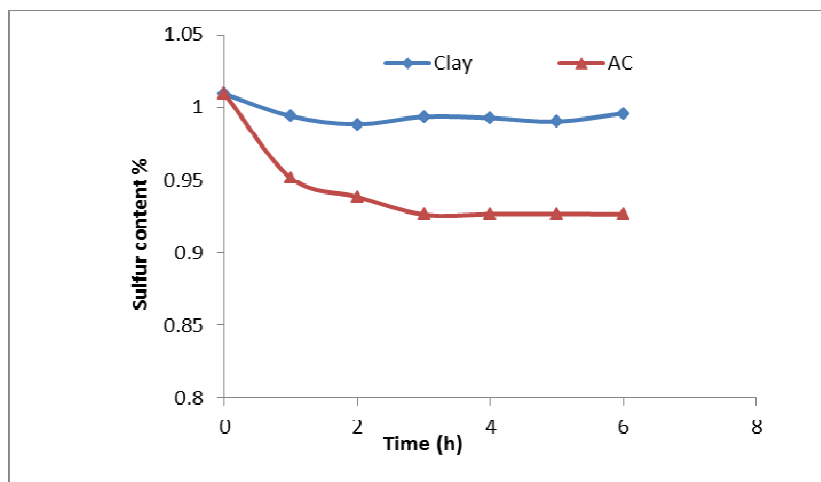
Diesel oil also was mixed with 5% by weight each of the following adsorbent materials: activated charcoal, granular H-Y type zeolite having SiO₂/Al₂O₃ molar ratio of 5.4 , granular H-MOR type zeolite without binder having SiO₂/Al₂O₃ molar ratio of 9 and molecular sieve at 30°C and 60°C and ambient pressure for 3 hrs. The filtrate was analyzed for sulfur content. The sulfur content was measured using EDXRF Sulfur Meter RX-360SH. The FTIR scans of diesel samples are obtained before and after desulfurization using Perkin Elmer spectrum one B FTIR spectrophotometer.

The mineralogical composition of the clays used in the adsorption study was examined by X-Ray Fluorescence, PW-1600 Spectrophotometer Philips, the ignition loss was determined by burning 1 g sample at 1000 °C till constant weight. Also the analysis for samples were performed using Perkin Elmer Clarus 580 Gas Chromatograph (GC), (FID) flame ionization detector. The chromatographic analysis was conducted according to the following program- Initial temperature of 30 °C maintained for 5min, increase at the rate of 4 °C per min to 250 °C and maintained for 30 min at 250 °C. Helium was used as a carrier gas at a pressure 48psi during the analysis.

3. RESULTS AND DISCUSSION

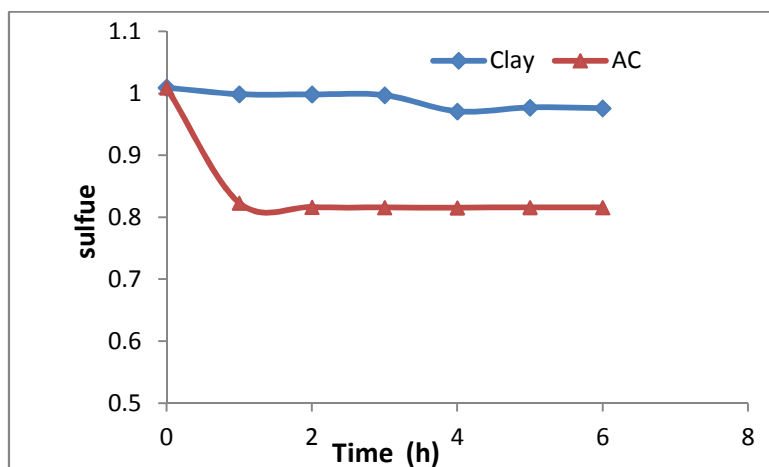
The X-ray analysis of the virgin clay was carried out in order to know its mineralogical nature and chemical composition. The analysis shows that the percentage of Al₂O₃ and SiO₂ in the sample is 7.29% and 41.5%, respectively. Whereas the percentages of other metals like Fe₂O₃, CaO, K₂O, MgO and Na₂O are 9.20%, 10.38%, 0.65%, 9.82% and 0.47%, respectively. The major constituents of the clay are aluminum, silicon, magnesium, iron, oxygen and calcium, which correspond to its chemical formula. Loss on ignition for the above clay is high as 22.08% this due to the larger amount of organic matter and soluble salts. The sulfur content was plotted with time hours using 5% wt and 10% wt activated charcoal and clay at 30 °C as in figure 1 and figure 2 below:

126 **Figure 1 Effect of time on desulfurization of diesel (5% activated charcoal and clay at**
 127 **30 °C)**



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130 **Figure 2. Effect of time on desulfurization of diesel (10% activated charcoal and clay**
 131 **at 30 °C)**



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133 It is clear from figures 1. and 2. that the three hours shaking are enough for activated
 134 charcoal to remove good amount of sulfur from diesel fuel while clay respond less even at 10
 135 % concentration. In other word It can be seen that optimum adsorption capacity were
 136 reached within 3hrs. indicating that all adsorption sites are saturated.
 137 The results showed that the sulfur content recovery was 5.73% after one hour shaking with
 138 5% activated charcoal and this removal was increased to about 8.2% by shaking for 3 hrs
 139 with activated charcoal. By increasing the percentage of activated charcoal to 10% the sulfur
 140 recovery was 9.79% after 3 hrs shaking and 1.5% with clay.
 141 Thus, by increasing the amount of commercial activated carbon and clay from 5% to 10%wt
 142 Fig. 2. The curve showed little decrease of sulfur content especially for activated charbon
 143 more than clay.

144 Desulfurization of Tawke diesel fuel containing about 1.0092%wt sulfur was studied over
 145 used adsorbent materials for three hours at 30 °C; 60 °C and ambient pressure.

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The results of adsorption studies on the desulfurization of Tawke diesel fuel over ion exchanged zeolites granular H-Y , granular H-MOR without binder , desiccant and activated charcoal are summarized in table 2. The results show that under present experimental conditions the adsorption capacity varied among activated charcoal, granular H-Y , granular H-MOR without binder and desiccant depending upon the nature of adsorption capacity of each adsorbent used in this process.

Table 2. Effect of temperature on desulfurization after 3 hours sorption with 5% of different adsorbents

Adsorbants	Sulfur content %wt at 30 °C	Sulfur content %wt at 60 °C
Mother	1.0092	1.0092
granular H-MOR type zeolite without binder	0.9992	0.9991
granular H-Y type zeolite	0.9638	0.9433
desiccant NO 17-1159	0.9810	0.9851
activated charcoal	0.9262	0.9103
clay	0.9969	0.9948

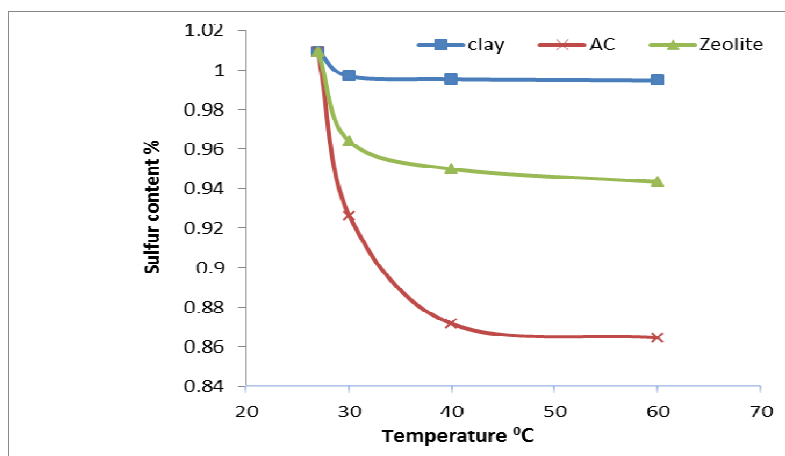
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Figure 3. Effect of temperature on desulfurization of diesel with with 5% of different adsorbents



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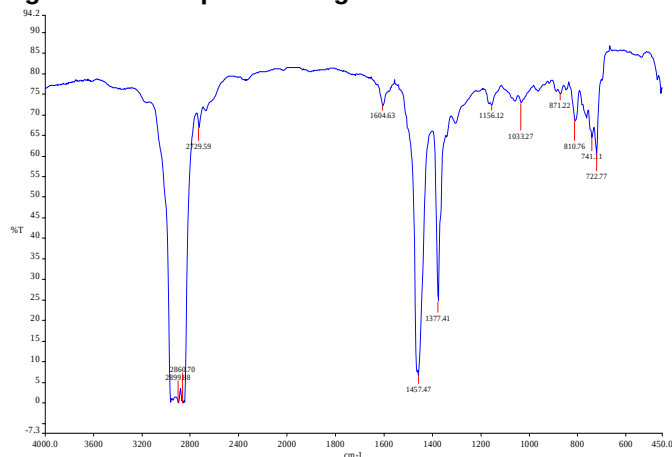
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Adsorptive desulfurization of diesel was also carried out at different temperatures i.e. 30, 40 and 60 °C as indicated in figure 3. The data show that the desulfurization by activated carbon increased more than clay and zeolite (H-Y type zeolite) as the temperature increased, while clay and zeolite respond very little. It may be attributed to the endothermic nature of the process, which is enhanced with the rise in temperature. The activated charcoal exhibited better performance in desulfurization of diesel than all zeolite types, it could adsorb both nitrogen species and refractory sulfur species in diesel while adsorption capacity for nitrogen species is much larger than that for sulfur species. The sulfur content after treatment with granular H-MOR type zeolite without binder is less than that treated with granular H-Y type zeolite this is due to the adsorption on MOR without binder affected by method of synthesis (clay particles) and MOR type zeolite more sensitive than Y type zeolite.

173 The color of diesel sample treated at 30 °C turned from red to light yellow, probably due to
174 the adsorption properties of used adsorbent materials which enable it to remove **colored**
175 **materials**.

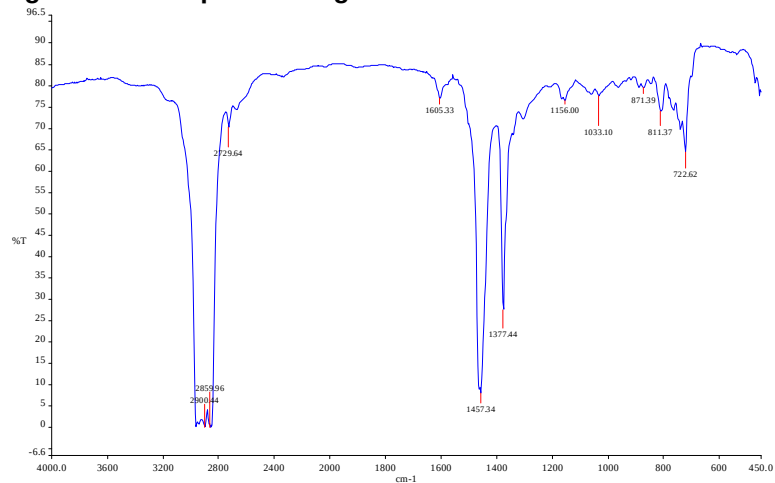
176 The infrared spectra of diesel samples were taken before and after desulfurization with
177 activated charcoal figure 4 and 5. The formation of peaks in the region of 2500-2675 cm⁻¹
178 giving information about thiols (S-H). Peaks at 1030-1060 cm⁻¹ are aromatic thiols,
179 moreover weak peaks between 800-700 cm⁻¹ are attributed to symmetric and asymmetric
180 vibration of the C-S stretching bonds which belongs to thiophenic and thiols compounds.
181 The significant suppression and changes in transmittance spectral band within the region of
182 1200-600cm⁻¹ indicates that a portion of organic sulfur compounds is suppressed. The
183 untreated diesel oil transmits more infrared light than the treated one, this decrease could be
184 attributed to the presence of detached sulfur compounds.[13,14]
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186 **Figure 4. FTIR spectra image of diesel before desulfurization with activated charcoal**



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Figure 5. FTIR spectra image of diesel after desulfurization with activated charcoal



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GC chromatogram of diesel fuel after treatment with 5%w activated charcoal at 30 °C **Figure 7. shows clear decrease of** intensity of some beaks In comparison with chromatogram of diesel fuel before treatment **Figure 6.** especially at the time of 15 and 16 min. this due to the sorption activity of used adsorbent material .

However, this was not a critical variable because of the complexity of diesel fuel, and there is no standard solutions for calibration, it is very difficult for us to use GC analysis to give more explanation.

Figure 6. Chromatogram of diesel fuel after treatment with 5%wt activated charcoal at 30 °C

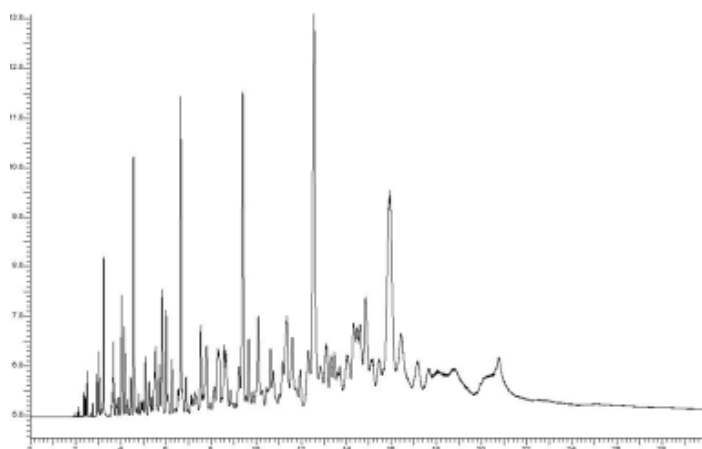
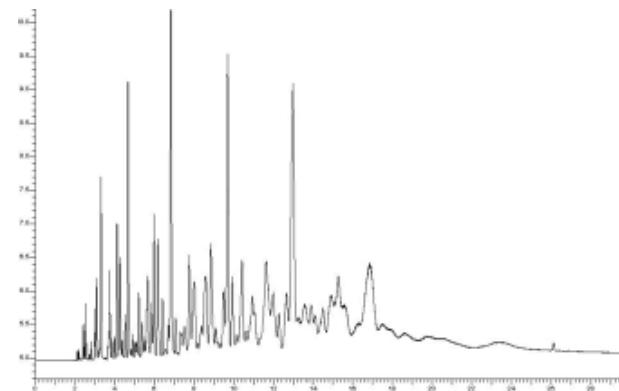


Figure 7. Chromatogram of diesel fuel before treatment



4. CONCLUSION

Based on our experiments it may be concluded that it is impossible to obtain low sulfur content in desulfurization process only with adsorption on used adsorbent materials. desulfurization by activated charcoal more efficient than the other adsorbents and give us a future perspective to focus on this type mainly and made some modification to increase the activity of the adsorbent.

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