

# **Desulphurization of Tawke Diesel Fuel by Adsorption on Na-Y Type Zeolite, Local Clay and Active Carbon**

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## **Authors' contributions**

*This work was carried out in collaboration between both authors. Author MKY designed the study and wrote the protocol. Authors MKY and SMS performed the statistical analysis, managed the literature search and wrote the first draft of the manuscript. Both authors read and approved the final manuscript.*

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## **ABSTRACT**

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 and infrared spectroscopy to improve the results of desulfurization process. 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 20%.

**Keywords:** *Desulfurization; diesel; adsorptive desulfurization; Na-Y type zeolite; active carbon; clay adsorbent.*

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## 1. INTRODUCTION

Sulfur compounds are undesirable in petroleum refining process. They tend to poison catalysts used in this process. Sulfur compounds are also responsible for causing several corrosion problems in pipeline, refining equipment, pumping, as well as poisoning the catalytic converters that used in automotive engines. Removal of these compounds is of great concern today. During combustion, sulfur compounds are converted mainly to sulfur dioxide (SO<sub>2</sub>), which is a major cause of air pollution and acid rains [1,2]. In order to prevent air pollution caused by exhaust gases, governments of many countries all over the world have assigned sulfur removal from transportation fuels since the last twenty years ago. For example, USA government limits the sulfur maximal content in on-road fuels to 15 ppm [3,4]. Identical or even stronger demands were made for the fuels produced in the European Union as 10 ppm [5]. Demands for clean diesel fuels in Iraq generally and in Kurdistan region especially are high. The removal of organic sulfur compounds from transportation fuels is becoming a more important issue in the recent years not only for environmental regulations but also because of the possibility that these fuels can be re-formed on-board to produce hydrogen-rich gas as a fuel for fuel cells for mobile, portable, and stationary applications. To reform these liquid fuels for fuel cell applications, the sulfur level should be further reduced close to zero ppm because the presence of even traces of sulfur is a poison to the reforming catalysts as well as electrode catalysts [6].

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

Adsorption is the most common HDS alternative method currently used to achieve ultra clean fuels [9]. Adsorption is a mass transfer process wherein molecules in a free phase become bound to a surface by intermolecular forces. It can be done under ambient 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  $\pi$ -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  $\pi$ -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-hydrodesulphurization 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. MATERIALS 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 gm/cm <sup>3</sup>	0.8334	ASTM D1217
API Gravity at 15.6 °C	38.08	ASTM D 1298
Water content, Ppm	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/m<sup>3</sup>), granular Na-Y type zeolite having SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 5.4, granular MOR type zeolite without binder having SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> 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 NH<sub>4</sub>NO<sub>3</sub> solution at 70°C to obtain NH<sub>4</sub>-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 METHODS

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 SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 5.4, granular H-MOR type zeolite without binder having SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> 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.

## 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 Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in the sample is 7.29% and 41.5%, respectively. Whereas the percentages of other metals like Fe<sub>2</sub>O<sub>3</sub>, CaO, K<sub>2</sub>O, MgO and Na<sub>2</sub>O 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 in hours using 5% wt and 10% wt activated charcoal and clay at 30°C (Figs. 1 and 2).

It is clear from Figs. 1. and 2. that the three hours shaking are enough for activated charcoal to remove good amount of sulfur from diesel fuel while clay respond less even at 10 % concentration. In other word it can be seen that optimum adsorption capacity were reached within 3hrs. indicating that all adsorption sites are saturated.

The results showed that the sulfur content recovery was 5.73% after one hour shaking with 5% activated charcoal and this removal was increased to about 8.2% by shaking for 3 hrs with activated charcoal. By increasing the percentage of activated charcoal to 10%, the sulfur recovery became 20% after 3 hrs of shaking and became 4% with clay.

As a result, the sulfur content is decreased with activated carbon more than with clay.

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

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.

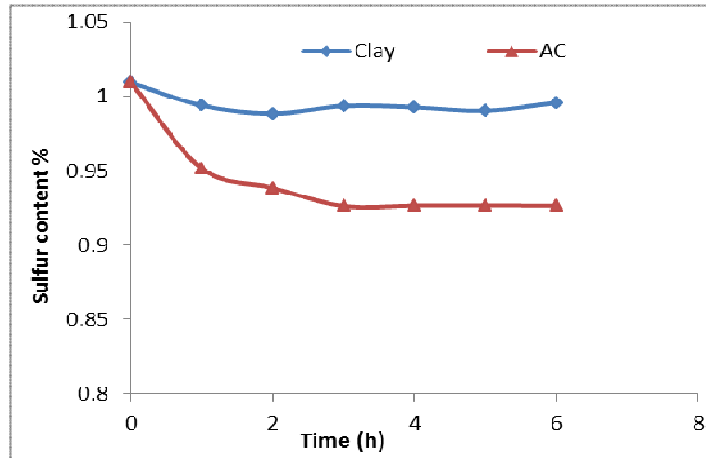


Fig. 1. Effect of time on desulfurization of diesel (5% activated charcoal and clay at 30°C)

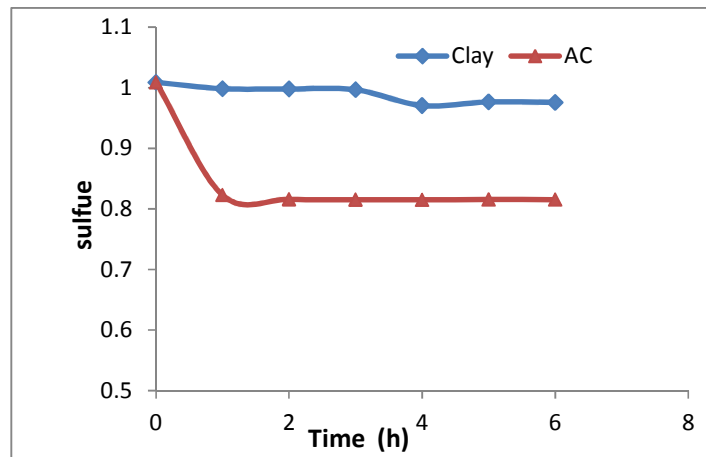


Fig. 2. Effect of time on desulfurization of diesel (10% activated charcoal and clay at 30°C)

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

Adsorptive desulfurization of diesel was also carried out at different temperatures i.e. 30, 40 and 60°C as indicated in Fig. 3. The data show that the desulfurization are increased by activated carbon more than by clay and zeolite (H-Y type zeolite) as the temperature increased, while clay and zeolite respond very little, this is probably due to the decrease of diesel viscosity for higher temperatures that favours the access to adsorption sites inside the pores.

nitrogen compounds, especially for the aromatic substituted sulfur ones. 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 probably due to the method used for the synthesis of both zeolite types.

The activated charcoal shows higher adsorptive capacity and selectivity for both sulfur and

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

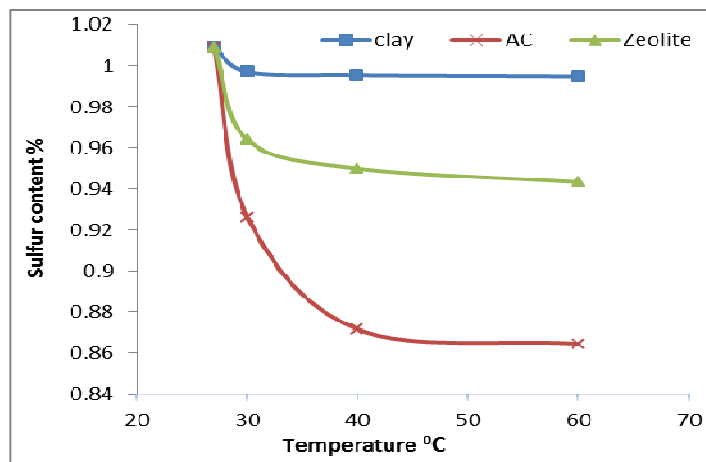


Fig. 3. Effect of temperature on desulfurization of diesel with with 5% of different adsorbents

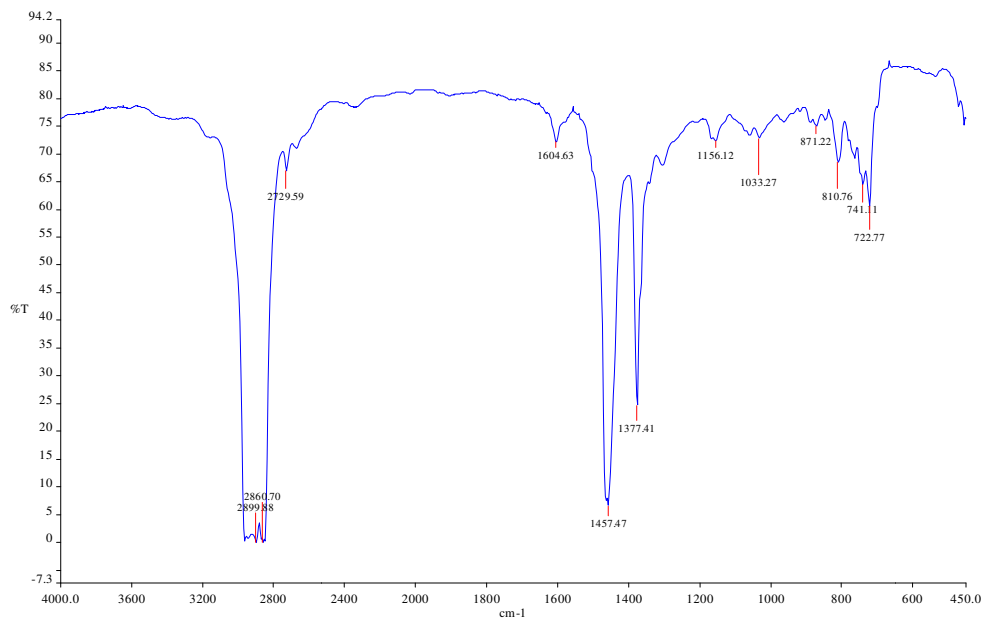
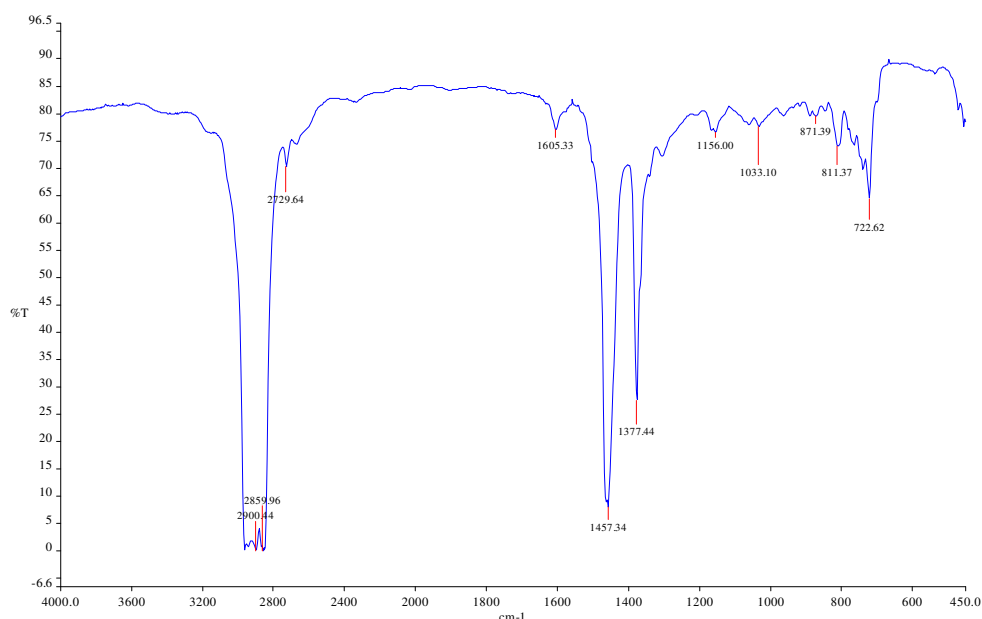


Fig. 4. FTIR spectra image of diesel before desulfurization with activated charcoal



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

The infrared spectra of diesel samples were taken before and after desulfurization with activated charcoal Figs. 4 and 5 (above). The formation of peaks in the region of 2500-2675  $\text{cm}^{-1}$  giving information about thiols (S-H). Peaks at 1030-1060  $\text{cm}^{-1}$  are aromatic thiols, moreover weak peaks between 800-700  $\text{cm}^{-1}$  are attributed to symmetric and asymmetric vibration of the C-S stretching bonds which belongs to thiophenic and thiols compounds. The significant suppression and changes in transmittance spectral band within the region of 1200-600  $\text{cm}^{-1}$  indicates that a portion of organic sulfur compounds is suppressed. The untreated diesel oil transmits more infrared light than the treated one, this decrease could be attributed to the presence of detached sulfur compounds [13,14].

#### 4. CONCLUSION

Low sulfur content is hard to be obtained by using granular Na-Y type zeolite, MOR type zeolite, molecular sieve 3A type and local clay. Desulfurization, by using the activated charcoal, is proved to be more efficient than with the adsorbents mentioned above. Thus, the focus will be on the latter type (i.e. activate charcoal) to obtain a low sulfur diesel in the future.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

#### REFERENCES

1. Speight JG. The Chemistry and Technology of Petroleum, 3<sup>rd</sup> Ed. Marcel Dekker New York; 1999.
2. Song C, Xiaoliang Ma. Ultra-deep desulphurization of liquid hydrocarbon fuels-chemistry and process. *Int. J. Green Eng.* 2004;1(2);167–191.
3. Babich IV, Moulijn JV. Science and technology of novel processes for deep desulfurization of oil refinery streams: a review *Fuel.* 2003;82(6):607–631.
4. Song C. An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel *Catal. Today.* 2003; 86; 211–263.
5. Tailleur R G, Ravigli J, Quenza S, Valencia N. Catalyst for ultra-low sulfur and aromatic diesel. *ApplCatal A-Gen.* 2005; 282:227-235
6. Parkinson G. Diesel Desulfurization Puts Refiners in a Quandary. *Chem Eng.* 2001; 108;37.
7. Fujikawa T, Kimura H, Kiriyaama K, Hagiwara K. Development of ultra-deep HDS catalyst for production of clean diesels. *Catal Today.* 2006;111(3-4):188-193.
8. Hernández-Maldonado AJ, Yan GRT. Desulfurization of transportation fuels by adsorption. *Catal Rev.* 2004;46(2):111-150.

9. Yang RT, Hernandez-Maldonado AJ, Cannella W. Desulfurization of transportation fuels with zeolite under ambient conditions. *Science*. 2003;301; 79–81.
10. Hernandez-Maldonado AJ, Yang RT. Desulfurization of diesel fuels by adsorption via pi-complexation with vapor-phase exchanged Cu(I)-Y zeolites. *J Am Chem Soc*. 2004;126;992-993.
11. Bhandari VM, Ko CH, Park JG, Han SS, Cho SH, Kim JN. Desulfurization of diesel using ion-exchanged zeolite. *Chem Eng Sci*. 2006;61;2599-2608.
12. Mikhail S, Zaki T, Khalil L. *Appl Catal A General*. 2002;227;256-260.
13. Roberto R, Coelho I, Hovell A, Lopes de Souza, Krishnaswamy R. Characterization of the functional chemical structure of sulphur in polyaromatic compounds from heavy petroleum. *Prepr. Pap.-Am. Chem. Soc., Div. Pet. Chem*. 2006;51(1-2);288-290
14. Stuart B. *infrared spectroscopy: fundamentals and applications*. John Wiley and Sons; 2004.

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