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Adsorptive Desulfurization of Crude Oil with Expanded Perlite
Genleştirilmiş Perlit ile Ham Petrolün Adsorptif Desülfürizasyonu

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Öz

Ham petrol; rafine edilerek kullanılması mümkün hale gelen, toplumun refahı, ekonomik kalkınması ve yaşam kalitesi için kritik öneme sahip fosil bir enerji kaynağıdır. Fosil yakıtların kullanımı sonucunda karbondioksit (CO_2), kükürt oksit (SO_x) ve diğer sera gazları açığa çıkmakta ve bu gazlar küresel iklim değişikliğinin ana nedeni olarak ifade edilmektedir. Bu nedenle bilim adamları, ham petrolde yanma reaksiyonları sonucu açığa çıkan SO_x gazlarının zararlı etkilerini en aza indirmek için yoğun çaba sarf etmektedirler. Sunulan bu çalışmada; volkanik bir kayaç türü olan ve ısıtılması sonucu genleşen ve gözenekli bir yapı kazanan genleşmiş perlit kullanılarak ham petrolün kükürt içeriği adsorptif kükürt giderme tekniği ile düşürülmeye çalışılmıştır. Bu amaçla 50 mL ham petrol numunesine ayrı ayrı 2, 4, 6, 8 ve 10 g genleştirilmiş perlit karıştırılmış ve daha sonra oda sıcaklığında 400 rpm'de bir saat boyunca manyetik karıştırıcı ile karıştırılarak adsorptif kükürt giderme işlemine tabi tutulmuştur. . Daha sonra santrifüj yardımıyla adsorbandan ayrılmış ve ASTM D 1552-03 yöntemine göre LECO 628S cihazı ile kükürt miktarı belirlenmiştir. Çalışma sonucunda, ham petroldeki kükürt miktarının %10,82 oranında azaldığı belirlenmiştir. Bu çalışma ile, genleştirilmiş ham perlitin kükürt giderme için iyi bir kapasiteye sahip olduğu, yenilenebilir nitelikte olduğu ve kükürt bileşiklerini uzaklaştırmak için kararlı bir yapıya sahip olduğu tespit edilmiştir.

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Abstract

Crude oil; is a fossil energy source that has become possible to be used by refining processes and has a critical importance for the welfare, economic development and quality of life of the society. As a result of the use of fossil fuels, carbon dioxide (CO_2), sulfur oxide (SO_x) and other greenhouse gases are released and these gases are expressed as the main cause of global climate change. For this reason, scientists are making an intense effort to minimize the harmful effects of SO_x gases released as a result of combustion reactions in crude oil. In this presented study; the sulfur content of crude oil has been tried to be reduced by an adsorptive desulfurization technique by using expanded perlite, which is a volcanic rock type and expands as a result of heating and takes on a porous structure. For this purpose, 50 mL samples of crude oil were treated separately with 2, 4, 6, 8 and 10 g of expanded perlite and then exposed to an adsorptive desulfurization process by mixing with a magnetic stirrer at 400 rpm for an hour at room temperature. Then, it was separated from the adsorbent with the help of a centrifuge and the amount of sulfur was determined by the LECO 628S device according to ASTM D 1552-03 method. As a result of the study, it was determined that the amount of sulfur in crude oil decreased by 10.82 %. The study's findings showed that the expanded crude perlite had a good capacity for sulfide loading, was renewably good, and had a stable structure for removing sulfur compounds.

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INTRODUCTION

Crude oil is a liquid hydrocarbon that forms underground due to chemical reactions and volcanic eruptions and is then preserved in porous rocks. It is also called the metamorphosis of organic material in the earth. Petroleum primarily comprises paraffin, naphthenes, olefins, and aromatic compounds.

According to its composition, crude oil is categorized. Light oil is defined as having high volatility and fluidity, whereas heavy oil has a lower fluidity and is more difficult to evaporate. Another element used in the classification of petroleum is the proportion of the sulfur element in its structure. Low-sulfur crude oil is known as "sweet oil" because it can be refined with ease. On the other hand, because oils containing too much sulfur must undergo additional processing, this kind of crude oil is known as sour (or bitter) oil (Kavak, 2022).

Sulfur in crude oil exists either as elemental sulfur or its compounds (for example, mercaptans, sulfides, disulfides, thiophenes, etc.) and has poor thermal stability. While refining crude oil, they decompose into hydrogen sulfide and simple organic sulfur compounds (Beşergil, 2007). Sulfur compounds cause environmental concerns as they contribute to atmospheric pollution. In addition, it has been proven by scientific studies that people get carcinogenic diseases due to exposure to a certain amount of sulfur compounds (Ahmad, 2016).

For all these reasons, methods such as oxidative desulfurization, adsorptive desulfurization, hydrodesulfurization, extraction, alkylation desulfurization, and microbe desulfurization are used in order to minimize the SOx gases found in crude oil and released as a result of combustion reactions (Li et al., 2018; Zhou et al., 2019; Wang et al., 2022; Vickers, 2017; Rezvani et al., 2019; Dharaskar et al., 2014; Yang et al., 2022; Dashtpeyma et al., 2022). Özkan and Özkan, (2022), tried to remove the amount of sulfur in crude oil by using the adsorptive desulfurization technique. Their studies using CZ as an adsorbent reduced the amount of sulfur in crude oil by 5.76 % (w/v). The behavior of mixed metal oxide TiO2-CeO2 adsorptively desulfurizing jet fuel with 1055 ppm sulfur was examined by Watanabe et al. in 2021. Through the interplay of electron donors and acceptors, the surface active oxygen species on TiO2-CeO_2 served as active sites and adsorbed sulfur molecules. It has been claimed that this mixed metal adsorbent may reduce the sulfur level of jet fuel to 1 ppm (Watanabe t al., 2021). Abd Al-Khodor and Albayati (2020), attempted to use the adsorptive desulfurization method using activated carbon to lessen the sulfur content of crude oil. Through their efforts, they were able to lower the sulfur content in crude oil from 2.5% to 1.8%. Ahmad et al. (2017), as a result of their efforts to remove the amount of sulfur in diesel and kerosene with montmorillonite functionalized with different metals such as Fe, Cr, Ni, Co, Mn, Pb, Zn, and Ag, succeeded in reducing the sulfur content in gas oil by 76% and the sulfur in diesel engines by 77%. The level of sulfur in crude oil was attempted to be reduced by Özkan (2022), by employing a multi-walled carbon nanotube functionalized with copper oxide nanoparticles. He obtained an adsorption efficiency of 5.44% by using the adsorptive desulfurization approach and experimenting with various adsorbent contact times, such as 60 and 120 minutes.

This research aimed to reduce the amount of sulfur in crude oil with expanded crude perlite (adsorbent). For this purpose, first; 2 g, 4 g, 6 g, 8 g, and 10 g adsorbents were weighed and added separately to 50 mL crude oil samples. The solution was stirred at 400 rpm for 60 minutes and 120 minutes at room temperature, and the mixture was subjected to adsorptive desulfurization. The adsorbent was removed from the solution medium with the help of a centrifuge and the amount of sulfur in the filtrate was measured using the ASTM method (ASTM D1552-03 std).

MATERIAL AND METHOD

The substances utilized in this study were all of the analytical purity and were purchased from Merck and Sigma-Aldrich. The crude oil sample we used in our analysis also originated in Kirkuk, Iraq. The chemical properties of the crude oil used in our study are given in Table 1.

Table 1. Chemical properties of crude oil

Chemical properties	Crude oil	Method
API gravity value	29.43	Calculation
Water & Sediment content (% v/v)	1 %	ASTM D-4007
Salt content (% w/v)	-	ASTM D-3230
Asphaltene content (% w/v)	0.3 %	ASTM D-6560
Total sulfur content (% w/v)	3.69 %	ASTM D-2622

Sulfur analysis

Expanded perlite samples weighing 2 g, 4 g, 6 g, 8 g, and 10 g each were weighed and placed separately in beakers with a 100 ml capacity. 50 mL of crude oil was then added to these beakers. To perform an adsorptive desulfurization process, it was agitated in a magnetic stirrer at 400 rpm for 60 and 120 minutes at room temperature. The petroleum/adsorbent solution from each beaker was combined, then transferred to 10-ml tubes and covered. After all test tubes were ready, the crude oil and adsorbent were separated by centrifuging them for 15 minutes at 4100 rpm. After that, 0.1 g of the petroleum sample that had been centrifugally separated from the adsorbent was added to 1 g of Com-Cat using a disposable dropper (a combustion catalyst made up of a WO_3, KH_2PO_4 mixture). After leaving the ceramic crucible produced by these operations in the LECO 628 S device's combustion chamber, sulfur was detected. According to the ASTM D 1552-03 standard, sulfur levels were tested. The technical specifications of the device used in the determination of sulfur are given in Table 2.

Table 2. The technical specifications of the device used in the determination of sulfur

Technical Specifications	Description (Values/Range)
Instrument Range	0.01 to 20 mg Sulphur
Precision (Sulphur)	0.005 mg or 1 % RSD (whicever is greater)
Nominal Sample Weight	up to 350 mg, 250 mg nominal
Detection Method	Infrared Absorption
Chemical Reagent	Magnesium Perchlorate (Anhydrous)
Gas Requirements	Oxygen, 99.5 % pure, 40 psi (2.8 bar)
Regulator Requirements	Oxygen, 0 to 125 psi (0 to 8.6 bar)
Furnace	600 to 1450 oC ±1 % of self point; Horizontal Resistance-type

RESEARCH FINDINGS AND DISCUSSION

The results obtained as a result of using expanded perlite as an adsorbent in the adsorptive desulfurization of crude oil are presented below (Table 3., Figure 1. and Figure 2.).

Table 3. Adsorptive desulfurization performance of expanded perlite

Sample Name		**Crude Oil**	**1**	**2**	**3**	**4**	**5**
Amount of Adsorbent (g)		-	2	4	6	8	10
Sulfur in Crude Oil (g/L)		36.875	36.875	36.875	36.875	36.875	36.875
Amount of adsorbed sulfur (g)	60 min	-	0.860	1.407	1.773	2.190	2.852
	120 min	-	1.197	2.254	3.413	3.860	4.723
Desulfurization Efficiency (%)	60 min	-	2.33	3.82	4.81	5.94	7.73
	120 min	-	3.25	6.11	9.26	10.47	10.82

As a result of using expanded perlite as an adsorbent with a contact time of 60 minutes; it is seen that sulfur is adsorbed in amounts ranging from 0.860 to 2.852 g. At the same time, as a result of contacting the adsorbent with crude oil for 120 minutes; it is clear from Table 3., and Figure 1. that desulfurization can be performed in varying amounts ranging from 1.197 to 4.723 g.

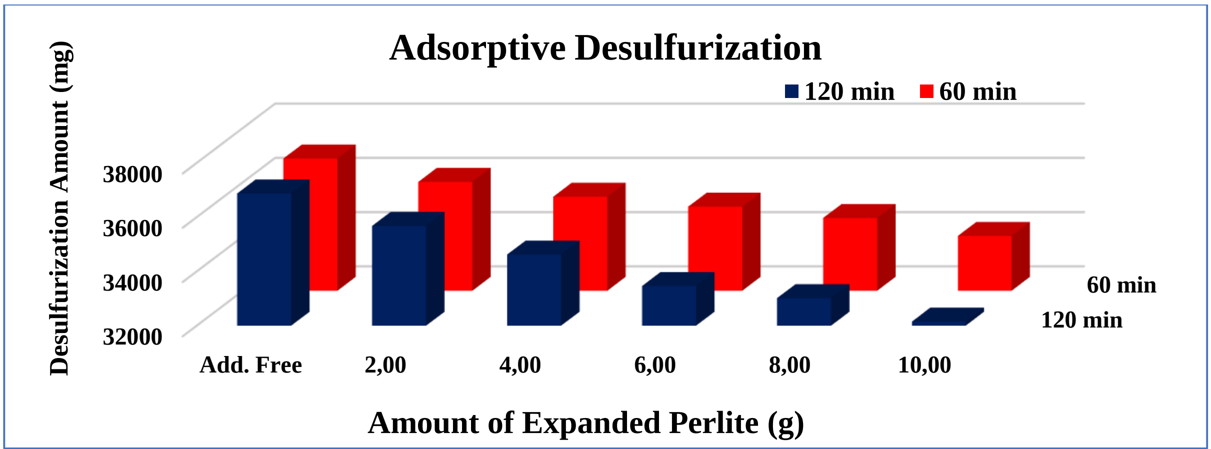

Figure 1. The effect of contact time and amount of expanded perlite on adsorptive desulfurization

Similarly, when Table 3. and Figure 2. are examined; as a result of 60 and 120 minutes of crude oil-adsorbent contact, desulfurization performance varying between 2.33 % and 10.82 % was determined.

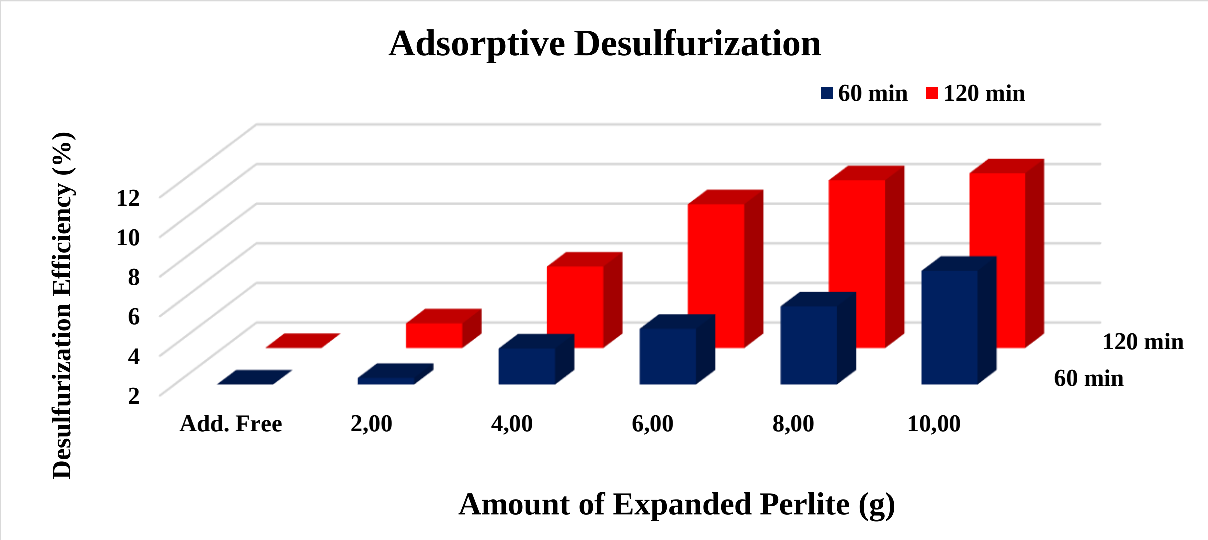

Figure 2. Adsorptive desulfurization efficiency of expanded perlite

In addition, when the results of this study are examined; it was determined that the desulfurization performance increased with the increase in the amount of adsorbent used and the contact time. It has been determined that the results of this study we have done are in agreement with the results of other studies (presented below) in the literature. Rajendran et al., (2020), as a result of the adsorptive desulfurization study, carried out using various adsorbents including carbon, mesoporous materials, metal oxide, clay, industrial waste, metal-organic framework, and zeolite-based materials, the amount of adsorbent, working time, initial adsorbate volume and operating temperature, etc. It has been stated that the factors affect the adsorbent performance significantly. Similarly, Khaled (2015), investigated the ability of MWCNT, graphene oxide, and activated carbon to remove thiophene and dibenzothiophene (DBT) from diesel fuel; all three adsorbents stated that DBT adsorbed more easily than thiophene. He also stated that the adsorption performance increased with the increasing amount of adsorbent. Multi-walled carbon nanotubes functionalized with aluminum oxide nanoparticles were employed by Gördük et al., (2022), in their research to lower the sulfur content of crude oil. They reported that their trials had a success rate of 4.75 % and that adding more adsorbent caused a reduction in the amount of sulfur in crude oil.

RESULTS

Considering the developing and changing world conditions, the need for energy is increasing day by day. This increasing energy need is generally met by fossil energy sources.

The increasing use of fossil energy sources such as crude oil causes more harmful gases such as SO_x to be released into the atmosphere and causes serious environmental problems such as air pollution. In the study carried out to provide a solution to this problem, the adsorptive desulfurization technique, which is one of the chemical desulfurization processes, was used, as was the heat-treated form of the perlite mineral, which is abundant in nature, namely expanded raw perlite. In this way, it has contributed to the solution of removing sulfur from crude oil, which is a serious problem for our world.

As a result of the study, it was determined that the desulfurization efficiency increased with the increase in the amount of absorbent and the contact time. The best result was obtained as a result of a contact time of 120 minutes and the use of 10 g adsorbent, and the sulfur content in crude oil was reduced by 10,82%. Compared with other desulfurization techniques; this study made a significant contribution to science by using expanded perlite, which is a derivative of the raw perlite mineral, which is abundant in nature, as it does not require complex processes, is easily applicable and has high desulfurization efficiency.

Conflict of Interest

The authors wish to declare that they have no conflict of interest

Authors contribution

The authors contributed equally to the study

REFERENCES

Abd Al-Khodor, Y. A., & Albayati, T. M. (2020). Adsorption desulfurization of actual heavy crude oil using activatedcarbon. *Eng. and Tech. J*, 38, 1441-1453.

Ahmad, W., Ahmad, I., Ishaq, M., & Ihsan, K. (2017). Adsorptive desulfurization of kerosene and diesel oil by Zn impregnated montmorollonite clay. *Arabian Journal of Chemistry*, 10, 3263-3269.

ASTM D1552-03(2000), *Standard test method for sulfur in petroleum products (hightemperature method)*. Annual Book of Standards (American Society for Testing and Materials (ASTM), West Conshohocken, PA) Vol. 05.01.

Beşergil, B. (2007). Ham petrolden petrokimyasallara. http://www.bayar.edu.tr/besergil/-hampetrolden_petrokimyasallara, 10.06.2015.

Dashtpeyma, G., Shabanian, S.R., Ahmadpour, J., & Nikzad, M. (2022). The investigation of adsorption desulfurization performance using bimetallic CuCe and NiCe mesoporous Y zeolites: Modification of Y zeolite by

H4EDTA-NaOH sequential treatment. *Fuel Processing Technology*, 235, 107379. https://doi.org/10.1016/j.fuproc.2022.107379

Dharaskar, S.A., Wasewar, K.L., Varma, M.N., Shende, D.Z., Tadi, K.K., & Yoo, C.K. (2014). Synthesis, characterization, and application of novel trihexyl tetradecyl phosphonium bis (2, 4, 4-trimethylpentyl) phosphinate for extractive desulfurization of liquid fuel. *Fuel Processing Technology*, 123, 1-10. https://doi.org/10.1016/j.fuproc.2014.02.001

Gördük, E., Özkan, V., Özkan, A. (2022). Alüminyum Oksit Nanopartikülleri İle Fonksiyonelleştirilmiş Çok Duvarlı Karbon Nanotüplerin Ham Petrol'de Adsorptif Desülfürizasyonu. Hoca Ahmet Yesevi 6. Uluslararası Bilimsel Araştırmalar Kongresi, Lenkeran, ISBN: 978-625-7464-86-4, 791-797. https://ww.yesevikongresi.org/

Kavak, Y and Haspolat, K. (2002). Farklı Yaklaşımlarla Enerji Kaynakları. Orient Yayınları, Gaziosmanpaşa–Çankaya/Ankara, Turkey.

Khaled, M. (2015). Adsorption performance of multiwall carbon nanotubes and graphene oxide for removal of thiophene and dibenzothiophene from model diesel fuel. *Research on Chemical Intermediates*, 41(12), 9817-9833.

Li, Y., Chi, K., Zhang, H., Du, P., Hu, D., Xiao, C., ... & Xu, C. (2018). The influence of hydrothermal crystallization temperature on a novel FDU-12 mesoporous composite assembled by ZSM-5 nanoclusters and its hydrodesulfurization performance for DBT and FCC diesel. *Fuel Processing Technology*, 180, 56-66. https://doi.org/10.1016/j.fuproc.2018.08.010

Özkan, A. (2022). Novel Research on the Use of Multi-Wall Carbon Nanotubes Functionalized with Copper Oxide Nanoparticles in the Adsorptive Desulfurization of Crude Oil: Laboratory Research. *ECS Journal of Solid State Science and Technology*, 11(9), 091012.

Özkan, V. and Özkan, A. (2022). Adsorptive Desulfurization of Crude Oil with Clinoptilolite Zeolite. *Natural and Engineering Sciences*, 7(3).

Rajendran, A., Fan, H.X., Feng, J., & Li, W.Y. (2020). Desulfurization on Boron Nitride and Boron Nitride-based Materials. *Chemistry–An Asian Journal*, 15(14), 2038-2059. https://doi.org/10.1002/asia.202000479.

Rezvani, M.A., Shaterian, M., Aghbolagh, Z.S., & Akbarzadeh, F. (2019). Synthesis and characterization of new inorganic-organic hybrid nanocomposite PMo11Cu@ MgCu2O4@ CS as an efficient heterogeneous nanocatalyst for ODS of real fuel. *ChemistrySelect*, 4(20), 6370-6376. https://doi.org/10.1002/slct.201900202

Srivastav, A., & Srivastava, V. C. (2009). Adsorptive desulfurization by activated alumina. *Journal of Hazardous Materials*, 170(2-3), 1133-1140.

Vickers, N.J. (2017). Animal communication: when I'm calling you, will you answer too? *Current biology*, 27(14), R713-R715. https://doi.org/10.1016/j.cub.2017.05.064

W. Ahmad. (2016). Sulfur in petroleum: petroleum desulfurization techniques. In Applying nanotechnology to the desulfurization process in petroleum engineering. IGI Global, 1-52.

Wang, J., Yang, B., Peng, X., Ding, Y., Yu, S., Zhang, F., ... & Guo, J. (2022). Design and preparation of polyoxometalate-based catalyst [MIMPs] 3PMo6W6O40 and its application in deep oxidative desulfurization with excellent recycle performance and low molar O/S ratio. *Chemical Engineering Journal*, 429, 132446. https://doi.org/10.1016/j.cej.2021.132446

Watanabe, S., Ma, X., & Song, C. (2021). Adsorptive desulfurization of jet fuels over TiO_2-CeO_2 mixed oxides: role of surface Ti and Ce cations. *Catalysis Today*, 371, 265-275. https://doi.org/10.1016/j.cattod.2020.07.071

Yang, N., Lu, L., Zhu, L., Wu, P., Tao, D., Li, X., ... & Zhu, W. (2022). Phosphomolybdic acid encapsulated in ZIF-8-based porous ionic liquids for reactive extraction desulfurization of fuels. *Inorganic Chemistry Frontiers*, 9(1), 165-178. https://doi.org/10.1039/D1QI01255J

Zhou, W., Zhou, A., Zhang, Y., Zhang, C., Chen, Z., Liu, L., ... & Tao, X. (2019). Hydrodesulfurization of 4,6-dimethyldibenzothiophene over NiMo supported on Ga-modified Y zeolites catalysts. *Journal of Catalysis*, 374, 345-359. https://doi.org/10.1016/j.jcat.2019.05.013