

Article

Efficient Oxidative Desulfurization of High-Sulfur Diesel via Peroxide Oxidation Using Citric, Pimelic, and α -Ketoglutaric Acids

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Abstract: The widespread use of diesel fuel for transportation, industry, and electricity generation causes several environmental issues via an increase in the amount of sulfur compound emissions. Commercial diesel fuel must be free of sulfur-containing compounds since they can cause several environmental problems. Considering the currently available processes to eliminate sulfur compounds, oxidative desulfurization (ODS) is one of the effective means for this purpose. This work presented a simple, low cost, and efficient ODS system of high-sulfur diesel fuels using peroxide oxidation with the aid of citric, pimelic, and α -ketoglutaric acids. The aim of the study was to investigate the potential of these acids as hydrogen peroxide (H_2O_2) activators for ODS and to optimize the reaction conditions for maximum sulfur removal. The results showed that citric, pimelic, and α -ketoglutaric acids were effective catalysts for the desulfurization of high-sulfur diesel with an initial sulfur content of 2568 mg L^{-1} , achieving a sulfur removal efficiency of up to 95%. The optimized reaction conditions were found to be 0.6 g of carboxylic acid dosage and 10 mL of H_2O_2 at 95°C . The desulfurization efficiency of the real diesel sample (2568 mg L^{-1}) was shown to be 27, 34, and 84.57%, using citric acid, α -ketoglutaric acid, and pimelic acid after 1 h, respectively. The effectiveness of the oxidation process was characterized by gas chromatographic pulsed flame photometric detector (GC-PFPD) and Fourier-transform infrared spectroscopy (FTIR) techniques. The experimental results demonstrated that the developed system exhibited high efficiency for desulfurization of real high-sulfur diesel fuels that could be a good alternative for commercial application with a promising desulfurization efficiency.

Keywords: oxidative desulfurization; diesel oil; citric acid; pimelic acid; α -ketoglutaric; solvent-extraction



Citation: Ahmed, B.S.; Hamasalih, L.O.; Aziz, K.H.H.; Salih, Y.M.; Mustafa, F.S.; Omer, K.M. Efficient Oxidative Desulfurization of High-Sulfur Diesel via Peroxide Oxidation Using Citric, Pimelic, and α -Ketoglutaric Acids. *Separations* **2023**, *10*, 206. <https://doi.org/10.3390/separations10030206>

Academic Editor: Kangmin Chon

Received: 8 February 2023

Revised: 5 March 2023

Accepted: 9 March 2023

Published: 15 March 2023



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1. Introduction

Environmental pollution is a major global challenge, with significant impacts on public health, ecosystems, and the economy. Pollutants released into the environment from various sources, such as transportation, industrial activities, and manufacturing plants, can have long-term effects on the environment and human health [1,2]. Diesel fuel is a widely used source of energy for transportation, industrial activities, and electricity generation. However, the combustion of diesel fuel also generates a significant amount of air pollutants, such as particulate matter, nitrogen oxides, and sulfur oxides [3,4]. The most prevalent pollutants in fossil fuels, such as gasoline and diesel, are naturally occurring organic compounds that contain sulfur. Sulfur oxides can cause acid rain, rain, soil pollution, and they damage the ecosystem, which can harm aquatic environments and damage buildings and infrastructure [5]. The increasing production and combustion of diesel fuels to cover fundamental requirements in various processes such as power generation, motorized road

vehicles, transportation, and industries resulted in a major source of air pollution, mainly through the emission of a large amount of high sulfur-containing gases [6,7]. Organo-sulfur compounds including methyl mercaptan, phenyl mercaptan, cyclohexylthiol, dimethyl sulfide, thiophenes, benzothiophene, and their derivatives, as well as inorganic sulfur compounds such as hydrogen sulfide, are abundant in crude oil [8,9]. In gasoline processing technologies, the presence of sulfur compounds also causes catalyst poisoning and corrode refinery equipment. The eradication of sulfur compounds has become necessary to obtain green fuel oil with a low sulfur content. The use of low-sulfur diesel fuel can significantly reduce air pollution from diesel fuel use and improve air quality, particularly in urban areas [10]. However, the implementation of such regulations and the adoption of cleaner technologies and fuels may require significant investments and changes in the way industries and consumers use and produce energy. Therefore, it is important to find a new and efficient desulfurization approach to reduce the amount of sulfur content in petroleum products from the standpoints of pollution, economy, and quality [11]. The development of efficient desulfurization processes has become increasingly important as society seeks to reduce the environmental impact of fossil fuel use, and to comply with increasingly stringent emissions regulations. By reducing the sulfur content in diesel fuels, these processes have the potential to significantly mitigate the environmental and health impacts of fossil fuel use, while maintaining the functionality of diesel fuels in a variety of applications. Numerous desulfurization processes were developed and implemented in the refining industry. These processes utilized a variety of techniques to reduce the sulfur content in diesel fuels, including hydrodesulfurization [12], oxidative desulfurization [13], selective adsorptive desulfurization [14], bio-desulfurization [15], and coupled oxidation solvent extraction desulfurization [16]. Hydrodesulfurization involves the use of hydrogen gas and a catalyst to break down sulfur-containing compounds, producing hydrogen sulfide as a byproduct. Oxidative desulfurization relies on the oxidation of sulfur-containing compounds using oxidizing agents, such as hydrogen peroxide or ozone. Adsorptive desulfurization utilizes adsorbent materials, such as activated carbon or metal oxides, to selectively capture sulfur compounds from the fuel. Bio-desulfurization employs microorganisms that can break down sulfur-containing compounds in diesel fuels. Hydrodesulfurization, a commonly used method in traditional refining processes, demonstrated its effectiveness in reducing the levels of thiols, mercaptans, sulfides, and disulfide-containing impurities. However, it was found to be less efficient in eliminating persistent heterocyclic organosulfur compounds, such as thiophene, benzothiophene, dibenzothiophene, and their sterically hindered derivatives [17]. Furthermore, the high cost and energy consumption associated with the utilization of large amounts of hydrogen under conditions of high temperature and pressure constitute a significant requirement [18]. As an efficient method for deep desulfurization process of diesel fuels, the oxidative desulfurization (ODS) process appears to be the most promising and efficient technology and attracted significant attention in removing organosulfur compounds from diesel fuels, as it operates under mild conditions and does not require the use of hydrogen [19]. At present, a variety of desulfurization processes based on adsorption and oxidation showed a good performance for the desulfurization of diesel fuels. Adsorptive desulfurization processes based on activated carbons [20], silica gel-supported TiO₂ [21], nanoporous activated carbons [22], the application of bimetallic nanoparticles onto activated carbon [23] were investigated. The utilization of carbon-supported heteropoly acids as catalysts in the oxidative desulfurization of model diesel fuel [24], the heterogeneous catalytic oxidation process, which is facilitated by ultrasound [25], and deep eutectic solvents [26] were also investigated to eliminate sulfur compounds from diesel fuels. The oxidative desulfurization process initially involves the oxidation of bivalent sulfur compounds to the hexavalent sulfone, whereby two oxygen atoms are added to the sulfur atom without disrupting any carbon-sulfur bonds. The resultant oxidized sulfone compounds can then be effectively separated from the fuel using solvent extraction, with appropriate solvents such as acetonitrile being used for this purpose [13]. Many interesting researches were

carried out in recent years that used catalytic desulfurization as a potent strategy for mitigating environmental issues [27,28]. Several metal complexes were used in the oxidative desulfurization process as homogeneous and heterogeneous catalysts. Diana et al. employed both peroxotungstate PW4 and a composite, consisting of PW4 immobilized in a trimethylammonium-functionalized SBA-15 (PW4@TMA-SBA-15), as catalysts for desulfurization of model and actual diesel fuels. The utilization of these catalysts resulted in a noteworthy 89% desulfurization efficiency of the actual diesel, which initially possessed a total sulfur content of 2300 mg/L [29]. The 1-octyl-3-methylimidazolium tetrachloroferates ($[\text{Omim}] \text{FeCl}_4$) was utilized as a catalyst, as well as an extractive solvent alone or impregnated on a silica gel in the oxidative desulfurization of both model and real diesel fuels. In conjunction with hydrogen peroxide as an oxidant, these methods were employed to achieve successful desulfurization [30,31]. The extractive–oxidative desulfurization approach based on a combination of ultrasound/UV irradiation/ $\text{H}_2\text{O}_2/\text{TiO}_2$ followed by water extraction was developed for the treatment of simulated fuel [32]. The mono lacunary phosphomolybdate supported on $\text{g-C}_3\text{N}_4$ nanocatalyst was prepared and used for oxidative desulfurization of a model and real diesel fuel under various reaction conditions [33]. Polyoxometalate modified alumina catalysts [34] and three-dimensional ordered mesoporous W-doped KIT-6 [35] in the presence of a H_2O_2 oxidant were also prepared and studied in the ODS processes. As a nanomaterial, a graphene-like boron nitride modified with carbon dots was synthesized and applied in catalytic ODS of dibenzothiophene in diesel fuel with a 93.5% efficiency [36].

The reported systems were efficient and promising technologies for oxidative desulfurization of real and model diesel fuels. However, these catalysts have complex preparation, high cost, and their raw materials are not easily available, which limits their application. In comparison to traditional metal-containing catalytic ODS methods, metal-free catalytic ODS techniques are thought to be more effective and promising methods in terms of safety, cost, and environmental considerations [28,37,38]. Metal-free catalysts are preferred for commercial applications because they avoid the use of expensive and sometimes dangerous metals [39]. Bronsted acids such as simple carboxylic acids promote the ODS process in the presence of H_2O_2 by forming active peroxyacids. In this work, the novel, efficient, and simple oxidative/extraction desulfurization system of high-sulfur diesel using H_2O_2 /carboxylic acid was designed and studied. The developed system was based on H_2O_2 activation via three carboxylic acids, namely citric acid, pimelic acid, and α -ketoglutaric acid following simple extraction with acetonitrile. The effect of operational conditions on the desulfurization efficiency was examined and optimized. Based on the results of gas chromatography, it was proven that the oxidation of the sulfur compounds produced extractable sulfones. This research offers a new perspective on the possible application of a cost-effective and straightforward H_2O_2 /carboxylic acid system for efficient removal of refractory sulfur compounds from real high-sulfur diesel fuels via an oxidative desulfurization technique.

2. Material and Methods

The present research utilized liquid H_2O_2 (30% GR Merck, Darmstadt, Germany), acetonitrile (99% Biochem, Beijing, China), citric acid (99% Merck, Darmstadt, Germany), pimelic acid (99% Merck, Darmstadt, Germany), and α -ketoglutaric acid (99% Merck, Darmstadt, Germany) in an oxidative/extraction desulfurization system to treat real high-sulfur diesel oil, which had an initial sulfur content of 2568 mg/L. Table 1 provides characteristics and structure of the carboxylic acids used in this work.

All the chemicals and solvents used in this study were of high purity and were used as received. The characteristics of the real diesel oil before and after the ODS process were analyzed based on the American Society for Testing and Materials (ASTM)'s methods, and the results are presented in Table 2.

Table 1. Chemical and physical information on citric acid, pimelic acid, and α -ketoglutaric acid.

Characteristics	Citric Acid	Pimelic Acid	α -Ketoglutaric Acid
Chemical formula	$C_6H_8O_7$	$C_7H_{12}O_4$	$C_5H_6O_5$
Molar mass	192.12 g/mol	160.17 g/mol	146.11 g/mol
Chemical structure			

Table 2. Presents an assessment of the diesel oil fractions before and after the treatment process.

Test	Test Methods	Before Treatment	After Treatment
Specific gravity@15.6 °C	ASTM D 1298	0.807	0.802
API gravity	ASTM	43.8	44.9
Flashpoint °C	ASTM D 93	70	71
Pour point °C	ASTM D 97	−21	−24
Vis.@50 °C/Cst	ASTM D 445	1.91	2
%Sulfur content	ED-XRF	0.2568	—
Distillation	ASTM	—	—
Initial B.P °C	—	188	190
Vol. at %10	—	208	214
Vol. at %50	—	238	240
Vol. at %70	—	260	262
Vol. at %90	—	298	300

The oxidative desulfurization experiments were carried out in a batch process, as illustrated in Figure 1. The initial concentration of the total sulfur content in the diesel fuels used in this study was 2568 mg/L. The high-sulfur diesel sample was procured from a petrol station in Sulaymaniyah, Iraq. The ODS reaction was performed in a temperature-controlled magnetic hot plate coupled with a 250-mL round-bottom flask. For each experimental trial, 50 mL of real diesel oil was introduced into the reactor, and continuously stirred at a constant mixing speed of 1100 rpm, while being heated to the desired reaction temperature of 95 °C, using the magnetic stirrer hot plate. In a typical procedure, the hot plate was set to a fixed temperature of 95 °C. Subsequently, 10 mL of hydrogen peroxide and 0.6 g of the desired carboxylic acid (citric acid, pimelic acid, or α -ketoglutaric acid) were added to the closed flask containing 50 mL of real diesel fuel. This protocol enabled the systematic evaluation of the performance of different carboxylic acids in the ODS process. The reaction was carried out under intense stirring at a speed of 1100 rpm, maintaining a temperature of 95 °C. The resulting reaction mixture was subsequently cooled to room temperature, and then a 1:1 volume ratio of acetonitrile was added to extract the oxidation products. The formed immiscible mixture was separated by means of a separation funnel having a capacity of 250 mL. The lower liquid phase, which represents the gas oil phase, was analyzed for its elemental sulfur content via energy dispersive X-ray fluorescence spectrometer in accordance with D-4294, and its sulfur-containing organic compounds were determined via gas chromatographic pulsed flame photometric detector (GC-PFPD). This analytical approach allowed for the identification and quantification of the sulfur-containing compounds present in the gas oil phase following oxidation.

In accordance with ASTM D4294, the total sulfur content in diesel samples was quantified using the Sulfur-in-Oil Analyzer (NEX QC, Austin, TX 78717, USA), an Energy-Dispersive X-Ray Fluorescence (ED-XRF) spectrometer (Analytik Ltd., Cambridge, CB24 4AA, United Kingdom). The infrared (IR) spectra were obtained from KBr pellets over the range of 400–4000 cm^{-1} using a Perkin-Elmer FT/IR spectrometer (Perkin-Elmer, Waltham, MA, USA). The conversion of sulfur compounds to sulfones was validated via gas chromatography (GC) using a CP-3800 instrument from Varian (Palo Alto, CA, USA),

equipped with a DB-17 column (30 m in length, 0.25 mm internal diameter, and 0.25 μm film thickness) containing a stationary phase of 50% phenyl and 50% methyl silicone. This specific column (Varian equivalent: CP-Sil 24 CB, CP7821) was designed for the separation of sulfur compounds. The GC was programmed to increase from 50 to 280 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{minute}$, with a 2 min hold at 50 $^{\circ}\text{C}$ and a final 20 min hold at 280 $^{\circ}\text{C}$.

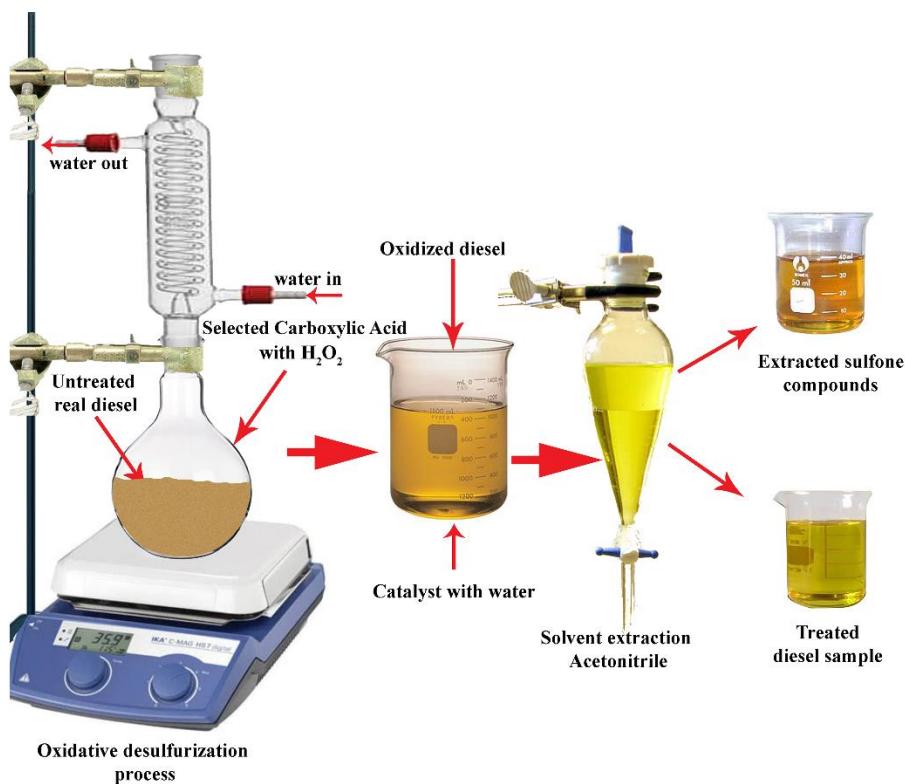


Figure 1. Schematic diagram of the operational desulfurization system.

3. Results and Discussion

3.1. Application of Oxidative Desulfurization System for Real Diesel Oil

Diesel fuel is a common fuel used in transportation, particularly in power generation, large trucks, and buses. It is produced as a medium distillate stream in refineries and has a boiling point range of 160–380 $^{\circ}\text{C}$. The most prominent compounds present in diesel fuels are benzothiophene and dibenzothiophene derivatives [11,40]. In the literature, carboxylic acids and homogeneous metallic systems, including polyoxometalates, were the dominant types of homogeneous catalysts that were reported. In ODS processes, simple carboxylic acids, specifically formic and acetic acids, are widely recognized as the most employed catalysts. During a typical ODS operation, refractory organic sulfur compounds such as dibenzothiophene and its derivatives undergo selective and efficient oxidation, resulting in the formation of their corresponding sulfoxides or sulfones, which can then be subsequently eliminated through solvent extraction (as illustrated in Figure 2). The oxidative desulfurization of a genuine diesel sample with a high sulfur content (2568 mg/L) was performed under carefully optimized experimental conditions, and the results of this study are presented in Figure 3. In this process, the desulfurization was accomplished through the formation of peracids (RCOOOOH), which were generated as a result of the reaction between H_2O_2 and carboxylic acids, followed by the production of sulfones via the peracids' reaction with the target sulfur-containing compounds in the diesel sample (as illustrated in Figure 2) [41]. Simple carboxylic acids such as formic and acetic acids were considered the most used catalysts in ODS processes. In typical ODS processes, refractory organic sulfur compounds, such as dibenzothiophene and its derivatives, can be selectively and efficiently oxidized to their corresponding sulfone or sulfoxides, which

could be removed subsequently in the process of solvent extraction (Figure 2). The ODS of a real high-sulfur diesel sample (2568 mg/L) was performed under optimized experimental conditions and the results are shown in (Figure 3). In this process, the desulfurization was carried out through peracids (RCOOOH) formation as a result of the reaction between H_2O_2 and carboxylic acid, followed by sulfone production via peracids reaction with target sulfur-containing compounds in the diesel sample (Figure 2). H_2O_2 gained widespread application as an oxidizing agent in various fields due to its stability, availability, and environmentally friendly nature. The effectiveness of this compound in various oxidative reactions is attributed to its distinctive characteristics, including its high oxidation potential and low toxicity, which render it a widely used chemical.

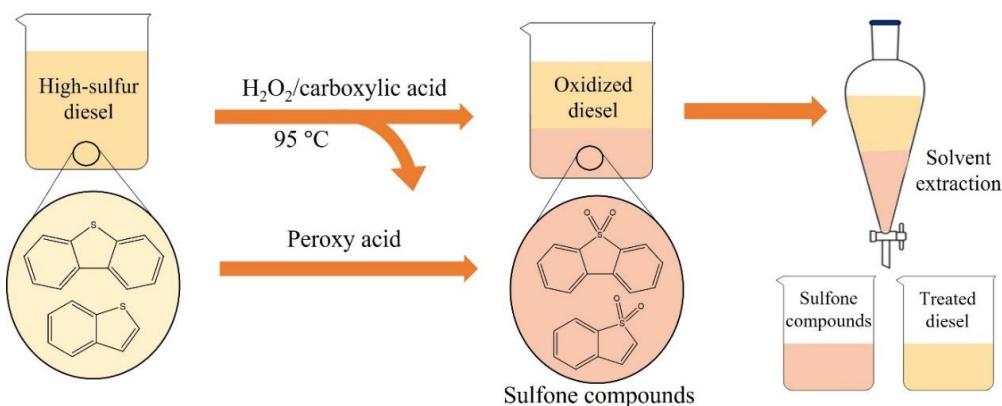


Figure 2. Schematic graphical mechanism pathway of ODS system via $\text{H}_2\text{O}_2/\text{carboxylic acid}$.

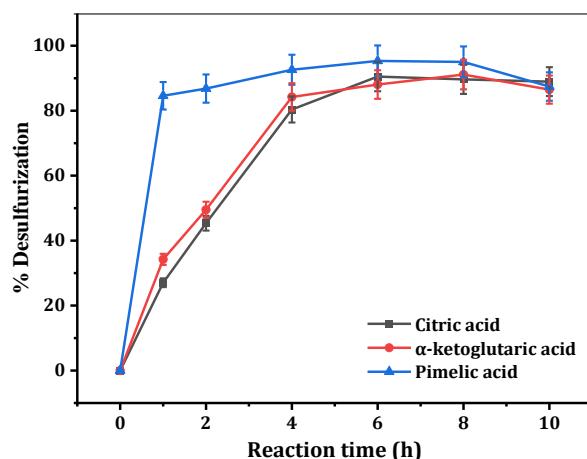


Figure 3. Oxidative desulfurization of untreated real diesel (2568 mg L^{-1}): carboxylic acids dosage = 0.6 g; H_2O_2 (30% w/w) = 15 mL.

From the results (Figure 3), it can be observed that the desulfurization efficiency under pimelic acid was better than citric acid and α -ketoglutaric acid. After one hour of treatment, the desulfurization rate reached more than 84% using pimelic acid. For α -ketoglutaric and citric acids, the percentage of desulfurization efficiency was 34 and 27% after the same treatment times, respectively. This superiority of pimelic acid can be attributed to its possession of a greater number of hydrophobic carbons that enhance its solubility in diesel fuel. The increased solubility of pimelic acid enabled it to interact more effectively with the sulfur-containing compounds in diesel fuel, leading to a higher level of desulfurization efficiency. These findings provide valuable insights into the molecular factors that influence the performance of activators in the H_2O_2 -based oxidative desulfurization process, thereby facilitating the development and optimization of ODS systems for industrial applications. Different materials that were utilized as H_2O_2 activators in ODS procedures for samples of high-sulfur diesel oil included isobutyraldehyde [42], dicarboxylic acids, and Brønsted

acidic ionic liquid supported on silica gel and formic acid [13,41]. The outcomes obtained in this study exhibited similar results to those of prior research and indicated the outstanding effectiveness of the analyzed carboxylic acids as a potential replacement for the present H_2O_2 activator employed in the process of oxidizing desulfurization for diesel fuels with high sulfur content.

3.2. Effect of Temperature, Hydrogen Peroxide, and Catalyst Doses

An assessment was conducted to investigate the effect of diverse quantities of hydrogen peroxide and chosen carboxylic acid on the percentage of desulfurization. This was achieved by introducing varying dosages of hydrogen peroxide and specific carboxylic acid into the system, while preserving the other experimental parameters constant. H_2O_2 concentration is a key parameter for the oxidative desulfurization process. Therefore, the impact of H_2O_2 concentration on the percentage of desulfurization was first investigated, and the results are shown in Figure 4. As the volume of 30% H_2O_2 was increased from 5 mL to 10 mL, a marked improvement in the efficacy of desulfurization was observed, rising from 58 to 88% when utilizing α -ketoglutaric acid as a catalyst. In contrast, there were no notable variations in the rate of desulfurization with the utilization of other carboxylic acids as catalysts. Based on these results, a quantity of 10 mL of H_2O_2 was selected to be an optimum oxidant volume for the developed system.

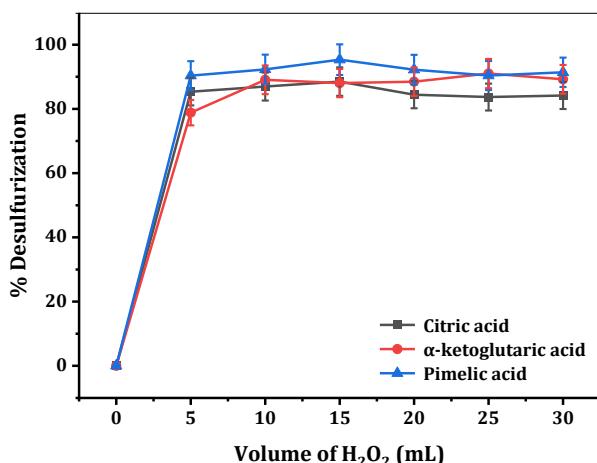


Figure 4. Optimization of (30% *w/w*) H_2O_2 addition for the oxidative desulfurization of diesel oil with a total sulfur content of 2568 mg L^{-1} ; Carboxylic acids dosage = 0.6 g at 95 °C after 6 h treatment.

A series of experiments was performed to determine the optimal dosages of carboxylic acids in the desulfurization process. To this end, a fixed amount of hydrogen peroxide (10 mL) was used while the dosages of carboxylic acids were varied. The results indicated that the highest efficiency of desulfurization was achieved when 0.6 g of each acid was used. Further increase in the number of acids led to a decrease in the solubility of the catalyst, as depicted in Figure 5. The efficiency of the oxidative desulfurization process is heavily influenced by the reaction temperature and contact time. A study was conducted to investigate the desulfurization efficiency at different oxidation temperatures and the results are presented in Figure 6. It was observed that the maximum desulfurization efficiency for the three selected carboxylic acids occurred at a temperature of 95 °C. As the reaction temperature increased, the probability of collision between the organosulfur compounds in the diesel sample and the active oxidant increased, resulting in improved desulfurization. Therefore, increasing the temperature has a positive impact on the overall desulfurization efficiency.

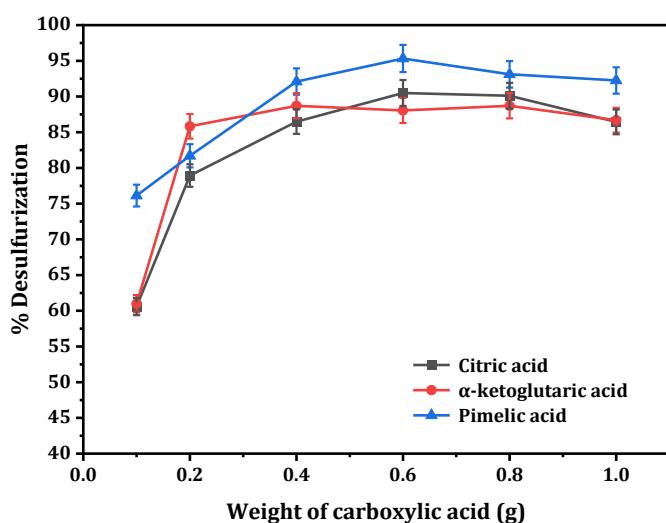


Figure 5. Optimization of carboxylic acids dosage for the oxidative desulfurization of real diesel (2568 mg L^{-1}) with $10 \text{ mL } 30\% \text{ H}_2\text{O}_2$ at 95°C after 6 h treatment.

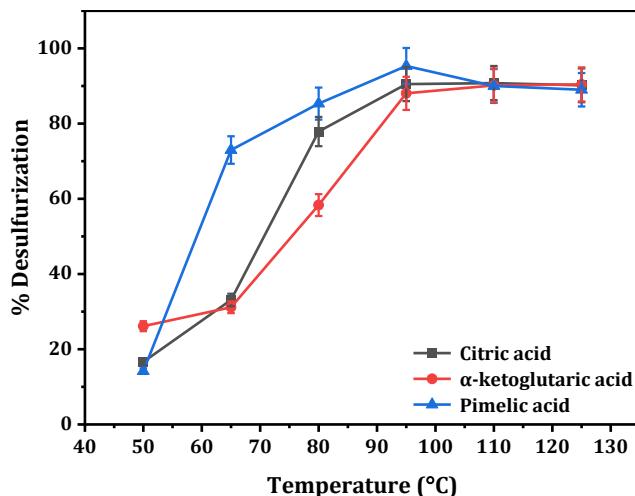


Figure 6. The influence of reaction temperature on oxidative desulfurization processes. Conditions: initial sulfur content of real diesel = 2568 mg L^{-1} , contact time = 6 h ; carboxylic acids dosage = 0.6 g ; H_2O_2 ($30\% \text{ w/w}$) = 10 mL .

Infrared spectroscopy (IR) is a powerful technique that yields information about the functional features of various petroleum constituents. The structure of the gas oil before oxidation was detected by IR and the results are presented in Figure 7A. The aliphatic C-H stretched at the range of 2955 and 2854 cm^{-1} for asymmetric and symmetric stretching of CH_3 groups, whereas CH_2 methylene groups have bands at 2924 cm^{-1} , the symmetric bending vibration of the methyl group appears at 1377 cm^{-1} , while methylene bending appears at 1463 cm^{-1} [43]. Figure 7B shows the IR spectrum of gas oil after oxidation; in these spectra, the sulfone band was observed at 1158 cm^{-1} for symmetric stretching and at 1305 cm^{-1} for asymmetric stretching [44]. These results indicated that the organic sulfur-containing compounds were converted to the corresponding sulfone. Furthermore, it was observed that the sulfone compounds were effectively eliminated through the implementation of solvent extraction utilizing acetonitrile, as illustrated in Figure 7C.

Gas chromatography was implemented in order to validate the conversion of recalcitrant sulfur compounds into extractable sulfones. The identification of certain sulfur compounds was facilitated by performing a comparative analysis between the chromatogram of the real diesel sample and those of standard organic compounds that contained sulfur, which are typically present in diesel samples. The obtained gas chromatographic pulsed

flame photometric detector (GC-PFPD) chromatograms of unoxidized and oxidized diesel oil are presented in Figure 8, after undergoing acetonitrile extraction. It is noteworthy that the GC peaks of sulfur compounds in the oxidized diesel oil were observed to shift in a heavier direction in comparison to those of the unoxidized sample. The obtained chromatograms demonstrated the conversion of organosulfur compounds into more polar molecules. This important finding indicates that most residual sulfur compounds present in the oxidized diesel oil were converted into sulfones through the process of oxidation. As a result of this transformation, the total sulfur content of the sample was reduced, suggesting the effectiveness of the oxidation process in eliminating sulfur compounds from diesel oil.

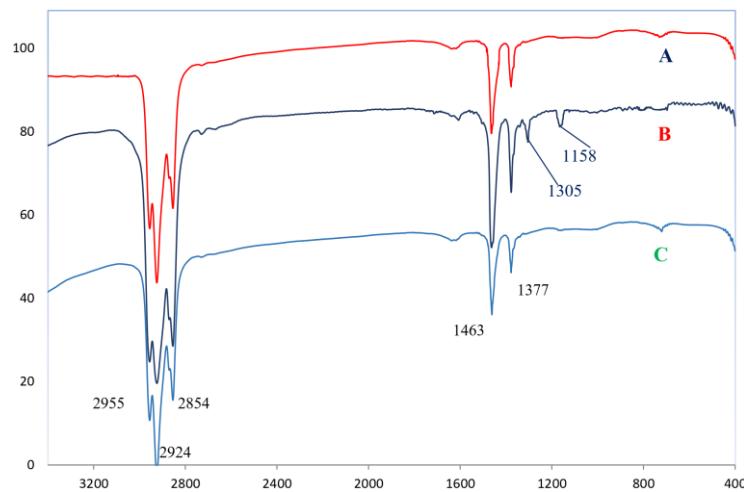


Figure 7. IR spectrum for gas oil, (A) before oxidation, (B) after oxidation (C) after solvent extraction.

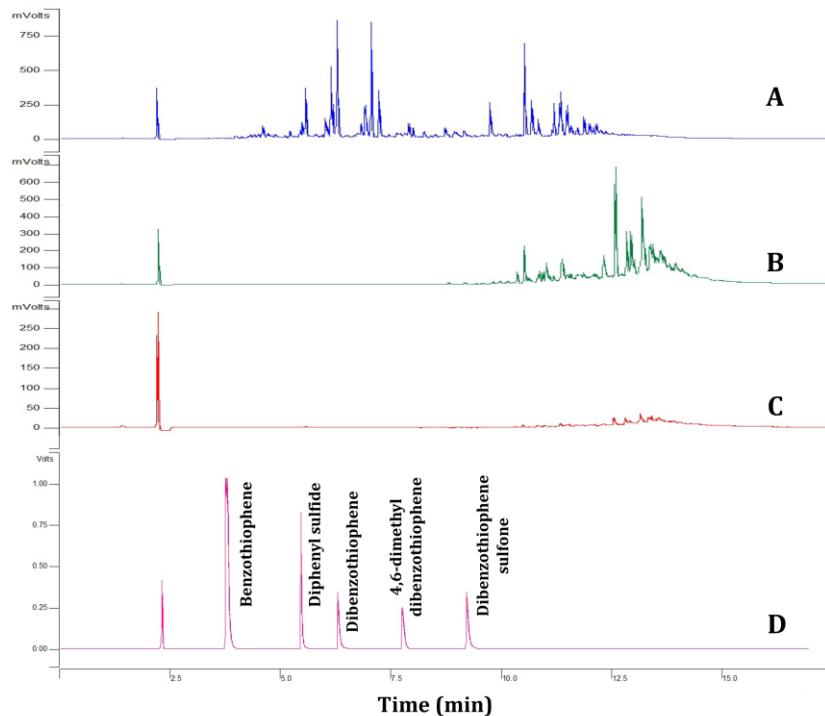


Figure 8. GC-FPD chromatograms: (A) unoxidized diesel oil, (B) oxidized diesel oil, (C) oxidized diesel oil, after extraction with acetonitrile, and (D) standard organosulfur compound.

4. Conclusions

In summary, an efficient oxidative desulfurization system that utilized citric acid, pimelic acid, and α -ketoglutaric acid as H_2O_2 activator was developed and designed for

effective extraction and oxidative desulfurization of real high-sulfur diesel fuels. The results of the experimental analysis confirmed the successful application of the developed ODS system for the removal of sulfur-containing compounds from the real high-sulfur diesel fuels with reasonable efficiency. Pimelic acid was identified as the most effective activator for H_2O_2 in the process of desulfurizing diesel fuel. This superiority can be attributed to the greater number of hydrophobic carbons present in pimelic acid, which confer upon it a heightened ability to dissolve in diesel fuel. The increased solubility of pimelic acid in diesel fuel enhances its interaction with the sulfur-containing compounds within the fuel, resulting in a greater degree of desulfurization efficiency. Further research may investigate alternative hydrophobic activators to further enhance the performance of the H_2O_2 -based ODS process. The optimal operational conditions were determined as 0.6 g carboxylic acid dose, 10 mL H_2O_2 at 95 °C. The designed oxidative-extraction coupling system demonstrated excellent desulfurization activity for real high-sulfur diesel and showed an attractive potential for industrial application. This study utilized solid-state catalysts that were both easily available and cost-effective. The findings presented in this research would provide a novel insight into the potential application of a simple and low-cost H_2O_2 /carboxylic acid system as a promising option for deep desulfurization of real high-sulfur diesel fuels using an oxidative desulfurization process. Utilizing a solid-state activator can significantly reduce the weight of the oxidant dose, reactor volume, storage needs, and transportation/shipping requirements. To estimate a true picture of the treatment cost, further investigation by using a pilot plant can be carried out where the actual energy requirement and the chemical usage can be properly calculated.

Author Contributions: Conceptualization, K.H.H.A. and B.S.A.; methodology, B.S.A.; software, F.S.M.; validation, L.O.H., K.H.H.A. and K.M.O.; formal analysis, B.S.A.; investigation, B.S.A.; writing—original draft preparation, K.H.H.A.; writing—review and editing, B.S.A., L.O.H., K.M.O., F.S.M. and Y.M.S.; visualization, K.H.H.A. and B.S.A.; supervision, K.H.H.A. and L.O.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Acknowledgments: The authors express their appreciation to the University of Sulaimani, Kurdistan Region, Iraq, for providing support to the study.

Conflicts of Interest: The authors disclose no conflict of interest.

References

1. Mustafa, F.S.; Aziz, K.H.H. Heterogeneous catalytic activation of persulfate for the removal of rhodamine B and diclofenac pollutants from water using iron-impregnated biochar derived from the waste of black seed pomace. *Process Saf. Environ. Prot.* **2023**, *170*, 436–448. [[CrossRef](#)]
2. Kumar, P.; Hama, S.; Abbass, R.; Nogueira, T.; Veronika, S.; Abhijith, K.; de Fatima, A.M.; Asfaw, A.; Aziz, K.H.; Cao, S.; et al. Potential health risks due to in-car aerosol exposure across ten global cities. *Environ. Int.* **2021**, *155*, 106688. [[CrossRef](#)] [[PubMed](#)]
3. Choi, A.E.S.; Roces, S.A.; Dugos, N.P.; Wan, M.W. Ultrasound assisted oxidative desulfurization: A comprehensive optimization analysis using untreated diesel oil. *Comput. Chem. Eng.* **2022**, *166*, 107965. [[CrossRef](#)]
4. Hai, T.; Alsharif, S.; Aziz, K.H.H.; Dhahad, H.A.; Singh, P.K. Deep learning optimization of a biomass and biofuel-driven energy system with energy storage option for electricity, cooling, and desalinated water. *Fuel* **2023**, *334*, 126024. [[CrossRef](#)]
5. Barilla, G.R.H.; Chen, C.A.W.; Valencia, M.Z.M.; Dugos, N.P.; Choi, A.E.S. Mixing assisted oxidative desulfurization using a synthesized catalyst of the activated carbon supported phosphotungstic acid: A process optimization study. *S. Afr. J. Chem. Eng.* **2022**, *42*, 61–71. [[CrossRef](#)]
6. Hossain, M.N.; Park, H.C.; Choi, H.S. A comprehensive review on catalytic oxidative desulfurization of liquid fuel oil. *Catalysts* **2019**, *9*, 229. [[CrossRef](#)]
7. Julião, D.; Gomes, A.C.; Pilling, M.; Valencia, R.; Ribeiro, J.C.; Goncalves, I.S.; Balula, S.S. Desulfurization of liquid fuels by extraction and sulfoxidation using H_2O_2 and [CpMo(CO) 3R] as catalysts. *Appl. Catal. B Environ.* **2018**, *230*, 177–183. [[CrossRef](#)]
8. Chandran, D.; Khalid, M.; Walvekar, R.; Mubarak, N.M.; Dharaskar, S.; Wong, W.Y.; Gupta, T.C.S. Deep eutectic solvents for extraction-desulphurization: A review. *J. Mol. Liq.* **2019**, *275*, 312–322. [[CrossRef](#)]

9. Jin, X.; Wu, J.; Silva, R.C.; Huang, H.; Zhang, Z.; Zhong, N.; Tutolo, B.M.; Larter, S. Alternate routes to sustainable energy recovery from fossil fuels reservoirs. Part 1. Investigation of high-temperature reactions between sulfur oxy anions and crude oil. *Fuel* **2021**, *302*, 121050. [[CrossRef](#)]
10. Choi, A.E.S.; Roces, S.A.; Dugoe, N.P.; Wan, M.W. Adsorption of sulfones from actual oxidized diesel oil in the frame of oxidative desulfurization: A process optimization study using activated clay. *J. Clean. Prod.* **2022**, *363*, 132357. [[CrossRef](#)]
11. Haruna, A.; Mercian, Z.M.A.; Musa, S.G.; Abubakr, S. Sulfur removal technologies from fuel oil for safe and sustainable environment. *Fuel* **2022**, *329*, 125370. [[CrossRef](#)]
12. Saleh, T.A. Carbon nanotube-incorporated alumina as a support for MoNi catalysts for the efficient hydrodesulfurization of thiophenes. *Chem. Eng. J.* **2021**, *404*, 126987. [[CrossRef](#)]
13. Ahmed, B.S.; Hamasalih, L.O.; Hamaaziz, K.H.; Omer, K.M.; Shafiq, I. Oxidative Desulfurization of Real High-Sulfur Diesel Using Dicarboxylic Acid/H₂O₂ System. *Processes* **2022**, *10*, 2327. [[CrossRef](#)]
14. Iruretagoyena, D.; Bikani, K.; Sunny, N.; Lu, H.; Kazarian, S.; Chadwick, D.; Pini, R.; Sahah, N. Enhanced selective adsorption desulfurization on CO₂ and steam treated activated carbons: Equilibria and kinetics. *Chem. Eng. J.* **2020**, *379*, 122356. [[CrossRef](#)]
15. Porto, B.; OliveIra, J.V.; Yamamoto, C.I.; Souza, A.A.; Souza, S.A.A. Heavy gas oil biodesulfurization by Rhodococcus erythropolis ATCC 4277: Optimized culture medium composition and evaluation of low-cost alternative media. *J. Chem. Technol. Biotechnol.* **2017**, *92*, 2376–2382. [[CrossRef](#)]
16. Gao, S.; Chin, X.; Xi, X.; Abro, M.; Afzal, W.; Abro, R.; Yu, G. Coupled oxidation-extraction desulfurization: A novel evaluation for diesel fuel. *ACS Sustain. Chem. Eng.* **2019**, *7*, 5660–5668. [[CrossRef](#)]
17. Jiang, W.; Xiao, G.; Gao, X.; An, X.; Leng, Y.; Zhu, L.; Zhu, W.; Li, H. In situ fabrication of hollow silica confined defective molybdenum oxide for enhanced catalytic oxidative desulfurization of diesel fuels. *Fuel* **2021**, *305*, 121470. [[CrossRef](#)]
18. Shafiq, I.; Shafique, S.; Akhter, P.; Yang, W.; Hussain, M. Recent developments in alumina supported hydrodesulfurization catalysts for the production of sulfur-free refinery products: A technical review. *Catal. Rev.* **2020**, *64*, 1–86. [[CrossRef](#)]
19. Mahboob, I.; Shafiq, I.; Shafique, S.; Akhter, P.; Amjad, U.; Hussain, M.; Park, Y. Effect of active species scavengers in photocatalytic desulfurization of hydrocracker diesel using mesoporous Ag₃VO₄. *Chem. Eng. J.* **2022**, *441*, 136063. [[CrossRef](#)]
20. Bu, J.; Gwie, C.G.; Dewiyanti, S.; Tasrif, M.; Borgna, A. Desulfurization of diesel fuels by selective adsorption on activated carbons: Competitive adsorption of polycyclic aromatic sulfur heterocycles and polycyclic aromatic hydrocarbons. *Chem. Eng. J.* **2011**, *166*, 207–217. [[CrossRef](#)]
21. Ren, X.; Liu, Z.; Dong, L.; Miao, G.; Liao, N.; Li, Z.; Xiao, J. Dynamic catalytic adsorptive desulfurization of real diesel over ultra-stable and low-cost silica gel-supported TiO₂. *AIChE J.* **2018**, *64*, 2146–2159. [[CrossRef](#)]
22. Triantafyllidis, K.S.; Deliyanni, E.A. Desulfurization of diesel fuels: Adsorption of 4, 6-DMDBT on different origin and surface chemistry nanoporous activated carbons. *Chem. Eng. J.* **2014**, *236*, 406–414. [[CrossRef](#)]
23. Saleh, T.A. Simultaneous adsorptive desulfurization of diesel fuel over bimetallic nanoparticles loaded on activated carbon. *J. Clean. Prod.* **2018**, *172*, 2123–2132. [[CrossRef](#)]
24. Ghabayra, R.; Nuttall, C.; Hodgkiss, S.; Craven, M.; Kozhevnikova, E.F.; Kozhevnikova, I.V. Oxidative desulfurization of model diesel fuel catalyzed by carbon-supported heteropoly acids. *Appl. Catal. B Environ.* **2019**, *253*, 309–316. [[CrossRef](#)]
25. Flores, R.; Rodas, A.; Gasperin, R. Oxidative desulfurization of diesel fuel oil using supported Fenton catalysts and assisted with ultrasonic energy. *Pet. Sci.* **2019**, *16*, 1176–1184. [[CrossRef](#)]
26. Sun, L.; Zhu, Z.; Su, T.; Liao, W.; Hao, D.; Chen, Y.; Zhao, Y.; Ren, W.; Ge, H.; Lu, H. Novel acidic eutectic mixture as peroxidase mimetics for oxidative desulfurization of model diesel. *Appl. Catal. B Environ.* **2019**, *255*, 117747. [[CrossRef](#)]
27. Abdurrahid, H.; Merican, Z.M.A.; Musa, S.G. Recent advances in catalytic oxidative desulfurization of fuel oil—A review. *J. Ind. Eng. Chem.* **2022**, *112*, 20–36.
28. Tanimu, A.; Tanimu, G.; Ganiyu, S.A.; Gambo, Y.; Alasiri, H.; Alhooshani, K. Metal-Free Catalytic Oxidative Desulfurization of Fuels—A Review. *Energy Fuels* **2022**, *36*, 3394–3419. [[CrossRef](#)]
29. Julião, D.; Mirante, F.; Ribeiro, S.O.; Gomes, A.C.; Valenca, R.; Casrto, B.; Balula, S.S. Deep oxidative desulfurization of diesel fuels using homogeneous and SBA-15-supported peroxophosphotungstate catalysts. *Fuel* **2019**, *241*, 616–624. [[CrossRef](#)]
30. Andevary, H.H.; Akbari, A.; Omidkhah, M. High efficient and selective oxidative desulfurization of diesel fuel using dual-function [Omin] FeCl₄ as catalyst/extractant. *Fuel Process. Technol.* **2019**, *185*, 8–17. [[CrossRef](#)]
31. Andevary, H.H.; Akbari, A.; Rajabi, Z.; Omidkhah, M. Towards a room temperature oxidative desulfurization of refractory compounds over 1-octyl-3-methylimidazolium tetrachloroferates/silica gel: The beneficial effects of immobilization. *Process Saf. Environ. Prot.* **2020**, *136*, 343–352. [[CrossRef](#)]
32. Sinhmar, P.S.; Tiple, A.; Gogate, P.R. Combined extractive and oxidative desulfurization approach based on ultrasound and ultraviolet irradiation with additives for obtaining clean fuel. *Environ. Technol. Innov.* **2021**, *22*, 101487. [[CrossRef](#)]
33. Moeinifar, B.; Chermahini, A.N. Mono lacunary phosphomolybdate supported on mesoporous graphitic carbon nitride: An eco-friendly and efficient catalyst for oxidative desulfurization of the model and real fuels. *J. Environ. Chem. Eng.* **2021**, *9*, 105430. [[CrossRef](#)]
34. Liu, Y.; Chu, J.; Lian, L.; Chen, Z.; Hong, L.; Wang, D.; Chen, W. Ultrafast Oxidative Desulfurization of Diesel Fuels by Mass Transfer Enhancement of Polyoxometalate Modified Alumina Catalysts. *Energy Fuels* **2021**, *35*, 2110–2120. [[CrossRef](#)]
35. Wang, B.; Dai, B.; Kang, L.; Zhu, M. Synthesis of three-dimensional ordered mesoporous W-doped KIT-6 for oxidative desulfurization catalyst of fuels. *Fuel* **2020**, *265*, 117029. [[CrossRef](#)]

36. Pedram-rad, T.; Eshaghi, Z.; Ahmadpour, A.; Kazemi, M.S.; Mohammadi, A.A. Carbon-dot Confined in Graphene-Analogous Boron Nitride for Enhanced Oxidative Desulfurization. *Arab. J. Chem.* **2022**, *15*, 104084. [[CrossRef](#)]
37. Lin, S.; Ng, S.-F.; Ong, W.-J. Life cycle assessment of environmental impacts associated with oxidative desulfurization of diesel fuels catalyzed by metal-free reduced graphene oxide. *Environ. Pollut.* **2021**, *288*, 117677. [[CrossRef](#)] [[PubMed](#)]
38. Wu, P.; Jia, Q.; He, J.; Lu, L.; Chen, L.; Zhu, J.; Peng, C.; He, M.; Xiong, J.; Zhu, W. Mechanical exfoliation of boron carbide: A metal-free catalyst for aerobic oxidative desulfurization in fuel. *J. Hazard. Mater.* **2020**, *391*, 122183. [[CrossRef](#)]
39. Jiang, W.; Zhu, K.; Li, H.; Zhu, L.; Hua, M.; Wang, C.; Yang, Z.; Chen, J.; Zhu, W. Synergistic effect of dual Brønsted acidic deep eutectic solvents for oxidative desulfurization of diesel fuel. *Chem. Eng. J.* **2020**, *394*, 124831. [[CrossRef](#)]
40. Betiha, M.A.; Rabie, A.M.; Ahmed, H.S.; Abdelrahman, A.A.; El-shahat, M.F. Oxidative desulfurization using graphene and its composites for fuel containing thiophene and its derivatives: An update review. *Egypt. J. Pet.* **2018**, *27*, 715–730. [[CrossRef](#)]
41. Houda, S.; Lancelot, C.; Blandchard, P.; Poinel, L.; Lamonier, C. Oxidative desulfurization of heavy oils with high sulfur content: A review. *Catalysts* **2018**, *8*, 344. [[CrossRef](#)]
42. Venkateshwar Rao, T.; Sain, B.; Kafola, S.; Nautiyal, B.R.; Sharma, Y.K.; Nanoti, S.M.; Garg, M.O. Oxidative desulfurization of HDS diesel using the aldehyde/molecular oxygen oxidation system. *Energy Fuels* **2007**, *21*, 3420–3424. [[CrossRef](#)]
43. Bhasarkar, J.B.; Chakma, S.; Moholkar, V.S. Investigations in physical mechanism of the oxidative desulfurization process assisted simultaneously by phase transfer agent and ultrasound. *Ultrason. Sonochem.* **2015**, *24*, 98–106. [[CrossRef](#)] [[PubMed](#)]
44. Kayan, G.Ö.; Kayan, A. Polyhedral Oligomeric Silsesquioxane and Polyorganosilicon Hybrid Materials and Their Usage in the Removal of Methylene Blue Dye. *J. Inorg. Organomet. Polym. Mater.* **2022**, *32*, 2781–2792. [[CrossRef](#)]

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