

Optimization of Desulfurization of 4-Methyldibenzothiophene and 4,6-Dimethyldibenzothiophene Using Mg/Al Layered Double Hydroxide Equipped with ZnO/TiO₂

Amri Amri^{1,2}, Nur Ahmad², Sahrul Wibiyani^{2,4}, Alfian Wijaya^{1,2}, Mardiyanto Mardiyanto³, Idha Royani⁴, Risfidian Mohadi⁴, and Aldes Lesbani^{2,4*}

¹Doctoral Program of Environmental Science, Postgraduate Program, Universitas Sriwijaya, Jl. Padang Selasa Bukit Besar, Palembang 30139, Indonesia

²Research Center of Inorganic Materials and Complexes, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, Jl. Padang Selasa Bukit Besar, Palembang 30139, Indonesia

³Department of Pharmacy, Universitas Sriwijaya, Jl. Palembang Prabumulih Km. 32, Ogan Ilir 30662, Indonesia

⁴Magister of Material Science, Graduate Program, Universitas Sriwijaya, Jl. Padang Selasa Bukit Besar, Palembang 30139, Indonesia

* **Corresponding author:**

email: aldeslesbani@pps.unsri.ac.id

Received: September 7, 2023

Accepted: March 21, 2024

DOI: 10.22146/ijc.88790

Abstract: The growth of heavy industry leads to an increase in sulfur dioxide emissions, impacting health, economy, and the fulfilment of the ecological needs for society. Sulfur removal is carried out using the oxidative desulfurization (ODS) method. In this study, layered double hydroxide materials of Mg/Al, Mg/Al-TiO₂, and Mg/Al-ZnO were successfully synthesized and analyzed using X-ray diffraction (XRD), Fourier-transform infrared (FTIR), and scanning electron microscope-energy dispersive spectroscopy (SEM-EDS) techniques. Those materials are used as catalysts for the desulfurization of 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). Composite Mg/Al catalysts with metal oxides provide superior desulfurization process efficiency and enhanced stability, making them highly effective for repeated use. The conversion percentage of desulfurization of 4-MDBT and 4,6-DMDBT increases with time. The n-hexane is a suitable solvent for desulfurization of 4-MDBT and 4,6-DMDBT. All catalysts exhibit significant heterogeneity that greatly aids in the separation process.

Keywords: desulfurization; 4-methyldibenzothiophene; 4,6-dimethyldibenzothiophene; layered double hydroxide; TiO₂/ZnO

INTRODUCTION

The rapid development of heavy industrial operations can undoubtedly result in a rise in the continuous emission of sulfur dioxide (SO₂) [1]. It is possible that this will result in considerable challenges for the economy and the health of the people, and it may also make it more difficult to satisfy the criteria that people have for an ecological environment that is both adequate and suitable [2]. Many different kinds of crops and human infrastructure have been affected as a result of acid rain that have been occurring on a regular basis in various regions of the world over the course of the last several decades [3]. These

events have been occurring in a variety of different places across the world. The reason for this is that sulfur oxides have the potential to react with the moisture that is present in the air or to be ingested by the air and rain, both of which can lead to the creation of acid rain [4].

The reduction of sulfur compounds can be accomplished using a number of different techniques, such as hydrodesulfurization, biological desulfurization, adsorptive desulfurization, oxidative-extractive desulfurization, and catalytic-oxidative desulfurization [5-7]. According to Chen et al. [8], conventional hydrodesulfurization techniques, which are used to

remove thiophene-derived chemicals like 4-methylthiophene (4-MDBT) and 4,6-dimethylthiophene (4,6-DMDBT), are said to necessitate harsh conditions, such as high temperature and pressure. These kinds of regulations result in increased operational costs and render it impossible to reduce the amount of sulfur present.

Oxidative desulfurization, often known as ODS, is the most prevalent method for removing sulfur from fuels. This is on account of its cheaper cost and increased activity towards aromatic sulfides when the circumstances are mild. Aromatic sulfur molecules undergo oxidation during this process, which results in the formation of sulfones. These sulfones are then extracted from the fuel by means of adsorbents or extractants. During the ODS process, a number of different oxidants are utilized. These oxidants include hydrogen peroxide (H_2O_2), air or oxygen, and Fenton's reagent. It is widely acknowledged that H_2O_2 is the most promising oxidant due to its high sulfur removal rate, low cost, and ability to generate water.

Metal-based catalysts, such as polyoxometalates, noble metals, superoxides, and metal oxides, have been demonstrated to perform extraordinarily well in the activity of oxygen hydrogen sulfide (OHS). This has been demonstrated through scientific research. For this reason, the development of highly active catalysts will be of the utmost importance to achieve high ODS performance targets [9]. Various approaches have been utilized to perform the desulfurization process, which has resulted in the formation of metal oxides, specifically transition metal oxides (ZnO , TiO_2 , and Fe_2O_3). Nevertheless, suppose these are utilized in the process of regeneration (repeated use), when the desulfurization ability is decreased. In that case, they are not as stable as they would be in any other circumstance. In order to improve the stability of metal oxides such as ZnO , TiO_2 metal oxide can be added to the metal oxide. However, this addition may decrease the desulfurization activity of the metal oxide [10]. As a consequence of this, it is absolutely necessary to enhance the structure of a metal oxidant catalyst in order to make it more stable. This is absolutely necessary for the catalyst to be utilized in the process of regeneration and for the desulfurization activity to be increased.

Layered double hydroxide (LDH) is a two-dimensional structure known as a hydrotalcite compound. Because of its unique structure, this LDH is an excellent candidate for use as a precursor in the production of mixed metal oxide catalysts. Mixed metal oxides can be obtained through the process of calcining LDH. During the first stage of the calcination process, water molecules and/or interlayer anions will be moved or decomposed. This is one of the factors that leads to the production of the porous structure of binary metal oxide. The unique characteristics of the binary metal oxides that are produced as a result can be utilized to enhance reactivity and/or mass transfer when these oxides are utilized in potential processes such as desulfurization [11].

Research was carried out by Ahmad et al. [12] on a composite of Ni/Al LDH with metal oxides (TiO_2 and ZnO) for the purpose of desulfurizing dibenzothiophene. Following the incorporation of Ni/Al LDH, the percentage of adsorption rose from 91.92% on TiO_2 to 99.88% on Ni/Al LDH/ TiO_2 , and from 95.36% to 99.90% on ZnO . In addition, the research showed that the material became more stable after the composite was applied. This was proved by the fact that there was no discernible decrease in the regeneration process over the course of three cycles. The desulfurization of 4-MDBT and 4,6-DMDBT was carried out within this inquiry's scope by using metal-oxidized (TiO_2 and ZnO) Mg/Al LDH catalysts. The purpose of this investigation was to improve the structural durability and efficiency of the desulfurization process at the same time. In the course of the investigation, both the stability of the regeneration process and the effectiveness of the desulfurization process were investigated.

■ EXPERIMENTAL SECTION

Materials

The investigation utilized acetonitrile (CH_3CN), *n*-pentane (C_5H_{12}), *n*-hexane (C_6H_{14}), *n*-heptane (C_7H_{16}), titanium(IV) oxide (TiO_2), and zinc(II) oxide (ZnO) acquired from Merck. Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), sodium hydroxide ($NaOH$), 4-MDBT

(C₁₃H₁₀S), and 4,6-DMDBT (C₁₄H₁₂S) were acquired from Sigma-Aldrich. Analytical-grade H₂O₂ was acquired from Smart-Lab, and distilled water (H₂O) was supplied by PT Bratachem, Indonesia.

Instrumentation

Validation of the success of the synthesis and preparation of Mg/Al LDH, Mg/Al-TiO₂, and Mg/Al-ZnO catalysts must be accomplished by first characterization. The X-ray diffractometer (Rigaku Miniflex-6000), the Fourier transfer infrared (Shimadzu Prestige-21), the SEM-EDS (SEM Quanta-650 Oxford), and the UV-vis spectrophotometer (EMC-18PC-UV) are the equipment/instruments that are used to determine whether or not the synthesis and catalyst preparation were successful.

Procedure

Mg/Al LDH catalyst synthesis

A solution of 0.75 M Mg(NO₃)₂ was combined with a solution of 0.25 M Al(NO₃)₃, both of which had a volume of 100 mL. This was done to prepare the Mg/Al LDH catalyst. In order to bring the solution's pH level up to 10, NaOH was added to it at a concentration of 2 M. This process continued until the solution reached a pH of 10. Stirring was carried out for a duration of 20 h at a temperature of 80 °C.

Catalyst preparation of Mg/Al-TiO₂ and Mg/Al-ZnO

Mg/Al LDH catalyst synthesis was the approach that was utilized in the preparation of the Mg/Al-TiO₂ and Mg/Al-ZnO catalysts [13]. After the mixing operation was completed, either 3.7 g of TiO₂ or ZnO was added to the M²⁺/M³⁺ solution in a ratio of 1:1, and the mixture was stirred for a period of 3 h. After that, 150 mL of NaOH with a concentration of 0.37 M was added to the mixture, and it was stirred for a period of 12 h at a temperature of 80 °C for the Mg/Al-TiO₂ and Mg/Al-ZnO catalysts. Finally, the catalysts were filtered, dried, and then calcined at 300 °C for 7 h.

Oxidative desulfurization optimization process of 4-MDBT and 4,6-DMDBT

A complex chemical process was carried out involving the production and transfer of 4-MDBT and 4,6-DMDBT in *n*-hexane at a concentration of 500 ppm. These compounds were then transferred to a catalytic

reaction flask with two branches. To prevent the evaporation of *n*-hexane, the flask was connected to a condenser. After adding 0.25 g of catalysts (Mg/Al LDH, Mg/Al-TiO₂, and Mg/Al-ZnO), 1 mL of 30% H₂O₂ was introduced. After the extraction process, a UV-vis spectrophotometer (EMC-18PC-UV) was used to assess the reaction. The extraction involved the use of 3 mL of acetonitrile for a duration of 10 min. Eq. (1) demonstrates the process of removing sulfur from 4-MDBT and 4,6-DMDBT:

$$\text{Sulfur removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

C₀ represents the total beginning concentrations of 4-MDBT and 4,6-DMDBT, whereas C_t represents the total final concentrations of 4-MDBT and 4,6-DMDBT.

The process of optimizing the oxidative desulfurization of 4-MDBT and 4,6-DMDBT was carried out with a number of different variations. These variations included time (10–60 min), catalyst weight (0.05–1 g), temperature variation (30–60 °C), solvent type, heterogeneity test, H₂O₂ oxidant dose (1.5–2.5 mL), and catalyst effectiveness in the reuse process (3 cycles).

RESULTS AND DISCUSSION

XRD Spectra

Fig. 1 shows the diffraction peaks of the catalysts, including Mg/Al LDH, Mg/Al-TiO₂, and Mg/Al-ZnO. The diffraction peaks of LDH were observed at various angles, indicating the presence of specific planes within the structure. These planes correspond to the hexagonal structure of Mg/Al LDH, as supported by JCPDF data 22-0452 [14]. The angles at which the peaks were obtained are 11.6°, 23.1°, 34.5°, 38.5°, 45.4°, 60.7°, and 62.0°, corresponding to the planes (003), (006), (012), (015), (018), (110), and (113), respectively. The peaks of the Mg/Al-TiO₂ catalyst can be observed at various angles, including 11.23°, 22.9°, 37.91°, 39.16°, 48.19°, 54.04°, 62.86°, and 70.36°. Based on JCPDS No. 21-1276 data [15], the peaks at 37.91° (101), 54.04° (211), 62.86° (002), and 70.36° (112) are indicative of TiO₂ material. The diffraction peaks observed on the Mg/Al-ZnO catalyst are found at angles of 2θ = 11.14° (003), 31.8° (100), 34.5° (002), 36.3° (101), 39.05° (015), 47.5° (002),

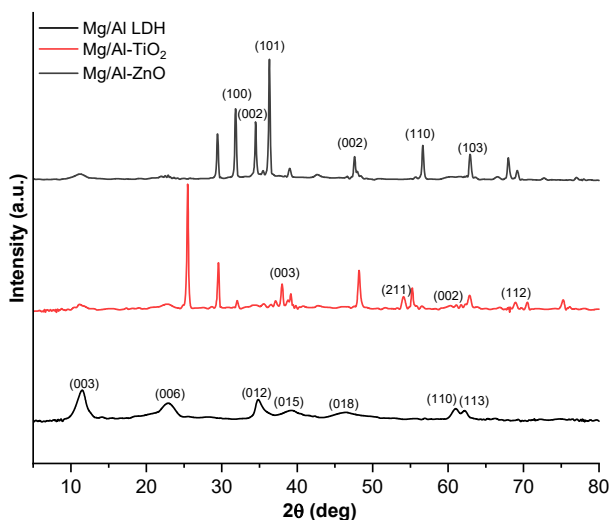


Fig 1. XRD diffraction patterns of the catalysts

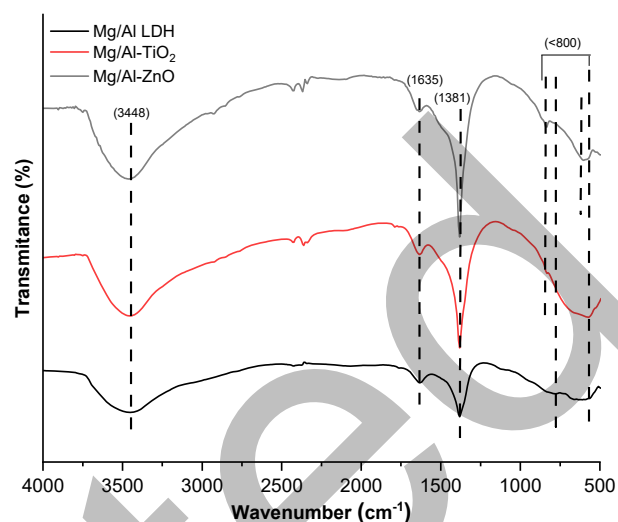


Fig 2. FTIR spectra of various catalysts

56.6° (110), and 62.90° (103). These specific peaks at certain angles are indicative of the presence of ZnO, according to the JCPDS 36-1451 data [13]. In the case of Mg/Al-TiO₂ and Mg/Al-ZnO materials, the peaks can be observed within the range of 9–12° and 60–62°, suggesting the presence of layered materials [16].

FTIR Spectra

Fig. 2 shows the FTIR spectra for the catalysts Mg/Al LDH, Mg/Al-TiO₂, and Mg/Al-ZnO. An interesting finding on the Mg/Al LDH catalyst was a peak observed at 3448 cm⁻¹. This peak suggests the existence of O-H groups that are formed from water molecules. The presence of OH bending vibrations is indicated by a peak at 1635 cm⁻¹ [17]. The presence of the NO₃⁻ anion in the interlayer and metal oxide groups (Mg-O and Al-O) is indicated by the appearance of peaks at 1381, 779, and 594 cm⁻¹ [18-20]. In composite catalysts, there is a peak at wavenumber < 800 cm⁻¹ that signifies the stretching modes of certain bonds. These bonds involve elements such as Mg, Al, Zn, and Ti [21-23].

EDS Spectra

Fig. 3 showcases the structure of Mg/Al LDH, Mg/Al-TiO₂, and Mg/Al-ZnO. Fig. 3(a) illustrates the irregular layered structure of the Mg/Al LDH material, which forms clusters resembling a sponge. Upon being combined with TiO₂ and ZnO (as shown in Fig. 3(b) and (c)), the surface structure of Mg/Al-TiO₂ and Mg/Al-ZnO

becomes more organized and consistent, exhibiting the presence of pores on the particle surface. The EDS results reveal the composition of the Mg/Al LDH material in terms of weight percentages: oxygen (O, 59.2%), magnesium (Mg, 17.9%), sodium (Na, 9.5%), nitrogen (N, 6.8%), and aluminum (Al, 6.6%). When combined with TiO₂, the weight percentage of O decreased from 59.2% to 53.9%, Mg decreased from 17.9% to 13.1%, and Al decreased from 6.6% to 5.1%. Interestingly, the addition of TiO₂ resulted in a significant increase in the Ti element by 22.5%. Similarly, the Mg/Al-ZnO material experiences a 28% increase in weight due to the addition of ZnO. The percentage of O decreased from 59.2% to 41.1%, Mg decreased from 17.9% to 17.4%, and Al decreased from 6.6% to 6.3%.

Effect of Time

Fig. 4 shows the relationship between reaction time and the ability of 4-MDBT and 4,6-DMDBT to be desulfurized with Mg/Al LDH, Mg/Al-TiO₂, and Mg/Al-ZnO catalysts. The influence of reaction time on the ability of 4-MDBT and 4,6-DMDBT to be desulfurized was studied for 10–60 min using a 0.25 g catalyst dosage of Mg/Al LDH, Mg/Al-TiO₂, and Mg/Al-ZnO. The effect of reaction time on the desulfurization of 4-MDBT and 4,6-DMDBT is significant, the longer the reaction time, the greater the percentage of sulfur removal of 4-MDBT and 4,6-DMDBT that happens.

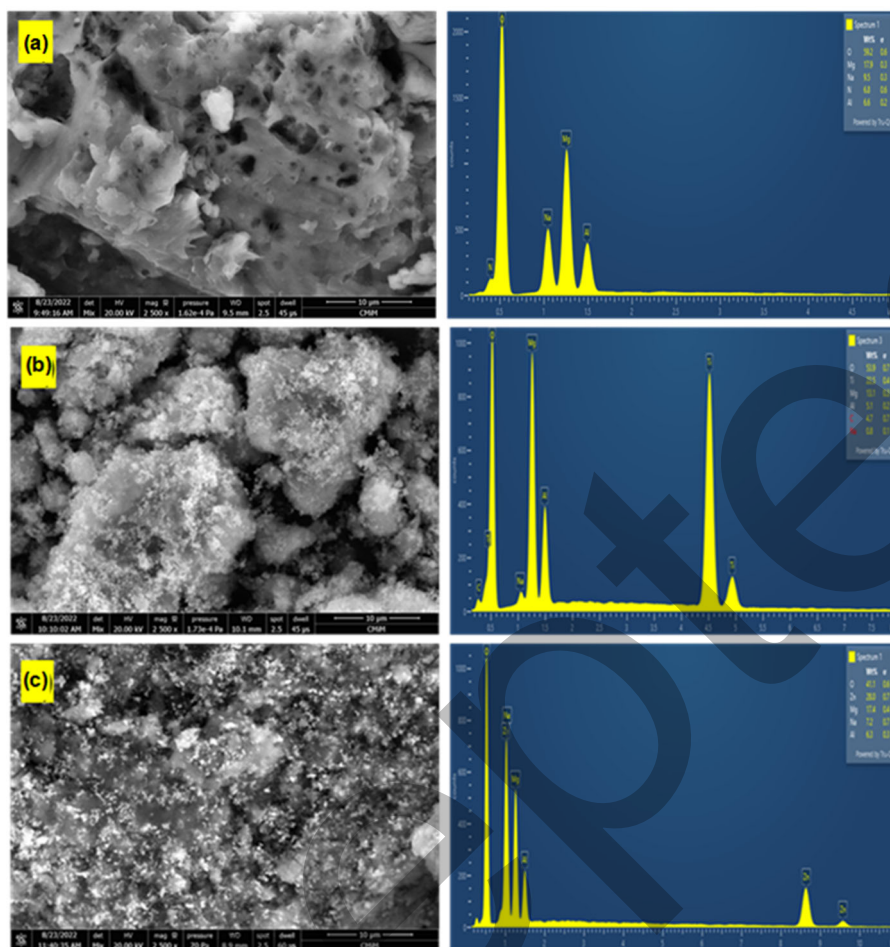


Fig 3. Surface morphology and EDS spectrum of (a) Mg/Al LDH, (b) Mg/Al-TiO₂, and (c) Mg/Al-ZnO

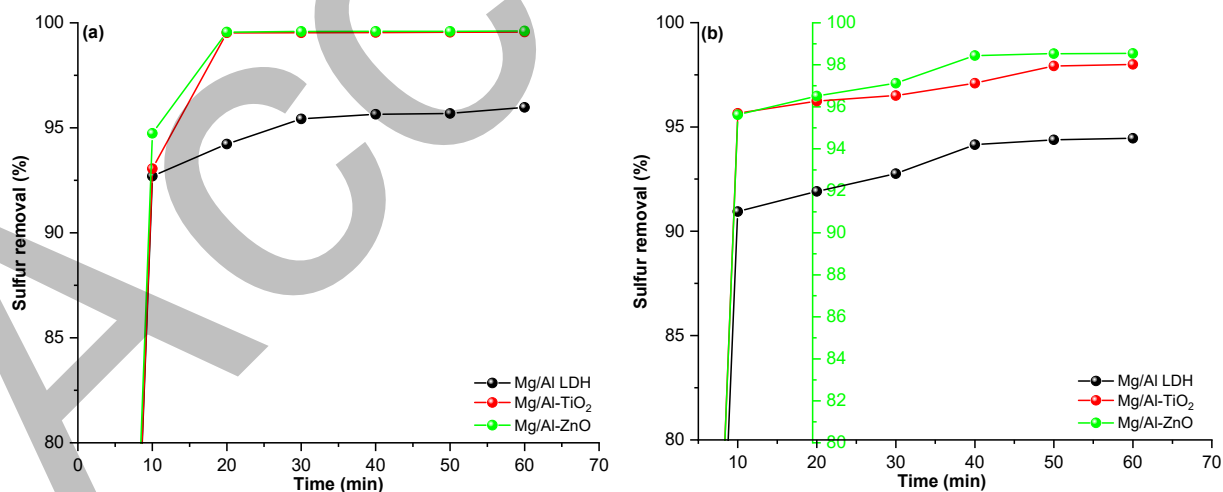


Fig 4. Effect of time on the desulfurization process of (a) 4-MDBT and (b) 4,6-DMDBT on various catalysts

The data obtained in Fig. 4(a) shows that the percentage sulfur removal of 4-MDBT with the optimum time on different catalysts was quite impressive. For the

Mg/Al LDH catalyst, it achieved a sulfur removal of 95.42% in 40 min. The Mg/Al-TiO₂ catalyst performed even better, reaching a sulfur removal of 99.52% in just

20 min. Similarly, the Mg/Al-ZnO catalyst also achieved a sulfur removal of 99.56% in 20 min. The sulfur removal percentages of 4,6-DMDBT were 94.15% (40 min) for Mg/Al LDH, 97.93% (50 min) for Mg/Al-TiO₂, and 98.42% (50 min) for Mg/Al-ZnO (Fig. 4(b)). Once the ideal duration had elapsed, the sulfur removal capacity of 4-MDBT and 4,6-DMDBT on the three catalysts remained relatively stable, with only a minor increase observed. The sulfur removal efficiency of 4-MDBT and 4,6-DMDBT on 3 different catalysts indicates that the combination of Mg/Al catalyst with TiO₂ and ZnO yields a higher percentage of sulfur removal compared to Mg/Al LDH. The enhanced reactivity and mass transfer in the desulfurization reaction can be attributed to the incorporation of metal oxides such as O-Ti-O and Zn-O [11]. Table 1 presents a comparison of the sulfur removal

data obtained in this investigation and the data reported in the referenced research.

Effect of Catalyst Dosage

Fig. 5 shows the effect of different catalyst dosages on the desulfurization of 4-MDBT and 4,6-DMDBT. The effect of catalyst dose on the desulfurization process of 4-MDBT and 4,6-DMDBT is critical, particularly in industry. This is because it can identify the efficacy of a catalyst, reducing the decrease in process costs caused by excessive catalyst utilization. Observations were done with dose variations of 0.05, 0.1, 0.25, 0.5, and 1 g, using each catalyst's optimum time. The results revealed the most effective catalyst dosage weight for sulfur removal of 4-MDBT and 4,6-DMDBT for each catalyst, namely Mg/Al LDH at 0.1 g for all desulfurization processes,

Table 1. Comparison of sulfur removal efficiency of 4-MDBT and 4,6-DMDBT in this study with the results of previous studies

Catalyst	Time	Types of compounds	Sulfur removal (%)	Ref.
Hexaammonium heptamolybdate tetrahydrate	3 h	4,6-DMDBT	89.20	[24]
TiO ₂ @NiAl	30 min	4-MDBT	99.48	[25]
ZnO@NiAl	30 min	4-MDBT	99.51	[25]
Mg/Al LDH	40 min	4-MDBT	95.42	This study
Mg/Al-TiO ₂	20 min	4-MDBT	99.52	This study
Mg/Al-ZnO	20 min	4-MDBT	99.56	This study
Mg/Al LDH	40 min	4,6-DMDBT	94.15	This study
Mg/Al-TiO ₂	50 min	4,6-DMDBT	97.93	This study
Mg/Al-ZnO	40 min	4,6-DMDBT	98.42	This study

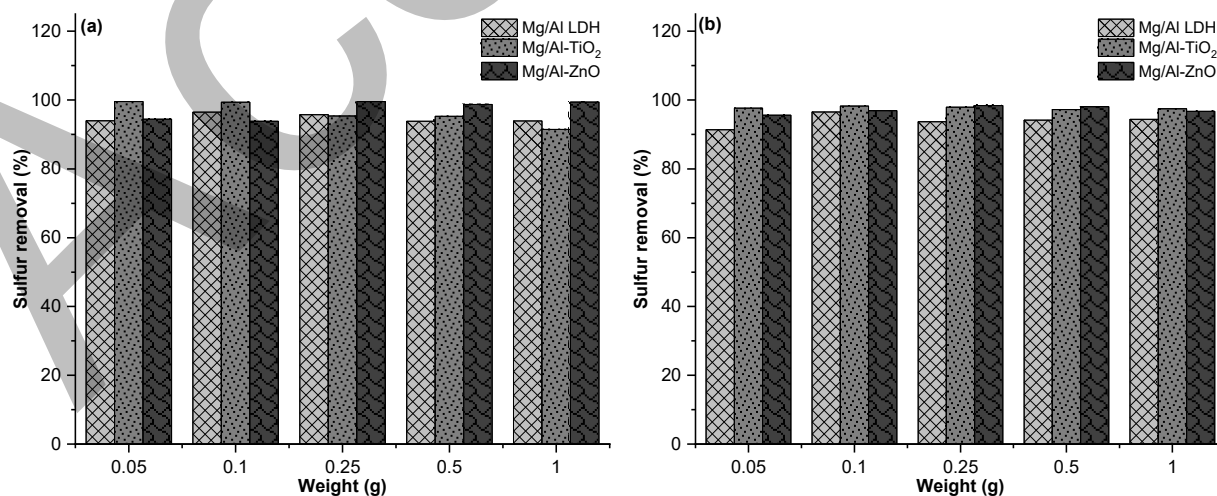


Fig 5. Effect of catalyst dosage on the desulfurization process of (a) 4-MDBT and (b) 4,6-DMDBT

Mg/Al-TiO₂ catalyst in 4-MDBT desulfurization at 0.05 and 0.1 g Mg/Al-TiO₂ in 4-MDBT desulfurization process, and Mg/Al-ZnO at 0.25 g (all desulfurization processes). Catalyst dose has been shown to have a significant impact on reaction rate and catalytic site number [26]. When the ideal dosage conditions are exceeded, the desulfurization process tends to slow and stabilize as the catalytic sites become saturated and face increased competition from oxidant molecules [16]. The sulfur removal percentages for 4-MDBT and 4,6-DMDBT utilizing Mg/Al LDH were 96.47% and 96.55%, respectively. Mg/Al-TiO₂ removed 99.54% and 98.26% of the sulfur from 4-MDBT and 4,6-DMDBT, respectively. Meanwhile, the percentage of sulfur removed from 4-MDBT and 4,6-DMDBT utilizing Mg/Al-ZnO is 99.56% and 96.9161%, respectively.

Effect of Temperature

The effect of temperature in the catalytic performance process of Mg/Al LDH, Mg/Al-TiO₂, and Mg/Al-ZnO catalysts was carried out using various temperatures, namely 30, 40, and 50 °C, as shown in Fig. 6. According to the results, as the temperature rises, so will the percentage of desulfurization of 4-MDBT and 4,6-DMDBT utilizing Mg/Al LDH, Mg/Al-TiO₂, and Mg/Al-ZnO catalysts. This can be seen at 30 °C, the sulfur removal percentage of 4-MDBT desulfurization rose from 93.22% to 95.44% and the percentage value of 4,6-DMDBT desulfurization rose from 93.67% to 94.65% at 50 °C. The same thing happened to the Mg/Al-TiO₂

catalyst, which increased from 30 °C with a sulfur removal percentage value of 99.31% on 4-MDBT and 97.93% on 4,6-DMDBT to 99.54% and 98.09%, respectively, at 50 °C. The sulfur removal of 4-MDBT on Mg/Al-ZnO also increased from 99.17% at 30 °C to 99.56% at 50 °C. However, when the temperature increased, the proportion of 4,6-DMDBT desulfurization reduced when utilizing the Mg/Al-ZnO catalyst. This is due to the creation of a product layer, which adds significant resistance and slows down the desulfurization process [27]. As a result, it can be stated that the Mg/Al-ZnO catalyst is suitable for the desulfurization of 4,6-DMDBT under low temperatures.

Effect of Solvent Type

Desulfurization of 4-MDBT and 4,6-DMDBT on a variety of catalysts, such as Mg/Al LDH, Mg/Al-TiO₂, and Mg/Al-ZnO, is illustrated in Fig. 7, which shows how different solvents have an effect on the process. Three different types of solvents were utilized: *n*-pentane, *n*-hexane, and *n*-heptane. In the desulfurizing process of 4-MDBT and 4,6-DMDBT, the utilization of catalysts such as Mg/Al LDH, Mg/Al-TiO₂, and Mg/Al-ZnO was shown to be efficient. The findings suggested that *n*-hexane was an effective solvent for the process. It was found that the Mg/Al-ZnO catalyst had the best percentage of sulfur removal for 4-MDBT and 4,6-DMDBT, followed by the Mg/Al-TiO₂ catalyst, and then finally, the Mg/Al LDH catalyst had the highest percentage.

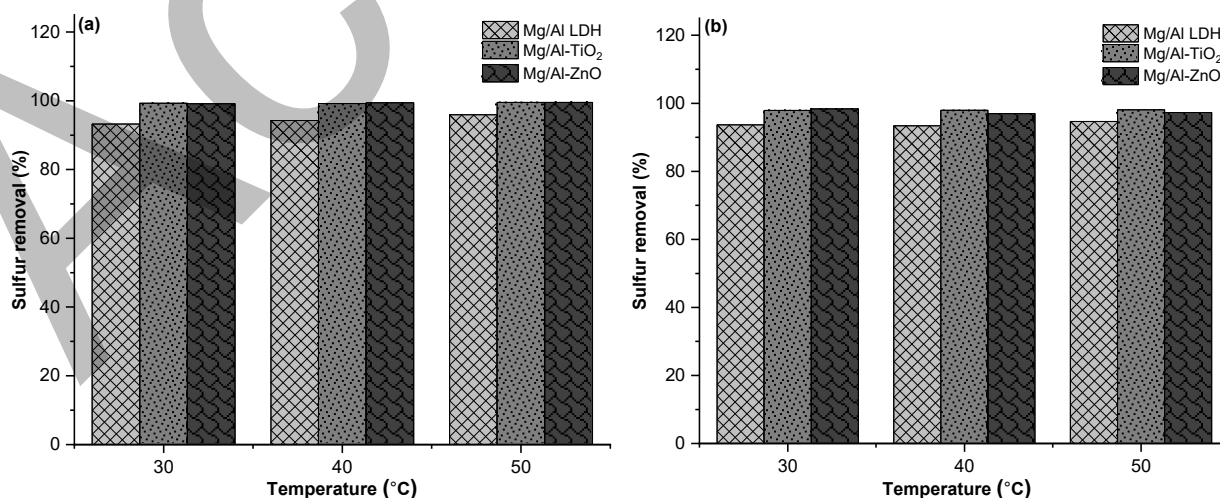


Fig 6. Effect of temperature on the desulfurization process of (a) 4-MDBT and (b) 4,6-DMDBT

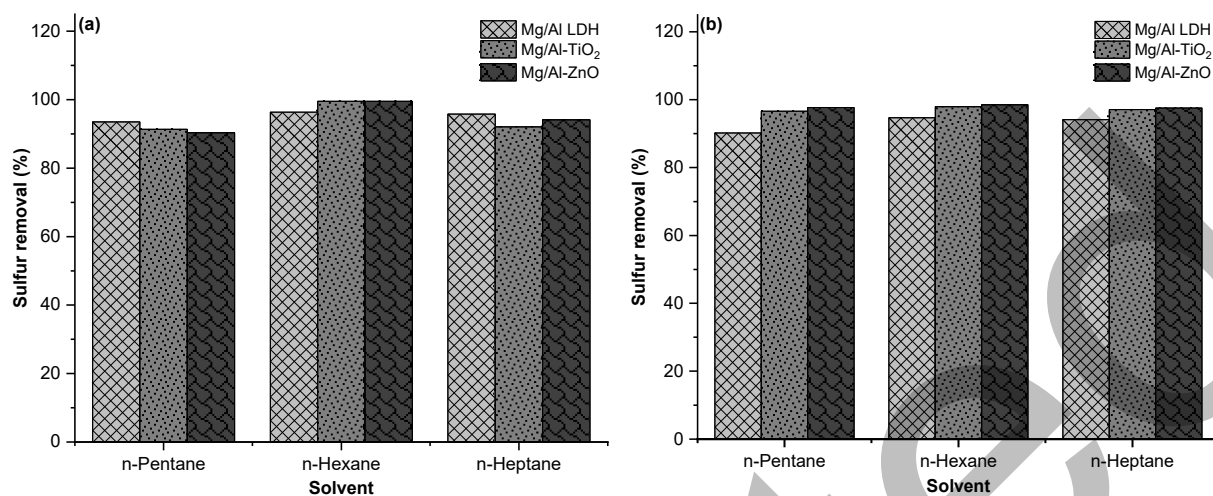


Fig 7. Effect of solvent type on the desulfurization process of (a) 4-MDBT and (b) 4,6-DMDBT

Catalyst Heterogeneity Test

The heterogeneity test is utilized to ascertain whether a catalyst exhibits homogeneity or heterogeneity. Homogeneous catalysts can easily dissolve in the reactants and products of a reaction, whereas heterogeneous catalysts do not dissolve and remain insoluble [16]. Testing for heterogeneity was performed by introducing various catalysts, including Mg/Al LDH, Mg/Al-TiO₂, and Mg/Al-ZnO, into a solution containing 4-MDBT and 4,6-DMDBT. The duration of the experiment was 10 min. Later on, the catalyst is collected and put through filtration to make sure that any remaining catalyst is removed. The desulfurization process is continued for 20–30 min without the presence

of a catalyst to observe any potential changes in sulfur removal. An unchanging percentage of sulfur removal suggests a system with varying components. Fig. 8 demonstrates that the percentage of sulfur removed during the desulfurization process of 4-MDBT and 4,6-DMDBT remains constant or shows little variation when the catalyst is taken out. Thus, it can be deduced that the Mg/Al LDH, Mg/Al-TiO₂, and Mg/Al-ZnO catalysts are of the heterogeneous variety [28]. Heterogeneous catalysts have the advantage of allowing for easy separation of products and catalysts, as well as the ability to be reused or regenerated [16].

Effect of Oxidant Addition

The choice and amount of oxidant play a crucial role

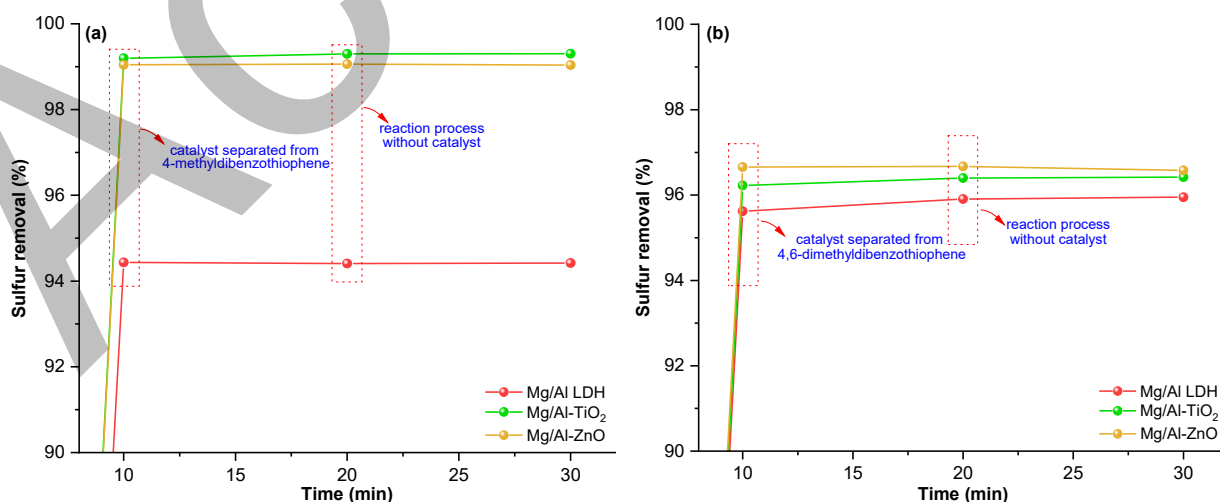


Fig 8. Catalyst heterogeneity test in the desulfurization process of (a) 4-MDBT and (b) 4,6-DMDBT

in determining the efficiency of desulfurization for 4-MDBT and 4,6-DMDBT. The reaction of H_2O_2 results in the formation of water is a harmless byproduct from an environmental standpoint. Testing was conducted on 4-MDBT and 4,6-DMDBT using Mg/Al LDH, Mg/Al- TiO_2 , and Mg/Al-ZnO. Different amounts of oxidant, specifically H_2O_2 volumes of 1.5, 2, and 2.5 mL, were used. The quantity of oxidant, in this instance H_2O_2 , plays a crucial role in determining the catalytic efficiency of Mg/Al LDH, Mg/Al- TiO_2 , and Mg/Al-ZnO catalysts during the desulfurization process of 4-MDBT and 4,6-DMDBT, as illustrated in Fig. 9. The results obtained indicated that the sulfur removal percentage on 4,6-DMDBT increased as the volume of oxidant dosage increased for the Mg/Al LDH, Mg/Al- TiO_2 , and Mg/Al-ZnO catalysts. Similar results were achieved in the sulfur removal of 4-MDBT using a Mg/Al- TiO_2 catalyst, with the removal efficiency increasing as the oxidant dosage volume increased. According to the findings of a previous study conducted by Guan et al. [29], an increase in the amount of oxidant led to an increase in desulfurization capacity. On the other hand, the effectiveness of Mg/Al LDH and Mg/Al-ZnO catalysts decreased with increasing H_2O_2 volume. The desulfurization of 4-MDBT decreased from 99.49% and 95.49% (+1.5 mL) to 99.05% and 95.43% (+2.5 mL). This indicates that the increase in the percentage of desulfurization of 4-MDBT is no longer influenced by the volume ratio of H_2O_2 oxidant [29].

Reusability of Catalyst

Efficient catalyst reuse is crucial for companies involved in ODS technology [30]. The experiment was conducted using *n*-hexane as a solvent and was carried out for 3 cycles. The catalyst recovery process was carried out using ultrasonic technology and then dried for future use. According to Fig. 10, it is evident that after 3 repetitions, all catalysts exhibited favorable outcomes. The Mg/Al LDH catalyst showed a slight decrease in the percentage of sulfur removal for 4-MDBT, going from 99.00% to 94.64%. Similarly, there was a decrease in the percentage of sulfur removal for 4,6-DMDBT, going from 93.83% to 86.02%. Unlike the Mg/Al- TiO_2 and Mg/Al-ZnO catalysts, the sulfur removal percentage value of the Mg/Al LDH catalyst is less stable. This is because TiO_2 and ZnO are added to each LDH, resulting in a more consistent 4-MDBT and 4,6-DMDBT sulfur removal percentage value for these two catalysts. There was a slight decrease in the sulfur removal percentage of 4-MDBT for both catalysts. On the Mg/Al- TiO_2 catalyst, the percentage decreased from 99.24% to 99.11%, while on the Mg/Al-ZnO catalyst, it decreased from 99.41% to 99.22%. The sulfur removal percentage on the Mg/Al- TiO_2 catalyst decreased slightly from 97.68% to 96.90%, while the sulfur removal percentage with the Mg/Al-ZnO catalyst decreased from 97.15% to 96.89%. Thus, it can be inferred that the catalysts Mg/Al- TiO_2 and Mg/Al-ZnO exhibit promising potential for application

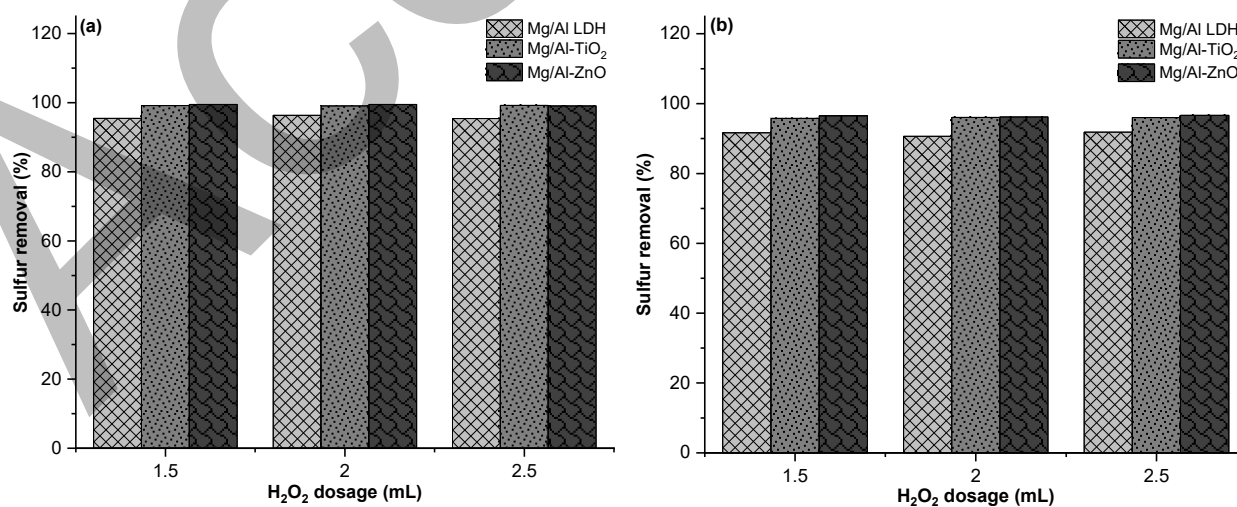


Fig 9. Effect of oxidant addition on the desulfurization process of (a) 4-MDBT and (b) 4,6-DMDBT

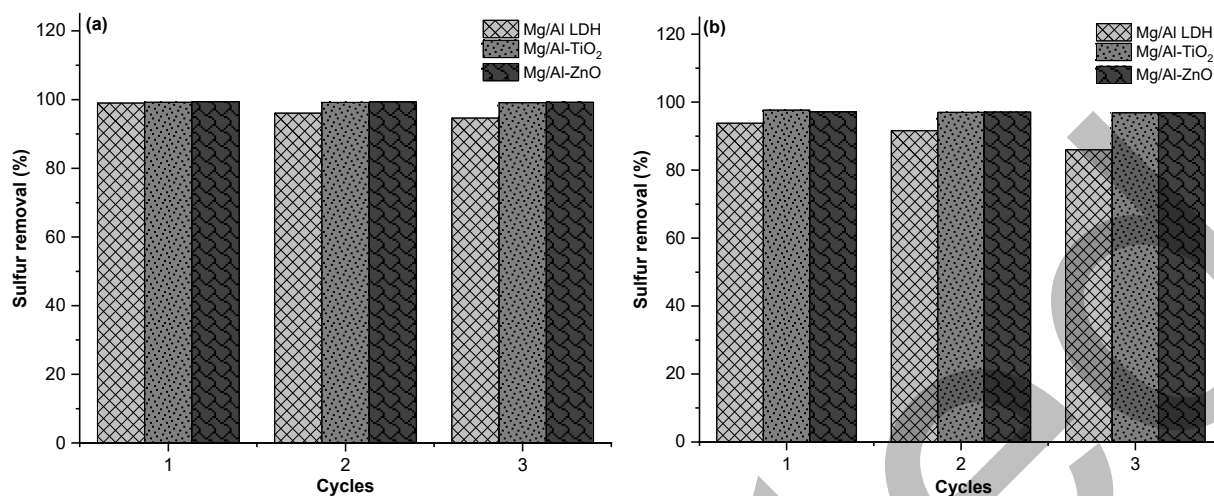


Fig 10. Reusability of catalyst in the desulfurization process of (a) 4-MDBT and (b) 4,6-DMDBT

in the desulfurization process of 4-MDBT and 4,6-DMDBT.

■ CONCLUSION

The production of Mg/Al LDH, Mg/Al-TiO₂, and Mg/Al-ZnO catalysts was successfully achieved in this study. The addition of TiO₂ and ZnO components to the Mg/Al LDH catalyst significantly improves the efficiency of sulfur removal during the desulfurization process of 4-MDBT and 4,6-DMDBT. As the temperature increases, the effectiveness of removing sulfur decreases. The choice of *n*-hexane as the solvent was suitable for the desulfurization process of 4-MDBT and 4,6-DMDBT. The behavior of all catalysts was found to be heterogeneous during the desulfurization process of 4-MDBT and 4,6-DMDBT. The recyclability of Mg/Al-TiO₂ and Mg/Al-ZnO materials outperformed that of Mg/Al LDH catalysts, indicating the long-lasting structural integrity of Mg/Al-TiO₂ and Mg/Al-ZnO. It is anticipated that catalysts like Mg/Al-TiO₂ and Mg/Al-ZnO will exhibit improved catalytic performance in fuel oil desulfurization, offering benefits to the petrochemical industry.

■ ACKNOWLEDGMENTS

We thank the Research Center for Inorganic Materials and Coordination Complexes at Universitas Sriwijaya and Hibah Profesi 2023 as additional research output Contract number SP DIPA-023.17.2.677515/2023 accordance with SK Rektor No. 0187/UN9.3.1/SK/2023

for the help and support so that this research can run smoothly and be completed.

■ CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this paper.

■ AUTHOR CONTRIBUTIONS

Amri performed conceptualization, investigation, original draft writing, manuscript revision, and visualization. Nur Ahmad performed investigation, visualization, and formal analysis. Sahrul Wibiyana and Alfian Wijaya conducted formal analysis, investigation, graphing, and visualization. Mardiyanto, Idha Royani, and Risfidian Mohadi carried out validation, ensured data accuracy, and performed visualization. Aldes Lesbani was responsible for funding acquisition, resource management, writing review and editing, supervision, methodology, and conceptualization. All authors have reviewed and endorsed the work's published version.

■ REFERENCES

- [1] Liu, P., Yang, S., Hu, J., and Wang, H., 2023, Numerical analysis of SO₂ removal characteristics in industrial flue gas desulfurization reactor by spray drying adsorption, *Sep. Purif. Technol.*, 323, 124475.
- [2] Lü, J., Fu, Y., Yu, H., Wang, H., Wang, Z., and Chen, H., 2024, Effect of relative humidity on the

- desulfurization performance of calcium-based desulfurizer, *J. Environ. Sci.*, 138, 179–188.
- [3] Li, W., Zhao, S., Yan, Y., Biney, B.W., Zhang, D., Alshiaani, N.H.A., Chen, K., Guo, A., and Xia, W., 2023, High-efficiency desulfurization adsorbents loaded with uniformly dispersed nano-metal particles prepared from phytoremediation, *J. Environ. Chem. Eng.*, 11 (5), 110409.
- [4] Jha, D., Maheshwari, P., Singh, Y., Haider, M.B., Kumar, R., and Balathanigaimani, M.S., 2023, A comparative review of extractive desulfurization using designer solvents: Ionic liquids & deep eutectic solvents, *J. Energy Inst.*, 110, 101313.
- [5] Mushtaq, A., Nadeem, M., Shaaban, I.A., Assiri, M.A., Sajid, M., Khan, M.A., Muhammad Asif, H., Nazar, Z., Hussain, S., and El-Bahy, Z.M., 2023, Catalytic oxidative desulfurization of thio-compounds by employing χ -Anderson-type polyoxometalates-porphyrin covalent organic framework (COF), *Tetrahedron*, 144, 133575.
- [6] Zaidi, Z., Gupta, Y., Gayatri, S.L., and Singh, A., 2023, A comprehensive discussion on fuel combustion and desulfurization technologies, *Inorg. Chem. Commun.*, 154, 110964.
- [7] Lu, L., Wei, W., Liu, F., Cao, W., Jin, H., Chen, Y., and Guo, L., 2023, Desulfurization mechanism of thiophene compounds in supercritical water, *Fuel*, 353, 129251.
- [8] Chen, M., Zou, C., Tang, W., and Cao, Y., 2023, Stable hydrogen bonding interactions in supramolecular deep eutectic solvents based on carbon quantum dots: For extraction and oxidative desulfurization, *Sep. Purif. Technol.*, 323, 124491.
- [9] Lim, S.H., Yongle, T.L., Bin Anwar, A.F., Kouk, Q.Y., Shiyun, K.L., Kok, P.C., and Chen, L., 2023, Boosting the carbo-catalytic of graphene nanoplatelets by ultrasonication for the oxidative desulfurization of dibenzothiophene, *FlatChem*, 41, 100534.
- [10] Wu, M., Chang, B., Lim, T.T., Oh, W.D., Lei, J., and Mi, J., 2018, High-sulfur capacity and regenerable Zn-based sorbents derived from layered double hydroxide for hot coal gas desulfurization, *J. Hazard. Mater.*, 360, 391–401.
- [11] Wu, M., Guo, E., Li, Q., Mi, J., and Fan, H., 2020, Mesoporous Zn-Fe-based binary metal oxide sorbent with sheet-shaped morphology: Synthesis and application for highly efficient desulfurization of hot coal gas, *Chem. Eng. J.*, 389, 123750.
- [12] Ahmad, N., Wijaya, A., Amri, A., Fitri, E.S., Arsyad, F.S., Mohadi, R., and Lesbani, A., 2022, Catalytic oxidative desulfurization of dibenzothiophene by composites based Ni/Al-oxide, *Sci. Technol. Indones.*, 7 (3), 385–391.
- [13] Ahmad, N., Yuliasari, N., Arsyad, F.S., Royani, I., desulfurization of dibenzothiophene by heterogeneous M^{2+} /Al-layered double hydroxide ($M^{2+} = \text{Zn, Mg, Ni}$) modified zinc oxide, *Iran. J. Catal.*, 13 (1), 35–45.
- [14] Sun, H., and Park, S.J., 2022, Bimetallic CuPd nanoparticle-decorated MgAl-LDH/g- C_3N_4 composites for efficient photocatalytic reduction of aqueous Cr(VI), *J. Ind. Eng. Chem.*, 111, 183–191.
- [15] Wang, Y., Zhang, Z., Wang, S., and Han, M., 2022, Integration of MgAl-layered double hydroxides into TiO_2 nanorods as photoanodes for enhanced photoelectrochemical water splitting, *Catal. Commun.*, 164, 106434.
- [16] Ahmad, N., Fitri, E.S., Wijaya, A., Amri, A., Mardiyanto, M., Royani, I., and Lesbani, A., 2022, Catalytic oxidative desulfurization of dibenzothiophene utilizing composite based Zn/Al layered double hydroxide, *Bull. Chem. React. Eng. Catal.*, 17 (4), 733–742.
- [17] Bokka, S., Singh, R., and Chowdhury, A., 2024, Efficacy of Mg-Al-layered double hydroxide nano-adsorbents for a multi-anionic mixed dye solution, *J. Mol. Liq.*, 396, 123984.
- [18] Wu, S., Liang, H., Zhang, Z., Zhang, Q., Han, Q., Wang, J., Gao, M., Fan, H., Yang, J., and Lang, J., 2022, The photocatalytic degradation and mechanism of rhodamine B by Zn-Al layered double hydroxide, *Opt. Mater.*, 131, 112636.
- [19] Lyu, P., Wang, G., Cao, Y., Wang, B., and Deng, N., 2021, Phosphorus-modified biochar cross-linked Mg-Al layered double-hydroxide composite for immobilizing uranium in mining contaminated soil,

- Chemosphere*, 276, 130116.
- [20] Wang, D., Repo, E., He, F., Zhang, X., Xiang, H., Yang, W., Min, X., and Zhao, F., 2022, Dual functional sites strategies toward enhanced heavy metal remediation: Interlayer expanded Mg-Al layered double hydroxide by intercalation with L-cysteine, *J. Hazard. Mater.*, 439, 129693.
- [21] Wang, L., Gao, X., Cheng, Y., Zhang, X., Wang, G., Zhang, Q., and Su, J., 2019, TiO₂@MgAl-layered double hydroxide with enhanced photocatalytic activity towards degradation of gaseous toluene, *J. Photochem. Photobiol., A*, 369, 44–53.
- [22] Sisca, V., Deska, A., Syukri, S., Zilfa, Z., and Jamarun, N., 2021, Synthesis and characterization of CaO limestone from Lintau Buo supported by TiO₂ as a heterogeneous catalyst in the production of biodiesel, *Indones. J. Chem.*, 21 (4), 979–989.
- [23] Estrada-Ruiz, M., Cosano, D., Esquivel, D., Romero-Salguero, F.J., and Ruiz, J.R., 2024, Synthesis and characterization of cobalt-based layered double hydroxides for light-driven CO₂ reduction, *Catal. Today*, 429, 114504.
- [24] Shao, B., Shi, L., and Meng, X., 2014, Deep desulfurization of 4,6-dimethyldienzothiophene by an ionic liquids extraction coupled with catalytic oxidation with a molybdc compound, *Ind. Eng. Chem. Res.*, 53 (16), 6655–6663.
- [25] Ahmad, N., Rohmatullaili, R., Hanifah, Y., Wibiyani, S., Amri, A., Wijaya, A., Mardiyanto, M., Mohadi, R., Royani, I., and Lesbani, A., 2023, Recycle performance of heterogeneous catalyst metal oxides-based layered double hydroxide for oxidative desulfurization process of 4-methyldibenzothiophene, *Bull. Chem. React. Eng. Catal.*, 18 (4), 548–558.
- [26] Zhou, S., He, J., Wu, P., He, L., Tao, D., Lu, L., Yu, Z., Zhu, L., Chao, Y., and Zhu, W., 2022, Metal-organic framework encapsulated high-loaded phosphomolybdc acid: A highly stable catalyst for oxidative desulfurization of 4,6-dimethyldibenzothiophene, *Fuel*, 309, 122143.
- [27] Ciro, E., Dell’Era, A., Hatunoglu, A., Bocci, E., and Del Zotto, L., 2023, Kinetic and thermodynamic study of the wet desulfurization reaction of ZnO sorbents at high temperatures, *Energies*, 16 (2), 792.
- [28] Vallés-García, C., Santiago-Portillo, A., Álvaro, M., Navalón, S., and García, H., 2020, MIL-101(Cr)-NO₂ as efficient catalyst for the aerobic oxidation of thiophenols and the oxidative desulfurization of dibenzothiophenes, *Appl. Catal., A*, 590, 117340.
- [29] Guan, S., Li, Z., Xu, B., Wu, J., Han, J., Guan, T., Wang, J., and Li, K., 2023, Deep eutectic solvents with multiple catalytic sites for highly efficient extractive and oxidative desulfurization, *Fuel*, 333 (Part 1), 126329.
- [30] Wang, F., Liu, Y., Lv, Y., Ren, J., Wang, R., and Jiao, W., 2022, Oxidative desulfurization of liquid fuels catalyzed by W₂C@C derived from metallophthalocyanine/phosphotungstic acid composites, *Sep. Purif. Technol.*, 281, 119953.