

ENHANCED PHOTOCATALYTIC PERFORMANCE OF CaAl LDH BY MODIFYING *MUNTINGIA CALABURA* EXTRACT FOR OXYTETRACYCLINE DEGRADATION

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Abstract

The persistent presence of oxytetracycline (OTC) in aquatic environments poses a serious ecological threat owing to its resistance to degradation and potential toxicity. To address these issues, this study explores an effective photocatalytic strategy utilizing CaAl layered double hydroxide (LDH) synthesized via a coprecipitation method. To enhance its photocatalytic performance, CaAl LDH was modified with bioactive compounds derived from a *Muntingia calabura* fruit extract, resulting in a CaAl LDH–MC material with improved structural stability and light absorption capability. X-ray diffraction, fourier transform infrared spectroscopy, ultraviolet diffuse reflectance spectroscopy, and scanning electron microscopy data confirmed that the incorporation of the *Muntingia calabura* extract significantly reduced the bandgap energy from 3.35 to 1.82 eV and yielded a more uniform particle morphology. Photodegradation performance was evaluated using OTC as a target pollutant with the highest degradation efficiency (66%) achieved under the optimal conditions: pH = 5, a catalyst mass of 30 mg, a temperature of 50°C, and an irradiation time of 120 min. The enhanced catalytic activity of CaAl LDH–MC was attributed to the improved charge separation and visible light absorption via extract modification. Compared with unmodified CaAl LDH, CaAl LDH–MC demonstrated superior photocatalytic efficiency and structural integrity, indicating its high application potential as a green and effective solution for environmental remediation.

Keywords: Photodegradation; Oxytetracycline; *Muntingia calabura*; Layered Double Hydroxide; Bandgap

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Introduction

The production of pharmaceuticals has increased annually by 13.34% (Alessandretti *et al.*, 2021). This increase contributes to the accumulation of pharmaceutical residues in the environment, particularly in water, which can cause significant toxicity and harm to both human health and aquatic ecosystems (Renuka *et al.*, 2024). Among various types of pharmaceutical products, antibiotics are among the primary contaminants frequently detected in aqueous environments (Zango *et al.*, 2024). Antibiotics in aquatic environments can promote antimicrobial resistance, posing serious risks to both human and animal health (Wang *et al.*, 2024a). According to a report published by the World Health Organization (2022), antibiotic residues contain strains of bacteria that have developed high anti-microbial resistance, and the resistance to antibiotics is considered a major global public safety concern with 4.95 million deaths. A common antibiotic that is frequently found in water pollution is oxytetracycline (OTC) (Yang *et al.*, 2020).

OTC is an antibiotic that is widely used in livestock, fisheries, and agriculture. However, OTC residues that are discharged into the environment (especially into water bodies) pose a serious problem owing to their toxic properties and high antimicrobial resistance. Photodegradation is a commonly used OTC removal method because it can effectively break down the OTC chemical structure into non-toxic compounds without producing secondary waste and is environmentally friendly (Pelosato *et al.*, 2022). The OTC photodegradation process involves the absorption of photon energy by semiconductor materials, which produce hydroxyl radicals ($\bullet\text{OH}$) as the main oxidative agent for degrading harmful pollutants (Ramadhini *et al.*, 2023). Previous research studies on OTC photodegradation have successfully used various photocatalytic materials such as $\text{CuFeS}_2@\text{Zn}$ (Vigneswaran *et al.*, 2025), Ag/TiO_2 (Nguyen *et al.*, 2023), BiVO_4 (Senasu *et al.*, 2021), metal-organic frameworks (Luo *et al.*, 2023), and layered double hydroxides (LDHs) (Cao *et al.*, 2025).

LDH has a high application potential in the field of antibiotic photodegradation. It consists of an ionic clay with a positively charged structure similar to that of brucite, in which anions are hydrated and intercalated between structural layers. LDHs have a general formula $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n}\cdot y\text{H}_2\text{O}$, in which M^{2+} and M^{3+}

refer to divalent and trivalent metal cations, respectively (Abriyanto *et al.*, 2024; Wibiyanto *et al.*, 2024; Amri *et al.*, 2025). The presence of the interlayer enables easy LDH modification to increase its photocatalytic efficiency. In addition, LDH exhibits a high ion exchange capacity, which supports its role in antibiotic degradation. The presence of trivalent cations (M^{3+} , such as Al) in LDHs results in bandgap energies above 3.0 eV, which decrease the LDH photocatalytic efficiency. Therefore, modifications using natural extracts were conducted to reduce the bandgap energy and thus make LDHs more suitable for photocatalytic applications (Molina-Muriel *et al.*, 2022; Jefri *et al.*, 2025).

LDHs are often modified with various materials to increase their functional efficiency and support more diverse and practical uses. For instance, Gholami *et al.* (2020) investigated the photocatalytic efficiency of biochar composites combined with ZnAl-LDH for gemifloxacin degradation. They found that the bandgap energies of Zn-Co-LDH and Zn-Co-LDH@BC decreased to 2.31 and 1.83 eV, respectively, with a degradation efficiency reaching 92.7% (Bansal and Pal, 2025). A modification of LDH with a *Uncaria Gambir* extract for tetracycline degradation successfully reduced the bandgap energy by 1.60-1.63 eV with a tetracycline degradation efficiency of 63.34% under the optimal conditions (Jefri *et al.*, 2025). Rohmatullaili *et al.* (2024a) also found that modifying MgAl LDH with a *Clitoria Ternatea* extract lowered its bandgap energy and enhanced its photocatalytic performance. The modification of NiAl-LDH with a *Butterfly pea* flower extract also produced promising results, including a reduced bandgap energy and tetracycline degradation efficiency of 93.61% (Rohmatullaili *et al.*, 2024b). In addition, Yu *et al.* (2021) developed a $\text{g-C}_3\text{N}_4/\text{LDH}$ material with a bandgap of 2.86 eV, which can degrade OTC with an efficiency up to 95.73%.

In recent years, the synthesis of inorganic materials from natural materials has developed rapidly with increasing focus on the principles of sustainability and environmental friendliness. This approach can potentially reduce the dependence on hazardous chemical reagents and minimize negative impacts on the environment. Among the various biological sources, *Muntingia calabura* is a potential candidate owing to its abundant content of bioactive compounds, such as flavonoids, tannins, and phenols. Flavonoids with high

concentrations not only demonstrate high antioxidant activities ($IC_{50} \leq 50 \mu\text{g/mL}$), but also act as stabilizing agents capable of increasing the stability of the material structure and sustaining the efficiency of the photocatalytic process (Nur *et al.*, 2021; Minh *et al.*, 2025).

In previous works, natural extracts composited with LDH exhibited high effectiveness in the photodegradation of antibiotic compounds. Therefore, in this study, a *Muntingia calabura* fruit extract was combined with CaAl LDH to produce a new photocatalytic material. Its objective was to develop a more environmentally friendly and sustainable catalyst for OTC degradation, contributing to the advancement of green remediation technologies.

Materials and Methods

Chemicals and Instruments

The materials used in this study included calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium hydroxide (NaOH), hydrochloric acid (HCl), ethyl acetate, isopropanol, triethanolamine, silver nitrate (AgNO_3), and benzoquinone, which were obtained from Merck. Distilled water was supplied by Dira Sonita, while *Muntingia calabura* fruits were procured from Palembang, South Sumatra. Oxytetracycline hydrochloride (OTC-HCl) in the powder form (1 g) was purchased from CV Total Pharmacy.

Several characterizations were performed using Fourier-transform infrared (FTIR) spectroscopy (Shimadzu Prestige-21), X-ray diffraction (XRD, Rigaku MiniFlex 600), ultraviolet-diffuse reflectance spectroscopy (UV-DRS, Jasco V-760, 200-800 nm), scanning electron microscopy-energy-dispersive X-ray spectroscopy (Quanta 650), and ultraviolet-visible (UV-Vis) spectroscopy (Biobase BK-UV 1800 PC) for the degradation analysis of OTC-HCl at a wavelength of 354 nm.

Preparation of *Muntingia calabura* Fruit Extract

The extraction of *Muntingia calabura* was performed by sorting the ripe fruits, washing them with distilled water, and slicing them to accelerate the drying process. The sliced fruits were dried in an oven at 50°C until they were completely dehydrated. The resulting dried material was ground into powder and extracted for 3 d in the dark via a maceration method using ethyl acetate as a solvent. The filtrate was evaporated using a rotary evaporator at 40°C to obtain a concentrated extract,

which was further dried in an oven at the same temperature for 24 h. The final extract was characterized via FTIR spectroscopy (Nur *et al.*, 2021).

Preparation of CaAl LDH Catalysts

CaAl LDH was synthesized via a coprecipitation method by mixing equal volumes of 0.75 M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.25 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solutions, adjusting the pH of the resulting mixture to 10 using NaOH, and stirring at 65°C for 24 h. The produced precipitate was separated, cleaned with distilled water, and dried at 80°C . The modification process was performed by adding 5 g of the *Muntingia calabura* extract to the CaAl-LDH mixture under the same conditions. The obtained product was filtered and dried at 70°C to synthesize the CaAl LDH-MC material (Karthikeyan and Meenakshi, 2019; Juleanti *et al.*, 2021).

OTC Photodegradation

The photodegradation of OTC was conducted in batches using the CaAl LDH and CaAl LDH-MC catalysts. A total of 20 mL of the OTC solution with a concentration of 20 mg/L was mixed with the catalyst and stirred in the dark for 30 min at 250 rpm. The resulting mixture was irradiated for 60 min using a 220-V UV lamp under continuous stirring. Subsequently, the catalyst mass (10-50 mg), solution pH (3-11), initial OTC concentration (20-40 mg/L), and reaction temperature ($30\text{-}50^\circ\text{C}$) were optimized. The pH adjustment was conducted using a 0.01 M HCl or NaOH solution. All experiments were performed in duplicate, and the kinetics data were analyzed using the Langmuir-Hinshelwood model (Rohmatullaili *et al.*, 2024c).

Photocatalyst Regeneration

The catalyst used in the OTC photodegradation process was regenerated via ultrasonication in 50 mL of distilled water for 60 min and dried at 50°C (Ahmed *et al.*, 2023). This procedure was repeated five times, and the regeneration efficiency (%R) was calculated as follows:

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

Here, C_0 represents the initial antibiotic amount, and C_t signifies the remaining antibiotic concentration after the photodegradation completion.

Free Radical Trapping

Free radical trapping was performed by adding specific trapping compounds to the OTC solution (30 mg/L, 30 mL) to identify the contribution of each reactive species. The utilized compounds included isopropanol (0.02 M) to capture hydroxyl radicals ($\bullet\text{OH}$), triethanolamine (0.01 M) for holes (h^+), benzoquinone (0.001 M) for superoxide radicals ($\bullet\text{O}_2^-$), and silver nitrate (0.1 M) for electrons (e^-). The resulting system was irradiated with UV light for 2 h, and the OTC degradation efficiency was measured to evaluate the relative role of each reactive species in the photodegradation mechanism.

Results and Discussion

FTIR Analysis

The successful synthesis of CaAl LDH and its modification with the *Muntingia calabura* extract were confirmed by FTIR (Figure 1). In the spectrum of CaAl LDH, the absorption peaks spanning from 3633 to 3479 cm^{-1} indicate the vibrational stretching of hydroxyl (OH^-) groups, which are likely derived from the hydroxyl groups located between LDH layers or adsorbed water molecules (Chouaybi *et al.*, 2025). Furthermore, the spectral peak at 1381 cm^{-1} indicates the presence of nitrate anions intercalated between LDH layers, whereas the peaks at 794 and 540 cm^{-1} are associated with metal-oxygen (Ca-O or Al-O) bonds reflecting a typical structure of LDH materials (Bekele *et al.*, 2019).

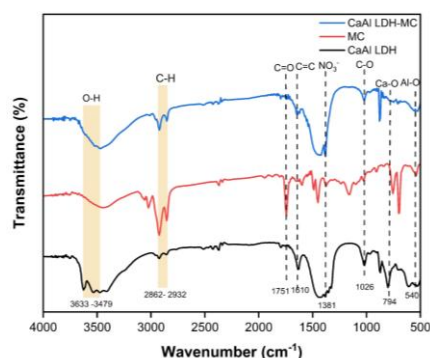


Figure 1. FTIR spectra of CaAl LDH-MC, the *Muntingia calabura* extract, and CaAl LDH

The spectra of the *Muntingia calabura* extract and CaAl LDH-MC composite contain absorption bands between 2862 and 2932 cm^{-1} associated with $=\text{C-H}$ bond stretching vibrations, suggesting that aliphatic moieties originated from organic

substances in the extract are present on the LDH surface. The band at 1751 cm^{-1} indicates the occurrence of stretching vibrations of carbonyl groups (C=O), which result from compounds such as ketones or aldehydes. In addition, the band at 1610 cm^{-1} can be associated with C=C aromatic bond frame vibrations or hydrogen bonding interactions occurring between different molecules. The band at around 1026 cm^{-1} indicates the stretching vibrations of the C-O group of the primary alcohol, which can be found in both the *Muntingia calabura* extract and CaAl LDH structure (Rasheed *et al.*, 2020).

XRD Analysis

Figure 2 shows the XRD patterns obtained for CaAl-LDH and its composite with *Muntingia calabura*. Typical diffraction peaks of CaAl LDH appear at 2θ values of 10° , 20° , 31.16° , 37.23° , 39° , 43.56° , 48.78° , and 55.87° , which correspond to the LDH reflection planes of (002), (004), (110), (106), (018), (114), (206), and (300) based on JCPDS No. 89-6723, respectively (Noorani Khomeyrani *et al.*, 2022). The peaks reflecting the (002), (004), and (110) planes are characteristic of pure LDH. The peak corresponding to the (002) plane was detected at $2\theta = 10^\circ$ with a gallery height of 0.443 nm, which was calculated using the Debye-Scherrer equation. This value is attributed to the intercalation of nitrate ions within the LDH structure (Mohadi *et al.*, 2021). The successful synthesis of the LDH composite with the *Muntingia calabura* extract was confirmed through the appearance of typical MC composite peaks at 2θ values of 36° (201) and 47.16° (102). These peaks confirm the presence of *Muntingia calabura* in the composite structure, indicating that bioactive compounds such as phenolic compounds in the extract play a vital role in the composite formation process (Vinayagam *et al.*, 2022). These interactions confirm the successful intercalation of organic compounds and enhanced LDH crystallinity.

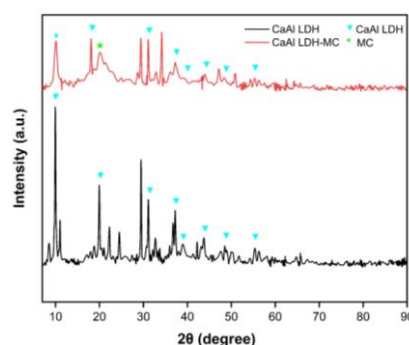


Figure 2. XRD patterns of CaAl LDH and CaAl LDH-MC

SEM Analysis

The surface morphologies and particle size distributions of CaAl LDH and CaAl LDH-MC are displayed in Figure 3 at a 2500 $\times$ magnification. Figure 3(a) shows that CaAl LDH has a tightly aggregated plate structure with uneven particle sizes and a high degree of agglomeration. After the modification with the *Muntingia calabura* extract (Figure 3(b)), the particle morphology becomes more defined, tends to be spherical, and the size distribution becomes more homogeneous.

The observed changes in morphology and the particle size distribution indicate that the bioactive compounds in the extract play a significant role in inhibiting particle agglomeration and crystal growth. This effect is likely caused by the compound's ability to stabilize the particle surface, resulting in a more dispersed and uniform structure (Vinayagam *et al.*, 2023; Bagherzadeh *et al.*, 2024). This phenomenon is consistent with the study conducted by Labanni *et al.* (2023), who found that natural compounds in plant extracts could act as complexation agents and stabilizers, thereby reducing interparticle forces.

UV-DRS Analysis

The modification of CaAl LDH was confirmed through UV-DRS (Figure 4(a)). Pure CaAl LDH exhibited absorption only in the UV region with a low intensity in the visible light region. After the modification with the *Muntingia calabura* extract, the absorption intensity in the 300–700 nm range significantly increased, particularly in the visible light region.

The bandgap energy was calculated using the Tauc plot method based on the following equation (Figure 4(b)):

$$(ah\nu)^n = A(h\nu - E_g) \quad (2)$$

The equation describes the relationship between the optical absorption coefficient (α) and photon energy ($h\nu$), where α is the absorption coefficient, h is Planck's constant, ν denotes the photon frequency, A represents a constant, and E_g refers to the optical bandgap energy of the material. Parameter n is an exponent that depends on the electronic transition properties with $n = 2$ for direct transitions and $n = 1/2$ for indirect transitions.

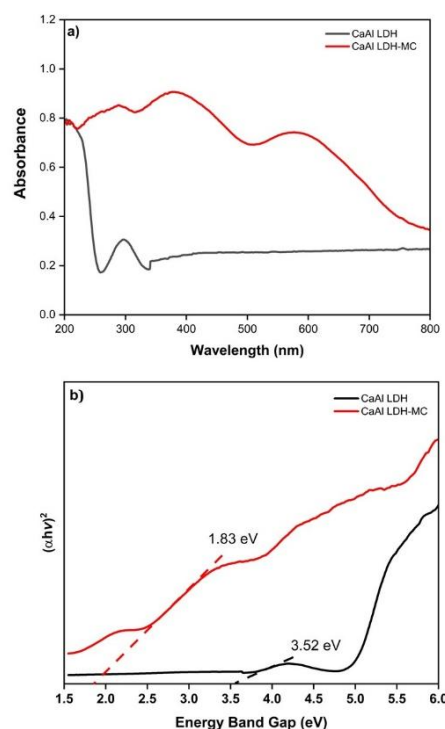


Figure 4. (a) UV-DRS spectra of CaAl LDH and CaAl LDH-MC. (b) Tauc plots showing the estimated bandgap energies

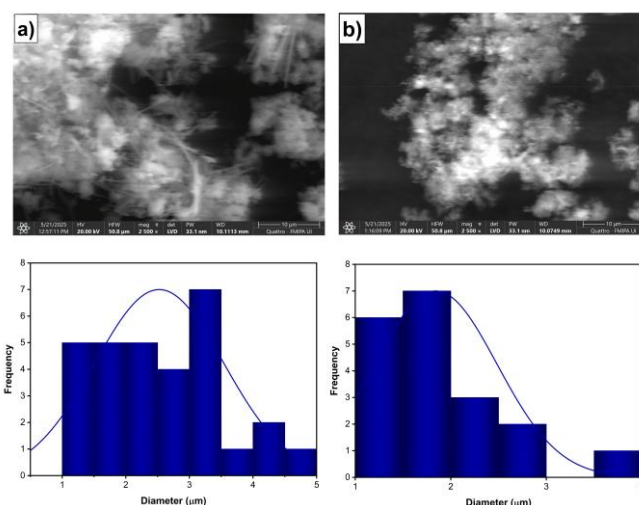


Figure 3. SEM images and particle size distributions of (a) CaAl LDH and (b) CaAl LDH-MC

The analysis results revealed a significant reduction in the bandgap energy from 3.35 eV to 1.82 eV after modification. This narrowing of the bandgap may be attributed to the incorporation of bioactive compounds that interact with surface metal centers, altering the electronic environment and potentially introducing localized energy levels within the forbidden band. These changes enhance the absorption of visible light and promote the separation and migration of photogenerated charge carriers (e^-/h^+), which are essential for the improved photocatalytic performance (Jansanthea *et al.*, 2024; Harshitha and Suresh, 2025).

The influences of light and dark conditions play a crucial role in evaluating the photocatalytic performance of materials. According to Figure 5, both CaAl LDH and CaAl LDH-MC exhibit a notable increase in the degradation efficiency under light irradiation. Specifically, CaAl LDH achieved a degradation efficiency of only 6-7% in the dark, which increased to approximately 10% under UV light exposure. In contrast, CaAl LDH-MC demonstrated a more pronounced enhancement with a degradation efficiency rising from 8% in the dark to 28% under illumination. This significant improvement in the degradation efficiency suggests that the modification of CaAl LDH with the *Muntingia calabura* fruit extract effectively enhances the photocatalytic activity toward OTC degradation. The bioactive compounds present in the extract likely improve light absorption and facilitate charge separation, thereby accelerating the photodegradation process (Elviera *et al.*, 2022). In conclusion, both CaAl LDH and its *Muntingia calabura*-modified counterpart are capable of OTC photodegradation with the latter demonstrating superior performance under UV light irradiation.

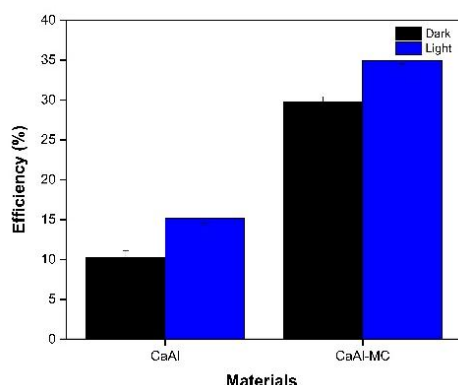


Figure 5. Degradation efficiencies of CaAl LDH and CaAl LDH-MC under the dark and light conditions

Effect of Reaction Parameters on OTC Photodegradation

Effect of pH

Variations in pH exert a strong effect on the OTC degradation efficiency (Figure 6(a)). The highest performance is achieved under acidic conditions, while a drastic decrease in the photodegradation efficiency occurs at neutral to basic pH values. At pH = 3, high concentrations of H^+ ions can inhibit OTC adsorption owing to the competition for active sites. Conversely, at pH = 9, excessive OH^- ions can interfere with the light absorption by the photocatalyst, thereby reducing the photodegradation efficiency (Paghaleh *et al.*, 2023).

The highest efficiency is achieved at pH = 5, which reflects the optimal balance between the adsorption process and photocatalytic activity. Under these conditions, the negatively charged catalyst surface promotes the migration of holes (h^+) as the primary oxidizer in the OTC degradation process. Additionally, the pH-dependent speciation of OTC HCl including cationic, zwitterionic, and anionic forms contributes to its differing reactivities during both the photolytic and photocatalytic processes (Akel *et al.*, 2020).

Effect of Catalyst Dosage

Figure 6(b) shows that increasing the catalyst dose improves the photodegradation efficiency of OTC. At a dose of 30 mg, the degradation efficiency of CaAl LDH-MC reaches 66%, while for CaAl LDH, this value is only around 35%. However, the increase in efficiency tends to reach a saturation point at higher doses, indicating a limited number of available active sites. Adding the catalyst beyond the optimal dose does not significantly improve the catalytic efficiency owing to the limited surface reactivity and possible shadowing effects, in which catalyst particles overlap and block the UV light penetration into the reaction system, thereby hindering the optimal photocatalytic activation (Huang *et al.*, 2025; Karcioğlu Karakaş and Dönmez, 2025). Based on these findings, a catalyst dosage of 30 mg was identified as the optimum dosing amount.

Effect of Reaction Time and Kinetic Analysis

The photocatalyst performance was also examined by comparing CaAl LDH and CaAl LDH-MC (Figure 6(c)). CaAl LDH-MC demonstrated a higher photodegradation efficiency than that of CaAl LDH characterized by a more significant decrease in the C/C_0 ratio during

120 min of irradiation. This shows that modifications with natural compounds can improve the catalyst performance, particularly through the optimization of electron transfer and increased formation of reactive oxygen species, which play an important role in the oxidation of target compounds (Chin *et al.*, 2025). A kinetic analysis of the reaction based on the Langmuir–Hinshelwood model (Figure 6(d)) shows that the reaction rate constant (k) of CaAl LDH–MC is greater than that of the unmodified material with a coefficient of determination (R^2) close to unity, confirming that this model adequately explains the OTC degradation mechanism. This finding indicates that the natural compound-based modification approach can potentially improve the photodegradation efficiency of organic pollutants.

Effects of Initial Concentration and Temperature

A more comprehensive study of the effects of other reaction parameters was conducted by evaluating variations in the OTC concentration (20–40 mg/L) and reaction temperature (30–50°C) (Figure 6(e)). These results indicate that CaAl LDH–MC consistently exhibits a higher photocatalytic activity compared with that of CaAl LDH across the entire range of the tested conditions with a degradation efficiency reaching 43–61%, while CaAl LDH achieves a degradation efficiency of only 10–27%.

This performance improvement is attributed to the successful surface modification using the

Muntingia calabura extract, which acts as a reducing agent and stabilizer during the synthesis process, resulting in a more active photocatalytic surface structure. This modification not only enhances the charge transfer efficiency but also strengthens the interactions between the catalyst surface and OTC molecules. Optimal conditions are achieved at an OTC concentration of 40 mg/L and reaction temperature of 50°C, which accelerate the photodegradation process by increasing the kinetic energy and collision frequency between reactant molecules (Liu *et al.*, 2025).

Overall, the results of this study confirm the potential utilization of natural materials as modifying agents in the development of LDH-based photocatalysts for the degradation of organic pollutants. The performances of the tested materials are compared with the results of previous studies in Table 1.

OTC Photodegradation Mechanism

To investigate the photocatalytic mechanism of OTC degradation by CaAl LDH and CaAl LDH–MC in detail, radical trapping assays were conducted to identify the main reactive species involved in the photodegradation process. The results of these assays provide a solid basis for identifying the dominant degradation pathway as well as clarifying the contribution of each active species to the photocatalytic system.

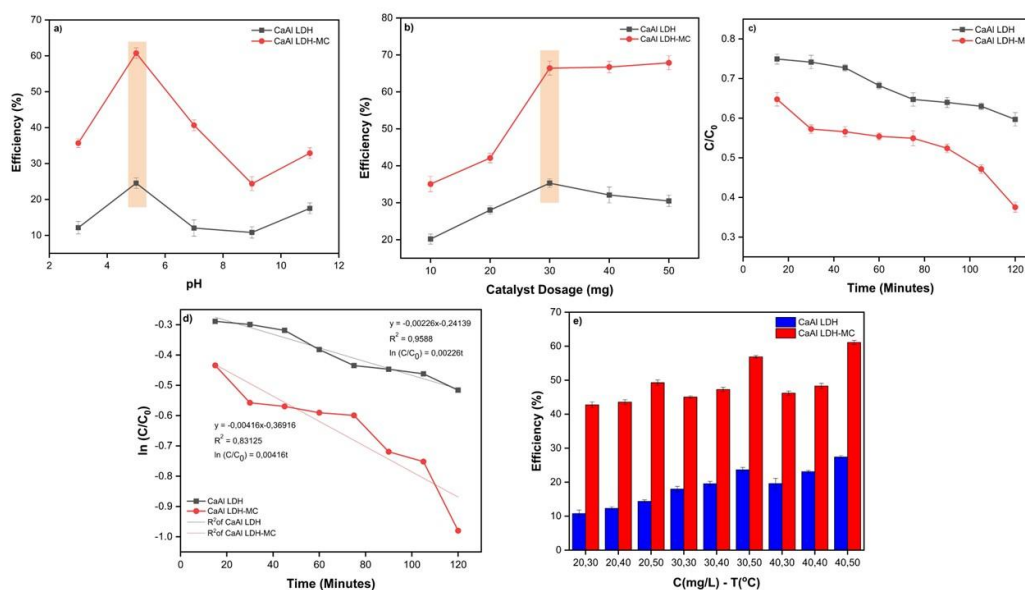


Figure 6. Effects of (a) pH, (b) the catalyst dosage, (c) the reaction time, (d) the Langmuir–Hinshelwood kinetic plot, and (e) the initial OTC concentration and temperature on OTC photodegradation

Table 1. Photocatalytic efficiencies of different catalysts toward OTC degradation

Material	pH	Catalyst (mg)	Time (min)	Initial Concentration (mg/L)	Temp (°C)	Degradation Efficiency (%)	Source
Zn ₃ In ₂ S	5	15	100	30	-	60.44	(Wang <i>et al.</i> , 2024b)
TiO ₂	-	100	60	10	30	56	(Wang <i>et al.</i> , 2023)
MIL-53(Fe)	5.7	200	60	300	-	54	(Dong <i>et al.</i> , 2025)
ZnO	4	1000	25	10	25	42.1	(Yildiz <i>et al.</i> , 2024)
GCN	6	10	180	10	25	40	(Chin <i>et al.</i> , 2023)
CaAl LDH	5	30	120	40	50	27.42	This work
CaAl LDH-MC	5	30	120	40	50	61.09	This work

As shown in Figure 7(a), a significant decrease in the degradation efficiency upon the addition of benzoquinone (BQ) and silver nitrate (SN) indicates that superoxide radicals ($\bullet\text{O}_2^-$) and photogenerated electrons (e^-) play crucial roles in the degradation process. A moderate decline in activity after the addition of isopropanol (IPA) suggests that hydroxyl radicals ($\bullet\text{OH}$) also contribute to OTC degradation, albeit to a lesser extent. Conversely, the negligible effect observed with triethanolamine (TEOA) confirms the minimal involvement of photogenerated holes (h^+) in this process.

Based on these findings, the proposed photocatalytic degradation mechanism of OTC by CaAl LDH-MC is illustrated in Figure 7(b). Upon UV irradiation, CaAl LDH-MC absorbs photons and promotes the transfer of electrons (e^-) from the valence band to the conduction band, generating electron-hole pairs. The excited electrons reduce the adsorbed oxygen (O_2) species on the catalyst surface to form reactive superoxide radicals ($\bullet\text{O}_2^-$), which are primarily responsible for initiating oxidative attacks on the aromatic rings and functional groups of OTC, ultimately producing less toxic and more biodegradable intermediates. In parallel, valence band holes (h^+) may oxidize water (H_2O) or hydroxide ions (OH^-) to form hydroxyl radicals ($\bullet\text{OH}$), which further contribute to the degradation process.

Accordingly, the overall photodegradation pathway can be represented by the following reactions:

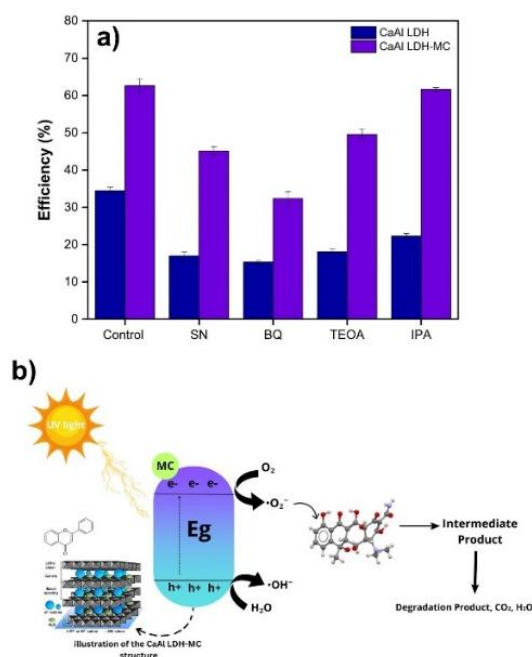
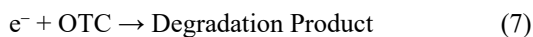
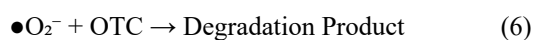
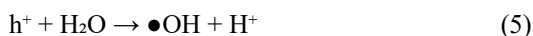
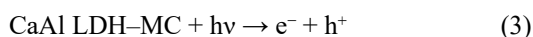


Figure 7. (a) Effect of various scavengers on the OTC degradation efficiency and (b) proposed photocatalytic mechanism of OTC degradation by CaAl LDH-MC under UV light irradiation

Reusability Study

The reusability assessment of photocatalysts under visible light irradiation is crucial for evaluating their structural stability and long-term applicability in environmental remediation. In this study, CaAl LDH and its modified counterpart, CaAl LDH-MC, underwent five successive OTC photodegradation cycles (Figure 8). After each cycle, the catalysts were cleaned using deionized water and ultrasonication to eliminate surface residues. A significant decline in the photocatalytic efficiency was observed for pristine CaAl LDH, dropping from 28% during the first cycle to

approximately 6% by the fifth cycle, which was likely due to the surface fouling by adsorbed OTC intermediates that blocked active sites and impeded mass transfer (Azadi *et al.*, 2024).

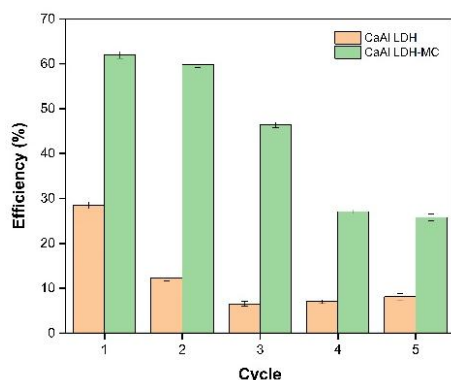


Figure 8. Photocatalyst reusability of CaAl LDH and CaAl LDH-MC over five cycles

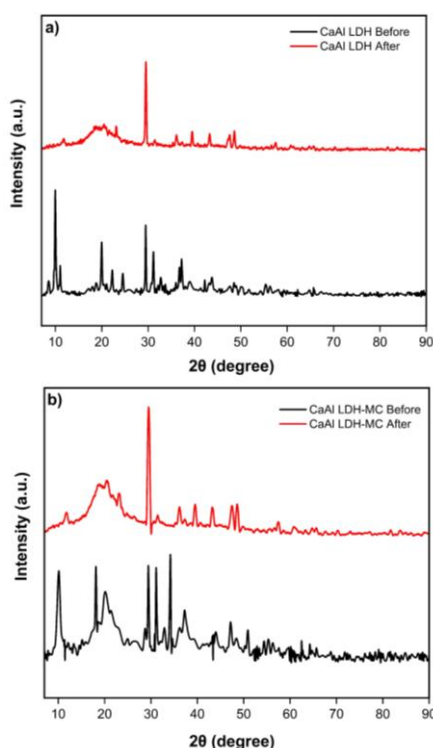


Figure 9. XRD patterns of (a) CaAl LDH and (b) CaAl LDH-MC obtained before and after regeneration

Conversely, CaAl LDH-MC exhibited remarkably enhanced stability, retaining consistent performance throughout the cycles. This effect is attributed to the presence of bioactive compounds

in the *Muntingia calabura* extract, which may enhance structural robustness, inhibit surface deactivation, and limit byproduct accumulation (Gizachew *et al.*, 2024). XRD structural analyses conducted before and after five cycles (Figure 9(a) and Figure (b)) revealed that CaAl LDH-MC exhibited only a slight decrease in crystallinity while maintaining a typical layered LDH structure. In contrast, CaAl LDH demonstrated more pronounced degradation of crystallinity characterized by a decrease in intensity and broadening of diffraction peaks. These findings indicate that modifications with natural extracts can improve the structural stability and reusability of photocatalytic materials.

Conclusions

In this study, CaAl LDH has been successfully modified using the *Muntingia calabura* fruit extract, as confirmed by the XRD, FTIR, UV-DRS, and SEM data. The addition of the extract plays a critical role in reducing the bandgap energy, increasing the visible light absorption, and producing a more uniform particle morphology. This study demonstrates that modifications with bioactive compounds significantly enhance the photodegradation efficiency of OTC by up to 66% under the optimal conditions while maintaining high performance over five reuse cycles. Such a natural material-based approach not only supports environmentally friendly synthesis processes but also produces efficient and economical photocatalysts. This work emphasizes the novelty of using biological compounds to improve the LDH performance and opens new avenues for future research studies on more complex waste treatment processes and other pollutants.

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