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Research Paper

Polyoxometalate-Assisted Layered Double Hydroxide for Facile Photocatalytic Methylene Blue and Malachite Green

Yulizah Hanifah[1*], Nur Ahmad[2]

[1]*National Research and Innovation Agency (BRIN), PUSPIPTEK, South Tangerang, 15331, Indonesia*
[2]*Research Center of Inorganic Materials and Coordination Complexes, Universitas Sriwijaya, Palembang, 30139, Indonesia*
***Corresponding author**: yuli065@brin.go.id*

Abstract
To increase the photodegradation activities of polyoxometalate, the co-precipitation approach has been used to prepare intercalated polyoxometalate compounds with ZnAl-LDH on methylene blue and malachite green dye. It is strongly advised to use the preparation catalyst LDH with polyoxometalate to create a successful method for anionic dye reduction. This study demonstrated the effectiveness environmentally method for intercalating ZnAl-LDH with polyoxometalate compound by employing methylene blu and malachite green dye as an organic pollutant. Additionally, the results showed that for pH = 7 for ZnAl-$SiW_{12}O_{40}$ on degraded malachite green, and the highest researching 94% on degradation methylene blue on ZnAl-$PW_{12}O_{40}$. Due to the rapid dissociation of the procion red reduction from the polyoxometalate photocatalytic activities, it was thought to have significant co-catalyst effects.

Keywords
Polyoxometalate, LDH, Photodgeradation, Methylene Blue, Malachite Green

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1. INTRODUCTION

Wastewater from dye-manufacturing and dye-consuming industries has long been a significant environmental issue. The dyes in these effluents decrease sunlight penetration and photosynthesis in aquatic ecosystems, while also raising the biochemical oxygen demand (Singh et al., 2003). Dyes are usually stable organic substances that are challenging to eliminate using biological treatment methods and often produce large amounts of wastewater containing complex synthetic dyes (Barciela et al., 2023). It is estimated that approximately 60-70% of these dyes are azo compounds, distinguished by their stable azo bonds ($-N=N^-$) connected to aromatic rings, which contribute to their persistence and potential risks to both ecosystems and human health, Nonetheless, alternative non-biological strategies, such as photocatalytic advanced oxidation processes, have shown promise in addressing these challenges can effectively eliminate them (Tseng et al., 2012). Photocatalysis of dyes entails generating highly reactive oxygen species (ROS), such as hydroxyl and superoxide radicals, which interact and bread down the dyes when exposed to a semiconductor and visible or ultraviolet (UV) light. Among different semiconductor oxides, TiO_2 and ZnS are commonly used for degrading organic pollutants because of their photoactivity, stability, and non-toxicity (Saefumillah et al., 2025). The most popular application of TiO_2 in photocatalytic degradation research in due to its low cost, alkali resistance to acid, non-toxicity, and photostability. Many elements have been doped on TiO_2 in recent years to increase its photochemical capacity (Feng et al., 2013). This could lower TiO_2 the bandgap increases element's absorption wavelength range into the visible range or improve the way the sun's light is uses but TiO_2 doped materials are frequently employed immediately (Nayak et al., 2025).

Polyoxometalate has the same character with TiO_2 commonly metal oxide. There exists a vast array of POM compositions and structural designs, which can be broadly classified into two primary classes: heteropoly anions and isopolyanions. The most commonly occurring kinds in the literature are heteropoly anions, such as the Keggin or well Dowson types. It is impossible to remove or chemically substitute element X (primary heteroatom) without endangering the anion degradation of the basic POM structure. However, removal of the metallic center can result in various structural alterations with consequents improved reactivity and mechanical qualities depending on reactional conditions, such as pH, temperature, or precursors (Gao et al., 2023). Because of their unique size and shape that resemble a metal-oxygen cluster structure, as well as several desirable properties that make them desirable for use in catalysis, biology, and magnetism, the class of metal-oxygen

cluster compounds known as polyoxometalates (POM), which are primarily based on V, Mo, and W ions in their highest oxidation states, are fascinating.

Malachite green (MG) triphenyl methane [$C_6H_5C(C_6H_4N(CH_3)_2)_2$]Cl is a cationic dark green dye, λmax = 617 nm, which is traditionally used as a dye. The structure of MG is given in wool, cotton, silk, jute, leather, paper, and certain fibers (Gessner and Mayer, 2000). MG renowned for its efficacy as both fungicide and parasiticide, has been utilized extensively in aquaculture and transportation to combat fungal infections in fish and extend the lifespan of fish suffering from scale damage. However, due to its classification as toxic triphenylmethane compound, MG carries potential risks of causing cancer and birth defects in humans, leading to its restriction or prohibition in several countries (Tian et al., 2011).

Similarly, methylene blue (MB), a thiazine dye with λmax = 664 nm, is one of the most widely used cationic dyes in textile dyeing, printing, paper, and leather industries (Ullah et al., 2017; Lobo et al., 2025). Although MB is employed in medicine as an antiseptic and diagnostic agent, excessive release of MB into water bodies poses environmental and health hazards, including eye burns, nausea, and methemoglobinemia upon prolonged exposure. Like MG, MB can strongly interact with negatively charged surfaces, making it persistent in the aquatic environment.

Currently, medication is absent on the market can effectively treat water mold as swiftly as MG. Despite concerns, MG remains unrestricted, particularly during transportation (Hu et al., 2021). MG and MB dye, as a cationic dye, can readily interacts with surfaces that carry a negative charge. It is essential to develop a method that is both environmentally friendly and effectively for breaking down methylene blue into non-toxic byproduct before it is disposed or used. Numerous approaches have been documented in the literature, such as photodegradation with catalysts (Asadzadeh-Khaneghah et al., 2021), oxidative degradation using nanoparticles, adsorption (Lobo et al., 2025; Patra et al., 2025) and ultrasound degradation (Bi et al., 2022).

Layered double hydroxides (LDHs) are a class of two-dimensional anionic clays with the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})^{x}/_{n}\cdot mH_2O$, where M^{2+} and M^{3+} represent divalent and trivalent metal cations, and A^{n-} denotes interlayer anions (Nayak et al., 2025). LDHs are attractive for photocatalytic and environmental applications due to their tunable metal composition, large surface area, and anion-exchange capacity (Xu et al., 2021) However, their photocatalytic efficiency is often restricted by several shortcomings, including rapid electron–hole recombination, relatively low conductivity, and limited light absorption. To address these limitations, intercalation of LDHs with functional guest species has been widely explored. Among these, polyoxometalates (POMs) are particularly promising due to their strong redox activity, excellent electron-accepting ability, and structural stability. Intercalating POMs into LDHs not only enhances charge separation and transfer but also broadens light-harvesting capability, thereby improving overall photocatalytic performance. Therefore, in this study, LDH–POM composites were developed to overcome the intrinsic drawbacks of pristine LDHs and to achieve enhanced photocatalytic activity.

Although intercalation of polyoxometalates into LDH hosts has been demonstrated to enhance catalytic and photocatalytic performance by improving charge separation and providing redox-active centers, recent reviews and original studies indicate that important challenges remain—namely the controlled assembly of POM pillars within LDH galleries, tuning of interfacial electronic coupling for efficient charge transfer, and comprehensive demonstration of improved photocatalytic metrics under conditions relevant to target applications. Recent efforts have produced POM-pillared LDHs with improved activity for CO_2 reduction and water oxidation (Zhao et al., 2018), and modular POM–LDH membranes via charge-driven self-assembly (Zhang et al., 2019) but these works also highlight the need for better control over interlayer architecture and systematic correlation between structure and photoelectronic performance. To address these gaps, the present study develops a (specify: e.g., reconstruction/anion-exchange/pillaring) strategy to intercalate [name/type of POM, e.g., Keggin-type $SiW_{12}O_{40}{}^{4-}$] into (M^{2+}/M^{3+}) LDH, and couples structural, spectroscopic, and photoelectrochemical characterization to demonstrate enhanced charge separation and photocatalytic activity compared to pristine LDH. This approach provides improved control of POM spatial arrangement and electronic interaction with the host layers, providing a clear advance over previously reported POM–LDH systems.

We created two novel polyoxometalate-intercalated ZnAlFe layered double hydroxide (POM-LDH) was synthesized throu gh water ion exchange of a precursor ZnAlFe LDH with polyoxometalate anions [P_2W_{17}] (Xu et al., 2021; Liu et al., 2025). The motivation on developing photocatalysis LDH materials looks from some success literature on degradation dye. The catalyst as degradation some cationic dye used layered material and polyoxometalate; methylene blue on Ni/Mg LDH (Hanifah et al., 2022) Intercalated NiAl-POM on degradation malachite green (Hanifah et al., 2023c); polyoxometalate for degradation malachite green (Hanifah et al., 2023b) ; procion red (Hanifah et al., 2023a). The ZnAlFe POM-LDH's adsorptive capability and photocatalytic activity. Previous works have demonstrated the effective breakdown and adsorptive removal of organic dyes ZnAl-LDH in aqueous solution using photocatalysis (Bi et al., 2022, 2011; Parida and Mohapatra, 2012).

In this work, we prepared material ZnAl-LDH intercalated with polyoxometalate (POM) by aqueous ion exchange of LDH as a precursor with two polyoxometalate anions $K_3[\alpha$-$PW_{12}O_{40}]$ (KPW) and $K_4[\alpha$-$SiW_{12}O_{40}]$ (KSiW). The photocatalytic activity of ZnAl-POM was assessed using the removal of cationic dye from aqueous solutions as a model reaction. Alongside characterizing the two synthesized POM-LDH materials, their photocatalytic performance was examined both theoretically and experimentally. Previous studies have demon-

strated that ZnAl-LDH is effective for degrading and adsorbing of dyes in aqueous solutions represent crucial steps towards sustainable water treatment technologies. It serves as beneficial catalyst support material for potential photocatalytic applications, owing to the high negative charge of POM that enhances its capability to degrade anionic dyes. Particularly LDH composite which plays a remarkable role in the reduction and remediation of environmental contaminants, has drawn a lot of attention to the photodegradation of organic pollutants in wastewater. For this reason, it has been named as one of the most hopeful materials photocatalysts.

2. EXPERIMENTAL SECTION

2.1 Materials

The substances employed in creating the samples were: sodium phosphate (Na_3PO_4), sodium carbonate (Na_2CO_3), zinc nitrate hexahydrate ($Zn(NO_3)_2$, sodium tungstate (Na_2WO_4), sodium hydroxide (NaOH), aluminum nitrate hexahydrate $Al(NO_3)_3$ and hydrogen chloride as a combined agent during the breakdown of organic dyes in water-based solutions. Chemicals used for analysis were sourced from reputable supplier such as Sigma Aldrich and Merck to ensure high quality and reliability. The synthetic dyes, methylene blue has a maximum absorbance of 665 nm and malachite green (λmax = 617 nm) were used as model cationic dye. A miniflux-6000 Rigaku XRD diffractometer was used radiation source to measure the materials crystallinity structure analysis was performed CuKα using a 30 kV voltage, 10 mA current, and a 2θ range spanning from 10 to 90 to investigate the crystallographic properties pf the materials. An analytical instrument known as the Shimadzu FTIR ALPHA Bruker (Platinum-ATR) by the KBr method and sample was scanned at 400-4000 cm^{-1} that used to analyze the molecular structure of the compounds. The UV-Vis Biobased BK-UV 1800 PC spectrophotometer was employed was employed to quality the extent of degradation thought absorbance measurements. SEM examination using the FEI Quanta 650 with an accelerating voltage of 30 V was uses to take the SEM ZnAl-LDH and ZnAl-composite was conducted to study the surface of the material.

2.2 Synthesis of Layered Double Hydroxide

The precursor ZnAl-LDH was synthesized via a coprecipitation technique [40] to promote the formation of the layered double hydroxide (LDH) phase. A mixed solution was prepared by dissolving 0.5 M $Zn(NO_3)_2{\cdot}6H_2O$ and 0.25 M $Al(NO_3)_3{\cdot}9H_2O$ in 100 mL of purified water, maintaining a molar ratio of Zn:Al = 2:1. Separately, 1.5 M $NaNO_3$ was introduced dropwise into the salt solution over a period of 2 h under vigorous stirring at room temperature. The pH was adjusted and maintained at 8.5 by the addition of 2 M NaOH solution. The resulting suspension was subsequently aged at 85°C for 18 h. The precipitate obtained was thoroughly washed with deionized water until a neutral pH was achieved, followed by vacuum drying at 60°C for 12 h to yield the ZnAl-LDH powder.

2.3 Synthesis of Polyoxometalate $K_3[\alpha\text{-}PW_{12}O_{40}]$ (KPW)

Keggin $K_3[\alpha\text{-}PW_{12}O_{40}]$, a polyoxometalate molecule, modifies LDH. After adding 2.4 g $Na_2WO_4.2H_2O$ in 1000 mL of acidic solution (which contained 100 mL of H_3PO_4 and 900 mL deionized water), the mixture attained a boiling point. 10 cc of HCl was added right away, and the mixture was allowed to cool. The insoluble was extracted from solution by adding 50 mL of diethyl ether and stirring for 10 minutes after the mixture had cooled. The hazy organic phase eventually gathered and dried causing the pure KPW to precipitate.

2.4 Composite LDH-Polyoxometalate

A polyoxometalate molecule called Keggin $K_4[\alpha\text{-}PW_{12}O_{40}]$ and $K_3[\alpha\text{-}PW_{12}O_{40}]$ is added to LDH. To prepare the composite, 2 g of LDH and 1 g pf polyoxometalate were combined with 1 mL of sodium hydroxide solution. The suspensions were quickly made while N_2 gas was present for two days. After that, the suspension was washed and allowed to dry at 80°C for 12 hours.

2.5 Photocatalytic Performance

The photocatalytic performance of the samples was first evaluated through adsorption-desorption equilibrium by dispersing the catalyst in dye solutions (20 mg/L methylene blue, MB, or 20 mg/L malachite green, MG) under dark conditions with continuous stirring for 30 minutes. Photodegradation experiments were then conducted by varying the catalyst dosage (0.02–0.10 g), contact time (10–120 minutes), and solution pH (3–11). The reactions were carried out under UV irradiation (λ = 365 nm), and aliquots of the suspensions were periodically withdrawn, centrifuged, and analyzed using a UV–Vis spectrophotometer at the respective maximum absorption wavelengths (λmax = 665 nm for MB and λmax = 617 nm for MG) to determine the residual dye concentration and calculate the degradation efficiency.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction analysis (XRD)

The XRD patterns of Zn/Al-LDH, POM (PW12O40 and $SiW_{12}O_{40}$), and their composites are presented in Figure 1. All samples were analyzed using CuKα radiation (λ = 1.54056 Å) over a 2θ range from 20 to 80 degrees. The pristine Zn/Al-LDH shows characteristic diffraction peaks at 2θ = 11.6°, 23.3°, 34.6°, 39.2°, 46.8°, and 60.9°, corresponding to the (003), (006), (012), (015), (018), and (110) planes, respectively, which are typical of layered double hydroxides with a hydrotalcite-like structure (Lesbani et al., 2025). The POMs exhibit distinct peaks in the range of 7–10° and 25–30°, which are attributed to the preserved Keggin-type structure of $PW_{12}O_{40}$ and $SiW_{12}O_{40}$ (Hanifah et al., 2023c). The peak of composite ZnAl-$SiW_{12}O_{40}$ was showed at 8.61, 25.27, 34.96, and 66.34, respectively which better than ZnAl-$PW_{12}O_{40}$. In the composite materials, the diffraction peaks of both Zn/Al-LDH and POM are observed, confirming the successful incorporation of POM into the LDH layers. The slight reduction in peak

intensity and broadening in the composite patterns indicate partial structural distortion, which suggests strong interaction between the LDH matrix and the POM units. Importantly, the characteristic reflections of the LDH remain visible, demonstrating that the layered structure is retained after composite formation. These results confirm the successful synthesis of Zn/Al-LDH/POM composites with integrated structural features from both components.

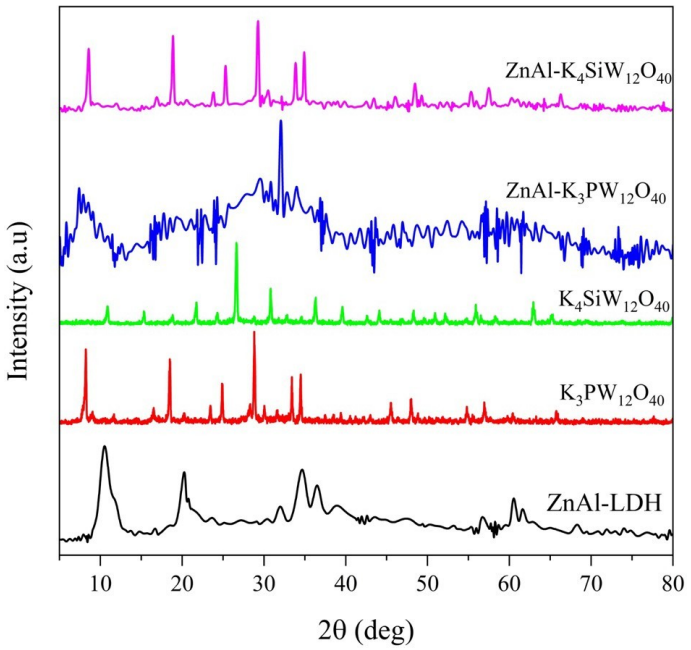

Figure 1. Diffractogram of ZnAl-LDH, $K_3PW_{12}O_{40}$, $K_4SiW_{12}O_{40}$, ZnAl-$PW_{12}O_{40}$, and ZnAl-$SiW_{12}O_{40}$

3.2 FTIR Analysis.

The infrared spectra of pristine LDH, LDH combined with polyoxometalate, and the pure polyoxometalate compound provided valuable information about the surface functional groups of the synthesized materials. All spectra were recorded in the range of 400–4000 cm^{-1}. The ZnAl-LDH and its composites displayed characteristic absorption bands, including a broad band at 3448 cm^{-1} corresponding to the O−H stretching vibration of interlayer water molecules, and a band at 1635 cm^{-1} associated with the bending vibration of H_2O. A strong absorption band was observed at 1381 cm^{-1}, which is attributed to the stretching vibration of interlayer CO_3^{2-}. Although nitrate precursors were used in the synthesis, carbonate is commonly detected in LDH materials because CO_3^{2-} anions have a higher affinity for interlayer sites and readily replace other anions during the coprecipitation process or subsequent exposure to atmospheric CO_2. This behavior has been widely reported in the literature, confirming the predominance of carbonate in the interlayer space.

In the lower region, bands between 400–800 cm^{-1} were associated with metal–oxygen and oxygen–metal–oxygen vibrations within the brucite-like layers, while a distinct band at 553 cm^{-1} was correlated with Ni−O stretching vibrations (Adim et al., 2025). The FTIR spectrum of the polyoxometalate exhibited characteristic bands at 1020 cm^{-1} (W−O), 979 cm^{-1} (W=O), and 925–789 cm^{-1} (W–O–W), consistent with previous reports (Hanifah et al., 2023a). In this study, $K_3PW_{12}O_{40}$ showed absorption bands at 976, 884, 740, and 594 cm^{-1}, while $K_4SiW_{12}O_{40}$ displayed peaks at 958, 865, 787, and 714 cm^{-1}. Following intercalation into the LDH structure, the composite spectrum exhibited altered absorption bands within the 976–594 cm^{-1} range, confirming successful modification of the LDH by polyoxometalate inclusion. Figure 2 depicts the preservation of the LDH structure supported with polyoxometalate.

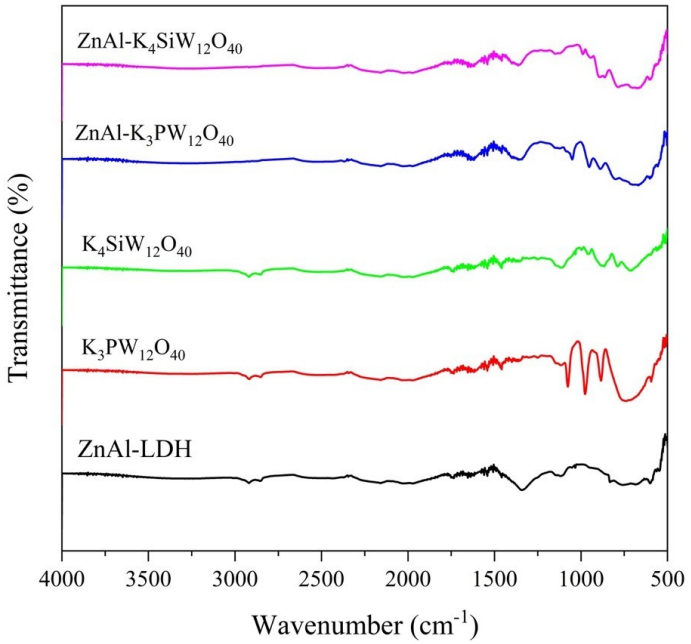

Figure 2. FTIR spectra of ZnAl-LDH, $K_3PW_{12}O_{40}$, $K_4SiW_{12}O_{40}$, ZnAl-$PW_{12}O_{40}$, and ZnAl-$SiW_{12}O_{40}$

3.3 SEM Analysis

SEM analysis illustrated the morphology of ZnAl-LDH in its LDH pristine form and in both LDH composite ZnAl-$PW_{12}O_{40}$ and ZnAl-$SiW_{12}O_{40}$ revealing aggregate pore structures, with ZnAl-polyoxometalate composite displaying distinct polyoxometalate distribution characterized by smaller particle sizes compared to pure ZnAl-LDH. The composite materials exhibited heterogeneous shapes worth notable aggregate formations. Figure 3 both samples prepare initially exhibited a characteristic lamellar structure of LDH, but ZnAl-LDH-POM displayed noticeable agglomeration compared to the precursor (Wang et al., 2021). It includes SEM images and particle size analysis using ImageJ, revealing mesoporous structure by particle sizes ranging were showed from 2 to 5 nm.

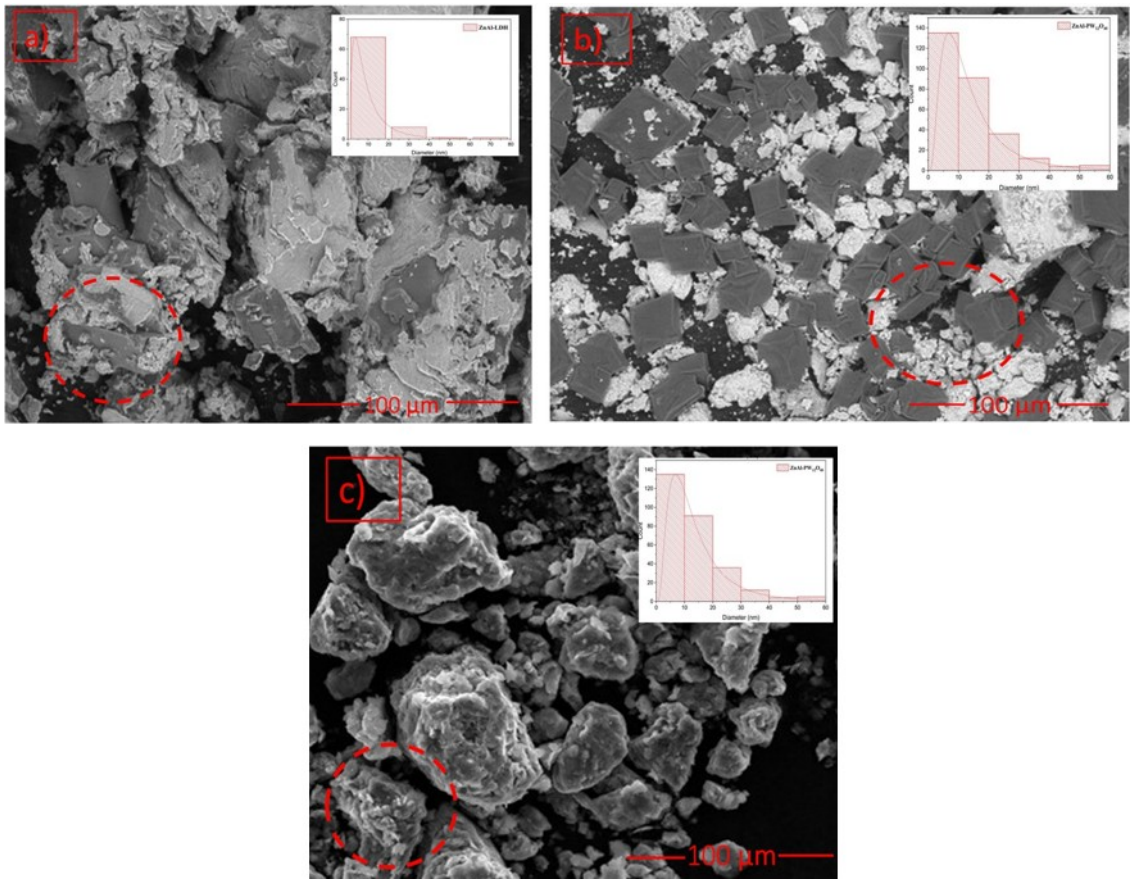

Figure 3. SEM Analysis of ZnAl-LDH, ZnAl-$K_4SiW_{12}O_{40}$, and ZnAl-$K_3PW_{12}O_{40}$

Table 1. The Percentage of Methylene Blue Degradation

Catalyst	% Degradation Methylene Blue	Time (minute)	Reference
Nb_2O_5/ZnAl-LDH	85	-	(Hanifah et al., 2023a)
CoMgAl-borate LDO	86	-	(Wang et al., 2021)
ZNCQD	96	90	(Bhuyan and Ahmaruzzaman, 2024)
MgZnCr-TiO_2	90	-	(Ma et al., 2017)
ZrCuFe-LDH/rGO	95	75	(Srivastava, 2024)
ZnCoFe/MgAl-LDH	74	3 h	(Abdel-Hady et al., 2022)
δ-Fe_2O_3/MgAl-LDH	86	4 h	(Srivastava, 2024)
ZnAl-[$PW_{12}O_{40}$]	92	2 h	In this study
ZnAl-[$SiW_{12}O_{40}$]	94a	2 h	In this study
MgAl-[$PW_{12}O_{40}$]	73	2 h	(Xu et al., 2021)
MgAl-[$SiW_{12}O_{40}$]	84	2 h	(Xu et al., 2021)
NiAl-[$PW_{12}O_{40}$]	82	2 h	(Bi et al., 2022)
NiAl-[$SiW_{12}O_{40}$]	86	2 h	(Bi et al., 2022)

3.4 UV-DRS Analysis

The UV-DRS analysis of LDH materials and their composites was carried out to determine their band gap energies, which are crucial parameters in evaluating photocatalytic activity for the degradation of organic pollutants. The results revealed that the band gap energy of ZnAl-LDH composites was lower (3.2 eV) compared to ZnAl-$PW_{12}O_{40}$ (3.4 eV) and ZnAl-$SiW_{12}O_{40}$ (3.7 eV) composites. Although ZnAl–LDH showed a smaller band gap than the ZnAl–POM composites, the composites exhibited enhanced photocatalytic degradation performance, mainly due to more efficient charge separation and the synergistic effect between LDH and POM. A smaller band gap implies

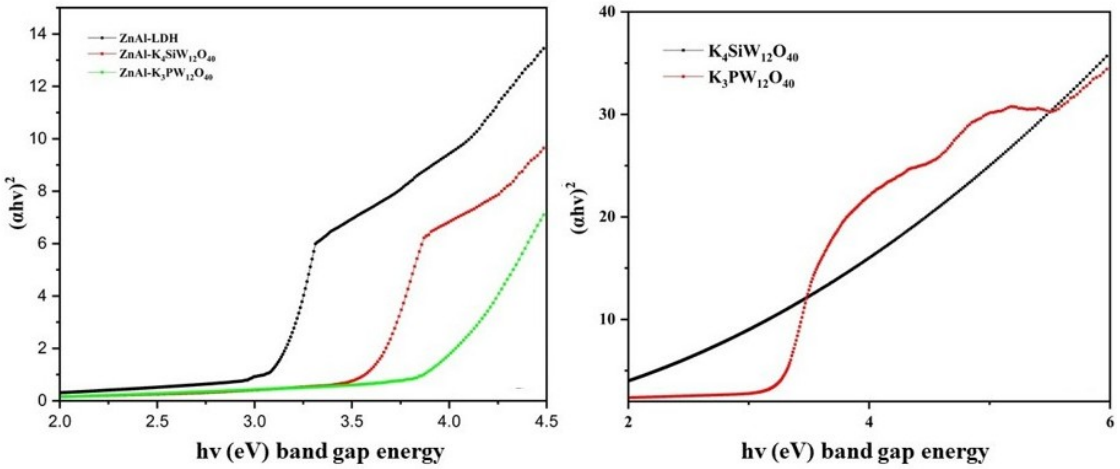

Figure 4. UV-DRS Analysis of LDH Composite and Polyoxometalate

Table 2. The Percentage of Malachite Green Degradation

Catalyst	% Degradation Malachite Green	Time (minute)	Reference
ZNCQD	99	-	(Bhuyan and Ahmaruzzaman, 2024)
Al-Li/Th-LDH@CNT	98	45	(Liao et al., 2017)
NiAl-LDH/polyoxometalate	89	-	(Bi et al., 2022)
ZnAl-gallate-LDH/polystsrene nanofibers	95	35	(Rabiee et al., 2020)
Magnetic ZnAl-LDH	-	6 h	(Rohmatullaili et al., 2024)
ZnAl-[$PW_{12}O_{40}$]	73	2 h	In this study
ZnAl-[$SiW_{12}O_{40}$]	74	2 h	In this study

enhanced visible-light absorption, which facilitates the generation of more hydroxyl (·OH) radicals, thereby improving the photodegradation efficiency of organic compounds (Lesbani et al., 2025). The band gap values derived from the Tauc plot are presented in Figure 4.

In addition, the photocatalytic mechanism can be explained as follows: when photoexcited electrons (e^-) in the conduction band (CB) react with adsorbed methylene blue (MB) molecules, MB radical anions are formed, leading to the degradation of MB. Meanwhile, the photogenerated holes (h^+) in the valence band (VB) can directly oxidize adsorbed MB molecules into MB radical cations, which subsequently undergo further transformation into mineralized end products. Moreover, when water molecules interact with the VB holes, ·OH radicals are produced, which act as powerful oxidizing species to accelerate dye degradation. The overall mechanism can be summarized by the following reactions:

$$\mathrm{ZnAl-LDH/POM} + h\nu \longrightarrow e^-_{CB} + h^+_{VB} \quad (1)$$

$$h^+ + H_2O \longrightarrow \cdot OH + H^+ \quad (2)$$

$$O_2 + 2H_2O + 2e^- \longrightarrow H_2O_2 + 2OH^- \quad (3)$$

$$H_2O_2 + e^- \longrightarrow \cdot OH + HO^- \quad (4)$$

$$H^+ + OH^- \longrightarrow H_2O \quad (5)$$

$$\cdot OH + \mathrm{dye} \longrightarrow MB^{\bullet+}/MG^{\bullet-} \longrightarrow \text{final product} \quad (6)$$

$$H^+ + \mathrm{MB/MG} \longrightarrow MB^{\bullet+}/MG^{\bullet-} \longrightarrow \text{final product} \quad (7)$$

3.5 Impact of Reaction Duration

The ideal reaction period for both the original material and composite was found to be 2 hours, during which methylene blue dye conversion was achieved. Extending the reaction time beyond this period showed diminishing return in terms of increased methylene blue degradation efficiency. The composite material achieved its highest conversion rate of 80% under these conditions, demonstrating that further prolonging rate of 80% under these conditions, demonstrating that further prolonging the reaction time does not significantly enhance the dye removal process. The percentage degradation of methylene blue for ZnAl-LDH, ZnAl-[$PW_{12}O_{40}$], ZnAl-[$SiW_{12}O_{40}$] were exceeded 74%, 73%, and 66% respectively. The degradation of malachite green for ZnAl-LDH, ZnAl-[$PW_{12}O_{40}$], ZnAl-[$SiW_{12}O_{40}$] were 83%, 93%, and 94% respectively. The effect of reaction time shown in Figure 5.

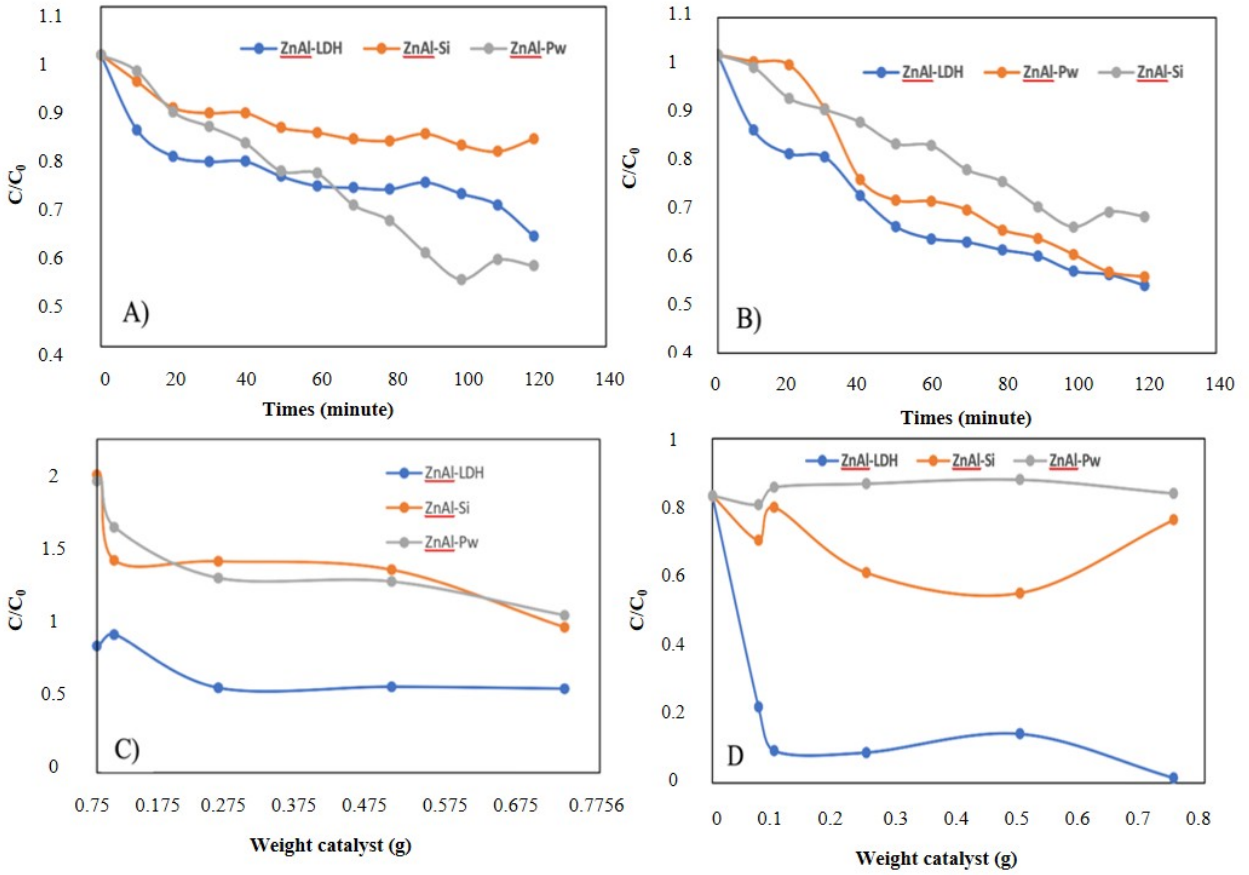

Figure 5. Effect Of A) Contact Time on the Degradation Malachite Green, B) Methylene Blue, and C) Weight Catalyst on Degradation Malachite Green, D) Methylene Blue

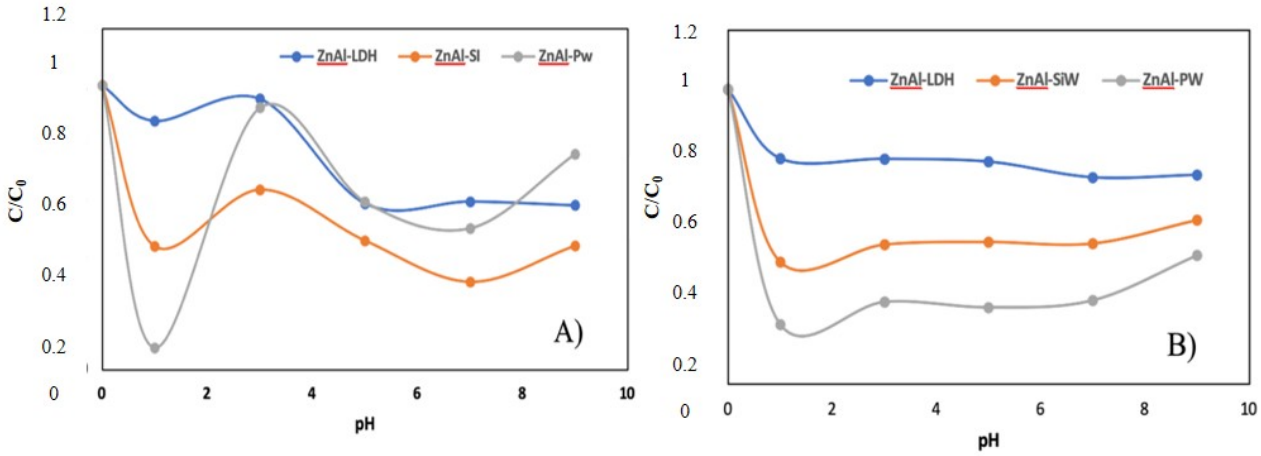

Figure 6. Effect of pH Degradation on Malachite Green (A) and Methylene Blue (B)

3.6 Impact of Catalyst Mass

Reported by Hanifah et al. (2023b) most effective degraded of malachite green using varying catalyst weights. In this study, a catalyst weight of 0.1 g was adequate for catalyzing methylene blue (initially at 20 ppm) using pristine ZnAl-LDH. Material composite, there are ZnAl-$PW_{12}O_{40}$, ZnAl-$SiW_{12}O_{40}$ were found 0.75 g all catalyst is effectively conversion of methylene blue as shown in Figure 5. The same variation on degradation malachite green shown in Figure 5. In this study, employing a catalyst weight below this threshold (0.02 g), is not much

enough to degrade, the maximum percentage degradation of methylene blue occurred at catalyst weights exceeding the specified range (e.g., 0.04 to 0.08). it may of using the highest amount of the material may result in achieving the highest percentage of degradation. It is because dosage used the more material that can bonded and degraded methylene blue than malachite green. However, the catalyst weight must be precisely calibrated. this study aligns the catalyst systems with experimental conditions. Figure 5 illustrates the influence of different catalyst masses on the degradation of methylene blue. The value %degradation for pristine material and composite material are quite similar.

3.7 Effect of pH

ZnAl-LDH pH 7, ZnAl-$SiW_{12}O_{40}$ and ZnAl-$PW_{12}O_{40}$ both are on pH 1 for degradation of methylene and degradation of malachite green are ZnAl-LDH pH 7, ZnAl-$SiW_{12}O_{40}$ pH 1 and ZnAl-$PW_{12}O_{40}$. The degradation of methylene blue through catalytic processes was investigated across varying solution pH levels (1, 3, 5, 7, 9, and 11). pH adjustments were made using NaOH and HCl prior to irradiation. It was observed in Figure 6 that the photodegradation characteristics vary among each material. LDH material which is ZnAl-LDH, ZnAl-$SiW_{12}O_{40}$ and ZnAl-$PW_{12}O_{40}$. ZnAl-LDH demonstrated the optimal pH that was obtained was at pH 7 respectively. The conditions used in the experiment, the optimal pH for LDH material was found to be pH 7, consistent with finding from other studies. However, the behavior of the composite material differed significantly, possibly attributed to the presence of polyoxometalate post-intercalation. This process of modification improves the formation of positively charged species, aiding in anionic interactions. There is a under UV irradiation, the photocatalytic reaction with the LDH-POM catalyst generates a positive charge hole (hvb+), and electrons (ecb) H_2O will generate a hydroxyl radical (·OH), capable of degrade methylene blue simpler intermediates. The composite materials, such as ZnAl-$PW_{12}O_{40}$. Exhibit optimal degradation of malachite green at pH 7, ZnAl-[$SiW_{12}O_{40}$] also shows optimal performance at pH 3. ZnAl-[$PW_{12}O_{40}$] at pH 1 and ZnAl-[$SiW_{12}O_{40}$] at pH 1 on degraded methylene blue. Figure 6 depict how pH influences the degradation of malachite green and methylene blue by catalysts, both LDH in printine and composite forms. Optimal degradation occurred at lower pH levels, at pH levels below 7, effective generating of OH· radicals occur, facilitating dye degradation and initiating the photodecomposition of polyoxometalate into ions.

4. CONCLUSIONS

The synthesis of intercalation resulted in the formation of a heterogeneous aggregate. By monitoring factors like pH, catalyst mass, degradation duration, researchers assessed. Degradation properties of pristine LDH and LDH composite materials. The ZnAl-$SiW_{12}O_{40}$ material exhibited the highest degradation percentage, achieving up to 94% degradation pH methylene blue compared to other composite material. The degradation of malachite green of ZnAl-$SiW_{12}O_{40}$ reaching to 74% on pH 7. The catalyst dosage used was 0.75 mg and optimum pH of ZnAl-$SiW_{12}O_{40}$was found pH 1. Nevertheless, its performance was markedly superior to that of pure LDH. The results indicate that the LDH composite has a strong photocatalytic activity for reducing methylene blue.

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REFERENCES

Abdel-Hady, E., R. Mahmoud, S. Hafez, and H. Mohamed (2022). Hierarchical Ternary ZnCoFe Layered Double Hydroxide As Efficient Adsorbent and Catalyst for Methanol Electrooxidation. *Journal of Materials Research and Technology*, **17**; 1922–1941

Adim, S., M. Eddahmi, A. Boussetta, M. Mansori, A. Essoumhi, and L. Bouissane (2025). Green Four-Component Reaction and Dye Adsorption Studies of New ZnCoAl-LDH and ZnCoCr-LDH Materials. *Journal of Organometallic Chemistry*, **1036**; 123719

Asadzadeh-Khaneghah, S., A. Habibi-Yangjeh, D. Seifzadeh, H. Chand, and V. Krishnan (2021). Visible-Light-Activated g- C_3N_4 Nanosheet/Carbon Dot/FeOCl Nanocomposites: Photodegradation of Dye Pollutants and Tetracycline Hydrochloride. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **617**; 126424

Barciela, P., A. Perez-Vazquez, and M. A. Prieto (2023). Azo Dyes in the Food Industry: Features, Classification, Toxicity, Alternatives, and Regulation. *Food and Chemical Toxicology*, **178**; 113935

Bhuyan, A. and M. Ahmaruzzaman (2024). Ultrasonic-Assisted Synthesis of Highly Efficient and Robust Metal Oxide QDs Immobilized-MOF-5/Ni-Co-LDH Photocatalyst for Sunlight-Mediated Degradation of Multiple Toxic Dyes. *Journal of Alloys and Compounds*, **972**

Bi, B., L. Xu, B. Xu, and X. Liu (2011). Heteropoly Blue-Intercalated Layered Double Hydroxides for Cationic Dye Removal From Aqueous Media. *Applied Clay Science*, **54**; 242–247

Bi, Y. G., Y. H. Zheng, L. Tang, J. Guo, and S. Q. Zhou (2022). Optimization of Process Parameters for Enhanced Degradation of Methylene Blue by Trough Ultrasonic. In *Journal of Physics: Conference Series*, volume 2152. IOP Publishing Ltd, page 012027

Feng, N., Q. Wang, A. Zheng, Z. Zhang, J. Fan, S. B. Liu, J. P. Amoureux, and F. Deng (2013). Understanding the High Photocatalytic Activity of (B, Ag)-Codoped TiO_2 Under Solar-Light Irradiation With XPS, Solid-State NMR, and

DFT Calculations. *Journal of the American Chemical Society*, **135**; 1607–1616

Gao, Y., C. M. Granadeiro, L. Cunha-Silva, J. Zhao, and S. S. Balula (2023). Peroxomolybdate@MOFs as Effective Catalysts for Oxidative Desulfurization of Fuels: Correlation Between MOF Structure and Catalytic Activity. *Catalysis Science & Technology*, **13**; 4785–4801

Gessner, T. and U. Mayer (2000). Triarylmethane and Diarylmethane Dyes. In *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley

Hanifah, Y., R. Mohadi, Mardiyanto, N. Ahmad, Suheryanto, and A. Lesbani (2023a). Photocatalytic of Anionic Dyes on Congo Red With M2+/Al (M2+ = Ni, Mg, and Zn) Layered Double Hydroxide Intercalated Polyoxometalate. *Communications in Science and Technology*, **8**; 43–49

Hanifah, Y., R. Mohadi, Mardiyanto, and A. Lesbani (2023b). Polyoxometalate Intercalated Layered Double Hydroxide for Degradation of Procion Red. *Ecological Engineering and Environmental Technology*, **24**; 109–116

Hanifah, Y., R. Mohadi, M. Mardiyanto, and A. Lesbani (2022). Photocatalytic Degradation of Malachite Green by NiAl-LDH Intercalated Polyoxometalate Compound. *Bulletin of Chemical Reaction Engineering and Catalysis*, **17**; 627–637

Hanifah, Y., R. Mohadi, M. Mardiyanto, and A. Lesbani (2023c). Polyoxometalate Intercalated MgAl-Layered Double Hydroxide for Degradation of Malachite Green. *Ecological Engineering and Environmental Technology*, **24**; 109–119

Hu, Q., Y. Cui, L. Zhang, M. Qian, L. Xiao, M. Yang, Z. Q. Yang, S. Rao, X. Gong, and J. Han (2021). An Ultrasensitive Analytical Strategy for Malachite Green Determination in Fish Samples Based on Bright Orange-Emissive Carbon Dots. *Journal of Food Composition and Analysis*, **102**; 104032

Lesbani, A., N. Ahmad, S. Wibiyan, A. Wijaya, Amri, Y. Hanifah, I. Royani, and R. Mohadi (2025). Improving Congo Red Dye Removal by Modification of Layered Double Hydroxide With Microalgae and Macroalgae: Characterization and Parametric Optimation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **706**; 135770

Liao, H., Y. Jia, L. Wang, Q. Yin, J. Han, X. Sun, and M. Wei (2017). Size Effect of Layered Double Hydroxide Platelets on the Crystallization Behavior of Isotactic Polypropylene. *ACS Omega*, **2**; 4253–4260

Liu, X., Y. Che, J. Liu, L. Liu, X. Wu, Z. Fan, Y. Deng, X. An, and X. Wu (2025). NH3-SCO Performance-Boosting for Ag-Based Catalysts at Low Temperature: Insight Into LDHs-Derived MgAl-LDO With Low Ag Loading. *Applied Catalysis B: Environmental*, **366**; 125031

Lobo, W. V., L. K. C. de Souza, V. Kumar, and F. A. de Freitas (2025). Eco-Friendly Adsorption of Methylene Blue and Remazol Brilliant Blue R From Effluents Using Chemically Modified Açaí Seeds. *Surfaces and Interfaces*; 106970

Ma, C., F. Wang, C. Zhang, Z. Yu, J. Wei, Z. Yang, Y. Li, Z. Li, M. Zhu, L. Shen, and G. Zeng (2017). Photocatalytic Decomposition of Congo Red Under Visible Light Irradiation Using MgZnCr-TiO2 Layered Double Hydroxide. *Chemosphere*, **168**; 80–90

Nayak, S. R., B. B. V. Sailaja, S. R. Tirukkovalluri, S. S. Singupilla, S. C. Jikamo, Raffiunisa, and N. R. Kadiyala (2025). Visible-Light-Driven Fe-Doped TiO_2@WO_3 Heterostructure Nanocomposites for Photocatalytic Degradation of Binary Dyes and Electrochemical Detection of Malathion. *Inorganic Chemistry Communications*, **180**; 114971

Parida, K. M. and L. Mohapatra (2012). Carbonate Intercalated Zn/Fe Layered Double Hydroxide: A Novel Photocatalyst for the Enhanced Photodegradation of Azo Dyes. *Chemical Engineering Journal*, **179**; 131–139

Patra, P., N. Chakraborty, G. R. Kiran, and S. G. Acharyya (2025). Remarkable Adsorption of Methylene Blue at Neutral pH Using Novel Freeze-Dried Hydrophilic Silica TEOS Cryogel. *Surfaces and Interfaces*; 107080

Rabiee, N., M. Bagherzadeh, A. Ghadiri, G. Salehi, Y. Fatahi, and R. Dinarvand (2020). ZnAl Nano Layered Double Hydroxides for Dual Functional CRISPR/Cas9 Delivery and Enhanced Green Fluorescence Protein Biosensor. *Scientific Reports*, **10**

Rohmatullaili, N. Ahmad, D. Erviana, Zultriana, D. Savira, R. Mohadi, and A. Lesbani (2024). ZnAl LDH-Based Derivative Materials As Photocatalysts: Synthesis, Characterization, and Catalytic Performance in Tetracycline Degradation. *Science and Technology Indonesia*, **9**; 457–469

Saefumillah, A., D. O. B. Apriandanu, R. Ramadhan, R. D. Fitria, Y. Yulizar, A. Shofiyani, W. Rahmalia, and A. H. Alimuddin (2025). Photocatalytic Degradation of Methylene Blue: Unraveling Structure-Activity Relationships and Performance Evaluation of Sol-Gel Synthesized TiO_2 Versus Commercial TiO_2 P25. *Journal of Molecular Structure*; 143277

Singh, K. P., D. Mohan, S. Sinha, G. S. Tondon, and D. Gosh (2003). Color Removal From Wastewater Using Low-Cost Activated Carbon Derived From Agricultural Waste Material. *Industrial & Engineering Chemistry Research*, **42**; 1965–1976

Srivastava, S. (2024). Recent Advances in Removal of Pharmaceutical Pollutants in Wastewater Using Metal Oxides and Carbonaceous Materials As Photocatalysts: A Review. *RSC Applied Interfaces*, **1**; 340–429

Tian, Y., P. Liu, X. Wang, and H. Lin (2011). Adsorption of Malachite Green From Aqueous Solutions Onto Ordered Mesoporous Carbons. *Chemical Engineering Journal*, **171**; 1263–1269

Tseng, Y. H., I. G. Chang, Y. Tai, and K. W. Wu (2012). Effect of Surface Plasmon Resonance on the Photocatalytic Activity of Au/TiO_2 Under UV/Visible Illumination. In *Journal of Nanoscience and Nanotechnology*. pages 416–422

Ullah, A. K. M. A., A. K. M. F. Kibria, M. Akter, M. N. I. Khan, A. R. M. Tareq, and S. H. Firoz (2017). Oxidative Degradation of Methylene Blue Using Mn_3O_4 Nanoparticles. *Water Conservation Science and Engineering*, **1**; 249–256

Wang, L., Z. Zhu, F. Wang, Y. Qi, W. Zhang, and C. Wang (2021). State-of-the-Art and Prospects of Zn-Containing Layered Double Hydroxides (Zn-LDH)-Based Materials

for Photocatalytic Water Remediation. *Chemosphere*, **278**; 130367

Xu, X., J. Wang, A. Zhou, S. Dong, K. Shi, B. Li, J. Han, and D. O'Hare (2021). High-Efficiency CO_2 Separation Using Hybrid LDH-Polymer Membranes. *Nature Communications*, **12**(1); 3069

Zhang, H., J. M. Jiang, L. Han, Y. Z. Lao, D. Zheng, Y. Y. Chen, S. J. Wan, C. W. Zheng, H. S. Tan, Z. G. Li, and H. X. Xu (2019). Uncariitannin, a Polyphenolic Polymer From *Uncaria gambier, Attenuates, Staphylococcus aureus* Virulence Through an MgrA-Mediated Regulation of α-Hemolysin. *Pharmacological Research*, **147**(14); 104328.

Zhao, X., S. Zhang, J. Yan, L. Li, G. Wu, W. Shi, G. Yang, N. Guan, and P. Cheng (2018). Polyoxometalate-Based Metal-Organic Frameworks as Visible-Light-Induced Photocatalysts. *Inorganic Chemistry*, **57**; 5030–5037

