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Research Article

Photocatalytic Degradation of Malachite Green by Layered Double Hydroxide Based Composites

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Abstract

Studies of LDH materials to be applied as photocatalyst for dye pollutant degradation have been developed. These interesting efforts are inseparable from the investigation of degradation performance and competitive synthetic methods. Composites based on Zn/Al and Mg/Al layered double hydroxides (LDHs) with ZnO and TiO_2 were prepared by coprecipitation-impregnation method following by calcination at 300 °C to forms Zn/Al-ZnO, Mg/Al-ZnO, Zn/Al-TiO_2, and Mg/Al-TiO_2. Composites were characterized by XRD, FTIR, SEM and UV-DRS. Photodegradation of malachite green (MG) was carried out, after optimization of pH, catalyst loading and contact time in batch system under UV irradiation. XRD and spectroscopic data shows composites were successfully formed indicated by formation of both pristine materials. Degradation of malachite green showed that composites as photocatalyst have higher catalytic activity than pristine LDHs. LDH-ZnO composite have better activity, energy band gap and degradation reusability than LDH-TiO_2. The Zn/Al-ZnO and Zn/Al-TiO_2 composites degraded 97.1% and 96.3% MG, whereas the Mg/Al-ZnO and Mg/Al-TiO_2 composites were able to degrade 99.8% and 98.6% MG, respectively.

Keywords: Malachite Green; Layered Double Hydroxide; Photocatalytic

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1. Introduction

The rapid advancement of industry, including industries that require dyestuff, is accompanied by the consequences of waste pollution. The stability of textile dyes compounds makes it difficult to decompose. This type of organic pollutant is carcinogenic and has high toxicity to the environment. Research efforts in degrading dyes are often carried out using photocatalysts [1–3]. Pollutant photodegradation is the most economical technique compared to sediment coagulation, adsorption, membrane separation and osmosis. Malachite green, a dye that is widely used in textile, leather and pharmaceuticals, was reported in a study to be degraded by a photocatalyst ZnO on Mg/Al-coated double hydroxide calcined to 500 °C (LDH) [4].

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Advanced materials that have easy modification for various purposes such as layered double hydroxide (LDH) have been reported to degrade organic pollutants. The general formula for LDH is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[(A^{n-})_{x/n}.yH_2O]^{x}$, with composition M is metallic element with valence 2+ and 3+ [5]. The LDH is relatively simple and economical to synthesize in both laboratory and industrial scales [6]. Research on LDH as a photocatalyst that degrades organic pollutants have been synthesized with various alternatives. Mg/AlNi^{3+} LDH was synthesized by coprecipitation in the presence of Na hypochloric as oxidizing media [7], and Pt modified ZnAl LDH was synthesized mechanochemically as a catalyst for degradation [8].

Modification of LDH is often carried out by composites with metal oxides because of the ability of the hexagonal layer to facilitate fast electron transfer [9]. Modifications of LDH-metal oxides, such as LDH-ZnO, result in dispersion of the active components. ZnO was composited with LDH to avoid aggregation [10]. The ZnO is an excellent photocatalyst due to its efficient photosensitivity, harmless nature and chemically stability [11,12]. Catalyst NiFe-LDH@ZnO@NF was hydrothermally synthesized to degrade Rhodamine B. However, the application of LDH-ZnO is the most widely used in the field of electrochemistry and is still very rarely used as a photocatalytic.

The composite between LDH and other metal oxides, namely TiO_2, provides the advantage of simplifying the filtration process and avoiding TiO_2 agglomeration [13]. TiO_2 has excellent photocatalytic activity, non-toxicity and commercial availability [3,14]. LDH material is used as a TiO_2 support material owing to its good dispersion, helps interaction and sedimentation rate within minutes or at the end of the catalysis process [14,15]. TiO_2 has high catalytic activity [16]. However, TiO_2 nanoparticles easily agglomerate, thereby reducing their catalytic activity. Many studies modify it with various support materials including LDH to degrade dyes [13] including: synthesis of NiAlCu LDH doped-TiO_2 using the hydrothermal method [14]; Mg/Al LDH-TiO_2 was prepared by coprecipitation with molar ratio M^{2+}/M^{3+} was 2 [5]; MgZn/Al-TiO_2 LDH synthesized by coprecipitation and ultrasonification was reported to degrade at 4 – 9 hours [3]; sol gel preparation of Mg/Al, Mg/Fe, and Zn/Al LDH-TiO_2 [16,17]. Many studies are still developing the advantages of LDH as a degradation photocatalyst.

Previous studies on the synthesis of LDH-ZnO or LDH-TiO_2 photodegradation catalysts using a calcination temperature of 500 °C or 550 °C include studies by Yan *et al.* [4], Elhalil *et al.* [11], Contreras-Ruiz *et al.* [16], Contreras-Ruiz *et al.* [17], and Hadnadjev-Kostic *et a*l. [26]. Those studies used relatively high calcination temperatures. This research therefore seeks to contribute to the lower consumption of calcined energy which is important for large-scale applications to be more energy efficient. This study modified Mg/Al LDH and Zn/Al LDH with metal oxides ZnO and TiO_2, respectively, but calcined at a lower temperature of 300 °C to be applied as degradation photocatalysts. The composites degraded malachite green (MG) as a model under UV light. The degradation activity was determined from the percent degradation of the dye and the apparent rate constant.

2. Materials and Methods

2.1 Chemicals and Instrumentation

All chemicals were used after received without specific treatment, $Al(NO_3)_3.9H_2O$ (Merck), $Mg(NO_3)_2.6H_2O$ (Merck), $Zn(NO_3)_2.6H_2O$ (Smart-Lab), TiO_2 (Merck), ZnO (LOBA Chemie), NaOH (Merck), Na_2CO_3 (Merck) and HCl (Mallinckrodt LabGuard). Water was supplied from Inorganic Materials and Complexes Research Group using resin ion exchange reverse method.

Analysis and characterization of materials were performed by Rigaku XRD Miniflex-6000 diffractometer by scanning at 1 deg/min. Analysis of IR was conducted using Shimadzu FTIR Prestige-21 using KBr method. Sample was scanned at 400–4000 cm^{-1}. Band gap analysis was carried out using JASCO V-760 UV-Vis Diffuse Reflectance Spectrometer. Degradation of malachite green was analyzed by UV-Vis Biobase BK-UV 1800 PC spectrophotometer at 617 nm.

2.2 Synthesis of Zn/Al LDH and Mg/Al LDH

LDH was synthesized by coprecipitation method according to a slight modification of the method reported by Lesbani *et al.* [18] and Rahmadan *et al.* [19]. The Zn/Al LDH was synthesized by means of 50 mL $Zn(NO_3)_2.6H_2O$ 0.75 M added with 50 mL $Al(NO_3)_3.9H_2O$ 0.25 M in a shaker for 2 hours. The mixture was added with NaOH and Na_2CO_3 with a mole ratio of 2:1 in 120 mL of distilled water, until the mixture had a pH of 10. This mixture was shaken again for 10 hours at a temperature of

80 °C. After the mixture was filtered and washed with distilled water then dried using an oven at a temperature of 110 °C then the LDH was weighed. The synthesis of Mg/Al LDH was carried out with the same procedure as above, but the salt used was Mg $(NO_3)_2.6H_2O$.

2.3 Synthesis of LDH-Metal Oxide Composite

50 mL solution of $Zn(NO_3)_2.6H_2O$ or $Mg(NO_3)_2.6H_2O$ with a concentration of 0.75 M was added with 50 mL $Al(NO_3)_3.9H_2O$ 0.25 M in a shaker for 2 hours, to prepared Zn/Al LDH or Mg/Al LDH. The mixture was added with NaOH and Na_2CO_3 with a mole ratio of 2:1 in 120 mL of distilled water, until the pH of the mixture was pH 10. This mixture was shaken again for 10 hours at a temperature of 80 °C. ZnO was dispersed in the mixture with a ratio of LDH pristine: ZnO was 1:1 by weight, then shaken for 3 hours. This mixture was then added with 150 mL of 0.37 M NaOH and stirred for 10 hours at a temperature of 70 °C. The mixture was washed with distilled water and filtered. Then the filtrate was calcined at a temperature of 300 °C in a furnace for 7 hours. The LDH-TiO_2 composite was made using the same procedure as above, but the oxide used was TiO_2.

2.4 Photodegradation Activity

The synthesized composites were used as a photocatalyst for the degradation of 5 mg/L malachite green as a model in 20 mL dye solution. Degradation in batch system with variable pH, catalyst loading, and contact time of degradation. The mixture of dye solution and photocatalyst was shaken for 20 minutes in the dark, then continued with the degradation process using UV light (4 × 20 watt with 352 nm). Photodegradation performance was analyzed by the determination of %degradation and kinetics. Determination of the apparent constant rate of degradation (k_{ap}) over time (t) according to the pseudo first order kinetics model equation $\ln (C_0/C) = k_{ap}.t$, where C_0 is the initial malachite green concentration and C is the concentration of malachite green after the degradation has progressed [12]. The desorption was carried out ultrasonically, and determination of catalyst reusability up to 5 cycles of use.

3. Result and Discussion

Layered double hydroxides (LDHs) are more commonly synthesized by coprecipitation. The synthesis paid attention to the arrangement of metal elements composition, anion intercalation and the ratio of carbonate to NaOH as a precipitant. This study uses the mole ratio of M^{2+}/M^{3+} was 3 and the mole ratio of $NaOH/Na_2CO_3$ was 2. The LDH pristine contains various ratios of valence metal 2+ (M^{2+}) to valence 3+ (M^{3+}). Li *et al.* [2] investigated that there was only a slight difference in %degradation by Cu doped Zn/Al LDH between the molar ratios of metals 3 and 4, 77% and 78%, respectively. Another study also used a M^{2+}/M^{3+} ratio of 3, but the synthesis was carried out by a combination of coprecipitation and hydrothermal methods to prepare Ba doped Zn/Al LDH [11]. The synthesis resulted in a higher percentage of degradation when using carbonate for interlayer anion than using

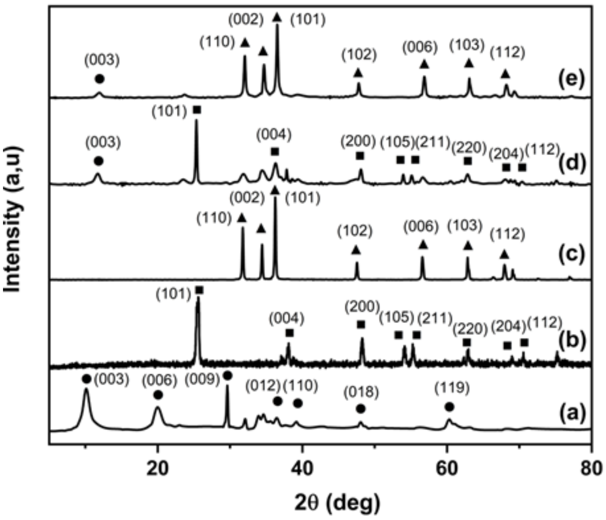

Figure 1. XRD pattern of Zn/Al LDH (a), TiO_2 (b), ZnO (c), Zn/Al-TiO_2 (d), and Zn/Al-ZnO (e).

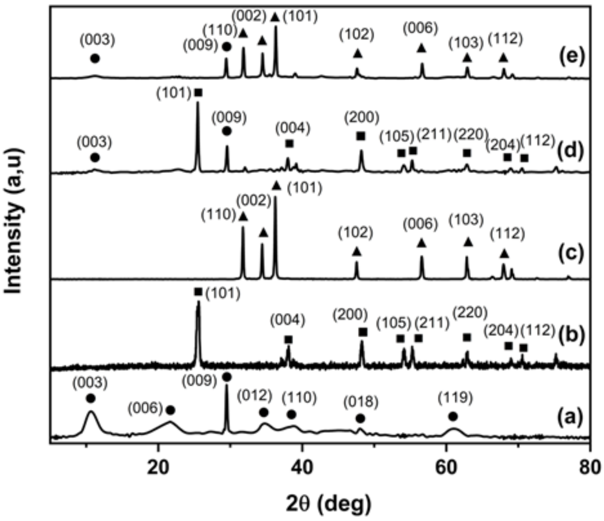

Figure 2. XRD pattern of Mg/Al LDH (a), TiO_2 (b), ZnO (c), Mg/Al-TiO_2 (d), and Mg/Al-ZnO (e).

sulfate, nitrate and chloride [21,22]. This study also used carbonate as counterion. Many variations in the molarity ratio between precipitating sodium hydroxide and carbonate have been reported. Li *et al.* [2], Yan *et al.* [4], and Hu *et al.* [20] used ratio $NaOH/Na_2CO_3$ was two. The presence of Al cations as 3+ valence metal in LDH increased photocatalytic activity, morphology, particle size and stability [11]. Optimization of the synthesis of Mg/Al LDH-TiO_2 obtained the optimum LDH-TiO_2 weight ratio was 1 [5]. This study also used a ratio of 1 by weight of LDH-metal oxide.

Pristine LDH, metal oxide and LDH-metal oxide composites were characterized using XRD to reveal the characteristic peaks of LDH and oxide, as shown in Figure 1 and Figure 2. The Zn/Al LDH has a unique peak indicating the layer structure at an angle of 2 theta 10.15°. The presence of interlayer anions is indicated by a peak of 60.0° and a metal oxide peak at 20–35° [11,18]. In this study, these peaks were seen in both pristine LDH and composite LDH. The pea at angle 12.1° was the peak (006) planes of Zn/Al LDH in the LDH-ZnO composite [23], while the peak that appears for Zn/Al-ZnO in this study was at 11.9°. Elhalil *et al.* [11] reported that the ZnO peak resulting from the calcination of Ba doped ZnAl LDH appeared at 31.8° (110), 34.5° (002), 36.3° (101), 47.6° (102), 56.6° (006), 62.9° (103), 68° (112) and 69.1° (201). The ZnO composite peaks in this study appeared at 31.8°, 34.5°, 36.3°, 47.5°, 56.6°, 68°, and 69.1° for Mg/Al-ZnO and 32°, 34.6°, 36.5°, 47.8°, 56.8°, 63°, 68.2°, and 69.3° for Zn/Al-ZnO. Contreras-Ruiz *et al.* [16] investigated the sol-gel synthesized Mg/Al-TIO_2 and Zn/Al-TiO_2 obtained peaks of 25° (101), 38° (004), 48° (200), 55° (105), and 63° (220). This study resulted in peaks of 25.5°, 37.9°, 48.2°, 55.2°, and 62.9° for Mg/Al-TIO_2 and 25.3°, 37.8°, 48°, 55.1°, and 67.2° for Zn/Al-TiO_2.

SEM investigated the morphology of the composites, which showed the distribution of metal oxides in LDHs. The SEM images represent that LDH-ZnO composites have a relatively more homogeneous morphology than LDH-TiO_2 composites. Figure 3 shows images of LDH-metal oxide composites magnified 5000 times, respectively.

The IR spectra of LDH between 3600 – 3200 cm^{-1} show the stretching vibration of the hydroxyl groups of water molecules located between layers and the hydroxyl is physically absorbed [11]. This study obtained a range of

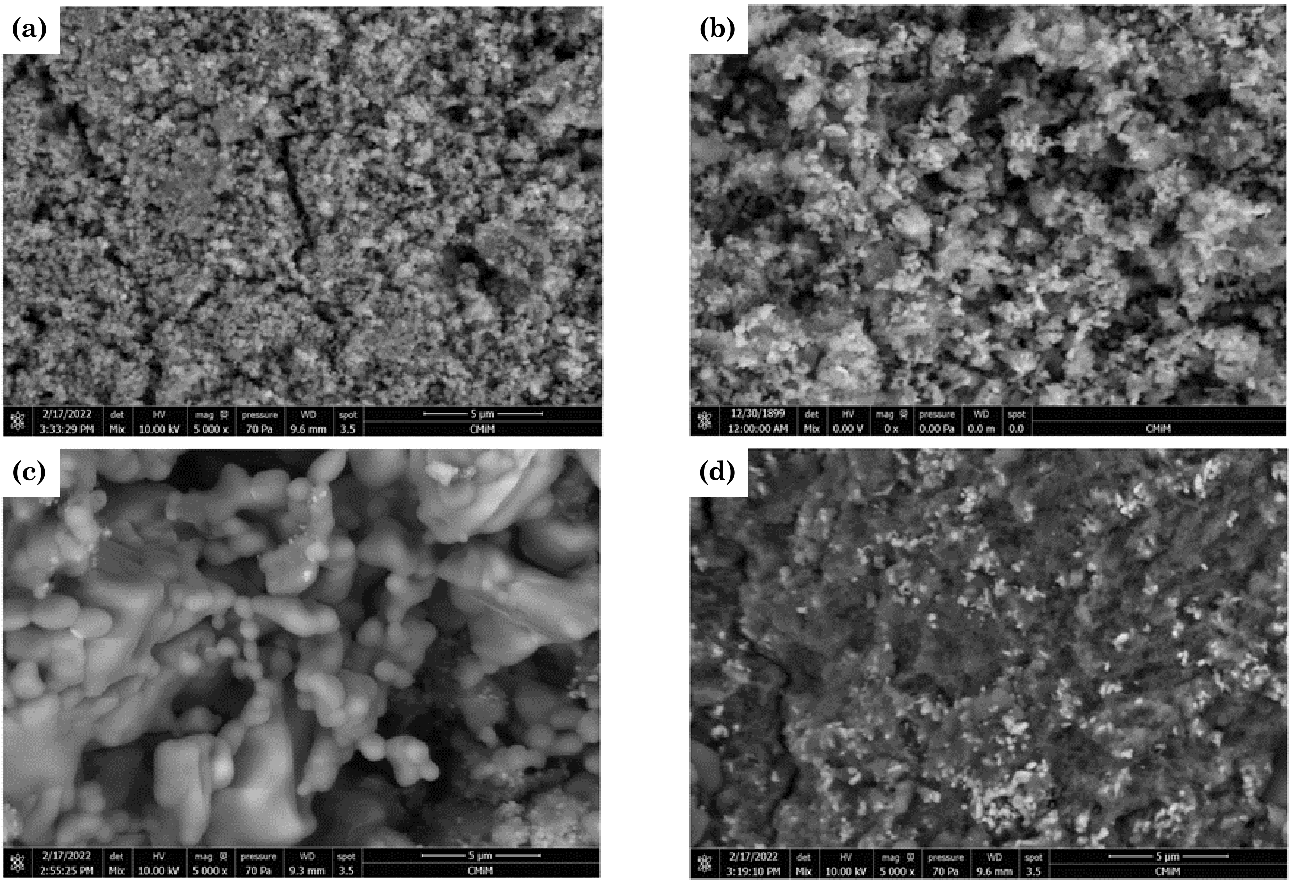

Figure 3. SEM images of composites Zn/Al-TiO_2 (a), Zn/Al-ZnO (b), Mg/Al-TiO_2 (c), and Mg/Al-ZnO (d).

spectra between 3464 to 3441 cm^{-1} in pristine LDHs and composites. Wijaya *et al.* [24] claimed that band 2368 cm^{-1} was the Zn−O vibration. In this study, band 2368 cm^{-1} was also found in both Zn/Al LDH and Mg/Al-ZnO. Hosseini *et al.* [6] claimed that the peak of CO_3 vibration was at 1381 cm^{-1}, while Zhao *et al.* [3] stated that the 1384 cm^{-1} band which was close to 1360 cm^{-1} showed stretching vibrations of the CO_3 group. In this study the carbonate band of all pristine LDH and composite LDH appeared at 1381 cm^{-1}. Contreras-Ruiz *et al.* [16] stated that the Ti−O band appears at 613 cm^{-1} and 614 cm^{-1} while the ZnO composite didn't show these bands. The Ti−O−Ti band appears at 551-556 cm^{-1}. In this study, it appeared that the 570 and 547 cm^{-1} bands belong to Mg/Al-TiO_2 and Zn/Al-TiO_2, respectively. Aoudjit *et al.* [15] conveyed that the band indicating the presence of M−O and O−M−O was in the 400-800 cm^{-1} range. Wijaya *et al.* [24] reported that a band of 462 cm^{-1} was the Zn−O vibration. The IR spectra of the catalysts in this study showed a band between 401 to 779 cm^{-1}. Figure 4 and Figure 5 represent the FTIR spectra of metal oxide, LDH and LDH-metal oxides composites.

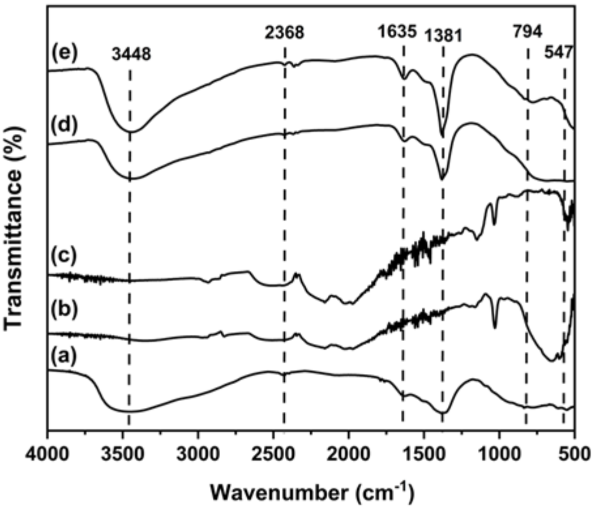

Figure 4. FTIR spectra of Zn/Al LDH (a), TiO_2 (b), ZnO (c), Zn/Al-TiO_2 (d), and Zn/Al-ZnO (e).

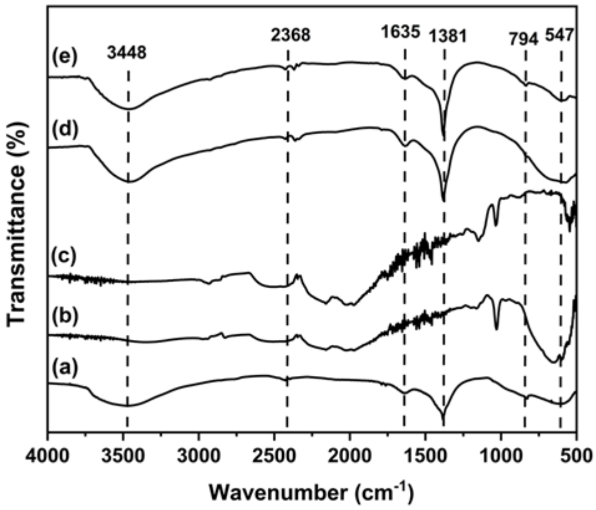

Figure 5. FTIR spectra of Mg/Al LDH (a), TiO_2 (b), ZnO (c), Mg/Al-TiO_2 (d), and Mg/Al-ZnO (e).

The UV-DRS spectrum of the composite is shown in Figure 6(a). On the coordinate axis of the spectrum there is a Kubelka-Munk absorption (KM function) which is the absorbance coefficient per scattering so that it is analogous to absorbance [2]. The composite response in absorbing radiation energy is effective in the UV region identified at peaks around 340 to 380 nm.

Figure 6(b) shows the band gap energies of pristine LDH and LDH-composite. According to Wijaya *et al.* [24], Zn/Ti LDH catalyst has a direct transition type so that the curve coordinates are the value $(ahv)^2$, where a is the absorptivity coefficient, h is the plank constant and v is the light frequency. The abscissa value

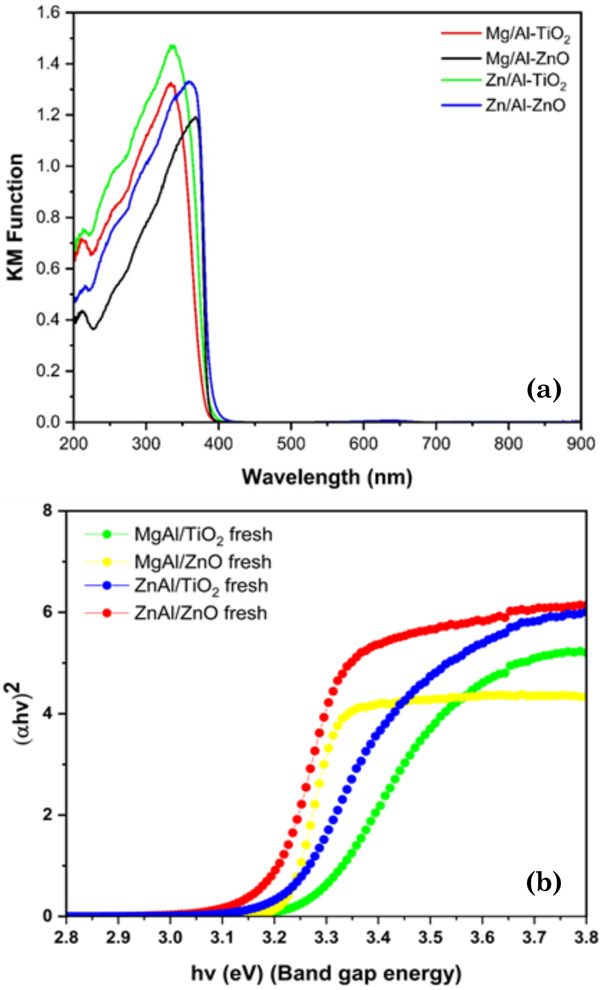

Figure 6. UV-DRS spectra (a) and Energy band gab (b) of LDH-TiO_2 and LDH-ZnO.

is hv or energy band gab, the energy band gab for Zn/Ti LDH was 3.35 eV. Hadnadjev-Kostic *et al.* [26] reported that Zn/Al LDH with metal molar ratio was 0.3 which was impregnated with TiO_2 with water medium had an energy band gab of 3.24 eV, whereas when impregnated in alkaline medium it had 3.21 eV. This study used alkaline media to composite metal oxides. The energy band gab Zn/Al-TiO_2 obtained was also 3.21 eV. The band gab energies of Mg/Al-TiO_2, Mg/Al-ZnO and Zn/Al-ZnO were 3.26, 3.21, and 3.19 eV, respectively. The energy of the Zn/Al-ZnO band gab is lower than that of Zn/Al-TiO_2, allowing the Zn/Al-ZnO photocatalyst to further trigger MG degradation. This is consistent with experimental data of higher value of kinetic rate (k_{ap}) in Section 3.1.4 and higher %degradation in Section 3.1.5. Likewise, the energy band gab of Mg/Al-ZnO is lower than that of Mg/Al-TiO_2. These data correspond to higher k_{ap} values in Section 3.1.4 and higher %degradation in Section 3.1.5 compared to degradation in the presence of Mg/Al-TiO_2.

The photocatalytic mechanism of the metal-oxide LDH composite was described by Wu *et al.* [12]. Due to the energy of UV irradiation, an effective separation of electron-hole pairs is formed. Photogenerated holes metal oxide could move to the valence band (VB) LDH. Photogenerated electrons in the conduction band (CB) LDH could migrate to the metal oxide CB. Photogenerated holes lead to the formation of $OH^\bullet$ by reacting with water or hydroxyl, while photogenerated electrons cause the formation of $O_2^{\bullet -}$ by reacting with oxygen. Both $OH^\bullet$ and $O_2^{\bullet -}$ are capable of degrading organic pollutants. The photocatalytic activity of the composite improves the material properties because LDH inhibits the recombination of electron-hole pairs of metal oxides.

3.1 Degradation of Malachite Green

3.1.1 Effect of pH on degradation

The photodegradation was carried out by taking into account the optimum pH perfor-

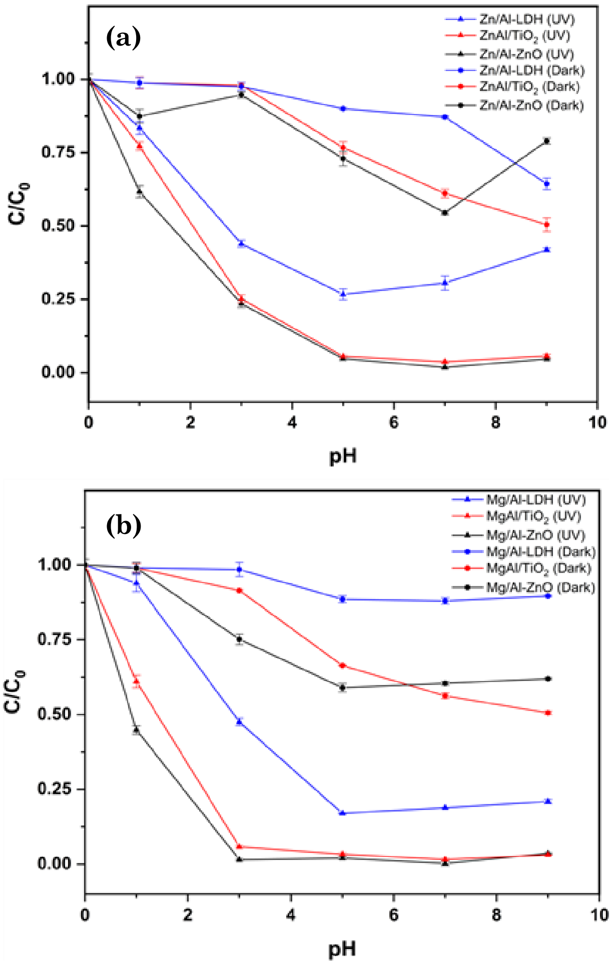

Figure 7. Effect of pH on MG degradation: by Zn/Al-LDH and Zn/Al-metal oxide (a) and by Mg/Al LDH and Mg/Al-metal oxide (b).

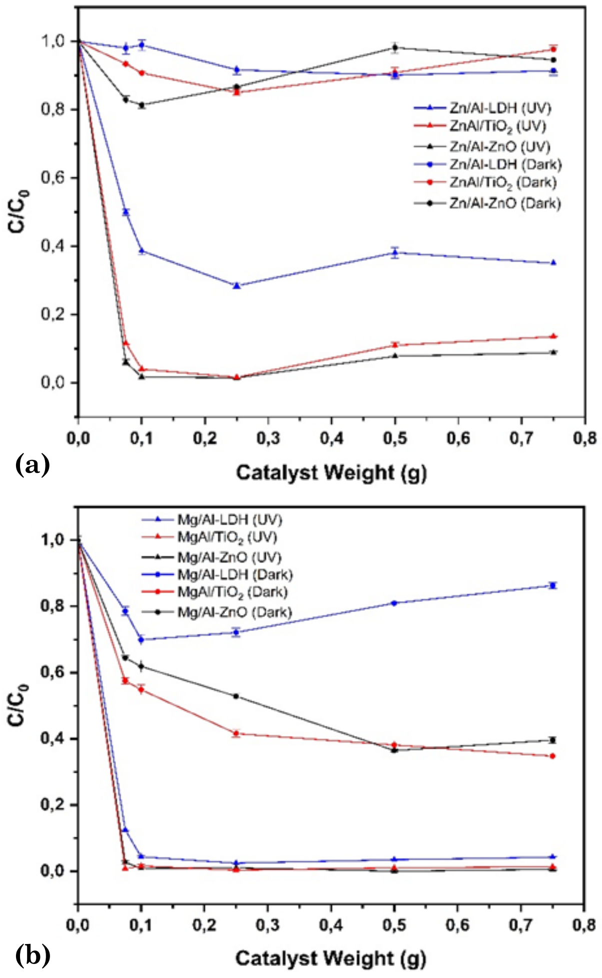

Figure 8. Effect of catalyst loading on MG degradation: by Zn/Al-LDH and Zn/Al-metal oxide (a) and Mg/Al LDH and Mg/Al-metal oxide (b).

mance of LDH pristine and each metal oxide LDH. The experimental results showed that the optimum pH was different between LDH pristine and LDH-metal oxide. Pristine LDH consisting of Mg/Al and Zn/Al LDHs has an optimum pH of 5, while Mg/Al-TiO_2, Mg/Al-ZnO, Zn/Al-TiO_2, Zn/Al-ZnO have an optimum pH of 7. Figure 7 shows the optimum pH in the photodegradation process for 120 minutes using a catalyst loading of 0.1 g. The optimum pH of the composite LDH is above the optimum pH of pristine LDH. Elhalil *et al.* [11] reported that there was a dissolution reaction and photodecomposition reaction of ZnO oxide to Zn^{2+} in LDH ZnO in acidic media, thereby reducing the degradation performance of the composite.

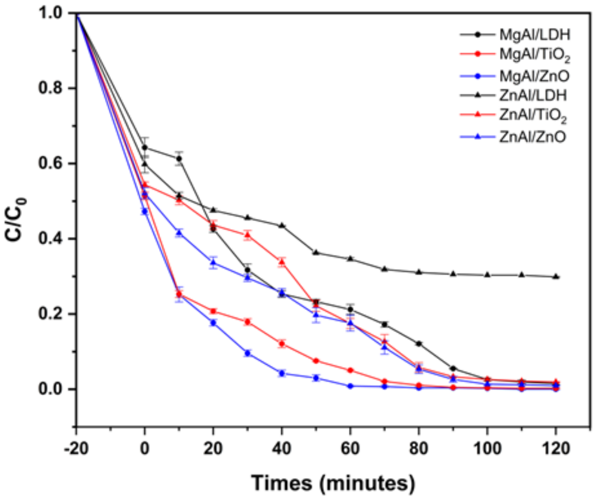

Figure 9. Effect of contact time on MG degradation by pristine LDH and composite LDH.

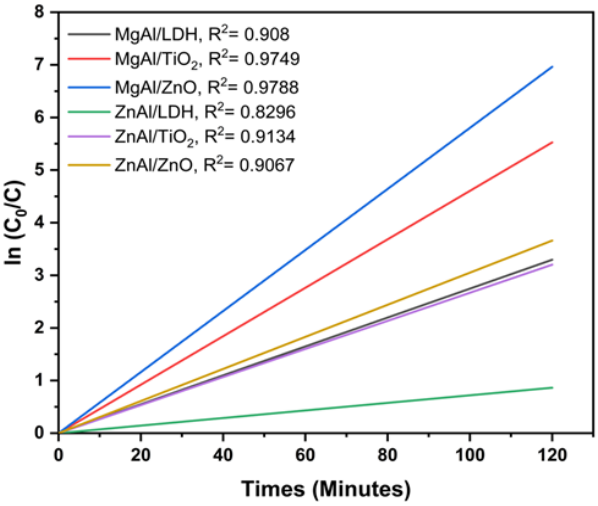

Figure 10. Kinetic curve based on pseudo first order kinetics model equation pristine LDH and LDH composite.

3.1.2 Effect of catalyst loading on degradation

Optimization of catalyst loading is carried out to avoid a shortage of catalyst and excessive catalyst weight. The optimum use of catalysts for both pristine LDH pristine and all composites is 0.25 g. Figure 8 shows the optimum catalyst loading at the optimum pH degradation conditions of each catalyst for 120 minutes of photodegradation. A slight decrease in degradation performance with the use of catalyst weight above the optimum weight can be caused by light refraction and reduced light penetration into the solution [11].

3.1.3 Effect of contact time on photodegradation

The effect of time on the performance of the catalyst in the malachite green degradation process showed a positive effect. The reduction of MG concentration during the first 20 minutes of contact was an adsorption process due to it takes place in dark conditions. UV radiation was turned on for up to 120 minutes to calculate percent degradation and kinetic parameters. Percent degradation by Mg/Al LDH was 96.7%, while that by Mg/Al-ZnO and Mg/Al-TiO_2 was 99.8% and 98.6%, respectively. LDHs modified with metal oxides allows the ability of the hexagonal layer to facilitate fast electron transfer so that it degrades better than pristine LDH [9]. Percent degradation of Zn/Al LDH was only 68.7%, while Zn/Al-ZnO and Zn/Al-TiO_2 composites degraded 97.1% and 96.3%, respectively. Figure 9 shows the reduction in MG concentration during contact time.

Table 1. Value of apparent constant (k_{ap}) of catalysts.

Catalysts	k_{ap} (mg/L.min)	Ref.
Zn/Co-Biochar	0.0260	[27]
Zn/Fe-Go/GS	0.0046	[28]
Mg/Al-TiO_2	0.0055	[16]
Mg/Fe-TiO_2	0.0043	[16]
Zn/Al-TiO_2	0.0060	[16]
ZnCo/Al LDH	0.0120	[29]
ZnO/ZnGaNO LDH	0.0200	[20]
Zn/Al LDH	0.0072	This study
Mg/Al LDH	0.0280	This study
Zn/Al-ZnO	0.0310	This study
Zn/Al-TiO_2	0.0270	This study
Mg/Al-ZnO	0.0580	This study
Mg/Al-TiO_2	0.0461	This study

LDH-ZnO composite had a higher %degradation than LDH TiO_2. This phenomena was in accordance with the apparent rate constant value which can also be higher than LDH-TiO_2. These results also agree with Yan *et al.* [4] who informed that ZnO has better organic compound degradation activity than TiO_2.

3.1.4 Kinetics of degradation

The degradation kinetics is based on pseudo first order kinetics model calculation as conveyed at experimental section. Figure 10 shows the curve ln (C_0/C) against time (t), the slope of the curve is the value of the apparent degradation rate constant, k_{ap} [15]. In this study, the k_{ap} value of degradation using composite LDH was better than pristine LDH because the degradation was more effective when the k_{ap} value was greater. Table 1 shows the value of the apparent constant (k_{ap}). In the table, it can be seen that the rate of degradation of the LDH-ZnO composite was better than the rate of LDH-TiO_2. Pseudo first order kinetics model allowed that the reaction rate (r) is comparable to the surface of the catalyst covered with pollutants, when the pollutant solutions are not concentrated. Therefore, because the k_{ap} rate constant is proportional to the reaction rate (r), the higher the k_{ap} value indicates the more efficient the degradation [16]. Table 1 shows the k_{ap} values of organic pollutant photodegradation catalysts produced by other studies, then compared with the k_{ap} values obtained by this study. The comparison shows that all composite k_{ap} values in this study are higher or better than all other research results. Even the pristine LDH k_{ap} value of Mg/Al LDH (0.028 mg/L minutes) was able to outperform the composite LDH from other previous studies. This result was in agreement with the higher %degradation of LDH-ZnO and information from Yan *et al.* [4] who stated that the degradation activity of ZnO was better than TiO_2.

3.1.5 Reusability of photocatalysts

The use of the catalyst is expected to be efficient so that it can be used repeatedly to degrade organic pollutants, this ability is known from the decrease in the percentage of degradation after several cycles of repeated use. Figure 11 shows a slight decrease in the degradation ability after reuse of the composite as a photocatalyst. After 5 cycles of using the catalyst there was a decrease in % degradation of Mg/Al LDH and Zn/Al LDH to 78.92% and 20.58%, respectively. The decrease in %degradation of LDH composites after 5 cycles of use by Zn/Al-ZnO, Zn/Al-TiO_2, Mg/Al-ZnO and Mg/Al-TiO_2 were 77.21%, 71.88%, 89.72%, 88.24%, respectively. The reusability of pristine LDH and composite LDH corresponded to the %degradation and apparent rate value. From the results of reusability, it can be seen that the LDH-ZnO was better than the LDH-TiO_2.

4. Conclusion

LDH-ZnO and LDH-TiO_2 composites which were synthesized by coprecipitation and followed by calcination at 300 °C have been succeeded in degrading malachite green as a model dye. XRD and FTIR characterization showed the presence of typical peaks or bands of metal oxide LDH. The results of the investigation carried out according to pH, catalyst loading and optimum contact time showed %degradation, degradation rate, and reusability of LDH-ZnO and LDH-TiO_2 composites were better

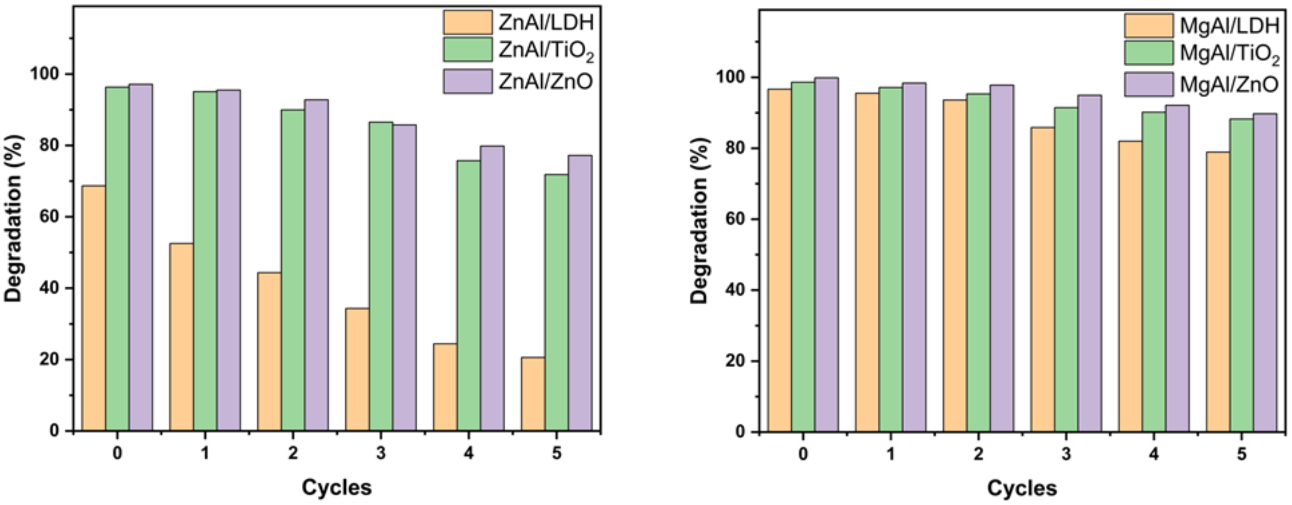

Figure 11. Reusability of pristine LDH and composite LDH in the fifth cycle.

than pristine LDH. LDH-ZnO composite has better activity, energy band gap and reusability degradation than LDH-TiO_2.

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