



Research Article

Photocatalytic Degradation of Malachite Green by NiAl-LDH Intercalated Polyoxometalate Compound

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Abstract

Composites based on layered double hydroxide with polyoxometalate $K_3[\alpha\text{-PW}_{12}\text{O}_{40}]$ and $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$ were synthesized to form NiAl- $[\text{SiW}_{12}\text{O}_{40}]$ and NiAl- $[\text{PW}_{12}\text{O}_{40}]$. The materials were characterized by XRD, FTIR, SEM, and UV-DRS and were then applied as a photocatalyst to degrade MG. The effects of catalyst loading, pH value, and contact times on photodegradation performance were carried out in this study. The results indicated that NiAl-LDH was successfully synthesized by showing the peak diffractions at angles 11.63°, 23.13°, and 35.16°. Both kinds of attained NiAl- $[\text{SiW}_{12}\text{O}_{40}]$ and NiAl- $[\text{PW}_{12}\text{O}_{40}]$ had typical structures of LDH that were proved by appearing diffraction at 2θ angles 10.76°, 26.59°, 30.8°, and 63.11° for NiAl- $[\text{PW}_{12}\text{O}_{40}]$ and at 2θ angles 8.26°, 11.34°, 29°, and 35.1° for NiAl- $[\text{SiW}_{12}\text{O}_{40}]$. The materials used for the fifth regeneration were characterized by FTIR, which still presents characteristics of LDH structure. The photocatalyst was applied for the first time to degrade MG. The decrease of band gap on NiAl pristine than LDH composite from 4.76 eV to 3.22 eV for NiAl- $[\text{SiW}_{12}\text{O}_{40}]$ and 3.78 eV for NiAl- $[\text{PW}_{12}\text{O}_{40}]$ respectively, was presented by DR-UV analysis. LDH composite shows improved degradation photocatalytic performance in comparison with LDH pristine. It was present by the %degradation MG performances were 68.94% for NiAl LDH, 84.51% for NiAl- $[\text{PW}_{12}\text{O}_{40}]$, and 88.91% for NiAl- $[\text{SiW}_{12}\text{O}_{40}]$. The degradation percentage indicates that the LDH-polyoxometalate composite has succeeded in increasing the ability of photodegradation catalytic and the regeneration ability of LDH pristine.

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1. Introduction

Layered double hydroxides (LDH), consisting of brucite-like layers with positively charged multimetal cations and interlayer compensating anions, have been applied to eliminate pollutants. LDH has the general formula $M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}(\text{A}^n)_{x/n}\cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are

divalent metal cations (Ca, Mg, Co, Fe, Cu, Ni, Mn) and trivalent metals (Al, Fe, Cr). The value of x is equal to the molar ratio of $M^{3+}/(M^{2+}+M^{3+})$, which is between 0.20 and 0.3; and A is the anion that is between the layers of valence n (Cl^- , NO_3^- , ClO_4^- , CO_3^{2-} , SO_4^{2-} and so on) [1]. The structure and characteristics of LDH give wide applications such as adsorbent [2], ion exchanger [3], and photocatalyst [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. Xue *et al.* [5] successfully modified NiFe LDH with polyoxometalate Keggin type $PW_{12}O_{40}^{3-}$ for water oxidation. The ZnAlFe-LDH was successfully degrading cationic dye and adsorbing removal [6]. According to Xu *et al.* [7], combining rare earth elements on LDH could endow the ability as a photocatalyst. It was assisted to their paper that MgAlCe-LDHs composed of different ratios of Ce^{2+} efficiently degrade methylene blue. NiAl-LDH doping with Fe^{3+} and reduced graphene oxide (RGO) improved photocatalytic performance on spoiling ciprofloxacin. Li *et al.* [8] informed Pt that modified ZnAl-LDH as a photocatalyst that effectively degrades ciprofloxacin. Furthermore, there are other researchers who have attention to modified LDH as a photocatalyst, such as Bi_2O_3 /LDHs doped with Pd(II) for degrading methylene blue [9], CoAl-LDH with Bi_2O_3 greatly degrades rhodamine B that reached the highest removal 90.36% [10], CrO_4^{2-} to replace interlayer anion on MgAl-LDH was efficiently enhanced photocatalysis performance for degrading methylene blue [11]. Polyoxometalate (POM) is a class of metal-oxygen cluster compounds that have a definite size and shape that make them attractive for application in catalysis and biology [12] and have been proven suitable for catalysis [13]. Polyoxometalate Keggin type has the most stable properties among other polyoxometalates [7]. In a previous report, we found the LDH intercalated with a large cluster anion could induce the function of cationic dye [14].

Recently, the application of LDH as a photocatalyst that degrades organic pollutants has been synthesized with various compounds. It is adopted strategies to decorate LDH-based materials to enhance efficiency performance in any application [15], including doping with noble metal [16], forming heterostructure with metal oxide [17], *etc.*, Yulisari *et al.* [18] reported that metal oxide (ZnO and TiO_2) modified LDH (Zn/Mg-Al) was synthesized as a catalyst for degrading malachite green, which is informed that LDH composite has better performance than LDH pristine. Gholami *et al.* [19] combining biochar with Zn-Co-LDH was composited for photocatalytic removal of gemifloxacin antibiotic. According to Amini *et al.* [20] inform succeeded in synthesizing of MgAl-POM, which was used for degradation dye, the percentage of degradation reached 97% for degraded rhodamine-B and 99% for degraded methylene blue. LDH has various morphological ad-

vantages and adjustable compositions, such as large interlayer spaces that form composites with other functional species are potential to be used as a photocatalyst [21,22] because its excess positive charge also produces more active sites, which are anions and water molecules can move freely and are easily exchanged, so that the LDH has the good ability as an anion exchange material. The LDH materials have a high capability of adsorption and tunable band gap, which can be used for anion-cation exchange and to provide a reaction site for the production of H_2 and O_2 from water splitting [23].

In this study, NiAl-LDH was composited with two different polyoxometalates (POM) types, Keggin $K_3[\alpha-PW_{12}O_{40}]$ and $K_4[\alpha-SiW_{12}O_{40}]$, which have additional charges by using the anion-exchange method which resulted in NiAl- $[PW_{12}O_{40}]$ and NiAl- $[SiW_{12}O_{40}]$ composite. The selection of the NiAl-LDH as catalyst materials and intercalate POM anions with the high negative charge for enhancing potential photocatalysis capability for cationic dye can endow the function of photodegradation malachite green (MG) dye. The material is applied as a photocatalyst to degrade malachite green dye. The prepared material was characterized using XRD, FTIR, SEM, and UV-DRS. Furthermore, application as a photocatalyst in this study carried out the photodegradation process, such as the catalyst loading, effect of pH, contact time, and regeneration of material.

2. Materials and Methods

2.1 Chemical and Instrumentation

Nickel nitrate (Merck), aluminum nitrate (Merck), sodium phosphate (Merck), sodium tungstate (Merck), sodium carbonate (Merck), sodium hydroxide (Merck), and hydrogen chloride (Mallinckrodt Lab Guard) were used in this research. Aquades was supplied from Inorganic materials and Complexes Research Group using the resin ion exchange reverse method. Characterization of materials was carried out by XRD Rigaku Miniflex-600. The sample scanned at scan speed 1 deg/min from 2theta range 5–70°. Analysis of IR was conducted using Shimadzu FTIR Prestige-21. The degradation of MG was analyzed by UV-Vis Biobase BK-UV 1800 PC spectrophotometer at 617 nm. UV-Vis Diffuse Reflectance Spectrometer for band gap analysis was carried out using JASCO V-760 and, SEM analysis was conducted by using SEM FEI Quanta 650. Polyoxometalate $K_3[\alpha-PW_{12}O_{40}].nH_2O$ and

$K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$ were synthesized according to previously reported literatures [24,25].

2.2 Synthesis of NiAl/LDH

NiAl-LDH was synthesized by a modified coprecipitation method by Lesbani *et al.* [26]. NiAl was synthesized by adding 18.75 g Zinc Nitrate 0.75 M mixed in water (100 mL) and 9.3 g aluminum nitrate 0.25 M dissolved in water (100 mL) in a stirrer for 2 h. Then, adjust the pH of the mixture to pH 10 by adding sodium hydroxide (2 M). This mixture was stirred for 6 h at 85 °C. The resulting product was washed and dried using an oven at a temperature of 110 °C then the NiAl LDH was weighted.

2.3 Preparation of Composite

The NiAl-LDH intercalated polyoxometalate compound was carried out by adding solution A (1 g of polyoxometalate into 50 L of distilled water) and solution B (2 g of NiAl-LDH into 1 M NaOH 25 mL) and mixed rapidly under the condition of N_2 gas for 24 h. Then the product was washed and dried. The sample obtained was LDH-polyoxometalate, carried out using XRD analysis, FT-IR spectrophotometer, SEM analysis and UV-DRS.

2.4 Photocatalytic Study

LDHs Pristine and LDH composite were applied as a photocatalyst to degrade MG 20 mg/L in a volume of 20 mL. Optimization degradation includes variations in pH at range (1, 3, 5, 7 and 9), for catalysts loading using variation at 0.075, 0.1, 0.25, 0.5, and 0.75 g respectively and degradation contact time using variation at

10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, and 120 minutes. Degradation is carried out using UV light. The percentage of degradation is determined based on the following equation formula:

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

where, C_0 is the initial dye concentration and, C_t is the dye concentration after degradation [27]. Determination of the reusability of the catalyst up to 5 cycles of regeneration of use and its desorption was carried out ultrasonically. The determination of the regeneration process and the degradation process had a similar procedure to fresh degradation [28].

3. Results and Discussion

3.1 Characterization of Materials

LDHs Pristine and LDH composite materials were characterized using XRD to show their structures before the degradation process. Figure 1 shows the XRD diffractions of material confirmed the good formation NiAl-LDH, $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$, $K_3[\alpha\text{-PW}_{12}\text{O}_{40}]$, NiAl- $[\text{SiW}_{12}\text{O}_{40}]$ composite, and NiAl- $[\text{PW}_{12}\text{O}_{40}]$ composite. The LDH layer structure is indicated by an angle of 2θ at 11.47° (003). There are also angles of 22.6° (006) and 34.69° (009) as anions between layers at an angle of 2θ at 61.62° (110) [29]. NiAl-LDH material was successfully synthesized by showing the peak diffractions at angles of 11.63° , 23.13° , and 35.16° . A typical principal diffraction peak is seen at $2\theta = 11.7$, 23.5, 35.1, 39.7, 47.3, 61.2, and 62.5 corresponding to the crystal plane (003), (006), (012), (015), (018), (110) and (113) from NiAl-

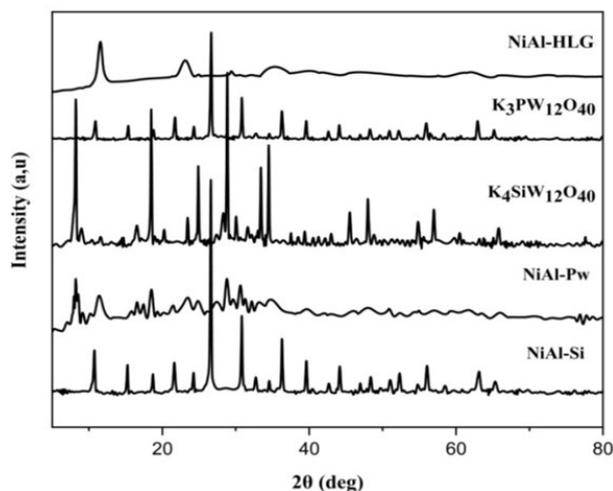


Figure 1. Diffractogram of catalyst (a) NiAl-LDH, (b) $K_3[\alpha\text{-PW}_{12}\text{O}_{40}]$, (c) $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$, (d) NiAl- $K_3[\alpha\text{-PW}_{12}\text{O}_{40}]$, (e) NiAl- $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$.

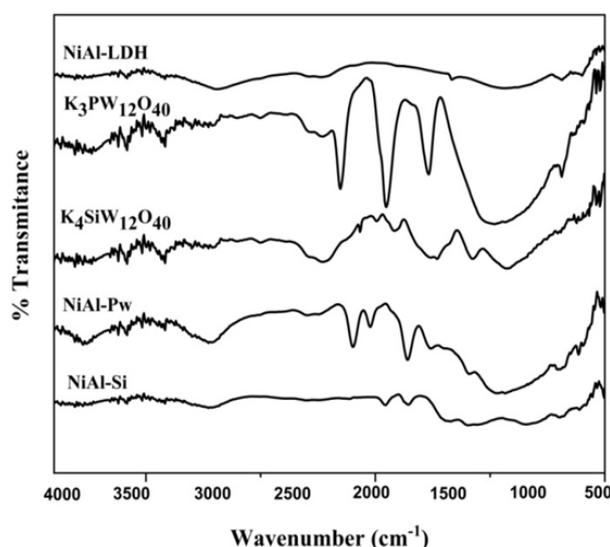


Figure 2. FTIR spectra of catalyst.

LDH, ensuring that the synthesis is successful [30]. The original compound of $K_3[\alpha\text{-PW}_{12}\text{O}_{40}]$ was shown at 2θ angles of $5\text{-}10^\circ$, $10\text{-}20^\circ$, and $25\text{-}30^\circ$ [31]. The peak is still present Pw in the NiAl- $K_3\text{-PW}_{12}\text{O}_{40}$ composite at angles 10.76° , 26.59° , 30.8° , and 63.11° . The presence of $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$ in LDH composite is indicated at 2θ angles 8.26° , 11.34° , 29° , and 35.1° .

Figure 2 represents the FTIR spectra of all synthesized LDH pristine and LDH composite within 4000 to 400 cm^{-1} . Characterization by FTIR was also carried out on LDH pristine and shows on LDH composite. All the prepared LDH displays peaks within the range 3420-

3480 cm^{-1} and 1620 to 1640 cm^{-1} , corresponding to the hydroxyl group vibration along with the stretching vibration of an interlayer water molecule. The LDH at 1348 cm^{-1} and 1361 cm^{-1} is attributed to the CO_3^- vibration mode and present the intercalated NO_3^- bending vibration [32]. The absorption band in the range of 500 to 800 cm^{-1} represents the bending and stretching vibration M-O and M-O-M and O-M-O.

The morphology of as-prepared NiAl-LDH was investigated by SEM analysis, as shown in Figure 3. A morphology can be observed for all NiAl-LDH samples, which validates LDH microsphere to the layered structure. LDH pristine and LDH composite their respective heterostructures. When LDH intercalated heterostructure is observed, a morphology that seems to result from the assembly of both layered materials is evidenced [33]. The morphology structure on synthesizing $[\text{SiW}_{12}\text{O}_{40}]$ which showed a block shape appearing on the surface material, which has similar to Lesbani *et al.* [34]. It is possible to appreciate the existence of platelet-shaped microcrystals. It can be seen that the LDH composite compared with LDH pristine, was polyporous, which implied adding polyoxometalate into the mixture solution can stick to

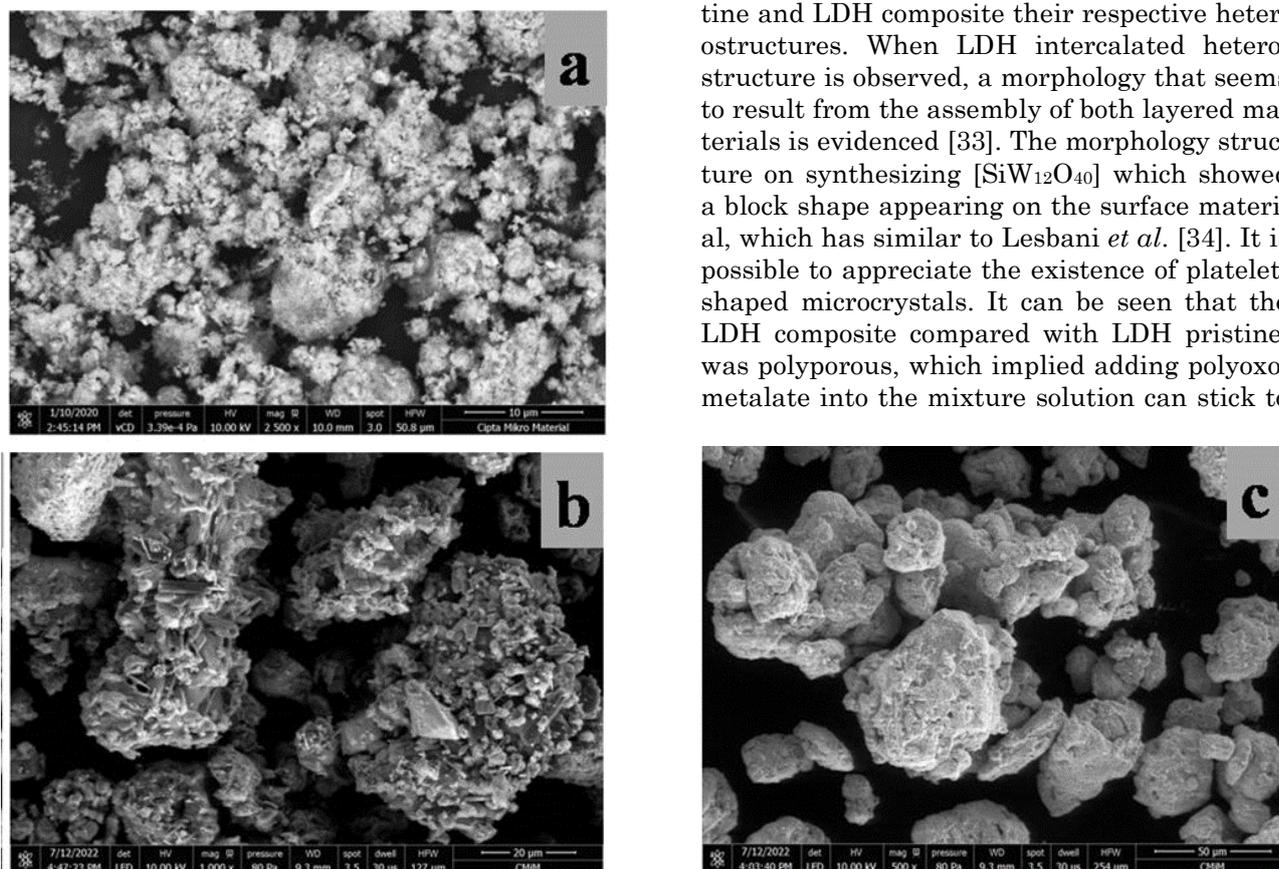


Figure 3. SEM of (a) NiAl-LDH, (b) NiAl- $[\text{SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$, (c) NiAl- $[\text{PW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$.

Table 1. EDX characterization of catalysts.

Element	NiAl-LDH (%wt)	NiAl-Pw (%wt)	NiAl-Si (%wt)
Ni	88.3	4.9	3.7
Al	1.3	1.7	1.0
W	-	44.7	19.5
P	-	0.7	-
Si	-	-	0.9
K	-	2.7	4.9
Cl	-	-	7.9
C	-	14.5	24.2
O	9.1	25.6	27.8
Na	-	4.9	9.6
N	1.4	-	-

the surface of the LDH composite. EDX analysis in Table 1 shows the percentages of Ni, Al, W, P, Si, K, Cl, C, O, and Na atoms. W appears after compositing into NiAl-[SiW₁₂O₄₀] and NiAl-[PW₁₂O₄₀].

3.2 Effect of Optimization Variables on Malachite Green Degradation

The degradation process by varying pH on LDH composite can affect the stability of the polyoxometalate structure in LDH. The pH media less than seven can create positively charged electron holes. These electron holes are not only influential in forming OH• radicals capable of degrading organic compounds on dye-stuffs but also cause photodecomposition of metal oxides into ions. Low pH conditions are also at risk for the dissolution of metal oxides into their ions [35].

Figure 4 shows the effect of media pH on MG degradation by catalysts based on NiAl-LDH. In the curve of C/C₀ against pH, the C/C₀ of the curve is the value of residual con-

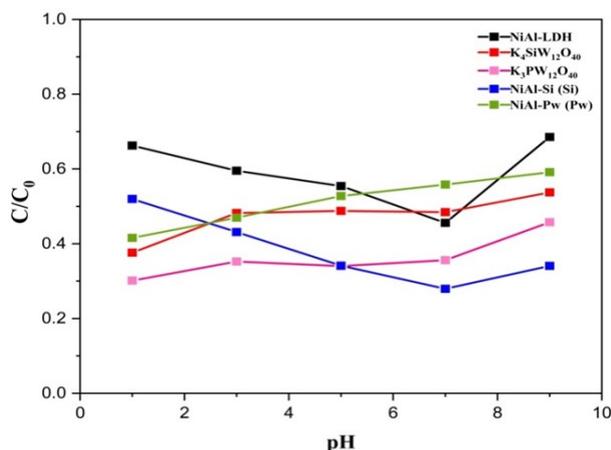


Figure 4. Effect of pH on MG degradation by catalysts.

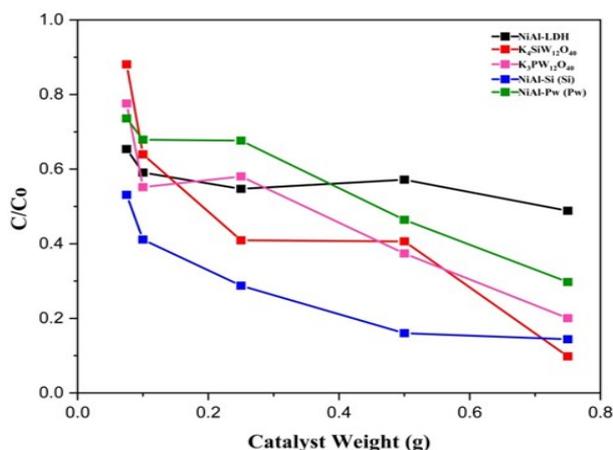


Figure 5. Effect of catalysts weight on MG degradation by catalysts.

centration, so the lower value of C/C₀ the higher %degradation. This causes pristine LDH and composite LDH to obtain a lower optimum pH, pH 7 for NiAl-LDH, pH 1 for K₃[α-PW₁₂O₄₀] and pH 1 for K₄[α-SiW₁₂O₄₀], while NiAl-[PW₁₂O₄₀] is optimum at pH one and NiAl-[SiW₁₂O₄₀] is optimum at pH 7. The effect of catalysts loading on the degradation process was carried out at the optimum pH of each material with treatment for 120 min. Figure 5 shows the results of various catalysts loading on the MG degradation process by LDH pristine and LDH composite, where it can be seen that NiAl-[PW₁₂O₄₀] and NiAl-[SiW₁₂O₄₀] have a significantly different degradation percentage.

3.3 Effect of Catalyst Loading on Degradation

Optimizing catalyst loading is carried out to avoid a shortage of catalysts and excessive catalyst weight. The optimum use of the catalyst for both LDH pristine and LDH composite is 0.75 g. Figure 5 shows the optimum catalyst loading at each catalyst's optimum pH degradation conditions for 120 min of photodegradation. A slight decrease in degradation performance with catalyst weight above the optimum weight can be caused by light refraction and reduced light penetration into the solution [35].

3.4 Effect of Contact Time on Photodegradation

The effect of time on the catalyst's performance in the MG degradation process showed a positive effect. The reduction of MG concentration during the first 20 minutes of contact was an adsorption process because it takes place in dark conditions. UV radiation was turned on for up to 120 min to calculate %degradation and kinetic parameters. The MG deg-

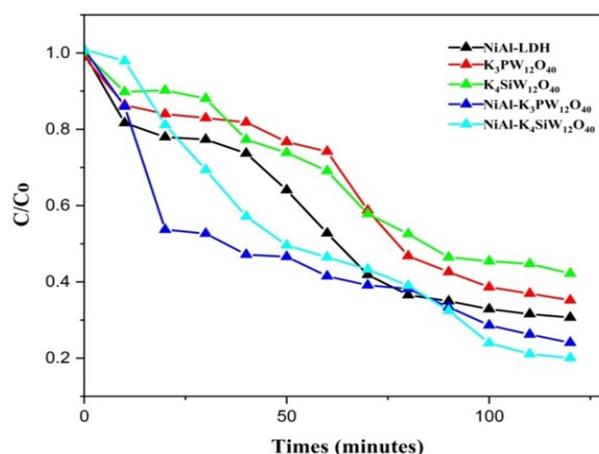


Figure 6. Effect of contact times on MG degradation by catalysts.

radiation rate on the LDH pristine and LDH composite are displayed in Figure 6. Figure 6 shows the MG degradation of effect varying time by LDH composite and LDH pristine as-based materials. The value of C/C_0 during 30 min of treatment increased by following the amount of MG degraded, especially for LDH composite. The percent MG degradation for NiAl-LDH, NiAl-[PW₁₂O₄₀], NiAl-[SiW₁₂O₄₀] was 68.94%, 84.51%, and 88.91%, respectively. The %degradation for K₃[α-PW₁₂O₄₀] and K₄[α-SiW₁₂O₄₀] was 57.75% and 73.32%, respectively. Furthermore, the degradation at 60 min for NiAl-[PW₁₂O₄₀] is slightly better than NiAl-[SiW₁₂O₄₀] caused that [SiW₁₂O₄₀] has a bigger charge which is 4⁻, than [PW₁₂O₄₀] which is 3⁻. Having a valence state of tungsten and nickel, both could enhanced redox reaction by electron transfer that can boost the decomposition of malachite green [36]. The splitting data of NiAl-[PW₁₂O₄₀] and NiAl-[SiW₁₂O₄₀] was shown at 90 min, then, NiAl-[SiW₁₂O₄₀] became superior compared to NiAl-[PW₁₂O₄₀]. According to the percentage degradation result

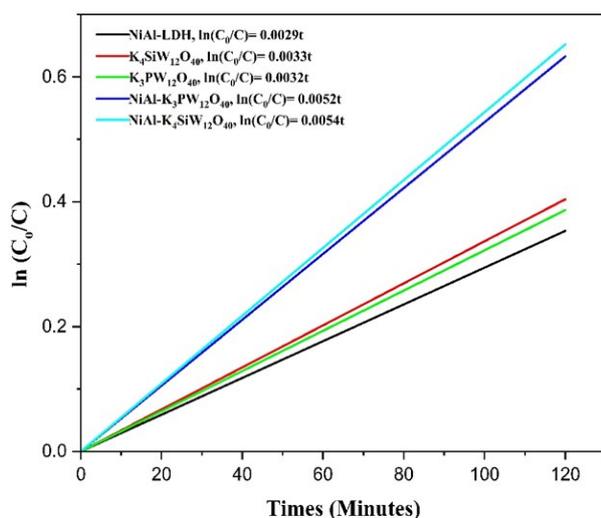


Figure 7. Kinetic curve based on pseudo first order kinetics model equation LDH pristine, polyoxometalate and LDH composite.

of composite catalyst NiAl-[PW₁₂O₄₀] and NiAl-[SiW₁₂O₄₀] has a better ability to degrade MG than pristine LDH. The NiAl-[SiW₁₂O₄₀] composites caused a degradation percentage that was not much different from that of the NiAl-[PW₁₂O₄₀] composites.

3.5 Kinetics of Degradation

The degradation kinetics is based on pseudo-first-order kinetics model calculation as conveyed in the experimental section. Figure 6 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} . In this study, the k_{ap} value of degradation using LDH composite was better than LDH pristine because the degradation was more effective when k_{ap} value was greater. Figure 7 and Table 2 show that the rate value catalyst of apparent degradation rate constant (k_{ap}) of NiAl-[SiW₁₂O₄₀] was better than the rate of NiAl-[PW₁₂O₄₀]. The value of r and k_{ap} for each material are 0.9637, 0.00527 for NiAl-[PW₁₂O₄₀] and 0.9949, 0.00543 for NiAl-[SiW₁₂O₄₀]. Pseudo-first-order kinetics model allowed that reaction rate (r) is comparable to the catalyst's surface 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 [37]. The comparison shows that all composite k_{ap} values in this study are higher or better than all other research results.

The UV-DRS spectrum of the composite is shown in Figure 8. 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 [42]. The composite response in absorbing radiation energy effectively in the UV region is identified at peaks around 220 to 400 nm. Figure 8 shows the band gap energies of LDH pristine and LDH composite. According

Table 2. The value catalyst of apparent degradation rate constant (k_{ap}).

Catalysts	k_{ap} (mg/L.min)	Ref.
Zn/Fe-GO/GS	0.0046	[38]
ZnAl-PW ₁₀ MO ₂	0.0022	[14]
ZnO/ZnGaNo	0.0026	[39]
Zn _x Cd _{1-x} S/ZnAl-LDH	0.0001	[17]
MgZnCr-TiO ₂	0.00003	[40]
ZnFe-CLDH	0.0021	[41]
Mg/Fe-TiO ₂	0.0043	[37]
NiAl-[SiW ₁₂ O ₄₀]	0.0054	In this study
NiAl-[PW ₁₂ O ₄₀]	0.0052	In this study

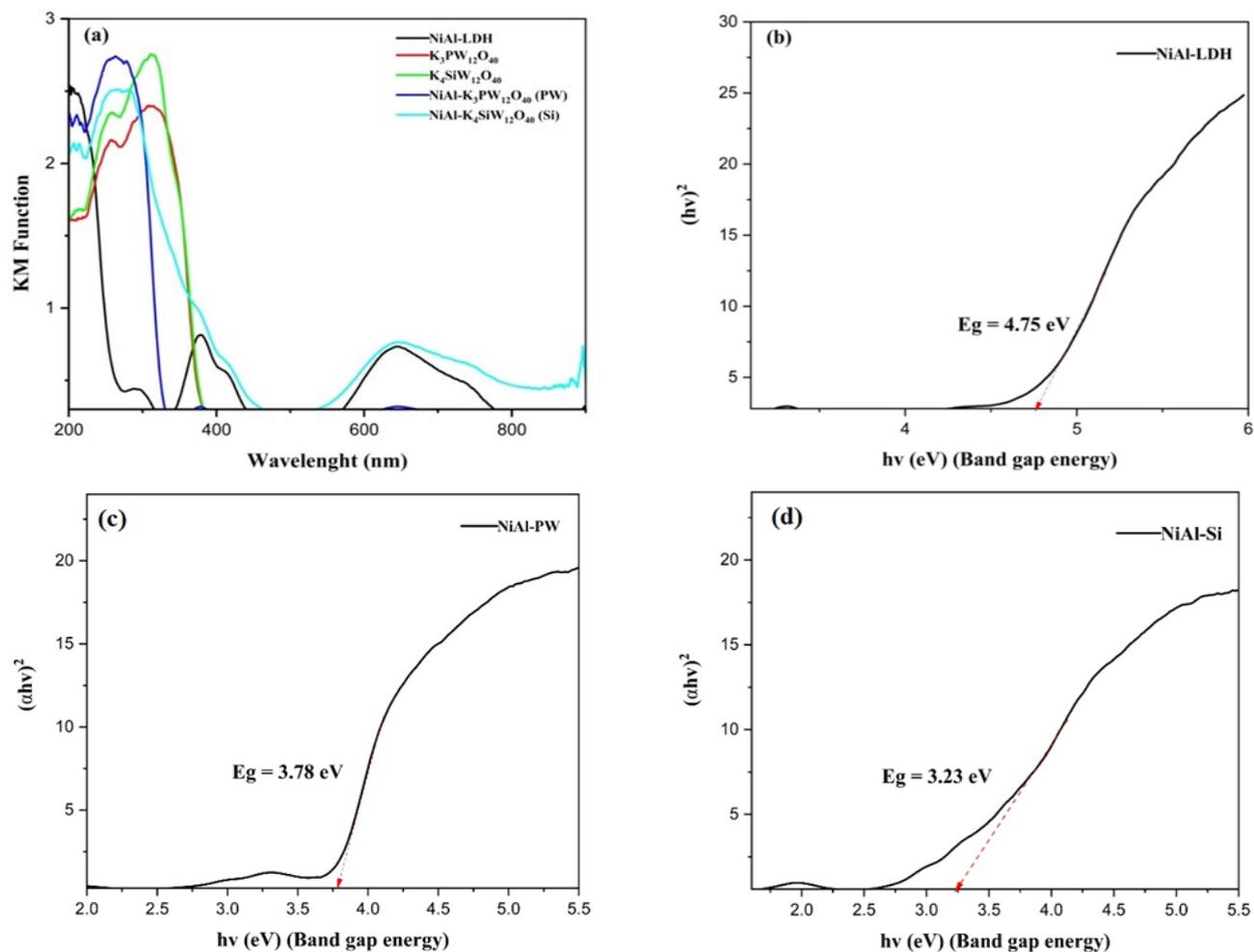


Figure 8. UV-DRS spectra and energy band gap (a) NiAl-LDH, (b) NiAl-[PW₁₂O₄₀] and (c) NiAl-[SiW₁₂O₄₀].

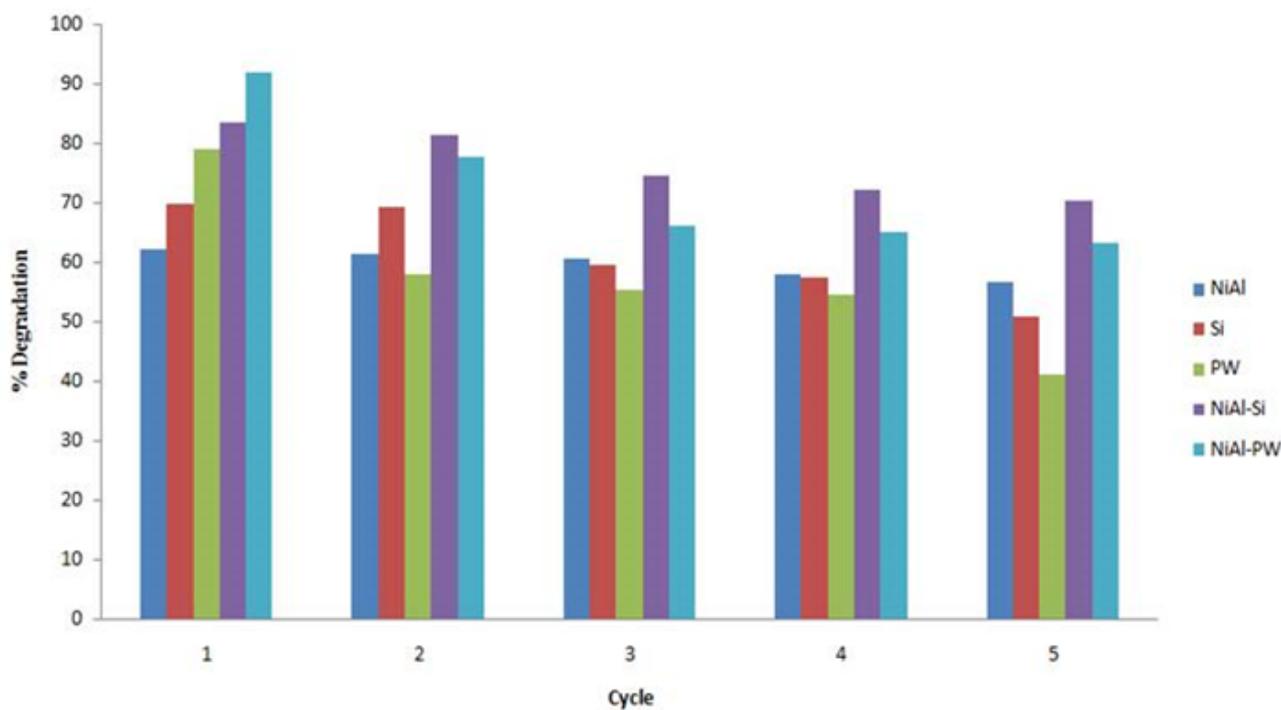


Figure 9. Regeneration of catalyst in the fifth cycle.

to Yuliasari *et al.* [18], LDH catalyst has a direct transition type, so that the curve coordinates are valued $(ah\nu)^2$, where a is the absorptivity coefficient, h is the plank constant, and ν is the light frequency [43]. The abscissa value is $h\nu$ or energy band gap. The energy band gap for NiAl-LDH was 4.77 eV. This study used polyoxometalate to composite NiAl-LDH. The band gap energies of NiAl-[PW₁₂O₄₀] and NiAl-[SiW₁₂O₄₀] were 3.78 eV and 3.23 eV, respectively. The band gap energy of both LDH composites is lower than LDH pristine. The decrease in band gap energy comparing LDH pristine and LDH composite may occur from the electron excitation event that generates more hydroxyl radicals that give a contribution to higher photodegradation efficiency. Each material corresponds to a higher k_{ap} value and %degradation. The band gap presence of LDH composite shows better efficient photocatalytic performance than LDH pristine, which are %degradation from 68.94% for NiAl-LDH to 88.91% for NiAl-[SiW₁₂O₄₀], which matched with theoretical band gap energies predictions. This study demonstrated that the photocatalytic performance of LDH materials depends on interlayer anion, metal combination, and cation ratio [44].

3.6 Regeneration of Catalyst

The use of the catalyst is expected to be efficient use repeatedly to degrade organic pollutants. This ability is known from the decrease in degradation percentage after several cycles of repeated use. Figure 9 shows a slight decrease in the degradation ability after the reuse of composite as a photocatalyst. After five cy-

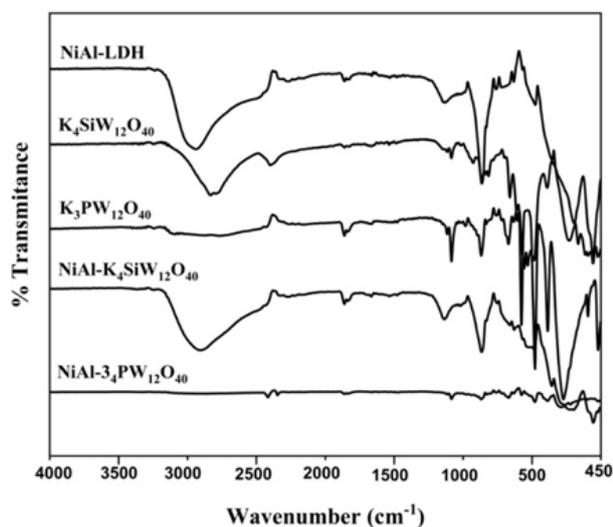


Figure 10. Spectra FTIR after regeneration 5 cyclee.

cles of using the catalyst, there was a decrease %degradation of NiAl-LDH 52.2%. The decrease in %degradation of LDH composite after five cycles of use by NiAl-[PW₁₂O₄₀] and NiAl-[SiW₁₂O₄₀] were 54.3% and 56.8%, respectively. The reusability of LDH pristine and LDH composite corresponded to the %degradation and apparent rate value. From the results of reusability, it can be seen that the NiAl-[SiW₁₂O₄₀] was better than the NiAl-[PW₁₂O₄₀].

Figure 10 shows the spectra FTIR of all materials NiAl-LDH, K₄[α -SiW₁₂O₄₀], K₃[α -PW₁₂O₄₀].nH₂O, NiAl-[SiW₁₂O₄₀] and NiAl-[PW₁₂O₄₀]. The representation of stretching and bending vibration of FTIR spectra confirmed the good formation of NiAl-LDH, K₄[α -SiW₁₂O₄₀], K₃[α -PW₁₂O₄₀], and both NiAl-[SiW₁₂O₄₀] and NiAl-[PW₁₂O₄₀]. The characterization by FTIR spectrum was also carried out on LDH composite that had to degrade MG to show the alteration after regeneration. The spectrum showed a band between 3420–3500 cm⁻¹ and about 1630-1583.6 cm⁻¹ offering the stretching vibration of the hydroxyl groups along the stretching vibration of an interlayer water molecule. The 1394 cm⁻¹ band represents CO₃ vibrations [45], and the peak at 1370-1960 cm⁻¹ also represents the intercalated NO₃⁻ bending vibration [46]. The W–O and W–O–W bands are in the 985.4 cm⁻¹ and 856.3 cm⁻¹, meaning characteristic material polyoxometalate on composite NiAl-[SiW₁₂O₄₀]. It also shows that bands on NiAl-[PW₁₂O₄₀] are 979.7 and 887.9 cm⁻¹ [47]. IR spectra data indicate that [SiW₁₂O₄₀] and [PW₁₂O₄₀] have remained in the NiAl-LDH. Figure 10 shows that these bands are still present for the catalyst that has degraded MG.

4. Conclusion

The LDH pristine and LDH composite has been successfully prepared and used for photodegradation MG. The materials synthesized optimally were well-oriented layer structures based on the characterization results. Modification of NiAl-LDH materials, which form composites with both polyoxometalate K₃[α -PW₁₂O₄₀] and K₄[α -SiW₁₂O₄₀] resulted in an enhanced capability for photodegradation of cationic dyes MG. Both composite NiAl-[PW₁₂O₄₀] and NiAl-[SiW₁₂O₄₀] composites also improved the regeneration performance of MG degradation compared to NiAl-LDH. The characterization results after fifth cycle regeneration using FTIR of materials that have degraded MG show that LDH pristine still has an LDH struc-

ture, and LDH composite also still has both LDH and polyoxometalate structure. The result of the investigation carried out according to pH, catalyst loading, and optimum contact time showed %degradation, degradation rate, and reusability of NiAl-[PW₁₂O₄₀] and NiAl-[SiW₁₂O₄₀] composites were better than LDH pristine. NiAl-[SiW₁₂O₄₀] composite has better performance activity, band gap energy, and reusability degradation than NiAl-[PW₁₂O₄₀].

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