Polyoxometalate Intercalated MgAl-Layered Double Hydroxide for Degradation of Malachite Green

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ABSTRACT

Improving the selectivity of photocatalysis of LDH pristine (MgAl-LDH) and LDH composite (MgAl-SiW$_{12}$O$_{40}$] and MgAl-[PW$_{12}$O$_{40}$]) was synthesized and used for degraded malachite green (MG). The effects of the amount of catalyst, pH value, and reaction times on degradation performance were discussed. MG degraded better composites than LDH pristine. The results indicated that MgAl-LDH was successfully synthesized by showing the peak diffractions at angles 10.39°(003), 20.17°(006), and 34.8°(009). Both kinds of attained MgAl-[SiW$_{12}$O$_{40}$] and MgAl-[PW$_{12}$O$_{40}$] had the typical structure of LDH that proved by appeared diffraction at 2θ angles 7.73°, 28.6°, 35.6° for MgAl-[PW$_{12}$O$_{40}$] and at 2θ angles 8.61°, 24.27°, 34.96° and 66.34° for MgAl-[SiW$_{12}$O$_{40}$]. The FTIR result indicates materials used for fifth regeneration, which confirmed the LDH composite structure. The fotodegradation activity of MG for pristine MgAl LDH (56.1%), composites MgAl-Pw (84.6%) and MgAl-Si (87.8%), respectively. The successful ability of photodegradation process by the percentage of degradation on material LDH-polyoxometalate composite showed the increasing of photodegradation catalytic and the regeneration ability of LDH pristine.

Keywords: LDH, polyoxometalate, photocatalytic, malachite green.

INTRODUCTION

Malachite green (MG) is the primary contaminant in water which are included organic pollutants and an organic dye used in industrial applications, especially in the aquaculture industry, due to as an antibacterial agent. Also used as dye material for wool, paper, leather, etc. on the other side, it has excellent outcomes with adverse effects such as mutagenesis, carcinogenicity also malformation especially for mammals (Salamat et al., 2019). Some contaminants of malachite green with high motilities and toxicities, mainly appear contaminant in aquatic organisms and accumulate in plants, which poses a potential risk to the ecosystem and human health (Patel et al., 2019) as a basic dye, malachite green is a toxic cationic dye, which is cannot efficiently biodegradable, thus BOD$_5$ in MG is almost to zero (Yong et al., 2014). Thus, its unbiodegradable removal from wastewater should be considered on the environment. Recently, various treatment practices to the removal of MG are adsorption (Burakov et al., 2018), extraction, biological degradation (Nasir et al., 2020) and application on photodegradation (Shahzad et al., 2016) have been used to reduce contaminants from wastewater (Gupta et al., 2018). Photocatalysis, a green treatment technology, is considered one of the most promising technologies because of its low cost, satisfactory performance, and high efficiency (Shi et al., 2019 and Lu et al., 2020). The photodegradation process is still considered as most favorable to remove dyes from water, thus of its high efficient

and simply eliminate (Nazir et al., 2020). The photocatalyst have been applied to eliminate dyes from aqueous, such as, industrial, activated carbon, biological waste materials and porous carbon (Zhang et al., 2018).

Layered double hydroxide (LDH) consisting of brucite-like layers with positively charged multimetal cations and interlayer compensating anion, have been applied to eliminate pollutants. LDH has general formula $M_{1-x}^{2+} M_x^{3+} (OH)_2]^{x+}$ $(A^n)_{x/n} \cdot mH_2O$ 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 $M^{3+}/(M^{2+}+M^{3+})$, where the value is between 0.20 and 0.33 ; and A is the anion that is between the layers of valence n (Cl^-, NO_3^-, ClO_4^-, CO_3^-, SO_4^- and so on) (Malherbe & Besse, 2000). Recently, LDH research has been related to adsorbents to remove pollutants from wastewater (organic and inorganic), energy storage and heavy metal ion (Yoshida et al., 2015; Behbahani et al., 2020). Single LDH is not considered an efficiently catalyst due to its morphology (Kaul et al., 2016). The structural characteristics of LDHs direct to the manipulation of morphology and active centers (such as electronic states, crystal faces, and defects) via various control synthesis techniques such as intercalated, immobilized etc, thereby significantly gaining performance of catalytic (Tonda et al., 2018 and Wang et al., 2019).

Thus, the current study report on the application of LDH as a photocatalyst that degrades organic pollutants have been synthesized with various compounds. According to Yulisari et al. (2022) reported that modified LDH (ZnAl and MgAl) with metal oxide (ZnO and TiO_2) as a catalyst for degrading malachite green, which is informed that LDH composite has better performance than LDH pristine. According to Gholami et al., (2020) Combining biochar with Zn-Co-LDH was composited for photocatalytic removal of gemifloxacin antibiotic. Sun et al. (2021) successfully synthesized NiCo-LDH composited with transition metal phosphide (Ni_2P) on degrade tetracycline to improve photocatalytic activity. Guo et al. (2021) reported their composite synthesize show the stronger degradation and inform the predominant photocatalytic performance on composite $CoAl-CeO_2$. Amini et al. (2017) informed the success in the synthesis LDH with anionic POM that was used for degradation dye which are rhodamine-B and methylene blue, the percentage of degradation reached 97% and
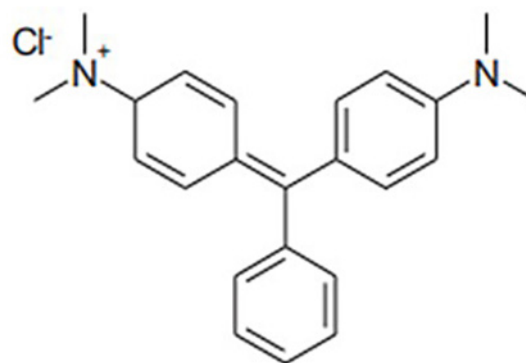
Figure 1. The structure of the malachite green (MG)

99%. LDHs have diverse morphological advantages and adjustable compositions, such as a interlayered arrangement of mortal ions, and broad chemical compositions and ability to exchange anions on these layers (Hu et al., 2019) and LDH materials have high tunable band gap and adsorption capacity which are capable for cation-anion-exchange and provide spatially separated redoks reaction sites (Mohapatra et al., 2016).

In the present study, MgAl pristine and MgAl composite which was composited with two different polyoxometalate (POM) type Keggin $K_3[\alpha-PW_{12}O_{40}]$ and $K_4[\alpha-SiW_{12}O_{40}]$ were synthesized using co-precipitation method and their photocatalytic performances were investigated such as the effect of pH, catalyst loading, contact time and regeneration of material. We select POM as intercalate to composite with MgAl-LDH due to POM anions have high negative charge for increasing the performance capability for cationic dye, that can endow the function of photodegradation malachite green (MG) dye. The material is applied as a photocatalyst to degrade MG dye. The prepared material were characterized using FTIR, XRD, SEM and UV-DRS. Furthermore, application as a photocatalyst in this study carried out the photodegradation process such as the effect of pH, catalyst loading, contact time and regeneration of material.

EXPERIMENTAL

Chemical and instrumentation

Magnesium nitrate, zinc nitrate, aluminium nitrate, sodium phosphate, sodium tungstate, sodium carbonate, sodium hydroxide and hydrogen chloride were used in this research. Malachite green (MG) is one of the

synthetic dyes which has formula $C_{23}H_{25}CIN_2$ (4-[(4-dimethylaminophenyl)-phenyl-methyl]-N) and maximum absorbance at λmax 616 nm. Characterization of materials was carried using Shimadzu FTIR Prestige-21. Analysis of XRD was conducted out by Rigaku XRD Miniflex-6000 diffractometer. 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 for SEM analysis was conducted by using SEM FEI Quanta 650. Polyoxometalate $K_3[\alpha\text{-PW}_{12}O_{40}].nH_2O$ and $K_4[\alpha\text{-SiW}_{12}O_{40}].nH_2O$ were synthesized according to previous reported literatures (Lesbani et al.,2014).

Synthesis of MgAl/LDH

An amount of 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 hours. MgAl-LDH was synthesized by a modified co-precipitation method by Lesbani et al. (2021). The pH of the mixture was adjusted to pH 10 by adding sodium hydroxide (2M). This mixture was stirred for 6 hours at 85 °C. The resulting product was washed and dried using an oven at a temperature of 110 °C then the MgAl LDH was weighted.

Preparation of composite

The composite were prepared by adding a solution A (1 g of polyoxometalate compound on 50 mL of distilled water) and solution as B (2 g of LDH with 25 mL of 1 M NaOH). The suspension is mixed rapidly under conditions of N_2 gas for 24 hours and then a product washed and dried. Characterization of the results of the intercalation material will be carried out using XRD analysis, FT-IR spectrophotometer, SEM analysis and UV-DRS.

Photocatalytic study

The composite was applied to degrade dye malachite green solutions. Firstly, using optimum catalyst weight with 20 mg/L malachite green was placed in the dark condition and magnetically stirred for 30 achieve a desorption equilibrium. For the photocatalytic test applied at a certain time interval, 20 mL of the suspension with 20 mg/L malachite green. Optimization degradation includes variations in pH at range (1, 3, 5, 7 and

9), for catalysts loading at 0.075, 0.1, 0.25, 0.5, and 0.75 g respectively and degradation contact time at 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, and 120 minutes. This degradation process is implemented using UV light. The percentage of degradation is defined based on the following equation formula: Percentage of Degradation (%) = (Co – Ct)/Together x 100, where Co is the initial dye concentration and Ct is the dye concentration after degradation (Hadnadjev-Kostic et al., 2017).

Regeneration experiment

In order to eximine the reproducibility of the photocatalyst, the suspension after first reaction (2.4) was centrifuged to collect a solid powder. The suspension was precipitate and separate from the solution. Then, the precipitate powder was dried at 70 °C for 24 h. The solid powder was subjected to the next photocatalytic reaction. The above procedure was repeated fifth time to confirm the repeatability of both LDH pristine and LDH composite photoacatalyst.

RESULTS AND DISCUSSION

LDH-based materials

Figure 2 shows the stepwise preparation synthesized catalyst. FT-IR analysis was utilized to determine the surficial groups of LDH. The composites were successfully synthesized. The characterization by FT-IR was also carried out on LDH pristine and LDH composite, it is all described on Figure 2. The FTIR spectrum showed a band between 3420–3500 cm⁻¹, which was indicated from brucite-like layers and interlayer water molecules. Interlayer water also gives medium-intensity (H_2O) absorption close to 1630 cm⁻¹. The 1381 cm⁻¹ band represents CO_3 vibrations (Zhao et al., 2018). The W-O and W-O-W bands are in the band 983-870 cm⁻¹ and 804.84 cm⁻¹ respectively (Wang et al., 2008). Figure 2 shows that these bands are still present in their typical LDH on catalyst LDH-polyoxometalate.

The MgAl-LDH and LDH composites were estimated by XRD on Figure 3. The result shows that the main components of LDH structure is that indicated angles 2θ at 10.39°(003), 20.17°(006), and 34.8°(009). Liu et al. (2022) when XRD patterns show the reflection of (006), (009), (012), (110) and (113), which can be indexed typically

of LDH materials, indicating its MgAl-LDH has been successfully (Zhou et al., 2020). The original diffraction of polyoxometalate compound $K_4[\alpha\text{-}SiW_{12}O_{40}]$, $K_3[\alpha\text{-}PW_{12}O_{40}]$ was shown at 2θ angles of 5-10°, 10-20°, 25-30° (Wang et al., 2008). Due to the use of both polyoxometalate on MgAl-LDH as composite LDH. Based on Figure 3, both peaks are still present of each type of

polyoxometalate in MgAl-$[PW_{12}O_{40}]$ that was at angles 7.73°, 28.6°, 35.6°. on the other hand, the presence of $K_4[\alpha\text{-}SiW_{12}O_{40}]$ in LDH is indicated at 2θ angles 8.61°, 24.27°, 34.96° and 66.34°. The composites were successfully synthesized.

The morphology of as-prepared MgAl-LDH was investigated by SEM analysis, as shown in Figure 4. Morphology can be observed for all
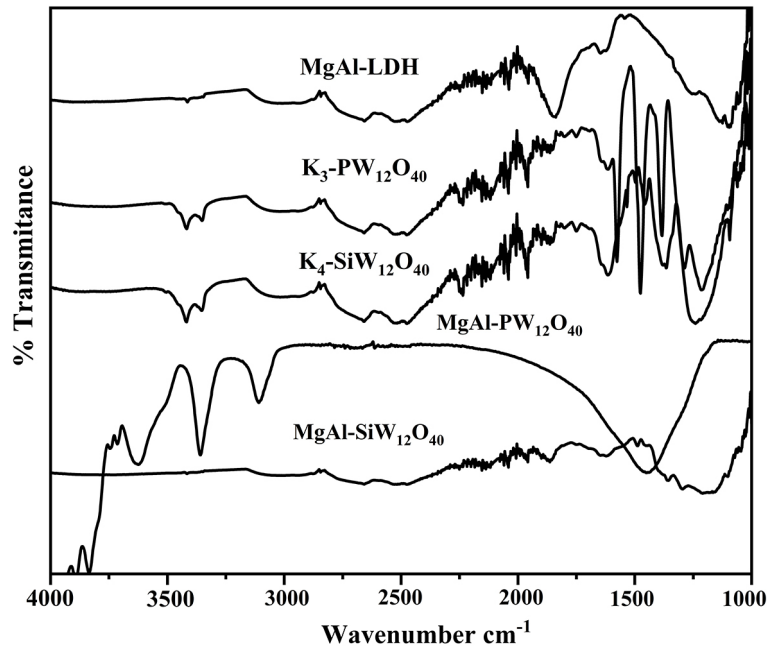

Figure 2. FTIR spectra of catalyst a) MgAl-LDH b) $K_3[\alpha\text{-}PW_{12}O_{40}]$ c) $K_4[\alpha\text{-}SiW_{12}O_{40}]$ d) MgAl-$[PW_{12}O_{40}]$ and e) MgAl-$[SiW_{12}O_{40}]$
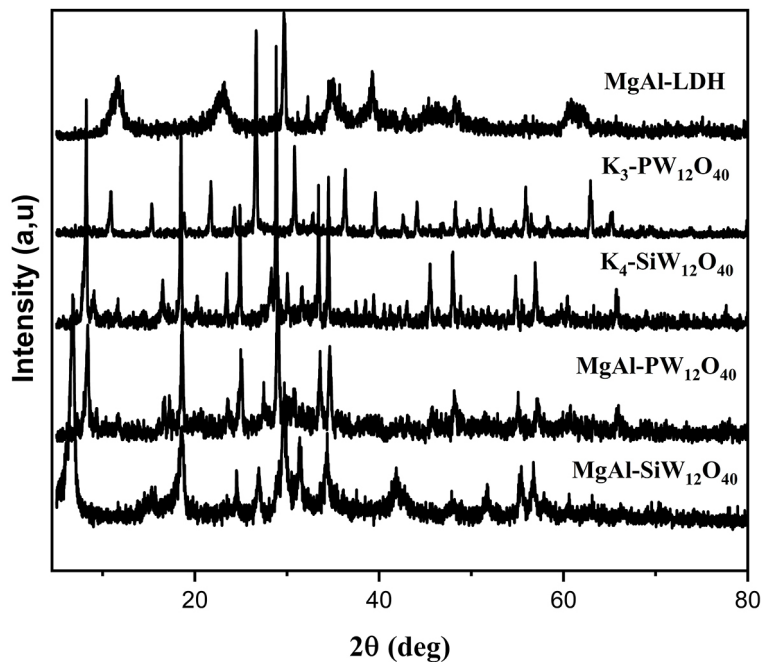

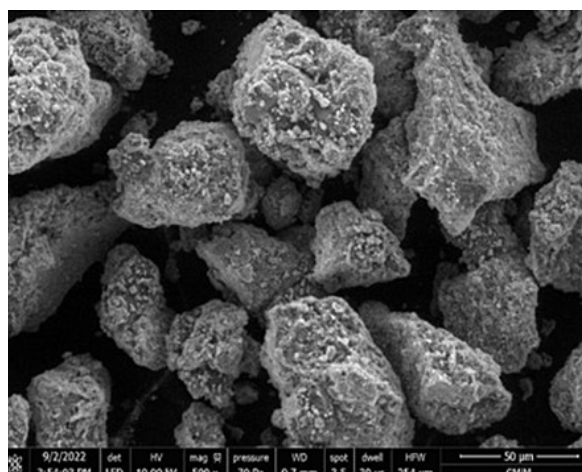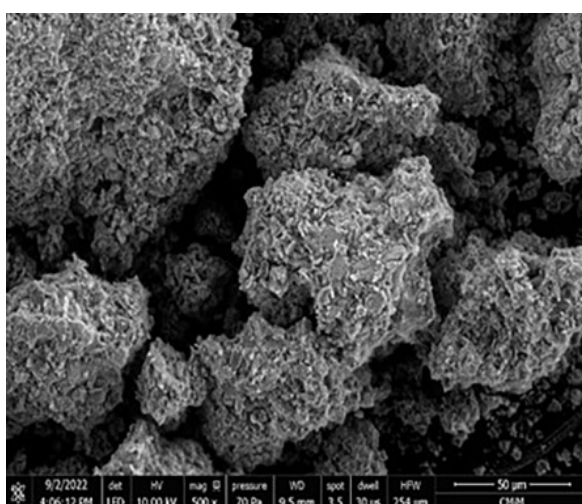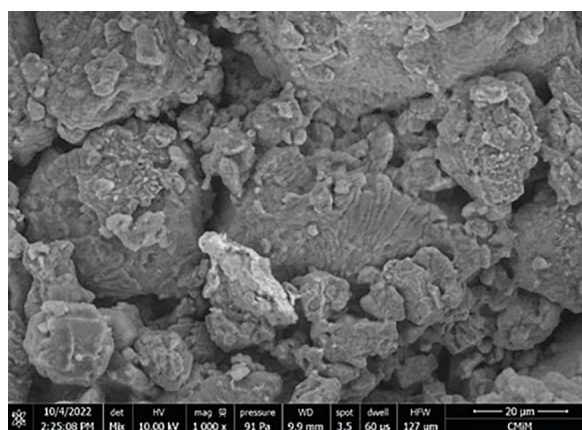**Figure 3.** Diffractogram of catalyst a) MgAl-LDH b) $K_3[\alpha\text{-}PW_{12}O_{40}]$ c) $K_4[\alpha\text{-}SiW_{12}O_{40}]$ d) MgAl-$[PW_{12}O_{40}]$ and d) MgAl-$[SiW_{12}O_{40}]$
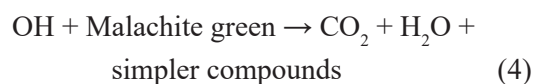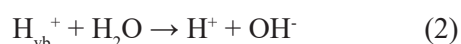
a)

b)

c)

Figure 4. SEM of (a) MgAl-LDH (b) MgAl-$[SiW_{12}O_{40}].nH_2O$ (c) MgAl-$[PW_{12}O_{40}].nH_2O$

MgAl-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 evidence. The morphology structure on synthesizing $[SiW_{12}O_{40}]$ which showed aggregate appearing on the surface material (Hanifah et al., 2022). It is possible to appreciate the existence of a platelet-shaped microcrystal. 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 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 MgAl-$[SiW_{12}O_{40}]$ and MgAl-$[PW_{12}O_{40}]$.

**Effect of optimization variables on malacite green degradation**

The presence of polyoxometalate on Mg degradation on pH in both composite MgAl-$[SiW_{12}O_{40}]$ and MgAl-$[PW_{12}O_{40}]$ can affect the stability of LDH structure. Enhancing the abundant of anionic can give the ability to form positively charged electron holes especially media on pH less than 7 that are effective in creating OH• radicals which has the capability to degrade dye stuff but also cause photodecomposition of polyoxometalate into ions. There is photocatalytic reaction UV irradiated catalyst MgAl-POM will produces a hole (h_{vb}^+) and electrons (e_{cb}) H_2O will form a hysroxyl radical (•OH) which able to degrade malachite green became simply intermediate. Process mechanism photocatalysis using MgAl-POM is shown at the following stage:

$$MgAl\text{-}[POM] + hv \rightarrow MgAl\text{-}[POM] \ (e_{cb}^- + h_{vb}^+) \quad (1)$$

$$H_{vb}^+ + H_2O \rightarrow H^+ + OH^- \quad (2)$$

$$H_{vb}^+ + OH^- \rightarrow •OH \quad (3)$$

$$OH + \text{Malachite green} \rightarrow CO_2 + H_2O + \text{simpler compounds} \quad (4)$$

This causes in this study MgAl-LDH was obtained at pH 7 while pH 1 for $K_3[\alpha\text{-}PW_{12}O_{40}]$ and pH 1 $K_4[\alpha\text{-}SiW_{12}O_{40}]$, while MgAl-$[PW_{12}O_{40}]$ is optimum at pH 1 and MgAl-$[SiW_{12}O_{40}]$ is optimum at pH 7. Figure 6 shows the effect pH on degrading malachite green by catalysts both LDH pristine and LDH composite. Catalysts loading on the degradation process also were examined in this study by implementing at the optimum pH in 120 minutes. Figure 7 show the results of various catalysts loading on degrading malachite green

Table 1. EDX of catalysts

| Element	MgAl-LDH (%wt)	MgAl-Pw (%wt)	MgAl-Si (%wt)
Mg	8.14	6.32	2.51
Al	5.20	6.85	1.62
W	-	2.15	32.54
P	-	-	7.82
Si	-	-	-
K	-	-	3.53
Cl	-	-	9.17
C	13.57	7.98	8.20
O	51.39	45.85	28.78
Na	2.58	4.1	5.83
N	9.12	-	-
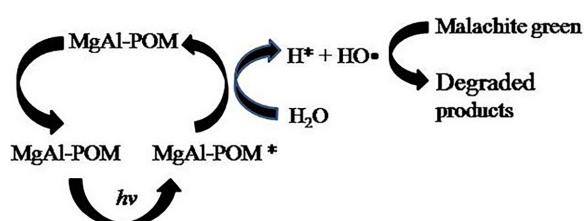
Figure 5. Process mechanism photocatalysis using MgAl-POM

process by both LDH composite and LDH pristine, where it can be seen that MgAl-[PW$_{12}$O$_{40}$] and MgAl-[SiW$_{12}$O$_{40}$] have a degradation percentage that was not much different. Figure 7 shows the effect of variations in MG degradation time by LDH composite and LDH pristine. The value of C/Co during 120 minutes of treatment had increased then with increasing time the amount of

MG degraded increased. The percent MG degradation for MgAl-LDH, MgAl-[PW$_{12}$O$_{40}$], MgAl-[SiW$_{12}$O$_{40}$] was 56.9%, 84.6%, 87.9%, respectively. The percent degradation for K$_3$[α-PW$_{12}$O$_{40}$] and K$_4$[α-SiW$_{12}$O$_{40}$] was 83%, 74.6%, respectively. It appears from the results of the percentage degradation that the catalyst LDH composite has a better ability to degrade MG than LDH pristine.

Regeneration of catalyst

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 degradation percentage after several cycles of repeated use. Figure 8 shows a slight decrease in the degradation ability after the reuse of composite as a photocatalyst. After 5 cycles of
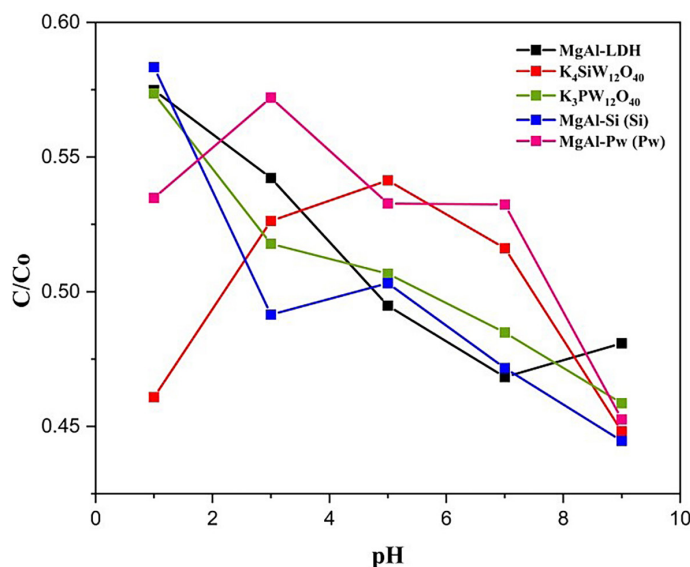
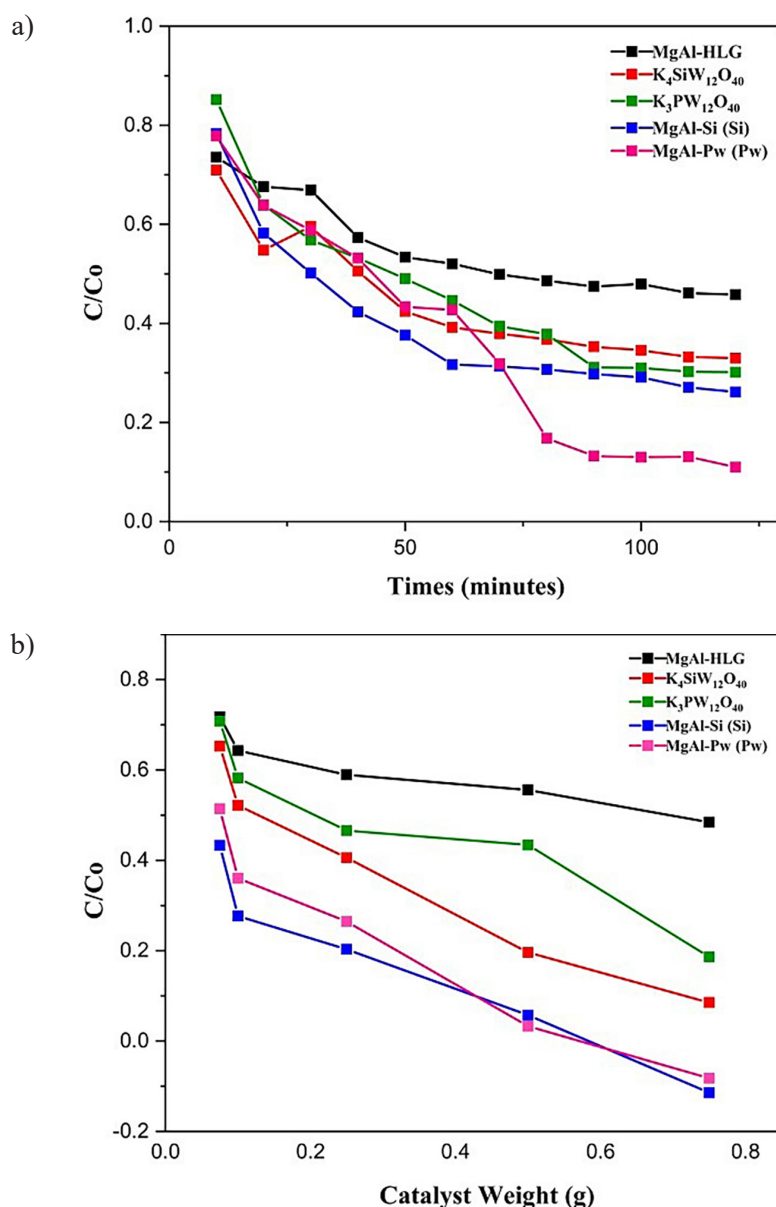**Figure 6.** Effect of pH on MG degradation by catalysts

a)

b)

Figure 7. Effect of a) times and b) catalysts weight on MG degradation by catalysts

using the catalyst there was a decrease %degradation of MgAl-LDH 46.1%. The decrease in %degradation of LDH composite after 5 cycles of use by MgAl-[PW$_{12}$O$_{40}$] and MgAl-[SiW$_{12}$O$_{40}$] were 78.4% and 80.4%, 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 MgAl-[SiW$_{12}$O$_{40}$] was better than the MgAl-[PW$_{12}$O$_{40}$]. Figure 6 shows the spectra FTIR of all materials MgAl-LDH, K$_4$[α-SiW$_{12}$O$_{40}$], K$_3$[α-PW$_{12}$O$_{40}$].nH$_2$O, MgAl-[SiW$_{12}$O$_{40}$] and MgAl-[PW$_{12}$O$_{40}$]. The representation of stretching and bending vibration of FTIR spectra confirmed the good formation of MgAl-LDH, K$_4$[α-SiW$_{12}$O$_{40}$], K$_3$[α-PW$_{12}$O$_{40}$], and both MgAl-[SiW$_{12}$O$_{40}$] and

MgAl-[PW$_{12}$O$_{40}$]. 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 and peak at 1359 cm^{-1} also represents the intercalated NO$_3^-$ 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 of polyoxometalate. It also shows that band on MgAl-[PW$_{12}$O$_{40}$] are 795.4 [47]. IR spectra data [PW$_{12}$O$_{40}$] have remained in the MgAl-LDH. Figure 10 shows that these bands are still present for the catalyst that has degraded MG.

Table 2. The value of %degradation malachite green

Catalyst	% degradation malachite green	Ref.
TiO_2/ZnO	69	Mohamed et al. (2018).
TiO_2 nanotubes	80	Prado et al. (2009)
Pc/ZSWP	79.2	Gupta et al. (2015)
CH/ZnO	54	Saad et al. (2020)
Guar gum/Al_2O_3	80	Pathania et al. (2016)
$FeTiO_2$	77	Asilturk et al. (2009)
MgAl-[$PW_{12}O_{40}$]	84.6	In this study
MgAl-[$SiW_{12}O_{40}$]	87.8	In this study
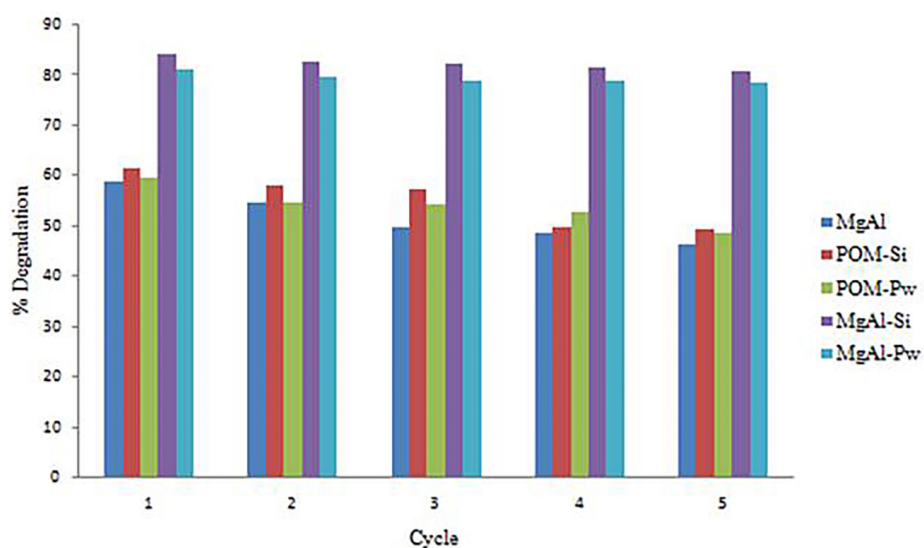
Figure 8. Regeneration of catalyst in the fifth cycle
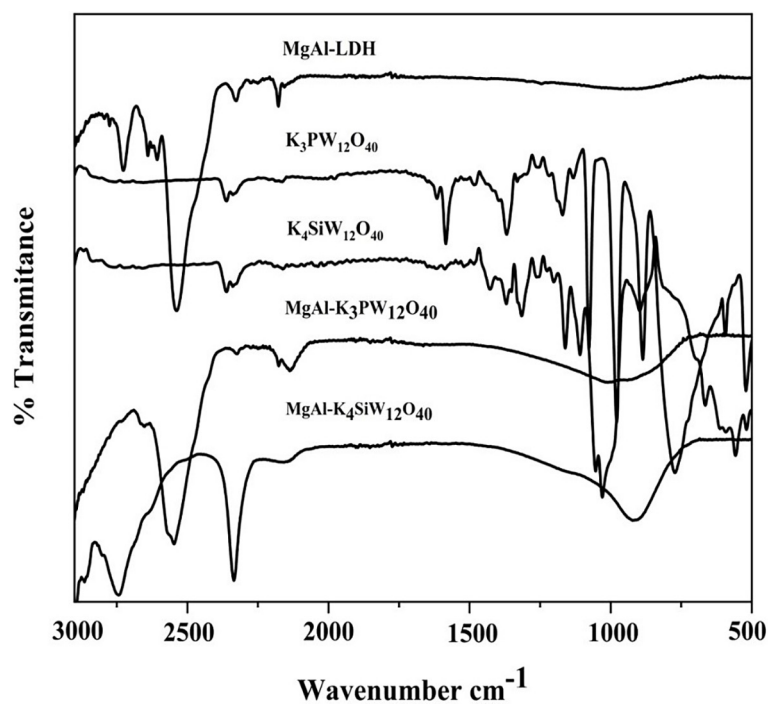
Figure 9. Spectra FTIR after regeneration 5 cycle

CONCLUSIONS

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. Modifying of MgAl-LDH materials, which form composites with both polyoxometalate $K_3[\alpha-PW_{12}O_{40}]$ and $K_4[\alpha-SiW_{12}O_{40}]$ resulted in an enhanced capability for photodegradation of cationic dyes MG. Both composite MgAl-$[PW_{12}O_{40}]$ and MgAl-$[SiW_{12}O_{40}]$ composites also improved the regeneration performance of MG degradation compared to MgAl-LDH. The characterization results after fifth cycle regeneration using FTIR of materials that have degraded MG show that LDH pristine still has an LDH structure, and LDH composite also still has 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 MgAl-$[PW_{12}O_{40}]$ and MgAl-$[SiW_{12}O_{40}]$ composites were better than LDH pristine. MgAl-$[SiW_{12}O_{40}]$ composite has better performance activity, band gap energy, and reusability degradation than MgAl-$[PW_{12}O_{40}]$.

Acknowledgements

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