COMMUNICATIONS IN SCIENCE AND TECHNOLOGY
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Photocatalytic of anionic dyes on Congo red with M^{2+}/Al (M^{2+}=Ni, Mg, and Zn) layered double hydroxide intercalated polyoxometalate

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Article history:
Received: 28 March 2023 / Received in revised form: 29 May 2023 / Accepted: 1 June 2023

Abstract

The modification catalysts of layered double hydroxide (LDH) with polyoxometalate based on Keggin type were prepared and characterized using X-Ray, FTIR, and SEM to confirm the layered double hydroxide structure. Intercalation was successfully synthesized and showed a heterogeneous aggregate resulted from SEM analysis. The degradation parameters of LDH pristine and LDH composite were determined by observing a number of factors such as pH, catalyst weight, and degradation time. The modification material resulted by preparation material LDH and polyoxometalate (POM) successfully resulted in the lower band gap value compared to material pristine LDH allowing LDH polyoxometalate as photocatalysts to show good photocatalytic activities. The NiAl-$SiW_{12}O_{40}$ material had the highest percentage of degradation removing Congo Red up to 86% degradation when compared to another composite material, yet it was still significantly better than LDH pristine. The result showed that the LDH composite presented excellent photocatalytic activity in reducing Congo Red.

Keywords: LDH; polyoxometalate; photocatalytic; Congo red

1. Introduction

Dye is among the critical industrial anionic direct extensively used in production that has been determined to pose health-confirmed hazards. One of the toxic anionic azo dyes, Congo Red (CR), due to its stable structure and high affinity toward water and organic solvents, has been used in various applications in industrial production to color textile industries, printing, paper and medical disinfectants [1]. Dye-related water contamination is hazardous to aquatic life and mutagenic to humans [2]. CR is one of the highly toxic dyes and is resistant to many treatment processes.

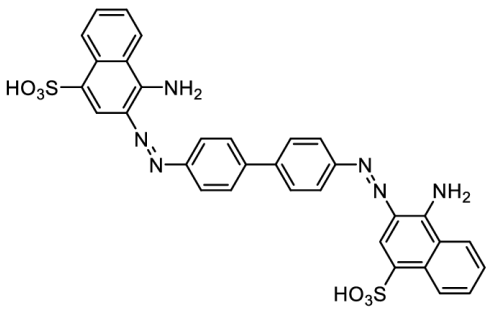

Fig. 1. The structures of the Congo Red

Nonetheless, despite their speed, some of them lose their suitability in removing any dangerous organics to restrict the introduction of enduring pollutants into the ecosystem [3]. Numerous methods for treating wastewater effluents are inexpensive, effective, and environmentally safe for decontaminating the synthetic colors. Photodegradation has been the subject of more recent research not only as a color converter but also as a decomposing substance. Photocatalytic dye removal in sunlight is one of the most intriguing and compelling processes [4]. Using a variety of pure and modified photocatalysts, photocatalysis has been thoroughly researched for the efficient degradation and removal of organic pollutants in an aqueous solution [5]. In view of its low cost, high efficiency, simple synthesis, and biocompatibility, LDH is one of those that are most frequently used [6]. Several studies have successfully examined and utilized LDH as a photocatalyst for pollutants and employed a MgAl-LDH catalyst to digest 70% of oxytetracycline and 90% of sodium naproxen [7,8]. In other studies, Rhodamine B was degraded using ZnAl-Ce, and ZnAl-LDH was modified [9]. Yang et al. successfully broke down Tetracycline from Zn/Fe LDH [10].

Due to the enhanced molecular level and charge density of POMs that incorporate transition metal elements, transition metal substituted POMs have significant catalytic characteristics [11]. The group of metal-oxygen clusters, known as polyoxometalates (POMs), has numerous uses in catalysis, waste management, and magnetism. POMs' essential

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https://doi.org/10.21924/cst.8.1.2023.1170

characteristics, such as composition, solubility, charge density, size, and form, impact the applications for which they are used. POM research is primarily interested in combining transition metal complexes to produce POM-based hybrids [12]. The band gap energy of polyoxometalate composite tends to be lower than that of the basic structure. Research [13] reported that the basic structure of the material, namely $Cu_5(bpy)_7.2H_2O$ had a band gap of 4.32 eV and polyoxometalate of 4.73 eV while as a composite it resulted in lower band gap of 1.83 eV and was able to be degraded. The same information is regarding the changes in lower band gap values-based material CoAl-LDH [14]. Rhodamine B was successfully destroyed by the polyoxometalate "$XM_{12}O_{40}$" (X = P, Si, M = W, Mo) [1]. Using CoW-TiO_2 nanocomposite made from Keggin-type cobalt-substituted phosphotungstates, Rafiee et al. [15] investigated the degradation of methyl orange, and when exposed to UV light, carbon nitride was produced with $H_3PW_{12}O_{40}$ doping [12].

A series of polyoxometalates containing $K_3PW_{12}O_{40}$ and $K_4SiW_{12}O_{40}$ intercalated with LDH (Mg, Ni, and Zn) were prepared using the coprecipitation method. The preparation of modified material LDH with polyoxometalate enhanced the photodegradation process. Multiple techniques were introduced to study morphology, composition and photoelectric characteristics (SEM, XRD, FTIR and UV-DRS). The photocatalytic performances of the synthesized and composited material were investigated under visible light for the degradation of Congo Red dye.

2. Materials and Methods

2.1. Chemical and instrument

This study employed sodium phosphate (Na_3PO_4), sodium tungstate (Na_2WO_4), sodium carbonate (Na_2CO_3), magnesium nitrate ($Mg(NO_3)_2$, zinc nitrate ($Zn(NO_3)_2$, aluminum nitrate ($Al(NO_3)_3$, sodium hydroxide (NaOH), and hydrogen chloride (HCl). All materials were purchased from Sigma Aldrich and Merck. One of the synthetic dyes, Congo Red ($C_{32}H_{22}N_6Na_2O_6S_2$) had a maximum absorbance of 498 nm. To characterize the materials, a Rigaku XRD Miniflex-6000 diffractometer CuKα as the radiation source, 30 kV voltage, 10 mA electricity, and 2θ ranging from 10° to 90° were used to determine the crystallinity structure. Shimadzu FTIR ALPHA Bruker (Platinum-ATR) carried performed the qualitative analysis of functional groups in a chemical compound. Meanwhile, the UV-Vis Biobase BK-UV 1800 PC spectrophotometer was used to measure the degradation. SEM analysis was performed to look at the surface image of a material (FEI Quanta 650).

2.2. Synthesis of (Mg, Zn, and Ni) LDH

To synthesize the LDH phase, the LDH precursors were modified by using a coprecipitation method approach to synthesize LDH[16] The specifics are displayed as follows. A mixture of 9.3 g of aluminum nitrate and 18.75 g of magnesium nitrate was stirred in water for 2 hours. Sodium hydroxide was then added to the mixture to change its pH into 10. The MgAl LDH was weighed after the mixture had been agitated for 6 hours at 85°C.

Lesbani et al. (2021) explained that the ZnAl-LDH is synthesized in the second step. Once pH 10 was achieved by adding sodium hydroxide (2M) and 100 mL each of zinc nitrate and aluminum nitrate, the mixture was agitated for 18 hours at 85°C. The third step referred to the synthesis of MgAl-LDH using the coprecipitation method by mixing 18.75 g magnesium nitrate 0.75 M with 9.3 g aluminum nitrate 0.25 M by adjusting sodium hydroxide to reach pH 10 and stirring for 2 hours. Then, the resulting product was washed and dried at a temperature of 80ºC.

2.3 Preparation of catalyst

LDH was modified with a polyoxometalate compound, Keggin $K_4[\alpha\text{-}SiW_{12}O_{40}]$ and $K_3[\alpha\text{-}PW_{12}O_{40}]$. The composite was mixed by adding 1 g polyoxometalate and 2 g LDH with the addition of sodium hydroxide 1 M. The suspensions were created rapidly under the condition of N_2 gas for 2 days. The suspension subsequently was cleaned and dried for 12 hours at 80°C.

2.4 Photocatalytic activity

The sample's photocatalytic activity was assessed in a 20 mg/L. In the first step, Congo Red was left in the dark and agitated for 30 minutes on a magnetic desorption equilibrium. The photodegradation technique used in optimizing degradation in 20 mg/L Congo Red comprised pH variations in 3-11, catalyst (0.02-0.1 g), and shaker based on contact time variation on the degradation process (10-120 minutes). Meanwhile, UV radiation was used to carry out the photodegradation process using UV light W (4x 20 watt) on the wavelength of 665 nm. After the photodegradation process, the degraded media was measured by UV light to measure the % of degradation. Based on the following equation formula, the percentage of degradation was then defined: The formula for percentage of degradation (%) was $(Co - Ct)/C_o \times 100$ where Co is the dye concentration before degradation and Ct is the dye concentration after degradation [17].

3. Results and Discussion

3.1. X-Ray diffraction analysis (XRD)

Figure 2 demonstrates the XRD pattern of pure LDH and LDH intercalating polyoxometalate nanoparticles synthesized using the coprecipitation method. The material determined the structure of the nanoparticle. Here, the typical peaks of NiAl-LDH were detected at 11.6º, 23.1º, and 35.1º. Meanwhile, the material pristine of SMgAl-LDH at 10.3º, 20.1º, and 34.8 º and ZnAl-LDH were detected at 10.3º, 20.1º, 34.6º, and 60.5º. The XRD spectra obtained for LDH composite intercalated with $K_3PW_{12}O_{40}$ were 8.26º, 11.34º, 29º, and 35.1º for NiAl-$PW_{12}O_{40}$, and for MgAl-$PW_{12}O_{40}$ it showed the peaks at 7.73º, 28.6º, and 35.6º. For ZnAl-$PW_{12}O_{40}$ the characteristic showed the peak at 10.76º, 26.59º, 30.8º and 63.11º. The second material intercalated using $K_4SiW_{12}O_{40}$ showed the peaks respectively at NiAl-$SiW_{12}O_{40}$ at 10.76º, 26.59º, 30.8º and peak at 7.73º, 28.6º and 35.6º MgAl-$SiW_{12}O_{40}$. For ZnAl-$SiW_{12}O_{40}$

it showed the characteristic peak at 8.61°, 25.27°, 34.96°, and 66.34°. The material composite of NiAl-LDH, MgAl-LDH and ZnAl-LDH showed the characteristic of LDH and polyoxometalate compound indicating that the preparation of material composite was successfully prepared. This result of material composite showed the successful preparation of material composite by showing the peaks of LDH material and polyoxometalate. Polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}]$ showed a diffraction peak at 2θ= 6-8°, usually at low range peak and high peak at 2θ = 24-29°, usually observed in Keggin type $[XM_{12}O_{40}]^{n-}$ [18].

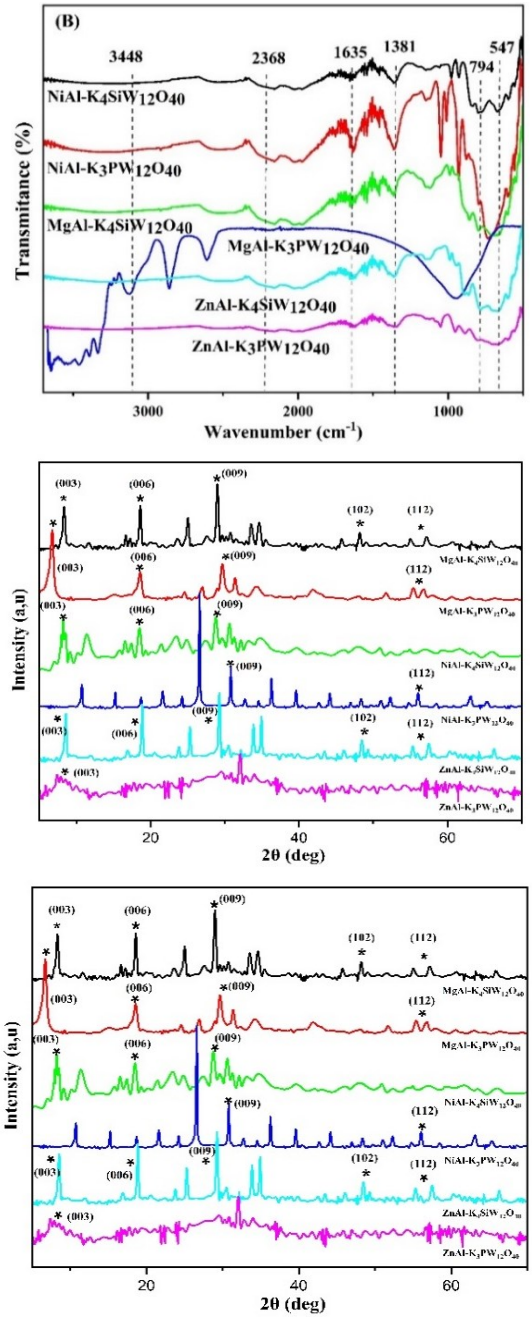

Fig. 2. Diffraction of LDH pristine (a) and LDH composite (b)

3.2 FTIR characterization

An infrared spectrum of LDH pristine, LDH composite, and polyoxometalate compound revealed the surface functional groups of LDH. There were six almost the same with the characteristic absorption bands in the FTIR figure of the LDH composite. The absorption band at 3448 cm^{-1} corresponded to The O-H stretching vibration of the water in interlayer LDH at1635 cm^{-1} showed the vibration of H_2O. The absorption band at 2368 cm^{-1} indicated for the vibration of CO and 1381 cm^{-1} corresponded to the CO_3^{2-}. The low wavenumber from 400 – 800 cm^{-1} could be attributed to the metal hydroxide sheets in the brucite-like lattice (M-O and O-M-O) (Li et al., 2018). FTIR spectrum of polyoxometalate contained the bands at 925-789 cm^{-1} (W-O-W), 979 (W=O), and 1020 cm^{-1} (W-O) [18]. Mirzaei et al. [19] interpreted α-Keggin SiW_{12} at bands 813, 882, 927, and 973 cm^{-1} for W-O. After LDH intercalated polyoxometalate compound, the spectrum of the LDH composite was successfully modified by showing the absorption band at 794 – 547 cm^{-1}. Figure 3 shows that generally LDH composites were maintained by support of polyoxometalate.

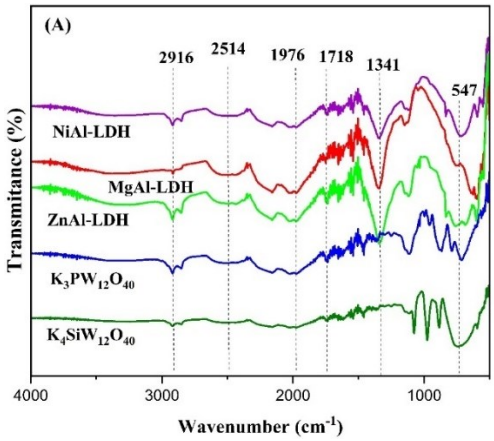

Fig. 3. FTIR spectra of LDH pristine (a) and LDH composite (b)

3.3 SEM analysis

The morphology of LDH pristine and LDH composite was investigated by SEM analysis as shown in Figure 4 showing an aggregate pore on the surface material of NiAl-LDH with a small variation. MgAl-LDH and ZnAl-LDH showed a similar pore aggregate; while, material composite NiAl-polyoxometalate showed polyoxometalate significantly distributed on the surface of LDH by showing various small particle size tricks to the NiAl-LDH. The composite material showed a heterogeneous shape with a small aggregate formation. Furthermore, SEM analysis on material composite showed the same character, indicating aggregate appearing on the surface material. [20] synthesized composite LDH with polyoxometalate appeared in aggregate formation. Figure 4 shows SEM image and particle size calculation using the ImageJ application for LDH pristine and LDH-polyoxometalate. The figure shows that the material was in the mesoporous shape in which all materials were in the range of particle size of 2-50 nm.

3.4 UV-DRS analysis

The characterization of LDH materials and composite materials was done using UV-DRS instruments to determine the band gap energy of the catalyst material and the ability of the catalyst to absorb light. In this study, the band gap energy

of material in degrading organic compounds was used. The results showed that the energy gap trend of the NiAl-LDH composite was better than that of the MgAl-LDH and ZnAl-LDH composite materials. This confirmed that NiAl-LDH had the better degradation of Congo Red compared to MgAl-LDH and ZnAl-LDH composite. [21] confirmed that the lower the band gap energy in producing more OH radicals, the easier the process of photodegradation of organic compounds will be.

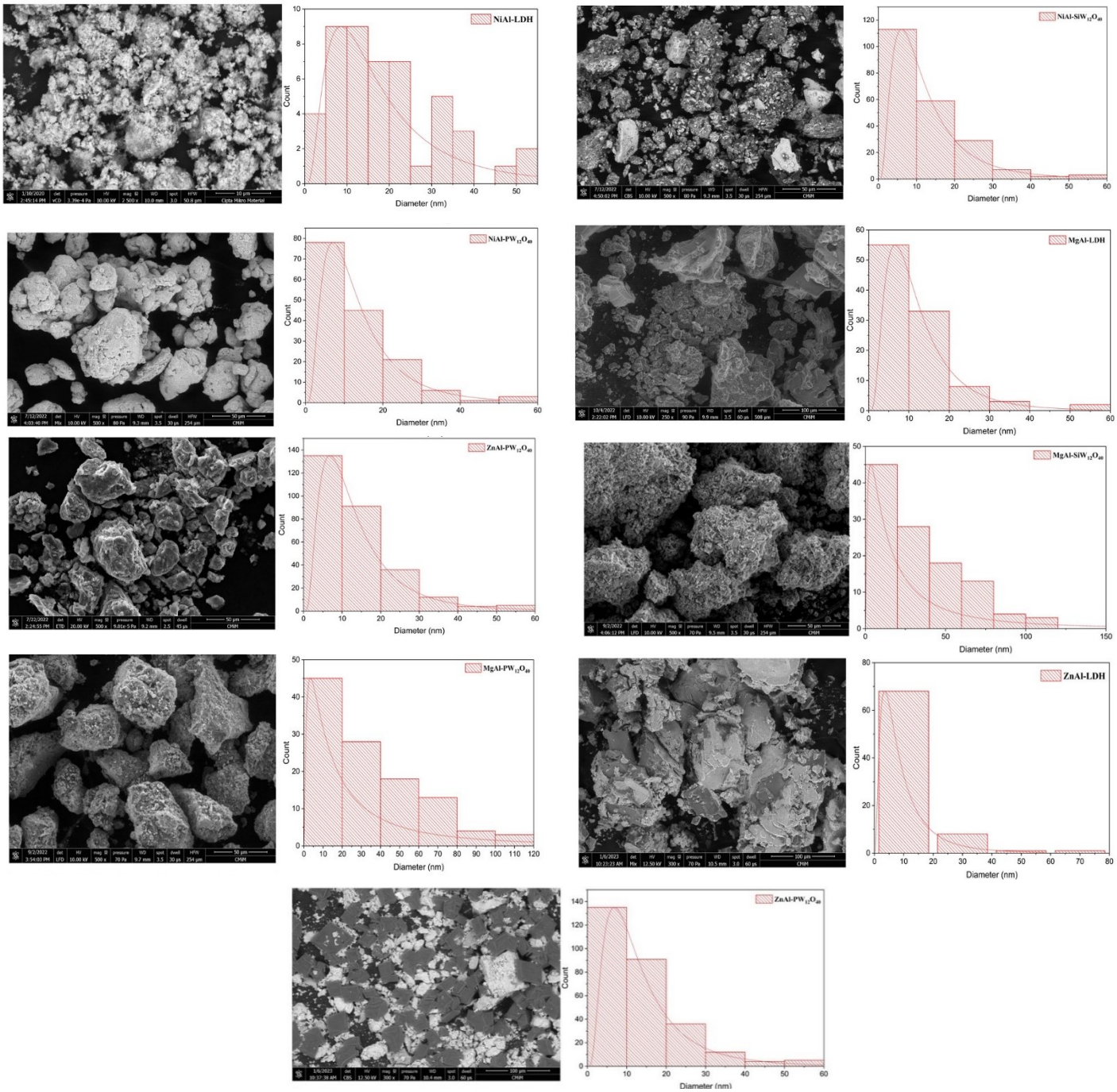

Fig. 4. SEM Analysis of LDH pristine and LDH composite

3.5 Effect of reaction time

The effect of reaction time for the material pristine and material composite was reached at 2 hours of reactions times. Increasing the reaction time for 2 hours was able to convert the Congo Red dye. Furthermore, extending the reaction time for one or more hours would no longer benefit the process in which it increased the time followed by the degradation of the amount of Congo Red. The highest conversion of the material composite was achieved at 80 %. The more reaction time would be exhausted for removing Congo Red. Here, the percentage degradation of Congo Red for MgAl-LDH, NiAl-LDH, ZnAl-LDH, MgAl-[$PW_{12}O_{40}$], MgAl-[$SiW_{12}O_{40}$], NiAl-[$PW_{12}O_{40}$], NiAl-[$SiW_{12}O_{40}$], ZnAl-[$PW_{12}O_{40}$], ZnAl-[$SiW_{12}O_{40}$] was 73%, 71%, 70%, 80%, 84%, 82%, 86%, 73%, and 66%, respectively.

3.6 Effect of catalyst weight

Hanifah et al. [22] reported that the degradation of

malachite green achieved its optimum condition using the highest variation of catalyst weight. In this research, the catalyst weight of 0.1 g met the 20-ppm reactant of Congo Red that was sufficient for catalyzing the Congo Red on material pristine of NiAl-LDH, MgAL-LDH, and ZnAl-LDH. For material composite, there were NiAl-$PW_{12}O_{40}$, NiAl-$SiW_{12}O_{40}$, MgAl-$PW_{12}O_{40}$, MgAl-$SiW_{12}O_{40}$, ZnAl-$PW_{12}O_{40}$, ZnAl-$SiW_{12}O_{40}$ found at 0.1 g. All catalysts were the effective conversion of Congo Red as shown in Figure 7. The use of catalyst weight under that value, in this research (0.02 g), was not quite much to degrade Congo Red during the above value (e.g., 0.04 to 0.08 g) reaching the maximum % degradation. The highest dosage material was used to reach the highest % degradation. Here, the higher the dosage used, the more material can bind and degrade Congo Red. Nevertheless, the catalyst weight should be on the precise value. This research in catalyst systems has been in accordance with the condition of the experiment. Figure 6 shows the results of various catalyst weights on degraded Congo Red. The material pristine and material composite had the value of %degradation that was not much different.

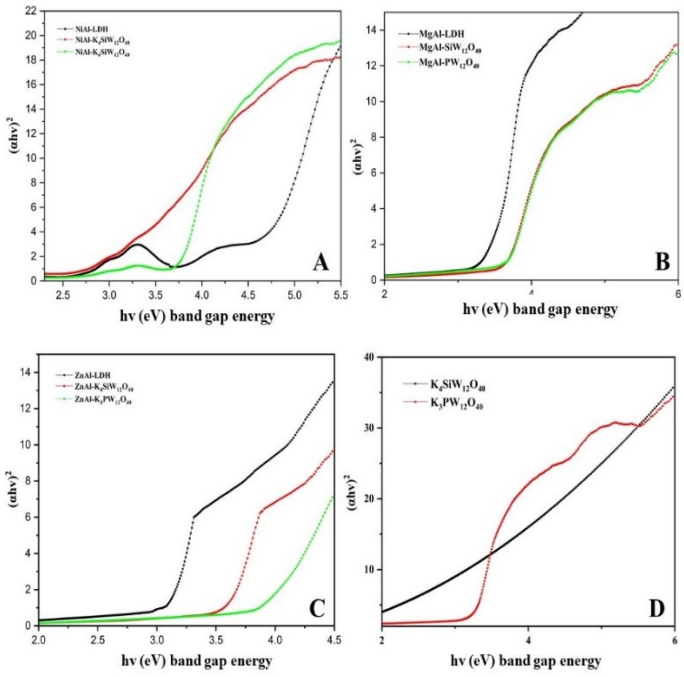

Fig. 5. UV-DRS Analysis of LDH pristine and LDH composite

3.6 Effect of catalyst weight

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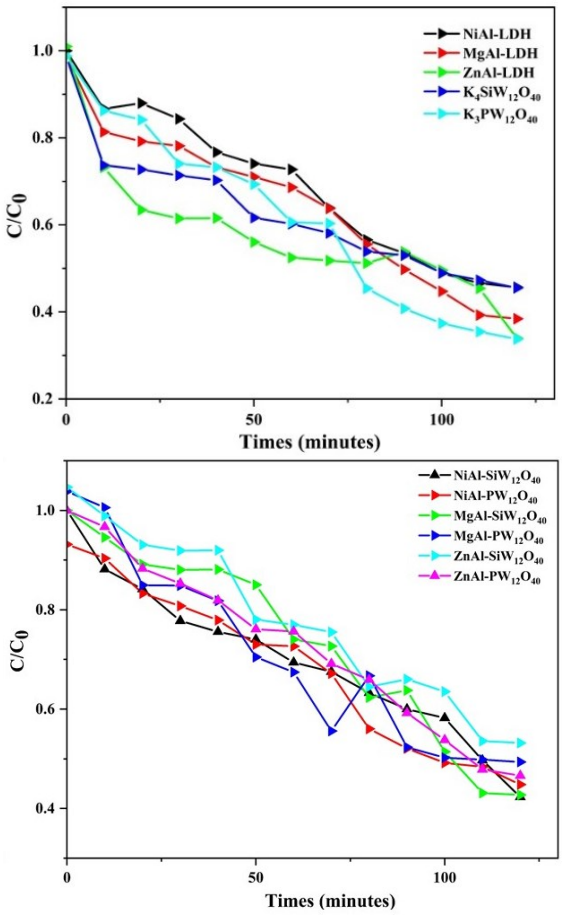

Fig. 6. Effect of time on degradation congo red

3.7 Effect of pH

The catalytic process degradation for Congo Red was studied as a function of the pH of the solutions (3, 5, 7, 9, and 11). The adjustment pH of the solution was carried out before irradiation using NaOH and HCl. Figure 7 shows that the photodegradation behavior for each material was different. LDH materials (i.e. NiAl-LDH, MgAl-LDH, and ZnAl-LDH) showed that the pH optimum obtained was at pH 7 respectively. In the experimental conditions, the optimum pH material LDH was factored at pH 7, such as the result from other author. The behavior of the material composite was kindly different probably due to the existence of polyoxometalate after intercalation. This modification process aimed at enhancing anionic that could form the positively charged electrons. A photocatalytic reaction of UV irradiated catalyst LDH-POM could produce a hole (h_{vb}^{+}), and electrons (e_{cb}) H_2O formed a hydroxyl radical (•OH), able to degrade Congo Red to be simply intermediated. Composite material such as MgAl-[$PW_{12}O_{40}$] was optimum at pH 1, MgAl-[$SiW_{12}O_{40}$] was optimum at pH 7, NiAl-[$PW_{12}O_{40}$] at pH 1 and NiAl-[$PW_{12}O_{40}$]

at pH 7, ZnAl-[$PW_{12}O_{40}$] at pH 5 and ZnAl-[$PW_{12}O_{40}$] at pH 1. Figure 7 shows the effect of pH on degrading Congo Red by catalysts, both LDH pristine and LDH composite. The optimum material degraded at lowest pH because of pH less than 7 is effective in forming OH• radicals, which can degrade dyestuff and cause the photodecomposition of polyoxometalate into ions.

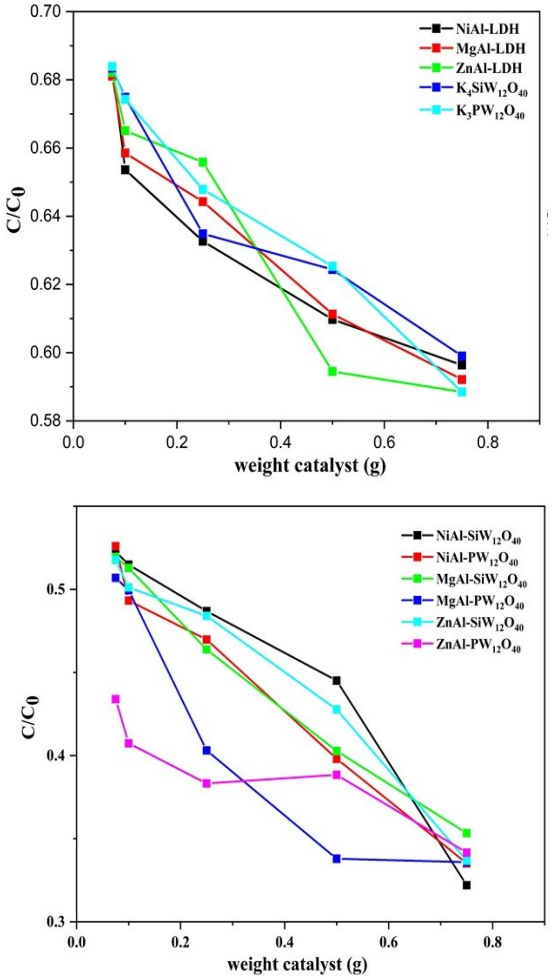

Fig. 7. Effect of catalyst weight on degradation Congo Red

Table 1. The value of %degradation Congo red

Catalyst	%degradation Congo red	Ref.
Nb_2O_5/ZnAl-LDH	85	[23]
CoMgAl-borate LDO	86	[24]
MgZnCr-TiO_2	90	[25]
Mg/Al-TiO_2	73	[26]
ZnAl-[$PW_{12}O_{40}$]	73	In this study
ZnAl-[$SiW_{12}O_{40}$]	66	In this study
MgAl-[$PW_{12}O_{40}$]	73	In this study
MgAl-[$SiW_{12}O_{40}$]	84	In this study
NiAl-[$PW_{12}O_{40}$]	82	In this study
NiAl-[$SiW_{12}O_{40}$]	86	In this study

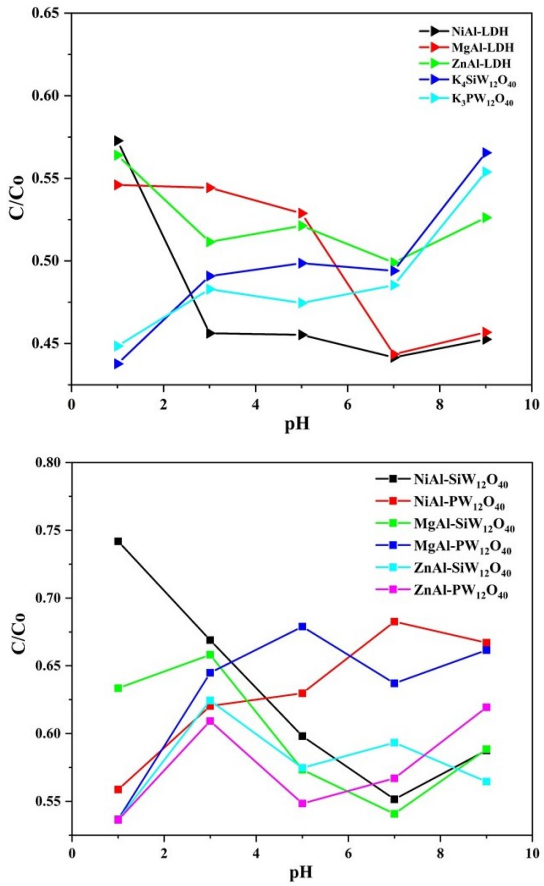

Fig. 8. Effect of pH on degradation Congo red

4. Conclusion

The successful synthesis of intercalation revealed a heterogeneous aggregate. By keeping the track of variables, including pH, catalyst weight, and degradation time, researchers were able to estimate the degradation characteristics of LDH pure and LDH composite. Here, the NiAl-$SiW_{12}O_{40}$ material had the highest percentage of degradation after Congo Red was removed, reaching up to 80% degradation compared to another composite material. The dosage catalyst was reached using 0.75 mg and the optimum pH of NiAl-$SiW_{12}O_{40}$ was reached at pH 7. However, it was still significantly better than LDH pure. The outcome demonstrated the strong photocatalyst activity of the LDH composite for reducing Congo Red.

Acknowledgements

The authors thank the Research Center of Inorganic Materials and Complexes FMIPA Universitas Sriwijaya for the valuable help in this research.

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