

Modification of pristine layered double hydroxide to form metal oxide composites as an anionic dye photodegradation catalysts

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Abstract

Pristine layered double hydroxide (LDH) clay material in the form of Mg/Al LDH was impregnated with metal oxides to form Mg/Al-metal oxide composite catalysts. These composites were then used as the catalysts for the photodegradation of Congo red (CR) dyes. The composites were calcined at a relatively low temperature of 300°C and characterized using SEM and DRUV. In this report, the photodegradation of CR as anionic dye was optimized based on the variables of pH, catalyst weight and time radiation. The stability of the catalyst was studied from the percent degradation in the recycling test. The catalyst characterization that has undergone 5th regeneration cycles was carried out using XRD and FTIR. The results of this study revealed that catalysis by Mg/Al-metal oxide composites resulted in a better percent degradation, rate constant and materials stability than pristine Mg/Al LDH. Mg/Al LDH, Mg/Al-TiO₂ and Mg/Al-ZnO catalyzed the photodegradation of CR by 65.97%, 73.06 % and 86.86%, respectively.

Keywords: Mg/Al LDH; photodegradation; congo red; TiO₂; ZnO

1. Introduction

Congo red (CR) an allergenic dye is a benzidine-anionic diazo dye. The aromatic amines of this dye can be metabolized into benzidine, which is a carcinogen [1]. The photocatalysis of degradation is an effective way for the fundamental removal of CR [2]. Recently, layered double hydroxide (LDH) is more frequently believed to be a potential photocatalyst. It has a formulation in the form of $[M^{II}_{1-x}M^{III}_x(OH)_2](A^n)_{x/n} \cdot mH_2O$ in which M^{II} symbolizes a divalent cation, M^{III} is a trivalent cation, and Aⁿ⁻ represents an organic or inorganic anion between 2 layers of the cationic structure [3]. The good photocatalytic activity of LDH is able to efficiently degrade organic dyes [4]. LDH synthesis is relatively simple and economical both in a laboratory scale and even in an industrial scale [5].

It is potential for LDH application if it has the same basic/pristine structure with another research field. Researches on the application of LDHs, among others, Mg/Al LDH in polyether sulfonate as energy storage device [6], Co/Al LDH in polyacrylonitrile for water purification [7], and PEG-Mg/Al LDH-FeO as material carrier for sorafenib was an anti-liver cancer drug [8]. In this case, MgPd/Al LDH was as a glycerol hydrogenolysis reaction catalyst [9] and Mg/AlAu LDH was as a nitrophenol hydrogenation catalyst [10]. Other applications in

the field of analytical sensors include Cu/Al LDH-graphene as a glyphosate sensor for an aquatic pollutant [11] and Mg/Al LDH as a sensor for volatile organic compounds [12].

LDH composited with metal oxide TiO₂ will facilitate electron transfer, thereby inhibiting recombination in the band gap for both. Photocatalytic degradation using TiO₂ and ZnO oxides are economical, and efficient approach compared to organic materials and easy to implement in managing any organic pollutants [3]. TiO₂ and ZnO are most commonly used as the photocatalysts for the degradation of organic pollutants [13]. LDH material is used as a TiO₂ support material because of its good dispersion to help to interact with pollutants [14]. ZnO, meanwhile, has the excellent chemical stability and photosensitivity efficiency of the catalyst [15]. LDH, when composited with ZnO, will avoid aggregation [16]. Al³⁺ cations when used in LDH-ZnO composite structures will be beneficial for catalytic activity and stability [17].

The relatively low band gap energy value of the catalyst facilitates photodegradation. TiO₂ material has a relatively low energy band gap of around 3.22. Similarly, the band gap energy of ZnO is only 3.21 eV; while ZnS is 3.54 eV [18,19]. Meanwhile, the band gap energy of NiO is higher around 3.6 - 4 eV [20]. Saju et al. obtained a band gap energy of NiO 3.67 - 3.77 eV [21]. Baliarsingh et al. varied the divalent cations of LDH, i.e. Zn, Ni and Co. The band gap energy data of structures containing Ni and Co are higher than those containing Zn, while those containing Cu absorbed radiation lower for photodegradation compared to those containing Zn [22].

Studies on the degradation of organic pollutants using

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composite photocatalysts based on Mg/Al LDH have been carried out. Mg/Al LDH modified with Ni³⁺ where Ni²⁺ was oxidized by NaClO during synthesis, and used to degrade CR [23]. The study of Mg/Al-TiO₂ and Zn/Al-TiO₂ with a ratio of M²⁺/M³⁺ = 2 found that Mg/Al-TiO₂ catalyzed the degradation of Orange II better than Zn/Al-TiO₂ [24]. Mg/Al-TiO₂ and Mg/Fe-TiO₂ were synthesized by solgel and calcined at 550°C and it showed that Mg/Al-TiO₂ had a better percentage phenol degradation than Mg/Fe-TiO₂. This study intended to compare the effect of using trivalent cations Al and Fe on the percent degradation [19]. Mg/Al LDH material was hydrothermally composited with two other materials: ZnO and C₃N₄ to form Mg/Al-ZnO-C₃N₄ as a catalyst for the degradation of methylene blue [25]; Mg,Zn/Al-TiO₂, which degraded rhodamine-B [26]; Mg,Zn/Cr-TiO₂ degraded CR [2] and Mg/Al-TiO₂ calcined at a temperature of 500°C to degraded dimethylphthalate [27].

Mg/Al LDH materials are often synthesized by coprecipitation technique. A number of researches involved calcining Mg/Fe-TiO₂ at 500°C as a photocatalyst for herbicide degradation [28]; calcining Mg/Al-TiO₂ at 450°C and 750°C as a photocatalyst for methyl orange degradation [29] and calcining Mg/Al-ZnO at 500°C as a photocatalyst for malachite green degradation [30]. Mg/Al LDH as pristine LDH needs to be modified to form its oxide structures, namely Mg/Al-TiO₂ and Mg/Al-ZnO to increase the catalytic ability in degrade CR. Higher catalytic ability is characterized by the increase in percent degradation and kinetic constant before and after modification. The novelty of this study included using a relatively low calcination temperature of 300°C for the preparation of Mg/Al-TiO₂ and Mg/Al-ZnO materials.

2. Materials and Methods

2.1. Materials and instrumental

The chemicals used in this study included Mg(NO₃)₂.6H₂O, Al(NO₃)₃.9H₂O, TiO₂, NaOH, Na₂CO₃ supplied from Merck, and ZnO produced from LOBA Chemie, HCl obtained from Mallinckrodt LabGuard, and water provided from Inorganic Materials and Coordination Complexes Research Group. The characterization of materials were performed by SEM Quanta-650 Oxford Instrument, DRUV Jasco V-760, Rigaku XRD Miniflex-6000 diffractometer, FTIR Bruker. Congo red was analyzed by UV-Vis Biobase BK-UV 1800 PC spectrophotometer at 497.8 nm.

2.2. Synthesis of Mg/Al LDH

Mg/Al LDH was synthesized by coprecipitation at pH 10 according to the modified procedure of Rahman et al. [31] and Yuliasari et al. [32]. The mole ratio of Mg²⁺/Al³⁺ is 3 by mixing 0.75 M Mg(NO₃)₂.6H₂O to 0.25 M Al(NO₃)₃.9H₂O to form 100 mL of solution. The solution was stirred for 2 hours before the pH was conditioned. The pH adjustment was carried out by adding 60 mL of 0.5 M NaOH and 60 mL of 0.25 M Na₂CO₃. After setting this pH, the mixture was stirred at a temperature of 80°C for 10 hours. Then the mixture was filtered, and the precipitate was washed with distilled water. The precipitate was dried at a temperature of 110°C and weighed.

2.3. Preparation of Mg/Al-Metal oxide composite

The Mg/Al-TiO₂ composite was prepared with the same initial procedure as the Mg/Al LDH synthesis, by mixing Mg(NO₃)₂.6H₂O and Al(NO₃)₃.9H₂O and alkalizing with NaOH and Na₂CO₃. After the mixture had been stirred for 10 hours, TiO₂ was added with a weight ratio of 1 between LDH and TiO₂. This was in accordance with Djeda's et al. report [24] that the best ratio of LDH / TiO₂ = 1. After the addition of the oxide, the mixture was stirred for 3 hours and then 0.37 M NaOH was added 150 mL and stirred for 10 hours at 70°C. The mixture was filtered, washed with distilled water and calcined for 7 hours at 300°C. Mg/Al-ZnO composite was prepared in the same way but the oxide used was ZnO.

2.4. Photodegradation of congo red by catalysts

The catalyst composite was added to a 20 mL CR solution with a concentration of 100 mg/L as a model dye and shaken for 60 minutes in a dark room. After the process, photodegradation was carried out with UV light using 4 lamps of 20 Watt 352 nm. Variations in the pH of the media solution, the weight of the catalyst and the time of degradation aimed to obtain the optimum conditions. The pseudo-first-order equation $\ln(C_0/C_t) = k_{ap}.t$, was used to determine the photodegradation kinetics rate constant (k_{ap}). According to Hadnadjev-Kostic [33], C_0 is the initial concentration of the dye after undergoing a time of 60 minutes with the catalyst in the dark room, and C_t is the concentration of CR after a certain photodegradation time (t). Furthermore, catalysts regeneration was carried out for 5 cycles with ultrasonic desorption.

3. Results and Discussion

3.1. Morphology and band gap energy of materials

The synthesized pristine LDH catalyst material and the prepared LDH-metal oxide composite catalysts were characterized using SEM to observe the morphology of each catalyst. Figure 1 shows the morphology condition of the

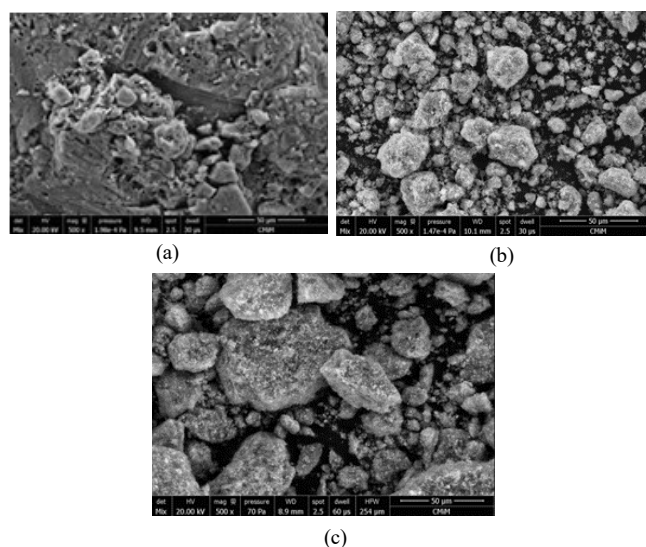


Fig. 1. SEM images of materials Mg/Al LDH (a) Mg/Al-TiO₂ (b) Mg/Al-ZnO (c)

catalysts indicating that Mg/Al-TiO₂ and Mg/Al-ZnO were rougher than Mg/Al LDH.

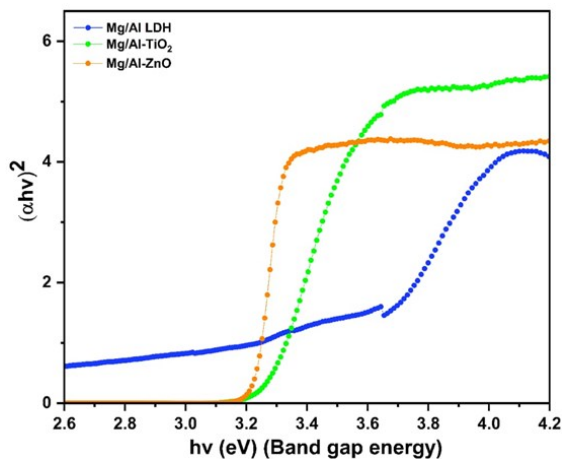


Fig. 2. Band Gap Energy of LDH Materials

The determination of band gap energy using DRUV is a material characterization that can show a catalytic ability including in the photodegradation process [25]. Figure 2 shows the energy band gap materials where the energy band gap composites LDH-Metal oxide only required less energy than LDH pristine and here Mg/Al-ZnO required the least energy. The band gap energies of Mg/Al LDH, Mg/Al-TiO₂ and Mg/Al-ZnO were 3.50 eV, 3.24 eV and 3.22 eV, respectively.

3.2. Effect of photodegradation process conditions

Photodegradation requires suitable conditions to achieve optimum results. One of the things that brings an effect is the pH condition of the media for being related to the nature of the catalyst and the interaction between the pollutant and the catalyst. Figure 3 shows the variation of pH to CR photodegradation for 120 minutes. At pH 8, it appeared that Mg/Al LDH produced the lowest C/C_0 or the highest CR photodegradation.

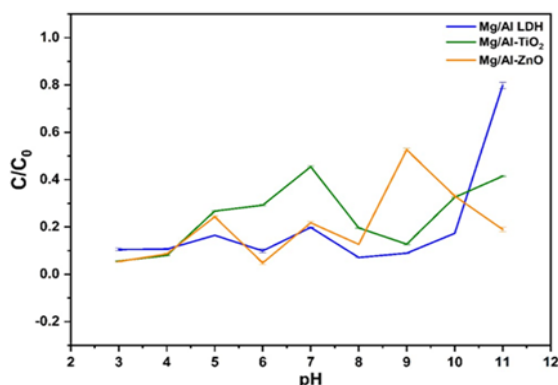


Fig. 3. Effect of pH on CR photodegradation

Research conducted by Ma et al. [2] chose to degrade CR with the help of MgZn/Cr-TiO₂ at a pH of around 9. This can be understood because at alkaline pH there is more OH⁻ so that more hydroxyl oxidizes pollutants. The modification of pristine LDH with metal oxides commonly enhances the photodegradation of pollutants [25]. CR is an anion, so it can be more compatible with the positive charge of the photocatalyst under acidic conditions. Figure 3 shows that

Mg/Al-TiO₂ had an optimum pH at pH 3, while Mg/Al-ZnO has an optimum at pH 6. Wang et al. [34] obtained a NiZn/Al LDH catalyst produced the optimum pH for photodegradation of Orange G an azo anionic dye at pH 5. Likewise, Chowdhury and Bhattacharyya [35] got the optimal NiCo/Ti LDH catalyst to degraded acid Red, and an azo anionic dye at pH 4. When degrading RhB a cationic dye, the optimal condition was pH 11. Shen et al. [36] investigated the photodegradation of ibuprofen an acid, this anti-inflammatory carboxylic acid got optimum at pH 3 with the help of Zn/AlLa LDH. The photodegradation of acid orange, an azo anionic dye, has also been carried out with the help of Mg/Fe TiO₂ and obtained a much better degradation at pH 2.5 than that of at pH 10. In addition, under acidic conditions the hydronium ion tends to cause the electron hole h⁺ to remain positively charged. Electron holes h⁺ also have an ability to oxidize pollutants [37]. This study found that the optimum pH when using Mg/Al ZnO was higher than using Mg/Al TiO₂. This was found to occur because according to Elhalil et al. under acidic conditions ZnO is at risk of being decomposed by electron holes h⁺ and dissolution into Zn²⁺ [17].

Variations in the weight of the catalyst used can affect the photodegradation process. The more catalysts used within certain limits will provide optimum conditions. Figure 4 shows the effect of catalyst weight on CR photodegradation for 120 minutes at the optimum pH of each material. It can be seen in the Figure that the heavier the catalyst used, the better the photodegradation tendency. The decrease in the photodegradation performance of the Mg/Al-ZnO catalyst at 0.1 g according to Elhalil et al. could be due to light being more difficult to penetrate into the media [17].

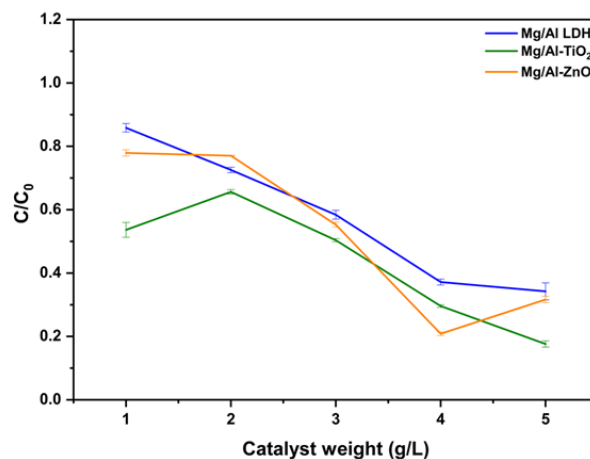


Fig. 4. Effect of catalyst weight on CR photodegradation

Variation in radiation times can indicate the optimum photodegradation time so that there is no inefficient excess of time. Figure 5 shows the photodegradation of CR at the optimum pH and weight of each catalyst over time. After contacting the catalyst with 100 mg/L of CR solution in the dark for 60 minutes, 41.5 mg/L, 26.3 mg/L and 47.5 mg/L CR was left as C₀ for Mg/Al LDH, Mg/Al-TiO₂ and Mg/Al-ZnO, respectively. The photodegradation results showed that after Mg/Al LDH was modified to LDH-metal oxide, it could improve the photodegradation performance. Mg/Al LDH, Mg/Al-TiO₂ and Mg/Al-ZnO catalyzed the photodegradation of CR by 65.97%, 73.06 % and 86.86%, respectively.

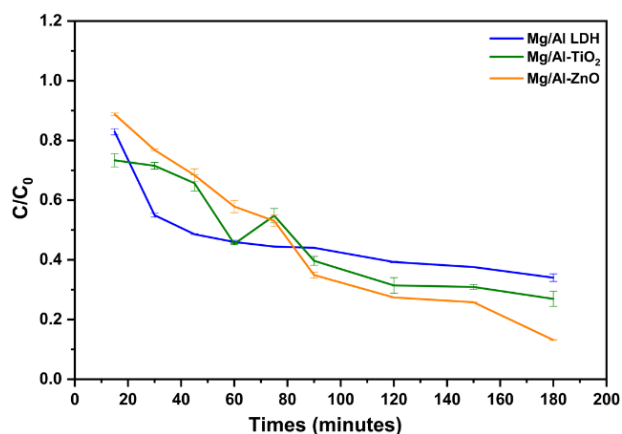


Fig. 5. Effect of time radiation on CR photodegradation

The results of studies that have been carried out by other researchers also showed the similar thing. Zn/Al LDH catalyzed 10% of sulfamethoxazole photodegradation and after being composited with TiO₂ can degraded by 98% [38]. Zn/Al LDH material after being composited with TiO₂ can increase the degradation ability of dodecylsulfate from 70% to 85% [14]. The degradation ability of Ni/Al LDH material, which degrades 30% of methyl orange, can be increased into 45% when composited with TiO₂ [39]. The Mg/Al LDH-ZnO composite was able to degrade 98% of green malachite, whereas before being composited with ZnO it was only able to degrade 32% [30].

Time variation data can be processed to obtain a constant rate of degradation if $\ln C_0/C$ is channeled against time in the form of a linear curve. The value of the slope of the curve is the rate constant value (k_{ap}). Figure 6 shows the value of k_{ap} which follows the pseudo-first order equation of degradation with Mg/Al LDH catalyst of 0.0077, Mg/Al-TiO₂ of 0.0085 and Mg/Al ZnO of 0.0103.

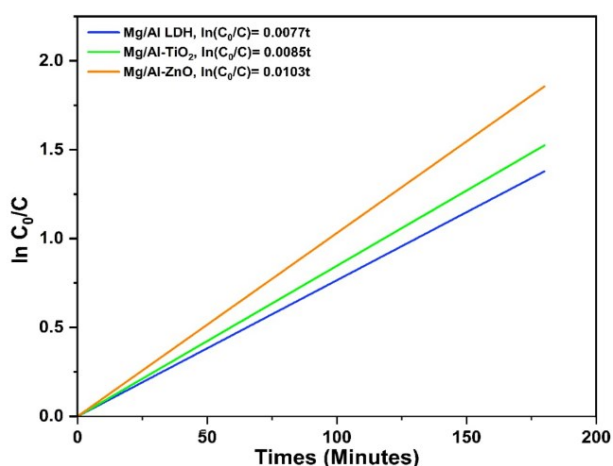


Fig. 6. CR photodegradation rate constant curve

From the results of the study, it appeared that the modified LDH-metal oxide k_{ap} was higher than the pristine LDH. This is in accordance with the results of other studies. The degradation constant of methyl orange increased by 0.0030 using Ni/Al LDH-TiO₂ compared to the pristine LDH of 0.0020 [14]. The degradation constant of rhodamine-B with a Zn/Al LDH catalyst of 0.0010 increased to 0.0037 after using Zn/Al LDH-TiO₂ [33]. Table 1 shows the k_{ap} values of CR photodegradation using various materials.

Table 1. Value of degradation rate constant

Materials	Dye	Value of k_{ap} (Minute ⁻¹)	Ref.
Cu,Mg/Al LDH	CR	0.0059	[40]
CuO	CR	0.0014	[41]
Au/Pd-TiO ₂	CR	0.0073	[42]
CuCl ₂	CR	0.0092	[43]
Fe ²⁺ (Sonication)	CR	0.0037	[44]
Fe ²⁺ (Fenton)	CR	0.0070	[44]
Mg/Al-TiO ₂	CR	0.0085	This study
Mg/Al-ZnO	CR	0.0103	This study

The modification of Mg/Al LDH to Mg/Al-TiO₂ will improve the physical properties of the material [24]. The CO₃²⁻ anion used also produces the best structural stability of LDH compared to SO₄²⁻, Cl⁻, and NO₃⁻ [45]. The most frequently used anion in the LDH interlayer is CO₃²⁻ [46]. Figure 7 shows that LDH-metal oxides, i.e. Mg/Al-TiO₂ and Mg/Al-ZnO were better in the regeneration of the material up to 5 photodegradation cycles than Mg/Al LDH as the pristine structure.

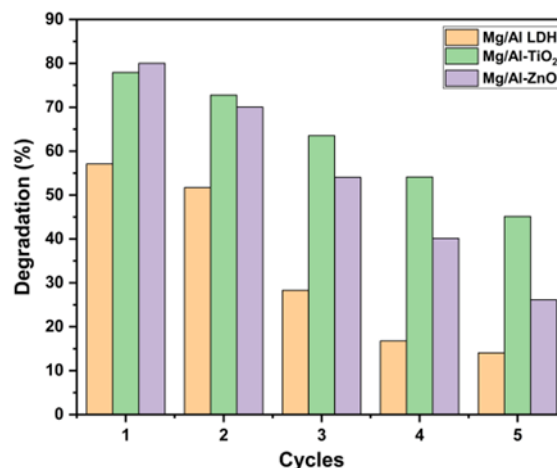


Fig. 7. Photodegradation catalyst regeneration cycle

Table 2. Dye degradation percentage of various material catalysts

Materials	Dye	Degradation	Concentration before contact	Ref.
LaBiFeO ₃ ,Mn5%/GNP	CR	12.00 %	100 mg/L	[47]
NiCoFe	CR	66.08 %	10 mg/L	[48]
MgZn/Cr-TiO ₂	CR	31.10 %	100 mg/L	[2]
Cr ₂ O ₃	CR	38.00 %	25 mg/L	[49]
Cr ₂ O ₃ (Fenton)	CR	34.00 %	25 mg/L	[49]
MCM-48/Ni ₂ O ₃	CR	68.20 %	25 mg/L	[50]
Mg/Al-TiO ₂	CR	73.06 %	100 mg/L	This Study
Mg/Al-ZnO	CR	86.86 %	100 mg/L	This Study

From the data, it appeared that the stability of Mg/Al-TiO₂ was better than that of Mg/Al-ZnO. This might be because, according to Elhalil et al., LDH-ZnO can undergo dissolution and photodecomposition [17]. Table 2 compares the catalytic abilities of various catalyst materials based on the percent

degradation. The dye concentrations are also informed before the catalyst comes into contact with the CR.

3.3. Material characterization after regeneration cycle

The catalyst material after 5th regeneration cycles in photodegradation of CR was analyzed by XRD. Figure 8 shows the XRD diffractogram of the catalysts. It can be seen in the figure that the Mg/Al LDH still had a peak 2 θ at 11.35° which is typical for the structure of the LDH cationic layer, and peaks 2 θ at 60.49° and 61.61° from the anionic interlayer, in addition to the presence of a peak 2 θ at 22.84°; 34.40°; and 38.64°.

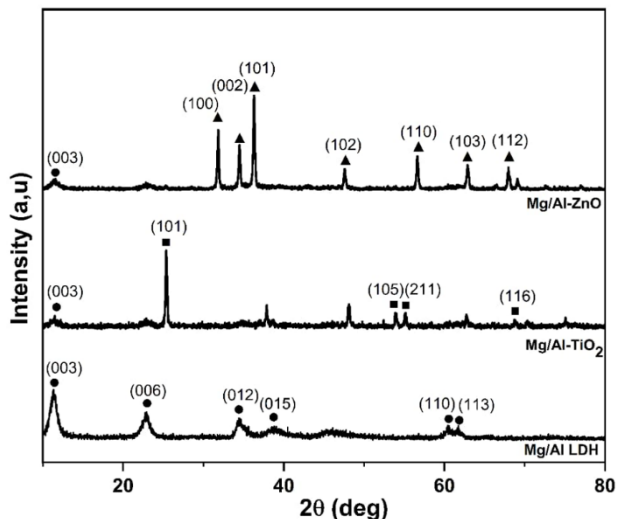


Fig. 8. Diffractogram of catalyst material after 5th regeneration cycles

According to Gholami et al. [4] and Yuliasari et al. [51] 2 θ LDH peaks at around 11°, 23°, 34°, 38°, 60° and 62° for the Miller index field 003, 006, 012, 015, 110 and 113. Mg/Al LDH after regeneration cycle still showed LDH peak at 2 θ at 11.36°, while the peak of TiO₂ appeared at 2 θ 25.37°; 53.93°; 55.06° and 68.77°. This result is in line with Mourid et al. [38] and Contreras-Ruiz et al. [19] stating that the TiO₂ peak of LDH-TiO₂ appeared at 2 θ around 25°, 54°, 55° and 69° with indexes of 101, 105, 211 and 116, respectively. While Mg/Al -ZnO still showed the typical peak of LDH at an angle of 2 θ 11.38°; and a typical peak of ZnO at an angle of 2 θ 31.81°; 34.46°; 36.28°; 47.55°; 56.59°; 62.89°; and 67.98°. According to Bhuvanawari et al. [25] and Elhalil et al. [17] the typical ZnO angle of LDH-ZnO appears at 2 θ around 32°, 34°, 36°, 48°, 56°, 63° and 68° with the indexes of 100, 002, 101, 102, 110, 103 and 112, respectively.

As shown in Figure 9, the analysis of the functional groups contained in the catalyst material after 5th regeneration cycle was carried out by FTIR. The 3428 cm⁻¹ band that appeared is in line with Palapa et al. [52] stating that the band around 3400 cm⁻¹ was the stretching OH vibration of LDH.

The presence of a band of 1365 cm⁻¹ is a stretching vibration of CO₃²⁻ as interlayer anion [26]. The band between 500 cm⁻¹ and 800 cm⁻¹ that appears according to Contreras-Ruiz et al. [19] about 600 cm⁻¹ is a vibration of Mg-OH and about 550 cm⁻¹ is a stretching vibration of the bond between metal elements and oxygen. The catalyst material that has been interacted with CR will be able to have CR groups as well, such as azo groups (N=N) and primary amine groups (NH₂). The 1620 cm⁻¹ band might be the vibration of the azo group or the primary amine

group. According to Nandiyanto et al. [53], the open chain azo group vibrations occurred at 1630-1575 cm⁻¹ while the bending vibrations of primary amines occurred at 1650-1590 cm⁻¹.

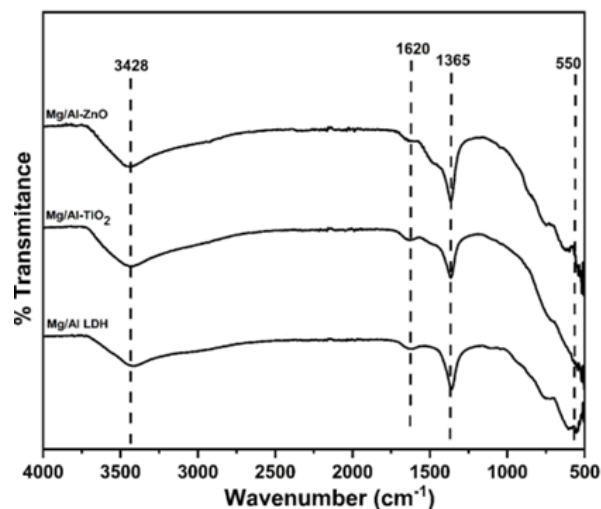


Fig. 9. FTIR spectra of catalysts after 5th regeneration cycles

4. Conclusion

From these findings, it is certain that pristine Mg/Al LDH modified into Mg/Al-TiO₂ and Mg/Al-ZnO composites have a better catalytic ability resulting in higher percent degradation and higher Congo red (CR) degradation rate constants. The percentage degradation and rate constant of Mg/Al-ZnO appeared to be slightly better than Mg/Al-TiO₂, but Mg/Al-TiO₂ seemed to have better regeneration stability than Mg/Al-ZnO. Regeneration up to 5 cycles proved the better stability of composites than pristine LDH. The XRD and FTIR characterizations were conducted on the material that had undergone 5 regeneration cycles. The XRD characterizations showed that the cationic layer was still possessed by all materials. The FTIR spectra also still showed hydroxy bands, interlayer anions and metal oxides, which indicated the good stability of the materials.

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