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Application of M^{2+} (Magnesium, Zinc)/Alumina-Metal Oxide Composites as Photocatalysts for the Degradation of Cationic Dyes

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ABSTRACT

The development of studies on layered double hydroxide (LDH) material as a photocatalyst for the degradation of dye pollutants continues to increase. LDH is an anionic clay, which is a natural or synthetic mixed metal hydroxide. Pristine LDH is written as M^{2+}/M^{3+} LDH, (M is metal ion). This study prepared pristine Mg/Al LDH and Zn/Al LDH composited with metal oxide TiO_2 and ZnO, respectively. Composite is denoted by M^{2+}/M^{3+}-metal oxide. The coprecipitation method used was accompanied by calcination of the composite at a temperature 300 °C that was not high. The prepared composites were morphologically characterized by SEM. The materials that had been used until the fifth cycle of regeneration were characterized by XRD and FTIR which still indicated the presence of LDH-metal oxide composite structure. The materials degraded cationic dyes namely rhodamine-B (RhB) and methylene blue (MB). RhB degraded better than MB by pristine LDH and composites. The percent degradation of RhB for pristine Mg/Al LDH, composites Mg/Al-TiO_2 and Mg/Al-ZnO were 53.1%, 59.8%, 62.8%, respectively. The percent RhB degradation for pristine Zn/Al LDH, composites Zn/Al-TiO_2 and Zn/Al-ZnO were 51.4%, 58.5%, 58.9%, respectively. The percentage of degradation indicates that the LDH-metal oxide composite has succeeded in increasing the photodegradation catalytic ability and the regeneration ability of LDH pristine.

Keywords: photodegradation, layered double hydroxide, TiO_2, ZnO, dyes.

INTRODUCTION

Sustainability of water availability is urgently needed for domestic consumption, energy production, industry and agriculture so that the treatment of waste containing pollutants becomes an important environmental issue. Synthetic dyes often become pollutants because they have a complex aromatic molecular structure that is difficult to degrade. These characteristics can be harmful to human health and aquatic life (Djeda et al., 2020; An et al., 2015). About 10-15% of the dyes that have been used in the dyeing process can be released into the wastewater stream (Singh et al., 2017).

The dye that is of concern to food safety regulators because it is a carcinogen and can cause sarcomas is cationic dye rhodamine-B (RhB). Products containing these dyes must provide a warning on the label, considering the illegal economic motive of counterfeiting (Zhou et al., 2019). Rhodamine-B staining is due to the conjugated structure of the C=O and C=N groups on the aromatic ring (Li et al., 2018). Another dye is methylene blue (MB), a cationic primary thiazine dye that

is very often used in the dye industry, including for dyeing cotton, silk, wool, printing, paper and paint. Thiazines are one of a group of organic compounds that contain a ring system consisting of sulfur atoms, and nitrogen atoms (Khan et al., 2022; Sintakindi & Ankamwar, 2020). Methylene blue in addition to being a carcinogen (Khairnar et al., 2020), can also cause digestive disorders, respiratory disorders, cyanosis, jaundice, necrosis, irritation, even mental disorders and blindness. Scopus data informs that articles on the photocatalysis degradation of methylene blue are increasing continuously (Khan et al., 2022). Figure 1 shows the structure of rhodamine-B and methylene blue.

A number of chemical and physical processes including precipitation, adsorption, ultrafiltration, air stripping, reverse osmosis and flocculation are being pursued to treat water from dyes. These methods also have limitations. Photocatalysis is being considered as an efficient process for the mineralization of toxic organic dyes (Muhammad & Garzali, 2019).

Recent research attention has become interested in applying layered double hydroxide (LDH) materials as photocatalysts for dye degradation. LDH is a clay material such as hydrotalcite, having the basic structure of the divalent 2+ and trivalent 3+ cation layers determined hexagonally on the hydroxide. The common formula for LDH is $[M^{2+}_{1-x}\ M^{3+}_{x}\ (OH)_2]_x + (A^{n-})_{x/n} \cdot mH_2O$, M^{2+} is a divalent cation (Mg^{2+}, Cu^{2+}, Zn^{2+}, etc), M^{3+} is a trivalent cation (Fe^{3+}, Cr^{3+}, Al^{3+}, etc); A^{n-} is an anion (NO_3^-, CO_3^{2-}, Cl^-, etc.). Pristine LDH is denoted by M^{2+}/M^{3+} LDH (M is metal ion). This positively charged layer causes anion intercalation through which anions can be exchanged. LDH has the advantages of high ion exchange capacity, adjustable composition, good stability, uniform distribution of cations, easy to synthesize and environmentally friendly (Contreras-Ruiz et al., 2019; Song et al., 2019; Zhang et al., 2016).

From various studies, semiconductor-based materials such as metal oxides also have the potential to be impregnated into LDH-metal oxide composites. Composite is written as M^{2+}/M^{3+}-metal oxide. This is done in addition to increasing the structural strength, but also composites can be used as photocatalysts in degrading dyestuffs (Djeda et al., 2020). The use of LDH containing metal oxides titanium dioxide (TiO_2) and zinc oxide (ZnO) will inhibit electron recombination, besides that the LDH layer facilitates electron transfer (Jaerger et al., 2021; Bhuvaneswari et al., 2019). LDH material is used as a TiO_2 support material because of its good dispersion, helps interact with pollutants and increases the sedimentation rate within minutes or at the end of the photocatalysis process (Jo et al., 2018; Aoudjit et al., 2018). ZnO is an excellent photocatalyst due to its efficient photosensitivity and good chemical stability (Elhalil et al., 2018; Wu et al., 2019). ZnO was composited with LDH as well in order to avoid aggregation (Ai et al., 2018).

Previous studies synthesized both pristine LDH and composite LDH by calcination technique at relatively high temperature. Ce doped Zn/Al LDH as catalyst for degradation rhodamine-B with 80-90% degradation required energy to calcination at 400-900 °C (Zhu et al., 2016). Zn/Al LDH as catalyst for degradation methylene blue 75% - 77% after required energy to calcination at 500-900 °C (Abderrazek et al., 2016). Zn/Al LDH as catalyst for degradation orange II required energy to calcination at 400-800 °C (Zhang et al., 2016). The relatively high temperature calcination technique in the preparation of LDH-TiO_2 or LDH-ZnO photocatalysts has also

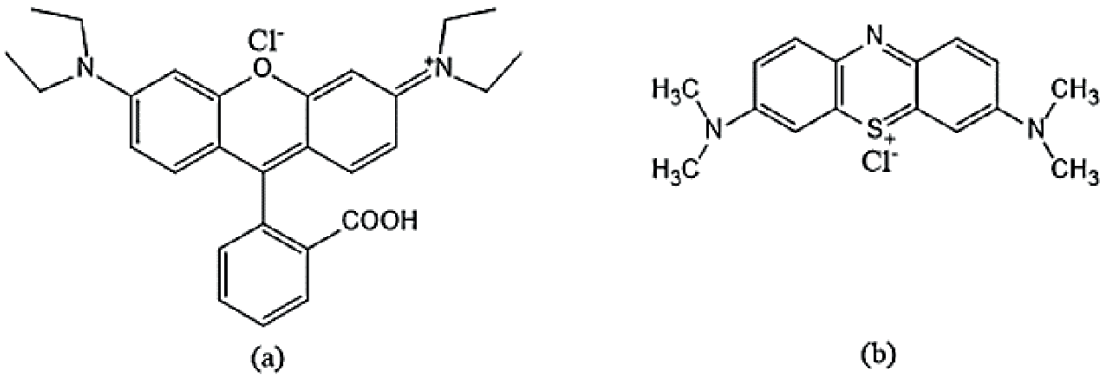

Figure 1. Structure of rhodamine-B (a) methylene blue (b)

been used for the degradation of organic pollutants. These studies using temperatures of 500 °C, 520 °C or 550 °C include research conducted by Contreras-Ruiz et al. (2016), Elhalil et al. (2018), Ni et al. (2018), Hadnadjev-Kostic et al. (2017), and Yan et al. (2016).

This research seeks to lower the calcination energy consumption of 300 °C, which is important for large-scale applications to be more energy efficient. M^{2+}/Al LDH (M^{2+}= Mg, Zn) materials were composited with metal oxides TiO_2 and ZnO, respectively, to form Mg/Al-TiO_2, Zn/Al-TiO_2, Mg/Al-ZnO, and Zn/Al-ZnO. These materials were used as a photocatalyst for the degradation of rhodamine-B dyes and methylene blue.

EXPERIMENT

Chemicals and instrumentations

All chemicals such as magnesium nitrate, zinc nitrate, aluminum nitrate, titanium dioxide, zinc oxide, sodium hydroxide, sodium carbonate and hydrogen chloride were used without specific treatment. Water was supplied from Inorganic Materials and Complexes Research Group employing resin ion exchange reverse method. Characterization of materials were carried out by Rigaku XRD Miniflex-6000 diffractometer. Analysis of IR was conducted using Shimadzu FTIR Prestige-21. Degradation of rhodamine-B and methylene blue were analyzed by UV-Vis Biobase BK-UV 1800 PC spectrophotometer at 554 nm and 662 nm, respectively.

Synthesis of Mg/Al LDH and Zn/Al LDH

LDH was synthesized according to a slightly modified co-precipitation method reported by Rahmadan et al. (2021) and Lesbani et al. (2021). Mg/Al LDH was synthesized by 50 mL 0.75 M magnesium nitrate added with 50 mL 0.25 M aluminum nitrate in a stirrer for 2 hours. The pH of the mixture was adjusted to pH 10 by adding sodium hydroxide and sodium carbonate with a mole ratio of 2:1 in 120 mL of distilled water. This mixture was stirred again for 10 hours at 80 °C. The precipitate was washed and dried using an oven at a temperature of 110 °C then the LDH was weighed. The synthesis of Zn/Al LDH was carried out with the same procedure as above, but the salt used was zinc nitrate.

Synthesis of LDH-metal oxide composite

Magnesium nitrate solution with 50 mL concentration of 0.75 M was added with 50 mL 0.25 M aluminum nitrate and stirred for 2 hours. The pH of the mixture was adjusted to pH 10 by adding sodium hydroxide and sodium carbonate with a mole ratio of 2:1 in 120 mL of distilled water. This mixture was stirred again for 10 hours at 80 °C. Titanium dioxide is dispersed in a mixture with a weight ratio of 1:1 between the resulting LDH and titanium dioxide, then stirred for 3 hours. This ratio is in accordance with the research results of Djeda et al. (2020). The mixture was added with sodium hydroxide again with a concentration of 0.37 M with a stirrer for 10 hours at a temperature of 70 °C. The precipitate was washed for calcination at 300 °C in a furnace for 7 hours. The LDH-ZnO composite was prepared by the same procedure as above, but the oxide used was zinc oxide.

Photodegradation activity

The composites were applied as photocatalysts for degrading 5 mg/L rhodamine-B or methylene blue in a volume of 20 mL. Optimization of degradation includes variations in pH, catalyst loading, and degradation contact time. The degradation is carried out using UV light. The percentage of degradation is determined based on the following equation formula: Percentage of Degradation (%) = $(C_o - C_t)/C_o$ x 100, where C_o is the initial dye concentration and C_t is the dye concentration after degradation (Hadnadjev-Kostic et al., 2017). Determination of the reusability of the catalyst up to 5 cycles regeneration of use and its desorption was carried out ultrasonically.

RESULTS AND DISCUSSION

Characterization of the prepared LDH-metal oxide

Characterization of LDH-metal oxide by SEM could inform the surface condition of the material. Figure 2 show the morphology of the composite at 1000 times magnification. Composites based on Mg/Al LDH appear to be smaller than composites based on Zn/Al LDH. The surface of the LDH-ZnO composites are more roughness than the LDH-TiO_2 composites.

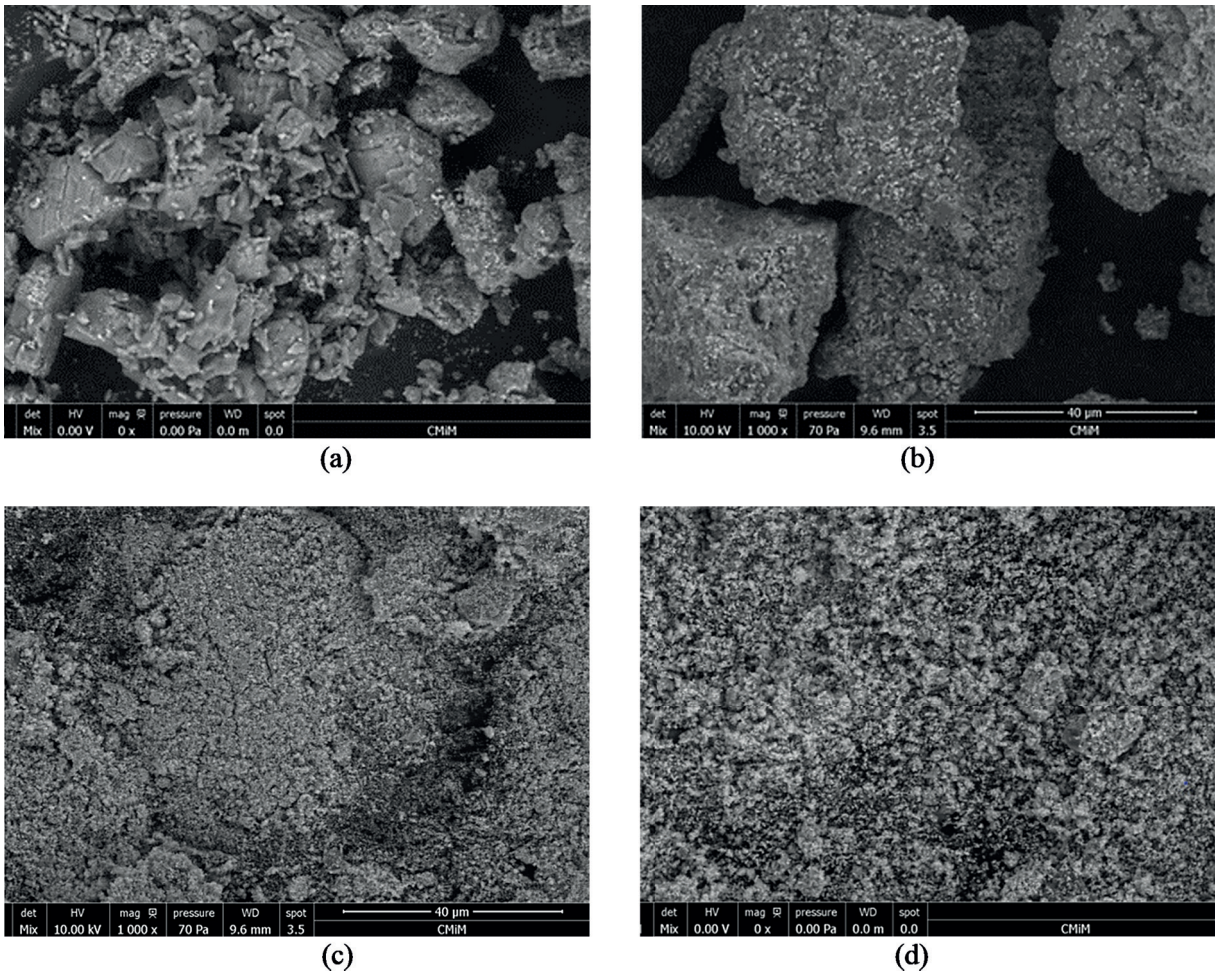

Figure 2. SEM images of composites Mg/Al-TiO_2 (a) Mg/Al-ZnO (b) Zn/Al-TiO_2 (c) Zn/Al-ZnO (d)

Characterization of LDH-based materials that have degraded dyes

Pristine LDHs and LDH composites materials that had degraded RhB were characterized using XRD to show that their structures were not damaged by the degradation process. 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 well as anions between layers at an angle of 2θ at 61.62°(110) Siregar (et al., 2022). Pristine LDH material that has degraded RhB still shows these LDH peaks. Mg/Al LDH peaks at angles 11.47°, 22.8°, 34.8°, 62.23°. The peaks of Zn/Al LDH were at angles 11.52°, 23.19°, 34.5°, 62.91°. The peaks of Mg/Al-TiO_2 at angles 11.57°, 22.9°, 62.84°. Mg/Al-ZnO peaks at angles 11.33°, 23.1°, 34.50°, 62.9°. Zn/Al-TiO_2 peaks at angles 11.66°, 34.58°, 62.85°. Zn/Al-ZnO peaks at angles 11.57°, 34.4°, 62.86°. The presence of TiO_2 in LDH was shown at 2θ angles 25°(101), 54°(105), 55°(211), 68°(116) (Contreras-Ruiz et al., 2019). These peaks are still present in the TiO_2 composite, Mg/Al-TiO_2 at angles of 25.48°, 54.00°, 55.20°, 67.92° and Zn/Al-TiO_2 at angles of 25.43°, 54°, 55.18°, 68.05°. The presence of ZnO in LDH is indicated at angles of 2θ 31.8° (110), 34.5° (002), 36.3°(101), 47.6°(102), 68°(112) (Elhalil et al., 2018). ZnO composites still showed these peaks, Mg/Al-ZnO at angles of 31.80°, 34.50°, 36.35°, 47.60°, 68.0° and Zn/Al-ZnO at angles of 31.79°, 34.45°, 36.25°, 47.5°, 67.94°. Figure 3 show the diffractogram of catalysts which have degraded RhB.

Characterization by FTIR was also carried out on LDH-based materials that had degraded RhB and MB. The IR spectra showed a band between 3420–3500 cm^{-1} and about 1630 cm^{-1} showing the stretching vibration of the hydroxyl groups. The 1381cm^{-1} band represents CO_3 vibrations (Hosseini & Akbari, 2016; Zhao et al., 2018). The M-O and O-M-O bands are in the band between 400 -800 cm^{-1}, (M = metal) (Aoudjit et al., 2018). Figure 4 shows that these bands are still present for the catalyst that has degraded RhB. The bands at 1700 cm^{-1} is COOH group vibrations (Singh et

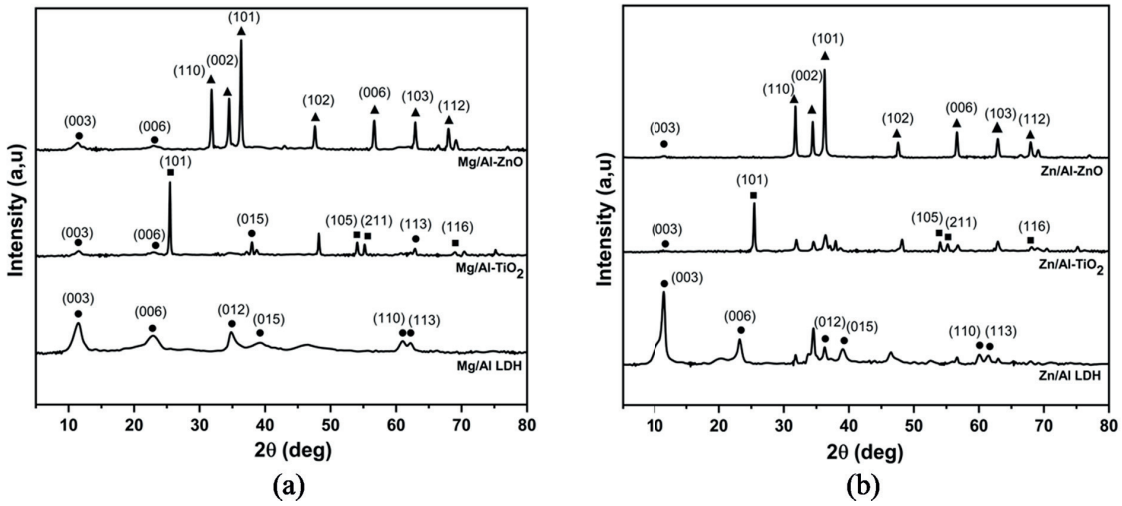

Figure 3. Diffractogram of catalysts which have degraded RhB:
catalysts based on Mg/Al LDH (a), catalysts based on Zn/Al LDH (b)

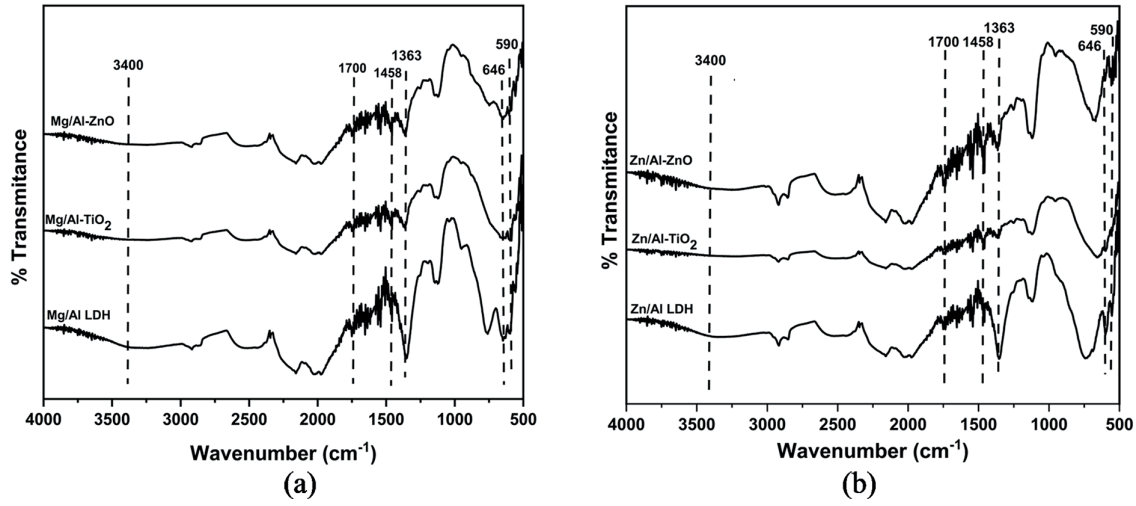

Figure 4. FTIR spectra of the catalysts after RhB degradation:
catalysts based on Mg/Al LDH (a), catalysts based on Zn/Al LDH (b)

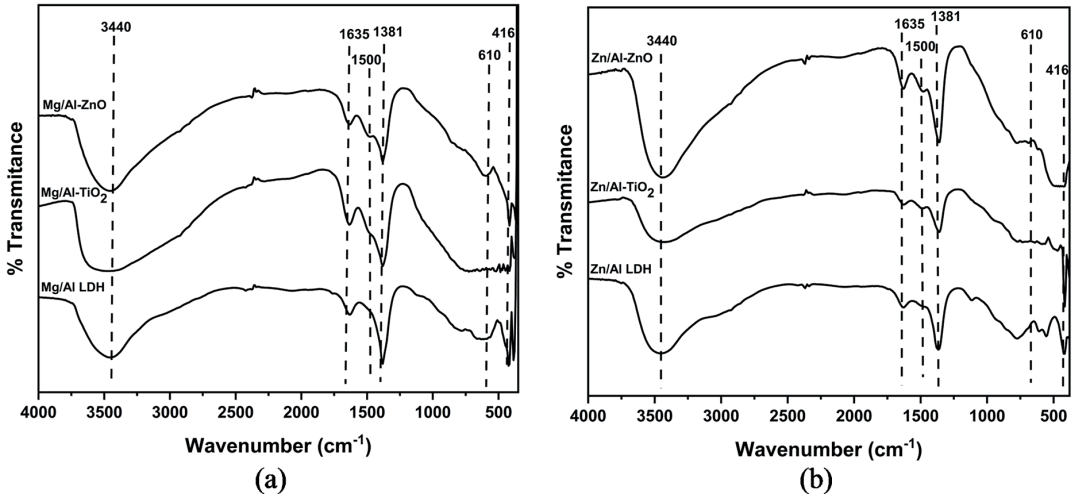

Figure 5. FTIR spectra of the catalysts after MB degradation:
catalysts based on Mg/Al LDH (a), catalysts based on Zn/Al LDH (b)

al., 2017), 1458 cm^{-1} is aromatic ring vibrations (Nandiyanto et al., 2019), these bands inform the interaction between the catalyst and RhB. Figure 5 shows the FTIR spectra of the catalyst that has degraded MB. Bands 1500 cm^{-1} is aromatic C=N vibrations, 610 cm^{-1} or between 570-705 cm^{-1} is C-S-C vibrations (Teng et al., 2020) indicating the interaction between the catalyst and MB.

Effect of optimization variables on Rhodamine-B degradation

The pH variation on degradation by LDH-metal oxide can affect the stability of the metal oxide structure in LDH. Media pH less than 7 also helps the formation of positively charged electron holes. These electron holes are not only effective in forming $OH^{\bullet}$ radicals which are capable of degrading dyestuffs 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 (Khairnar et al., 2020; Elhalil et al., 2018). This causes pristine LDH to obtain a lower optimum pH, pH 7 for Mg/Al LDH and pH 3 for Zn/Al LDH, while LDH-metal oxide is optimum at pH 9. Figure 6 shows the effect of media pH on RhB degradation by catalysts based on LDH.

The effect of catalysts loading on the degradation process was carried out at the optimum pH of each material with treatment for 300 minutes. Figure 7 show the results of various catalysts loading on the RhB degradation process by Mg/

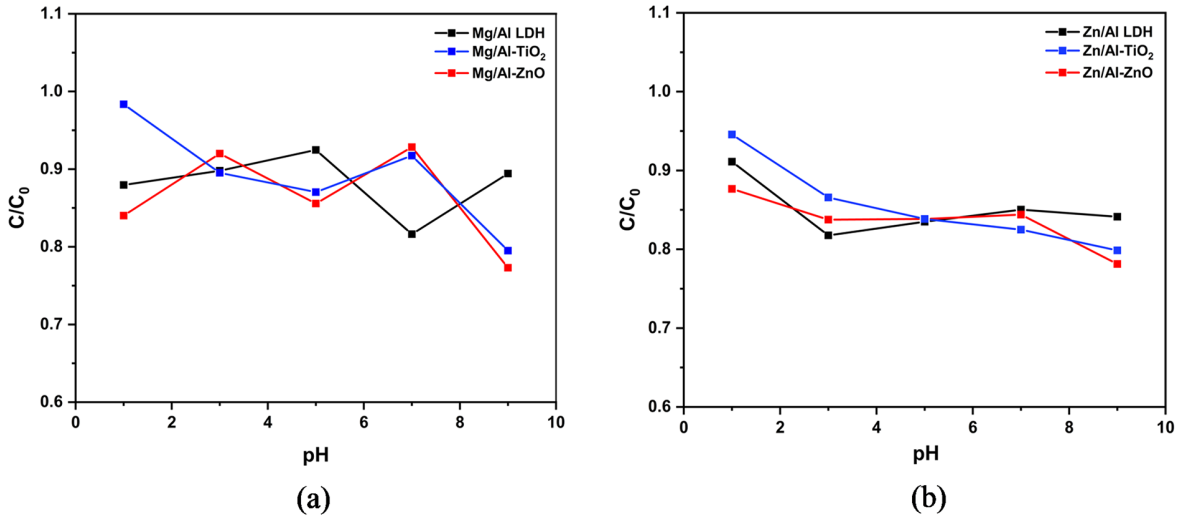

Figure 6. Effect of pH on RhB degradation by catalysts: based on Mg/Al LDH (a), based on Zn/Al LDH (b)

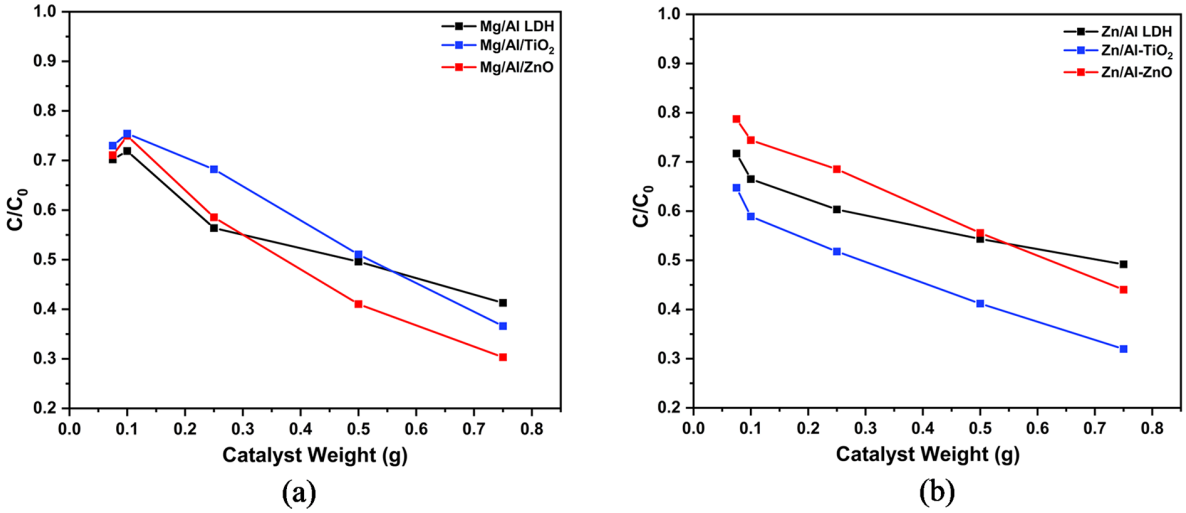

Figure 7. Effect of catalyst loading on RhB degradation by materials: based on Mg/Al LDH (a), based on Zn/Al LDH (b)

Al LDH and Zn/Al LDH-based materials, where it can be seen that LDH-TiO_2 and LDH-ZnO have a degradation percentage that was not much different. Figure 8 show the effect of variations in RhB degradation time by Mg/Al LDH and Zn/Al LDH based materials. The value of C/Co during 30 minutes of treatment had increased quite sharply then with increasing time the amount of RhB degraded increased. The percent RhB degradation for Mg/Al LDH, Mg/Al-TiO_2, Mg/Al-ZnO was 53.1%, 59.8%, 62.8%, respectively. The percent degradation for Zn/Al LDH, Zn/Al-TiO_2, Zn/Al-ZnO was 51.4%, 58.5%, 58.9%, respectively. It appears from the results of the percentage degradation that the composite catalyst LDH-TiO_2 and LDH-ZnO has a better ability to degrade RhB than pristine LDH. The LDH-TiO_2 composites caused a degradation percentage that were not much different from that of the LDH-ZnO composites.

The efficiency of using a material for use in pollutant degradation depends also on its reusability. Figure 9 show the regeneration cycle for LDH-based catalysts which were used repeatedly in RhB degradation for up to 5 cycles. Each degradation was carried out for 120 minutes at optimum pH and catalysts loading. It appears in the regeneration results that the composite catalyst LDH-TiO_2 and LDH-ZnO has a much better ability to degrade RhB than pristine LDH, especially after 5 regeneration cycles.

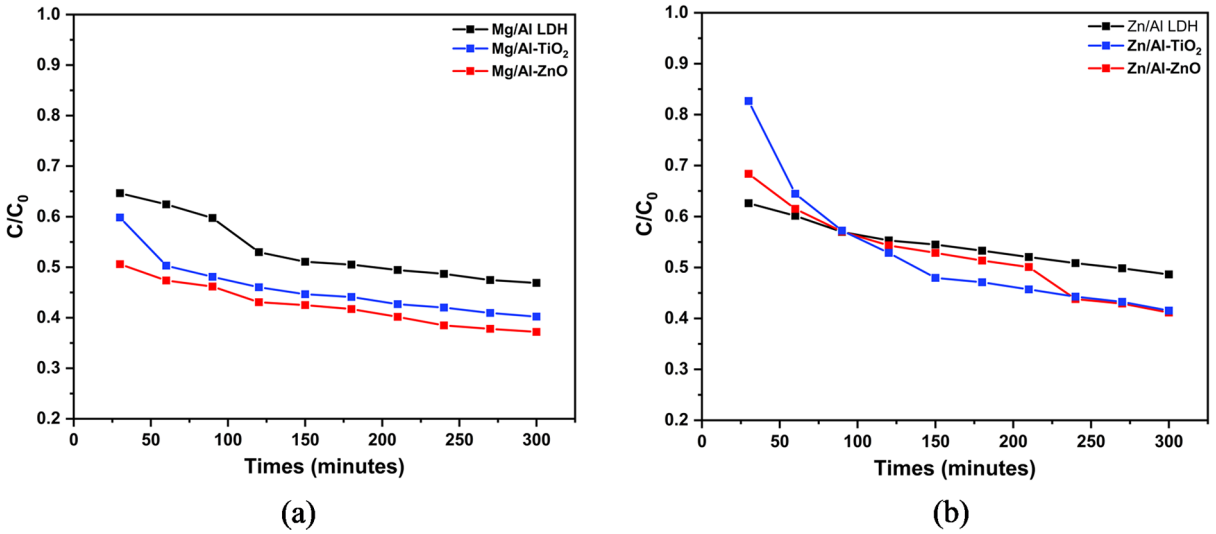

Figure 8. Effect of contact time on RhB degradation by catalysts: based on Mg/Al LDH (a), based on Zn/Al LDH (b)

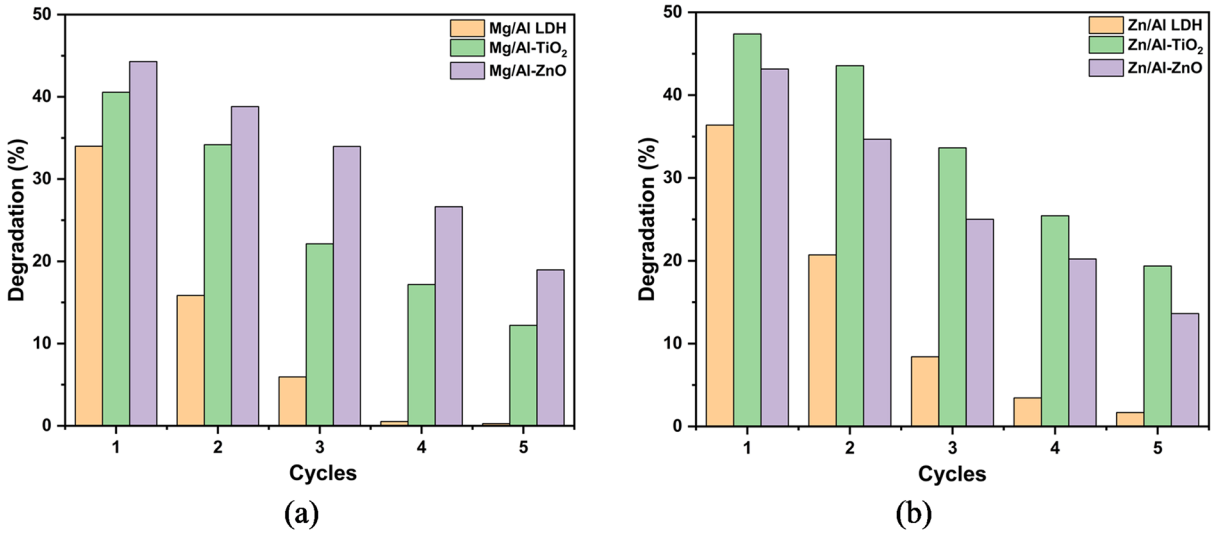

Figure 9. Regeneration cycle of RhB degradation by catalysts: based on Mg/Al LDH (a), based on Zn/Al LDH (b)

The effect of optimization variables on the degradation of methylene blue

The degradation of MB dye is also affected by pH. Figure 10 show the effect of pH and optimum pH for MB degradation catalyzed by LDH-based materials. MB degradation obtained an optimum pH of 9, except by Mg/Al LDH based composites. The Mg/Al-TiO_2 material produced the optimum at pH 7 and the optimum Mg/Al-ZnO at pH 5. Khairnar et al. (2020) claimed that the optimum pH for MB degradation catalyzed by SnO_2 was in the acidic region, because under alkaline conditions there was a risk of MB agglomeration. Khan et al. (2022) in their review informed that MB photodegradation can be carried out at medium pH, but alkaline conditions can also be advantageous in terms of the formation of $OH^{\bullet}$ radicals which degrade MB.

The effect of catalyst loading on MB degradation by an LDH-based catalyst is shown in Figure 11.The small residual MB concentration after being catalyzed by pristine LDH indicates the amount of catalyst loading causes an intense interaction between MB as cationic dye and the negative charge of the catalyst in alkaline media, considering the optimum pH for degradation is pH 9. Catalyst loading at a certain amount can refract light, besides that it can cause the light needed for the degradation process to not penetrate well

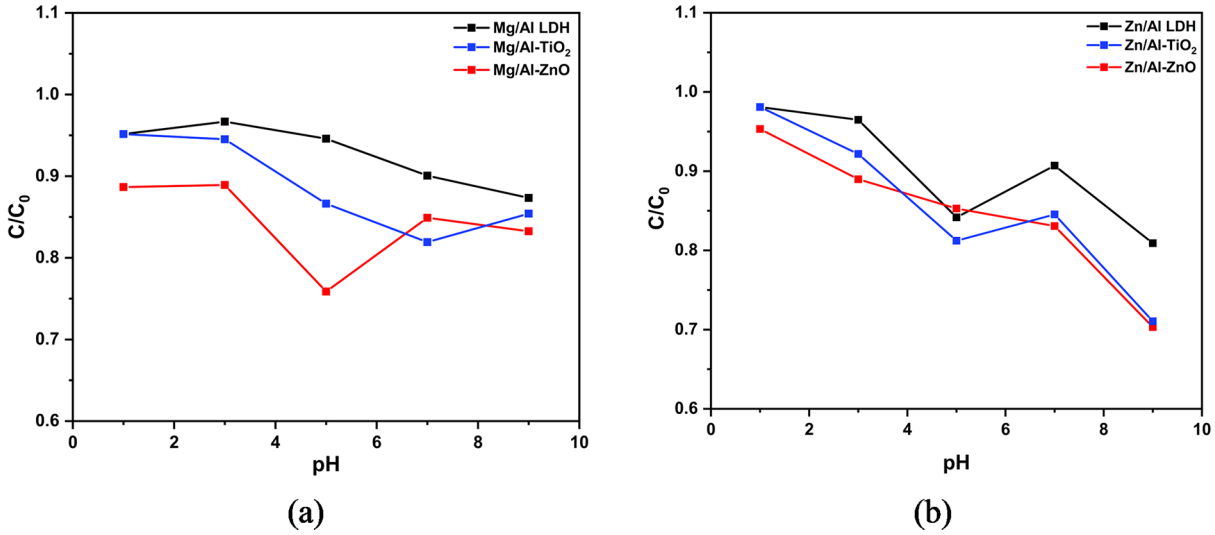

Figure 10. Effect of pH on MB degradation by catalysts: based on Mg/Al LDH (a), based on Zn/Al LDH (b)

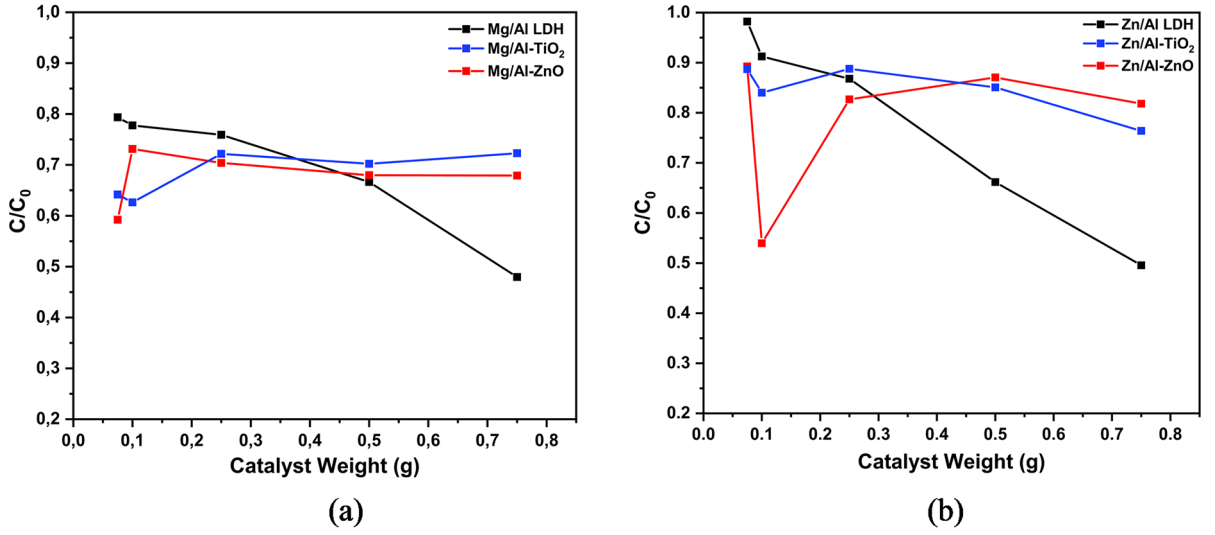

Figure 11. Effect of catalyst loading on MB degradation by catalysts: based on Mg/Al LDH (a), based on Zn/Al LDH (b)

into the media, thereby reducing the ability of the LDH-metal oxide (Elhalil et al., 2018). Figure 12 present the effect of contact time on the catalytic ability of LDH based materials when degrading MB. The percent MB degradation for Mg/Al LDH, Mg/Al-TiO_2, Mg/Al-ZnO was 8.7%, 15.5%, 24.9%, respectively. The percent degradation for Zn/Al LDH, Zn/Al-TiO_2, Zn/Al-ZnO were 16.1%, 22.1%, 30.6%, respectively. These results indicate that the modified Mg/Al LDH or Zn/Al LDH to form LDH-metal oxide composites can increase the catalytic ability to degrade MB.

The ability of a material to catalyze degradation may change after repeated use. Figure 13 show the regeneration cycle of an LDH based material catalyzing MB degradation. Khairnar et al. (2020) stated that there is a risk of dissolution from ZnO to Zn^{2+} in degrading MB. The results showed that in the first cycle the degradation of LDH-ZnO was slightly better than LDH-TiO_2, but in the next cycle LDH-TiO_2 appeared to be superior to LDH-ZnO.

CONCLUSIONS

Modification of Mg/Al LDH and Zn/Al LDH materials which respectively form composites with metal oxides TiO_2 and ZnO resulted in an increased photodegradation capability of cationic

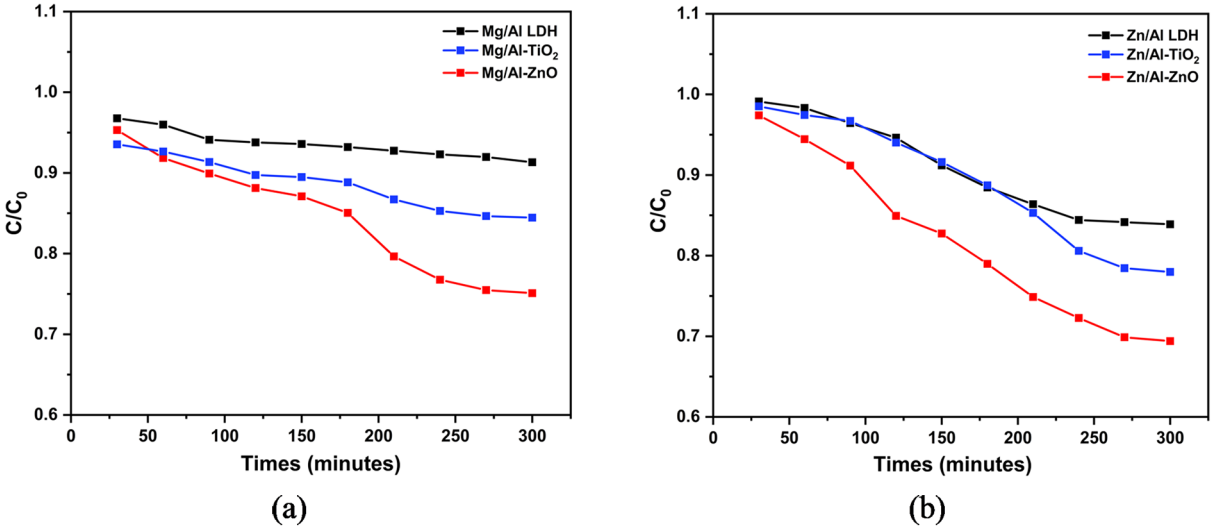

Figure 12. Effect of contact time on MB degradation by: Mg/Al LDH based catalysts (a), Zn/Al LDH based catalysts (b)

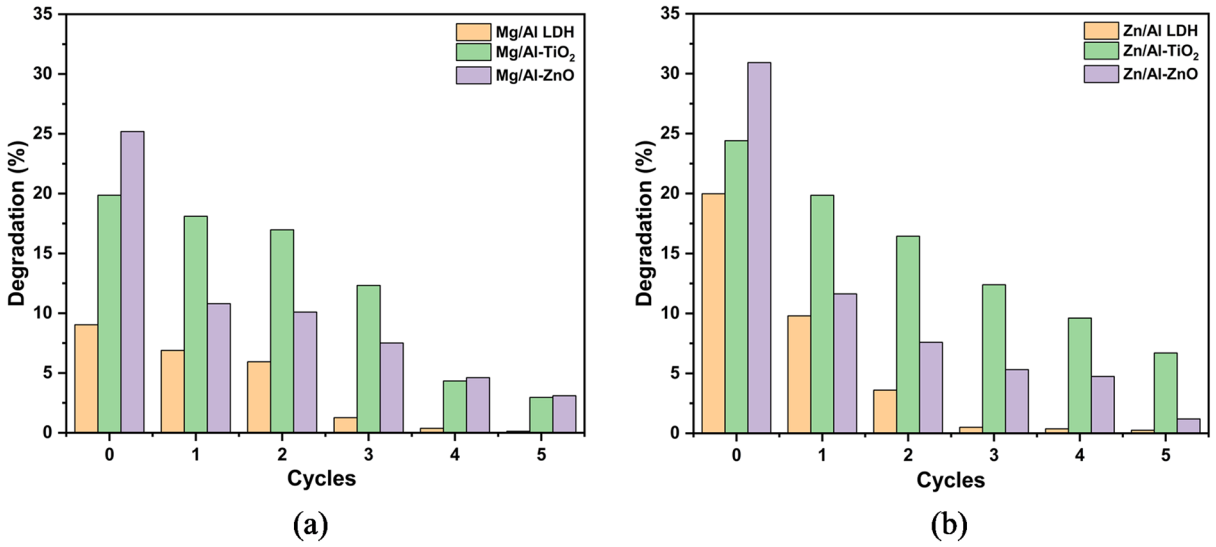

Figure 13. MB degradation regeneration cycle by: Mg/Al LDH based catalysts (a), Zn/Al LDH based catalysts (b)

dyes rhodamine-B and methylene blue. The preparation of Mg/Al-TiO_2 and Zn/Al-TiO_2 composites as well as Mg/Al-ZnO and Zn/Al-ZnO composites also improved the regeneration performance of RhB and MB degradation compared to LDH in the basic structure of Mg/Al LDH and Zn/Al LDH. LDH-ZnO composites allow it to be used as an alternative to LDH-TiO_2 in degrading dyestuffs. The results of characterization using XRD or FTIR of materials that have degraded RhB and MB show that LDH pristine still have an LDH structure and composites also still have LDH-metal oxide structure.

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