

STUDY ON THE DEGRADATION FOR RHODAMINE-B IN WATER USING Cu^{2+} DOPED HYDROTALCITE COMPOUNDS

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ABSTRACT

We report on the synthesis of CuMgAl hydrotalcite compounds by the coprecipitation method, using nitrate salts with Mg^{2+} , Al^{3+} , Cu^{2+} , and Na_2CO_3 , controlled pH = 9.5 by NaOH 2.0 M. The characteristics of the compound were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM) images, energy dispersive X-ray spectrum (EDS), nitrogen adsorption/desorption isotherms (BET), and UV-Vis diffuse reflectance spectra. As a result, samples with a double hydrotalcite layer structure indicated that able to absorb light in the visible range. The conversion for the rhodamine-B degradation increased as the doped Cu^{2+} ratio in samples from 0 to 3.0. These results showed that 3th CuMgAl2.0, CuMgAl2.5, and Cu-MgAl3.0 samples excellent degraded for rhodamine-B under visible light.

Keywords: Hydrotalcites; coprecipitation; characterization; photocatalyst; conversion.

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NGHIÊN CỨU KHẢ NĂNG XỬ LÝ RHODAMIN-B TRONG NƯỚC BẰNG CÁC VẬT LIỆU TỔNG HỢP HYDROTANXIT CÂY Cu^{2+}

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TÓM TẮT

Chúng tôi báo cáo kết quả tổng hợp các vật liệu hydrotanxit CuMgAl theo phương pháp đồng kết tủa sử dụng các muối nitrat của Mg^{2+} , Al^{3+} , Cu^{2+} và Na_2CO_3 , ở pH = 9,5 điều chỉnh bởi NaOH 2,0 M. Đặc trưng cấu trúc vật liệu được tiến hành bằng gián đồ XRD; ảnh TEM; phổ EDS, đường đẳng nhiệt hấp phụ/ giải hấp phụ N_2 (BET), phổ UV-Vis DRS. Kết quả phân tích cho thấy, các mẫu vật liệu tổng hợp đều có cấu trúc lớp kép của hydrotanxit và đều có khả năng hấp thụ ánh sáng trong vùng nhìn thấy. Độ chuyển hóa rhodamin-B tăng khi tỉ lệ Cu^{2+} được cấy trong các mẫu từ 0 – 3,0. Các kết quả thu được cho thấy 3 mẫu vật liệu CuMgAl2,0, CuMgAl2,5 và Cu-MgAl3,0 có khả năng phân hủy rhodamin-B rất tốt dưới ánh sáng khả kiến của đèn LED 30 W.

Từ khóa: Hydrotanxit; đồng kết tủa; đặc trưng cấu trúc; quang xúc tác; độ chuyển hóa

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1. Introduction

Hydrotalcite compounds, and bihydroxide layers have been interested in many applications, including adsorption, a catalyst for organic synthesis, petrochemical catalysts, photocatalysts, etc [1]. Hydrotalcites with the nominal formula as $Mg_{0.667}Al_{0.333}(OH)_2(CO_3)_{0.167}(H_2O)_{0.5}$, Zaccagnite $Zn_4Al_2(OH)_{12}(CO_3) \cdot 3H_2O$ have been known. Hydrotalcite materials contain different ratios of M^{2+}/M^{3+} synthesized (M^{2+} : such as Mg^{2+} , Zn^{2+} , etc; M^{3+} : Al^{3+} , Fe^{3+} , etc. After that, hydrotalcites have modified with transition metals or their oxides to create new materials [1]. Materials ZnAl-LDH, ZnFeAl-LDH, FeOOH-LDH [2]; HT, HT/TiO₂, HT/TiO₂/Fe, etc [3]; Zn-Al-Ti [4], synthesized to study for degradation of methylene blue in water under UV or visible light. The layered double hydrotalcite and hydroxide compounds have been synthesized and studied to photodegrade rhodamine-B in water, such as Cu-Ti-hydrotalcite [5]; Zn/Ti-LDH and Ag/LDH [6]. Materials like hydrotalcite and layered double hydroxide have also been synthesized for the fields of organic catalysis, petrochemical such as MgCuAl- used to selectively oxidize styrene [7], Mg-Al [8] for green hydrocarbon synthesis through decarboxylation process, Zn-Cu-Ti [9] for oxidation reaction CO, Cu-Al catalyst for alkylation reaction indole using benzaldehyde agent [10], etc. The general characterizations of hydrotalcites, modified hydrotalcites or layered double hydroxides are synthesized from salts of valence metal II and III or II and IV, ensured their molar ratios within the optimal limits

($M^{2+} : M^{3+} = 2: 1$ or $3: 1$ or $4: 1$; $M^{2+} : M^{4+} = 5: 1$ or $5: 2$ ratio), at high pH from 9.0 – 10.0. Based on the reference to the above documents [7], we synthesized Cu²⁺ doped hydrotalcites with different Cu²⁺ ratios and applied as a catalyst for rhodamine-B degradation in water under 30W LED light (6500K).

2. Experimental methods

2.1. Preparation of the catalysts

The compounds were synthesized following the materials [5, 7]: $Al(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ (Merck) are simultaneously dissolved in 150 mL of deionized water. The reaction vessel was placed on a magnetic stirrer, stirring the sample at room temperature for 30 min, and obtain a homogeneous solution. Next, 25 mL of 0.6M Na_2CO_3 (Merck) was added dropwise into the reaction vessel, and vigorously stirred for 60 minutes at room temperature. The entire mixture was transferred to a 400 mL beaker, and the pH of the mixture was adjusted with NaOH 2M solution to pH = 9.5 to obtain the gel. Then, the gel was stirred on the stirrer for 60 minutes. The aging of the gel was performed in a Teflon vessel at 100°C for 24 h. After gel aged, the product was filled, washed with hot deionized water (70 °C) several times to pH = 7.0. The solid was dried at 80 °C for 24 h to obtain samples of hydrotalcite materials (denoted MgAl) and Cu²⁺ doped hydrotalcites (indicated CuMgAln - n is the ratio of Cu in the sample) (Table 1). The samples were then crushed with an agate pestle and used to research on their characterization and photocatalysis.

Table 1. Samples of hydrotalcite and Cu²⁺ doped hydrotalcites (CuMgAl)

No.	Denote	Molar ratios Cu : Mg : Al : CO ₃	Nominal Formula	Value of d ₀₀₃ (Å)
1	MgAl	0 : 7.0 : 3.0 : 1.5	$Mg_{0.7}Al_{0.3}(OH)_2(CO_3)_{0.15} \cdot mH_2O$	7.830
2	CuMgAl0.5	0.5 : 6.5 : 3.0 : 1.5	$Mg_{0.65}Cu_{0.05}Al_{0.3}(OH)_2(CO_3)_{0.15} \cdot mH_2O$	7.667
3	CuMgAl1.0	1.0 : 6.0 : 3.0 : 1.5	$Mg_{0.6}Cu_{0.1}Al_{0.3}(OH)_2(CO_3)_{0.15} \cdot mH_2O$	7.767
4	CuMgAl1.5	1.5 : 5.5 : 3.0 : 1.5	$Mg_{0.55}Cu_{0.15}Al_{0.3}(OH)_2(CO_3)_{0.15} \cdot mH_2O$	7.825
5	CuMgAl2.0	2.0 : 5.0 : 3.0 : 1.5	$Mg_{0.5}Cu_{0.2}Al_{0.3}(OH)_2(CO_3)_{0.15} \cdot mH_2O$	7.762
6	CuMgAl2.5	2.5 : 4.5 : 3.0 : 1.5	$Mg_{0.45}Cu_{0.25}Al_{0.3}(OH)_2(CO_3)_{0.15} \cdot mH_2O$	7.859
7	CuMgAl3.0	3.0 : 4.0 : 3.0 : 1.5	$Mg_{0.4}Cu_{0.3}Al_{0.3}(OH)_2(CO_3)_{0.15} \cdot mH_2O$	7.794
8	CuMgAl3.5	3.5 : 3.5 : 3.0 : 1.5	$Mg_{0.35}Cu_{0.35}Al_{0.3}(OH)_2(CO_3)_{0.15} \cdot mH_2O$	7.865

Value d₀₀₃: Distance between two inner layers

2.2. Studying characterization of the catalysts

The structure of the compound was investigated by the X-ray diffraction methods. The elements of catalysts were measured by the EDS (Energy Dispersive spectrometry) in the Faculty of Chemistry - Hanoi University of Science - VNU. TEM images of materials were measured at the Hanoi National Institute of Hygiene and Epidemiology. The nitrogen adsorption/desorption isotherms were collected in the Institute of Chemistry - Vietnam Academy of Sciences. UV-Vis diffraction spectrum (UV-Vis DRS) was run on U-4100 Spectrophotometer in the Faculty of Chemistry – Thai Nguyen University of Education - Thai Nguyen University.

2.3. Investigating catalytic activity of synthetic material samples for rhodamine-B (Rh-B)

To investigate the adsorption capacity of synthesized material samples, we conducted the following survey: Using 0.2 g of synthetic material samples to carry out the adsorption with the 250 mL rhodamine-B and its 30 ppm concentration in the dark. After every 15 minutes, the sample was centrifuged and measured at the 553 nm optical absorbance to determine the concentration of Rh-B.

To investigate the photochemical degradation ability of synthetic material samples, we surveyed as follows: Using 0.2 g of synthetic material samples to conduct the adsorption with 250 mL rhodamine-B, 30 ppm concentration in the dark for 30 minutes to reach adsorption equilibrium. After adsorption in the dark, 1.2 mL of 30% H₂O₂ was added to a glass beaker containing rhodamine-B. The catalytic performance of synthesized samples was examined by the ability to decompose rhodamine-B under LED lighting over time. After every 30 minutes, samples were taken out, centrifuged and measured the molecular absorbance at 553 nm to determine the Rh-B concentration at the time of sampling. From there, it is possible to calculate the conversion of Rh-B by lighting time.

2.4. Determination of rhodamine-B concentration in water (blended samples)

A calibration curve for determining the concentration of rhodamine-B in water was created by the photometric method. Rhodamine-B was measured at the 553 nm optical absorbance. The rhodamine-B concentration arranged from 1.0 to 10.0 ppm. We get the equation the standard curve to determine the rhodamine-B concentration as $y = 0.1692x + 0.001$. $R^2 = 0.9993$. After centrifugation to remove material samples, the remaining rhodamine-B concentration in the solution was determined by measuring the molecular absorbance on UV-Vis 1700 instrument in the Faculty of Chemistry - Thai Nguyen University of Education and calculated using the standard curve method.

3. Results and discussion

3.1. Characterizations of the synthesized compounds

3.1.1. XRD analysis

Figure 1 shows XRD results of 8 samples that all samples have characteristic peaks for hydroxalcite-like crystal structure. Values d_{003} at angle $2\theta = 11.57$, d_{006} at angle $2\theta = 23.45$ and d_{110} at angle $2\theta = 60.9$ are used to calculate the lattice parameters of the material (distance between metal ions and thickness of bruxite layer) [7]. The results follow: parameter a ranges from $3.044 - 3.056\text{\AA}$, parameter c reaches $22.92 - 23.53\text{\AA}$. These parameters a and c are quite similar to the results in the document [7]. The distance between the two inner layers (d_{003}) reported in Table 1 shows that the values of d_{003} vary in the range of $7.667 - 7.859\text{\AA}$ characterizing for the bruxite structure of hydroxalcites with CO₃²⁻ ion between the layers. The peak intensity and peak height at the 11.57° diffraction angle decrease when the increasing ratio of doped Cu²⁺ in the samples. However, doped Cu²⁺ materials still retain the most basic characterizations of materials with hydroxalcite-like structure. Therefore, the implantation of the Cu²⁺ ion into hydroxalcite

structure not only slightly changed the morphology bruxite-like structure of hydrotalcite compounds but also gained the modified materials with high catalytic activity.

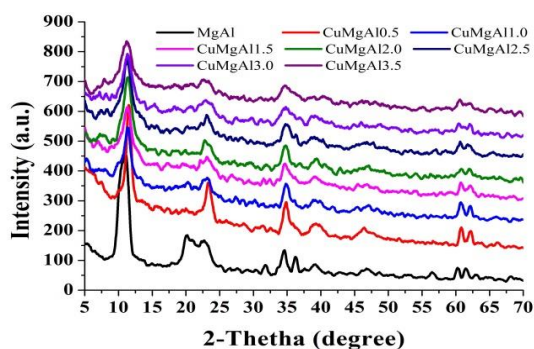
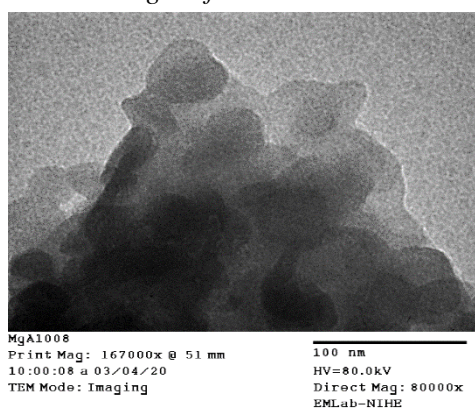
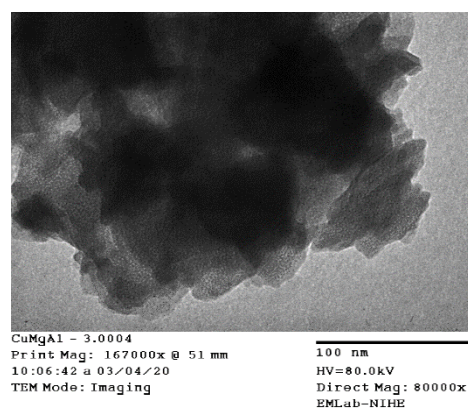


Figure 1. XRD patterns of synthesized samples denoted MgAl, CuMgAl0.5 – CuMgAl3.5

3.1.2. TEM images of materials



A



B

Figure 2. Two TEM images of MgAl (A) and CuMgAl3.0 (B) materials

3.1.3. Energy dispersive spectrometry (EDS)

The obtained results as analyzing elements Mg, Al, Cu, O in 3 samples MgAl, CuMgAl2.0 and CuMgAl3.0 are shown in Table 2 below. The ratios of elements Mg : Al and Cu : Mg : Al does not coincide with the theoretical calculation ratios for synthesizing materials (Mg : Al = 7 : 3; Cu : Mg : Al = 2 : 5 : 3 or 3 : 4 : 3). These results explain that a part of Al(OH)₃, Zn(OH)₂ is dissolved at the high pH values causing a reduction of the Al³⁺ or Zn²⁺ amount in the sample. On the other hand, the EDS spectrum analysis method is based on the determination of SEM image points, so it is not possible to accurately reflect the total percentage of each element in the material. Typically, we must decompose the sample and determine the percent of elements by AAS or ICP-MS spectroscopy.

Table 2. Percent of elements Mg, Al, Cu, O in the synthesized samples

Sample	MgAl	CuMgAl2.0	CuMgAl3.0
Element		% element	
O	70.95	64.34	69.05
Mg	19.68	10.83	11.61
Al	9.37	10.46	8.68
Cu		14.38	10.66

TEM images of the two prepared samples denoted as MgAl and CuMgAl3.5 in Figure 2 clearly showed the double layered structure of hydrotalcite material. The layers have an uneven size which is a common feature of hydrotalcites. When doped with a dosage of Cu²⁺ = 0.35 molar. The TEM image of the material shows the color uniformity of hydrotalcite layers and small porous holes appear inside the plates. This result confirmed that the homologous replacement of Cu²⁺ with Mg²⁺ takes place inside the hydrotalcite networks due to the similar octagonal geometry of Cu²⁺ and Mg²⁺ [7]. The mesoporous systems are consistent with the results obtained when analyzing the nitrogen adsorption/desorption isotherms.

3.1.4. Nitrogen adsorption/desorption isotherms of materials

The analysis results of nitrogen adsorption/desorption isotherms (BET) in Figure 3 show that the composites samples have adsorption and desorption curves depending on type IV with a broad H3 type hysteresis loop attributed to the presence of mesopores according to IUPAC classification [2, 7]. The results are entirely consistent with the structure of hydrotalcite materials. BET surface area and average pore diameter of the MgAl, CuMgAl2.0 and CuMgAl3.0 materials are 47.39; 79.15 and 36.02 m²/g; 17.52; 15.22 and 12.35 nm.

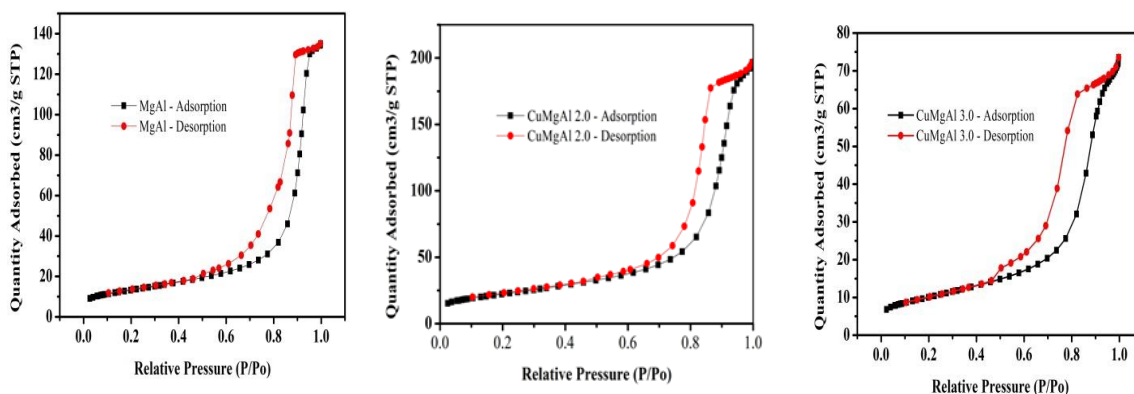


Figure 3. Nitrogen adsorption/desorption (BET) of 3th MgAl, CuMgAl2.0 and CuMgAl3.0 samples

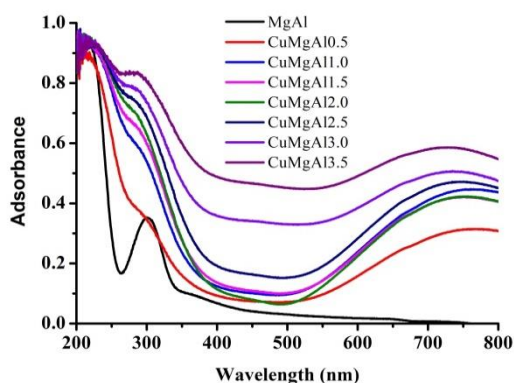


Figure 4. UV-Vis DRS of materials

3.1.5. UV-Vis Diffraction spectrum of material samples

UV-Vis DRS spectrum of composites samples is shown in Figure 4. The MgAl hydrotalcite sample has two absorption wave areas of 210 - 240 nm and 260 - 320 nm and the maximum absorption wavelength is about 360 nm. When Cu²⁺ ion was doped into a network of hydrotalcite, the absorption bank shifted strongly to the visible area. The maximum absorption wavelength increases with Cu²⁺ dosage in samples from 0.5 to 3.5. Besides increasing of adsorption wavelength, the absorption shoulders also shift to the red zone when increasing the amount of Cu²⁺ in

the sample. The doped Cu²⁺ hydrotalcite materials absorb approximately from 395 to 495 nm. Therefore, from the results of UV-Vis DRS spectrum analysis above, it is possible to predict samples of doped Cu²⁺ with high photocatalytic activity under visible light (LED light 30 W).

3.2. Catalytic performance of the synthetic samples for rhodamine-B degradation

3.2.1. Results of the 30 ppm Rh-B adsorption capacity of synthetic samples

Using synthetic samples to conduct surveys of their adsorption capacity for 30 ppm Rh-B. the results show that all examined samples are negligible adsorption for Rh-B. The adsorption results are similar to documents [2, 5]. UV-Vis spectra of Rh-B after 120 minutes of adsorption in the dark on samples are shown in Figure 5 (materials MgAl, CuMgAl1.0 and CuMgAl3.0).

3.2.2. Results of the survey on the photocatalytic ability of synthetic samples

a. Effect of doped Cu²⁺ dosage and irradiation time

Investigation of the 30 ppm Rh-B degradation progressing using synthesized compounds,

the results obtained in Figure 6 show that as the irradiation time increases, the Rh-B conversion rate on all of the doped Cu²⁺ samples increase (except for MgAl sample, Rh-B transformation only reaches about 22% after 240 minutes of irradiation). Especially, 3 photocatalytic samples (CuMgAl2.0, CuMgAl2.5 and CuMgAl3.0) have the best catalytic activity for the Rh-B photodegradation (Rh-B conversion rate on these 3 material samples can reach 90 - 92% after only 30 minutes of irradiation under LED light 30 W). This is due to the role of Cu²⁺ ion in the material samples due to producing the electron (e⁻) and hole (h⁺) pairs

and hydroxyl (OH[•]) radicals following by equations (1 – 7) below [3], [11], [12].

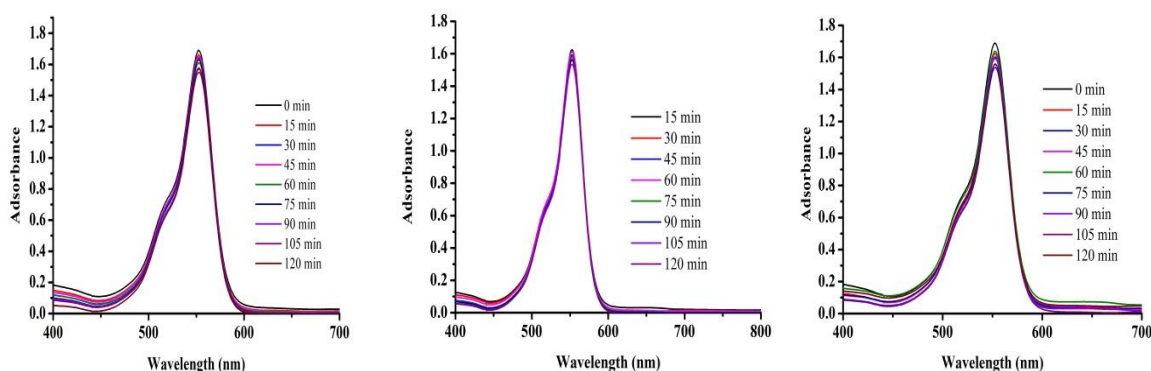
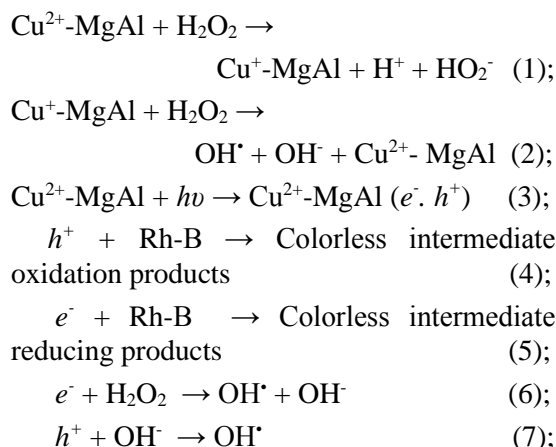


Figure 5. Survey results of 30 ppm Rh-B adsorption capacity on samples of synthetic materials MgAl, CuMgAl1.0 and CuMgAl3.0

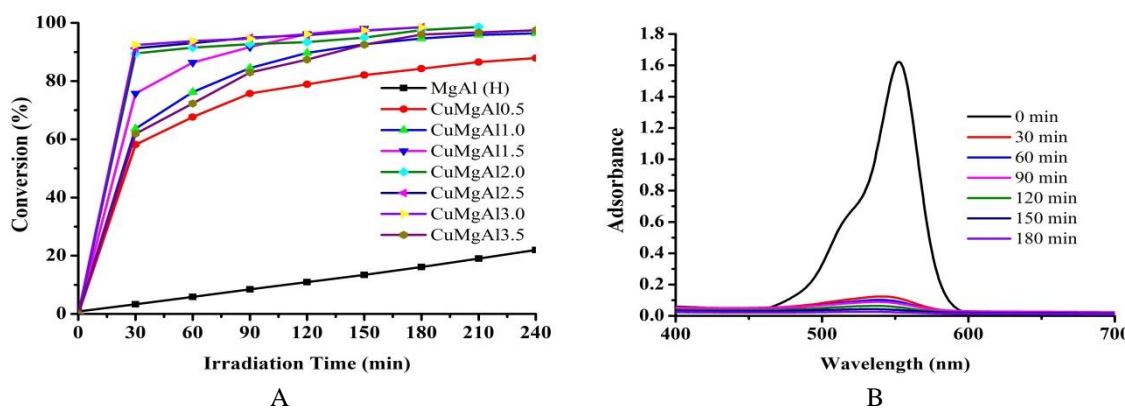


Figure 6. Rh-B conversion on synthetic materials (A) and UV-Vis spectrum of Rh-B after 180 minutes irradiation with 30 W LED of CuMgAl3.0 sample (B)

b. Investigate the effect of environmental pH on the catalytic activity of materials

Environmental pH has a significant influence on the catalytic activity of the examined material (sample CuMgAl2.0) (Figure 7). In a strongly acidic environment (pH = 2.0), the catalytic activity of the investigated sample decreases markedly. Possibly due to the destruction of the material structure, the amount of Cu²⁺ in the sample is dissolved which reduces the number of catalyst centers. The catalytic activity of the material also decreases at pH = 10.0 compared to the

optimal pH range from 4.0 to 8.0. This may be due to the increased viscosity of the solution at high pH reducing the possibility of diffusion of Rh-B and light absorption of materials. Therefore, the optimal pH range for the Rh-B degradation of materials is 4.0 – 8.0.

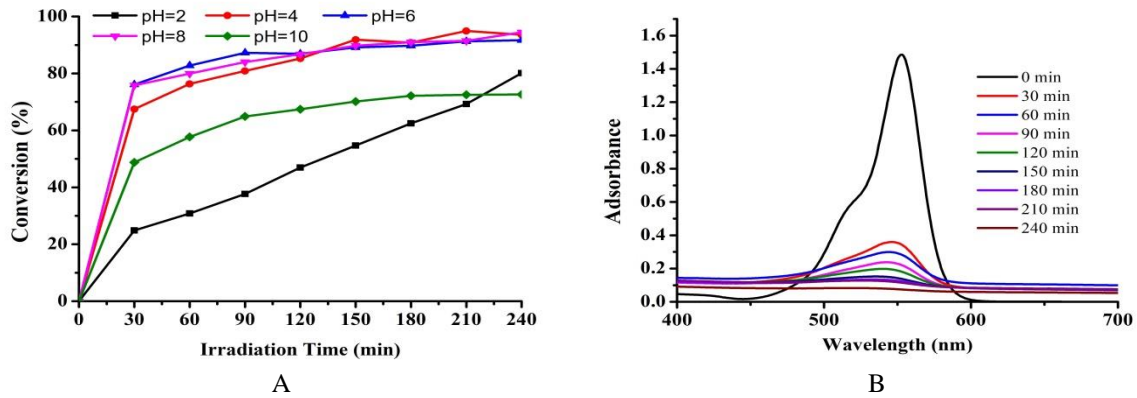


Figure 7. Rh-B conversion on CuMgAl_{2.0} sample (A) and UV-Vis spectrum of rhodamine-B after 240 minutes of lighting by 30 W LED at pH = 8.0 (B)

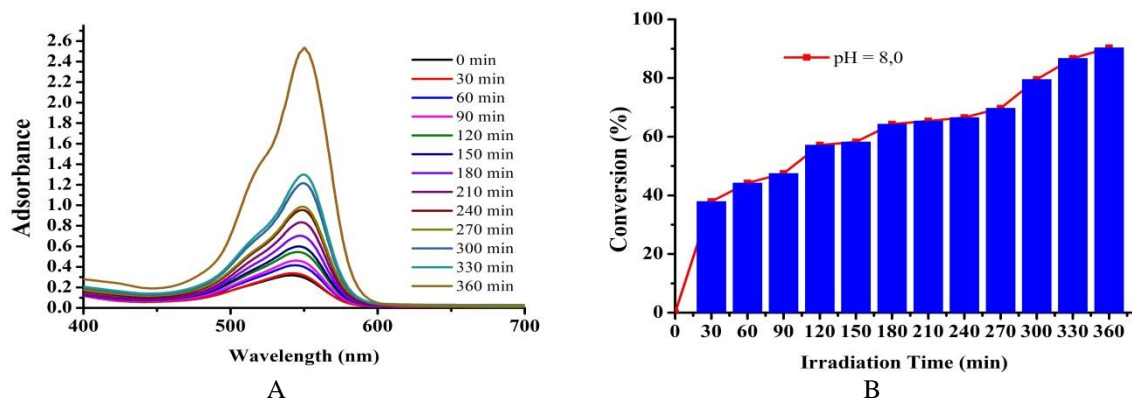


Figure 8. UV-Vis spectra of dye textile in waste water of sedge mat weaving village - Quynh Phu district - Thai Binh province (A) and dye conversion of CuMgAl_{2.0} sample after 360 min irradiation (B)

c. Wastewater treatment results of sedge mat weaving village (Quynh Phu District - Thai Binh)

Using sample material CuMgAl_{2.0} to investigate the ability to dye decompose in wastewater of sedge mat weaving village - Quynh Phu district - Thai Binh province.

Diluting the wastewater sample 30 times with distilled water, then pH solution is adjusted to reach 8.0 by solution HCl 0.1N and NaOH 0.1N. 0.2 g of CuMgAl_{2.0} and 1.2 mL of H₂O₂ 30% is used to add to a glass containing 250 mL of diluted wastewater sample. Conducting a survey experiment, after about 30 minutes of sampling, centrifuging and spectral scanning on the UV-Vis 1700 machine, we get the results shown in Figure 8

below. The color conversion in waste water increases gradually over time illumination. The absorbance peak height of the dye mixture at 550 nm also decreases simultaneously. After 360 minutes of irradiation, the solution becomes colorless completely, the conversion of color chemicals reaches about 90%. Therefore, the survey results show the practical applicability of the synthetic materials to Textile dye wastewater treatment.

4. Conclusion

The material samples were successfully synthesized by the co-precipitation method. The characterizations of synthetic materials have confirmed that they have the double

layered structure of hydrotalcite and have a strong absorption edge shifting to the visible light area. In general, synthetic material samples have low Rh-B adsorption capacity. On the contrary, they have a high ability to photodegrade for Rh-B when irradiated by the light of 30 W LED together with the presence of H₂O₂ 30%. 3 samples of CuMgAl_{2.0}, CuMgAl_{2.5} and CuMgAl_{3.0} have the highest Rh-B conversion rate and the best photocatalytic activity at the optimal pH = 8.0. Some of the synthesized materials with an optimal Cu²⁺ doped ratio are the ability to apply directly in practice for the treatment of textile dye wastewater (the conversion of color chemicals for the sedge mat weaving wastewater can reach about 90% after 360 min irradiation).

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