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Enhanced oxidation of rhodamine B using Mg-Cu-Al hydrotalcite/chitosan composites as catalysts

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ABSTRACT

A series of Mg-Cu-Al hydrotalcite/chitosan materials have been synthesized via a co-precipitation method, in which chitosan is synthesized from chitin extraction from waste shrimp shells. The obtained solids were characterized by XRD, BET, EDX, IR techniques. The materials have a well crystallized hydrotalcite structure and medium surface area. It was observed that Mg-Cu-Al hydrotalcite/chitosan catalysts exhibited the high activity in catalyzing enhanced oxidation of rhodamine B solution with H_2O_2. 95% of 100 mg/L of rhodamine B solution could be decolourized by Mg-Cu-Al hydrotalcite/chitosan composite with the presence of hydrogen peroxide at room temperature for 150 minutes. Therefore, Mg-Cu-Al hydrotalcite/chitosan is a promising and reasonable catalyst for use in the enhanced oxidation of rhodamine B.

1. Introduction

Hydrotalcite, which is a typical layered anionic clay with a general formula of $[M^{II}_{1-x} M^{III}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}.mH_2O$ [1-2], exists in both natural mineral form and can be synthesized, is cheap and easy to find, environmentally friendly. Hydrotalcites used as catalysts [3-4], ion exchangers [5], adsorbents [6]. In recent years, some researchers have developed organic-inorganic composites which are capable of combining the physical properties of the components to obtain new structural or functional properties. Polymer composites could be prepared by dispersing inorganic materials in an organic polymer matrix to create new hybrid materials [7-8]. Chitosan, which is low cost and available on a largre quantity, has the features like non-toxicity, biodegradability. Therefore, it attracts the interest of researchers using for the removal of toxic ions [2],[9]. The hybrid materials between hydrotalcites and chitosan contained hydroxyl and amino groups promising a high capacity in the removal of dyes from aqueous solution. Rhodamine B is one of the widely used dyes in textiles and food stuffs [10]. Rhodamine B pollution from effluents affected strongly on human life due to its toxic nature. The residues of rhodamine B in the waste water may be removed by the traditional methods of the wastewater treament such as sedimentation, flocculation and chemical coagulation, filtration and aeration. However, these techniques have some disadvantages such as toxic by-products, energy consumption and require large areas for treatment. On the contrary, the advanced oxidation process is considered to be the most effective treatment methods because it can decompose organic compounds by generating strong oxidizing substances, such as hydroxyl radical (HO•) [11].

In this study, the Mg-Cu-Al hydrotalcite/chitosan materials were synthesized and used as heterogeneous catalysts for the degradation of rhodamine B aqueous solution in the presence of hydrogen peroxide.

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2. Experimental

Chitosan in this study was synthesized from shrimp shells, collected from waste shrimp shells from seafood markets. After being washed, shrimp shells were treated with HCl and NaOH to obtain chitin, then chitin was converted to chitosan by using 40% NaOH for 48 hours at 120°C. The Mg-Cu-Al hydrotalcite was prepared by the slow addition of two solutions. The first solution contains the nitrates salts of the following metals: $Mg(NO)_3.6H_2O$ (99%), $Cu(NO_3)_2.3H_2O$ (98%) and $Al(NO_3)_3.9H_2O$ (98%) with the molar ratio of Mg : Cu : Al shown in Table 1 and the second solution contains aqueous solutions simultaneously of KOH and Na_2CO_3. The second solution was dropwised into the first one at constant pH at 9-10 for 30 minutes with vigorous stirring at room temperature. Then, 6.0 grams of chitosan was dispersed in the CH_3COOH solution that was added. The resulting gel-like material was heated at 65°C for 24 hours. The precipitate was filtered, washed with deionized water up to pH = 7 and dried at 80°C for 24 hours. The dried Mg-Cu-Al hydrotalcite/chitosan composite was ground to powder form and was characterized by physical techniques of Power X-ray diffraction (XRD), Energy dispersive spectroscopy (EDS) and Fourier transform infrared (FT-IR) prior to use as catalysts for the advanced oxidation of rhodamine B.

The oxidation reaction of rhodamine B was carried out in a beaker with H_2O_2 solution as the oxidizing agent. 0.2 grams of catalyst was added in 100 mL rhodamine B with the desired initial concentration. H_2O_2 solution was put into at once. The mixture was stirred and maintained at room temperature (26-28°C), pH = 6 (the pH of the solution at normal conditions). The reaction was conducted for a total time of 150 minutes. Every 30 minutes, 5 mL of the reaction mixture was taken with a pipette and the solution was filtered to measure the UV-VIS molecular absorption spectrum at the maximum absorption wavelengths of rhodamine B (553 nm) on a Jasco V-730 UV-Vis spectrometer. The degradation efficiency of rodamine B in the oxidation processes (%) could be given by:

$$\text{Degradation Efficiency (\%)} = \frac{C_o - C}{C_o} \times 100\%$$

Where C_o and C are the initial concentration and the measured concentration of rhodamine B at a given time, respectively.

3. Results and discussion

Four samples of Mg-Cu-Al hydrotalcite/chitosan composite are prepared by the coprecipitation method with the ratio of metals and chitosan are presented in Table 1. The two samples designated as TH00 and TH03 are represented catalysts for testing the characteristic of XRD.

Power X-ray diffraction patterns for two samples (TH00 and TH03) are displayed in Fig. 1. The presence of an intense peak (003) at 11.9° followed by two smaller peaks (006) and (012) at 23.9° and 35.2°, respectively confirmed that synthesized products showed a typical structure of layered double hydroxides [12-13]. The other broad peaks at higher 2-theta are presented as the diffraction peaks by (015), (018) confirming the formation of a well-crystallized hydrotalcite structure [14-15].

Table 1: The molar ratio of metals and chitosan in samples of Mg-Cu-Al hydrotalcite/chitosan composite

Samples	The molar ratio of metals and chitosan
TH00	0.07 mol Mg : 0.00 mol Cu : 0.03 mol Al + 6 g chitosan
TH01	0.06 mol Mg : 0.01 mol Cu : 0.03 mol Al + 6 g chitosan
TH02	0.05 mol Mg : 0.02 mol Cu : 0.03 mol Al + 6 g chitosan
TH03	0.04 mol Mg : 0.03 mol Cu : 0.03 mol Al + 6 g chitosan

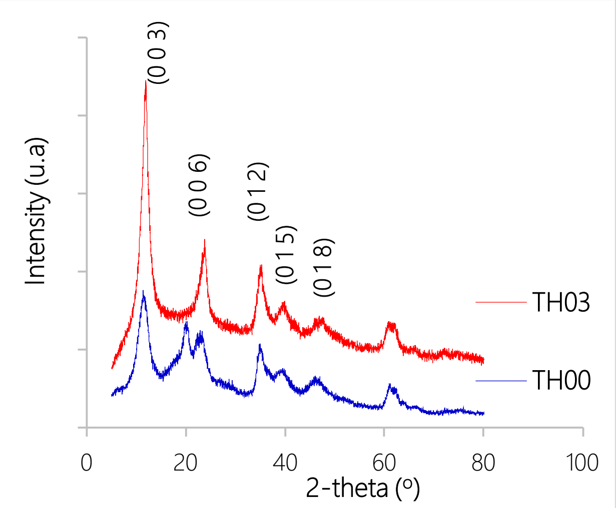

Figure 1: XRD patterns of TH00 and TH03 samples.

The FT-IR analysis was used to determine the chemical composition of Mg-Cu-Al hydrotalcite/chitosan composite. Fig. 2A shows the results of the FT-IR spectra, a broad and strong band at 3387 cm^{-1} is probably assigned to the O-H stretching (from the brucite-like layer) overlapped with N-H ($-NH_2$)

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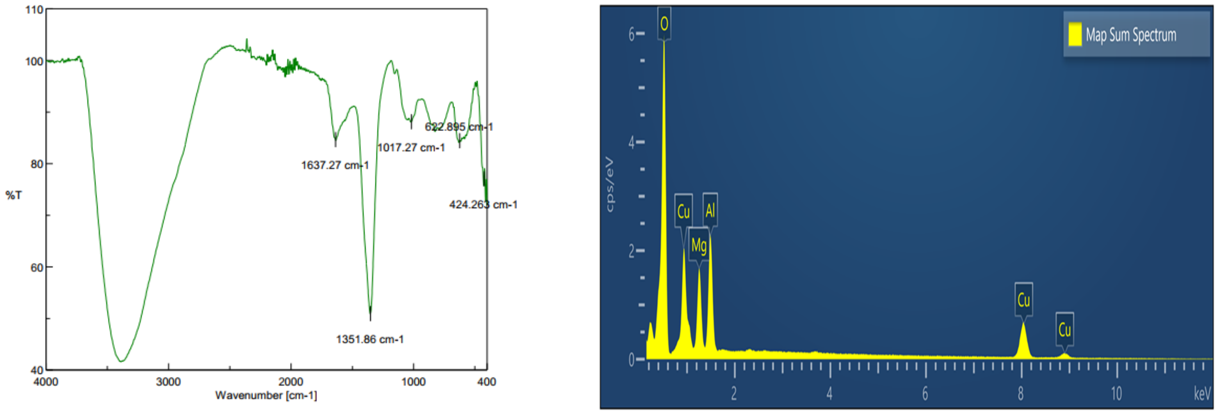
stretching in chitosan [7]. The weak band at 1637 cm^{-1} is corresponded to the bending mode of interlayer water molecules while the strong band at 1351 cm^{-1} is relative to the asymmetric stretching mode of the carbonate species [15, 16]. The bond in lower wavelength spectrum (424 cm^{-1} to 622 cm^{-1}) corresponded to Metal ion-OH vibration and O-Metal ion-O stretching [7]. The EDS analysis method indicated the presence of all components. EDS pectra of the TH03 sample in Fig. 2B show the signals of Cu, Mg, Al, O.



(A)

(B)

Figure 2: FT-IR (A) and EDS (B) spectra of the TH03 sample.

The catalytic activity of all synthesized Mg-Cu-Al hydrotalcite/chitosan composites in the oxidation of rhodamin B with concentration 100 mg/L was carried out in the same reaction conditions in addition a blank test without catalyst. The results were showed in Fig. 3.

It can be seen from the results that the blank experiment shows very low degradation effficiency. As for the catalyst sample with Cu-free (TH00) exhibits a rather low degradation effficiency about 10-11%. However, the degradation efficiency of rhodamine B sharply increases from 10% on TH00 sample to 80-95% on Mg-Cu-Al hydrotalcite/chitosan composite. The results indicate an obvious synergetic effect between copper ions, basic sites and H_2O_2 on the oxidation of rhodamine B [15,17].

The results from Fig. 3 also indicate that the degradation efficiency of rhodamine B rises rapidly during the first 90 min and then gradually stabilizes. These results demonstrate the catalytic role of copper ions in the oxidation of rhodamine B. Copper ions in the crystal lattice of Mg-Cu-Al hydrotalcite/chitosan composite perform as active sites the decomposition of H_2O_2 to form $HO^\bullet$ radicals which strongly influence the oxidation efficiency of rhodamine B. Therefore, Cu^{2+} ions are introduced into hydrotalcite lattice, the degradation efficiency of rhodamine B increases monotonically with the amount of copper. The activity of catalysts rises in the order of TH00 < TH01 < TH02 < TH03 (Fig. 3).

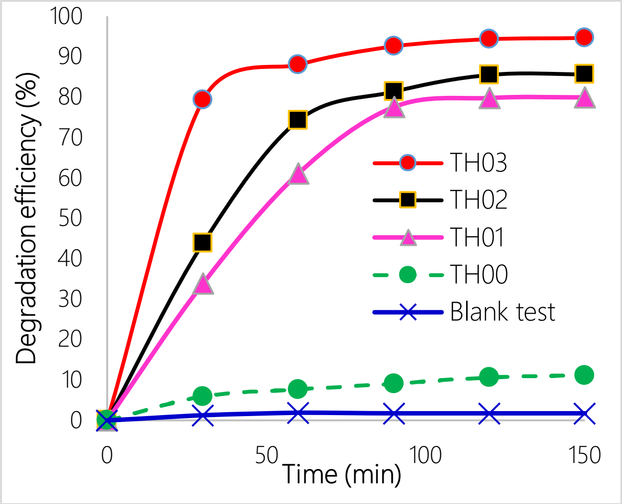


Figure 3: Effect of copper contents in Cu-doped hydrotalcites on the degradation efficiency of rhodamine B (100 mg/L of rhodamine B, 0.20 g of catalyst, 3.0 mL of H_2O_2, room temperature, pH = 6 (the pH of the solution at normal conditions)).

The amount of H_2O_2 in a reaction is also an important parameter for decomposition, therefore a series of experiments were performed on the oxidation of of rhodamine B (100 mg/L) with different volumes of H_2O_2 solution over the Mg-Cu-Al hydrotalcite/chitosan catalyst (TH03). The results from the effect of addition of H_2O_2 are summarized in Fig. 4.

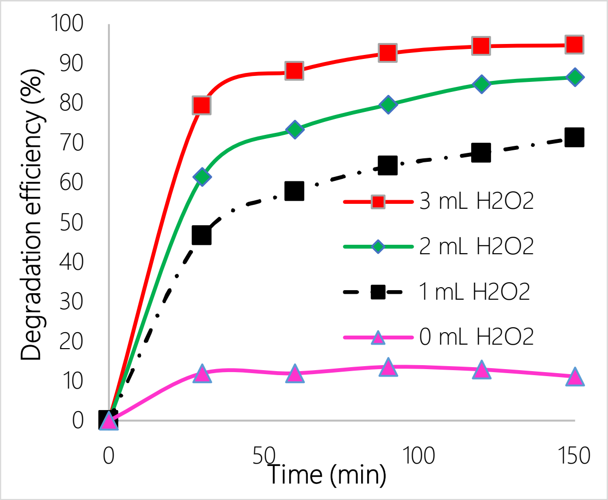


Figure 4: Effect of H_2O_2 amounts on the degradation efficiency of rhodamine B on TH03 catalyst sample (100 mg/L of rhodamine B, 0.20 g of catalyst, room temperature and pH = 6 (the pH of the solution at normal conditions)).

In case no H_2O_2 oxidant was added into the reaction, about 12-13% of rhodamine B was physically adsorbed on the catalyst. When the addition of H_2O_2 inceases from 1 to 3 mL, the degradation level of rhodamine B increases from 46 to 95%. This occurrence could be illustrated that when the addition volume of H_2O_2 rises, more hydroxyl radicals are available to attack the aromatic rings of dye molecules, therefore the rate of reaction enhances [18-19].

In terms of the application, the pollutant concentration is one of the most important parameters to study the dependence of removal efficiency on the initial concentration of dye. Fig. 5 reveals the results obtained from investigation effect of various initial dye concentrations on the degradation of rhodamine B. The degradation efficiency of dyes exhibits decreases from 95% to 80% with the increases of rhodamine B concentrations from 100 to 200 mg/L and the fixed amount of H_2O_2 in the experiments. This is due to the fact that at the lower concentration, many active sites are available on the catalyst surface with an excess of hydroxyl radicals; hence the percent degradation of dye increases. However, at the higher concentration the degradation efficiency is lower. The reason could be due to the formation of several layers of dye molecules adsorbed on the catalyst surface, which then prevent direct contact of the catalyst with hydroxyl radicals when the catalytic oxidation reaction occurs. The effect of the initial dyes concentrations on the efficiency of dye degradation was investigated by many researchers and the obtained results were the same [18,20-23].

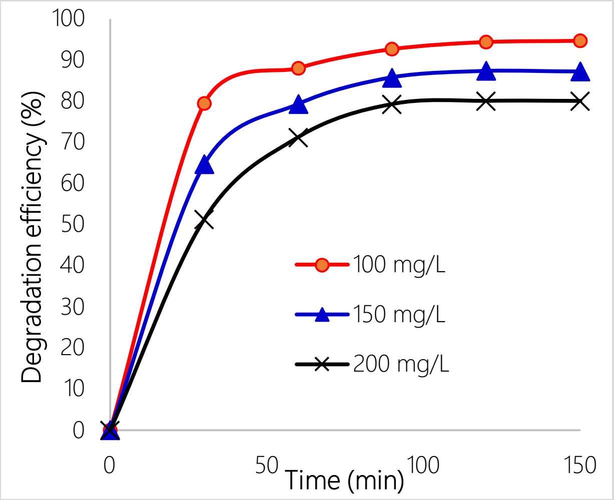


Figure 5: Effect of rhodamine B concentration on the degradation efficiency over TH03 catalyst sample (100 mg/L, 150 mg/L, 200 mg/L of rhodamine B, 0.20 g of catalyst, 3.0 of mL H_2O_2, room temperature and pH = 6 (the pH of the solution at normal conditions)).

4. Conclusion

The composites of Mg-Cu-Al hydrotalcite/chitosan were successfully synthesized by using co-precipitation method. The physical characterization using XRD and IR showed with the successful combination of hydrotalcite and chitosan to form composite materials with many functional groups. The EDS measurement results from the hydrotalcite/chitosan composite indicated that the Mg, Al, Cu and O elements were dominant in the sample. It is shown that in this study the prepared Mg-Cu-Al hydrotalcite/chitosan is a promising catalyst for rhodamine B removal. The highest degradation efficiency of rhodamine B was found on TH03 sample around 94-95% under mild conditions. The results also indicate the role of copper ions for the destruction of rhodamine B with the presence of H_2O_2 as an oxidant. Using chitosan as the support could not only increase the catalytic efficiency of the catalyst and reduce the cost as well as the quantity of metal required but also bring inherent advantages to the environment due to the green property, abundance, and stability of chitosan.

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