



## Photodecolorization of methylene blue using CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> prepared by low-temperature combustion method

Jucheng Zhang<sup>a,b</sup>, Ying He<sup>\*a,b</sup>, Yuqian Liu<sup>a,b</sup>, Xianlan Chen<sup>a,b</sup>, Yashun Chen<sup>a,b</sup> and Guowei Zhang<sup>a,b</sup>

<sup>a</sup>Key Laboratory of Natural Pharmaceutical and Chemical Biology of Yunnan Province, Mengzi, China

<sup>b</sup>School of Science Honghe University, Mengzi, China

### ABSTRACT

The CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst has been prepared by the low-temperature combustion method. And the photo-activity of the catalyst was investigated for decoloration methylene blue. The X-ray powder diffraction (XRD) was employed to characterize the catalysts. The concentrations of CuO, volume of H<sub>2</sub>O<sub>2</sub>, temperature of reaction system and the light source were studied. The results indicated CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst could efficient photodecoloration methylene blue (MB) under irradiation by solar and fluorescent lamp.

**Keywords:** low-temperature combustion method, CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, photo-decoloration, methylene blue

### INTRODUCTION

Dyes, the majority of them do not readily biodegrade and characterize by high chemical oxygen demand, represent potential environmental pollutants. There are many literatures reporting that many semiconductors have used to remove some pollutants with photoreaction, such as TiO<sub>2</sub>, ZnO, Er<sup>3+</sup>:YAlO<sub>3</sub>/TiO<sub>2</sub>, CdSe/ZnS[1-4].

Copper oxide (CuO), is a p-type semiconductor, has used as a passive and active component in solar cell technology and photovoltaic applications[5]. CuO supported on Al<sub>2</sub>O<sub>3</sub> has been widely studied for detecting gases and removal SO<sub>2</sub>, NO etc,[6,7] it is a biosensor for detecting Aspergillus niger fungi[8]. And it has used to catalyst some organic reaction, oxidize levulinic acid[9]. The CuO/Al<sub>2</sub>O<sub>3</sub> catalyst, which has prepared by consecutive impregnation method, has used degraded azo dyes[10,11]. and S.S. Ashour indicates that the mixed oxide catalysts often have catalytic properties that are superior to those of pure oxides[12].

In this work, the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is prepared by low-temperature combustion method and characterized by X-ray powder diffraction (XRD), the photo-activity has investigated on light source, concentration of CuO, system temperature and H<sub>2</sub>O<sub>2</sub> concentrations. The results suggest the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst has good photo-activity for decolorizing dye under irradiation.

### EXPERIMENTAL SECTION

#### 2.1 Materials

Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, CO(NH<sub>2</sub>)<sub>2</sub>, Methylene Blue (MB), H<sub>2</sub>O<sub>2</sub>(30%) were purchased from China National Medicines Corp. All reagents were analytical grade and used as received without further purification. Ultrapure water was employed in all experimental work. Methylene Blue solution was made at a concentration 0.01%.

#### 2.2 Preparation of the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

The CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by the low-temperature combustion method. The Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, CO(NH<sub>2</sub>)<sub>2</sub> were solved by distilled water in a beaker with stirring, and the mixture solution was

condensed in the crucible on electro cooker, then the sample was sintered at 300 °C for 20 min and at 550 °C for 4 h in a muffle furnace. The catalysts were prepared containing 0, 5, 7, 9, 11, 13, 15 wt.% CuO, respectively. The samples were named C0, C5, C7, C9, C11, C13, C15.

### 2.3 General reaction conditions

In each trial, 0.2 g catalyst was added to 200 mL 2 ppm aqueous MB solution and avoided irradiation 12 h, then the mixture was stirred under irradiation. After the allotted reaction time had elapsed, stirring was stopped and centrifuged, then the solution was detected at 664 nm by TU-1901 UV-vis spectrophotometer (Beijing Purkinje General Instrument Co. Ltd., China).

### 2.4 The decoloration ratio (DR)

The decolorization ratio is according the next equation:

$$\text{DR (\%)} = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

Where the  $A_0$  and  $A_t$  are the initial and final absorbance value of MB solution respectively.

## RESULTS AND DISCUSSION

### 3.1 Wide-angle XRD

The XRD was employed to characterize the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. Figure 1 shows an XRD pattern of CuO doped  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and the data indicate the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts have prepared by the low-temperature combustion method.

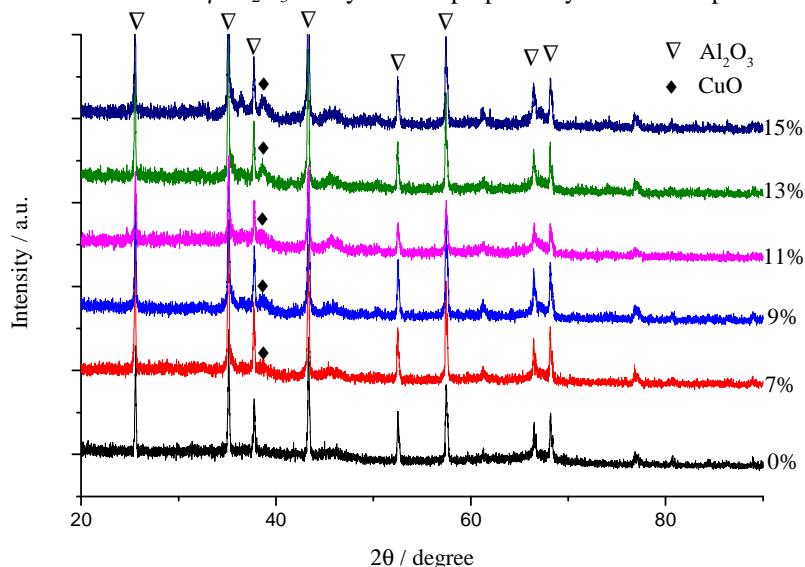


Figure 1. XRD pattern for the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts

In the literatures, the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts have prepared by the consecutive impregnation method, so the CuO is absorbed at the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. But in this work, the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts have prepared by solution, so CuO homogeneously incorporated in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. According to the XRD spectra, there are no obvious CuO peak appears which indicated the CuO is non-crystalloid phase [11].

### 3.2 Compare the decoloration activity between CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

The decolorization rate for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were investigated at the same conditions. In the trails, 0.9mL H<sub>2</sub>O<sub>2</sub> was injected in the reaction system, the temperature was controlled at 37 °C by a water cycle system, and irradiation with 36w fluorescent lamp. The data show in figure 2.

Figure 2 show the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> could photo-decolorize MB under irradiation, the DR is 28.5%. The catalyst C13, 13 % CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, decolorized ratio is 98.3%, far higher than  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The result indicated the CuO is the activity composition in catalyst.

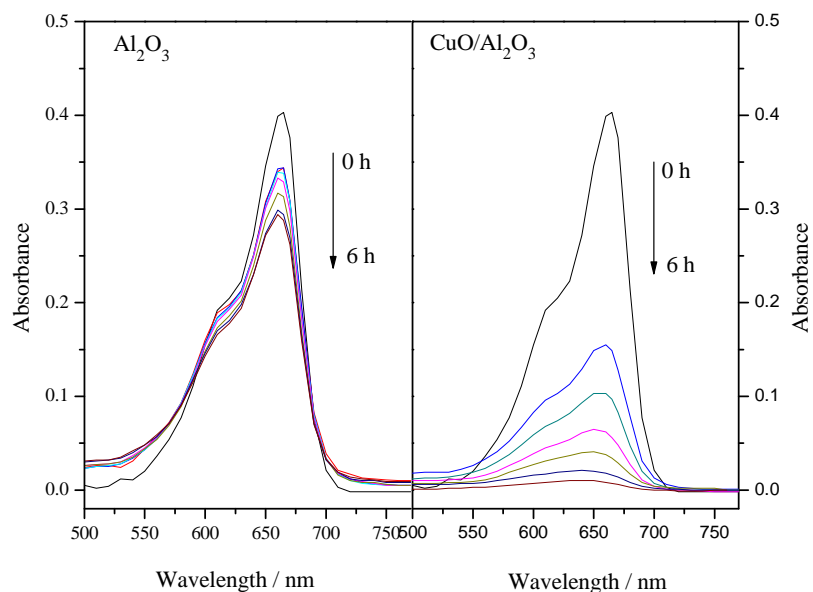


Figure 2. The spectra of MB which was decolorized in present  $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$  respectively

### 3.3 Effect of CuO content

The effect of different proportion of CuO in the  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  catalyst on photo-decoloration of the dye MB was investigated. The different catalysts, including 0, 5, 7, 9, 11, 13 and 15% CuO respectively, were employed to decolorize the MB at the same conditions. The results show in figure 3.

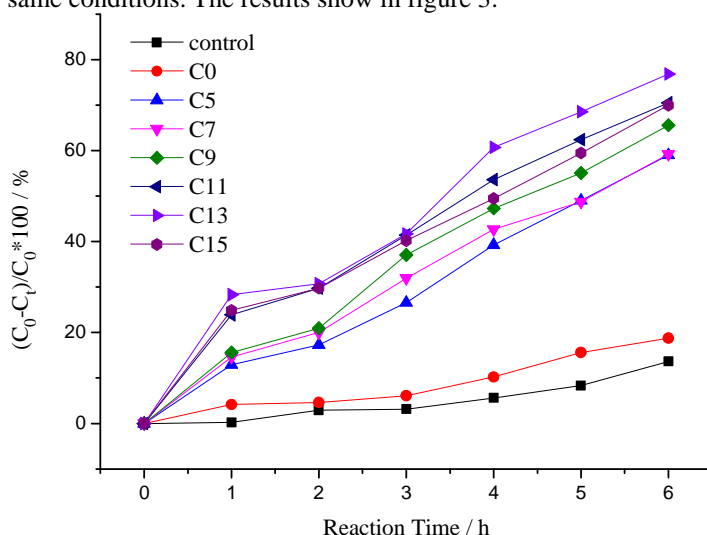


Figure 3. The decoloration ratio against reaction time with different catalyst, 0%, 5%, 7%, 9%, 11%, 13%, 15% CuO

Figure 3 shows the decoloration ratio after 6 h increased with the CuO concentration from 0 to 13%, then the decolorization decrease with the increasing concentration of CuO in catalyst. The reason is the content of CuO increased in catalyst could produce more photo-electron, and then transited to MB to cause the decoloration. But the excessive CuO in catalyst decrease the activity site in  $\gamma\text{-Al}_2\text{O}_3$ , so the dye molecular could not efficiency absorption at catalyst.

### 3.4 The effect of light source

Three type light sources were employed to investigate the influence on decolorization ratio. The reaction worked under solar irradiation in room temperature without control, but the other reaction system worked in 25 °C with a cycle water system. The results show in figure 4.

Figure 4 shows the catalysts have more activity with solar, and the DR with ultraviolet light was lower than other two light sources. For controlling the experiment conditions, the fluorescent lamp was employed as light source in next trials. And the energy gaps of catalyst will be studied in future.

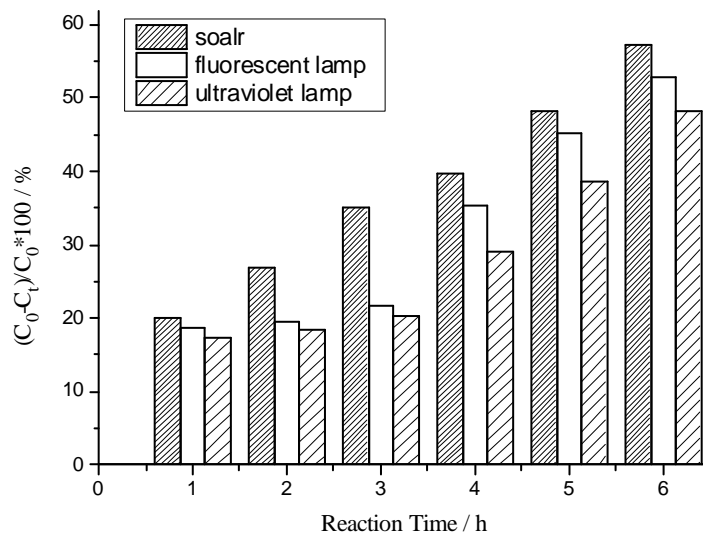


Figure 4. The effect of the light source

### 3.5 The concentration of H<sub>2</sub>O<sub>2</sub>

The influence of H<sub>2</sub>O<sub>2</sub> on DR was investigated. The different volume of H<sub>2</sub>O<sub>2</sub> was added to system from 0.1mL to 1.3mL. The data show in figure 5.

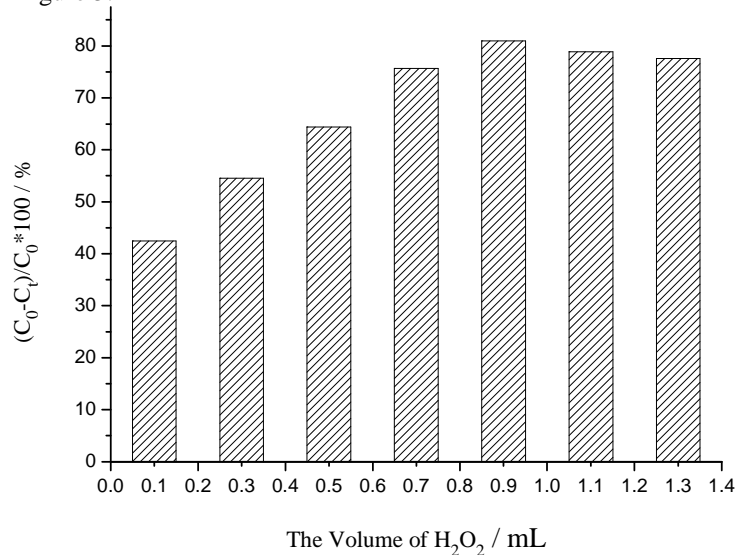


Figure 5. The effect of the volume of H<sub>2</sub>O<sub>2</sub>

Figure 5 shows the DR increased with the volume of H<sub>2</sub>O<sub>2</sub>, from 0.1 mL to 0.9 mL, but the DR descent with the further increased H<sub>2</sub>O<sub>2</sub>, from 0.9 mL to 1.3 mL. So the best H<sub>2</sub>O<sub>2</sub> content is 4.5 mL/L.

### 3.6 The effect of temperature

The effect of the temperature of reaction system on DR was also investigated. A cycle water pump was used to control the temperature of the mixture system at 25, 32 and 37°C. The results were shown in figure 6 and table 1.

Table 1. The effect of temperature on decoloration ratio (%)

Time / h	25 °C	32 °C	37°C
0	0	0	0
1	36.7	30.3	60.2
2	54.5	47.9	75.7
3	63.3	64.0	86.5
4	64.0	67.0	92.4
5	69.3	77.9	96.8
6	81.0	88.8	98.4

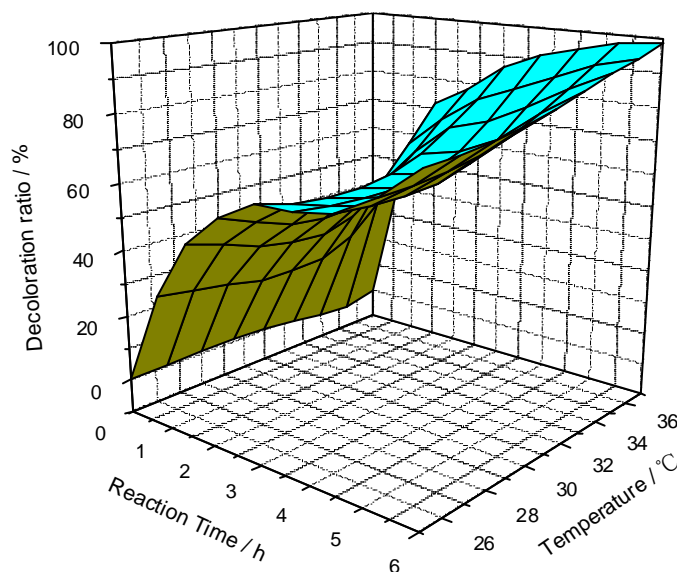


Figure 6. The effect of reaction temperature in different time

Figure 6 and table 1 show the DR increased with the increased temperature from 25 to 37 °C. After 6 h, the DR is 98.4% at 37 °C, this result suggest the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst has more activity in higher temperature, and the initial speed at 37 °C is higher than the other. The reason is the higher temperature is beneficial to H<sub>2</sub>O<sub>2</sub> to produce O<sub>2</sub><sup>·-</sup> and MB or degraded product in adsorption and desorption of on the catalyst surface.

### 3.7 The recycle trial

To investigate the stability of the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, recycling trials were conducted at the same conditions. After the initial reaction, the catalyst was separated and washed with distilled water, then sintered 5h at 550 °C in a muffle furnace. Figure 7 shows the decoloration ratios obtain on the first use of the catalyst and the subsequent recycled use. It evidence that the catalyst maintained practically the same activity in the second reaction.

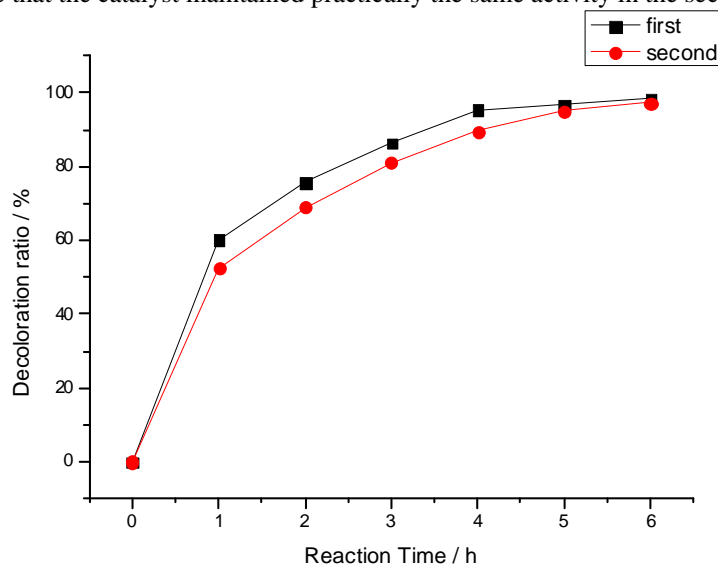


Figure 7. Decoloration ratios over fresh and recycled CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

## CONCLUSION

This work prepared the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst by low-temperature combustion method at first time, and the photo-activity was investigated by methylene blue decoloration ratio. The decoloration rate increased with the contents of CuO in catalyst increased from 0% to 13%, but decreased at content above 13%. The data showed that the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was capable of rapidly decolorizing 98.4% MB with 0.9 mL 30% H<sub>2</sub>O<sub>2</sub> at 37 °C under irradiation after 6 h.

This work illuminates that the low-temperature combustion method can prepare high activity CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, and this method also can use to prepare the other catalysts.

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