

## Research Article

# The Use of a Nanoscale Copper Catalyst in the Catalytic Decomposition of Water Polluted with Organic Dyes

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A supported copper catalyst was used as a catalyst for the decomposition of organic dyes using a commercial chlorinating agent. The catalytic process achieved complete decomposition in only 2 min. Different catalyst to dye concentration ratios is studied to determine the optimal conditions. The catalyst is fully characterized using XRD, SEM, and EDX analysis.

## 1. Introduction

The removal of organic and inorganic pollutants is an aim shared by many researchers throughout the world [1–6]. Polluted water has led to many environmental issues and hazardous effects, including health effects on humans and many aquatic organisms [7–10]. Heavy metals are commonly removed by adsorbents and ion exchangers to ensure total removal [11–14]. The situation is somewhat different for organic pollutants because it is nearly impossible to remove 100% of organic pollutants from an aqueous stream through adsorption processes. In addition, industrial waste water containing large amounts of organic pollutants will require an enormous amount of adsorbent, which will again require environmentally safe removal. In this case, the catalytic decomposition of organic pollutants may be the best choice to remove these pollutants [15–20]. Photocatalytic decomposition is a commonly used removal method [15, 16], but this system is mainly used at lab scale because the whole system should be subjected to ultraviolet irradiation for a long period of time, making large-scale implementation difficult. Environmentally safe oxidants such as hydrogen peroxide are also used either as catalysts or to promote thermal decomposition [21]. The use of hydrogen peroxide is also limited by the fact that it is considered to be a mild oxidant, meaning that even in catalytic decomposition it will not totally decompose the organic pollutants into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , potentially resulting in more organic pollution fragments.

The use of excited molecular oxygen may be the solution to this problem. For example, singlet oxygen has distinct properties that enable it to be highly reactive, achieving total decomposition of the organic pollutant. The fact that the reaction of singlet oxygen is considered to occur via a free-radical mechanism means that the decomposition will occur in only a few minutes.

This study reports the removal of organic dye (pollutants) with a system consisting of a 5% solution of sodium hypochlorite (commercial grade), oxygen gas, and a supported copper oxide catalyst to generate singlet oxygen.

## 2. Experimental

**2.1. Materials.** Methyl orange (Merck), sodium hypochlorite solution (commercial), oxygen gas (99.99%), aluminum hydroxide (Merck), and copper nitrate trihydrate (Merck) were used in these experiments.

**2.2. Catalyst Preparation.** First, aluminum hydroxide was calcined at  $550^\circ\text{C}$  for 3 hours to convert it into  $\text{Al}_2\text{O}_3$ . Copper was loaded as copper nitrate (20%) on the resulting gamma alumina by impregnation with stirring for 2 h and then dried and calcined at  $450^\circ\text{C}$  for 3 hours.

**2.3. Reaction Design.** Oxygen was introduced to a 0.5 mL solution of 5% sodium hypochlorite at 100 ppm from methyl

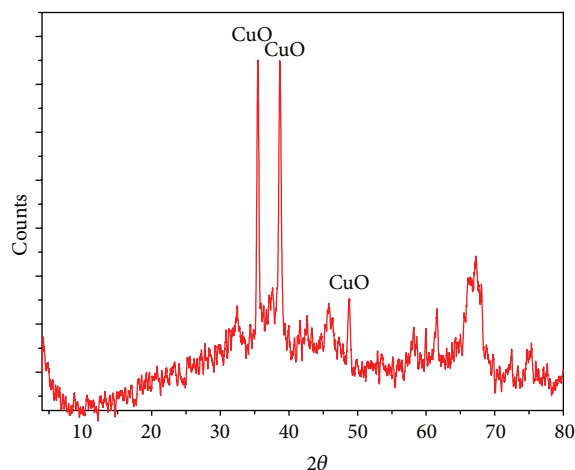


FIGURE 1: XRD of CuO catalyst deposited on alumina.

orange by passing oxygen at 20 mL/min in an open system. Copper oxide catalyst was added (0.5 g), and samples from methyl orange were collected and separated by centrifuge at several time points for analysis. For comparison, the same reaction was performed with and without catalyst and with and without oxygen.

#### 2.4. Instruments and Techniques

**2.4.1. X-Ray Diffraction Analysis (XRD).** X-ray diffractograms of the samples under investigation were collected using a Bruker D8 Advance instrument with CuK $\alpha$ 1 radiation and a secondary monochromator operated at 40 kV and 40 mA.

**2.4.2. SEM and EDX Analysis.** Scanning electron microscopy (SEM) images were collected and EDX analysis was performed using a JXA-840 Electron Probe Micro Analyzer (JEOL).

**2.4.3. Total Organic Carbon.** Organic carbon content was measured using a Multi N/C total organic carbon measurement instrument (Analytik Jena, model 2100/2100 S).

### 3. Results and Discussion

**3.1. XRD.** The XRD patterns of the supported CuO catalyst over alumina are shown in Figure 1. This figure clearly shows that a pure phase of CuO was formed over an amorphous phase of gamma alumina.

**3.2. SEM and EDX.** Figure 2 shows the SEM image of the 20 wt% CuO/Al<sub>2</sub>O<sub>3</sub> catalyst. This image clearly shows that the CuO crystals appear as separated aggregates at different intervals over the alumina surface. The EDX analysis of these aggregates (Figure 3) showed that these aggregates are mainly composed of CuO.

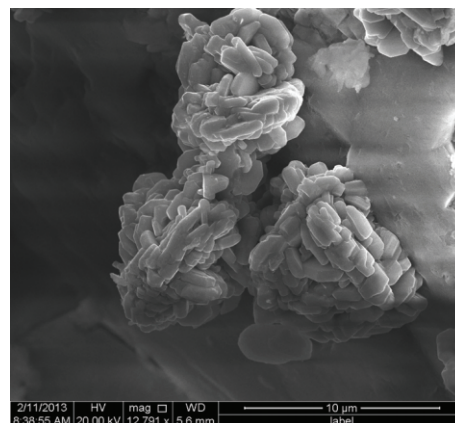


FIGURE 2: SEM of CuO on alumina.

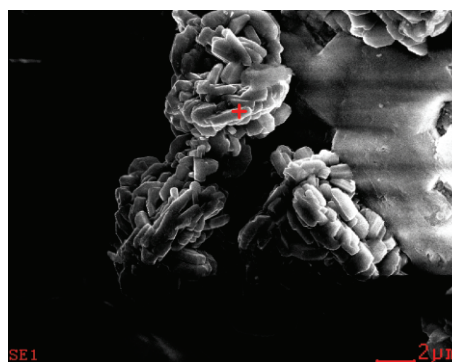
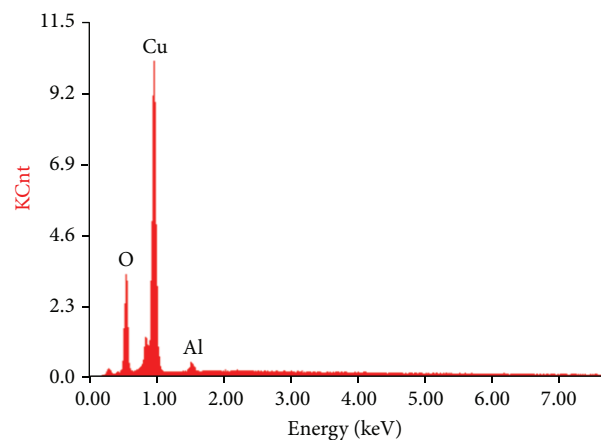


FIGURE 3: EDX spectra of CuO agglomerates.

**3.3. Catalytic Decomposition of Organic Dye.** Figure 4 shows that the rate of catalytic decomposition of the copper catalyst with chlorate solution and oxygen is much higher than that of the chlorate solution alone and that passing oxygen with catalyst in the absence of chlorate does not promote decomposition.

The previous results can be explained in light of the mode of decomposition of the dye. Passing oxygen without chlorate, even in the presence of a catalyst, does not induce decomposition because molecular oxygen is stable under

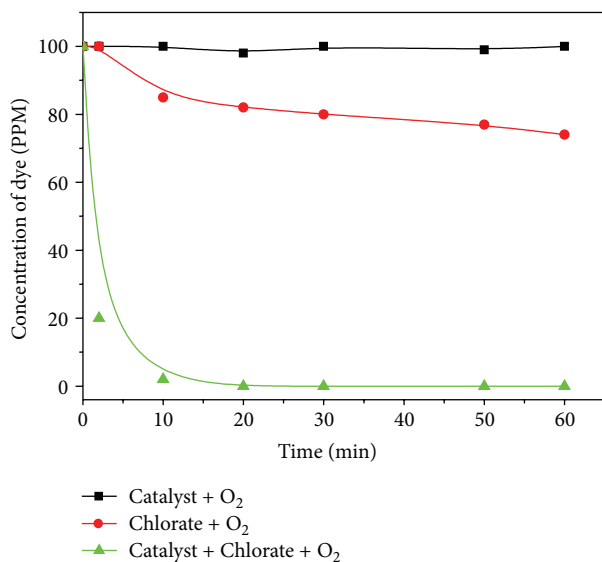


FIGURE 4: Comparison of the catalytic decomposition activity of catalyst with oxygen only, chlorate solution with oxygen, and catalyst with oxygen and chlorate.

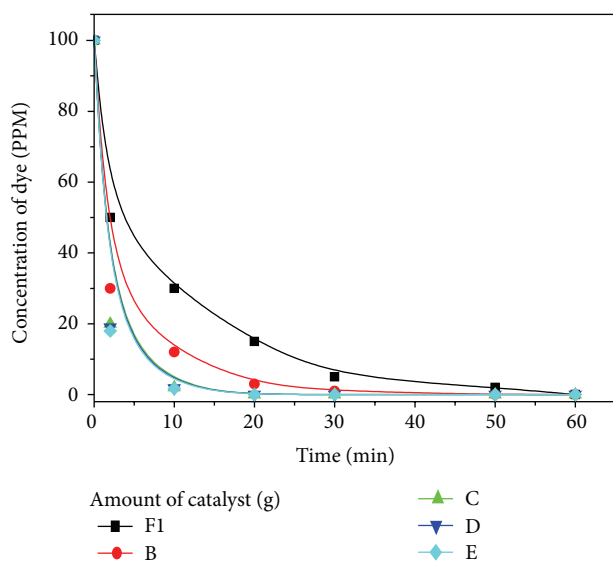
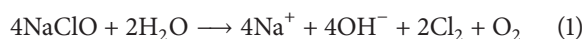


FIGURE 5: Effect of the amount of catalyst on the decomposition of the dye.

these conditions, and it is very difficult to decompose the dye at room temperature.

In the presence of chlorate solution (5% sodium hypochlorite), the decomposition will occur according to the following equation:



The nascent oxygen produced in the previous equation could be used in the oxidation of the organic dye, and the  $\text{Cl}_2$  produced could also decolorize the dye [22]. In the combined presence of the catalyst, oxygen, and chlorate, a sudden effervescence of a huge amount of gases occurs, and depolarization can be visually observed in only a few

minutes. This can only be explained by assuming that a singlet oxygen is produced and that the dye acts as a sensitizer [23]. However, because the concentration in Figure 3 was calculated by the UV-Vis spectra, the decolorization and decomposition cannot be differentiated. To differentiate between these outcomes, a sample after 60 min of reaction was measured for the total organic carbon (TOC), and the results showed that in the presence of catalyst, chlorate, and oxygen, the organic carbon is nearly absent after 60 min.

Figure 5 compares the effects of different dye amounts on the decomposition of the organic dye. This curve clearly shows that optimal catalysis is achieved at 0.5 g of catalyst.

## 4. Conclusions

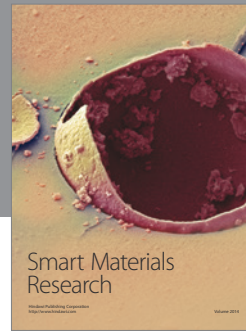
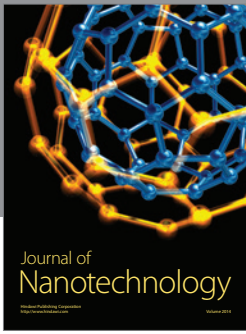
The following conclusions can be drawn from the research presented previously.

- (1) The system of a copper catalyst, a solution of commercial chlorate, and any organic dye pollutant could be effective in the decomposition of organic pollutants.
- (2) The aforementioned system can be easily scaled up at low cost to achieve effective pollutant removal.
- (3) The decomposition followed a free-radical reaction mechanism and produced singlet oxygen.

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