Decolorization of Reactive Orange 16 Dye by Copper Oxide System
(Penyahwarnaan Pewarna Reaktif Jingga 16 oleh Sistem Kuprum Oksida)

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ABSTRACT

The decolorization of reactive orange 16 dye (RO16) from aqueous solution by CuO/H_2O_2 was investigated. The amount of dye removed was determined by measuring the concentration of the dye at its characteristic wavelengths by UV-Vis spectrophotometer. The effects of CuO dose, H_2O_2 concentration and UV light on the decolorization of the dye were investigated. It was found that the removal rate increased with increasing mass of CuO and increasing concentration of H_2O_2. The combination of CuO, H_2O_2 and UV light was the best system with dye removal of 100% after 6 h. The removal efficiency observed was in the order: $CuO/UV/H_2O_2 > CuO/H_2O_2 > CuO/UV = CuO > UV/H_2O_2 > H_2O_2 > UV$.

Keywords: Copper oxide; decolorization; dye; H_2O_2; UV light

ABSTRAK

Penyahwarnaan pewarna reaktif jingga16 (RO16) daripada larutan akueus oleh CuO/H_2O_2 telah dikaji. Jumlah pewarna yang disingkirkan telah ditentukan dengan mengukur kepekatan pewarna pada panjang gelombang ciri menggunakan spektrofotometer UV-nampak. Kesan dos CuO, kepekatan H_2O_2 dan cahaya UV ke atas penyahwarnaan pewarna telah dikaji. Kadar penyingkiran didapati meningkat dengan peningkatan jisim CuO dan kepekatan H_2O_2. Kombinasi CuO, H_2O_2 dan cahaya UV adalah sistem terbaik dengan penyingkiran 100% pewarna selepas 6 jam. Kecekapan penyingkiran adalah mengikut turutan: $CuO/UV/H_2O_2 > CuO/H_2O_2 > CuO/UV = CuO > UV/H_2O_2 > H_2O_2 > UV$.

Kata kunci: Cahaya UV; H_2O_2; kuprum oksida; penyahwarnaan; pewarna

INTRODUCTION

The textile dyeing and printing industries are among several industries responsible for the pollution of aquatic ecosystems. Over 700,000 tons of approximately 10,000 different types of dyes and pigments are produced annually worldwide (Nigam et al. 2001). Nearly 50% of these dyes are azo-type dyes (Bauer et al. 2001). About 20% of dye of the total world production is assumed to be discharged in industrial effluents during the textile dyeing process (Azbar et al. 2004). Up to 50% of reactive dyes, 8-20% of disperse dyes and 1% of pigments may be lost directly into effluents during the dyeing process (McMullan et al. 2001). Removal of color in wastewater generated by the textile industries is a current issue of discussion and regulation all over the world. Among the reactive dyes, the textile azo dyes have attracted the most attention with regard to its' high environmental impact due to their widespread use, their potential to form toxic aromatic products and their low removal rate during primary and secondary treatment

A variety of physical and chemical treatment methods are presently available for these dyes. Nevertheless these methods merely transfer the dye to a solid phase which requires further treatment (Zollinger 1991). Biological processes such as sequenced anaerobic or aerobic digestion have been proposed in the treatment of textile wastewater, but they are limited due to the fact that many of the dyes are non-biodegradable (Carneiro et al. 2004).

During the last two decades advanced oxidation processes (AOPs), through combination of powerful oxidizing agents (catalytic initiators) with UV or near-UV light, have been applied for the removal of refractory organic pollutants and xenobiotics.

The destructive oxidation of dyes and textile effluents has recently received considerable attention since colored aromatic compounds have proven to be degraded effectively by a variety of AOPs. Among these processes, heterogeneous photocatalysis was found as an emerging destructive technology leading to the total mineralization of most of organic pollutants (Karkmaz et al. 2004; Mozia et al. 2005). The use of hydrogen peroxide in wet oxidation of organic compounds is also another option. Unfortunately the literature on the use of metal oxide and hydrogen peroxide is very scarce (Baldrain et al. 2006; Gemeay et al. 2008). The aim of this work was to evaluate the possibility of alternative treatment for removal of dye-containing wastewater by copper oxide systems.

MATERIALS AND METHODS

MATERIALS

Reactive orange 16 dye, RO16, (Aldrich) and copper oxide, CuO, (Fluka) were used as received without further purification. Hydrogen peroxide (9.8 M) solution (Merck) was diluted to 1.0 M prior to use. The RO16 dye stock solution of 1000 mg/L was prepared by dissolving 1.0 g of dye into 1.0 L deionised water while the working solution of desired concentration was prepared by dilution of the stock solution.

EXPERIMENTAL

The decolorization of RO16 was carried out by batch experiment at room temperature. At the beginning of each test run, 1 L of 25 mg L^{-1} RO16 was mixed with appropriate amount of CuO and H$_2$O$_2$. Continuous mixing of the mixture was provided by a magnetic stirrer at a constant rate for 6 h. Aliquot (5 mL), withdrawn at predetermined time intervals and filtered through Millipore membrane filter (0.45 μm), was analyzed by Perkin Elmer Lambda 20 UV-vis spectrophotometer at maximum wavelength of 492 nm to determine the concentration of the dye. The UV-vis spectra were recorded in the range of 350-700 nm. The effect of UV light on the removal of RO16 in the presence and absence of CuO and H$_2$O$_2$ was carried out by using Blak-Ray B100 AP long wave (365 nm) UV lamp.

RESULTS AND DISCUSSION

EFFECT OF CuO

The decolorization of RO16 dye in the presence of various amount of CuO is illustrated in Figure 1. The decolorization was very rapid during the initial stage followed by a very slow decolorization rate. The rapid stage could be attributed to the fast adsorption of the dye molecules on adsorption sites, which increases with increasing amount of CuO, while the slow rate may be attributed to the diffusion of the dye molecules within the CuO particles. Adsorption equilibrium was attained after 2 h of reaction time.

EFFECT OF H$_2$O$_2$

In the presence of 1 g of CuO, 28% of the RO16 dye was removed by adsorption process. However, the color removal was doubled upon addition of 4.9 mM of H$_2$O$_2$. This enhancement was attributed to the presence of hydroxyl radicals, which are able to unselectively degrade many organic pollutants, produced via CuO-catalyzed decomposition of H$_2$O$_2$. Although a continuous improvement in color removal was observed with increasing H$_2$O$_2$ concentration as depicted in Figure 2, the increment of color removal was not directly proportional to the increase of H$_2$O$_2$ concentration. This phenomenon could be explained by the hydroxyl radical scavenging effect of H$_2$O$_2$. According to Walling (1975), at high concentration,
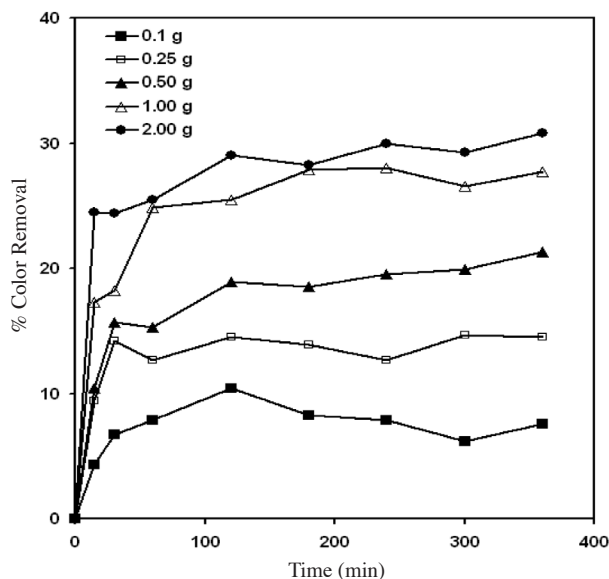

FIGURE 1. The decolorization of RO16 dye in the presence of various amount of CuO, (pH 5-6, [RO16] = 25 mgL^{-1})
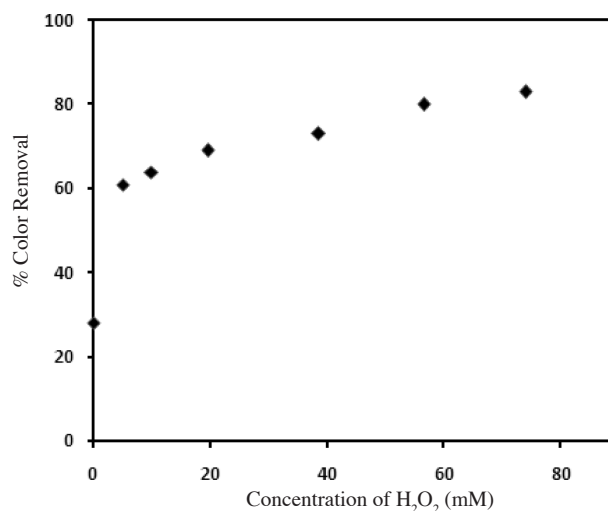

FIGURE 2. Decolorization of RO16 aqueous solutions by different initial concentration of H$_2$O$_2$. (CuO = 1g, pH 5-6, [RO16]= 25 mg L^{-1})

H$_2$O$_2$ acts as a scavenger of the hydroxyl radicals to produce perhydroxyl radical (1) which also capable of reacting with hydroxyl radicals to form water and oxygen (2):

$$H_2O_2 + •OH \rightarrow H_2O + HO_2• \qquad (1)$$

$$HO_2• + •OH \rightarrow H_2O + O_2 \qquad (2)$$

In additon, the availability •OH radical also reduces through recombination process shown below

$$•OH + •OH \rightarrow H_2O_2• \qquad (3)$$

Therefore the slight improvement in color removal observed at high H$_2$O$_2$ concentration is due to the

competition for the HO• radicals between the three reactions above and the oxidation of RO16 dye molecules and its intermediate.

EFFECT OF CuO DOSAGE IN THE PRESENCE OF H_2O_2

In order to determine the effect CuO dosage, in the presence of H_2O_2 solution, on the removal of RO16, the mass of CuO was varied from 0.0 to 5.0 g while the concentration of H_2O_2 was fixed at 56.6 mM. Figure 3 shows that the color removal was very low in the absence of CuO indicating that RO16 dye is difficult to be oxidized by H_2O_2. However, it increases significantly upon addition of CuO due to the production of higher amount of hydroxyl radical through decomposition of H_2O_2 by CuO. The increment in color removal became less significant when the mass of CuO used was above 2.0 g.

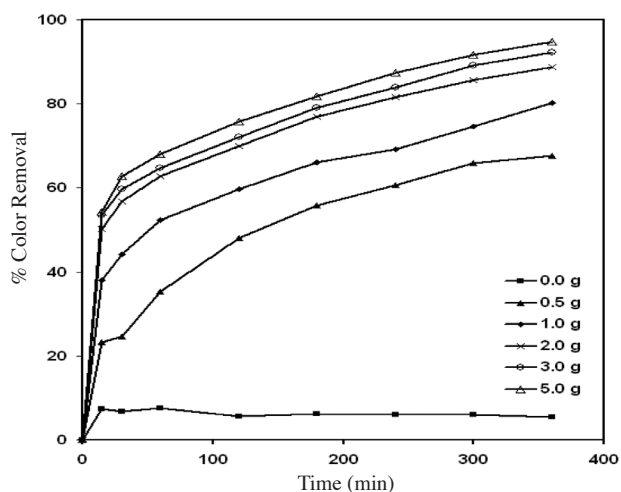FIGURE 3. Decolorization of RO16 by different amount of powdered copper oxide. (Conc. of H_2O_2 = 56.6 mM, pH 5-6, [RO16] = 25 mgL^{-1})

Since the presence of metal ions in H_2O_2 solution has been reported to enhance color removal (Xu et al. 2004; Yang et al. 1998), the possibility of having Cu^{2+} ions in the reaction mixture was investigated using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). The analysis showed that 3.5 ppm of Cu^{2+} ions were present in the aqueous solution after 6 h of reaction time, indicating the leaching out of the ions from the CuO particles. A set of experiment was conducted by introducing 3.5 ppm of Cu^{2+} ions into the dye-H_2O_2 mixture to investigate the possible contribution of Cu^{2+} ion in color removal through homogeneous oxidation reaction. As depicted in Figure 4, an approximately 36% of color removal was observed. Comparison in term of percentage of color removal with those obtained from CuO and CuO/H_2O_2 system, signifies the contribution of Fenton-like oxidation on decolorization of RO16 dye by the CuO/H_2O_2 system. In addition to Fenton-like reaction
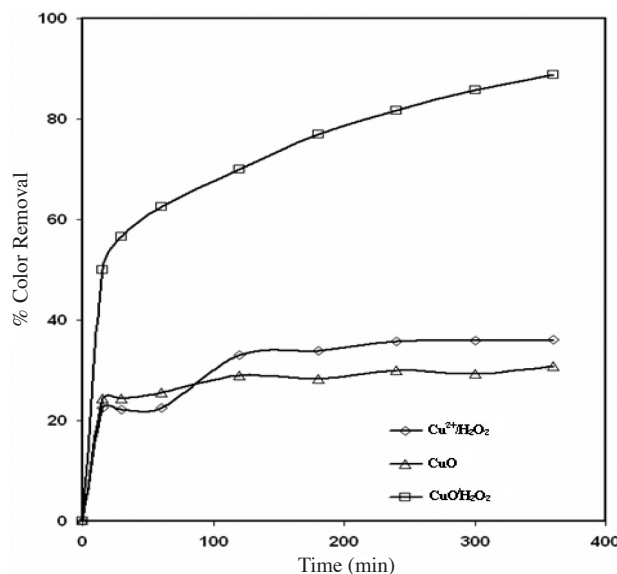

FIGURE 4. Decolorization of RO16 by CuO, CuO/H_2O_2 and Cu^{2+}/H_2O_2 system. (CuO = 2g, Cu^{2+} = 3.5 mgL^{-1}, Conc. of H_2O_2 = 56.6 mM, pH 5-6,[RO16] = 25 mgL^{-1})

that lead to the formation of OH·, decomposition of H_2O_2 by CuO via heterogeneous catalysis has also been reported to yield hydroxyl and superoxide radicals (Drijver et al. 1999). Hence, it can be concluded that the presence of hydroxyl and superoxide radical from decomposition of H_2O_2 by homogeneous and heterogeneous catalysis, along with sorption process by CuO, have led to a significant improvement in the color removal of RO16 by the CuO/H_2O_2 system.

EFFECT OF UV IRRADIATION

The effect of UV irradiation on the decolorization of RO16 was also investigated. There was no observable loss of color when the dye is irradiated with UV which suggests that the dye is resistant to direct UV-photolysis. The combined action of UV and H_2O_2 however produced an increase of 10% in decolorization compared to that of H_2O_2 alone due to the reaction of hydroxyl radicals generated upon photolysis of hydrogen peroxide (De et al. 1999). A higher percentage of removal by CuO/H_2O_2 showed that copper- catalyzed decomposition of H_2O_2 was more efficient than that of UV-catalyzed in producing the hydroxyl radical responsible for the oxidation of the dye. Similar percentage of color removal was observed for CuO and CuO/UV which implies that UV radiation has negligible effect both on the dye and the CuO. For CuO/UV/H_2O_2 system, a complete color removal was observed after 6 h of irradiation. The high efficiency of this process is due to the formation of more hydroxyl radical which is attributed to copper-catalyzed (homogeneous and heterogeneous) and UV-catalyzed decomposition of H_2O_2. Table 1 summarized the results for the color removal of RO16 by all system investigated in this work.

TABLE 1. The percentage of decolorization of reactive orange 16 dye by various systems

System	Color removal (%)	System	Color removal (%)
CuO	30.8	CuO/UV	29.5
H_2O_2	5.5	CuO/ H_2O_2	88.8
UV	0.2	CuO/ H_2O_2/UV	100.0
H_2O_2/UV	15.8		

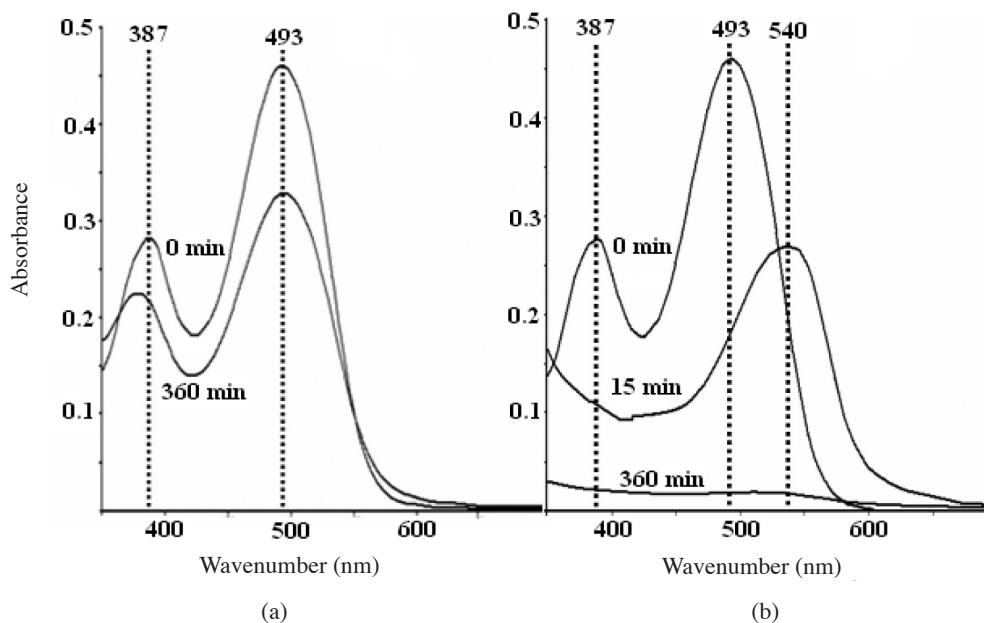Mass of CuO = 2 g, [H_2O_2] = 56.6mM, [RO16] = 25 mg L^{-1} Reaction time = 6 h

FIGURE 5. UV-Vis absorption spectral changes of RO16 recorded at different time intervals
by (A) CuO and (B) CuO/UV/H_2O_2 process

UV/VIS SPECTRA

The UV-vis spectral changes during decolorization of RO16 by all the systems employed were shown in Figure 5. Except for the reduction in the intensity of the peaks at 387 and 493 nm, no significant changes were observed for CuO, H_2O_2, and CuO/UV. The recorded spectra were represented by Figure 5(a). Drastic changes, however, were observed for CuO/H_2O_2 and CuO/H_2O_2/UV systems (Figure 5(b)). After 15 minutes of reaction time, the 387 nm peak disappeared while the 493 nm peak red shifted to 540 nm, which its intensity then decreases with increasing reaction time. For the CuO/H_2O_2/UV system, this band disappeared after 6 h. The red shifting of the 493 nm peak to 540 nm is possibly due to the oxidation of the functional groups presence which is accompanied by color change from orange red to dark red which was observed visually. The decrease in intensity of the 540 nm peak suggests that the decolorization of the dye progressed possibly through the destruction of the azo bond by the hydroxyl radicals.

CONCLUSION

The efficiency in decolorization of RO16 was in the following order: CuO/UV/H_2O_2 > CuO/H_2O_2 > CuO/UV = CuO > UV/H_2O_2 > H_2O_2 > UV. A complete color removal of RO16 within 6 h is possible when using CuO/U UV V/ H_2O_2 system through adsorption and oxidation processes. The enhancement of removal efficiency is attributed to the presence of hydroxyl radicals generated from copper-catalyze, homogeneous and heterogeneously, and UV–catalyze decomposition of H_2O_2.

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