



Synthesis of CuO-ZnO Nanocomposite and Its Photocatalytic Activity

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ABSTRACT

In this paper, CuO-ZnO nanocomposite was synthesized and its photocatalytic dye degradation ability from colored wastewater was studied. Basic Red 18 (BR18) and Basic Violet 16 (BV16) were used as model dyes. The characteristics of CuO-ZnO were investigated using Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscope (SEM) and X-ray diffraction (XRD). Photocatalytic dye degradation by CuO-ZnO was studied by UV-Vis spectrophotometer. The effects of CuO-ZnO dosage, initial dye concentration and salt on dye degradation were evaluated. The results indicated that CuO-ZnO as a photocatalyst could be used to degrade dyes from wastewater. Prog. Color Colorants Coat. 9 (2016), 207-215 © Institute for Color Science and Technology.

1. Introduction

The rapid increase in the manufacture and consumption of synthetic dyes during the past century has been quite. Colored water and wastewater is one of the main concerns of developing countries. Synthetic dyes have complex aromatic structure and they are difficult to remove from wastewater. Synthetic dyes are of environmental interest, because 700,000 t of them are produced in the world annually. About 15% of the total world production of dyes is lost during textile dyeing which is released in textile effluents. The release of these colored wastewaters in the ecosystem is a dramatic source of aesthetic pollution, eutrophication and perturbation of aquatic life. In addition, the stability of their molecular structures renders them resistant to biological or even chemical degradation.

Some of dyes produce toxic and carcinogenic intermediates by hydrolysis, oxidation, etc. Thus they should be treated suitably from water and wastewater [1-9].

Several methods such as adsorption, biological, filtration, coagulation and ozonation were used to treat wastewater. Each method has its advantages and disadvantages. For example, adsorption is nondestructive, since it just transfers dyes from water to another phase, thus causing secondary pollution. Consequently, regeneration of the adsorbent materials and post-treatment of solid wastes, which are expensive operations, are needed. Due to the large degree of aromatics present in dye molecules and the stability of modern dyes, conventional biological

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treatment methods are ineffective for decolorization and degradation [4, 6].

The advanced oxidation technology (AOT) is an emerging technology aimed at the degradation of air, water and wastewater pollutants, especially refractory organic substances. AOT degrades pollutants using strong oxidants such as hydroxyl radicals (HO[•]). The advantages of AOT over competing processes are: (1) complete degradation, (2) no waste disposal problem, (3) low cost and (4) only mild temperature and pressure conditions are necessary. The mechanism of heterogeneous photocatalytic degradation of dyes was investigated in detail [10 -16].

In this paper, CuO-ZnO nanocomposite was synthesized and characterized. The photocatalytic dye degradation ability of CuO-ZnO from colored wastewater was investigated in details. Basic Red 18 (BR18) and Basic Violet 16 (BV16) were used as model dyes. The characteristics of CuO-ZnO were investigated using Fourier transform infrared (FTIR), scanning electron microscope (SEM) and X-ray diffraction (XRD). Photocatalytic dye degradation was studied by UV-Vis spectrophotometer. The effect of CuO-ZnO dosage, initial dye concentration and salt on dye degradation was evaluated.

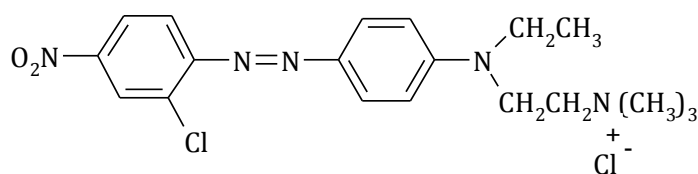
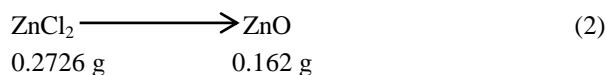
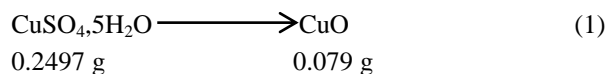
2. Experimental

2.1. Chemicals

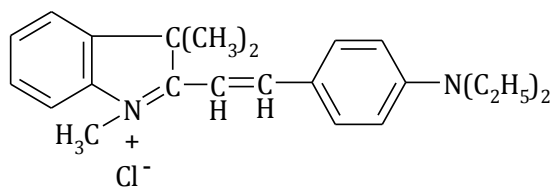
Basic Red 18 (BR18) and Basic Violet 16 (BV16) were obtained from Ciba and used without further purification. Figure 1 shows the chemical structure of dyes. Other chemicals were obtained from Merck.

2.2. Synthesize of CuO-ZnO nanocomposite

CuO-ZnO nanocomposite was synthesized in our laboratory. ZnCl₂ (0.2726 g), CuSO₄·5H₂O (0.2497 g) and NaOH (0.4 g) were dissolved in distilled water (30 mL). This solution was sealed and left static at 80°C for 24 h, and then cooled to room temperature. The final precipitate was separated by centrifuge, washed several times with distilled water and absolute alcohol to remove the possible residues and then dried at 80°C for 12 h [17]. The value of CuO and ZnO in as-prepared Nanocomposite was 67.2% ZnO and 32.8 %CuO, respectively (Equations 1 and 2).



(a)



(b)

Figure 1: The chemical structure of dyes (a) BR18 and (b) BV16.

2.3. Characterization

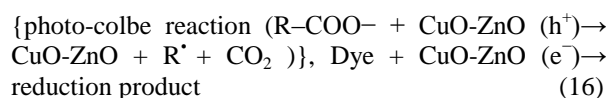
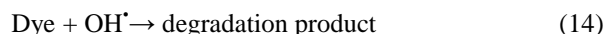
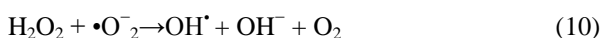
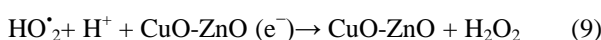
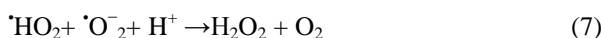
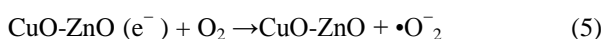
The functional groups of the material were studied using Fourier transform infrared (FT-IR) spectroscopy (Perkin-Elmer Spectrophotometer Spectrum One) in the range of 4000-450 cm^{-1} . The morphological structure of the material was examined by scanning electron microscopy (SEM) using a LEO 1455VP scanning microscope. Crystallization behavior of the material was identified by XRD model Siemens D-5000 diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at room temperature.

2.4. Reactor and Photocatalytic dye degradation

Experiments were carried out in a batch mode photo-reactor. The irradiation source was a UV-C lamp (200-280 nm, 9W, Philips), which was placed in the inner quartz tube of the reactor.

The photocatalytic dye degradation experiments were conducted by mixing various amounts of CuO-ZnO (0 - 0.35 g) in photo-reactor containing 800 mL dye solution (20mg/L) at 25 °C. The solution samples were withdrawn from the reaction medium at regular time intervals. The CuO-ZnO was separated from solution and the change on the absorbance at maximum wavelength (λ_{max}) of dyes (489 nm for BR18 and 547 nm for BV16) was monitored by UV-Vis spectrophotometer (Perkin-Elmer Lambda 25).

A mechanism of the photocatalytic degradation of BR18 and BV16 can be described by following steps (Equations 3-17):



The effect of CuO-ZnO dosage on the photocatalytic dye degradation was investigated by contacting 800 mL of dye solution (20 mg/L) at room temperature (25 °C) for 4 h. Different amounts of CuO-ZnO (0, 0.05, 0.15, 0.25 and 0.35 g) were applied.

The effect of initial dye concentration on the photocatalytic dye degradation was studied. The CuO-ZnO (0.35 g) was added to 800 mL of dye solution with different concentrations (10, 20, 30 and 40 mg/L). The effect of salt on the photocatalytic dye degradation was studied. Different salts (Na_2SO_4 , NaCl and NaHCO_3) (0.02 mol) were added to 800 mL of dye solution (20 mg/L) containing CuO-ZnO (0.35 g) at room temperature (25 °C).

To study the dye adsorption by CuO-ZnO nanocomposite experiments were conducted without UV irradiation. The dye adsorption ability of CuO-ZnO is very low (<2.5% for BR18 and <3.5% for BV16). Thus, dye adsorption by composite was not further studied.

3. Results and discussions

3.1. Characterization

The FT-IR spectrum of CuO-ZnO nanocomposite is shown in Figure 2. It has two peaks at 3450 cm^{-1} and 500-600 cm^{-1} which indicate O-H stretching vibration and metal-oxygen vibration, respectively. The peak at 1625 cm^{-1} was attributed to OH bending of molecular water [18]. The SEM micrograph of the CuO-ZnO (Figure 3) shows a relatively homogeneous particle size distribution of CuO-ZnO.

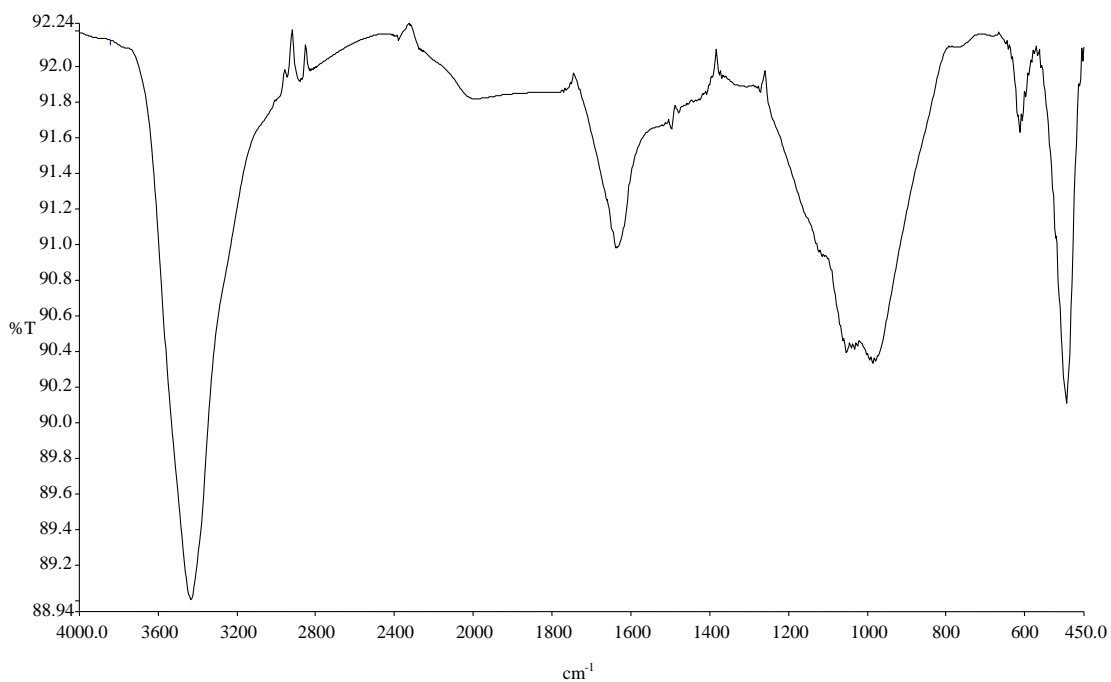
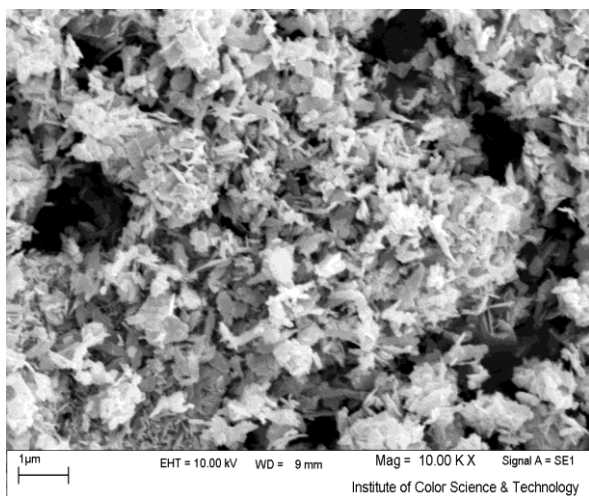
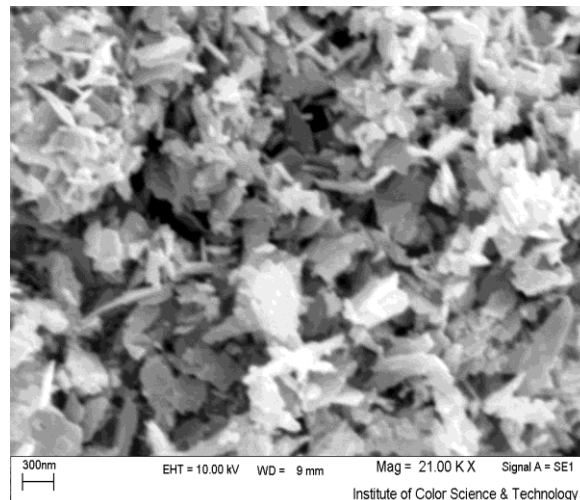


Figure 2: FT-IR spectrum of CuO-ZnO nanocomposite.



(a)



(b)

Figure 3: SEM images of CuO-ZnO nanocomposite.

Figure 4 illustrates the X-ray diffraction (XRD) pattern of the zinc oxide/copper oxide nanocomposite. Diffraction peaks are in good agreement with those of the standard patterns of hexagonal wurtzite ZnO (JCPDS Card No. 36-1451) and monoclinic CuO (JCPDS Card No. 05-0661). In Figure 4, there are two sets of diffraction peaks for the zinc oxide/copper oxide nanocomposite sample, which are correspondingly ascribed to hexagonal wurtzite ZnO and monoclinic CuO, and no peaks of other phases and impurities were detected [19].

3.2. Effect of operational parameters on dye degradation

3.2.1. CuO-ZnO dosage

Figure 4 shows the effect of CuO-ZnO dosage on the

photocatalytic dye degradation. The photodegradation in the absence of CuO-ZnO is 2 % and 1.5 % for BR18 and BV16, respectively (Figure 5). Considering that the UV alone is not effective to oxidize dyes in the colored wastewater samples, it needs to be activated by a catalyst. It is observed that the simultaneous use of CuO-ZnO with UV to a certain extent yielded a significant improvement of dye degradation compared to that of the UV degradation alone (Figure 5).

CuO-ZnO is an effective photocatalyst by utilizing light energy to create e^-/h^+ pairs on its surface. The e^-/h^+ pairs are then available for degradation processes, which usually involve the formation of reactive oxygen species, such as HO^\bullet and $O_2^{\bullet-}$, which then further contribute to the degradation of pollutants.

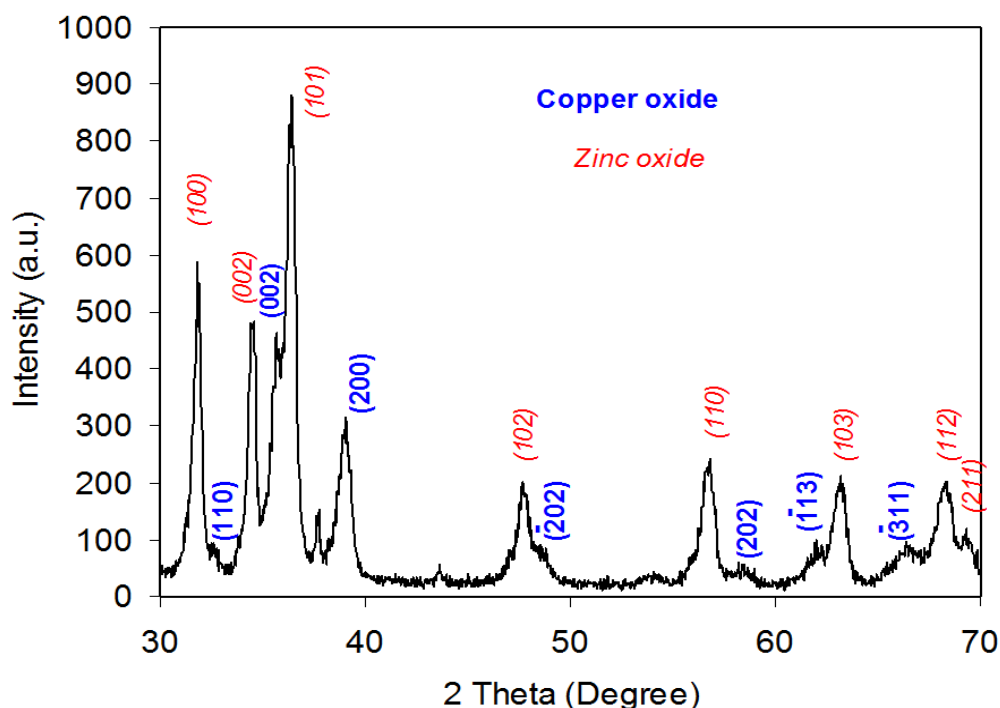


Figure 4: XRD pattern of CuO-ZnO nanocomposite.

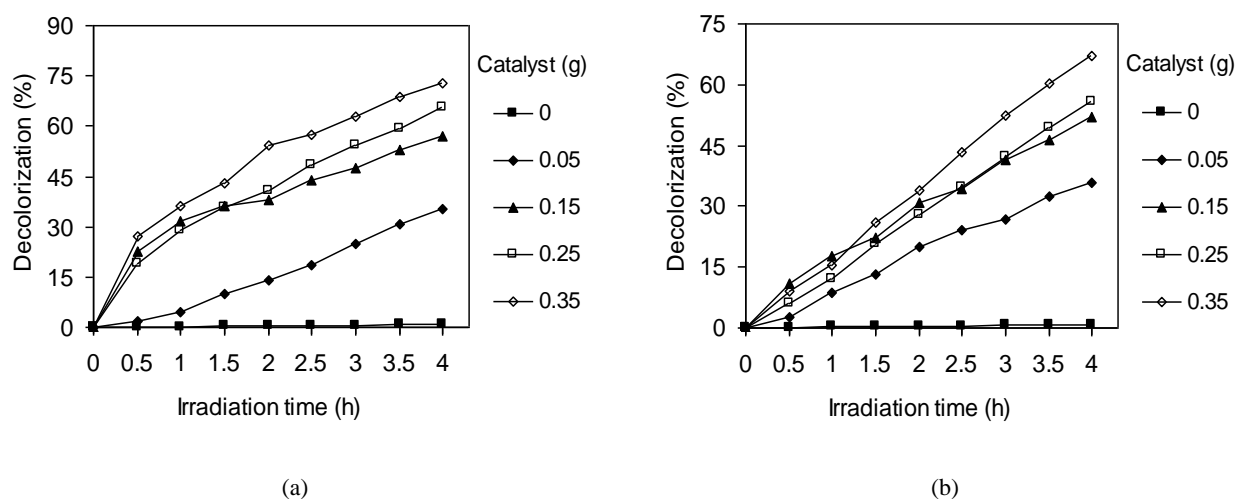


Figure 5: CuO-ZnO nanocomposite dosage effect on degradation of dyes using UV/CuO-ZnO nanocomposite (a) BR18 and (b) BV16.

3.2.2. Salt

Inorganic anions (salts) exist in wastewater. These materials may compete for the active sites on the CuO-ZnO surface or deactivate the CuO-ZnO and, subsequently, decrease the degradation rate of the target dyes. Hydroxyl radical is high reactive and non-selective radical. It reacts with non-target compounds present in the background water matrix such as dye auxiliaries in the dye bath. It causes higher HO[•] demand to accomplish the desired degree of degradation, or complete inhibition of advanced degradation rate and efficiency [20].

Figure 6 shows the effect of salts on the photocatalytic dye degradation using CuO-ZnO. The anionic species could inhibit dye degradation through their scavenging effects on the HO[•] radicals. To generate sufficient levels of HO[•] for the photocatalytic dye degradation in the presence of high levels of sulfate, a higher catalyst dose should be used.

3.2.3. Initial dye concentration

Figure 7 presents the effect of initial dye concentration on the photocatalytic dye degradation at different time intervals. The results showed that dye degradation decreases by increasing the initial dye concentration. With the increase of dye concentration, the possible cause is the interference from intermediates formed upon degradation of the parental dye molecules. Such suppression would be more pronounced in the presence of an elevated level of degradation intermediates formed upon an increased initial dye concentration [10].

3.3. Degradation and mineralization of dyes

The UV-Vis spectra of the dyes at $200 \text{ nm} \leq \lambda \leq 650 \text{ nm}$ during the degradation process using UV/CuO-ZnO at different time intervals were studied (Figure 8). The results showed that the maximum absorbance in visible region decreases because chromophore of dyes is the most active sites for degradation attack.

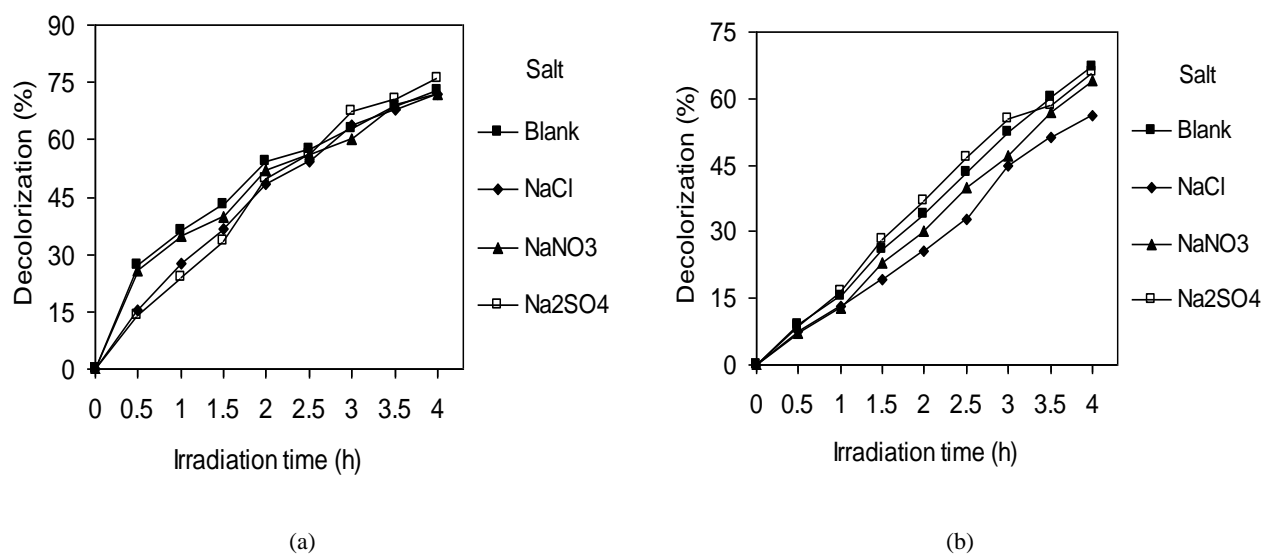


Figure 6: Salt (inorganic anion) effect on degradation of dyes using UV/CuO-ZnO nanocomposite (a) BR18 and (b) BV16.

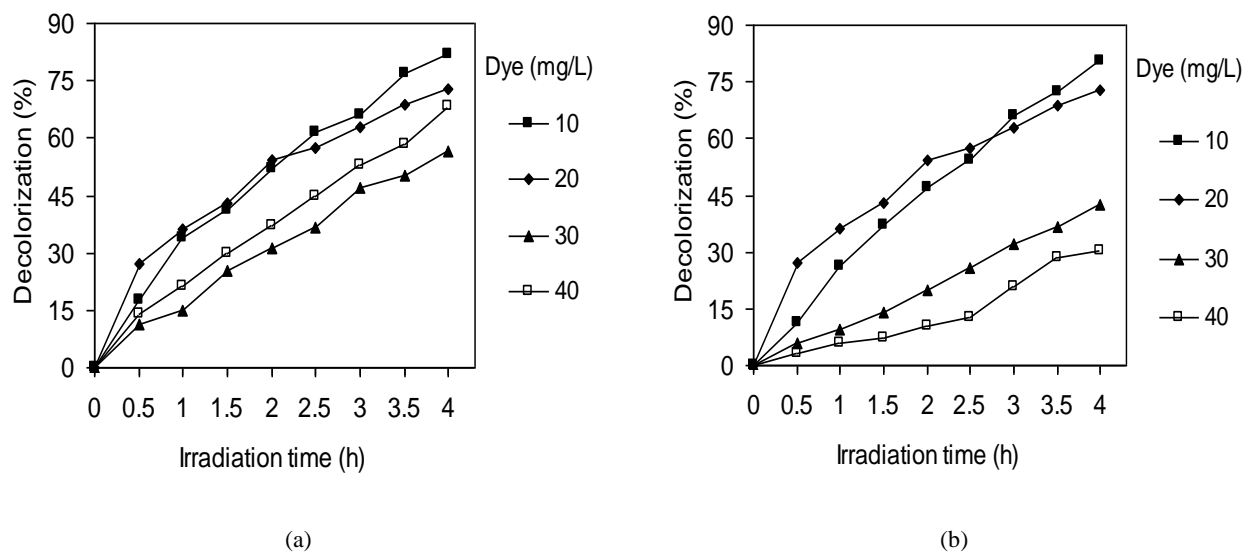
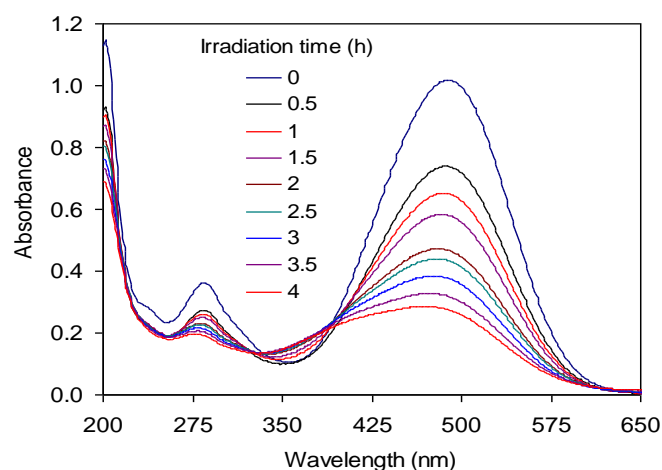
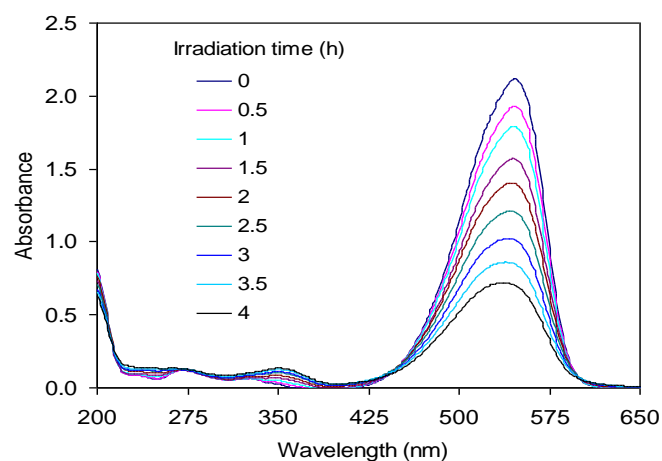


Figure 7: Dye concentration effect on the degradation of dyes using UV/CuO-ZnO nanocomposite (a) BR18 and (b) BV16.



(a)



(b)

Figure 8: UV-Vis spectrum of dyes during the degradation process using UV/CuO-ZnO nanocomposite (a) BR18 and (b) BV16.

4. Conclusion

In this paper, CuO-ZnO was synthesized and characterized. The photocatalytic dye degradation and mineralization ability of CuO-ZnO in the presence of hydrogen peroxide (H_2O_2) from colored textile wastewater was studied. Reactive dyes were used as model compounds. The effects of CuO-ZnO dosage, initial dye concentration and salt on photocatalytic dye

degradation were evaluated. The photodegradation with UV in the absence of CuO-ZnO presents a low performance for dye degradation from solutions (≤ 5). The synergistic effects of CuO-ZnO and UV were observed because of the catalytically performance of CuO-ZnO for production of hydroxyl radicals. It can be concluded that the CuO-ZnO could be used as a photocatalyst to degrade dyes in wastewater.

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