Property of Cu$_2$O-CuO/ZSM-5 nanocomposite and degradation process of azo dye AO7 without sacrificial agent (H$_2$O$_2$)

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ABSTRACT

In this study, Cu$_2$O-CuO/ZSM-5 nanocomposite was synthesized by the impregnation method, and its catalytic performance for the destruction of AO7 in aqueous solutions was investigated. The morphology, structure and surface element valence state of Cu$_2$O-CuO/ZSM-5 were characterized by transmission electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. The operating conditions on the degradation of AO7 by Cu$_2$O-CuO/ZSM-5, such as initial pH values, concentration of AO7 and catalyst dosage were investigated and optimized. The results showed that the sample had good catalytic activity for destruction of AO7 in the absence of a sacrificial agent (e.g. H$_2$O$_2$); it could degrade 91% AO7 in 140 min at 25°C and was not restricted by the initial pH of the AO7 aqueous solutions. Cu$_2$O-CuO/ZSM-5 exhibited stable catalytic activity with little loss after three successive runs. The total organic carbon and chemical oxygen demand removal efficiencies increased rapidly to 69.36% and 67.3% after 120 min of treatment by Cu$_2$O-CuO/ZSM-5, respectively.

Key words | AO7, Cu$_2$O-CuO nanocomposite, degradation, wastewater treatment. ZSM-5

INTRODUCTION

Organic dyes in wastewater give rise to water eutrophication, inducing increase of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) of the water body, and impose a high risk for the environment and human beings (Tsuda et al. 2001). Among them, azo dyes have attracted extensive attention due to their significant loss during manufacture and hard-degradation and toxicity (Forgacs et al. 2004). Thus, development of the methods to degrade them has attracted extensive attention. Various physical and chemical treatment technologies, such as adsorption and flocculation (Ahmad & Hameed 2010), electrochemical (Chen et al. 2013), and advanced oxidation processes (AOPs) have been reported (Pera-Titus et al. 2004; Liotta et al. 2009). However, nondestructive physical approaches usually result in the transfer of the azo dyes from water to another phase, which could lead to production of various secondary pollutants (Cooper 1993; Galindo et al. 2001). In recent years, AOPs have been widely investigated as promising and efficient methods to treat hardly degradable organic pollutants due to their high efficiency and easy operation. (Malato et al. 2009; Fu et al. 2010).

In recent years, copper oxides (Cu$_2$O and CuO) have been extensively used for catalytic degradation of organic dye due to their high efficiency, visible-light sensitivity, abundance, inexpensiveness, and environmental friendliness (Zheng et al. 2009; Kuo et al. 2014). In general, the catalytic activity of a catalyst is related to specific surface area. Larger specific surface area means more active sites for reaction and adsorption of molecules. The ZSM-5 zeolite not only has large specific surface area, but also provides abundant Brønsted acid sites (Al-OH) to adsorb alkaline groups or corresponding molecules. So the ZSM-5 zeolite has been used for support in this paper and exhibited a good ability for dispersed Cu$_2$O and CuO nanocomposites which show high degradation efficiency for AO7.

In this paper, a facile approach for preparing Cu$_2$O-CuO/ZSM-5 nanocomposite is presented and the morphology and structure of the composite samples are characterized. The catalytic degradation performance of Cu$_2$O-CuO/ZSM-5 for AO7 without a sacrificial agent was investigated including the effects of various factors such as initial pH, concentration of AO7, operating temperature and catalyst reusability. The reaction intermediates and valence state of active copper in the Cu$_2$O-CuO/ZSM-5 catalyst was investigated by Fourier transform infrared (FTIR)
and X-ray photoelectron spectroscopy (XPS) measurements, respectively.

EXPERIMENTAL

Preparation of Cu$_2$O-CuO/ZSM-5

Cupric acetate monohydrate and ZSM-5 were purchased from Aladdin Industrial Corporation and Huang Ma Chemical Industry Co., Ltd, respectively. All chemicals were analytical grade reagents and were used as received without further purification. A certain amount of Cu(CH$_3$COO)$_2$$\cdot$H$_2$O (1.2566 g) was dissolved in 40 mL deionized water until a clear solution was obtained. Then 5 g ZSM-5 was added to the above solution under strong stirring for 30 min. The suspension was treated ultrasonically for 2 h to ensure the ZSM-5 was well dispersed, then dried at 60 °C for 6 h. Finally, the powder was calcined at 350 °C for 5 h. For comparison, Cu$_2$O-CuO nanocomposite without using ZSM-5 was prepared by the same method.

Characterization of Cu$_2$O-CuO/ZSM-5

Morphology of the samples was taken by transmission electron microscope (TEM) (Philips Tecnai 12). XPS was recorded using an X-ray photoelectron spectroscopy (PerkinElmer, PHI Quantera II) with an Al Kα (hv = 1486.6 eV) X-ray source, and samples were dried under vacuum at 80 °C before detection. The samples were compensated for charging with a low-energy electron beam, and the peak of C1s (binding energy = 284.4 eV) was used to correct for sample charging. X-ray diffraction (XRD) patterns of the catalyst were obtained using a Bruker D8 advance operating at 40 kV and 30 mA with nickel-filtered Cu Kα radiation at the scanning rate of 10° min$^{-1}$ from 5° to 80°.

Degradation experiment and analytical methods

Solutions of 25 ml AO7 with different concentrations (range from 0.01 mM to 0.15 mM) and the desired Cu$_2$O-CuO/ZSM-5 powder were stirred for different time intervals (20, 40, 60, 80, 100, 120, and 140 min) under solar irradiation. Then the suspensions were centrifuged at 4,500 rpm for 3 min to remove solid particles. The concentration of AO7 in the obtained clear solution was determined by measuring the absorbance at $\lambda_{\text{max}}$ = 484 nm with a UV–vis spectrophotometer (T6, Beijing Purkinje General Instrument Co., Ltd) and a calibration curve. The initial pH values were controlled using 0.1 M NaOH or 0.1 M HCl, and measured with a pH meter (METTLER TOLEDO, FE20).

Degradation efficiency ($\eta$) of AO7 was calculated by the following expression:

$$\eta = \frac{(C_0 - C)}{C_0}$$

$C_0$ and $C$ are the initial concentration of AO7 and the instant concentration of AO7 at the corresponding time, respectively.

The mineralization process of AO7 was investigated by FTIR spectrometer (Nicolet IZ10FTIR), COD (Shimadzu, Japan), and total organic carbon (TOC) (Lianhua, China).

RESULTS AND DISCUSSION

TEM, XRD and XPS analysis

From Figures 1(a) and 1(b) it can be clearly seen that for Cu$_2$O-CuO/ZSM-5, copper oxide particles were evidently observed on the surface of the ZSM-5. In Figure 1(c), for pure ZSM-5 and Cu$_2$O-CuO/ZSM-5, typical characteristic peaks corresponding to ZSM-5 ($\theta = 8.02^\circ$, 8.87°, 23.12°, 23.97°, 24.42°) can be clearly observed, which meant the structure of ZSM-5 in the catalyst mainly remained. The decrease of intensity of the typical characteristic peaks corresponding to ZSM-5 of the sample could be the result of Cu$^+$ and Cu$_2$O cations introduced to ZSM-5 pores partially during the preparation process (Ravenelle et al. 2010). New peaks at $\theta = 35.7^\circ$ and 38.8° appeared (Figure 1(c)), which is attributed to the diffraction of monoclinic CuO (PDF No. 05-0661).

As shown in Figure 1(d), the Cu 2p3/2 spectra could be separated into two peaks at 932.38 eV and 934.50 eV, which were assigned to Cu$^+$ and Cu$_2$O, respectively (Espinós et al. 2002; Wang et al. 2002; Zheng et al. 2009), indicating that both the Cu$_2$O (CuO) and Cu$^+$ (Cu$_2$O) species were present on the sample surface, which seemed not to agree with the XRD analysis and that may be ascribed to trace element information that cannot be detected by XRD, and the process of thermal dehydration of copper(II) acetate monohydrate (Zhang et al. 2005), which showed that the major mass loss at 222 °C is attributed to the loss of the acetate anion as gaseous carbon dioxide and water.

Effect of the catalyst dosage, initial pH and the initial concentration of AO7

The effect of catalyst dosage on the bleaching of AO7 is shown in Figure 2(a). It can be observed that the
degradation efficiency increased markedly with an increase in dosage from 0.4 g/L to 1.2 g/L, and with further increase in the catalyst dosage above 1.2 g/L, the degradation efficiency was almost unaltered. When the catalyst dosage was only 1.2 g/L, about 91% of AO7 was bleached after 140 min. For the sake of comparison, in all subsequent experiments, 1.2 g/L of catalyst was used. In addition, under the same conditions, the degradation efficiency of Cu$_2$O-CuO was 27.8% after 140 min. For pure ZSM-5, only 2.9% of AO7 was bleached after 140 min.

The initial solution pH value and the initial concentration of dye are known to be the important parameters for bleaching of dye in waste water (Merka et al. 2011). The effect of initial pH values (4.0, 6.0, 8.0 and 10.0) and the initial concentrations of AO7 (0.01, 0.03, 0.05, 0.10, 0.15 mM or 3.50, 10.51, 17.52, 35.03, 52.55 mg/L) is shown in Figures 2(b) and 2(c). As can be seen in Figure 2(b), the catalyst shows high activity for bleaching of AO7 in a wide pH range: 91.5%, 90.2%, 85.8%, and 94.2% of AO7 was bleached for the initial pH values of 4.0, 6.0, 8.0, and 10.0 after 140 min, respectively. Furthermore, in alkaline conditions, for which the initial pH values were 11.0 and 11.8, about 92.3% and 91.8% of AO7 were bleached after 140 min (not shown), which meant along with the increase in pH value (>10) the bleaching efficiency decreased slightly. The catalyst for bleaching AO7 was not restricted by the initial pH value of the AO7 dye aqueous solution.

The effect of different initial AO7 concentrations (0.01, 0.03, 0.05, 0.10, and 0.15 mM) was also investigated. As can be seen in Figure 2(c), after 140 min, all of the AO7 degradation efficiencies were above 65% under the different concentrations of AO7, which were 65.9%, 86.1%, 91%, 89.8%, and 86.8%, respectively. Increase in the initial concentration of AO7 from 0.01 to 0.05 mM increases the degradation efficiency appreciably, and with further increase in the initial concentration above 0.05 mM, the degradation efficiency decreases slightly. The results presented in the form of the initial rate of AO7 degradation as a function of initial dye concentration are shown in Figure 2(d). It was observed that the initial degradation rate increased obviously with the increase of initial AO7 concentration. It can be noticed that the decolorization
The rate does not obey the first-order kinetic process. The result may be explained by the higher initial dye concentration being beneficial to more AO7 adsorbed by ZSM-5 and reacting with Cu2O and CuO.

In all subsequent experiments, 0.05 mM of initial AO7 concentration was used. The catalyst could destroy AO7 effectively for a broad initial concentration of AO7, which could have potential applications in catalysis fields in environmental treatment.

**Effect of the temperature and recyclability**

The influence of various operating temperatures on the bleaching of AO7 is shown in Figure 3(a). After 140 min, 89.1%,
88.6%, 82.2%, and 60.5% of AO7 was bleached at 20 °C, 30 °C, 40 °C, and 50 °C, respectively. According to Figure 2(b), 94.2% of AO7 was bleached when the operating temperature was 25 °C. Obviously, the optimal operating temperature is 25 °C, and if the operating temperature varied about 10–15 °C, the degradation efficiency of AO7 decreased slightly. But when the reaction temperature reached 50 °C, the degradation efficiency decreased fast. That may because overly high temperatures did not facilitate the adsorption of dye molecules by ZSM-5 and reaction with Cu2O and CuO.

The stability of the catalyst was also studied. Three cyclic experiments were performed under optimal conditions. As shown in Figure 3(b), the degradation efficiency of three cyclic experiments was 90%, 89.6%, and 86.9%, respectively. The catalyst exhibited stable catalytic activity with little loss after three cycles, which emphasized the chemical stability of Cu2O-CuO/ZSM-5.

**UV–vis spectroscopy, FTIR spectroscopy**

Figure 4(a) shows typical UV–vis spectra obtained during the bleaching of AO7 in an aqueous solution by Cu2O-CuO/ZSM-5. According to the spectrum obtained before the bleaching process (0 min), there are two peaks in the visible region, which correspond to the hydrazone form (484 nm) and the azo form (430 nm) of AO7 (Stylidi et al. 2004; Yue et al. 2014). These forms originate from intermolecular hydrogen-bonding tautomeric interactions between the β-hydrogen of the corresponding azo linkage and the oxygen of the naphthyl group, respectively (Stylidi et al. 2004; Yue et al. 2014). The peaks in the UV region (511 and 229 nm) correspond to π–π* transitions in the naphthalene and benzoic rings of AO7, respectively (Feng et al. 2000; Yue et al. 2014). It can be seen from Figure 4(a) that all the four main peaks (485, 430, 311, and 229 nm) of AO7 obviously decrease after 50 min. Two hours later, the peaks almost disappear completely, and no new absorption bands appear in either the visible or the ultraviolet spectral regions. The results suggest that the hydrazone form (485 nm) and the azo form (430 nm) of AO7 could be decomposed almost completely (Feng et al. 2000), and it may also represent the benzoic and naphthalene rings of mineralized AO7 obviously. It should be noted that control experiments under otherwise identical conditions showed that AO7 is almost stable with the treatment of pure ZSM-5.

![Figure 4](https://iwaponline.com/wst/article-pdf/73/11/2747/460680/wst073112747.pdf)
In order to further investigate the bleaching process and intermediates, FTIR measurement was used. Figures 4(b) and 4(c) are the FTIR spectra of AO7 aqueous solution before and after treatment by the catalyst, respectively. In Figure 4(b), the peak at 1,506 cm\(^{-1}\) is attributed to the bending vibration mode \(\delta(N-H)\) of the hydrazone form of AO7 or to the azo bond (\(-N=\equivN-\)) vibrations or aromatic ring vibrations sensitive to interaction with the azo bond (Vinodgopal et al. 1996; Bauer et al. 1999; Stylidi et al. 2004; Yue et al. 2014). The bands at 1,452, 1,559, 1,599, and 1,622 cm\(^{-1}\) are attributed to C=C aromatic skeletal vibrations (Stylidi et al. 2003; Yue et al. 2014). Additionally, the band at 1,622 cm\(^{-1}\) is also assigned to a combination of phenyl ring vibrations with stretching of the C=N group of the hydrazone form of the azo dye (Stylidi et al. 2003; Yue et al. 2014). The bands located at 1,319 and 1,402 cm\(^{-1}\) can be linked to O–H bending vibrations, while the band at 1,255 cm\(^{-1}\) is linked to the stretching vibrations of C–N of the hydrazone form of AO7 (Vinodgopal et al. 1996). Finally, the bands at 1,036 and 1,122 cm\(^{-1}\) are assigned to the coupling between benzene mode 1 and \(v_3(SO_3)\), while the band at 1,209 cm\(^{-1}\) is linked to the \(v_{as}(SO_3)\) stretching mode (Bauer et al. 1999). The FTIR absorption spectrum of AO7 after 120 min of treatment by Cu\(_2\)O-CuO/ZSM-5 is also given. As shown in Figure 4(c), the decreased intensity of the 1,506 cm\(^{-1}\) band implies the destruction of the chromophore part (i.e., \(-N=\equivN-\)) of AO7 (Yue et al. 2014). In particular, intensities of all peaks (1,255, 1,506, 1,559, and 1,622 cm\(^{-1}\)) linked to the hydrazone form of AO7 decreased remarkably (Yue et al. 2014), and intensities of the majority of the peaks (660–895 cm\(^{-1}\)) linked to C–H vibrations of the aromatic ring also decreased remarkably, which means the aromatic rings were mostly destroyed, which is consistent with the analysis of the UV–vis spectra.

In addition, the COD and TOC of the AO7 aqueous solution were determined after 120 min of treatment by Cu\(_2\)O-CuO/ZSM-5 (experimental conditions: \(T = 25^\circ\text{C}\), \([\text{AO7}]_0 = 0.05 \text{mM}\), pH = 10.0, catalyst dosage = 1.2 g/L). The TOC and COD removal efficiency increased rapidly to 69.36% (the TOC of the AO7 aqueous solution before and after treatment by Cu\(_2\)O-CuO/ZSM-5 was 13.53 mg/L and 4.146 mg/L, respectively) and 67.3% (the COD of the AO7 aqueous solution before and after treatment by Cu\(_2\)O-CuO/ZSM-5 was 25.1 mg/L and 8.2 mg/L, respectively) after 120 min of treatment, respectively. The results indicate that most of the AO7 was mineralized by Cu\(_2\)O-CuO/ZSM-5, and a part was decomposed into small molecules, which is consistent with the analysis of the UV–vis and FTIR spectra.

**CONCLUSION**

In summary, we have prepared Cu\(_2\)O-CuO/ZSM-5 by the impregnation method and used it to remove AO7 from water. The Cu\(_2\)O-CuO/ZSM-5 exhibited satisfactory catalytic activity for degradation of AO7 without the assistance of a sacrificial agent (e.g. H\(_2\)O\(_2\)), and was not restricted by the initial pH of the AO7 aqueous solution. Both the TOC and COD removal efficiencies of AO7 aqueous solution were above 67% after 120 min treatment by Cu\(_2\)O-CuO/ZSM-5. The catalyst exhibited stable catalytic activity with little loss after three successive runs. In addition, the method and raw materials for preparing a copper-based catalyst are simple and inexpensive, and the degradation of AO7 does not need special equipment, so the Cu\(_2\)O-CuO/ZSM-5 catalyst has potential applications in the treatment of dyes in wastewater containing AO7. In future work, we will use real effluent containing different dyes (including AO7) to detect the degradation performance of Cu\(_2\)O-CuO/ZSM-5, and try to further study the mechanism of degradation of AO7.

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