Research Article

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Abstract: The effects of Cu$^{2+}$ on the catalytical degradation of acid chrome blue K (ACBK) in UV-TiO$_2$ and H$_2$O$_2$ processes were studied. In these two processes, Cu$^{2+}$ markedly depressed the catalytical degradation of ACBK by its interaction with ACBK. Through this interaction, the new complex Cu(ACBK)$_2$ formed. The formation of this new complex was favorable to protect some groups in ACBK from the oxidation of reactive oxygen generated in UV-TiO$_2$ and H$_2$O$_2$ processes, and consequently had suppressing effects on degradation of ACBK. In addition, Cu$^{2+}$ also inhibited the degradation of ACBK in UV-TiO$_2$ process by influencing the adsorption of ACBK on the surface of TiO$_2$ particles.

Keywords: Copper ions • Acid chrome blue K • Photocatalytical degradation

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1. Introduction

Numerous investigations have focused on TiO$_2$ photocatalysis in recent years, particularly owing to its application for the mineralization of undesirable organic contaminants to CO$_2$, H$_2$O and inorganic constituent [1]. Dyestuffs from the textile and photographic industries are becoming a major source of environmental contaminations [2,3]. Some conventional methods such as flocculation, reverse osmosis and activated carbon adsorption have been used to decolorize the textile wastewater [4]. Activated carbon adsorption process for the removal of dyes is an accepted practice, but the cost of treatment is high. Otherwise, the methods just separate the dyes from the textile wastewater, thereby leading to the difficulties in the complete removal of color. The advanced oxidation technologies, such as TiO$_2$-mediated photocatalysis and photo-Fenton processes [5-8], have been investigated to degrade dye pollutants during the past few years.

The occurrence of dissolved metal ions is rather common in natural waters and industrial wastewaters. For example, such transition or posttransition metal ions as Cu$^{2+}$, Zn$^{2+}$, Al$^{3+}$, and Fe$^{3+}$ are often contained in the wastewaters of textile factories [9]. They can significantly influence the photocatalytic reactions for removal of the pollutants [10-13]. The degradation of acid red B was inhibited by the trace quantities of Mn$^{2+}$; Ni$^{2+}$, and also depressed the photocatalytical degradation of cationic blue X-GRL; but Ca$^{2+}$, Mg$^{2+}$ and Al$^{3+}$ could enhance the degradation of acid red B [14]. The decrease in the degradation rate could be caused by precipitation of dissolved metals as hydroxides onto the surface of catalyst [15]. Fe$^{3+}$ inhibited the degradation of alizarin red and malachite green by altering the electron-transfer pathway involving dyes, O$_2$ and TiO$_2$ particles [10]. On the contrary, metal ions such as Fe$^{2+}$ and Ag$^+$ could scavenge photogenerated electrons on the catalyst surface, reduce the non-desired electron/hole recombination, result in an increased rate of active oxygen species, and has positive effect on pollutants' degradation [16,17]. Besides, some metal ions also reacted with the dyestuffs; did this reaction have some effects on the oxidation of these dyes?

In this experiment, an azo dye: acid chrome blue K (ACBK) was used to study the effects of Cu$^{2+}$ on the catalytical degradation of some dyes. In pH 5.0 buffer solution, ACBK was degraded quickly in TiO$_2$-UV or in
H₂O₂ processes. But the degradation rate was inhibited with the addition of Cu²⁺. The changes in the spectra indicated there was an interaction between ACBK and Cu²⁺. With this interaction, a new compound Cu(ACBK)₂ formed. This interaction was favorable to protect ACBK from the oxidation of some active oxygen generated in TiO₂-UV and H₂O₂ processes, consequently had suppressing effects on the degradation of ACBK. Otherwise, Cu²⁺ depressed the photocatalytical degradation of ACBK in UV-TiO₂ process by influencing the adsorption of ACBK on TiO₂ particles surface.

2. Experimental Procedures

2.1 Apparatus and reagents
A Model S4100 spectrometer (Scinco Instruments, Korea), equipped with Lappro Plus Software, was used to measure the spectra of ACBK. A Mode pHS-25 pH meter (Shanghai Precise Science Instrument, Shanghai, China) was used to measure the pH of the buffer solutions. A Model Analyst 400 Atomic Absorption Spectrometer (PerkinElmer, USA) was used to measure the concentration of Cu²⁺. A Model Zetasizer Nano Z instrument (Malvern, England) was used to measure Zeta potential of TiO₂. A Model Liqui TOC II total organic carbon analyzer (Elementar CO. Germany) was used to measure the change of total organic carbon during irradiation times. A Model TG16-WS high speed centrifuge (Changsha Xiangyi Centrifuge Instrument, Hunan, China) was used to separate P25 TiO₂ from the solutions. A home made batch reactor was used to study the photo-catalytical degradation of ACBK with P25 TiO₂. Irradiation was provided by a 110 W middle-pressure mercury light (Shanghai Yadong Light Instrument, China) placed in a plugging tube in the center of the reactor. A Pyrex cylindrical jacket located around the plugging tube contained circulating water to avoid heating of the solution.

P25 TiO₂ powder (Degussa CO. Germany) was used as the catalyst without pretreatment. Stock ACBK solution (5.000 mmol L⁻¹) was prepared by dissolving 1.466 g ACBK (Shanghai Chemical Reagents Company, China) in 500 mL deionized water. Stock solution of Cu²⁺ (0.100 mol L⁻¹) was prepared by dissolving CuCl₂•2H₂O in 100 mL deionized water. A pH 5.0 buffer solution was prepared with acetic acid and sodium acetate. It was used to adjust the acidity of solutions. Hydrogen peroxide (30% H₂O₂) was used to oxidize ACBK. All other reagents were of laboratory reagent-grade and were used without further purification. Deionized water was used throughout the experiment.

2.2 Methods

2.2.1 Degradation of ACBK with P25 TiO₂ and UV-light
A 10-mL aliquot of ACBK stock solution, 50 mL of pH 5.0 buffer solution and known volume of Cu²⁺ were added into a 1-L flask. The solutions were diluted to 1 L with deionized water. Then 0.5 g of P25 TiO₂ was added to these solutions to form the suspensions. The suspensions were magnetically stirred in the dark for approximately 60 minutes prior to irradiation to permit an adsorption/desorption equilibrium to be reached. The suspensions were added to the batch reactor. At given irradiation time intervals (5 min), 16 mL aliquots were collected and consequently centrifuged to remove the catalyst particles. The supernatants were analyzed with S4100 spectrometer. The degradation efficiency (δ) of ACBK was defined as:

$$\delta (%) = \frac{100 - A}{A_0} \times 100\%$$

Where A₀ was the maximal absorbance of supernatant at 0 minute and the A was that at given time. The Cu²⁺ concentration in supernatant was analyzed with atomic absorption spectroscopy. With the same process, the adsorption of ACBK on the surface of TiO₂ particles was studied. Into a series of 100 mL flasks, 5.0 mL pH 5.0 buffer solution, known volume of Cu²⁺ and 0.05 g P25 TiO₂ were added. The suspensions were diluted to 100 mL with deionized water and were magnetically stirred for approximately 60 minutes. The zeta potential of P25 TiO₂ in these solutions was measured with Zetasizer Nano Z instrument.

2.2.2 Degradation of ACBK with H₂O₂
A 0.1-mL aliquot of ACBK stock solution (5.0 mmol L⁻¹), 0.5 mL of pH 5.0 buffer, and known volume of Cu²⁺ were added into 10.0 mL calibrate flask. The solutions were diluted to 10.0 mL with deionized water and were mixed thoroughly. 3.0 mL of these solutions were added into optical cell. Consequently, 0.400 mL of 30% H₂O₂ was added into the solution quickly. The spectra of the solutions at given time intervals (3 minutes) were measured against water with S4100 spectrometer. The decolorizing efficiency (δ) of ACBK in H₂O₂ process was calculated with the same method in above experiment.

2.2.3 Interaction between Cu²⁺ and ACBK
Into a series of 10-mL calibrated flasks, 0.1 mL of ACBK stock solution (5.0 mmol L⁻¹), 0.5 mL of pH 5.0 buffer and known volume of Cu²⁺ were added. The solutions were diluted to 10.0 mL with deionized water and were mixed thoroughly. The solutions were measured at 519 and 543 nm against water respectively. By means of spectra
3. Results and Discussions

3.1 Degradation of ACBK in UV-TiO₂ process

ACBK is a type of azo dye. Its structure is shown in Fig. 1. It can be degraded in the existence of TiO₂ with the UV-light irradiation. The photocatalytical degradation of ACBK in TiO₂ dispersion in the presence and absence of Cu²⁺ was illustrated in Figs. 2 and 3.

![Figure 1. The structure of ACBK and the complex ion Cu(ACBK)₂²⁺.](image)

During UV-light irradiation, the characteristic absorption band of ACBK decreased rapidly in the absence of Cu²⁺, as the spectra in Fig. 2A shown. In the presence of Cu²⁺, the absorbance of ACBK also decreased; but the degradation rate was depressed by the addition of Cu²⁺, as the spectra in Fig. 2B, C and D shown. Cu²⁺ markedly hindered the degradation of ACBK. These experimental results also could be found in Fig. 3. After 40 minutes, almost all of ACBK were degraded in Cu²⁺-free dispersions. There just about 91.6%, 86.1%, 79.5%, 73.7%, 73.9% and 73.4% of ACBK were degraded when 0.0025, 0.0050, 0.0100, 0.0200, 0.0300 and 0.0400 mmol L⁻¹ Cu²⁺ were added into suspensions respectively. The depressing effects reached a maximum with the addition of 0.0200 mmol L⁻¹ Cu²⁺. No further depressing effects was observed with the addition of more Cu²⁺. Moreover, the hypsochromic shifts of the absorption maximum were pronounced in the presence of Cu²⁺.

For the dyes’ photocatalytical degradation process, it was necessary for dyes to adsorb on the surface of catalyst [19]. The adsorption efficiency of ACBK on the surface of TiO₂ particles decreased obviously with the addition of Cu²⁺ into the ACBK/TiO₂ dispersion. There was about 5% of ACBK was adsorbed on TiO₂ in absence of Cu²⁺. By contrast, the adsorption efficiency of ACBK was just about 1% with the addition of 0.0400 mmol L⁻¹ Cu²⁺. The adsorption of ACBK on TiO₂ particles surface was mainly through electrostatic interaction. So the charge property of TiO₂ particles was very important for this adsorption. The zeta potential recorded as a function of the TiO₂ particles’ charge property in the presence and absence of Cu²⁺ displayed in Fig. 4B. The zeta potential of TiO₂ particles exhibited concomitant in the presence and absence of Cu²⁺. Here the decrease in adsorption efficiency was not caused by the change of TiO₂ particles' charge property. In pH 5.0 buffer solution, the surface of P25 TiO₂ particles was positively charged because the pH of zero charge point of P25 TiO₂ was pH 6.25 [19]. It was favorable for the adsorption of negatively charged ACBK, while the adsorption of cationic metal ions was relatively insignificant [20]. As the Fig. 5A shows, the adsorption of Cu²⁺ on TiO₂ was just about 5%. In pH 5.0 buffer solution, more “>TiOH₂“ and “>TiOH“ formed on the surface of TiO₂. The formation of these groups was not favorable for the adsorption of Cu²⁺ [21]. In addition, during the irradiation, the concentration of Cu²⁺ remained unchanged, as the experimental results in the Fig. 5B indicated. It was well known that some transition metal ions decreased the formation of reactive oxygen species by scavenging electrons on the catalysis surface. During this process, the metal ion was reduced [10]. In this experiment, during UV-light irradiation, the concentration of Cu²⁺ remained unchanged. The reduction of Cu²⁺ was not observed in this experiment. Accordingly, we deduced that the decrease of degradation rate in the presence of Cu²⁺ was not caused by the decrease of active oxygen species. The hypsochromic shifts of the absorption maximum in the presence of Cu²⁺ inferred the interaction between ACBK and Cu²⁺ [18]. Maybe this interaction was the main reason for the decreasing of ACBK's adsorption on the surface of TiO₂ and for the inhibition effects of Cu²⁺ on catalytical degradation of ACBK.
Figure 2. Spectral change of 0.050 mmol L⁻¹ ACBK (A) and 0.050 mmol L⁻¹ ACBK with 0.0100, 0.0200 and 0.0300 mmol L⁻¹ Cu²⁺ (B, C and D) at pH 5.0 buffer solutions with 0.05% P25 TiO₂ and UV-light at given time intervals. Spectra from 1 to 12 denote irradiation times from 0 to 55 min with 5 min intervals.

Figure 3. The degradation of 0.050 mmol L⁻¹ ACBK with controlled Cu²⁺ concentrations (0.000, 0.0025, 0.0050, 0.0100, 0.0200, 0.0300 and 0.0400 mmol L⁻¹) at pH 5.0 buffer solution with 0.05% P25 TiO₂ and UV-light at different times.

Figure 4. The adsorption of ACBK on the surface of P25 TiO₂ (A) and the change of Zeta potential of P25 TiO₂ (B) at different concentration of Cu²⁺.

Figure 5. The adsorption of Cu²⁺ on P25 TiO₂ (A) and the change of Cu²⁺ concentration during the irradiation time (B).

Figure 6. The change of TOC and degradation efficiency of 0.0500 mmol L⁻¹ ACBK in the absence (A) and presence of 0.0300 mmol L⁻¹ Cu²⁺ (B).
To investigate the mineralization of ACBK in presence and absence of Cu\(^{2+}\), the TOC of ACBK/TiO\(_2\) dispersion was measured under UV-light irradiation. The experimental results are shown in Figs. 6A and B. During irradiation time, the TOC of the solution decreased slightly in the presence and absence of Cu\(^{2+}\). The TOC decreased as little as 9.57% in Cu\(^{2+}\) free solution. However with the addition of 0.0300 mmol L\(^{-1}\) Cu\(^{2+}\), the decrease of TOC was just 6.90%. The higher decolorizing efficiency and lower TOC removal efficiency indicated the rather facile cleavage of the chromophoric groups and the comparatively difficult mineralization of organic pollutants.

3.2 Oxidation of ACBK with H\(_2\)O\(_2\)

To investigate the role of the Cu\(^{2+}\) ions in more detail, H\(_2\)O\(_2\), as an integral component of several chemical oxidation technologies including Fenton, photo-Fenton, UV-based chemical oxidation [22,23], was used to oxidize ACBK without adsorption effects being considered. The experimental results were presented in Figs. 7 and 8.

As the spectra in Fig. 7A shows, ACBK could be degraded efficiently in aqueous solutions with the addition of H\(_2\)O\(_2\). After 45 min of reaction, about 91.2% ACBK decomposition was observed. However, a slower degradation of ACBK occurred in the presence of Cu\(^{2+}\), as the Fig. 7B, C and D shows. In the presence of 0.0050, 0.0100, 0.0150, 0.0200, 0.0300 and 0.0400 mmol L\(^{-1}\) Cu\(^{2+}\), just 73.6%, 56.4%, 37.6%, 15.0%, 7.8% and 8.5% ACBK decomposition was achieved in 45 min. The depressing effects also reached to a maximum with the addition of 0.0200 mmol L\(^{-1}\) Cu\(^{2+}\). No further depressing effects was observed with the addition of more Cu\(^{2+}\). Moreover, the experimental results in Fig. 8B shows that the decolorizing efficiency was proportional to the reacting times, indicating that the degradation rate of ACBK exhibited concomitant in the presence of 0.0300 and 0.0400 mmol L\(^{-1}\) Cu\(^{2+}\). In this process, the reaction between ACBK and H\(_2\)O\(_2\) was a homogeneous reaction. Hence there were no adsorption effects on the decomposition of ACBK. Moreover, similar to the results in “UV-TiO\(_2\)” process, the hypsochromic shifts of the absorption maximum were pronounced in the presence of Cu\(^{2+}\), too. The hypsochromic shifts of the absorption maximum in presence of Cu\(^{2+}\) was presumed to the interaction between ACBK and Cu\(^{2+}\). In order to clarify the role of Cu\(^{2+}\), interaction between ACBK and Cu\(^{2+}\) was examined by spectra correction technique.

Figure 7. Spectral change of 0.050 mmol L\(^{-1}\) ACBK (A) and 0.050 mmol L\(^{-1}\) ACBK with 0.0100, 0.0200 and 0.0300 mmol L\(^{-1}\) Cu\(^{2+}\) (B, C and D) at pH 5.0 buffer solutions with H\(_2\)O\(_2\) at different times. Spectra from 1 to 16 denote reacting times from 0 to 45 min with 3 min intervals.
The spectra correction technique was a new spectral method to study the interaction between ligands and some metal ions or proteins [18, 24]. In this work, it was used to study the interaction between ACBK and Cu²⁺. The effective fraction (η) of ACBK binding to Cu²⁺ and its binding ratio (γ) were calculated [18], as shown in Fig. 9.

As seen in Fig. 9A, γ of ACBK to Cu²⁺ remained constant (about 2) when ACBK concentration was bigger than 0.02 mmol L⁻¹. Here ACBK was enough to react with all Cu²⁺ with the formation of a new compound Cu(ACBK)₂. As Fig. 9B indicates, η of ACBK increased with the addition of more Cu²⁺, indicating that more and more ACBK was bound to Cu²⁺. When the Cu²⁺'s concentration reached to 0.0250 mmol L⁻¹, almost all ACBK was bound to Cu²⁺ with little free ACBK existing in solutions [24]. It is relevant to note that 100-η (%) and δ (%) displayed identical change characteristics. With the addition of 0.0050, 0.0100, 0.0150, 0.0200 and 0.0300 mmol L⁻¹ Cu²⁺, the percent of free ACBK (100-η (%)) was about 81.5, 61.9, 43.1, 25.1 and 0%, respectively. Correspondingly, the decolorizing efficiency (δ) of ACBK was about 72.4, 55.8, 36.8, 23.1 and 12.4%. This identical change characteristics were presumed to the result from the formation of stable Cu(ACBK)₂. In the presence of 0.0250 mmol L⁻¹ or more Cu²⁺, all ACBK was bound to Cu²⁺ with the formation of Cu(ACBK)₂. So η reached to near 100%. Nonetheless, some Cu(ACBK)₂ would dissociate to Cu²⁺ and free ACBK. These free ACBK was degraded immediately by the H₂O₂ in solution. Clearly, the degradation rate was controlled by the dissociation rate, thereby leading to a constant degradation rate in the presence of 0.0250 mmol L⁻¹ or more Cu²⁺, as the experimental results in Fig. 8B shows. With the addition of Cu²⁺, ACBK interacted with Cu²⁺. Then new compounds Cu(ACBK)₂ (the structure was shown in Fig. 1) formed. This formation of these new compounds could protect some groups in ACBK from the oxidation of reactive oxygen, which were provided in UV-TiO₂ and H₂O₂ process.

4. Conclusions
Cu²⁺ obviously has detrimental effects on the catalytical degradation of ACBK in UV-TiO₂ and H₂O₂ process. These inhibition effects were mainly caused by the interaction ACBK and Cu²⁺ in pH 5.0 buffer solution. Through this interaction, Cu(ACBK)₂ formed. This interaction was favorable for protecting some groups in ACBK from the oxidation of reactive oxygen generated in UV-TiO₂ and H₂O₂ process, and consequently had suppressing effects on degradation of ACBK. Otherwise, the addition of Cu²⁺ also influenced the adsorption of ACBK on the surface of TiO₂, and consequently influenced the degradation of ACBK.

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