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The effects of copper ions on the catalytical degradation of azo dye acid chrome blue K

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_2O_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_2O_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_2O 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

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H_2O_2 processes. But the degradation rate was inhibited with the addition of Cu^{2+}. The changes in the spectra indicated there was an interaction between ACBK and Cu^{2+}. 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 TiO_2-UV and H_2O_2 processes, consequently had suppressing effects on the degradation of ACBK. Otherwise, Cu^{2+} depressed the photocatalytical degradation of ACBK in UV-TiO_2 process by influencing the adsorption of ACBK on TiO_2 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 Cu^{2+}. A Model Zetasizer Nano Z instrument (Malvern, England) was used to measure Zeta potential of TiO_2. 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 TiO_2 from the solutions. A home made batch reactor was used to study the photo-catalytical degradation of ACBK with P25 TiO_2. 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 TiO_2 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 Cu^{2+} (0.100 mol L^{-1}) was prepared by dissolving $CuCl_2 \cdot 2H_2O$ 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% H_2O_2) 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 TiO_2 and UV-light

A 10-mL aliquot of ACBK stock solution, 50 mL of pH 5.0 buffer solution and known volume of Cu^{2+} were added into a 1-L flask. The solutions were diluted to 1 L with deionized water. Then 0.5 g of P25 TiO_2 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:

$$\delta\ (\%) = 100 - A / A_0 \times 100\% \qquad (1)$$

Where A_0 was the maximal absorbance of supernatant at 0 minute and the A was that at given time. The Cu^{2+} concentration in supernatant was analyzed with atomic absorption spectroscopy. With the same process, the adsorption of ACBK on the surface of TiO_2 particles was studied. Into a series of 100 mL flasks, 5.0 mL pH 5.0 buffer solution, known volume of Cu^{2+} and 0.05 g P25 TiO_2 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 TiO_2 in these solutions was measured with Zetasizer Nano Z instrument.

2.2.2 Degradation of ACBK with H_2O_2

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 Cu^{2+} 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% H_2O_2 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 H_2O_2 process was calculated with the same method in above experiment.

2.2.3 Interaction between Cu^{2+} 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 Cu^{2+} 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

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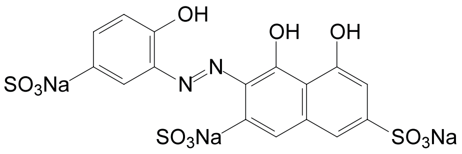
correction technique [18], the binding number (γ) of ACBK on Cu^{2+} and the effective fraction (η) of ACBK to Cu^{2+} were calculated. At last, 3.0 mL of the solutions were added into other series flasks with the addition of 0.400 mL of 30% H_2O_2. One hour later, the absorbance of these solutions were measured against water.

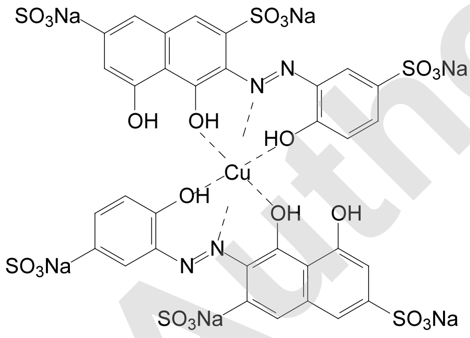
3. Results and Discussions

3.1 Degradation of ACBK in UV-TiO_2 process

ACBK is a type of azo dye. Its structure is shown in Fig. 1. It can degraded in the existence of TiO_2 with the UV-light irradiation. The photocatalytical degradation of ACBK in TiO_2 dispersion in the presence and absence of Cu^{2+} was illustrated in Figs. 2 and 3.



ACBK



$Cu(ACBK)_2$

Figure 1. The structure of ACBK and the complex ion $Cu(ACBK)_2^{2+}$.

During UV-light irradiation, the characteristic absorption band of ACBK decreased rapidly in the absence of Cu^{2+}, as the spectra in Fig. 2A shown. In the presence of Cu^{2+}, the absorbance of ACBK also decreased; but the degradation rate was depressed by the addition of Cu^{2+}, as the spectra in Fig. 2B, C and D shown. Cu^{2+} 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 Cu^{2+}-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} Cu^{2+} were added into suspensions respectively. The depressing effects reached 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 hypsochromic shifts of the absorption maximum were pronounced in the presence of Cu^{2+}.

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 TiO_2 particles decreased obviously with the addition of Cu^{2+} into the ACBK/TiO_2 dispersion. There was about 5% of ACBK was adsorbed on TiO_2 in absence of Cu^{2+}. By contrast, the adsorption efficiency of ACBK was just about 1% with the addition of 0.0400 mmol L^{-1} Cu^{2+}. The adsorption of ACBK on TiO_2 particles surface was mainly through electrostatic interaction. So the charge property of TiO_2 particle was very important for this adsorption. The zeta potential recorded as a function of the TiO_2 particles' charge property in the presence and absence of Cu^{2+} displayed in Fig. 4B. The zeta potential of TiO_2 particles exhibited concomitant in the presence and absence of Cu^{2+}. Here the decrease in adsorption efficiency was not caused by the change of TiO_2 particles' charge property. In pH 5.0 buffer solution, the surface of P25 TiO_2 particles was positively charged because the pH of zero charge point of P25 TiO_2 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 Cu^{2+} on TiO_2 was just about 5%. In pH 5.0 buffer solution, more "$>TiOH_2^+$" and "$>TiOH$" formed on the surface of TiO_2. The formation of these groups was not favorable for the adsorption of Cu^{2+} [21]. In addition, during the irradiation, the concentration of Cu^{2+} 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 Cu^{2+} remained unchanged. The reduction of Cu^{2+} was not observed in this experiment. Accordingly, we deduced that the decrease of degradation rate in the presence of Cu^{2+} was not caused by the decrease of active oxygen species. The hypsochromic shifts of the absorption maximum in the presence of Cu^{2+} inferred the interaction between ACBK and Cu^{2+} [18]. Maybe this interaction was the main reason for the decreasing of ACBK's adsorption on the surface of TiO_2 and for the inhibition effects of Cu^{2+} on catalytical degradation of ACBK.

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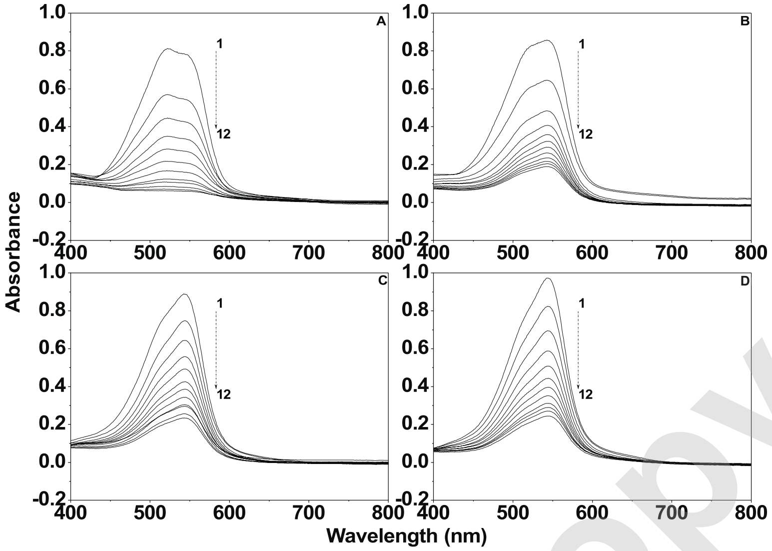

Figure 2. Spectral change of 0.050 mmol L^{-1} ACBK (A) and 0.050 mmol L^{-1} ACBK with 0.0100, 0.0200 and 0.0300 mmol L^{-1} Cu^{2+} (B, C and D) at pH 5.0 buffer solutions with 0.05% P25 TIO_2 and UV-light at given time intervals. Spectra from 1 to 12 denote irradiation times from 0 to 55 min with 5 min intervals

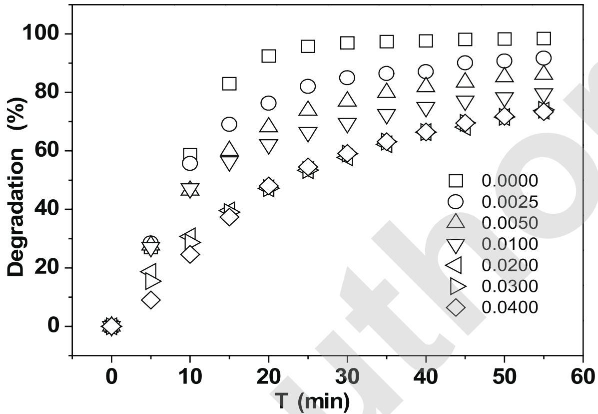

Figure 3. The degradation of 0.050 mmol L^{-1} ACBK with controlled Cu^{2+} concentrations (0.000, 0.0025, 0.0050, 0.0100, 0.0200, 0.0300 and 0.0400 mmol L^{-1}) at pH 5.0 buffer solution with 0.05% P25 TIO_2 and UV-light at different times.

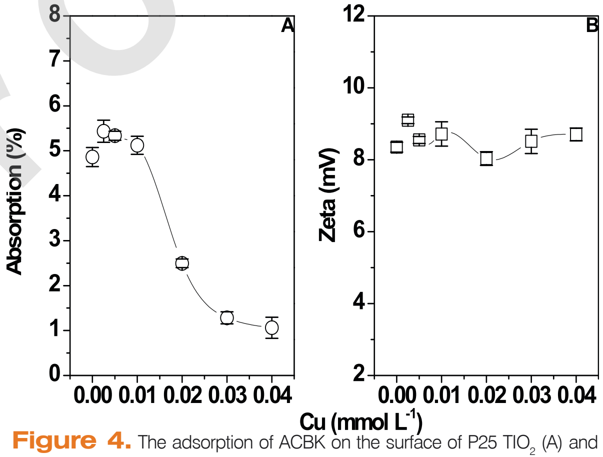

Figure 4. The adsorption of ACBK on the surface of P25 TIO_2 (A) and the change of Zeta potential of P25 TIO_2 (B) at different concentration of Cu^{2+}.

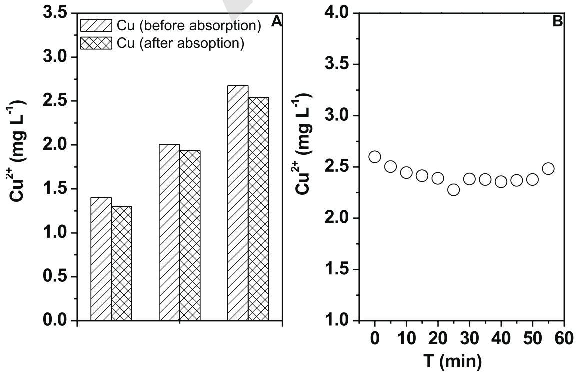

Figure 5. The adsorption of Cu^{2+} on P25 TiO_2 (A) and the change of Cu^{2+} concentration during the irradiation time (B).

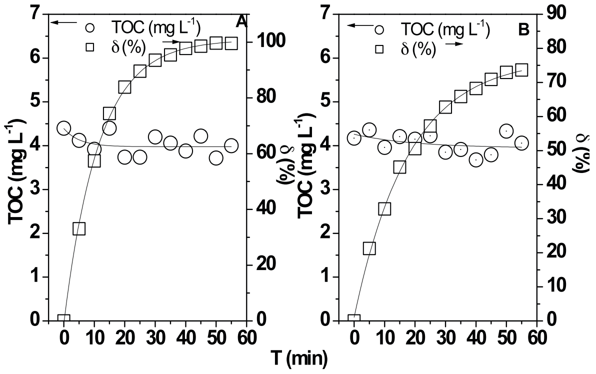

Figure 6. The change of TOC and degradation efficiency of 0.0500 mmol L^{-1} ACBK in the absence (A) and presence of 0.0300 mmol L^{-1} Cu^{2+} (B).

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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_2O_2

To investigate the role of the Cu^{2+} ions in more detail, H_2O_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_2O_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_2O_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.

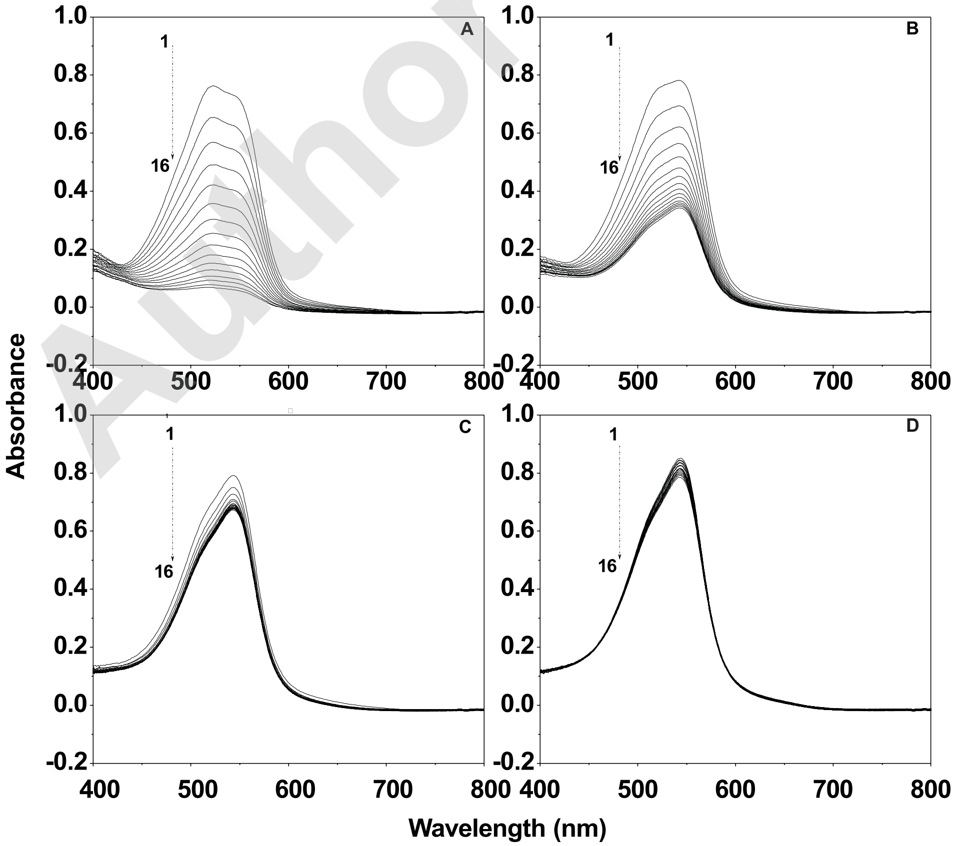

Figure 7. Spectral change of 0.050 mmol L^{-1} ACBK (A) and 0.050 mmol L^{-1} ACBK with 0.0100, 0.0200 and 0.0300 mmol L^{-1} Cu^{2+} (B, C and D) at pH 5.0 buffer solutions with H_2O_2 at different times. Spectra from 1 to 16 denote reacting times from 0 to 45 min with 3 min intervals.

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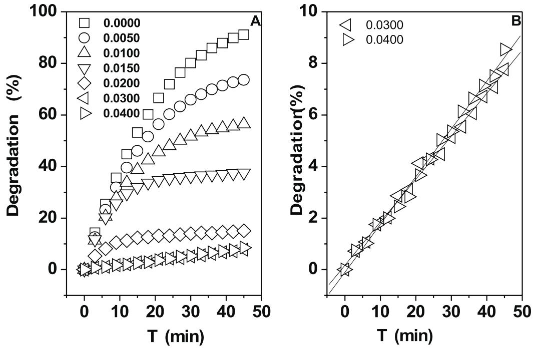

Figure 8. The degradation of 0.050 mmol L^{-1} ACBK with controlled Cu^{2+} concentrations (0.000, 0.0050, 0.0100, 0.0150, 0.0200, 0.0300 and 0.0400 mmol L^{-1}) at pH 5.0 buffer solutions with H_2O_2 at different times (A). Plots of δ vs. time with the addition of 0.0300 and 0.0400 mmol L^{-1} Cu^{2+} (B).

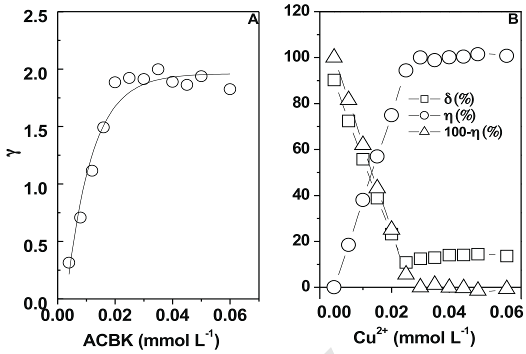

Figure 9. Variations of γ (A), η, 1-η (B) of the solutions at pH 5.0 containing 0.050 mmol L^{-1} ACBK and Cu^{2+} from 0 to 0.060 mmol L^{-1}, and variation of degradation efficiency δ (B) of ACBK in above solutions with H_2O_2.

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3.3 Interaction between ACBK and Cu^{2+}

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 Cu^{2+}. The effective fraction (η) of ACBK binding to Cu^{2+} and its binding ratio (γ) were calculated [18], as shown in Fig. 9.

As seen in Fig. 9A, γ of ACBK to Cu^{2+} remained constant (about 2) when ACBK concentration was bigger than 0.02 mmol L^{-1}. Here ACBK was enough to react with all Cu^{2+} with the formation of a new compound $Cu(ACBK)_2$. As Fig. 9B indicates, η of ACBK increased with the addition of more Cu^{2+}, indicating that more and more ACBK was bound to Cu^{2+}. When the Cu^{2+}'s concentration reached to 0.0250 mmol L^{-1}, almost all ACBK was bound to Cu^{2+} 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} Cu^{2+}, 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 Cu^{2+}, all ACBK was bound to Cu^{2+} with the formation of $Cu(ACBK)_2$. So η reached to near 100%. Nonetheless, some $Cu(ACBK)_2$ would dissociate to Cu^{2+} and free ACBK. These free ACBK was degraded immediately by the H_2O_2 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 Cu^{2+}, as the experimental results in Fig. 8B shows. With the addition of Cu^{2+}, ACBK interacted with Cu^{2+}. 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-TiO_2 and H_2O_2 process.

4. Conclusions

Cu^{2+} obviously has detrimental effects on the catalytical degradation of ACBK in UV-TiO_2 and H_2O_2 process. These inhibition effects were mainly caused by the interaction ACBK and Cu^{2+} 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-TiO_2 and H_2O_2 process, and consequently had suppressing effects on degradation of ACBK. Otherwise, the addition of Cu^{2+} also influenced the adsorption of ACBK on the surface of TiO_2, and consequently influenced the degradation of ACBK.

Acknowledgements

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