

The Effects of Copper Ions on the Catalytic Degradation of Azo Dye Acid Chrome Dark Blue

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The effect of Cu^{2+} on the catalytic degradation of Acid chrome dark blue (ACDB) in UV-TiO₂ process and Fenton process was studied. In these two processes, Cu^{2+} markedly inhibited the degradation of ACDB. These inhibition effects had an obvious relationship with the concentration of Cu^{2+} . The experimental results indicated that in pH 5.0 buffer solution, ACDB reacted with Cu^{2+} with the formation of new complex $\text{Cu}(\text{ACDB})_2$. This interaction was favorable to protect some groups in ACDB from the oxidation of reactive oxygen species generated in UV-TiO₂ process and Fenton process, and consequently had suppressing effects on degradation of ACDB.

Keywords: Copper ions, Acid chrome dark blue, Photocatalytical degradation, Fenton-process

INTRODUCTION

Numerous investigations have focused on TiO₂ photocatalysis in recent years, particularly owing to its application for the mineralization of undesirable organic contaminants to CO₂, H₂O and inorganic constituents [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. On the other hand, these 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 TiO₂-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 post transition metal ions as Cu^{2+} , Zn^{2+} , Al^{3+} and Fe^{3+} are often found in the wastewaters of textile factories [9]. They can significantly influence the photocatalytic reactions for the removal of the pollutants [10-13]. The degradation of acid red B was inhibited by the trace quantities of Mn^{2+} ; Ni^{2+} also depressed the photocatalytic 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 the catalyst [15]. Fe^{3+} inhibited the degradation of alizarin red and malachite green by altering the electron-transfer pathway involving dyes, O₂ and TiO₂ particles [10]. On the contrary, metal ions such as Fe^{2+} and Ag^+ scavenged photogenerated electrons on the catalysis surface, reduced the non-desired electron/hole recombination, resulted in an increased rate of active oxygen species, and had positive effect on pollutants' degradation

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[16,17]. Besides, some metal ions also reacted with the dyestuffs; but did this reaction have any effects on the oxidation of these dyes?

In this work, the effect of metal ion Cu^{2+} on the catalytic degradation of azo dye acid chrome dark blue (ACDB) has been investigated in aqueous TiO_2 dispersions and Fenton reagent. In pH 5.0 buffer solution, Cu^{2+} markedly depressed the catalytic degradation of ACDB in UV- TiO_2 and Fenton reagent process. The adsorption of ACDB on TiO_2 particles surface was examined in the absence and presence of Cu^{2+} . The change of Cu^{2+} concentration during the UV light irradiation was also explored to obtain more details on the effect of Cu^{2+} . Experimental results strongly suggested that Cu^{2+} interacting with ACDB protected some groups in ACDB from the oxidation of some active oxygen, and consequently had depressing effects on the catalytic degradation of ACDB.

EXPERIMENTAL

Apparatus and Reagents

A Model S4100 spectrometer (Scinco Instruments, Korea) was used to measure the spectra of ACDB with Lappro Plus Software. A Mode pH-25 acidity 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 voltage of TiO_2 . A Model TG16-WS high speed centrifuge (Changsha Xiangyi Centrifuge Instrument, Hunan, China) was used to separate P25 TiO_2 from the solutions. A 110 w middle-pressure mercury light (Shanghai Yadong Light Instrument, China) was used as UV-light source. A home-made batch reactor was used to research the photo-catalytic degradation of ACDB with P25 TiO_2 .

P25 TiO_2 powder (Degussa CO. German) was used as the catalyst without pretreatment. Stock ACDB solution (5.000 mM) was prepared by dissolving 0.6055 g ACDB (Shanghai Chemical Reagents Company, China) in 500 ml deionized water. Stock solution of Cu^{2+} (0.100 M) was prepared by dissolving $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 ml deionized water. Buffer solutions with pH 5.0 were prepared with acetic acid and sodium acetate. They were used to adjust the acidity of

solutions. 30% H_2O_2 and 200 mg l^{-1} Fe^{3+} were used as Fenton agent to oxidize ACDB. All other reagents were of laboratory reagent-grade quality and were used without further purification. Deionized water was used throughout the experiment.

Methods

Degradation of ACDB with P25 TiO_2 and UV-light. 10 ml of ACDB stock solution, 50 ml of pH 5.0 buffer solution and known volume of Cu^{2+} were added into 1000 ml flask. The solutions were diluted to 1000 ml with deionized water. 0.5 g of P25 TiO_2 was added into these solutions to form the suspensions. The suspensions were magnetically stirred in the dark for approximately 60 min prior to irradiation to permit an adsorption/desorption equilibrium to be reached. The suspensions were added into a batch reactor. At the 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 ACDB was defined as $\delta (\%) = A_0/A \times 100\%$, where A_0 was the maximal absorbance of supernatant at 0 min and A at the given time. The Cu^{2+} concentration in supernatant was analyzed with atomic absorption spectrometer. 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 were added. The suspensions were diluted to 100 ml with deionized water and were magnetically stirred for approximately 60 min. The Zeta voltage of P25 was measured with Zetasizer Nano Z instrument.

Degradation of ACDB in Fenton process. 0.1 ml of ACDB stock solution (5.0 mM), 0.5 ml of pH 5.0 buffer, known volume of Cu^{2+} (1.0 mM) and 0.05 ml Fe^{3+} (200 mg l^{-1}) was 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 was added into optical cell. Consequently, 0.100 ml of 30% H_2O_2 was added into the solution quickly. The spectra of the solutions at given time intervals (2 min) were measured against water with S4100 spectrometer. The degradation efficiency (δ) of ACDB was calculated with the same method as in the above experiment.

Interaction between Cu^{2+} and ACDB. Into a series of 10 ml calibrated flasks, 0.1 ml of ACDB stock solution (5.0 mM), 0.5 ml of pH 5.0 buffer and known volume of Cu^{2+} (1.0 mM)

were added. The solutions were diluted to 10.0 ml with deionized water and were mixed thoroughly. The solutions were measured at 541 and 569 nm against water, respectively. By means of spectra correction technique [18], the binding number (γ) of ACDB on Cu^{2+} and the effective fraction (η) of ACDB to Cu^{2+} were calculated. The solutions in the optical cell were returned completely into the flasks. Then 0.05 ml of Fe^{3+} (200 mg l^{-1}) was added into these solutions, respectively. At last, 3.0 ml of the solutions were added into other series flasks with the addition of 0.100 ml of 30% H_2O_2 . After 1 h, the absorbance of these solutions was measured against water.

RESULTS AND DISCUSSIONS

Degradation of ACDB in UV-TiO₂ Process

ACDB is a kind of azo dye. Its structure is shown in Fig. 1. It can be degraded in the presence of TiO_2 with the UV-light irradiation. The photocatalytic degradation of ACDB in TiO_2 dispersion in the presence and absence of various concentrations of Cu^{2+} are illustrated in Figs. 2 and 3.

The absorbance of ACDB always decreased exponentially with the irradiation time, as the experimental results show in Fig. 2. It indicates that ACDB could be degraded in UV-TiO₂ process. However, compared with the spectra in Figs. 2A and B, the absorbance of ACDB decreased more rapidly in the Cu^{2+} -free dispersion than in the presence of Cu^{2+} . Thus, the

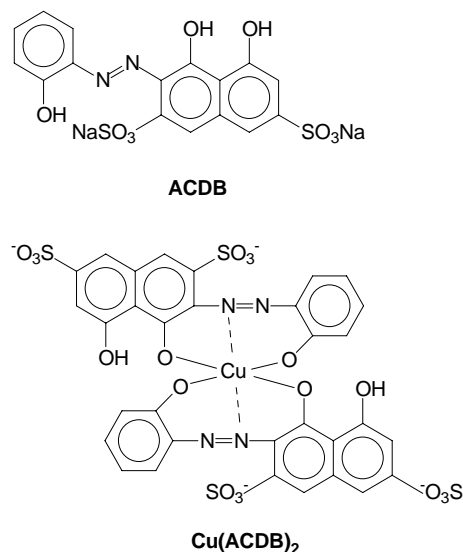


Fig. 1. The structure of ACDB and the complex ion $\text{Cu}(\text{ACDB})_2^{2-}$.

addition of Cu^{2+} suppressed the photodegradation of ACDB. This experimental result can also be found in Fig. 3 which shows that the addition of Cu^{2+} has had detrimental effects on the degradation rate of ACDB. On the other hand, this inhibition effect has an obvious relationship with the concentration of Cu^{2+} . After 40 min, almost all of ACDB were degraded in Cu^{2+} -free dispersions. But when 0.005 mM and

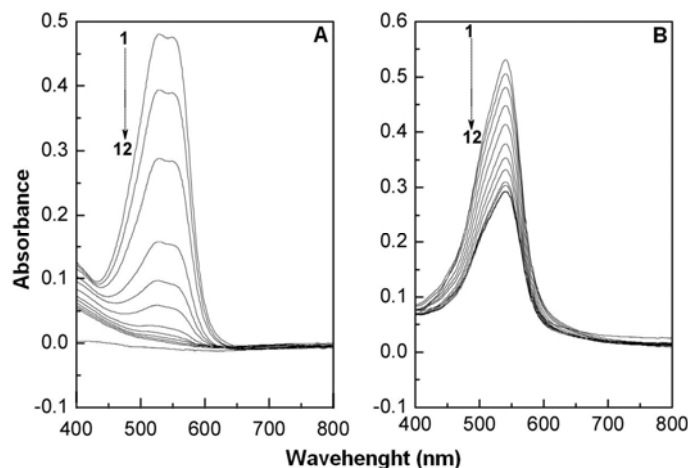


Fig. 2. Spectral change of 0.050 mM ACDB (A) and 0.050 mM ACDB with 0.020 mM Cu^{2+} (B) at pH 5.0 buffer solutions with 0.05% P25 and UV-light at given time intervals (Spectra 1 to 12 denote irradiation times from 0 to 55 min with 5 min intervals).

0.010 mM Cu^{2+} were added into dispersions, respectively, just about 70% and 50% of ACDB were degraded in this process. The depressing effect reached a maximum with the addition of 0.020 mM Cu^{2+} . With the addition of more Cu^{2+} , there were no obvious enhancements on its inhibition effects.

For the dyes' photocatalytic degradation process, at first, it was necessary for the dyes to adsorb on the surface of the catalyst [19]. From Fig. 4A, the adsorption of ACDB on TiO_2 surface was about 18%. With the addition of Cu^{2+} , the extent of adsorption didn't change significantly. When Cu^{2+} concentration changed from 0 to 0.0400 mM, the adsorption just changed from 19% to 17%. The adsorption of ACDB on TiO_2 surface was mainly through electrostatic interaction. The Zeta voltage of TiO_2 particle was very important for this adsorption. As Fig. 4B shows, with the addition of Cu^{2+} , the Zeta voltage of TiO_2 didn't change significantly. It was about 9 mV all the time. In pH 5.0 buffer solutions, 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 ACDB, while the extent of adsorption of cationic metal ions was relatively insignificant [20]. As Fig. 5A shows, the adsorption of Cu^{2+} on TiO_2 was just about 19%. This adsorption didn't change with the addition of more Cu^{2+} . In pH 5.0 buffer solution, some of the " $-\text{OH}$ ", which was on the surface of TiO_2 particles, formed " $-\text{OH}_2^+$ ". The formation of " $-\text{OH}_2^+$ " was not favorable for the covalent interaction between Cu^{2+} and " O " in " $-\text{OH}$ " [21]. In addition, during the irradiation process, there was no obvious change on the concentration of Cu^{2+} , as the experimental

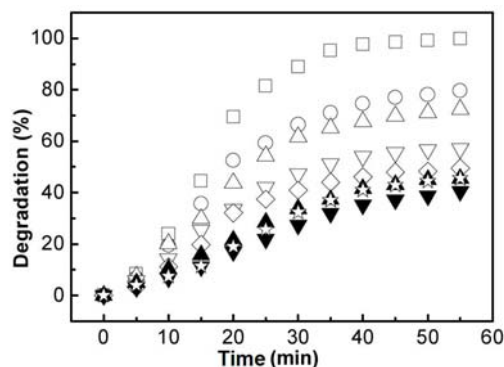


Fig. 3. The %degradation-time plots of 0.050 mM ACDB with Cu^{2+} ion at pH 5.0 buffer solution with 0.05% P25 and UV-light. Copper concentrations are: (\square) 0.0000, (\circ) 0.0025, (\triangle) 0.0050, (∇) 0.0075, (\diamond) 0.0100, (\blacktriangle) 0.0200, (\blacktriangledown) 0.0300 and (\star) 0.0400 mM.

results in Fig. 5B indicated. It is 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 is reduced [10]. In this experiment, the concentration of Cu^{2+} did not change significantly during the irradiation time. The reduction of Cu^{2+} was not significant. So the terminal effects on the photocatalytic degradation of ACDB could not be attributed to the decrease of reactive oxygen species caused by the addition of Cu^{2+} . However, by comparison of the spectra in Figs. 2A and 2B, it was found that with the addition of Cu^{2+} , the spectra

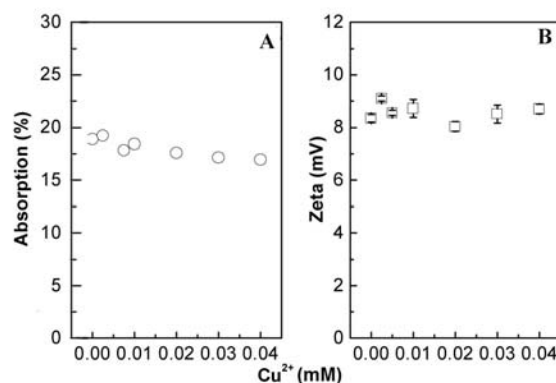


Fig. 4. The adsorption of ACDB on the surface of P25 (A) and the change of Zeta voltage of P25 (B) at different concentration of Cu^{2+} .

The Effects of Copper Ions on the Catalytic Degradation

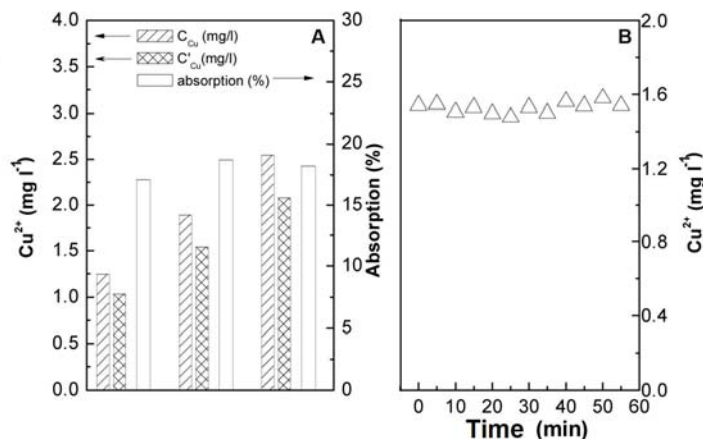


Fig. 5. The adsorption of Cu²⁺ on P25 (A) and the change of Cu²⁺ concentration during the irradiation time (B).

of ACDB changed significantly. This change indicated the interaction between ACDB and Cu²⁺. This interaction was perhaps responsible for the Cu²⁺ inhibition effects on catalytic degradation of ACDB.

Degradation of ACDB in Fenton Agent

•OH can be generated by inter-reaction of hydrogen peroxide with Fe²⁺ and Fe³⁺ [22] and it can oxidize almost all the organic substances and mineralize them to carbon dioxide and water owing to their high oxidation potential. Thus, the Fenton-treatment has attracted much interest for the destruction of dyestuffs in wastewater [23,24]. In this experiment, we also used Fenton reagent to study the effects of Cu²⁺ on the catalytic degradation of ACDB.

From the spectra in Fig. 6A and B, the ACDB's absorbance decreased obviously with variable irradiation times in the absence of Cu²⁺, or in the presence of Cu²⁺. It indicated that ACDB was degraded by the hydroxyl radicals generated in Fenton type reagent. Similar to the ACDB degradation in UV-TiO₂ process, ACDB degraded more quickly in Cu²⁺-free solutions than in the solutions with the existence of Cu²⁺, as the experimental results in Fig. 6B shows. These suppressing effects also had an obvious relationship with Cu²⁺ concentration. With the addition of more Cu²⁺, the suppressing effects became more obvious.

In the Cu²⁺-free solutions, almost 85% of ACDB was degraded after 30 min, but just 58%, 35%, 23% and 12% of ACDB were degraded when 0.005, 0.010, 0.015 and 0.025 mM Cu²⁺ were added into solutions, respectively, as the

experimental results in Fig. 7 indicated. The suppressing effects also reached to maximal when the concentration of Cu²⁺ was about 0.025 mM. In the Fenton process, there was no adsorption of ACDB on catalysis, which was investigated in UV-TiO₂ process. Just like the experimental results in UV-TiO₂ process, we also found that ACDB spectra changed obviously with the addition of Cu²⁺. Maybe the investigation of interaction between ACDB and Cu²⁺ could provide some information about the Cu²⁺'s inhibiting effects on the degradation of ACDB.

Interaction of ACDB and Cu²⁺

The spectra correction technique was a new spectral method to study the interaction of ligands and some metal ions or proteins [18,25]. In this work, it was used to study the interaction of ACDB and Cu²⁺. The effective fraction (η) of ACDB bound to Cu²⁺ and its binding ratio (γ) were calculated [18], as shown in Fig. 8.

As Fig. 8B indicates, η of ACDB binds to Cu²⁺ increased with the increasing of Cu²⁺ concentration. When the Cu²⁺ concentration reached to 0.0200 mM, almost all ACDB binds to Cu²⁺ ion and there was little free ACDB in the solutions [25]. From Fig. 8A, γ of ACDB to Cu²⁺ remained constant when Cu²⁺ concentration was less than 0.0200 mM. Therefore a new compound Cu(ACDB)₂ formed. When Cu²⁺ was over 0.0200 mM, Cu²⁺ was excessive. There was almost no free ACDB in the solutions [26]. Other interesting results that we found were that the change of 100- η (%) and that of δ (%) of ACDB had obvious corresponding relationship. With the

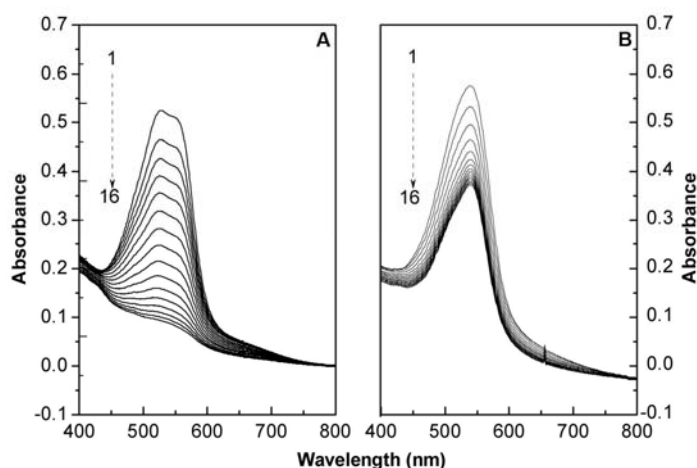


Fig. 6. Spectral change of 0.050 mM ACDB (A) and 0.050 mM ACDB with 0.010 mM Cu^{2+} (B) at pH 5.0 buffer solutions with 1% H_2O_2 and $10 \text{ mg l}^{-1} \text{Fe}^{3+}$ at different times (Spectra 1 to 16 denote irradiation times from 0 to 30 min with 2 min intervals).

addition of more Cu^{2+} , more ACDB were bound to Cu^{2+} resulting in the formation of new compounds. When the concentration of free ACDB decreased, the δ of ACDB decreased, too. When Cu^{2+} reached to 0.0200 mM, all ACDB were bound to Cu^{2+} . So η reached to nearly 100%. Consequently, the δ (%) of ACDB almost decreased to 0. When more Cu^{2+} was added, there were no free ACDB. The degradation efficiency of ACDB remained 0, too. In this process, with the addition of Cu^{2+} , ACDB interacted with Cu^{2+} . Then new compounds of $\text{Cu}(\text{ACDB})_2$ (the structure is shown in Fig. 1) formed. This formation of new compounds could protect some groups in ACDB from the oxidation of reactive oxygen species, which were generated in UV- TiO_2 and Fenton processes.

CONCLUSIONS

Cu^{2+} had a strong suppressing effect on the catalytic degradation of ACDB in UV- TiO_2 process and Fenton reagent process by interacting with ACDB and the formation of $\text{Cu}(\text{ACDB})_2$. The interaction between Cu^{2+} and ACDB protected some groups in ACDB from the oxidation of active oxygen generated in UV- TiO_2 process and Fenton reagent process. Addition of Cu^{2+} enhanced the formation of $\text{Cu}(\text{ACDB})_2$, which subsequently decreased the concentration

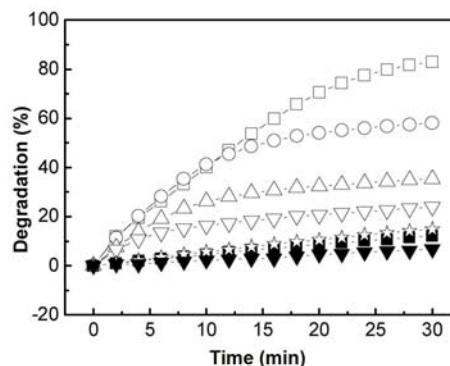


Fig. 7. The %degradation-time plots of 0.050 mM ACDB with Cu^{2+} ion at pH 5.0 buffer solutions with 1% H_2O_2 and $10 \text{ mg l}^{-1} \text{Fe}^{3+}$. Copper concentrations are: (□) 0.0000, (○) 0.0050, (△) 0.0100, (▽) 0.0150, (■) 0.0250, (☆) 0.1000 and (▼) 0.2000 mM.

of free ACDB and suppressed the catalytic degradation of ACDB. However, Cu^{2+} didn't interfere with the generation of active oxygen and the adsorption of ACDB on TiO_2 particles surface.

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The Effects of Copper Ions on the Catalytic Degradation

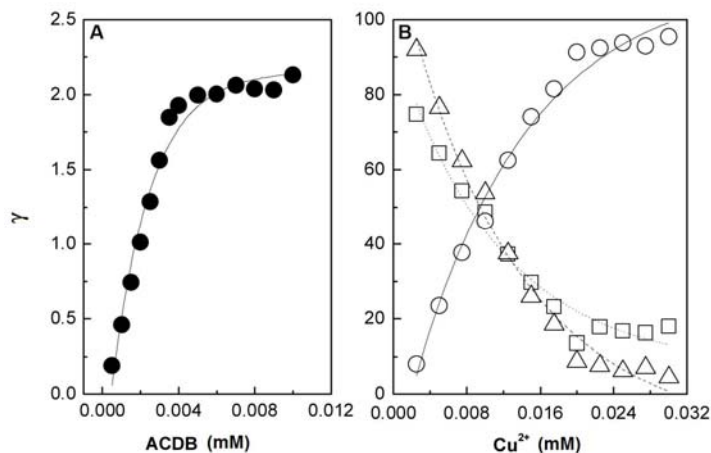


Fig. 8. Variations of γ (A), η (○: %, B, $1-\eta$ (△: %, B) of the solutions at pH 5.0 containing 0.050 mM ACDB and Cu^{2+} from 0 to 0.030 mM, and variation of degradation efficiency δ (□: %, B) of ACDB in above solutions with 1% H_2O_2 and $10 \text{ mg l}^{-1} \text{ Fe}^{3+}$ after 1 h.

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Fan *et al.*

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