



## Effects of Cu(II) and humic acid on atrazine photodegradation

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### Abstract

This work was designed to explore the characteristics of photodegradation of herbicides in the copper-polluted water body. The results showed that Cu(II) alone could induce a photo Fenton-like reaction to enhance the degradation of atrazine, in which hydroxyl radical ( $\cdot\text{OH}$ ) was a main active species. Humic acids restrained atrazine degradation, nevertheless, when introducing Cu(II), the photodegradation was accelerated, in which singlet oxygen ( $^1\text{O}_2$ ) replaced  $\cdot\text{OH}$  acting as the prevailing species. A feasible mechanism for the photochemical process was also proposed, which is helpful for better understanding the environmental photochemistry of atrazine in the copper-polluted water.

**Key words:** humic acids; Cu(II); photodegradation; hydroxyl radical; singlet oxygen

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### Introduction

Organic herbicides are largely introduced to environment due to their wide usage in agriculture, that poses great risks to human health and ecological security. Photodegradation is believed to play an important role in the environmental fate of this type of refractory contaminants (Sakellarides et al., 2003). The components of water could impact the phototransformation of organic herbicides significantly (Zhang et al., 2006).

Humic acids (HA), the most universal natural component in natural water, could be excited to triplet states ( $^3\text{HA}^*$ ) after absorbing sunlight, followed producing reactive oxygen species (ROS) and hydrated electron (Lou and Xie, 2006), which have significant effects on photochemical transformation of herbicides occurring in the environment. In addition, functional groups in HA such as  $-\text{OH}$ ,  $-\text{COOH}$  may complex with metal ions to form a HA-metal complex, which can be sensitized by illumination to form ROS and then participate in the photodegradation of organic compounds. Typically, the coexistence of Fe and HA could accelerate the photodegradation of atrazine significantly (Ou et al., 2007).

Copper is a common pollutant found in surface water with an allowable concentration up to 100  $\mu\text{g/L}$  (Roy, 1997). In the water body polluted by the wastewater from the industries like electroplating and smelting its concentration can reach a few  $\text{mg/L}$  (Santos-Echeandia et al.,

2008). It is believed that copper enables to induce a Fenton-like reaction, which enhances the degradation of organic contaminants in the aqueous phase (Ciésła et al., 2004). It is well known that the typical Fenton reaction ( $\text{Fe}^{2+} + \text{H}_2\text{O}_2$ ) takes place only at an acidic range (near pH 3) which weakens its function on natural photochemistry. Comparatively, photo Fenton-like reaction using Cu ions as the catalytic element shows acceptable activity in a wider pH range (3–8) (Masarwa et al., 1988; Yip et al., 2005). Thus, the photodegradation of organic contaminants in the presence of Cu has gained increasing attention (Liu et al., 2007).

Copper may be chelated with HA to form a copper-HA complex, which is likely to play a different role from that of copper or HA individually. Until now, the photodegradation of herbicides with the presences of HA and Cu complex is not known well. The objectives of this work were to preliminarily investigate the role of copper in the photodegradation of herbicides in the absence or presence of HA, and to explore the potential mechanism.

### 1 Materials and methods

#### 1.1 Chemicals

Atrazine (purity  $\geq 98\%$ , Sigma Aldrich Chemical Co., USA) was served as the target herbicide in present work. Its saturated vapor pressure was  $4 \times 10^{-5}$  Pa ( $20^\circ\text{C}$ ) and the solubility in water was 33  $\text{mg/L}$  ( $20^\circ\text{C}$ ). HA with a purity of 98% was purchased from MP Biomedical,

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Inc. (USA), which was composed of 49.5 wt.% carbon, 43.3 wt.% oxygen, and 5.1 wt.% hydrogen. Milli-Q water (resistivity  $\geq 18 \text{ M}\Omega\text{-cm}$ ) was used for preparation of stock solution. All stock solutions were stored at  $4^\circ\text{C}$  in the dark and used within 1 month. 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, Tokyo Chemical Industry Co., Ltd., Japan) and 2,2,6,6-tetramethyl-4-piperidone monhydrate (TEMP, USA) were used for electron spin resonance (ESR) experiment to detect hydroxyl radical ( $\cdot\text{OH}$ ) and singlet oxygen ( $^1\text{O}_2$ ), respectively.

## 1.2 Photochemical experiments and analysis

Irradiation of the solution in a cylindrical quartz tube was conducted in a climate incubator (Linpin Co., Ltd., China) equipped with a xenon lamp with a full wavelength (200–800 nm). Experiments were performed under an irradiation intensity of  $120 \text{ W/m}^2$  and temperature  $(25 \pm 3)^\circ\text{C}$ . The initial pH was adjusted to  $6.1 \pm 0.1$  by  $0.1 \text{ mol/L}$  HCl or NaOH. The solutions were always magnetically stirred during the irradiation. The light exposure experiment lasted for 60 hr and was sampled on an interval.

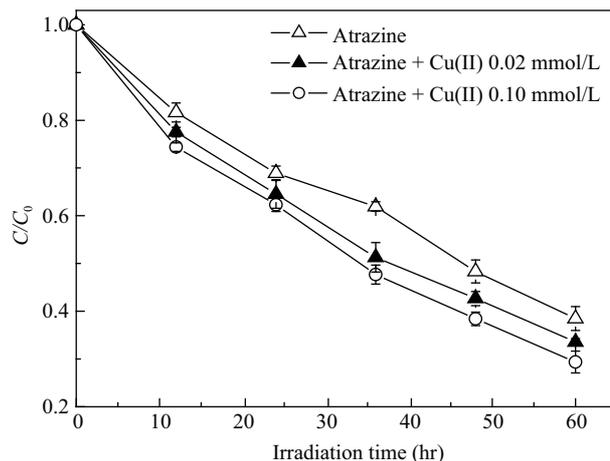
High performance liquid chromatography (Waters-2695, PDA-2996, USA) was used to determine atrazine concentration. A mixture of methanol and water (65/35, V/V) at a constant flow rate of  $1.0 \text{ mL/min}$  was used as the mobile phase and the detector wavelength was set at 220 nm. All the experiments were repeated in triplicates, and recovery rate of the analysis was  $99.3\% \pm 1.4\%$ . The fluorescence spectra were recorded with the excitation wavelength at 350 nm and the emission wavelength from 370 to 600 nm. ESR experiment was carried out using a Bruker model ESR-200 spectrometer (Germany). Our pre-experiments showed almost no degradation of atrazine at the visible range. Therefore, the degradation in the full wavelength could be considered as the results from UV irradiation. Thus, the ESR experiment was operated using an Hg lamp (100 W) as the light source which had a similar spectrum to the xenon lamp in UV range. Typical spectrometer parameters were fixed at a central magnetic field of 3350 G, scan range of 100 G, amplitude modulation of 2 G and microwave power of 20 mW.

## 2 Results and discussion

### 2.1 Effects of Cu(II) on the photodegradation of atrazine

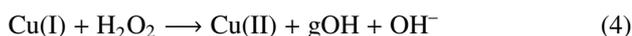
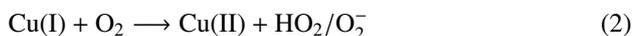
The effects of Cu(II) on the photodegradation of atrazine are illustrated in Fig. 1, which shows an enhanced degradation of atrazine with increasing concentration of Cu(II). The group in the presence Cu(II) with  $0.10 \text{ mmol/L}$  shows a higher degradation rate than that with  $0.02 \text{ mmol/L}$ . The photodegradation rate increased from 61.5% to 70.4% after 60 hr irradiation with increasing Cu(II) from 0 to  $0.10 \text{ mmol/L}$ .

It has been documented that Fenton-like reaction could be induced upon irradiation in the presence of Cu(II) (Ghiselli et al., 2004). The following reactions were



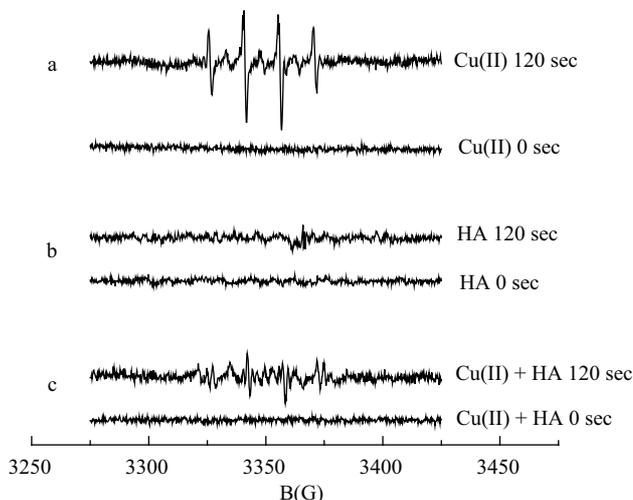
**Fig. 1** Effect of Cu(II) on the photodegradation of atrazine. Initial atrazine concentration  $5 \text{ mg/L}$ .

potential pathways:



When illuminated, Cu(II) in the solution absorbed photons and then transformed into Cu(I) (Reaction (1)). The transient Cu(I) is reoxidized to Cu(II) with concomitant formation of superoxide radical in the presence of  $\text{O}_2$  (Reaction (2)) (Sykora 1997; Konrad et al., 2005). The formed  $\text{O}_2^{\cdot-}/\text{HO}_2\cdot$  then transformed into  $\text{H}_2\text{O}_2$  by disproportionation reaction (Reaction (3)). Accordingly, the system containing Cu(I) and  $\text{H}_2\text{O}_2$  is able to perform a Fenton-like reaction (Sykora, 1997; Konrad et al., 2005) to generate  $\cdot\text{OH}$  (Reaction (4)).

To understand whether  $\cdot\text{OH}$  was generated in the solution of Cu(II), ESR DMPO trapping technique was used. The ESR spectrum of the DMPO- $\cdot\text{OH}$  spin adduct in the presence of Cu(II) is shown in Fig. 2a. No signal could be detected in the dark in Cu(II) and DMPO solution, whereas



**Fig. 2** ESR signals of  $\cdot\text{OH}$  in the solution under irradiation. (a) Cu(II) ( $0.1 \text{ mmol/L}$ ) alone; (b) HA ( $10 \text{ mg/L}$ ); (c) Cu(II) ( $0.1 \text{ mmol/L}$ ) + HA ( $10 \text{ mg/L}$ ). The signals were recorded at 0 and 120 sec irradiation, DMPO  $40 \text{ mmol/L}$ . 0 sec: in the dark, 120 sec: under irradiation of 120 sec.

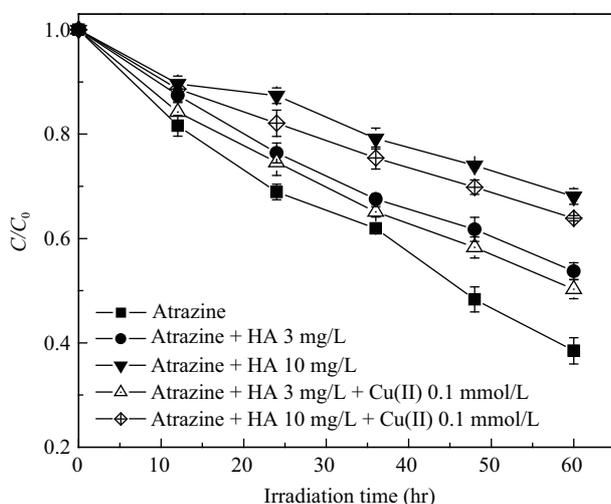
remarkably characteristic signals for DMPO- $\cdot$ OH adduct were observed under the illumination. The ESR results confirm that  $\cdot$ OH was generated in the presence of Cu(II) under the illumination, which could explain the enhanced photodegradation of atrazine.

## 2.2 Effects of Cu(II) and humic acid (HA) on the photodegradation of atrazine

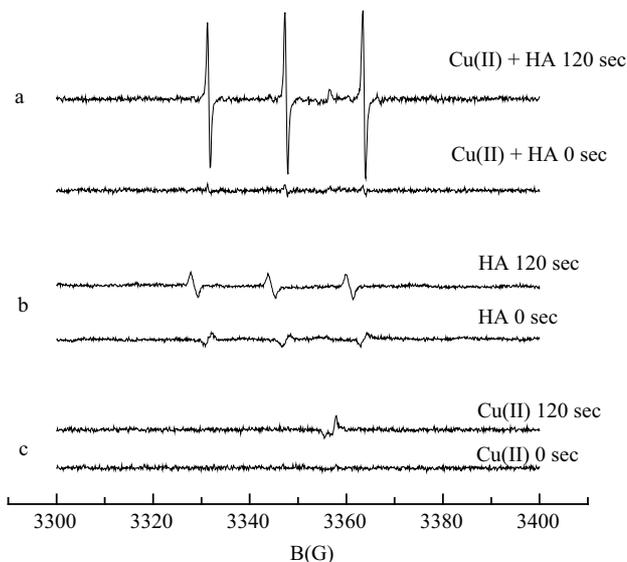
To understand the Cu(II) effect in the presence of HA, the effect of HA alone on the photodegradation of atrazine was investigated. Different concentrations of HA (0, 3 and 10 mg/L) were added into atrazine solutions respectively, and the results are shown in Fig. 3. It was observed that the photodegradation were restrained with the addition of HA. HA is well-known light absorbing substance, and it was inevitable that HA competed with atrazine for the available photons (Ou et al., 2009). Therefore, with increasing HA concentration, the photons consumed by HA increased, causing that the photodegradation was retarded. On the other hand, it is assumed that atrazine might be bound to the HA, which could also restrain the photolysis. Hua et al. (2000) reported that aromatic reticular formation of HA adsorbed herbicide, which led to the herbicide poorly absorbing light. Meantime, ESR spectra of HA under the irradiation (Fig. 2b) had not signals of  $\cdot$ OH, indicating that  $\cdot$ OH was not the major ROS in the HA solution.

The effect of coexisting HA with Cu(II) on the photodegradation is also shown in Fig. 3. When Cu (0.1 mmol/L) was added into the solution containing HA of 3 mg/L, the photodegradation of atrazine gently increased from 46.1% to 50% after 60 hr irradiation. Similar promoting effect of Cu(II) was observed in the solution containing HA of 10 mg/L. In comparison, the degradation rate increase to 70.4% in the group of Cu alone (Fig. 1).

The ESR spectra in Fig. 2c show that there was no significant signal of  $\cdot$ OH in the coexistence of HA and Cu. Therefore, it was likely that other active species was generated and functioned in the photodegradation according to the promoting effect of Cu with the presence of HA. Considering that singlet oxygen ( $^1\text{O}_2$ ) is another



**Fig. 3** Effect of Cu(II) on the photodegradation of atrazine in the presence of HA. Initial atrazine concentration: 5 mg/L; HA: humic acid.



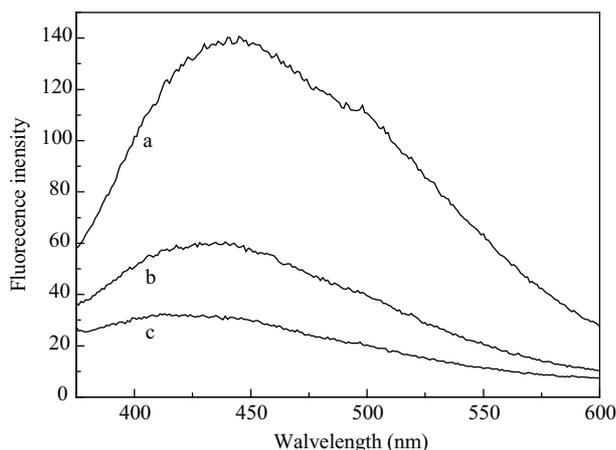
**Fig. 4** ESR signals of  $^1\text{O}_2$  in the solutions under irradiation. a: Cu(II) (0.1 mmol/L) + HA (10 mg/L); b: HA (10 mg/L); c: Cu(II) (0.1 mmol/L). The signals were recorded at 0 sec and 120 sec irradiation, respectively, TEMP: 40 mmol/L.

important ROS in the photodegradation (Ou, 2007), we tried to detect  $^1\text{O}_2$  in the solution using ESR measurement and the results are shown in Fig. 4. A strong triplet ESR signal of  $^1\text{O}_2$  could be observed in the coexistence of Cu(II) and HA under the illumination (Fig. 4a), suggesting that  $^1\text{O}_2$  was a main radical species in the group of HA and copper. While in the presence of HA alone, the  $^1\text{O}_2$  signal was much lower (Fig. 4b). It suggested that the positive effect of  $^1\text{O}_2$  on the degradation was limited, which could not overcome the inhibition of HA itself resulting from competition of photon with the target contaminants or bonding with the contaminants. Additionally, Cu alone could not produce  $^1\text{O}_2$  (Fig. 4c), but it could enhance  $^1\text{O}_2$  signals as coexisting with HA, indicating that Cu intensified the photo-sensitization of HA which led to an increase in the photodegradation.

Together with unobvious  $\cdot$ OH signal in the coexistence of HA and Cu(II) (Fig. 2c), the spectrum in Fig. 4a also suggested that Cu(II)-HA complex was in favor of producing  $^1\text{O}_2$  rather than  $\cdot$ OH under the irradiation. The oxidation potential of  $^1\text{O}_2$  ( $E = 2.2$  V) is lower than that of  $\cdot$ OH ( $E = 2.8$  V), which was likely to be one of reasons for the lower photodegradation rate in the coexistence than that in the Cu alone. Another possible reason for the lower degradation in the presence of HA was that the binding of Cu with HA decreased the amount of free  $\text{Cu}^{2+}$ , which could be confirmed by HA fluorescence spectrum (Fig. 5). The characteristic peak at 445 nm was attributed to absorption of  $\cdot$ OH,  $\cdot$ COOH of HA. When Cu(II) was added in, the fluorescence was significantly quenched, suggesting the formation of Cu(II)-HA complex.

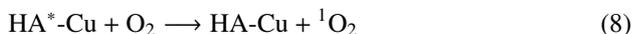
## 2.3 Proposed photodegradation scheme

From the above results, Cu could enhance the photodegradation of atrazine in water.  $\cdot$ OH and  $^1\text{O}_2$  played different roles in the degradation. From Reactions (1)–(4), without HA, Cu induced a photo Fenton-like reaction to

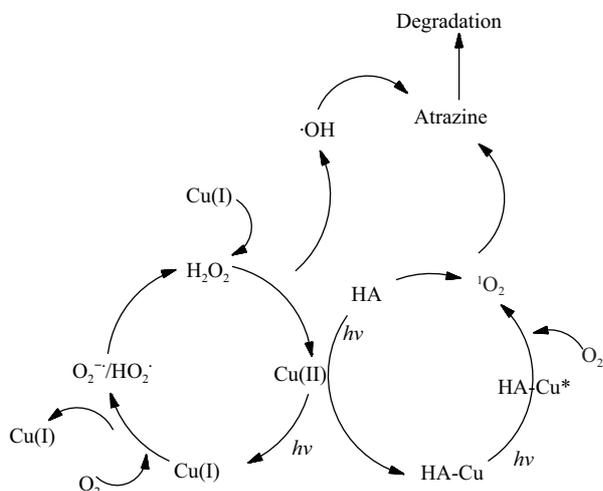


**Fig. 5** Fluorescence quenching spectrum of HA provoked by Cu(II). line a: HA 3 mg/L; line b: HA 3 mg/L + 0.02 mol/L Cu(II); line c: HA 3 mg/L + 0.1 mmol/L Cu(II).

enhance the degradation, in which  $\cdot\text{OH}$  was the main ROS. On the other hand, in the coexistence of Cu and HA,  $^1\text{O}_2$  instead of  $\cdot\text{OH}$  became the predominant active species. HA is likely indispensable for the formation of  $^1\text{O}_2$ . Based on the above discussion, the photochemical reactions in the presence of HA could be proposed as the following Reactions (5)–(8), and a scheme for the Cu(II) cycling and main reactions in Cu-HA systems is proposed in Fig. 6.



As is well known, HA could be excited by photo to form  $\text{HA}^*$  (Reaction (5)), which could react with  $\text{O}_2$  to produce  $^1\text{O}_2$  (Reaction (6)) (Zepp et al., 1987), but its signals were too weak (Fig. 5b). Therefore, the positive effect of HA could not compensate the inhibition of HA on the degradation, and consequently HA addition led to a decline of photodegradation. Alternatively, when adding Cu(II), HA-Cu complex formed might be excited to  $\text{HA}^*-\text{Cu}$  by photon (Reaction (7)), then  $^1\text{O}_2$  was produced (Reaction



**Fig. 6** Scheme for the Cu(II) cycling and main reactions in HA-Cu systems.

(8)), which played a major role in the photolysis of atrazine in the coexistence of Cu and HA.

### 3 Conclusions

The photodegradation of atrazine in the presence of Cu were investigated in the present work. The results suggest that Cu could enhance the photodegradation of atrazine. Cu alone promoted the photodegradation by induced  $\cdot\text{OH}$  generation from the Fenton-like reaction, while in the presence of HA, Cu-HA complex also enhanced the degradation by production of  $^1\text{O}_2$ . The results implied that atrazine was inclined to be degraded more quickly in the water polluted by copper. Different radical species mechanisms in the processes could help to understand the environmental photochemistry in the copper-polluted water.

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