

Removal of Chelated Copper by TiO₂ Photocatalysis: Synergetic Mechanism Between Cu (II) and Organic Ligands

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ABSTRACT: UV/TiO₂ photocatalysis of chelated copper in aqueous solutions has been performed starting from Cu(II)-tartaric acid, Cu(II)-citric acid, Cu(II)-EDTA and Cu(II)-DTPA, in the presence of oxygen and at acidic pH. The photocatalytic reaction obeys first-order kinetic equation. The influence of Cu(II) on photocatalytic oxidation of organic ligands and how the various organics will affect the treatment of Cu(II) were described. A significant synergistic effect was observed between the reduction of Cu(II) and oxidation of organic ligands. The results prove that TiO₂ photocatalysis is an effective approach for removing chelated copper from wastewater.

KEY WORDS: TiO₂ photocatalysis, chelated copper, Organic ligands, Synergistic mechanism.

INTRODUCTION

Recently, it has been demonstrated that photocatalysis is a promising technology applicable for the treatment of pollutants. Electron-hole pairs will be consistently generated from semiconducting TiO₂ under irradiation. When electron-hole pairs are trapped by the contaminant (e.g., organic pollutants and/or metal ions) on surface, redox reactions will be initiated[1]. Thus, photocatalysis process involves photocatalytic oxidation of organic pollutants and reduction of metal ions.

It is well known that TiO₂ photocatalysis is effective for removing dissolved transition metal ions from an aqueous solution[1], such as Tl(I) [2], Mn(II) [3,4],

Cr(VI) [5], Hg(II) [6,7], Pb(II) [8,9], Cd(II) [10,11], Cu(II) [9,12,13], Ni(II) [9,14], Zn(II) [9,11] and so on.

TiO₂ photocatalysis has also been successfully applied to remove organic pollutants. Basic and applied researches on this subject have been performed extensively all over the world. Photocatalyst can mineralise a large range of organic pollutants including some of the most refractory ones (e.g., pesticides, herbicides, dyes, surfactants and electroplating additives) [15]. Over the last decades, there have been considerable research works on photocatalytic degradation of organic pollutants, such as chlorinated aliphatic hydrocarbons[16],

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sucrose[17], salicylic acid[18], phenol[19], nitrobenzene[20], EDTA [21], azo dyes [22] and so on.

EthyleneDiamineTetraacetic Acid (EDTA), Citric acid (Cit), Tartaric acid (Tart) and Diethylene Thiamine Pentacetate Acid (DTPA) have been widely employed in electroplating copper process[23]. Chelating agents and Cu(II) ions will form chelated copper complexes. Consequently, the speciation, transformation, cycling, transport of Cu(II) and organic ligands will be affected in the environment. Photocatalytic degradation of chelated copper is quite different from that of Cu(II)-alone and organic ligand-alone. Therefore, it should be paid more attention to investigating the photocatalytic degradation of chelated copper. However, to the best of our knowledge, this area has not been reported in relevant literatures.

EXPERIMENTAL SECTION

Materials

Distilled water was utilized to prepare the simulated wastewater. All experiments were carried out under the following conditions:

solution volume, 500 mL

initial Cu (NO₃)₂ concentration [23], 7.5×10⁻⁴ mol/L

initial pH, 3.0 ± 0.2 (either HNO₃ or NaOH was used to adjust the suspension to desired pH)

temperature, fixed at 26 ± 0.5 °C

TiO₂ concentration, 2.0 g/L

Aqueous solutions of Cu(II) were complexed 1:1 molar with EDTA, citric acid, tartaric acid and DTPA. The suspensions were held in the dark for more than 12 hours before UV-irradiation. Cu (NO₃)₂ and chelating reagents were of guaranteed-reagent grade, the others were of analytical-reagent grade. All reagents were supplied by Aladdin Reagent (China) Co., Ltd. and used without further purification.

TiO₂ nanoparticles (Degussa P-25, mainly anatase, surface area: ca. 50 m²/g, particle size: ca. 21 nm) were oven dried at 105 °C for 2 h before use.

Photoreactor and procedure

All experiments were conducted with a photoreactor equipment which has been described elsewhere[24]. The UV light source was a high-pressure Hg straight lamp of 300 W, with dominant wavelength 365 nm. A 500 mL three-necked flask was utilized as reaction container.

The three necks were employed as sampling, temperature monitoring and aerating ports, respectively. To keep TiO₂ in suspension, the suspensions were aerated at a flow rate of 300 mL/min. A magnetic stirrer at high rotating speed was also used to conserve the suspension in vessel. The average light intensity in solutions was about 8 MW/cm².

In order to ensure establishment of adsorption/desorption equilibrium, the suspensions were held in the dark for 30 minutes prior to UV irradiation. Time was measured from the moment at which the lamps were turned on. At regular time intervals, 7 mL of the solutions were withdrawn through the sampling port. The samples were centrifuged at 8000 r/min for 20 min to separate the solids and the supernatant. TiO₂ particles were filtered out, supernatant was collected and analysed for determining copper and organic ligands concentrations. After 60 min irradiation, the final pH values of samples were determined.

All samples were filtered through a 0.22 μm MSI Filter Membrane (Teflon) before analysis. Cu(II) concentration was analyzed using HITACHI Z-2000 Polarized Zeeman Atomic Absorption Spectrophotometer (GB/T 7475-1987). The concentrations of citric acid and tartaric acid (GB/T 5009.157-2003), EDTA and DTPA (GB/T 23323-2009) were analyzed using a Shimadzu LC-20A High-performance Liquid Chromatograph. The chromatogram for the ligands and the condition of chromatography refer to annex A. An alcohol thermometer and a pH meter (PHS-3C) were used to determine temperature and pH, respectively.

Preliminary studies

Percentage contents of various species in complex systems

The values of stability constants for the four copper complexes and corresponding proton binding constants of the ligands were summarized (Table 1)[25]. The stability constants are logarithms. The magnitude of the stability constant quantitatively expresses the stability of the complex.

The total concentration of Cu(II) in solution can be expressed as Eq. (1):

$$c_M = [M] \sum_{i=0}^N \beta_i [L]^i \quad (1)$$

The total concentration of ligand in solution can be expressed as Eq. (2):

$$c_L = [L] + [M] \sum_{i=1}^N i \beta_i [L]^i \quad (2)$$

Table 1: Stability constants of the copper complexes and proton binding constants of ligands

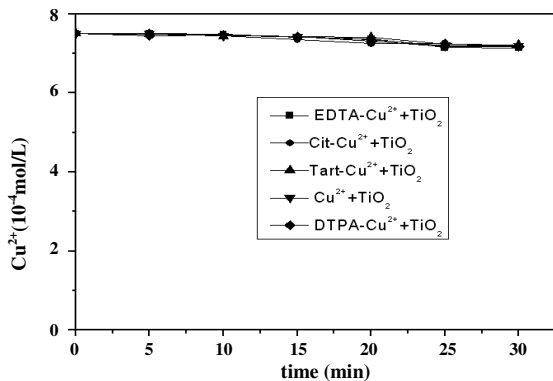
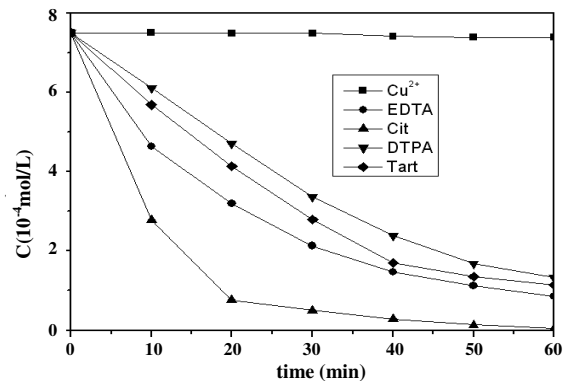
| Ligand | Stability Constants | Proton Binding Constants |
|----------|--|--|
| EDTA | CuL=18.8, CuHL=21.8, Cu(OH)L=21.2 | HL=10.34, H ₂ L=16.58, H ₃ L=19.33, H ₄ L=21.40, H ₅ L=23.0, H ₆ L=23.9 |
| Citrate | CuL=18.0, CuHL=22.3, CuH ₂ L=28.3 | HL=16, H ₂ L=22.1, H ₃ L=26.5, H ₄ L=29.5 |
| Tartaric | CuL=3.2, CuL ₂ =5.1, CuL ₂ =5.8, CuL ₄ =6.2 | HL=4.1, H ₂ L=7.0 |
| DTPA | CuL=20.5, CuHL=24.5, Cu ₂ L=26.0 | HL=10.56, H ₂ L=19.25, H ₃ L=23.62, H ₄ L=26.49, H ₅ L=28.43 |

Table 2: Percentage contents of various Cu species

| Species | Cu(OH) ₂ (aq) | Cu ²⁺ | CuL | CuHL | CuH ₂ L | Cu(OH)L |
|-----------------------|--------------------------|------------------|-------|-------|--------------------|---------|
| Cu ²⁺ | | 100 | | | | |
| EDTA-Cu ²⁺ | | | 49.87 | 49.87 | | |
| Cit-Cu ²⁺ | | 18.71 | | | 81.21 | |
| DTPA-Cu ²⁺ | | 1.7 | 8.94 | 89.36 | | |
| Tart-Cu ²⁺ | | 95.40 | 4.59 | | | |

Table 3: Suspension pH variations before/after experiments

| Sample | Cu ²⁺ | EDTA-Cu ²⁺ | DTPA-Cu ²⁺ | Tart-Cu ²⁺ | Cit-Cu ²⁺ |
|-------------------|------------------|-----------------------|-----------------------|-----------------------|----------------------|
| Before experiment | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| After experiment | 2.73 | 6.89 | 5 | 4.44 | 3.63 |

**Fig. 1: Dark adsorption of the Cu²⁺-alone, EDTA-Cu²⁺, Cit-Cu²⁺, Tart-Cu²⁺ and DTPA-Cu²⁺ (initial concentrations: 7.5×10⁻⁴ mol/L, molar ratio of Cu²⁺/organic ligands: 1/1)****Fig. 2: Photolysis of Cu²⁺-alone and organic ligand-alone (initial concentrations: 7.5×10⁻⁴ mol/L)**

The percentage contents of various species can be calculated through Eq. (3):

$$\phi_i = \frac{[ML_i]}{C_M} = \frac{\beta_i [L]^i}{1 + \sum_{i=1}^N \beta_i [L]^i} \quad (3)$$

Where c_M is the total concentration of metal ions in mol/L, $[M]$ is the concentration of free copper ion in mol/L, β_i is the total stability constant, N is maximum coordination number, $[L]$ is the concentration of free ligand in mol/L, c_L is the total concentration of ligand in mol/L.

By substitution of $c_M = 7.5 \times 10^{-4}$ mol/L, $c_L = 7.5 \times 10^{-4}$ mol/L, $[H^+] = 10^{-3}$ and all the data in Table 1 into Eqs. (1), (2) and (3), respective, major Cu(II) species distribution can be calculated (Table 2). The complexes with percentage of total components less than or equal to 1% were neglected.

Model calculations indicate that free copper ion, CuL/CuHL, CuH₂L, CuHL are the predominant Cu(II) species in Cu(II)-Tart, Cu(II)-EDTA, Cu(II)-Cit, Cu(II)-DTPA systems, respectively.

Results process and presentation

The kinetics of photocatalytic degradation of compounds usually follows the Langmuir – Hinshelwood scheme [26,27]: Eq. (4):

$$r = -\frac{d_c}{d_t} = \frac{kKc}{1+Kc} \quad (4)$$

where K is apparent adsorption equilibrium constant, k is the first-order kinetic constant and used to characterize the photocatalytic rate, t is the illumination time.

In order to calculate the rate at any time, it is assumed that the photocatalysis follows the first-order kinetic model as Eq. (5). The assumption is reasonable, because the concentration of the reactant is comparatively low [26,27]. The kinetics was monitored by measuring copper or organic ligand concentration at various times. Eq. (5):

$$\ln(C_0/C_t) = kt \quad (5)$$

Where C_t is the concentration of copper or organic ligand at a certain interval of time in mol/L; C_0 is the initial concentration of copper or organic ligand in mol/L.

Photolysis and dark adsorption experiments

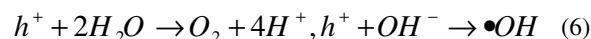
Photolysis and dark adsorption experiments were also performed. Dark adsorption experiments were carried out in order to examine the adsorption of copper on TiO₂ powder without illumination. Photolysis experiments of copper and organic ligands were conducted by illumination in absence of TiO₂. Dark adsorption results of the Cu(II) in Cu(II)-alone and copper complex system, photolysis results of the Cu(II)-alone and organic ligand-alone were depicted (Figs. 1 and 2). From Fig. 2, it is obvious that no measurable variations of the copper concentrations can be observed. The results indicate the complete absence of photoreaction. The degradation of organic ligands to a certain extent

was found in organic ligand-alone systems (Fig. 2). The experimental results presented here show that organic ligands undergo a photolytic/photocatalytic oxidation reaction, while copper undergoes a photocatalytic reduction.

Results and Discussion

Variations of the suspension pH

The pH values of suspensions were summarized (Table 3) after experiments. The pH decreased in Cu(II)-alone system. Such a phenomenon can be explained by the fact that water and OH⁻ would be oxidized by holes, which can be generated from photocatalytic reduction of Cu(II) on TiO₂ surface. Moreover, hydration reaction will occur if Cu(II) is in solution. As a result, the system's acidity may be further increased, although the hydration of Cu(II) is not the main contribution. Eq. (6):



On the contrary, the pH increased in the presence of organic acids after experiments. The increase of pH may be attributed to hydrogen generation by the following reaction: Eq. (7):



The hydrogen ions are mainly generated from the ionization of organic acid. Such a reaction may possibly occur competitively with the reduction reaction of Cu(II). In this case, Cu(II) declines more quickly [28]. Moreover, in the presence of organic acids, the photogenerated holes are consumed through Eq. (8):



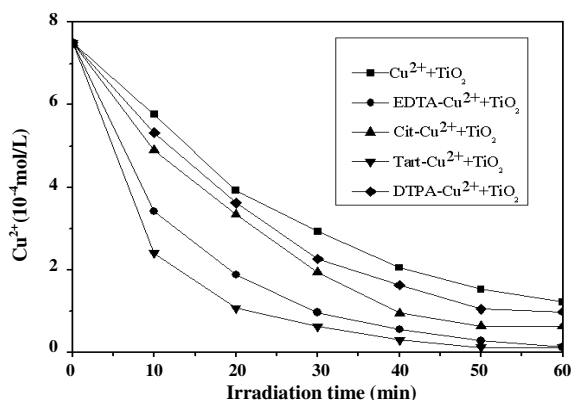
As a consequence, the ionization of organic acid will be accelerated. While both the hydrogen ion and acid radical will be consumed through the reactions above (Eqs.(7) and (8)). Thus, both Eqs.(7) and (8) make contribution to the pH increases. The solution pH increased in the complex systems, while the increase of pH facilitated the removal of Cu(II). Nevertheless, the pH decreased in Cu(II)-alone system, while the removal of Cu(II) would be hindered.

Influence of organic ligands on photocatalytic reduction of Cu(II)

The reduction of Cu(II) concentration was described as a function of irradiation time in control experiment (Cu(II)-alone) and complex systems (Fig. 3). Reaction rate

Table 4: Kinetic results of Cu-photocatalytic reduction

| Sample | Cu ²⁺ | EDTA-Cu ²⁺ | Cit-Cu ²⁺ | Tart-Cu ²⁺ | DTPA-Cu ²⁺ |
|-------------------------------------|------------------|-----------------------|----------------------|-----------------------|-----------------------|
| k ^a (min ⁻¹) | 0.0339 | 0.0883 | 0.0466 | 0.1049 | 0.0379 |
| RSQ ^b | 0.9933 | 0.9622 | 0.9483 | 0.9659 | 0.9698 |

^a First order rate constant obtained using Ep.(4);^b RSQ= R-squared.**Fig. 3: Cu-photocatalytic reduction in Cu²⁺-alone and complex systems (initial Cu²⁺ concentrations: 7.5×10⁻⁴ mol/L, molar ratio of Cu²⁺ / organic ligands:1/1)**

constant can be calculated according to Cu(II) concentration at various times. The results (Table 4) indicate that the decreasing order of Cu(II) reaction rate in complex systems is Eq. (9):

$$r_{\text{Cu(II)-Tart}} > r_{\text{Cu(II)-EDTA}} > r_{\text{Cu(II)-Cit}} > r_{\text{Cu(II)-DTPA}} \quad (9)$$

Where $r_{\text{Cu(II)-Tart}}$, $r_{\text{Cu(II)-EDTA}}$, $r_{\text{Cu(II)-Cit}}$, $r_{\text{Cu(II)-DTPA}}$ are Cu(II) reaction rate in Cu(II)-Tart, Cu(II)-EDTA, Cu(II)-Cit, Cu(II)-DTPA systems, respectively.

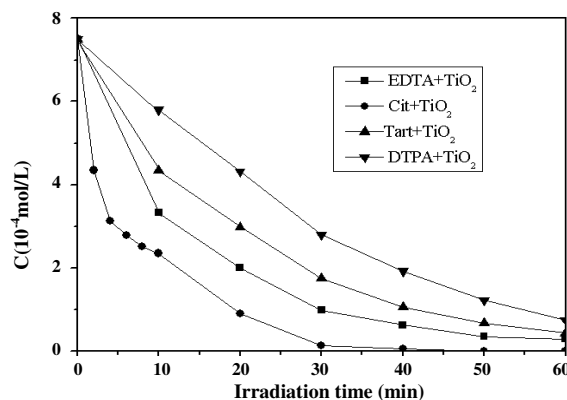
The accelerating effect of organic ligands on the rate of Cu(II) reduction can be expressed as: Eq. (10):

$$\frac{r_{\text{Cu(II)-EDTA}}}{r_{\text{Cu(II)}}} = 2.60, \quad \frac{r_{\text{Cu(II)-Cit}}}{r_{\text{Cu(II)}}} = 1.37, \\ \frac{r_{\text{Cu(II)-Tart}}}{r_{\text{Cu(II)}}} = 3.09, \quad \frac{r_{\text{Cu(II)-DTPA}}}{r_{\text{Cu(II)}}} = 1.12 \quad (10)$$

In contrast with control experiment (Cu(II)-alone), EDTA, citric acid, tartaric acid and DTPA enhanced Cu(II) reduction rate by 2.60, 1.37, 3.09 and 1.12 times, respectively. The results imply that photocatalytic oxidation of organic ligands can catalyze the removal of Cu(II). It is explained by the fact that if no organics are

Table 5: Kinetic results of the organic ligand-alone photocatalysis by TiO₂

| Sample | EDTA | citric acid | tartaric acid | DTPA |
|-------------------------------------|--------|-------------|---------------|--------|
| k ^a (min ⁻¹) | 0.0882 | 0.1083 | 0.0527 | 0.0219 |
| RSQ ^b | 0.9819 | 0.9791 | 0.9931 | 0.9949 |

^a First order rate constant obtained using Ep.(4);^b RSQ= R-squared.**Fig. 4: Organic ligand-alone photocatalytic oxidation by TiO₂ (initial ligands concentrations: 7.5×10⁻⁴ mol/L)**

present, water will be oxidized by Eq. (6). However, the ionization of water is too low to facilitate the consumption of holes in system. As a consequence, photocatalytic reduction of Cu(II) may be limited by the low rate of water oxidation. In the presence of organic ligands, the holes are consumed through Eq. (8). The electrons will be mainly consumed by Cu(II). Therefore, the recombination of electrons and holes will be inhibited. Ultimately, Cu(II) reaction rate can be enhanced remarkably (Eq. (10)). In addition, as discussed above, the increased pH will also facilitate the removal of Cu(II).

However, it is quite different in the accelerating effects of different organic ligands on the rate of Cu(II) reduction. Tartaric acid was more susceptible to promote the photocatalytic reduction of Cu(II). It may be attributed to the fact that Cu(II)-Tart is less stable than the other complexes and free tartaric acid is the major form in Cu(II)-Tart system. While chelated ligands are the major forms in other complex systems (Table 2). As discussed above, it is obvious that free ligands will consume more holes than complexes. Consequently, the employment of tartaric acid is a more feasible strategy for photocatalysis in complex system. Finally, the reaction will catalyze the removal of Cu(II) (see Eq. (10)).

There were more free organic ligands in Cu(II)-Cit system than in Cu(II)-EDTA system (Table 2). Therefore, citric acid seems to enhance the Cu(II) reduction rate compared with EDTA. However, the results show that it is not the case (Eq. (10)). The phenomenon can be explained by the fact that the major species CuL and CuHL in Cu(II)-EDTA system are less stable than CuH₂L in Cu(II)-Cit system (Tables 1 and 2). Moreover, the solution pH increased considerably higher in Cu(II)-EDTA system than in Cu(II)-Cit system (Table 3). The higher pH is, the more OH⁻ there will be. Apparently, OH⁻ is beneficial for the removal of Cu(II).

Compared with Cu(II)-DTPA system, it was not only photocatalytic oxidation rate of the organic ligands was more favorable, but also the number of free organic ligands was greater in Cu(II)-Cit system. Even though the major species CuH₂L is more stable (Tables 1 and 2) and the solution pH increased a bit lower in Cu(II)-Cit system (Table 3), the enhancement of citric acid on Cu(II) reduction rate is slightly higher than that of DTPA (Eq. (10)).

The phenomena indicate that the stability constant is a major factor controlling the accelerating effect of organic ligands on the rate of Cu(II) reduction, but not the only one. The rate is also related to the photocatalytic oxidation rate of organic ligands and the solution pH.

Influence of Cu(II) on photocatalytic oxidation of organic ligands

Concentrations of EDTA, citric acid, tartaric acid and DTPA in absence of Cu(II) were depicted here as a function of irradiation times (Fig. 4). The kinetic results are also presented (Table 5). The decreasing order of organic ligand reaction rate is Eq. (11):

$$r_{\text{Cit}} > r_{\text{EDTA}} > r_{\text{Tart}} > r_{\text{DTPA}} \quad (11)$$

Where r_{Cit} , r_{EDTA} , r_{Tart} , r_{DTPA} are organic ligand reaction rate in respective ligand-alone systems.

Similarly, concentrations of EDTA, citric acid, tartaric acid and DTPA oxidation were also depicted as a function of irradiation times in complex systems. The oxidation rate of organic ligands (Table 6) indicate that the decreasing order of organic ligand reaction rate in complex systems is Eq. (12):

$$r'_{\text{Cu(II)-Cit}} > r'_{\text{Cu(II)-Tart}} > r'_{\text{Cu(II)-EDTA}} > r'_{\text{Cu(II)-DTPA}} \quad (12)$$

Table 6: Kinetic results of organic ligands photocatalytic oxidation in complex systems

| Sample | EDTA-Cu ²⁺ | Cit-Cu ²⁺ | Tart-Cu ²⁺ | DTPA-Cu ²⁺ |
|-------------------------------------|-----------------------|----------------------|-----------------------|-----------------------|
| k ^a (min ⁻¹) | 0.1915 | 0.2403 | 0.2122 | 0.0798 |
| RSQ ^b | 0.9502 | 0.9219 | 0.9850 | 0.9975 |

^a First order rate constant obtained using Ep.(4);

^b RSQ= R-squared

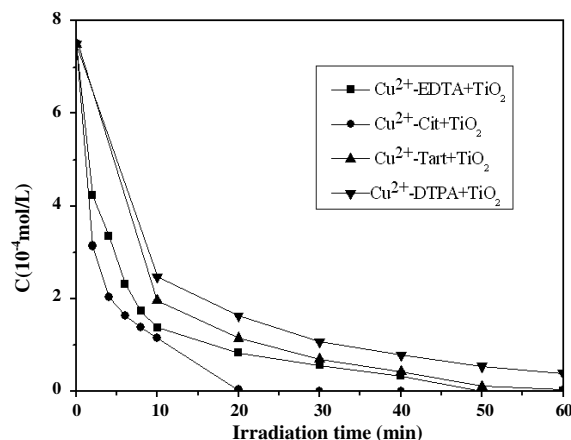


Fig. 5: Photocatalytic oxidation of organic ligands in complex systems by TiO₂ (initial organic ligands concentrations: 7.5×10⁻⁴ mol/L, molar ratio of Cu²⁺/organic ligands: 1/1)

Where $r'_{\text{Cu(II)-Cit}}$, $r'_{\text{Cu(II)-Tart}}$, $r'_{\text{Cu(II)-EDTA}}$, $r'_{\text{Cu(II)-DTPA}}$ are organic ligand reaction rate in Cu(II)-Cit, Cu(II)-Tart, Cu(II)-EDTA, Cu(II)-DTPA systems, respectively.

The accelerating effect of Cu(II) on the rate of organic ligand oxidation can be expressed as: Eq. (13):

$$\frac{r_{\text{Cu(II)-EDTA}}}{r_{\text{EDTA}}} = 2.17, \quad \frac{r_{\text{Cu(II)-Cit}}}{r_{\text{Cit}}} = 2.22, \\ \frac{r_{\text{Cu(II)-Tart}}}{r_{\text{Tart}}} = 4.03, \quad \frac{r_{\text{Cu(II)-DTPA}}}{r_{\text{DTPA}}} = 3.64 \quad (13)$$

In contrast with the control experiment (organic ligand-alone), Cu(II) significantly improved EDTA, citric acid, tartaric acid and DTPA reaction rate by 2.17, 2.22, 4.03 and 3.64 times, respectively. The results indicate that Cu(II) can accelerate the oxidation of organic ligands. The reasons are ascribed to the fact that the photogenerated electrons are consumed by Cu(II). The consumption of electrons will inhibit the recombination of electrons and holes. Alternatively, the holes will be mainly consumed by organic ligand and

the reaction rate of organic ligand will be increased obviously (Eq. (13)).

Nevertheless, Cu(II) caused different accelerating effects on the reaction rate of different organic ligands. The more profound influence of Cu(II) on tartaric acid than the others can be explained by the fact that Cu(II)-Tart is less stable than the other complexes. Copper ions are the major form in Cu(II)-Tart system, while chelated copper ions are the major forms in the other complex systems (Table 2). Thus, Cu(II) was more susceptible to be reduced in Cu(II)-Tart system, as a result, the recombination of electrons and holes would be inhibited. Consequently, the degradation of tartaric acid would be accelerated.

It has been also noticed that the reaction rate of DTPA was much lower than that of citric acid and EDTA in control experiment (Eq. (11)), whereas Cu(II) increased the oxidation rate of DTPA more remarkably than citric acid and EDTA (Eq. (13)). The results show that the accelerating effect of Cu (II) on the rate of organic ligands oxidation strongly depends on the magnitude of their own reaction rates. That is, the lower the organic ligand oxidation rate is, the more considerably Cu(II) increases the oxidation rate of them.

The reaction rate of EDTA was almost the same as that of citric acid (Eq. (11)). However, there were more free organic ligands in Cu(II)-Cit system than that in Cu(II)-EDTA system (Table 2). Therefore, the result leads to the enhancement of Cu(II) on citric acid oxidation rate is slightly higher than that of Cu(II) on EDTA (Eq. (13)).

Tartaric acid oxidation rate was higher than EDTA in their complex system (Eq. (12)), whereas it is clearly contrary to the result of control experiment (Eq. (11)). Thereby, complexes (formed by chelating agents and copper) altered the behaviors of organic ligands photocatalytic oxidation.

CONCLUSIONS

On the basis of experimental results, we conclude that photocatalytic oxidation of organic ligands can catalyze the reduction of Cu(II). However, the accelerating effects of different organic ligands on the rate of Cu(II) reduction differ distinctly. The solution pH values increase along with the extent of organic ligands are oxidized. The pH variation affects the enhancement of organic ligands on Cu(II) reduction rate. In addition,

Cu(II) can also accelerate the photocatalytic oxidation of organic ligands. Nevertheless, Cu(II) cause different accelerating effects on the reaction rates of different organic ligands. Chelating agents and copper can form complexes, which alter the behaviors of organic ligands photocatalytic oxidation.

A significant synergistic effect is observed between the reduction of Cu(II) and simultaneous oxidation of various organic ligands. It has been demonstrated that TiO₂ photocatalysis is an effective approach for removing chelated copper from wastewater.

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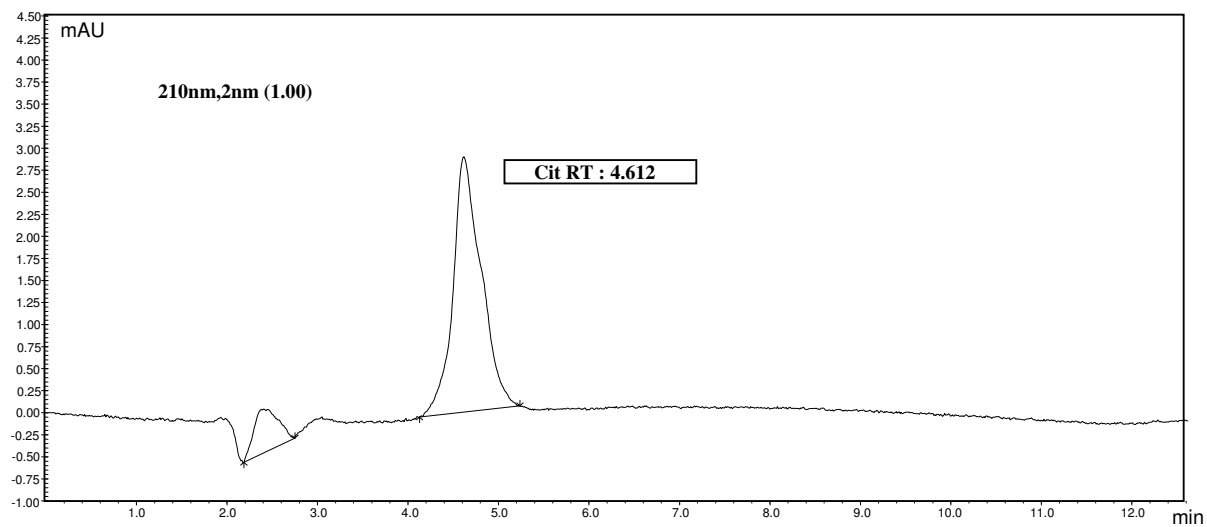
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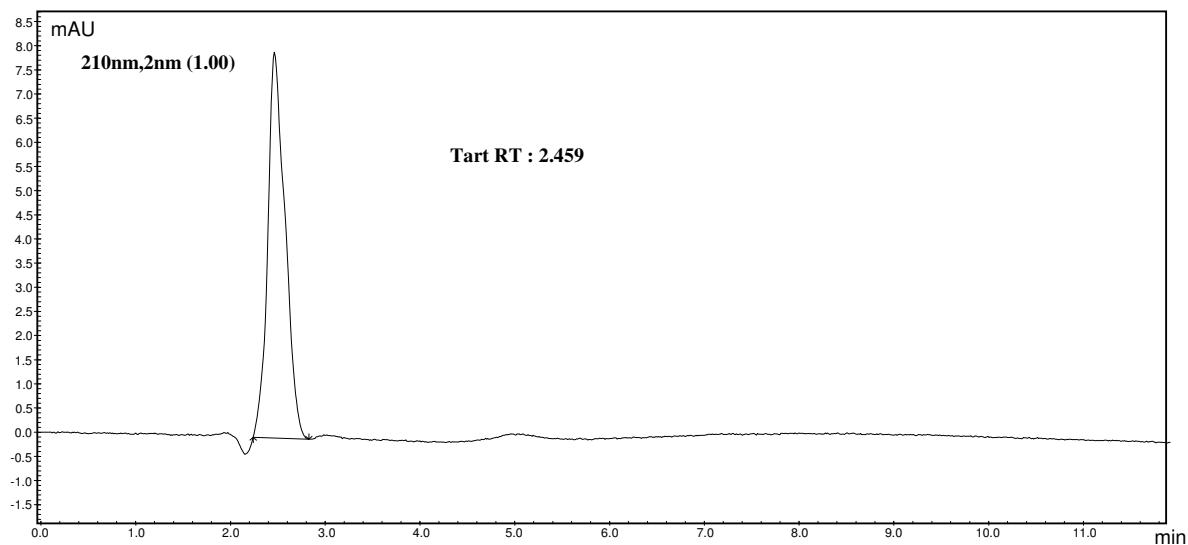
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Appendix**Citric acid****HPLC conditions**HPLC column : C₁₈, 5 μ m, 4.6 mm \times 250 mm;Mobile phase : 0.01 mol/L diammonium phosphate, adjusted to pH 2.7 \pm 0.2 with phosphoric acid, passed through 0.45 μ m film;

Flow rate : 1 mL/min;

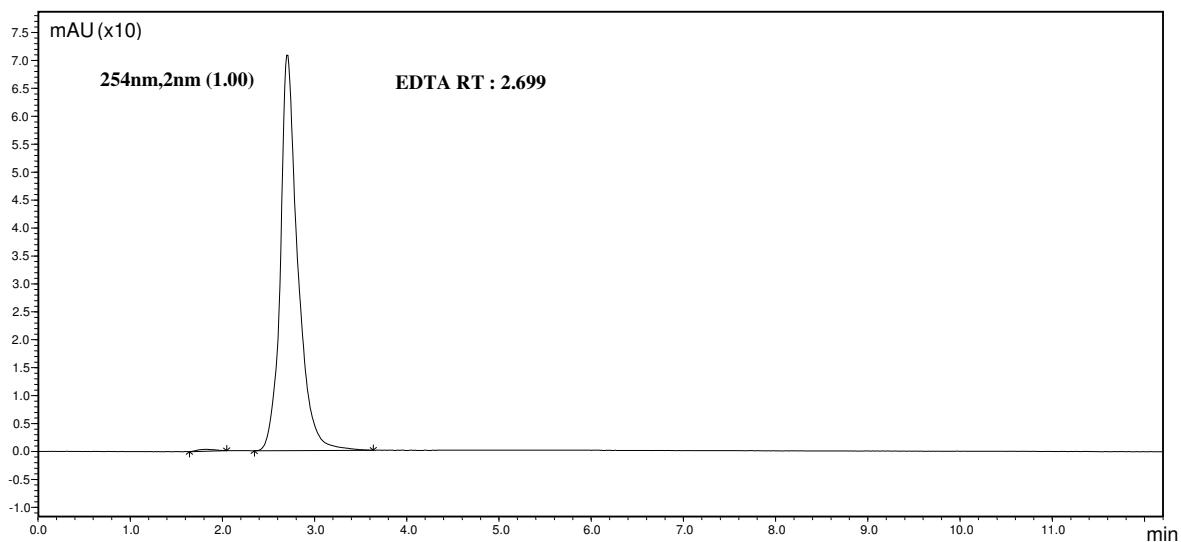
Detector wavelength : 210 nm;

Column temperature : 30 $^{\circ}$ C;Injection volume : 20 μ L**Tartaric acid****HPLC conditions**HPLC column : C₁₈, 5 μ m, 4.6 mm \times 250 mm;Mobile phase : 0.01 mol/L diammonium phosphate, adjusted to pH 2.7 \pm 0.2 with phosphoric acid, passed through 0.45 μ m film;

Flow rate : 1 mL/min;

Detector wavelength : 210 nm;

Column temperature : 30 $^{\circ}$ C;Injection volume : 20 μ L

EDTA

HPLC column : C₁₈, 5 μ m, 4.6 mm \times 250 mm;

Mobile phase : A : B=2 : 8

A : acetonitrile

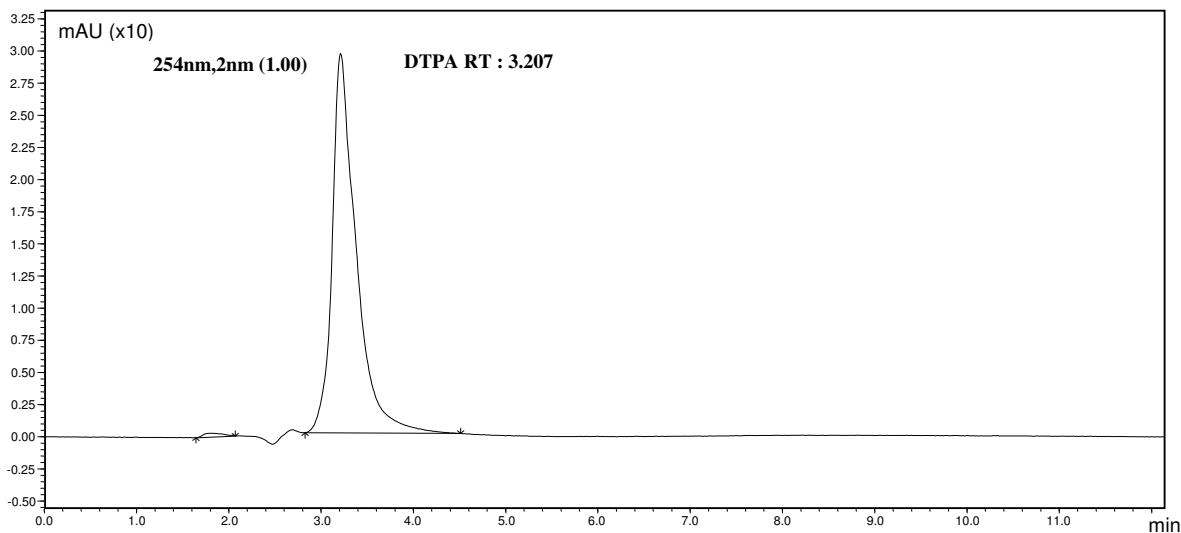
B : Cation of reagents II: Accurately weigh 0.645 g tetrabutylammonium bromide and 2.31 g ammonium acetate in 1 L volumetric flask, and dilute to the scale with water. Adjusted to pH 4.0 \pm 0.2 with acetic acid, passed through 0.45 μ m film;

Flow rate : 1 mL/min;

Detector wavelength : 254 nm;

Column temperature : 30 $^{\circ}$ C;

Injection volume : 20 μ L

DTPA

HPLC column : C₁₈, 5 μ m, 4.6 mm \times 250 mm;

Mobile phase : A : B=2 : 8

A : acetonitrile

B : Cation of reagents II: Accurately weigh 0.645 g tetrabutylammonium bromide and 2.31 g ammonium acetate in 1 L volumetric flask, and dilute to the scale with water. Adjusted to pH 4.0 \pm 0.2 with acetic acid, passed through 0.45 μ m film;

Flow rate : 1 mL/min;

Detector wavelength : 254 nm;

Column temperature : 30 $^{\circ}$ C;

Injection volume : 20 μ L