Cu(II) Catalytic Reduction of Cr(VI) by Tartaric Acid Under the Irradiation of Simulated Solar Light

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Abstract

Cu(II) catalytic reduction of Cr(VI) by tartaric acid under the irradiation of simulated solar light was investigated through batch experiments at pHs from 3 to 6 and at temperatures from 15°C to 35°C. Results demonstrated that introduction of Cu(II) could markedly improve reduction of Cr(VI) in comparison with tartaric acid alone. Optimal removal of Cr(VI) was achieved at pH 4. Reduction of Cr(VI) increased with increasing temperatures and initial concentrations of Cu(II) and tartaric acid. The catalytic role of Cu(II) in the reduction of Cr(VI) was ascribed to the formation of Cu(II)-tartaric acid complex, which generated active reductive intermediates, including Cu(I) and tartaric acid radicals through a pathway of metal–ligand–electron transfer with light. Cu(II) photocatalytic reduction of Cr(VI) by tartaric acid followed pseudo zero-order kinetics with regard to Cr(VI), and the activation energy was calculated to be 21.48 kJ/mol. To date, such a role of Cu(II) has not been reported. The results from the present study are helpful in fully understanding the photochemical reductive behavior of Cr(VI) in the presence of both tartaric acid and Cu(II) in soil and aquatic environments.

Key words: catalytic reduction; Cr(VI); Cu(II); simulated solar light; tartaric acid

Introduction

CHROMIUM IS EXTENSIVELY utilized in industries such as leather tanning, electroplating, and pulp producing owing to its unique properties (Palmer and Wittbrodt, 1991). As a result of leakage, unsuitable storage, or improper waste disposal, chromium pollution is becoming more and more serious all over the world. Chromium exists in several oxidation states, but only the states of hexavalent [Cr(VI)] and trivalent [Cr(III)] are dominantly prevalent in the environment (Jiang *et al.*, 2012). However, they exhibit quite different properties. The Cr(VI) species with high solubility and mobility is very harmful to humans, animals, and plants. In contrast, the Cr(III) species with less solubility and mobility is one of the micronutrients in humans. In addition, Cr(III) is easily absorbed onto the surfaces of clay minerals, readily precipitates in Cr(OH)₃, or forms complexes with organic ligands (Eary and Rai, 1988). Thus, one of the feasible methods to minimize chromium pollution in the environment is to convert Cr(VI) into Cr(III).

It has been reported that Cr(VI) can be effectively reduced to Cr(III) by many reductants such as zerovalent iron (Puls *et al.*, 1999; Melitas *et al.*, 2001; Zhou *et al.*, 2008), divalent iron (Fendorf and Li, 1996; Buerge and Hug, 1997; Seaman *et al.*, 1999), sulfide (Thornton and Amonette, 1999; Lan *et al.*, 2005, 2006), vitamin C (Xu *et al.*, 2004, 2005), zerovalent zinc (Guo *et al.*, 2012), and other minerals (Zhou *et al.*, 2012). It is known that numerous organic compounds exist in aquatic and soil environments. Therefore, the reduction of Cr(VI) by organic compounds also attracts significant attention. Nevertheless, it has been found that the reduction of Cr(VI) by organic matter alone is very slow (Deng and Stone, 1996; Li *et al.*, 2007). For example, Deng and Stone (1996) reported that only about 10 μM Cr(VI) was reduced to Cr(III) by the organic compounds with α-hydroxyl and α-carbonyl carboxylic acids within 200 h. Li *et al.* (2007) pointed out that the removal of Cr(VI) by citric acid alone at pH 4.5 was very slow, and <5% of 50 μM Cr(VI) was converted to Cr(III) within 22 h. A weak reaction between Cr(VI) and soil humic substances (SHSs) under weakly acidic and neutral conditions was also observed (Wittbrodt and Palmer, 1995, 1996a, 1996b).

In recent years, it has been discovered that many transition metal ions, such as Mn(II) and Fe(III), can dramatically catalyze Cr(VI) reduction by organic acids (Kabir-ud-Din *et al.*, 2000; Li *et al.*, 2007; Lan *et al.*, 2008). The reduction rate of Cr(VI) by citric acid is markedly enhanced by the addition

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of Mn(II), and the rate constant increases by about 45 times as compared with that in the absence of Mn(II) (Li *et al.*, 2007). It has been suggested that the formation of complex between Mn(II) and citric acid can improve the activity of α -OH group in citric acid, and then produce Cr(VI)-citric acid-Mn(II), which may accelerate the reduction of Cr(VI) (Kabir-ud-Din *et al.*, 2000; Lan *et al.*, 2008). Wittbrodt and Palmer (1996a) observed that the reduction of Cr(VI) by the SHS was accelerated by Fe(III). In the reaction system, Fe(III) was rapidly reduced to Fe(II) by the SHS. Then, Fe(II) transformed Cr(VI) to Cr(III) and meanwhile, Fe(III) was generated. So, a ternary cyclic system of Cr-Fe-SHS formed enhanced the reduction of Cr(VI). The photoreduction rate of Cr(VI) by aquatic dissolved organic matter increased with iron concentration (Gaberell *et al.*, 2003). Sun *et al.* (2009) further found that the Fe(III) photocatalytic reduction of Cr(VI) was positively correlated with the number of α -OH groups in organic acids, and reported that the rate constants involving the four acids were in the following order: tartaric acid (with two α -OH groups) > citric acid (with one α -OH group) $\approx$ malic acid (with one α -OH group) $\gg$ *n*-butyric acid (without α -OH group). It was suggested that the enhancement of Cr(VI) reduction by organic acids in the presence of Fe(III) may involve the next few steps (Hug *et al.*, 1997; Gaberell *et al.*, 2003; Sun *et al.*, 2009; Tian *et al.*, 2010). First, the Fe(III)-organic complexes were quickly formed in the reaction system. Then, Fe(II) and reductive radicals such as $R^\bullet$ and $HO_2^\bullet$ were generated through a pathway of metal-ligand-electron transfer under the irradiation of light, which converted Cr(VI) to Cr(III) step by step. Finally, Fe(III) and organic acids formed the complexes again. The steps mentioned earlier also constituted a cyclic system of the catalytic reaction and enhanced the reduction of Cr(VI).

It is known that Cu(II) exists in soil and water environments. We hypothesize that Cu(II), similar to Fe(III), forms the complexes with organic acids, which can also generate Cu(I) and some reductive free radicals through a pathway of metal-ligand-electron transfer under the irradiation of light. Therefore, it is likely that Cu(II) may catalyze Cr(VI) reduction by organic acids with light. To the best of our knowledge, so far, such a role of Cu(II) has not been reported. This study aimed at investigating the catalytic role of Cu(II) in the Cr(VI) reduction by tartaric acid and the factors affecting this reaction through batch experiments.

Materials and Methods

Materials

All the chemicals used were of analytic reagent and used without further purification. $K_2Cr_2O_7$, used as a source of hexavalent chromium, was dried at 120°C for 2 h before weighing. The stock solutions of Cr(VI), Cu(II), and tartaric acid were prepared with deionized water and their concentrations were 4, 8, and 40 mM, respectively. 1,5-Diphenylcarbazide (DPC; purchased from Sigma-Aldrich Company), acting as the chromogenic agent, was prepared by dissolving 0.25 g DPC in 100 mL acetone, which was stored in an amber bottle and then kept in a refrigerator before use. 2,2'-Biquinoline, a characteristic reagent for Cu(I), was also obtained from Sigma-Aldrich Company. NaOH and HCl were used to adjust the initial

pH of solutions. All the glassware used in the experiments was soaked in 1 M HCl for at least 6 h and thoroughly rinsed with tap water and then deionized water.

Experiments

Cu(II) photocatalytic reduction of Cr(VI) by tartaric acid was conducted in an XPA-7 photochemical reactor (Xujiang Electromechanical Plant) that was equipped with a magnetic stirrer and a device controlling temperature. A 500-W xenon lamp was used as a light source of simulated solar light at the wavelengths from 300 to 800 nm, which was positioned inside a cylindrical Pyrex vessel surrounded by a circulating water Pyrex jacket to cool the lamp. The schematic diagram was illustrated in our previous paper (Tian *et al.*, 2010). For typical photocatalytic reactions, the stock solutions of Cu(II) and tartaric acid were introduced into a 50 mL quartz tube, and the mixed solution was diluted with deionized water to $\sim$ 35 mL. Then, 0.1 M NaOH and HCl were used to adjust the initial pH to the desired values (3, 4, 5, and 6). Third, the solution was diluted to 39 mL with deionized water again and kept in a thermostatic bath at the desired temperatures (15–35°C) for 30 min. Finally, 1 mL Cr(VI) stock solution was added to the tube and the total volume of the solution was 40 mL. The solution was rapidly mixed before being placed in the photochemical reactor. The temperature was maintained with the thermostatic bath, and the solution was stirred with a magnetic bar at 500 rpm during the irradiation. At appropriate time intervals, 1 mL aliquot of solution was withdrawn from the quartz tube using a pipette for Cr(VI) analysis.

The reduction of Cr(VI) by tartaric acid in the presence of Cu(II) in dark as a control was also performed in the photochemical reactor under the other same conditions. The initial concentrations of Cu(II), tartaric acid, and Cr(VI) were 400, 1,000, and 100 μ M, respectively.

Analytical methods

Cr(VI) concentrations in the solution were determined by the DPC colorimetric method (Jiang *et al.*, 2012). One milliliter sample was added to the mixture of 1 mL DPC and 1 mL H_2SO_4 (1:20 v/v), which was used to adjust the pH for color development. The volume was adjusted to 10 mL with deionized water. The concentration of Cr(VI) was measured by monitoring its absorbance at 540 nm with an Alpha-1502 Spectrophotometer. Cu(I), an intermediate, was detected using 2,2'-biquinoline acting as the chromogenic agent, which was extracted with isoamyl alcohol (Wei and Qian, 2002) and the absorbance was measured at 545 nm (see Supplementary Fig. S1 for the adsorption curve). The concentration of tartaric acid in the stock solution was measured on a high-performance liquid chromatography (Waters 2487). The mobile phase consisted of 25 mM diammonium phosphate at pH 2.8 with 3% (v/v) MeOH. Lichrospher C_{18} (5 μ m, 250 $\times$ 4.6 mm) was used as the separation column, and the component in the effluent was detected at 214 nm. The concentrations of Cu(II) in the stock solution were determined by atomic absorption spectrometry (HITACHI 180-80). Total organic carbon (TOC) in aqueous solution was determined with Shimadzu TOC-L analyzer. Oxygen was used as carrier gas with a pressure of 200 kPa at the following velocity of 150 mL/min.

Results and Discussion

Effect of Cu(II) on the Cr(VI) reduction by tartaric acid

The Cr(VI) reduction by tartaric acid in the presence and absence of Cu(II) is illustrated in Fig. 1. Almost no reduction of Cr(VI) was observed within 2 h without light whether in the presence of Cu(II) or not. The results showed that the reduction of Cr(VI) by tartaric acid alone was very slow, and the effect of Cu(II) on the removal of Cr(VI) by tartaric acid without light was negligible. The irradiation of simulated solar light weakly affected the reduction of Cr(VI) by tartaric acid, and the removal percentage of Cr(VI) increased by $\sim 5\%$ as compared with the experiment in the dark. However, 100 μM Cr(VI) was almost completely removed within 80 min in the presence of 400 μM Cu(II) with the simulated solar light, demonstrating that Cu(II) can significantly improve photochemical reduction of Cr(VI) by tartaric acid.

It has been reported that Mn(II) without light can strongly catalyze the reduction of Cr(VI) by citric acid under weakly acidic conditions because of the formation of Cr(VI)-citric acid-Mn(II) complex (Li *et al.*, 2007; Lan *et al.*, 2008), and Fe(III) photocatalytic reduction of Cr(VI) by organic acids with $\alpha\text{-OH}$ is extremely fast due to the formation of a photochemically active complex, which releases stronger reductants by shuttling electrons (Sun *et al.*, 2009). Similar to Fe(III), Cu(II) reacted with tartaric acid to form a complex and also had a lower oxidation state, Cu(I). Under the irradiation of light, Cu(II)-tartaric acid complex produced Cu(I) and tartaric acid radicals through a pathway of metal-ligand-electron transfer. To prove this hypothesis, a full-length scan experiment was performed and it verified the formation of Cu(II)-tartaric acid complex (Supplementary Fig. S2). Furthermore, we introduced 2,2'-biquinoline into the reaction system and a red complex in isoamyl alcohol solution as extracting agent was observed, which confirmed the generation of Cu(I) during the reaction (Wei and Qian, 2002). A similar result was also reported by Ciesla *et al.* (2004), who revealed that Cr(III)-EDTA complex could generate a Cr(II) center and the EDTA $^{\bullet}$ radicals by a photoinduced inner sphere electron transfer.

Cr(VI) photochemical reduction is a complicated reaction. Hug *et al.* (1997) reported that Fe(III) photocatalytic reduc-

tion of Cr(VI) by oxalic acid involved four processes: (1) photolysis of Fe(III)-oxalate and formation of products such as Fe(II)-oxalate, $\text{CO}_2^{\bullet-}$, and $\text{O}_2^{\bullet-}$; (2) reactions of Cr(VI) and Cr(VI) intermediates [Cr(V), Cr(IV)] with Fe(II), $\text{HO}_2^{\bullet}$ / $\text{O}_2^{\bullet-}$, and $\text{CO}_2^{\bullet-}$ in the presence of oxalic acid; (3) other reactions, including the reaction of Fe(II) and reactive oxygen species; and (4) formation of Fe(III)-oxalate. Based on the determination of previously discussed intermediates by this study and the mechanism proposed by Hug *et al.* (1997) and taking into account the fact that an irradiation of simulated solar light could also cause a slow photoreduction of Cr(VI) by tartaric acid alone (Fig. 1), it was hypothesized that organic radicals could also be yielded due to the absorption of light by tartaric acid itself. In the presence of both Cu(II) and tartaric acid, Cu(I) ($E^\circ_{\text{Cu(II)/Cu(I)}} = 0.153 \text{ V}$) (Lide, 2005) along with organic radicals and $\text{CO}_2^{\bullet-}$ converted Cr(VI) to Cr(III) step by step, accompanied with the reproduction of Cu(II). Again, Cu(II)-tartaric acid complex formed. Consequently, a cycle process of converting Cu(II) to Cu(I) in the reaction system was established. The main reactions mentioned earlier were summarized as follows:

In order to further investigate the effect of irradiation on Cr(VI) reduction, the solution after the reactions for 30 and 60 min with light was transformed to an amber bottle (see insert in Fig. 1). It was observed that Cr(VI) was still reduced. The reaction rate was much slower than that with light, but faster than that in the dark. This demonstrated that Tar intermediates continuously converted Cr(VI) to Cr(III) according to Equation (8).

In addition, TOC in aqueous solution was determined and it was observed that $\sim 4\%$ of TOC by the end of the reaction

FIG. 1. Reduction of Cr(VI) by tartaric acid at pH 4 and 25°C. Experimental conditions: $c[\text{Cr(VI)}]_0 = 100 \mu\text{M}$, $c(\text{tartaric acid})_0 = 1 \text{ mM}$. $\square$ 0 μM Cu(II) with light; $\blacksquare$ 400 μM Cu(II) with light; $\triangle$ 0 μM Cu(II) without light; $\blacktriangle$ 400 μM Cu(II) without light.

was removed. The decrease of TOC after the reaction possibly resulted from the release of CO_2 , as summarized in Equations (5), (6), and (8).

Effect of pH on the photochemical reduction of Cr(VI) by tartaric acid

The effect of initial pH on the reduction of Cr(VI) by tartaric acid in the presence and absence of Cu(II) was investigated, and the results are shown in Fig. 2. In the absence of Cu(II), the reduction rate of Cr(VI) by tartaric acid obviously increased with pH decreasing from 6 to 3, although all the reactions were slow. However, a different tendency of pH effect on the Cr(VI) reduction in the presence of Cu(II) was observed. The removal of Cr(VI) increased with pH increasing from 3 to 4, but decreased with pH increasing from 4 to 6. The optimal removal of Cr(VI) was achieved at initial pH 4. The phenomenon observed in this study was not completely consistent with the phenomena described in the literature (Hug *et al.*, 1997; Sun *et al.*, 2009), in which it was reported that Fe(III)-photocatalytic reduction of Cr(VI) increased with pH decreasing from 3.0 to 4.5 in the presence of tartaric acid (Sun *et al.*, 2009), and decreased almost linearly with pH increasing above pH 5.5 in the presence of oxalic acid (Hug *et al.*, 1997). This implied that the effect of pH on the reduction of Cr(VI) by organic acids assisted by transition metal ions might be complicated.

Cr(VI) mainly exists in the form of HCrO_4^- at pH from 1 to 6 and CrO_4^{2-} (or $\text{Cr}_2\text{O}_7^{2-}$ at a high concentration) above pH 7 (Kotas and Stasicka, 2000). Cr(VI) in the form of HCrO_4^- at pH 3–6 was reduced to Cr(III) as follows:

According to Equation (9), the rate of Cr(VI) reduction was closely related to the concentration of H^+ in the solution. The solution pH by the end of the reaction was measured and it was found that in the all tests, pH increased, which demonstrated that the reaction is consuming H^+ . Therefore, the increase of H^+ concentration enhanced the conversion of Cr(VI) into Cr(III). As a result, in the absence of Cu(II),

FIG. 2. Effect of pH on Cu(II) photocatalytic reduction of Cr(VI) by tartaric acid with 500 W xenon lamp at 25°C. Experimental conditions: $c[\text{Cr(VI)}]_0 = 100 \mu\text{M}$, $c(\text{tartaric acid})_0 = 1 \text{ mM}$, and $c[\text{Cu(II)}]_0 = 400 \mu\text{M}$. Initial pH: ■ 3 (□ control without Cu(II)); ◆ 4 (◇ control); ● 5 (○ control); ▲ 6 (Δ control).

~30% of the initial Cr(VI) was reduced by tartaric acid at pH 3 within 2 h, but only <10% of the initial Cr(VI) was converted to Cr(III) at higher pH.

Tartaric acid exists in three states in water:

Obviously, the decrease of H^+ concentration caused the equilibrium of Equation (10) to shift to the right, resulting in increased Cu(II)-tartaric acid complex. Thus, the reduction of Cr(VI) was significantly enhanced due to more production of Cu(II)-tartaric acid complex with high photochemical activity. However, a low concentration of H^+ (high pH value) is not conducive to the transformation of Cr(VI) to Cr(III) as previously discussed. Another negative effect on Cr(VI) reduction rate with pH increasing from 4 to 6 possibly resulted from an increase of Cu(II) hydrolysis, which does not benefit the formation of Cu(II)-tartaric acid complex. Therefore, the optimal pH for Cr(VI) removal by tartaric acid in the presence of Cu(II) was 4 in a pH range of 3–6.

Effects of initial concentration of Cu(II) and tartaric acid on the photochemical reduction of Cr(VI)

Effects of the initial concentrations of Cu(II) and tartaric acid on the photochemical reduction of Cr(VI) with an irradiation of 500 W xenon lamp at pH 4 and 25°C were further investigated, and results are depicted in Figures 3 and 4, respectively. In the presence of 1 mM tartaric acid, the removal of Cr(VI) significantly increased with the initial concentration of Cu(II) from 0 to 1,200 μM (Fig. 3). Obviously, with the initial concentration of Cu(II) increasing, more photochemically active complexes of Cu(II)-tartaric acid formed in the reaction system, which accelerated the reduction of Cr(VI). However, in the absence of Cu(II), a slight increase in the reduction of Cr(VI) was observed with increasing the initial concentration of tartaric acid from 0.5 to 4 mM, but it was enlarged in the presence of 400 μM Cu(II) (Fig. 4). This result further confirmed that the reduction of Cr(VI) by tartaric acid alone was weak and Cu(II) played an important role in accelerating Cr(VI) removal with light.

FIG. 3. Effect of Cu(II) concentration on photocatalytic reduction of Cr(VI) by tartaric acid with 500 W xenon lamp at pH 4 and 25°C. Experimental conditions: $c[\text{Cr(VI)}]_0 = 100 \mu\text{M}$, $c(\text{tartaric acid})_0 = 1 \text{ mM}$. $c[\text{Cu(II)}]_0$: □ 0 μM ; ■ 100 μM ; ▲ 200 μM ; ◆ 400 μM ; ● 800 μM ; — 1,200 μM .

FIG. 4. Effect of the concentration of tartaric acid on Cu(II) photocatalytic reduction of Cr(VI) with 500 W xenon lamp at pH 4 and 25°C. Experimental conditions: $c[\text{Cr(VI)}]_0 = 100 \mu\text{M}$, $c[\text{Cu(II)}]_0 = 400 \mu\text{M}$. $c(\text{tartaric})_0$: ■ 0.5 mM [□ control without Cu(II)]; ◆ 1 mM (◇ control); ● 2 mM (○ control); ▲ 4 mM (Δ control).

The reaction of Cr(VI) removal by tartaric acid with or without Cu(II) could be described as a pseudo zero-order kinetics model as the decrease of $c[\text{Cr(VI)}]/c[\text{Cr(VI)}]_0$ was almost linear with reaction time (Figs. 3 and 4). The reaction rate constant (k) and correlation coefficient (R^2) are listed in Table 1. The rate constants of Cr(VI) reduction by 1 mM tartaric acid in the presence of 100, 200, 400, 800, and 1,200 μM Cu(II) increased by 5.6, 8.56, 11.8, 15.5, and 18.8 times, respectively, as compared with that in the absence of Cu(II). The removal rates of Cr(VI) increased with the initial concentration of tartaric acid alone from 0.5 to 4 mM, but as previously discussed, the amplitude was much small in comparison with that in the presence of Cu(II).

Effect of temperatures on photochemical reduction of Cr(VI)

The effect of temperatures on the photochemical reduction of Cr(VI) by 1 mM tartaric acid at pH 4 with and without Cu(II) is illustrated in Fig. 5. In the absence of Cu(II), the temperature exerted a very weak impact on the reduction of Cr(VI) by tartaric acid, and almost no difference in the reaction rate was observed when the temperature increased from 15°C to 35°C. However, in the presence of 400 μM

FIG. 5. Effect of temperature on Cu(II) photocatalytic reduction of Cr(VI) by tartaric acid with 500 W xenon lamp at pH 4. Experimental conditions: $c[\text{Cr(VI)}]_0 = 100 \mu\text{M}$, $c(\text{tartaric acid})_0 = 1 \text{ mM}$, and $c[\text{Cu(II)}]_0 = 400 \mu\text{M}$. ■ 15°C [□ control without Cu(II)]; ◆ 25°C (◇ control); ● 35°C (○ control).

Cu(II), the temperature played an important role in accelerating the removal of Cr(VI) by tartaric acid. Cr(VI) with an initial 100 μM was almost completely converted to Cr(III) within 2 h at 15°C, but it took only 1 h at 35°C. The rate constants were 0.89, 1.29, and 1.60 $\mu\text{M}/\text{min}$ at 15, 25, and 35°C, respectively.

The activation energy (E_a) for the Cu(II) photocatalytic reduction of Cr(VI) by tartaric acid was evaluated by plotting $\ln k$ versus $1/T$ (K^{-1}), and the value was 21.48 kJ/mol.

Conclusions

Cu(II) markedly catalyzed Cr(VI) reduction by tartaric acid with light under weakly acidic conditions. The reaction rate was improved with the increase in temperature and the initial concentrations of Cu(II) and tartaric acid. The optimal removal of Cr(VI) by tartaric acid assisted with Cu(II) was achieved at pH 4. Cu(II) photocatalytic reduction of Cr(VI) by tartaric acid obeyed the pseudo zero-order reaction, and the activation energy was 21.48 kJ/mol. It was proposed that the formation of Cu(II)-tartaric acid complex in the reaction system was important, which can produce actively reductive intermediates, including organic acid radicals, Cu(I), and $\text{CO}_2^{\bullet-}$ through a pathway of metal–ligand–electron transfer, leading to rapid conversion of Cr(VI) to Cr(III) step by step. Therefore, the results from the present study are helpful to fully understand the photochemical reductive behavior of Cr(VI) in the presence of both tartaric acid and Cu(II) in soil and aquatic environments.

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Author Disclosure Statement

No competing financial interests exist.

TABLE 1. PSEUDO ZERO-ORDER RATE CONSTANT (k) AND CORRELATION COEFFICIENT (R^2) FOR PHOTOCATALYTIC REDUCTION OF 100 μM Cr(VI) BY TARTARIC ACID IN THE PRESENCE OF Cu(II) AT pH 4 AND 25°C

Conditions	$k(\mu\text{M}/\text{min})$	R^2
1 mM tartaric acid–0 μM Cu(II)	0.11	0.9694
1 mM tartaric acid–100 μM Cu(II)	0.61	0.9913
1 mM tartaric acid–200 μM Cu(II)	0.94	0.9969
1 mM tartaric acid–400 μM Cu(II)	1.29	0.9948
1 mM tartaric acid–800 μM Cu(II)	1.70	0.9950
1 mM tartaric acid–1,200 μM Cu(II)	2.06	0.9922
0.5 mM tartaric acid–400 μM Cu(II)	1.01	0.9957
2 mM tartaric acid–400 μM Cu(II)	1.39	0.9940
4 mM tartaric acid–400 μM Cu(II)	1.56	0.9972

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