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Oxidative degradation of organic pollutants using cuprous oxide in acidic solution: hydroxyl radical generation

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ABSTRACT

In this study, cuprous oxide (Cu_2O) particles were synthesized by a precipitation method, and were used to degrade synthetic dyes (i.e. rhodamine B (RhB), methylene blue (MB), reactive brilliant red X-3B (RR X-3B), orange II, and crystal violet (CV)). Cu_2O was most effective copper species to induce the generation of H_2O_2 and degrade RhB at acidic condition, compared to nanoscale zero-valent copper (nZVC), cupric oxide (CuO) and cupric ions (Cu^{2+}). Mechanism investigation of the Cu_2O/acid system showed that the corrosion of Cu_2O in acidic conditions (pH < 4) was accompanied by electron transfer from Cu_2O to molecular oxygen, which led to the simultaneous generation of Cu^{2+} and H_2O_2. Moreover, hydroxyl radical ($^\bullet OH$) was produced via the Fenton-like reaction between Cu_2O and H_2O_2, which was identified as the main reactive oxidant for RhB removal based on the results of radical scavenging experiments and electron paramagnetic resonance spectroscopy. The results clearly showed that the solution pH was the most significant impact factor on RhB (15 mg L^{-1}) removal using 36 mg L^{-1} Cu_2O, and 77.5% RhB was removed within 30 min at initial pH 3.0 compared to only 10.9% at initial pH 4.0 but there was no RhB removal at initial pH ≥ 5.

Keywords: Cuprous oxide; Rhodamine B; Hydrogen peroxide; Hydroxyl radical

1. Introduction

Wastewater from dyeing processes is one of the most challenging types of industrial wastewater to be treated because of the massive amount of water, deep colors and the significant change of water quality [1,2]. Approximately 21–377 m^3 of water is consumed for one tonne of textile products, and the chemical consumption varies typically from 10% to over 100% of the weight of the cloth [3]. Moreover, with the development of the dyestuff industry and the advancement of post-finishing technology, the extensive use of various new types of auxiliaries and dyes have led to increasingly complex components in this type of wastewater. Recently, Fenton or Fenton-like systems, accompanying $^\bullet OH$ generation in aqueous iron/hydrogen peroxide (H_2O_2) systems have been widely studied in degrading synthetic dyes [4,5]. However, Fenton or Fenton-like systems often require the external addition of abundantly large amounts H_2O_2, which can induce a high cost of US$ 390–500 for industrial grade H_2O_2 per tonne and has the potential risk in regard to transport, handling and storage [3]. It reinforces the need to find some economically and technically viable alternatives in the treatment of printing and dyeing wastewater.

A viable option is to degrade any dyes in the system by the in situ generation of $H_2O_2/^\bullet OH$ [6–9]. Zero-valent iron (ZVI), zero-valent aluminum (ZVAl), and zero-valent copper (ZVC)/acid systems are studied because of high reactivity without additional oxidant such as H_2O_2 and persulfate [6–8,10–12]. In addition, in our previous studies, we compared the degradation of 2,4-dichlorophenol (2,4-DCP) by ZVC, ZVI, ZVAl, and zero-valent/tungsten (ZVW) acid

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systems, and ZVC/acid system showed the stronger reactivity [12]. Furthermore, H_2O_2 was generated by electron transfer from zero-valent metals (ZVMs) to O_2, while releasing low-valent metal ions, and $^\bullet OH$ was produced via low-valent metal ions induced Fenton-like reactions. Therefore, we envisage that direct addition of a low-valent copper species may have higher reactivity even better than ZVC. Besides, cuprous oxide (Cu_2O) is a good choice due to the instability of cuprous ions in solution. As an excellent semiconductor photocatalyst, Cu_2O has attracted extensive interest in the application of water splitting, solar-energy conversion and photocatalytic environmental remediation under visible light irradiation due to its lower direct band gap (2.2 eV), low toxicity, good environmental acceptability and ready availability [13,14]. Further, with regard to the standard electrode potential of Cu^{2+}/Cu^{+} (0.160 V), it is more negative than that of O_2/H_2O_2 (0.695 V) and Cu^{2+}/Cu (0.337V) [7]. Theoretically, Cu_2O has the ability to be generated in situ H_2O_2 in acidic conditions and is more reactive with oxygen than ZVC. Thus, we believe the Cu_2O/acid system has potential and is worth to study.

In this work, Cu_2O powder was synthesized via a precipitation method, and was characterized by using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Moreover, we investigated the oxidation capacity of the Cu_2O/acid system for degrading synthetic dyes. Compared to ZVC, copper oxide (CuO), and copper ions (Cu^{2+}), the oxidation efficiency in the system at different initial pH and the concentration of in situ formed H_2O_2 at initial pH = 3.0 are discussed. The effect of Cu_2O dosage and the degradation efficiency of various dyes in Cu_2O/acid system were also discussed. Moreover, mechanism of the Cu_2O/acid system was determined by measuring the corrosion of Cu^{2+} and the H_2O_2 production under aerobic and anaerobic conditions. In addition, the $^\bullet OH$ radical was demonstrated by the inhibition of the scavengers (i.e. tert-butanol, Ethanol) and electron paramagnetic resonance (EPR) measurement.

2. Materials and methods

2.1. Materials and reagents

Rhodamine B (RhB, ≥99%), methylene blue (MB, ≥99%), reactive brilliant red X-3B (RR X-3B, ≥99%), orange II (≥99%), and crystal violet (CV, ≥99%), copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$, ≥99%), L-ascorbic acid, tert-butanol (TBA), sulfuric acid, ethanol (EtOH), sodium hydroxide (NaOH) were of analytic grade and supplied by Chendu Kelong Chemical Reagent Factory, (Chengdu, China). Nanoscale zero-valent copper (nZVC, 30 nm, ≥99.9%), 5,5-dimethyl-1-pyrrpline-N-oxide (DMPO), and catalase (≥3,000 unit/mg) were purchased from Aladdin Industrial Corporation, (Shanghai, China).

In a typical procedure, $CuSO_4{\cdot}5H_2O$ (2.4968 g, 0.01 mol) was dissolved in 50 mL of ultrapure water at 25°C, then 70 mL NaOH (4 mol L^{-1}) was slowly added into the $CuSO_4$ solution, and stirred for 30 min. After this, 100 mL L-ascorbic acid solution (0.1 mol L^{-1}) was added drop wise, and the mixture was continuously stirred for another 30 min. The generated flocculent precipitates were cleaned by ultrapure water and ethanol several times, and dried under vacuum at 60°C for 8 h. Similarly, CuO was also prepared in a precipitation procedure. $CuSO_4{\cdot}5H_2O$ (2.4968 g, 0.01 mol) was dissolved in 50 mL of ultrapure water, and NaOH (4 mol L^{-1}) was dropwise added into the solution at 80°C. After stirring for 30 min, the black product was washed several times with ultrapure water and absolute alcohol. Finally, the as-obtained precipitate was dried in vacuum at 80°C.

2.2. Experimental procedure

All the experiments were performed in 250 mL glass flasks with a total solution volume of 200 mL, under constant stirring with a PTFE-coated magnetic stirrer and with the temperature controlled at 25°C in ultrapure water. All the experiments were open to the atmosphere. The pH was adjusted to the desired value using 0.1 M H_2SO_4 and 0.1 M NaOH. Each run was initiated by simultaneously adding the desired dosage of substrates and catalysts. Quenching experiments with TBA, EtOH, and catalase were performed by adding the desired quencher into the reaction solution in advance. Samples were extracted from the flasks at the predetermined time, and the concentration of RhB samples were immediately measured by a UV-vis spectrometer after filtration with a glass fiber membrane of 0.70 μm pore size. All the experiments were performed in dark conditions, in duplicate, and the presented data are the average values of the results.

2.3. Analytical and characteristic methods

The pH value in system was monitored by pH meter (Shanghai Leici Apparatus Fac., China). The concentration of H_2O_2 was determined by a photometric method using the chromogenic reaction of titanium complexing hydrogen peroxide. The total concentration of dissolved copper (TCu) in the reaction mixture was measured using an UV-vis spectrometer at 454 nm (Text S1). Hydroxyl radical ($^\bullet OH$) was determined by EPR measurement, employing 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin trapper at room temperature on a Bruker model EPR JES-FA200 spectrometer (Karlsuhe, Germany). The concentration of RhB was measured on a UV-vis spectrometer (Mapada UV-1800, Shanghai, China) at 554 nm (MB at 644 nm, Reactive red X-3B at 540 nm, Orange II at 484 nm, CV at 590 nm). Moreover, the generated Cu_2O particles were characterized using (XRD, X'Pert Pro MPD diffractometer) and (SEM, JSM-7500F).

3. Results and discussion

3.1. Characterization of Cu_2O

Fig. 1a shows the XRD patterns of the fabricated catalyst, which has a number of peaks that can be well-indexed to Cu_2O (PDF#05-0667). It has seven sharp peaks at 29.6°, 36.4°, 42.3°, 52.5°, 61.4°, 73.5° and 77.4°, corresponding to (110), (111), (200), (211), (220), (311), and (222) of Cu_2O, respectively. Moreover, no other impurity phases, such as CuO and Cu, were detected, and the result demonstrates that Cu_2O has been successfully fabricated. Moreover, SEM images (Fig. 1b) show that the Cu_2O particles have an approximate cubic block structure, and the side lengths are about 200–500 nm.

3.2. Efficiency of RhB removal by various copper species at different initial pH

Previous studies [7] had reported that the generation of hydrogen peroxide by ZVC was pH-dependent, because the pH strongly affects the dissolution of Cu^+ and Cu^{2+} from ZVC as well as the evolution of the hydroxyl radical. Thus, the effect of different copper species, including Cu_2O, nZVC, CuO and $CuSO_4$, under different initial pH conditions on RhB removal, was investigated.

Copper oxide and copper salts theoretically cannot produce higher valent copper species by dissolution or oxidation of oxygen, but cuprous oxide and ZVC can, and the results from Fig. 2 also indirectly confirms it. As Fig. 2 shows, in the presence of CuO and Cu^{2+}, the target organic substance was not degraded, however the RhB concentration decreased when nZVC and Cu_2O were spiked into the acidic solutions. Specifically, within 30 min of reaction time, the addition of nZVC degraded RhB by 18.4%, 26.5%, 27.7% and 3.5% at pH 2.00, 2.50, 3.00, and 4.00, respectively. Much more than this, after Cu_2O was added into acidic RhB solution, the removal degradations of RhB in 30 min were 48.0%, 69.4%, 77.5% and 10.9% at pH 2.00, 2.50, 3.00, and 4.00, respectively. In addition, these four different copper species had zero efficiency on degrading RhB at pH 5.00 and pH 9.00. From the above results, it is considered that the pH value is the key parameter affecting the Cu_2O/acid system. Furthermore, less RhB was removed on decreasing the initial pH from 3.0 to 2.0. This may be due to the generation of oxonium ion ($H_3O_2^+$) [15], which increases the stability of the in situ generated H_2O_2, and the scavenging effect of $^{\bullet}OH$ by the excess H^+ [16]. Besides, in the situation pH > 3, the oxidation efficiency rapidly decreases, not only resulting in the generation of in situ H_2O_2 but also due to the decomposition of H_2O_2 [15].

3.3. Effect of Cu_2O dosage on RhB oxidation

The effect of Cu_2O dosage on the degradation of RhB was investigated by varying the catalyst dosage from 18 mg L^{-1} to 108 mg L^{-1} (0.25 mM to 1.50 mM in copper), and the results are shown in Fig. 3. The degradation efficiency of RhB

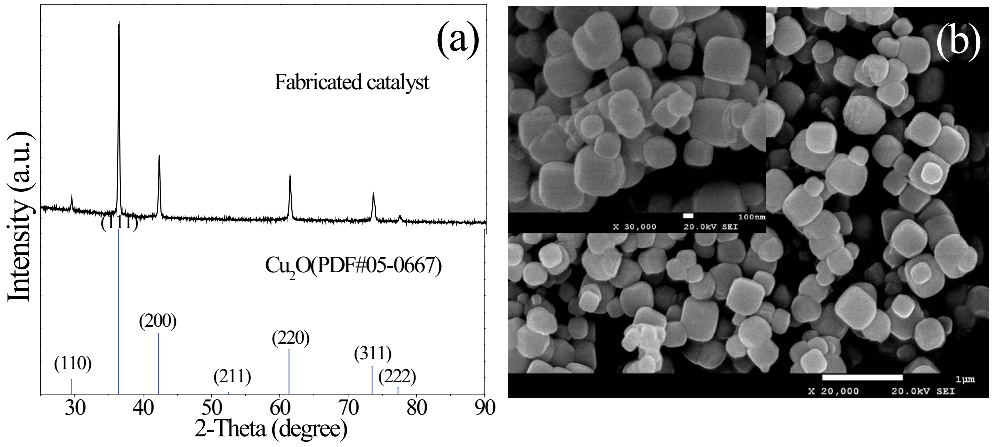

Fig. 1. (a) X-ray diffraction patterns from the catalyst and (b) SEM images of the fabricated Cu_2O powder.

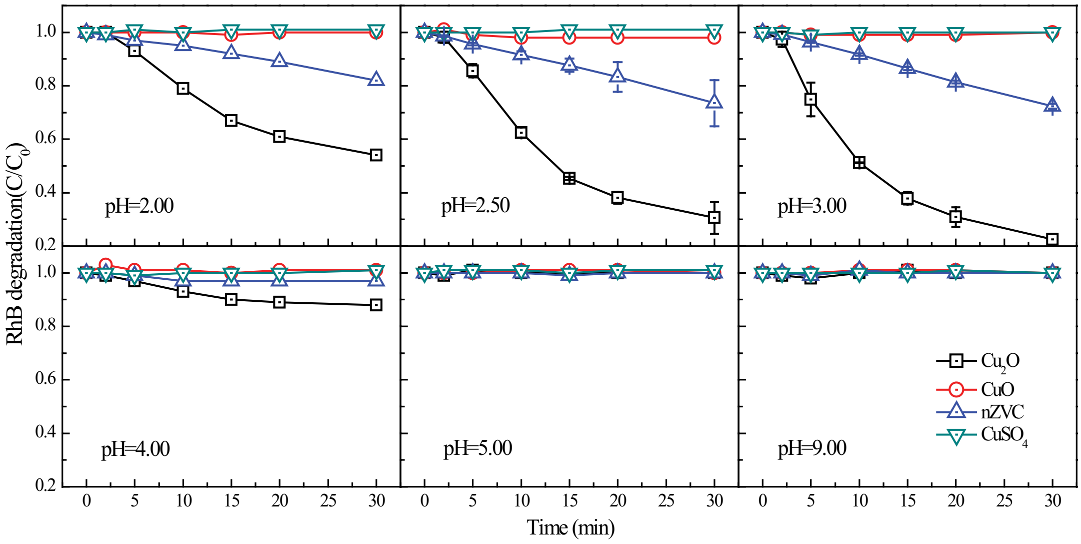

Fig. 2. Comparation of various copper species on the removal of RhB ($[RhB]_0$ = 15 mg L^{-1}, $[copper]_0$ = 0.50 mM).

increased gradually as the dosage of Cu_2O increased from 18 to 72 mg L^{-1} (0.25 to 1.00 mM) in copper. For example, the removal of RhB at 30 min increased from 42.1% with 18 mg L^{-1} (0.25 mM in copper) Cu_2O to 86.9% with 72 mg L^{-1} (1.00 mM in copper) Cu_2O at an initial pH 3.0. However, when the dosage of Cu_2O was increased to 108 mg L^{-1} (1.50 mM in copper), the degradation of RhB did not improve, or even decrease, compared with the dosage of Cu_2O at 72 mg L^{-1}. In order to understand the cause of this phenomenon, the pH value of the reaction process was detected. As Fig. 3 shows, for the case of 108 mg L^{-1} Cu_2O in solution, the pH value increased rapidly from 3.00 to 4.05 within 10 min, and up to 4.68 within 15 min. When the pH value of the reaction solution reaches 4.0, the reaction system cannot efficiently degrade organics. This explains why, in the case of higher Cu_2O loadings (>72 mg L^{-1} in copper), the removal of RhB does not increase significantly.

3.4. Ubiquitous degradation efficiency of various dyes in the Cu_2O/acid system

To explore the oxidation capacity of the Cu_2O/acid process, five different synthetic dyes, i.e.RhB, MB, reactive brilliant red X-3B (RR X-3B), orange II, and CV, were spiked into the reaction system individually. Furthermore, the degradation efficiencies of different dyes in 30 min are shown in Fig. 4, where it is noticeable that all five organics were degraded more or less via the Cu_2O/acid process. To be specific, the degradation rates of RhB, MB, RR X-3B, Orange II, and CV, in 30 min were 77.5%, 62.9%, 72.2%, 76.5%, and 68.0%, respectively.

3.5. Proposed mechanism of the Cu_2O/acid solution system

3.5.1. Production of H_2O_2 in the process of copper corrosion

It has been reported that H_2O_2 could be formed via a one-step two-electron direct reduction route [Eq. (1)] [17]. In the acidic solution, the generation of H_2O_2 requires low-valent copper species to provide electrons, and •OH was produced by Fenton-like reaction between low-valent copper species and H_2O_2. Specifically, Cu_2O [Eq. (2)] and nZVC can be electron donors, but CuO and Cu^{2+} cannot. In other words, in the presence of CuO or Cu^{2+}, H_2O_2 was not generated in the acidic solution, and there will be no •OH production. Moreover, CuO has low adsorption capacity. Therefore, CuO and Cu^{2+} has no ability to degrade organics under acidic condition. Fig. 5a shows that at pH = 3.0, in the presence of CuO or Cu^{2+}, no H_2O_2 was generated during the reaction. However, 37.5 and 12.5 μM of H_2O_2 were detected in 30 min after Cu_2O and nZVC were spiked into the solution, respectively. These results confirmed why CuO and Cu^{2+} have no degradation ability, and Cu_2O is the best copper species, compared to nZVC, CuO, and Cu^{2+}, to generate H_2O_2 in acidic conditions.

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \quad (1)$$

$$Cu_2O - 2e^- + 2H^+ \rightarrow 2Cu^{2+} + H_2O \quad (2)$$

As described in section 3.2, the pH value is the key factor affecting the whole reaction process, and in order

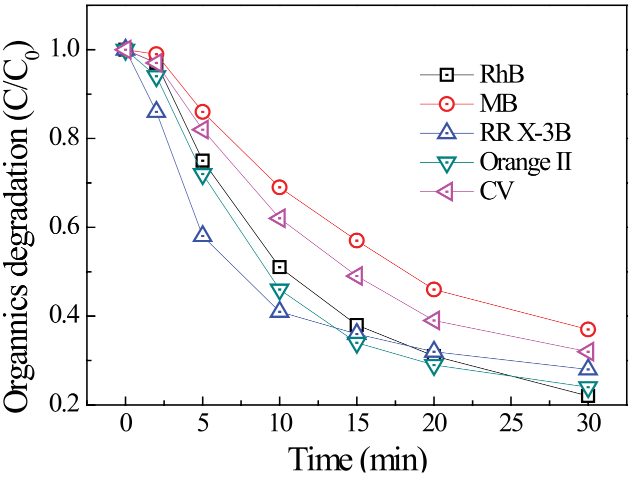

Fig. 4. Degradation efficiency of various organic dyes in the Cu_2O/acid process ($[substrate]_0$ = 15 mg L^{-1}, $[Cu_2O]_0$ = 36 mg L^{-1}).

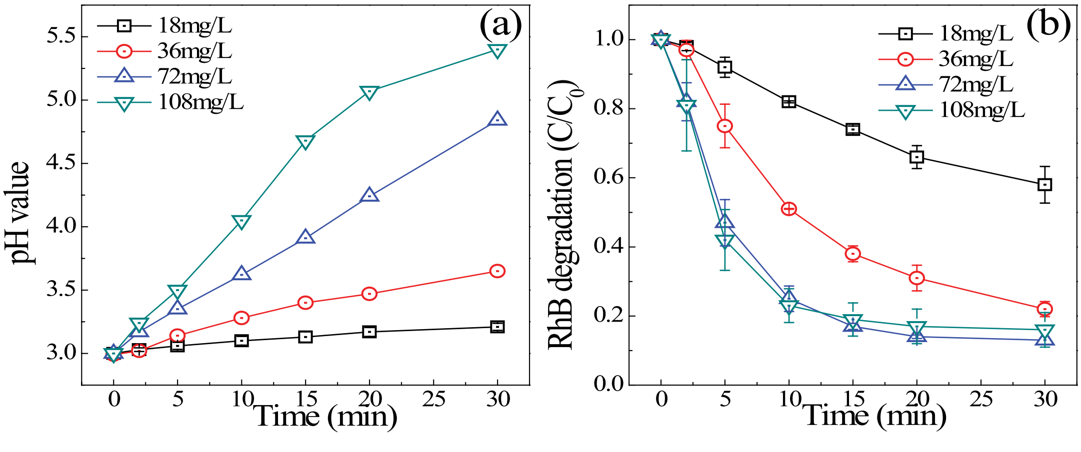

Fig. 3. (a) Real-time pH changes on different Cu_2O dosage in system and (b) Effect of Cu_2O dosage (in copper) on RhB removal in reaction solution ($[RhB]_0$ = 15 mg L^{-1}, pH_0 = 3.0).

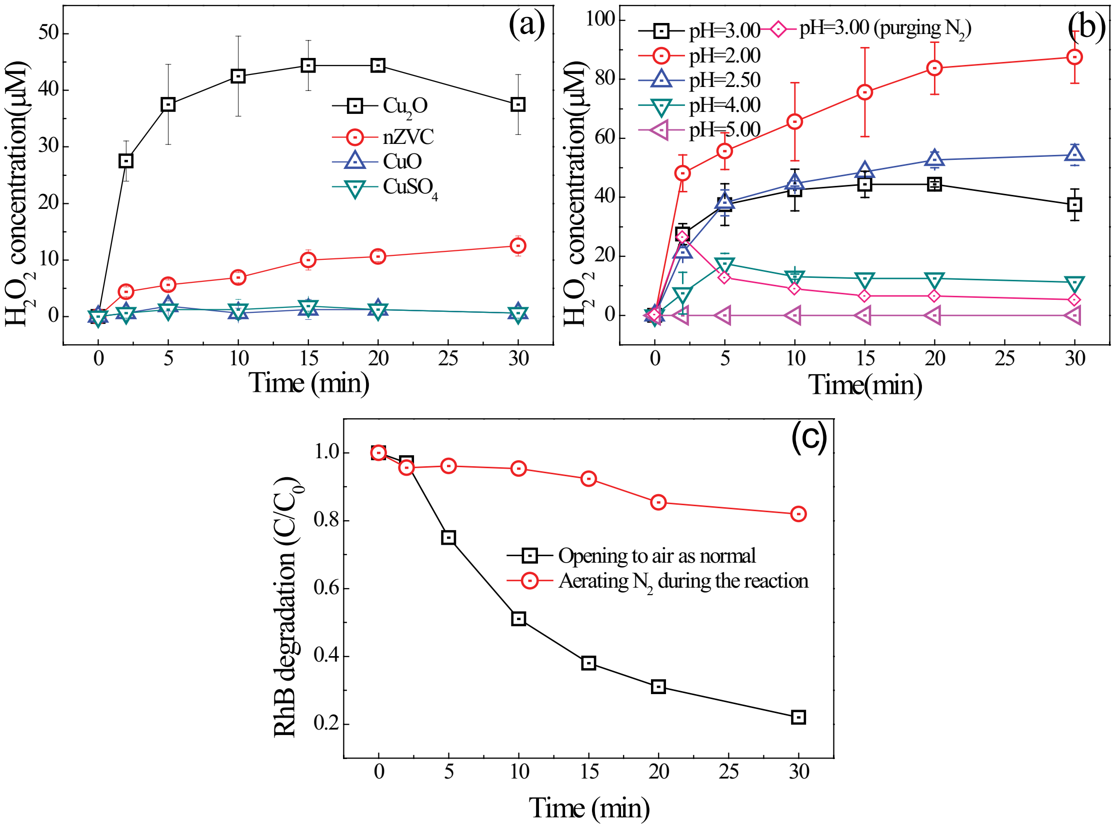

Fig. 5. (a) Concentration of in situ generated H_2O_2 during the reaction in the presence of different copper species at pH = 3.0, (b) concentration of in situ generated H_2O_2 during the reaction at different initial pH and purging N_2 at pH = 3.0 and (c) degradation of RhB in Cu_2O acidic system in normal and purging N_2 condition. ($[RhB]_0$ = 15 mg L^{-1}, $[copper]_0$ = 0.50 mM).

to investigate the production of H_2O_2 in more detail in the Cu_2O/acid process, the concentration of in situ generated H_2O_2 and the total concentration of copper (TCu) during the reaction at different initial pH were detected. As shown in Figs. 5b and S1a, with the initial pH value in the system decreasing from 5.0 to 2.0, the concentration of in situ generated H_2O_2 and TCu increased, and no cuprous ions in the process were detected. Specifically, at the initial pH = 2.0, the concentration of H_2O_2 reached 87.5 μM, and the TCu reached 53.28 μM, while at the initial pH = 3.0, it was 37.5 and 30.96 μM, respectively. Nonetheless, Fig. 2 shows that the degradation of RhB was better than for pH = 2.0 with the pH = 3.0. This results from, as discussed in section 3.2, H_2O_2 would be more stable at pH < 3.0. In addition, it's worth noting that after 20 min of reaction, the concentration of in situ formed H_2O_2 decreased slightly at initial pH = 3.0. This maybe was the result of the reduction of H_2O_2 production and being more effectively decomposed into $^{\bullet}OH$, which is a main kind of reactive radical for degrading RhB in Cu_2O/acid system. Thus, from Figs. 5b and S1a it is clear that the production of hydrogen peroxide is accompanied by the dissolution of cuprous oxide. More precisely, the generation of H_2O_2 requires electrons which can be provided by the process of the corrosion of Cu_2O in an acidic condition. In addition, 36 mg L^{-1} Cu_2O was added to degrade 77.5% RhB (15 mg L^{-1}) in 30 min at an initial pH = 3.0 (Fig. 2). At this dosage, 30.96 μM (1.98 mg L^{-1}) of copper ions were detected (Fig. S1a), but the dissolved Cu^{2+} could be reused by adding Fe^0 [9,18] or reducing agents (RAs) (i.e. hydroxylamine (HA), N-methylhydroxylamine, L-ascorbic acid, p-hydroquinone, and sodium nitrite) [19], and be removed by adsorbents (i.e., carbon nanotubes, zeolite, graphene oxide, fly ash and activated carbon) [20–23].

Furthermore, to prove molecular oxygen is also needed as an electron acceptor to form H_2O_2, the accumulation of H_2O_2 and TCu, and the degradation of RhB were measured in a nitrogen-equilibrated suspension and compared with the condition of an oxygen-equilibrated suspension (open to the atmosphere). N_2 gas was aerated for 15 min before the reaction with unceasing purging during the whole process. From Fig. 5b, 44.4 μM H_2O_2 was generated rapidly at the initial pH 3.0 within the first 15 min and then reduced to 37.5 μM at 30 min. On the contrary, negligible generation of H_2O_2 in the nitrogen-equilibrated suspension were found, and only a small amount of H_2O_2 was formed at first, which may be related to the adsorbed oxygen on the surface of the catalyst [24]. Moreover, 77.5% RhB was effectively removed in the Cu_2O/acid system at initial pH 3.0, when open to the air as normal. Conversely, there was little RhB removed when aerating N_2 during the reaction, and only a small amount of H_2O_2 was generated in 30 min (Figs. 5b and c). In addition, as can be seen in Fig. S1b, 21.2 μM Cu^{2+} was produced within 30 min under the nitrogen-equilibrated condition, however, 31.0 μM Cu^{2+} was found in the oxygen-equilibrated suspension. Thus,

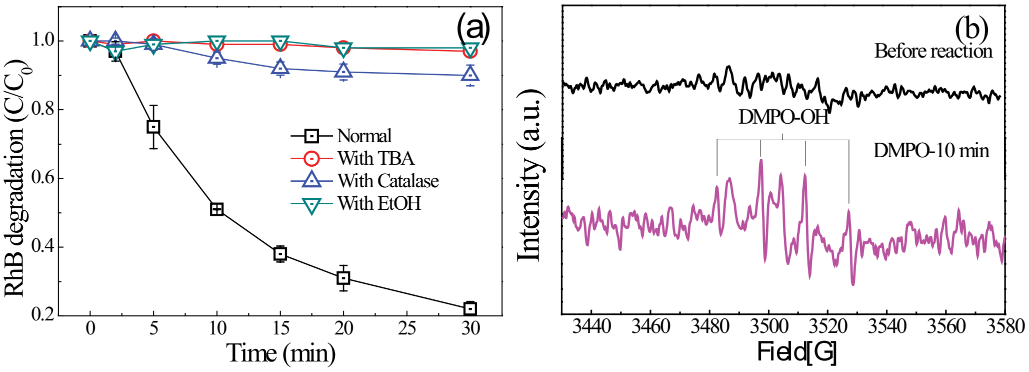

Fig. 6. (a) Effect of the addition of TBA and EtOH ($^{\bullet}$OH scavenger), catalase (decomposing H_2O_2) on the degradation of RhB ($[Cu_2O]_0 = 36$ mg L^{-1}, $[TBA]_0 = 150$ mg L^{-1}, $[EtOH]_0 = 200$ mg L^{-1}, $[Catalase]_0 = 200$ mg L^{-1}, $pH_0 = 3.0$]) and (b) EPR spectra of DMPO-OH adduct. ($[RhB]_0 = 15$ mg L^{-1}, $[Cu_2O]_0 = 1,000$ mg L^{-1}, $[DMPO]_0 = 2$ mM, $pH_0 = 3.0$).

the corrosion of Cu_2O has two possible pathways: release of Cu^{2+} by H^+ via Eq. (2), and release of Cu^{2+} by dissolved oxygen via Eq. (3).

$$Cu_2O + \frac{1}{2}O_2 + 2H_2O \rightarrow 2Cu^{2+} + 4OH^- \qquad (3)$$

3.5.2. Generation of $^{\bullet}$OH radical

In ZVMs acidic systems [7,25], H_2O_2 was used as the precursor of $^{\bullet}$OH which was believed to be the reactive oxygen species (ROS) responsible for the degradation of organic pollutants. In addition, following the conclusion of previous research [26], catalase, which is an important enzyme in all the tissues of all known animals, can catalyze the decomposition of H_2O_2 into water molecules and molecular oxygen. Furthermore, researchers [27] have demonstrated that alcohols containing α-H, such as ethanol (EtOH), can scavenge the $^{\bullet}$OH, whose reaction rate constant is 1.2×10^9–2.8×10^9 M^{-1} s^{-1}, and even without α-H, tert-butanol (TBA) can also effectively react with $^{\bullet}$OH whose reaction rate constant is 3.8×10^8–7.6×10^8 M^{-1} s^{-1}. Thus, in order to investigate the speculation that the production of $^{\bullet}$OH, as ROS generated by H_2O_2 involved in the Cu_2O/acid system, 200 mg L^{-1} catalase, 150 mg L^{-1} TBA and 200 mg L^{-1} EtOH were spiked into the reaction solution.

The results are shown in Fig. 6a, where the process of removing RhB was notably hindered in the addition of catalase, TBA and EtOH. For instance, about 77.5% RhB was degraded at 30 min by the Cu_2O/acid process. On the contrary, only 7.76% RhB was removed with the addition of 200 mg L^{-1} catalase, and there was no obvious degradation of RhB in the presence of TBA and EtOH. As shown in Fig. S2, after adding TBA, catalase and EtOH in the Cu_2O/acid process, TCu was not much different from normal condition. This indicates that the presence of scavengers did not affect the corrosion of Cu_2O, but reacted with the H_2O_2 or $^{\bullet}$OH generated in the process. Therefore, through the inhibited process of degrading RhB, it confirms that H_2O_2 is the crucial intermediate for producing $^{\bullet}$OH, which is responsible for degrading RhB in the Cu_2O/acid system.

In order to further investigate the ROS involved in the system, EPR spectroscopy was undertaken on 5,5-dimethyl-1-pyrrpline-N-oxide (DMPO) as the spin trap agent. Previous study [28] concluded that DMPO is a good probe for $^{\bullet}$OH, because the reaction forms DMPO-OH adducts which can be discerned by determination in EPR. Thus, two samples were prepared (1) adding DMPO but without Cu_2O in the system, (2) adding both DMPO and Cu_2O and reacting for 10 min. As the results show in Fig. 6b, no peaks were identified in the EPR spectrum for single DMPO without Cu_2O dosing. However, when both Cu_2O and DMPO were added in the process, DMPO-OH adducts were observed. To be specific, at 10 min, a four-line EPR spectrum, in which ratio of the four peaks in a typical EPR spectrum for $^{\bullet}$OH was 1:2:2:1, was observed suggesting that $^{\bullet}$OH was formed in the Cu_2O/acid system. A relatively weak EPR spectrum was also identified in a bimetallic Fe-Al/acid system [29] due to the generation of $^{\bullet}$OH from the corrosion of Fe/Al in the acidic aqueous solution. These results further demonstrate the generation of $^{\bullet}$OH in Cu_2O/acid system.

$$\equiv Cu^+ + H_2O_2 \rightarrow Cu^{2+} + {}^{\bullet}OH + OH^- \qquad (4)$$

According to the above analysis, the mechanism of oxidative degradation of organics via the Cu_2O/acid system is proposed as follows. Firstly, the reaction should start with the corrosive dissolution of Cu_2O through two pathways of release for Cu^{2+} by the H^+ and the dissolved oxygen, in other words, Cu_2O is the electron donor to provide one electron. Then molecular oxygen, as the electron acceptor combining with H^+ in the aqueous solution, is converted into H_2O_2. Whereafter, $^{\bullet}$OH is generated via the reduction of Cu_2O with the in situ formed H_2O_2. Besides, the formation of $^{\bullet}$OH via a Fenton-like reaction between transition metal oxides or ions and H_2O_2 has been reported [30–32]. Specifically, in the Cu_2O/acid system, $^{\bullet}$OH was generated via a Fenton-like reaction between Cu_2O and H_2O_2 (Eq. 4). Based on the discussion above, a feasible mechanism for the degradation of organic pollutants for the Cu_2O acidic process is proposed in Fig. 7.

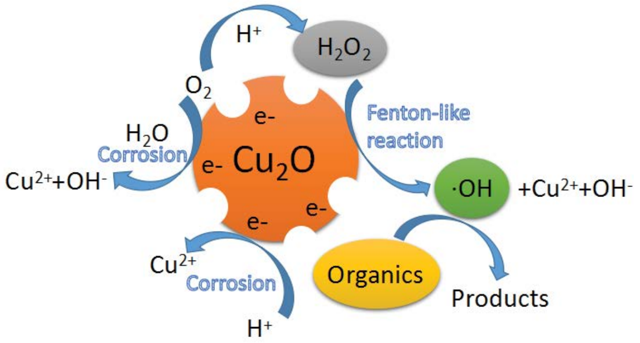

Fig. 7. Proposed mechanism of Cu_2O/acid system.

4. Conclusions

In this study, Cu_2O was synthesized via a precipitation method, and the Cu_2O acidic system showed a more powerful capacity for oxidative degradation of organic pollutants and more generation of H_2O_2 compared to the ZVC/acid system. This shows that Cu_2O can not only be used as a recognized good photocatalyst [33,34], but also provide excellent degradation of organics in the absence of light. In addition, the system had an optimum condition for degrading RhB at initial pH 3.0 and negligible oxidative degradation at initial pH > 4. Moreover, with the increase of Cu_2O dosage, the degradation efficiency did not show an obvious increase due to the superfluous Cu_2O loadings that made the pH in the system rapidly increase to 4.0. The mechanism investigation showed that the degradation of RhB by the Cu_2O/acid system started with the corrosion of Cu_2O, as the electron donor, by H^+ and molecular oxygen. Meanwhile, molecular oxygen, as the electron acceptor, combined with H^+ to produce H_2O_2. Then the $^\bullet OH$ radical, mainly responsible for the degradation of RhB, was generated via the heterogeneous Fenton-like reaction between in situ formed H_2O_2 with Cu_2O. In addition, the production of $^\bullet OH$ was identified through adding $^\bullet OH$ radical scavengers (TBA and EtOH), catalase and conducting EPR monitoring experiments with DMPO. In general, this study describes a novel application that has high potential for degrading refractory organic matters in the treatment of wastewater.

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References

[1] M. Zhang, J.L. Gong, G.M. Zeng, P. Zhang, B. Song, W.C. Cao, H.Y. Liu, S.Y. Huan, Enhanced degradation performance of organic dyes removal by bismuth vanadate-reduced graphene oxide composites under visible light radiation, Colloid Surf., A, 559 (2018) 169–183.

[2] A.A. Isari, A. Payan, M. Fattahi, S. Jorfi, B. Kakavandi, Photocatalytic degradation of rhodamine B and real textile wastewater using Fe-doped TiO_2 anchored on reduced graphene oxide (Fe-TiO_2/rGO): characterization and feasibility, mechanism and pathway studies, Appl. Surf. Sci., 462 (2018) 549–564.

[3] A. Asghar, A.A.A. Raman, M.A.W.D. Wan, Advanced oxidation processes for in-situ production of hydrogen peroxide/hydroxyl radical for textile wastewater treatment: a review, J. Cleaner Prod., 87 (2015) 826–838.

[4] P. Marcinowski, E. Zapalowska, J. Maksymiec, J. Naumczyk, J. Bogacki, Hydraulic fracturing flow-back fluid treatment by ZVI/H_2O_2 process, Desal. Wat. Treat., 129 (2018) 177–184.

[5] A. Ikhlaq, M. Kazmi, F. Javed, H. Fatima, A. Akram, S. Asif, UV/H_2O_2/iron loaded rice husk ash based advanced oxidation process for the removal of safranin from wastewater, Desal. Wat. Treat., 126 (2018) 306–313.

[6] W. Liu, H. Zhang, B. Cao, K. Lin, J. Gan, Oxidative removal of bisphenol A using zero valent aluminum-acid system, Water Res., 45 (2011) 1872–1878.

[7] G. Wen, S.J. Wang, J. Ma, T.L. Huang, Z.Q. Liu, L. Zhao, J.L. Xu, Oxidative degradation of organic pollutants in aqueous solution using zero valent copper under aerobic atmosphere condition, J. Hazard. Mater., 275 (2014) 193–199.

[8] A.D. Bokare, W. Choi, Zero-valent aluminum for oxidative degradation of aqueous organic pollutants, Environ. Sci. Technol., 43 (2009) 7130–7135.

[9] R. Yamaguchi, S. Kurosu, M. Suzuki, Y. Kawase, Hydroxyl radical generation by zero-valent iron/Cu (ZVI/Cu) bimetallic catalyst in wastewater treatment: heterogeneous Fenton/Fenton-like reactions by Fenton reagents formed in-situ under oxic conditions, Chem. Eng. J., 334 (2018) 1537–1549.

[10] C.R. Keenan, D.L. Sedlak, Factors affecting the yield of oxidants from the reaction of nanoparticulate zero-valent iron and oxygen, Environ. Sci. Technol., 42 (2008) 1262–1267.

[11] C.E. Noradoun, I.F. Cheng, EDTA degradation induced by oxygen activation in a zerovalent iron/air/water system, Environ. Sci. Technol., 39 (2005) 7158–7163.

[12] P. Zhou, J. Zhang, Y. Zhang, G. Zhang, W. Li, C. Wei, J. Liang, Y. Liu, S. Shu, Degradation of 2,4-dichlorophenol by activating persulfate and peroxomonosulfate using micron or nanoscale zero-valent copper, J. Hazard. Mater., 344 (2017) 1209–1219.

[13] C.H. Kuo, C.H. Chen, M. Huang, Seed-mediated synthesis of monodispersed Cu_2O nanocubes with five different size ranges from 40 to 420 nm, Adv. Funct. Mater., 17 (2010) 3773–3780.

[14] C.H.B. Ng, W.Y. Fan, Shape evolution of Cu_2O nanostructures via kinetic and thermodynamic controlled growth, J. Phys. Chem. B, 110 (2006) 20801–20807.

[15] N.K. Daud, B.H. Hameed, Acid Red 1 dye decolorization by heterogeneous Fenton-like reaction using Fe/kaolin catalyst, Desalination, 269 (2011) 291–293.

[16] C.L. Hsueh, Y.H. Huang, C.C. Wang, C.Y. Chen, Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system, Chemosphere, 58 (2005) 1409–1414.

[17] G.D. Fang, D.M. Zhou, D.D. Dionysiou, Superoxide mediated production of hydroxyl radicals by magnetite nanoparticles: demonstration in the degradation of 2-chlorobiphenyl, J. Hazard. Mater., 250 (2013) 68–75.

[18] Q. Ji, J. Li, Z. Xiong, B. Lai, Enhanced reactivity of microscale Fe/Cu bimetallic particles (mFe/Cu) with persulfate (PS) for p-nitrophenol (PNP) removal in aqueous solution, Chemosphere, 172 (2017) 10–20.

[19] W. Li, P. Zhou, J. Zhang, Y. Zhang, G. Zhang, Y. Liu, X. Cheng, Generation of reactive oxygen species by promoting the Cu(II)/Cu(I) redox cycle with reducing agents in aerobic aqueous solution, Water Sci. Technol., 78 (2018) 1390–1399.

[20] B. Hayati, A. Maleki, F. Najafi, H. Daraei, F. Gharibi, G. Mckay, Super high removal capacities of heavy metals (Pb^{2+} and Cu^{2+}) using CNT dendrimer, J. Hazard. Mater., 336 (2017) 146–157.

[21] X. Lu, W. Fei, X. Li, K. Shih, E.Y. Zeng, Adsorption and thermal stabilization of Pb^{2+} and Cu^{2+} by zeolite, Ind. Eng. Chem. Res., 55 (2016) 8767–8773.

[22] E. Pehlivan, S. Cetin, Application of fly ash and activated carbon in the removal of Cu^{2+} and Ni^{2+} ions from aqueous solutions, Energy Source, 30 (2008) 1153–1165.

[23] S.T. Yang, Y. Chang, H. Wang, G. Liu, C. Sheng, Y. Wang, Y. Liu, A. Cao, Folding/aggregation of graphene oxide and its application in Cu^{2+} removal, J. Colloid Interface Sci., 351 (2010) 122–127.

[24] E.A. Lewis, W.B. Tolman, Reactivity of dioxygen-copper systems, Cheminform, 104 (2004) 1047–1076.

[25] M. Stieber, A. Putschew, M. Jekel, Treatment of pharmaceuticals and diagnostic agents using zero-valent iron--kinetic studies and assessment of transformation products assay, Environ. Sci. Technol., 45 (2011) 4944.

[26] P. Chelikani, I. Fita, P.C. Loewen, Diversity of structures and properties among catalases, Cell. Mol. Life Sci., 61 (2004) 192–208.

[27] P. Neta, R.E. Huie, A.B. Ross, Rate Constants for reactions of inorganic radicals in aqueous solution, J. Phys. Chem. Ref. Data, 17 (2009) 1027–1284.

[28] C. Tan, N. Gao, Y. Deng, J. Deng, S. Zhou, J. Li, X. Xin, Radical induced degradation of acetaminophen with Fe_3O_4 magnetic nanoparticles as heterogeneous activator of peroxymonosulfate, J. Hazard. Mater., 276 (2014) 452–460.

[29] J. Fan, H. Wang, L. Ma, Oxalate-assisted oxidative degradation of 4-chlorophenol in a bimetallic, zero-valent iron-aluminum/air/water system, Environ. Sci. Pollut. Res., 23 (2016) 16686–16698.

[30] F. Duarte, F.J. Maldonado-Hódar, A.F. Pérez-Cadenas, L.M. Madeira, Fenton-like degradation of azo-dye Orange II catalyzed by transition metals on carbon aerogels, Appl. Catal., B, 85 (2009) 139–147.

[31] M. Masarwa, H. Cohen, D. Meyerstein, D.L. Hickman, A. Bakac, J.H. Espenson, Reactions of low-valent transition-metal complexes with hydrogen peroxide. Are they Fenton-like or not? 1. The case of Cu^{+}_{aq} and Cr^{2+}_{aq}, J. Am. Chem. Soc., 110 (1988) 4293–4297.

[32] D.A. Nichela, A.M. Berkovic, M.R. Costante, M.P. Juliarena, F.S.G. Einschlag, Nitrobenzene degradation in Fenton-like systems using Cu(II) as catalyst. Comparison between Cu(II)- and Fe(III)-based systems, Chem. Eng. J., 228 (2013) 1148–1157.

[33] B.F. Sun, H.L. Li, X.Y. Li, X.W. Liu, C.H. Zhang, H.Y. Xu, X.S. Zhao, Degradation of organic dyes over Fenton-Like Cu_2O-Cu/C catalysts, Ind. Eng. Chem. Res., 57 (2018) 14011–14021.

[34] C.Y. Kuo, C.H. Wu, J.T. Wu, Y.C. Chen, Preparation of immobilized Cu_2O using microwave irradiation and its catalytic activity for bisphenol A: comparisons of Cu_2O/H_2O_2 and visible-light/Cu_2O/H_2O_2 systems, Water Sci. Technol., 70 (2014) 1428–1433.

Supporting information

S1. Method of TCu concentration detection

The total concentration of dissolved copper (TCu) was determined using a UV-vis spectrometer (Mapada UV-1800). Samples (5 mL) were withdrawn from the reaction solution at specific time intervals after filtration with a glass fiber membrane (pore size: 0.45 μm). The 1 mL filtered sample, 0.5 mL 0.2 M phosphoric acid-phosphate buffer, 0.5 mL 10 mM NP, 0.5 mL 0.1 M L-ascorbic acid, and 7.5 mL Milli-Q water (18.25 MΩ cm) were mixed to create Cu^{+}-NP complex solution. The concentration of TCu was detected by a UV-vis spectrometer at 454 nm.

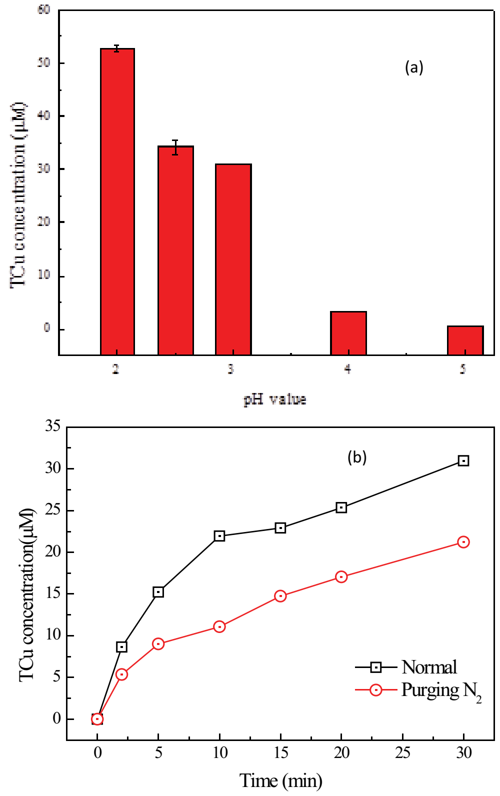

Fig. S1. (a) TCu concentration at different initial pH after reacted for 30 min and (b) TCu concentration in Cu_2O acidic system in normal and purging N_2 condition. ($[RhB]_0$ = 15 mg L^{-1}, $[Cu_2O]_0$ = 36 mg L^{-1})

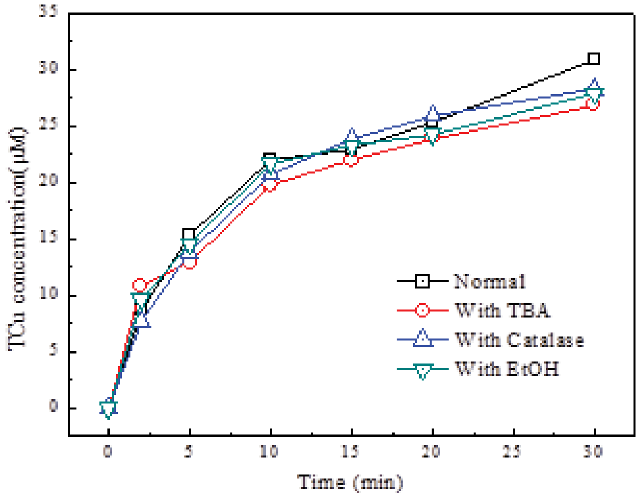

Fig. S2. Effect of TBA and EtOH (•OH scavenger), catalase (decomposing H_2O_2) on TCu concentration in Cu_2O acidic system, under aerobic atmosphere condition. ($[RhB]_0$ = 15 mg L^{-1}, $[Cu_2O]_0$ = 36 mg L^{-1}, pH_0 = 3.0, [TBA] = 20 mM, [catalase] = 200 mg L^{-1}, [EtOH] = 150 mg L^{-1})