



Copper–catalyzed activation of molecular oxygen for oxidative destruction of acetaminophen: The mechanism and superoxide-mediated cycling of copper species



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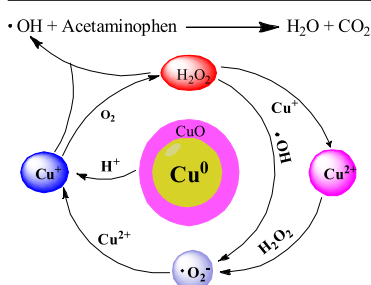
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HIGHLIGHTS

- The ZVC/air system was effective in degradation of ACT.
- The Cu^+ was responsible for activation of O_2 to produce H_2O_2 .
- The $\cdot\text{O}_2^-$ was formed via the decomposition of H_2O_2 in the ZVC/air system.
- It was proved that the $\cdot\text{O}_2^-$ mediated the copper cycling by reduction of Cu^{2+} to Cu^+ .

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the commercial zero-valent copper (ZVC) was investigated to activate the molecular oxygen (O_2) for the degradation of acetaminophen (ACT). 50 mg/L ACT could be completely decomposed within 4 h in the ZVC/air system at initial pH 3.0. The H_2O_2 , hydroxyl radical ($\cdot\text{OH}$) and superoxide anion radical ($\cdot\text{O}_2^-$) were identified as the main reactive oxygen species (ROSS) generated in the above reaction; however, only $\cdot\text{OH}$ caused the decomposition and mineralization of ACT in the copper-catalyzed O_2 activation process. In addition, the in-situ generated Cu^+ from ZVC dissolution not only activated O_2 to produce H_2O_2 , but also initiated the decomposition of H_2O_2 to generate $\cdot\text{OH}$. Meanwhile, the H_2O_2 could also be partly decomposed into $\cdot\text{O}_2^-$, which served as a mediator for copper cycling by reduction of Cu^{2+} to Cu^+ in the ZVC/air system. Therefore, $\cdot\text{OH}$ could be continuously generated; and then ACT was effectively degraded. Additionally, the effect of solution pH and the dosage of ZVC were also investigated. As a result, this study indicated the key behavior of the $\cdot\text{O}_2^-$ during Cu–catalyzed activation of O_2 , which further improved the understanding of O_2 activation mechanism by zero-valent metals.

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1. Introduction

The development of green technologies to dispose organic pollutants is one of the most important goals in oxidation chemistry (Piera and Bäckvall, 2008). Molecular oxygen is a cheap, ecologically benign and most readily available oxidant. Thus,

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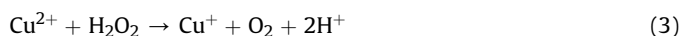
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oxidation of the organic contaminants using molecular oxygen is particularly attractive (Joo and Cheng, 2006; Keenan and Sedlak, 2008). However, the direct oxidation of the organic pollutants by molecular oxygen is often kinetically unfavored, due to both the weak oxidation capacity and quite stable nature of the ground triplet state of molecular oxygen under ambient conditions (Xu et al., 2013).

On the other hand, previous studies have also confirmed the zero-valent metals, including zero-valent iron (ZVI) (Ai et al., 2013; Joo and Cheng, 2006; Keenan and Sedlak, 2008), zero-valent aluminium (ZVAL) (Liu et al., 2011, 2014) and zero-valent copper (ZVC) (Dong et al., 2014; Wen et al., 2014), could activate molecular oxygen to generate more powerful reactive oxygen species (ROSSs), such as hydrogen peroxide (H_2O_2), superoxide radical anion ($\cdot\text{O}_2^-$) and hydroxyl radical ($\cdot\text{OH}$). Those ROSSs could effectively degrade many organic contaminants. For example, Waite's group reported that the ZVI/ O_2 could effectively degraded carbothiolate herbicide and molinate at initial pH of 4–8.1 (Joo et al., 2004). Similar to ZVI, the ZVAL/ O_2 was also able to remove many organic pollutants at initial pH < 4.0 (Liu et al., 2014). Compared with ZVI and ZVAL, the ZVC was seldom studied for using as an O_2 -activator to remove organic pollutants, so the mechanism underlying was still less understood. Recently, Dong et al (Dong et al., 2014), found that the nanoscale ZVC(nZVC)/air was effective in degradation of azo contaminants at neutral pH, mainly due to the breaking of the $-\text{N}=\text{N}-$ bond of the azo compound via the Cu(I)-catalyzed sandmeyer reaction. However, their nZVC/air system could not degrade azo free contaminants.

In addition, studies focusing on the potential cytotoxicity and genotoxicity of copper have also attracted particular interest (Hu et al., 2016; Lytle and Liggett, 2016; Wang et al., 2015). Generally, the toxicity of copper is often explained by generation of harmful ROSSs as a result of the transformation between its oxidation states (including Cu^0 , Cu^+ and Cu^{2+}) (Adam et al., 2015; Meng et al., 2016). For example, the released cuprous copper (Cu^+) from the dissolution of Cu^0 can be quickly oxidized to cupric copper (Cu^{2+}) with the concomitant generation of H_2O_2 , which is the precursor of $\cdot\text{OH}$ that can damage cells via non-selective oxidation of proteins (Eq. (1)) (Pham and Waite, 2014). While, Cu^{2+} can also be reduced to Cu^+ in sunlit surface waters by reaction with photo-generated ROS (H_2O_2 and/or $\cdot\text{O}_2^-$) (Eqs. (2) and (3)) (Buerge-Weirich and Sulzberger, 2004; Pham et al., 2013). Because ROSSs differed markedly with respect to their oxidizing/reducing activities, identifying the kinds of ROSSs generated during the cycling between the different copper species was important to understand its toxicity. Although a large number of studies on copper have been reported (Awual et al., 2016; Bang et al., 2016; Kim and Metcalfe, 2007; Xu et al., 2013), none of those works have convincingly elucidated the mechanism and pathway of generating the ROSSs. Therefore, there is need for a systematic study of the nature of the oxidant formed and the transformations occurring between the various species present.



In this study, we investigated the ability of the commercial ZVC powder to activate the molecular oxygen for the degradation of acetaminophen (ACT), one of the mostly used drugs detected in water. We identified the ROSSs generated during this process and evaluated the roles of different ROSSs played in the degradation of ACT. This studies indicated the key behavior of the $\cdot\text{O}_2^-$ during the cycling of copper species, which further improve the understanding

in the toxicity of copper in natural waters and environments of significance to human health.

2. Materials and methods

2.1. Materials

Copper powder (>99.9%), CuCl ($\geq 99.95\%$), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (99.9%), NaOH, HCl (36–38%), H_2O_2 (30%), ethylenediamine and ACT ($\geq 99.0\%$) were analytical-grade and purchased from Aladdin, Inc., China. Methanol, *tert*-butyl alcohol (TBA) and ethylacetate were HPLC-grade and acquired from Sinopharm Chemical Reagent Co., Ltd, China. Horseradish peroxidase (POD, ≥ 300 units/mg), 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), Xanthine, *N,N*-Diethyl-*p*-phenylenediamine sulfate (DPD, 98.5%) and Superoxide Dismutase (SOD) were purchased from J & K Chemical Technology. Xanthine Oxidase, *N,O*-Bis(trimethylsilyl)trifluoroacetamide/Trimethyl chlorosilane (BSTFA/TMCS, 99:1, *v/v*) and Bathocuproine sulfonate disodium salt hydrate (97%) were obtained from Sigma-Aldrich. Deionized water was produced from a Millipore-Q system with a resistance of 18.2 M Ω and used throughout the experiments.

2.2. Aerobic degradation of ACT

Experiments were performed in the 250 mL glass beakers equipped with magnetic stirrer at room temperature ($20 \pm 2^\circ\text{C}$). A 100 mL ACT solution with a concentration of 50 mg/L was oxygen-saturated through continuous stirring for 30 min before reaction. In addition, prior to reaction, desired amount of ZVC was washed in 100 mL of HCl solution (pH 1.0) for 5 min and rinsed three times with deionized water. Without drying, the washed ZVC particles were added to the oxygen-saturated ACT solution. The aqueous pH was adjusted using NaOH or HCl. The beakers were open to the air to prevent the depletion of dissolved oxygen during the reaction. At the given reaction time intervals, samples were taken out using a 2.5 mL syringe and filtered through a 0.22 μm Suporfone film to remove the solid particles. The concentration of the ACT and the content of the total organic carbon (TOC) were measured immediately with a high performance liquid chromatography (HPLC) system (Agilent 1260, USA) and a TOC analyzer (TOC-L CPH, Shimadzu), respectively. Data were plotted as mean of duplicates, and error bars indicated deviation from the mean.

2.3. Analytical method

The concentration of ACT was measured using a HPLC equipped with a Diode Array Detector (243 nm) (Moctezuma et al., 2012) and a reversed phase ZORBAX Eclipse XDB-C18 column (4.6 mm \times 150 mm, 5 μm). The eluent consisted of 30/70 (*v/v*) of methanol/water with a flow rate of 1.0 mL min/L at 40 $^\circ\text{C}$. Hydrogen peroxide was analyzed using the DPD-POD method developed by Bader et al. (Bader et al., 1988). Typically, 0.4 mL of phosphate buffer solution (pH 6) and 0.1 mL of 0.01 mol/L bipyridine solution were premixed in a quartz cell, followed by the addition of 2 mL of the sample, and 30 μL of 1% DPD reagent in 0.1 mol/L H_2SO_4 , and 30 μL of POD reagent successively. The absorbance at 551 nm was measured after the addition of the POD. Formation of Cu^+ was determined by spectrophotometric measurement of the Cu^+ complex with bathocuproine according to Moffett et al. (Moffett et al., 1985). After the sample was taken at the predetermined time, 20 mM ethylenediamine was added before the addition of bathocuproine as a masking ligand to prevent the interference of Cu^{2+} . The orange complex of Cu^+ and bathocuproine was measured on a UV-Vis spectrophotometer at 484 nm immediately. Total copper ion (TCu) was quantified by the Inductively Coupled Plasma (ICP, OPTIMA

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