



# Activation of hydrogen peroxide during the corrosion of nanoscale zero valent copper in acidic solution



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## ABSTRACT

Activation of hydrogen peroxide ( $H_2O_2$ ) and its mechanism were investigated during corrosion of nanoscale zero valent copper (nZVC) in acidic aqueous solution. As the radical probe compound, benzoic acid (BA) degradation was completely achieved after 25 min in the nZVC/ $H_2O_2$  system at initial pH 3.0.  $H_2O_2$  can accelerate the corrosion of nZVC to release  $Cu^+$  resulting in the further activation of  $H_2O_2$  via a Fenton-like reaction in acidic aqueous solution. The released  $Cu^+$  during the corrosion of nZVC is the main effective copper species to activate  $H_2O_2$  to produce  $\cdot OH$  in the nZVC/ $H_2O_2$  system. Hydroxyl radical ( $\cdot OH$ ) was verified as the primary reactive oxidant which is responsible for BA degradation in the nZVC/ $H_2O_2$  system owing to the intense inhibition of BA degradation with the addition of excess *tert*-butyl alcohol (TBA). Moreover, acidic aqueous solution facilitates the degradation of BA and optimum initial pH for BA degradation is 3.0. Higher nZVC dosage could enhance the degradation rate of BA. In addition, the present study put forward an interesting idea to make full use of intermediate  $Cu^+$  to activate  $H_2O_2$  during corrosion of nZVC to degrade organic contaminants.

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## 1. Introduction

With the increasing influence of human activities, synthetic organic chemicals were frequently used and released into lakes or rivers that led to the sustained deterioration of water resources. Hence, advanced oxidation processes (AOPs) has fascinate practitioners of water treatment resulting from the generation of highly and unselective oxidizing radicals such as hydroxyl radical ( $\cdot OH$ ) which can effectively degrade or mineralize recalcitrant pollutants [1].

In recent literatures, zero valent metals, which could activate molecular oxygen to induce the generation of reactive oxygen species (ROS), are receiving increasing attention, including nanoscale zero valent iron (nZVI) [2–4] and zero valent aluminium (ZVAL) [5–8]. Such as, Joo and coworkers [3] reported that carbthiolate herbicide, molinate, could be effectively degraded during dissolution of nZVI in acidic aerobic aqueous solution (pH < 4.8) via *in situ* generation of  $H_2O_2$  which subsequent transform into  $\cdot OH$  by Fenton reaction. It is similar to nZVI, the corrosion of ZVAL could induce the simultaneous generation of  $Al^{3+}$  and  $H_2O_2$  resulting from the electron transfer from ZVAL to  $O_2$  in acidic condi-

tions (pH < 4), and showed the observably ability on 4-chlorophenol degradation [7]. All these being showed,  $H_2O_2$  generated by electron transfer from zero valent metals or low valent ions to  $O_2$  is a key intermediate. However, *in situ* generation of  $H_2O_2$  is feeble and could reduce performance efficiency of zero valent metals to activate  $H_2O_2$ .

Moreover, copper, one of the major redox-active transition metals [9], which has been reported to be an activator of  $H_2O_2$  to activate  $H_2O_2$  to produce  $\cdot OH$  via the catalytic redox cycle of  $Cu(II)/Cu(I)$  [10–14]. Nevertheless,  $Cu(I)$  was seldom used to activate  $H_2O_2$  resulting from it is unstable and easily oxidized to  $Cu(II)$  by oxygen or other oxidants in aqueous solutions [15–17]. In order to expand the application of Cu material in Fenton-like system, many researchers have made copper chelated complexes (e.g. Cu-EDTA and  $Cu(OH)PO_4$ ) [18,19], copper electrode-based [20] and copper-metal bimetallic composite catalysts [21] to induce the generation of  $\cdot OH$  which could degrade the organic contaminants in heterogeneous Fenton-like systems. However, the application of Cu materials in homogeneous Fenton-like system was severely limited by the instability of  $Cu^+$ .

Whereas, the current literatures reported that some reducing agents (e.g. L-ascorbic acid and hydroxylamine) could be employed to reduce  $Cu(II)$  into intermediate  $Cu(I)$  to induce the chain reactions of copper resulting in the generation of  $\cdot OH$  via a homogeneous Fenton-like reaction [22–24], which put forward

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that the instantaneous intermediate Cu(I) could be a prominent activator of  $\text{H}_2\text{O}_2$  to induce the generation  $\bullet\text{OH}$ . Moreover, it has been reported recently that the corrosive dissolution of zero valent copper and accompanying reduction of oxygen could induce the simultaneous generation of intermediate Cu(I) [25]. Therefore, it is a potential capacity for nanoscale zero valent copper (nZVC) to release  $\text{Cu}^+$  during the corrosion of nZVC to activate  $\text{H}_2\text{O}_2$  resulting in  $\bullet\text{OH}$  formation to degrade organic contaminants. According to our review, there is no report on the use of  $\text{Cu}^+$  to activate  $\text{H}_2\text{O}_2$  to degrade organic contaminants during nZVC corrosion. Based on the highly reaction rate constant with  $\bullet\text{OH}$  [26], the relatively simple chemical structure, and the stable property with conventional oxidants, benzoic acid (BA) was employed as  $\bullet\text{OH}$  probe in this study [27,28].

The presented work studied the BA degradation efficiency in the nZVC/ $\text{H}_2\text{O}_2$  system and specifically focused on the mechanism of the nZVC/ $\text{H}_2\text{O}_2$  system, identification of primary reactive oxidants, and the effects of initial pH and nZVC dosage.

## 2. Materials and methods

### 2.1. Materials

Nanoscale zero valent copper (nZVC, >99.9%, size: 10–30 nm), zero valent copper (ZVC, >99.9%, average particle size: 5  $\mu\text{m}$ ), and neocuproine hemihydrate (NCP, >98%) were purchased from Aladdin Industrial Corporation. BA ( $\geq 99.5\%$ ), and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  ( $\geq 99.0\%$ ) were supplied by Sigma-Aldrich. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%), *tert*-butyl alcohol (TBA), potassium titanium oxalate, sodium sulfite, sulfuric acid, and sodium hydroxide from Chengdu Kelong chemical reagent factory were of analytic purity. Ammonium acetate and methanol (MA) from Sigma-Aldrich were of HPLC grade. Pure oxygen gas ( $\text{O}_2$ ,  $\geq 99.2\%$ ) and pure nitrogen gas ( $\text{N}_2$ ,  $\geq 99.99\%$ ) were stored in gas cylinders.

### 2.2. Experimental procedure

The activation of  $\text{H}_2\text{O}_2$  by nZVC was carried out at  $12 \pm 1^\circ\text{C}$  with 500 mL glass flask under a constant stirring rate in Milli-Q water (18.25  $\text{M}\Omega\text{cm}$ ). Most of the experiments were operated open to the air. However, for some experiments requiring aerobic or anaerobic aqueous solutions, pure  $\text{O}_2$  or pure  $\text{N}_2$  was bubbled into the reactor for 15 min prior to the initiation of the reaction to investigate the effect of dissolved oxygen (DO). The desired pH value was adjusted by 1 M  $\text{H}_2\text{SO}_4$  and 1 M NaOH. Each reaction was switched on by simultaneous adding the desired dosage of BA, nZVC, and  $\text{H}_2\text{O}_2$ . TBA was beforehand added into the reaction solution to perform the quenching experiment. For some experiments, NCP was used as Cu(I)-chelating to investigate the role of  $\text{Cu}^+$  in the process. After filtration with the glass fiber membrane (pore size: 0.45  $\mu\text{m}$ ), the samples were withdrawn from the reaction solution and simultaneously mixed with a small amount of sodium sulfite (1 M).

### 2.3. Analytical methods

The concentration of BA in the samples was analyzed on reverse-phase HPLC chromatography (Waters, e2695) equipped with a 2489  $\lambda$  UV absorbance detector. The binary phase composition was methanol/0.1% ammonium acetate (30:70, v/v) and detection wavelength was 227 nm for BA. The concentration of  $\text{H}_2\text{O}_2$  in the samples was measured by UV-vis spectrometer (UV-1800, Shanghai MAPADA Instrument Co., Ltd.) at 400 nm after chelated by potassium titanium oxalate. The pH in the aqueous solution was measured by a pH meter (Shanghai Leici Apparatus Fac., PHB-4). Total concentration of dissolved copper (TCu) were measured by a PerkinElmer® PinAAcle 900T flame atomic absorption

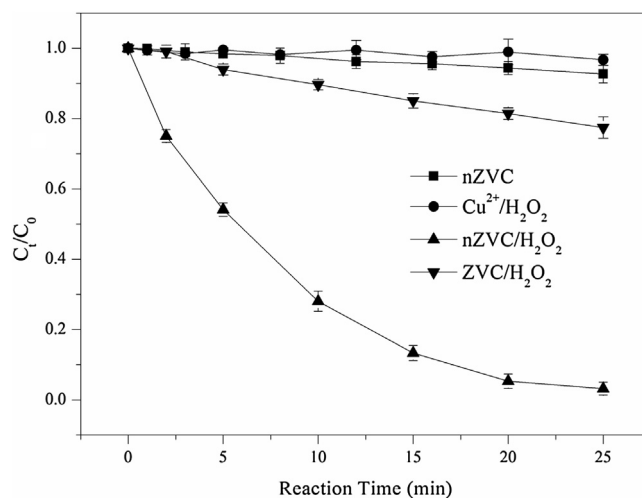


Fig. 1. Degradation of BA in the nZVC/ $\text{H}_2\text{O}_2$  system.  $[\text{BA}]_0 = 20 \mu\text{M}$ ,  $[\text{H}_2\text{O}_2]_0 = 1 \text{mM}$ ,  $[\text{nZVC}]_0 = 40 \text{mg/L}$ ,  $[\text{Cu}^{2+}]_0 = 40 \text{mg/L}$ ,  $\text{pH}_0 = 3.0$ .

spectrometer (FAAS) (Shelton, CT, USA) equipped with two hollow multi-element cathode lamps. Accumulation concentration of  $\text{Cu}^+$  ( $\text{TCu}^+$ ) was determined by spectrophotometric method after chelated with NCP [29].

## 3. Results and discussions

### 3.1. Degradation efficiency of BA in the nZVC/ $\text{H}_2\text{O}_2$ system

Fig. 1 shows the removal of BA in the nZVC/ $\text{H}_2\text{O}_2$  system at acidic aqueous solution (initial pH 3.0). Less than 8% BA was degraded by the nZVC system after 25 min when the dosage of nZVC is 40 mg/L. And 22.5% BA was degraded in the ZVC/ $\text{H}_2\text{O}_2$  system. Surprisingly, the BA was completely degraded in the nZVC/ $\text{H}_2\text{O}_2$  system after 25 min. The above results clearly demonstrated that the nZVC/ $\text{H}_2\text{O}_2$  system is an effective system to degrade BA in acidic aqueous solution. In contrast, no BA removal was observed in the  $\text{Cu}^{2+}/\text{H}_2\text{O}_2$  system with the same dosage of  $\text{Cu}^{2+}$  which can infer that  $\text{Cu}^{2+}$  is not an efficiency activator for  $\text{H}_2\text{O}_2$  in the acidic aqueous solution.

### 3.2. Identification of primary reactive oxidants

In the previous studies [10,11,30], it has been suggested that  $\bullet\text{OH}$  could be formed in the copper-catalyzed decomposition of  $\text{H}_2\text{O}_2$  system. In order to investigate the contribution of  $\bullet\text{OH}$  in the nZVC/ $\text{H}_2\text{O}_2$  system on BA degradation, TBA was introduced into the nZVC/ $\text{H}_2\text{O}_2$  system because of its higher reaction rate constant with  $\bullet\text{OH}$  ( $6.0 \times 10^8 \text{M}^{-1} \text{s}^{-1}$ ) [26]. Fig. 2 shows that 92.0% BA was degraded in the nZVC/ $\text{H}_2\text{O}_2$  system after 25 min. In contrast, less than 14% BA was degraded after 25 min with the addition of 5 mM TBA (the nZVC/ $\text{H}_2\text{O}_2$ -TBA system). Hence, it is followed that  $\bullet\text{OH}$  is the primary reactive oxidant of the nZVC/ $\text{H}_2\text{O}_2$  system.

### 3.3. Effective copper species to activate $\text{H}_2\text{O}_2$

It has been reported that  $\text{Cu}^+$  is an effective activator for  $\text{H}_2\text{O}_2$  to induce the generation of  $\bullet\text{OH}$  by the Fenton-like reaction (Eq. (1)) [10,11,30]. However,  $\text{Cu}^+$  could be rapidly oxidized to  $\text{Cu}^{2+}$  by oxidizing agents in aqueous solution [15–17]. Thus, the variation of  $\text{Cu}^+$  concentration is not detected by spectrophotometric method employing NCP as a chromogenic agent for  $\text{Cu}^+$  (detection limit  $\sim 100 \mu\text{g/L}$ ) [29,30]. Whereas, with the addition of NCP in advance, the accumulation of  $\text{Cu}^+$  ( $\text{TCu}^+$ ) as the reaction proceeded was detected in the nZVC/ $\text{H}_2\text{O}_2$  system at pH 3.0. As shown

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