



pH-Dependent reactivity of oxidants formed by iron and copper-catalyzed decomposition of hydrogen peroxide



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HIGHLIGHTS

- ▶ We examine the nature of oxidants formed by iron and copper-catalyzed Fenton systems.
- ▶ Hydroxyl radical is the dominant oxidant under acidic conditions.
- ▶ High-valent metal complexes are formed under neutral and alkaline conditions.

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ABSTRACT

The decomposition of hydrogen peroxide catalyzed by iron and copper leads to the generation of reactive oxidants capable of oxidizing various organic compounds. However, the specific nature of the reactive oxidants is still unclear, with evidence suggesting the production of hydroxyl radical or high-valent metal species. To identify the reactive species in the Fenton system, the oxidation of a series of different compounds (phenol, benzoic acid, methanol, Reactive Black 5 and arsenite) was studied for iron- and copper-catalyzed reactions at varying pH values. At lower pH values, more reactive oxidants appear to be formed in both iron and copper-catalyzed systems. The aromatic compounds, phenol and benzoic acid, were not oxidized under neutral or alkaline pH conditions, whereas methanol, Reactive Black 5, and arsenite were oxidized to a different degree, depending on the catalytic system. The oxidants responsible for the oxidation of compounds at neutral and alkaline pH values are likely to be high-valent metal complexes of iron and copper (i.e., ferryl and cupryl ions).

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1. Introduction

For decades, there have been questions about the identity of the reactive oxidant produced when hydrogen peroxide reacts with Fe(II) (Goldstein et al., 1993). According to the literature (Goldstein et al., 1993; Goldstein and Meyerstein, 1999), in the initial stage of the reaction, an inner-sphere complex is formed between Fe(II) and H₂O₂ (i.e., a iron(II)-peroxide complex). This transient species decomposes into reactive oxidants (either ·OH via a one-electron transfer from iron to peroxide ligand, or ferryl ion, Fe(IV) via a two-electron transfer). Since Haber and Weiss (1934) first proposed a mechanism involving ·OH, many researchers have produced evidence supporting the free radical mechanism using electron spin resonance spectroscopy with spin trapping (Yamazaki and Piette, 1991; Yagi et al., 1992, 1993) and analysis of the oxidation products of probe compounds (Halliwell and Gutteridge, 1981; Baker and Gebicki, 1984) to implicate ·OH. Other

groups have hypothesized the production of Fe(IV) from the reaction, using the formation of non-hydroxylated oxidation products and the inability of ·OH scavengers to prevent the oxidation of probe compounds as evidence against the ·OH-based reaction (Sutton, 1989; Goldstein and Czapski, 1990; Goldstein et al., 1993; Bossmann et al., 1998). They also have questioned the methods used for identification of ·OH (Goldstein et al., 1993).

A possible explanation for the discrepancy between the two groups is a shift in the reaction mechanism under different conditions (Hug et al., 2001; Hug and Leupin, 2003; Katsoyiannis et al., 2008). For example, the effect of 2-propanol on arsenite oxidation by the Fenton reaction is pH-dependent. At pH values below 5, 2-propanol can prevent As(III) oxidation while it has little effect under circumneutral conditions, which is consistent with a shift in the oxidant from ·OH to Fe(IV) as pH increases. This assertion was supported by studies on the oxidation of organic compounds by nanoparticulate zero-valent iron (nZVI) in the presence of oxygen (i.e., the Fe⁰/O₂ system) (Keenan and Sedlak, 2008a,b; Lee and Sedlak, 2008) that showed a similar shift from ·OH to Fe(IV) with increasing pH. However, a more recent study that used sulfoxides

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as probes suggested that Fe(IV) was not the oxidant formed at circumneutral pH values (Pang et al., 2011). The failure of sulfoxides to quench the oxidant at neutral pH was suggested as the critical evidence against the production of Fe(IV) because a previous study had documented a rapid reaction between $\text{Fe}=\text{O}^{2+}$ and sulfoxide. The authors suggested that the pH-dependence of the formation of oxidation products and the inability of oxidant scavengers such as 2-propanol to stop As(III) oxidation was attributable to complex reactions involving radical intermediates or surface-bound $\cdot\text{OH}$.

Similarly, there has been a debate on the reactive oxidant for the copper-catalyzed Fenton-like reaction. Several previous studies have produced evidence for and against the formation of $\cdot\text{OH}$, and cupryl ions (Cu(III), analogous to Fe(IV) in the iron-catalyzed reaction) have most often been suggested as the alternative oxidant to $\cdot\text{OH}$ (Johnson et al., 1985, 1988; Eberhardt et al., 1989). However, little is known about whether solution pH can affect the nature of the reactive oxidants formed from the copper-catalyzed system.

The objectives of the present study were to assess changes in nature of oxidants produced in iron- and copper-catalyzed decomposition of H_2O_2 by employing a comprehensive set of probe compounds under similar conditions. For this purpose, a series of experiments were carried out using various probe compounds that exhibit different reactivities with $\cdot\text{OH}$ and high-valent metal species. The iron and copper catalyzed Fenton (-like) systems were evaluated over 3–11, and the effect of oxidant scavengers on reaction kinetics and product yields were examined.

2. Materials and methods

2.1. Reagents

All chemicals were of reagent grade (Sigma–Aldrich) and were used without further purification, except for 2,4-dinitrophenyl hydrazine (DNPH). DNPH was recrystallized three times from acetonitrile prior to use. Deionized water (18 M Ω cm Milli-Q water from a Millipore system) was used to prepare all solutions. Fe(II) and Fe(III) stock solutions (10 mM) were prepared by dissolving ferrous sulfate and ferric perchlorate, respectively, in a 0.1 mM HClO_4 solution. The copper(II) stock solution (10 mM) was prepared from cupric sulfate. As(III) and As(V) stock solutions (10 mM) were prepared by dissolving sodium arsenite and sodium arsenate, respectively, in 10 mM HCl. H_2O_2 was used either neat (30% w/v) or from a 10 mM stock solution. Stock solutions of phenol (10 mM), benzoic acid (10 mM), Reactive Black 5 (RB5) (1 mM) were also prepared and stored at 4 °C until use.

2.2. Experimental setup and procedure

All experiments were performed in 125-mL Pyrex flasks (100 mL reaction solution) at room temperature (20 \pm 2 °C). A pH buffer solution was not used for reactions at pH 3–5. For these experiments, initial pH was adjusted using either 1 N HClO_4 or 1 N NaOH solution. 1 mM Buffer solutions of 2-(N-morpholino)ethanesulfonic acid (MES) and piperazine-N,N'-bis(ethanesulfonic acid) (PIPES) were used for reactions at pH 6 and 7, respectively. Borate buffer (1 mM) was used for reactions at pH 8–10. The experiments were initiated by adding an aliquot of freshly prepared stock solution of H_2O_2 to a pH-adjusted solution containing the probe compound and the metal ion. Reaction samples were withdrawn using a 10-mL glass syringe at predetermined timed intervals, and filtered immediately using a 0.45- μm nylon syringe filter. At least triplicate runs for each experiment were carried out, the mean values and standard deviations of which are presented.

2.3. Oxidation of probe compounds

Phenol, benzoic acid, methanol, RB5, and As(III) were used as probe compounds to assess the reactive oxidants produced. Aromatic compounds such as benzoic acid and phenol are not effectively oxidized by Fe(IV), whereas methanol, As(III), and RB5 are believed to be more susceptible to oxidation by high-valent metal species. More details regarding the selection of probe compounds based on their reactivity with reactive oxidants are described elsewhere (Keenan and Sedlak, 2008a). The oxidative transformation of the probe compounds (for phenol, benzoic acid, and RB5), or the formation of their oxidation products (for benzoic acid, methanol, and As(III)), were measured after a certain time of reaction. 1,10-Phenanthroline and EDTA were used to quench the reactions within the iron and copper-containing reaction vessels, respectively. *tert*-Butanol and dimethyl sulfoxide (DMSO) were tested for their ability to scavenge the reactive oxidants. In all the experiments, iron and copper without H_2O_2 did not lead to significant removal or oxidative transformation of probe compounds. Details regarding the selection of probe compounds and their reactivity with reactive oxidants are described elsewhere (Keenan and Sedlak, 2008a).

2.4. Analytical methods

The concentration of formaldehyde was determined using DNPH derivatization, followed by HPLC and UV absorbance detection at 350 nm (Zhou and Mopper, 1990). Phenol, benzoic acid, and *p*-hydroxybenzoic acid (i.e., the oxidation product of benzoic acid) were analyzed using HPLC with UV detection at both 255 and 270 nm. Separation was performed on a Dionex – Acclaim C18 column (250 \times 4.6 mm, 5 μm), using both an aqueous solution of 10 mM nitric acid, and neat acetonitrile as the eluents, at a flow rate of 1.0 mL min^{-1} . The concentration of arsenate (As(V), the oxidation product of As(III)) was measured spectrophotometrically using the molybdenum blue method (Dhar et al., 2004). RB5 was directly analyzed by measuring visible light absorbance at 597 nm.

3. Results

3.1. Oxidation of phenol and benzoic acid

The oxidative removal of phenol and benzoic acid were examined at pH 3–11 in the Fe(III)/ H_2O_2 , the Fe(II)/ H_2O_2 , and the Cu(II)/ H_2O_2 systems (Fig. 1a and b). In the Fe(III)/ H_2O_2 system, both phenol and benzoic acid were completely oxidized at pH 3, whereas less than 25% loss of the compound was observed at pH values above 3. The Fe(II)/ H_2O_2 system exhibited nearly complete removal of the compound up to pH 5 for both phenol and benzoic acid. In the Cu(II)/ H_2O_2 system, the oxidation of both phenol and benzoic acid exhibited optimal removal at pH values ranging from 5.5 to 6.5. However, the copper-catalyzed reaction removed more than twice as much phenol (75%) as benzoic acid (30%). The production of *p*-hydroxybenzoic acid (pHBA) from the oxidation of benzoic acid followed a similar trend to the removal of benzoic acid in the Fe(III)/ H_2O_2 , the Fe(II)/ H_2O_2 , and the Cu(II)/ H_2O_2 systems (Supplementary material (SM), Fig. SM-1). When hydroxylamine (a Cu(II) reducing agent) was added in the Cu(II)/ H_2O_2 system, the production of pHBA was greatly enhanced with increasing yields with decreasing pH (Fig. SM-1b).

3.2. Oxidation of methanol

The oxidation of methanol by Fe(III)/ H_2O_2 , Fe(II)/ H_2O_2 , and Cu(II)/ H_2O_2 systems was examined by measuring its primary oxidation product, formaldehyde (HCHO) (Fig. 2a). The oxidation of

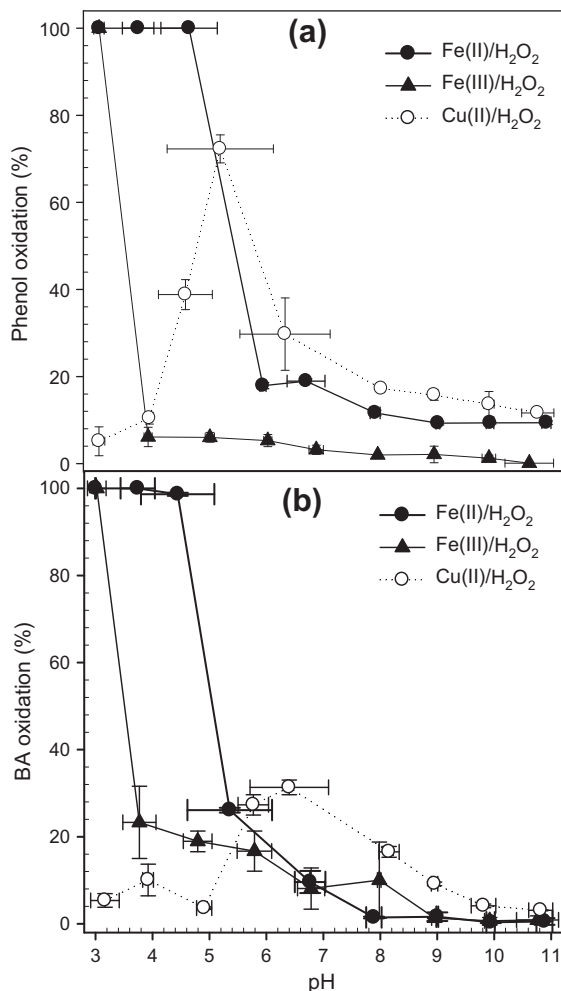


Fig. 1. Oxidative removal of phenol (a) and benzoic acid (b) as a function of pH; $[\text{Fe(II)}]_0 = [\text{Fe(III)}]_0 = [\text{Cu(II)}]_0 = [\text{Phenol}]_0 = [\text{Benzoic acid}]_0 = 0.1 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$; $[\text{Borate buffer}]_0 = 1 \text{ mM}$ at pH 8–10; reaction time = 1 h; and horizontal error bars represent pH variations during the reaction.

methanol exhibited trends that differed from those of phenol and benzoic acid. In the $\text{Fe(III)}/\text{H}_2\text{O}_2$ system, between 10 and 50 μM of HCHO was produced for reactions in the pH range of 3–7. In the $\text{Fe(II)}/\text{H}_2\text{O}_2$ system, the HCHO yield was usually higher, with a distinct maximum around pH 6, which was similar to the trend observed when methanol was oxidized by nZVI in the presence of oxygen (Keenan and Sedlak, 2008a). The yield of HCHO in the $\text{Cu(II)}/\text{H}_2\text{O}_2$ system increased with increasing pH with between 50 and 100 μM produced at pH values above 7.

The production of HCHO from the oxidation of methanol was also quantified in the presence of equal concentrations of DMSO (Fig. 2b). The control experiments performed with DMSO alone did not show any significant production of HCHO (Fig. SM-2). As is apparent from comparison of Fig. 2a and b, the introduction of DMSO inhibited HCHO production under acidic pH conditions more than under circumneutral or alkaline pH conditions.

3.3. Oxidation of RB5 and As(III)

The transformation of RB5 also exhibited a strong pH-dependence (Fig. 3a). As was the cases for phenol and benzoic acid, the iron-catalyzed systems exhibited efficient removal of the compound, with the percent removed decreasing with increasing pH over the range of 3–8. Less than 20% of the RB5 was removed at

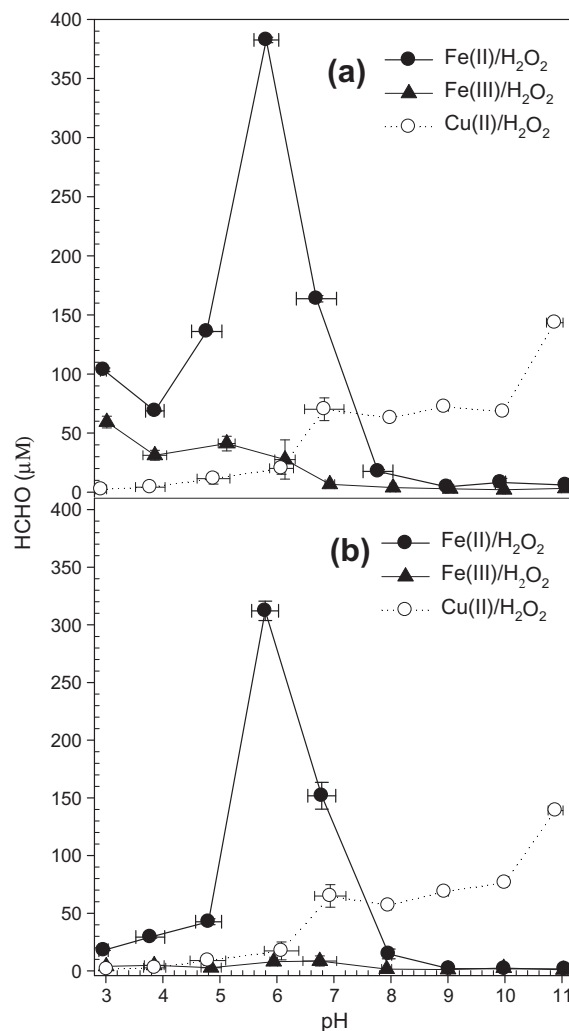


Fig. 2. Formation of HCHO as a function of pH in the absence (a) and the presence (b) of DMSO as a function of pH; $[\text{Fe(II)}]_0 = [\text{Fe(III)}]_0 = [\text{Cu(II)}]_0 = 0.1 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 1 \text{ mM}$; $[\text{Methanol}]_0 = [\text{DMSO}]_0 = 200 \text{ mM}$; $[\text{MES buffer}]_0 = 1 \text{ mM}$ at pH 6; $[\text{PIPES buffer}]_0 = 1 \text{ mM}$ at pH 7; $[\text{Borate buffer}]_0 = 1 \text{ mM}$ at pH 8–10; reaction time = 1 h; and horizontal error bars represent pH variations during the reaction.

pH values between 8 and 10. At pH 11, the removal of the compound increased in both systems, indicating that reactive oxidants are formed under the extreme alkaline conditions. In contrast to the iron-catalyzed systems, the $\text{Cu(II)}/\text{H}_2\text{O}_2$ system exhibited better RB5 removal under neutral and alkaline conditions, which was similar to the trend observed for the oxidation of methanol (Fig. 2a). In the $\text{Cu(II)}/\text{H}_2\text{O}_2$ system, the addition of 100 mM *tert*-butanol lowered the removal of RB5 by less than 20% under neutral and alkaline conditions.

For experiments involving As(III) oxidation (Fig. 3b), a much lower concentration of H_2O_2 (0.2 mM) was used because As(III) is directly oxidized by H_2O_2 , particularly under alkaline conditions. In the $\text{Fe(II)}/\text{H}_2\text{O}_2$ system, the formation of more than 0.04 mM As(V) was observed over the entire pH range. A decrease in As(V) formation was observed at pH values between 8 and 9. The addition of *tert*-butanol significantly inhibited As(III) oxidation under acidic conditions, and the inhibitory effect diminished with increasing pH. The $\text{Fe(III)}/\text{H}_2\text{O}_2$ system exhibited less As(V) formation under acidic conditions and nearly identical behavior with the $\text{Fe(II)}/\text{H}_2\text{O}_2$ system under alkaline conditions. The $\text{Cu(II)}/\text{H}_2\text{O}_2$ system was not effective in oxidizing As(III) under any of the employed conditions possibly due to less production of oxidants

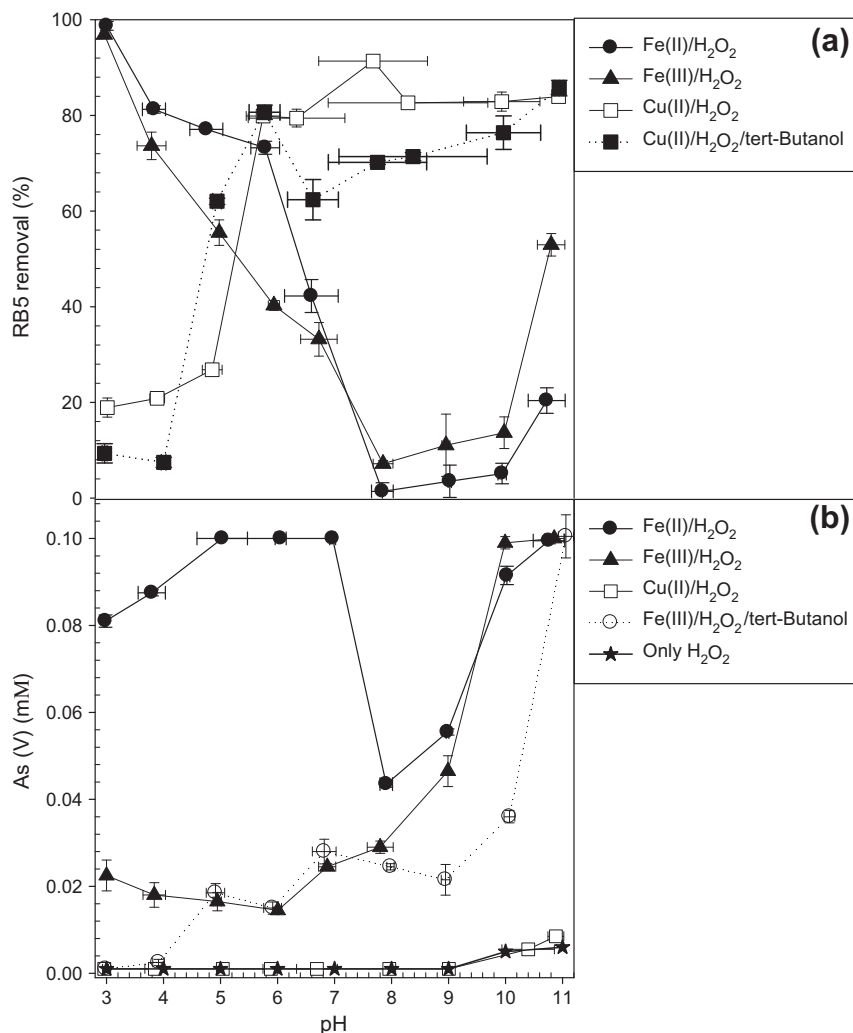


Fig. 3. Oxidative removal of RB5 (a) and oxidation of As(III) into As(V) (b) as a function of pH; (a): $[\text{Fe(II)}]_0 = [\text{Fe(III)}]_0 = [\text{Cu(II)}]_0 = 0.1 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$; $[\text{RB5}]_0 = 0.01 \text{ mM}$; $[\text{tert-butanol}]_0 = 100 \text{ mM}$; Reaction time = 1 h; (b): $[\text{Fe(II)}]_0 = [\text{Fe(III)}]_0 = [\text{Cu(II)}]_0 = [\text{As(III)}]_0 = 0.1 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 0.2 \text{ mM}$; $[\text{tert-butanol}]_0 = 100 \text{ mM}$; reaction time = 1 h; and horizontal error bars represent pH variations during the reaction.

with a lower concentration of H₂O₂ (The Cu(II)/H₂O₂ system is slower than the Fe(III)/H₂O₂ system.). Under alkaline conditions where the Cu(II)/H₂O₂ reaction is fast enough, the produced oxidants appear to have low reactivity toward As(III).

3.4. Competitive oxidation of methanol versus As(III)

To compare the reactivity of the oxidants formed under different pH conditions, the competitive oxidation of methanol and As(III) was investigated in the presence of Fe(II) and H₂O₂ at pH 3 and 7, respectively (Fig. 4a and b). The formation of HCHO and As(V) from the solution containing both methanol and As(III) was measured at varying ratios of As(III) and methanol by increasing the concentration of As(III) at a fixed initial concentration of methanol. The concentration of As(V) increased as more As(III) was added, and less HCHO was produced under both pH conditions. The formation ratio of oxidation products (i.e., [As(V)] divided by [HCHO]) exhibited a linear correlation with the input ratio of As(III) and methanol (i.e., [As(III)] divided by [methanol]) under both pH conditions (see the insets of Fig. 4a and b). However, the slope for the linear plot at pH 3 was approximately two hundred times lower than that at pH 7 (i.e., 10 at pH 3 versus 1.9×10^3 at pH 7, respectively).

4. Discussion

4.1. Evidence for the pH-dependent shift in the reaction mechanism

The specific pH-dependencies of oxidation for different compounds are the primary evidence for the production of multiple reactive oxidants in the Fenton (-like) systems. Although the pH-dependent oxidation of benzoic acid, methanol, and As(III) in the Fenton systems has been reported previously (Hug et al., 2001; Hug and Leupin, 2003; Katsoyiannis et al., 2008), more extensive data with more compounds under different conditions were presented in this study, which strengthened the hypothesis that the reactive oxidant shifts with pH. In addition, a similar pH-dependency was observed for the first time in the copper-catalyzed Fenton-like reaction.

In iron-catalyzed systems, the oxidative removal of phenol and benzoic acid was predominant under acidic conditions (Fig. 1a and b), showing the same trend as that observed for production of pHBA (Fig. SM-1a). The ratios of the production of pHBA to the loss of benzoic acid (i.e., $\Delta[\text{pHBA}]$ divided by $\Delta[\text{BA}]$) were almost constant as 0.16–0.18 in the pH range of 3–5 (Fig. SM-1c), indicating that the oxidative removal of benzoic acid is mainly due to $\cdot\text{OH}$. On the basis of the reported product ratio from the reaction of

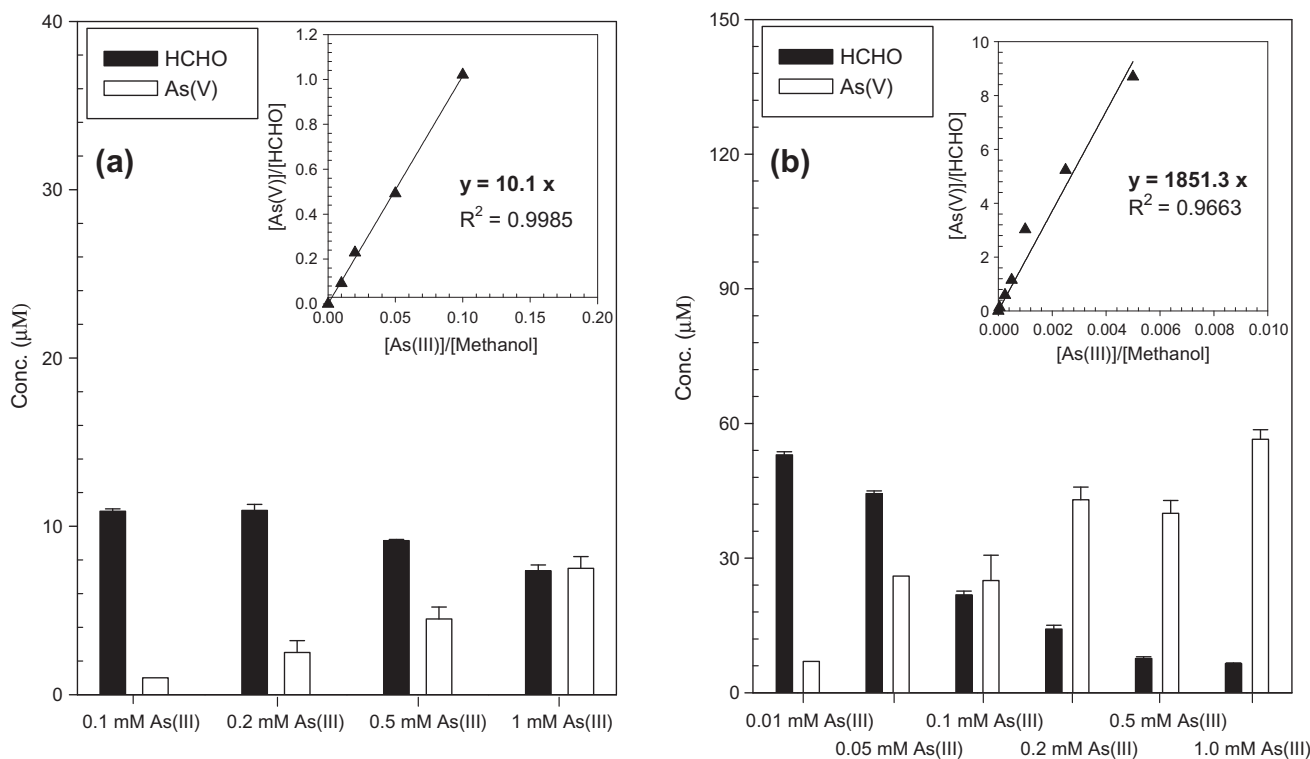


Fig. 4. Competitive oxidation of methanol and As(III) in the Fe(II)/H₂O₂ system at pH 3 (a) and pH 7 (b); (a) [Fe(II)]₀ = 0.01 mM; [H₂O₂]₀ = 0.1 mM; [As(III)]₀ = 0.1, 0.2, 0.5, 1.0 mM; [Methanol]₀ = 10 mM; [PIPES buffer]₀ = 1 mM at pH 7; reaction time = 1 h; (b) [Fe(II)]₀ = 0.01 mM; [H₂O₂]₀ = 0.1 mM; [As(III)]₀ = 0.01, 0.05, 0.1, 0.2, 0.5, 1.0 mM; [Methanol]₀ = 200 mM; [PIPES buffer]₀ = 1 mM at pH 7; and reaction time = 1 h.

benzoic acid with $\cdot\text{OH}$ (i.e., *o*-HBA:*m*-HBA:*p*-HBA = 1.7:2.3:1.2) (Klein et al., 1975), the yields of total hydroxybenzoic acids were calculated as 68–77%. In contrast to phenol and benzoic acid, methanol, RB5, and As(III) were significantly oxidized at pH 6 and 7 in both iron-catalyzed systems (Figs. 2a, 3a and b), suggesting that reactive oxidants other than $\cdot\text{OH}$ are formed at neutral pH values (Keenan and Sedlak, 2008b). This assertion is supported by the competitive oxidation of methanol and As(III) (Fig. 4a and b). At pH 3, the oxidation of As(III) is more favored over that of methanol by a factor of 10, which is consistent with the known kinetics of the $\cdot\text{OH}$ reactions; the reported second rate constants for the reactions of $\cdot\text{OH}$ with methanol and As(III) are 9.7×10^8 (Buxton et al., 1988) and $8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Klaning et al., 1989), respectively. However, the selectivity factor for As(III) relative to methanol increased by up to 1800 at pH 7, indicating that much more selective oxidants than $\cdot\text{OH}$ are formed under neutral conditions.

The oxidation of all compounds began to slow down above pH 8 in the iron-catalyzed systems due to the low solubility of iron (both Fe(III) and Fe(II)). Interestingly the removal efficiencies of RB5 and As(III) were recovered under alkaline conditions (Fig. 3a and b). It appears that under alkaline conditions, the Fenton reaction still produces oxidants that have different reactivities than those produced under neutral conditions.

The effects of $\cdot\text{OH}$ scavengers are additional evidence for the production of alternative oxidants. The complete prevention of removal of phenol and benzoic acid by the addition of excess *tert*-butanol (Fig. SM-4) implies that a stronger oxidant, likely $\cdot\text{OH}$ is mainly responsible for the oxidation of these compounds. The addition of DMSO and *tert*-butanol most effectively inhibited the oxidation of compounds under lower pH conditions (methanol oxidation in Fig. 2b, As(III) oxidation in Fig. 3b), which also supports the hypothesis that $\cdot\text{OH}$ is the major oxidant under acidic conditions, and that more selective oxidants are dominant under neutral and alkaline conditions.

Different trends for the various compounds were also exhibited by the copper-catalyzed Fenton-like system. In the Cu(II)/H₂O₂ system, the oxidation of phenol and benzoic acid was maximized at around pH 5.5–6.5 (Fig. 1a and b), whereas the oxidation of methanol and RB5 proceeded over a broad range of acidic, neutral and alkaline conditions (Figs. 2 and 3a). The low oxidation efficiency of the compounds under acidic conditions is attributed to the slower kinetics of the reduction of Cu(II) into Cu(I) by H₂O₂; indeed when 5 mM hydroxylamine was added as the Cu(II)-reducing agent, benzoic acid was completely oxidized under such acidic conditions (data not shown). The catalytic decomposition of H₂O₂ by Cu(II) is accelerated as pH increases (Fig. SM-3) as the deprotonated form of H₂O₂ (HO₂⁻, pK_a of H₂O₂ = 11.6) is the major electron-donor responsible for the reduction of Cu(II). The enhanced decomposition of H₂O₂ under alkaline conditions may lead to the increase in the production of reactive oxidants, which to some extent explains the trends of methanol and RB5 oxidation. However, the oxidants formed under alkaline conditions, do not appear to be effective in oxidizing phenol and benzoic acid (Fig. 1a and b), indicating that the predominant oxidant at the high pH values is not $\cdot\text{OH}$. The partial hydroxylation of benzoic acid was detected in the pH region where the removal of benzoic acid was pronounced in the Cu(II)/H₂O₂ system (Fig. SM-1b), suggesting the involvement of $\cdot\text{OH}$ in the oxidation of benzoic acid. When the Cu(II)/H₂O₂ system was kinetically activated by the addition of hydroxylamine, the hydroxylation of benzoic acid was greatly enhanced, with higher yields at lower pH values (Fig. SM-1b) indicating that acidic conditions favor the production of $\cdot\text{OH}$ in the Cu(II)/H₂O₂ system, as in the iron-catalyzed systems.

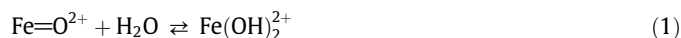
4.2. Possibility of surface-bound $\cdot\text{OH}$

An alternative explanation for the pH-dependent oxidation of compounds is that the behavior which is unexplained by free $\cdot\text{OH}$

may be attributable to the formation of surface-bound $\cdot\text{OH}$, and not to the presence of high-valent metal species (Pang et al., 2011). It may be possible that under neutral and alkaline conditions, that $\cdot\text{OH}$ is formed, and is bound to the surface (or the immediate vicinity) of insoluble metal species (iron and copper hydroxides or oxides). In this case, selective oxidation of compounds can occur depending on the affinity of a given compound for the surface of the heterogeneous metal species. However, evidence for alternative oxidants was found even under the conditions in which most of iron and copper species are present in soluble forms, which is inconsistent with the involvement of surface-assisted reactions. For example, in the $\text{Fe(II)}/\text{H}_2\text{O}_2$ system, the alternative oxidation behaviors of compounds (Figs. 1–3) were apparent even at pH values less than 7, where 0.1 mM Fe(II) is highly soluble (Fig. SM-5). The different competitive kinetics at pH 3 versus pH 7 (Fig. 4a and b) were also found among conditions of Fe(II) solubility (i.e., 10 μM). In addition, in the $\text{Cu(II)}/\text{H}_2\text{O}_2$ system, the pH-dependent inhibitory effect of *tert*-butanol on RB5 oxidation (below and above pH 5) was shown even when using the filtered solution of Cu(II) (Fig. SM-6).

4.3. Nature of alternative oxidants produced by the Fenton-type reactions

The alternative oxidants produced under circumneutral and alkaline conditions are likely high-valent iron and copper species (i.e., Fe(IV) and Cu(III)). There may be more than one species of Fe(IV) and Cu(III) formed by the Fenton (-like) reactions. For example, metal-oxo (e.g., $\text{Fe}=\text{O}^{2+}$, $\text{Cu}=\text{O}^+$) and metal-hydroxo complexes (e.g., Fe(OH)_2^{2+} , Cu(OH)_2^+) are possible species, and these oxo and hydroxo complexes may be interconvertible by the fast hydration and dehydration equilibrium (Reaction (1)) (Pestovsky and Bakac, 2004, 2006a,b).



However, DMSO (an oxygen acceptor from the metal-oxo complexes) failed to quench the methanol oxidation reaction under neutral and alkaline conditions (compare Fig. 2a and b), excluding the possibility of the formation of metal-oxo complexes in the systems; the second order rate constants for the reaction of FeO^{2+} with methanol and DMSO are reportedly 5.72×10^2 and $1.26 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, respectively (Pestovsky and Bakac, 2004, 2006a,b). This observation is in agreement with a recent study that reported the failure of sulfoxides to scavenge oxidants formed by the Fe^0/O_2 system (Pang et al., 2011). Therefore, it is possible that the hydroxo complexes may be the primary forms of high-valent metal complexes produced by the Fenton (-like) reactions (Reactions (2) and (3)).



As previously mentioned, the different behaviors in the oxidation of methanol versus RB5 (or As(III)) suggest that the oxidants under alkaline conditions are different from those produced under neutral conditions, which could be due to pH-dependent speciation of the metal-hydroxo species (e.g., Fe(OH)_2^{2+} , Fe(OH)_3^+ , Fe(OH)_5^- , etc. for Fe(IV) species). The oxidation power of metal-hydroxo species typically decreases with increasing concentrations of hydroxo ligand, which serves as an electron donor (Bard et al., 1985). It is possible that RB5 and As(III) are more vulnerable than methanol to oxidation by the Fe(IV) -hydroxo complexes occurring under alkaline conditions. However, to produce critical evidence for the presence of these complexes further study is needed.

5. Conclusions

The observations from this study provide new evidence that oxidants other than, and more selective than $\cdot\text{OH}$ are produced by the iron and copper-catalyzed Fenton (-like) reactions, and that they are mostly favored under neutral and alkaline conditions. The oxidants produced at neutral and alkaline pH values appear to be high-valent metal complexes of iron and copper. They are suggested to be the forms of Fe(IV) - or Cu(III) -hydroxo complexes. When the Fenton (-like) systems are applied to water treatment processes under circumneutral conditions, they can exhibit a higher efficiency than the $\cdot\text{OH}$ -based oxidation processes in transforming a specific group of contaminants. These selective oxidants may avoid undesired reactions with water constituents, such as natural organic matter. The Fenton (-like) systems may also be useful in disinfection. Selective oxidants, such as Fe(IV) and Cu(III) , should be more stable than $\cdot\text{OH}$ in natural water, allowing greater exposure to microorganisms. They are also expected to produce less toxic byproducts compared to chlorine-based disinfectants.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2013.01.073>.

References

- Baker, M.S., Gebicki, J.M., 1984. The effect of pH on the conversion of superoxide to hydroxyl free-radicals. *Arch. Biochem. Biophys.* 234, 258–264.
- Bard, A.J., Parsons, R., Jordan, J., 1985. *Standard Potentials in Aqueous Solution*. Marcel Dekker, New York.
- Bossmann, S.H., Oliveros, E., Gob, S., Siegwart, S., Dahlen, E.P., Payawan, L., Straub, M., Worner, M., Braun, A.M., 1998. New evidence against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced fenton reactions. *J. Phys. Chem. A* 102, 5542–5550.
- Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical-review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals ($\cdot\text{OH}/\text{O}^-$) in aqueous-solution. *J. Phys. Chem. Ref. Data* 17, 513–886.
- Dhar, R.K., Zheng, Y., Rubenstone, J., van Geen, A., 2004. A rapid colorimetric method for measuring arsenic concentrations in groundwater. *Anal. Chim. Acta* 526, 203–209.
- Eberhardt, M.K., Ramirez, G., Ayala, E., 1989. Does the reaction of Cu^+ with H_2O_2 Give OH radicals – a study of aromatic hydroxylation. *J. Org. Chem.* 54, 5922–5926.
- Goldstein, S., Czapski, G., 1990. Transition metal ions and oxygen radicals. *Int. Rev. Exp. Pathol.* 31, 133–164.
- Goldstein, S., Meyerstein, D., 1999. Comments on the mechanism of the "Fenton like" reaction. *Acc. Chem. Res.* 32, 547–550.
- Goldstein, S., Meyerstein, D., Czapski, G., 1993. The Fenton reagents. *Free Radical Biol. Med.* 15, 435–445.
- Halliwell, B., Gutteridge, J.M.C., 1981. Formation of a thiobarbituric-acid-reactive substance from deoxyribose in the presence of iron salts – the role of superoxide and hydroxyl radicals. *FEBS Lett.* 128, 347–352.
- Haber, F., Weiss, J., 1934. The catalytic decomposition of hydrogen peroxide by iron salts. *Proc. Roy. Soc. A* 147, 332–351.
- Hug, S.J., Canonica, L., Wegelin, M., Gechter, D., von Gunten, U., 2001. Solar oxidation and removal of arsenic at circumneutral pH in iron containing waters. *Environ. Sci. Technol.* 35, 2114–2121.
- Hug, S.J., Leupin, O., 2003. Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction. *Environ. Sci. Technol.* 37, 2734–2742.

- Johnson, G.R.A., Nazhat, N.B., Saadallanazhat, R.A., 1985. Reaction of the aquocopper(I) ion with hydrogen-peroxide – evidence against hydroxyl free-radical formation. *J. Chem. Soc. Chem. Commun.* 25, 407–408.
- Johnson, G.R.A., Nazhat, N.B., Saadallanazhat, R.A., 1988. Reaction of the aquacopper(I) ion with hydrogen-peroxide – evidence for a Cu(III) (cupryl) intermediate. *J. Chem. Soc. Faraday Trans. 1* (84), 501–510.
- Katsoyiannis, I.A., Ruettimann, T., Hug, S.J., 2008. PH dependence of Fenton reagent generation and As(III) oxidation and removal by corrosion of zero valent iron in aerated water. *Environ. Sci. Technol.* 42, 7424–7430.
- Keenan, C.R., Sedlak, D.L., 2008a. Factors affecting the yield of oxidants from the reaction of manoparticulate zero-valent iron and oxygen. *Environ. Sci. Technol.* 42, 1262–1267.
- Keenan, C.R., Sedlak, D.L., 2008b. Ligand-enhanced reactive oxidant generation by nanoparticulate zero-valent iron and oxygen. *Environ. Sci. Technol.* 42, 6936–6941.
- Klaning, U.K., Bielski, B.H.J., Sehested, K., 1989. Arsenic(IV) – a pulse-radiolysis study. *Inorg. Chem.* 28, 2717–2724.
- Klein, G.W., Bhatla, K., Madhavan, V., Schuler, R.H., 1975. Reaction of hydroxyl radicals with benzoic acid: isomer distribution in the radical intermediates. *J. Phys. Chem.* 79, 1767–1774.
- Lee, C., Sedlak, D.L., 2008. Enhanced formation of oxidants from bimetallic nickel-iron nanoparticles in the presence of oxygen. *Environ. Sci. Technol.* 42, 8528–8533.
- Pang, S.Y., Jiang, J., Ma, J., 2011. Oxidation of sulfoxides and arsenic(III) in corrosion of nanoscale zero valent iron by oxygen: evidence against ferryl ions (Fe(IV)) as active intermediates in Fenton reaction. *Environ. Sci. Technol.* 45, 307–312.
- Pestovsky, O., Bakac, A., 2004. Reactivity of aqueous Fe(IV) in hydride and hydrogen atom transfer reactions. *J. Am. Chem. Soc.* 126, 13757–13764.
- Pestovsky, O., Bakac, A., 2006a. Aqueous ferryl(IV) ion: kinetics of oxygen atom transfer to substrates and oxo exchange with solvent water. *Inorg. Chem.* 45, 814–820.
- Pestovsky, O., Bakac, A.A., 2006b. Identification and characterization of aqueous ferryl(IV) ion. *Abstr. Pap. Am. Chem. Soc.* 232, 682.
- Sutton, H.C., 1989. Formate oxidation induced by a copper peroxy complex produced in Fenton-like reactions. *J. Chem. Soc. Faraday Trans.* 85, 883–893.
- Yagi, K., Ishida, N., Komura, S., Ohishi, N., Kusai, M., Kohno, M., 1992. Generation of hydroxyl radical from linoleic-acid hydroperoxide in the presence of epinephrine and iron. *Biochem. Biophys. Res. Commun.* 183, 945–951.
- Yagi, K., Komura, S., Ishida, N., Nagata, N., Kohno, M., Ohishi, N., 1993. Generation of hydroxyl radical from lipid hydroperoxides contained in oxidatively modified low-density-lipoprotein. *Biochem. Biophys. Res. Commun.* 190, 386–390.
- Yamazaki, I., Piette, L.H., 1991. EPR spin-trapping study on the oxidizing species formed in the reaction of the ferrous ion with hydrogen-peroxide. *J. Am. Chem. Soc.* 113, 7588–7593.
- Zhou, X.L., Mopper, K., 1990. Determination of photochemically produced hydroxyl radicals in seawater and fresh-water. *Mar. Chem.* 30, 71–88.