Editor Choice Paper

A novel homogeneous Fenton-like system with Fe(III)–phosphotungstate for oxidation of organic compounds at neutral pH values

Changha Lee [1], David L. Sedlak *

Department of Civil and Environmental Engineering, 657 Davis Hall, University of California, Berkeley, CA 94720, United States

ABSTRACT

Ferric ion (Fe[III]) catalyzes the decomposition of hydrogen peroxide (H_2O_2) into strong oxidants such as hydroxyl radical ($^\bullet OH$) and ferryl ion (Fe[IV]) through the redox cycling of the iron couple (Fe[II]/Fe[III]). The use of these reactions for the catalytic oxidation of organic compounds is usually limited to the acidic pH region due to the low solubility of Fe(III) and the low efficiency of oxidant production at neutral pH values. The addition of phosphotungstate ($PW_{12}O_{40}^{3-}$), a polyoxometalate, extends the working pH range of the Fe(III)/H_2O_2 system up to pH 8.5. $PW_{12}O_{40}^{3-}$ forms a soluble complex with iron that converts H_2O_2 into oxidants. The coordination of Fe(II) by $PW_{12}O_{40}^{3-}$ also alters the mechanism of the reaction of Fe(II) with H_2O_2 at neutral pH, resulting in formation of an oxidant capable of oxidizing aromatic compounds. The base-catalyzed hydrolysis of $PW_{12}O_{40}^{3-}$ gradually results in inactivation of the catalyst. In the absence of Fe(III), $PW_{12}O_{40}^{3-}$ was completely hydrolyzed after 1 day at pH 7.5, whereas the Fe(III)–$PW_{12}O_{40}^{3-}$ complex was active for at least 4 days under the same conditions.

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1. Introduction

Over the last two decades, the advanced oxidation processes that employ hydrogen peroxide (H_2O_2) and iron have been extensively studied as methods for the oxidation of recalcitrant contaminants in drinking water, industrial wastewater, and soils [1]. Under acidic conditions, Fenton's reagent (i.e., Fe(II)/H_2O_2) rapidly converts H_2O_2 into a stoichiometric amount of hydroxyl radical ($^\bullet OH$) (reaction (1)):

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + {}^\bullet OH + OH^- \quad k_2 = 63\,M^{-1}\,s^{-1} \quad [2] \quad (1)$$
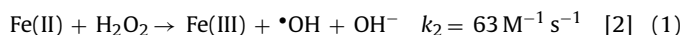
While this process has been used for the treatment of water containing toxic organic compounds [3–5], the formation of ferric precipitates after the treatment produces large amounts of waste. To avoid this problem, a low concentration of Fe(III) relative to H_2O_2 can be used for the catalytic conversion of H_2O_2 into $^\bullet OH$ (i.e., reaction (2) followed by reaction (1)). The application of this treatment process has been limited because the rate of reaction (2) is slow:
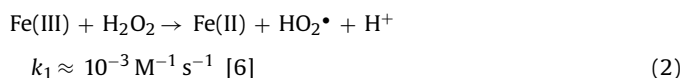
$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2{}^\bullet + H^+$$
$$k_1 \approx 10^{-3}\,M^{-1}\,s^{-1} \quad [6] \qquad (2)$$

Both the Fe(II)/H_2O_2 and the Fe(III)/H_2O_2 systems are typically used only under acidic pH conditions (<pH 3), and as a result the addition of strong acids and bases is required before and after the process. The low efficiency of these systems under neutral pH conditions is attributable to two factors. First, Fe(III) forms insoluble precipitates of amorphous Fe(III)–oxyhydroxides, which produce very low yields of oxidants from reactions with H_2O_2 [7,8]. Second, at these pH values, the reaction of Fe(II) with H_2O_2 does not always produce $^\bullet OH$. The oxidant formed at neutral pH values, which appears to be ferryl ion (Fe[IV]), is capable of oxidizing short chain aliphatic alcohols and arsenite [9–11], but cannot oxidize aromatic organic compounds and other recalcitrant contaminants [11].

The addition of iron-chelating agents such as ethylenediaminetetraacetate (EDTA) [12], tetraamino macrocyclic ligands (TAML) [13], and porphyrins [14] can be used to extend the useful range of the Fe(III)/H_2O_2 system to neutral pH conditions by preventing iron precipitation and producing a more reactive oxidant [15,16]. However, these organic ligands scavenge the oxidants produced by the system, lowering the efficiency of contaminant oxidation, and resulting in a need to continuously supply ligands. The ligands also pose secondary environmental risks because they can mobilize toxic metals [17].

The addition of phosphotungstate ($PW_{12}O_{40}^{3-}$, a type of polyoxometalate) may provide an alternative approach for extending the useful range of the Fe(III)/H_2O_2 system without using organic ligands. $PW_{12}O_{40}^{3-}$ forms soluble complexes with Fe(III) under neutral pH conditions [18], and is relatively nontoxic and resistant to oxidation [19,20]. It also retains its catalytic activity when it is covalently bound to silica surfaces [21]. The objective of the present

* Corresponding author. Tel.: +1 510 643 0256; fax: +1 510 642 7483.
E-mail address: sedlak@ce.berkeley.edu (D.L. Sedlak).
[1] Present address: School of Urban and Environmental Engineering, Ulsan National Institute of Science and Technology (UNIST), 194 Banyeon-ri, Ulsan 698-805, South Korea.

study was to evaluate the potential for $PW_{12}O_{40}^{3-}$ to enhance oxidant production in the Fe(III)/H_2O_2 system under neutral pH conditions. For this purpose, the oxidation of compounds that are known to react with $^\bullet$OH or Fe(IV) (i.e., benzoate and methanol) by the Fe(III)/H_2O_2 system was studied under various conditions in the absence and presence of $PW_{12}O_{40}^{3-}$.

2. Experimental

2.1. Reagents

All chemicals except for 2,4-dinitrophenyl hydrazine (DNPH) were of reagent grade and were used without further purification. DNPH was recrystallized three times from acetonitrile. All chemicals were obtained from Fisher Scientific Inc. except for DNPH, ferrous sulfate, and benzoic acid, which were obtained from Sigma–Aldrich Co. All solutions were prepared using 18 MΩ Milli-Q water from a Millipore system. The Fe(III) stock solution (50 mM) was prepared daily by dissolving ferric perchlorate (Fe(ClO$_4$)$_3$·9H$_2$O) in 0.1 N HClO$_4$. When necessary, 50 mM ferrous sulfate (in 0.1 mM HCl) and 100 mM H_2O_2 stock solutions were also prepared prior to experiments. Silica-immobilized $PW_{12}O_{40}^{3-}$ (SiO$_2$–$PW_{12}O_{40}^{3-}$) was prepared by a sol–gel hydrothermal method, and the catalyst prepared by this method typically has a $PW_{12}O_{40}^{3-}$ content of 20 wt% and a BET surface area of 326 m^2/g [18,21].

2.2. Oxidation of probe compounds

Benzoate and methanol were used as probe compounds for detecting oxidants. Details regarding the reactivity of probe compounds with $^\bullet$OH and Fe(IV) are described elsewhere [11]. In most of the experiments, the disappearance of 0.5 mM benzoate was observed to quantify oxidant production. For some experiments, an excess of methanol (i.e., 200 mM) was employed to ensure that all of the oxidants reacted with the probe compound, and its major oxidation product (i.e., HCHO) was quantified.

All experiments on the oxidation of probe compounds were performed in 60 mL Pyrex vials at room temperature (20 ± 2 °C) under air-saturation ([O$_2$]$_0$ = 0.25 mM). Borate buffer solutions (2 mM) were used for most of the experiments (pH 6–9). 1.5 mM piperazine-N,N'-bis(ethanesulfonic acid) (PIPES; 1.5 mM) was used as a buffer for the experiments with 200 mM methanol at pH 7. The solution pH usually decreased during the reaction with borate buffer solutions (by 0.2–1 units). The pH was measured throughout each experiment, and the average pH value was calculated for each experiment.

The experiments were initiated by adding an aliquot of H_2O_2 stock solution to a pH-adjusted solution containing the probe compound, Fe(III), and $PW_{12}O_{40}^{3-}$. Samples were withdrawn at pre-determined time intervals using a 5-mL glass syringe and immediately filtered through a 0.22-μm nylon syringe filter. For the experiments with benzoate, 25 μL of methanol was added to the 5 mL samples to quench the reaction. All of experiments were carried out in triplicate, and average values and standard deviations are presented.

2.3. Analytical methods

Benzoate (BA) was analyzed using high-performance liquid chromatography (HPLC) with UV absorbance detection at 270 nm. The concentration of HCHO was determined by HPLC with UV absorbance detection at 350 nm after DNPH derivatization [22]. Separation was performed on a Waters Symmetry C18 column (150 mm × 4.6 mm, 5 μm), using water with 10 mM nitric acid and acetonitrile as the eluent, at a flow rate of 1.0 mL min^{-1}. UV/visible

absorbance of $PW_{12}O_{40}^{3-}$ and iron solutions were analyzed using a Perkin Elmer Lambda 14 spectrophotometer with a quartz cell with a 1-cm optical path length. The concentration of H_2O_2 was quantified spectrophotometrically by either the titanium sulfate method [23] or the N,N-diethyl-p-phenylenediamine (DPD) method (for measuring H_2O_2 concentration less than 1 mM [24]).

3. Results

3.1. Enhanced oxidation of benzoate in the Fe(III)/H_2O_2 system in the presence of $PW_{12}O_{40}^{3-}$

The oxidative degradation of benzoate (BA) and the decomposition of H_2O_2 in the Fe(III)/H_2O_2 system were investigated in the absence and presence of $PW_{12}O_{40}^{3-}$. In the absence of $PW_{12}O_{40}^{3-}$, the concentration of BA decreased by only 14% over 4 h with 1 mM Fe(III) and 50 mM H_2O_2 (Fig. 1a), while 62% of H_2O_2 was decomposed (Fig. 1b). Increasing the concentration of Fe(III) to 4 mM resulted in the loss of approximately 33% of BA as the rate of H_2O_2 decomposition increased (complete decomposition after 2 h). Control experiments conducted in the absence of H_2O_2 indicate that adsorption of BA on Fe(III)–oxyhydroxides accounted for approximately 33% of the observed loss of BA (4 mM Fe(III) only in Fig. 1a).

The addition of $PW_{12}O_{40}^{3-}$ (1 mM) enhanced the rate of BA loss (Fig. 1c), and decreased the rate of H_2O_2 decomposition (Fig. 1d). With 1 mM Fe(III) in the presence of $PW_{12}O_{40}^{3-}$, 43% of BA was transformed in 4 h, whereas the H_2O_2 concentration decreased by only 8%. Increasing the concentration of Fe(III) enhanced both the rate of BA loss and the rate of H_2O_2 decomposition. No significant removal of BA was observed in the absence of H_2O_2 (Fig. 1c).

3.2. pH Dependence

The Fe(III)/$PW_{12}O_{40}^{3-}$/H_2O_2 system exhibited a higher degree of BA oxidation and less H_2O_2 decomposition than the Fe(III)/H_2O_2 system after 3 h over pH values ranging pH 6.3–8.8. In both the Fe(III)/H_2O_2 and Fe(III)/$PW_{12}O_{40}^{3-}$/H_2O_2 systems, BA removal decreased, while the loss of H_2O_2 increased with increasing pH (Fig. 2a and b). These trends were most clearly evident in the Fe(III)/$PW_{12}O_{40}^{3-}$/H_2O_2 system above pH 7.5. The calculated H_2O_2 utilization efficiency (i.e., Δ[BA]/Δ[H_2O_2] × 100) in the Fe(III)/$PW_{12}O_{40}^{3-}$/H_2O_2 system was approximately 3.5% at pH values ranging from 6.3 to 7.7, and decreased to approximately 0.5% at pH 8.4 (Fig. 2c). The H_2O_2 utilization efficiency in the Fe(III)/H_2O_2 system was less than 0.5% over the entire pH range.

3.3. Effect of aging

$PW_{12}O_{40}^{3-}$ hydrolyzes into PO_4^{3-} and WO_4^{2-} under neutral pH conditions [25,26]. To investigate the stability of the Fe(III) complexes with $PW_{12}O_{40}^{3-}$, a stock solution containing 2 mM Fe(III) and 1 mM $PW_{12}O_{40}^{3-}$ was prepared, and aged in borated-buffered solution at 7.5. An aliquot of the stock solution was withdrawn on a daily basis, and the transformation of BA and the decomposition of H_2O_2 were examined after adding 0.5 mM BA and 50 mM H_2O_2.

The catalytic activity of the Fe(III) complexes with $PW_{12}O_{40}^{3-}$ gradually decreased over 7 days as $PW_{12}O_{40}^{3-}$ underwent hydrolysis. The rate of the BA transformation decreased (Fig. 3a), and the rate of H_2O_2 decomposition increased (Fig. 3b) as Fe(III)–$PW_{12}O_{40}^{3-}$ aged. The solution of Fe(III)–$PW_{12}O_{40}^{3-}$ turned turbid as the solution aged possibly due to the formation of iron precipitates. $PW_{12}O_{40}^{3-}$ aged for 1 day in the absence of Fe(III) lost all of its catalytic activity with respect to BA oxidation when Fe(III) and H_2O_2 were added to the aged solution (no. 12 in Table 1), indicating that $PW_{12}O_{40}^{3-}$ is stabilized by Fe(III) complexation.

Table 1
Effects of reagent concentrations, a $^\bullet OH$ scavenger (*tert*-butanol), and $SiO_2-PW_{12}O_{40}^{3-}$ on BA degradation, H_2O_2 decomposition and H_2O_2 utilization efficiency.

No.	Fe(III)]$_0$ (mM)	[H_2O_2]$_0$ (mM)	[$PW_{12}O_{40}^{3-}$]$_0$ (mM)	[BA]$_0$ (mM)	pH (pH_i, pH_f, pH_{ave})	Reaction time, additives, etc.	BA removal (%)	H_2O_2 decomposition (%)	Efficiency (%) (Δ[BA]/Δ[H_2O_2]) × 100)
1	2	50		0.5	7.5, 7.2, 7.3	4 h	14 ± 4.6	70 ± 5.8	0.20 ± 0.064
2	2	50	1	0.5	8.0, 6.6, 7.0	4 h	87 ± 7.4	26 ± 3.2	3.4 ± 0.64
3	2	50	1	2	8.0, 6.3, 6.4	4 h	46 ± 2.8	23 ± 1.6	8.2 ± 0.39
4	2	50	1	5	8.0, 6.1, 6.2	4 h	27 ± 1.3	20 ± 1.1	14 ± 0.50
5	2	25	1	0.5	8.0, 6.6, 6.8	4 h	74 ± 9.0	25 ± 0.38	5.9 ± 0.36
6	2	5	1	0.5	8.0, 7.0, 7.1	4 h	56 ± 5.1	35 ± 2.5	16 ± 0.94
7	2	50	2	0.5	8.0, 6.2, 6.5	4 h	87 ± 4.4	14 ± 2.5	6.2 ± 0.58
8	2	50	0.5	0.5	8.0, 6.5, 6.8	4 h	89 ± 8.0	29 ± 3.8	3.1 ± 0.30
9	2	50	0.25	0.5	8.0, 6.8, 7.2	4 h	67 ± 4.3	31 ± 3.0	2.1 ± 0.053
10	2	50		0.5	7.5, 7.2, 7.3	4 h, 200 mM *tert*-butanol	13 ± 4.3	85 ± 0.18	0.15 ± 0.050
11	2	50	1	0.5	8.0, 6.8, 7.1	4 h, 200 mM *tert*-butanol	16 ± 0.21	20 ± 2.1	0.81 ± 0.075
12	2	50	1[a]	0.5	7.0, 8.1, 8.5	4 h	11 ± 0.34	46 ± 9.1	0.23 ± 0.023
13	2	50		0.5	7.0, 8.3, 8.4	4 h, 10 mM WO_4^{2-}	17 ± 3.0	69 ± 2.5	0.24 ± 0.022
14	2	50	1[b]	0.5	8.0, 7.2, 7.4	4 h	31 ± 2.5	54 ± 2.9	0.58 ± 0.067
15	2	50	5[b]	0.5	8.0, 6.8, 7.0	4 h	50 ± 4.6	33 ± 3.8	1.5 ± 0.020

[a] Aged for 1 day at pH_{ave} 7.5 in the absence of Fe(III).
[b] $SiO_2-PW_{12}O_{40}^{3-}$ (1 mM as $PW_{12}O_{40}^{3-} \approx 2.9$ g/L $SiO_2-PW_{12}O_{40}^{3-}$).

3.4. Effects of reagent concentrations, a $^\bullet OH$ scavenger, $SiO_2-PW_{12}O_{40}^{3-}$, and methanol as a probe compound

The efficiency of the BA degradation in the Fe(III)/$PW_{12}O_{40}^{3-}$/H_2O_2 system was investigated varying the initial concentrations of H_2O_2, BA, and $PW_{12}O_{40}^{3-}$ (nos. 1–9 in Table 1). Increasing the initial concentration of BA from 0.5 to 5 mM increased the H_2O_2 utilization efficiency from 3.4 to 14% mainly through increased loss of BA (nos. 2–4 in Table 1). Decreasing the concentration of H_2O_2 from 50 to 5 mM resulted in a similar degree of enhancement (nos.
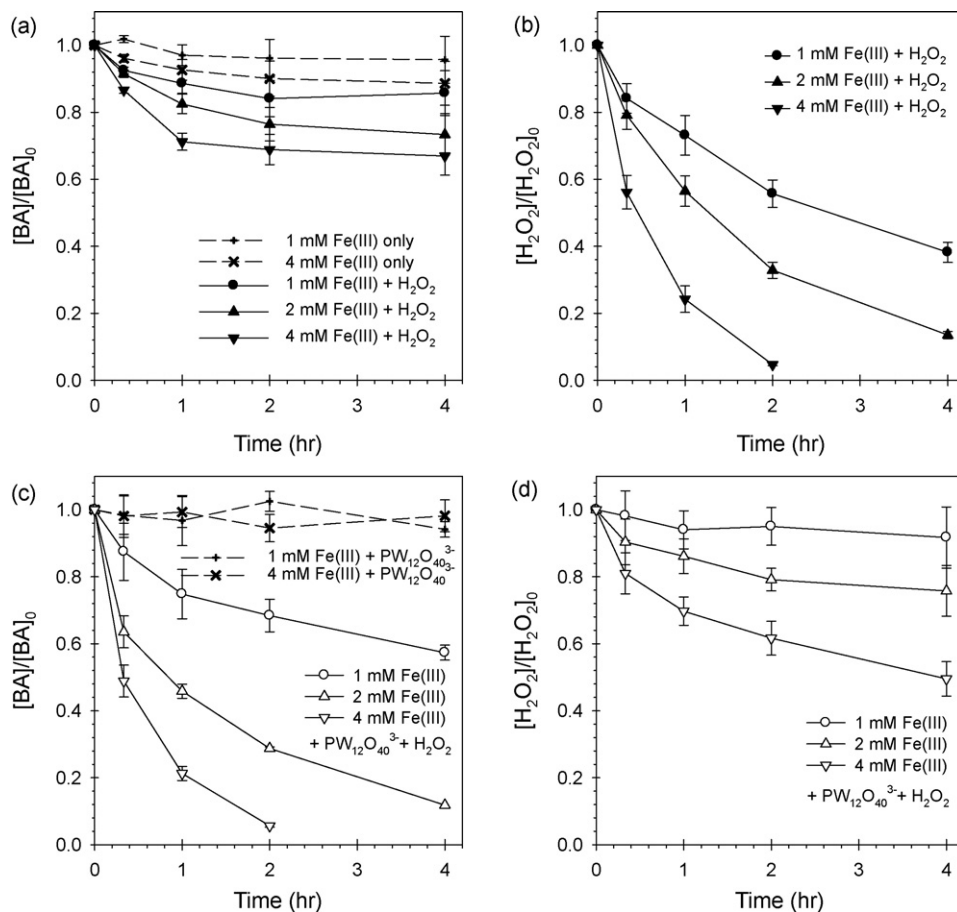

Fig. 1. BA loss and H_2O_2 decomposition in the Fe(III)/H_2O_2 and the Fe(III)/$PW_{12}O_{40}^{3-}$/H_2O_2 systems ([H_2O_2]$_0$ = 50 mM; [$PW_{12}O_{40}^{3-}$]$_0$ = 1 mM; [BA]$_0$ = 0.5 mM; pH_i 7.5, pH_{ave} 7.3 for the Fe(III)/H_2O_2 system; pH_i 8.0, pH_{ave} 7.0 for the Fe(III)/$PW_{12}O_{40}^{3-}$/H_2O_2 system).
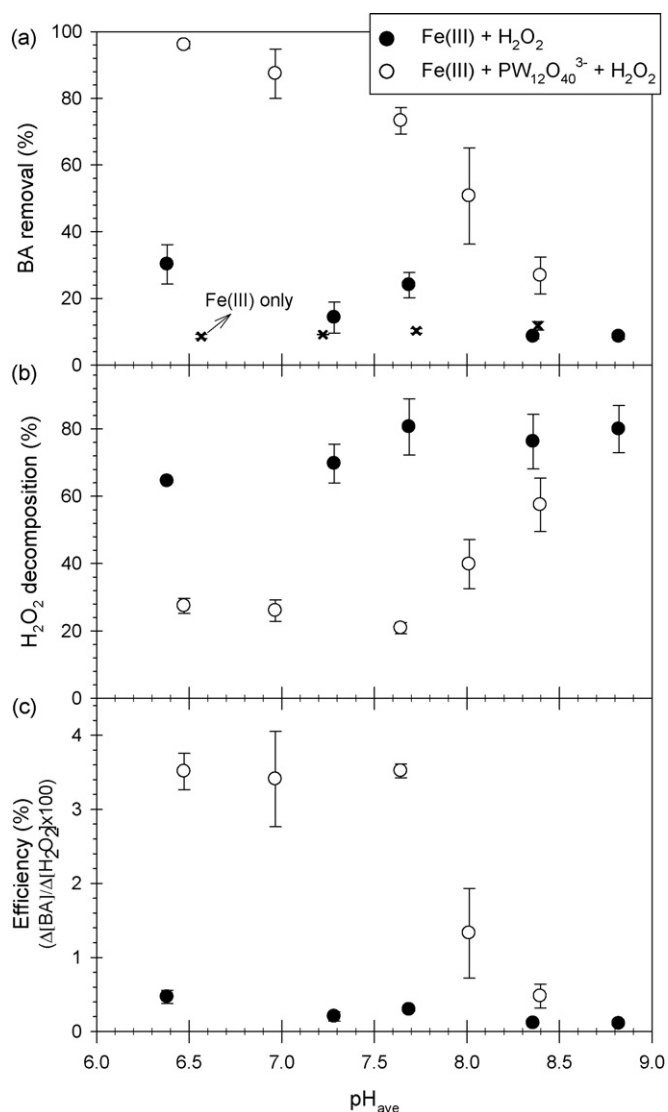
Fig. 2. Effect of pH on BA degradation (a), H_2O_2 decomposition (b), and the H_2O_2 utilization efficiency (c) in the $Fe(III)/H_2O_2$ and the $Fe(III)/PW_{12}O_{40}^{3-}/H_2O_2$ systems ([$Fe(III)]_0 = 2$ mM; [$H_2O_2]_0 = 50$ mM; [$PW_{12}O_{40}^{3-}]_0 = 1$ mM; [$BA]_0 = 0.5$ mM; reaction time = 4 h).

2, 5 and 6 in Table 1) because H_2O_2 competes with BA for the oxidant. When the concentration of $PW_{12}O_{40}^{3-}$ was reduced from 2 to 0.25 mM, the H_2O_2 utilization efficiency decreased from 6.2 to 2.1% (nos. 2 and 7–9 in Table 1).

In the presence of $PW_{12}O_{40}^{3-}$, the addition of 200 mM *tert*-butanol, which is an efficient $^{\bullet}OH$ scavenger, lowered the extent of BA transformation, and reduced the H_2O_2 utilization efficiency (no. 11 in Table 1). In the absence of $PW_{12}O_{40}^{3-}$, there was little change in BA transformation or H_2O_2 decomposition upon addition of *tert*-butanol (nos. 1 and 10 in Table 1).

Relative to homogeneous $PW_{12}O_{40}^{3-}$, $SiO_2-PW_{12}O_{40}^{3-}$ exhibited a much lower H_2O_2 utilization efficiency (nos. 14 and 15 in Table 1).

To measure maximum yields of oxidant, an excess of methanol (i.e., 200 mM), which is known to react with both $^{\bullet}OH$ and $Fe(IV)$ [11], was used as a probe compound, and its oxidation product, formaldehyde (HCHO) was quantified. In the $Fe(III)/H_2O_2$ system, the yields of HCHO were approximately 6% at neutral pH values (nos. 1 and 2 in Table 2), whereas the $Fe(III)/PW_{12}O_{40}^{3-}/H_2O_2$ system with 1–2 mM $PW_{12}O_{40}^{3-}$ exhibited HCHO yields ranging from 42 to 64% (nos. 3 and 4 in Table 2).
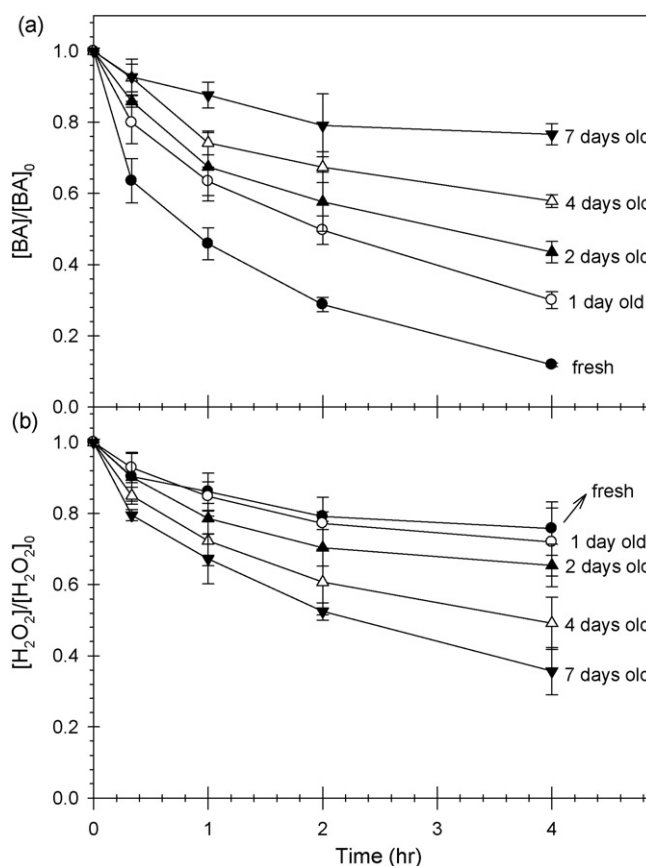
Fig. 3. Effect of aging (at pH_{ave} 7.5) on BA degradation (a) and H_2O_2 decomposition (b) in the $Fe(III)/PW_{12}O_{40}^{3-}/H_2O_2$ system ([$Fe(III)]_0 = 2$ mM; [$H_2O_2]_0 = 50$ mM; [$PW_{12}O_{40}^{3-}]_0 = 1$ mM; [$BA]_0 = 0.5$ mM; pH_i 8.0, pH_{ave} 7.0).

4. Discussion

4.1. Catalytic decomposition of H_2O_2 by Fe(III)

The formation of $^{\bullet}OH$ in the $Fe(III)/H_2O_2$ system under acidic pH conditions usually has been explained by a free radical mechanism (reactions (1)–(4)):

$$Fe(III) + HO_2^{\bullet} \rightarrow Fe(II) + O_2 + H^+ \quad k_3 = 2.5 \times 10^5\,M^{-1}\,s^{-1}$$

$$[27, 28] \tag{3}$$

$$Fe(II) + HO_2^{\bullet} \xrightarrow{H^+} Fe(III) + H_2O_2 \quad k_4 = 1.2 \times 10^6\,M^{-1}\,s^{-1}$$

$$[29] \tag{4}$$
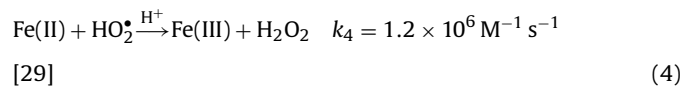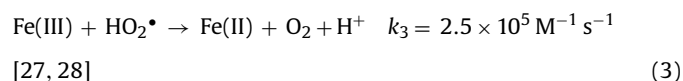
In this mechanism, the rate-determining step is the slow reduction of Fe(III) by H_2O_2 (reaction (2)), which is followed by the Fenton reaction to produce $^{\bullet}OH$ (reaction (1)). The $HO_2^{\bullet}$ produced from reaction (2) either reduces Fe(III) or oxidizes Fe(II) (reactions (3) and (4)). In the presence of high concentration of H_2O_2, Fe(III) is the predominant species of iron ([$Fe(II)]/[Fe(III)] < 0.005$ [6]), and the rate of reaction (4) is slow compared to reaction (3). According to reactions (1)–(3), the theoretical yield of $^{\bullet}OH$ from H_2O_2 ($\Delta[^{\bullet}OH]/\Delta[H_2O_2] \times 100$) is 67% because three moles of H_2O_2 are consumed for every two moles of $^{\bullet}OH$ produced (i.e., reaction (1) + 2 × reaction (2) + reaction (3)). The highest observed yield of HCHO from the oxidation of methanol in the $Fe(III)/H_2O_2$ system at pH 2.6 (69%; no. 5 in Table 2) is consistent with the theoretical value.
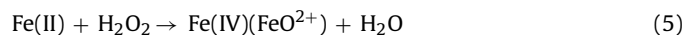
Under neutral pH conditions, Fe(III) forms the amorphous precipitates of Fe(III)–oxyhydroxides consisting of iron centers linked

Table 2
Methanol oxidation into HCHO, the H_2O_2 decomposition, and the H_2O_2 utilization efficiency.

No.	[Fe(III)]$_0$ (mM)	[H$_2$O$_2$]$_0$ (mM)	[PW$_{12}$O$_{40}$$^{3-}$]$_0$ (mM)	[Methanol]$_0$ (mM)	pH (pH$_i$, pH$_f$, pH$_{ave}$)	Reaction time	HCHO formed (mM)	H$_2$O$_2$ decomposed (mM)	Efficiency (%) (Δ[HCHO]/Δ[H$_2$O$_2$] × 100)
					Conditions				
1	2	1		200	7.0, 6.5, 6.7	4 h	$(5.7 \pm 0.38) \times 10^{-2}$	1	5.7 ± 0.38
2	2	1		200	8.0, 7.8, 7.9	4 h	$(5.5 \pm 0.26) \times 10^{-2}$	1	5.5 ± 0.26
3	2	1	1	200	8.0, 6.8, 7.0	10 h	0.42 ± 0.029	1	42 ± 2.9
4	2	1	2	200	8.0, 6.1, 6.4	10 h	0.64 ± 0.017	1	64 ± 1.7
5	2	1		200	2.5, 2.6, 2.6	10 h	0.69 ± 0.037	1	69 ± 3.7

together by oxy and hydroxyl bridges. These heterogeneous Fe(III) species are known to generate very low yields of oxidants from the catalytic decomposition of H_2O_2 [7,8], which is consistent with our observations for the oxidation of BA and methanol (Fig. 1a and b; nos. 1 and 2 in Table 2). The low yield of oxidants from the heterogeneous iron catalysts is believed to be due to reactions occurring on or near the surface that directly decompose H_2O_2 into water and oxygen [8].

In addition, the reaction of Fe(II) with H_2O_2 produces oxidants other than •OH under neutral pH conditions. In the absence of Fe(II)-complexing ligands, Fe(IV) appears to be the predominant oxidant produced at pH values above 5 (reaction (5) [9,10]). Fe(IV) rapidly oxidizes methanol to HCHO, but does not react with BA or other aromatic compounds [11]:

$$Fe(II) + H_2O_2 \rightarrow Fe(IV)(FeO^{2+}) + H_2O \qquad (5)$$

4.2. Production of oxidants by iron-PW$_{12}$O$_{40}$$^{3-}$ complexes

$PW_{12}O_{40}^{3-}$ forms soluble complexes with Fe(III) and Fe(II) [18]. The stoichiometry between iron and $PW_{12}O_{40}^{3-}$ in these complexes is not precisely known, but it appears that a single molecule of $PW_{12}O_{40}^{3-}$ is capable of coordinating several iron atoms because the rate of BA transformation continues to increase as the ratio of Fe(III) to $PW_{12}O_{40}^{3-}$ increases from 1:1 to 4:1 (Fig. 1c). The Fe(III)/Fe(II)–$PW_{12}O_{40}^{3-}$ complexes are believed to catalyze the conversion of H_2O_2 into oxidants through a mechanism analogous to reactions (1)–(4). An equimolar mixture of Fe(III) and $PW_{12}O_{40}^{3-}$ under neutral pH conditions produced a 64% yield of HCHO (no. 4 in Table 2), which is approximately equal to the predicted maximum, whereas the yields of HCHO were around 5.6% under similar conditions in the absence of $PW_{12}O_{40}^{3-}$ (nos. 1 and 2 in Table 2).

The identity of the oxidant produced in the Fe(III)/$PW_{12}O_{40}^{3-}$/H_2O_2 system is still unclear. The significant degradation of BA observed at neutral pH values and the inhibition of the BA degradation by the addition of tert-butanol (no. 11 in Table 1) suggest that the oxidant produced in the Fe(III)/$PW_{12}O_{40}^{3-}$/H_2O_2 system is much more reactive than the Fe(IV) species formed by the Fenton reaction under neutral pH conditions (reaction (5)). Nonetheless, solution-phase •OH does not appear to be the only oxidant formed in this system because the BA degradation did not behave as expected when the concentrations of BA, H_2O_2, and •OH scavengers were varied: the fraction of •OH that react with BA ($f_{•OH,BA}$) can be expressed by equation (6), and the H_2O_2 utilization efficiency for BA degradation (Δ[BA]/Δ[H_2O_2]) should be approximately proportional to the $f_{•OH,BA}$ value.

$$f_{•OH,BA} = k_{•OH,BA}[BA]/(k_{•OH,BA}[BA] + k_{•OH,H2O2}[H_2O_2]$$
$$+ \sum k_{•OH,S}[S]) \qquad (6)$$

where $k_{•OH,H2O2}$ is 2.7×10^7 M^{-1} s^{-1}, $k_{•OH,BA}$ is 5.9×10^9 M^{-1} s^{-1} [30], and $\sum k_{•OH,S}$[S] represents the rate constants and concentrations of other •OH scavengers (e.g., tert-butanol).

In the presence of 0.5 mM BA and 50 mM H_2O_2, the $f_{•OH,BA}$ value is calculated to be 0.68. When the concentration of BA increases by an order of magnitude (from 0.5 to 5 mM) or the concentration of H_2O_2 decreases by an order of magnitude (from 50 to 5 mM), the calculated $f_{•OH,BA}$ value increases from 0.68 to 0.96. However, the observed H_2O_2 utilization efficiency increased by approximately a factor of five under these conditions (from 3.4 to 14–16%; nos. 2, 4, and 6 in Table 1), which indicates that the oxidant formed in this system is more reactive with H_2O_2 than BA. In addition, the inhibitory effect of tert-butanol on the BA degradation is not as high as predicted by its •OH rate constant ($k_{•OH,tert\text{-}butanol} = 6.6 \times 10^8$ M^{-1} s^{-1} [30]): addition of 200 mM tert-butanol should have decreased the H_2O_2 utilization efficiency of BA by almost two orders of magnitude in the presence of 0.5 mM BA and 50 mM H_2O_2, compared to the factor of four decrease observed in Table 1 (no. 11). The inconsistency between experimental observations and predictions based on •OH reaction rates suggests that other oxidants such as caged •OH [31] or a more reactive Fe(IV) species coordinated by $PW_{12}O_{40}^{3-}$ are produced in the presence of $PW_{12}O_{40}^{3-}$.

4.3. Stability of Fe(III)–PW$_{12}$O$_{40}$$^{3-}$ complexes

The production of oxidants during the catalytic decomposition of H_2O_2 does not alter the structure or reactivity of $PW_{12}O_{40}^{3-}$ as verified by the observation that the UV absorption band of Fe(III)–$PW_{12}O_{40}^{3-}$ ($\varepsilon_{255nm} \approx 35,000$ M^{-1} cm^{-1}) was not significantly changed after the reaction (under the conditions of no. 2 in Table 1; data not shown). However, $PW_{12}O_{40}^{3-}$ undergoes stepwise hydrolysis, to ultimately produce PO_4^{3-} and WO_4^{2-}, under neutral and alkaline pH conditions [25,26]. The hydrolysis rate increases with pH, with half lives of $PW_{12}O_{40}^{3-}$ at pH 7 and 8 estimated to be 75 and 19 min, respectively, at 20 °C [25]. This process explains the reduction in H_2O_2 utilization efficiency observed when a $PW_{12}O_{40}^{3-}$ solution was stirred for 1 day at pH 7.5 before adding Fe(III) (0.58%; no. 12 in Table 1). A similar H_2O_2 utilization efficiency was observed when 10 mM WO_4^{2-} (i.e., the major hydrolyzed product of $PW_{12}O_{40}^{3-}$) was added to the Fe(III)/H_2O_2 system under identical conditions (no. 13 in Table 1).

The Fe(III)–$PW_{12}O_{40}^{3-}$ complexes appear to be more resistant to hydrolysis than uncomplexed $PW_{12}O_{40}^{3-}$. The catalytic activity of Fe(III)–$PW_{12}O_{40}^{3-}$ gradually decreased when the catalyst was aged for 7 days at pH 7 (Fig. 3). The Fe(III)–$PW_{12}O_{40}^{3-}$ complexes likely consist of a sandwich-type structure with two Keggin fragments linked by metal atoms. Such structures are known to be more stable under neutral pH conditions than the typical Keggin-type polyoxometalates, $XW_{12}O_{40}^{n-}$ [32].

Despite the enhanced stability of the catalyst, the gradual loss of the Fe(III)–$PW_{12}O_{40}^{3-}$ complexes by hydrolysis may still restrict the use of this system. $PW_{12}O_{40}^{3-}$ is not used commonly in water treatment or manufacturing applications and it is therefore difficult to predict the cost of a full-scale treatment system. Further research may be needed to develop more stable forms of iron-

polyoxometalate catalysts or less expensive ways of producing POM.

4.4. Reuse of $PW_{12}O_{40}^{3-}$

The retention and subsequent reuse of $PW_{12}O_{40}^{3-}$ is also necessary for the cost-effective application of the Fe(III)/$PW_{12}O_{40}^{3-}$/H_2O_2 system. It may be possible to use nanofiltration to retain the Fe(III)–$PW_{12}O_{40}^{3-}$ complexes while allowing water, salts, and dissolved solutes to pass through a treatment system. For example, Kim et al. [33] have recently demonstrated the hybrid system of the homogeneous Fenton-like oxidation using Fe(III)–tetrasulfophthalocyanine (Fe(III)–TsPc) with nanofiltration under acidic pH conditions [33]. Use of a supported catalyst such as SiO_2–$PW_{12}O_{40}^{3-}$ also could be used to retain $PW_{12}O_{40}^{3-}$. However, SiO_2–$PW_{12}O_{40}^{3-}$ exhibited a much lower H_2O_2 utilization efficiency than $PW_{12}O_{40}^{3-}$ (i.e., 3.4% for $PW_{12}O_{40}^{3-}$ vs. 0.58% for SiO_2–$PW_{12}O_{40}^{3-}$; nos. 2 and 14 in Table 1), probably due to the limited sites for the Fe(III) complexation on the catalyst surface. As a result, a supported catalyst may require a larger amount of $PW_{12}O_{40}^{3-}$ than the homogeneous system.

5. Conclusions

The Fe(III)/$PW_{12}O_{40}^{3-}$/H_2O_2 system is a new homogeneous Fenton-like system that is capable of oxidizing recalcitrant organic compounds under neutral pH conditions. Catalytic reactions of iron–$PW_{12}O_{40}^{3-}$ complexes convert H_2O_2 into strong oxidants with a higher efficiency. Due to the use of $PW_{12}O_{40}^{3-}$, which is a relatively nontoxic and resistant to oxidation, this system offers many advantages over other Fenton-like systems using organic ligands in terms of the system efficiency and environmental safety. The Fe(III)/$PW_{12}O_{40}^{3-}$/H_2O_2 system can be useful for treatment of water contaminated with toxic organic compounds, but issues associated with the eventual loss of activity and approaches for retaining and reusing the catalyst need to be further investigated for its effective application.

References

[1] J.J. Pignatello, E. Oliveros, A. Mackay, Crit. Rev. Environ. Sci. Technol. 36 (2006) 1–84.
[2] C. Walling, A. Goosen, J. Am. Chem. Soc. 95 (1973) 2987–2991.
[3] R.J. Bigda, Chem. Eng. Prog. 12 (1995) 62–66.
[4] Z. Wanpeng, Y. Zhihua, W. Li, Water Res. 30 (1996) 2949–2954.
[5] M.-J. Liou, M.-C. Lu, J. Mol. Catal. A: Chem. 277 (2007) 155–163.
[6] J.D. Laat, H. Gallard, Environ. Sci. Technol. 33 (1999) 2726–2732.
[7] C.K.-J. Yeh, W.-S. Chen, W.-Y. Chen, Prac. Period Hazard. Toxic Radioact. Waste Manage. 8 (2004) 161–165.
[8] A.-C. Ndjou'ou, J. Bou-Nasr, D. Cassidy, Environ. Sci. Technol. 40 (2006) 2778–2783.
[9] S.J. Hug, O. Leupin, Environ. Sci. Technol. 37 (2003) 2734–2742.
[10] I.A. Katsoyiannis, T. Ruettimann, S.J. Hug, Environ. Sci. Technol. 42 (2008) 7424–7430.
[11] C.R. Keenan, D.L. Sedlak, Environ. Sci. Technol. 42 (2008) 1262–1267.
[12] S. Nam, V. Renganathan, P.G. Tratnyek, Chemosphere 45 (2001) 59–65.
[13] T.J. Collins, Acc. Chem. Res. 35 (2002) 782–790.
[14] N.A. Stephenson, A.T. Bell, J. Am. Chem. Soc. 127 (2005) 8635–8643.
[15] W.H. Koppenol, J.F. Liebman, J. Phys. Chem. 88 (1984) 99–101.
[16] C.R. Keenan, D.L. Sedlak, Environ. Sci. Technol. 42 (2008) 6936–6941.
[17] B. Nowack, H.B. Xue, L. Sigg, Environ. Sci. Technol. 31 (1997) 866–872.
[18] C. Lee, C.R. Keenan, D.L. Sedlak, Environ. Sci. Technol. 42 (2008) 4921–4926.
[19] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171–198.
[20] J.T. Rhule, C.L. Hill, D.A. Judd, Chem. Rev. 98 (1998) 327–357.
[21] B. Yue, Y. Zhou, J. Xu, Z. Wu, X. Zhang, Y. Zou, S. Jin, Environ. Sci. Technol. 36 (2002) 1325–1329.
[22] X. Zhou, K. Mopper, Mar. Chem. 30 (1990) 71–88.
[23] G.M. Eisenberg, Ind. Eng. Chem. Anal. 15 (1943) 327–328.
[24] M.E. Balmer, B. Sulzberger, Environ. Sci. Technol. 33 (1999) 2418–2424.
[25] J.H. Kyle, J. Chem. Soc. Dalton Trans. (1983) 2609–2612.
[26] A. Jürgensen, J.B. Moffat, Catal. Lett. 34 (1995) 237–244.
[27] W.G. Rothschild, A.O. Allen, Radiat. Res. 8 (1958) 101–110.
[28] J.D. Rush, B.H.J. Bielski, J. Phys. Chem. 89 (1985) 5062–5066.
[29] G.G. Jayson, B.J. Parsons, Trans. Faraday Soc. 68 (1972) 236–242.
[30] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 17 (1988) 513–886.
[31] C. Walling, K. Amarnath, J. Am. Chem. Soc. 104 (1982) 1185–1189.
[32] C.M. Tourné, G.F. Tourné, F. Zonnevijlle, J. Chem. Soc. Dalton Trans. (1991) 143–155.
[33] J.-H. Kim, P.-K. Park, C.-H. Lee, H.-H. Kwon, S. Lee, J. Membr. Sci. 312 (2008) 66–75.