



## Stabilization of hydrogen peroxide using phthalic acids in the Fenton and Fenton-like oxidation

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### H I G H L I G H T S

- ▶ The stabilization of H<sub>2</sub>O<sub>2</sub> was evaluated in Fenton reactions with a stabilizer.
- ▶ The life time of hydrogen peroxide was prolonged by a stabilizer, phthalic acid.
- ▶ The stabilization is mainly due to the inhibition of catalytic activity of dissolved iron species.
- ▶ The stabilization effect was pH dependent and was negligible at above pK<sub>a2</sub>.

### A R T I C L E I N F O

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### A B S T R A C T

The stabilization of hydrogen peroxide was evaluated in Fenton reaction with phthalic acid as a stabilizer. The stabilization effect was high at a low pH < pK<sub>a1</sub> and the effect was negligible at a high pH above pK<sub>a2</sub> in both Fenton and Fenton-like reactions. While the lifetime of hydrogen peroxide was prolonged by phthalic acid, the stabilization could not contribute on the increase of the reaction rate in the current Fenton and Fenton-like experimental systems because the systems were all well mixed systems. The interaction between dissolved iron and phthalic acid was spectroscopic monitored in variable pH over pK<sub>a1</sub> and pK<sub>a2</sub> of phthalic acid. Ferrous iron was well stabilized and the initial concentration was kept after mixing with phthalate while ferric iron was removed from the aqueous phase by the phthalic acid. It could be concluded that the stabilization by phthalic acid is due to inhibition of catalytic activity of dissolved iron and minimizes the self-decomposition of hydrogen peroxide. The stabilization is affected by ionization state of the organic acid.

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### 1. Introduction

Oxidation is one of the most popular reactions to treat organic and inorganic contaminants in water and soil environments. Hydrogen peroxide and ozone are the most common oxidants and have been used in numerous environmental applications. The oxidants generate more powerful species when they are coupled with UV and catalysts such as titanium oxide or ferrous iron (Glaze et al., 1993; Pignatello et al., 1999; Nogueira et al., 2005; Watts et al., 2005; Liu et al., 2006; Martinez et al., 2007; Laat et al., 2011; Almeida et al., 2012; Matfonova and Batoev, 2012; Zhu et al., 2012). When the hydrogen peroxide is coupled with ferrous iron, the mixture of hydrogen peroxide and ferrous iron is called a Fenton's reagent (Fenton and Fenton, 1894). Ferrous iron

initiates and catalyzes the decomposition of hydrogen peroxide resulting in the generation of reactive species and oxidation of target contaminants. The reactive species include hydroxyl radical, one of the strongest oxidizing species.

Fenton reactions have been intensively studied and applied to water and wastewater treatments. Fenton reactions have also been successfully tested for soil and groundwater remediation using naturally occurring iron minerals in subsurface environment, so-called Fenton-like reactions (Hinchee et al., 1990; Prasad and Watts, 1997; Baciocchi et al., 2004; Watts and Teel, 2005; Du et al., 2012; Munoz et al., 2012; Xu and Wang, 2012). In water and wastewater treatments, a rapid production of hydroxyl radical is preferred for a quick treatment, however, in the remediation of soil and groundwater, the rapid generation of reactive species such as hydroxyl radical is not favorable because the reactive species usually has a short life-time and a relatively long time is required to flow through a soil layer with a low hydraulic conductivity. Therefore, the rapid

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generation of these reactive species leads to waste of the hydrogen peroxide. Consequently, a large amount of hydrogen peroxide is needed to treat the contaminants adsorbed on soil surfaces and placed in a deep soil layer. The stabilization of hydrogen peroxide is necessary for an effective and complete removal of organic contaminants from subsurface environments. A few stabilizers were investigated for the stabilization of hydrogen peroxide. Phosphate is the most frequently studied stabilizer for hydrogen peroxide (Watts and Dilly, 1996; Kakaria and Watts, 1997; Watts et al., 1999; Baciocchi et al., 2003, 2004). Phosphate (Kakaria and Watts, 1997; Watts et al., 1999) retards decomposition of hydrogen peroxide by lowering the available dissolved iron concentration through either precipitation of iron species or formation of stable complexes. Recently, Watts and co-workers reported that organic acids (Watts et al., 2007) also inhibited the self-decomposition of hydrogen peroxide in Fenton-like reactions. The stability of hydrogen peroxide is dependent on the type of subsurface solids and phytate, citrate, and malonate showed relatively better performance in the stabilization out of ten tested organic acids. They also reported that phytate was the most effective stabilizer increasing the half-life of hydrogen peroxide to about 50 times (Watts et al., 2007). Jung and co-workers evaluated the lifetime of  $\text{H}_2\text{O}_2$  in Fenton's reaction and Fenton-like reactions and they concluded  $\text{H}_2\text{O}_2$  was more stable in the Fenton-like reaction than in the Fenton's reaction and the lifetime of  $\text{H}_2\text{O}_2$  was also highly affected by the solution pH, and a pH buffered acidic condition was preferred (Jung et al., 2009). Recently an improved remediation efficiency was reported using stabilizers and chelating agents in Fenton-like process (Vicente et al., 2011). They reported that  $\text{KH}_2\text{PO}_4$  has a negligible stabilization effect but L-ascorbic acid, garlic and citric acid give a certain decrease of the hydrogen peroxide conversion. Previous studies also showed that the lifetime of hydrogen peroxide could be an indicator of the efficiency of Fenton's and Fenton-like oxidation in soils (Baciocchi et al., 2003, 2004). Many studies were conducted to investigate the catalytic decomposition of hydrogen peroxide in homogeneous aqueous solution and in mineral catalyzed Fenton-like systems (Lin and Gurol, 1998; Laat and Gallard, 1999; Watts et al., 1999; Kwan and Voelker, 2003).

More detail studies are needed to understand the stabilization mechanism and to use the hydrogen peroxide stabilized Fenton reactions on practical purposes. A reasonable hypothesis is the catalytic inhibition of transition metal which is used for Fenton reactions. Organic acids make complexes with transition metals inhibiting the catalytic activity. Sometimes the complexes can lead to precipitation. However, the ionization states of organic acids vary depending on solution pH and the different organic acid species are likely to make various metal-organic acid complexes. The permanent removal of iron species from aqueous phase can stabilize hydrogen peroxide and simultaneously terminate the Fenton reaction. A stabilization of hydrogen peroxide by reducing the catalytic activity is preferred. The reduced activity will likely improve the delivery of hydrogen peroxide to the contaminants in a deep soil layer.

In this study, the stability of hydrogen peroxide was evaluated in the presence of an organic acid, phthalic acid. The formation of complexes with organic acids was monitored at varied solution pH and iron-organic acid complexes were tested for a model contaminant, nitrobenzene.

## 2. Experiments

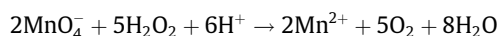
### 2.1. Materials

Hydrogen peroxide (30%), nitrobenzene, hydrochloric acid, hexane (HPLC grade), potassium hydrogen phthalate were purchased

from Sigma-Aldrich (Milwaukee, WI). Ferrous sulfate and ferric chloride were obtained from Duksan Chemical (Korea). All chemicals were reagent grade and used without further purification. A Thermo Scientific Barnstead NANOpure™ water purification system was used to purify water used in all experiments to > 18 M $\Omega$  cm.

### 2.2. Spectroscopic studies of hydrogen peroxide-iron complexes

Spectroscopic investigation was conducted for ferrous and ferric iron in the presence of stabilizers. The absorbance of UV-Vis range of the iron-organic acid complexes was measured in the variable solution pH over all  $\text{pK}_a$  of the phthalic acid. The dissolved iron was measured using an atomic absorption spectroscopy (Perkin Elmer AA-100) equipped with an acetylene flame before and after making complexes. The concentration of the remaining was determined with redox titration using potassium permanganate. It is known that  $\text{H}_2\text{O}_2$  reacts stoichiometrically with permanganate at about 60 °C as shown by the redox equation below (Flotron et al., 2005).



The  $\text{pK}_a$  of phthalic acid are variable depending on the isomers. The  $\text{pK}_{a1}$  of *o*-phthalic acid, *m*-phthalic acid, and *p*-phthalic acid are 2.89, 3.54, and 3.51 respectively and the  $\text{pK}_{a2}$  of the isomers are 5.51, 4.60, and 4.82 respectively. In the current study, *o*-phthalic acid was the major component (99.8%).

### 2.3. Oxidation of nitrobenzene in Fenton and Fenton-like reactions

Oxidation reactions were carried out in batch reactors using Erlenmeyer flasks. Nitrobenzene was dissolved into deionized water and the reaction initiated by introducing hydrogen peroxide and ferrous sulfate or ferric chloride. The initial concentration of nitrobenzene, hydrogen peroxide, and iron are 200 mg L<sup>-1</sup>, 1.03 M and 0.017 M respectively ( $\text{H}_2\text{O}_2/\text{Fe} = 60$ ). The dissolved phthalic acid was 0.05 M. All reaction conditions of Fenton-like reactions are identical with Fenton reaction except the iron source using hematite (Kanto Chemical) or magnetite (Aldrich) instead of ferrous or ferric iron. At each scheduled sampling time, 5 mL of solution was taken and moved to a 20 mL vial containing hexane. The vials were shaken for 30 on an orbital shaker and the hexane transferred to a GC auto-sampler vials. Nitrobenzene was quantified using a GC-FID (HP-5890). At each sampling time, the remaining hydrogen peroxide was also determined.

## 3. Results and discussion

### 3.1. Complex of iron-phthalic acids

Each aqueous solution of phthalic acid, ferrous sulfate, and ferric chloride was analyzed with a UV-vis spectrophotometer and the mixture of phthalic acid and ferrous or ferric iron was monitored in UV-vis range with variation of solution pH (Figs. 1 and 2). The solution pH was adjusted with HCl and NaOH to 2.6 (< $\text{pK}_{a1}$ ), to 4.1 (between  $\text{pK}_{a1}$  and  $\text{pK}_{a2}$ ), and to 6.5 (> $\text{pK}_{a2}$ ). The absorption spectrum of phthalate was not changed with the addition of ferrous iron below  $\text{pK}_{a1}$  and between  $\text{pK}_{a1}$  and  $\text{pK}_{a2}$ . The spectrum was changed only above  $\text{pK}_{a2}$  indicating that ferrous iron interacted or made complexes with fully ionized phthalate. Dissolved iron was quantified and no significant change was observed before or after making mixture.

In the case of ferric iron, the spectroscopy of phthalate was changed in all three pH ranges indicating that ferric iron interacted with ionized phthalate and non-ionized phthalate. The

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