

Stabilization of hydrogen peroxide using tartaric acids in Fenton and fenton-like oxidation

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Abstract—The stabilization of hydrogen peroxide is a key factor in the efficiency of a Fenton reaction. The stability of hydrogen peroxide was evaluated in a Fenton reaction and Fenton-like reactions in the presence of tartaric acid as a stabilizer. The interactions between ferrous or ferric iron and tartaric acid were observed through spectroscopic monitoring at variable pH around pK_{a1} and pK_{a2} of the stabilizer. Ferric iron had a strong interaction with the stabilizer, and the strong interaction was dominant above pK_{a2} . At a low pH, below pK_{a1} , the stabilizing effect was at its maximum and the prolonged life-time of hydrogen peroxide gave a higher efficiency to the oxidative degradation of nitrobenzene. In Fenton-like reactions with hematite, the acidic conditions caused dissolution of iron from an iron oxide, and an increase in iron species was the result. Tartaric acid showed a stabilizing effect on hydrogen peroxide in the Fenton-like system. The stabilization by tartaric acid might be due to an inhibition of catalytic activity of dissolved iron, and the stabilization strongly depends on the ionization state of the stabilizer.

Keywords: Fenton Oxidation, Fenton-like Reactions, Stabilization, Hydrogen Peroxide, Life-time, Tartaric Acid

INTRODUCTION

Fenton reactions are advanced oxidation processes that have been used frequently in the oxidative degradation of numerous organic contaminants. Many researchers have worked on the reaction mechanisms and kinetics [1-7], and numerous organic compounds have been tested including pharmaceutical wastewater [8-12]. They concluded the Fenton reaction is one of the most powerful oxidation reactions and very feasible for decomposition of organic compounds. Fenton reactions also have been successfully tested for removing organic contaminants in soil and groundwater, and it is known that Fenton reactions occur by just injecting hydrogen peroxide into a soil layer without catalysts such as titanium oxide or ferrous iron. Naturally occurring iron minerals in subsurface environment work as catalysts instead of ferrous iron, and this reaction is called a Fenton-like reaction [5,10,13-23]. Fenton-like reactions also generate hydroxyl radicals, which are very strong oxidizing species, and have all the advantages of Fenton reactions. A Fenton-like reaction can be applied to sites heavily contaminated by organic compounds for quick treatment. This technology is especially feasible for eliminating toxic organic contaminants that inhibit biological degradation.

One of the advantages of Fenton reactions is a very fast reaction rate in comparison with biological treatments. The generation of hydroxyl radicals is very fast, and oxidation with a hydroxyl radical needs to be done within minutes due to the short life-time of the

radical [19,24-26]. When hydrogen peroxide is mixed with enough ferrous iron, the reaction occurs very vigorously and the reaction terminates quickly upon consumption of the hydrogen peroxide. More oxidants produce more reactive radicals and this leads to quick treatments. In water and wastewater treatments, a rapid production of reactive radicals is preferred for a quick treatment when the reaction is not limited by mass transfer. However, when applied to soil or groundwater, the rapid generation of reactive species is not favorable because the reactive species usually have a short life-time and unnecessary rapid generation of the species wastes the hydrogen peroxide [17,27]. Fenton-like reactions in soil and groundwater remediation are not homogeneous and it might take days or months for reactant to flow to contaminants in a deep soil layer or into a less permeable layer. Therefore, the protection of hydrogen peroxide from unnecessary decomposition is necessary to have it flow into a deep layer, leading to effective removal of organic contaminants from subsurface environments.

Without catalysts such as ferrous iron, self-decomposition of H_2O_2 is not significant; therefore, a way to protect H_2O_2 is to avoid iron species from contacting the H_2O_2 . However, permanent exclusion of iron species from the reaction system leads to a very slow reaction and degradation of contaminants cannot be achieved. Phosphate [14,19] retards decomposition of hydrogen peroxide by lowering the available dissolved iron concentration through either precipitation of iron species or formation of stable complexes. Watts and co-workers reported that organic acids also inhibit the self-decomposition of hydrogen peroxide in Fenton-like reactions, and the stability of hydrogen peroxide is dependent on the type of subsurface solids [26]. However, there are no additional reports show-

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ing the mechanism of the stabilization of hydrogen peroxide. Jung and co-workers evaluated the lifetime of H_2O_2 in Fenton reactions and Fenton-like reactions and concluded that the lifetime of H_2O_2 was also highly affected by the solution pH, and a pH buffered acidic condition was preferred [28]. Recently, Kim et al. reported that malonic acid has stabilization ability for hydrogen peroxide in Fenton and Fenton-like reactions [29].

In this study, the stability of hydrogen peroxide was evaluated in the presence of an organic acid, tartaric acid. The interaction between tartaric acid and ferrous or ferric iron was monitored at varied solution pH. Fenton reactions were tested for an organic contaminant, nitrobenzene, in the presence of tartaric acid. Fenton-like reactions were also tested using iron oxides instead of soluble ferrous or ferric iron with tartaric acid.

EXPERIMENTS

1. Materials

Hydrogen peroxide (Junsei, 30%), nitrobenzene (Sigma-Aldrich), hydrochloric acid (Merck, 37%), hexane (J.T. Barker, HPLC grade), and tartaric acid (SAMCHUN) were used for the Fenton reactions. Ferrous sulfate (heptahydrate) and ferric chloride (hexahydrate) were obtained from Duksan Chemical (Korea). All chemicals were reagent grade and used without further purification. A Barnstead NANO-pure system was used to purify the water used in all experiments to $>18\text{ M}\Omega\text{-cm}$.

2. Spectroscopic Studies of Hydrogen Peroxide-iron Complexes

Spectroscopic investigation was conducted for ferrous and ferric iron in the presence of tartaric acid. The concentration of tartaric acid and iron species was varied to get clear absorption spectroscopy and to identify the interaction between the organic acid and iron species. The absorbance in UV-Vis range was monitored for the iron-organic acid complexes. Solution pH level was varied over all pK_a of tartaric acid. The dissolved iron was measured before and after the complexation by using an atomic absorption spectrometer (Perkin Elmer AA-100) equipped with an acetylene flame. The remaining hydrogen peroxide was determined with redox titration using potassium permanganate (Junsei, grade reagent). It is known that H_2O_2 reacts stoichiometrically with permanganate at about 60°C by a redox equation [30].

The pK_a of tartaric acids are variable depending on the isomers. The pK_{a1} of L-tartaric acid and meso-tartaric acid are 2.98 and 3.22, respectively, and the pK_{a2} of the isomers are 4.34 and 4.82 respectively. In the current study, $C_4H_6O_6$ L-tartaric acid was the major component.

3. Oxidation of Nitrobenzene in Fenton and Fenton-like Reactions

Oxidation reactions were in batch reactors using Erlenmeyer flasks. Nitrobenzene was dissolved into deionized water, and the reaction was initiated by introducing hydrogen peroxide and ferrous sulfate or ferric chloride. The initial concentration of nitrobenzene, hydrogen peroxide, and iron was 200 mg/L, 1.03 M and 0.017 M, respectively ($H_2O_2/Fe=60$). The dissolved tartaric acid was 0.05 M. The study was not carried out under controlled solution pH, but the pH changes were monitored because common inorganic and organic pH buffers interfere with the species in the

reactors and make an effect on the reaction. The Fenton reaction was performed using multiple injections of nitrobenzene testing the continuous use of remaining hydrogen peroxide due to stabilization. An aliquot of nitrobenzene was repeatedly spiked after every sampling time until nitrobenzene accumulated. Organic buffers can be decomposed by the Fenton reaction and some organic acids are known to have a stabilizing effect. Some inorganic buffers also make complexes with iron species. Phosphate, a common pH buffer, was used as a H_2O_2 stabilizer in a few previous studies. The initial solution pH was adjusted using HCl and NaOH, and the pH variation was monitored at every sampling time. All reaction conditions of Fenton-like reactions are identical with the Fenton reaction except the source of iron was hematite (Kanto Chemical, 0.017 M) instead of ferrous or ferric iron. At each scheduled sampling time, 5 mL of solution was taken and extracted using hexane on an orbital shaker for 30 min. The hexane phase was transferred to GC auto-sampler vials. Nitrobenzene was quantified using a GC-FID (Agilent, 7890A). At each sampling time, the remaining hydrogen peroxide was also determined.

RESULTS AND DISCUSSION

1. Complex of Iron-organic Acids

The individual absorption spectra of tartaric acid, ferrous sulfate, and ferric chloride were obtained, and the absorption spectra of the mixture of tartaric acid and ferrous iron or the mixture of tartaric acid and ferric iron were also obtained in UV-Vis range. Spectra data were collected at a variation of solution pH between pK_{a1} and pK_{a2} . The pK_{a1} and pK_{a2} of tartaric acid are 2.98 and 4.34, respectively. Neutral tartaric acid has an absorption in the UV range with a maximum wavelength of 212 nm. Two new absorption peaks at 230 nm and 300 nm appeared upon the addition of ferrous iron, indicating that tartaric acid interacted with ferrous iron. At pH 3.50 the absorption spectra of ferrous iron and tartaric acid changed, as shown in Fig. 1. Absorbance of tartaric acid increased over the range of 212 nm to 400 nm with characteristic peaks at 350 nm, indicating there were interactions between the organic acid and ferrous iron. In the case of $>pK_{a2}$, pH 4.50, a dramatic change of absorption spectra was observed at wavelengths between 212 nm to 265.6 nm and between 310 nm to 500 nm. This indicates tartaric acid interacts strongly with ferrous iron at $pH > pK_{a2}$ where anionic forms are dominant. For ferric iron, the absorption spectra of ferric iron changed as the solution pH increased. The absorption spectra at pH 3.50 and pH 4.50 were the same as shown in Fig. 2. The absorption spectra of the mixture of ferric iron and tartaric acid changed from the individual spectra. At pH 2.50, absorption intensity increased over the wavelength longer than 300 nm. At pH 3.5 and 4.5, absorption intensity increased over the visible range from 270 nm to 520 nm for both pH ranges. In general, the spectrum of tartaric acid was changed over all three pH ranges, indicating ferric iron interacts with tartarate and non-ionized tartaric acid. Dissolved iron was measured and no significant change was observed before or after making the mixtures. Organic acids interact with transition metals, including iron, and when they work as ligands, organic acid-transition metal complexes can form inhibiting the catalytic activity, whereas the complexes

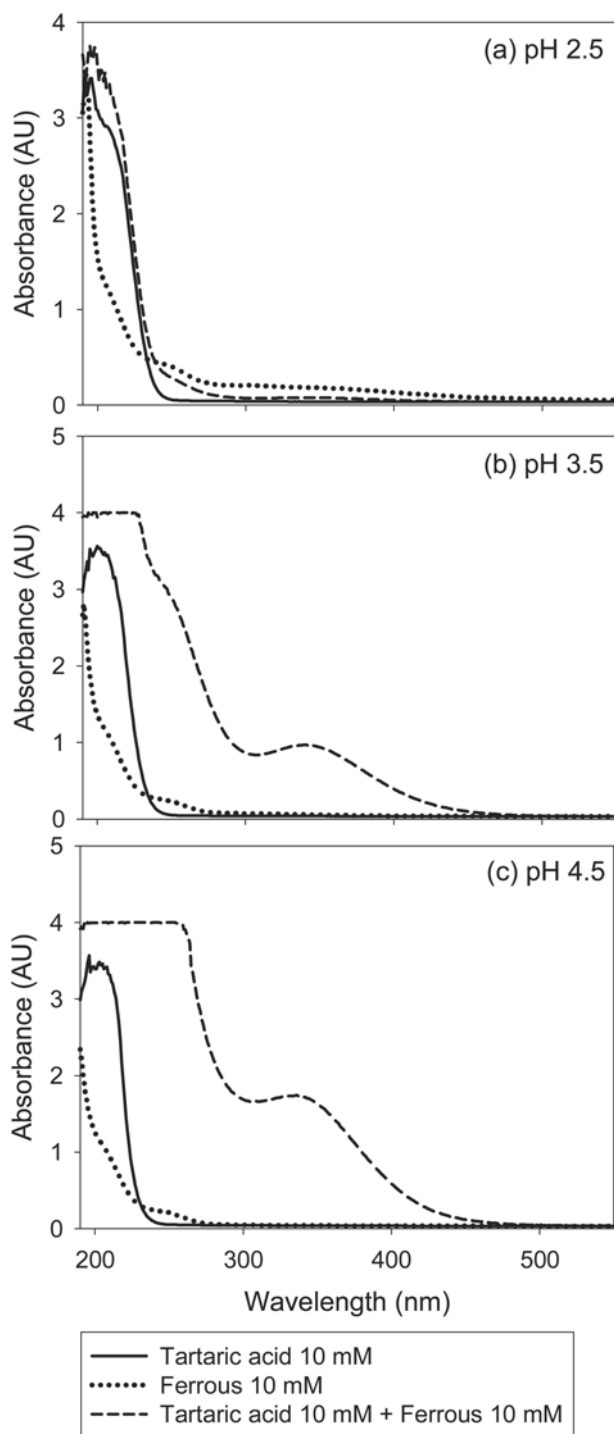


Fig. 1. The absorption spectrum of tartaric acid with the addition of ferrous iron.

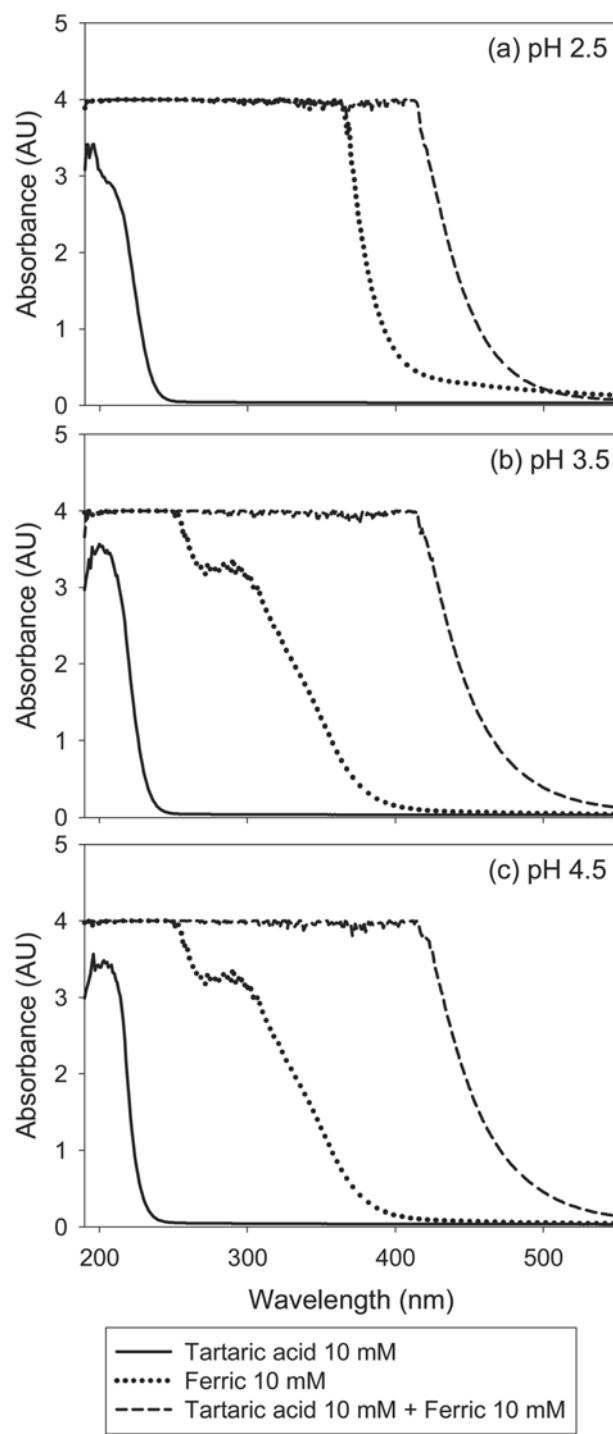


Fig. 2. The absorption spectrum of tartaric acid with the addition of ferric iron.

can lead to precipitation. Organic acid-metal complexes have been studied in water and soil environments and complex formation constants are dependent on the solution pH [31-33]. Jansen et al. reported mobility of Fe(II) and Fe(III) in acidic forest soils by dissolved organic matter, and the solution pH affected the solubilization of metal organic matter complex [32]. Jung et al. showed that ferric iron made a complex with phthalic acid and was removed

by precipitation [28]. However, the ionization states of organic acids vary depending on solution pH, and different organic acid species are likely to make various metal-organic acid interactions or complexes. The permanent removal of iron species from an aqueous phase may stabilize hydrogen peroxide but also terminate the Fenton reaction. The stabilization of hydrogen peroxide by reduced catalytic activity is preferred rather than a complete removal of cata-

lytic activity. The reduced activity will likely improve the delivery of hydrogen peroxide to the contaminants in a deep soil layer and help control the release of hydroxyl radicals.

2. Stabilization of H_2O_2 in a Fenton's Reaction

Stability of H_2O_2 was tested in the presence of ferrous iron and tartaric acid under variable pH conditions. The solution pH was adjusted to three ranges before the experiment was started: 2.55 ($< \text{pK}_{\text{a}1}$), 3.62 (between $\text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}2}$), and 4.48 ($> \text{pK}_{\text{a}2}$). Decomposition of H_2O_2 was determined in 48 hours and the solution pH and concentration of soluble iron were monitored simultaneously (Fig. 3). H_2O_2 quickly decomposed in the presence of ferrous or ferric iron without the stabilizer. However, the stability of H_2O_2 dramatically increased after tartaric acid was added, indicating the organic acid worked as a stabilizer. Initial pH of the solution was adjusted to three ranges: below $\text{pK}_{\text{a}1}$, between $\text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}2}$, and

above $\text{pK}_{\text{a}2}$. However, the solution pH decreased early during the reaction as the result of the Fenton reaction. Laat and Gallard studied the catalytic decomposition of hydrogen peroxide using ferric species. They summarized major reaction kinetic constants from their study and others'. Most of the reactions among iron species, water, and hydrogen peroxide produce a proton, but some of the reactions make a hydroxyl ion as shown below [34].

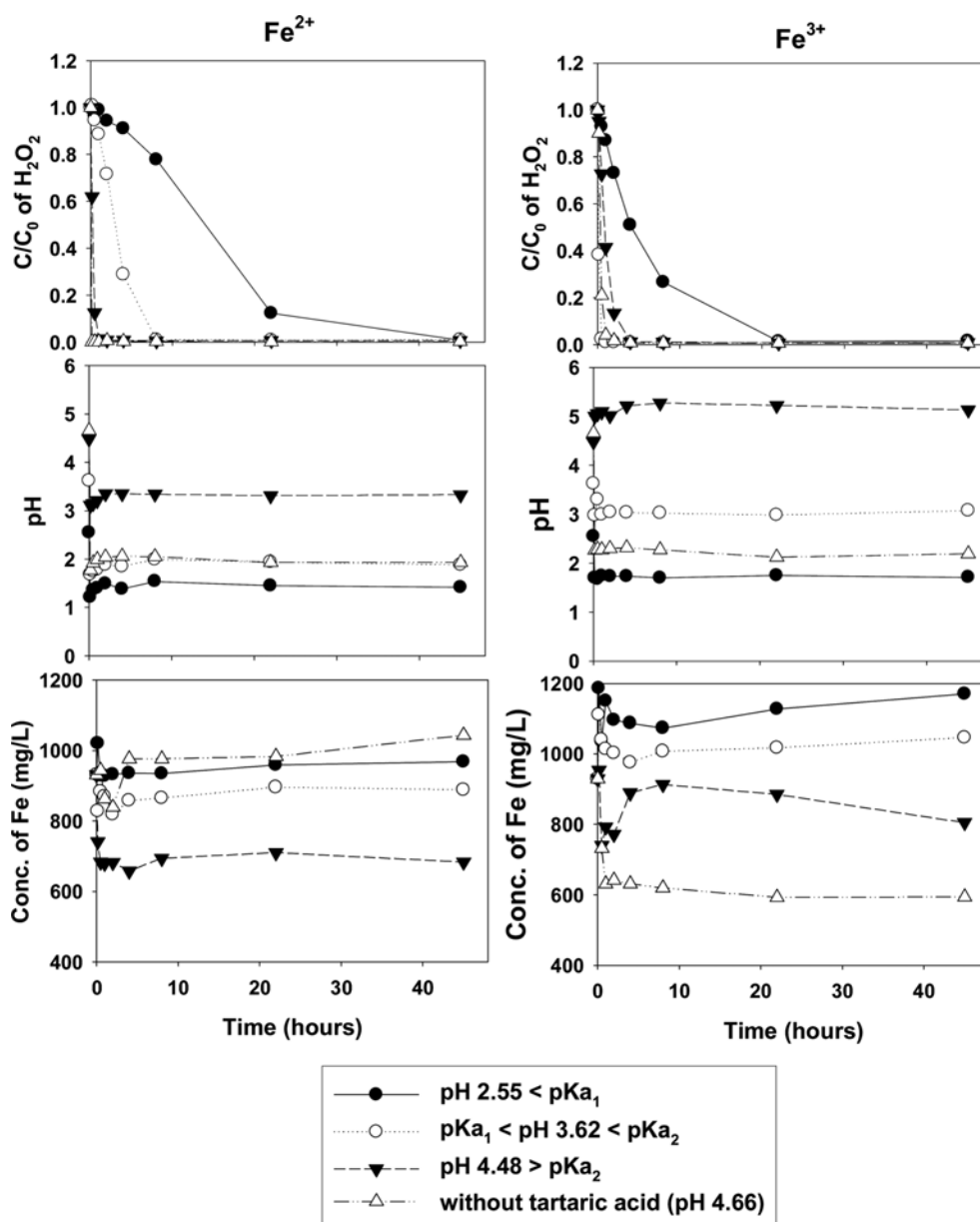
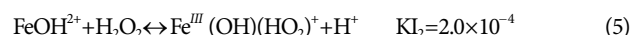
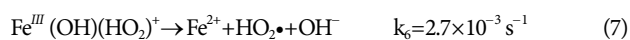


Fig. 3. Stabilization of hydrogen peroxide with tartaric acid in the presence of ferrous and ferric iron.



A pH drop was observed upon the addition of iron into the hydrogen peroxide solution in this study, indicating the pH drop was the result of a Fenton reaction.

The tendency of the pH effect on the stability is clear even though the initial pH was not sustained over the whole reaction period. In general, at low starting pH where the tartaric acid is in neutral form,

tartaric acid has a better stabilizing effect on both ferrous and ferric iron. Concentration of soluble iron fluctuated for the first four hours and then stabilized during the rest of the reaction period. This indicates the oxidation reaction includes complex reactions between iron species and other stabilizers or ions, and the reactions affect the concentration of dissolved iron. However, the detailed reactions were not identified in the current study. The iron concentration of a $\text{pH} > \text{pK}_{\text{a}1}$ system remained relatively high in both the ferrous and the ferric systems and the iron concentration without-stabilizer kept high in the $\text{pH} > \text{pK}_{\text{a}1}$ ferrous system, but the concentration decreased to about 600 mg/L for the ferric system

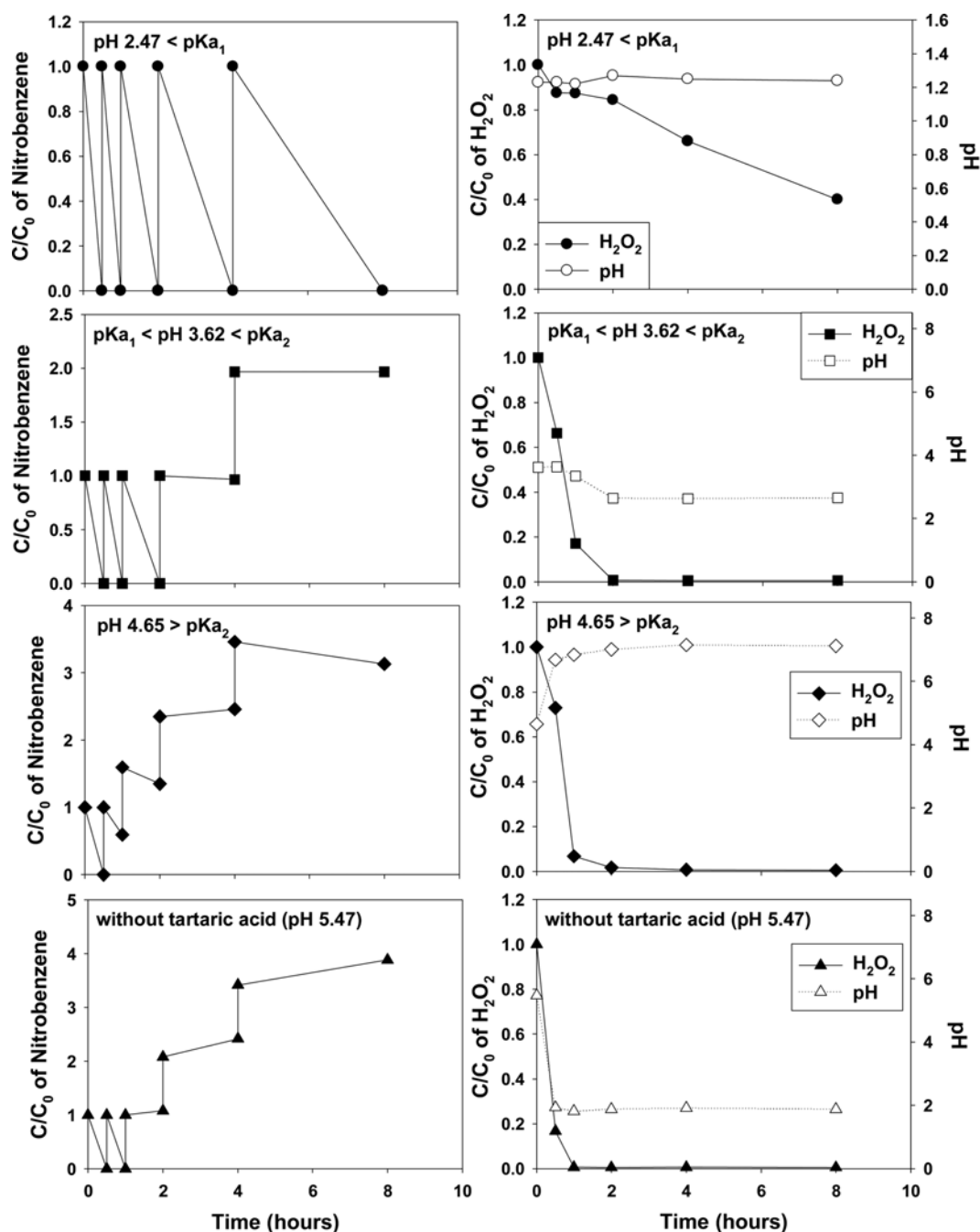


Fig. 4. Fenton oxidation of nitrobenzene in the presence of tartaric acid as a stabilizer and ferrous iron.

without-stabilizer indicating precipitation occurred. The fluctuation in the iron concentration might be connected to the competition between the complexing effects of tartaric acid and the pH. The increase of iron concentration in the middle of the reaction might be due to the dissolution of precipitated species. This indicates that tartaric acid interacts with the dissolved iron and makes the iron soluble in water. However, the neutral form of tartaric acid-iron interaction lowered the catalytic activity of the Fenton reaction, while the interaction of ionized tartaric acid-ferrous or ferric iron at high pH worked as catalysts for the Fenton reaction decomposing H_2O_2 . The current results demonstrated that the soluble

iron stabilized by an organic acid has a very low catalytic activity for the Fenton reaction. Enough iron in soluble states and ionized tartaric acid, which is supposed to make a strong interaction with ferrous or ferric iron, cannot contribute to the stabilization.

3. Oxidation of a Model Contaminants in Fenton Reaction with Stabilizer

The Fenton reaction stabilized with tartaric acid was applied to a model contaminant, nitrobenzene. The remaining H_2O_2 was determined at every sampling time as shown in Fig. 4. Injected nitrobenzene was rapidly oxidized and an aliquot of nitrobenzene was repeatedly spiked after every sampling time to test the longevity of

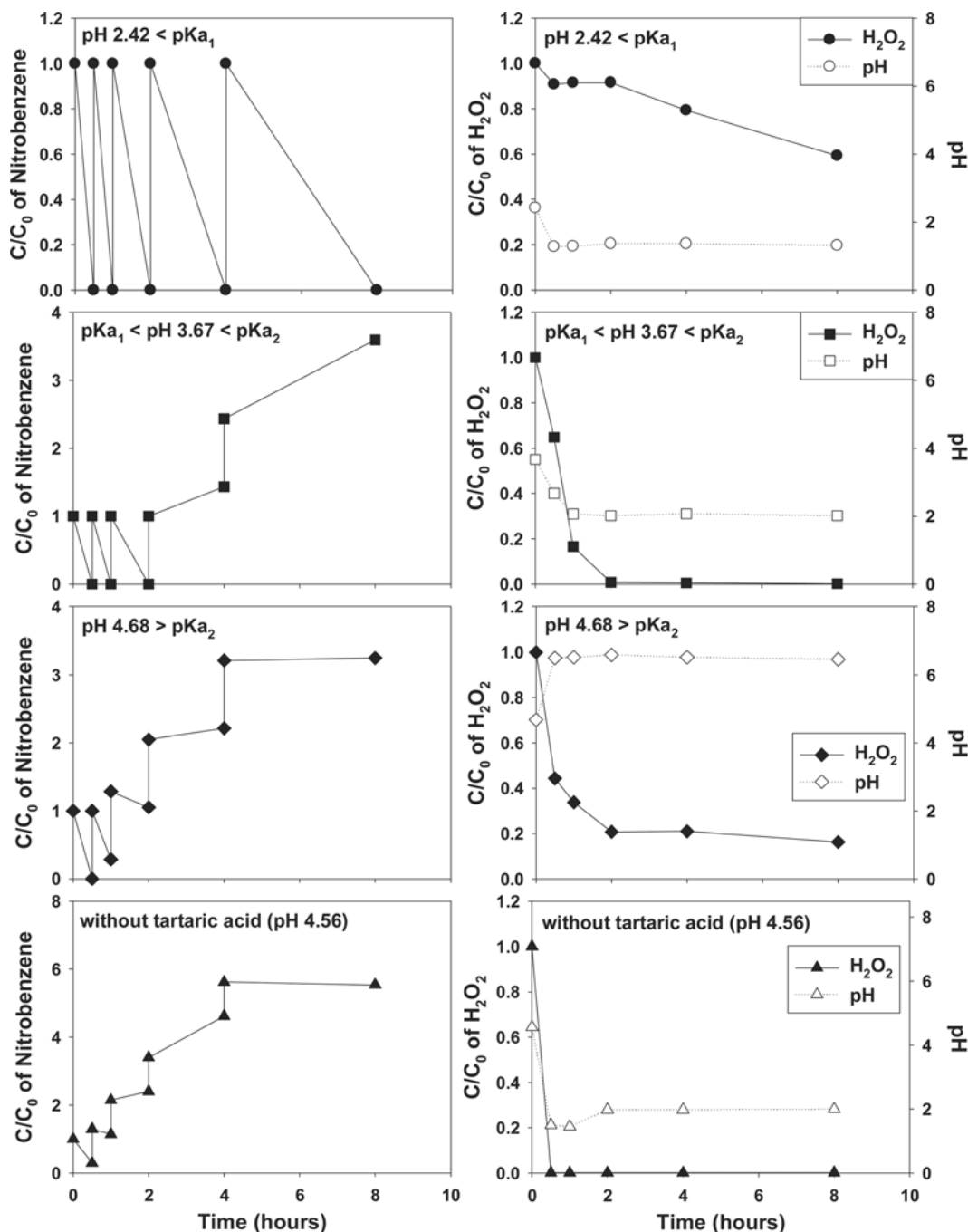


Fig. 5. Fenton oxidation of nitrobenzene in the presence of tartaric acid as a stabilizer and ferric iron.

the reaction system. The newly added mass of nitrobenzene was expressed as the determined concentration at each sampling time. In the $\text{pH} < \text{pK}_{\text{a}1}$ system, nitrobenzene was spiked six times, and five times the nitrobenzene was completely decomposed, and in the sixth was partly removed. In the pH range of $\text{pK}_{\text{a}1} < \text{pH} < \text{pK}_{\text{a}2}$, the first three times the target spike resulted in a complete removal and in the fourth spike, accumulated. However, for the $\text{pH} > \text{pK}_{\text{a}2}$ system, only the first spike was oxidized, and from the second spike, the concentration of the remaining target compound increased. The longevity of the Fenton reaction without tartaric acid was low due to the quick decomposition of H_2O_2 in a few hours. The run of oxidation ability of the system matched the complete decomposition of H_2O_2 . The H_2O_2 was used up at the sampling time of 24 hr, corresponding to where the oxidation reaction stopped in the $\text{pH} < \text{pK}_{\text{a}1}$ system (data is plotted up to 8 hrs). As the solution pH increased, the stability of H_2O_2 decreased and H_2O_2 was used up in a few hours. A similar trend of stabilization of hydrogen peroxide and reactivity for nitrobenzene was obtained in the test for ferric iron with repeated spikes of nitrobenzene after each sampling. The exception was at $\text{pH} > \text{pK}_{\text{a}2}$ where stabilization of H_2O_2 was observed but no effective removal of the target compound was obtained, indicating the stabilization of H_2O_2 was due to a strong interaction between stabilizer and ferric iron or permanent removal of iron species (concentration of dissolved iron was not available for this experiment) (Fig. 5). The longevity of reactivity was found to be completely related to the stability of H_2O_2 . This means that stabilization of H_2O_2 leads to greater efficiency of the Fenton reaction with a given amount of H_2O_2 .

4. Stabilization H_2O_2 in a Fenton-like Reaction

It takes at least a few months to treat contaminated soil and groundwater through in-situ chemical oxidation due to slow mass transfer in soil layers. Therefore, cost-effective processes with relatively slow reaction rates are preferred rather than a fast reaction in a range of minutes, which is preferred in off-site reactors. The stability of H_2O_2 is more important in soil and groundwater remediation because it takes a relatively long time for H_2O_2 to flow through a soil layer into adsorbed contaminants. Whereas, the reaction kinetic is an important factor in an advanced oxidation of off-site or ex-situ systems. The H_2O_2 stabilizer, tartaric acid, was applied to a Fenton-like reaction with hematite, and the pH of the solution was varied from below $\text{pK}_{\text{a}1}$ to above $\text{pK}_{\text{a}2}$. Without tartaric acid, H_2O_2 quickly decomposed and was used up in a few hours. However, significant stabilization was obtained with the stabilizer in the order of $\text{pH} < \text{pK}_{\text{a}1}$, $\text{pK}_{\text{a}1} < \text{pH} < \text{pK}_{\text{a}2}$, and $\text{pH} > \text{pK}_{\text{a}2}$. The dissolved iron concentration was monitored as shown in Fig. 6. The concentration of soluble iron was about 40–80 mg/L and 30–65 mg/L for $\text{pH} < \text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}1} < \text{pH} < \text{pK}_{\text{a}2}$, respectively. However, the iron concentration of $\text{pH} > \text{pK}_{\text{a}2}$ was less than 30 mg/L and that of the control system was less than 20 mg/L. The dissolution of iron oxide could be enhanced by surface complexation with organic acid. The dissolution can be increased by the acidity and bidentate complex formation [35]. Soluble iron species were released from the hematite surface and more iron species can accumulate in an acidic condition such as below $\text{pK}_{\text{a}1}$. The Fenton-like reactions might involve both a homogeneous reaction with dissolved iron species and a heterogeneous reaction on the surface of the iron oxide. The het-

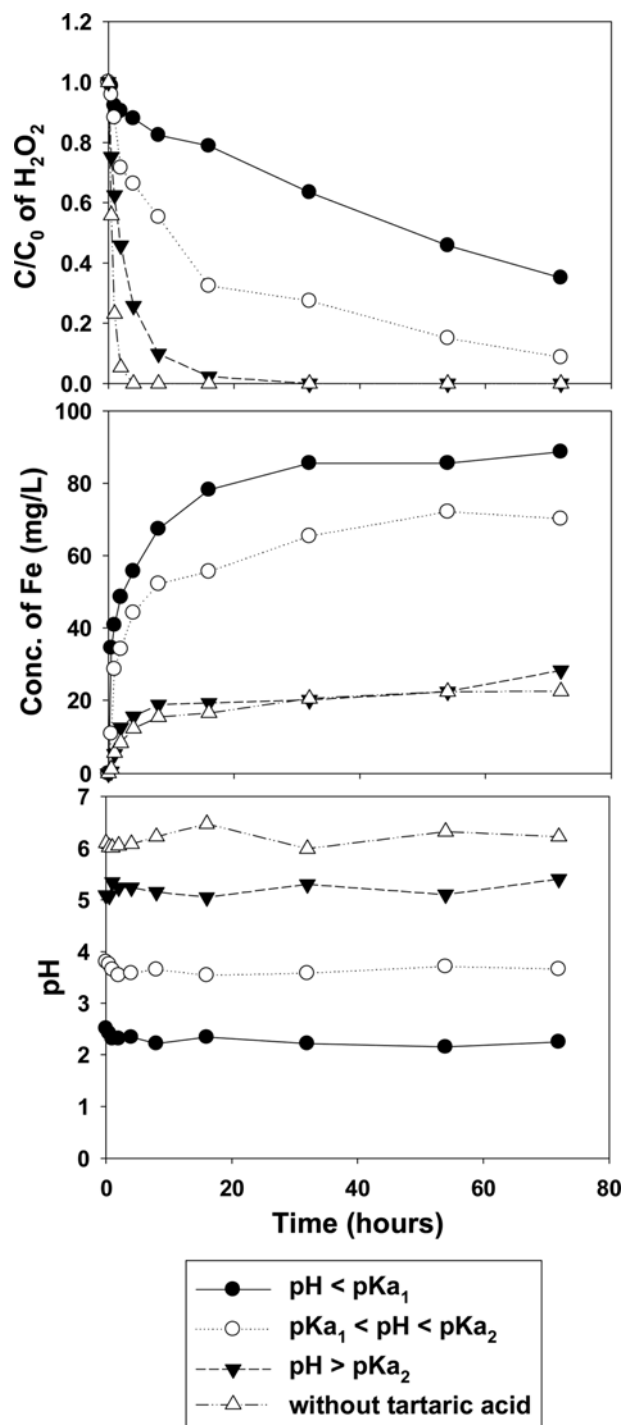


Fig. 6. Fenton-like oxidation of nitrobenzene in the presence of tartaric acid as a stabilizer and the stability of hydrogen peroxide.

erogeneous reaction can contribute to the decomposition of hydrogen peroxide.

CONCLUSION

Stability of H_2O_2 is a very important factor when using Fenton and Fenton-like reactions for soil and groundwater remediation. Tartaric acid was applied as the stabilizer of H_2O_2 . Ferrous and fer-

ric iron interacted with tartaric acid and the stabilized iron had low reactivity with H_2O_2 . The interaction was dependent on the available iron species and the solution pH. The degradation rates were also dependent on the solution pH, indicating the stabilizing effect and mechanisms are highly affected by which species of the stabilizer are present. Fully ionized organic acid was expected to interact strongly with iron and to give better inhibition to the catalytic effect. The lower pH, $\text{pH} < \text{pK}_{\text{a}1}$, was more effective at stabilization. The stabilization of H_2O_2 was also effective in a Fenton-like reaction with hematite. It can be concluded that stabilization is achieved by inhibiting the catalytic effect of soluble iron by an interaction between iron and stabilizer. Additionally, stabilization is highly affected by the available species of organic acid. The current study shows that an appropriate stabilization of H_2O_2 with organic acid improves the oxidative degradation performance and provides an alternative cost effective technology.

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