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Hydroxyl radical yields in the Fenton process under various pH, ligand concentrations and hydrogen peroxide/Fe(II) ratios

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HIGHLIGHTS

- •OH yield differs not much after 3 h of reaction in the pH range 1.5–5.
- •OH yield increases significantly after 24 h of reaction in the pH range 2.7–3.5.
- Pyrophosphate forms a stable complex with Fe(III) and terminates the Fenton process.
- Sulfate decreases the •OH yield in the Fenton process.
- At the low sulfate concentration applied the Fenton process is not terminated.

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ABSTRACT

The Fenton process, one of several advanced oxidation processes, describes the reaction of Fe(II) with hydrogen peroxide. Fe(II) is oxidized to Fe(III) that reacts with hydrogen peroxide to Fe(II) and again initiates the Fenton reaction. In the course of the reactions reactive species, e.g. hydroxyl radicals, are formed. Conditions such as pH, ligand concentrations and the hydrogen peroxide/Fe(II) ratio may influence the OH radical yield. It could be shown that at pH < 2.7 and >3.5 the OH radical yield decreases significantly. Two ligands were investigated, pyrophosphate and sulfate. It was found that pyrophosphate forms a complex with Fe(III) that does not react with hydrogen peroxide and thus, the Fenton reaction is terminated and the OH radical yields do not further increase. The influence of sulfate is not as strong as that of pyrophosphate. The OH radical yield is decreased when sulfate is added but even at higher concentrations the Fenton reaction is not terminated.

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1. Introduction

The Fenton reaction is named after Henry J. H. Fenton and describes the reaction of Fe^{2+} with H_2O_2, as in 1894, Fenton reported that H_2O_2 oxidizes tartaric acid in the presence of Fe(II) salts (Fenton, 1894). Several decades later it was proposed that the oxidative species generated by the Fenton reaction is the hydroxyl radical (•OH) (Haber and Weiss, 1934). The formed •OH, one of the most powerful oxidants ($E^\circ = 2.73$ V), are nonselective and fast reacting with organic and inorganic compounds. Fe(II) reacts with H_2O_2 to Fe(III) and •OH (reaction 1). The Fenton reaction is conducted under acidic conditions (Barb et al., 1951).

$$\mathrm{Fe(II)} + H_2O_2 \rightarrow \mathrm{Fe(III)} + OH^- + {}^\bullet OH \qquad (1)$$

Fe(III) formed in reaction 1 can be reduced by H_2O_2 to Fe(II) (reaction 2) and again initialize reaction 1. Reported reaction rate constants for reaction 1 vary from 40 to 80 $M^{-1}\,s^{-1}$ while reaction 2 was found to be several orders of magnitude slower (Pignatello et al., 2006).

$$\mathrm{Fe(III)} + H_2O_2 \rightarrow \mathrm{Fe(II)} + HO_2^\bullet + H^+ \qquad (2)$$

Reactions 1 and 2 summarize the overall Fenton reactions. In more detail it is assumed that in the first step H_2O_2 adds to Fe^{2+}

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giving a hydroperoxy complex (reaction 3) that decomposes yielding •OH and Fe(III) (reaction 4) (von Sonntag, 2008)

$$Fe^{2+} + H_2O_2 \rightleftarrows FeOOH^{+} + H^{+} \tag{3}$$

$$FeOOH^{+} + H^{+} \rightleftarrows FeOH^{2+} + {}^{\bullet}OH \tag{4}$$

It is expected, that the hydroperoxy complex could also decompose yielding Fe(IV) and OH^{-}• (reaction 5) (von Sonntag, 2008). Fe(IV) has been suggested as a second reactive species besides •OH (Hug and Leupin, 2003) in particular at higher pH when no •OH are formed.

$$FeOOH^{+} \rightleftarrows FeO^{2+} + {}^{\bullet}OH^{-} \tag{5}$$

Fe(III) that is formed in reaction (4) forms a hydroperoxy complex with H_2O_2 that decomposes unimolecularly to yield Fe(II) and HO_2• (reactions 6–9) (De Laat and Le, 2005).

$$Fe^{3+} + H_2O_2 \rightleftarrows Fe^{III}(HO_2)^{2+} + H^{+}\ K = 3.1 \times 10^{-3} \tag{6}$$

$$FeOH^{2+} + H_2O_2 \rightleftarrows Fe^{III}(OH)(HO_2)^{+} + H^{+}\ K = 2 \times 10^{-4} \tag{7}$$

$$Fe^{III}(HO_2)^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet}\ k = 2.7 \times 10^{-3}\ s^{-1} \tag{8}$$

$$Fe^{III}(OH)(HO_2)^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet} + OH^{-}\ k = 2.7 \times 10^{-3}\ s^{-1} \tag{9}$$

According to reactions (10)–(12) HO_2• can recombine yielding H_2O_2 which can contribute to the Fenton reaction (Bielski et al., 1985).

$$O_2^{\bullet -} + H^{+} \rightleftarrows HO_2^{\bullet} \tag{10}$$

$$O_2^{\bullet -} + HO_2^{\bullet} + H_2O \rightarrow H_2O_2 + O_2 + OH^{-}\ k = 9.7 \times 10^{7}\ M^{-1}\ s^{-1} \tag{11}$$

$$2\ HO_2^{\bullet} \rightarrow H_2O_2 + O_2\ k = 8.3 \times 10^{5}\ M^{-1}\ s^{-1} \tag{12}$$

Besides the reaction of Fe(II) with H_2O_2 Fe(II) can also be oxidized to Fe(III) by oxygen present in the solution without yielding •OH. The reaction rates of these autoxidation reactions depend on the iron species (reactions 13–15). The more OH^{-} are bound to the Fe(II), the faster the reaction (King, 1998).

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{\bullet -}\ k = 9.2 \times 10^{-7}\ M^{-1}\ s^{-1} \tag{13}$$

$$Fe(OH)^{+} + O_2 \rightarrow Fe(OH)^{2+} + O_2^{\bullet -}\ k = 6.95\ M^{-1}\ s^{-1} \tag{14}$$

$$Fe(OH)_2 + O_2 \rightarrow Fe(OH)_2^{+} + O_2^{\bullet -}\ k = 8.75 \times 10^{5}\ M^{-1}\ s^{-1} \tag{15}$$

Besides Fe(III) superoxide is formed in the autoxidation reactions (reactions 13–15) that can recombine to hydrogen peroxide (reactions 10–12) and contribute to the Fenton reaction.

Fig. 1 shows the fractions of Fe(II) present in aqueous solution at different pH. At pH below 9 the predominant species is Fe^{2+}, which indicates that at acidic and neutral pH autoxidation (reaction 13) is very slow and can be neglected, if no ions that accelerate the reaction, e.g. CO_3^{2-}/HCO_3^{-}, are present. At higher pH (>9) autoxidation becomes more relevant as the predominant species is $Fe(OH)_2$ which reacts faster with O_2 (reaction 15). As the Fenton reaction is not conducted at such high pH, the reaction of $Fe(OH)_2$ with O_2 can be neglected.

As the Fenton process describes a reaction that generates •OH (reaction 1) it is assigned to the advanced oxidation processes (AOPs). The reaction takes place under acidic conditions. Therefore, the Fenton reaction is not often applied as most of the treated waters are in a neutral to slightly basic pH range. The only efficient field of application are acidic industrial wastewaters because no pH shift is needed and the used chemicals are easy to handle compared to other advanced oxidation processes.

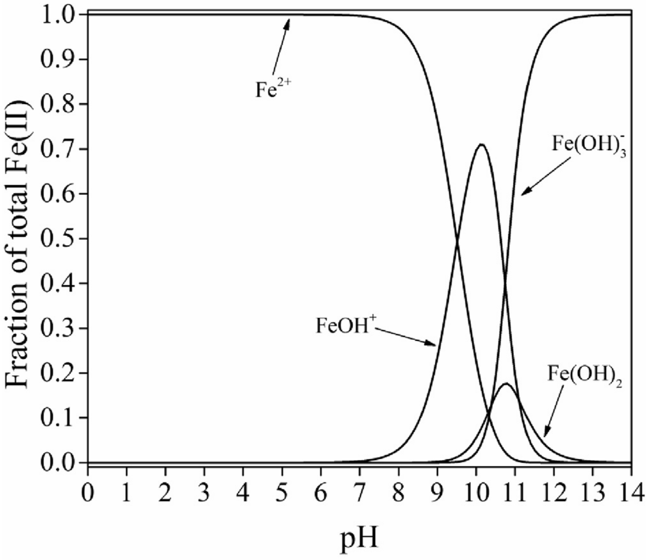

Fig. 1. Iron(II) speciation diagram in aqueous solution as a function of pH at 25 °C and ionic strength of 1 M based on data from (Turner et al., 1981).

If other transition metals than Fe(II) are present (e.g. Cu(I), Fe(III)) the reaction is called Fenton-type or Fenton-like. There are several other Fenton-based reactions known, e.g. photo-Fenton, electro-Fenton and sono-Fenton reactions (Wang and Xu, 2012).

The Fenton process is a very complex and not fully understood sequence of reactions. When inorganic ions are present in the solution it becomes even more complex. Some inorganic ions, e.g. Cl^{-} and Br^{-} can act as •OH scavenger, as they are very reactive towards •OH ($k(Cl^{-} + {}^{\bullet}OH) = 3 \times 10^{9}\ M^{-1}\ s^{-1}$ (Grigorev et al., 1987) and •$k(Br^{-} + {}^{\bullet}OH) = 1.1 \times 10^{10}\ M^{-1}\ s^{-1}$ (Zehavi and Rabani, 1972)). They can be present in high concentration in waters to be treated suppressing the reaction of •OH with contaminants. The reaction of chloride with •OH yields $Cl_2^{\bullet -}$ that reacts more selectively than •OH and decreases the oxidation rate. Besides scavenging of •OH chloride can form complexes with Fe(III). These Fe(III)-chlorocomplexes are less reactive towards H_2O_2 and decrease the •OH yield as reaction 2 is suppressed (De Laat and Le, 2006). However, due to the high reaction rate constant of chloride with •OH the scavenging effect is much more important than the inhibition caused by the complexation. Other inorganic ions, e.g. phosphate form complexes with Fe(III) which are less reactive towards H_2O_2 (Lu et al., 1997). In this case the catalytic cycle of the Fenton reaction is disrupted as there is no reduction of Fe(III) to Fe(II) possible. The Fenton reaction can also be affected by other ligands in the contrary way. Wells and Salam observed that increasing the concentration of some halides, sulfate and tripolyphosphate accelerates the reaction of Fe(II) with H_2O_2 (Wells and Salam, 1967, 1968). Also some chelating ligands, e.g. EDTA and oxalate, can accelerate the reaction of Fe(II) with H_2O_2 when forming Fe(II) complexes that are more reactive towards H_2O_2 ($k(Fe(II)\text{-}C_2O_4^{2-} + {}^{\bullet}OH) = 1 \times 10^{4}\ M^{-1}\ s^{-1}$ (Park et al., 1997) and $k(Fe(II)\text{-}EDTA + {}^{\bullet}OH) = 1.75 \times 10^{4}\ M^{-1}\ s^{-1}$ (Rush and Koppenol, 1986)). The reaction of the Fe(II)-EDTA complex with H_2O_2 is supposed not to yield •OH, as the product does not undergo reactions that are characteristic for •OH, but behaves more like a FeO(II)-EDTA complex (Rush and Koppenol, 1986). Stability

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