Unraveling the sigmoidal profiles in Fenton catalysis: Toward mechanistic elucidation

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ABSTRACT

Fenton reactions are widely known and have been employed to degrade different pollutants in various environmental matrices. However, some controversies related to the Fenton mechanism remain unresolved. Although not comprehensively understood, kinetic sigmoidal profiles with an initial induction period have frequently been reported for Fenton systems. A thorough kinetic study was carried out at different temperatures involving Fenton reactions promoted by Fe^{3+} and Fe^{2+} and under the influence of radical scavengers. Catalysis supported by Fe^{2+} displayed the usual pseudo-first-order profile, while Fe^{3+} catalysis showed a sigmoidal pattern. The sigmoidal profiles were correlated to a pseudo-elementary autocatalytic mechanism developed by Finke and Watzky (F–W). The use of the F–W equation indicates that a certain amount of oxidative species must be generated to promote the substrate degradation. This correlation is a breakthrough in the understanding of Fenton catalysis.

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1. Introduction

Fenton catalysis has been known since 1894 [1], and its importance has grown since this reaction proved to be very useful in wastewater treatment. Currently, this reaction is widely utilized in the degradation of different contaminants, being considered one of the most relevant advanced oxidation processes (AOPs).

Although they are widely employed and studied, the complex chemistry of Fenton reactions still incites some controversies [2,3], mainly related to the production of radicals and oxidative species and their relevance in the substrate degradation. Another aspect that has frequently been reported is the appearance of an induction period during Fenton catalysis, especially when a low concentration of catalyst is used. This induction period corresponds to an initial slow step of the reaction where no significant consumption of the substrate is observed. After this initial period, the degradation of the substrate is suddenly observed, which is usually related to the formation of intermediate species necessary for it. This overall behavior follows a kinetic sigmoidal profile [4].

This induction period has been observed during the degradation of different organic species, such as dyes [5], benzene derivatives [6,7], and ethylenediaminetetraacetic acid (EDTA) [8].

During the study by Liu and co-workers, the induction period in EDTA degradation by the Fenton reaction was compared to the one existent combustion reactions, which are induced by heat [8]. The authors discuss the lack of explanation for this reaction profile, which has been observed in AOPs and also in other chain reactions, such as during the autoxidation of hydrocarbons. Unlike that observed for AOPs, the sigmoidal profile of hydrocarbon oxidation is well described in the literature, and the induction period is attributed to the time required to form the peroxides responsible for the degradation of hydrocarbons [9]. An induction period has also been observed for phenol degradation catalyzed by copper ions, which are also able to catalyze the decomposition of hydrogen peroxide [10]. Even though some authors have described this behavior and attributed this mechanism to an autocatalytic process, this kinetic profile has not been correctly investigated until now [8,11].

The reasons for the lack of novel kinetic mechanisms in Fenton reactions are mainly related to the incorrect use of a universally accepted first-order equation, which sometimes does not describe the exact mechanism of the reaction. This fit is often justified with the application of high concentrations of hydrogen peroxide and catalyst, aiming to optimize the reactions and promote a higher degradation rate. This optimization generates an excess of radicals in the reactions, which has been used as an argument to impose the application of a pseudo-first-order mechanism.
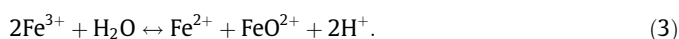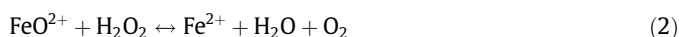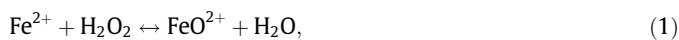
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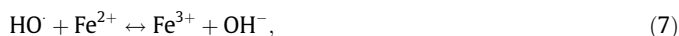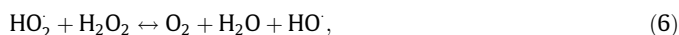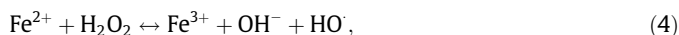 *E-mail address:* zamora@ufpr.br (P. Peralta-Zamora).

1.1. Kinetic aspects of the Fenton reaction and evolution of the ferric ion mechanism

In 1984, H.J.H Fenton first described the reaction of ferrous sulfate and hydrogen peroxide with tartaric acid, aiming to provide a test for the presence of this acid, since the mixture of these species with an alkali provided a characteristic violet color. Already, in that year, Fenton realized that Fe^{3+} ions were not as active in the reaction as Fe^{2+} ions [1].

In 1932, Bray and Gorin [12] proposed a mechanism of a chain reaction involving the formation of ferryl oxide:

$$Fe^{2+} + H_2O_2 \leftrightarrow FeO^{2+} + H_2O, \tag{1}$$

$$FeO^{2+} + H_2O_2 \leftrightarrow Fe^{2+} + H_2O + O_2 \tag{2}$$

$$2Fe^{3+} + H_2O \leftrightarrow Fe^{2+} + FeO^{2+} + 2H^+. \tag{3}$$

The reverse of reaction (3) would be the termination step of the chain reaction. High-valent metal complexes constituted of Fe^{4+} are still mentioned as oxidative agents in neutral medium [13], especially in highly stabilized environments. It was Haber and Weiss, in 1934 [14], who would first propose the formation of the hydroxyl radical and provide the path for further studies on the Fenton mechanism. They also studied the reaction catalyzed by Fe^{3+} ions and proposed the reactions (4) to (8). According to Haber and Weiss, the primary and rate-determining step of the reaction initiated by Fe^{3+} would be described by reaction (8). They also proposed that the hydroperoxyl radical (HO_2) would be consumed by parallel reactions [14], according to reaction (6).

$$Fe^{2+} + H_2O_2 \leftrightarrow Fe^{3+} + OH^- + HO^{\cdot}, \tag{4}$$

$$HO^{\cdot} + H_2O_2 \leftrightarrow H_2O + HO_2^{\cdot}, \tag{5}$$

$$HO_2^{\cdot} + H_2O_2 \leftrightarrow O_2 + H_2O + HO^{\cdot}, \tag{6}$$

$$HO^{\cdot} + Fe^{2+} \leftrightarrow Fe^{3+} + OH^-, \tag{7}$$

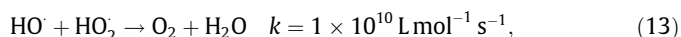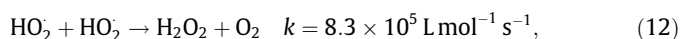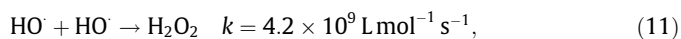$$Fe^{3+} + HO_2^- \leftrightarrow Fe^{2+} + HO_2^{\cdot}. \tag{8}$$

In 1950, Barb, Baxendale, George, and Hargrave [15] gave an essential step in the comprehension of H_2O_2 decomposition catalyzed by ferric ions. Assuming an analogy between Fe^{3+} and other trivalent metals, such as Co^{3+}, the authors proposed that H_2O_2 would react with Fe^{3+} forming HO_2^- in two consecutive electron transfer steps, reactions (9) and (10). The hydroperoxyl radical (HO_2) would be an intermediate of this process.

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe^{2+} + HO_2^{\cdot} + H^+. \tag{9}$$

$$Fe^{3+} + HO_2^{\cdot} \leftrightarrow Fe^{2+} + O_2 + H^+, \tag{10}$$
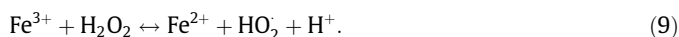
It is currently accepted that Fenton reactions are initiated by reactions (4) and (9). It is well known that reaction (9) presents a much lower velocity than reaction (4) ($0.01\ L\ mol^{-1}\ s^{-1}$ vs. 63 L $mol^{-1}\ s^{-1}$) [14]. The "conventional Fenton process" occurs when hydrogen peroxide decomposition is initiated by the catalysis promoted by soluble Fe^{2+} ions (reaction (4)), and when other catalysts are utilized the reaction is usually reported as "Fenton-like."

Velocities of Fenton reactions are remarkably affected by pH. Optimum reaction rates are achieved under acidic pH, usually in a range of 2.8–4.0. Above this range, less active iron species are generated due to iron precipitation, and the use of chelating agents is often required [16–19]. Moreover, it is reported that less acidic conditions facilitate the iron redox cycle and raise the oxidizing capability of Fenton reactions [20]. The role of molecular oxygen in Fenton reactions is still a matter of debate. However, it is admitted that its presence is relevant in the formation of reactive oxygen species under metabolic conditions at low hydrogen peroxide concentrations. At high hydrogen peroxide concentrations, the effect of molecular oxygen is manifested after the attack of the hydroxyl radical to the organic substrate by forming peroxo-organic radicals that favor the mineralization process [21].

Fenton reactions are also dependent on the concentrations of catalyst and oxidant. These concentrations are usually optimized, aiming to achieve higher contaminant mineralization and velocity rates. As a result, excessive concentrations of iron and hydrogen peroxide are employed, even though hydrogen peroxide concentrations are limited by the recombination of the oxidative radicals promoted by an unproductive excess of hydrogen peroxide, such as represented by reactions (5) and (6). The rate constants of some radical recombination reactions can reach $10^{10}\ L\ mol^{-1}\ s^{-1}$ [22], which suggests that they constitute inevitable side reactions during every Fenton process:

$$HO^{\cdot} + HO^{\cdot} \rightarrow H_2O_2 \quad k = 4.2 \times 10^9\ L\ mol^{-1}\ s^{-1}, \tag{11}$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad k = 8.3 \times 10^5\ L\ mol^{-1}\ s^{-1}, \tag{12}$$

$$HO^{\cdot} + HO_2^{\cdot} \rightarrow O_2 + H_2O \quad k = 1 \times 10^{10}\ L\ mol^{-1}\ s^{-1}, \tag{13}$$

Fenton reactions and their applications have been thoroughly revised in the literature, which includes the use of this reaction in the presence of light and the electrogeneration of H_2O_2, among other combined processes [23,24]. Although the previously mentioned equations have been used to explain the Fenton reaction mechanism, the literature has cited the appearance of an induction period that cannot be explained using the models developed so far.

1.2. The Finke and Watzky mechanism

Sigmoidal profiles can be ascribed to the Finke and Watzky (F–W) mechanism, which was first described in 1997 by Murielle Watzky and Richard Finke while studying the formation of P_2W_{15}-$Nb_3O_{62}^{9-}$ polyoxoanion and Bu_4N^+-stabilized $Ir(0)_{\sim300}$ nanoclusters. The authors observed that a slow nucleation step was followed by autocatalytic growth of the nanoclusters, which then would catalyze the hydrogenation of cyclohexene (C_6H_{10}) [4]. The consumption of cyclohexene exhibited an autocatalytic kinetic profile that was adjusted to the equation derived from the system represented by the following reactions:

$$A \xrightarrow{k1} B, \tag{14}$$

$$A + B \xrightarrow{k2} 2B, \tag{14a}$$

$$B + H_2 + C_6H_{10} \xrightarrow{k3} B + C_6H_{12}. \tag{14b}$$

In this system, the induction period previous to the beginning of cyclohexene hydrogenation was due to the time required to form enough B (Bu_4N^+-stabilized $Ir(0)_{\sim300}$ nanoclusters). As one can observe, B is a product of the first step (reaction (14)) and a reagent in the subsequent steps ((14a) and (14b)). The third step ((14b))