Krzysztof BARBUSIŃSKI[*]

FENTON REACTION - CONTROVERSY CONCERNING THE CHEMISTRY

REAKCJA FENTONA - KONTROWERSJE DOTYCZĄCE CHEMIZMU

Abstract: There is something intriguing and at the same time fascinating that a simple reaction (of Fe^{2+} ions with H_2O_2), which was observed by H.J.H. Fenton over 110 years ago, proves to be very difficult to describe and understand. As yet the nature of the oxidizing species obtained in Fenton reaction is still a subject of deliberation, which may be explained by the fact that it is very common in both chemical and biological systems and in natural environment. It is a paradox that the Fenton reaction is successfully used in environmental protection (for example in wastewater treatment and remediation of groundwater) and it is thought to be a factor, which causes damage to biomolecules and plays a major role in the aging process and a variety of diseases. This article presents a short review on radical and non-radical mechanisms of the Fenton reaction postulated in literature, possible reaction pathways as well as various points of view in this field.

Keywords: Fenton reaction, Fenton reagent, Fenton chemistry, hydroxyl radical, ferryl ion

Introduction

The oxidation of organic substrates by iron(II) and hydrogen peroxide is called the "*Fenton chemistry*", as it was first described by H.J.H. Fenton who first observed the oxidation of tartaric acid by H_2O_2 in the presence of ferrous iron ions [1]. Alternatively, the name of "*Fenton reaction*" or "*Fenton reagent*" is often used. We know that the Fenton reagent defined as a mixture of hydrogen peroxide and ferrous iron is currently accepted as one of the most effective methods for the oxidation of organic pollutants.

The Fenton reagent has been known for more than a century but its application as an oxidizing process for destroying hazardous organics was not applied until the late 1960s [2, 3]. After this time comprehensive investigations showed that the Fenton reagent is effective in treating various industrial wastewater components including aromatic amines [4], a wide variety of dyes [5-7], pesticides [8-10], surfactants [11-13], explosives [14] as well as many other substances. As a result, the Fenton reagent has been applied to treat a variety of wastes such as those associated with the textile industry,

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[*] Institute of Water and Wastewater Engineering, Silesian University of Technology, ul. Konarskiego 18, 44-100 Gliwice, Poland, tel. 032 237 11 94, email: krzysztof.barbusinski@polsl.pl

chemical manufacturing, refinery and fuel terminals, engine and metal cleaning etc. [7, 15]. The Fenton reagent can also effectively be used for the destruction of toxic wastes and non-biodegradable effluents to render them more suitable for secondary biological treatment [16]. Moreover, the importance of Fenton chemistry has been long recognised among others in food chemistry and material ageing [17].

Currently we know that the efficiency of the Fenton reaction depends mainly on H_2O_2 concentration, Fe^{2+}/H_2O_2 ratio, pH and reaction time. The initial concentration of the pollutant and its character as well as temperature, also have a substantial influence on the final efficiency. Moreover, there is wide spread experience in the practical use of Fenton reagent for degradation of organic substrates in wastewater and other wastes.

More than 110 years after the Fenton reaction was discovered we know that this oxidation system is based on the formation of reactive oxidizing species able to efficiently degrade the pollutants of the wastewater stream. The nature of these species is still under discussion and it has been a subject of controversy in the past and recent Fenton oxidation related literature [18-22]. Two reaction pathways for the first step of Fenton chemistry have been advanced: a radical pathway, which considers an $OH^\bullet$ radical production and a non-radical pathway considering ferryl ion production [23].
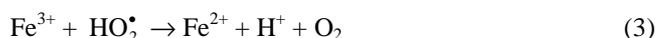
This paper presents a short review on the radical and non-radical mechanisms of the Fenton reaction postulated in literature. The possible reaction pathways and various points of view in this field are also discussed.

Fenton chemistry - the controversies

Radical and non-radical pathways

Although the Fenton reagent has been known for more than a century and has been proven long since as a powerful oxidant, the mechanism of the Fenton reaction is still under intense and controversial discussion [18]. The radical ($OH^\bullet$) and non-radical mechanism (mainly ferryl ion) of the Fenton reaction are discussed in literature. Two years after Fenton's death the hydroxyl radical mechanism was mentioned for the first time in 1931 by Haber and Willstätter [24] in a paper on radical chain mechanisms [25]. They suggested that $OH^\bullet$ could be produced by one-electron reduction of H_2O_2 by $HO_2^\bullet$ (today known as a very slow reaction in the absence of catalytic redox cycling metals) and that $OH^\bullet$ could abstract hydrogen from a carbon-hydrogen bond and initiate radical chain reactions [24]. Following on in 1932 Haber and Weiss suggested $OH^\bullet$ production by one-electron reduction of H_2O_2 by Fe^{2+} [26-28]. According to the classic interpretation of Haber and Weiss [28], the reaction of iron(II) with hydrogen peroxide (H_2O_2) in aqueous solution leads to the formation of radicals $OH^\bullet$ and $HO_2^\bullet$ as active intermediates in the reactions (1 and 2) described below [18, 29]. However, their paper is not concerned with oxidation of organic compounds. The reaction (1) is called the Fenton reaction (or classical Fenton reaction), although Fenton never wrote it [26].

In 1946, Baxendale, Evans and Park [30] suggested that $OH^\bullet$ from reaction 1 adds to carbon double bonds and can thereby initiate a polymerisation reaction. The original mechanism of Haber and Weiss has been subsequently modified in 1951 by Barb et al [31]. The free radical mechanism proposed by Barb et al [31] consists of the following steps [29]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad (1)$$

$$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \qquad (2)$$

$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + H^+ + O_2 \qquad (3)$$

$$Fe^{2+} + HO_2^\bullet \rightarrow Fe^{3+} + HO_2^- \qquad (4)$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \qquad (5)$$

It is a chain reaction with step (1) serving as chain initiation, steps (4) and (5) as termination and the cycle (1)-(2)-(3) forms the chain which is the site of O_2 evolution [29]. More than two decades later Walling [32] presented further evidence of the involvement of hydroxyl radicals in the oxidation of various organic compounds by the Fenton reagent [18].

According to the theory presented above the chemistry related to the use of Fenton reagent is the chemistry of this radical. Therefore, taking into consideration that the Fenton reaction can also involve several other cations of metals (M^{n+}), the processes connected with the reactions similar to Fenton reaction may be characterized as follows [33]:

$$(M^{n+}) + H_2O_2 \rightarrow (M^{n+1}) + OH^- + OH^\bullet \qquad (6)$$
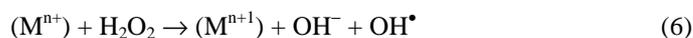
For a long time the importance of the Fenton reaction in the production of OH radicals in solution has been a subject of controversy [23]. The hydroxyl radical production by the Fenton reaction has been questioned by several studies suggesting that the reaction between H_2O_2 and iron(II) produces the ferryl ion (FeO^{2+}, an oxidizing Fe(IV) species), which is then the active intermediate species in the Fenton chemistry. Bray and Gorin (1932) [34] were the first to propose iron(IV) as the active intermediate in the Fenton chemistry and they postulated that iron(II) and iron(III) are connected through equilibrium. Bray and Gorin suggested the reactions (7) and (8) but their paper was not concerned with the oxidation of organic substances [23, 26]:

$$Fe^{2+} + H_2O_2 \rightarrow FeO^{2+} + H_2O \qquad (7)$$

$$FeO^{2+} + H_2O_2 \rightarrow Fe^{2+} + H_2O + O_2 \qquad (8)$$
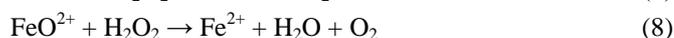
The mechanism for the decomposition of hydrogen peroxide by Haber and Weiss had been also criticised by George [35] and Abel [36] by the late 1940s [37].

The aqueous ferryl species $[Fe(IV)O]^{2+}$ has been shown to be a reactive oxidant, exhibiting both single-electron hydrogen abstraction chemistry and two-electron oxidation of alcohols to ketones [38]. Accumulated evidence shows that the ferryl species $[Fe(IV)O]^{2+}$ can be formed under a variety of conditions including those related to the ferrous ion-hydrogen peroxide system known as the Fenton's reagent [39].

Kremer [29] concluded that it is difficult to accept the existence of free radical mechanism because this mechanism either in the formulation of Haber and Weiss or in that of Barb et al, recognizes only Fe^{2+} and Fe^{3+} as the forms of iron in the system. In the free radical mechanism, reaction (2) becomes insignificant at low $[H_2O_2]$ as a mode of reaction of $OH^\bullet$. Hydroxyl radical could then react with Fe^{2+} and produce Fe^{3+} (reaction (9)). As an alternative, $OH^\bullet$ could react with Fe^{3+} (reaction (10)):

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \qquad (9)$$

$$Fe^{3+} + OH^{\bullet} \rightarrow FeOH^{3+} \tag{10}$$

If this reaction occurred it would be even more plausible to assume that the pair $Fe^{3+} + OH^{\bullet}$ (as products of reaction 1) would not become separated at all and the species $FeOH^{3+}$ would appear instead. It can be stated that the species $FeOH^{3+}$ is merely the protonated form of FeO^{2+} ($FeO^{2+} + H^+ \rightarrow FeOH^{3+}$) [29].

Fenton reaction in biological systems

All animals need O_2 for efficient production of the energy in mitochondria. This requirement for O_2 obscures the fact that it is a toxic mutagenic gas - aerobes survive only because they have evolved antioxidant defences. The field of antioxidants and free radicals is often perceived as focused around the use of antioxidant supplements to prevent human disease. In fact, antioxidants and free radicals permeate the whole of life, creating the field of redox biology. Free radicals are not all detrimental but not all antioxidants are beneficial. Life is a balance between the two: antioxidants serve to keep down the levels of free radicals, permitting them to perform useful biological functions without too much damage [40].
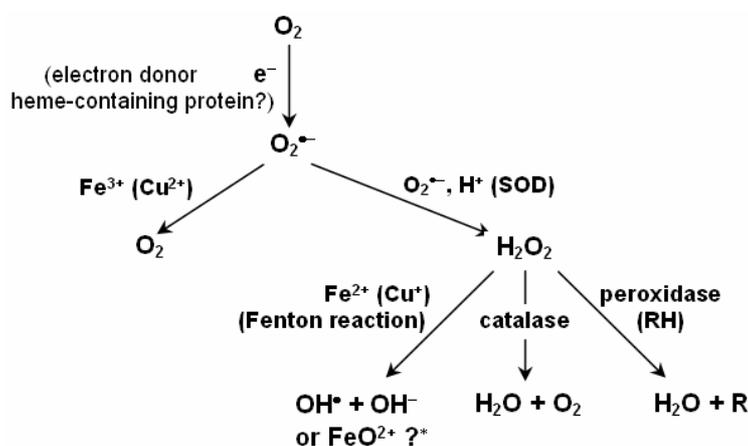

Fig. 1. Schematic representation of the sequence of events involved in Fenton reaction [41] (modified). Initially, electron donors can convert oxygen to superoxide anion ($O_2^{\bullet-}$), which is rapidly converted to hydrogen peroxide. Hydrogen peroxide can further form hydroxyl radicals ($OH^{\bullet}$) or ferryl ion (FeO^{2+}) in the actual Fenton reaction in the presence of ferrous or cuprous ions (which are simultaneously oxidized to ferric or cupric ions). SOD - superoxide dismutase; RH/R - reducing agent in oxidized and reduced form

All aerobes suffer damage when exposed to O_2 concentrations not only higher than normal, but also even at normal O_2 levels. Many scientists believe that O_2 toxicity is due to excess formation of the superoxide radical $O_2^{\bullet-}$. This is the superoxide theory of O_2 toxicity [40]. Although oxygen is a powerful oxidant, the triplet ground state of dioxygen constitutes a kinetic barrier for the oxidation of biological molecules, which are mostly in the singlet state. However, the unpaired orbitals of dioxygen can sequentially

accommodate single electrons to yield $O_2^{\bullet-}$, H_2O_2, the highly reactive $OH^{\bullet}$ and water. Superoxide radical ($O_2^{\bullet-}$) dismutates (via spontaneous or enzyme-catalysed reactions) to produce H_2O_2 (Fig. 1 [41]). Superoxide radical can also reduce and liberate Fe^{3+} from ferritin or liberate Fe^{2+} from iron-sulphur clusters. Subsequently highly reactive oxygen species can be formed via the Fenton reaction [42].

It is also commonly accepted that the oxidizing intermediates involved in Fenton reactions cause damage to biomolecules and play a major role in the aging process and a variety of diseases such as cancer [43]. The Fenton reaction has been found to be the key reaction in the oxidation of membrane lipids, oxidation of amino acids and in the reactions where biological reduction agents are present, such as ascorbic acid or thiols. Its occurrence is also supposed in heart diseases, such as ischemia and reperfusion [33].

The nature of the species responsible for this damage is however still unclear. Most studies implicate the highly reactive hydroxyl radical as responsible for the damage [44-46] and other studies champion the involvement of high valent metal species [47, 48]. The reactions with Fe(IV) have been implicated in biological processes and proposed to be involved in damage to the cellular components. For example, in the case of Fe^{2+} chelates with ADP, *ortho*-phosphate, or EDTA, the oxidant formed from H_2O_2 behaves differently than it is expected for $OH^{\bullet}$ and it has been proposed to be the ferryl FeO^{2+}. Caged or bound $OH^{\bullet}$, often denoted as $[Fe–H_2O_2]^{2+}$ or $[FeOOH]^{+}$, might also account for the noted differences [42, 49]. Many scientists even question the importance and occurrence of the Fenton reaction in biological systems due to supposedly low concentrations of H_2O_2 and "free iron" in the systems. They also claim that the high and indiscriminate reactivity of the hydroxyl radical limits its ability to diffuse and cause more extensive damage to biomolecules [43].

Competitive kinetic studies have been performed to compare the reactivity of the oxidizing intermediates generated in the Fenton reaction with authentic $OH^{\bullet}$ generated by radiolysis of water or photolysis of H_2O_2 [50]. Rahhal and Richter [51] examined Fe^{II}(EDTA) oxidation and suggested that an oxidant other than $OH^{\bullet}$ was generated in this system. Rush and Koppenol [52], having studied a number of chelated iron complexes using stopped-flow spectrophotometry, concluded that a metallo-oxo species was generated in neutral solutions, while $OH^{\bullet}$ was predominant in acidic solutions of nonchelated iron. Sutton et al [53] arrived at the opposite conclusion that unchelated iron generated a metallo-oxo species as the primary oxidant while $OH^{\bullet}$ was predominant when chelated iron was present. Several review articles and research papers have suggested a rationalization for this discrepancy in which it is argued that under certain conditions, the metallo-oxo species or $OH^{\bullet}$ can be generated in both systems. A recent study, based on the assumption that 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO)–OH adducts are formed solely from $OH^{\bullet}$, has suggested that there is more than one type of oxidizing intermediate present, and that the ratio between the amount of $OH^{\bullet}$ and metallo-oxo species depends on the chelated ligand [49].

Yamazaki and Piette [54] are proposed three possible pathways of the Fenton reaction. The dominant ones depend very much on the nature of the iron chelator being used. These three reaction paths comprised production of hydroxyl radicals, ferryl species, and nonoxidizing species, respectively. Prousek [55] has reviewed various

aspects of the participation of Fenton chemistry in biology and medicine. He also concluded that both hydroxyl radical and ferryl ion can be formed under a variety of the Fenton and Fenton-like reactions.

Fenton reaction in natural waters

In natural waters exposed to solar radiation, reactive intermediates are formed which then take part in photooxidation reactions [33, 43]. The Fenton reaction is often perceived as a possible source of $OH^\bullet$ in sunlight waters [56, 57]. Other sources include photolysis of nitrate(III) [58], nitrate(V) [59], metal to ligand-charge-transfer reactions [60], photoFenton reactions [56] as well as dioxygen-independent organic sources [61]. Both H_2O_2 and Fe(II) are photochemically produced in these sunlight waters. H_2O_2 is formed via the disproportionation of the superoxide ($O_2^{\bullet-}$), produced by the reduction of oxygen by photoexcited dissolved organic matter (DOM). The concentrations of H_2O_2 and $O_2^{\bullet-}$ may be further increased in their production by microflora [33]. Fe(II) on the other hand is produced by the photoreduction of Fe(III), which may be O_2 assisted. The process is usually increased by complexation with the organic ligands such as DOM [62].

While several studies have suggested that $OH^\bullet$ is the oxidizing species involved in the oxidative processes connected with Fenton reaction, other possibilities have not been ruled out [43]. For example, a study of the reduction of dissolved iron species by humic acid has suggested that in addition to the $OH^\bullet$ radical another oxidant may be involved in the Fenton reactions in the seawaters at neutral pH (7.0-7.5) [63]. Studies on the oxidation of arsenic [64] have indicated that $OH^\bullet$ is involved in the oxidation of arsenic(III) to arsenic(IV), which occurs readily at low pH, but that high-valent metal species may be formed also at high pH, which does not readily oxidize arsenic(III). Other studies [65] suggest that at nanomolar levels of Fe(II) the oxidation of Fe(II) by H_2O_2 in the seawater predominantly involves the $FeOH^+$ species at pH 6-8.
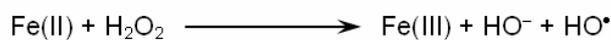
Possible mechanisms of the Fenton reaction

Many studies examining the nature of reactive oxidizing species in the Fenton reaction have been conducted and many possible mechanisms of reaction were presented. Some of them are presented below. As an example, the simple free radical pathway scheme (Fig. 2) can be shown [43, 66] but the mechanism of the Fenton reaction has been suggested to be more complicated than presented in Figure 2. Since iron has a variable valency, its oxidation by H_2O_2 may occur via a one or two electron transfer (reactions (11) and (12), respectively):

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + OH^\bullet \tag{11}$$

$$Fe(II) + H_2O_2 \rightarrow Fe(IV) + 2\,OH^- \tag{12}$$
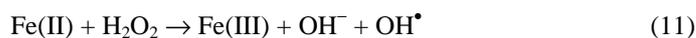
Some studies therefore suggest that the classical Fenton reaction occurs using only Fe(II) as an electron donor to H_2O_2. Such would be an outer sphere electron transfer reaction with no direct bonding interactions between the electron donor and the acceptor, (Mechanism I, Figure 3). On the other hand, recent studies have shown and favored the inner sphere electron transfer mechanisms, which involve direct bonding between the iron and H_2O_2. This interaction could produce a metal-peroxo complex, Fe(II) HOO which may react further to generate either $HO^\bullet$ radicals (one-electron oxidant) or

Fe(IV)O (two electron oxidant), (Mechanism II, Figure 3). The key question therefore is which of these species is the major oxidant in these reactions [43].

Fenton Reaction

$$Fe(II) + H_2O_2 \longrightarrow Fe(III) + HO^- + HO^\bullet$$

Haber–Weiss Reaction (Superoxide Driven Fenton Reaction)

$$H_2O_2 + Fe(II) \longrightarrow Fe(III) + HO^- + HO^\bullet$$

$$O_2 \qquad\qquad O_2^{\bullet -}$$
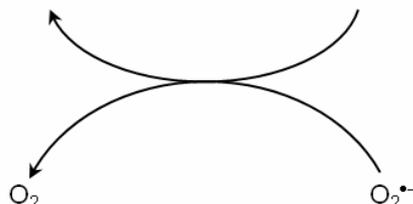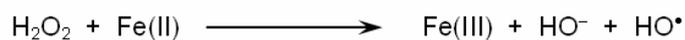
Haber–Weiss Net Reaction

$$O_2^{\bullet -} + H_2O_2 \xrightarrow{\textit{Fe(II)/Fe(III)}} O_2 + HO^- + HO^\bullet$$
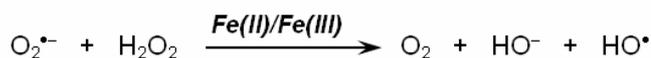
Fig. 2. Basic free radical mechanisms for the Fenton and Haber-Weiss reaction [43, 66]

Mechanism I ┊ **Mechanism II**

$$Fe(II) + H_2O_2 \rightleftharpoons Fe(II)\,OOH + H^+$$
„Bound HO"

Outer sphere electron transfer ┊ *Inner sphere electron transfer*

$$Fe(III) + [H_2O_2]^{-\bullet} \qquad Fe(III)O^- + HO^\bullet + H^+$$

$$Fe(III) + HO^- + HO^\bullet \longleftarrow Fe(IV)=O + H_2O$$
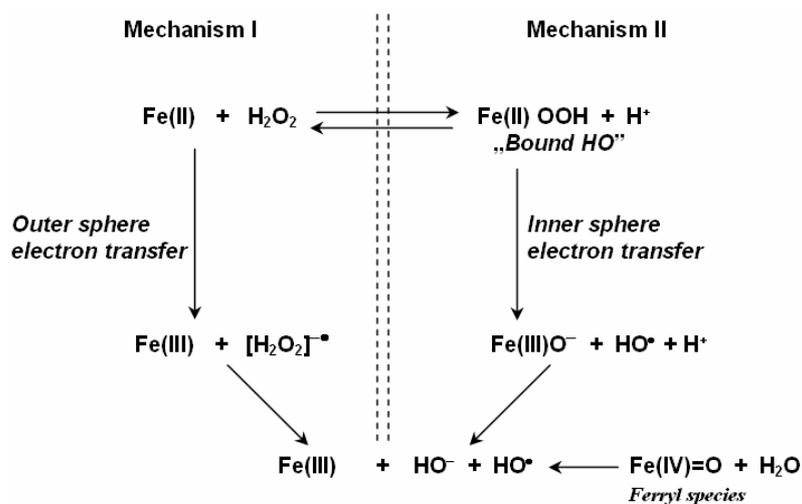*Ferryl species*

Fig. 3. Basic reactions and intermediates involved in the classic Fenton and the metal centered Fenton reactions [43]

Various pathways have been proposed [19, 29, 67, 68] including: non-radical mechanisms, radical mechanisms involving oxygen centred radicals and reactions of

highvalent metal species (Fig. 4). Due to the importance of Fenton reactions in biological and environmental systems elucidation of the nature of species involved in these reactions has been the subject of many studies. These studies have been carried out at varying pH using both organic and inorganic metal complexes and employing a variety of free radical techniques of analysis (usually indirect).
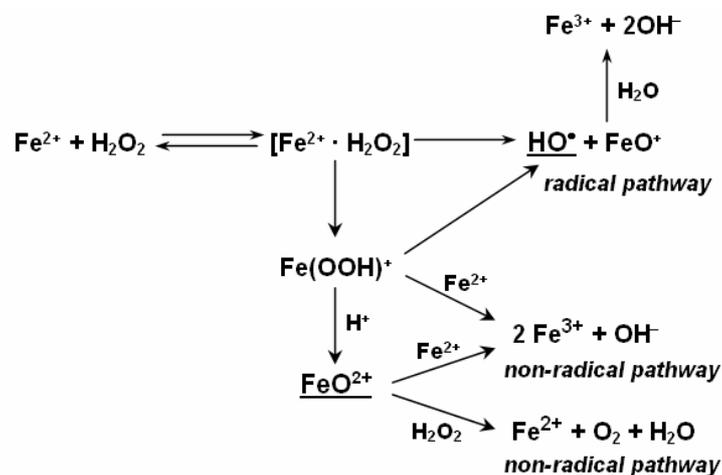

Fig. 4. Possible reaction pathways for the Fenton reaction in absence of organic substrates [43]
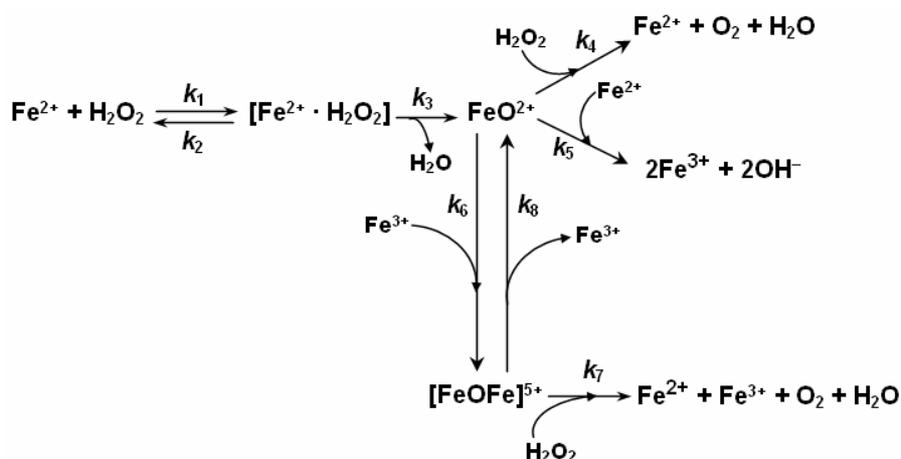

Fig. 5. Proposed non-radical mechanism for the Fenton reaction [29]

Kremer [29] proposed a non-radical mechanism for the Fenton reaction (Fig. 5). He suggested that the reaction starts with the reversible formation of a primary intermediate $\{Fe^{2+} \cdot H_2O_2\}$ from Fe^{2+} and H_2O_2 (exchange of a H_2O molecule in the hydration shell of Fe^{2+} ions by H_2O_2). A secondary intermediate FeO^{2+} is formed from the primary complex by the loss of H_2O. This species is the key intermediate in the reaction. It can react either

with Fe^{2+} ions to produce Fe^{3+} (k_5) or with H_2O_2 to produce O_2 (k_4). FeO^{2+} can further react with Fe^{3+} and form a binuclear species $[FeOFe]^{5+}$ (k_6). This species can react with H_2O_2 to produce O_2 (k_7) or to decompose back to FeO^{2+} and Fe^{3+} (k_8). Kremer pointed out that there is an error in the analysis of Barb et al [31], because they assumed a steady state is attained in $[Fe^{2+}]$ whereas in fact $[Fe^{2+}]$ goes to zero [1].

More recent studies [64, 69] show that the Fenton chemistry mechanism cannot be restricted to the mechanism of Barb et al [31] or to the one of Bray and Gorin [34]. Indeed, these studies postulate the existence of an active intermediate, which should be a weak acid at pK_a around 2 providing OH$^{\bullet}$ and iron(III) formation at low pH values or ferryl ion at high pH values. This hypothesis explains the observed OH$^{\bullet}$ radical production for equimolar concentrations of diluted reagents in water and pH values lower than 2 [64, 69, 70]. Thus, according to the pH value, the active intermediary is OH$^{\bullet}$ (radical pathway) or the ferryl ion (non-radical pathway) [23].

Ensing and co-workers [71] demonstrate the spontaneous formation of ferryl ion ($Fe^{IV}O^{2+}$) in an aqueous solution of iron(II) and hydrogen peroxide by means of first principles molecular dynamics simulations confirming the model first proposed by Bray and Gorin. Their simulations disfavour but do not rule out completely the Haber and Weiss OH$^{\bullet}$ radical mechanism (which is, especially in biochemistry, often taken as synonymous to Fenton chemistry). In the initial step of the iron catalysed hydrogen peroxide dissociation, a very short-lived OH$^{\bullet}$ radical and the L–Fe^{III}–OH^{-} complex always appears first. This radical has no independent existence as it abstracts a hydrogen either immediately or in a short transfer via one or two solvent molecules from a water ligand to form a dihydroxoiron(IV) complex, or even directly from the OH ligand to form the ferryl ion; in both these cases neutralizing itself to a water molecule. When other ligands than water molecules are used, such as chelating agents, the radical may scavenge these ligands.
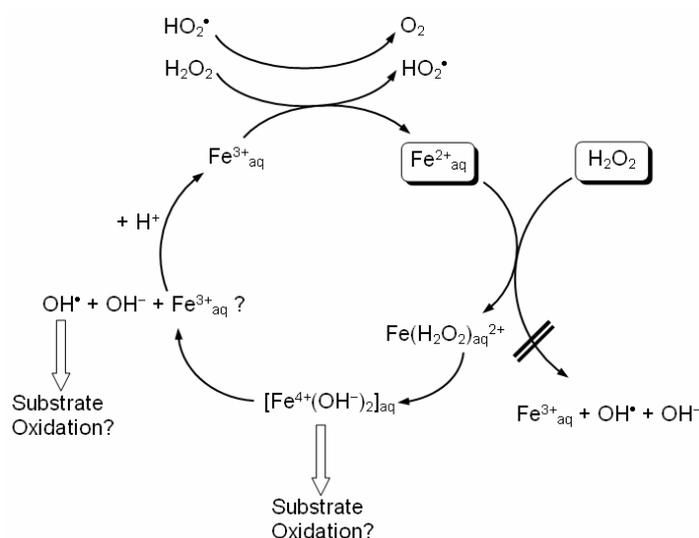

Fig. 6. Mechanistic presentation of possible reactions involved in the thermal Fenton reaction with simplified notations used for the various iron complexes [18]

Bossmann et al [18] studied the degradation of 2,4-dimethylaniline (2,4-xylidine) by means of the H_2O_2/UV method and both Fenton and photochemically enhanced Fenton reactions. The comparison of the reaction products of 2,4-xylidine clearly demonstrated that H_2O_2 photolysis and both Fenton reactions involved different reactive intermediates. While hydroxylated aromatic amines were formed during H_2O_2 photolysis, 2,4-dimethylphenol was the most important intermediate in both Fenton and photochemically enhanced Fenton reactions. The genesis of 2,4-dimethylphenol may only be explained by an electron-transfer mechanism. The authors concluded that during the reaction of Fe_{aq}^{2+} with H_2O_2 a cationic iron intermediate possessing an unusual charge (most likely the ferryl ion Fe_{aq}^{4+}) was formed. Reaction pathways shown in Figure 6 may be significantly important to understand the mechanism of the Fenton reaction.

Summary

The Fenton reaction generally occurs in chemical and biological systems as well as in the natural environment. The importance of Fenton chemistry has been long recognised among others in food chemistry, material ageing and in environmental engineering in particular. The nature of the oxidizing species obtained in Fenton reaction is still a controversial subject. It is something intriguing and at the same time fascinating that a simple reaction (of Fe^{2+} ions with H_2O_2), observed by H.J.H. Fenton over one hundred years ago, proves to be very difficult to describe and understand. It is a paradox, that the Fenton reaction is successfully used in environment protection (for example in wastewater treatment and remediation of groundwater) and it is thought to be a factor, which causes damage to biomolecules and plays a major role in the aging process and a variety of diseases.

A lot of research was done to determine the nature of the species involved in Fenton reactions at various systems and conditions such as the influence of pH and the presence of ligands. Some researchers claimed that the results of this study clearly show that $OH^{\bullet}$ radical is a major species in the Fenton reaction. Another group of the scientists have provided an alternative interpretation of the Fenton reaction mechanism including formation of reactive oxidizing iron species such as ferryl ion. It is important to notice that the high valent metal species are generally unavailable (especially at neutral or acidic pH) from an independent source. Therefore, it is difficult to demonstrate their involvement in Fenton reactions. The formation or involvement of the ferryl species in the Fenton reactions is indirectly deduced from the presence of species having different reactivity from that of the hydroxyl radical [49]. In addition, most of the studies done to determine the nature of species involved in Fenton and Fenton-like reactions have been found to be inconclusive due to the limitations in their methodology [43]. Hence it appears that on the basis of these results it is difficult to clearly conclude which theory is true.

Considering the fact that Fenton reaction is common in chemical, biological, and environmental systems where conditions may be very diverse, it is highly probable that there is more than one universal Fenton mechanism. It is possible that both hydroxyl radicals and ferryl ions can coexist in Fenton chemistry (Fenton and Fenton-like reactions) and depending on the environmental conditions or operating parameters, one

of them will predominate. Given the above doubts, it is desirable to carry out further in-depth research either prove the above hypothesis or prove that there is only one mechanism (radical or non-radical) of the Fenton reaction.

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REAKCJA FENTONA - KONTROWERSJE DOTYCZĄCE CHEMIZMU

Instytut Inżynierii Wody i Ścieków, Politechnika Śląska, Gliwice

Abstrakt: Jest coś intrygującego i jednocześnie fascynującego w tym, że prosta reakcja (jonów Fe^{2+} z H_2O_2) zaobserwowana przez H.J.H. Fentona ponad 110 lat temu jest tak trudna do opisania i pełnego zrozumienia. Jak dotąd natura utleniających czynników powstających w reakcji Fentona jest przedmiotem ciągłych kontrowersji, co może być tłumaczone faktem, że reakcja ta występuje powszechnie zarówno w systemach chemicznych, jak i biologicznych, a także w środowisku przyrodniczym. Jest również paradoksem, że z jednej strony reakcja Fentona jest z powodzeniem stosowana w ochronie środowiska (np. w oczyszczaniu ścieków czy remediacji wód gruntowych), a z drugiej strony jest ona czynnikiem powodującym uszkodzenia molekuł biologicznych, a także odgrywa główną rolę w procesach starzenia się oraz wielu chorobach. Artykuł przedstawia krótki przegląd dotyczący rodnikowego i nierodnikowego mechanizmu reakcji Fentona postulowanego w literaturze naukowej, możliwe drogi przemian chemicznych, a także różne punkty widzenia w tym zakresie.

Słowa kluczowe: reakcja Fentona, odczynnik Fentona, chemizm procesu Fentona, rodnik hydroksylowy, jon ferrylowy