Chinese Chemical Letters 35 (2024) 109579

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

The degradation pathways of contaminants by reactive oxygen species generated in the Fenton/Fenton-like systems

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ARTICLE INFO

Article history:
Received 15 September 2023
Revised 4 January 2024
Accepted 24 January 2024
Available online 30 January 2024

Keywords:
Fenton
Hydroxyl radical
Superoxide radical
Singlet oxygen
Hydroperoxyl radical
High-valent iron

ABSTRACT

Reactive oxygen species (ROSs) in Fenton process are of great importance in treating contaminants in wastewater. It is crucial to understand their chemical properties, formation, and reaction mechanisms with contaminants. This review summarizes the reactive oxygen species in Fenton process, including hydroxyl radical ($^{\bullet}OH$), superoxide radical ($O_2^{\bullet-}$), singlet oxygen ($^1O_2$), hydroperoxyl radical ($HO_2^{\bullet}$), and high-valent iron. $^{\bullet}OH$ shows a trend to react with chemistry groups with abundant electrons through H-atom abstraction, radical adduct formation and single electron transfer. Electron transfer is discovered to be an important pathway when $^1O_2$ degrades organic pollutants. Ring-opening and β-scission are proposed to be the possible ways of $^1O_2$ to certain contaminants. Proton abstraction, nucleophilic substitution, and single electron transfer are proposed to explain how $O_2^{\bullet-}$ degrade pollutants. As the conjugated acid of $O_2^{\bullet-}$, radical adduct formation and H-atom abstraction are reported for the reaction mechanisms of hydroperoxyl radical. High-valent iron in Fenton, namely Fe(IV), reacts with certain pollutants *via* single- or two-electron transfer. This review is important for researchers to understand the ROSs produced in Fenton and how they react with pollutants.

1. Introduction

Due to the continuous growth of global population and limited water resources, water pollution has been regarded as one of the most leading environmental issues. Wastewater treatment plants (WWTPs) are built worldwide to mediate this crisis. They serve to remove harmful contaminants and reduce them to a level that can be accepted by humans. However, some pollutants that cannot be degraded by traditional WWTPs have been detected in natural water environment. Due to the lack of understanding and control of such pollutants, as well as their potential risks, they are named "Emerging contaminants" (ECs) [1].

ECs are released from human activities, which means they have been in the water environment for a long time [1]. Although ECs levels detected in municipal sewage, surface water, and drinking water are low, they are highly persistent and not easily degraded [2]. They may enter the global water environment in different ways such as the release of hospital wastewater, industrial production wastewater, agricultural water, water discharged from sewage treatment plants [3]. Due to the lack of substantial guidelines, these compounds cover a wide range, including pharmaceuticals and personal care products (PPCPS), endocrine interference compounds (EDCs), antibiotics, dyes, pesticides, flame retardants, and microplastics [2,4].

Fenton process (FP), one of the most effective advanced oxidative processes (AOPs) [5], was first discovered in 1894 by Henry J. Fenton who reported the reaction between ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2) to eliminate tartaric acid. In addition to its achievements in cancer therapy, Fenton process have demonstrated considerable effectiveness in the degradation of refractory

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https://doi.org/10.1016/j.cclet.2024.109579
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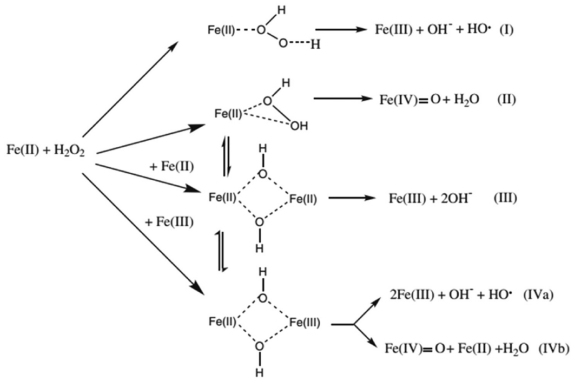

Fig. 1. The competing reactions in Fenton at different pH. Reprint with permission [6]. Copyright 2011, Springer Nature.

contaminants such as PPCPs, EDCs, dyes and antibiotics in water system.

The possible competing pathways of the Fenton system has been proposed by Freinbichler *et al*. in Fig. 1 [6]. This diagram explains the predominant reactions when environmental parameters (*e.g.*, pH, the gerne of ligands and concentration of O_2) change [6–12]. Path I stands for the classical Fenton reaction that generates hydroxyl radical and path II represents the way involving ferryl species. Both the reactive species own great oxidative capacity [6,13]. Path III is predominant when the Fe(II) concentration is beyond that of H_2O_2. Paths IVa and IVb become important when the concentration of Fe(III) and Fe(II) is equal [6,13].

To date, numerous research has been done on the pathways of the Fenton/Fenton-like reactions. Meanwhile, extra stimuli like light and electricity has been introduced to improve the degradation efficacy of the Fenton/Fenton-like systems with certain catalytic materials [14]. Based on this situation, many improved Fenton systems have been proposed and investigated, such as electro-Fenton, photo-Fenton and heterogenous Fenton, to enhance the decontamination capacity of the systems [15]. Chelating agents is a kind of ligands that form complex with Fe ions. Adding chelating agents to Fenton/Fenton-like systems has attract attention since it enables Fe(III) to dissolve even at high pH, largely overcoming the drawbacks of Fenton [16,17]. The whole Fenton/Fenton-like system is a complicated process that generates many kinds of reactive oxygen species (ROSs), including hydroxyl radicals (•OH), superoxide radicals ($O_2^{\bullet-}$), singlet oxygen ($^1O_2$) and high-valent iron (Fe(IV)). The interaction between ROSs can be summarized in three sections: chain initiation, chain propagation and chain termination [18]. It explains the generation of radicals such as hydroxyl radicals and hydroperoxide radicals, the reaction of ROSs with organic compounds, and the end of the production of reactive intermediates and the termination from the reaction.

Since ROSs of Fenton process are the main substances to degrade contaminants, many researchers are committed to improving the production of ROSs to promote the efficiency of Fenton process. Numerous researchers have devoted themselves to investigating the formation, determination, and properties of these ROSs [19–24]. For instance, the oxidative effect of $SO_4^{\bullet-}$, •OH and $O_2^{\bullet-}$ to degrade norfloxacin was studied in the persulfate/Fe_3O_4-supported N-doped wood carbon catalysts system [25]. Singlet oxygen generated in the PMS activation by metal organic framework derived Fe_2O_3/Mn_3O_4 composites is critical to the degradation of tetracycline [26].

Reviews published in the field of Fenton/Fenton-like include the reaction rate constants of ROS [27,28], the determination of ROSs [28–31], photo-Fenton [19,32-40], electro-Fenton [41–48], Fenton processes for wastewater treatment [20,21,28,31,49-54], Fenton based on catalysts [55–60] and heterogeneous Fenton processes (Table 1) [29,30,61-67]. Although many reviews have been published in the Fenton/Fenton-like field, the review on the reaction mechanisms of ROS and organic contaminants in the Fenton/Fenton-like system has not been published. Nonetheless, it is important to pay attention to the reaction mechanisms since the possible degradation pathways of contaminants can be a good guide to understanding and utilizing ROSs in AOPs. Therefore, this article reviews several main reactive oxidation species in Fenton process and discusses their reaction mechanisms with certain contaminants.

2. ROSs in Fenton process

2.1. Hydroxyl radicals (•OH)

Hydroxyl radicals is the most common and promising radical in Fenton process, which is relatively easy to generate and has the highest reactive rate with pollutants. The standard potential of •OH reaches 2.18 V (E^0(•OH, H^+/H_2O) = 2.18 V), and the second-order rate constant with pollutants is in the range from 10^7 to 10^{10} L mol^{-1} s^{-1} [28,68,69].

In conventional Fenton process, hydroxyl radicals can be produced through the reaction between Fe^{2+} and H_2O_2 shown in Eq. 1, which is known as Fenton reaction [70]. However, the following reaction of Fe^{3+} produced in Eq. 1 with H_2O_2 is the rate-limiting step [31]. The reaction rate of Eq. 1 is so much faster than that of Eq. 2, which results in: (1) the increase of pH due to the vast amount of OH^-, and (2) the accumulation of Fe^{3+}, thus producing iron sludge [71–76]. The existence of iron sludge and unsuitable pH in aqueous environment impede the production of •OH severely [75,77,78]. Therefore, numerous novel methodologies have been studied to improve the cycle of Fe^{2+}/Fe^{3+}.

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2{}^{\bullet} + H^+ \quad (2)$$

In the process of searching for new strategy to refine the conventional Fenton process, it was found that though •OH is highly reactive, its life span is extremely short [68,79-81].

Systematic cognition of mechanism and kinetic analysis would be great tools to improve the effective appliance of Fenton process in organic degradation. However, the mechanism of the entire oxidation is usually hard to elucidate due to the complexity of reactions. Therefore, the first step of the system is important.

It is widely accepted that the hydroxyl radicals eliminate organics *via* three main methods: hydrogen atom transfer (HAT), radical adduct formation (RAF) and single electron transfer with •OH (SET) [82–84]. The reaction mechanisms are shown below (Eqs. 3-5).

$$\text{HAT: } A + {}^{\bullet}OH \rightarrow A(\text{-H}) + H_2O \quad (3)$$

$$\text{RAF: } A + {}^{\bullet}OH \rightarrow AOH \quad (4)$$

$$\text{SET: } A + {}^{\bullet}OH \rightarrow A^+ + OH^- \quad (5)$$

Accordingly to An *et al*., •OH is prone to abstract the H atom on -NH, -OH and -CH when attacking organic contaminants [82]. The dissociation energy of H-OH is 499 kJ/mol, which is slightly higher than that of C-H bonds in saturated hydrocarbons. This energy decreases to around 360 kJ/mol if the H atom is on the α-position of a molecule containing a single double bond [85,86]. In

Table 1
Reviews published in the Fenton/Fenton-like field.

Categories	Main contents	Refs.
Photo-Fenton	Promotive catalysts and refinenation	[19,32-40]
Electro-Fenton	Application, progresses and pollutants treatment	[41–48]
Fenton for waste water treatment	Processes, performances, properties of catalysts and detection of ROSs	[20,21,28,31,49-54]
Fenton based on catalysts	Types of catalysts and improvement of the process	[55–60]
Heterogeneous Fenton	Working mechanisms and catalyst performance	[29,30,61-67]

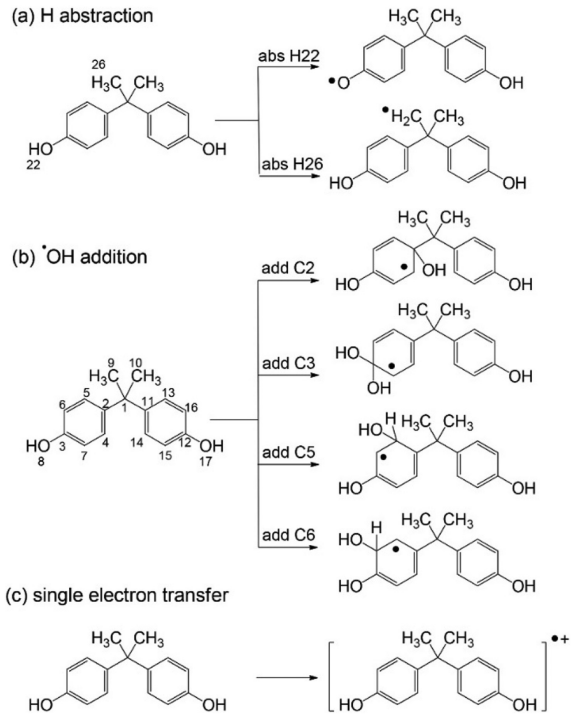

Fig. 2. The three possible degradation pathways of BPA mediated by hydroxyl radical. Reprinted with permission [89]. Copyright 2017, Elsevier.

summary, primary H has lower possibility to be abstracted than secondary and tertiary H for compounds containing alkane functional groups. The electrophilic character of •OH is shown in addition reactions, especially for the double bonds connecting with a group that abundant in electrons [87]. •OH tends to reacts with C=C and C=N bonds instead of C=O due to the lack of electrons [85,86]. Schuler and Albarran [88] discovered that •OH reacts with C=C at a rate close to diffusion mode, which ensures that •OH can readily react with benzenoid hydrocarbons, especially with the electron-releasing substituents such as -OH and $-NH_2$.

Xiao *et al*. [89] studied the possible pathway and mechanism of how •OH degraded bisphenol A (BPA, a kind of endocrine disrupting contaminant) in certain environments through comparing the calculated enthalpies (ΔH_R^0), Gibbs free energy (ΔG_R^0), height of activation energy barrier and second-rate order constant with theoretical value. In their experiment, BPA was prepared with an initial concentration of 10 μmol/L in phosphate buffer (pH of 7.55). They concluded that the degradation was enhanced due to the presence of H_2O_2. The combination of H_2O_2 and UV was proved to be a •OH-meditated process in this case. They found that H abstraction would produce different BPA radicals. The abstraction of H in 26th position by •OH needed more energy and form a relatively unstable BPA radical (Fig. 2). However, the abstraction of H22 would result in the formation of a stable phenoxide radical [89].

RAF is also observed in the reaction between •OH and BPA, which can be classified as an electrophilic addition process. Hydroxyl radicals, as a sort of natural electrophile, can generate several intermediates when adding to the aromatic ring, a nucleophile. This addition typically occurs at the *ortho*, *meta*, and *para* positions of the ring, while it is disadvantageous to occur at the *ortho* position (C5) owing to its higher energy need. In contrast, additions to C2 and C6 are much easier. The •OH addition to C3 is most frequent and the produced gemdiol will then experience the loss of water, followed by the formation of a ketone [90].

It has been proven that the aforementioned RAF and HAT are the predominant pathways when •OH reacts with most refractory organic pollutants [91–93]. Similar conclusion was made by Bo *et al*. when they investigated how •OH degraded tyrosol (TY, a phenolic compound often presented in olive oil mill wastewater) [94]. Thermodynamic calculations in case of Gibbs free energy (ΔG) and energy barrier ($\Delta G^{\neq}$) were carried out, unveiling that RAF routes were more favorable to occur than HAT. In addition, Bo *et al*. performed a kinetic analysis in the temperature range of 273 K to 313 K. They come to the conclusion that the rate constants of RAF with •OH were several times higher than those of HAT, which was consistent with the results of thermodynamic analysis [94]. Tong *et al*. studied the degradation of syringic acid initiated by •OH and found that HAT dominated the rapid reactions at pH 3. At pH of 6, there would be an extra RAF route where an •OH was added to the benzene ring [95]. It is noticeable that Sanches-Neto *et al*. combined quantum chemistry calculations and reaction rate theory to investigate how •OH attack picloram (a toxic herbicide) for the first time. They pointed out that hydroxyl radical mediated addition was the main degradation pathway [96].

Direct SET process has been rarely studied. Wojnarovits and Takacs [86] believed that there was an rearrangement of H_2O surrounding the charge center and this was not conducive to single electron transfer. An *et al*. studied the mechanism of how •OH reacted with dimethyl phthalate (DMP) in aqueous solution and found that SET process was the least possible initial reaction and concluded that RAF and HAT were two main reaction types because OH-adducts and methyl related radicals were detected to be the dominated intermediates [82]. Zhao *et al*. have investigated the •OH degradation in the irradiated TiO_2/Titanate (TiO_2/TNT) system, in which •OH was generated by accepting electrons and holes from UV-light excited TiO_2. The conclusion was that the BPA radical cation was first generated when •OH transferred single electron to neutral BPA that was further oxidized into hydroxylated BPA compounds [97]. Organic compounds like BPA and DMP would be mineralized into CO_2 and H_2O.

The main reaction mechanism mentioned above (HAT, RAF and SET) may occur spontaneously. In addition to the most studied pathway: HAT-RAF, Dejan *et al*. discovered through DFT calculation and experiment that there was one new pathway for hydroxyl radical named radical adduct formation and hydrogen atom abstraction (RAF-HAA) when investigating the reaction between •OH and a certain derivations of coumarin: 4-hydroxycoumarin, where •OH was produced from typical Fenton reaction and further detected by EPR spectrometer [98]. Firstly, due to the different reaction locations of the addition of •OH, several intermediates were produced,

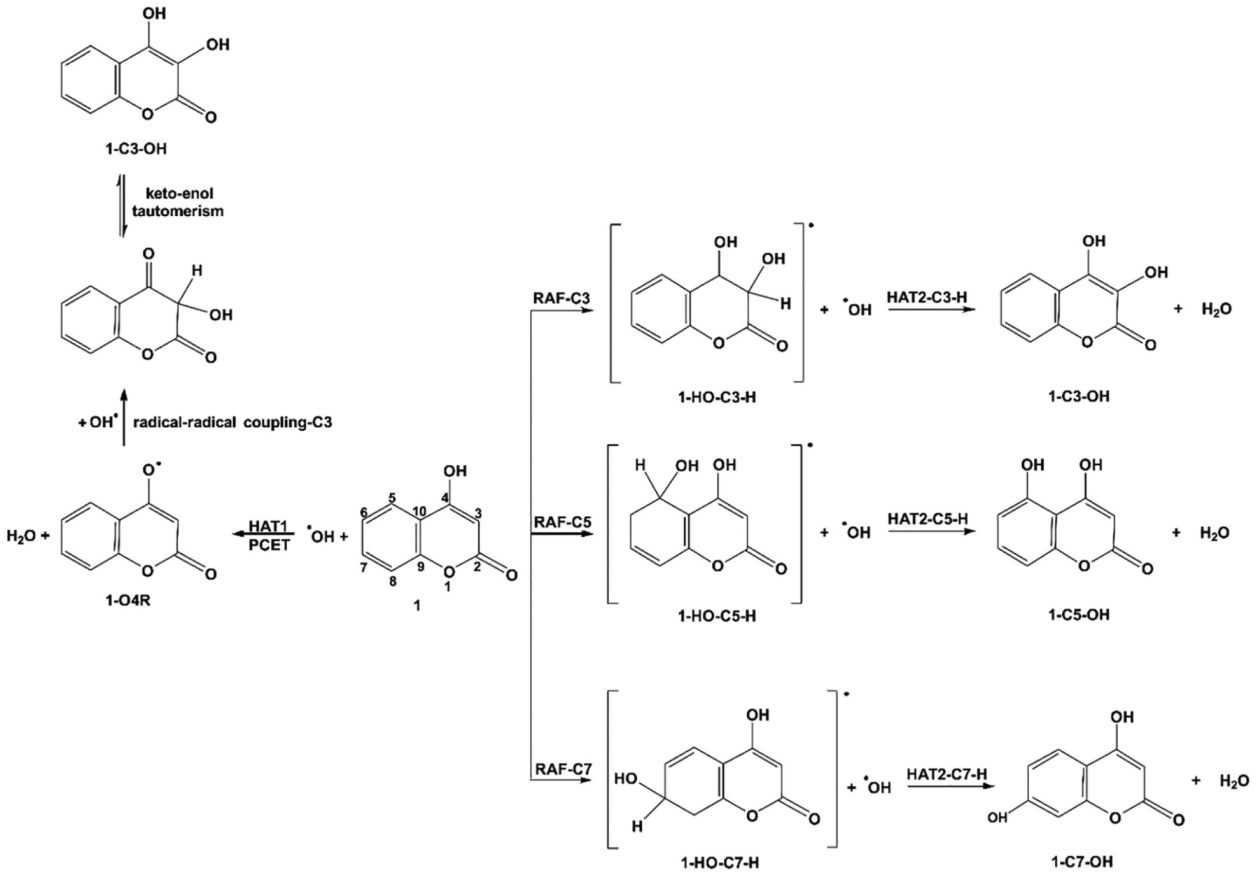

Fig. 3. The possible pathways of the reaction between •OH and 4-hydroxycoumarin. Reprinted with permission [98]. Copyright 2020, Elsevier.

which further reacted with another •OH to produce stable compounds that were proved to be less toxic than the initial molecules. It was concluded that this newly found mechanism can be utilized for other stable compounds without H-donating groups (Fig. 3).

2.2. Superoxide ions ($O_2^{\bullet-}$)

$O_2^{\bullet-}$ has a redox potential of 2.4 V, which is slightly lower than that of •OH [99]. Unlike most peroxide species, $O_2^{\bullet-}$ tends to become unstable at temperature above 348 K [100]. The lifespan of $O_2^{\bullet-}$ varies from 1 min to 3000 min in different pH environments [21,101-103]. $O_2^{\bullet-}$ can be generated *via* numerous methods such as radiolysis, photolysis and some biochemical methods involving certain bacteria [104]. As for the water under sunlight, $O_2^{\bullet-}$ is mainly produced *via* the reaction of dissolved oxygen molecule with electron donors [105–108]. In water, superoxide ions form hydroperoxy radical ($HO_2^{\bullet}$) through proton transfer (Eq. 6). The generated $HO_2^{\bullet}$ undergoes further reactions to form hydrogen peroxide and water (Eqs. 7 and 8) [109]. Besides, metals (*i.e.*, Fe, Mn and Cu) in water can also react with $O_2^{\bullet-}$ to accelerate this decay process (Eqs. 9 and 10) [110–112].

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet} \quad (6)$$

$$HO_2^{\bullet} + O_2^{\bullet-} \rightarrow HO_2^{-} + O_2 \quad (7)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (8)$$

$$M^{(n+1)+} + O_2^{\bullet-} \rightarrow M^{n+} + O_2 \quad (9)$$

$$M^{n+} + O_2^{\bullet-} + 2H^+ \rightarrow M^{(n+1)+} + H_2O_2 \quad (10)$$

The reactivity of $O_2^{\bullet-}$ in aqueous system is not as strong as we imagine mainly due to these aforementioned decay reactions. Therefore, many research has been carried out to improve the production of $O_2^{\bullet-}$ and explore the reaction mechanisms of superoxide ions with organic pollutants.

Generally, superoxide radicals react with organic contaminants mainly through several following ways: (1) Proton abstraction; (2) nucleophilic substitution and (3) single electron transfer [100]. Eq. 11 shows proton abstraction and the formed carbon-based radicals will then react with dissolved oxygen to produce peroxy compounds, which are further transformed into oxidation products (Eqs. 12-14) [113]. When there are no protons, $O_2^{\bullet-}$ are prone to attack positively charged contaminants because of its strong nucleophilicity [114,115]. Besides, $O_2^{\bullet-}$ will disproportionate in water forming oxygen molecule or its conjugated acid-$HO_2^{\bullet}$, as shown in Eq. 15 [100,116-121]. Water-induced disproportionation of $O_2^{\bullet-}$ in dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and acetonitrile (AcN) was investigated by Che *et al.* [122]. It turned out that a hydrogen bond formation between water molecule and sulfoxide of DMSO and DMF (or nitrile group of AcN) fixed H_2O, making H_2O protons less likely to interact with other compounds [122]. Several researches about dynamics of disproportionation of $O_2^{\bullet-}$ had been proposed for a long time. They showed that $O_2^{\bullet-}$ disproportionation reached the highest point at pH that was equivalent to the pK_a of $HO_2^{\bullet}$ and reached equilibrium at pH 14 [123]. In addition, nucleophilic reactions and one-electron transfer, both as the essential properties of $O_2^{\bullet-}$, has been involved in early studies [124–126]. Nucleophilic reactions of $O_2^{\bullet-}$ were typically reported in the cases of reacting with alkyl halides, whereas the single elec-

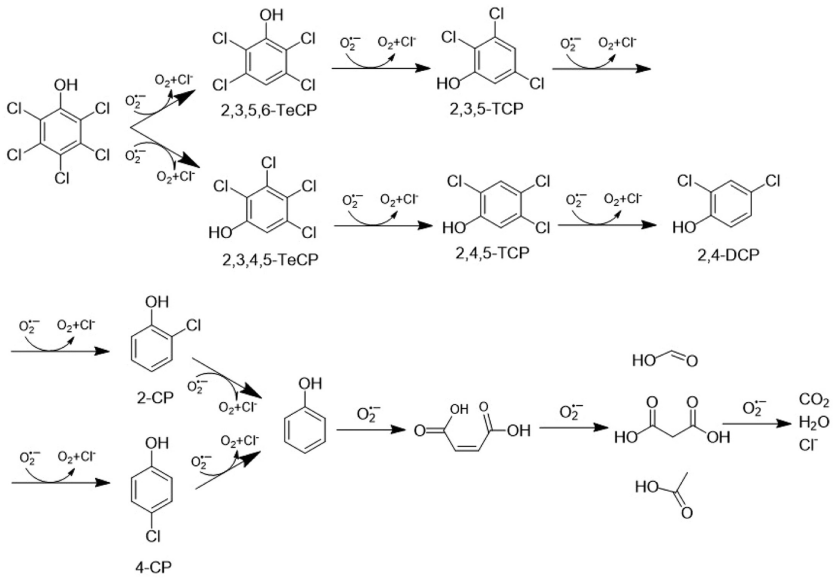

Fig. 4. The PCP degradation by $O_2^{\bullet-}$ generated from bismuth silicate crystal ($Bi_{12}SiO_{20}$, BSO) through photocatalytic method. Reprinted with permission [130]. Copyright 2011, Elsevier.

tron transfer was broadly used in the reaction with metal complexes [127–129].

$$RH + O_2^{\bullet-} \rightarrow R^{\bullet} + HOO^- \quad (11)$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \quad (12)$$

$$ROO^{\bullet} + O_2^{\bullet-} \rightarrow ROO^- + O_2 \quad (13)$$

$$ROO^- \rightarrow \text{Oxidation products} \quad (14)$$

$$2O_2^{\bullet-} + H_2O \rightarrow O_2 + HO_2^{\bullet} + OH^- \quad (15)$$

In some special process, superoxide radicals play an important role. Li *et al*. have demonstrated that superoxide ions were the decisive ROS in photocatalytic degradation of pentachlorophenol (PCP) under a xenon lamp in the range of 300–800 nm [130]. Li *et al*. tried to investigate how degradation of PCP can be improved by photocatalysis involving bismuth silicate crystal ($Bi_{12}SiO_{20}$, BSO), and oxygen vacancies on the BSO surface can enhance the interfacial electron transfer effectively [130]. To further understand the entire degradation process, the mechanism was posted by Li *et al*. as well (Fig. 4). Carbon atoms on benzene ring in PCP molecules tended to be electrophile because of the higher electronegativity of Cl and thus having the trend of withdrawing electrons [131–133]. Meanwhile, the electron-releasing ability of $O_2^{\bullet-}$ made bonds between carbon and chlorine atoms more susceptible to be attacked, leading to elimination of chlorine atoms in PCP molecules one by one and the generation of phenol. The phenol molecule was further degraded into CO_2 and H_2O [130]. Kalu and White [134] documented the possible degradation pathways of hexachlorobenzene (HCB) induced by $O_2^{\bullet-}$, which was generated from 0.3 cm-thick chlorine electrode in the DMF/DMSO solution. They suggested that a series of nucleophilic addition happened to the Cl group and then an intermediate called orthoquinone was generated, which would be further converted to HCO_3^- [134]. The reaction of superoxide ions with halogenated compounds have been widely studied due to its nucleophilic and reductive properties [135–137].

The findings of Li *et al*. emphasized the important role of $O_2^{\bullet-}$ again [138]. They focused on the refinement of the electro-Fenton technology, which was coupled with W-doped CeO_2 (W/CeO_2) composites as catalysts to degrade ciprofloxacin (CIP), a persistent antibiotic pollutant that has been increasingly abused by human. They found that the introduction of W increased the maximum loading amount oxygen vacancies (OVs), which was helpful for the subsequent formation of $O_2^{\bullet-}$. It was proposed that $O_2^{\bullet-}$ mainly attacked the N atoms on the piperazine ring of CIP molecule, broke the bonds between carbon atoms, added oxygen molecules, thus forming an compound structured $C_{17}H_{16}FN_3O_5$, which was further oxidized into inorganic substances (CO_2 and H_2O) [138]. Besides, Dong *et al*. found that the important degradation of carbamazepine (CBZ) by $MoSe_2$/PMS system was initiated by $O_2^{\bullet-}$. UV–visible light served as the driving force for $MoSe_2$ activation to emit electrons and holes, which can convert oxygen molecule to $O_2^{\bullet-}$. The radical transformed CBZ into its exited state-iminostilbene and oxidized it further into stable compounds [139]. Wu *et al*. proposed a new insight into the UV/ferrate(VI) system degrading phenolic contaminants [140]. They found that $O_2^{\bullet-}$ started the destruction of 2,4-DCP by attacking the Cl atom on the benzene ring, as shown in Fig. 5. Chloride atom at C2 position was firstly attacked by $O_2^{\bullet-}$ to form parachlorophenol superoxide radical, which reacted with $O_2^{\bullet-}$ again to produce 4-chlorocatechol by losing a H_2O [141]. It is worth noting that BPA degradation can also be partially attributed to the presence of superoxide radical. Superoxide radicals in the C_{60}@AlCl-LDO (ZnAlTi layer double oxide) system were generated from the excitation of molecule oxygen by the photo-yielded electrons trapped by Ag and LDO. Then the generated $O_2^{\bullet-}$ facilitated the elimination of the aromatic rings in BPA [141]. When effective degradation of BPA involves superoxide radical, it is usually the result of the synergetic effect of several ROSs such as hydroxyl radical and hydroperoxyl radical [142,143]. However, the effective degradation of BPA merely by superoxide radical has been rarely reported.

2.3. Hydroperoxyl radical ($HO_2^{\bullet}$)

As the conjugated radical of superoxide radicals (Eq. 6), $HO_2^{\bullet}$ is an important ROS in Fenton reaction system (Eqs. 2 and 8). The redox potential of $HO_2^{\bullet}$ is 1.7 V, which is lower than that of su-

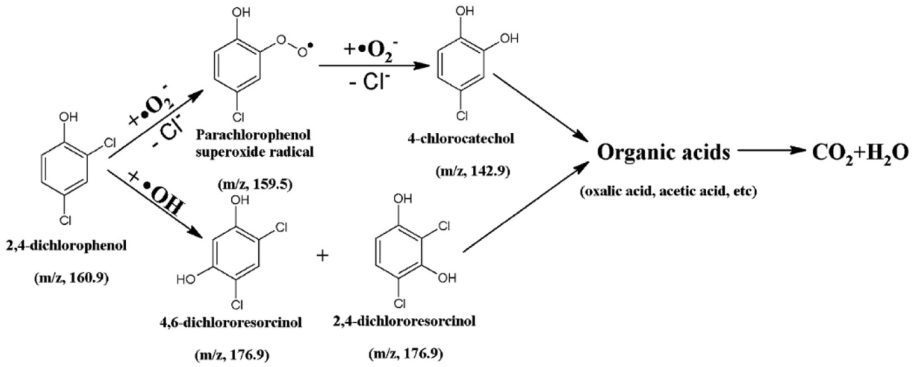

Fig. 5. The degradation pathways of 2,4-DCP by superoxide radical. Reprinted with permission [140]. Copyright 2020, Elsevier.

peroxide radicals (2.4 V) [144,145]. In AOPs, especially Fenton process, hydroxyl radical always receives attention due to its great oxidizing ability. Hydroperoxyl radical has been named "The forgotten radical" by Aubrey D.N.J. De Grey [146]. Traditional investigated mechanisms for $HO_2^{\bullet}$ include RAF (Eq. 16) and hydrogen atom abstraction (HAA). However, the HAA mechanism is special since it happens through two similar pathways: HAT (Eq. 17) and proton-coupled electron transfer (PCET) (Eq. 18) [147–149]. Although the research on $HO_2^{\bullet}$ in AOP process is limited, there are experimental results revealing the mechanism about how $HO_2^{\bullet}$ reacts with certain kinds of compounds in aqueous phase.

$$AH + HOO^{\bullet} \rightarrow [AH\text{-}OOH]^{\bullet} \quad (16)$$

$$AH + HOO^{\bullet} \rightarrow A^{\bullet} + H_2O_2 \quad (17)$$

$$A^{\bullet} + HOO^{\bullet} \rightarrow A\text{-}OOH \quad (18)$$

Dusan *et al*. investigated the oxidation process of hydroperoxyl radical and coumarin and demonstrated the details of the oxidation pathways (Fig. 6) [147]. They suggest that there are two possible pathways for this reaction: (1) Mere HAA and (2) RAF-HAA. The OH group on the coumarin molecule donates a H atom to $HO_2^{\bullet}$, followed by a radical-radical coupling (RRC) to produce a relative unstable intermediate containing two ketos. A keto-enol conversion occurs to form the final stable compound. However, there are several pathways in the RAF-HAA mechanism. Hydroperoxyl radicals are added to the benzene ring or the C atom next to OH group to generate a radical, which undergoes a H-atom abstraction on the carbon atom that has been added [147].

Apart from the reaction mechanism of $HO_2^{\bullet}$ in water, the role it plays and its effect are also investigated. After adjusting the concentration of $HO_2^{\bullet}$ by controlling pH, Zhao *et al*. found that $HO_2^{\bullet}$ can enhance the degradation of *p*-nitrophenol (*p*-NP) by hydroxyl radical on a great extent [150]. In order to make $HO_2^{\bullet}$ the predominant ROS, a large amount of H_2O_2 was added to the acidic solution containing *p*-NP and oxygen, and pulse radiolysis was employed for the entire reaction system. It is found that *p*-NP was converted into phenoxy-like radicals, which underwent ring-opening reaction mediated by $HO_2^{\bullet}$ and the formed diketone (Fig. 7).

Although the reaction mechanisms of $HO_2^{\bullet}$ with pollutants have been investigated, the current researches regarding $HO_2^{\bullet}$ are not sufficient and comprehensive and more investigation needs to be carried out. For example, the quantitative measurement of $HO_2^{\bullet}$ in aqueous environment is of a great vacancy. The rate constants of $HO_2^{\bullet}$ and contaminants are needed to evaluate the reactive capacity of the radical. The lack of basic data of $HO_2^{\bullet}$ limits its further study in the biochemical and environmental fields.

2.4. Singlet oxygen ($^1O_2$)

Singlet oxygen is regarded as a special molecular oxygen with two low states lying: O_2 ($^1\Delta_g$) and O_2 ($^1\Sigma_g^+$). However, the latter tends to convert to the former owing to the short lifespan of O_2 ($^1\Sigma_g^+$), which is only 10^{-12} s [151,152]. Compared with hydroxyl radicals and sulfate radicals, singlet oxygen has lower standard redox potential: $E^0 = 1.52$ V, while this value for $^{\bullet}OH$ and $SO_4^{\bullet-}$ is around 2.8 V and 2.7 V, respectively [152]. The generation methods of singlet oxygen have been broadly investigated during the past several decades and the reported approaches are as follows: (1) The activation of PMS and PDS by metals and their composites [153,154]; (2) the conversion from superoxide radicals under catalysis [100]; and (3) the photosensitized excitation of triplet dioxygen [155].

It is noted that singlet oxygen reacts with organic compounds mainly through four pathways including electron transfer, reactions with alkene, reactions to form endoperoxides and reactions with sulfate to produce sulfoxides [156–159]. Singlet oxygen possesses a high reactivity with electron-rich groups in organic compounds, which provides $^1O_2$ with a trait to degrade numerous PPCPs. The degradation effect of sulfamethoxazole (SMX) by singlet oxygen generated from PMS activation by *p*-benzoquinone (*p*-BQ) has been investigated [160]. The findings of Zhou *et al*. demonstrated the special properties of singlet oxygen by observing that the species tended to attack the sulfanilic group of SMX instead of the isoxazole ring [160]. The amine group at the benzene ring was attacked by singlet oxygen to form nitroso-SMX and nitro-SMX (Fig. 8). In addition, there was another intermediate named hydroxy—SMX produced by the hydroxylation of aniline ring. In addition, the generation of singlet oxygen can be facilitated when the pyridine nitrogen in thiacloprid (THIA) combined with PMS. Liu *et al*. discovered that thiacloprid (THIA) can be degraded by $^1O_2$ through several paths, among which electron transfer played an essential role [153]. In the presence of PMS, electrons of N atom transferred to the methylene bridge and the next saturated carbon atom, making them more likely to be attacked by singlet oxygen. It was reported that cyanoimino group can also be attacked by singlet oxygen to form nitroso-THIA and nitro-THIA and subsequently induced the loss of corresponding molecular nitrous oxide.

Moreover, the reaction of singlet oxygen and ofloxacin in $LaNiO_3$/PMS system has been carried out. In this system, $^1O_2$ was generated from the reaction of carboxylic acid and oxygen, both of which came from the decomposition of peroxycarboxylic acid. Their reaction pathways (Fig. 9) were summarized as follows [161]: Piperazinyl substituent was attacked by $^1O_2$ to eliminate the methyl and the produced compound can react further with singlet oxygen *via* two pathways: (1) Hydroxylation and (2) decarboxylation. The chemical compound generated through the former

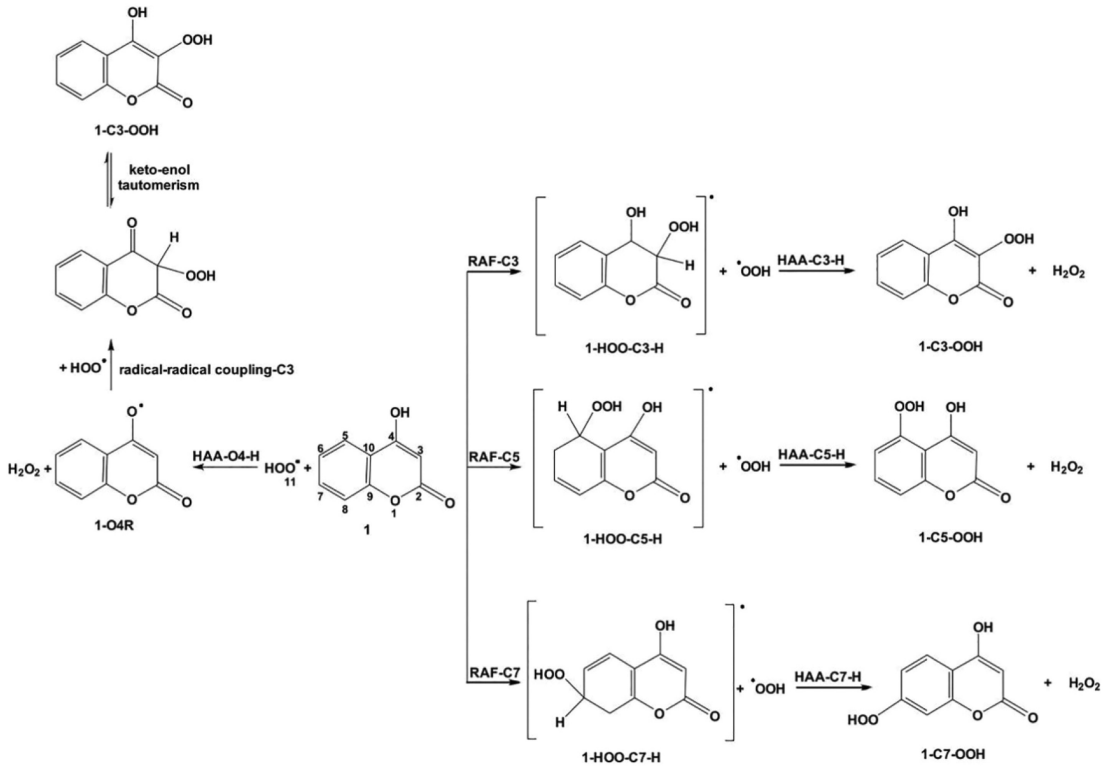

Fig. 6. The possible pathways for $HO_2^{\bullet}$ to degrade coumarin. Reprinted with permission [147]. Copyright 2021, Elsevier.

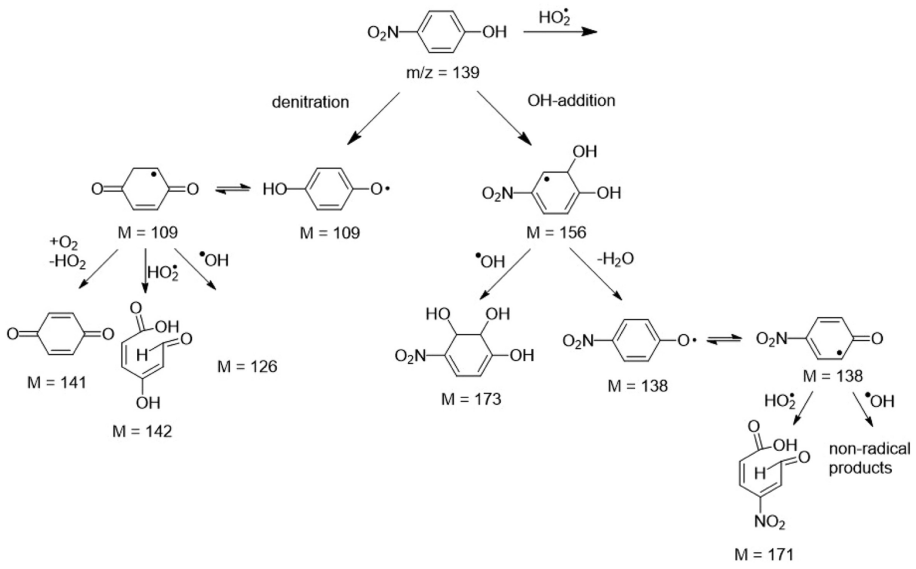

Fig. 7. The degradation mechanism of *p*-NP in the presence of $HO_2^{\bullet}$, $^{\bullet}OH$ and H_2O_2 in acidic solution (pH 2) through pulse radiolysis. Reprint with permission [150]. Copyright 2013, Elsevier.

pathway underwent ring-opening and a series of subsequent reactions, while demethylation triggered by $^1O_2$ occurred to the oxazinyl substituent of the latter.

Singlet oxygen has been widely proved to be effective in degrading BPA. The generation of $^1O_2$ in the $NaBiO_3$/HCL system was proved to be related with lattice oxygen since a linear relationship between singlet oxygen-production and composite loading was established by Ding *et al.* [162]. Singlet oxygen attacked the central carbon atom connecting the two aromatic rings through a β-scission to generate phenol and 4-isopropenylphenol (Fig. 10) [163]. The isopropyl of 4-isopropenylphenol was easily attacked by singlet oxygen or hydroxyl radicals, rendering the formation of 4-hydroxyacetophenone [164]. There was an extra conversion from 4-hydroxyacetophenone to *p*-hydroquinone according to the research of Zhang *et al.* [164]. These intermediate products often underwent ring opening reactions and further oxidation mediated by singlet oxygen, thus completing the whole reaction chain [165]. Similar pathways were also proposed by Zhang *et al.* when they focused on the generation of $^1O_2$ with the involvement of Bi composites [166]. In the summary, reaction pathways are found to be similar in case of the degradation of BPA *via* singlet oxygen. The breaking of C-C bond in the middle of BPA molecule is widely accepted as

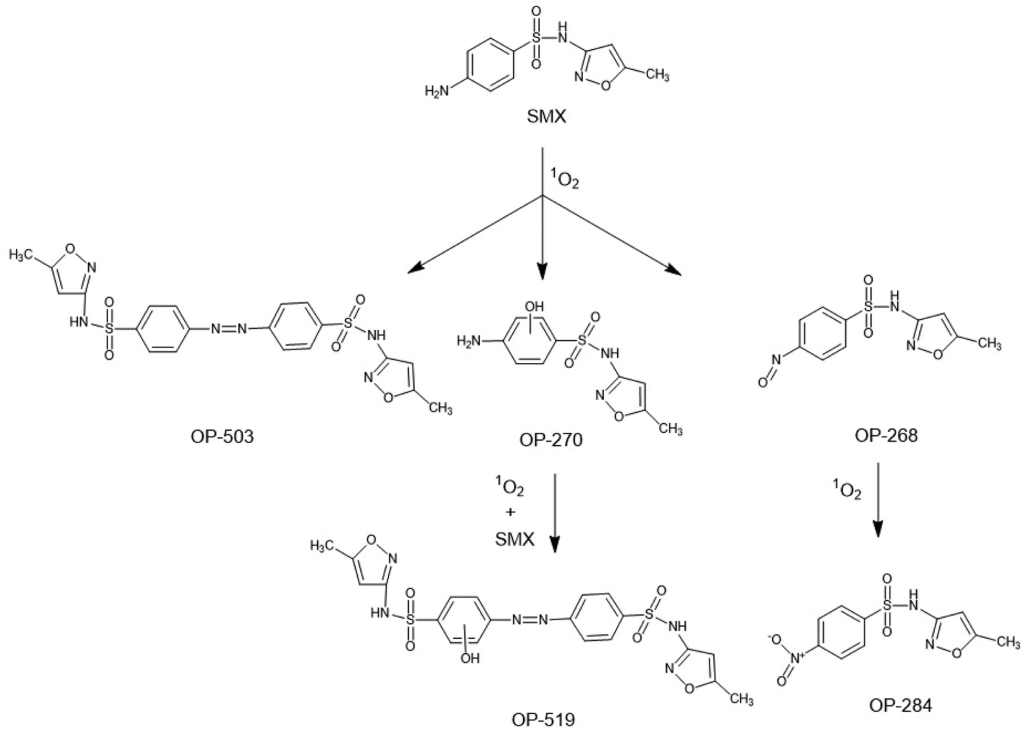

Fig. 8. The proposed degradation pathways of SMX in the presence of singlet oxygen. Reprint with permission [160]. Copyright 2017, Elsevier.

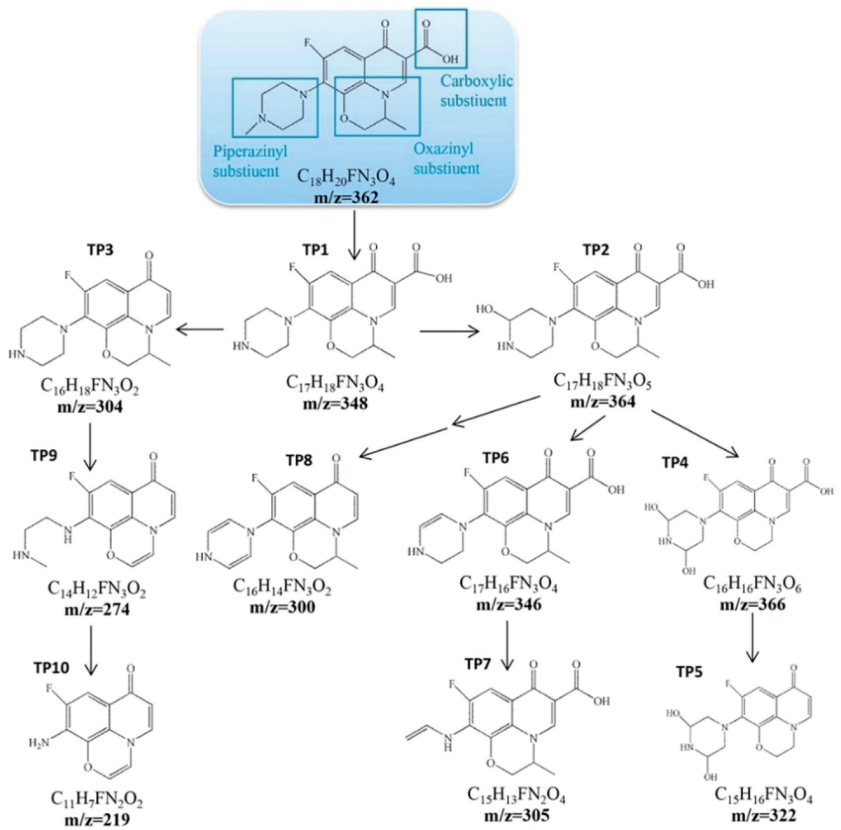

Fig. 9. The possible OFX degradation pathways in $LaNiO_3$/PMS system. Reprinted with permission [161]. Copyright 2019, Elsevier.

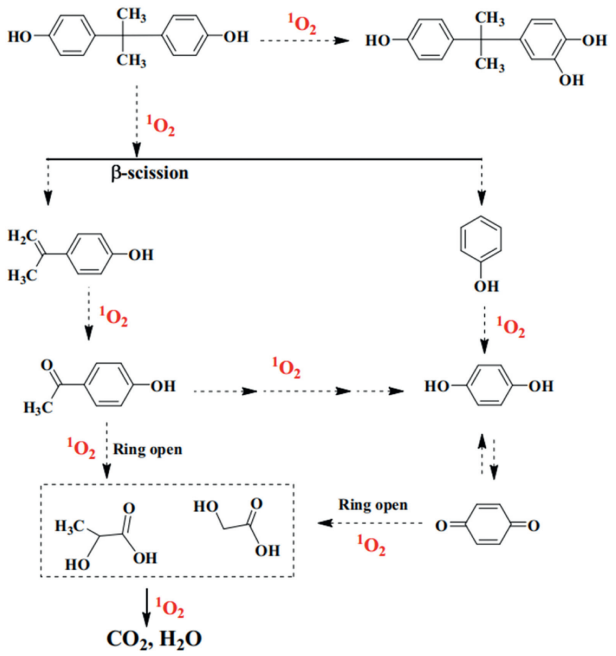

Fig. 10. Mechanism about how singlet oxygen from $NaBiO_3$ degrades BPA. Reprinted with permission [163]. Copyright 2016, Elsevier.

the initial step of the mechanism. This is mainly because hydroxyl groups have the ability to give electrons, making the carbon atom at the central position a vulnerable site to be attacked [166–168].

As a popular ROS in Fenton system, singlet oxygen has been applied in the treatment of a variety of organic pollutant. Meanwhile, many techniques based on $^1O_2$ have been established due to its oxidation ability and easy generation. However, Lu *et al.* suspected the authentic degradation capacity of $^1O_2$-dominant processes and investigated the performance of singlet oxygen in a non-photochemical system [169]. They concluded that the importance of singlet oxygen was overestimated in the environmental without the involvement of sunlight because of the quickly quenching of $^1O_2$ by water. They also pointed out that EPR technology, which is regarded as the direct monitor of $^1O_2$, may convey the misleading signals. Similar phenomenon has also been reported by Nardi *et al.* in their research about $^1O_2$ detection through EPR [170]. They found an overestimated signal given by EPR device when 2,2,6,6,-tetramethylpiperidine (TEMP) served as a probing agent to detect $^1O_2$ and concluded that the deprotonation of TEMP radical cation and its reaction with oxygen would give a misleading ERP signal since it had nothing to do with singlet oxygen.

2.5. High-valent iron (Fe(IV))

In Fenton and Fenton-like processes, hydroxyl radical is widely considered as the main ROS responsible for the oxidation of organic contaminants, followed by superoxide radicals [171]. High-valent iron (Fe(IV)), a newly discovered oxidizing agent several decades ago, is proposed as another oxidant. The redox potential value of Fe(IV) is beyond 1.2 V [172]. Fe(IV) usually exists as $(H_2O)_5Fe^{IV}{=}O^{2+}$ in acidic and neutral aqueous media [173]. This ferryl ion can be generated typically through Fenton reaction when ozone is involved (Eq. 19) [172–176]. Besides, ferryl ion species can be generated in Fenton process and then undergoes the reaction with hydrogen peroxide based on the research by Christina. R. (Eqs. 20-22) [174,175].

$$Fe^{II} + O_3 \rightarrow Fe^{IV}O^{2+} + O_2 \quad (19)$$

$$[Fe(OH)(H_2O)_5]^+ + H_2O_2 \rightarrow [Fe(OH)(H_2O_2)(H_2O)_4]^+ + H_2O \quad (20)$$

$$[Fe(OH)(H_2O_2)(H_2O)_4]^+ \rightarrow [Fe(OH)(H_2O)_4]^{2+} + {}^{\bullet}OH + OH^- \quad (21)$$

$$[Fe(OH)(H_2O_2)(H_2O)_4]^+ \rightarrow [Fe(OH)(H_2O)_4]^{3+} + 2OH^- \quad (22)$$

Compared with hydroxyl radicals, high-valent irons have lower reactivity but higher selectivity to organic compounds. Though the generation of Fe(IV) can be achieved by Fenton reactions, it is severely affected by the parameters of solution according to Hug *et al.* [176] and Pignatello *et al.* [177]. Fe(IV) rather than ·OH is prone to be produced in a higher pH range when 2-propanol is used as

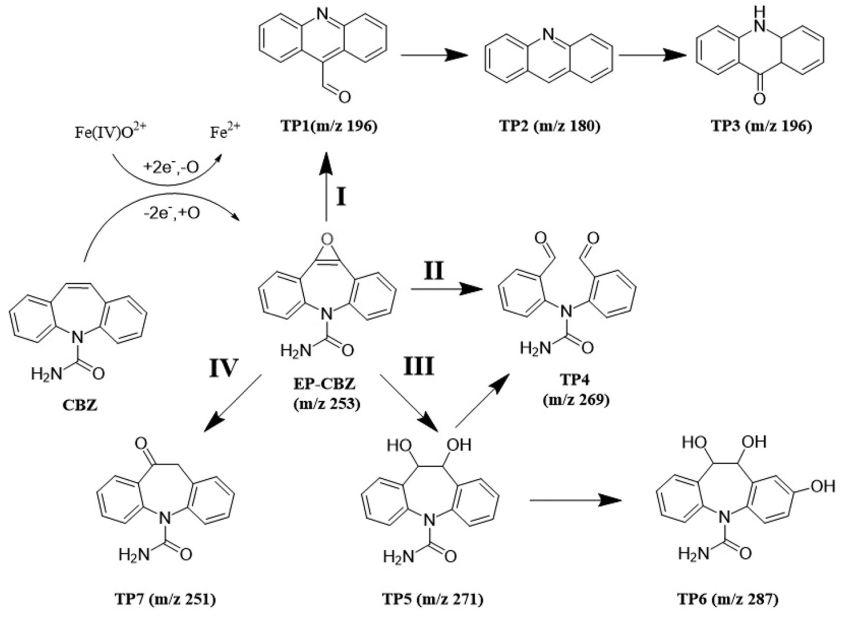

Fig. 11. The possible pathway for $Fe(IV){=}O^{2+}$ to degrade CBZ through electron transfer. Reprinted with permission [180]. Copyright 2021, Elsevier.

the quencher for the Fenton reaction, while Pignatello *et al*. illustrated that a mixture of •OH and ferryl ions is generated under a low pH around 2.8.

It was postulated that Fe(IV) degrades organic contaminants mainly through electron transfer [178]. Pestovsky *et al*. did a research about reaction of Fe(IV)=O with cyclobutanol. They concluded that cyclobutanol would undergo a ring opening pathway through a single electron transfer, while the oxidation of cyclobutanol to cyclobutanone by Fe(IV) occurred when the reaction involves two electrons transfer [179]. Ma *et al*. proposed a possible pathway for the degradation of CBZ by Fe(IV)=O generated in the FeS_2/PS system [181]. The initial intermediate was EP-CBZ as shown in Fig. 11. Ma *et al*. hold the opinion that Fe(IV) species attacked carbon atoms on positions 1 and 2 through electron transfer, resulting in the cleavage of olefin bonds between C1 and C2 [178,180].

Based on the determination method of Fe(IV)=O in the aqueous solution, many researches have published the mechanism and contribution of high-valent irons. According to the findings of Kong *et al*., Fe(II) tended to react with O_2 to generate hydrogen peroxide and then Fe(IV)=O formed through the reaction of $Fe(II)OH^+$ and H_2O_2 in neutral and alkaline environment [181]. Sun *et al*. investigated the contribution of Fe(IV)=O in oxidizing As(III) to As(V) in alkaline solution [182]. Oxygen molecules absorbed on the surface of pyrite reacted with Fe(II) to yield intermediates, which can later be transformed into Fe(IV) through breaking the O-O bond. Sun *et al*. finally concluded that the oxidation of As(III) to As(V) can be accelerated by Fe(IV) at a high pH value (9.0–11.0). In acidic environment, Fe(III) on the surface of pyrite may be converted to Fe(IV)=O, which accelerated the decomposition of hydroperoxide to oxygen molecules, thus facilitating the oxidation of As(III) to As(V) [182]. Lai *et al*. found a good method to remove atrazine (ATZ) by activating PDS with natural titanomagnetite and gave evidence that Fe(IV) were involved in the degradation of ATZ [183]. Fe(IV) was mainly generated from Fe(II) on the surface of Ti. The elimination of ATZ was synergistically induced by •OH and $SO_4^{\bullet-}$. However, it was difficult to quantitively determine the contribution of high-valent iron-oxo specie in this system. In addition, the research about direct degradation pathways of high-valent iron to organic contaminants is lacking since recent study pays more attention to the evidence of existence, formation and auxiliary role of Fe(IV) in the advanced oxidation process [184,185].

3. Conclusion

This article reviewed several reactive oxidation species in Fenton process. The generation of the species are summarized and the reaction mechanisms of the species with organic contaminants are discussed in detail. Hydroxyl radical, as the most promising ROS in Fenton, reacts with organic contaminants through H-abstraction, radical addition, and single electron transfer. Special groups that are vulnerable to attack by •OH are summarized, while there is little explicit research on single electron transfer. As a reductant and nucleophile, superoxide ions display obvious tendency to attack halogenated groups. As for hydroperoxyl radicals, only specific reactions such as HAA and RAF-HAA are observed and the further reaction mechanism of this ROS is unknown. Singlet oxygen, as an oxidation specie with high reactivity, tends to oxidize electron-enriched substitutes mainly through electron transfer. Nevertheless, the real oxidation ability of $^1O_2$ has been suspected. Recent investigation on Fe(IV) has been concentrated on its generation and determination. Several researches have shifted their attention to the role it plays in the metal-composite system, while the direct degradation pathway of Fe(IV) to organic contaminants or metal ions is still lacking.

The consensus regarding the main oxidizer in Fenton (•OH or Fe(IV)) under specific conditions has not been reached. In addition to the •OH that has received the most attention, the oxidation capacity of other free radicals generated in the Fenton/Fenton-like systems still needs to be explored. The transformation of superoxide radical to other ROS such as •OH and $^1O_2$ still needs to be investigated. The main method to determine the contribution of ROS to organic degradation is ROS scavenging method, and other methods need to be explored. Besides, there is still lacking of direct detection of hydroperoxyl radical and Fe(IV) species and the accuracy of the detection methodology for some ROS is controversial, which seriously impede the in-depth research for these ROS. More detailed reaction mechanisms for Fenton system must be further investigated to improve the treatment efficiency.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 22176102 and 21806081), Natural Science Foundation of Tianjin (No. 19JCQNJC07900), Fundamental Research Funds for the Central Universities, Natural Science Foundation of Jiangsu Province in China (No. BK20230410) and Natural Science Research of Jiangsu Higher Education Institution of China (No. 23KJB610010).

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