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To cite this version:

Feilong Dong, Chuyun Fu, Mingbao Feng, Da Wang, Shuang Song, et al.. Simultaneous generation of free radicals, $Fe(V)$ and $Fe(V)$ by ferrate activation: A review. Chemical Engineering Journal, 2024, 481, pp.148669. $10.1016/j.cej.2024.148669$. hal-04390371

HAL Id: hal-04390371 <https://hal.science/hal-04390371v1>

Submitted on 12 Jan 2024

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Chemical Engineering Jo[u](https://doi.org/10.1016/j.cej.2024.148669)rnal 481 (2024) 148669

<https://doi.org/10.1016/j.cej.2024.148669>

Review

Simultaneous generation of free radicals, Fe(IV) and Fe(V) by ferrate activation: A review

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Keywords: Ferrate High-valent iron intermediates Free radicals Activation Mechanism Degradation

ABSTRACT

Ferrate (Fe $^{VIO_4^2}$, Fe(VI)) is a green and effective oxidant that has been extensively studied for removing organic pollutants in water and wastewater. However, practical applications of ferrate are limited due to selfdecomposition at nearly neutral pH and low removal efficiency for electron-deficient pollutants. Therefore, recent research has focused on activating Fe(VI). Although various methods for enhancing Fe(VI) oxidation efficacy have been explored and reviewed extensively, there remains a gap in the systematic comparison of the different highly reactive species involved in the Fe(VI) activation process. To bridge this gap, this review aims to comprehensively present the mechanisms, strategies, and efficiencies of generating key reactive species, including sulfate radicals (SO⁴), hydroxyl radicals (\bullet OH), and intermediate iron species (Fe(IV) and Fe(V)), in the Fe(VI) activation system. We observed that both iron intermediates and free radicals react at much higher rate constants than their Fe(VI) precursor, resulting in rapid abatement of organic pollutants. The oxidation characteristics of these active species in Fe(VI) activation are discussed. Finally, the practicability of each Fe(VI) activating strategy is evaluated for rapid and efficient removal of organic pollutants in water and wastewater.

1. Introduction

As a green and efficient oxidant, ferrate (Fe ${^{VI}O_4^2}$, Fe(VI)) is widely used to remove organic pollutants, algae, and toxic metals $[1-6]$. Fe(VI) can effectively degrade pollutants under neutral or alkaline conditions [7–9]. Additionally, Fe(VI) has the capability of sterilization and disinfection, which can inactivate bacteria and pathogens during water treatment [10]. Among the various forms of Fe(VI), such as $H_3FeO_4^+$, H_2FeO_4 , HFeO₄, and FeO₄², the protonated HFeO₄ form dominates at neutral pH. HFeO₄ has a larger spin density on the oxo ligands, and its oxidation capacity is stronger than $FeO₄²$ [11–13]. The intermediate forms with oxidation states of $+$ 4 such as $\text{Fe}^{\text{IV}}\text{O}_3^{2}$ and $\text{Fe}^{\text{IV}}\text{O}_4^{4}$ (Fe(IV)), and $+$ 5 such as Fe $\mathrm{^VO_4^{3-}}$ (Fe(V)) are produced by Fe(VI) through electron acquisition $[14–18]$. The reactivity of Fe(IV) and Fe(V) are two to five orders of magnitude higher than that of Fe(VI), which can degrade most

of refractory organic compounds and form non-toxic or low-toxic products [19–21]. In addition, the low-valent iron oxidation state, Fe (III), is subsequently generated during Fe(VI) self-decomposition or oxidation of pollutants. This is beneficial because Fe(III) has an excellent flocculation ability to remove suspended particles, phosphates, radionuclides, and metals in wastewater [21–24].

Although Fe(VI) can efficiently degrade pollutants, it still has several following limitations. First, the mineralization degree of some refractory pollutants by Fe(VI) oxidation is low $[25,26]$. Fe(VI) and intermediate iron species (Fe(IV) and Fe(V)) may resist degrading organic pollutants without electron-rich groups [27,28]. Second, pH has a great influence on the stability and oxidation capacity of Fe(VI) in aqueous solution [29–31]. Therefore, innovative methods for improving the reactivity of Fe(VI) oxidation system have been recently developed.

For instance, the oxidation capacity of Fe(VI) can be enhanced by

* Corresponding authors. *E-mail addresses:* ivylin0225@163.com (Q. Lin), vsharma@tamu.edu (V.K. Sharma). activating Fe(VI), which involves generating highly reactive species sulfate radicals (SO₄), hydroxyl radicals (\bullet OH), iron(IV) (Fe^{IV}O₄⁴ or Fe^{IV}O₃²), and iron(V) (Fe^VO₄²) [32–35]. The generation of SO₄² $(E_{\text{SO4}}^0_{\bullet}$ =2.5–3.1 V versus NHE) and \bullet OH ($E_{\bullet}^0_{\bullet}$ = 1.8–2.7 V versus NHE) performed non-selective oxidation toward organic pollutants, leading to the occurrence of ring-opening process and elevated the mineralization [36–39]. Additionally, Fe(IV) and Fe(V) are mainly derived from the Fe (VI) self-decay process and the reduction reaction between Fe(VI) and reductants, which may effectively resist the pH implication on the oxidation by Fe(VI) $[40, 41]$. Nowadays, there are some reviews on Fe (VI) applications [18,28]. However, the generation mechanism and comparison of free radicals and highly reactive iron intermediates in various Fe(VI) activation systems have not been comprehensively reviewed.

This review elucidates insights into self-decomposition in water that forms reactive species and the mechanisms giving high-valent iron intermediates and radical species during Fe(VI) activation (Fig. 1). First, Fe(VI) can combine with sulfur-containing salts to generate sulfate radical. Second, the generation pathway of hydroxyl radical in Fe(VI) activation system mainly includes Fe(VI) self-decomposition, Fentonlike process and the reaction of sulfate radical with H_2O . Similarly, other radicals, e.g., $\text{°O}_2^{\text{}}$, HO $_2^{\text{}}$, may be generated by Fe(VI) self-decomposition and more reactions with assistive technology. Fe(VI) reacts with various reagents, e.g., oxidants, reducing agents and photocatalysts to form high-valent iron intermediates [42–45]. The superiority of Fe(VI) activation system is proved by the improvement of pollutant mineralization by free radicals and the resistance to pH by Fe(IV) and Fe(V). Besides, the quenching experiments are summarized to distinguish the contributions of various active species in Fe(VI) activation system. Significantly, the advantages and disadvantages of Fe(VI) activation to form high reactive species are given, including the adaptability to pH variation, characteristics of oxidizing species, and effects on products. This review facilitates optimizing the Fe(VI) oxidation system and may guide the practical applications of Fe(VI) in water treatment.

2. Mechanism of oxidation by ferrate(VI) in water

Ferrate is typically a dark purple or violet solid, which is paramagnetic $[46]$. A dry solid Fe(VI) is stable, but it is susceptible to selfdecomposition in humid environment [47]. At present, the methods for preparing ferrate mainly include electrochemical methods, wet chemical methods, and dry chemical methods, nevertheless the

preparation costs of all three are relatively high [28]. Among them, electrochemistry is the most common method. Considering the stability and economy, sodium ferrate and potassium ferrate are often used in degradation research, which has a good application prospect [48]. Fe (VI) has a strong oxidizing ability, which is stronger than common oxidants (e.g., chlorine, H_2O_2 , permanganate) [49]. Fe(VI) has reduction potentials of $+ 2.20$ V and $+ 0.70$ V (versus NHE) under acidic and alkaline conditions [49,50], respectively, which can effectively remove organic compounds containing electron-donating groups, e.g., hydroxyl moiety of phenolic groups, double bonds, and amine groups. According to Eq. (1) [51], Fe(VI) directly oxidizes organic pollutants to form Fe (III)/Fe(II) and low molecular weight products. Fe(VI) gains electrons by reacting with water or by attacking the electron-rich groups of pollutants to form intermediate iron species of Fe(IV) and Fe(V), which can also rapidly attack contaminants (Eqs. (2) – (6)) [51,52]. Sharma et al. [53] found that when Fe(VI) was used to degrade cyanide, the reactivity of iron was as follows: Fe(V) *>* Fe(IV) *>* Fe(VI). Hence, researchers have attempted to generate more $Fe(IV)$ and $Fe(V)$ by combining with reducing agents, e.g., carbon nanotubes, biochar [40,44,54], oxidants, e. g., periodate, peracetic acid [55,56], composite materials [32,57], and assistive technologies [58], e.g., irradiation of ultraviolet A lightemitting diode to improve the reactivity of Fe(VI) system, which is discussed in more detail in section 3.4. However, these high-valent iron species only selectively attack the electron-rich groups of pollutants, which causes a low mineralization rate in the Fe(VI) alone system [59,60].

On the other hand, the consumption of Fe(VI) in solutions includes self-decomposition and direct oxidation of pollutants. The excessive selfdecomposition of Fe(VI) cannot increase the content of Fe(IV) and Fe(V), but causes a dramatic reduction in the oxidation capacity of Fe(VI). The self-decomposition of ferrates ultimately generates Fe(III) and $O₂$ (Eqs. (7)–(12)) [51,61]. The hydrolysis of Fe(III) gives Fe(OH)₃, which catalyzes the self-decomposition of Fe(VI) [61,62]. Of note, the self-decay of Fe(VI) is significantly dependent on pH [63]. Lower pH increases the oxidation ability of Fe(VI), but the decomposition becomes much faster. Conversely, Fe(VI) has good stability at a higher pH, while its oxidation capacity is weakened [64,65]. A research described the selfdecomposition of Fe(VI) was weakest at pH 9.4–9.7 in the dilute solution [64]. And others explained the reason of reducing pH could improve the oxidation performance of Fe(VI) was because the protonation of Fe (VI) could be promoted under low pH conditions, and the protonated ferrate form had good oxidizing properties [61].

Fig. 1. Methods for generating reactive species by Fe(VI) activation.

 $HFe^{VI}O₄ + pollutant \rightarrow Fe(II)/Fe(III) + pollutant (oxidized)$

 $HFe^{VI}O₄ + e⁻ \rightarrow HFe^VO₄²$

(3) $HFe^VO₄² + e₁ \rightarrow HFe^{IV}O₄³$

(1)

(2)

(4) (5) (6)

$$
2HFe^{VI}O_4 + 4H_2O \rightarrow 2H_3Fe^{IV}O_4 + 2H_2O_2
$$

$$
HFeVO42 + Pollutant \rightarrow Fe(II)/Fe(III) + Pollutant (oxidized)
$$

$$
H_3Fe^{IV}O_4 + \text{ Pollutant} \rightarrow Fe(II)/Fe(III) + \text{ Pollutant (oxidized)}
$$

$$
4HFe^{VI}O_4 + 6H_2O \to 4Fe(OH)_3 + 4OH^+ + 3O_2
$$
\n(7)

(8) $4Fe^{VI}O₄² + 10H₂O \rightarrow 4Fe(OH)₃ + 8OH + 3O₂$

$$
4\text{FeO}_4^2 + 20\text{H}^+ \to 4\text{Fe(III)} + 10\text{H}_2\text{O} + 3\text{O}_2\tag{9}
$$

$$
2HFeVO42 + 4H2O \to 2Fe(OH)3 + 4OH + O2
$$
\n(10)

$$
2HFe^{IV}O_4^{3+} + 5H_2O \rightarrow 2Fe(OH)_3 + 6OH + 1/2O_2
$$
\n(11)

$$
HFe^{IV}O_4^{3-} + 3H_2O + e^- \rightarrow Fe(OH)_3 + 4OH^-(12)
$$

Overall, Fe(VI) can gain electrons by reacting with water or by attacking the pollutants to form $Fe(IV)$ and $Fe(V)$, and these irons rapidly oxidize pollutants containing electron-donating groups. However, the excessive self-decomposition and selectivity of Fe(VI) limit the oxidative capacity of Fe(VI) system. Hence, it is necessary to consider the reactive performance of Fe(VI) applications and minimize the undesired reactions. The coupling strategies of Fe(VI) and other substances to enhance the oxidizing capacity of Fe(VI) system should be considered.

3. Iron(V), iron(IV) and radicals in Fe(VI) activation

3.1. Sulfur-containing radical generation by Fe(VI) activation

The sulfur-containing radicals, e.g., SO_4^{\bullet} , are strong single-electron oxidants, which can attack most refractory organic matter [66,67]. To enhance the reactivity of Fe(VI) oxidation system, combining sulfurcontaining salts with Fe(VI) to form sulfur-containing radicals, e.g., SO₄ and SO₅, was one of the satisfactory approaches. The sulfurcontaining salts mainly include persulfate (PS), e.g., peroxymonosulfate (PMS), peroxydisulfate (PDS), sulfite, and thiosulfate (TS) [58,68,69]. The mechanism of sulfur-containing radicals generation by Fe(VI) activation by sulfite is shown in Eqs. (13)–(26) [37,69–72].

$$
HFeVIO4 + HSO3/SO32 \rightarrow HFeVO42 + SO32
$$
 (13)

$$
SO_3^{\bullet-} + O_2 \to SO_5^{\bullet-} \tag{14}
$$

 $SO_5^{\bullet-} + HSO_3^{\bullet}/SO_3^{2-} \rightarrow SO_4^{\bullet-} + SO_4^{2-}$ (15)

 $SO_4^{\bullet+} + H_2O \rightarrow SO_4^{2-} + \bullet OH + H^+$ (16)

 $SO_4^{\bullet-}$ / \bullet OH + pollutant $\rightarrow SO_4^{2-}$ + pollutant (oxidized) (17)

 $Fe(III) + HSO₅ \rightarrow Fe(II) + SO₅⁺ + H⁺$ (18)

 $\text{Fe(II)} + \text{HSO}_5^{\bullet} \rightarrow \text{Fe(III)} + \text{SO}_4^{\bullet} + \text{OH}^{\bullet}$ (19)

$$
\gamma\text{-Fe}_2\text{O}_3 + \text{HSO}_5 \rightarrow \text{Fe}^{\text{III}}\text{-OH} + \text{SO}_4^{\bullet} + \text{OH}^- \tag{20}
$$

 $\text{Fe(III)} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe(II)} + \text{S}_2\text{O}_8^{\bullet}$ •- (21)

 $Fe(II) + S_2O_8^{2-} \rightarrow Fe(III) + SO_4^{2-} + SO_4^{\bullet}$ (22)

 $Fe^{VI}O₄² + SO₃[•] \rightarrow Fe^VO₄³ + SO₃$ (23)

 $HFe^VO₄² + SO₃[•] \rightarrow HFe^{IV}O₄³ + SO₃$ (24)

 $4HFe^{VI}O_4 + 3S_2O_3^2 + 2OH^- + 3H_2O \rightarrow 4Fe(OH)_3 + 6SO_3^2$ (25)

$$
HFeVIO4 + S2O32 \to HFeIVO3 + S2O42
$$
 (26)

Fe(VI) and its products, e.g., Fe(II) and Fe(III), undergo electron transfer with sulfur-containing salts to promote the formation of highly reactive sulfur-containing radicals. In the sulfite-Fe(VI) system, Fe(VI) first reacts with HSO_3^2/SO_3^2 to generate SO_3^{\bullet} , which was then is oxidized by oxygen to form SO_5^2 , which may subsequently react with HSO_3/SO_3^2 to produce SO_4^{\bullet} (Eqs. (13) – (15)) [37]. Due to the presence of water, a SO_4^\bullet may also react with H₂O to form \bullet OH (Eq. (16) [37]. Both SO_4^\bullet and •OH can oxidize the target pollutants (Eq. (17) [37]. In this activation process, there is a possibility of Fe(VI) self-decomposition that produces Fe(II)/Fe(III) (Eqs. (1) , (5) – (12)) [51,61]. Then Fe(II)/Fe(III) can also promote the generation of sulfur-containing radicals. In the Fe(VI)-PS system (Eqs. (18) – (22)) [71], Fe(III) can react with HSO₅ or S₂O₈² to form SO_5^{\bullet} and $S_2O_8^{\bullet}$, which can be further formed SO_4^{\bullet} . The reduced iron (III) species ($γ$ -Fe₂O₃) may thus contribute to the SO₄^{*} generation (Eq. (20) [71]. Table 1 presents possible reactions and their corresponding rate constants that are involved in the generation of sulfur-containing radicals in the activation of Fe(VI). The process of Fe(VI) activating also generates Fe(V) and Fe(IV) to effectively enhance the removal efficiency of pollutants (Eqs. (13) , (23) and (24)) [72–74], which is discussed in more detail in section 3.4.

Table 2 exhibits the degradation efficiency of organic compounds by SO^{*} in Fe(VI) system. Wu et al. [75] combined Fe(VI) with PMS that enhanced degradation of atrazine to 81.5 %. Comparatively, Fe(VI)-PS and Fe(VI)–H₂O₂ systems had removal efficiency of 65.7 % and 15.9 %, respectively. Feng et al. [69] showed that the combination of Fe(VI) and PMS had synergistic effects, and SO_4^{\bullet} , Fe(V) and Fe(IV) could enhance the degradation rates of four fluoroquinolones. Gong et al. [76] found that the oxidation process of sulfamethoxazole by Fe(VI)-PMS can be further enhanced by ultraviolet A irradiation.

Hydroxylamine also could accelerate the circulation of Fe(III) and Fe (II) to form more ${SO_4^{\bullet}}$ during the pollutant degradation in the Fe(VI) and sulfur-containing salts system [71]. Zhang et al. [37] found that the reaction rate of chloramphenicol could be improved in Fe(VI)-TS system with molar ratio of [TS]/[Fe(VI)] of 1:8 (69 %, within 120 min), which was much higher than that of Fe(VI) alone (32 %). Importantly, SO₄, Fe (V), and Fe(IV) had synergistic effects on the degradation of pollutants in water.

Overall, the coupling of Fe(VI) and sulfur-containing salts involves the reaction of Fe(VI) with sulfur-containing salts to generate primary sulfur-containing species, e.g., SO_3^{\bullet} , SO_4^{\bullet} , and SO_5^{\bullet} , and Fe(VI) gaining electrons to form $Fe(V)$ and $Fe(IV)$ (Fig. 2). This system not only can rapidly degrade pollutants, but also generate non-toxic final products such as $Fe(OH)_3$ and SO_4^2 , which has a broad advantageous prospect.

Table 2

Fig. 2. Generation of SO₄⁺ by Fe(VI) activation. Fe(VI) and its products can react with sulfur-containing salts to form SO_4^{\bullet} and \bullet OH, which have powerful oxidation capacity.

3.2. Hydroxyl radical generation in the activation of Fe(VI)

Fe(VI) has a powerful oxidation capacity to eliminate various pollutants containing electron-rich moieties. However, it has less capability of opening the benzene rings of organics to achieve complete mineralization $[6,14,84,85]$. In contrast, \bullet OH is non-selective to attack benzene rings to form hydroxylation products. The methods of •OH generation by Fe(VI) activation can improve the reactivity of Fe(VI) system and enhance the mineralization degree of pollutants [86,87]. The generation of •OH by Fe(VI) activation can be divided into two pathways. On the one hand, sulfur-containing salts are directly stimulated to produce •OH, or indirectly through the reaction of $SO_4^{\bullet\bullet}$ with H₂O to form •OH (Eqs. (16) and (27) [37]. Fe(VI) self-decomposition and Fenton-like processes can generate •OH (Eqs. (4), (28)–(36)) [76,83,88–90]. Significantly, pH may be the major factor influencing the generation of different reactive species (e.g., \bullet OH, SO $_{4}^{\bullet}$, Fe(IV) and Fe(V)) [91]. Generally, •OH may be formed in the oxidation and self-decay processes of Fe(VI) at both acid and basic conditions. It is well known that •OH exhibited a higher redox potential (2.7 V) in acid solution than in alkaline solution (1.8 V), accounting for more important roles [92]. The removal efficiency of •OH decreased with increasing pH. As for Fe(IV) and Fe(V), Wang et al. $[93]$ elaborated that Fe(IV) and Fe(V) were primarily produced in the Fe(VI)-activation system under alkaline conditions in comparison to •OH. Considering Fe(IV) and Fe(V) owned 2–5 orders of magnitude higher reactivity than Fe(VI), the oxidation performance of •OH greatly decreased with the increase of pH. Thus, Fe(IV) and Fe(V) were the main reactive species under higher pH conditions. High-valent iron species were easily hydrolyzed to produce H_2O_2 under acid conditions, which can further react with low-valent iron, e.g., Fe(II) and Fe(III), to generate \bullet OH [90]. In addition, other assistive technologies, e.g., ultrasoundand illumination, can alsopromote thegeneration of \bullet OH in the Fe(VI) system (Eqs. (32)–(35)) [90]. For example, in the Fe (VI)-ultrasound system, $H₂O$ was thermally cavitated by ultrasound to form \bullet OH, and \bullet OH was recombined to form H_2O_2 . The Fenton-like reaction occurred from the reactions involved in the $Fe(VI)$ –H₂O₂ system to further generate •OH.

$$
HSO5 + hv \rightarrow SO4• + \bullet OH
$$
 (27)

 $H_2Fe^VO₄² + H_2O + H⁺ \rightarrow Fe(OH)₃ + H_2O₂$ (28)

 $2Fe^{IV}O_3^2 + 2H_2O + 4H^+ \rightarrow 2Fe(OH)_3 + H_2O_2$ (29)

 $Fe(OH)₃ + 2H⁺ \rightarrow [Fe(OH)]²⁺ + 2H₂O$ (30)

 $[Fe(OH)]^{2+} + hv \rightarrow Fe(II) + \bullet OH$ (31)

$$
H_2O + Ultrasound \rightarrow \bullet OH + \bullet H \tag{32}
$$

$$
2\bullet \text{OH} \to \text{H}_2\text{O}_2 \tag{33}
$$

 $Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2^{\bullet} + H^+$ (34)

$$
HO_2^{\bullet} + H_2O_2 \rightarrow O_2 + H_2O + \bullet OH
$$
 (35)

$$
Fe(II) + H2O2 + H+ \to Fe(III) + \bullet OH + H2O
$$
 (36)

Table 2 shows the removal efficiency of pollutants by \bullet OH in Fe(VI)containing system. Phenolic substances could be effectively degraded into small molecules, e.g., CO_2 and H_2O , by \bullet OH during the Fe(VI) selfdecomposition [10,57,94,95]. Except for the self-decomposition of Fe (VI), the reaction of $SO_4^{\bullet-}$ and H_2O can also produce \bullet OH to degrade pollutants. Zhang et al. [74] found that both SO^{*} and \bullet OH could be generated in the Fe(VI)-sulfite system. •OH was also the main active species in the process of pollutant degradation. Furthermore, •OH and SO⁺ could assist high-valent iron species to further improve the degradation of ciprofloxacin [71]. Chen et al. [91] tried to combine $Na₂SO₃$ -Fe(VI) and NaHSO₃-Fe(VI) system together. The result showed that the presence of H^+ could improve the continuous degradation ability of Fe (VI) system, and several active species, e.g., \bullet OH, SO $_{4}^{\bullet}$, Fe(V) and Fe(IV), synergistically oxidized pollutants. Recently, Shu et al. [96] demonstrated that mineral zincite could activate Fe(VI) system for carbamazepine degradation. The existence of zincite promoted the Fe(V) generation and boosted the Fenton reaction by inhibiting the conversion from Fe(II) to Fe(III). The adducts of Lewis acid-Fe(VI) could initiate the formation of organic radical, e.g., R-COO^{*}, which together with highvalent irons and • OH were reactive species to oxidize pollutants.

In general, the generation of "OH not only occurs in Fe(VI)-sulfurcontaining system ($SO_4^{\bullet-}$ react with H₂O), but also appears in the selfdecomposition of Fe(VI) or Fenton-like reaction (Fig. 3). The latter system usually happened under acidic conditions. Although •OH plays a secondary role in the Fe(VI)-containing oxidation system, its oxidative capacity cannot be ignored in most cases. The current studies have confirmed the existence of •OH in the Fe(VI)-containing system, the

Fig. 3. Generation of hydroxyl radical by Fe(VI) activation. The selfdecomposition of Fe(VI) or Fenton-like reaction can generate •OH to enhance the oxidizing ability of Fe(VI) activation system.

strong oxidizing ability of •OH and its wide application in the field of pollutant degradation enhanced the mineralization ability of Fe(VI) system.

Investigations into the Fe(VI) activation system have highlighted the critical roles of Fe(IV), Fe(V) and free radicals, particularly \bullet OH. The detection of •OH radicals has conventionally employed molecules like methanol and ethanol, chosen for their high diffusion-controlled rate constants $[71]$. However, these alcohols may also interact with $Fe(V)$ and Fe(IV), thus complicating the attribution of observed effects solely to •OH radicals in Fe(VI)-activated systems [6]. An alternative approach involves the use of methyl phenyl sulfoxide (PMSO), whose conversion to methyl phenyl sulfone (PMSO $_2$) is indicative of the presence of highvalent iron intermediates and reactive oxygen species, especially •OH [97]. This pathway has been substantiated through methodologies such as kinetic modeling and density functional theory, providing a clearer distinction between the contributions of various reactive species [6]. Moreover, sodium azide (NaN3) is particularly effective, exhibiting rapid reaction kinetics with both \bullet OH ($k = 2.5 \times 10^9 \,\mathrm{M}^{-1} \mathrm{s}^{-1}$) and SO $_4^\bullet$ $(k = 1.2 \times 10^{10} \text{ M}^{-1} \text{s}^{-1})$ [98,99]. Additionally, *tert*-butanol (TBA) is employed to preferentially quench •OH, given its lower reactivity with SO_4^\bullet (values of k for reactions of TBA with $\bullet\mathrm{OH}$ and SO_4^\bullet are 3.8–7.6 \times 10^8 M⁻¹s⁻¹ and 4.0–9.1 × 10⁵ M⁻¹s⁻¹, respectively) [100]. Furthermore, trichloromethane (TCM) is used to quench superoxide radicals ($^{\bullet}$ O₂) ($k = 1 \times 10^{10} \,\mathrm{M}^{-1} \mathrm{s}^{-1}$) [101]. These quenching agents thus enable a more specific determination of the roles of •OH and other reactive species in the Fe(VI) activation system.

3.3. Generation of superoxide and peroxyacetyl radicals in the activation of Fe(VI)

Other types of radicals like superoxide ($^{\bullet}O_{2}^{-}$, HO₂) and peroxyacetyl $(CH_3C(O)OO^{\bullet})$ may also be in the Fe(VI) activated system degrading pollutants (Eqs. (7)–(11), (37)–(44), (46)) [17,51,56,81–83]. In the Fe (VI) activated system, Fe(III), O_2 , H_2O_2 , Fe(IV), and Fe(V) are formed. Then O_2 can accept electrons to generate O_2^- (Eq. (42) [82]. The degradation efficiency of organic compounds by $^{\bullet}O_{2}^{-}$ in the Fe(VI) system is summarized in Table 2. The $\textdegree O_2^-$ may oxidize organic pollutants simultaneously [102,103]. Wu et al. [104] combined UV and Fe(VI) to degrade 2,4-dichlorophenol. The active Fe(IV) and Fe(V) produced many free radicals, e.g., O_2^- , H₂O₂, O₂, and \bullet OH, under UV irradiation. Among these, \textbf{O}_2^- had a strong oxidative capacity, which could replace the *ortho-position* Cl⁻ of 2,4-dichlorophenol to form bisphenols and organic acids. Li et al. [100] also proposed a novel solar/PMS/Fe(VI) system to removal antibiotic-resistant bacteria. Both the quenching experiments and EPR technique demonstrated the generation of $\mathrm{^{\bullet}O}_{2}$, $^{1}O_{2}$, and high-valent irons that contributed to disinfection (Fig. 4).

$$
2H_2FeVO42 + 2H2O + 2H+ \to 2Fe(OH)3 (aq) + 2H2O2
$$
 (37)

 $Fe^{VI}O₄² + 2H₂O₂ \rightarrow Fe^{IV}O₄⁴ + H₂O + O₂ + 2H⁺$ (38)

$$
Fe^{IV}O_4^{4-} + H_2O_2 + 4H^+ \rightarrow Fe(OH)_{2\ (aq)} + 2H_2O + O_2
$$
 (39)

Fig. 4. The mechanism of $^{\bullet}O_{2}^{-}$, $^1O_{2}$ and high-valent irons formation in a novel solar/PMS/Fe(VI) system. High-valent irons, $\rm{^{\bullet}O_{2}^{-}}$ and $\rm{^1O_{2,}}$ which are generated by a series reactions of Fe(VI) and PMS, can inactivate antibiotic-resistant bacteria. Modified with permission of Elsevier from Ref. [100].

 $HFe^{VI}O_4 + H_2O_2 + OH^- \rightarrow Fe^{IV}O_3^{2-} + 2H_2O + O_2$ (40)

 $HFe^VO₄² + H₂O₂ + H₂O \rightarrow Fe(OH)_{3 (aq)} + O₂ + 2OH⁻$ (41)

 $O_2 + e^- \rightarrow$ O_2 (42)

 $H_2O_2 \rightarrow 2\bullet OH$ (43)

 $H_2O_2 + \bullet OH \rightarrow HO_2^{\bullet} + H_2O$ (44)

 $\text{°O}_2^{\text{-}} + \text{e}^{\text{-}} + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^{\text{-}}$ (45)

 $Fe^{VI}O₄² + CH₃C(0)OO⁻ \rightarrow Fe^VO₄³ + CH₃C(0)OO[•]$ (46)

$$
FeVIO42 + CH3C(O)OO- \to FeIVO32 + CH3C(O)O- + O2
$$
 (47)

The redox potential of Fe(VI) is higher in acidic conditions than in alkaline conditions. Hence, the weak alkaline system, e.g., HCOOH, CH3COOH, is considered to improve Fe(VI) degradation [105,106]. Manoli et al. $[56]$ found that Fe(VI)-peracetic acid could form $CH_3C(O)$ OO[•]/CH₃C(O)O[•] and enhance the removal of CBZ. However, the present of CH₃C(O)OO[•]/CH₃C(O)O[•] was not as major oxidant. The main effect of peracetic acid was due to co-existing hydrogen peroxide that promote the transformation of $Fe(VI)$ to $Fe(IV)$ and $Fe(V)$ (Eqs. (46) and (47) [56], which was further discussed in the next section.

Fe(III) and Fe(II) can directly or indirectly active H_2O_2 to produce $HO₂[•]$ (Eq. (34) [90]. Furthermore, the self-decomposition of $H₂O₂$ can indirectly form HO_2^{\bullet} (Eqs. (43) and (44) [107]. However, there are limited studies focusing on such radicals for the degradation of pollutants. Two primary reasons of limiting factors of their applications as follow. First, these radicals are generated slowly and infrequently. Second, these radicals are short-lived [108–110], which can be transformed into other substances rapidly by Eqs. (35), (45) and (47) [56,90]. Therefore, the oxidizing properties may not be significant.

Compared with Fe(VI), free radicals, e.g., $SO_4^{\bullet\bullet}$, \bullet OH, $^\bullet$ O₂, performed a better non-selectivity for pollutants degradation, which was beneficial to promote the ring-opening or hydroxylation reactions of contaminants [111]. Thus, the coupling of Fe(VI) and free radicals generation could effectively improve the mineralization rate of pollutants. Wu et al. [104] found that the mineralization rate of 2,4-DCP in the UV/Fe(VI) system (40.6 %) was significantly higher than that of Fe(VI) alone oxidation (less 10 %), which could be attributed to the attack of \degree O₂. Gong et al. [76] combined Fe(VI) with PMS to removal sulfamethoxazole under ultraviolet A irradiation. It was proven that the mineralization efficiency of sulfamethoxazole in stepwise addition of Fe(VI) (47 %) was enhanced compared to one-off dosing (35 %) or stepwise dosing of PMS (22 %). Because the intermediates produced by sulfamethoxazole could compete for SO₄⁺ with the parent compound in stepwise addition of Fe(VI). In general, free radicals have a higher tendency to mineralize organic

pollutants than Fe(VI) $[85]$. The coupling of free radicals and Fe(VI) could overcome the limitations of Fe(VI) oxidation alone [91], which could be a future research directions of Fe(VI) oxidation technology.

3.4. Fe(IV) and Fe(V) formation in activated Fe(VI) system

It is known that the presence of water constituents in natural waters could interfere with the pollutant oxidation by the above radicals in the Fe(VI)-based system [110,112,113]. The formation modulation of Fe (IV) and Fe(V) with higher oxidizing capability than Fe(VI) has attracted increasing attention due to their selective oxidation properties [59,60,114–116].

Most previous research focused on the combination of reducing substances, e.g., carbon nanotubes, biochar, sulfites, and TS, with Fe(VI) to promote the formation of Fe(IV) and Fe(V) $[40, 44, 54]$. Sun et al. [54] found that heterogeneous carbon nanotubes could accelerate the oxidation of bromophenols by promoting the formation of Fe(IV) and Fe (V) at pH 7.0–9.0. Hydroxyl moiety of phenolic on carbonaceous substances can interact with Fe(VI) as an electron shuttle to promote the generation of Fe(IV) and Fe(V) $[54,74]$. Tian et al. $[40]$ used the redoxactive moieties (Hydroxyl moiety of phenolic) on biochar to accelerate the reduction of Fe(VI) to form Fe(IV) and Fe(V) by electron shuttle.

Except for traditional reducing agents, the reaction of Fe(VI) and sulfur-containing reducing agents can form Fe(IV) and Fe(V) to enhance the reactivity of the Fe(VI) system. During these reactions, intermediate radicals, e.g., SO₃, rapidly donate electrons for Fe(VI) to form Fe(IV) and Fe(V) (Eqs. (13) , (23) and (24)) [72–74]. The formation of Fe(IV) and Fe(V) can rapidly degrade most refractory organic compounds (Eqs. (5) and (6) $[117-119]$. For example, Shao et al. $[60]$ used calcium sulfite $(CaSO₃)$ to improve the oxidation of Fe(VI), because $CaSO₃$ accelerated the reduction of Fe(VI) to Fe(V) and Fe(IV) through the one-electron transfer step (Fig. 5a). Besides, $S_2O_3^2$ and SO_3^2 can promote the rapid conversion of Fe(VI) into Fe(V) and Fe(IV) (Eqs. (13) , (23) – (26)) $[120]$. Notably, different Fe(VI)-sulfite systems had different major reactive species. This phenomenon may be ascribed to the different reaction conditions, such as Fe(VI)/sulfite molar ratio, and medium conditions [60].

Recent investigations have shown that the combination of Fe(VI) with other known oxidants such as PMS, H_2O_2 , peracetic acid, and periodate could trigger the generation of highly reactive Fe(IV) and Fe (V) intermediates [5,30,42,69]. It was found that the *in-situ* and *ex-situ* H2O2 functioned as the reducing agent with Fe(VI) to accelerate the removal of SMX at pH 8.0 [30]. The degradation efficiency was unaffected by the coexisting inorganic ions and dissolved organic matter. Quenching experiments and chemical probe analysis suggested the critical role of Fe(IV) and Fe(V) intermediates, generated by one/twoelectron transfers from Fe(II) or H_2O_2 to Fe(VI). Furthermore, Manoli et al. [56] proposed that Fe(VI) and peracetic acid could jointly accomplish the fast degradation of multiple pharmaceuticals in water in 60 s at pH 9.0. Mechanistic explorations suggested the Fe(IV), Fe(V) and acetylperoxyl radicals as the dominant species. Subsequent in-depth work used the probe compounds (i.e., benzoic acid and PMSO) to verify the predominant role of Fe(IV) and Fe(V) (Fig. 5b). It is interesting to observe that peracetic acid did not serve as the Fe(VI) activator but elevated the oxidation capacity of these highly reactive intermediates as the ligand. This would stabilize these species and make their oxidation surpass the self-decay rates. More recently, the similar role of periodate as the Fe(IV) and Fe(V) ligand was also proposed for the Fe(VI)/periodate system, in which the synergistic oxidation of various micropollutants can be achieved in 2 min (Fig. 5c) [42,55]. The less influence induced by the water matrices indicated the selective oxidation of the combined system. Further demonstration of the Fe(IV) and Fe(V) intermediates was performed using the Mossbauer spectroscopy and PMSO experiments.

It is also a good strategy to encapsulate Fe(VI) in the frame material to obtain the composite materials containing Fe(VI). Wu et al. [32]

Fig. 5. Mechanism of Fe(IV) and Fe(V) formation in activated Fe(VI) system. (a) CaSO₃ reduced Fe(VI) to Fe(IV) and Fe(V) through the one-electron transfer step. Reproduced with permission from Ref. [60]. (b) peracetic acid and (c) periodate served as the ligand to elevate the oxidation capacity of Fe(IV) and Fe(V). Reproduced with permission from Ref. [5] and [42]. (d) cMnO₂ accelerated the formation of Fe(IV) and Fe(V) by surface-promoted mechanism. Reproduced with permission from Ref. [121].

inserted Fe(VI) into Ca/Al-layered double hydroxide (Ferrate-LDH) to treat phenol solution. Ferrate-LDH generated Fe(III)/Fe(II) on the surface of LDH, which inhibited the self-decomposition of Fe(VI) and prolonged the existence time of Fe(VI). Recently, Shu et al. [57] also prepared a Fe(VI)-Ti/Zn LDH composite to enhance the removal of imidacloprid under visible light. In this system, Fe(VI) extracted photoelectrons from LDH to generate Fe(IV) and Fe(V), and its products, e. g., Fe(III) particles, could combine with LDH as a heterojunction photocatalyst to efficiently removal pollutants. In addition, Luo et al. [121] observed that Fe(VI) could combine with the vacancies in colloid manganese dioxide (cMnO₂) to form a precursor complex (cMnO₂ – Fe(VI) *), which had higher oxidation potential than Fe(VI) to rapidly generate Fe(IV) and Fe(V) (Fig. 5d).

Comparatively, Fe(IV) and Fe(V) have higher resistance to pH variations than Fe(VI) alone $[41, 43]$. The oxidation capacity of Fe(VI) is limited under alkaline conditions, which interferes with the removal of pollutants in the Fe(VI) system [64,65]. The methods described above for promoting the generation of Fe(IV) and Fe(V) can provide the advantages of effectively degrading contaminants over a wider pH range. Tian et al. $[40]$ found that Fe(IV) and Fe(V) still remained high reactivity at pH 8. Fe(IV) and Fe(V) oxidation significantly improved the removal rates of all studied pollutants. And the reaction rate constants in Fe(VI)/ biochar system were 3–14 times higher than that in sole Fe(VI) at alkaline conditions. Pan et al. [43] also demonstrated that Fe(IV) and Fe (V) had excellent oxidation capacity for various pollutants degradation at the pH value of 9. The removal of carbamazepine in $g-C_3N_4$ -Fe(VI)visible light system, which had main active species Fe(IV) and Fe(V), was 2 times higher than that in control systems. Furthermore, Gao et al. [41] studied the yield of PMSO₂ in Fe(VI)/sulfur reducing agents system at a pH range of 8–10, which represented the formation of Fe(IV) and Fe (V). Although under alkaline conditions, a large amount of Fe(VI) still transformed into Fe(IV) and Fe(V). Especially in the Fe(VI)/TS system, the conversion rate of PMSO to $PMSO₂$ reached more than 90 %, which had a high oxidation potential. In general, the new technologies to improve the reactivity and pH adaptability of Fe(VI) oxidation by promoting the formation of Fe(IV) and Fe(V) have gained increasing attention.

4. Perspective

Fe(VI) is a multifunctional water treatment agent due to its strong oxidation, sterilization, coagulation, precipitation, and absorption capabilities. However, several shortcomings such as poor stability and pH dependence, limit its practical applications. The strategies effectively mitigated these drawbacks by activating Fe(VI), which induced the generation of free radicals and intermediate iron species, thus increasing the reactivity of the Fe(VI) system. The free radicals, e.g., \bullet OH, SO $_{\rm T}^{\bullet}$, and $_{\rm COZ}^{\bullet}$ have a higher oxidizing ability and non-selectivity, which can break $\mathrm{O_{2}}$ have a higher oxidizing ability and non-selectivity, which can break the chemical bonds of refractory organics, e.g., ring-opening, transferring larger molecular weight organics to smaller molecular weight. In contrast, high-valent irons had certain resistance to aqueous substrates and pH variation [122]. Therefore, the methods for promoting the active species generation by Fe(VI) activation can alleviate the problem in the Fe(VI) alone oxidation process.

Except Fe(VI)-based oxidation systems, some common advanced oxidation processes (AOPs) could also generate Fe(IV), Fe(V), and free radicals. For example, Kang et al. [123] activated PMS by hematite to generate Fe(IV), which accelerated the degradation of compounds. Similarly, Fe(IV) was identified as the main reactive species in the combined system of Fe^{2+} , peracetic acid and ultraviolet-A irradiation [124]. However, these AOPs typically require acidic conditions for optimal performance. Table 3 provides the advantages and disadvantages of Fe(VI) activation methods. Compared to AOPs, Fe(VI) activation methods exhibited excellent oxidation performance over a wider pH range and served as in-situ iron sources to trigger the free radical reaction [91]. The activation of Fe(VI) for the generation of active species, notably SO₄, is a widely studied approach in environmental applications. These SO₄⁻ are favored due to their higher redox potential and longer half-life (30–40 μs) compared to other free radicals like •OH with a half-life of less than 1 µs [125–127]. This extended half-life of SO_4^{\bullet} is advantageous for the degradation of pollutants, as cited in studies [127]. The generation of sulfur-containing radicals through Fe(VI) activation thus shows promising applicability in pollutant degradation. However, current methods employing Fe(VI) coupled with free radicals, predominantly SO₄, have potential environmental drawbacks, such as water acidification and increased biotoxicity [128,129]. This underscores the need for further research into the oxidation effects of different radicals and their practical applicability in real-world scenarios. Additionally, while the generation of free radicals enhances the mineralization capacity of the Fe(VI) system, this process is highly susceptible to interference from the water matrix due to its non-selective oxidation nature [111]. In contrast, Fe(IV) and Fe(V) display more resilience to variations in water composition and pH, but may not achieve complete mineralization of pollutants [41]. Consequently, relying solely on either free

Table 3

Advantages and disadvantages of the reactive species generation by AOPs and Fe (VI) activation.

Note: Δ means not acceptable, ΔΔ means acceptable, ΔΔΔ means a recommendation

radicals or iron intermediates for pollutant removal in the Fe(VI) activation may not be effective in practical applications. To address these limitations, a synergistic approach that combines the oxidation capabilities of free radicals, Fe(IV), and Fe(V) within the Fe(VI) activation system presents a promising avenue. Developing such synergistic oxidation technologies could potentially offer more effective and environmentally sustainable solutions for abatement of pollutants.

5. Conclusions

Fe(VI) has a strong oxidizing property to attack electron-rich groups of pollutants. However, the Fe(VI) oxidation system was limited by a strong degree of pH dependency and confined mineralization rate, which became the bottleneck in the future application of Fe(VI). To overcome aforementioned shortcomings, the coupling of Fe(VI) and free radicals generation was shown to be the efficient method. The generated free radicals without selectivity may benefit the ring-opening reaction of pollutants, which may mineralize pollutants thoroughly. Fe(VI) promotes the formation of free radicals by activating sulfate or peroxide, while Fe(IV) and Fe(V) are also formed by Fe(VI) accepting electrons from \bullet OH and SO $_{4}^{\bullet}$. Hence, the activation mechanism of free radicals, e. g., SO_4^{\bullet} , \bullet OH, \bullet O₂, and HO₂, by Fe(VI) presented herein may guide future investigations. The combination of Fe(VI) and sulfur-containing salts can form SO_4^{\bullet} , the self-decomposition of Fe(VI) or the reaction between SO_4^{\bullet} and H_2O can generate \bullet OH. In addition, several methods to promote the formation of Fe(IV) and Fe(V) were also presented. Compared with Fe(VI) alone, the coupling of Fe(VI) and free radicals generation can remove pollutants more effectively and rapidly. According to the characteristics of different reactive species generation systems, the stimulation of SO_4^{\bullet} by Fe(VI) may be more advantageous. Furthermore, free radicals, Fe(IV), and Fe(V) oxidation have their own advantages and disadvantages in water treatment. Therefore, the

coupling of free radicals and intermediate high-valent irons can not only degrade pollutants effectively, but also improve the environmental applicability. The simultaneous activation of free radicals and intermediate iron species in Fe(VI) system is expected to overcome challenges facing the practical application of Fe(VI) oxidation technology, which may be a key research direction in the future.

CRediT authorship contribution statement

Feilong Dong: Conceptualization, Funding acquisition, Writing – review & editing. **Chuyun Fu:** Formal analysis, Data curation, Writing – original draft. **Mingbao Feng:** Conceptualization, Formal analysis, Writing – original draft. **Da Wang:** Writing – original draft, Writing – review & editing. **Shuang Song:** Funding acquisition, Writing – review & editing. **Cong Li:** Conceptualization, Writing – review & editing. **Eric Lichtfouse:** Formal analysis, Writing – original draft, Writing – review & editing. **Jinzhe Li:** Writing – review & editing. **Qiufeng Lin:** Conceptualization, Writing – review & editing. **Virender K. Sharma:** Conceptualization, Formal analysis, Writing – original draft, Writing – review & editing.

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.

Data availability

Data will be made available on request.

Acknowledgments

This work was financially supported by the Zhejiang Provincial Natural Science Foundation of China (Grants LQ22E080018), and the National Natural Science Foundation of China (No. 52100015, 22076168).

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