Application of Fe(VI) in abating contaminants in water: State of art and knowledge gaps

Shuchang Wang¹,², Binbin Shao¹,², Junlian Qiao¹,²,³, Xiaohong Guan (✉)¹,²,³

¹ State Key Laboratory of Pollution Control and Resources Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China
² Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China
³ International Joint Research Center for Sustainable Urban Water System, Tongji University, Shanghai 200092, China

HIGHLIGHTS
• The properties of Fe(VI) were summarized.
• Both the superiorities and the limitations of Fe (VI) technologies were discussed.
• Methods to improve contaminants oxidation/disinfection by Fe(VI) were introduced.
• Future research needs for the development of Fe (VI) technologies were proposed.

ARTICLE INFO
Article history:
Received 25 August 2020
Revised 4 October 2020
Accepted 4 October 2020
Available online 4 November 2020

Keywords:
Ferrate
Oxidation
Disinfection
Coagulation
Enhancement

ABSTRACT
The past two decades have witnessed the rapid development and wide application of Fe(VI) in the field of water de-contamination because of its environmentally benign character. Fe(VI) has been mainly applied as a highly efficient oxidant/disinfectant for the selective elimination of contaminants. The in situ generated iron(III) (hydr)oxides with the function of adsorption/coagulation can further increase the removal of contaminants by Fe(VI) in some cases. Because of the limitations of Fe(VI) per se, various modified methods have been developed to improve the performance of Fe(VI) oxidation technology. Based on the published literature, this paper summarized the current views on the intrinsic properties of Fe(VI) with the emphasis on the self-decay mechanism of Fe(VI). The applications of Fe (VI) as a sole oxidant for decomposing organic contaminants rich in electron-donating moieties, as a bi-functional reagent (both oxidant and coagulant) for eliminating some special contaminants, and as a disinfectant for inactivating microorganisms were systematically summarized. Moreover, the difficulties in synthesizing and preservings Fe(VI), which limits the large-scale application of Fe (VI), and the potential formation of toxic byproducts during Fe(VI) application were presented. This paper also systematically reviewed the important nodes in developing methods to improve the performance of Fe(VI) as oxidant or disinfectant in the past two decades, and proposed the future research needs for the development of Fe(VI) technologies.

© The Author(s) 2020. This article is published with open access at link.springer.com and journal.hep.com.cn

1 Introduction
In the past few years, a large number of toxic and harmful trace organic contaminants (TrOCs) and inorganic substances have been frequently detected in various water bodies and the eutrophication of natural water bodies has
become a serious environmental concern (Conley et al., 2009; Tran et al., 2018; Ashoori et al., 2019; Rojas and Horcajada, 2020). These environmental problems pose great threats to human health, and they are harmful to the sustainable development of the society. Hence, great efforts should be made to control the water pollution.

Among various water treatment reagents, iron-based reagents have gained much attention, for iron is an earth-abundant material and an essential element for most living organisms. Iron offers a unique range of valence states (0, I, II, III, IV, V and VI). The high-valent iron species, which are commonly called ferrates (Fe(IV), Fe(V), and Fe(VI)), possess stronger oxidation ability than most traditional water treatment oxidants (e.g., O3, Cl2, H2O2, KMnO4), and the concentrations of toxic byproducts resulting from ferrates oxidation are generally low (Sharma, 2011; von Gunten, 2018; Wang et al., 2018a). Hence, because of the environmentally benign character of high-valent iron species and the more convenient synthesis methods of Fe (VI) compared to those of Fe(V) and Fe(IV), the application of Fe(VI) for abating the water pollution problems has become a research hotspot over the past two decades.

The studies on Fe(VI) and its application can be roughly divided into three categories: 1) clarifying the properties of Fe(VI) so as to provide the theoretical basis for the practical application of Fe(VI) (Lee et al., 2004; Sharma, 2010; Lee et al., 2014); 2) evaluating the feasibility of Fe (VI) technologies to abate various contaminants in water (Lee et al., 2009; Chen et al., 2019b; Manoli et al., 2020), exploring the influence of coexisting components on the removal of target contaminants (Jiang et al., 2015; Feng et al., 2016; Luo et al., 2019), and the formation of toxic byproducts resulting from ferrates oxidation are generally low (Sharma, 2011; von Gunten, 2018; Wang et al., 2018a). Hence, because of the environmentally benign character of high-valent iron species and the more convenient synthesis methods of Fe (VI) compared to those of Fe(V) and Fe(IV), the application of Fe(VI) for abating the water pollution problems has become a research hotspot over the past two decades.

2 Properties of Fe(VI)

2.1 The redox and acid-base properties of Fe(VI)

Fe(VI) is a powerful oxidant and disinfectant with a redox potential of + 2.2 V (vs NHE) in the acidic solution, which is higher than those of most other chemical oxidants applied in water treatment (Table 1) (Jiang, 2007; Ghernaout and Naceur, 2012; Sharma et al., 2016). However, the redox property of Fe(VI) is highly pH-dependent. The redox potential of Fe(VI) drops to + 0.7 V (vs NHE) under alkaline conditions. The decrease in the redox potential of Fe(VI) with increasing pH can be ascribed to the shift of Fe(VI) species with pH. Fe(VI), with three pKa values (1.5, 3.5, and 7.3), has four protonation states: H3FeO4+, H2FeO4, HFeO4−, and FeO42− (Eqs. (1)-(3)) (Rush et al., 1996; Sharma et al., 2001a). Under environmentally-relevant conditions (pH 4.0–9.0), HFeO4−, and FeO42− are the dominant Fe(VI) species (Fig. 1). Using calculations based on the density functional theory (DFT), Kamachi et al. (2005) found that the monoprotonated Fe(VI) (HFeO4−) has a larger spin density on the oxo-ligands than the deprotonated Fe(VI) (FeO42−) does, resulting in the higher oxidation ability of HFeO4− compared to FeO42−. Consistent with the finding of Kamachi et al. (2005), the reaction rate constants of HFeO4− with most compounds are reported to be 1 to 4 orders of magnitude higher than those of FeO42− with various compounds (Rush et al., 1996; Lee et al., 2009; Sharma, 2011; Sharma, 2013).

\[
\text{H}_3\text{Fe}^{\text{VI}}\text{O}_4^+ \rightleftharpoons \text{H}^+ + \text{H}_2\text{Fe}^{\text{VI}}\text{O}_4^- \quad \text{pK}_{a1} = 1.5 \quad (1)
\]
\[
\begin{align*}
\text{H}_2\text{FeVIO}_4^{-} + 8\text{H}^{+} + 8\text{e}^{-} & \rightarrow \text{Fe}^{3+} + 4\text{H}_2\text{O} \quad E^0 = 2.20 \\
\text{FeO}_2^{-} + 4\text{H}_2\text{O} + 3\text{e}^{-} & \rightarrow \text{Fe(OH)}_3 + 5\text{OH}^{-} \quad E^0 = 0.70
\end{align*}
\]

Sarma et al. (2012) recently investigated the self-decay mechanism of Fe(VI) in strongly acidic solution (pH 1.0–3.0) based on the oxygen-18 isotope fractionation method, stopped-flow kinetics, spectroscopic measurements, and DFT calculations. The self-decay of Fe(VI) first undergoes the rapid condensation and dimerization of the monomeric protonated Fe(VI) starting material, leading to the formation of the metastable \( \mu_1,2\)-oxo dimerate(VI) prior to intramolecular oxo-coupling with a rate constant of \( \sim 185 \text{ s}^{-1} \) at pH 1.0 (Eq. (4)). This will result in the rapid

**Fig. 1** Influence of pH on the speciation of Fe(VI).

\[
\begin{align*}
\text{H}_2\text{FeVIO}_4^{-} & \rightarrow \text{HFeVIO}_4^{-} \quad \text{pK}_{a2} = 3.5 \\
\text{HFeVIO}_4^{-} & \rightarrow \text{H}^{+} + \text{FeVIO}_4^{2-} \quad \text{pK}_{a3} = 7.3
\end{align*}
\]

2.2 Self-decay of Fe(VI)

2.2.1 The self-decay mechanism of Fe(VI) in strongly acidic solution (pH 1.0–3.0)

Sarma et al. (2012) recently investigated the self-decay mechanism of Fe(VI) in strongly acidic solution (pH 1.0–3.0) based on the oxygen-18 isotope fractionation method, stopped-flow kinetics, spectroscopic measurements, and DFT calculations. The self-decay of Fe(VI) first undergoes the rapid condensation and dimerization of the monomeric protonated Fe(VI) starting material, leading to the formation of the metastable \( \mu_1,2\)-oxo dimerate(VI) prior to intramolecular oxo-coupling with a rate constant of \( \sim 185 \text{ s}^{-1} \) at pH 1.0 (Eq. (4)). This will result in the rapid

**Table 1** Redox potential of different oxidant used in water treatment

| Oxidant (VI) | Reactions | \( E^0 \) (V/NHE) | Reference |
|-------------|-----------|-------------------|-----------|
| Ferrate(VI) | \( \text{FeO}_2^{-} + 8\text{H}^{+} + 8\text{e}^{-} \rightarrow \text{Fe}^{3+} + 4\text{H}_2\text{O} \) | 2.20 | Sharma et al., 2016 |
| Permanganate | \( \text{MnO}_2^{2-} + 8\text{H}^{+} + 5\text{e}^{-} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \) | 1.51 | Sharma et al., 2016 |
| Ozone | \( \text{O}_3 + 2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{O}_2 + \text{H}_2\text{O} \) | 2.08 | Ghernaout and Naceur, 2012 |
| Hypochlorite | \( \text{ClO}^{-} + \text{H}_2\text{O} + 2\text{e}^{-} \rightarrow \text{Cl}^{-} + 2\text{OH}^{-} \) | 0.84 | Jiang, 2007 |

2.2.2 The self-decay mechanism of Fe(VI) in strongly acidic solution (pH 1.0–3.0)

It was well documented that pH is one of the most vital factors affecting the kinetics and mechanism of Fe(VI) self-decay. The lowest self-decay rate of Fe(VI) occurs at pH 9.4–9.7 (Carr, 2008) and at pH below or above this pH range, the stability of Fe(VI) decreases rapidly with the decrease or increase of the pH value (Sharma, 2011). However, up to now, there is no consensus on the mechanism of Fe(VI) self-decay. Some researchers reported that the self-decay of Fe(VI) is first-order while other researchers insisted that its self-decay is second-order or mixed first and second-order dependence on Fe(VI) concentration. It’s imperative to understand the current views on the self-decay mechanism of Fe(VI) so as to clarify the self-decay mechanism of Fe(VI) and guide the practical application of Fe(VI) technologies.

2.2.3 The self-decay mechanism of Fe(VI) in strongly acidic solution (pH 1.0–3.0)

It was well documented that pH is one of the most vital factors affecting the kinetics and mechanism of Fe(VI) self-decay. The lowest self-decay rate of Fe(VI) occurs at pH 9.4–9.7 (Carr, 2008) and at pH below or above this pH range, the stability of Fe(VI) decreases rapidly with the decrease or increase of the pH value (Sharma, 2011). However, up to now, there is no consensus on the mechanism of Fe(VI) self-decay. Some researchers reported that the self-decay of Fe(VI) is first-order while other researchers insisted that its self-decay is either second-order or mixed first and second-order dependence on Fe(VI) concentration. It’s imperative to understand the current views on the self-decay mechanism of Fe(VI) so as to clarify the self-decay mechanism of Fe(VI) and guide the practical application of Fe(VI) technologies.
generation of the aquated diferrate(V) peroxide species as well as the aquated diferrate(IV) (Scheme 1) (Sarma et al., 2012; Lee et al., 2014).

\[
\frac{-d[\text{Fe(VI)}]}{dt} = \frac{k_1 k_2}{k_{-1}[\text{H}_2\text{O}]} + k_2 \{[\text{H}_3\text{FeO}_4]^+\}^2, \quad (4)
\]

where \(k_1\) and \(k_{-1}\) are the forward and reverse rate constants for converting two equivalents of \([\text{H}_3\text{FeO}_4]^+\) into \([\text{H}_4\text{Fe}_2\text{O}_7]^2+\) and \(\text{H}_2\text{O}\), respectively, and \(k_2\) is the microscopic rate constant for O-O bond formation. Conversely, the intermolecular water attack mechanism, the alternative pathway of the oxo-coupling, is not favorable within this pH range due to the higher energy barrier. Then the aquated diferrate(IV) undergoes disproportionation, forming ferrous and ferrate(VI) or ferric and diferrate(IV) instead of oxidizing the water within the experimental time scale. Particularly, the former reaction plays the dominant role in the disproportionation process, and ultimately affords \(\text{O}_2\) and the ferric products (Sharma et al., 2002; Sharma, 2011).

It’s worth noting that in the self-decay process of Fe(VI), aside from diferrate(VI), all the other intermediates can’t accumulate to the detectable level due to the faster consumption rate than the generating rate. Considering that \(k_{-1}[\text{H}_2\text{O}]\) is much larger than \(k_2\) at pH 1.0 or under less acidic conditions in the presence of Fe(VI) of sufficiently high concentration, the rate of Fe(VI) disappearance approaches \((k_1/k_{-1}[\text{H}_2\text{O}])[([\text{H}_3\text{FeO}_4]^+])^2\). Substituting \([\text{H}_4\text{Fe}_2\text{O}_7]^2+\) for \((k_1/k_{-1}[\text{H}_2\text{O}])[([\text{H}_3\text{FeO}_4]^+])^2\) can thus give Eq. (5).

\[
\frac{-d[\text{Fe(VI)}]}{dt} = k_2 \{[\text{H}_4\text{Fe}_2\text{O}_7]^2+\}. \quad (5)
\]

Consequently, Fe(VI) decay follows a simple first-order rate law at pH 1.0 (Sarma et al., 2012). However, as the pH value increases, the decay kinetics of Fe(VI) transits from first-order to second-order, which is corroborated by the increased sensitivity of the self-decay rate to Fe(VI) concentration.

2.2.2 The self-decay mechanism of Fe(VI) in weakly acidic and near-neutral solution (pH 3.0–9.0)

Many studies have been carried out in weakly acidic and near-neutral buffer solution to simulate the self-decay kinetics of Fe(VI) in the natural environment. Lee et al. (2014) found the self-decay of Fe(VI) is second-order concerning the Fe(VI) concentration at pH 2.0–8.0 in 10 mM phosphate-buffered solution, which is consistent with the viewpoint in the literature (Lee and Gai, 1993; Rush et al., 1996). The apparent second-order rate constant of Fe(VI) self-decay is highly pH-dependent, which increases by more than 4 orders of magnitude as the pH value decreases from 8.0 to 2.0. Similar to the proposed self-decay mechanism in the strongly acidic solution (Sarma et al., 2012), the self-decay process of Fe(VI) also starts with the dimerization of two Fe(VI) and the formation of the diferrate(VI) intermediate in weakly acidic and near-neutral solution, which subsequently undergoes rate-limiting O–O bond formation via intramolecular O–O coupling (Lee et al., 2014; Chen et al., 2018a). However, the newly formed oxo-coupled diferrate(V) would transform into diferrate(V) (\(\text{Fe}^{2+}\text{–O–Fe}^{3+}\)) and then liberate \(\text{H}_2\text{O}_2\) by two consecutive hydrolysis steps (Scheme 1) rather than generating \(\text{O}_2\). Moreover, Fe(V) ends up as Fe(III) (Rush and Bielski, 1989; Rush et al., 1996). The major reaction equations and the reaction sequence involved in the self-decay process of Fe(VI) in phosphate-buffered solution at pH 7.0 are shown in Table 2 and Scheme 2 (Lee et al., 2014), respectively.

Discordantly, Jiang et al. (2015) proposed that the second-order kinetic model can only be adopted to describe the homogenous decay of Fe(VI) within this pH range in 10 mM phosphate-buffered solution while the self-decay kinetics of Fe(VI) can be well fitted by mixed first- and second-order dependence on Fe(VI) concentration in 10 mM borate-buffered solution, which can be modeled by the following equation (Luo et al., 2020):

\[
\frac{-d[\text{Fe(VI)}]}{dt} = k_1[\text{Fe(VI)}] + k_2[\text{Fe(VI)}]^2, \quad (6)
\]

where \(k_1\) and \(k_2\) represent the rate constant of the first- and second-order decay of Fe(VI), respectively.

Since phosphate can complex with the in situ generated iron(III) (hydr)oxides, which would otherwise catalyze the self-decay of Fe(VI), and excess phosphate can also consume Fe(VI), the aforementioned disputes can be attributed to the different types and concentrations of buffer solutions employed in different studies. Considering the concentration of phosphate in natural water is much lower than that used in the experiments, the self-decay kinetics of Fe(VI) in the real practice is more similar to that in borate-buffered solution than that in phosphate-buffered solution. Thus, the self-decay of Fe(VI) is likely to obey the mixed first- and second-order rate law in the real water environment within the pH range of 3.0 to 9.0.

2.2.3 The self-decay mechanism of Fe(VI) in weakly basic solution (pH 9.0–10.0)

Recently, Luo et al. clarified the self-decay mechanism of Fe(VI) at pH 9.0 and 10.0 in 10 mM phosphate-buffered solution based on the kinetic data and the modeling results (Luo et al., 2020). They found the self-decay process of Fe(VI) follows first-order kinetics due to water attack, for the formation of O–O bond via oxo-coupling is unfavorable because of the high activation barrier within this pH range (Scheme 1). Water attack can be deemed as the addition of one-OH and one proton to two separate oxygen ligands in Fe(VI), forming the hydrolyzed Fe(V) intermediate.
species. After stripping one H₂O₂ through the electron transfer between H₂O₂ and the central iron atom, the deprotonated Fe(IV) is thus generated. The newly formed deprotonated Fe(IV) further undergoes dimerization, forming diferrate(IV) species, which subsequently self-decomposes and leads to the formation of Fe(III) and H₂O₂. However, the self-decay mechanism of Fe(VI) is quite different in the presence of Ca²⁺ within this pH range (Ma et al., 2016). It was reported that the coexisting Ca²⁺ can activate Fe(VI) by bringing the two FeO⁴⁻₂⁻ ions together to facilitate O−O coupling to generate a peroxo species, and the self-decay of Fe(VI) is in accordance with the second-order rate law in weakly basic solution.

In sum, although the self-decay mechanism of Fe(VI) is strongly dependent on pH, the influence of other experimental conditions including the type and the concentration of buffer solution as well as the coexisting components can’t be neglected. However, the influences of these factors on the self-decay mechanism of Fe(VI) have seldom been investigated. Moreover, it remains unclear why the self-decay rate of Fe(VI) is the lowest at pH 9.4–9.7. Thus, it’s worth further exploring the self-decay mechanism of Fe(VI) with the emphasis on the above unknown territory in the future.

2.3 Oxidizing mechanism of Fe(VI)

Fe(VI) is a powerful oxidant, which can efficiently oxidize...
various contaminants, including inorganics, organics, and the secondary metabolites of microorganisms (Sharma, 2011; Sharma et al., 2016; Fan et al., 2018; Islam et al., 2018). Except the reactions of Fe(VI) with selenite and some cyanides, the reactions of Fe(VI) with most inorganics and TrOCs follow the second-order kinetics (Johnson and Bernard, 1992; Sharma et al., 1998; Yngard et al., 2007; Yngard et al., 2008), which can be expressed as:

\[
k_{\text{app}} \frac{[\text{Fe}^{\text{VI}}]}{[\text{X}]} \approx \sum_{j=1}^{4} k_{ij} \alpha_i \beta_j \frac{[\text{Fe}^{\text{VI}}]}{[\text{X}]}, \quad (7)
\]

where \(k_{ij}\) is the species-specific second-order rate constant for the reaction between the Fe(VI) species \(i\) and the target contaminant species \(j\), \(\alpha_i\) and \(\beta_j\) represent the proportion of the Fe(VI) species \(i\) and the target contaminant species \(j\), respectively.

The essence of the redox reaction is the electron transfer between the oxidants and reductants. Hence, the premise of determining the oxidation mechanism under different reaction conditions is to clarify the electron transfer mechanism. Broadly speaking, there are three possible electron transfer ways: 1) \(1-e^-\) transfer, 2) \(2-le^-\) transfer (total of \(2-e^-\)), and 3) \(2-e^-\) (oxygen-atom) transfer (Sharma, 2011; Sharma et al., 2011). Goff and Murmann are the first to investigate the electron transfer mechanism using oxygen isotopic labeling method (Goff and Murmann, 1971). Based on the reaction pathway of \(^{18}\text{O}\) and the reaction stoichiometry, they suggested that Fe(VI) oxidized \(\text{SO}_3^{2-}\) through oxygen-atom transfer. However, the oxo-group exchange between the solvent water and high-valent iron was neglected (Pestovsky and Bakac, 2006). Therefore, the proposed oxygen-atom transfer mechanism between Fe(VI) and \(\text{SO}_3^{2-}\) might not be reliable. The rate constants for the oxidation of inorganics by Fe(VI) were correlated with thermodynamic reduction potentials to understand the reaction mechanism. Based on this method, Sharma found a linear relationship between \(\log k\) and \(1-e^-\) transfer potentials for iodide, cyanides, and superoxide, and a linear relationship between \(\log k\) and \(2-e^-\) transfer potentials for diverse oxy-compounds, including nitrogen, sulfur, selenium, and arsenic (Sharma, 2010). The linear relationships can be mathematically expressed by Eqs. (8) and (9). It’s worth mentioning that this method is also applicable to determining the mechanism of TrOCs oxidation by Fe(VI) (Fig. 2) (Sharma, 2010; Sharma et al., 2011; Sharma, 2013).

\[
\log(1-e^-) = 6.39 - 1.83E_{(1)}^0, \quad (8)
\]

\[
\log(2-e^-) = 4.44 - 3.09E_{(2)}^0, \quad (9)
\]

However, sometimes several electron transfer pathways occur simultaneously (Sharma et al., 1997; Sharma et al., 2011), and the electron transfer potentials of some compounds are not available in the literature. Therefore, the combination of the reaction stoichiometry and the products-analysis or other methods is necessary to clarify the electron transfer mechanism (Zimmermann et al., 2012; Chen et al., 2018b; Huang et al., 2018). Although the

![Scheme 2](image-url)  
**Scheme 2** Schematic illustration of the self-decay of Fe(VI) at pH 7.0.

**Fig. 2** \(\log k\) as a function of the standard one-electron reduction potential \((E_{(1)}^0)\) (a) and standard two-electron reduction potential \((E_{(2)}^0)\) (b) for the reaction of Fe(VI) with inorganic/organic substrates at 25°C.
application of the premix pulse radiolysis apparatus, one of the spectroscopic apparatuses, was limited in the past due to the inaccessibility of the apparatuses and the harsh experimental conditions (Sharma, 2002; Sharma and Cabelli, 2009), the spectroscopic technique has become the most direct method for the products-analysis now. It can provide solid evidence for the generation of Fe(V)/Fe(IV) or other reactive oxidant species (ROS), and light up the way for exploring the electron transfer mechanism. Particularly, the X-ray absorption fine structure (XAFS) spectroscopy and Mössbauer spectroscopy are able to detect Fe(V)/Fe(IV) in situ, which will promote the application of spectroscopic technique in investigating the oxidation mechanism of Fe(VI) (Novak et al., 2018; Liang et al., 2020).

### 3 Superiorities of applying Fe(VI)

Fe(VI) is generally employed as either oxidant or disinfectant but seldom be used solely as the coagulant due to its relative high price, although its reduced product, Fe(III), can also work as the coagulant. Therefore, this section mainly summarizes the superiorities of applying Fe (VI) as a sole oxidant for decomposing organic contaminants rich in electron-donating moieties, as a bifunctional reagent (both oxidant and coagulant) for eliminating some special contaminants, and as a disinfectant for inactivating microorganisms.

#### 3.1 Oxidation of organics rich in electron-donating moieties

Fe(VI) is effective for abating TrOCs in water with second-order rate constants ranging from $<0.1$ to $10^5$ M$^{-1}$·s$^{-1}$ (Lee et al., 2009; Sharma, 2013). It is highly selective in oxidizing TrOCs. It was reported that Fe(VI) also has eximious predominance in oxidizing cyanotoxins and reducing their toxicity. Moreover, it can efficiently oxidize organics containing electron-donating moieties such as phenols, anilines, amines, and olefins. However, the reactions between Fe(VI) and organics containing electron-withdrawing moieties such as carboxylic acids and alkanes are sluggish. The mechanistic analysis showed that the mechanism of oxidizing the aforementioned organics containing electron-donating moieties include electrophilic oxidation, hydrogen abstraction, $1$−$e^-$ transfer (Fe(VI)-Fe (V)), and subsequent $2$−$e^-$ transfer (Fe(VI)-Fe(IV) or Fe (V)-Fe(III)) (Lee et al., 2009; Yang et al., 2011; Yang et al., 2012; Sharma, 2013; Chen et al., 2019b).

#### 3.1.1 Microcystins

Microcystins (MCs), a class of hepatotoxic monocyclic heptapeptides, released by cyanobacteria is among the most problematic cyanotoxins (de Figueiredo et al., 2004). It was reported that Fe(VI) can swiftly degrade MCs within the environmentally-relevant pH range. While undesirable toxic byproducts were generated in the process of MCs oxidation by some conventional chemical oxidants such as Cl$_2$, NH$_2$Cl, and O$_3$, the concentrations of the harmful byproducts associated with Fe(VI) oxidation are relatively low (Jiang et al., 2014). Previous study has determined that the second-order rate constants for the reaction of Fe(VI) with MC-LR, one of the most abundant species of the MCs, are in the range of $8.1\pm0.08$ M$^{-1}$·s$^{-1}$ to $1.3\pm0.1 \times 10^2$ M$^{-1}$·s$^{-1}$ within the pH range of 7.5−10.0 (Jiang et al., 2014). Through a series of reaction steps including the hydroxylation of the aromatic ring, the cleavage of the olefinic double bonds, and the fragmentation of the cyclic MC-LR structure (Jiang et al., 2014; Mura et al., 2017; Islam et al., 2018), the ecotoxicity of MC-LR can be significantly reduced.

#### 3.1.2 Phenols

In recent years, the widespread occurrence endocrine-disrupting chemicals (EDCs) in the aquatic environment, which can cause potential toxicity to aquatic organisms and human beings, has raised great concerns. The phenolic moiety, a substructure of many important classes of EDCs such as steroid estrogens and alkylphenols, is responsible for the biological effects of EDCs, and it can be efficiently decomposed by Fe(VI) through electrophilic oxidation mechanism (Lee et al., 2005).

It has been determined that the second-order rate constants for the reactions of phenol, 17α-ethynylestradiol (EE2), 17β-estradiol (E2), bisphenol-A (BPA), triclosan (TCS), and 4-methylphenol with Fe(VI) at pH 7.0 are $7.7 \times 10^4$ M$^{-1}$·s$^{-1}$, $7.3 \times 10^2$ M$^{-1}$·s$^{-1}$, $7.6 \times 10^5$ M$^{-1}$·s$^{-1}$, $6.4 \times 10^2$ M$^{-1}$·s$^{-1}$, $1.1 \times 10^3$ M$^{-1}$·s$^{-1}$, and $6.9 \times 10^2$ M$^{-1}$·s$^{-1}$, respectively (Lee et al., 2005; Lee et al., 2009). The rate constant of HFeO$_4$ with dissociated phenol is greater than that of HFeO$_4$ with undissociated phenol and the former is about $2.1 \times 10^4$ M$^{-1}$·s$^{-1}$ while the latter is about $1.0 \times 10^2$ M$^{-1}$·s$^{-1}$ (Lee et al., 2005). Furthermore, the estrogenic activities of EE2, estrone (E1), E2, estriol (E3) (Li et al., 2008; Lee and von Gunten, 2010) as well as their transformation intermediates (Lee et al., 2008) can be significantly attenuated by Fe(VI) with low concentrations while the decomposition of these organic contaminants by other conventional oxidants like Cl$_2$ and O$_3$ often leads to the generation of carcinogenic byproducts (Lee and von Gunten, 2010; Lane et al., 2015). It was found that the reaction between Fe(VI) and the phenolic contaminant is initiated abstracting an electron from the phenolic contaminant by Fe(VI), forming phenoxyl radicals and Fe(V) (Huang et al., 2001a). The phenoxyl radicals subsequently undergo a 2-electron oxidation with the Fe (V) species or couple with each other at different positions via O−C or C−O−C bonds, forming dimers, trimers, and
tetramers (Scheme 3) (Huang et al., 2001a), which are less toxic (Huang et al., 2001a; Chen et al., 2019b). Moreover, the second-order rate constants for the reactions of Fe(VI) with phenols, especially the dissociated phenols, are linearly correlated with both the Hammett substituent constants and $pK_a$ values of the substituted phenols, for the reactions are sensitive to the substituent effect (Lee et al., 2005). Based on these results, it’s convenient to predict the rate constants for the reactions between Fe(VI) and phenolic compounds of complex structures.

### 3.1.3 Anilines and amines

Fe(VI) also shows an appreciable reactivity to antibiotics with aniline or amine moieties in the water because these moieties are susceptible to Fe(VI) attack. The second-order rate constants for the oxidation of aniline, sulfamethoxazole (SMX), and ciprofloxacin (CIP) by Fe(VI) at pH 7.0 are $6.6 \times 10^3 \text{M}^{-1}\cdot\text{s}^{-1}$, $1.8 \times 10^3 \text{M}^{-1}\cdot\text{s}^{-1}$, and $4.7 \times 10^2 \text{M}^{-1}\cdot\text{s}^{-1}$, respectively (Lee et al., 2009). Due to the presence of amine group in ampicillin (AMP) besides the thioether, the oxidation rate constant of AMP is much higher than that of penicillin G (PENG) or cloxacillin (CLOX) (Karlesa et al., 2014). The reactivity of Fe(VI) to aniline or amine moieties is in the order of aniline group $>$ glycine (primary (1°) amine) $>$ dimethylamine (secondary (2°) amine) $>$ trimethylamine (tertiary (3°) amine) in the pH range of 6.0–8.0 (Lee and von Gunten, 2010; Yang et al., 2012). The free radical mechanism for the reaction between Fe(VI) and excess amounts of anilines was suggested based on EPR measurements (Scheme 4) (Huang et al., 2001b), where the steps (II) and (III) are the rate-determining steps, and the oxidation mechanism would not change with the electron-richness of the compound (Sharma, 2013). Similar to the correlation between the oxidation rate constants of phenols by Fe(VI) and the Hammett substituent constants, the oxidation rate constants of anilines by Fe(VI) are also strongly correlated to $\sigma^+$. However, aliphatic amines are decomposed by Fe(VI) via an oxygen-atom transfer step, involving the breaking of the N-H bond of amines, whose strength would ultimately affect the second-order rate constants (Sharma, 2013). Besides, it’s worth pointing out that pH can not only affects the rate constants significantly but also sometimes affect the reaction mechanism, resulting in the generation of different oxidation products at various pH. Taking the oxidation of sulfonamides by Fe(VI) as an example, Fe(VI) preferentially attacks the isoxazole moiety and the aniline moiety under neutral and basic conditions while the cleavage of S-N bond dominates in acidic conditions (Sharma et al., 2006a; Sharma et al., 2006b).

### 3.1.4 Olefins

Since olefin is also one of the electron-donating moieties, the organic contaminants containing olefin moieties can also be readily oxidized by Fe(VI). It was found that Fe (VI) rapidly oxidized carbamazepine (CBZ) by electrophilic attack at the olefinic group in the central heterocyclic ring, leading to ring-opening, with the second-order rate constant of $70 \text{M}^{-1}\cdot\text{s}^{-1}$ at pH 7.0 (Hu et al., 2009). And...
over 98.6% of tetracycline (TC) can be swiftly decomposed within 60 s with the [Fe(VI)]₀/[TC]₀ ratio of 1:10, especially under high pH conditions, which can be ascribed to the attack of olefinic bonds by Fe(VI) (Yang and Doong, 2008; Ma et al., 2012). However, the change of TOC during TC oxidation by Fe(VI) was generally very minor (Yang and Doong, 2008; Ma et al., 2012), and the residual transformation organics might also pose threat to the organisms. Thus, the removal of the parent compounds shouldn’t be the only index to evaluate the feasibility of Fe(VI) application under different conditions because the toxicity of the generated oxidation products might vary with the reaction mechanism. Consequently, a comprehensive evaluation of the oxidation efficacy of Fe(VI) is required in combination with the removal of the parent compounds and the attenuation of the ecotoxicity of the transformation products in the real practice.

3.2 Elimination of some contaminants by Fe(VI) via both oxidation and coagulation

Some contaminants, including organophosphorus compounds, organoarsenic compounds, and some heavy metals, are difficult to be directly removed while their oxidized products are apt to be removed via coagulation or adsorption. Considering the versatility of Fe(VI), removing these contaminants by Fe(VI) oxidation followed by coagulation is an attractive option for mitigating the environmental risks of these contaminants.

3.2.1 Organophosphorus and organoarsenic compounds

Among various technologies to remove organophosphorus, the commonly used pesticides, from water, Fe(VI) shows prominent advantage due to its dual function as both oxidant and coagulant (Yang et al., 2012; Sharma et al., 2016). It was found that chlorpyrifos, an organophosphorus compound, can be completely oxidized by Fe(VI) in the water at pH 7.0 within 300 s with the [Fe(VI)]₀/[chlorpyrifos]₀ ratio of 100:1 (Liu et al., 2019). The mechanism of chlorpyrifos removal by Fe(VI) is its transformation to inorganic phosphate, which can be easily adsorbed on the surface of and incorporated into the structure of the in situ generated γ-Fe₂O₃/γ-FeOOH core/shell nanoparticles at low Fe/P mass ratios (Kralchevska et al., 2016a).

Similarly, transferring organoarsenic compounds by Fe(VI) to inorganic arsenate and subsequently immobilizing the generated arsenate by the in situ generated iron(III) (hydr)oxide nanoparticles are effective for abating organoarsenic compounds. Both roxarsone (ROX) and p-arsanilic acid (p-ASA), the two widely used organoarsenic compounds in the worldwide, contain electron-donating
moieties and are readily oxidized by Fe(VI) (Xie and Cheng, 2019). It was found that the second-order rate constant for the reaction of Fe(VI) with ROX is 305 M$^{-1}$·s$^{-1}$ at pH 7.0, and over 95% of total As can be removed within 10 min at [Fe(VI)]$_0$/[ROX]$_0$ ratio of 20:1 (Yang et al., 2018a). Moreover, in comparison with the TOC removal in O$_3$, HClO, and KMnO$_4$ treatment systems (Yang et al., 2018b), the TOC removal in the oxidation process of p-ASA by Fe(VI) is 1.6 to 38 times higher, which mainly ascribed to the in situ generated iron(III) (hydr)oxide nanoparticles. Generally, in the conversion of organoarsenic compounds by Fe(VI), -AsO(OH)$_2$ group is first cleaved from aromatic ring (Czaplicka et al., 2014; Yang et al., 2018a; Yang et al., 2018b). The released inorganic As(III) species can be further oxidized by Fe(VI) to As(V) species, which greatly increases the affinity of organoarsenic compounds with solid surfaces and reduces their mobility in the water (Jain et al., 2009). The second-order rate constant of Fe(III) with Fe(VI) ($k_{\text{app}[\text{Fe}^7\text{Ti}^3\text{O}_5\text{S}(-\text{As})^{(\text{OH})3}]} = 2.5 \times 10^6$ M$^{-1}$·s$^{-1}$) is comparable with those of As(III) with other oxidants ($k_{\text{app}[\text{HOCl}+\text{As}^{(\text{OH})3}]} = 4.3 \times 10^3$ M$^{-1}$·s$^{-1}$, $k_{\text{app}[\text{O}_2+\text{As}^{(\text{OH})3}]} = 5.5 \times 10^2$ M$^{-1}$·s$^{-1}$ and $k_{\text{app}[\text{H}_2\text{O}_2+\text{As}^{(\text{OH})3}]} = 7.2 \times 10^2$ M$^{-1}$·s$^{-1}$) (Sharma et al., 2007). It’s worth pointing out that the newly formed As(V) species can not only be efficiently absorbed on the surface of the iron(III) (hydr)oxide nanoparticles but also be embedded into the tetrahedral sites of the $\gamma$-Fe$_2$O$_3$ spinel structure (Prucek et al., 2015). The chemical adsorption and the formation of inner-sphere complexes alleviate the inhibition effects of the background matrices and avoid the leaching of metal ions back into the environment (Liu et al., 2017).

### 3.2.2 Heavy metals

Some low-valence-state heavy metals like Ti(I) (Liu et al., 2017), and Mn(II) (Goodwill et al., 2016), pose greater environmental risks than their counterparts in high-valence-state due to the high solubility of the former. Some other low-valence-state heavy metals like Sb(III) (Lan et al., 2016) and As(III) are not only more toxic but also more difficult to be separated from water than their high-valence-state species. Thus, oxidizing these low-valence-state heavy metals to the high-valence-state species and then separating them through coagulation or co-precipitation is a viable option. Considering Fe(VI) can serve as both oxidant and coagulant, it has advantages over the traditional mechanisms. It should be noted that the coagulation mechanism of Fe(VI) for different heavy metals is not identical but depends on the ionic radiiuses and the electronic structures of the heavy metal ions (Prucek et al., 2015).

In addition, some of the heavy metals are easily complexed with other components in the water, forming stable complexes that are difficult to remove, such as the cyanide (CN$^-$)-complexed heavy metals in the basic coke plant effluents. Interestingly, Fe(VI) can also deal with this kind of contaminants by breaking the complexes and oxidizing both CN$^-$ and heavy metals. Previous study has reported that the uncomplexed CN$^-$ can be oxidized by Fe (VI) through sequential $1^{-}\text{e}^{-}$ transfer, generating Fe(OH)$_3$, CO$_2$, and NO$_2$ (Sharma et al., 1998), and the reaction kinetics is first-order with respect to each reactant (Sharma et al., 1998). The second-order rate constant of CN$^-$ with Fe(VI) is about 605 M$^{-1}$·s$^{-1}$ at pH 8.0 (Sharma et al., 1998). Although it is lower than those of CN$^-$ with O$_3$, HClO, and H$_2$O$_2$ (Gurrol and Bremen, 1985; Kepa et al., 2008; Moussavi et al., 2018), combing the oxidation capability of Fe(VI) and the coagulation capability of iron (III) offers an efficient approach to eliminate the CN$^-$ complexed heavy metals from water. It was found that 91.23% of CN$^-$ (1.0 mM) can be oxidized and 98.96% of Cu$^{2+}$ (0.094 mM) can be removed in minutes when 2.0 mM Fe(VI) was adopted to deal with the industrial wastewater containing cyanide-complexed Cu$^{2+}$ (Seung-Mok and Diwakar, 2009). And the reaction kinetics is first-order with respect to each reactant. However, it should be noted that the performance of Fe(VI) depend on the type of heavy metals, which can affect both the rate of breaking the complexes by Fe(VI) and the reaction mechanism. It has been demonstrated that the rate law for the reaction of Fe(VI) with Zn(CN)$_4^{2-}$/Cd(CN)$_4^{2-}$ is different from that of Fe(VI) with Cu(CN)$_4^{2-}$, which can be written as (Ynggard et al., 2007; Ynggard et al., 2008):

$$
\frac{d[\text{Fe(VI)}]}{dt} = k[\text{Fe(VI)}][\text{M(CN)}]^{4-}_{4}^{0.5},
$$

where M represents Zn or Cd. Although the oxidation rates of most CN$^-$-complexed heavy metals are slower than that of uncomplexed CN$^-$, the oxidation of Zn(II)-cyanide or Cu(I)-cyanide by Fe(VI) was found to be the exception (Sharma et al., 2005).

In sum, Fe(VI) is expedient in treating cyanide complexed heavy metals owing to its versatility and environmental friendliness (Sharma et al., 1998). Likewise, Fe(VI) also exhibits great potential in the elimination of other organics-complexed heavy metals.

### 3.3 Inactivation of microorganisms

Fe(VI) is an environmental benign disinfectant with the ability of damaging the genome and the oxidant-sensitive protein structures of microorganisms, hindering their growth and reproduction (Hu et al., 2012; Yan et al., 2020). Previous studies have demonstrated that Fe(VI) can effectively inactivate a wide variety of microorganisms including cyanobacteria (Sharma, 2007), bacteriophage MS2 (Hu et al., 2012), f2 virus (Schink and Waite, 1980), norovirus (Manoli et al., 2020), Bacillus cereus, Escherichia coli, Staphylococcus aureus (Sharma, 2007), micro-
algae (Fan et al., 2018), and so on. It was reported that a Fe (VI) CT dose of about 3.5 (mg·min)/L was required for the 2 log removal of *Escherichia coli* at pH 7.0, and at a Fe(VI) CT dose of 2.0 (mg·min)/L at pH 7.0, a 2 log removal of MS2 can be obtained (Hu et al., 2012; Manoli et al., 2020). Although the disinfection performance of the conventional disinfectants closely associates with pH in addition to the type of microorganisms, the influence of pH on the disinfection performance of Fe(VI) is less than that of other conventional disinfectants, which further demonstrates the superiority of Fe(VI) technologies.

Moreover, Fe(VI) is an alternative disinfectant to deal with the cyanobacterial issues of the source water. It was found that Fe(VI) disinfection can induce the formation of coagulant aid secreted by cyanobacteria (Ma and Liu, 2002), and decrease the electrostatic repulsion between the cyanobacterial cells, which thus cause the formation of cell agglomerates (Kubiňáková et al., 2017). Another advantage of Fe(VI) is that it can inactivate cyanobacterial cells without affecting cyanobacterial cell integrity or releasing the cyanotoxins (Fan et al., 2018). Even if Fe(VI) does induce the significant cell lysis, the released cyanotoxins are not the problems since they can be rapidly eliminated by Fe(VI) as mentioned in Section 3.1.1. Furthermore, the inactive cyanobacteria can be adsorbed by the in situ generated iron(III) (hydro)oxides (Deng et al., 2017), which decreases the turbidity of the water and reduces the required dosage of the extra coagulant. Thus, Fe(VI) is a promising option to treat the microorganisms-bearing water. Nevertheless, the dose of Fe(VI) should be strictly controlled since the microbial cell lysis and the toxins released that result from the excess addition of Fe(VI) would further increase the operation cost and the environmental risks (Fan et al., 2018).

4 Limitations of applying Fe(VI)

As introduced above, Fe(VI) has long been recognized as a multifunctional water treatment reagent with obvious advantages in tackling different kinds of contaminated water, it also has some disadvantages limiting its wide application. This section mainly summarized the limitations of applying Fe(VI) in real practice.

4.1 Difficulty in synthesizing and preserving Fe(VI)

The premise of applying Fe(VI) in real practice is its easy synthesis. The published synthesis methods of Fe(VI) so far include wet chemical method (Thompson et al., 1951), electrochemical method (Mácová et al., 2009), and thermal method (Dedushenko et al., 2009). However, the synthetic routes of all these methods are long and tedious, which are time-consuming and costly. Moreover, the instability of Fe (VI) in solid and aqueous phases remains an impediment to its utilization in large scale (Schmidbaur, 2018).

4.2 Potential environmental risks associated with the halide ions

Fe(VI) is traditionally considered as a green oxidant without producing any hazardous halogenated byproducts. Previous studies have proposed that it can be used as a pre-oxidant in source water to control disinfection byproducts (DBPs) formation in subsequent chlorine or chloramine disinfection (Liu et al., 2020). It is often stated in the literature that one major advantage of Fe(VI) oxidation over ozonation is that Fe(VI) can’t oxidize bromide (Br ) and thus does not lead to the generation of bromate (BrO3 ) (Sharma, 2011). Besides, it was believed that the formation of the iodinated disinfection byproducts (I-DBPs) is also not an issue for Fe(VI) oxidation (Wang et al., 2018a). Fe (VI) can oxidize iodide (I ) to the highly reactive hypoiiodous acid (HOI) through 2 − e − transfer, which can be transformed to iodate (IO3 ) swiftly by disproportionation or further oxidation by Fe(VI) (Shin et al., 2018). Unlike other commonly used oxidants such as O3, NH2Cl, KMnO4, and HOCl, the second-order rate constant of Fe (VI) with HOI (kapp[Fe(VI)-HOI] = 1.03 × 105 M−1·s−1 at pH 7.2) is higher than that of Fe(VI) with I− (kapp[Fe(VI)-I−] ~ 2.0 × 104 M−1·s−1 at pH 7.0) (Krachchevska et al., 2016b; Wang et al., 2018a; Wang et al., 2020). Therefore, the accumulation of the highly reactive HOI and the associated I-DBPs can be well inhibited (Wang et al., 2018a). In addition to being able to inhibit the formation of I-DBPs, Fe(VI) is effective for degrading these I-DBPs in iodine-containing water (Sun et al., 2019). Overall, in the past two decades, all the above advantages of Fe(VI) suggested that Fe(VI) oxidation is a promising option for halogenated byproducts mitigation during the treatment of halide-containing water.

Nonetheless, great attention should still be paid to the potential environmental risks associated with the halide ions when Fe(VI) is applied. Because most of the studies on Fe(VI) application were conducted in phosphate-buffered solutions under weakly-basic condition in the past, which is very different from the real situations. Thus, the previous viewpoints on the possible formation of the potentially carcinogenic halogenated byproducts should be re-evaluated. It was found that the concentration of the generated BrO3 might exceed the US drinking water maximum contaminant level when Fe(VI) oxidizes Br in the absence of phosphate under weakly-acidic condition (Huang et al., 2016). Moreover, the decay rate of Fe(VI) increases with increasing Br− concentration in borate-buffered solutions while the change of the decay rate of Fe (VI) is not obvious in the presence of elevated Br− concentration in phosphate-buffered solutions (Jiang et al., 2016a). Thus, it can be inferred that the presence of phosphate inhibits the generation of the halogenated byproducts when halide ions are oxidized by Fe(VI). The influence of phosphate can be attributed to the complexation between phosphate and Fe, including Fe(VI), Fe(V),
Fe(IV), Fe(III), and Fe(II), which would affect the reaction process from the following aspects: 1) stabilizing Fe and increasing the contact time between oxidants and reductants; 2) decreasing the reactivity of ferrates (Huang et al., 2018); 3) inhibiting the catalytic effect of the iron(III) particles on the decomposition of H₂O₂ and increasing the concentration of H₂O₂ (Huang et al., 2016; Jiang et al., 2016a). The effects of the elevated H₂O₂ concentration on the generation of the brominated products are quite intricate. On one hand, H₂O₂ can reduce HOBr to Br⁻, inhibiting the accumulation of the highly reactive HOBr and the production of both BrO₃⁻ and brominated products (Huang et al., 2016; Jiang et al., 2016a). On the other hand, the reactions between H₂O₂ and Fe(VI)/Fe(III)/Fe(II) can also induce the formation of the highly reactive oxidants including Fe(V), Fe(IV), and HO²⁻, which might also contribute to the formation of BrO₃⁻ (Huang et al., 2016; Zhu et al., 2020). With regard to I-DBPs, although H₂O₂ can reduce HOI, the regenerated I⁻ and the difficulty in forming stable IO₃⁻ might increase the possibility of forming I-DBPs in iodine-containing water (Wang et al., 2020). Therefore, the potential of forming halogenated byproducts in real practice might be underestimated if phosphate is used as buffer. Further investigations should be carried out under environmentally relevant conditions to determine the possible formation of the halogenated byproducts and the contribution of ferrates and different reactive oxygen species.

In some cases, the halide concentrations in potable water are high due to the seawater erosion and anthropogenic activities (Gong and Zhang, 2013), and there are a variety of components that can also consume Fe(VI). The insufficient dosing of Fe(VI) can lead to the formation of BrO₃⁻ or other halogenated byproducts. Taking I⁻ oxidation as an example (Fig. 3), when there is excess I⁻ over Fe(VI), ferrates (Fe(IV), Fe(V), and Fe(VI)) can oxidize I⁻ to I₃⁻ species accompanied with the formation of I₂, both of which may react with residue organics yielding I-DBPs (Kralchevska et al., 2016b; Wang et al., 2018a). The reaction between Fe(VI) and I⁻ can be presented by Eq. (11) (Kralchevska et al., 2016b).

\[
2\text{HFe}^{VI}\text{O}_4^- + 6\text{I}^- + 5\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 + 2\text{I}_3^- + 6\text{OH}^- + \frac{1}{2}\text{O}_2
\]

Besides, the halogenated organics can also act as the potential halogen sources of the toxic halogenated byproducts. Previous studies have demonstrated that Fe(VI) can induce the deiodination/debromination reactions during the degradation of brominated/iodinated organics such as tetrabromobisphenol A (TBBPA) (Yang et al., 2014; Han et al., 2018), 3-bromophenol (3-BrP) (Sun et al., 2019), and iodinated X-ray contrast media (ICMs) (Dong et al., 2018). Considering the reactions between the highly reactive iodine/bromine species and the organic transformation intermediates, the release of halide ions inevitably accompanies with the formation of the halogenated byproducts (Dong et al., 2018; Han et al., 2018; Sun et al., 2019). The newly formed halogenated byproducts might be more toxic than the parent compounds. Therefore, if Fe(VI) is not enough to further degrade these halogenated byproducts and stabilize the inorganic halogen intermediates, the newly formed halogenated byproducts would pose a serious threat to the public health (Wang et al., 2020).

In addition, the coexistence of Br⁻ and I⁻ as well as pH can affect the generation of the halogenated byproducts. It was reported that high concentrations of Br⁻ can remarkably restrain the transformation of I⁻ to stable IO₃⁻, which potentially increases the risk of forming iodinated byproducts (Zhang et al., 2016). It was also documented that in the Fe(VI)/I⁻/BPA system, the production of the iodinated byproducts increased with increasing

Fig. 3 Illustration of the formation of I-DBPs when NOM is oxidized by Fe(VI) in the presence of excess I⁻.
pH (Wang et al., 2020). This was because the reactivity of Fe(VI) with HOI decreased with the increasing pH while the reactivity of HOI with BPA increased with elevating pH (Wang et al., 2020). Furthermore, the newly formed iodinated byproducts could not be completely decomposed by Fe(VI) within a short time scale due to the low oxidation ability of Fe(VI) at high pH. On the contrary, the pH lower than 7.5 favors the formation of HOBr and BrO₃⁻ (Jiang et al., 2016a). Hence, care should be taken when Fe (VI) is applied at extreme pH conditions with high concentrations of halide ions.

5 Methods to improve contaminants oxidation/disinfection by Fe(VI)

Although Fe(VI) shows great superiorities in abating various contaminants, the rapid self-decay of Fe(VI) in the water and the sluggish reactivity of Fe(VI) with some contaminants limit its application. Thus, various methods have been developed in the past two decades to overcome the limitations of Fe(VI), which are summarized in Fig. 4. According to the commonalities and characteristics of these methods, they can be divided into three categories: 1) the sustained released of Fe(VI); 2) the in situ activation of Fe(VI), and 3) the replacement of Fe(VI) with Fe(V)/Fe(IV).

5.1 Sustained release of Fe(VI)

Since the self-decay of Fe(VI) results in great loss of its oxidation capacity, Yuan et al. fabricated the encapsulated K₂FeO₄ samples, whose encapsulating wall and encapsulated core are paraffin wax and K₂FeO₄ solid respectively, in 2008 (Yuan et al., 2008b). With the protection of paraffin wax, K₂FeO₄ solid can be slowly released into the water and be consumed by the target contaminants immediately, thus remarkably abate the negative effects arising from Fe (VI) self-decay. Consequently, the encapsulated K₂FeO₄ is effective in degrading various TrOCs and reducing the COD value of the contaminated water even under extreme pH conditions (Yuan et al., 2008b; Wang et al., 2009). Chen et al. (2019a) modified the encapsulated K₂FeO₄ samples by replacing paraffin wax with chitosan and a buffer layer between the wall material and the oxidant was added to prevent Fe(VI) from reacting with the wall material.

Similarly, the removal of TrOCs by Fe(VI) can be improved by applying Fe(VI) in multiple-dosing mode rather than in single-dosing mode (Feng et al., 2016; Yan et al., 2020). Compared with the encapsulated K₂FeO₄ samples, multi-step dosing of Fe(VI) is more environmentally-friendly since no additional materials are introduced into the water. However, these two methods can only enhance the removal of the organic contaminants that can be oxidized by Fe(VI) but has limited effect on the organic contaminants that are refractory to Fe(VI) oxidation.

5.2 In situ activation of Fe(VI)

Sharma et al. demonstrated the enhanced oxidation of ammonia by Fe(VI) in UV-irradiated TiO₂ suspensions in
2001 (Sharma et al., 2001b). It was found that both Fe(V) and Fe(IV) can be obtained through the photoreduction of Fe(VI) (Eqs. (12)-(13)).

$$\text{FeO}_4^{2-} + e_{cb} \rightarrow \text{FeO}_3^{4-}$$  \hspace{1cm} (12)

$$\text{FeO}_3^{4-} + e_{cb} \rightarrow \text{FeO}_4^{2-}$$  \hspace{1cm} (13)

The in situ generated highly reactive Fe(V)/Fe(IV) can significantly increase the removal of the contaminants that are refractory to Fe(VI) oxidation, and accelerate the removal of contaminants, which alleviates the impact of Fe(VI) self-decay on the oxidation capacity of Fe(VI) (Sharma et al., 2001b). Thus, the development of photo-activated Fe(VI) technologies, including UV/TiO$_2$/Fe(VI) (Xing et al., 2002; Yuan et al., 2008a) and UV/Fe(VI) (Wang et al., 2010; Aslani et al., 2017; Wu et al., 2020), attracted great attention in the following two decades. However, the mechanism is still controversial. While Wang et al. (2010) suggested that HO$^*$ generated by photochemical process and Fe(VI) self-decay was the dominant ROS contributing to the oxidation of organic phosphorus, Aslani et al. (2017) deemed that both Fe(V) and HO$^*$ were responsible for the degradation of haloacetic acids in UV/Fe(VI) process. Recently, however, it was concluded that it was O$_2$** rather than Fe(V)/Fe(IV) promoting the degradation of phenolic contaminants in UV/Fe(VI) process (Wu et al., 2020). The disparity in the reported mechanisms can be ascribed to the different experimental conditions (e.g., pH value, Fe(VI) dose, and UV fluence rate) and the different properties of contaminants. However, the practical application of these methods is limited by many factors, such as the poor light transmittance of Fe(VI) solution, the high energy consumption resulting from the coexisting components, and so on (Loeb et al., 2019).

5.2.2 Silica gel/Persyoxonomosulfate (PMS)/Ammonia-enhanced Fe(VI) technologies

The development of Fe(VI) in situ activation technologies has ushered in an unprecedented climax, and more and more new technologies have appeared since 2017. Manoli et al. (2017a) found that the solid silica gel (SiO$_2$) could remarkably enhance the oxidation of caffeine (CAF) by Fe(VI) at pH 8.0, while the increased removal of fluorquinolones by Fe(VI) in the presence of persyoxonomosulfate (PMS) was achieved (Feng et al., 2017b). Besides, ammonia was reported to be able to promote the oxidation of flumequine by Fe(VI) (Feng et al., 2017a). However, the aforementioned studies only focused on the effects of various reagents on the kinetics of the oxidation of contaminants by Fe(VI). The relevant reaction mechanism and the type of the dominating oxidants of these reaction systems warrant in-depth investigation.

5.2.3 ABTS/Acid-activated Fe(VI) technologies

Dong et al. (2017) found that ABTS, acting as the electron shuttle, accelerated the reaction of DCF with Fe(VI) over a wide pH range. It was proposed that Fe(VI) can oxidize ABTS to ABTS**, which was responsible for the enhanced oxidation of DCF (Dong et al., 2017). However, the potential promoting effects of the in situ generated Fe(V)/Fe(IV) were not considered.

The oxidative transformation of organics by Fe(VI) was also promoted due to acid dosing (Manoli et al., 2017b). Manoli et al. ascribed the enhanced removal of organics by acid-activated Fe(VI) technology to the participation of Fe(V)/Fe(IV), even though no direct evidence was provided for the generation of Fe(V)/Fe(IV) (Manoli et al., 2017b).

5.2.4 Sulfur(IV)-activated Fe(VI) technologies

Fe(VI)-reducing agent system is efficient to generate high-valent iron-oxo intermediates, resulting in the rapid decomposition of organic contaminants. Among various available reductants, sulfur(IV)-based reductants have attracted the greatest interest due to their environmental friendliness (Feng et al., 2018). SO$_4^{2-}$, the final reaction product of the sulfur(IV)-based reductants, can also be accommodated within conventional water treatment processes. Guan et al. (2016) initiated the research on applying S$_2$O$_5^{2-}$ to activate Fe(VI) in 2016, which set off an upsurge of research on sulfur(IV)-Fe(VI) (Zhang et al., 2017; Feng and Sharma, 2018; Sun et al., 2018). Based on the EPR analysis and the quenching experiments, Zhang et al. (2017) ascribed the extraordinarily fast degradation of TrOCs to the formation of the free radicals (i.e., SO$_4^{2-}$, *OH, SO$_4^{+}$, and SO$_2^{*}$) rather than the high-valent iron-oxo intermediates while Sun et al. (2018) indicated that SO$_4^{2-}$ was the dominating ROS in the SO$_3^{2-}$/Fe(VI) system. However, Feng and Sharma proposed the involvement of Fe(V)/Fe(IV) in the rapid oxidation of TMP in the SO$_3^{2-}$/Fe(VI) system although they did not provide direct evidences (Feng and Sharma, 2018).

Recently, Shao et al. (2020) systemically investigated the influence of [SO$_3^{2-}$]$_0$/[Fe(VI)]$_0$ molar ratio on the variation of the dominating ROS in the SO$_3^{2-}$/Fe(VI) system. Interestingly, Fe(V) was identified as the primary active oxidant for the oxidation of contaminants at a [SO$_3^{2-}$]$_0$/[Fe(VI)]$_0$ molar ratio of 0.1–0.3. As the [SO$_3^{2-}$]$_0$/[Fe(VI)]$_0$ molar ratio increased, the contribution of Fe(V) to the abatement of contaminants decreased while SO$_4^{2-}$ and *OH were identified to be the dominant ROS (Shao et al., 2020). Since the reactivity of different ROS to different contaminants is very different, it’s of great importance to control the [SO$_3^{2-}$]$_0$/[Fe(VI)]$_0$ molar ratio within a reasonable range in the real practice considering the properties of the target contaminants and water matrix. It was found that SO$_3^{2-}$ dosed at low concentration was
not effective to activate Fe(VI) but SO$_3^{2-}$ dosed at high concentration would consume the generated active oxidants. Therefore, we further proposed to apply the sparingly soluble CaSO$_3$ instead of Na$_2$SO$_3$ to effectively reduce the negative effect caused by excessive sulfite (Shao et al., 2019). CaSO$_3$ could promote the generation of sparingly soluble CaSO$_3$ instead of Na$_2$SO$_3$ to effectively abate the contaminants. Therefore, we further proposed to apply the Fe(V)/CaSO$_3$ process with Fe(V)/Fe(IV) as the main oxidants, and even some of the refractory contaminants can be efficiently oxidized (Shao et al., 2019). Although the oxidation rate constants of the target contaminants are slightly lower than those in the Fe(VI)/Na$_2$SO$_3$ system, the amount of the target contaminants removed in the Fe(VI)/CaSO$_3$ system is comparable to or higher than that in the Fe(VI)/Na$_2$SO$_3$ system under the same Fe(VI) dose and other reaction conditions. Hence, the Fe(VI)/CaSO$_3$ process with Fe(V)/Fe(IV) as the main reactive oxidants is a promising method to enhance the abatement of contaminants.

\[
\text{HFeVIO}_4 + \text{SO}_3^{2-} \rightarrow \text{HFeVVO}_2 + \text{SO}_4^{2-} + \text{SO}_3^{-} \\
k = 10^3 - 10^4 \text{M}^{-1} \cdot \text{s}^{-1} \quad (14)
\]

\[
\text{SO}_5^{-} + \text{O}_2 \rightarrow \text{SO}_4^{-} \\
k = 1.1 \times 10^9 \text{M}^{-1} \cdot \text{s}^{-1} \quad (15)
\]

\[
\text{SO}_4^{2-} + \text{SO}_3^{2-} \rightarrow \text{SO}_5^{-} + \text{SO}_3^{-} \\
k = 1.0 \times 10^8 \text{M}^{-1} \cdot \text{s}^{-1} \quad (16)
\]

\[
\text{SO}_4^{2-} + \text{SO}_3^{2-} \rightarrow \text{SO}_5^{-} + \text{SO}_3^{-} \\
k = 5.6 \times 10^8 \text{M}^{-1} \cdot \text{s}^{-1} \quad (17)
\]

\[
\text{SO}_4^{2-} + \text{OH}^{-} \rightarrow \text{SO}_5^{-} + \text{HO}^{-} \\
k = 7.3 \times 10^9 \text{M}^{-1} \cdot \text{s}^{-1} \quad (18)
\]

\[
\text{Fe}^{VII}O_4^{2-} + \text{SO}_3^{-} \rightarrow \text{Fe}^{V}O_4^{3-} + \text{SO}_3 \\
k = 1.9 \times 10^8 \text{M}^{-1} \cdot \text{s}^{-1} \quad (19)
\]

\[
\text{Fe}^{V}O_4^{3-} + \text{SO}_3^{-} \rightarrow \text{Fe}^{IV}O_4^{4-} + \text{SO}_3 \\
(20)
\]

### 5.3 Replacement of Fe(VI) with Fe(V)/Fe(IV)

In addition to the introduction of Fe(V)/Fe(IV) through the in situ activation of Fe(VI), applying Fe(V) or Fe(IV) directly instead of Fe(VI) is also a promising option to elevate the removal of contaminants by high-valent iron oxides in some cases. It has been proposed in the last century that aqueous Fe(IV) can be in situ generated from Fe$_{aq}^{2+}$ and O$_3$ in the strongly acidic solution conveniently (Loegager et al., 1992). And the kinetic study of the aqueous Fe(IV) with aromatic substrates carried out in 2002 demonstrated the effectiveness of this method (Mártil et al., 2002). The in situ generated Fe(IV) can degrade the target contaminants in seconds to minutes (Mártil et al., 2002; Pestovsky and Bakac, 2004), which alleviates the negative effects of the self-decay of ferrates. Subsequently, many studies also highlighted the superiority of the in situ generated Fe(IV) species produced by Fe$_{aq}^{2+}$ and some other oxygen-atom donors such as hypochlorous acid (Liang et al., 2020), peroxydisulfate (Wang et al., 2018b), hydrogen peroxide (Bataineh et al., 2012), and peracetic acid (Kim et al., 2019) under certain reaction conditions. The in situ generation of Fe(IV) offers an arena for promoting the abatement of contaminants, however, there are still some limitations. For most of the above methods should be carried out under acidic conditions, their application in the environmentally-relevant conditions is limited. And considering excess Fe$_{aq}^{2+}$ would consume Fe(IV) and thus decrease the overall oxidation capacity of the reaction systems, the doses of the reactants should be strictly controlled.
Besides, special attention should also be payed to the formation of the unwanted byproducts, for the introduced oxygen-atom donors might increase the concentration of the nonselective ROS.

6 Research gaps in applying Fe(VI) for abating contaminants in water in real practice

In sum, Fe(VI) is a versatile water treatment reagent, which integrates various functions such as oxidation, disinfection, and coagulation/adsorption. It can effectively and selectively remove contaminants from water and reduce the environmental risks of the transformation intermediates of contaminants. Despite the great advancement made in the field of Fe(VI) technologies in the past two decades, the application of Fe(VI) in real practice still has several important limitations. Research and development in this area are necessary to overcome or mitigate these limitations and to expand the use of Fe(VI). Based on this review, the key areas for future research are proposed as follows:

1) Development of economical and simple Fe(VI) synthesis method. The available synthesis methods of Fe(VI) at this stage are all time-consuming and uneconomical, which greatly limit the application of Fe(VI). Hence, developing an economical and simple Fe(VI) synthesis method is the pre-requisite for the large-scale application of Fe(VI).

2) Clarifying the self-decay mechanism of Fe(VI). The removal of contaminants by Fe(VI) is closely associated with the stability of Fe(VI) in the water. However, the self-decay mechanism of Fe(VI) under different reaction conditions are controversial. Thus, clarifying the self-decay mechanism of Fe(VI), especially the reasons for the relative high stability of Fe(VI) in the range of pH 9.4–9.7, is of significance for developing the innovative methods to enhance the stability of Fe(VI).

3) Determination of the contribution of Fe(V)/Fe(IV) and the reactivities of ferrates toward various organic contaminants. Our recent study revealed that methyl phenyl sulfoxide (PMSO) was mainly degraded by Fe(IV) and Fe(V) rather than by Fe(VI) per se and Fe(V) played a dominant role when PMSO was degraded by Fe(VI) (Zhu et al., 2020). The contributions of Fe(IV) and Fe(V) were previously underemphasized, and Fe(VI) was less reactive toward organic contaminants than what we expected. Considering that Fe(VI), Fe(V), and Fe(IV) are selective oxidants, the contributions of Fe(V) and Fe(IV) on the degradation of TrOCs by Fe(VI) vary with the properties of TrOCs, so it’s worthwhile to further investigate the relationship between the contributions of Fe(V) and Fe(IV) and the properties of TrOCs. Moreover, the reaction rate constants for the reactions of Fe(VI)/Fe(IV) with various organic contaminants should be determined to better understand the mechanisms of organic contaminants by Fe(VI).

4) Establishment of the quantitative structure-activity relationship models. Currently, only a limited number of typical compounds are selected as the target contaminants in the studies regarding the abatement of organic contaminants by ferrates. Since the organic contaminants in the realistic water generally possess complex structures, those published studies seem to be not representative, and it’s difficult for engineers to accurately assess the feasibility of Fe(VI) technologies in the real practice based on the existing information. Considering ferrates exhibit different reactivity to TrOCs with different structures, establishing quantitative structure-activity relationship models might be a promising method. Because they not only provide new insights into the mechanism for the reactions of ferrates with different kinds of TrOCs but also provide the basis for the selection of the appropriate Fe(VI) activation methods in the real practice.

5) The potential environmental risks associated with the coexisting components. The performance of Fe(VI) is susceptible to the coexisting components in the water, and the generation of the undesired byproducts, especially halogenated byproducts, caused by the coexisting components, has not attracted enough attraction. Thus, it’s necessary to make a thorough inquiry into these issues in the future to figure out the mechanism of the production of the undesired byproducts so as to maximize the oxidation ability of Fe(VI) and decrease the environmental risks associated with the coexisting components. Moreover, the interaction among different kinds of contaminants and the resultant impacts on the generation of the byproducts by Fe(VI) technologies should also be fully considered.

6) Development of the enhanced Fe(VI) technologies. A variety of modified Fe(VI) technologies have been developed to enhance the removal of contaminants by Fe(VI). However, some of the methods have defects in practical operation and materials preparation, some of the methods might increase the environmental risks associated with the transformation intermediates, and the improvement in removing Fe(VI) refractory contaminants by some of the methods is limited. Therefore, the innovative Fe(VI) technologies, which are green, economical, and efficient should be focused on as a hot point.

7) Comprehensive evaluation of the role of the in situ generated iron(III) oxide particles. While most of the studies highlighted the significant role of the in situ generated iron(III) (hydr)oxide particles on elevating the removal of contaminants by coagulation/adsorption, the potential adverse impacts of the (hydr)oxide particles on the turbidity of the water were rarely investigated. And the researches on removing contaminants by Fe(VI) synergistic oxidation coagulation/adsorption are also limited. Consequently, it’s of great importance to make a comprehensive evaluation of the role of the in situ generated iron(III) (hydr)oxide particles so as to provide
more insightful information for Fe(VI) synergistic oxidation coagulation/adsorption.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant No. 21976133) and the National Key Research and Development Program of China (No. 2019YFC1805202).

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

Ashoori N, Teixido M, Spahr S, Lefèvre G H, Sedlak D L, Luthy R G (2019). Evaluation of pilot-scale biochar-amended woodchip bioreactors to remove nitrate, metals, and trace organic contaminants from urban stormwater runoff. Water Research, 154: 1–11
Aslanli H, Nasser S, Nabizadeh R, Meselehgahia A, Alimohammadi M, Nazmara S (2017). Haloacetic acids degradation by an efficient Ferrate/UV process: Byproduct analysis, kinetic study, and application of response surface methodology for modeling and optimization. Journal of Environmental Management, 203: 218–228
Bataineh H, Pestovsky O, Bakac A (2012). pH-induced mechanistic changeover from hydroxyl radicals to iron(IV) in the Fenton reaction. Chemical Science (Cambridge), 3(5): 1594–1599
Carr J D (2008). Kinetics and product identification of oxidation by ferrate(VI) of water and aqueous nitrogen containing solutes. In: ACS Symposium Series: American Chemical Society. Washington DC: American Chemical Society, 189–196 (Ferrates)
Chen B Y, Kuo H W, Sharma V K, Den W (2019a). Chitosan encapsulation of ferrate(VI) for controlled release to water: Mechanistic insights and degradation of organic contaminant. Scientific Reports, 9(1): 18268
Chen G, Lam W W Y, Lo P K, Man W L, Chen L, Lau K C, Lau T C (2018a). Mechanism of water oxidation by ferrate(VI) at pH 7–9. Chemistry: A European Journal, 24(70): 18735–18742
Chen J, Qi Y, Pan X, Wu N, Zuo J, Li C, Qu R, Wang Z, Chen Z (2019b). Mechanistic insights into the reactivity of Ferrate(VI) with phenolic compounds and the formation of coupling products. Water Research, 158: 338–349
Chen J, Xu X, Zeng X, Feng M, Qu R, Wang Z, Nesnas N, Sharma V K (2018b). Ferrate(VI) oxidation of polychlorinated diphenyl sulfides: Kinetics, degradation, and oxidized products. Water Research, 143: 1–9
Conley D J, Pael H W, Howarth R W, Boesch D F, Seitzinger S P, Havens K E, Lancelot C, Likens G E (2009). Controlling eutrophication: Nitrogen and phosphorus. Science, 323(5917): 1014–1015
Czaplicka M, Bratek L, Jaworek K, Bonarski J, Pawlak S (2014). Photo-oxidation of p-arsanilic acid in acidic solutions: Kinetics and the identification of by-products and reaction pathways. Chemical Engineering Journal, 243: 364–371
de Figueiredo D R, Azeiteiro U M, Esteves S M, Gonçalves F J M, Pereira M J (2004). Microcystin-producing blooms: A serious global public health issue. Ecotoxicology and Environmental Safety, 59(2): 151–163
Dedushenko S K, Perfiliev Y D, Sapykin A A (2009). Mössbauer Study of Iron in High Oxidation States in the K–Fe–O System. Berlin: Springer Berlin Heidelberg, 877–882
Deng Y, Wu M, Zhang H, Zheng L, Acosta Y, Hsu T T D (2017). Addressing harmful algal blooms (HABs) impacts with ferrate(VI): Simultaneous removal of algal cells and toxins for drinking water treatment. Chemosphere, 186: 757–761
Dong H, Qiang Z, Lian J, Qu J (2017). Promoted oxidation of diclofenac with ferrate (Fe(VI)): Role of ABTS as the electron shuttle. Journal of Hazardous Materials, 336: 65–70
Dong H, Qiang Z, Liu S, Li J, Yu J, Qu J (2018). Oxidation of iopamidol with ferrate (Fe(VI)): Kinetics and formation of toxic iodinated disinfection by-products. Water Research, 130: 200–207
Fan J, Lin B H, Chang C W, Zhang Y, Lin T F (2018). Evaluation of potassium ferrate as an alternative disinfectant on cyanobacteria inactivation and associated toxin fate in various waters. Water Research, 129: 199–207
Feng M, Cizmas L, Wang Z, Sharma V K (2017a). Activation of ferrate (VI) by ammonia in oxidation of fluomequine: Kinetics, transformation products, and antibacterial activity assessment. Chemical Engineering Journal, 323: 584–591
Feng M, Cizmas L, Wang Z, Sharma V K (2017b). Synergistic effect of aqueous removal of fluoroquinolones by a combined use of peroxymonosulfate and ferrate(VI). Chemosphere, 177: 144–148
Feng M, Jinadatha C, Mcdonald T J, Sharma V K (2018). Accelerated oxidation of organic contaminants by ferrate(VI): The overlooked role of reducing additives. Environmental Science & Technology, 52(19): 11319–11327
Feng M, Sharma V K (2018). Enhanced oxidation of antibiotics by ferrate(VI)-sulfur(VI) system: Elucidating multi-oxidant mechanism. Chemical Engineering Journal, 341: 137–145
Feng M, Wang X, Chen J, Qu R, Sui Y, Cizmas L, Wang Z, Sharma V K (2016). Degradation of fluoroquinolone antibiotics by ferrate(VI): Effects of water constituents and oxidized products. Water Research, 103: 48–57
Ghernaout D, Naceur M W (2012). Ferrate(VI): In situ generation with ferrate (VI) ion (FeO42−): Kinetics, degradation of organic compounds and the formation of coupling products. Water Research, 158: 338–349
Goff H, Murmann R K (1971). Mechanism of isotopic oxygen exchange and reduction of ferrate (VI) ion (FeO42−). Journal of the American Chemical Society, 93(23): 6058–6065
Gong T, Zhang X (2013). Determination of iodide, iodate and organo-iodine in waters with a new total organic iodine measurement method. Chemosphere, 186: 757–761
Goodwill J E, Mai X, Jiang Y, Reckhow D A, Tobiason J E (2016). Oxidation of manganese(II) with ferrate: Stoichiometry, kinetics, products and impact of organic carbon. Chemosphere, 159: 457–464
Guan X, Dong H, Wang H, Fan W, Qiao J (2016). A method for rapid removal of organic pollutants from water by intermediate iron.
Lee Y, Zimmermann S G, Kieu A T, von Gunten U (2009). Ferrate (Fe(VI)) application for municipal wastewater treatment: A novel process for simultaneous micropollutant oxidation and phosphate removal. Environmental Science & Technology, 43(10): 3831–3838
Li C, Li X Z, Graham N, Gao N Y (2008). The aqueous degradation of bisphenol A and steroid estrogens by ferrate. Water Research, 42(1–2): 109–120
Liang S, Zhu L, Duan W, Yang P T, Wang S L, Wei C, Liu C, Feng C (2020). Fe2+/HClO reaction produces Fe(IV)O2+: An enhanced advanced oxidation process. Environmental Science & Technology, 54(10): 6406–6414
Liu H, Chen J, Wu N, Xu X, Qi Y, Jiang L, Wang X, Wang Z (2019). Oxidative degradation of chlorpyrifos using ferrate(VI): Kinetics and reaction mechanism. Ecotoxicoology and Environmental Safety, 170: 259–266
Liu J, Lujan H, Dhungana B, Hockaday W C, Sayes C M, Cobb G P, Sharma V K (2020). Ferrate(VI) pretreatment before disinfection: An effective approach to controlling unsaturated and aromatic halo-disinfection byproducts in chlorinated and chloraminated drinking waters. Environment International, 138: 105641
Liu Y, Wang L, Wang X, Huang Z, Xu C, Yang T, Zhao X, Qi J, Ma J (2017). Highly efficient removal of trace thallium from contaminated source waters with ferrate: Role of in situ formed ferric nanoparticle. Water Research, 124: 149–157
Loeb S K, Alvarez P J J, Brame J A, Cates E L, Choi W, Crittenjen D, Dionysiou D D, Li Q, Li-Puma G, Quan X, Sedlak D L, David Waite T, Westerhoff P, Kim J H (2019). The technology horizon for photocatalytic water treatment: Sunrise or sunset? Environmental Science & Technology, 53(6): 2937–2947
Loegager T, Holcman J, Sehested K, Pedersen T (1992). Oxidation of ferric ions by ozone in acidic solutions. Inorganic Chemistry, 31(17): 3523–3529
Luo C, Feng M, Sharma V K, Huang C H (2019). Oxidation of pharmaceuticals by ferrate(VI) in hydrolyzed urine: Effect of major inorganic constituents. Environmental Science & Technology, 53(9): 5272–5281
Luo C, Feng M, Sharma V K, Huang C H (2020). Revelation of ferrate(VI) unimolecular decay under alkaline conditions: Investigation of involvement of Fe(IV) and Fe(V) species. Chemical Engineering Journal, 388: 124134
Ma J, Liu W (2002). Effectiveness and mechanism of potassium ferrate(VI) preoxidation for algae removal by coagulation. Water Research, 36(4): 871–878
Ma L, Lam W W, Lo P K, Lau K C, Lau T C (2016). Ca2+-induced oxygen generation by FeO2− at pH 9–10. Angewandte Chemie International Edition in English, 55(9): 3012–3016
Ma Y, Gao N, Li C (2012). Degradation and pathway of tetracycline hydrochloride in aqueous solution by potassium ferrate. Environmental Engineering Science, 29(5): 357–362
Máčová Z, Bouzek K, Hives J, Sharma V K, Terryn R J, Baum J C (2009). Research progress in the electrochemical synthesis of ferrate (VI). Electrochimica Acta, 54(10): 2673–2683
Manoli K, Maffettone R, Sharma V K, Santoro D, Ray A K, Passalacqua K D, Carnahan K E, Wobus C E, Sarathy S (2020). Inactivation of murine norovirus and fecal coliforms by ferrate(VI) in secondary effluent wastewater. Environmental Science & Technology, 54(3): 1878–1888
Manoli K, Nakhla G, Feng M, Sharma V K, Ray A K (2017a). Silica gel-enhanced oxidation of caffeine by ferrate(VI). Chemical Engineering Journal, 330: 987–994
Manoli K, Nakhla G, Ray A K, Sharma V K (2017b). Enhanced oxidative transformation of organic contaminants by activation of ferrate(VI): Possible involvement of Fe3+/Fe4+ species. Chemical Engineering Journal, 307: 513–517
Mártire D O, Caregnato P, Furlong J, Allegretti P, Gonzalez M C (2002). Kinetic study of the reactions of oxoiron(IV) with aromatic substrates in aqueous solutions. International Journal of Chemical Kinetics, 34(8): 488–494
Moussavi G, Pourakbar M, Aghayani E, Mahdavianpour M (2018). Investigating the aerated UV/P(Co) process simultaneously generating hydroxyl and sulfate radicals for the oxidation of cyanide in aqueous solution and industrial wastewater. Chemical Engineering Journal, 350: 673–680
Mura S, Malfatti L, Greppi L, Innocenzi P (2017). Ferrates for water remediation. Reviews in Environmental Science and Biotechnology, 16(1): 15–35
Novak P, Kolar M, Machala L, Siskova K M, Karlicky F, Petr M, Zboril R (2018). Transformations of ferrates(IV,V,VI) in liquids: Mossbauer spectroscopy of frozen solutions. Physical Chemistry Chemical Physics, 20(48): 30247–30256
Pestovsky O, Bakac A (2004). Reactivity of aqueous Fe(IV) in hydride and hydrogen atom transfer reactions. Journal of the American Chemical Society, 126(42): 13757–13764
Pestovsky O, Bakac A (2006). Aqueous ferryl (IV) ion: Kinetics of oxygen atom transfer to substrates and oxo exchange with solvent water. Inorganic Chemistry, 45(2): 814–820
Prucek R, Tucek J, Kolarik J, Huskova I, Filip J, Varma R S, Sharma V K, Zboril R (2015). Ferrate(VI)-prompted removal of metals in aqueous media: Mechanistic delineation of enhanced efficiency via metal entrenchment in magnetic oxides. Environmental Science & Technology, 49(4): 2319–2327
Rai P K, Lee J, Kailasa S K, Kwon E E, Tsang Y F, Ok Y S, Kim K H (2018). A critical review of ferrate(VI)-based remediation of soil and groundwater. Environmental Research, 160: 420–448
Rojas S, Horcajada P (2020). Metal–organic frameworks for the removal of emerging organic contaminants in water. Chemical Reviews, 120(16): 8378–8415
Rush J D, Bielski B H J (1989). Kinetics of ferrate(V) decay in aqueous solution: A pulse-radiolysis study. Inorganic Chemistry, 28(21): 3947–3951
Rush J D, Zhao Z, Bielski B H J (1996). Reaction of ferrate(VI)/ferrate (V) with hydrogen peroxide and superoxide anion: A stopped-flow and premix pulse radiolysis study. Free Radical Research, 24(3): 187–198
Sarma R, Angeles-Boza A M, Brinkley D W, Roth J P (2012). Studies of the di-iron(VI) intermediate in ferrate-dependent oxygen evolution from water. Journal of the American Chemical Society, 134(37): 15371–15386
Schink T, Waite T D (1980). Inactivation of λ virus with ferrate(VI). Water Research, 14(12): 1705–1717
Schmidbaur H (2018). The history and the current revival of the oxo chemistry of iron in its highest oxidation states Fe\textsuperscript{VI}–Fe\textsuperscript{VIII}. Journal of Inorganic and General Chemistry, 644: 536–559

Seung-Mok L, Diwakar T (2009). Application of ferrate(VI) in the treatment of industrial wastes containing metal-complexed cyanides: A green treatment. Journal of Environmental Sciences-China, 21(10): 1347–1352

Shao B, Dong H, Feng L, Qiao J, Guan X (2020). In Seung-Mok L, Diwakar T (2009). Application of ferrate(VI) in the treatment of industrial wastes containing metal-complexed cyanides: A green treatment. Journal of Environmental Sciences-China, 21(10): 1347–1352

Sharma V K (2007). Disinfection performance of Fe(VI) in water and wastewater: A review. Water Science and Technology, 55(1–2): 225–232

Sharma V K (2010). Oxidation of inorganic compounds by ferrate (VI) and ferrate (V): One-electron and two-electron transfer steps. Environmental Science & Technology, 44(13): 5148–5152

Sharma V K (2011). Oxidation of inorganic contaminants by ferrates (VI, V, and IV)–kinetics and mechanisms: A review. Journal of Environmental Management, 92(4): 1051–1073

Sharma V K (2013). Ferrate(VI) and ferrate(V) oxidation of organic compounds: Kinetics and mechanism. Coordination Chemistry Reviews, 257(2): 495–510

Sharma V K, Burnett C R, Millero F J (2001a). Dissociation constants of the monoprotic ferrate(VI) ion in NaCl media. Physical Chemistry Chemical Physics, 3(11): 2059–2062

Sharma V K, Burnett C R, O’connor D B, Cabelli D (2002). Iron(VI) and iron(V) oxidation of thiocyanate. Environmental Science & Technology, 36(19): 4182–4186

Sharma V K, Burnett C R, Rivera W, Joshi V N (2001b). Heterogeneous photocatalytic reduction of ferrate(VI) in UV-irradiated titania suspensions. Langmuir, 17(15): 4598–4601

Sharma V K, Burnett C R, Yngard R A, Cabelli D E (2005). Iron(VI) and iron(V) oxidation of copper(I) cyanide. Environmental Science & Technology, 39(10): 3849–3854

Sharma V K, Cabelli D (2009). Reduction of oxyiron(V) by sulfite and thiosulfate in aqueous solution. Journal of Physical Chemistry A, 113 (31): 8901–8906

Sharma V K, Chen L, Zboril R (2016). Review on high valent FeV\textit{i} (ferrate): A sustainable green oxidant in organic chemistry and transformation of pharmaceuticals. ACS Sustainable Chemistry & Engineering, 4(1): 18–34

Sharma V K, Dutta P K, Ray A K (2007). Review of kinetics of chemical and photocatalytical oxidation of arsenic(III) as influenced by pH. Journal of Environmental Science and Health Part A-Toxic/hazardous Substances & Environmental Engineering, 42(7): 997–1004

Sharma V K, Luther G W, Millero F J (2011). Mechanisms of oxidation of organosulfur compounds by ferrate(VI). Chemosphere, 82(8): 1083–1089

Sharma V K, Mishra S K, Nesnas N (2006a). Oxidation of sulfonamide antimicrobials by ferrate(VI). Environmental Science & Technology, 40(23): 7222–7227 (Fe\textit{VI}O\textit{V}O\textit{IV})

Sharma V K, Mishra S K, Ray A K (2006b). Kinetic assessment of the potassium ferrate(VI) oxidation of antibacterial drug sulfamethoxazole. Chemosphere, 62(1): 128–134

Sharma V K, Rivera W, Smith J O, O’brien B (1998). Ferrate(VI) oxidation of aqueous cyanide. Environmental Science & Technology, 32(17): 2608–2613

Sharma V K, Smith J O, Millero F J (1997). Ferrate(VI) oxidation of hydrogen sulfide. Environmental Science & Technology, 31(9): 2486–2491

Sharma V K, Zboril R, Varma R S (2015). Ferrates: Greener oxidants with multimodal action in water treatment technologies. Accounts of Chemical Research, 48(2): 182–191

Shin J, von Gunten U, Reckhow D A, Allard S, Lee Y (2018). Reactions of ferrate(VI) with iodide and hypoiodous acid: Kinetics, pathways, and implications for the fate of iodine during water treatment. Environmental Science & Technology, 52(13): 7458–7467

Sun S, Jiang J, Qiu L, Pang S, Li J, Liu C, Wang L, Xue M, Ma J (2019). Activation of ferrate by carbon nanotube for enhanced degradation of bromophenols: Kinetics, products, and involvement of Fe(V)/Fe(IV). Water Research, 156: 1–8

Sun S, Pang S, Jiang J, Ma J, Huang Z, Zhang J, Liu Y, Xuc L, Liu Q, Yuan Y (2018). The combination of ferrate(VI) and sulfite as a novel advanced oxidation process for enhanced degradation of organic contaminants. Chemical Engineering Journal, 333: 11–19

Talaiekhohzani A, Talaei M R, Rezania S (2017). An overview on production and application of ferrate(VI) for chemical oxidation, coagulation and disinfection of water and wastewater. Journal of Environmental Chemical Engineering, 5(2): 1828–1842

Thompson G W, Ockerman L T, Schreyer J M (1951). Preparation and purification of potassium ferrate(VI). Journal of the American Chemical Society, 73(3): 1379–1381

Tian S Q, Wang L, Liu Y L, Ma J (2020). Degradation of organic pollutants by ferrate/biochar: Enhanced formation of strong intermediate oxidative iron species. Water Research, 183: 116054

Tran N H, Reinhard M, Gin K Y H (2018). Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions: A review. Water Research, 133: 182–207

von Gunten U (2018). Oxidation processes in water treatment: Are we on track? Environmental Science & Technology, 52(9): 5062–5075

Wang H L, Liu S Q, Zhang X Y (2009). Preparation and application of sustained release microcapsules of potassium ferrate(VI) for dinitrobutyl phenol (DNBP) wastewater treatment. Journal of Hazardous Materials, 169(1–3): 448–453

Wang X, Liu Y, Huang Z, Wang L, Wang Y, Li Y, Li J, Qi J, Ma J (2018a). Rapid oxidation of iodide and hypoiodous acid with ferrate and no formation of iodoform and monoiodoacetic acid in the ferrate/HA system. Water Research, 144: 592–602

Wang X S, Liu Y L, Xu S Y, Zhang J, Li J, Song H, Zhang Z X, Wang L, Ma J (2020). Ferrate oxidation of phenolic compounds in iodine-containing water: Control of iodinated aromatic products. Environmental Science & Technology, 54(3): 1827–1836

Wang Z, Jiang J, Pang S, Zhou Y, Guan C, Gao Y, Li J, Yang Y, Qiu W, Jiang C (2018b). Is sulfate radical really generated from peroxydi-
sulfate activated by iron(II) for environmental decontamination? Environmental Science & Technology, 52(19): 11276–11284
Wang Z P, Huang L Z, Feng X N, Xie P C, Liu Z Z (2010). Removal of phosphorus in municipal landfill leachate by photochemical oxidation combined with ferrate pre-treatment. Desalination and Water Treatment, 22(1–3): 111–116
Wu S, Liu H, Lin Y, Yang C, Lou W, Sun J, Du C, Zhang D, Nie L, Yin K, Zhong Y (2020). Insights into mechanisms of UV/ferrate oxidation for degradation of phenolic pollutants: Role of superoxide radicals. Chemosphere, 244: 125490
Xie X, Cheng H (2019). A simple treatment method for phenylarsenic compounds: Oxidation by ferrate(VI) and simultaneous removal of the arsenate released with in situ formed Fe(III) oxide-hydroxide. Environment International, 127: 730–741
Xing H, Yuan B, Wang Y, Qu J (2002). Photocatalytic detoxification of microcystins combined with ferrate pretreatment. Journal of Environmental Science and Health Part A-Toxic/hazardous Substances & Environmental Engineering, 37(4): 641–649
Yan X, Sun J, Kenjiahan A, Dai X, Ni B J, Yuan Z (2020). Rapid and strong biocidal effect of ferrate on sulfidogenic and methanogenic sewer biofilms. Water Research, 169: 115208
Yang B, Ying G G, Chen Z F, Zhao J L, Peng F Q, Chen X W (2014). Ferrate(VI) oxidation of tetrabromobisphenol A in comparison with bisphenol A. Water Research, 62: 211–219
Yang B, Ying G G, Zhang L J, Zhou L J, Liu S, Fang Y X (2011). Kinetics modeling and reaction mechanism of ferrate(VI) oxidation of benzo triazoles. Water Research, 45(6): 2261–2269
Yang B, Ying G G, Zhao J L, Liu S, Zhou L J, Chen F (2012). Removal of selected endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) during ferrate(VI) treatment of secondary wastewater effluents. Water Research, 46 (7): 2194–2204
Yang S, Doong R (2008). Preparation of potassium ferrate for the degradation of tetracycline. In: ACS Symposium Series: American Chemical Society. Washington, DC: ACS Publications, 404–419 (Ferrates)
Yang T, Liu Y, Wang L, Jiang J, Huang Z, Pang S Y, Cheng H, Gao D, Ma J (2018a). Highly effective oxidation of roxarsone by ferrate and simultaneous arsenic removal with in situ formed ferric nanoparticles. Water Research, 147: 321–330
Yang T, Wang L, Liu Y, Jiang J, Huang Z, Pang S Y, Cheng H, Gao D, Ma J (2018b). Removal of organoarsenic with ferrate and ferrate resultant nanoparticles: Oxidation and adsorption. Environmental Science & Technology, 52(22): 13325–13335
Yngard R, Damrongsiiri S, Osathaphan K, Sharma V K (2007). Ferrate (VI) oxidation of zinc-cyanide complex. Chemosphere, 69(5): 729–735
Yngard R A, Sharma V K, Filip J, Zboril R (2008). Ferrate(VI) oxidation of weak-acid dissociable cyanides. Environmental Science & Technology, 42(8): 3005–3010
Yuan B, Ye M, Lan H (2008b). Preparation and properties of encapsulated potassium ferrate for oxidative remediation of trichloroethylene contaminated groundwater. In: ACS Symposium Series: American Chemical Society. Washington, DC: ACS Publications, 378–388 (Ferrates)Yuan B L, Li X Z, Graham N (2008a). Aqueous oxidation of dimethyl phthalate in a Fe(VI)-TiO2-UV reaction system. Water Research, 42(6–7): 1413–1420
Zhang J, Zhu L, Shi Z, Gao Y (2017). Rapid removal of organic pollutants by activation sulfite with ferrate. Chemosphere, 186: 576–579
Zhang M S, Xu B, Wang Z, Zhang T Y, Gao N Y (2016). Formation of iodinated trihalomethanes after ferrate pre-oxidation during chlorination and chloramination of iodide-containing water. Journal of the Taiwan Institute of Chemical Engineers, 60: 453–459
Zhu J, Yu F, Meng J, Shao B, Dong H, Chu W, Cao T, Wei G, Wang H, Guan X (2020). Overlooked role of Fe(IV) and Fe(V) during organic contaminants oxidation by Fe(VI). Environmental Science & Technology, 54(15): 9702–9710
Zimmermann S G, Schmukat A, Schulz M, Benner J, Gunten U, Ternes T A (2012). Kinetic and mechanistic investigations of the oxidation of tramadol by ferrate and ozone. Environmental Science & Technology, 46(2): 876–884

Dr Xiaohong Guan is a professor of Municipal Engineering at Tongji University, China. She obtained her Ph.D. from Hong Kong University of Science and Technology in Environmental Engineering, China. Prof. Guan also holds B.S. and M.S. degrees from Tongji University in Environmental Engineering. Research and educational activities in her Lab at Tongji University are focused on novel physical and chemical processes for water pollution control, with an emphasis on developing technologies for heavy metals and emerging organic contaminants removal. She is a recipient of the 2015 NSFC Outstanding Youth Foundation and the Second prize of Natural Sciences of Ministry of Education of China. She had been invited to talk at Gordon Conference because of the originality of her research. Now she serves as the associate editors of Water Research and Journal of Hazardous Materials.