



## Commentary

## Water decontamination by reactive high-valent iron species

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The occurrence of emerging organic contaminants (EOCs) in water bodies has received increasing attention worldwide. EOCs, such as pharmaceuticals and pesticides, when present in trace concentrations, cannot be effectively removed by conventionally designed treatment processes in most wastewater treatment plants. Therefore, advanced oxidation processes (AOPs) have been developed as promising alternatives for trace-level EOC elimination using radicals (e.g., hydroxyl radicals and sulfate radicals) and non-radical pathways. However, these reactive species are generally nonselective and also exhibit excellent reactivity with background water constituents, leading to excess consumption of oxidants and the possible generation of toxic secondary pollutants [1]. Accordingly, selective oxidants have recently become a subject of considerable interest, mainly including singlet oxygen and high-valent metal species [2]. They could preferentially attack electron-rich moieties, resulting in selective degradation of EOCs. Reactive high-valent iron species include ferrate [Fe(VI)], Fe(IV), and Fe(V), and are often referred to as active ferrate species. They possess attractive chemical properties and have raised renewed interest in iron-based catalytic AOPs to remove EOCs in practical water decontamination. Fe(IV)/Fe(V) species mainly exist as  $\text{Fe}^{\text{V}}\text{O}_4^{3-}$  and  $\text{Fe}^{\text{IV}}\text{O}_4^{4-}$  or  $\text{Fe}^{\text{IV}}\text{O}_3^{2-}$ , and can be generated from Fe(VI) (ferrate,  $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ ). Fe(VI) is capable of simultaneously inducing coagulation, adsorption, oxidation, and disinfection in water decontamination. These unique properties can be explained by the fact that: (1) when oxidizing EOCs, Fe(VI) can be reduced to Fe(III) oxides/hydroxides that act as coagulants, (2) the generated  $\gamma$ -FeOOH and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> with core-shell structures can adsorb EOCs in water, (3) Fe(IV) and Fe(V) species with significantly higher reactivity and selectivity (2–6 orders of magnitude more reactive) compared with Fe(VI) [3] are generated, which greatly enhances EOCs oxidation, and (4) Fe(VI) can inactivate or kill many microorganisms, such as *Escherichia coli*, murine norovirus and methicillin-resistant *Staphylococcus aureus* without disinfection by-products.

Compared with typical radicals such as  $\cdot\text{OH}$  or  $\text{SO}_4^{\cdot-}$ , despite their lower oxidizing ability, Fe(IV) and Fe(V) species mediate EOC oxidation through various reaction channels (oxygen atom, hydrogen atom, hydride, electrophilic addition, and electron transfer) at a relatively low rate [4], and are more durable and longer-lived (Table S1). That is, they have

higher steady-state concentrations and, therefore, exhibit similar pseudo-first-order rate constants to  $\cdot\text{OH}$  or  $\text{SO}_4^{\cdot-}$  for EOC oxidation [5]. Additionally, Fe(IV) and Fe(V) show an extremely strong selectivity toward EOCs under neutral or near-neutral conditions, making them highly resistant to interference from water matrix constituents [6]. However, the majority of generated Fe(IV) and Fe(V) species undergo self-decay, and Fe(IV) species can react with  $\text{H}^+$  to generate Fe(II) under acidic conditions ( $k = 0.1 \text{ s}^{-1}$  at pH 1.0) [7]. This leads to the generation of Fe(II) and Fe(III) species rather than EOC oxidation, resulting in an underutilization of high-valent iron-oxo intermediates [8]. Thus, how to optimize the production, stability, and oxidation ability of Fe(IV) and Fe(V) species for water decontamination is a promising research direction.

### 1. Generation of Fe(IV)/Fe(V) species

Fe(IV)/Fe(V) species can be produced by direct synthesis of Fe(IV) or Fe(V) salts, ferrate Fe(VI) decomposition or reduction, and Fe(II) or Fe(III) oxidation. The synthesis of Fe(IV)/Fe(V) salts (e.g.,  $\text{K}_3\text{FeO}_4$ ,  $\text{Na}_4\text{FeO}_4$ ) was reported using a thermal method as early as the 1950s [9], but few attempts have been made since then due to the high energy consumption and instability of products. The formed Fe(IV) and Fe(V) salts readily decompose to produce Fe(III), making it difficult to produce, store, and transport Fe(IV)/Fe(V) salts, further limiting practical applications.

In recent decades, it has been reported that Fe(IV) and Fe(V) species can be obtained through the decomposition or reduction of Fe(VI) via the addition of metal ions (e.g.,  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ), acids (e.g., HCl), carbonaceous materials (e.g., carbon nanotubes) and reductants (e.g.,  $\text{SO}_3^{2-}$ ) [10]. In detail, the addition of acids induces the formation of Fe(VI) protonated species (i.e.,  $\text{HFe}^{\text{VI}}\text{O}_4^-$ ), which decompose via the formation of  $\text{Fe}^{\text{VI}}_2\text{O}_7^{2-}$  followed by O–O coupling to produce  $\text{Fe}^{\text{IV}}_2\text{O}_6$  [2–11]. The addition of trace acids generates more reactive Fe(IV) and Fe(V) intermediates, beneficial to the degradation of recalcitrant EOCs. However, the magnitude of the enhancement depends on the rates of competing reactions between Fe(IV)/Fe(V) species and EOCs, as well as their self-decomposition rates, which are closely related to EOC moieties.

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Received 27 July 2023; Received in revised form 6 December 2023; Accepted 11 December 2023

Available online 14 December 2023

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Fe(VI) can also be reduced by some radicals (e.g., hydrated electrons and  $\cdot\text{CH}_2\text{OH}$ ) to produce Fe(V) and be activated by carbonaceous materials to generate Fe(IV) and Fe(V) species, improving EOCs oxidation [10].

The Fe(II)/Fe(III) oxidation may also produce Fe(IV)/Fe(V) species. For example, the Fe(III) oxidation by  $\cdot\text{OH}$  in carbonate, pyrophosphate, and phosphate solutions at pH 10.4 can generate Fe(IV) in the form of Fe(IV) ligands, the lifetime of which varies depending on the ligand coordinated to central Fe [12]. The oxidation of Fe(II) by oxygen-atom donors (e.g.,  $\text{O}_3$ ,  $\text{HClO}$ , and  $\text{Na}_2\text{S}_2\text{O}_8$  [13]) under strongly acidic conditions can also produce Fe(IV). The electrogeneration of Fe(IV) and Fe(V) was recently reported in Fe(III)-assisted electrochemical oxidation [5] or Fe(II)-modified electrochlorination [14] for EOC oxidation.

It should be noted that pH is a crucial influencing factor in the production of Fe(IV) and Fe(V) species via either Fe(VI) reduction or Fe(II)/Fe(III) oxidation. However, its effects vary across different processes and even differ from those observed in the traditional Fenton reaction [15]. In general, the contribution of Fe(IV) decreases significantly with the increase in solution pH. More specifically, approximately 82% of produced Fe(IV) species are available for EOC degradation at pH 1.0 but contribute little at pH 7.5 [16]. Fe(IV) and Fe(V) species can be generated by Fe(VI) reduction under alkaline conditions, whereas their production by Fe(II) oxidation occurs at acidic or near-neutral pH [17]. In addition, the transition metal/iron-based catalysts applied in AOPs stimulate the production of high-valence metal oxide species (Fig. 1a). For example, transition metal salts (e.g.,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  [18] and permanganate [19]), transition metal oxides (e.g.,  $\alpha\text{-Fe}_2\text{O}_3$  [20]), transition metal complexes [e.g.,  $\text{Fe}(\text{dpa})\text{Cl}_2$  [21]], and single-atom catalysts (e.g.,  $\text{Fe}_{\text{SA}}\text{-N-C}$  [22]) can improve the yield of Fe(IV)/Fe(V) species.

Although there are various methods for Fe(IV)/Fe(V), current production methods have the disadvantages of complicated synthesis procedures, harsh operating conditions, and low utilization of active ferrate species due to the addition of reductants or oxidants, potentially introducing secondary undesirable species. These drawbacks limit the practical applications of active Fe(IV)/Fe(V) species. Therefore, it is imperative to develop easily operating, highly efficient, direct, economical, and sustainable production methods for Fe(IV) and Fe(V) species in future studies.

## 2. Detection of Fe(IV)/Fe(V) species

Methyl phenyl sulfoxide (PMSO) is a typical probe compound for detecting and measuring liquid Fe(IV) and Fe(V) since it can be oxidized by Fe(IV)/Fe(V) species to generate methyl phenyl sulfone ( $\text{PMSO}_2$ ) (Fig. S1a) [4]. The existence of Fe(IV) and Fe(V) can be confirmed by measuring PMSO and  $\text{PMSO}_2$  using high-performance liquid chromatography (HPLC) at 194 nm. The PMSO/ $\text{PMSO}_2$  method can only determine whether Fe(IV)/Fe(V) species occur but cannot identify which one is actually present.

In terms of the detection of solid Fe(IV) and Fe(V) species, Mössbauer spectra are commonly used to analyze the valence of iron, including Fe(VI), Fe(V), Fe(IV), Fe(III), and Fe(II) (Fig. S1b) [13]. The *in-situ* absorption spectrometer, consisting of a tungsten lamp emitting powerful light and a highly sensitive detector ( $\sim\text{ms}$ ), can record changes in iron species. Additionally, density-functional theory (DFT) calculations assist in determining the first favorable reaction step between Fe(VI) and reductants by calculating the activation energy and Gibbs free energy to determine the Fe(IV) or Fe(V) formation (Fig. S1c and S1d) [23]. In summary, detection methods have progressed due to advancements in materials sciences and characterization techniques. However, it is still ambiguous to detect Fe(IV) and Fe(V) separately, let alone quantify their individual concentrations, which warrants further investigation.

## 3. Roles of Fe(IV)/Fe(V) species in water decontamination

Fe(V) was reported to be a selective oxidant in spite of limited data, and exhibits greater reactivity than Fe(IV). Taking the oxidation of amino acids as an example, Fe(V) preferentially attacks the side chain via two-electron transfer, whereas  $\cdot\text{OH}$ , a major reactive oxygen species in AOPs, reacts by addition to the ring of the organic molecule [24]. The decontamination kinetics and performance of Fe(V) were reported to depend on pH and the nature of EOC molecules (e.g., structure and protonation equilibrium), and those for Fe(IV) species are affected by pH and co-existing metal ions [12]. Niu et al. found that Fe(IV)/Fe(V) species did not alter the oxidation mechanisms of EOCs, but enhanced the degradation

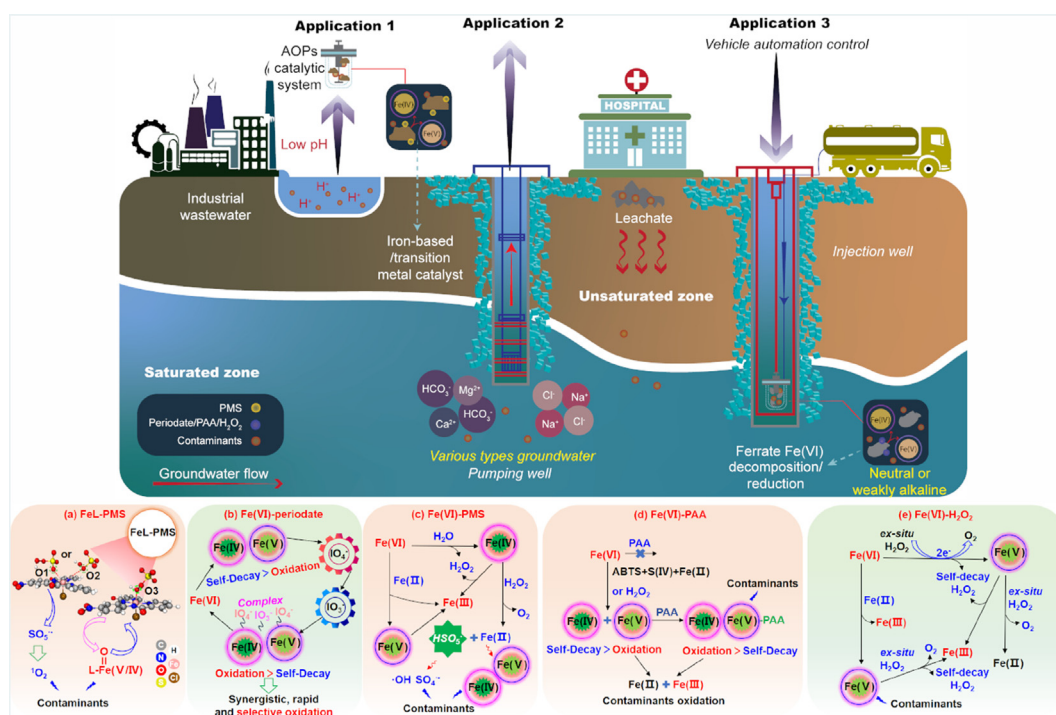


Fig. 1. Generation mechanisms of Fe(IV) and Fe(V) species in transition metal-based catalyst-induced AOPs system (a) [21]; and in typical Fe(VI) decomposition/reduction systems: Fe(VI)-periodate system (b) [25], Fe(VI)-PMS system (c) [26], Fe(VI)-PAA system (d) [4], and Fe(VI)- $\text{H}_2\text{O}_2$  system (e) [23].

rate [25]. Cheng et al. claimed that  $\text{Fe}^{\text{IV}}=\text{O}$  species promoted the oxidizing ability, pH tolerance, as well as stability of a single-atom Fe–N–C activated PMS system for water decontamination [22]. Overall, water decontamination studies using Fe(IV)/Fe(V) species are currently limited, and the few existing articles generally identify the significant roles of Fe(IV)/Fe(V) species in EOC oxidation without exploring the oxidation mechanisms. It is desirable that future studies conduct thorough investigations on the interaction of Fe(IV)/Fe(V) species with EOCs.

#### 4. Synergistic oxidation by Fe(IV)/Fe(V) species combined with other processes

Synergistic oxidation involving Fe(IV)/Fe(V) species together with other processes is generally achieved by Fe(VI)-based AOPs, such as Fe(VI)- $\text{H}_2\text{O}_2$  system, Fe(VI)-peroxymonosulfate (PMS) system, Fe(VI)-periodate system, and Fe(VI)-peracetic acid (PAA) system, where Fe(IV)/Fe(V) species work together with other radicals and oxidants in EOCs removal. It should be noted that oxidants play different roles in Fe(VI)-based systems. For example,  $\text{H}_2\text{O}_2$  and PMS act as activators of Fe(VI), while PAA works as a stabilizer of Fe(IV)/Fe(V) species. Niu et al. first reported the synergistic, rapid, and selective oxidation ability of periodate/iodate-modulated Fe(IV)/Fe(V) intermediates toward multiple EOCs (Fig. 1b) [25]. They demonstrated that Fe(IV)/Fe(V) species were the main oxidants rather than various radicals or singlet oxygen, and periodate/iodate was not behaving as the activators due to their low reactivity with Fe(VI) (only  $0.82 \text{ M}^{-1} \text{ s}^{-1}$ ) but rather as Fe(IV)/Fe(V) ligands. PMS is considered an effective oxidizer and activator of Fe(VI). The Fe(VI)-PMS system was found to be highly efficient for sulfamethoxazole degradation, and Fe(IV)/Fe(V) species contributed to 49.7% of the degradation (Fig. 1c) [26]. The application of the Fe(VI)-PAA system resulted in much faster degradation of EOCs compared to Fe(VI) or PAA used separately. Fe(IV) and Fe(V) intermediates were predominant reactive species, while organic radicals [e.g.,  $\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$  or  $\text{CH}_3\text{C}(\text{O})\text{O}^\bullet$ ] made little contribution (Fig. 1d) [4]. Recently, the promoting effect of  $\text{H}_2\text{O}_2$  received attention for EOC oxidation. The Fe(VI)- $\text{H}_2\text{O}_2$  system provided superior oxidation compared with the sole use of Fe(VI), presumably due to the catalytic role of  $\text{H}_2\text{O}_2$  (*in-situ* or *ex-situ*), facilitating the generation of Fe(IV)/Fe(V) species. In addition,  $\text{O}_2^{\bullet-}$  and  $\bullet\text{OH}$  that are often involved in EOC degradation were excluded in Fe(VI) and Fe(VI)- $\text{H}_2\text{O}_2$  systems (Fig. 1e) [23]. The contribution of produced Fe(IV)/Fe(V) species varies in different systems, and is affected by factors such as the nature of EOCs, oxidants, and reaction conditions. The universal rules or primary influencing factors are obscure at the current stage of research.

#### 5. Environmental implications

Owing to their high oxidation potential and selectivity toward recalcitrant EOCs, reactive high-valent iron species, especially Fe(IV) and Fe(V), have intriguing potential in practical water decontamination, such as wastewater treatment, water purification as well as groundwater remediation. They can be applied as single or multiple AOPs and incorporated into existing remediation techniques, such as permeable reactive barriers and *in-situ* chemical oxidation for groundwater remediation. Unfortunately, current studies have largely been conducted on single AOPs at a laboratory scale, resulting in findings that are still far from practical application. A critical obstacle for the practical applications of Fe(IV)/Fe(V) is the intricacies of production methods. Consequently, the controllable generation in AOPs should be a priority for future research to find a viable solution. Although a few studies have reported on the superior oxidation performance of Fe(IV)/Fe(V) intermediates toward EOCs and their high resistance to complex water matrices, the direct evidence for the formation or involvement of such species is greatly missing. This discrepancy can be attributed to deficient analytical tools, theoretical calculations, and modeling. Therefore, the development and application of new analytical techniques and calculation methods are a

top priority for mechanism investigation and reactivity tuning of ferrates for water decontamination. The production of undesirable byproducts in the presence of water matrices and resulting risks after treatment are also largely neglected and should be evaluated in practical applications.

#### Author contributions

Y.H.Z.: conceptualization, writing–original draft; L.S.: writing–review & editing; W.B.W.: conceptualization, writing–review & editing.

#### Declaration of competing interests

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 article.

#### Acknowledgments

This study is supported by the Shanghai Sailing Program (21YF1449200), Fundamental Research Funds for the Central Universities (22120210534), National Natural Science Foundation of China (42177386) and National Key Research and Development Program of China (2020YFC1808200).

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eehl.2023.12.002>.

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