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Metal ion-induced enhanced oxidation of organic contaminants by ferrate: a review

Christopher V. Marbaniang¹ · Krishnamoorthy Sathiyam¹ · Thomas J. McDonald¹ · Eric Lichtfouse²  · Poulami Mukherjee¹ · Virender K. Sharma¹ 

Abstract

The global contamination of water resources by organic contaminants such as pharmaceuticals and pesticides is calling for advanced remediation techniques, yet conventional water treatments are incomplete or generate toxic byproducts such as chlorinated compounds. As a consequence, safer methods such as treatment with ferrate are needed. Here, we review the utilization of ferrate(VI), the tetraoxy anion FeO_4^{2-} , with emphasis on synthesis and activation of ferrate. Ferrate synthesis is done by wet, thermal, and electrochemical processes. An increase in the oxidation capacity can be obtained by activation of ferrate(VI), which generates highly reactive high-valent iron species such as iron(V) and iron(IV) species. We present activation of ferrate(VI) by iron(III), copper(II), and colloidal Mn(IV), which are present in natural minerals. We compare various ferrate(VI)–metal ion systems to reveal the most effective systems to remove organic contaminants from contaminated water.

Keywords Ferrate · High-valent iron · Kinetics · Pharmaceuticals · Removal · Mechanisms

Abbreviations

MNV	Murine norovirus
QB	Qubevirus durum
ATL	Atenolol
CAF	Caffeine
ACE	Artificial sweetener
SET	Single-electron transfer
OAT	Oxygen-atom transfer
PMSO	Methyl phenyl sulfoxide
PMSO ₂	Methyl phenyl sulfone
EWT	Emergency water treatment
SMX	Sulfamethoxazole
CBZ	Carbamazepine
DCF	Diclofenac

SIZ	Sulfisoxazole
GCE	Glassy carbon electrode

Introduction

One of the human rights includes water, but a significant population of many countries lacks safe drinking water (Everard 2019). The contamination in source water is a worldwide concern, which is continuously increasing due to the high use of pesticides to meet the demand for food security, the high consumption of pharmaceuticals and personal care products by the human population, and the increasing industrialization of the society (Hoek van Dijke et al. 2022; Morin-Crini et al. 2022). The effluents from agriculture, health care, and industrial activities contribute to water contamination (Anand et al. 2022; Cizmas et al. 2015; Fan et al. 2021; Kovalakova et al. 2021, 2020). Conventional treatment plants are not made to remove a wide range of contaminants, especially emerging ones, and obtaining safe drinking water is challenging and requires innovative approaches (Hejase et al. 2022; Lim et al. 2022; Von Gunten 2018; Winkler and Van Loosdrecht 2022). Furthermore, treatments like chlorination generate potentially toxic halogenated and nitrogenous byproducts (Dong et al. 2019; Richardson and Ternes 2022; Sharma et al. 2014, 2017b). Iron-based technologies

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have emerged as attractive approaches to address the challenges of currently used treatment processes to achieve water sustainability (Brillas 2022; Garcia et al. 2021; He et al. 2023; Luo et al. 2021a; Parvulescu et al. 2022; Sharma et al. 2017a; Wang et al. 2022).

Iron (Fe) has a range of valence states (0, II, III, IV, V, and VI) (Sharma et al. 2015a, b). Iron in low-valent oxidative forms, such as Fe(0), Fe(II), and Fe(III), has been applied in nanotechnology, medicine, biocatalysis, energy, and environmental remediation (Brillas 2022; El Kateb et al. 2022; Gupta et al. 2022; Hong et al. 2022; Li et al. 2021b). Among the high-valent iron species, Fe(IV) and Fe(V) are implicated in biological oxidation reactions (Sharma 2013a; Soler et al. 2022; Zhang et al. 2021c). Iron in +6 oxidation states (iron(VI)) has been investigated for many decades that have potential applications in super iron batteries, green synthesis, and remediation of contaminants (Sharma et al. 2016). The most studied role of iron(VI) is in the remediation processes (He et al. 2022; Sailo et al. 2017; Sharma et al. 2015a, b; Sharma 2010a, 2011; Sharma et al. 2022; Wang et al. 2021a; Yates et al. 2014; Zhang and Jiang 2022). Here, we review ferrate(VI) with focus on ferrate synthesis, ferrate activation and application to remove organic contaminants.

Ferrate(VI)

Alkali and alkaline salts of tetraoxy anions of iron(VI) ($\text{Fe}^{\text{VI}}\text{O}_4^{2-}$), commonly called ferrates, have been investigated to remove a wide range of contaminants in water and wastewater (El Kateb et al. 2022; He et al. 2023; Liu et al. 2022; Tian et al. 2022; Wu et al. 2022; Zhang and Jiang 2022). Salts of sodium and potassium ferrate(VI) (Na_2FeO_4 and K_2FeO_4) have been used in studying their roles in the remediation of inorganic and organic contaminants. Since 1950, three approaches have been applied to synthesize these salts (Cataldo-Hernández et al. 2018; Sharma 2008; Sharma et al. 2009; Zboril et al. 2014). The synthesis of K_2FeO_4 was produced by heating a mixture of potassium nitrate and iron(III) oxides up to 1100 °C. However, this thermal approach gave a ferrate product of low purity, below 50%. The high purity of the ferrate(VI) salt (~90%) could be obtained by replacing potassium nitrate with sodium peroxide and heating the mixture to 600 °C. Significantly, this approach lowered the heating temperature; however, sodium peroxide is expensive compared to potassium nitrate.

In the wet chemical approach, salts of Fe(III) and iron(III) oxides were oxidized by hypochlorite under high alkaline conditions, e.g., with more than 10 M hydroxide ion (Perfiliev and Sharma 2008). Using sodium hydroxide and potassium hydroxide as an alkaline medium in the wet method yielded Na_2FeO_4 and K_2FeO_4 , respectively. The high

purity of K_2FeO_4 , 98% and higher, could be obtained from Na_2FeO_4 by exchanging the sodium ion with the potassium ion. This was possible because of the lower solubility of K_2FeO_4 than Na_2FeO_4 in water (5406 Sharma 2010; 3631 Luo, Z. 2011). The electrochemical method involved oxidizing iron rode (Fe(0)), Fe(II) salts, and oxides and salts of Fe(III) under a high alkaline medium to generate either Na_2FeO_4 or K_2FeO_4 . The strength of the alkaline solution and temperature in the synthetic procedure determine the yield of the salts of ferrate(VI). The overlap of potentials in the oxygen evolution decreases the conversion of Fe(III) to ferrate(VI).

Some researchers have used an inert anode-like boron-doped electrode (BDE) to overcome the drawback of electrochemical synthesis of ferrate(VI) (Macova et al. 2009; Sánchez-Carretero et al. 2010) (Macova et al. 2009). More details of ferrate synthesis are in published reviews (Sharma et al. 2013, a, b). Overall, large-scale solid synthesis of ferrate(VI) has many practical problems, such as high temperature for dry preparation, i.e., thermal approach, low product yield involving many reaction steps, i.e., wet chemical approach, and the formation of residual passive film on the electrode surface and the interference of competitive oxygen evolution reaction, i.e., electrochemical approach. Furthermore, both wet chemical and electrochemical approaches require high concentration of OH^- , e.g., 10 M or higher. The direct use of $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ ion solutions produced by these methods has limitations because of their high pH that raises the pH of the treated water. Also, the high pH reduces the efficacy of $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ by decreasing the oxidation power, i.e., a decrease in rates with an increase in pH. High amounts of $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ would be needed to achieve the desired efficacy at high pH that would further increase the pH of the treated water and the treatment cost.

Novel methods to surmount the harsh conditions of synthesizing $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$, such as 10 M or higher NaOH in wet synthesis, are thus needed to achieve $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ synthesis at lower pH. The potential of electrochemical preparation is too close to the one of oxygen evolution reactions, but electrodes based on smart iron-containing materials may overcome such inherent conditions. However, attention must be focused on lowering the pH since decreasing pH decreases the stability of the $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ ion. Ideally, the synthesized solution should have a pH of 9.0–10.5, the range at which $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ is the most stable for several hours.

The issue of the inherent instability of $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ ion may be addressed by generating it in situ, or at the site of use. This would still require innovation in the procedures used to generate $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ ion, i.e., liquid with low pH that eliminates current shortcomings of synthesis methods. Considering the advances made in materials/nanomaterials, an improvement is needed to develop the starting material, or iron(III) oxide/hydroxide, to synthesize $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ ion.

A hybrid approach of synthesizing liquid $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ with enhanced stability of several weeks has been used, and the pH was at least three units lower than the high alkaline solution produced by either the wet chemical or electrochemical method (Sharma 2015). This approach presents opportunities to improve the applicability of $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$, especially in treating solid surfaces to inactivate a wide range of bacteria and viruses (Sharma and Jinadatha 2020). However, the potential of the $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ solution, prepared by the hybrid approach, in treating polluted water is unknown due to a lack of testing. Future research may include improving the stability of $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ solutions from weeks to months, so that activated ferrate can be utilized similarly to bleach in many applications. Testing the liquid $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ solution to solve emerging environmental concerns provides the confidence that this iron-based molecule is not restricted to laboratory research.

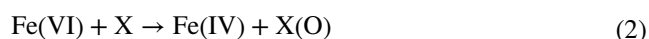
Ferrate(VI) can perform multi-modal actions to induce simultaneous oxidation, coagulation, and disinfection in sludge and water treatment (5421 Sharma 2007; 7516 Le 2004; 3241 Lee 2009; 7959 Kralchevska 2016; 7025 Sharma 2015; 9956 Zhang 2020; 10,118 Zheng 2020; 9957 Cui 2018; 10,881 Rougé V. 2022; 9888 Meng 2019; 10,877 Islam 2018; 9428 Shin J. 2018). Ferrate(VI) is reduced to lower oxidation state iron(III) oxides/hydroxides, which have performed superior being coagulants for the removal of metals such as (arsenic, copper, cadmium, and thallium) and nutrients like phosphate ion (Filip et al. 2011; Goodwill et al. 2019; Johnson and Lorenz 2015; Kolarík et al. 2018; Prucek et al. 2013, 2015; Wang et al. 2020; Yang et al. 2018). Importantly, the generated iron(III) oxides/hydroxides ($\gamma\text{-Fe}_2\text{O}_3$ and $\gamma\text{-FeOOH}$) possess core-shell structures from $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ successfully captured metals from water. $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ has also been shown to be a powerful disinfectant. Ferrate(VI) has shown its inactivation of bacteria and virus-like *Bacillus cereus* *Escherichia coli*, MS2 Bacteriophage, murine norovirus (MNV), Qubevirus durum (QB), and bacteriophages f2 (Sharma and Jinadatha 2020; Sharma 2007). Importantly, ferrate(VI) destroys capsid proteins, genome, and MS2, inhibiting the regeneration of the virus in water.

In the past decade, the research on the application of ferrate(VI) to oxidize emerging contaminants (X) has increased (Cui et al. 2018; Karlesa et al. 2014; Kim et al. 2015; Kovalakova et al. 2021; Li et al. 2021a; Luo et al. 2021a; McBeath and Graham 2021; Meng et al. 2019; Shao et al. 2019; Shin et al. 2018a, 2018b; Sun et al. 2016; Wang et al. 2021a; Yang et al. 2020; Zhang et al. 2021a; Zhao et al. 2018b, 2018c; Zheng et al. 2021; Zhu et al. 2021). Ferrate(VI) is considered a strong oxidant in an acidic medium (+2.2 V vs. NHE), while it is a mild oxidant in alkaline conditions (+0.7 V vs. NHE) (Delaude and Laszlo 1996; Sharma 2013a). Contaminants with electron-rich moieties like aniline, phenolic, and thiol functionalities have

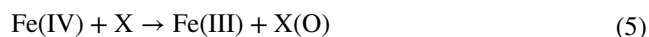
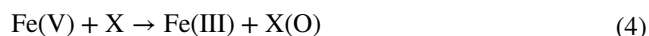
shown high reactivity with ferrate(VI) (He et al. 2022; Jiang 2015; Sharma et al. 2011; Sharma 2013b). Ferrate(VI) had sluggish reactivity with X that contains electron-deficient functional groups. The dose of ferrate(VI) to remove X depends on the oxidation capacity, which is discussed in the next section.

Oxidation capacity of ferrate(VI)

Numerous studies revealed that the oxidation capacity, expressed as moles of electron equivalent per mole of ferrate(VI), to degrade X depends on the participation of generated intermediate iron(V) ((Fe(V)) and iron(IV) ((Fe(IV))) species in reactions. Fe(V) and Fe(IV) are produced by when ferrate(VI) oxidizes X by one-electron and two-electron (or oxygen atom) transfer steps, respectively (reactions 1 and 2) (Huang et al. 2018, 2021; Sharma 2010b, 2013b; Sharma et al. 2011; Tian et al. 2020):



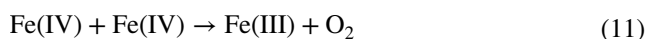
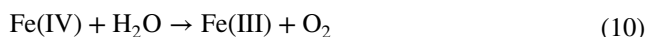
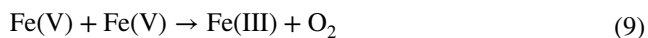
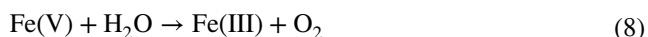
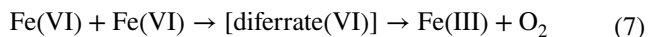
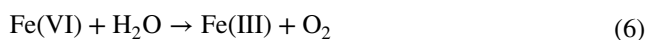
Further reactions of X with Fe(V) and Fe(IV) can increase the oxidation capacity of ferrate(VI) (reactions 3–5). The reaction of Fe(V) with X can proceed by either one-electron (reaction 3) or two-electron transfer (reaction 4) steps. The formed Fe(IV) in reaction 3 can subsequently react with X to oxidize it (reaction 5):



When the oxidation of X by ferrate(VI) occurs by one-electron steps, i.e., reactions 1, 3, and 5), each mole of ferrate(VI) would be able to oxidize 3 mol of X, yielding an oxidation capacity of 3.0. However, if the oxidation of X happens by the initial two-electron step (reaction 2), followed by one-electron transfer (reaction 5) processes, only 2 mol of X would be oxidized by ferrate(VI), giving an oxidation capacity of 2.0.

Additional reactions that may also simultaneously occur during the oxidation of ferrate(VI) with X are the reactions of ferrate(VI), Fe(V), and Fe(IV) with water and themselves (reactions 6–11) (Karlesa et al. 2014; Lee et al. 2005, 2009; Lee and von Gunten 2010; Sharma et al. 2015a, b; Sharma et al. 2016; Sun et al. 2018a, b; Wang et al. 2021a). These reactions would decrease the oxidation capacity of ferrate(VI) because ferrate(VI) is consumed by such

un-desired reactions rather than ferrate species reacting with X (i.e., desired reactions):



Reactions (6), (8), and (10) proceed by the first order, suggesting independent of the concentration of ferrate species. Reactions (7), (9), and (11) follow second-order reactions and thus, depend on the concentrations of ferrate species. The kinetics of the reactions (6)–(11) are pH dependent. Generally, three patterns have been seen for ferrate(VI) and Fe(V) species. Under high acidic conditions, reactions follow first-order kinetics. At neutral pH, the reactions are of second-order kinetics. In an alkaline medium, the reactions are of second-order kinetics. More details of pH dependence of the reactions are given in reviewed articles (Sharma et al. 2015a, b; Sharma et al. 2022).

Oxidation of X by ferrate(VI) and its intermediate species (Fe(V) and Fe(IV)) (reactions 1–5) are pH dependent with the general trend of increase in rates with the decrease in pH. Rates of reactions also vary with the nature of X. Therefore, the oxidation capacity of ferrate to degrade X depends on the type of X and pH. Furthermore, the oxidation capacity would usually vary between 1.0 and 3.0. The experimental conditions may be applied to obtain the optimum oxidation capacity of degraded X by ferrate(VI). As mentioned above, tuning the chemistry of the reaction between ferrate(VI) and X is needed to increase the participation of highly reactive iron intermediate Fe(V) and Fe(IV) in oxidative reactions. In recent years, a concept of "activated ferrate(VI)" has been introduced that achieves this objective and is discussed in the next section.

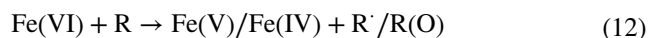
Activation of ferrate(VI)

The production of iron(V) and iron(IV) from ferrate(VI) in high concentrations at short time scales has been given the term "activated ferrate(VI)", which has shown high potential in treating contaminants of low reactivity (or recalcitrant organic molecules) in water and wastewater (Cao et al. 2021; Feng et al. 2017a, b; Feng et al. 2017a, b; Ghosh et al. 2019;

Lee et al. 2009; Manoli et al. 2022, 2017a, 2017c; Shao et al. 2019; Sharma et al. 2015a, b; Spellman et al. 2022; Wang et al. 2021b; Zhu et al. 2021). Some examples of recalcitrant contaminants are caffeine (CAF) (i.e., psychostimulants), flumequine and trimethoprim (i.e., antibiotics), acesulfame potassium (i.e., artificial sweetener), and Atenolol (ATL) (i.e., β -blocker) (Ghosh et al. 2019; Manoli et al. 2019; Pan et al. 2020). Many investigations are in progress on activating ferrate(VI) by different activators that could generate Fe(V) and Fe(IV) to enhance the oxidation of recalcitrant contaminants in water.

One of the initial approaches to activate ferrate(VI) in mild alkaline pH (i.e., pH 9.0) in water was by adding a small amount of nitric acid, hydrochloric acid, and acetic acid without significant change in pH (Manoli et al. 2017b). This acid activation could oxidize caffeine, acesulfame potassium, and atenolol in seconds, while without such activation, degradation of the contaminants occurred in minutes-hours. For example, the activated ferrate(VI) exhibited a 30% increase in the removal of caffeine, acesulfame, and atenolol. It was observed that the activated Fe(VI) showed an increased reduction in caffeine, artificial sweetener (ACE), and atenolol by 30% (Manoli et al. 2017b). An increase in the amount of acid addition led to the complete removal of these contaminants (Manoli et al. 2017b). Enhanced removal of contaminants for a wide range of pharmaceuticals and pesticides in wastewater effluent by acid-ferrate(VI) combinations has been demonstrated.

Later approaches have applied reductants (R) to generate iron(V) and iron(IV) from ferrate(VI) (reaction 12) (Feng et al. 2018; He et al. 2023; Shao et al. 2019; Spellman et al. 2022; Sun et al. 2018a, b, 2019a; Zhang et al. 2017):



A detailed study on using inorganic reductants was conducted, which showed varied increased removal of pharmaceuticals by ferrate(VI)-reductant system. This research showed that Fe(V) and Fe(IV) may be formed selectively by initial single-electron transfer (SET) and oxygen-atom transfer (OAT) reductant, respectively (e.g., Fig. 1) (Sharma 2010b, 2013b; Sharma et al. 2011). Reductants of SET like bisulfite (SO_3^{2-}) and thiosulfate ($\text{S}_2\text{O}_3^{2-}$) showed enhanced removal in a shorter time scale of 30 s (Feng et al. 2018). Comparatively, OAT reductants like hydroxylamine, arsenite, nitrite, ammonia, amines, and creatinine took minutes to have similar removal percentages of pharmaceuticals. Researchers have focused on using bisulfite as a reductant to study the enhanced phenomena of oxidizing contaminants by ferrate(VI).

In recent years, silica and carbonaceous surfaces have also been applied to enhance the oxidation of contaminants in water (Cao et al. 2021; Pan et al. 2020; Sun et al. 2019a,

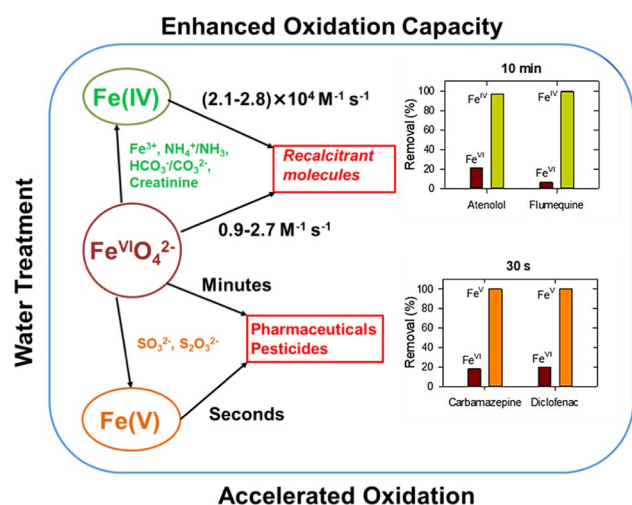


Fig. 1 Effect of reductants on the activation of ferrate(VI) to remove contaminants in water. The addition of one-electron reductants like sulfite gives Fe(V) from ferrate(VI), which could completely remove pharmaceuticals and pesticides in 30 s. Comparatively, two-electron reductants such as creatinine generate Fe(IV) that removes recalcitrant contaminants completely in 10 min. Note that without reductants, the removal of different contaminants by only ferrate(VI) was lower than 20%. The potential ligands such as borate, phosphate, carbonate, and ammonia for the Fe(V) and Fe(IV) determine the magnitude of the increased effect of reductants on the ferrate(VI)

b; Tian et al. 2020). Silica has an acidic character and may behave like the small addition of acid to ferrate(VI) to increase the oxidation of contaminants. It seems that carbonaceous surfaces possess functional moieties that may be acting as reductants to generate Fe(V) and Fe(IV) to cause enhanced oxidation of pollutants in the heterogeneous system of Fe(VI)–carbonaceous solids. An example of carbonaceous surfaces is biochar and hydrochar that contain functional groups like C=O groups as reductants to produce Fe(V)/Fe(IV), which yielded increased removal of pharmaceuticals and pesticides under mild alkaline conditions.

Activation of ferrate(VI) by metal ions

An interest in applying alkaline earth (Ca(II), Al(III), and Sc(III)) and transition metals ions (Co(II), Ni(II), Fe(II), Fe(III), Cu(II), Mn(II), and Mn(IV)) in combination with ferrate(VI) has been forthcoming in order to understand their role in increased removal of contaminants in water (Sharma et al. 2022; Zhang and Jiang 2022; Zhang et al. 2021b; Zhao et al. 2018a, 2018b; Zheng et al. 2020). A thought of applying the metal ion was to enhance the decomposition of Fe(VI) to increase the concentration of Fe(V)/Fe(IV) in a short time period for enhanced degradation of contaminants in water. Additionally, the structures and properties of Fe(IV) and Fe(V) may vary advantageously with the metal

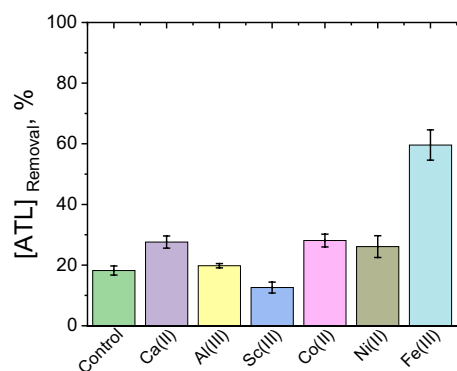


Fig. 2 Removal of atenolol (ATL) by ferrate(VI)–metal ion systems. (Experimental conditions: [atenolol]=5.0 μ M, [ferrate(VI)]=100 μ M, [Metal ion]=100 μ M, [borate buffer]=2.0 mM, pH 9.0). In applying ferrate(VI) only, the removal of atenolol was ~18%. Most ions showed minimal influence on the removal efficiency of ferrate(VI)–metal ions. The addition of Fe(II) to ferrate(VI) had increased removal efficiency to ~60%. Data were taken from Zhang et al. (2021b) with the permission of the American Chemical Society)

ions in the mixed solution of Fe(VI)–metal ions–contaminant present in a solution like synthesized salts of Fe^{VI} having different metal ions (Delattre et al. 2000; Herber and Johnson 1979; Yu and Licht 2008). In other words, this approach may allow modulating the reactivity of ferrate(VI) to increase its oxidation power.

A summary of tested metal ions is presented in Fig. 2. The addition of Ca(II) has shown an increase in the decomposition of ferrate(VI); however, the removal of atenolol did not increase significantly. Al(III), Sc(III), and Co(II) also had almost no noticeable enhanced removal of atenolol. Ni(II) showed increased removal of atenolol by ferrate(VI). Ni(II) is known to have a solid influence on decomposing the ferrate(VI) even in trace amounts in solution (Licht et al. 1999). The addition of Fe(III) to ferrate(VI) had the highest enhanced removal of atenolol in water. The comparative results of Fig. 2 indicate that the type of metal ions has a role in enhancing the removal effects of metal ions when combined with ferrate(VI) in water. The variation of metal ions may be related to the competing rate constants of the self-decomposition of Fe(V)/Fe(IV) by metal ions.

Figure 2 suggests that most of the metal ions, except Fe(III), were able to destabilize Fe(V)/Fe(IV) at a higher rate than the reaction rates of the intermediate iron species with the atenolol. Interestingly, this negative effect of the metal ions was not predominant in using Fe(III) in the ferrate(VI)–atenolol system. This is significant because Fe(III) is routinely used as a coagulant in treatment plants. We have therefore presented a detailed review of Fe(III) in enhancing the removal of contaminants by ferrate(VI) in the next section. Other metal ions, Cu(II) and Mn(IV), may either present inherently in contaminated water or exist in

natural minerals; hence, we have also briefly discussed these metal ions in the following section.

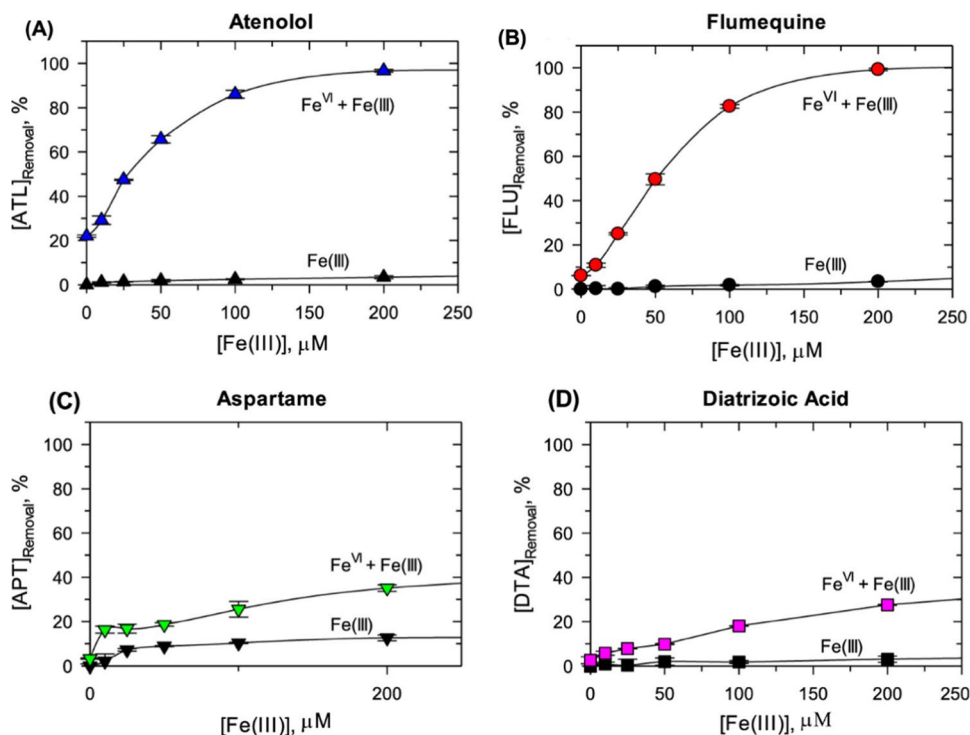
Activation of ferrate(VI) by iron(III)

Initial testing of Fe(III) influence on the activation of ferrate(VI) was carried out on four contaminants, atenolol, flumequine, aspartame, and diatrizoic acid, which have varied molecular structures (Fig. 3) (Zhang et al. 2021b). Importantly, these contaminants have sluggish reactivity with ferrate(VI) with corresponding second-order rate constants at pH 9.0 are $(5.0 \pm 0.4) \times 10^{-1}$, $(3.4 \pm 0.1) \times 10^{-1}$, $(8.2 \pm 1.0) \times 10^{-1}$, and $(5.3 \pm 0.1) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ for atenolol, flumequine, aspartame, and diatrizoic acid, respectively. The slow reactivity could be seen in the minimal removal efficiency of the contaminants by only ferrate(VI) (i.e., less than 20%) (Fig. 3). However, with increasing addition of Fe(III) to the same solution of ferrate(VI), resulted in increased removal of the contaminants in water. Complete removal of atenolol and flumequine was obtained with increasing Fe(III) concentration (Fig. 3a, b). Aspartame and diatrizoic acid also showed increased removal, but maximum removal was up to 35% (Fig. 3c, d). The results of Fig. 3 clearly showed the significant role of Fe(III) in enhancing the removal of pollutants by ferrate(VI). Furthermore, the oxidizing species, Fe(V)/Fe(IV), generated from ferrate(VI)–Fe(III) mostly contributed to enhance the removal of the contaminants. The Fe(V) and Fe(IV) species are much more reactive

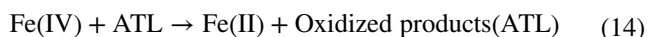
than ferrate(VI) (Sharma 2002, 2011) to cause the increasing removal of contaminants from Fe(VI) alone. The enhancement of Fig. 3 was also observed in the oxidation of sulfamethoxazole (i.e., antibiotic) by ferrate(VI)–Fe(III) system in borate buffer (Shao et al. 2019). It appears that the reactivity of Fe(V)/Fe(IV) species differed with the molecular structure of each contaminant to yield different percentages of removal by the Fe(VI)–Fe(III).

The importance of Fe(V)/Fe(IV) species in the oxidation of contaminants by ferrate(VI)–Fe(III) has been explored by the selective oxidation of methyl phenyl sulfoxide (PMSO) to methyl phenyl sulfone (PMSO₂). The methyl phenyl sulfoxide is known to probe high-valent iron species (Shao et al. 2019, 2020). Fe(V)/Fe(IV) species react much faster with contaminants than with ferrate(VI) (Sharma 2002, 2011), and therefore, the comparative formation rate of methyl phenyl sulfone usually indicates the generation of Fe(V)/Fe(IV) in the ferrate(VI)–Fe(III) system. In the ferrate(VI)–Fe(III)–contaminant system, the stoichiometric formation of methyl phenyl sulfone was seen, indicating that the Fe(V)/Fe(IV) caused the enhanced removal of contaminants by ferrate(VI)–Fe(III) system. Interestingly, the help of kinetic modeling of the oxidation of atenolol was sought to distinguish which of the two Fe(V) and Fe(IV) were the major species responsible for giving increased removal of atenolol in the ferrate(VI)–Fe(III) system. The modeling was able to demonstrate that the major oxidative species was Fe(IV), and the calculated second-order rate constant for reaction with atenolol was obtained as

Fig. 3 Effect of Fe(III) on removal of (A) atenolol, (B) flumequine, (C) aspartame, and (D) diatrizoic acid by Fe^{VI}–Fe(III) system. (Experiments conditions: [Contaminant] = 5.0 μM, [Fe(VI)] = 100.0 μM, pH 9.0 ([borate buffer] = 2.0 mM), reaction time = 10 min). Herein, Fe(III) removed much of the studied contaminants in 10.0 min. The removal of atenolol by ferrate(VI) was ~20%, which increased to ~100% by adding 200 μM Fe(III). In the case of other contaminants, the removal efficiency of Fe(III) was low (≤10%). With the addition of 200 μM Fe(III), the removal efficiency increased to 100, 35, and 30% for flumequine, aspartame, and diatrizoic acid, respectively. Adapted from (Zhang et al. 2021b) with the permission of the American Chemical Society



$(6.3 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, which is much higher than that of the reaction between ferrate(VI) and atenolol (i.e., $(5.0 \pm 0.4) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$). Reactions (13) and (14) may thus describe the enhancement of the oxidation of atenolol by the addition of Fe(III) to ferrate(VI):



Both reactions (13), (14) have pH dependence, and therefore, the magnitude of enhancement would vary with pH (Dong et al. 2017; Lee et al. 2014; Luo et al. 2021a, 2021b, 2020). Effect of water constituents of natural water like carbonate and phosphate ions on the removal efficiency of ferrate(VI)–Fe(III) was examined (Baum et al. 2021; Luo et al. 2021a, 2019). The studied contaminant was diatrizoic acid at 5.0 mM carbonate and phosphate at pH 9.0. Carbonate had no effect on the removal of diatrizoic acid with efficiencies of $19.7 \pm 1.9\%$ and $16.2 \pm 2.2\%$ without and with carbonate. However, phosphate ion decreased the efficiency to $5.5 \pm 0.5\%$, similar to previous studies (Huang et al. 2018, 2021). Details of the reasoning behind inorganic constituents of water have been well studied and explained elsewhere, in which the role of ligands of Fe(V) and Fe(IV) was provoked (Huang et al. 2018; Luo et al. 2019). Fe(V)- and Fe(IV)-complexes behave differently than un-complexed Fe(V) and Fe(IV) species because oxidation mechanisms are varied from the change of the coordination sphere around the central iron element (Guo et al. 2019; Morimoto et al. 2011; Park et al. 2011). Natural organic matter showed a decrease in the removal efficiency of the contaminants by the ferrate(VI)–Fe(III) system. In addition to the influence of organic moieties as ligands on Fe(V)/Fe(IV) species, the competitive consumption of natural organic matter by ferrate(VI) may decrease the oxidation capacity of ferrate(VI)–Fe(III) (Feng et al. 2016; Lee et al. 2020; Luo et al. 2015).

Figure 4 shows the removal of diatrizoic acid investigated in lake water and river water by the ferrate(VI)–Fe(III) system. The water samples were collected from the Brazos River water and Bryan Lake, the City of Bryan in Texas (Zhang et al. 2021b). The samples were mixed with diatrizoic acid to test for the effect of the amount of ferrate(VI) on the removal of diatrizoic acid from the lake water and river water samples in a borate buffer at pH 8.0 (Zhang et al. 2021b). Diatrizoic acid was removed 100% from water at pH 8.0 after 10 min of the reaction by applying an increasing amount of ferrate(VI) ($> 200.0 \mu\text{M}$) while maintaining the ([ferrate(VI)]/[Fe(III)] = 0.5 (Zhang et al. 2021b). Figure 4 further depicts that $> 400.0 \mu\text{M}$ amounts of ferrate(VI) in the ferrate(VI)–Fe(III) were needed for the complete removal

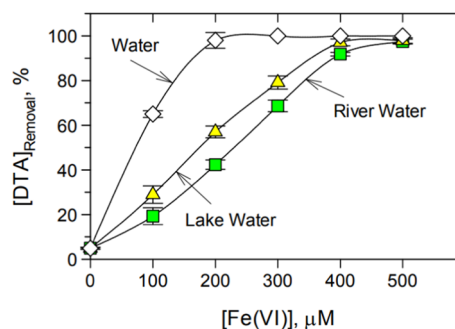


Fig. 4 Effect of concentration of ferrate(VI) on the removal of diatrizoic acid in surface waters collected from Brazos River and Lake Bryan by ferrate(VI)–Fe(III) system at a fixed molar ratio of 0.5 ([ferrate(VI)]/[Fe(III)]) at pH 8.0. (Experimental conditions: [diatrizoic acid]=5.0 μM. [borate buffer]=2.0 mM and reaction time=10 min). The constituents of natural water samples like lake and river water decreased the removal efficiency of diatrizoic acid by ferrate(VI)–Fe(III) system. The decrease in efficiency could be compensated by increasing the amount of ferrate(VI) in the mixed solution of ferrate(VI) and Fe(III). As shown herein, 200.0 μM of ferrate(VI) in a mixed solution was needed, while about 400.0 μM was required to completely remove sulfamethoxazole in ions and natural organic water-containing water samples. (Adapted from (Zhang et al. 2021b) with permission of the American Chemical Society)

of diatrizoic acid. Overall, the magnitude of contaminant removal in real water samples will vary with pH, inorganic constituent concentrations, and the levels and types of natural organic matter (Zhang et al. 2021b). The optimization of the pH and concentration of ferrate(VI) and the molar ratio of ferrate(VI) to Fe(III) could be required to achieve high efficiency in removing contaminants from water (Zhang et al. 2021b).

In another real water application of the ferrate(VI)–Fe(III) system, 1.0 L of pharmaceutical industrial wastewater in China was used as the sample, maintained at 4 °C, and adjusted to a pH of 9.0 (Mao et al. 2022). The filtered (0.45 syringe) wastewater sample was spiked with 5.0 μM of sulfamethoxazole (Mao et al. 2022). The successful removal of sulfamethoxazole from industrial wastewater could be optimized using the ferrate(VI)–Fe(III) combination rather than ferrate(VI) alone. More recently, a set laboratory-scale batch of studies assessed the effects of the Fe(VI):Fe(III) ratio and Fe dosage to produce drinking water in emergency disaster and disease-outbreak scenarios (Zheng et al. 2020). The study revealed that the joint use of ferrate(VI) and Fe(III) salts as an oxidant in the emergency water treatment (EWT) process had simultaneously and effectively removed chemical and microbial contaminants from water (Zheng et al. 2020). The cost-effectiveness of ferrate(VI) in the usage of water treatment was discussed, wherein the addition of Fe(III) into ferrate(VI) lowered the overall treatment cost-effectiveness (Zheng et al. 2020). Additionally, a modest amount of acid inherently present in Fe(III)

liquid used in treatment plants would be beneficial in removing contaminants in water (Zheng et al. 2020).

Activation of ferrate(VI) by copper(II) ions

Recently, copper(II) performance was thoroughly researched to comprehend and define the extent of its efficacy in activating ferrate(VI) to enhance the oxidation of sulfamethoxazole (Shi et al. 2022). Results on the enhanced effect of Cu(II) on the removal of sulfamethoxazole by ferrate(VI) are presented in Fig. 5 (Shi et al. 2022). In 10 min, the removal of sulfamethoxazole by ferrate(VI) alone was ~60.0% at pH 8.0. However, the addition of Cu(II) to ferrate(VI) yielded the complete removal of sulfamethoxazole. A similar effect of Cu(II) was also observed at pH 7.0 and 8.0. Increased removal of sulfamethoxazole was seen with the increasing amount of Cu(II) to ferrate(VI) at pH 8.0. A wide range of contaminants having different structures (e.g., bisphenols) could also be removed effectively by the ferrate(VI)–Cu(II) combination at pH 8.0.

The enhanced effect of Cu(II) was described by the following reactions (15)–(17):

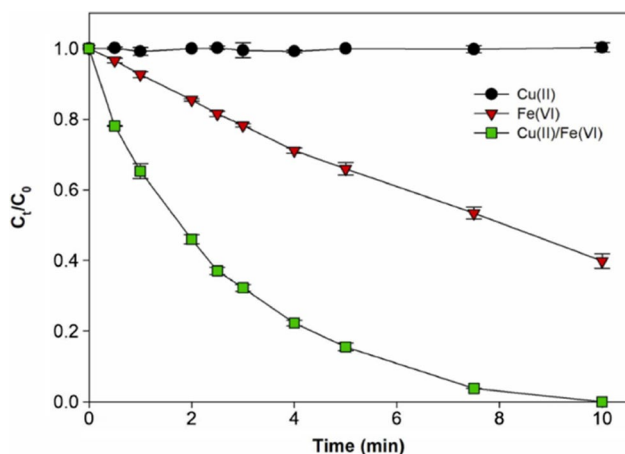
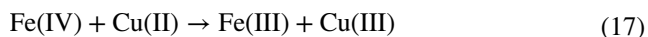
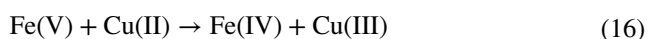


Fig. 5 Degradation of sulfamethoxazole by ferrate(VI) in the presence of Cu(II). (Reaction conditions: [sulfamethoxazole]₀ = 5.0 μM, [ferrate(VI)]₀ = 50.0 μM, [copper(II)]₀ = 20.0 μM, pH = 8.0, and T = 20 °C) Degradation of sulfamethoxazole by copper(II), ferrate(VI), and ferrate-Cu(II) system. Copper(II) did not give any degradation of sulfamethoxazole. However, ferrate(VI) showed degradation of up to 60% removal in 10.0 min. When copper(II) was added to ferrate(VI), the sulfamethoxazole degradation rate increased, which gave complete removal in 10.0 min. (Adapted from (Shi et al. 2022) with the permission of Elsevier Inc.)

As discussed in the previous section, Fe(V) and Fe(IV) species have a high potential to oxidize contaminants in water. An additional oxidant in the reaction was Cu(III), which also has the ability to oxidize contaminants by the ferrate(VI)–Cu(II) system. Both kinds of high-valent iron and copper were supported by different analytical methods (Shi et al. 2022). The Fe(V)/Fe(IV) species were identified by the stoichiometric conversion of methyl phenyl peroxide to methyl phenyl sulfone. The identification of Cu(III) was explored by spectroscopic techniques.

The influence of inorganic and organic constituents on the removal of sulfamethoxazole by ferrate(VI)–Cu(II) was investigated at pH 8.0 (Shi et al. 2022). Most inorganic ions (cations and anions), except carbonate ion, had no effect on the removal efficiency. The negative effect of carbonate ion may be related to the formation of Cu(II)–carbonate complex and that inhibited the formation of highly reactive oxidative species. The decrease in the removal efficiency in the presence of natural organic matter was seen for the oxidation of sulfamethoxazole by ferrate(VI)–Cu(II), similar to the oxidation system of ferrate(VI)–Fe(III) (Zhang et al. 2021b). It seems that natural organic matter and its functional moieties could remove oxidative species (Fe(IV), Fe(IV), and Cu(III) through competitive reactions to decrease the ability to oxidize the contaminant. This could be further shown by the increase in inhibitory effect with an increase in the concentration of natural organic matter. The presence of carbonate and natural organic matter in surface water also decreases the removal efficiency of sulfamethoxazole by the ferrate(VI)–Cu(II) system. The influence of other copper species, Cu(I), has also indicated its removal of contaminants by ferrate(VI) (Sharma et al. 2005, 2008; Yngard et al. 2008). Importantly, finalized state of copper was Cu(II), which could be removed by coagulation by Fe(III) oxides/hydroxide, produced by ferrate(VI), similar to many previous studies (Ghosh et al. 2008).

Activation of ferrate(VI) by colloidal manganese dioxide

Colloid manganese dioxide (cMnO₂) is usually found in natural water and water treatment processes (Yu et al. 2020; Zhang et al. 2020a, b). Researchers have used different types of colloidal manganese dioxide (αMnO₂, βMnO₂, γMnO₂, and δMnO₂) in removing contaminants in water and in carrying out organic oxidation reactions (Luo et al. 2022). Therefore, colloidal manganese dioxide combined with ferrate(VI) seeks enhancement of contaminants removal. A detailed study was performed using sulfamethoxazole, and the results are presented in Fig. 6a. (Luo et al. 2022). Among the various types of colloidal manganese dioxide, only amorphous manganese dioxide (cMnO₂) in

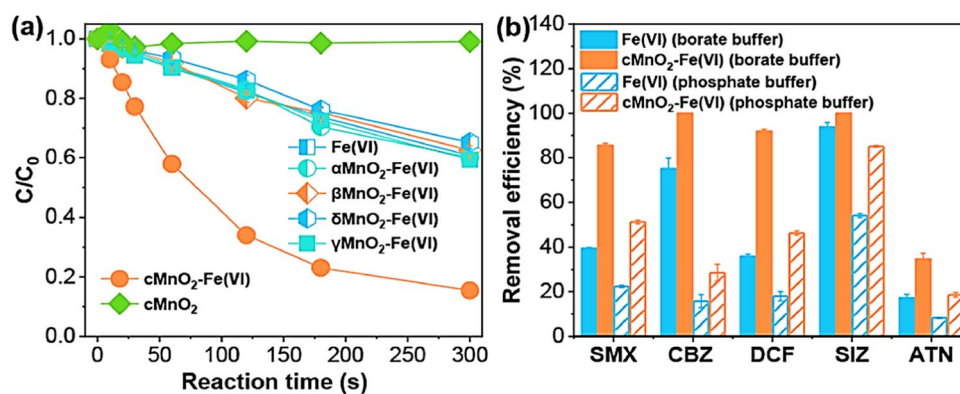


Fig. 6 **a** Effects of various crystal-shapes MnO₂ on activation of ferrate(VI) to remove sulfamethoxazole and **b** Degradation efficiencies of five representative pollutants after reaction 5.0 min in ferrate(VI) and cMnO₂-ferrate(VI) systems with borate or phosphate buffer, SMX-sulfamethoxazole, CBZ-carbamazepine, DCF-diclofenac, SIZ-sulfisoxazole, and ATN. (Experimental conditions: [SMX]₀=[CBZ]₀=[DCF]₀=[SIZ]₀=[ATN]₀=5.0 μM, [ferrate(VI)]₀=50.0 μM, [cMnO₂]₀=50.0 μM, [phosphate buffer]₀=[borate buffer]₀=20.0 mM, [αMnO₂]₀=[βMnO₂]₀=[γMnO₂]₀=[δMnO₂]₀=150 mg L⁻¹, pH=8.0). cMnO₂-amorphous shape manganese dioxide, which had varied disorder structures of

short-range order and long-range disorder structure, possesses more surface area and defects having more surface defects and active sites. **a** Shows that such active sites could promote the activation of ferrate(VI) to increase the oxidation of sulfamethoxazole. **b** Depicts that cMnO₂ induced similar activation of ferrate(VI) was also seen in oxidizing other contaminants. However, the magnitude of enhancement of oxidation of contaminations by such cMnO₂-induced activation of ferrate(VI) differs due to different moieties in the molecular structures of contaminants. Adapted from Luo et al. (2022) with the permission of Elsevier

combination with ferrate(VI) had an increasing effect on the oxidation of sulfamethoxazole compared to ferrate(VI) alone. The characterization of different phases of manganese dioxide revealed that colloidal manganese dioxide has an amorphous phase with a large surface area and surface defects (Luo et al. 2022), thereby contains a large number of active sites to interact with ferrate(VI) to result in enhanced oxidation of sulfamethoxazole. The ease of oxidation of sulfamethoxazole by ferrate(VI)-cMnO₂ was supported by determining the activation energy of the reaction, which was 20.6 kJ mol⁻¹, lower than the activation energy obtained as 25.6 kJ mol⁻¹ in the reaction of sulfamethoxazole by ferrate(VI) only (Luo et al. 2022).

The enhanced effect of ferrate(VI)-cMnO₂ was also tested against carbamazepine (CBZ), diclofenac (DCF), sulfisoxazole (SIZ), and atenolol in borate and phosphate buffer at pH 8.0 (Fig. 6b). Results showed higher removal efficiency of the contaminants by ferrate(VI)-cMnO₂ than that of ferrate(VI) alone in both buffers in solution. It was noticed that phosphate buffer had lower removal efficiency than borate buffer, similar to previous studies (Huang et al. 2018). Significantly, removal efficiency by the cMnO₂-induced activation of ferrate(VI) varied with the structure of the organic contaminants (Fig. 6b).

Identification of reactive intermediates, Fe(V) and Fe(IV), in the ferrate(VI)-cMnO₂ system was initially investigated by measuring the amount of methyl phenyl sulfone from the conversion of methyl phenyl sulfoxide (Luo et al. 2022). A higher amount of methyl phenyl sulfone was observed than only ferrate(VI), indicating higher concentrations

of Fe(V) and Fe(IV) to yield an enhanced effect of the ferrate(VI)-cMnO₂. It was suggested that cMnO₂ forms a complex with ferrate(VI) (ferrate(VI)-cMnO₂) to ease the oxidation of contaminants. Such complexation was initially explored by Raman spectroscopy (Fig. 7a). The stretching vibrations of [MnO₆] in cMnO₂ were seen in the region of 574–638 cm⁻¹ (Cheng et al. 2014). The vibration intensity was affected in the presence of ferrate(VI), which showed a decrease in this band. The band at 783 cm⁻¹ of ferrate(VI) for the Fe–O oscillator also showed influence due to the complex formation (Sitter et al. 1985). Overall, bands observed in Raman spectroscopy indicate the complex formation between ferrate(VI) and cMnO₂.

The ferrate(VI)-cMnO₂ complex was further investigated by in situ electrochemical measurements. The open-circuit potential of the GCE (glassy carbon electrode), coated with cMnO₂ (cMnO₂-GCE), increased with the addition of ferrate(VI) (Fig. 7b). When sulfamethoxazole was added into the ferrate(VI) containing solution, the potential decreased, which was interpreted that the complex formed reacted with sulfamethoxazole to cause such decrease. Comparatively, the glassy carbon electrode without coating with cMnO₂ had a small decrease when sulfamethoxazole was added into the ferrate(VI) containing solution. This finding inferred a higher oxidation ability of postulated ferrate(VI)-cMnO₂ to oxidize sulfamethoxazole than ferrate(VI) (Fig. 7b). More details of electrochemical measurement are given elsewhere (Luo et al. 2022).

The influence of cations (Ca²⁺ and Mg²⁺) and anion (SO₄²⁻) on the removal of sulfamethoxazole by

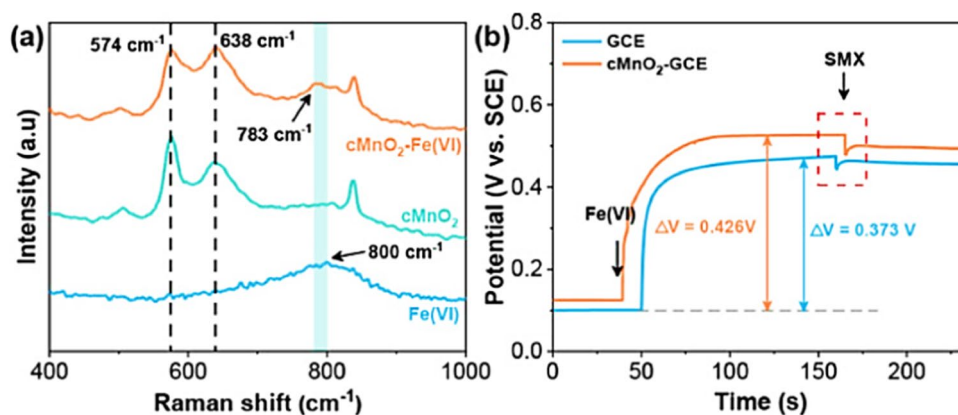


Fig. 7 a In situ Raman spectra of ferrate(VI), cMnO_2 , and cMnO_2 -ferrate(VI). (Experimental conditions: $[\text{ferrate(VI)}]_0 = 3.0 \text{ mM}$, $[\text{cMnO}_2]_0 = 3.0 \text{ mM}$). **b** The change of open-circuit potential with or without cMnO_2 (SMX-sulfamethoxazole, GCE-glassy carbon electrode). **a** Suggests the change in cMnO_2 and ferrate(VI) vibration bands when mixed compared to individual cMnO_2 and ferrate(VI). Bands at 574–638 cm^{-1} are from cMnO_2 , while the band at 800 cm^{-1} is from ferrate(VI). Both bands are

affected by the presumed complex ferrate(VI)- cMnO_2 . **b** Shows the oxidation potential of glassy carbon electrode (GCE) with and without the coating of cMnO_2 . Oxidation potential decreased by adding sulfamethoxazole in ferrate(VI) containing solution, which was more in the GCE coated with cMnO_2 , indicating the possibility of the ferrate(VI)- cMnO_2 complex. (Adapted from (Luo et al. 2022) with the permission of Elsevier, Inc.)

ferrate(VI)- cMnO_2 was examined (Luo et al. 2022). The cations were found to increase sulfamethoxazole's oxidation rate by ferrate(VI)- cMnO_2 . It seems that the cations have a positive role through interaction with negative surfaces of cMnO_2 and, therefore, a possibility of a stronger complex with negatively charged ferrate(VI) (FeO_4^{2-}). The stronger complex in the presence of Ca^{2+} and Mg^{2+} has a higher ability to oxidize sulfamethoxazole than the absence of these ions in the ferrate(VI)- cMnO_2 system. The SO_4^{2-} had no significant influence on oxidation. The sulfamethoxazole degradation rate also increased in the lake and river waters (Luo et al. 2022). This positive influence of inorganic and organic constituents of natural water needs further mechanisms to optimize the ferrate(VI)- cMnO_2 to remove a wide variety of contaminants present in treatments (Luo et al. 2022).

Conclusion

The oxidation of contaminants by ferrate(VI) can be accelerated with increased removal efficiency by producing Fe(V) and Fe(IV) species in the ferrate(VI)-metal ion system. Both Fe(V) and Fe(IV) have much higher reactivity than ferrate(VI) in the following order: $\text{Fe(V)} > \text{Fe(IV)} > \text{ferrate(VI)}$. The preference for generating Fe(V) may take precedence over producing Fe(IV) in the ferrate(VI)-reductant system, which may take seconds to oxidize contaminants compared to Fe(IV), which requires minutes to degrade the recalcitrant organic contaminants completely. Natural metal ions, Fe(III), Cu(II), and Mn(IV),

showed enhanced removal of a wide variety of contaminants when combined with ferrate(VI). Fe(III) ions addition has shown promise among the metal ions because they are already used as coagulants at water treatment facilities. Furthermore, the Fe(III) coagulant has an acidity that may also enhance the removal efficiency of contaminants. Additionally, the addition of Fe(III) to ferrate(VI) may be cost-effective because of the less required dosage of ferrate(VI) compared to achieving the same removal efficiency at a much higher amount of ferrate(VI) alone. Advantageous multimodal actions of ferrate(VI) as a disinfectant and coagulant would create a comprehensive, advanced treatment process by the ferrate(VI)-Fe(III) system. The exploitation of the ferrate(VI)-Fe(III) system in continuous-flow treatment technology may be investigated to overcome real-time challenges in treating contaminated water and wastewater.

Many studies on ferrate(VI) activation by various homogeneous and heterogeneous activators are forthcoming; however, a mechanistic understanding of the system is far from clear. In-depth comprehension will assist investigators in modulating ferrate(VI) reactivity with contaminants. Importantly, researchers should work on creating natural metal ion-based activators that could be recycled. In these directions, researchers may take advantage of the advancement made in bioinspired materials that may be efficient activators of ferrate(VI). These activators must be least influenced by inorganic and organic constituents of water, which are present in much higher concentrations than the targeted contaminants. The objective may be to combine the robust catalyst with ferrate(VI) to treat water with high removal efficiency.

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Declarations

Conflict of interest The authors have not disclosed any competing interests.

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