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# Ferrates: Greener Oxidants with Multimodal Action in Water Treatment Technologies

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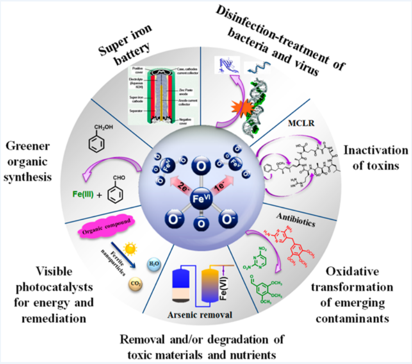

**CONSPECTUS:** One of the biggest challenges for humanity in the 21st century is easy access to purified and potable water. The presence of pathogens and toxins in water causes more than two million deaths annually, mostly among children under the age of five. Identifying and deploying effective and sustainable water treatment technologies is critical to meet the urgent need for clean water globally. Among the various agents used in the purification and treatment of water, iron-based materials have garnered particular attention in view of their special attributes such as their earth-abundant and environmentally friendly nature. In recent years, higher-valent tetraoxy iron(VI) ($Fe^{VI}O_4^{2-}$, Fe(VI)), commonly termed, ferrate, is being explored for a broad portfolio of applications, including a greener oxidant in synthetic organic transformations, a water oxidation catalyst, and an efficient agent for abatement of pollutants in water. The use of Fe(VI) as an oxidant/disinfectant and further utilization of the ensuing iron(III) oxides/hydroxide as coagulants are other additional attributes of ferrate for water treatment. This multimodal action and environmentally benign character of Fe(VI) are key advantages over other commonly used oxidants (e.g., chlorine, chlorine dioxide, permanganate, hydrogen peroxide, and ozone).

This Account discusses current state-of-the-art applications of Fe(VI) and the associated unique chemistry of these high-valence states of iron. The main focus centers around the description and salient properties of ferrate species involving various electron transfer and oxygen-atom transfer pathways in terms of presently accepted mechanisms. The mechanisms derive the number of electron equivalents per Fe(VI) (i.e., oxidation capacity) in treating various contaminants. The role of pH in the kinetics of the reactions and in determining the removal efficiency of pollutants is highlighted; the rates of competing reactions of Fe(VI) with itself, water, and the contaminants, which are highly pH dependent, determine the optimum pH range of maximum efficacy.

The main emphasis of this account is placed on cases where various modes of ferrate action are utilized, including the treatment of nitrogen- and sulfur-containing waste products, antibiotics, viruses, bacteria, arsenic, and heavy metals. For example, the oxidative degradation of N- and S-bearing contaminants by Fe(VI) yields either Fe(II) or Fe(III) via the intermediacy of Fe(IV) and Fe(V) species, respectively (e.g., $Fe^{VI} \rightarrow Fe^{IV} \rightarrow Fe^{II}$ and $Fe^{VI} \rightarrow Fe^{V} \rightarrow Fe^{III}$). Oxidative transformations of antibiotics such as trimethoprim by Fe(VI) generate products with no residual antibiotic activity. Disinfection and inactivation of bacteria and viruses can easily be achieved by Fe(VI). Advanced applications involve the use of ferrate for the degradation of cyanobacteria and microcystin originating from algal blooms and for covalently embedding arsenic and heavy metals into the structure of formed magnetic iron(III) oxides, therefore preventing their leaching.

Applications of state-of-the-art analytical techniques, namely, *in situ* Mössbauer spectroscopy, rapid-freeze electron paramagnetic resonance, nuclear forward scattering of synchrotron radiation, and mass spectrometry will enhance the mechanistic understanding of ferrate species. This will make it possible to unlock the true potential of ferrates for degrading emerging toxins and pollutants, and in the sustainable production and use of nanomaterials in an energy-conserving environment.

## 1. INTRODUCTION

Of the six billion people living on earth today, about 20% are devoid of access to safe drinking water. By the year 2025, approximately two-thirds of the world's population will confront severe water shortages.[1] Access to purified water is one of the biggest challenges that researchers face in the 21st century. The identification and deployment of effective and sustainable water treatment technologies is critical to meet the urgent global needs of clean water.[2] Among the various purification and treatment methods that are available, iron-based technologies are attractive as they are environmentally

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friendly and use an earth-abundant material. Moreover, some iron-containing materials are magnetic and can be easily removed or recycled after culmination of the treatment procedure, thus rendering their application more sustainable.

Iron offers a unique range of valence states (0, II, III, IV, V, and VI) and polymorphs exemplified by $Fe_2O_3$ and FeO(OH) species, which have found varied applications in nanotechnology, medicine, biocatalysis, energy, and environmental remediation. A wide range of minerals containing iron in +II and +III oxidation states have been found terrestrially as well as on Mars, which include goethite, magnetite, hematite, maghemite, and akaganeite. Zero-valent iron (ZVI) is considered a catalyst and a highly efficient and environmentally friendly reductant for *in situ* groundwater treatment, while Fe(II) and Fe(III) species have been used extensively in both, homogeneous and heterogeneous catalysis.

Iron is also an essential element for most living organisms as illustrated by the iron−porphyrin complex which participates in the binding and transport of molecular oxygen. In the past few years, higher-valent iron intermediates have been hypothesized to play a role in the reaction mechanisms of various heme and nonheme enzymes, such as taurine $\alpha$-ketoglutarate dioxygenase (TauD), chloroperoxidase, iron-dependent halogenase SyrB2, and cytochrome P450.[3,4] These enzymes may possess $Fe^{IV}{=}O$ and $Fe^{V}{=}O$ sites to enable the oxidation of C═C and C−H moieties that are difficult to activate conventionally.[3] Several research groups have synthesized model compounds in nonaqueous environments containing higher-valent iron with organic ligands to understand the mechanism of biological oxidation reactions.[5]

In recent years, the research on simple oxo-compounds of high-valent iron species, commonly called ferrates ($Fe^{VI}O_4^{2-}$, Fe(VI); $Fe^{V}O_4^{3-}$, Fe(V); and $Fe^{IV}O_4^{4-}$, Fe(IV)) in aqueous solution has come to the forefront due to the applications of ferrates in energy materials, green organic synthesis, and waste remediation.[6−8] This Account provides an overview of the current status of the synthesis and characterization of ferrates including the reaction mechanisms involving electron and oxygen-atom transfers. Ferrates are emerging multifunctional agents for disinfection, oxidation, and coagulation that can make a meaningful contribution to addressing the challenging demands of sustaining the water supply in the 21st century.

## 2. SYNTHESIS AND CHARACTERIZATION OF FERRATES

Three strategies are often deployed for the synthesis of sodium and potassium salts of Fe(VI) ($Na_2FeO_4$ and $K_2FeO_4$) which include wet chemical, electrochemical, and thermal approaches (Figure 1). In the wet chemical method, iron(III) oxides (e.g., $Fe_2O_3$) or their salts (e.g., $FeCl_3$, $Fe(NO_3)_3$) are oxidized by hypochlorite ($OCl^-$) in highly alkaline solution, prepared by using NaOH; a highly soluble $Na_2FeO_4$ is obtained in this procedure. A much less soluble $K_2FeO_4$ salt, with high purity (98%) of Fe(VI), is precipitated from the solution of $Na_2FeO_4$ by adding KOH.[9] Ozone usage instead of $OCl^-$ has been found to generate $Na_2FeO_4$, albeit in low yield.[9]

The electrochemical method, a relatively cleaner process, involves the use of iron electrode (Fe(0)), Fe(II) salts, and oxides and salts of Fe(III) (Figure 1).[10] The synthetic efficiency for obtaining Fe(VI) is dictated by the composition of the iron precursors, temperature, and the strength of the alkaline solution; the optimum yield of Fe(VI) is usually obtained in 14 M NaOH. Temperature influences the synthetic outcome via two competing processes. With increasing temperature, fresh surface of the bulk anode material is created that leads to an increase in yield efficiency, but self-decay of Fe(VI) is simultaneously accelerated, which is detrimental to the yield of Fe(VI). The main drawback is the overlap of potentials of the oxidation of Fe(III) to Fe(VI) and oxygen evolution. Progress is, however, being made to overcome this problem by using an inert anode (e.g., boron-doped electrode, BDE) and by employing molten hydroxides as an electrolysis medium.[10] Both methodologies have minimized the influence of the composition of anode material in Fe(VI) synthesis; related additional approaches have been reviewed.[10]

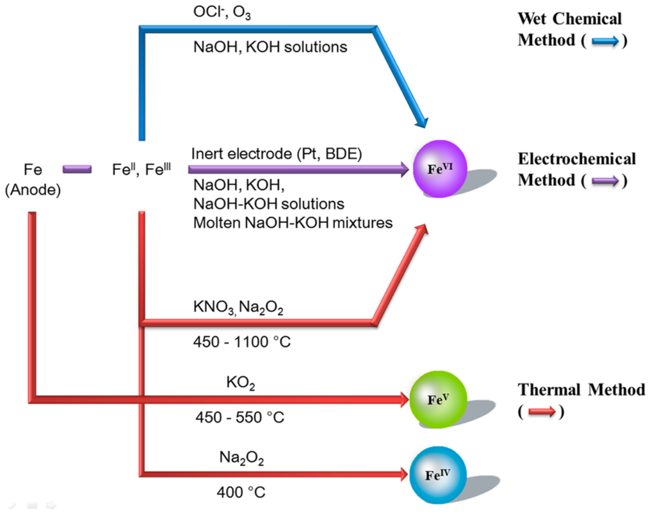

**Figure 1.** Available approaches for the synthesis of ferrates.

The thermal synthesis of Fe(VI) entails heating a mixture of iron(III) oxides and $KNO_3$ above 1100 °C to produce $K_2FeO_4$ (Figure 1) with low purity (∼30%). In recent years, such impracticably high temperatures have been lowered below 600 °C by using a mixture of iron(III) oxide and $Na_2O_2$;[11] high yield of $Na_2FeO_4$ (>90%) is obtained. Under a stream of oxygen, a sodium salt of Fe(IV), $Na_4FeO_4$, is obtainable by heating a mixture of $Fe_2O_3$ and $Na_2O_2$ (the molar ratio of Fe:Na = 1:2) at 370 °C.[11]

The stability of ferrates in solid phase remains an impediment to the utilization of these compounds in energy and environmental applications. The use of Fe(VI) in remediation necessitates its stability in water. Some progress has been made in stabilizing the $Fe^{VI}O_4^{2-}$ ion in liquid phase by invoking a hybrid process that uses thermal and wet processes to generate Fe(VI) solution which is stable for 2 weeks; this is in contrast to the typical aqueous stability of Fe(VI) that lasts only for hours.[12]

Several solid compounds of Fe(IV), Fe(V), and Fe(VI) have been prepared using the aforementioned synthetic methods and were characterized using Fourier transform infrared (FTIR) spectroscopy, neutron and X-ray diffractions, X-ray absorption near edge structure (XANES), and Mössbauer spectroscopy.[11] Mössbauer spectroscopy represents a powerful tool to distinguish different valence states of iron as the values of the isomer shift ($\delta$) are highly sensitive to the oxidation state (OS) of iron in ferrates; $\delta$ values decrease with an increase in OS (see Figure 2).[11] Thus, Mössbauer spectroscopy is a crucial technique for monitoring sample purity and identifying the intermediate states (Fe(V) and Fe(IV)) during transformation of Fe(VI) to Fe(III).

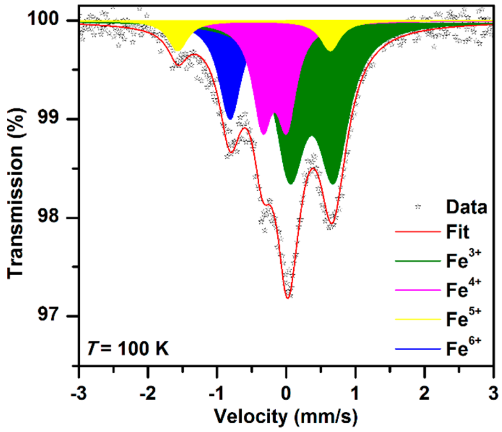

**Figure 2.** Mössbauer spectra of Fe(VI), Fe(V), Fe(IV), and Fe(III) species formed together during disproportionation of ferrate(IV) in a water/ethanol environment. The sample was treated by rapid-freeze technique and spectrum measured at 100 K.

## 3. KINETICS, MECHANISMS, AND SELECTED APPLICATIONS OF FERRATES

Fe(VI) is a strong oxidizing agent with redox potentials of +2.2 and +0.7 V (vs NHE) in acidic and basic solutions, respectively. In an acidic environment, the redox potential of Fe(VI) is the highest among the currently used chemical oxidants such as hypochlorite, chlorine dioxide, ozone, and permanganate. However, the redox potential order under basic conditions is ozone > chlorine dioxide > hypochlorite > Fe(VI) > permanganate. Significantly, Fe(VI) had no reactivity with $Br^-$ ion,[8] a common constituent of treated water, whereas ozone, chlorine dioxide, and hypochlorite react to form potentially toxic brominated byproducts.[13] Thus, Fe(VI) exhibits multiple advantages as an oxidant/disinfectant.

This section discusses the kinetics and mechanisms of various reactions involving ferrates, as well as their applicability in the degradation of persistent compounds and micropollutants, and in treatment of bacteria, viruses, heavy metals, and arsenic.

### 3.1. Kinetics of Ferrate Reactions: Effect of pH

The kinetics of the reactions with various compounds (X) having a broad range of molecular and structural variations have been studied to gain insight into the chemistry of ferrates.[8,14−18] The efforts have been focused on environmentally relevant compounds such as sulfur- and nitrogen-containing compounds (e.g., sulfide, bisulfite, thiols, cyanides, amines, and amino acids), emerging pollutants including endocrine disruptors and antibiotics (e.g., alkylphenols, sulfonamides, $\beta$-lactams, and $\beta$-blockers), and cyanotoxins (e.g., microcystin-LR). Most of the reaction kinetics have been studied using a stopped-flow spectrometry technique. Reactions have been under pseudo-order conditions in which $[X] \gg [Fe(VI)]$ and the concentration of Fe(VI) is monitored using a maximum absorbance of Fe(VI) at 510 nm ($\epsilon_{510\,nm} = 1150\ M^{-1}cm^{-1}$; Figure 3).[19] To examine the reactivity of Fe(V) and Fe(IV) with these compounds, a premix pulse radiolysis approach was applied.[8] This setup consists of two syringes, mounted in a double syringe drive; Fe(VI) solution is in one syringe, and substrate solution is another syringe. Both solutions are promptly injected into the optical cell followed by exposure to an ionizing pulse. The spectra for Fe(V) and Fe(IV) were used to determine the reactive rate constants in aqueous solution (Figure 3).

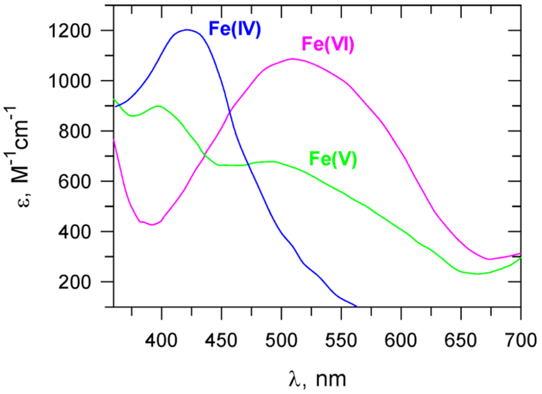

**Figure 3.** UV−visible spectra of Fe(VI), Fe(V), and Fe(IV) in 1 M NaOH. Reprinted with permission of ref 19. Copyright 1986 American Chemical Society.

The kinetic measurements of reactions of Fe(VI) with X have been carried out mostly in the neutral to basic pH range. In the acidic pH range, however, reactions of Fe(VI) with water and X are generally too rapid to follow. Also, the lack of interest of environmental chemists and engineers in performing kinetic measurements beyond the environmental pH range has resulted in fewer investigations under acidic media. Only a handful of studies on the reactivity of Fe(V)/Fe(IV) with X could be performed due to a lack of access to pulse radiolysis apparatus in the community. The values of $k_{app}$ for the reaction of Fe(VI) varied in the range from $10^{-2}$ to $10^{5}$ $M^{-1}$ $s^{-1}$ while the reactions of Fe(V) had $k_{app}$ in the range from $10^{2}$ to $10^{6}$ $M^{-1}$ $s^{-1}$ (Figure 4).

In the basic pH range, $k_{app}$ mostly decreased with pH, but in acidic solution, the trend was less clear. In the acidic pH range with Fe(VI), some compounds showed a decrease in rate constant with increasing pH (e.g., tryptophan, Trp; and ethylenediaminetetraacetate, EDTA), while glycine (Gly) showed the opposite trend (Figure 4a).[15] The reaction of Fe(V) with Gly displayed a maximum for the value of $k_{app}$ as a function of pH. However, gluconic acid exhibited a continued decrease in $k_{app}$ with increasing pH (Figure 4b).[15] Cyanide is the only pollutant that has been studied for the comparative oxidizing capability of ferrates in various oxidation states. An examination of Figure 4 suggests the rates for the reactivity of ferrates with cyanide to be Fe(V) > Fe(IV) > Fe(VI). The trends seen in Figure 4 were quantitatively modeled using the speciation of both Fe(VI) and various compounds; details of such models have been reviewed for the oxidation of X by ferrates.[8,15,20]

### 3.2. Mechanisms of Ferrate Reactions

Numerous reactions occur in the Fe(VI)−X reaction systems (Figure 5). These reactions involve, (i) the generation of Fe(V) and Fe(IV) through 1-$e^-$ and 2-$e^-$ transfer processes, (ii) production of radical species which can also generate Fe(V) and Fe(IV) species, (iii) further reactions of Fe(V) and Fe(IV) with contaminants, (iv) self-decompositions of Fe(VI), Fe(V), and Fe(IV) species, (v) reactions of ferrates with reactive oxygen species, $O_2^{\bullet-}$, and $H_2O_2$, produced from self-decompositions.

The second-order rate constants, stoichiometry, and products of the reactions have been used to delineate the mechanism of the reactions of Fe(VI).[8,15,20,21] Other mechanistic tools used were the correlations of rate constants with 1-$e^-$ transfer and 2-$e^-$ transfer potentials ($E^0_{(1)}$ and

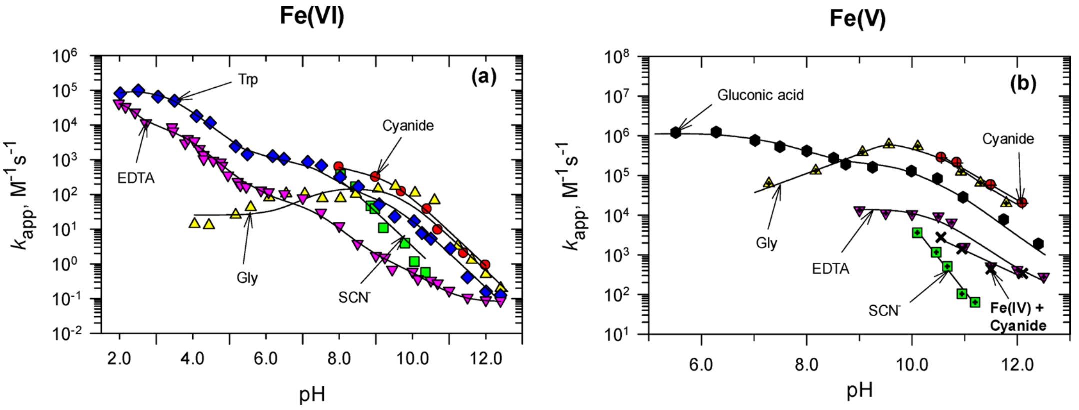

**Figure 4.** pH dependence of the reactivity of ferrates with various compounds (X): (a) Fe(VI) and (b) Fe(V).

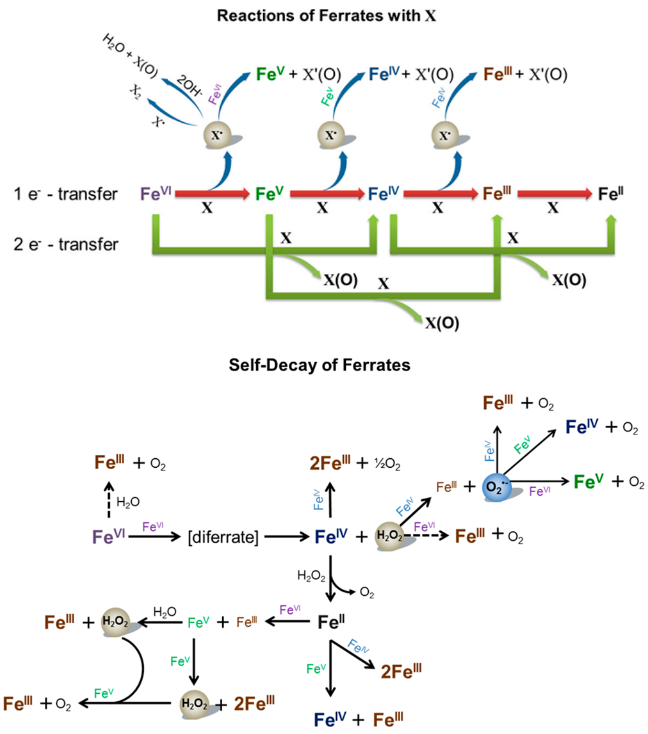

**Figure 5.** Possible reaction steps during the oxidation of compound (X) by ferrate species.

$E^0_{(2)}$).[15] Among the inorganic contaminants, cyanides and sulfide reacted via a 1-e$^-$ transfer step and three-electron equivalents per Fe(VI) could be observed. Other compounds, namely, oxy-compounds of sulfur, selenium, arsenic, and nitrogen, likely go through an initial 2-e$^-$ transfer step. For example, the oxidation of arsenite ($AsO_3^{3-}$) to arsenate ($AsO_4^{3-}$) occurred via oxygen-atom transfer (OAT),[8] thus suggesting the transfer of four-electrons-equivalents per Fe(VI).

The mechanism of oxidation of organic compounds by Fe(VI) involves a range of electron equivalents per Fe(VI) (i.e., oxidation capacity). Fe(VI) was found to oxidize three molecules of ascorbic acid (Asc) because of sequential oxidation in which Fe(V) and Fe(IV) further reacted with Asc (Fe(VI)/Fe(V)/Fe(IV) + 3Asc → Fe(III) + 3Asc$^{\bullet -}$).[15] Fe(VI) could transfer four electrons (or two O atoms) to cysteine (Cys) ($FeO_4^{2-}$ + Cys → Fe(II) + Cys($O_2$)). Three-electron transfer was observed in the oxidation of methionine (Met) (2Fe(VI) + 3Met →2Fe(III) + 3Met(O)). In the oxidation of ascorbic and sulfur compounds, Fe(VI), Fe(V), and Fe(IV) reacted with the parent molecules instead of undergoing self-decomposition to release oxygen, and therefore three- or four-electron equivalents per Fe(VI) were identified. In the preceding systems, the intermediate iron species, Fe(V) and Fe(IV), reacted with Asc; demonstrating the three-electron equivalent oxidation capacity of Fe(VI). However, a recent study performed by Lee et al.[18] on the iron(VI) 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) system showed only a one-electron equivalent oxidation capacity of Fe(VI) (Fe(VI) + ABTS → Fe(III) + ABTS$^{\bullet +}$) because Fe(V), produced in the first step, self-decomposed to Fe(III) and $H_2O_2$/$O_2$ rather than reacting with ABTS.

The mechanism of OAT has been investigated in detail by studying the oxidation of tryptophan (Trp) by $Fe^{18}O_4^{2-}$ ion.[22] The analysis of oxidized products (OPs) at pH 7.0 gave *N*-formylkynurenine (NFK) as the major product (Figure 6). Significantly, the OAT transfer from $Fe^{18}O_4^{2-}$ ion to NFK was demonstrated by reacting $Fe^{18}O_4^{2-}$ ion with Trp. Another major finding was that the increase of pH to 9.0 resulted in the formation of different OPs, namely, 4-hydroxyquinoline (4-OH Q) and kynurenic acid (Kyn-A) being the major candidates (Figure 6).

In a recent study, OAT from Fe(VI) to dibenzothiophene (DBT) resulted in the formation of a corresponding sulfone which could be enhanced in the presence of a solid surface of silica (Figure 7).[23]

In summary, Fe(VI) provides different oxidation capacities to oxidize contaminants while Fe(VI) reduced to Fe(III) or Fe(II). The rates of each of the reactions are pH dependent (Figure 4), and hence the oxidation capacity of Fe(VI) may vary with pH. The oxidation capacity involves self-decay reactions of ferrates, which not only vary with pH but can also change orders between first and second orders.[8,20,21] The self-decay of ferrate species and their reactions among themselves generate $Fe^{III}$ and reactive oxygen species (ROS) as their final products.[18] The ROS may also participate by reacting with contaminants.

### 3.3. Ferrates in Degradation of Persistent Compounds and Micropollutants

Persistent organic pollutants (POPs) are a group of lipophilic chemicals that can remain in water, soils, and sediments for decades to centuries and are resistant to chemical oxidation. Besides POPs, micropollutants, which are present in nanograms to micrograms per liter levels, exert toxic effects even at low concentrations, especially when present as mixtures.[1] Studies

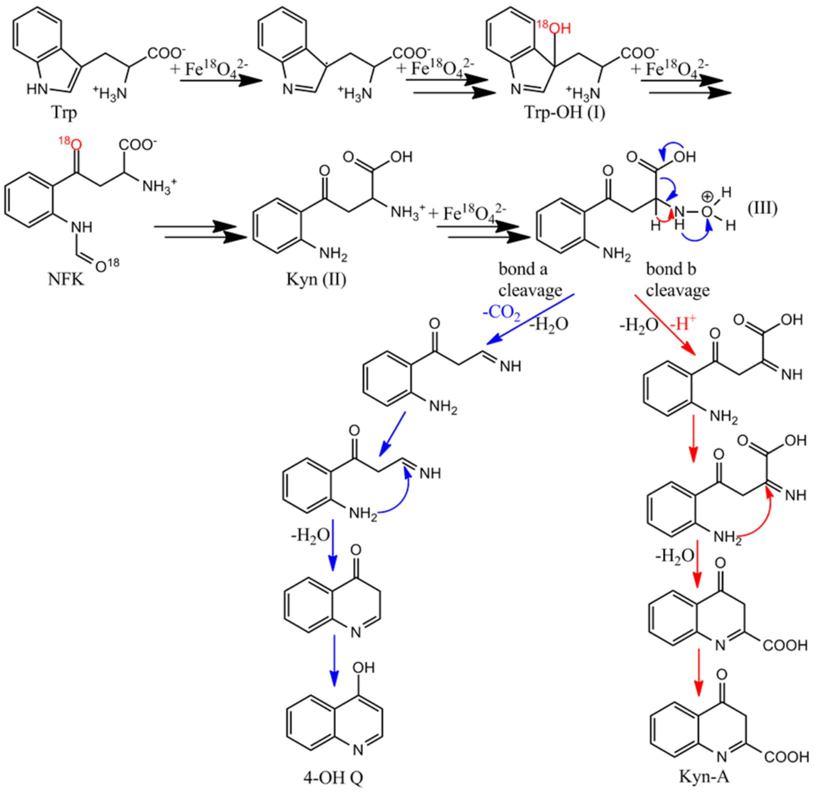

**Figure 6.** Products observed in the oxidation of Trp by Fe(VI). Reprinted with permission of ref 22. Copyright 2013 American Chemical Society.

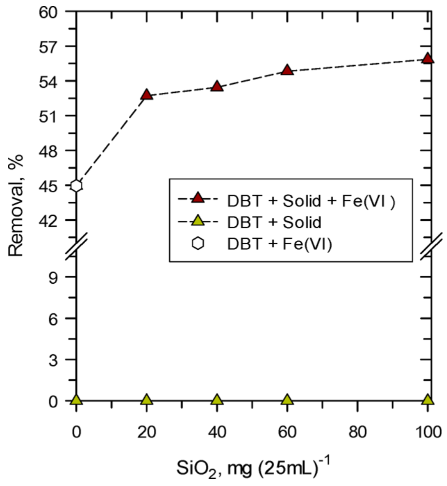

**Figure 7.** Effect of silica gel addition on DBT oxidation by Fe(VI) ($[DBT]_0$ = 106 $\mu$M, $[Fe(VI)]/[DBT]_0$ = 3.3, pH = 8.0, $t$ = 25 °C). Reprinted with permission of ref 23. Copyright 2014 Elsevier B. V.

on the degradation of POPs and micropollutants by Fe(VI) have been performed.[14,24−26] The trends for reaction rates of ferrates again reinforce the dependence of the oxidation capacity of Fe(VI) on pH. Nevertheless, the values of $k_{app}$ in Figure 4a under treatment conditions (pH ∼ 7.0−8.0) suggest that the contaminants would be degraded by 10 mg $L^{-1}$ Fe(VI) with half-lives ranging from seconds to minutes. However, if Fe(VI) cannot degrade POPs, Fe(V) and Fe(IV) would degrade these molecules because of their relatively higher reactivity (see Figure 4a,b). This was recently shown for the oxidation of extremely resistant contaminants, perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA).[25] Solid compounds of Fe(V) ($K_3FeO_4$) and Fe(IV) ($Na_4FeO_4$) were added directly into PFOS and PFOA solutions; both Fe(V) and Fe(IV) could degrade fluoro-compounds while Fe(VI) had almost no reactivity (Figure 8). These results reflect the dominance of Fe(V)/Fe(IV) reactions with fluoro-compounds over the self-decay of the ferrates.

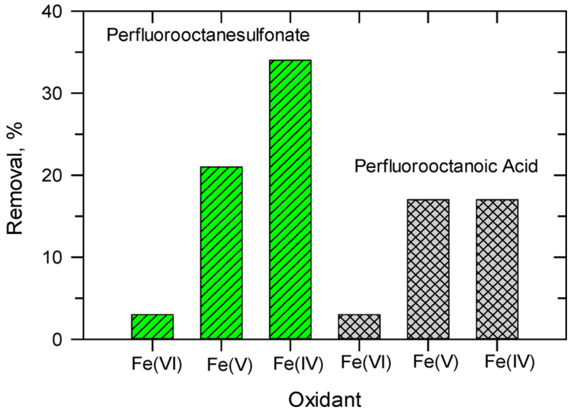

**Figure 8.** Degradation of perfluorooctylsulfonate and perfluorooctanoic acid by different higher-valent iron species at pH 9.0. Reproduced with permission of ref 25. Copyright 2014 Springer.

Another example is the degradation of dibutyl phthalate (DBP) and dimethyl phthalate (DMP) by Fe(VI)−$TiO_2$ under UV light (Figure 9);[26] $TiO_2$ nanoparticles (P25 Degussa) were suspended in stated Fe(VI) solutions. Neither DBP nor DMP decomposed amply with either the Fe(VI) or $TiO_2$/UV systems alone but could be degraded when Fe(VI) was present in the photocatalytic system. The $TiO_2$/UV system may produce conduction band electrons ($e^-_{cb}$), which reacted with Fe(VI) to generate Fe(V)/Fe(IV) species, (Fe(VI) + $e^-_{cb}$ →

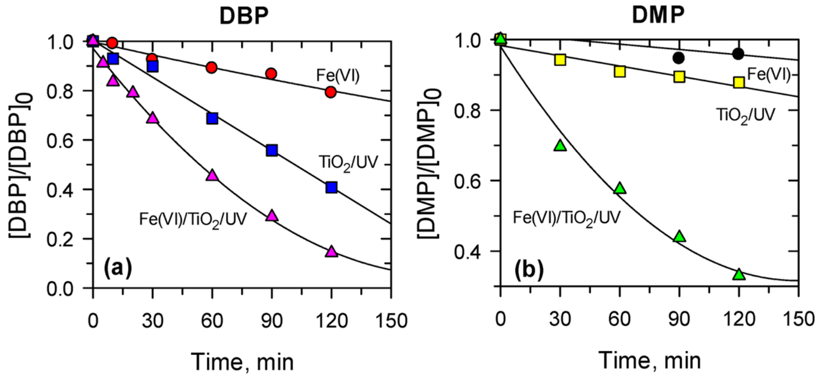

**Figure 9.** Photocatalytic degradation of by the Fe(VI)−$TiO_2$−UV system at pH 9.0 (Reproduced with permission of ref 26. Copyright 2010 Springer.): (a) DBP and (b) DMP.

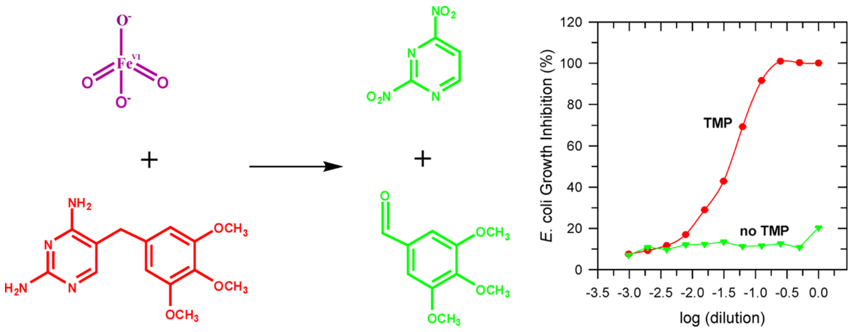

**Figure 10.** Identified oxidized products (left) and antibiotic tests against *E. coli* (right) in the treatment of TMP by Fe(VI). Reprinted with permission from ref 27. Copyright 2011 American Chemical Society.

Fe(V); Fe(V) + $e^-_{cb}$ → Fe(IV)), thus causing the degradation of recalcitrant contaminants. This Fe(VI)-enhanced photocatalytic oxidation of contaminants in aqueous $TiO_2$ suspensions has been reviewed.[26]

The oxidative treatment of micropollutants has been pursued in our laboratory, and the compounds studied include typical endocrine disruptors (nonylphenol and ocylphenol) and pharmaceuticals (sulfonamides, $\beta$-lactams, and $\beta$-blockers).[27−29] The kinetics of the reactions showed the removal of micropollutants in seconds to minutes by Fe(VI), and the results have been in agreement with other studies, performed on a wide range of micropollutants in wastewater using Fe(VI).[14,24,30] Studies on the oxidation of sulfamethoxazole (SMX) and trimethoprim (TMP) by Fe(VI) showed complete removal of SMX and TMP by Fe(VI), and the stoichiometries of the reactions were 4:1 and 5:1 (Fe(VI):([SMX] or [TMP])). The product analysis showed the oxidation of amines to nitro-groups; the oxidative transformation of TMP ultimately resulted in the formation of 3,4,5-trimethoxybenzaldehyde and 2,4-dinitropyrimidine (Figure 10).[27]

The complete removal of amine moieties implies the elimination of the antibiotic activity of TMP (Figure 10, left);[27,31] the oxidized products of TMP[26] revealed that they did not exhibit any antibiotic activity against *Escherichia coli* (*E. coli*; Figure 10, right). A similar oxidative treatment of triclosan, an antimicrobial drug present in consumer products, by Fe(VI) showed loss of its toxicity against the alga *Pseudokirchneriella subcapitana*.[32] Fe(VI) by itself or in conjunction with titania is thus a good candidate for the oxidative degradation of antibiotics in water.[26]

### 3.4. Treatment of Bacteria and Viruses

A number of studies have shown the effectiveness of Fe(VI) for inactivation of viruses and bacteria.[33] Treatment of water from different sources with Fe(VI) achieved more than 99.9% kill rates of total coliform. Most of the disinfection studies have been carried out on *E. coli*, and its inactivation over several log units has been demonstrated. Importantly, Fe(VI) could inactivate sulfite-reducing clostridia and aerobic spore-formers (Figure 11),[33] both chlorine resistant bacteria. Chlorination was able to inactivate aerobic spore-bearers slightly over 1-log unit, but Fe(VI) reduced this species by 3-log units.[33] Similarly,

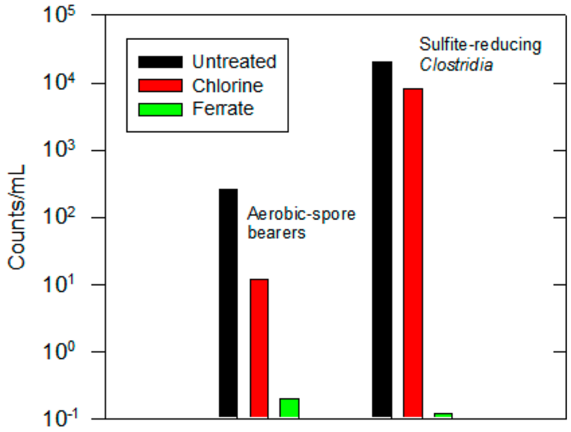

**Figure 11.** Disinfection of river water by Fe(VI) over 30 min contact time (sodium ferrate(VI), 2 mg/L as Fe; hypochlorite, 3.5 mg/L chlorine). Reproduced with permission of ref 33. Copyright 2005 IWA Publishing.

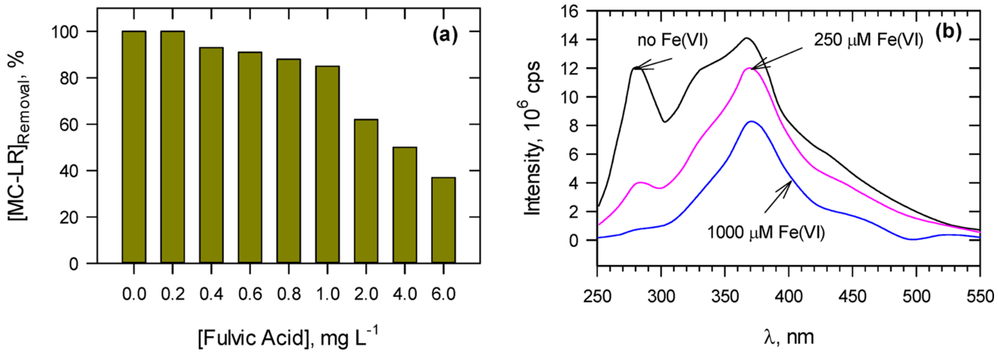

**Figure 12.** (a) Effect of fulvic acid on the removal of MC-LR by Fe(VI). Experimental conditions: [Fe(VI)] = 10 μM; [MCLR] = 0.5 μM; pH 9.0. Reproduced with permission of ref 35. Copyright 2014 American Chemical Society. (b) SSF spectra of HA before and after the addition of Fe(VI). Reproduced with permission of ref 36. Copyright 2013 Elsevier Ltd.

sulfite-reducing clostridia being resistant to chlorination was completely inactivated by Fe(VI).[33]

Other bacterial species that have been found to be susceptible to Fe(VI) are *Bacillus cereus*, *Streptococcus bovis*, *Staphylococcus aureus*, *Shigella flexneri*, *Streptococci faecalis*, and *Salmonella typhimurium*. Fe(VI) also effectively inactivates a wide range of viruses, and the requisite contact times have been established, the latest work being on the inactivation of bacteriophage MS2 by Fe(VI).[34] Treatment of Fe(VI) can also damage the capsid protein and genome.[34]

In our laboratory, the work on oxidative treatment of the potent cyanotoxin, microcystin-LR (MC-LR), in drinking water by Fe(VI) has been initiated[35] wherein Fe(VI) could successfully degrade MC-LR in buffered and lake water samples. The analyses of products showed that Fe(VI) attacked several moieties of MC-LR. Remarkably, the degradation byproducts of MC-LR had no significant biological toxicity as assessed by protein phosphatase (PP1) activity.[35] Natural organic matter (NOM; e.g., fulvic acid, FA) had a significant effect on the removal efficiency (Figure 12a); MC-LR and FA compete in their reactions with Fe(VI). The potential reactivity of NOM (e.g., sedimentary humic acid, HA) with Fe(VI) has been studied independently using synchronous scan fluorescence (SSF) spectral technique (Figure 12b).[36]

A decrease in SSF intensity was observed by adding Fe(VI). The peak at 287 nm, corresponding to the low molecular weight (MW) fraction of HA, almost completely disappeared. The peak at 364 nm, representing the high MW fraction of HA, still had significant remaining intensity. Overall, the dosages of Fe(VI) for removing micropollutants/toxins would vary with the nature and source as well as concentration of NOM present in contaminated water.

In summary, ferrates are highly efficient not only in the treatment of a wide spectrum of bacterial strains but also in the degradation of toxins produced by microorganisms, e.g., cyanobacteria.

### 3.5. Ferrates in Removal of Heavy Metals and Arsenic

Fe(VI) as a coagulating agent is highly effective in removing metals and nonmetals from water. The main iron species responsible for the coagulation/co-precipitation are nanocrystalline iron(III) oxides/hydroxides, produced via the reduction of Fe(VI). Our own efforts have centered on removing arsenite, arsenate, and metals in metal−cyanide complexes,[37,38] wherein Fe(VI) efficiently removes Cd, Cu, and Zn (though not Ni). Fe(VI) alone, and in combination with Al(III) and Fe(III) ions, can completely remove arsenic from water.[38] Figure 13 presents the removal of arsenic at varying concentrations of Fe(VI) and Al(III) ions. The addition of a small amount of Fe(VI) to an aqueous arsenite solution, followed by precipitation via Al(III) salts, removed the arsenic to amounts below the detection limit (<1 μg L$^{-1}$ or <1 ppb). Overall, iron has been applied extensively for removing arsenic from water, and specifically, Fe(IV) has been suggested in iron-catalyzed oxidation of As(III) by $O_2$ and $H_2O_2$.[39]

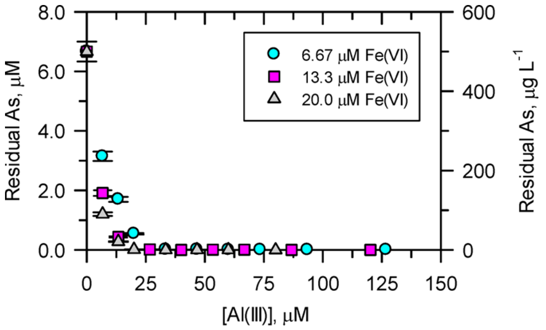

**Figure 13.** Removal of arsenite by Fe(VI)/Al(III) salts at pH 6.5. The initial arsenic concentration was 500 μg L$^{-1}$. Reprinted with permission of ref 37. Copyright 2009 Elsevier B. V.

The matrix components, nitrate, phosphate, silicate, and NOM increased the required concentrations of Fe(VI) for the removal of arsenic; the mechanism has been pursued using surface and spectroscopic techniques.[40] Importantly, a significant amount of arsenic was covalently incorporated into the structure of the nanocrystalline iron(III) oxide (Figure 14). A

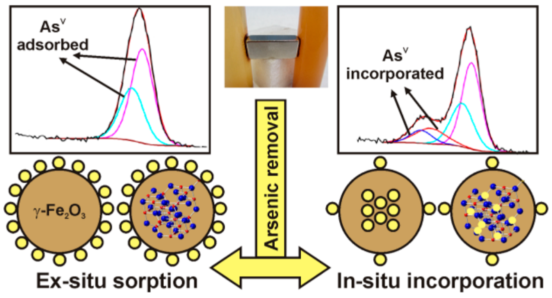

**Figure 14.** Different mechanisms of arsenic removal by Fe(III), ex situ sorption (left) and Fe(VI) induced in situ covalent structural incorporation (right). Reprinted with permission from ref 40. Copyright 2013 American Chemical Society.

detailed examination, using high-resolution X-ray photoelectron spectroscopy (see Figure 14) and in-field $^{57}$Fe Mössbauer spectroscopy, showed that arsenic was *in situ* covalently embedded in the tetrahedral sites of the Fe(III) spinel structure that was formed during the reduction of Fe(VI), thus achieving highly efficient arsenic removal. Interestingly, no arsenic was bound inside the structure of iron(III) oxide when arsenic was added *ex situ* into the solution containing solid iron(III) oxides, produced independently via the reduction of Fe(VI) in deionized water (Figure 14).

The mechanistic studies on the Fe(VI)-promoted removal of free metal ions are currently pursued through the surface and spectroscopic analysis of the final iron(III) oxides product. The role of inherent properties of metal ions (e.g., ionic radius) is being explored to ascertain their structural incorporation into the crystal structures of different iron(III) oxides such as ferrite and $\gamma$-$Fe_2O_3$ nanoparticles. Importantly, firmly bound arsenic and heavy metals, observed in the case of Fe(VI) treatment, would not leach back to the aquatic environment. Furthermore, Fe(III) nanoparticles containing metals are strongly magnetic and could be separated from the treated water using an external magnet.[40]

Most of the aforementioned examples described in the literature are restricted to the laboratory scale operations, although some pilot scale applications have recently been performed.[41,42]

## 4. CONCLUSION AND FUTURE ASPECTS

Undoubtedly, ferrates represent a highly promising and environmentally friendly class of agents exhibiting multimodal activity due to their high oxidation capacity combined simultaneously with disinfection and coagulation effects in a single dose. However, the effects of water quality parameters (e.g., concentrations of bromide ions, alkalinity, and characteristics of NOM) need to be established to learn about the efficacy of Fe(VI) in treating polluted water.

The high pH of treatment water with an alkaline ferrate solution remains a great concern. There are still challenges in terms of ferrate synthesis, stability control, mechanisms of action, and large scale applications. Solid Fe(VI) requires special storage and packaging to avoid exposure to humidity, which decomposes it to Fe(III). A complex approach that stabilizes Fe(VI) for a few weeks in aqueous medium may enhance opportunities to utilize Fe(VI) in treatment processes. However, the large scale production of Fe(VI) would require additional research to resolve engineering and economic challenges.

Several examples describe the successful use of Fe(VI) in the abatement of inorganic pollutants. However, similar studies on remediation of organic contaminants using ferrates are rather limited. Advanced analytical techniques such as liquid chromatography−high-resolution mass spectrometry may help identify and quantify the oxidized products. It is important to scrutinize the environmentally benign nature of ferrate treatment processes, especially if followed by a biodegradation protocol which enables the mineralization of organics via hybrid oxidation−biodegradation approach.

Adequate progress has been made in understanding the mechanism of the reactions of Fe(VI) in alkaline medium. However, similar studies are almost unknown under acidic conditions, and limited studies conducted so far have shown no clear trends. Therefore, delineation of the mechanism of the oxidative chemistry of Fe(VI) in acidic solution can be made by extending the kinetic and product studies; the involvement of different protonated species of Fe(VI) and pollutants in oxidative mechanism will be clarified. Furthermore, direct evidence for the formation of intermediate iron species, Fe(IV) and Fe(V), in the oxidation of compounds by Fe(VI) can be provided by using rapid freezing of reaction solution in a time scale of milliseconds, followed by their characterization via Mössbauer and EPR spectroscopy techniques. An application of synchrotron radiation may also aid in establishing highly unstable Fe(IV) and Fe(V) species.

Fe(V) and Fe(IV) react orders of magnitude faster than Fe(VI); however, to date, no study has been performed to investigate the oxidation of any emerging contaminants (e.g., pharmaceuticals and personal care products) by Fe(V) and Fe(IV). These studies will assist in understanding the role of Fe(IV) and Fe(V) during oxidation processes. In addition, understanding the oxidative properties of Fe(V) and Fe(IV) may enable one to harness three or four electron equivalents oxidation capacity of Fe(VI) in treating polluted water.

Finally, the mechanisms of the disinfection and coagulation properties of Fe(VI) must be understood. A challenging task, for example, would be to delineate the concomitant degradation of cyanobacteria and associated toxins by Fe(VI). Further studies on the mechanism of disinfection are needed to explore the sites of the attacks in pathogens, e.g., genetic damage and ensuing changes in gene expression, or direct damage to proteins. In any coagulation studies, advancements in comprehending the mechanisms of removal of metals and radioactive elements in the presence and absence of natural organic matter will be rewarding. Advanced surface analytical techniques in studying the coagulation/co-precipitation processes of Fe(VI) will also provide insight into the possible leaching of metals after their removal through embedding/sorption into solid iron(III) oxide/hydroxide precipitates. Lastly, these investigations may stimulate the sustainable applications of these earth-abundant, iron-based materials in greener chemical transformations, an area that has been least explored.

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### Notes

The authors declare no competing financial interest.

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**Rajender S. Varma** was born in India and earned his Ph.D. from Delhi University in 1976. After postdoctoral research at Robert Robinson Laboratories, Liverpool, U.K., he was a faculty member at Baylor College of Medicine and Sam Houston State University prior to joining the Sustainable Technology Division at the U.S. Environmental Protection Agency in 1999. He has over 40 years of research experience in management of multidisciplinary technical programs ranging from natural products chemistry to development of more environmentally friendly synthetic methods using microwaves, ultrasound, and so on. Lately, he has focused on greener approaches to assembly of nanomaterials and sustainable applications of magnetically retrievable nanocatalysts in benign media.

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