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Accelerated Oxidation of Organic Contaminants by Ferrate(VI): The Overlooked Role of Reducing Additives

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Abstract

This paper presents an accelerated ferrate(VI) ($\text{Fe}^{\text{VI}}\text{O}_4^{2-}$, Fe^{VI}) oxidation of contaminants in 30 s by adding one-electron and two-electron transfer reductants ($\text{R}_{(1)}$ and $\text{R}_{(2)}$). An addition of $\text{R}_{(2)}$ (e.g., NH_2OH , As^{III} , Se^{IV} , P^{III} , and NO_2^- , and $\text{S}_2\text{O}_3^{2-}$) results in Fe^{IV} initially, while Fe^{V} is generated with the addition of $\text{R}_{(1)}$ (e.g., SO_3^{2-}). $\text{R}_{(2)}$ additives, except $\text{S}_2\text{O}_3^{2-}$, show the enhanced oxidation of 20–40% of target contaminant, trimethoprim (TMP). Comparatively, enhanced oxidation of TMP was up to 100% with the addition of $\text{R}_{(1)}$ to Fe^{VI} . Interestingly, addition of $\text{S}_2\text{O}_3^{2-}$ (i.e., $\text{R}_{(2)}$) also achieves the enhanced oxidation to 100%. Removal efficiency of TMP depends on the molar ratio ($[\text{R}_{(1)}]:[\text{Fe}^{\text{VI}}]$ or $[\text{R}_{(2)}]:[\text{Fe}^{\text{VI}}]$). Most of the reductants have the highest removal at molar ratio of ~ 0.125 . A $\text{Fe}^{\text{VI}}\text{--}\text{S}_2\text{O}_3^{2-}$ system also oxidizes rapidly a wide range of organic contaminants (pharmaceuticals, pesticides, artificial sweetener, and X-ray contrast media) in water and real water matrices. Fe^{V} and Fe^{IV} as the oxidative species in the $\text{Fe}^{\text{VI}}\text{--}\text{S}_2\text{O}_3^{2-}$ -contaminant system are elucidated by determining removal of contaminants in oxygenated and deoxygenated water, applying probing agent, and identifying oxidized products of TMP and sulfadimethoxine (SDM) by $\text{Fe}^{\text{VI}}\text{--}\text{S}_2\text{O}_3^{2-}$ systems. Significantly, elimination of SO_2 from sulfonamide (i.e., SDM) is observed for the first time.

Graphical Abstract

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Associated Content

Notes

The authors declare no conflicts of interest.

Introduction

Iron (Fe) is the second most abundant metal after aluminum in the earth's crust and is easily available. Iron plays many important roles in physiological processes, industrial synthesis, and remediation of pollutants in water.(1–7) In the decontamination field, iron-based technologies have been researched for many decades, including nanoscale zerovalent iron (nZVI), iron-based reactants/catalysts (e.g., Fe^{2+} , Fe^{3+} , Fe_3O_4 , and Fe_2O_3) in advanced oxidation processes (Fe-AOPs), and high-valent iron-oxo units based systems (e.g., $\text{Fe}^{\text{IV}}=\text{O}$, $\text{Fe}^{\text{V}}=\text{O}$, and $\text{Fe}^{\text{VI}}=\text{O}$).(8–12) Among the high-valent iron remediation technologies, ferrate(VI) ($\text{Fe}^{\text{VI}}\text{O}_4^{2-}$, Fe^{VI}) has been receiving great attention due to its multiple roles as oxidant, disinfectant, and coagulant.(13–15) Examples include depollution of flue gases, pesticides, estrogens, and antibiotics, inactivation of bacteria, and viruses as well as coagulation of toxic metals and radionuclides.(15–17)

Fe^{VI} has shown high effectiveness in decontaminating organic pollutants from water. (12,15,18) However, oxidation of certain organics takes the time of minutes to hours to react with Fe^{VI} . This reactivity of Fe^{VI} decreases its oxidation capacity (i.e., electron equivalent per Fe^{VI}). Furthermore, due to simultaneous consumption of Fe^{VI} by unwanted reaction with water, a slow reaction with pollutants requires higher dosages of the oxidant, particularly at pH relevant to treatment conditions (pH 7.0 and 8.0).(15,19) These limitations restrict the applications of Fe^{VI} to efficiently oxidize a wide range of pollutants in water.

This paper presents a systematic innovative strategy to tune the chemistry of Fe^{VI} by selectively adding one-electron (S(IV)) and two-electron (or oxygen-atom transfer) reducing agents (hydroxylamine (NH_2OH), arsenite (AsO_3^{3-}), selenite (SeO_3^{2-}), phosphite (PO_3^{3-}), nitrite (NO_2^-), iodide (I^-), and thiosulfate ($\text{S}_2\text{O}_3^{2-}$)) (see Supporting Information (SI) Text S1)(20–25) that initially generate the short-lived Fe^{V} and Fe^{IV} species, respectively (i.e., $\text{R}_{(1)}$ (i.e., $\text{Fe}^{\text{VI}} \rightarrow \text{Fe}^{\text{V}}$),(26) and $\text{R}_{(2)}$ (i.e., $\text{Fe}^{\text{VI}} \rightarrow \text{Fe}^{\text{IV}}$).(27) Fe^{V} and Fe^{IV} have 2–5 orders of reactivity higher than that of Fe^{VI} with reactivity order of $\text{Fe}^{\text{V}} > \text{Fe}^{\text{IV}} > \text{Fe}^{\text{VI}}$.(28–31) Our current results showed that the initially generated Fe^{V} had the highest enhancement (up to 100%), while oxygen-atom transfer reductants, except $\text{S}_2\text{O}_3^{2-}$, gave moderate enhancement (up to 40%) by producing Fe^{IV} . This feature of enhancement has not been reported in literature.

Recent studies carried out on enhancing the oxidation of contaminants in 15 s were restricted to few reductants that gave the contradictory results, and the description of observed findings was inconsistent.(32–34) In the earlier work on Fe^{VI} –S(IV) system,

enhancement was proposed solely due to activation of S(IV) by Fe^{VI} yielding SO₃^{•-}, SO₄^{•-}, and [•]OH without any role of intermediate Fe^V/Fe^{IV} species. Later work investigated the combined use of the reductants (S(IV), S₂O₃²⁻, dithionite (S₂O₄²⁻), pyrosulfite (S₂O₅²⁻), and AsO₃³⁻) with Fe^{VI} to oxidize N,N-diethyl-3-toluamide (DEET) in 10 s.(32) This study claimed that only sulfate radicals (SO₄^{•-}) caused the enhancement in the Fe^{VI}-S(IV) system.(32) Additionally, this study found no enhanced oxidation of DEET by adding S₂O₃²⁻ and AsO₃³⁻ to Fe^{VI} at a high ratio (4:1) of [S₂O₃²⁻/AsO₃³⁻]:[Fe^{VI}].(32) Interestingly, our current study demonstrated the accelerated oxidation of contaminants by Fe^{VI} even using S₂O₃²⁻ and AsO₃³⁻ when the ratio was much lower. Our previous work on Fe^{VI}-S(IV) system showed that multiple oxidizing species (Fe^V/Fe^{IV}, SO₄^{•-}, and [•]OH) were responsible to cause enhancement of oxidation of antibiotics in water in 15 s.

Our work presented herein suggested that only Fe^V/Fe^{IV} species are involved in enhancing the oxidation of a wide range of contaminants in water at a lower ratio of [S(IV)/S₂O₃²⁻]:[Fe^{VI}]. Importantly, we demonstrated the critical roles of molar ratios of R₍₁₎/R₍₂₎ to Fe^{VI} and kind of reductants (i.e., initial one-electron versus oxygen-atom transfer) to observe the magnitude of enhancement and involved oxidizing species in the combination of Fe^{VI} with the reductants. Moreover, SO₃²⁻ and S₂O₃²⁻ are sulfur-based reductants but have different chemistry in reaction with Fe^{VI} (i.e., R₍₁₎ and R₍₂₎). We examined the Fe^{VI}-S₂O₃²⁻ system in details for oxidizing a wide range of contaminants. We have applied density functional theory (DFT) calculations to demonstrate the two-electron transfer in the initial step of the Fe^{VI}-S₂O₃²⁻ system. Also, S₂O₃²⁻ was attractive to us because it is a commercially available salt with high stability. Comparatively, SO₃²⁻ is not stable in water(35) and is used in gaseous form (SO₂ (g)) at large facilities involving storage and handling issues. A system of Fe^{VI}-S₂O₃²⁻ is an attractive alternate in enhancing oxidation of contaminants in large scale applications.

The objectives of current paper are to (i) demonstrate the enhanced reactivity of Fe^{VI} by adding R₍₁₎ and R₍₂₎ at trace levels with a focus on S₂O₃²⁻ to decontaminate organics in water in 30 s. Sixteen organic contaminants of different categories and structures (artificial sweetener, pesticides, pharmaceuticals, and X-ray contrast medium, see SI Table S1) were selected. These compounds carry public health concerns and have shown low reactivity with Fe^{VI} alone,(12) (ii) identify the reactive oxidizing species causing accelerated oxidation of contaminants including recalcitrant compounds by Fe^{VI}-R₍₁₎ and Fe^{VI}-R₍₂₎ systems, (iii) learn the transformation products and reaction pathways of two representative pharmaceuticals (TMP and SDM) by Fe^{VI}-R₍₁₎ systems, and (iv) exhibit tuned reactivity of Fe^{VI} (i.e., Fe^{VI}-S₂O₃²⁻ system) to rapidly remediate the organic contamination in real water matrices.

Materials and Methods

Chemicals and Reagents

Detailed information on all test organic contaminants, buffer chemicals and preparation of reaction solutions is provided in SI Text S2.

Oxidation of Organic Contaminants

All batch experiments were conducted in a series of 100 mL glass jars under constant stirring rate (400 rpm) with a magnetic stirrer. Elimination of each contaminant or their mixtures by Fe^{VI} with or without $\text{S}_2\text{O}_3^{2-}$ was initiated by mixing equal solution volumes of 10 mL, and the final pH values of reaction solutions were kept at 8.00 ± 0.05 . The concentration of Fe^{VI} was maintained at $100.0 \mu\text{M}$, and the ratios of $[\text{S}_2\text{O}_3^{2-}]:[\text{Fe}^{\text{VI}}]$ in the system varied from 0 to 5.0 for aqueous removal of TMP ($5.0 \mu\text{M}$). Similar removal experiments of TMP were performed by preadding seven other reducing agents (i.e., NH_2OH , AsO_3^{3-} , NO_2^- , SeO_3^{2-} , PO_3^{3-} , I^- , and SO_3^{2-}) with different test concentrations, followed by Fe^{VI} oxidation. The optimized ratio of $[\text{S}_2\text{O}_3^{2-}]:[\text{Fe}^{\text{VI}}]$ at 1:8 (0.125) was used to oxidize all organic contaminants at environmentally relevant concentration (i.e., $1.0 \mu\text{M}$) in either ultrapure water or real water samples (river and lake water). After 30 s of oxidation, a $20.0 \mu\text{L}$ NH_2OH solution (1 M, $[\text{NH}_2\text{OH}]:[\text{Fe}^{\text{VI}}] = 10.0$) was added to quench the reactions. Samples were transferred into high performance liquid chromatography (HPLC) vials and subsequently analyzed using the HPLC method (see details in SI Text S3 and S4).

Analytical Procedures

Two inorganic reactive radicals (i.e., $\cdot\text{OH}$ and/or $\text{SO}_4^{\cdot-}$), possibly produced in the oxidation system, were measured using the room-temperature electron paramagnetic resonance (EPR) technique.(34,36) Detailed information is provided in SI Text S4.

Results and Discussion

$\text{Fe}^{\text{VI}}\text{-R}_{(2)}$ Systems

Initially, accelerated removal of TMP by Fe^{VI} was examined at pH 8.0 by adding $\text{R}_{(2)}$ additives at various concentrations. Herein, tested $\text{R}_{(2)}$ act as two-electron transfer reducing species were evident through initial step of the reduction of Fe^{VI} by reductants. Initial steps of different reductants were supported by experimental finding using ^{18}O -labeled salt of Fe^{VI} (i.e., $\text{K}_2\text{Fe}^{18}\text{O}_4$) that demonstrated transfer of oxygen-atom from the oxidant to reductants (e.g., NO_2^- to NO_3^- and PO_3^{3-} to PO_4^{3-}).(24,37) The DFT calculations on the $\text{Fe}^{\text{VI}}\text{-AsO}_3^{3-}$ system also provided preferable oxygen-atom transfer as first step of the reaction.(22,38) More details of the individual reductant as $\text{R}_{(2)}$ are given in SI Text S1.

Without $\text{R}_{(2)}$ additives, the removal of TMP by Fe^{VI} was $\sim 16\%$, which rapidly increased following the introduction of $\text{R}_{(2)}$ into the $\text{Fe}^{\text{VI}}\text{-TMP}$ mixed solution (Figure 1a). In solutions containing TMP and $\text{R}_{(2)}$ (i.e., no Fe^{VI}), no oxidation of TMP was observed (SI Figure S1). This suggested that the enhancement of TMP was due to the reactive species generated by the interactions between Fe^{VI} and $\text{R}_{(2)}$. The maximum removal of TMP oxidation for $\text{R}_{(2)}$ was up to $\sim 25\%$, at a molar ratio of 0.1 ($[\text{R}_{(2)}]:[\text{Fe}^{\text{VI}}]$) (Figures 1a and b). At molar ratios greater than 0.1, enhanced oxidation of TMP decreased. At high levels of NH_2OH and AsO_3^{3-} (i.e., $[\text{R}_{(2)}]:[\text{Fe}^{\text{VI}}] = 10.0$ and 5.0 , respectively), oxidation of TMP ceased. Importantly, a molar ratio of 10.0 using hydroxylamine as a quenching reagent was sufficient to stop the oxidation of the contaminant by Fe^{VI} . Increasing the concentration of selenite resulted in an initial decrease to $\sim 6\%$, followed by no effect due to further increase in the molar ratios of selenite to Fe^{VI} (Figure 1b). An increase in concentration of PO_3^{3-}

showed no decrease in removal of TMP (Figure 1b). This trend is similar to NO_2^- , in which the maximum removal of TMP was ~30% at a molar ratio of 1.0 (Figure 1c). In this additive, eliminating oxygen from the air by purging with nitrogen showed no difference in removal of TMP (Figure 1c).

The results shown in Figure 1 may be explained by the sequence of reactions taking place in the $\text{Fe}^{\text{VI}}\text{-R}_{(2)}\text{-TMP}$ system (Reactions 1–5). In absence of $\text{R}_{(2)}$, TMP is oxidized only by Fe^{VI} (Reaction 1). However, when $\text{R}_{(2)}$ is added, Reaction 2 occurs, generating Fe^{IV} species (speculative as $\text{HFe}^{\text{IV}}\text{O}_3^-$), which can react with TMP (Reaction 3). Fe^{IV} species are much more reactive than parent Fe^{VI} and therefore, enhancement in removal of TMP was observed by adding $\text{R}_{(2)}$ to $\text{Fe}^{\text{VI}}\text{-TMP}$ solutions (Figure 1). However, Fe^{IV} may also react with $\text{R}_{(2)}$ (Reaction 4). Self-decomposition reaction of Fe^{IV} may also happen (Reaction 5).(39)

Results of Figure 1 suggest that enhancement due to $\text{R}_{(2)}$ is related to the concentrations of generated Fe^{IV} , added $\text{R}_{(2)}$, and the competitive rate constants of Reactions 2–5. At low concentration of $\text{R}_{(2)}$, Fe^{IV} produced from Reaction 2 seems to be reacting with TMP (Reaction 3) to yield enhancements in removal (Figure 1). However, with increasing concentrations of $\text{R}_{(2)}$, Reaction 4 begins to dominate and causes the decreasing concentration of Fe^{IV} , that is, less Fe^{IV} species is available to oxidize TMP (i.e., $\text{TMP(oxidized products)}$), which results in the decreasing trend in the removal of TMP. Incomplete removal of TMP by the $\text{Fe}^{\text{VI}}\text{-R}_{(2)}$ system suggests that Reaction 5 may be significant to result in the disappearance of Fe^{IV} itself(39) rather than the oxidation of TMP.

The rate constants of Reactions 2–5, shown to describe results of Figure 1, are currently unknown in literature to describe fully enhancement in removal of TMP under $\text{Fe}^{\text{VI}}\text{-R}_{(2)}$ systems under studied conditions. Determination of these rate constants would require modified premix pulse radiolysis technique.(29,30,39) It seems that the rate constants of

Reactions 2 and 4 vary with the type of $R_{(2)}$, which gave different patterns of the oxidation of TMP with increasing molar ratios of $R_{(2)}$ to Fe^{VI} . Furthermore, Reactions 1–5 are a simplistic representation of involved reactions and complex chemistry, which may be existing in a particular Fe^{VI} - $R_{(2)}$ additive system.

Fe^{VI} -Iodide System

The addition of iodide resulted in ~41% removal at a molar ratio of 0.1 ($[I^-]:[Fe^{VI}]$) (Figure 2a). Further increase in this molar ratio decreased the removal of TMP, and complete inhibition of TMP was observed at the molar ratio of 1.0 (Figure 2a). A formation of I_3^- in the reaction of Fe^{VI} with I^- has been observed, which produced through initial one-electron transfer step ($Fe^{VI} + I^- \rightarrow Fe^V + I^\bullet$) (SI Text S1).(20) The generated Fe^V may react with TMP to enhance the oxidation of TMP. However, a recent study proposed oxygen-atom transfer step that gave Fe^{IV} species in initial step ($Fe^{VI} + I^- \rightarrow Fe^{IV} + HOI/OI^-$) (SI Text S1).(40) The Fe^{IV} species may also increase the oxidation of TMP. Formation of different oxidized products has been observed in the reaction of O_3 with I^- .(41) Formed HOI has high reactivity with aromatic compounds, which suggests that TMP may also be oxidized by HOI in the Fe^{VI} - I^- system.(40) These reactive species would yield the enhanced oxidation of TMP observed in our study. It appears that at molar ratios greater than 0.1 ($[I^-]:[Fe^{VI}]$), the reactions of Fe^V/Fe^{IV} with I^- start competing with that of these intermediate iron species with TMP to cause decrease in enhanced effect of I^- to oxidize TMP.

Fe^{VI} -Sulfite System

Sulfite ion also showed the enhancement, with complete elimination of TMP at a molar ratio of 0.25 ($[SO_3^{2-}]:[Fe^{VI}]$) (Figure 2b). A detailed examination of the oxidation of SO_3^{2-} by Fe^{VI} showed that SO_3^{2-} acts as $R_{(1)}$ (see SI Text S1).(26) Enhanced oxidation of contaminants by Fe^{VI} - SO_3^{2-} system, studied only at a molar ratio of 4.0 ($[SO_3^{2-}]:[Fe^{VI}]$), was also reported in our previous study and other investigations.(32,34) Figure 2b shows that the increasing ratios had no decreasing effect on TMP removal until the molar ratio of 5.0. However, when the molar ratio was greater than 5.0, enhanced oxidation of TMP decreased and no enhancement could be obtained at the molar ratio of 20.0 (SI Figure S2). When nitrogen was purged in Fe^{VI} - SO_3^{2-} -TMP solution, enhanced removal efficiency decreased, and maximum removal of TMP was ~83% in the molar ratio between 0.5 and 1.0 (Figure 2b). In the molar ratio range of 1.0–5.0, a linear decrease to 60% was observed in TMP removal (Figure 2b).

Reactions 6–10 may describe the results in Figure 2b. A SO_3^{2-} ion reduced Fe^{VI} to Fe^V with the formation of a $\bullet SO_3^-$ (Reaction 6, for example, $k_6 = (2.0 \pm 0.2) \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$, pH 11.4). This radical also reduced Fe^{VI} to give Fe^V (Reaction 7, for example, $k_7 = (1.9 \pm 0.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, pH 11.4).(26) Fe^V species react with TMP to enhance the oxidation of TMP (Reaction 8). Fe^V is 3–5 orders of magnitude higher in reactivity than Fe^{VI} .(28) hence the observed enhancement in TMP oxidation (see Figure 2). Furthermore, Fe^V is much more reactive than Fe^{IV} species produced by $R_{(2)}$, and results in substantially more enhancement caused by $R_{(1)}$ compared to $R_{(2)}$ (Figure 2b versus Figure 1). However, Fe^V may react with SO_3^{2-} without the formation of Fe^{IV} species (Reaction 9, e.g., $k_9 = (3.9 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, pH 11.4).(26) The self-decomposition of Fe^V species to Fe^{III} may also occur (Reaction

10, $k_{10} = (\sim 7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}, \text{pH } 11.4)$. (42) Both Reactions 9 and 10 caused the elimination of the reactive Fe^{V} species, responsible for enhancing the removal of TMP.

Concentrations of Fe^{V} produced and TMP in $\text{Fe}^{\text{VI}}\text{-SO}_3^{2-}\text{-TMP}$ solutions and the competitive rate constants of Reactions 6–10 at pH 8.0 would ultimately determine the magnitude of enhancement of the target contaminant and their variation with the ratio of SO_3^{2-} to Fe^{VI} . Additional oxidant species ($\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$) are formed ($\text{SO}_3 + 2\text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O}$; $\bullet\text{SO}_3^- + \text{O}_2 \rightarrow \bullet\text{SO}_5^- \rightarrow \bullet\text{SO}_4^-$; and $\bullet\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{H}^+ + \bullet\text{OH}$), (34,43) in which no decrease in enhancement of TMP removal at $[\text{SO}_3^{2-}]:[\text{Fe}^{\text{VI}}] = 0.1\text{--}5.0$ is observed. (32,34) Formation of such radicals has been evidenced in previous investigations. (32,34) However, at ratios higher than 5.0, Reactions 9 and 10 are most likely to occur to cause the decrease in enhanced oxidation of TMP by $\text{Fe}^{\text{VI}}\text{-SO}_3^{2-}$ system (SI Figure S2). Interestingly, when no oxygen existed in the solution mixture, enhanced oxidation of TMP still occurred. The values of rate constants for Reactions 7–9 at pH 8.0 are needed to fully understand the observed trend of enhancement in Figure 2b.

$\text{Fe}^{\text{VI}}\text{-Thiosulfate System}$

Enhancement of TMP removal was also seen when $\text{S}_2\text{O}_3^{2-}$ was used as a reductant, with complete removal of TMP observed at a ratio of 0.125 (Figure 2c). In the mixture of $\text{TMP-S}_2\text{O}_3^{2-}$ solutions, no removal of TMP was seen (SI Figure S1), therefore, the enhancement of TMP removal (Figure 2c) is due to this reducing additive in the $\text{Fe}^{\text{VI}}\text{-TMP}$ mixed solution. Removal of oxygen (i.e., nitrogen purging) in $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}\text{-TMP}$ solution had no significant difference from TMP removal in air saturated solutions (Figure 2c). At a molar ratio ($[\text{S}_2\text{O}_3^{2-}]:[\text{Fe}^{\text{VI}}]$) greater than 0.125, enhancement of TMP oxidation decreased. When this molar ratio reached 5.0, no oxidation of TMP occurred (or complete inhibition). The

magnitude of enhanced effect depends on the pH and the concentrations of contaminant (see SI Figure S3).

Based on the results observed in Figure 2c, $\text{S}_2\text{O}_3^{2-}$ as an additive was selected to investigate the acceleration and enhancement of 16 organic contaminants at pH 8.0. Except the unstable sulfite,(35) all other additives are pollutants and unsuitable for use as additives in treatment processes using Fe^{VI} . A molar ratio of $\text{S}_2\text{O}_3^{2-}$ to Fe^{VI} was selected at 0.125, which demonstrated complete removal of TMP. As shown in Figure 3, the presence of $\text{S}_2\text{O}_3^{2-}$ in the Fe^{VI} -contaminant system could increase the removal percentages of all contaminants in 30 s, as compared to Fe^{VI} only. Interestingly, complete removal of typical electron-rich moieties containing pharmaceuticals (CMZ, DCF, PPN, SDM, TMP, and ENR) was found, similar to oxidation of TMP (see Figure 2b). Notably, removals of other recalcitrant contaminants were also significant (20–40%). The results of Figure 3 suggest that a wide range of organic contaminants can be rapidly removed by the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system. Considering the coexistence of various pharmaceuticals in the water environment, elimination of six pharmaceuticals present in a mixture solution by the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system was also studied at pH 8.0. Again, complete removal of all tested contaminants was found after 30 s (SI Figure S4). These observations further suggest the applicability of $\text{S}_2\text{O}_3^{2-}$ in enhancing the oxidation of organic contaminants by Fe^{VI} in water.

Results of the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system at low molar ratios ($[\text{S}_2\text{O}_3^{2-}]:[\text{Fe}^{\text{VI}}] = 0.125$) were similar to those obtained in the $\text{Fe}^{\text{VI}}\text{-SO}_3^{2-}$ system. Our initial thought was that the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system may be generating directly Fe^{V} and $\text{S}_2\text{O}_3^{\bullet-}$ (Reaction 11) to result in enhanced oxidation of contaminants. However, experimental findings of the oxidation of $\text{S}_2\text{O}_3^{2-}$ by Fe^{VI} suggested oxygen atom transfer from Fe^{VI} to $\text{S}_2\text{O}_3^{2-}$ to produce Fe^{IV} and $\text{S}_2\text{O}_4^{2-}$ (Reaction 12 and see SI Text S1).

To further clarify whether $\text{S}_2\text{O}_3^{2-}$ behaves like $\text{R}_{(1)}$ additive (i.e., Reaction 11) or $\text{R}_{(2)}$ (i.e., Reaction 12), DFT calculations were performed to learn the favorable step of the reaction between Fe^{VI} and $\text{S}_2\text{O}_3^{2-}$ (SI Text S5). All the species involved were optimized and the changes of Gibbs free energy (ΔG) were individually calculated for Reactions 11 and 12. Compared to the positive value ($\Delta G = 34.66$ kJ/mol) of Reaction 11, Reaction 12 had a negative value ($\Delta G = -50.67$ kJ/mol), indicating the spontaneity of two-electron transfer reaction (SI Figure S5). Thus, the results of DFT calculations are also in good agreement with the prediction based on the relationship of the rate constant with the potential of redox pair, $\text{S}_2\text{O}_4^{2-}/\text{S}_2\text{O}_3^{2-}$.(27)

Notably, results of enhancement in the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system differed from those obtained in the $\text{Fe}^{\text{VI}}\text{-R}_{(2)}$ system (Figure 2b versus Figure 1). We therefore proposed that the reaction between Fe^{VI} and $\text{S}_2\text{O}_3^{2-}$ produced indirectly Fe^{V} species to cause initial enhancement seen in Figure 2c. The final oxidized product observed in the reaction between Fe^{VI} and $\text{S}_2\text{O}_3^{2-}$ is SO_3^{2-} (Reaction 13).(44,45)

The generated SO_3^{2-} produced Fe^{V} species (see Reaction 6) to result in initial enhancement of the oxidation of TMP in the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system. The second-order rate constants for the reactivity of Fe^{VI} with $\text{S}_2\text{O}_3^{2-}$ and $\text{S}(\text{IV})$ ($\text{HSO}_3^- + \text{SO}_3^{2-}$) are $6.01 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ and $1.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at pH 8.0.(23,45,46) This suggests that produced SO_3^{2-} in Reaction 13 can react with Fe^{VI} to form Fe^{V} (see Reaction 6). Radicals, that is, $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$, can only be generated in the presence of oxygen.(34) Participation of $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ to cause this enhancement was ruled out by performing the experiments under nitrogen environment (i.e., no oxygen from air). In 30 s, Fe^{VI} would not produce significant oxygen from its self-decomposition.(47) Results showed no significant difference in enhancing the oxidation of TMP by $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system (see Figure 2b). This suggests that oxygen has a minimal, if any, role in carrying out oxidation of TMP by $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ mixed solution in 30 s. Similar results were also observed in oxidizing other organic contaminants (i.e., no obvious difference with and without oxygen in oxidation of APT, ATL, CAF, DCF, and ENR, SI Figure S6), suggesting no possible role of $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ in the enhanced oxidation of organic pollutants by $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system.

The room-temperature electron paramagnetic resonance (EPR) measurements with 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as the spin trap reagent were conducted to probe the formation of $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$.(34,36) Compared with the EPR spectrum of the $\text{Fe}^{\text{VI}}\text{-TMP-DMPO}$ system, no new signal was observed after introducing $\text{S}_2\text{O}_3^{2-}$ at a low ratio (1:8) of $[\text{S}_2\text{O}_3^{2-}]:[\text{Fe}^{\text{VI}}]$ (SI Figure S7). The observed EPR signals in the control group were assigned as $\bullet\text{OH}$, generated at a low yield (<4%) by Fe^{VI} self-decay in water.(19) The unchanged EPR intensity indicated that no $\text{SO}_4^{\bullet-}$ was produced and also $\bullet\text{OH}$ was not further formed in the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system, therefore not contributing to the significantly enhanced oxidation of organic contaminants. Similar results were observed following introduction of the lower ratio (1:8) of $[\text{SO}_3^{2-}]:[\text{Fe}^{\text{VI}}]$ and $[\text{I}^-]:[\text{Fe}^{\text{VI}}]$ (SI Figure S7). Furthermore, $\text{SO}_3^{\bullet-}$ can also be ruled out in the system: it is a precursor to the production of $\text{SO}_4^{\bullet-}$.(34,43)

The role of $\text{Fe}^{\text{IV}}/\text{Fe}^{\text{V}}$ intermediates on $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ -contaminant system was further explored using dimethyl sulfoxide (DMSO) as the probing reagent for the high-valent iron species. DMSO is selectively oxidized by $\text{Fe}^{\text{V}}=\text{O}$ and $\text{Fe}^{\text{IV}}=\text{O}$ species through oxygen atom transfer to produce the corresponding sulfone (DMSO_2). (11,48,49) Such reactions differ from the reaction pathways involved in radicals-based oxidation.(50) The oxidation of TMP was followed by adding 1 mM DMSO into $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ -TMP system. Interestingly, oxidation of TMP was almost inhibited in the presence of DMSO (i.e., no difference in TMP removal by Fe^{VI} with and without $\text{S}_2\text{O}_3^{2-}$) (SI Figure S8). This suggests that the $\text{Fe}^{\text{IV}}/\text{Fe}^{\text{V}}$

species generated in $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ -TMP solution were captured by DMSO and thus, unavailable to oxidize TMP. It should be pointed out that Fe^{VI} has a very slow reactivity with DMSO ($k \sim 1.0 \text{ M}^{-1} \text{ s}^{-1}$ at pH 8.0)(51) and no significant reaction between Fe^{VI} and DMSO was expected in 30 s ($t_{1/2} \sim 690 \text{ s}$). Therefore, the dominant reactive species for oxidation of organic pollutants in $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system were $\text{Fe}^{\text{IV}}/\text{Fe}^{\text{V}}$ species. Another study has reported different rate constant for the reaction of Fe^{VI} with DMSO (i.e., $16 \text{ M}^{-1} \text{ s}^{-1}$, giving $t_{1/2}$ of Fe^{VI} consumption by 1 mM of DMSO = 43 s).(45) However, excessive Fe^{VI} (100.0 μM) used in our study would ensure the enhanced effect, which could still be seen at less magnitude because of less molar ratio of $\text{S}_2\text{O}_3^{2-}$ to Fe^{VI} than 0.125. As shown in SI Figure S8, the oxidation of TMP completely stopped by the presence of DMSO in the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system. In other words, both rate constants applied in previously reported studies suggest that the reaction of Fe^{VI} with DMSO had a minimal role, and inhibition of the degradation of TMP by the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system was due to elimination of $\text{Fe}^{\text{IV}}/\text{Fe}^{\text{V}}$ species by DMSO; suggesting the generation of such highly reactive iron species to enhance the oxidation of contaminants by the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system. Additionally, the oxidized product of DMSO by the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system was identified as DMSO_2 (SI Figure S9).

Overall, enhanced oxidation of TMP by the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system was most likely by direct production of Fe^{IV} (Reaction 12) and indirect generation of Fe^{V} species (Reaction 6), which reacted with TMP (Reactions 3 and 8). With increasing concentration of $\text{S}_2\text{O}_3^{2-}$ (or $[\text{S}_2\text{O}_3^{2-}]:[\text{Fe}^{\text{VI}}]$). The intermediate reactive iron species, Fe^{IV} and Fe^{V} , may be removed by their reactions with $\text{S}_2\text{O}_3^{2-}$ (Reactions 14 and 15). Reaction 14 is presumably occurring through oxygen-atom transfer from Fe^{IV} to $\text{S}_2\text{O}_3^{2-}$ yielding Fe^{II} , similar to the one proposed earlier.(45) The rapid reaction of Fe^{V} with $\text{S}_2\text{O}_3^{2-}$ may also happen (e.g., $k_{15} = (2.1 \pm 0.1) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, pH 11.4). The Fe^{II} , produced in Reaction 14, may consume the main oxidant, Fe^{VI} (Reaction 16, that is, $k_{16} = \sim 10^5 \text{ M}^{-1} \text{ s}^{-1}$, pH 12.1).(26) Reaction 16 would terminate the production of Fe^{V} and Fe^{IV} , the responsible species to cause enhanced oxidation of TMP by $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system. Furthermore, the reductants $\text{R}_{(2)}$ would produce Fe^{II} as one of reduced species of Fe^{VI} (see Reaction 4 or 14) before converting to final Fe^{III} species (Reaction 16). It appears that excess $\text{S}_2\text{O}_3^{2-}$ (or $[\text{S}_2\text{O}_3^{2-}]:[\text{Fe}^{\text{VI}}] > 1.0$), not only eliminates the $\text{Fe}^{\text{IV}}/\text{Fe}^{\text{V}}$ species (Reactions 14 and 15), but also causes the consumption of Fe^{VI} (Reaction 15). It seems no Fe^{VI} was available to oxidize TMP at excess concentration of $\text{S}_2\text{O}_3^{2-}$ and no degradation of TMP was observed (see Figure 2c).

Available rate constants for Reactions 15 and 16 are at high alkaline medium (i.e., pH 11.4 and 12.1), and these reactions would occur at much faster rates at pH 8.0. For example, the rate constant for the reaction of Fe^{VI} with Fe^{II} was estimated to be greater than $1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at pH 5.0.(19) The initial step of Reaction 16 produces Fe^{V} (i.e., $\text{Fe}^{\text{VI}} + \text{Fe}^{\text{II}} \rightarrow \text{Fe}^{\text{V}} + \text{Fe}^{\text{III}}$). The subsequent reaction of Fe^{V} with Fe^{II} would produce Fe^{IV} ($\text{Fe}^{\text{V}} + \text{Fe}^{\text{II}} \rightarrow \text{Fe}^{\text{IV}} + \text{Fe}^{\text{III}}$). Similarly, Fe^{IV} may also react with Fe^{II} to form Fe^{III} ($\text{Fe}^{\text{IV}} + \text{Fe}^{\text{II}} \rightarrow 2\text{Fe}^{\text{III}}$), which may terminate reaction. The rate constant of Reaction 14 is not known. The pattern of the oxidation of TMP in Figures 1 and 2 as well as SI Figure S2 may be explained fully by knowing the rate constants of reactions involved in the oxidation of TMP by Fe^{VI} -reducing additive system. At a molar ratio of 0.125 ($[\text{S}_2\text{O}_3^{2-}]:[\text{Fe}^{\text{VI}}]$), contributions of different involved reactions in the system provide optimum levels of $\text{Fe}^{\text{IV}}/\text{Fe}^{\text{V}}$ to cause maximum oxidation of TMP. Again, the values of rate constants of all possible reactions at different pH are needed to understand this optimum ratio of 0.125.

Oxidized Products (OPs) of TMP and SDM by $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ System

The OPs of TMP and SDM by $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system were investigated at pH 8.0 and a molar ratio of 0.125 ($[\text{S}_2\text{O}_3^{2-}]:[\text{Fe}^{\text{VI}}]$), which had complete removal of contaminants (see Figure 3). Based on the molecular weights and previous study,(34) OPs of TMP were named as OP-338, OP-322, OP-308, OP-306, OP-304, OP-292, OP-212, and OP-196. MS/MS spectra and possible structures of the fragments of SDM and its OPs are presented in SI Figure S10. SDM has five fragments (m/z 218.02295, 156.07666, 108.04427, 92.04943, and 65.03873 (SI Figure S10a). These structures were proposed as the sequential losses of the aniline group from SDM (m/z 311.08060), the SO_2 group from m/z 218.02295, the amino and methoxyl groups from m/z 156.07666, the residual aniline group from SDM (m/z 311.08060) and the loss of $-\text{NH}_2\text{C}$ group from m/z 92.04943. OPs of SDM were classified as OP-356, OP-340, OP-327, OP-326, OP-324, OP-311, OP-295, and OP-276 (SI Figure S10b--S10i). The molecular compositions of these OPs were suggested by the good mass error (<3 ppm) between the experimental and theoretical m/z values. Results are summarized in SI Tables S3 and S4.

Some of the OPs in the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system were not found in the oxidation of TMP and SDM by $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ systems (SI Tables S3 and S4).(52–56) This again indicates the absence of $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ species during the enhanced elimination of TMP and SDM by $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system. OPs were also determined independently in the oxidation of TMP and SDM by Fe^{VI} alone, $\text{Fe}^{\text{VI}}\text{-I}^-$, and $\text{Fe}^{\text{VI}}\text{-SO}_3^{2-}$, which also yielded the same products as obtained by $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system (SI Tables S3 and S4). This further suggests that the oxidizing species in the $\text{Fe}^{\text{VI}}\text{-I}^-$, $\text{Fe}^{\text{VI}}\text{-SO}_3^{2-}$, and $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ systems at this lower ratio were likely the same oxidants, that is, $\text{Fe}^{\text{IV}}/\text{Fe}^{\text{V}}$ species.

The OPs and reaction pathways of TMP by the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system were the same as those reported earlier (SI Figure S11).(34) Based on the reaction mechanisms of Fe^{VI} oxidation of sulfonamides (e.g., sulfamethoxazole (SMX)) and the OPs of SDM produced by the other oxidation systems,(52,54,57) two initial transformation pathways of SDM by the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system are suggested (Figure 4). The salient feature of reaction pathways was the formation of OP-276 through SO_2 elimination and rearrangement of OP-340 (Pathway I).

The SO₂ elimination has been commonly suggested in the oxidation of sulfonamides by SO₄^{•-}, (52,58) but was first observed in the oxidation of SDM by the Fe^{VI}-R₍₁₎ system. In pathway I, the amino group in the benzene ring of SDM was oxidized to generate OP-326, which was further oxidized to form OP-324 with NO group and OP-340 with NO₂ group at the same reaction moiety. Afterward, OP-356 was formed via hydroxylation of OP-340. A similar reaction pathway was reported in the oxidation of SMX by Fe^{VI} alone under basic and neutral pH conditions. (57) Transformation of OP-340 resulted in OP-276. Herein, the nitro group could have deactivated the benzene ring, but involvement of highly reactive Fe^{IV}/Fe^V species may achieve further reaction of OP-340 to give the formation of OP-356. Generally, Fe^{IV}/Fe^V species have shown activation of C–H bond of organic molecules. (59,60) Pathway II was initiated by deamination of SDM to produce OP-295, and then two sequential hydroxylations occurred to produce OP-311 and OP-327, respectively (Figure 4). Deamination of SDM may be similar to the finding observed in oxidation of amino acids by ferrate species. (61,62) Formation of hydroxylated products (i.e., OP-311 and OP-327) may be occurring through involvement of Fe^{IV}/Fe^V species. A similar hydroxylation of the benzene ring of the parent molecule has also been observed in the oxidation of SMX and flumequine by Fe^{VI} alone. (57,63) Furthermore, we have independently studied the oxidation of benzene by Fe^{VI} and Fe^{VI}-S₂O₃²⁻ systems at pH 8.0 after 30 s. The formation of phenol, generated by hydroxylation of benzene and confirmed by the HPLC spectra of the phenol standard, was observed in both systems (SI Figure S12). Molar yields of phenols were low (without thiosulfate: [phenol]_{formed}/[Fe(VI)]_{consumed} = 0.41 μM/6.5 μM ≈ 0.06; with thiosulfate: [phenol]_{formed}/[Fe(VI)]_{consumed} = 0.83 μM/43.0 μM ≈ 0.02). High-valent iron species produced in the system of Fe^{VI}-S₂O₃²⁻ would react with phenol to give additional products. This may explain lower molar ratio of formed phenol to consumed Fe^{VI}. Reactivity of Fe^V with phenol is three-orders of magnitude higher than the reactivity of Fe^{VI} with phenol. (47) An independent study on the reaction of Fe(V) with phenol has shown several products are formed. (47) A detailed investigation of the oxidized products in the system of Fe^{VI}-thiosulfate-benzene would clarify this possibility. Nevertheless, hydroxylation of benzene by high-valent species is very likely as suggested by our results. Basically, the generation of Fe^{IV}/Fe^V species caused hydroxylation of benzene. This is supported by an independent DFT study on the reactivity of Fe^{IV} species with benzene. (64) Calculations showed the feasibility of the formation of phenol from the hydroxylation of benzene by Fe^{IV} species.

Environmental Implications

The results clearly demonstrate that the establishment of a Fe^{VI}-reducing agent system is a highly effective tool to generate high-valent iron-oxo intermediates for rapid water depollution. This was further tested in applying the Fe^{VI}-S₂O₃²⁻ system in different water matrices. Investigated six pharmaceuticals were CMZ, DCF, ENR, PPN, SDM, and TMP at 1.0 μM. An optimum molar ratio of 0.125 ([S₂O₃²⁻]:[Fe^{VI}]) at pH 8.0 was applied to investigate oxidation of these pharmaceuticals in both river water and lake water. The reactions were quenched in 30 s, and results are depicted in SI Figure S13. Interestingly, S₂O₃²⁻ addition to Fe^{VI} could also enhance the removal percentages of target pharmaceuticals present in river water and lake water. In river water, four of the six pharmaceuticals could be removed completely (SI Figure S13a). Removal of CMZ and ENR

was ~80%. In lake water, removal of pharmaceuticals was less than that in river water (SI Figure S13b). Eliminations of DCF, PPN, SDM, and TMP were ~80%, whereas removal of CMZ and ENR was ~50%. It is likely that water constituents in natural waters such as anions, cations, and dissolved organic matters are influencing the removal of the target contaminants by the oxidizing species present in the $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ mixed solution. These results demonstrated that $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system can be adopted for efficient and rapid remediation of natural waters polluted with organic micropollutants. However, dosages (or amount) of Fe^{VI} for eliminating organic contaminants would vary with the characteristics of treated water. In the application of $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system, the formed products are nontoxic $\text{Fe}(\text{OH})_3$ and SO_4^{2-} . Furthermore, generated $\text{Fe}(\text{OH})_3$ has remarkable efficiency of removing metals and phosphate.(65–67)

Significantly, some of the reducing agents (e.g., $\text{S}_2\text{O}_3^{2-}$, NH_2OH , and NO_2^-) have been applied to quench the reaction between Fe^{VI} and contaminants without realizing that the added quencher may greatly influence the oxidative processes. Significantly, quenching the reaction depends on the molar ratio of quencher to Fe^{VI} , which varies with the type of quencher. For example, this study suggested ten times more molar concentration of NH_2OH than that of Fe^{VI} would be needed to inhibit the reaction of Fe^{VI} with the target contaminant. However, if $\text{S}_2\text{O}_3^{2-}$ is used to quench the reaction, only five-time the concentration of $\text{S}_2\text{O}_3^{2-}$ compared to Fe^{VI} would be sufficient. The results presented herein will guide researchers in future studies on the oxidation of contaminants by Fe^{VI} .

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Oxidation of TMP by Fe^{VI} and two-electron reducing additives (R₂), a, hydroxylamine; b, phosphite, selenite, and arsenite) system in air saturated solutions, and (c) nitrite under air saturated and anoxic conditions. (Experimental conditions: [TMP]₀ = 5.0 μM, [Fe^{VI}]₀ = 100.0 μM, pH 8.00 ± 0.05, reaction time = 30 s).

Figure 2.

Oxidation of TMP by Fe^{VI}-iodide (a), Fe^{VI}-sulfite (b), and Fe^{VI}-thiosulfate (c) systems in air saturated solutions. (Experimental conditions: [TMP]₀ = 5.0 μM, [Fe^{VI}]₀ = 100.0 μM, pH 8.00 ± 0.05, reaction time = 30 s).

Figure 3.

Oxidation of organic contaminants by Fe^{VI} with and without $S_2O_3^{2-}$ in air saturated solution. (Experimental conditions: $[Contaminant]_0 = 1.0 \mu M$, $[Fe^{VI}]_0 = 100.0 \mu M$, $[S_2O_3^{2-}]_0 = 12.5 \mu M$, pH 8.00 ± 0.05 , reaction time = 30 s). (APT-aspartame, ATL-atenolol, ATZ-atrazine, BZF-bezafibrate, CAF-caffeine, CMZ-carbamazepine, DMS-dexamethasone, DTA-diatrizoic acid, DCF-diclofenac, ENR-enrofloxacin, FLU-flumequine, IBP-ibuprofen, DEET-*N,N*-diethyl-3-toluamide, PPN-propranolol, SDM-sulfadimethoxine, TMP-trimethoprim).

Figure 4.

Proposed reaction pathways of sulfadimethoxine (SDM) by $\text{Fe}^{\text{VI}}\text{-S}_2\text{O}_3^{2-}$ system at pH 8.00 in air saturated solution.