

Ferrate(VI) Oxidation of Hydrogen Sulfide

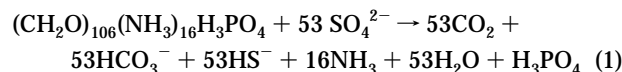
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The rates of oxidation of hydrogen sulfide with Fe(VI) were made anaerobically as a function of pH (7–12) and temperature (5–15 °C). The reaction was found to be first order for each reactant. The rates decrease with an increase in pH. The energy of activation was found to be $30.1 \pm 4.9 \text{ kJ mol}^{-1}$ at pH = 12. When the concentrations of $[\text{H}_2\text{S}]_{\text{T}}$ ($[\text{H}_2\text{S}] + [\text{HS}^-]$) are in excess, the ratio of $[\text{H}_2\text{S}]_{\text{T}}$ consumed to $[\text{Fe(VI)}]$ consumed was 1.51 ± 0.14 at pH = 7.0 and 2.50 ± 0.13 at pH = 9.0 and 11.3. Thiosulfate was the main product at pH = 7.0; sulfite, thiosulfate, and sulfate were identified as the products of the reactions at pH = 9.0 and 11.3. In an excess of $[\text{Fe(VI)}]$ over $[\text{H}_2\text{S}]_{\text{T}}$, the hydrogen sulfide is fully oxidized to sulfate. A mechanism in which Fe(VI) oxidizes H_2S by a one-electron process is proposed. Experiments were conducted to test the Fe(VI) removal efficiency of sulfide in groundwater and wastewater. The results indicate that Fe(VI) can be used as an effective oxidant to remove hydrogen sulfide from wastewaters.

Introduction

The formation of hydrogen sulfide occurs in a number of areas such as well water, lakes, oil fields, anaerobic sewage, and industrial wastewaters (1). Anthropogenic activities that generate hydrogen sulfide include paper mills, chemical plants, tanneries, and textile mills (1). Hydrogen sulfide is produced as a byproduct from anaerobic bacterial oxidation of plants by the reduction of sulfate by the following reaction:



The generation of hydrogen sulfide in wastewater collection systems presents serious sewer maintenance problems not only due to the toxic nature and noxious odor of the gas but also because of corrosive attack from the oxidized form of hydrogen sulfide upon the concrete sewers (2). Corrosion is due to the formation of sulfuric acid, which forms from oxidation of hydrogen sulfide in the presence of aerobic bacteria such as *Thiobacilli*:



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The corrosion caused by sulfide in sewage systems may be controlled by oxidizing sulfide with various oxidants such as oxygen, hydrogen peroxide, hypochlorites, chlorine, and potassium permanganate (3–5). Oxidation of hydrogen sulfide by oxygen has been studied in detail (4, 6–8). It has been found that hydrogen sulfide oxidation by oxygen is a relatively slow process and becomes practical only under pressurized conditions (3). Sulfide oxidation by oxygen can also be enhanced by transition metal ions and their complexes (2, 9–11). In a study (9) of metal-4,4',4'',4'''-tetrasulphthalocyanine complex $[\text{M(II)}-\text{TSP}]$; $\text{M} = \text{Co}, \text{Ni}, \text{Cu}$ catalyzed autooxidation of hydrogen sulfide, it was found that the catalytic activity of CoTSP was greater than either NiTSP or CuTSP. The oxidation catalyzed by CoTSP followed enzyme-like kinetics. The reaction rate of the catalyzed reaction at $[\text{CoTSP}] = 0.5 \text{ nM}$ and $\text{pH} = 8.3$ was 400 times higher than the uncatalyzed reaction (9). The maximum advantage of a Co^{II} TSP in wastewater occurred when the dissolved oxygen concentrations were 4 ppm or higher. At low levels of oxygen ($\leq 1 \text{ ppm}$) found in sewers, the oxidation rates were doubled in the presence of 1000 nM Co^{II} TSP (2).

Sulfide oxidation by peroxide is slow, but it is faster than the oxidation by oxygen (12). Hypochlorite, chlorine, and potassium permanganate were found to be potential oxidizers for sulfide as their reactions are completed within 5 min of contact time (5). One promising advanced oxidation process involves the use of iron in a +6 valence state, Fe(VI), to oxidize hydrogen sulfide in aqueous solutions. Fe(VI) ion is a powerful oxidizing agent throughout the entire pH range with a reduction potential varying from +2.2 to +0.7 V in acidic and basic solutions, respectively (13). Fe(VI) ion decomposes by a complex disproportionation mechanism (14, 15). Fe(VI) has shown promise in its ability to remove contaminants in wastewater effluents (16–20). Research studies have indicated that Fe(VI) acts as a coagulant and is more effective than other coagulants such as aluminum, ferric, or ferrous salts (21). The applicability of Fe(VI) to remove metals, nonmetals, and radionuclides has been investigated (22). Studies on Fe(VI) reacting with certain inorganic and organic substrates indicate its applicability in remediation of contaminants in industrial effluents (23–30), and it has been suggested to be an ideal substitute for other commonly used oxidants, particularly chlorine (15). In this paper, we have investigated the Fe(VI) oxidation of hydrogen sulfide in aqueous solution. Fe(VI) has also been evaluated as an oxidant for removal of sulfide from groundwater and wastewater.

Experimental Section

All chemicals used were of reagent grade (Sigma, Aldrich) and were used without further purification. Solutions were prepared with water that had been distilled and then passed through 18 MΩ Milli-Q water purification system. Potassium ferrate (K_2FeO_4) of high purity (98% plus) was prepared by the method of Thompson et al. (31). The Fe(VI) solutions were prepared by addition of solid samples of K_2FeO_4 to deoxygenated 0.005 M $\text{Na}_2\text{HPO}_4/0.001 \text{ M}$ borate, pH 9.0, where the solutions are most stable. A molar absorption coefficient $\epsilon_{510\text{nm}} = 1150 \text{ M}^{-1} \text{ cm}^{-1}$ was used for the calculation of $[\text{Fe(VI)}]$ at pH = 9.0 (15). The H_2S stock solutions were prepared by dissolving rinsed $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ crystals in degassed water. The stock solutions were standardized iodometrically and stored under a nitrogen atmosphere. Anaerobic solutions of sulfide were prepared in degassed 0.01 M phosphate and adjusted to the desired pH with either phosphoric acid or sodium hydroxide.

Stoichiometry of the Fe(VI) oxidation of hydrogen sulfide was examined at pH 7.0, 9.0, and 11.3 at 23 °C. In these

experiments, equal volumes (10 cm³) of Fe(VI) and hydrogen sulfide were mixed. The pH of the reaction mixtures was measured to ensure that the reaction occurred at the specified pH. The Fe(VI) concentrations ranged from 70 to 140 μM, while the concentration of sulfide ranged from 85 to 3025 μM. The methylene blue method of Cline (32) was used to quantify the hydrogen sulfide concentration before and after each reaction with Fe(VI). A volume (0.1–1 cm³) from the reaction mixture (depending on the concentration of hydrogen sulfide) was added to a 10 cm³ flask that contained 5 cm³ of Milli-Q water. An amine-sulfuric acid reagent (0.5 cm³) and FeCl₃ solution (0.15 cm³) were added to the flask, and the solution was immediately mixed. An addition of 1.6 cm³ ammonium phosphate solution was made after 5 min. The absorbance measurements were made after 15 min using a Hewlett-Packard Model 8452A spectrophotometer. The analytical precision of our hydrogen sulfide determinations was less than 5%.

In the product analysis experiments, the concentrations of hydrogen sulfide solutions were 10 times the Fe(VI) concentrations, and the products analyzed were sulfite, thiosulfate, and sulfate ions. A Waters ion chromatographic system was used for analysis of these ions in samples (33). Samples were injected immediately (<15 s) after the completion of the reaction.

Kinetic studies were carried out by using a stopped-flow system (34). Experiments were carried out under pseudo-first-order conditions. The concentration of hydrogen sulfide was kept in excess and ranged from 4.0 to 9.5 × 10⁻⁴ M, while the Fe(VI) concentrations were 50–75 × 10⁻⁶ M. Experiments were initiated with the measurements of the spontaneous decay of Fe(VI) under the given conditions, the rate of which was used as a correction factor for runs in which Fe(VI) was mixed with a sulfide solution. The contribution from the Fe(VI)–Fe(VI) reaction was less than 0.1% in our studies. With our kinetic system, we were able to determine the rate of the reactions only at high pH (11.0–12.6) and low temperatures (5–15 °C). The reactions were too fast at low pH and high temperatures.

The usefulness of Fe(VI) to remove sulfide from groundwater (GW) and wastewater (WW) was tested at various concentrations of Fe(VI). Wastewater samples were collected from primary effluent at the Oso Treatment Plant in Corpus Christi, TX. The samples were filtered through a 0.45-μm filter before performing experiments. Groundwater samples were collected from two monitoring wells at Padre Island National Sea Shore, TX. Removal experiments were performed at the sites without filtration. Experiments were conducted by mixing equal volumes (10 cm³) of Fe(VI) and sample. The hydrogen sulfide concentrations were determined before and after the reactions by the methylene blue method (32).

Results and Discussion

Kinetic Studies. In the first series of experiments, the reaction rates of Fe(VI) with hydrogen sulfide were determined at pH = 12.0 and 15 °C. The rate expression for the reaction can be expressed as

$$-d[\text{Fe(VI)}]/dt = k[\text{Fe(VI)}]^m [\text{H}_2\text{S}]_T^n \quad (3)$$

where [Fe(VI)] and [H₂S]_T are the concentrations of Fe(VI) and total hydrogen sulfide ([H₂S] + [HS⁻]), respectively; *m* and *n* are the orders of the reaction; and *k* is the reaction rate constant. Kinetic studies were done under pseudo-first-order conditions in which excess of [H₂S]_T was used. Under such conditions eq 3 becomes

$$-d[\text{Fe(VI)}]/dt = k_1[\text{Fe(VI)}]^m \quad (4)$$

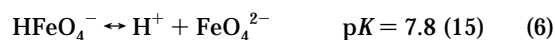
where

$$k_1 = k[\text{H}_2\text{S}]_T^n \quad (5)$$

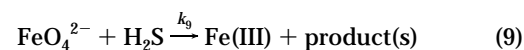
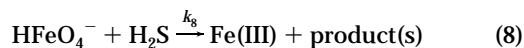
Reactions were conducted by measuring the absorbance of Fe(VI) at 600 nm wavelength as a function of time. A successive integration model for the absorption of Fe(VI) as a function of time gave the best fit indicating the reaction is first order with respect to Fe(VI) with *k*₁ = 1.43 ± 0.07 s⁻¹. To detect any interference from the products of the reaction mixtures, the reactions were also monitored at 650 nm wavelength and pH = 12, and *k*₁ was found to be 1.38 ± 0.08 s⁻¹. The similar rate constants at 600 and 650 nm wavelengths suggest that the products of the reaction mixture do not cause any interference. The reaction order with respect to hydrogen sulfide was determined by plotting log *k*₁ vs log [H₂S]_T. The slope of the line was found to be 1.10 ± 0.07; *r* = 0.99), indicating that the reaction is first order with respect to [H₂S]_T. The rate constant at different levels of hydrogen sulfide were found to be *k* = 2179 ± 190 M⁻¹ s⁻¹ at pH = 12 and 15 °C.

The effect of temperature on the reaction of Fe(VI) with hydrogen sulfide was studied at pH = 12.0. The plot of log *k* vs 1/*T* was linear (*r* = 0.987) and gave an activation energy of 30.1 ± 4.9 kJ mol⁻¹. It should be pointed out that the activation energy contains terms due to the effect of temperature on the dissociation of H₂S and HFeO₄⁻. The energy of activation for the Fe(VI) oxidation of H₂S is lower than oxidation by Cr(VI), H₂O₂, and O₂ as their activation energies are 43.6 ± 1.5, 39 ± 2, and 57 ± 4 kJ mol⁻¹, respectively (8, 12, 35).

The rate of the reaction was also determined as a function of pH (11.0–12.6) at 15 °C. The rates were found to decrease with an increase in pH. The change in *k* as a function of pH can be described by considering equilibrium of Fe(VI) and hydrogen sulfide:



The two forms of Fe(VI) can react with the two forms of hydrogen sulfide. To understand which of the two equilibria (eqs 6 and 7) is controlling the rates, the effect of ionic strength on the rates of hydrogen sulfide oxidation was examined in NaCl solutions at pH = 11.0 and 15 °C. The rate constants were found to be 5302 ± 890 M⁻¹ s⁻¹ and 5454 ± 652 M⁻¹ s⁻¹ in 0.05 and 0.10 M NaCl solutions, respectively. These results are the same within the experimental error as found in solutions without NaCl (4662 ± 334 M⁻¹ s⁻¹) and indicate that reaction is independent of ionic strength or that one of the reactive species has no charge (H₂S). Thus, reactions 8 and 9 are controlling rates that appear to be more favorable due to the repulsion of the negatively charged species in reaction.



With this in mind, the observed rate constants can be given by

$$k[\text{Fe(VI)}] = k_8[\text{HFeO}_4^-] + k_9[\text{FeO}_4^{2-}] \quad (10)$$

which can be simplified to

$$k = k_8\alpha(\text{HFeO}_4^-) + k_9\alpha(\text{FeO}_4^{2-}) \quad (11)$$

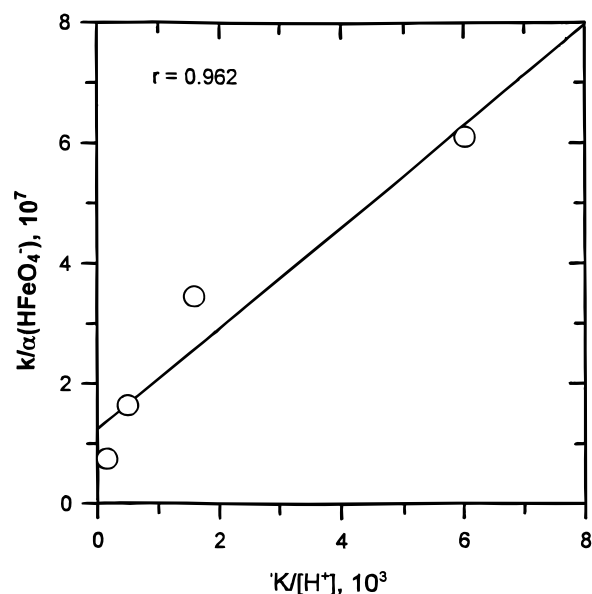


FIGURE 1. Plot of $k/\alpha(\text{HFeO}_4^-)$ versus $(K/[\text{H}^+])$ at 15 °C.

The fractions $\alpha(i)$ can be estimated from

$$\alpha(\text{HFeO}_4^-) = [\text{HFeO}_4^-]/[\text{Fe(VI)}] = [\text{H}^+]/(K + [\text{H}^+]) \quad (12)$$

$$\alpha(\text{FeO}_4^{2-}) = [\text{FeO}_4^{2-}]/[\text{Fe(VI)}] = K/(K + [\text{H}^+]) \quad (13)$$

where $K = 1.58 \times 10^{-8}$ is the equilibrium constant for reaction 6. The rearrangement of eq 13 gives

$$k/\alpha(\text{HFeO}_4^-) = k_8 + k_9(K/[\text{H}^+]) \quad (14)$$

A plot of $k/\alpha(\text{HFeO}_4^-)$ versus $(K/[\text{H}^+])$ shown in Figure 1 gives $k_8 = (1.24 \pm 0.78) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $k_9 = (8.41 \pm 1.67) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$. These results suggest that the protonated species of Fe(VI), HFeO_4^- , is the most reactive species while the deprotonated form, FeO_4^{2-} is relatively unreactive. The protonation of Fe(VI) destabilizes this species by reducing the electron-donating capacity of the ligands and making it more reactive (37). The enhanced reactivity of HFeO_4^- as compared to FeO_4^{2-} was also observed in oxidation of ascorbate and thiourea by Fe(VI) (38, 39).

Stoichiometry and Product(s) Studies. Stoichiometric experiments of the oxidation of hydrogen sulfide with Fe(VI) were conducted at pH = 7.0, 9.0, and 11.3. The results of the final changes of reactants ($\Delta[\text{H}_2\text{S}]_{\text{T}}/[\text{Fe(VI)}]_{\text{T}}$) versus the initial ratio $[\text{H}_2\text{S}]_{\text{T}}/[\text{Fe(VI)}]_{\text{T}}$ are shown in Figure 2. The stoichiometry increases initially with an increasing ratio of $[\text{H}_2\text{S}]_{\text{T}}/[\text{Fe(VI)}]_{\text{T}}$ in the reaction mixture and then becomes constant as $[\text{H}_2\text{S}]_{\text{T}}/[\text{Fe(VI)}]_{\text{T}} \geq 8$. The limiting stoichiometry is 1.51 ± 0.14 , 2.52 ± 0.10 , and 2.41 ± 0.17 at pH = 7.0, 9.0 and 11.3, respectively.

To understand the variation in the stoichiometry with pH, the products analysis of the reaction mixtures were made at a ratio of $[\text{H}_2\text{S}]_{\text{T}}/[\text{Fe(VI)}]_{\text{T}} = 10$. Thiosulfate ($\text{S}_2\text{O}_3^{2-}$) was the only reaction product found at pH 7.0 and accounted for only 24% of consumed sulfide. When the reaction occurred at pH 7.0, it was observed that the solution turned cloudy. The opacity of the solution may point to the formation of elemental sulfur. Spectrophotometric measurements suggest that Fe(II) formed during the oxidation process. At pH 9.0 and 11.3, three products were identified: SO_3^{2-} (8–9%), $\text{S}_2\text{O}_3^{2-}$ (12%), and SO_4^{2-} (11–12%). The three products account for approximately 43–45% of the consumed sulfide. The oxidation of sulfide with numerous oxidants under alkaline conditions suggest that the formation of polysulfide ion occurs

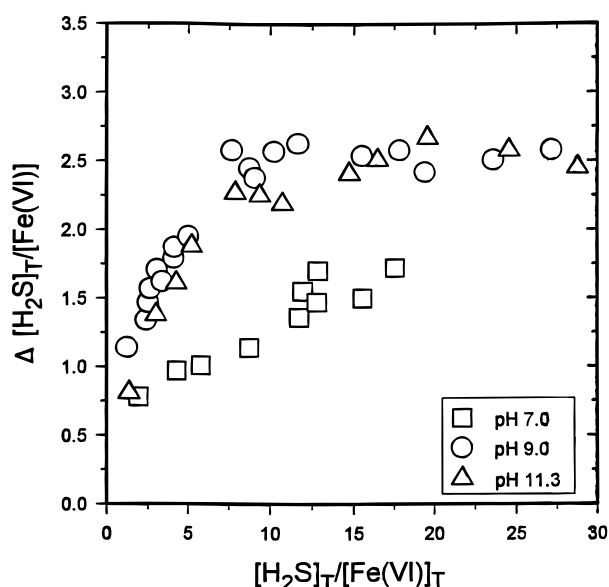
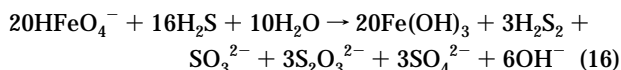
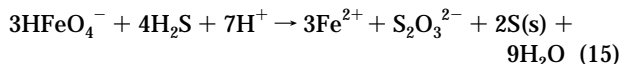


FIGURE 2. Stoichiometry of $\Delta[\text{H}_2\text{S}]_{\text{T}}/[\text{Fe(VI)}]_{\text{T}}$ as a function of $[\text{H}_2\text{S}]_{\text{T}}/[\text{Fe(VI)}]_{\text{T}}$ at pH = 7.0, 9.0, and 11.3 at 23 °C.

(40, 41). Therefore, polysulfide may be a fourth and unmeasured product produced from the oxidation of sulfide by Fe(VI).

The oxidation of hydrogen sulfide by Fe(VI) may occur through a chain reaction because of (i) the initial variation in stoichiometry with $[\text{H}_2\text{S}]_{\text{T}}/[\text{Fe(VI)}]_{\text{T}}$ and (ii) the measured limiting stoichiometry is greater than the predicted stoichiometry from simple electron balance in alkaline medium.



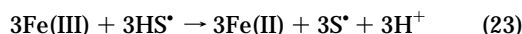
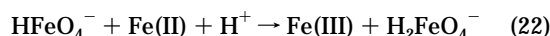
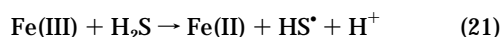
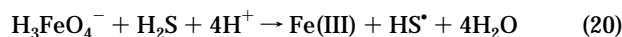
The results of the oxidation of sulfite by Cr(VI) were explained by considering pentavalent and tetravalent chromium (42). In a study of permanganate oxidation of sulfite, direct spectroscopic evidence for manganate(VI) and manganate(V) ions was given (43). Recently, it has been shown that the reduction of Fe(VI) by ascorbic acid (AH^-) occurs through a one-electron transfer with the formation of an ascorbic radical ($\text{A}^{\cdot-}$). The measured stoichiometry, $[\text{A}^{\cdot-}]/[\text{Fe(VI)}] = 3$ when $[\text{AH}^-] > [\text{Fe(VI)}]$. The yield of $\text{A}^{\cdot-}$ dropped with a decrease in the ratio of $[\text{AH}^-]/[\text{Fe(VI)}]$. It is likely that similar to ascorbic acid, hydrogen sulfide oxidation by Fe(VI) is occurring through one-electron transfer with the formation of ferrate species, Fe(V), Fe(IV), Fe(III), Fe(II), and HS^{\cdot} . Fe(V) and Fe(IV) species disappear either by first-order kinetics or biomolecular kinetics depending on pH (37). It is possible that the Fe(V), Fe(IV), and Fe(III) once formed may also react with hydrogen sulfide. The reaction of Fe(V) and Fe(IV) species with inorganic and organic compounds are 3–5 orders of magnitude faster than Fe(VI) (44–46). The lack of formation of Fe(V) and Fe(IV) species in our experiments further suggests that Fe(V) and Fe(IV) must be reacting faster with hydrogen sulfide than Fe(VI) does. In our experiments, Fe(V) and Fe(IV) reactions with hydrogen sulfide would go to completion by the time the reaction mixture are measured optically. We also did not observe the HS^{\cdot} radical as its spontaneous decay ($k = 6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at pH = 7.0) is much faster than the spontaneous decay of $\text{A}^{\cdot-}$ ($3.76 \pm 0.72 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at pH = 9.0 and 24 °C) (38, 47). The initial variation in the stoichiometry suggests that the HS^{\cdot} radical probably competes with hydrogen sulfide for the ferrate

species. Our results also indicate that the first step of the overall reaction mechanism is the rate-controlling step. A probable chain mechanism for the oxidation of hydrogen sulfide by Fe(VI) is proposed in which it is postulated that, similar to Fe(VI), other ferrate species also undergo one-electron reduction with abstraction of hydrogen atom from the reductant species. In this mechanism, the species, Fe(V) and HS[•] are chain carriers to give propagation steps. The overall rates of propagation steps would not be much larger than the rate of initiation step; therefore, a short chain is expected. A short chain of 2.7–6.0 was observed for the disappearance of Fe(VI) with reducing radical (Gly[•]) flux of $7.5 \times 10^{-2} \mu\text{M/s}$ (44).

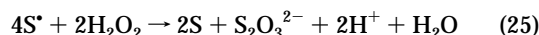
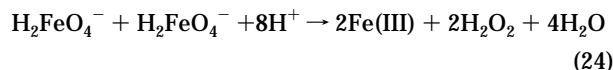
Mechanism.

pH = 7.0

Initiation and Propagation Steps

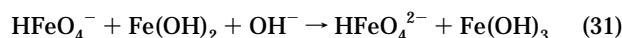
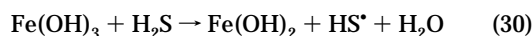


Termination Steps



pH = 9.0–11.3

Initiation and Propagation Steps



Termination Steps

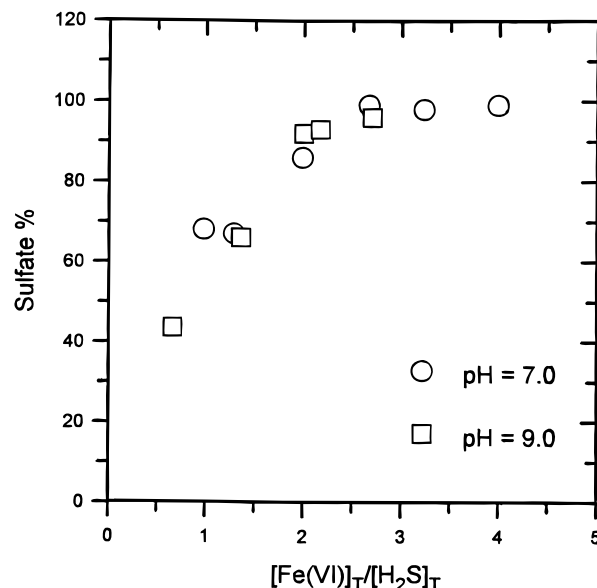
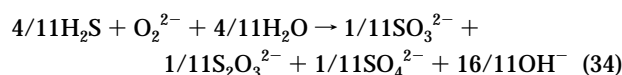
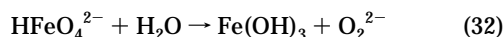
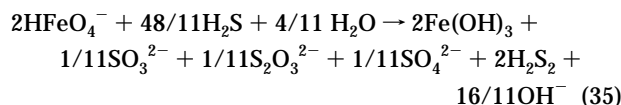


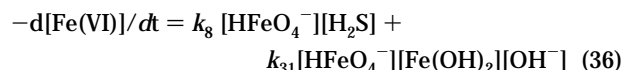
FIGURE 3. Percent of sulfate formed to consumed hydrogen sulfide as a function of $[\text{H}_2\text{S}]_T/[\text{Fe(VI)}]_T$ at pH = 7.0 and 9.0 at 23 °C.

The summation of eqs 17–25 at pH = 7.0 gives eq 15. The observed limiting stoichiometry at pH 7 is close to the predicted stoichiometry from eq 15. In alkaline medium, the summation of eqs 26–34 gives an eq 35.



The observed stoichiometry ~ 2.5 is close to the predicted stoichiometry from eq 35, but it does not explain that only 43% of the consumed H_2S forms thiosulfate, sulfite, and sulfate. A possible explanation is that the stable product of Fe(VI), Fe(III), may also be oxidizing hydrogen sulfide before the analysis of the reaction mixture (49). It should be pointed out that the most stable and most often observed polysulfides formed from the oxidation of H_2S are HS_4^- and HS_5^- (2, 9). Attempts were made to observe these species spectroscopically during kinetics runs at pH = 12 and 15 °C. Although we did not observe the buildup of these species during the reaction, we cannot rule out the formation of HS_4^- and HS_5^- species. These species may further react with ferrate species or may be unseen due to interference from Fe(III) complexes.

The rate of disappearance of Fe(VI) in alkaline medium can be written by considering



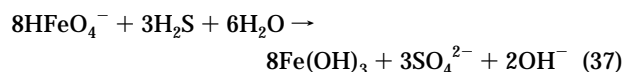
This agrees with the observed rate law provided the second term is much smaller than the first. This is a good approximation under our conditions since Fe(II) reduces Fe(VI) at a rate of $k \sim 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (44) while $k_8 = 1.24 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

The next series of experiments examined the application of excess Fe(VI) at pH 7.0 and pH 9.0 while maintaining a constant sulfide concentration. Hydrogen sulfide concentrations were kept at constant concentration (91 μM), and Fe(VI) concentrations were varied (60–360 μM). The concentrations of hydrogen sulfide were undetectable with the addition of Fe(VI) at both values of pH. The percentage of the sulfate formed to the hydrogen sulfide consumption is shown in Figure 3 against the molar ratio of Fe(VI) and total hydrogen sulfide. Fe(VI) concentrations needed were 2.5 or more times the total hydrogen sulfide concentrations for

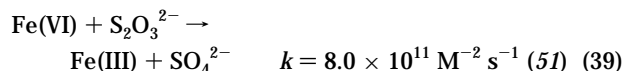
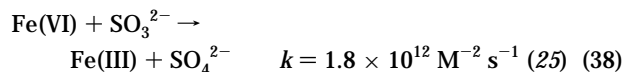
TABLE 1. Removal of Sulfide by Fe(VI) in Groundwater (GW) and Wastewater(WW)

sample	S (salinity)	pH	[Fe(VI)] _T (μM)	[H ₂ S] _T (μM)		[H ₂ S] _T removal (%)	[Fe(VI)] _T / [H ₂ S] _T
				before	after		
GW1	7	8.3	135	75.4	3.6	90.4	1.8
			222	75.4	2.2	94.2	2.9
GW2	95	8.0	540	364	239	34.3	1.5
			1015	364	56.4	84.5	2.8
			1502	364	1.6	99.5	4.1
			1801	364	0.6	99.8	4.9
WW	<2	7.8	22.1	71.4	13.4	81.2	0.31
			54.3	71.4	0.20	99.7	0.76
			75.2	71.4	0.10	99.8	1.05

complete conversion of sulfide to sulfate. This stoichiometry ([Fe(VI)]/[H₂S]_T) of ~2.5 is close to the mass balance equation (eq 37) for complete conversion of hydrogen sulfide to sulfate.



These results indicate that Fe(VI) is oxidizing the sulfur intermediates to sulfate at both pH values. This is possible because the Fe(VI) disproportionation rates are slower (15, 50) and Fe(VI) can easily react with S₂O₃²⁻ and SO₃²⁻ since half-lives for their reactions are less than 7 s at pH = 9.0 under our experimental conditions (eqs 38 and 39).



Furthermore, the Fe(V) and Fe(IV) species would also react with sulfur intermediates. The rate constants of Fe(V) with sulfur compounds, cysteine and cystine, are $4.0 \pm 0.8 \times 10^9$ and $1.95 \pm 0.02 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively at pH = 12.4 (44). These rate constants are 4–6 orders of magnitude faster than Fe(VI) reaction with cysteine and cystine (44). We suspect that the relative rates of Fe(V) and Fe(IV) oxidation with sulfur intermediates must be very fast. It is interesting that there is probably a build of H₂S₂ or S⁰ species when [H₂S]_T > [Fe(VI)]_T while sulfate was the product when [Fe(VI)]_T > [H₂S]_T. This suggests that H₂S₂ and S⁰ species are also reacting with ferrates. In the autooxidation of hydrogen sulfide, the sulfate was formed as the product when [O₂] > [H₂S]_T, and elemental sulfur was formed as one of the products when [O₂] < [H₂S]_T (2, 40).

Sulfide Removal Studies. Table 1 gives the results of the Fe(VI) removal efficiency of hydrogen sulfide from groundwater and wastewater samples at various concentrations of Fe(VI). As the concentration of Fe(VI) increases, the removal efficiency increases. For GW1, the ratio [Fe(VI)]_T/[H₂S]_T was found to be 3 for removing 95% or more sulfide present in groundwater. In the case of GW2, this ratio was 4 for removing 99% of the sulfide. In both samples, the ratios are more than expected from the laboratory experiments (see Figure 3). The higher ratios indicate that Fe(VI) is not only reacting with sulfide but also with other components present (e.g., metals, organic sulfide) in the groundwater samples. This may also be the reason for the higher ratio for the GW2 samples that had a higher salinity (S) than GW1. It may be possible that GW2 contains more of other components than GW1. For wastewater samples, less Fe(VI) was required for complete removal of sulfide. Overall, our results indicate that Fe(VI) can be used to effectively remove sulfide in aqueous solutions.

TABLE 2. Comparison of Reactivity of Hydrogen Sulfide with Cr(VI), Mn(VII), and Fe(VI)

oxidant	reductant	half-life ^a	k, (M ⁻¹ s ⁻¹)	ref
Cr(VI)	hydrogen sulfide	hours–days	<1.2 × 10 ⁻⁵	35
Mn(VII) ^b	hydrogen sulfide	minutes		4
Fe(VI)	hydrogen sulfide	≤seconds	2.2 × 10 ³	this work
Fe(VI)	cysteine	≤seconds	7.6 × 10 ²	46
Fe(VI)	thiourea	≤minutes	4.2 × 10 ¹	39

^a Based on 5-fold or more oxidant concentration than reductant (100 μM). ^b No rate constant was given.

Comparison with Other Oxidants. The results of the Fe(VI) oxidation of hydrogen sulfide are compared with similar tetroxy anions in the first transition series CrO₄²⁻ and MnO₄⁻ in Table 2. Fe(VI) is the most powerful oxidizing agent, and the oxidizing power increases from Cr to Mn to Fe. The reduction potential for Cr(VI)/Cr(III) [$E^\circ(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = 1.33 \text{ V}$ in acidic medium, $E^\circ(\text{CrO}_4^{2-}/\text{Cr(OH)}_3) = -0.12 \text{ V}$ in basic medium] and Mn(VII)/Mn(IV) [$E^\circ(\text{MnO}_4^-/\text{MnO}_2) = 1.669$ and 0.558 V at pH 1 and 14, respectively] (52) are significantly lower than that of Fe(VI)/Fe(III) (2.20 and 0.72 V in acid and basic medium). Therefore, Fe(VI) is expected to be more powerful oxidant than chromium and manganese tetroxy anions.

The reactivity of Fe(VI) with hydrogen sulfide is also compared with organic sulfur compounds in Table 2. The reactivity of Fe(VI) decreases in the order sulfide > cysteine > thiourea. In a study of amino acids with Fe(VI), it was found that cysteine, containing the –SH group, gave higher rates as compared to other amino acids (44). Studies of aliphatic sulfur compounds oxidation by Fe(VI) also indicated that the nucleophilicity on the sulfur atom determined the rate of oxidation (53).

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Supporting Information Available

Two tables and two figures showing further experimental results (3 pp) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the Supporting Information from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St. NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagination, volume number, and issue number) and prepayment, check or money order for \$12.00 for photocopy (\$14.00 foreign) or \$12.00 for microfiche (\$13.00 foreign), are required. Canadian residents should add 7% GST. Supporting Information is also available via the World Wide Web at URL <http://www.chemcenter.org>. Users should select Electronic Publications and then Environmental Science and Technology under Electronic Editions. Detailed instructions for using this service, along with a description of the file formats, are available at this site. To down-load the Supporting Information, enter the journal subscription number from your mailing label. For additional information on electronic access, send electronic mail to si-help@acs.org or phone (202)872-6333.

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