

Arsenic(III) Oxidation by Iron(VI) (Ferrate) and Subsequent Removal of Arsenic(V) by Iron(III) Coagulation

YUNHO LEE,[†] IK-HWAN UM,[‡] AND JEYONG YOON^{*,†}

School of Chemical Engineering, College of Engineering, Seoul National University, San 56-1, Shilim-dong, Gwanak-gu, Seoul 151-742, Korea, and Department of Chemistry, Ewha Womans University, 11-1, Daehyun-dong, Seodaemun-gu, Seoul 120-750, Korea

We investigated the stoichiometry, kinetics, and mechanism of arsenite [As(III)] oxidation by ferrate [Fe(VI)] and performed arsenic removal tests using Fe(VI) as both an oxidant and a coagulant. As(III) was oxidized to As(V) (arsenate) by Fe(VI), with a stoichiometry of 3:2 [As(III):Fe(VI)]. Kinetic studies showed that the reaction of As(III) with Fe(VI) was first-order with respect to both reactants, and its observed second-order rate constant at 25 °C decreased nonlinearly from $(3.54 \pm 0.24) \times 10^5$ to $(1.23 \pm 0.01) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ with an increase of pH from 8.4 to 12.9. A reaction mechanism by oxygen transfer has been proposed for the oxidation of As(III) by Fe(VI). Arsenic removal tests with river water showed that, with minimum 2.0 mg L^{-1} Fe(VI), the arsenic concentration can be lowered from an initial 517 to below $50 \mu\text{g L}^{-1}$, which is the regulation level for As in Bangladesh. From this result, Fe(VI) was demonstrated to be very effective in the removal of arsenic species from water at a relatively low dose level (2.0 mg L^{-1}). In addition, the combined use of a small amount of Fe(VI) (below 0.5 mg L^{-1}) and Fe(III) as a major coagulant was found to be a practical and effective method for arsenic removal.

Introduction

Arsenic (arsenites [As(III)] and arsenates [As(V)]) contaminations of natural waters and wastewaters have been serious problems in many countries. The high concentration of arsenic found in drinking water resources has raised concern in many parts of the world, including the Bengal Delta (Bangladesh and West Bengal, India) (1), the Red River Delta (Vietnam) (2), and the western United States (3). In Bangladesh especially, an estimated 40 million people are at risk of developing cancer due to chronic arsenic poisoning (4). The U.S. EPA recently decreased the maximum concentration level (MCL) of arsenic in drinking water from 50 to $10 \mu\text{g L}^{-1}$ (5) due to the fatal toxicity of arsenic on human health (6).

Most arsenic pollution of natural waters is known to originate from the oxidative weathering or reductive dissolution of As-containing minerals in its most common oxidation state, As(III) (7). As(III) is more toxic and mobile than As(V), so it is highly desirable to oxidize As(III) species

for enhancing the immobilization of arsenic. Therefore, many conventional arsenic removal procedures involve a pretreatment for As(III) oxidation, followed by the adsorption or coprecipitation of the As(V) formed using adsorbents or coagulants, such as metal oxyhydroxides (8). Until now, many oxidants or oxidant-generating systems have been tested for the oxidation of As(III); oxygen and ozone, hydrogen peroxide, manganese oxides, UV/iron systems, and TiO_2/UV systems (ref 9 and references cited therein). However, considering the high toxicity of arsenic and the disastrous effects of its contamination of groundwater in Bangladesh, the development of more efficient arsenic treatment (oxidation) technologies is still required.

Recently, ferrate [Fe(VI), iron in +6 oxidation state] has gained great attention as an environmentally friendly oxidant and coagulant for water and wastewater treatment (10–12). Fe(VI) is a known powerful oxidant over the entire pH range; its redox potentials are 2.20 and 0.72 V in acidic and basic media, respectively (13). Fe(VI) has been reported to be especially effective for treating various nitrogen- and sulfur-containing contaminants in water (ref 12 and references cited therein). It has also been proven to be a good coagulant for removing various toxic metals, nonmetals (14), and radionuclides (15) due to its ability to produce ferric ions [Fe(III)] as decomposition byproducts. In addition, several studies demonstrated that Fe(VI) could be used simultaneously as an oxidant and a coagulant for the treatment of various wastewater (16–18). Nevertheless, little attention has been paid to Fe(VI) as both an oxidant and a coagulant for the removal of arsenic species from waters. Considering that the removal of arsenic requires two steps, these being its oxidation and subsequent coagulation, our assumption is that Fe(VI) might be the ideal candidate for the removal of arsenic due to its dual functions as an oxidant and as a coagulant.

To our knowledge, there have been only two studies on the reaction of As(III) with Fe(VI) in aqueous solutions. Schreyer et al. (19) first reported the stoichiometric relationship of As(III) oxidation by Fe(VI) for the purpose of developing an analytical method for Fe(VI). Recently, Fan et al. (20) reported a preliminary study for the As(III) oxidation by Fe(VI) with the aim of applying Fe(VI) to the removal of arsenic from wastewater. However, neither study provided the kinetics or the mechanisms for the oxidation of As(III) by Fe(VI), even though the kinetics and mechanisms of the Fe(VI) oxidation of various (in)organic compounds in aqueous solution had been reported (12).

Therefore, the main objective of this study was to investigate the kinetics and mechanisms of the As(III) oxidation reaction by Fe(VI) and (re)determine its stoichiometry. In addition, we intended to evaluate and compare the efficiency of Fe(VI) and Fe(III) in terms of their arsenic removals from water.

Experimental Section

Materials and Chemicals. All the chemicals were of reagent grade or better and were used without further purification. NaAsO_2 (Sigma) and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma) were used as the sources of arsenite [As(III)] and arsenate [As(V)], respectively. The ultrapure water ($18 \text{ M}\Omega \cdot \text{cm}$) was prepared by a Barnstead purification system. Potassium ferrate (K_2FeO_4) was prepared by hypochlorite oxidation of ferric nitrate according to the method of Delaude and Laszlo (21). It had purity higher than 96% checked by the chromite titration method (22) and was stored in a desiccator until needed.

* Corresponding author e-mail: jeyong@snu.ac.kr, phone: +82-02-880-8927; fax: +82-02-876-8911.

[†] Seoul National University.

[‡] Ewha Womans University.

Stoichiometry. The stoichiometry of the As(III) oxidation with Fe(VI) was examined by an analysis of the products after the complete reaction of Fe(VI) with As(III). The reaction was initiated by mixing equal volumes (5 mL) of Fe(VI) and As(III) solutions, and the reaction products were analyzed after 1 min [As(III) oxidations were actually completed within 1 s in all cases; see Kinetic Studies]. Each solution was prepared in 5 mM Na₂HPO₄/1 mM borate buffer (pH 9.0) as phosphate, which is a complexing agent for Fe(III), prevents not only the precipitation of Fe(III) (10) but also the arsenic removal by Fe(III) coagulation. The experiments were performed both in O₂-purged (oxic) and N₂-purged (anoxic) conditions in order to find the effects of oxygen on the overall stoichiometry. The Fe(VI) concentrations ranged from 0 to 173 μ M, while the As(III) concentration was fixed at 100 μ M. A molar absorption coefficient, $\epsilon_{510\text{ nm}} = 1,150\text{ M}^{-1}\text{ cm}^{-1}$ was used for the calculation of Fe(VI) concentrations at pH 9.0 (23). The analysis of As(V) was performed using ion chromatography (DX-120, Dionex) equipped with a Dionex Ion Pac AS14 (4 mm \times 250 mm) column and conductivity detection. The eluent solution was 8 mM Na₂CO₃/1 mM NaHCO₃. The ferrous [Fe(II)] and ferric [Fe(III)] ions were analyzed by the 1,10-phenanthroline colorimetric (24) and potassium thiocyanate colorimetric methods (25), respectively.

Kinetics. The kinetic studies of the As(III) oxidation with Fe(VI) were performed with an Applied Photophysics SX-17MV stopped-flow spectrophotometer equipped with a Nesalb RTE-110 constant-temperature circulating bath to keep the temperature in the reaction chamber at the appropriate temperature within $\pm 0.1^\circ\text{C}$ (26). All the kinetic experiments were carried out at 25 $^\circ\text{C}$, except the experiments for the determination of the activation energy, in 50 mM phosphate buffer and under pseudo-first-order conditions with respect to the Fe(VI). The pH of the solution was adjusted using concentrated HClO₄ (70%, Aldrich) or NaOH (50%, Fisher). The As(III) concentration was kept at an excess and ranged from 1000 to 5000 μ M, while the Fe(VI) concentration was around 80 μ M. The progress of the reactions was monitored by the decay of Fe(VI) absorbance at 510 nm under various experimental conditions. The rate constants represent the average values of six experimental runs at each As(III) concentration.

Arsenic Removal from River Water. The arsenic removal experiments were undertaken using water from the Nakdong River, Korea. The removal of arsenic by Fe(VI) is composed of two steps, these being the oxidation of As(III) to As(V) by Fe(VI) and the subsequent removal of the As(V) by its coagulation with the Fe(III) produced by the reduction of the Fe(VI). The detailed procedures are as follows: As(III) was spiked into the river water ([As(III)]₀ = 517 $\mu\text{g L}^{-1}$, pH 7.8). Then, various concentrations of Fe(VI) ([Fe(VI)] = 0–6 mg L⁻¹ as Fe) were applied by the addition of concentrated Fe(VI) stock solution ([Fe(VI)] = 400 mg L⁻¹ as Fe, freshly prepared just before the addition) to the river water (1 L) containing the As(III). After 1 min of rapid mixing (oxidation step), the pH of the solutions was adjusted to around 6.3–6.6 using HClO₄ (5%) to enable the proper coagulation of Fe(III). At this stage, the distinct purple color of Fe(VI) rapidly disappeared, confirming that all the remaining Fe(VI) had been converted to Fe(III). The half-life for the Fe(VI) self-decomposition to Fe(III), which is known as acid-catalyzed reaction, is less than 1 s at a pH below 7 when the initial concentration of Fe(VI) is within 2–6 mg L⁻¹ as Fe (27). The solution was then coagulated and sedimented using standard jar testing, that is one minute of rapid mixing (150 rpm), 30 min of slow mixing (25 rpm), and 30 min of sedimentation. After settlement, a portion of the upper clear solution was decanted and filtered through a 0.45- μm nylon filter (Whatman), and the resulting solution was analyzed by

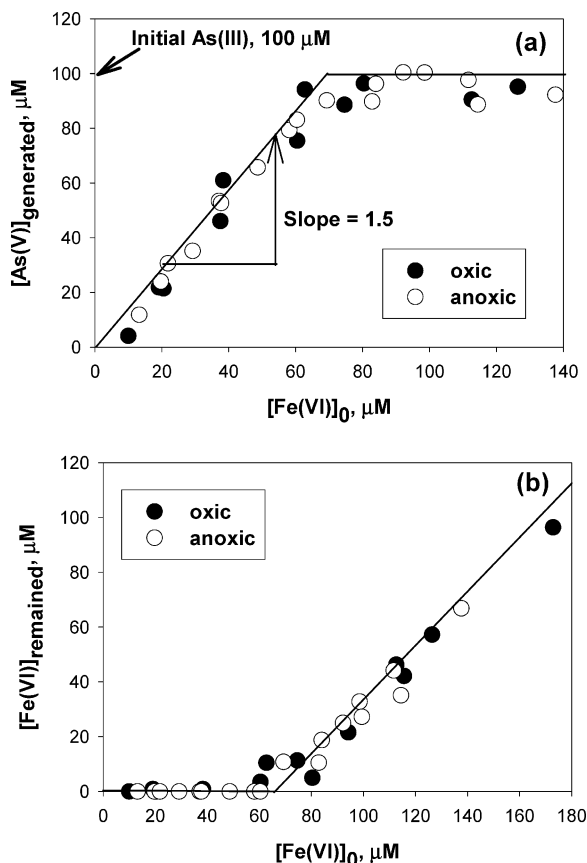


FIGURE 1. Concentration plot for (a) As(V) generated and (b) Fe(VI) remaining after the complete reaction of 100 μM As(III) with various initial concentrations of Fe(VI) (0–170 μM) at pH 9.0 under both oxic (O₂ bubbling) and anoxic (N₂ bubbling) conditions. The line represents the 3:2 [As(III):Fe(VI)] stoichiometry of the reaction.

ICP-MS (Elan 6100, Perkin-Elmer) for total arsenic concentration.

To compare the arsenic removal efficiencies of Fe(VI) and Fe(III), the exact same coagulation experiments (without the 1-min preoxidation step) were carried out using Fe(III) instead of Fe(VI). The Fe(III) stock solution (0.3 M) was freshly prepared from FeCl₃·6H₂O (8). In the experiment with the combined use of Fe(VI) and Fe(III), the river water containing As(III) was preoxidized by 0.5 mg L⁻¹ Fe(VI) and then used in the same coagulation experiments by adding 2 or 4 mg L⁻¹ Fe(III) as a supplementary coagulant.

Analysis of Nakdong River (Korea) Water. Before the analysis, all the samples were filtered through a 0.45- μm cellulose nitrate membrane (Whatman). The pH was measured with a pH meter (420A, Orion), and the DOC (dissolved organic carbon) was measured with a TOC analyzer (820, Sivers). The total alkalinity was measured by titration according to a Standard Method (28). The dissolved iron ion was analyzed using an ICP-AES (Optima 3000, Perkin-Elmer).

Results and Discussion

Stoichiometry and Reaction Product(s) Studies. Figure 1a,b shows the concentrations of the As(V) generated and Fe(VI) remaining, respectively, after the complete reaction of As(III) (100 μM) with Fe(VI) (0–180 μM) under both oxic (air purging) and anoxic (N₂ purging) conditions at pH 9.0. As the concentration of initial Fe(VI) in the reaction mixture increased from 0 to ca. 70 μM , As(V) was linearly formed with a gradient of 1.5 (Figure 1a), and the added Fe(VI) was completely consumed (Figure 1b). As the initial Fe(VI)

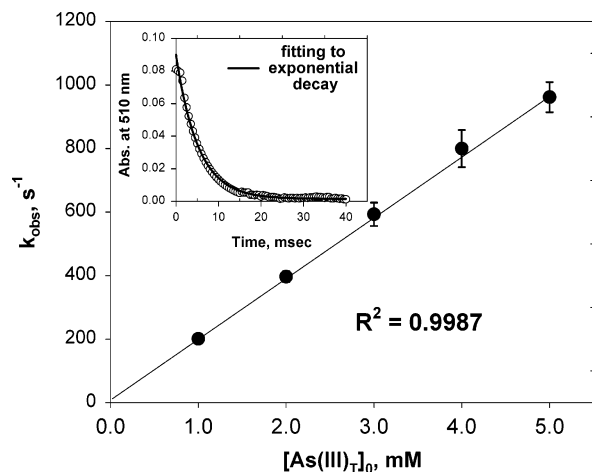


FIGURE 2. Typical plot of the observed first-order decay rate constant of Fe(VI) (k_{obs}) vs $[\text{As(III)}]_0$ for As(III) oxidation by Fe(VI) at pH 9.0 (50 mM phosphate buffer) and 25 °C. The inset figure shows the first-order decay for the reaction of Fe(VI) with 1 mM As(III) from the reduction in the absorbance at 510 nm.

concentration greater than 70 μM was applied, the generated As(V) was maintained constant at 100 μM , which is equal to the initial concentration of As(III) (Figure 1a), and the concentration of Fe(VI) linearly increased with a gradient of 1 (Figure 1b). These results clearly indicate that As(III) was converted to As(V) with a stoichiometry of 3:2 [As(III):Fe(VI)]. Only Fe(III) was identified as a reaction product of the Fe(VI) (not Fe(II)). The stoichiometry and reaction products of the As(III) oxidation by Fe(VI) were not affected by the presence of dissolved oxygen (O_2), indicating that the oxygen atom of As(V) did not originate from the dissolved O_2 . This result is consistent with previous reports where the oxygen atom of sulfate (SO_4^{2-}), produced from the Fe(VI) oxidation of sulfite (SO_3^{2-}), originated solely from Fe(VI) (29).

Kinetic Studies. The reaction rates for the Fe(VI) oxidation of As(III) were measured at various As(III) concentrations and pH values ($[\text{As(III)}]_0 = 1\text{--}5\text{ mM}$, pH 8.4–12.9). The rate expression for the reaction between Fe(VI) and As(III) can be expressed as

$$-\text{d}[\text{Fe(VI)}]_{\text{T}}/\text{d}t = k[\text{Fe(VI)}]_{\text{T}}^a[\text{As(III)}]_{\text{T}}^b \quad (1)$$

where $[\text{Fe(VI)}]_{\text{T}}$ and $[\text{As(III)}]_{\text{T}}$ are the molar concentrations of the total Fe(VI) ($\text{H}_n\text{FeO}_4^{n-2}$) and As(III) species ($\text{H}_n\text{AsO}_4^{n-3}$), respectively; a and b are the orders of the reaction; k is the rate constant of the reaction between Fe(VI) and As(III). The kinetic experiments were undertaken under pseudo-first-order conditions for Fe(VI) where an excess of As(III) was used ($[\text{Fe(VI)}]_{\text{T}} < 0.1\text{ mM}$ and $[\text{As(III)}]_{\text{T}} > 1\text{ mM}$). Under these conditions, eq 1 can be rewritten as

$$-\text{d}[\text{Fe(VI)}]_{\text{T}}/\text{d}t = k_{\text{obs}}[\text{Fe(VI)}]_{\text{T}}^a \quad (2)$$

where

$$k_{\text{obs}} = k[\text{As(III)}]_{\text{T}}^b \quad (3)$$

The pseudo-first-order decay rate constants of Fe(VI) (k_{obs}) were obtained by measuring the decrease in the absorbance of Fe(VI) at 510 nm wavelength as a function of time. The reactions were monitored at least until nine half-life decays of Fe(VI) were attained. The inset in Figure 2, as representative data ($[\text{As(III)}]_{\text{T}} = 1\text{ mM}$), shows that the 510 nm absorbance profile of Fe(VI) fitted well to a single-exponential decay curve

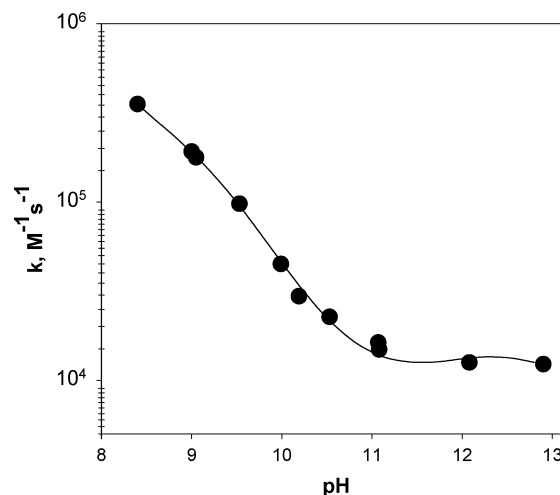
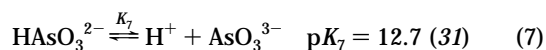
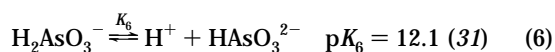
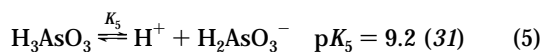
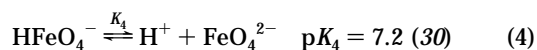


FIGURE 3. pH dependence of the second-order rate constant of As(III) oxidation by Fe(VI) (k) in 50 mM phosphate buffer at 25 °C. The solid line represents the fitting line of experimental data.

($R^2 > 0.99$), confirming that the reaction is first-order with respect to Fe(VI) ($a = 1$). Then, k_{obs} values were determined at various concentrations of As(III) at pH 9.0 (50 mM phosphate buffer) and 25 °C. In all cases, the decay of Fe(VI) was confirmed to be first-order with respect to Fe(VI) ($R^2 > 0.99$). Figure 2 clearly shows the linearity of k_{obs} with respect to $[\text{As(III)}]_{\text{T}}$ ($R^2 > 0.99$), confirming this reaction to also be first-order with respect to As(III) ($b = 1$). From the slope in Figure 2, the second-order rate constant for the reaction between Fe(VI) and As(III), $k = (1.92 \pm 0.04) \times 10^5\text{ M}^{-1}\text{ s}^{-1}$ was obtained at pH 9.0 and 25 °C.

In the next series of experiments, the second-order rate constants for the reactions between Fe(VI) and As(III) (k) were measured at various pH values (pH 8.4–12.9). As shown in Figure 3, the second-order rate constants (k) were found to decrease nonlinearly with increasing pH from 8.4 to 11.1 and to be constant in the pH range from 11.1 to 12.9. The reaction rate was too fast to be measured below pH 8.4. This variation in the k value as a function of pH (pH 8.4–12.9) can be explained by considering the following species distribution of Fe(VI) and As(III) at the given pH conditions (eqs 4–7) and Figure 4):



According to the above equilibria for Fe(VI) (HFeO_4^- and FeO_4^{2-}) and As(III) (H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-} , and AsO_3^{3-}), eight different reactions (2×4) are possible between Fe(VI) and As(III). However, the reactions of HFeO_4^- with ionized species of As(III) (H_2AsO_3^- , HAsO_3^{2-} , and AsO_3^{3-}) are expected to be negligible since the $\text{p}K_a$ value of HFeO_4^- ($\text{p}K_4 = 7.2$) is much lower than that of H_3AsO_3 , the first ionization constant of As(III) ($\text{p}K_5 = 9.2$), by 2.0 $\text{p}K_a$ units indicating that there is little possibility of the occurrence for these reactions as shown in Figure 4. In addition, it is unlikely that the rates of HFeO_4^- with ionized species of As(III) are much greater than that of HFeO_4^- with H_3AsO_3 due to the strong repulsion between the negatively charged species. Therefore, the

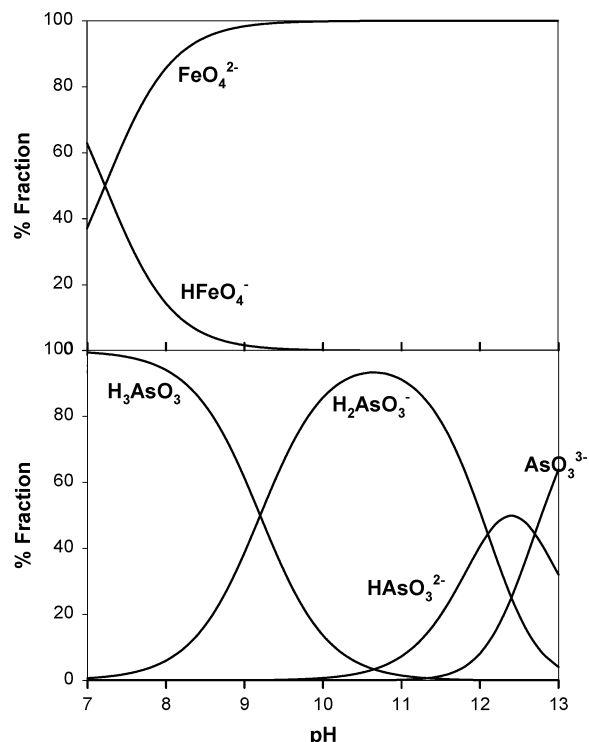
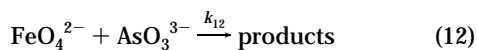
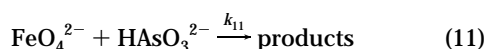
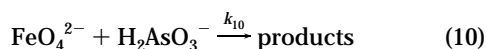
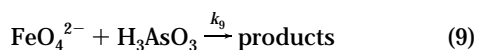
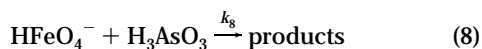


FIGURE 4. Species distributions of Fe(VI) and As(III) as a function of pH.

following five reactions (reactions 8–12) can be considered as possible reactions between the Fe(VI) and As(III) species under the given pH conditions (pH 8.4–12.9) to explain formally the dependence of reaction rates on pH:



When considering the above five reactions, the decay rate of the Fe(VI) as a function of pH can be expressed as

$$-d[\text{Fe(VI)}]_T/dt = k_8[\text{HFeO}_4^-][\text{H}_3\text{AsO}_3] + k_9[\text{FeO}_4^{2-}][\text{H}_3\text{AsO}_3] + k_{10}[\text{FeO}_4^{2-}][\text{H}_2\text{AsO}_3^-] + k_{11}[\text{FeO}_4^{2-}][\text{HAsO}_3^{2-}] + k_{12}[\text{FeO}_4^{2-}][\text{AsO}_3^{3-}] \quad (13)$$

Then, the second-order rate constant (k) can be written as eqs 15 and 16 using the equilibrium constants of the Fe(VI) (K_4) and As(III) species (K_5 , K_6 , and K_7) as shown in eqs 4–7, respectively:

$$-d[\text{Fe(VI)}]_T/dt = k[\text{Fe(VI)}]_T[\text{As(III)}]_T \quad (14)$$

where

$$k = \alpha_0\beta_0k_8 + \alpha_1\beta_0k_9 + \alpha_1\beta_1k_{10} + \alpha_1\beta_2k_{11} + \alpha_1\beta_3k_{12} \quad (15)$$

and

$$\alpha_0 = \frac{[\text{HFeO}_4^-]}{[\text{Fe(VI)}]_T} = \frac{[\text{H}^+]}{[\text{H}^+] + K_4} \quad \alpha_1 = \frac{[\text{FeO}_4^{2-}]}{[\text{Fe(VI)}]_T} = \frac{K_4}{[\text{H}^+] + K_4}$$

$$\beta_0 = \frac{[\text{H}_3\text{AsO}_3]}{[\text{As(III)}]_T} = \frac{[\text{H}^+]^3}{T} \quad \beta_1 = \frac{[\text{H}_2\text{AsO}_3^-]}{[\text{As(III)}]_T} = \frac{K_5[\text{H}^+]^2}{T}$$

$$\beta_2 = \frac{[\text{HAsO}_3^{2-}]}{[\text{As(III)}]_T} = \frac{K_5K_6[\text{H}^+]}{T} \quad \beta_3 = \frac{[\text{AsO}_3^{3-}]}{[\text{As(III)}]_T} = \frac{K_5K_6K_7}{T} \quad (16)$$

where

$$T = [\text{H}^+]^3 + K_5[\text{H}^+]^2 + K_5K_6[\text{H}^+] + K_5K_6K_7$$

The individual values of the five rate constants (k_8 , k_9 , k_{10} , k_{11} , and k_{12}) were determined to best fit the experimental data using a multiple regression analysis. (The solid line in Figure 3 represents the results of the best fit.) The determined rate constants were $k_8 = (2.50 \pm 0.09) \times 10^6$, $k_9 = (2.67 \pm 0.04) \times 10^5$, $k_{10} = (1.02 \pm 0.16) \times 10^4$, $k_{11} = (1.73 \pm 0.78) \times 10^4$, and $k_{12} = (9.20 \pm 7.26) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. The relatively large uncertainty for k_{11} and k_{12} indicates that reactions 11 and 12 do not contribute significantly as compared with the other reactions 8–10 to the overall reactivity of Fe(VI) with As(III).

Then, the following two points are significant: First, the protonated species of Fe(VI) (HFeO_4^-) reacts more rapidly than the unprotonated species (FeO_4^{2-}) with H_3AsO_3 (k_8 is 9.4 times larger than k_9). This increased reactivity of the Fe(VI) upon protonation has also been observed in many other studies (12) and can be rationalized by considering the higher oxidative power of the Fe(VI) when protonated (13). Second, FeO_4^{2-} reacts faster with the nonionic species of As(III) (H_3AsO_3) than with the ionic species (H_2AsO_3^- , HAsO_3^{2-} , and AsO_3^{3-}) (k_9 was ca. 20 times larger than k_{10} , k_{11} , and k_{12}). This result can be understood by considering the greater charge repulsion between the two ionized species, FeO_4^{2-} and ionized As(III). Similar results have also been reported in other studies (12).

Next, the effect of the ionic strength on the rate of As(III) oxidation by Fe(VI) was examined in NaCl solutions at pH 11.08 and 25 °C. The second-order rate constants (k) determined were $k = (1.49 \pm 0.02) \times 10^4$, $(2.27 \pm 0.11) \times 10^4$, and $(2.86 \pm 0.23) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ with 0, 0.5, and 1.0 M NaCl, respectively. At pH 11.08, the main species of Fe(VI) and As(III) are FeO_4^{2-} , H_2AsO_3^- , and HAsO_3^{2-} , all of which are ionized species (Figure 4). One explanation for the slight increase in the reaction rate between ionized species of Fe(VI) (FeO_4^{2-}) and As(III) (H_2AsO_3^- and HAsO_3^{2-}) with increasing the concentration of NaCl can be found from the “Activated Complex Theory”, which supports that the reaction rate between like charged species can be raised with an increase in the ionic strength of an aqueous solution (32).

In addition, such an increase in the reaction rate can be related with the changes in pK_a values of Fe(VI) and As(III) species with the increase in the ionic strength. However, the pK_a values of Fe(VI) and As(III) are known to decrease with the increase of ionic strength (30, 33), indicating that more deprotonated species of Fe(VI) and As(III) are present at pH 11.08. Accordingly, in higher ionic strength, the reaction rate between Fe(VI) and As(III) is likely to decrease due to the more charge repulsion between deprotonated species of Fe(VI) and As(III), which is contrary to the measured rate dependence on ionic strength.

Finally, the effect of temperature on the rate of As(III) oxidation by Fe(VI) was investigated with temperatures ranging from 15 to 35 °C at 5 °C intervals and at pH 10.19. The temperature dependency for the reaction was found to

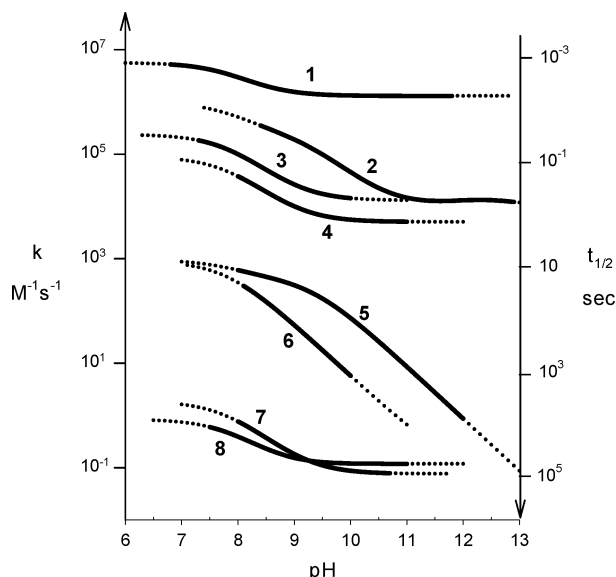


FIGURE 5. Reaction-rate constants (second-order) and half-time values of different compounds in the presence of Fe(VI) as a function of pH. Assumptions for $t_{1/2}$ scale: (i) $[\text{Fe(VI)}] = 100 \mu\text{M}$, (ii) $[\text{compound}] \ll [\text{Fe(VI)}]_{\text{const}}$, (iii) 1:1 stoichiometry $[\text{compound}:\text{Fe(VI)}]$ of all compounds with Fe(VI). Compounds: 1, ascorbate (34); 2, As(III) (this study); 3, mercaptoethanesulfonate (35); 4, hydrazine (36); 5, cyanide (39); 6, thioxane (40); 7, hexafluoro-2-propanol (37); 8, ammonia (38).

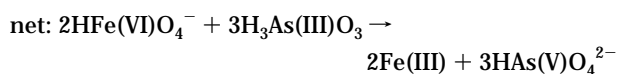
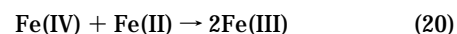
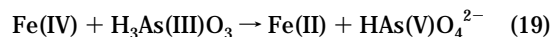
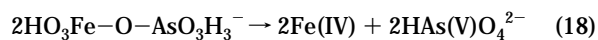
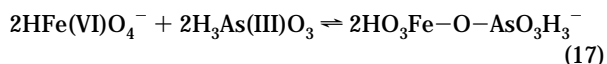
be small, and this can be understood considering the high speed of the Fe(VI)/As(III) reaction. The plot of $\log k$ versus $1/T$ (K^{-1}) gave a linear plot (data not shown). The activation energy (E_a) was calculated to be 21.3 kJ mol^{-1} from the slope of the linear plot. This activation energy contains terms due to the effect of temperature on the dissociation of HFeO_4^- , H_3AsO_3 , H_2AsO_3^- , and HAsO_3^{2-} .

Fe(VI) has been considered a very selective oxidant, and its reaction rates (second order) with various organic or inorganic compounds range from about $10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at the lower end up to $10^7 \text{ M}^{-1} \text{ s}^{-1}$ in the pH range of 7–13 (10, 12). Figure 5 shows the second-order rate constants (k) of a few selected compounds with Fe(VI) and the half-time values for their degradation ($t_{1/2}$) in the presence of Fe(VI) as a function of pH (under pseudo-first-order assumption for compounds, that is, $[\text{compound}] \ll [\text{Fe(VI)}]_{\text{const}}$ and $[\text{Fe(VI)}] = 100 \mu\text{M}$). As shown in Figure 5, Fe(VI) reacts very fast ($k > 10^3 \text{ M}^{-1} \text{ s}^{-1}$) with ascorbate (34), mercaptoethanesulfonate (thiol) (35), and hydrazine (36) as well as As(III) (this study) with $t_{1/2}$ below approximately 1 s. However, the rate constants of Fe(VI) with hexafluoro-2-propanol (alcohol) (37) and ammonia (38) are relatively very low ($k < 1 \text{ M}^{-1} \text{ s}^{-1}$) with $t_{1/2}$ above 10^3 s. The rate constants of Fe(VI) with cyanide (39) and thioxane (40) belong between those two groups ($1 < k < 10^3 \text{ M}^{-1} \text{ s}^{-1}$). From a compilation of the rate constants of Fe(VI) with various compounds (10, 12), the reaction of Fe(VI) with As(III) was found to be in a very fast reaction group ($k > 10^4 \text{ M}^{-1} \text{ s}^{-1}$). This indicates that the As(III) present in waters containing various background compounds having lower reaction rate ($k < 10^3 \text{ M}^{-1} \text{ s}^{-1}$) can be selectively oxidized by Fe(VI).

In addition, as high levels of arsenic in groundwater are known to correlate with high concentrations of carbonate species (above hundreds of milligrams per liter) (1), the interference effect of carbonate species on the As(III) oxidation by Fe(VI) needs to be examined. Separate experiments were then performed to show that the reaction of Fe(VI) with carbonate species is relatively very slow ($k \ll 0.1 \text{ M}^{-1} \text{ s}^{-1}$ at pH 9.0). This result indicates that even the presence

of hundreds of milligrams of carbonate species per liter does not interfere in the As(III) oxidation by Fe(VI).

Mechanism. The following reactions (eqs 17–20) were proposed as the mechanism of the As(III) oxidation by Fe(VI). In this reaction scheme, the main species of Fe(VI), As(III), and As(V) at pH 7 were selected for their simplicity. A similar reaction scheme has been proposed for oxidation reactions of sulfite (SO_3^{2-}) and selenite (SeO_3^{2-}) with ferrate [Fe(VI)] by Johnson and Bernard (41). The oxidation reaction was proposed to proceed via oxygen transfer based on their stoichiometric and kinetic results:



Reaction 17, which is the formation step of Fe(VI)–As(III) adduct, indicates that the As(III) is oxidized by Fe(VI) via the direct transfer of an oxygen from the Fe(VI) to the center atom of the As(III) (oxygen transfer mechanism). Reaction 18 represents that the Fe(VI)–As(III) adduct produces Fe(IV) and arsenate [As(V)] by an internal redox process. Then, according to Johnson and Bernard (41), sulfite and selenite showed slight mechanistic differences in their reactions with Fe(VI) despite the similarities in their structures. They proposed that the Fe(VI)–sulfite adduct solely undergoes the internal redox process forming sulfate (SO_4^{2-}) and an Fe(IV) intermediate, whereas the Fe(VI)–selenite adduct undergoes not only this internal redox process but reacts with another selenite to produce selenate (SeO_4^{2-}) and Fe(II). These different mechanistic explanations were based on their kinetic results, where the reaction of selenite with Fe(VI) was of a mixed first- and second-order with respect to selenite, but the reaction of sulfite with Fe(VI) was solely first-order with respect to sulfite. Since the reaction of As(III) with Fe(VI) was found to be a first-order reaction but not a second-order reaction with respect to As(III) for the As(III) concentration range used (as shown in Figure 2), we therefore propose that the Fe(VI)–As(III) adduct can only undergo an internal redox process (eq 18) as is the case with sulfite. This argument can be further supported from the standard reduction potentials (E°) [i.e., the E° values of As(III), sulfite, and selenite at basic aqueous solution are -0.67 , -0.94 , and 0.03 V , respectively (42), indicating that As(III) and sulfite are much more easily oxidized than selenite]. Therefore, the Fe(VI)–selenite adduct can have a longer lifetime enough to react with other selenite rather than Fe(VI)–As(III) and Fe(VI)–sulfite adducts because it is more resistant to oxidation than As(III) and sulfite.

Reactions 19 and 20 indicate that Fe(IV) oxidizes not only another As(III) to produce Fe(II) and As(V) but also Fe(II) to generate 2 mol of Fe(III) as the final iron products. It should be noted that the elements (oxygen and hydrogen) and charges are not balanced in eqs 18–20. This is because the exact formula and structure of Fe(IV), which is known to be a highly reactive species, was not elucidated although its existence in aqueous solution has been shown (43). The net equation for this reaction scheme clearly shows a 3:2 stoichiometry for the As(III) oxidation by Fe(VI).

It is possible that Fe(VI) can oxidize substrates by one-electron transfer process, generating Fe(V) and a radical.

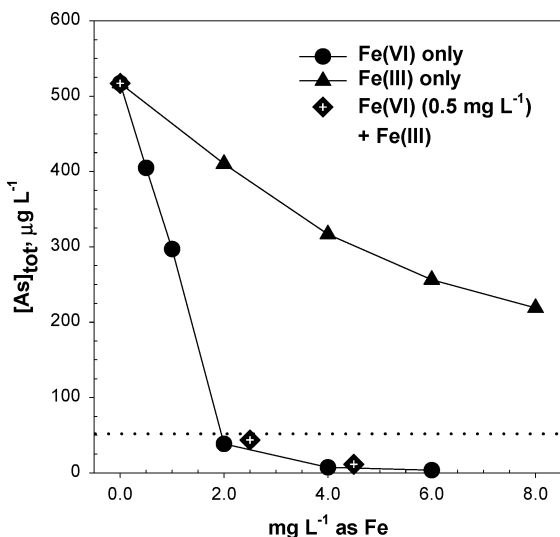


FIGURE 6. Arsenic removal from river water (Nakdong River in Korea) by Fe(VI) only (0–6 mg L⁻¹), Fe(III) only (0–8 mg L⁻¹), and combined use of Fe(VI) (0.5 mg L⁻¹) and Fe(III) (2 and 4 mg L⁻¹). Initial arsenic concentration: 517 μg L⁻¹ As(III). The bottom dotted line represents the drinking water regulation level of arsenic in Bangladesh, 50 μg L⁻¹.

However, this radical was only observed in a reaction of Fe(VI) with organic molecules, such as phenol (44) and aniline (45), during EPR spectroscopy studies. Other studies also suggested one-electron transfer process, but no experimental evidences were given (12). On the other hand, the proposed two-electron transfer process in this study for As(III) oxidation by Fe(VI) is consistent with not only our experimental data but also other studies in the literature on the oxidation of inorganic oxyanions by Fe(VI), such as sulfite (SO₃²⁻) and selenite (SeO₃²⁻) (41). This two-electron-transfer mechanism involves the oxygen transfer from FeO₄²⁻ to SO₃²⁻, which was proven by Goff and Murmann during their isotopic ¹⁸O tracer study (29). Therefore, the proposed mechanism that the reaction of Fe(VI) with As(III) proceeds via the formation of adduct and then two-electron transfer via oxygen transfer step appears to be a reasonable suggestion, although no experimental evidences were given to support the proposed mechanism.

Removal Studies. Studies on the removal of arsenic were carried out on the Nakdong River (Korea) water. The pH, total alkalinity and dissolved organic carbon concentration of the river water were 7.8, 30 mg L⁻¹ (as CaCO₃), and 4.45 mg L⁻¹, respectively. The original iron level [Fe(II) and Fe(III)] in the water was quite low (below 0.1 mg L⁻¹), and the arsenic removal without iron addition was not observed. As shown in Figure 6, 2.0 mg of Fe(VI) L⁻¹ effectively removed the arsenic species, lowering the arsenic concentration from an initial 517 to below 50 μg L⁻¹, which satisfies the regulation level for As in Bangladesh. In contrast, the addition of Fe(III), even up to ca. 8 mg L⁻¹, failed to achieve an effective reduction in the arsenic concentration below to the arsenic regulation level. This large difference in the removal efficiency of Fe(VI) and Fe(III) can support the argument that Fe(VI) not only oxidizes As(III) to As(V) but also acts as a coagulant of the arsenic. Besides, Fe(VI) was proven to be very effective in the removal of arsenic species from water at relatively lower levels (2.0 mg L⁻¹) as compared with Fe(III).

More interestingly, as shown in Figure 6, the effective removal of arsenic species was achieved by the combined use of very small amounts of Fe(VI) (0.5 mg L⁻¹) and Fe(III) (2.0 and 4.0 mg L⁻¹) as supplementary coagulants. When considering that Fe(VI) is not currently commercially available and is a relatively expensive chemical, arsenic removal by

Fe(VI) alone is not an economical method. However, the combined use of a small amount of Fe(VI) (below 0.5 mg L⁻¹) as an oxidant for As(III) with Fe(III) as a major coagulant could be a practical method for the effective treatment of arsenic species in waters and wastewaters.

Acknowledgments

This work was supported by Grant R01-2003-000-10053-0 from the Basic Research Program of the Korea Science & Engineering Foundation. Financial support from the Brain Korea 21 project is also acknowledged. The authors thank Prof. V. K. Sharma for his review of the manuscript and Dr. L. Delaude for his comments on the preparation of K₂FeO₄.

Supporting Information Available

Two tables showing the second-order rate constants of As(III) oxidation by Fe(VI) and the characteristics of Nakdong River water. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Nickson, R.; McArthur, J.; Burgess, W.; Ahmed, K. M. *Nature* **1998**, *395*, 338.
- (2) Berg, M.; Tran, H. C.; Nguyen, T. C.; Pham, H. V.; Schertenleib, R.; Giger, W. *Environ. Sci. Technol.* **2001**, *35*, 2621.
- (3) Reid, J. J. *Am. Water Works Assoc.* **1994**, *86*, 44.
- (4) Smith, A. H.; Lingas, E. O.; Rahman, M. *Bull. World Health Org.* **2000**, *78*, 1093.
- (5) Smith, A. H.; Lopipero, P. A.; Bates, M. N.; Steinmaus, C. M. *Science* **2002**, *296*, 2145.
- (6) Pontius, F. W.; Brown, K. G.; Chen, C.-J. *J. Am. Water Works Assoc.* **1994**, *86*, 52.
- (7) Cullen, W. R.; Reimer, K. J. *Chem. Rev.* **1989**, *89*, 713.
- (8) Hering, J. G.; Chen, P. Y.; Wikie, J. A.; Elimelech, M.; Liang, S. *J. Am. Water Works Assoc.* **1996**, *88*, 155.
- (9) Lee, H.; Choi, W. *Environ. Sci. Technol.* **2002**, *36*, 3872.
- (10) Carr, J. D.; Kelter, P. B.; Tabatabai, A.; Splichal, D.; Erickson, J.; McLaughlin, C. W. *Proc. Conf. Water Chlorination Chem. Environ. Impact. Health Effects* **1985**, *5*, 1285.
- (11) Jiang, J. Q.; Lloyd, B. *Water Res.* **2002**, *36*, 1397.
- (12) Sharma, V. K. *Adv. Environ. Res.* **2002**, *6*, 143.
- (13) Wood, R. H. *J. Am. Chem. Soc.* **1958**, *80*, 2038.
- (14) Bartzatt, R.; Cano, M.; Johnson, L.; Nagel, D. J. *Toxicol. Environ. Health* **1992**, *35*, 205.
- (15) Potts, M. E.; Churchwell, D. R. *Water Environ. Res.* **1994**, *66*, 107.
- (16) Waite, T. D.; Gray, K. A. *Stud. Environ. Sci.* **1984**, *23*, 407.
- (17) De Luca, S. J.; Cantelli, M.; De Luca, M. A. *Water Sci. Technol.* **1992**, *26*, 2077.
- (18) White, D. A.; Franklin, G. S. *Environ. Technol.* **1998**, *19*, 1157.
- (19) Schreyer, J. M.; Thompson, G. W.; Ockerman, L. T. *Anal. Chem.* **1950**, *22*, 691.
- (20) Fan, M.; Brown, R. C.; Huang, C. P. *Int. J. Environ. Pollut.* **2002**, *18*, 91.
- (21) Delaude, L.; Laszlo, P. *J. Org. Chem.* **1996**, *61*, 6360.
- (22) Schreyer, J. M.; Thompson, G. W.; Ockerman, L. T. *Anal. Chem.* **1950**, *22*, 1426.
- (23) Bielski, B. H. J.; Thomas, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 7761.
- (24) Tamura, H.; Goto, K.; Yotsuyanagi, T.; Nagayama, M. *Talanta* **1974**, *21*, 314.
- (25) Skoog, D. A.; West, D. M.; Holler, F. J. *Analytical Chemistry, An Introduction*, 6th ed.; Saunders College Publishing: 1994; p 418.
- (26) Um, I. H.; Buncel, E. *J. Org. Chem.* **2000**, *65*, 577.
- (27) Rush, J. D.; Zhao, Z.; Bielski, B. H. J. *Free Radical Res.* **1996**, *24*, 187.
- (28) Clesceri, L. S.; Greenberg, A. E.; Eaton, A. D. *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; American Public Health Association: Washington, DC, 1998.
- (29) Goff, H.; Murmann, R. K. *J. Am. Chem. Soc.* **1971**, *93*, 6058.
- (30) Sharma, V. K.; Burnett, C. R.; Millero, F. J. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2059.
- (31) Sadiq, M.; Zaidi, T. H.; Mian, A. A. *Water, Air, Soil Pollut.* **1983**, *20*, 369.
- (32) Stumm, W.; Morgan, J. J. *Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters*, 3rd ed.; John Wiley & Sons: New York, 1996.
- (33) Baes, C. F.; Mesmer, J. R. E. *The Hydrolysis of Cations*; John Wiley & Sons: New York, 1986; p 367.

- (34) Cyr, J. E.; Bielski, B. H. J. *Free Radical Biol. Med.* **1991**, *11*, 157.
- (35) Read, J. F.; Adams, E. K.; Gass, H. J.; Shea, S. E.; Theriault, A. *Inorg. Chim. Acta* **1998**, *281*, 43.
- (36) Johnson, M. D.; Hornstein, B. J. *Inorg. Chim. Acta* **1994**, *225*, 145.
- (37) Norcross, B. E.; Lewis, W. C.; Gai, H.; Noureldin, N. A.; Lee, D. G. *Can. J. Chem.* **1997**, *75*, 129.
- (38) Sharma, V. K.; Bloom, J. T.; Joshi, V. N. *J. Environ. Sci. Health* **1998**, *A33*, 635.
- (39) Sharma, V. K.; Rivera, W.; Smith, J. O.; O'Brien, B. *Environ. Sci. Technol.* **1998**, *32*, 2608.
- (40) Read, J. F.; Boucher, K. D.; Mehlman, S. A.; Watson, K. J. *Inorg. Chim. Acta* **1998**, *267*, 159.
- (41) Johnson, M. D.; Bernard, J. *Inorg. Chem.* **1992**, *31*, 5140.
- (42) Bard, A. J.; Parsons, R.; Jordan, J. *Standard Potentials in Aqueous Solution*; Marcel Dekker: New York, 1985.
- (43) Rush, J. D.; Bielski, B. H. J. *J. Am. Chem. Soc.* **1986**, *108*, 523.
- (44) Huang, H.; Sommerfeld, D.; Dunn, B. C.; Eyring, E. M.; Lloyd, C. R. *J. Phys. Chem. A* **2001**, *105*, 3536.
- (45) Huang, H.; Sommerfeld, D.; Dunn, B. C.; Lloyd, C. R.; Eyring, E. M. *J. Chem. Soc., Dalton Trans.* **2001**, 1301.

Received for review March 7, 2003. Revised manuscript received September 15, 2003. Accepted September 22, 2003.

ES034203+