

# Ferrate(VI) Oxidation of Aqueous Cyanide

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The rates of oxidation of cyanide with Fe(VI) were measured as a function of pH (8.0–12) and temperature (15–30 °C). The reaction was found to be first order for each reactant. The rates decrease with increasing pH. The energy of activation was found to be  $38.9 \pm 1.0$  kJ mol<sup>-1</sup> at pH 9.0. The removal of cyanide by oxidation with Fe(VI) was studied at pH 7.5, 9.0, and 12.0. Fe(VI) removal efficiency was greater at pH 9.0 than at pH 7.5 and 12.0. At pH 9.0, Fe(VI) molar consumption was nearly equal to that of oxidized cyanide. Cyanate and nitrite ions were identified as the products of the reaction at pH 7.5. The experiments indicated 1:1 stoichiometric conversion of cyanide to nitrite ion at pH 9.0 and 12.0. Experiments were conducted to test the Fe(VI) removal efficiency of cyanide in electroplating rinsewater. The results indicate that Fe(VI) has the potential to serve as a reliable and safe oxidative treatment for removing cyanide in wastewater effluent.

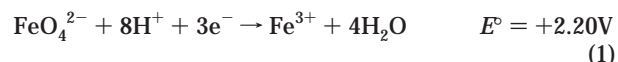
## Introduction

Cyanide, a highly toxic substance, is present in wastes of gold refining, metal plating, chemical manufacturing, and iron and steel industries (1). To comply with Federal and State regulations, the treatment of wastewater is required before the safe discharge of cyanide wastes. The ultimate goal of the wastewater treatment is to achieve a zero discharge level of undesirable contaminants in its effluent. The metal finishing industry defines the term zero discharge as no measurable cyanide in the effluent wastewater and no environmental impact resulting from the discharged wastewater. Attainment of zero discharge level has become the new standard by which treatment plants will be judged.

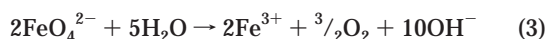
Cyanide exists in three forms in wastewater: free cyanide such as hydrogen cyanide; simple cyanide such as sodium cyanide or potassium cyanide; complex cyanide such as iron cyanide, nickel cyanide, and copper cyanide. Total cyanide is the sum of simple and complex cyanides but excludes other ligands such as cyanate and thiocyanate. The most common oxidative technique for the destruction of cyanide wastes is alkaline chlorination. This method, although adequate, has many disadvantages such as high chemical costs, formation of cyanogen chloride, chloride contamination, and incomplete decomposition of some metal cyanide complexes (2, 3). Other methods such as electrolytic decomposition, ozonation, electrodialysis, catalytic oxidation, reverse osmosis, ion exchange, genetic engineering applications, and photocatalytic oxidation (2, 4–9) are evolving to

meet the demands of tighter discharge limits. Another promising oxidation process involves the use of iron in a +6 valence state, Fe(VI) as  $\text{FeO}_4^{2-}$ , to oxidize cyanide in water.

Fe(VI) ion is tetrahedral in structure, all Fe–O bonds are equivalent with covalent character (10). Fe(VI) species are strong oxidizing agents that can be seen from the reduction potentials of reactions 1 and 2 in acidic and alkaline solutions, respectively (10).



The spontaneous oxidation of Fe(VI) in water forms molecular oxygen (11).



The rates of this reaction are very slow at pH 9–10 and are fast below and above this pH range; the rate with respect to Fe(VI) is second order below pH 9 and first order above pH 10 (12, 13). Kinetic measurements suggest a reaction scheme (eqs 4–6) in which hydrogen ferrate ion ( $\text{HFeO}_4^-$ ) reacts with another ferrate ion ( $\text{FeO}_4^{2-}$ ) to give a dimer that is reduced by water to give oxygen (12, 13).



Fe(VI) has been evaluated as a multipurpose wastewater chemical for coagulation, disinfection, and oxidation (14–18). The reactivity of Fe(VI) with certain inorganic and organic contaminants suggests its usefulness in remediation of contaminants in industrial effluents (19–22). Recently, experiments were conducted to test Fe(VI) removal efficiency of sulfide in groundwater and wastewater (23). The results indicated the effectiveness of Fe(VI) in removing sulfide from wastewaters. In this paper, we report the Fe(VI) oxidation of free cyanide in water. We have also evaluated Fe(VI) as an oxidant for removing cyanide from electroplating rinsewater.

## Experimental Section

Fe(VI) as  $\text{K}_2\text{FeO}_4$  was prepared according to the method of Thompson et al. (24). Solutions were prepared with water that had been distilled and then passed through an 18 MΩ Milli-Q water purification system. The Fe(VI) solutions were prepared by addition of solid samples of  $\text{K}_2\text{FeO}_4$  to 0.001 M borate/0.005 M  $\text{Na}_2\text{HPO}_4$ , pH 9.0, where the solutions are most stable. The phosphate serves as a complexing agent for Fe(III), which otherwise precipitates rapidly as a hydroxide that interferes with the optical monitoring of the reaction and accelerates the spontaneous decomposition of Fe(VI). A molar absorption coefficient  $\epsilon_{510\text{ nm}} = 1150\text{ M}^{-1}\text{ cm}^{-1}$  was used for the calculation of Fe(VI) concentration at pH 9.0 (12). Cyanide solutions were prepared by dissolving recrystallized KCN in 0.01 M phosphate and were adjusted to the desired pH with either phosphoric acid or sodium hydroxide.

Kinetic experiments were carried out using a stopped-flow system (25). The studies were done under pseudo-

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first-order conditions. The concentration of cyanide was kept in excess and ranged from  $1.5$  to  $9.0 \times 10^{-3}$  M, while the Fe(VI) concentrations ranged from  $100$  to  $125 \times 10^{-6}$  M. Experiments were initiated with decay of Fe(VI) absorbance at  $510$  nm under the given conditions. Rate constants represented an average of nine experimental runs per cyanide concentration.

The stoichiometric experiments were carried out by mixing equal volumes ( $5 \times 10^{-3}$  L) of Fe(VI) and cyanide solutions together. The concentration of cyanide was kept between  $232$  and  $250 \times 10^{-6}$  M at each pH (pH 7.5, 9.0, and 12.0), and Fe(VI) concentrations ranged from  $46$  to  $508 \times 10^{-6}$  M. Cyanide concentrations were determined before and after mixing with Fe(VI) using high performance ion chromatography (HPIC). The HPIC system consisted of a DEAE-5pw ( $75$  mm  $\times$   $7.5$  mm) ion exchange column connected in-line to a silver electrode in a Waters 464 electrochemical detector. The eluent was a solution of  $50 \times 10^{-3}$  M LiOH and  $0.25 \times 10^{-3}$  M Na<sub>2</sub>EDTA pumped at a flow rate of  $2.0 \times 10^{-3}$  L/min. Nitrite and nitrate analysis were accomplished by using Waters IC-Pak A HR ( $75$  mm  $\times$   $4.6$  mm) ion exchange column connected in-line to a Waters 431 conductivity detector. The mobile phase was a solution of 2% borate/gluconate buffer (pH 8.5) set at a flow rate of  $1.0 \times 10^{-3}$  L/min.

The analysis of carbon from oxidation of cyanide by Fe(VI) was conducted using FTIR (Mattson GL2020). The reaction mixtures were acidified with phosphoric acid to pH 4.0 before collecting FTIR spectra. The blank solution in FTIR studies consisted of mixing of equal volumes ( $5 \times 10^{-3}$  L) of Fe(VI) in  $0.001$  M borate/ $0.005$  M phosphate buffer and  $0.01$  M phosphate used as cyanide preparing solvent.

Rinsewater experiments were conducted to determine the efficiency of Fe(VI) in removing free and total cyanide from an untreated industrial water sample. Water samples were collected from the Corpus Christi Army Depot's (CCAD) electroplating facility in Corpus Christi, TX. Several electroplating processes used at CCAD contain cyanide compounds. The rinsewater used for each process collects in a central holding tank. Water used in the processing operation originated from the local municipal water supply and was drinking water quality. The collected rinsewater is then processed through the pretreatment system. Typical rinsewater usually contains cadmium, copper, iron, and silver in concentrations varying from  $20$  to  $200 \times 10^{-6}$  M. The rinsewater sample was diluted to a concentration of  $232 \times 10^{-6}$  M free cyanide and reacted with various concentrations of Fe(VI) solutions. The samples were then analyzed for remaining free cyanide by HPIC as described before. Fe(VI) efficiency to remove total cyanide was also tested. Total cyanide was quantitatively determined by an established method (26).

## Results and Discussion

**Kinetics Studies.** In the first series of experiments, the reaction rates of Fe(VI) with cyanide were determined at pH 9.0 and  $22^\circ\text{C}$ . The rate expression for the reaction between Fe(VI) and cyanide is given by

$$-d[\text{Fe(VI)}]/dt = k[\text{Fe(VI)}]^m[\text{CN}_T]^n \quad (7)$$

where  $[\text{Fe(VI)}]$  and  $[\text{CN}_T]$  are molar concentrations of Fe(VI) and cyanide ( $\text{HCN} + \text{CN}^-$ ), 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 an excess of cyanide was used. Under these conditions, eq 7 can be written as

$$-d[\text{Fe(VI)}]/dt = k_1[\text{Fe(VI)}]^m \quad (8)$$

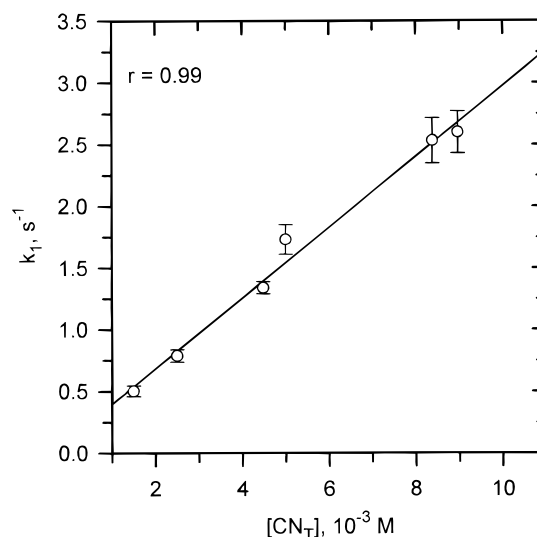


FIGURE 1. Values of  $k_1$  ( $\text{s}^{-1}$ ) vs  $[\text{CN}_T]$  at pH 9.0 and  $22^\circ\text{C}$ .

where

$$k_1 = k[\text{CN}_T]^n \quad (9)$$

Reactions were carried out by measuring the absorbance of Fe(VI) at  $510$  nm wavelength as a function of time. The reactions were followed for at least 2 half-lives. A successive integration model for the absorption of Fe(VI) as a function of time gave the best fit for an exponential value of 1, indicating that the reaction is first order with respect to Fe(VI). Various  $k_1$  values were determined at different concentrations of cyanide at pH 9.0 and  $22^\circ\text{C}$  (Figure 1). The linearity of the plot shows that reaction is first order with respect to  $[\text{CN}_T]$ . The half-lives in the studied cyanide concentrations ( $1.50$ – $8.96 \times 10^{-3}$  M) were found to be  $0.27$ – $1.38$  s at pH 9.0 and  $22^\circ\text{C}$ . The reactions were also monitored at  $600$  nm wavelength, pH 9.0, to detect any interference from the products of the reaction mixture. The similar rate constants at  $510$  and  $600$  nm suggest that the products of the reaction mixture do not cause any interference.

The effect of temperature on the reaction of Fe(VI) with cyanide was studied as a function of temperature,  $15$ – $30^\circ\text{C}$  at pH 9.0 (see Table 1). The plot of  $\log k$  vs  $1/T$  was linear ( $r^2 = 0.998$ ) and gave an activation energy of  $38.9 \pm 1.0$  kJ  $\text{mol}^{-1}$ . This activation energy contains terms due to the effect of temperature on the dissociation of  $\text{HFeO}_4^-$  and  $\text{HCN}$ . In comparison, the oxidation of aqueous cyanide by ozone did not show any temperature effect in  $26$ – $80^\circ\text{C}$  (27). In the next series of experiments, reaction rates were determined as a function of pH ( $8.0$ – $12.0$ ) at  $22^\circ\text{C}$ . Reaction rates were too fast to measure at pH lower than  $8.0$ . The rates were found to decrease nonlinearly with an increase in pH (Figure 2). The change in  $k$  as a function of pH can be described by considering the equilibria of Fe(VI) and cyanide.



The two forms of Fe(VI) can react with two forms of cyanide.

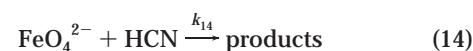
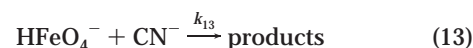
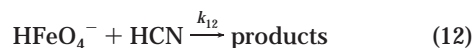
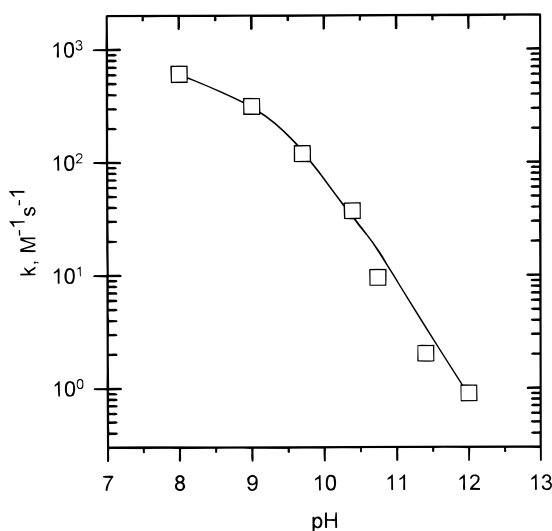


TABLE 1. Fe(VI) Oxidation of Cyanide and Nitrite at Different Values of pH and Temperature

| pH             | $k, \text{M}^{-1} \text{s}^{-1}$ |          |             |               |          |
|----------------|----------------------------------|----------|-------------|---------------|----------|
|                | 15 °C                            | 20 °C    | 22 °C       | 25 °C         | 30 °C    |
| <b>Cyanide</b> |                                  |          |             |               |          |
| 8.0            |                                  |          | 605 ± 60    |               |          |
| 9.0            | 214 ± 10                         | 275 ± 25 | 315 ± 22    | 376 ± 14      | 475 ± 39 |
| 9.7            |                                  |          | 120 ± 10    |               |          |
| 10.4           |                                  |          | 37.2 ± 2.7  |               |          |
| 10.7           |                                  |          | 9.51 ± 0.51 |               |          |
| 11.4           |                                  |          | 2.02 ± 0.25 |               |          |
| 12.0           |                                  |          | 0.90 ± 0.08 |               |          |
| <b>Cyanate</b> |                                  |          |             |               |          |
| 8.1            |                                  |          |             | 10.8 ± 0.5    |          |
| 8.4            |                                  |          |             | 11.0 ± 0.5    |          |
| 8.7            |                                  |          |             | 13.8 ± 0.8    |          |
| 9.0            |                                  |          |             | 11.0 ± 1.0    |          |
| 9.4            |                                  |          |             | 12.0 ± 0.8    |          |
| <b>Nitrite</b> |                                  |          |             |               |          |
| 8.1            |                                  |          |             | 11.5 ± 0.3    |          |
| 8.6            |                                  |          |             | 2.09 ± 0.10   |          |
| 9.2            |                                  |          |             | 0.42 ± 0.01   |          |
| 9.6            |                                  |          |             | 0.083 ± 0.016 |          |
| 9.9            |                                  |          |             | 0.058 ± 0.009 |          |

FIGURE 2. Values of rate constants ( $k, \text{M}^{-1} \text{s}^{-1}$ ) as a function of pH at 22 °C.

The rate of Fe(VI) disappearance as a function of pH can be written as

$$-d[\text{Fe(VI)}]/dt = k_{12}[\text{HFeO}_4^-][\text{HCN}] + k_{13}[\text{HFeO}_4^-][\text{CN}^-] + k_{14}[\text{FeO}_4^{2-}][\text{HCN}] + k_{15}[\text{FeO}_4^{2-}][\text{CN}^-] \quad (16)$$

By using the equilibrium values from eqs 10 and 11, the  $k$  can be written as

$$k = \alpha_1 \alpha_3 k_{12} + \alpha_1 \alpha_4 k_{13} + \alpha_2 \alpha_3 k_{14} + \alpha_2 \alpha_4 k_{15} \quad (17)$$

where  $\alpha_1 = [\text{H}^+]/([\text{H}^+] + K_{10})$ ;  $\alpha_2 = K_{10}/([\text{H}^+] + K_{10})$ ;  $\alpha_3 = [\text{H}^+]/([\text{H}^+] + K_{11})$ ;  $\alpha_4 = K_{11}/([\text{H}^+] + K_{11})$ . Initially, when eq 17 was solved, it was found that the data can be fitted by using eqs 12 and 14. The determined values for  $k_{12}$  and  $k_{14}$  were  $949 \pm 19$  and  $437 \pm 8 \text{M}^{-1} \text{s}^{-1}$ , respectively. Alternatively, we have also found that eqs 12 and 13 can also fit the data

and values of the rate constants,  $k_{12}$  and  $k_{13}$  were  $958 \pm 53$  and  $13661 \pm 692 \text{M}^{-1} \text{s}^{-1}$ , respectively. This is not surprising considering that products of  $\alpha_2 \alpha_3$  and  $\alpha_1 \alpha_4$  parallel each other as a function of pH. To distinguish the two set of values, the effect of ionic strength on the rates of cyanide oxidation by Fe(VI) was examined in NaCl solutions at pH 9.0 and 25 °C. The rate constants were found to be  $397 \pm 31$  and  $392 \pm 15 \text{M}^{-1} \text{s}^{-1}$  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 ( $376 \pm 14 \text{M}^{-1} \text{s}^{-1}$ ) and indicate that either the reaction is independent of ionic strength or that one of the reactive species has no charge (HCN). In addition, it is unlikely that ionized species ( $\text{HFeO}_4^-$ ) will react with ionized species ( $\text{CN}^-$ ) at a faster rate than with unionized species (HCN). This is supported by other studies (23, 36, 37) in which Fe(VI) reacts faster with protonated species than with unprotonated species. This further suggests the contribution of  $k_{14}$  rather than  $k_{13}$  in determining the rates of cyanide oxidation by Fe(VI). The fit (the solid line in Figure 2) through the experimental data represents the use of eqs 12 and 14.

**Removal and Product(s) Study.** The experiments on the removal of cyanide by Fe(VI) were conducted at pH 7.5, 9.0, and 12.0. Figure 3 shows the amount of cyanide consumed after reacting with a specific amount of Fe(VI). The cyanide concentrations in mixture were determined when no purple color of Fe(VI) was noticed. As the concentration of Fe(VI) increases, the consumed amount of cyanide increases. At pH 9.0, the amount of cyanide consumed was nearly equal to the amount of Fe(VI) added in the reaction mixture. A linear regression of initial data points was conducted at pH 9.0, and the ratio of cyanide consumed to Fe(VI) consumed was found to be  $1.06 \pm 0.12$ . At pH 7.5, higher amounts of Fe(VI) were required for complete removal of cyanide. The cyanide was not completely removed at pH 12.0 even with the addition of higher amounts of Fe(VI). In a separate experiment, it was found that the final product of Fe(VI) was Fe(III). The addition of potassium thiocyanate to the final reaction mixture gave a characteristic red ferric thiocyanate complex color.

The variation of Fe(VI) efficiency in removing cyanide at different pH values is related to the simultaneous reaction of Fe(VI) with water in the reaction mixture (eqs 3–6) (Table 2). At pH 7.5, reduction of Fe(VI) by water is lower but significant when cyanide is reacting with Fe(VI) in our

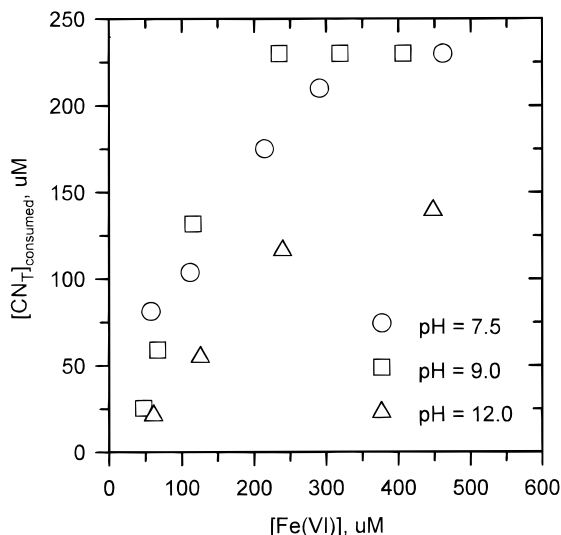


FIGURE 3. Plot of cyanide consumed vs [Fe(VI)] at different pH (initial cyanide: 250  $\mu$ M, pH 7.5; 232  $\mu$ M, pH 9.0; 250  $\mu$ M, pH 12.0).

TABLE 2. Pseudo-First-Order Rate Constants for Reactions of Fe(VI) with Water and Cyanide

| pH   | Fe(VI) + water <sup>a</sup> (s <sup>-1</sup> ) | Fe(VI) + cyanide <sup>a</sup> (s <sup>-1</sup> ) |
|------|--|--|
| 7.5  | $1.8 \times 10^{-2}$ (12)                      | $2.0 \times 10^{-1}$                             |
| 9.0  | $5.0 \times 10^{-5}$ (12)                      | $9.4 \times 10^{-2}$                             |
| 12.0 | $2.0 \times 10^{-3}$                           | $2.2 \times 10^{-4}$                             |

<sup>a</sup> The rate constants were estimated using [Fe(VI)] =  $250 \times 10^{-6}$  M.

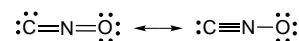
experimental conditions. Therefore, a higher amount of Fe(VI) needs to be used for complete removal of cyanide at pH 7.5. The rate constant for decomposition of Fe(VI) by water at pH 12.0 is faster than decomposition of cyanide by Fe(VI) in experimental conditions studied. This suggests an incomplete removal of cyanide by Fe(VI) at pH 12.0. At pH 9.0, Fe(VI) solution is the most stable and Fe(VI) reaction with cyanide is faster by approximately 3 orders of magnitude than its reaction with water (Table 2). Therefore, Fe(VI) has a maximum efficiency for removing cyanide at pH 9.0.

Figure 4 shows the formation of nitrite as one of the products in the oxidation of cyanide by Fe(VI) at different pH. At pH 7.5, the molar amount of nitrite formed was less than the molar amount of cyanide removed. The slope of the line between nitrite formation and cyanide removed is  $0.59 \pm 0.03$  and indicates that nitrite formation accounts for only ~60% of the cyanide removed. This suggests the formation of another product at this pH. We have found cyanate ( $\text{CNO}^-$ ) as the other product from oxidation of cyanide by Fe(VI) (see Figure 4). The sum of  $\text{NO}_2^-$  and  $\text{CNO}^-$  was found to be nearly equal to the cyanide consumed in the reaction mixture. Figure 4 also shows the amount of nitrite formed as the amount of cyanide reacted at pH 9 and 12. The slope of the resulting line was  $0.98 \pm 0.05$ , which indicates a 1:1 stoichiometric conversion of cyanide to nitrite ion. We have also investigated the fate of carbon in Fe(VI) oxidation of cyanide. The peak for carbon dioxide at  $2460 \text{ cm}^{-1}$  in the FTIR spectral study was observed, which indicates the formation of  $\text{CO}_2$  ( $\text{HCO}_3^-$ ) as the other final product of cyanide oxidation.

Considering the observed rate law and stoichiometry in our study, we propose a free radical mechanism (eqs 18–24). It is postulated that Fe(VI) reduces to Fe(V) by cyanide with the formation of cyanyl radical (eq 18). The formation of cyanyl radical has been observed by nitroso spin trap technique in the oxidation of cyanide by horseradish

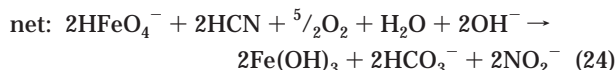
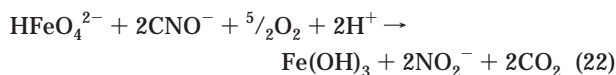
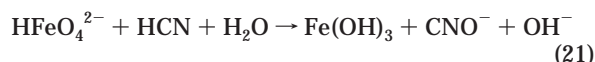
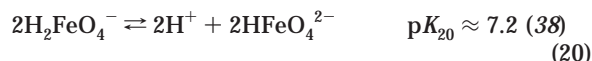
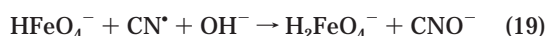
peroxidase/ $\text{H}_2\text{O}_2$  (29). The cyanyl radical further reacts with Fe(VI) to form Fe(V) and cyanate (eq 19). Cyanate was the product of cyanide oxidation at  $\text{TiO}_2$  and ZnO surfaces (30, 31). Titanium dioxide photocatalytic oxidation of cyanide resulted in cyanate that further oxidized to nitrate via nitrite (9, 32). The decomposition of cyanide ion from wastewater has been carried out by using different oxidizing agents, e.g., potassium peroxydisulfate, hydrogen peroxide, potassium chromate, and potassium permanganate (33). It was found that potassium permanganate was most effective at pH 10 and that cyanate formed during oxidation. The oxidation of cyanide by ozone also resulted in cyanate formation (2). A chain free radical mechanism was suggested for the kinetics of cyanide oxidation (2, 34).

Both cyanide and cyanate will further react with Fe(V), resulting in the observed reaction products (eqs 21 and 22). The reaction of Fe(V) with inorganic and organic compounds are 3–5 orders of magnitude faster than Fe(VI) (35–37). Fe(VI) was not considered to react with cyanate because of its slower reactivity (Table 1). Therefore, Fe(V) will react preferentially with cyanate (eq 22). The reaction involves the inherent oxygen in the reaction system, similar to proposed reaction of  $\text{OH}^\bullet$  radicals with cyanide (2). The C–N triple bond is weak in cyanate due to resonance



and donation of electron(s) from C to Fe(V) with  $\text{OH}^-$  attached to N would yield to  $\text{CO}_2$  and  $\text{NO}_2^-$ .

#### mechanism



In our results at pH 7.5, we have found cyanate as the product of the reaction in addition to nitrite and bicarbonate. The possible explanation is that Fe(V) may not be fully converting cyanate to nitrite (reaction 22) due to its simultaneous self-decomposition at this pH. In an alkaline medium, Fe(V) species decay by bimolecular reactions (with itself) that are strongly pH dependent. The rates are of the order of  $10^7 \text{ M}^{-1} \text{ s}^{-1}$  and increase with a decrease in pH (40).

The rate of disappearance of Fe(VI) in our experiments can be written by considering



The steady-state approximation of cyanyl radical would yield eq 26. Equation 26 is similar to the observed rate law for eq 16 where  $2k_{18} \sim k_{12} + k_{14}$ .



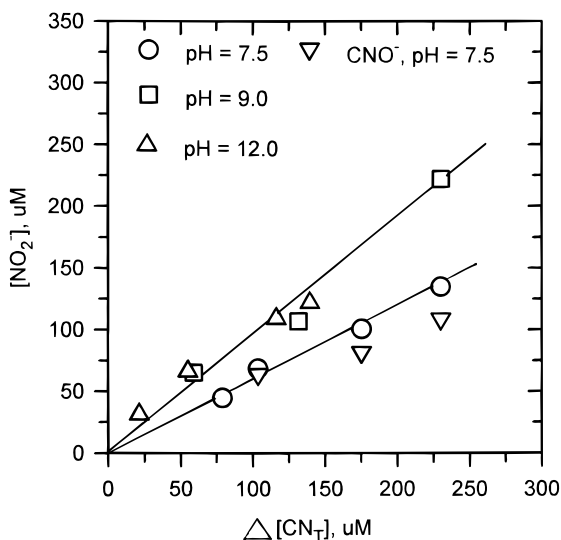


FIGURE 4. Plot of nitrite formation vs cyanide consumed at different pH ([Fe(VI)] = 48–508  $\mu$ M).

$$-d[\text{Fe(VI)}]/dt = 2k_{18}[\text{HFeO}_4^-][\text{HCN}] \quad (26)$$

We have also investigated the kinetics of nitrite oxidation by Fe(VI) at 25 °C. The rate constants at different pH are given in Table 1 and vary from  $1.15 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$  at pH 8.05 to  $5.8 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  at pH 9.9. These rate constants are in reasonable agreement with earlier reported values for the oxidation of nitrite by Fe(VI) (41). The rates for nitrite oxidation by Fe(VI) are approximately 2 orders of magnitude slower than cyanide oxidation rates. Nitrate byproduct was identified during oxidation of nitrite by Fe(VI), and the overall stoichiometry of the reaction has been suggested as (41)



**Rinsewater Study.** The experiments on the removal of free cyanide from rinsewater by Fe(VI) were conducted in diluted rinsewater. The samples were diluted by a factor of 4. The results are shown in Figure 5 and compared with removal experiments of Fe(VI) with cyanide in deionized water at pH 9.0 (control). Since the rinsewater had a similar pH and concentration as the control solution, it was expected that treatment with the same molar amount of Fe(VI) would remove all free cyanide in the rinsewater. However, after treatment with an equimolar amount of Fe(VI), the rinsewater still showed the presence of free cyanide. It was found that an excess of >2.5 times the molar amount of Fe(VI) was required to oxidize all the cyanide in the rinsewater. This is not surprising due to competing reactions between Fe(VI) with cyanide, complexed cyanide, and other organic and inorganic components present in rinsewater.

The Fe(VI) efficiency to remove total cyanide present in rinsewater sample containing 630  $\mu$ M total cyanide was also tested. It was found that when twice the molar amount of Fe(VI) to cyanide (based on the total amount) was added to the sample (pH 8.6), ~90% of the total cyanide was removed. When the rinsewater pH was adjusted to 9.1 and 9.8, it yielded ~90% total cyanide removal. Application of a secondary treatment of Fe(VI) had no effect in removing additional total cyanide. The cyanide complexation with metal may be the cause for inability of Fe(VI) in removing the last 10% of the cyanide. In comparison, it was found in cyanide oxidation by ozone that the rate of decomposition of complex cyanide varied with the stability of the complex. Cyanide complexes such as nickel, zinc, and copper were readily oxidized by

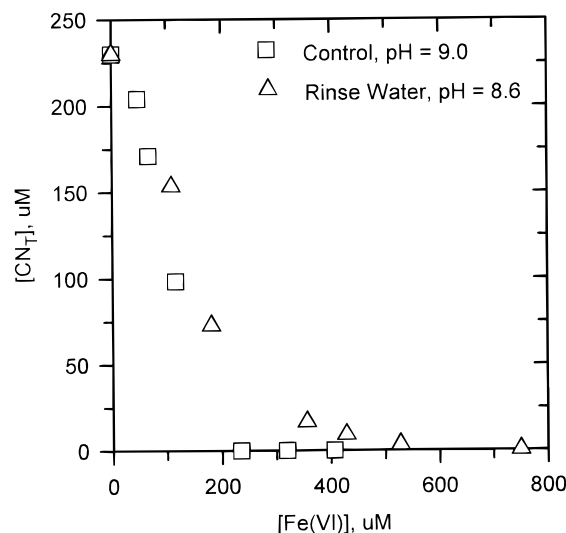


FIGURE 5. Removal of cyanide from rinsewater by Fe(VI).

ozone while cobalt cyanide, iron(II) cyanide, and iron(III) cyanide were resistant to ozonation (42, 43). Alkaline chlorination and ozone treatment are traditional methods for destruction of cyanide wastes.

Alkaline chlorination is a proven technology for cyanide destruction but it suffers from the use of gaseous chlorine and the formation of a toxic intermediate, cyanogen chloride (5). The ozone method requires the excess amount of ozone because of mass transfer limitation on the reaction rate (2, 44). In addition, ozonation involves high capital investment and operational costs associated with electric power (45). The other chemical oxidation methods, employing electrolysis, chlorine dioxide, Caro's acid, and hydrogen peroxide suffer from high chemical costs, incomplete treatment, and/or formation of undesirable residue (46–49). Fe(VI) appears to have a better potential to serve as a reliable and safe oxidative treatment for removing cyanide in wastewater effluent. The destruction of cyanide with Fe(VI) can be accomplished in minutes with the formation of simple byproducts  $\text{CO}_2$  ( $\text{HCO}_3^-$ ) and  $\text{NO}_2^-$  ( $\text{NO}_3^-$ ) that are less harmful to the environment. Moreover, Fe(VI) can easily be prepared and is a selective oxidant (12–14, 19). Fe(VI) can also be used as multipurpose wastewater treatment chemical for wastewater and drinking water disinfection, oxidation, purification, and coagulation.

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