Removal of Cyanide by Ferrate(VI) Ion

By

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The removal of cyanide by ferrate(VI) ion was investigated at $pH = 7.5$ and 9.0. Ferrate(VI) removal efficiency is greater at $pH = 9.0$ than at $pH = 7.5$. Nitrite ion as one of the products of a reaction was identified at $pH = 9.0$. The experiments indicated 1:1 stoichiometric conversion of cyanide to nitrite ion and ferrate(VI) molar consumption was nearly equal to that of oxidized cyanide. The reaction rates of ferrate(VI) with cyanide were determined in the pH range 8.0-9.7. The rates increase with a decrease in pH. Ferrate(VI) efficiency to remove cyanide was also tested in rinse water. The results suggest that ferrate(VI) is a promising oxidizer to destroy cyanide in rinse water.

The ultimate goal of the waste water treatment plant is to achieve a zero discharge level in its effluent. The term "zero discharge" is defined by the metal finishing industry as no measurable contaminants in the effluent waste water. and no environmental impact resulting from discharged waste water. Because federal and state regulatory agencies are tightening effluent restrictions. the attainment of the zero discharge level has become the new standard by which waste water treatment plants will be judged. Discharge limits are being lowered for parameters such as ion concentration. mass load limits. aquatic toxicity assessment criteria. and most importantly for pretreatment discharge requirements[1]. The most profound consequences of adopting a goal of "zero discharge" has been the steady growth in the technological race to find efficient and cost effective treatment methods for removing toxic and hazardous materials from waste water effluent.

Of the many toxic compounds found in the metal finishing industry. free cyanide and complexed cyanide waste waters present unique treatment problems[2]. Traditional methods found in industrial treatment plants. such as alkaline-chlorination. electrolytic decomposition. and ozonation present their own inherent problems and could fail to effect complaince with lower discharge limits[3,4]. New or improved methods such as electrodialysis. reverse osmosis. ion exchange. genetically engineered bacteria. and advanced oxidation processes are evolving to better meet the challenge posed by lower discharge limits[5-8]. One promising advanced oxidation process involves the use of iron in a +6 valence state to destroy residual cyanide in wastes.

Ferrate (VI)

Potassium ferrate (K_2FeO_4) is easily prepared in relatively pure form and is very stable and safe. X-ray diffraction studies of solid ferrate (VI) crystals revealed that the crystalline structure of the negative ion is tetrahedral[9]. It is believed that in an aqueous solution. ferrate(VI) is present as the FeO_4^{2-} ion. An extensive study of the decomposition rate of Fe(VI) over a wide pH range has identified two protonated forms[10]

$$H_2FeO_4 \leftrightarrow H^+ + HFeO_4^- \quad pK_1 = 3.5 \qquad (1)$$

$$HFeO_4^- \leftrightarrow H^+ + FeO_4^{2-} \quad pK_2 = 7.8 \qquad (2)$$

Ferrate(VI) ion is a powerful oxidizing agent throughout the entire pH range with a reduction potential varying from +2.2V to +0.7V in acidic and basic solution , respectively[11].

$$FeO^{2-} + 8H^+ + 3e^- \rightarrow Fe^{+3} + 4H_2O \quad E^0 = +2.20V \qquad (3)$$

$$FeO_4^{2-} + H_2O + 3e^- \rightarrow Fe(OH)_3 + 5OH^- \quad E^0 = +0.72 \qquad (4)$$

A large number of compounds have been oxidized with ferrate (VI). and it has been shown that ferrate(VI) is a strong but selective oxidizer.[10, 12]

Experimental Procedure

Potassium ferrate (K_2FeO_4) was synthesized according to the method of Thompson et al.[13]. The potassium ferrate salt had a purity of >95%. Potassium cyanide was obtained from Fluka Chemical. and was recrystallized before use.

All solutions were prepared from deionized water which had been processed by a Mill-Q Plus water purification system. Ferrate(VI) solutions were prepared by dissolving potassium ferrate crystals in a 0.001M borate buffer solution at pH 9.0. Potassium cyanide solutions were prepared in a .012M Na_2HPO_4 buffer solution, and the desired pH of the solutions was attained/adjusted by the addition of phosphoric acid. All solutions were filtered through 0.22 µm filters prior to use.

Stopped-flow experiments were carried out with a Rapid Kinetic Accessory (Applied Photophysics, UK), attached to a UV/Vis diode array spectrophotometer (Hewlett-Packard model 8452A). Kinetic runs were acquired and interpreted using OLIS Diode Array software (On-Line Instrument Systems Inc.) which had been interfaced with the diode array spectrophotometer.

Kinetic studies of the ferrate(VI) reactions with cyanide were carried out under pseudo-first order conditions. The concentration of cyanide was kept in excess and covered the range of 1.5 to 9.0 mM. Reactions were monitored at the maximum absorbance of ferrate(VI) at 510 nm. The experiments were conducted at 22-23°C. Rate constants were corrected for the spontaneous decay of Fe(VI) and represent averages of nine experimental runs per cyanide concentration.

Removal studies were done by mixing equal volumes, 10 mL, of each ferrate(VI) and cyanide solutions. The cyanide concentration in the reaction mixture was kept at 232 µM for each pH at which the studies were conducted (pH = 7.5, and 9.0) and ferrate(VI) concentrations were varied from 125 µM to 500 µM. Cyanide concentrations, before and after mixing, were determined by using a Waters high performance liquid chromatography (HPLC) system. A DEAE-5PW (75x7.5 mm) ion exchange column coupled to an electrochemical detector fitted with a silver electrode was used to quantitate cyanide. The eluent used was 50 mM LiOH/0.25 mM Na_2EDTA solution delivered at a flow rate of 2.0 mL/min. Products of the reaction mixtures were analyzed for nitrite and nitrate by using HPLC. An IC-Pak A HR (75x4.6 mm) ion exchange column coupled to a conductivity detector was used for detection of nitrite and nitrate. The anion analytical eluent was a borate/gluconate buffer solution at a pH of 8.5 and was delivered at a flow rate of 1.0 mL/min.

Results and Discussion

Cyanide Removal Studies

Ferrate(VI) efficiency in removing cyanide was studied at pH = 7.5 and 9.0. Figure 1 shows the amount of cyanide remaining after reacting with a specific amount of ferrate(VI). As the concentration of ferrate(VI) increases, the removal efficiency increases. At pH = 9.0, the amount of cyanide removal was nearly equal to the amount of ferrate(VI) added in the reaction mixture. The removal efficiency of ferrate(VI) is greater at pH = 9.0 than at pH = 7.5 (Figure 1). At pH = 7.5, the ferrate(VI) in solution reacts not only with cyanide, but also with itself and therefore, more ferrate(VI) is required to remove a given amount of cyanide.

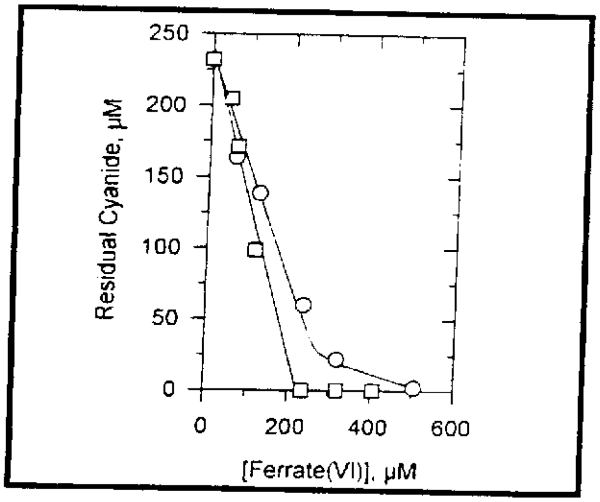

Fig. 1-Removal of cyanide by ferrate(VI) (□-pH = 9.0 ,○ - pH= 7.5).

Figure 2 shows the nitrite formation in reaction of cyanide with ferrate(VI) at pH = 9.0. Product

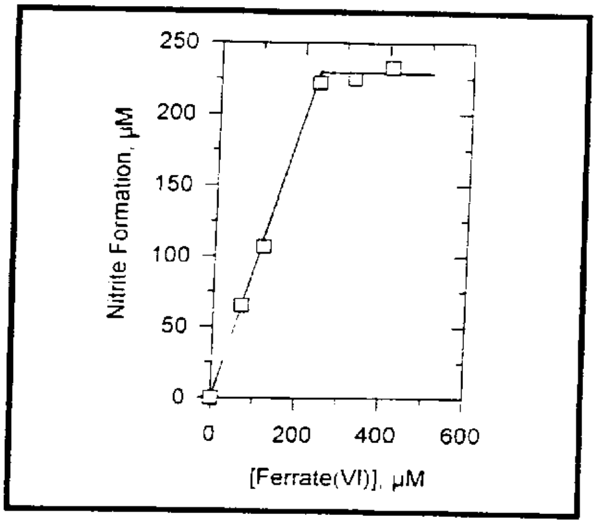

Fig. 2-Formation of nitrite in the reaction of cyanide with ferrate(VI) at pH 9.0

analysis did not reveal the presence of nitrate as a product of a reaction. It is interesting to note that the amount of cyanide removed is equal to the amount of nitrite formed (Figure 3).

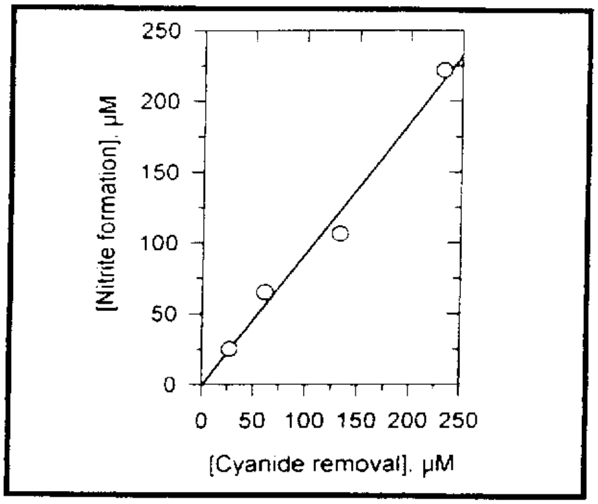

Fig. 3- Nitrite formation vs. cyanide removal at pH = 9.0

Kinetic Studies

Kinetic measurements were made to observe the proceed rate of oxidation of cyanide with ferrate(VI). Figure 4 shows a typical relationship between pseudo-first order rate constant (k_1) and cyanide concentration at pH = 9.0. The slope of the resultant line gives an overall rate constant (k) for the reaction of cyanide with ferrate(VI). Overall rate constants were also determined at pH = 8.0 and 9.7 and the values are given in Table 1. The oxidation rates are pH dependent and decrease with increasing pH. This pH dependence may reflect the speciation of both ferrate(VI) and cyanide species [14].

Table 1
Reactivity of Fe(VI) With Cyanide
At Various pH (22-23°C)

pH	**k, M^{-1} s^{-1}**
8.0	605 ± 60
9.0	315 ± 22
9.7	120 ± 10

Rinse Water Study

In this study, a sample was taken from a cadmium plating rinse tank. The rinse water had an initial concentration of 7342 μM cyanide. The sample was diluted with deionized water in order to test the cyanide removal efficiency of ferrate(VI) under commonly encoutered conditions. Equal volumes of ferrate(VI) solution at pH = 9.0 (559 μM) and diluted sample (551 μM cyanide) were mixed. The final pH of the mixture was 9.2. It was found that 70 % of the cyanide was removed and converted to nitrite. This lower efficiency is probably related to the reaction of ferrate(VI) with other rinse water components (e.g. metal-cyanide complexes). Future work will include ferrate(VI) experiments with metal cyanides which will more fully characterize the usefulness of ferrate(VI) in rinse water.

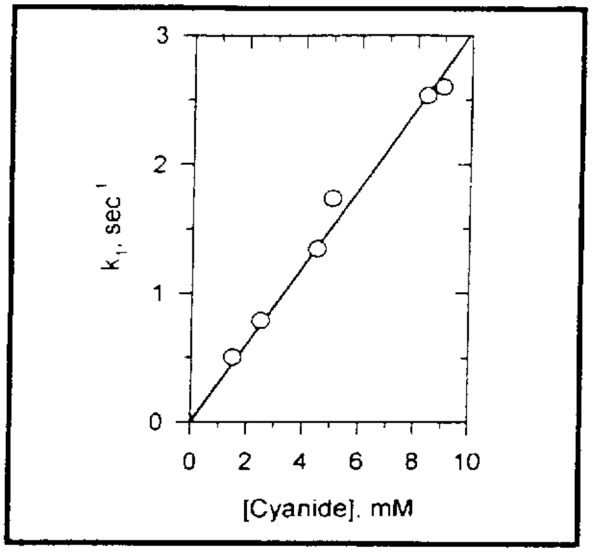

Fig. 4- Kinetics Studies of Ferrate(VI) oxidation of cyanide at pH = 9.0.

Summary and Conclusions

1. The efficiency of ferrate(VI) to remove cyanide was investigated at pH = 7.5 and 9.0. Product analysis of a reaction identified the nitrite ion as a product of a reaction. The results indicate that a lesser amount of ferrate(VI) is required to remove cyanide at pH = 9.0 than at pH = 7.5. The results also indicate that upon oxidation of each mole of cyanide at pH = 9.0, approximately 1 mole of ferrate(VI) is consumed, and while 1 mole of nitrite ion is formed as the reaction product.
2. The rates of ferrate(VI) reaction with cyanide were investigated in the pH range 8.0 - 9.7. According to the kinetic results obtained with a stopped-flow spectrophotometer, the rate decreases with increasing pH.

3. Ferrate(VI) removal efficiency was tested in rinse water at pH = 9.2. This experiment was promising, and ferrate(VI) appears to exhibit significant potential as an oxidizer for removal of cyanide from rinse water.

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