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FERRATE(VI) FOR WASTE WATER TREATMENT : OXIDATION OF CYANIDE IN AQUEOUS MEDIUM

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Abstract : The higher valence state of iron i.e., Fe(VI) was employed for the oxidation of one of an important toxic ion, cyanide in the aqueous medium. Cyanide was oxidized into cyanate, which is 1,000 times less toxic to cyanide and often accepted for its ultimate disposal. It was to be noted that Fe(VI) is a very powerful oxidizing agent and can oxidize most of the cyanide within few minutes i.e., *ca* 5 mins of contact. The data was obtained by the UV-Visible measurements for the Fe(VI) decomposition. The UV-Visible data was used to evaluate the overall rate constant for second order redox reaction between ferrate(VI) and cyanide. Also the pseudo first order rate constant was calculated as keeping the cyanide concentration in excess.

Key Words : Ferrate(VI), cyanide, wastewater, oxidation

INTRODUCTION

The increased level of industrialization/urbanization poses serious threat for the environment. The usual methods used for wastewater treatment is either, sometimes, ineffective or the chemicals used for the purpose releases several hazardous by-products which, ultimately become burden for the environment.[1-7)] Hence, with the changed scenario it always worth concerning to innovate or to modify the existing technologies for waste treatment by some alternative chemicals that can have good efficiency/selectivity and also possess more environmentally friendly. In this context the role of ferrate(VI), the higher oxidation state of iron showed very promising behavior as possess very high oxidative capacity (redox potentials of Fe(VI)/Fe(III) couple (E^0 (FeO_4^{2-}/Fe^{3+}) and E^0 ($FeO_4^{2-}/Fe(OH)_3$ are 2.20 and 0.72, respectively at pH 1 and 14) and the by-products obtained followed by the reduction of Fe(VI) i.e., Fe(III) are not harmful for human being or environment.[8)] Hence, the application of Fe(VI) in various waste water treatment strategies are likely to play a key role as a greener chemical for the next generation.

During last couple of decades much interest has been intended in the preparation and possible application of ferrate in waste treatment technologies. The reaction of ferrate(VI) with variety of organic/inorganic compounds were performed and the studies were focused to evaluate the kinetic parameters of possible reactions. Most of the reactions of Fe(VI) with a variety of compounds were reported to be first-order with respect to both reactants. The reported second order reaction rate constants of Fe(VI) ranged from about 10^{-2} to 10^{7} M^{-1} s^{-1}, however, it de-

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pends on several factors such as pH, initial Fe(VI) concentration, temperature and also the nature of reacting compounds. The degradation of phenol and chlorophenols by potassium ferrate was carried out and it was reported that within few minutes of contact (ca 5 mins) most of these organic compounds are degraded.[9-11] Fe (VI) was reported to oxidize amino acids in neutral to alkaline solutions.[12-14] The oxidation was strongly pH dependent. Reducing compounds such as ascorbic acid in large excess reduce Fe(VI) to Fe(III).[15] Further, the multifunctional use of ferrate was examined for the real wastewater treatment obtained from Sewage Treatments Works of Thames Water, UK. The results were compared with AS (aluminum sulfate) and FS (ferrous sulfate) and it was reported that ferrate (VI) can reduce 50% more color ($Vis_{400\text{-}abs}$), 30% more COD and kill 10% more bacteria from the wastewater.[16] In a line studies reveal that ferrate(VI) was fairly effective and efficient to kill *E.Coli,* total *coliforms* and *f2 Coliphage* viruses.[17-19] Chao[20] used potassium ferrate(VI) for wastewater treatment and reported that it replaces several chemicals utilized for odor control of sludge, mainly aggressive odors caused by ammonia and sulphides, through the formation of precipitates with iron compounds. Ferrate(VI) applied to sludge also has the double effect of transforming ammonia into nitrates, such that this product took the place of sulphates, acting as an electron acceptor, thus preventing the development of further odors when biosolids are utilized. In a line, we prepared the ferrate by modified method[9] and were further used for the cyanide oxidation in aqueous medium.

MATERIALS AND METHODS

Reagents and Materials

The chemicals used were of AR/GR grade. Potassium cyandide, Duksan Pure Chemical, Co.Ltd., Korea, sodium hypochlorite solution 12%, Junsei Chemical Co. Ltd., Japan, iron(III) nitrate enneahydrate, Kanto Chemical Co. Ltd. Inc. Japan, n-hexane, Matsunoem Chemicals Ltd., Japan, anhydrous ether and methanol, J. T. Baker, Mexico, potassium hydroxide, Junsei Chemical Co. Ltd., Japan, Whatman filter paper (GF/C), England and the PYREX Brand 36060® Fritted Funnel (10-15 μ), Cole-Palmer International, USA were used.

Preparation of Ferrate(VI)

The potassium ferrate(VI) was prepared by adopting partially the method described elsewhere.[9] In this method we have taken directly the sodium hypochlorite rather than preparing the potassium hypochlorite. 300 mL of chilled NaClO (12%) solution was taken in a beaker and 90 g of solid KOH was added slowly in this solution and the resulting suspension was cooled down *ca* 2℃. The precipitate formed was filtered with GF/C filter paper, as to obtain a clear yellow and highly alkaline NaClO solution. Again the solution was cooled and filtered by GF/C filter paper if any precipitate being formed. In this solution, 20 g of pulverized ferric nitrate was added slowly for more than 2 hrs with constant and vigorous stirring under cooling conditions (<8℃). Further, after complete addition of ferric nitrate, we stirred the solution for *ca* 30 mins. It is to noted that the cold and highly alkaline conditions favored for the oxidation of Fe(III) to Fe(VI). Also the time given with stirring may result for enhanced yield with even low concentration of NaClO used. The color of the solution readily changed to purple. Further, *ca* 50 g of solid KOH was added slowly as the temperature should not go beyond 15℃. The solution mixture was allowed to cool down as to stand it in the refriegerator for ca 40 mins. The resulting dark purple slurry was filtered with a glass filter (medium porosity 10~15 μ), after which the filtrate was discarded, and the precipitate was washed with cold 3M KOH solution (*ca* 100 mL (20x5)). The filtrate from the washings was collected and taken in a flask and added *ca* 150 g of KOH slowly under cooling conditions. The potassium ferrate was readily precipitated. Again filtered with the GF/C filter paper. The filtrate was discarded and the solid was washed with cold 3M KOH solutions (*ca* 50 mL) and the filtrate was collected in a beaker. Similar, reprecipitation was carried out at least for 3 times to remove any impurity if present. Finally, the solid was flushed with n-hexane (four times x 10 mL), dry methanol (two times x 5 mL) and diethyl ether (two times x 10 mL). The final product was collected carefully, almost black in color and stored in a vacuum desiccator. The obtained potassium ferrate(VI) was analyzed for its purity at pH 9.0 (0.001 mol/L Borate + 0.005 mol/L Na_2HPO_4) and at 510 nm using UV-Visible spectrophotometer (with the standard molar absorbance 1150 M^{-1} cm^{-1} at 510 nm and pH 9.0)[21)] and were found to be 98% plus purity.

Methodology

UV-Visible measurements

The UV-Visible Spectrophotometer, OPTIZEN 2120UV, Megasys Co. Ltd, Korea was used to find out the absorbance of the solutions. First we performed the experiments with blank i.e., taking the known concentration of Fe(VI) in phosphate buffer (pH 10) prepared by 0.005 M Na_2HPO_4 + 0.001 M Na_3PO_4 and observed the absorbance at different time intervals. Further, the similar experiments were done in presence of cyanide concentrations and observed the absorbance at different time intervals. The necessary self-decomposition correction for Fe(VI) was corrected with the blank.

Measurements with cyanide probe

To determine the cyanide concentration we used the cyanide probe (Orion Cyanide Electrode 9606, Ionplus annexed with Orion pH meter 720A, USA). The cyanide electrode was calibrated by using the standard cyanide solutions at pH~10 (phosphate buffer). The experimental cyanide solution with known initial concentration was taken in phosphate buffer pH 10 and the required concentration of Fe(VI) was added. Hence, The equilibrium bulk cyanide concentration was measured.

RESULTS AND DISCUSSION

Species in Aqueous Solutions

Several spectroscopic studies enabled that various protonated and deprotonated species of ferrate(VI) are present in solution and these species are prevalent at different solution pH, which basically depends on the acidic dissociation constant of that particular species. Figure 1 depicts the percentage speciation of these species with the function of pH. The speciation was calculated using the known pK_a's values i.e., pK_{a1} =1.6, pK_{a2} = 3.5 and pK_{a3} = 7.3,[22-24)] at Fe(VI) concentration 1.0 mmol/L. Figure 1 clearly indicate that $HFeO_4^-$ and FeO_4^{2-} are predominant in neutral and alkaline pH, in which Fe(VI) was known to be relatively stable towards its spontaneous decomposition to ferric ion (Fe(III)) [25)], we also observed in our studies. The figure also indicate that at pH~10 the only species i.e., FeO_4^{2-} exists in aqueous solutions.

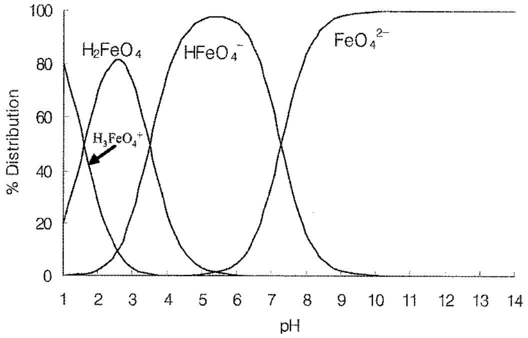

Figure 1. Speciation of ferrate(VI) species in aqueous solutions [Concentration of Fe(VI): 1 mmol/L].

Decomposition of Ferrate

The spontaneous decomposition of Fe(VI) was measured at 510 nm and at various pH values using the initial Fe(VI) concentration 1.0 mmol/L at room temperature. The results obtained are shown in Figure 2. It is clear that with decreasing the pH, the ferrate(VI) stability decreases rapidly. Also at pH 5, after *ca* 420 secs, the color of the solution becomes yellow due to the conversion of Fe(VI) into Fe(III). Hence, no more data were recorded after 420 sec at this pH.

It was assumed that the self-decomposition of Fe(VI) is to be proceeded with two primary reactions (i.e., eq., 1 and 2; the reaction of hydrogen Fe(VI) species is only represented).[26-27) In the first step, Fe(VI) combines with another Fe(VI) molecule producing the diferrate ($Fe_2O_7^{2-}$), a dimeric intermediate of Fe(VI). In the second step, the diferrate is reduced to ferric ion ($Fe_2(OH)_2(H_2O)_8^{4+}$) producing oxygen through water oxidation. Of these two steps, the forward reaction of first step was suggested as a rate-determining step. Hence, with keeping in view we determined the rate constant for second order rate law and values were shown graphically in Figure 3.

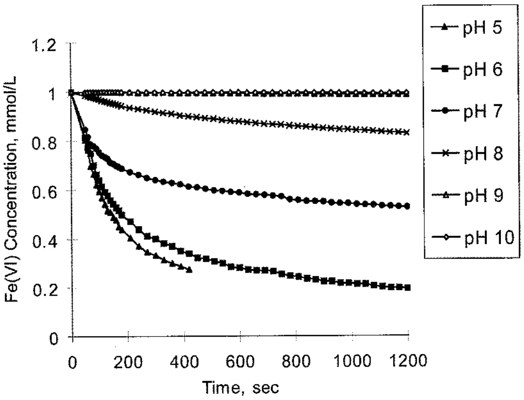

Figure 2. The change of Fe(VI) concentration as a function of time at various pH values [Initial concentration of Fe(VI): 1 mmol/L].

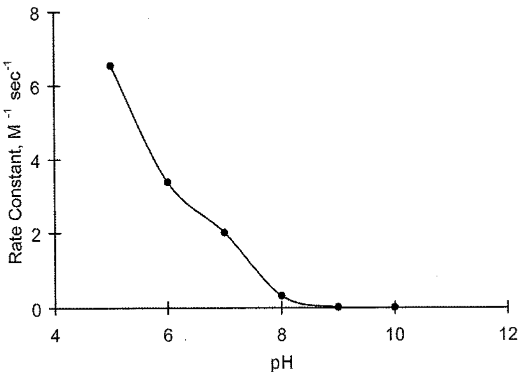

Figure 3. Second order rate constant for the reduction of Fe(VI) at various pH values [Initial concentration of Fe(VI) : 1.0 mmol/L].

Earlier, the Graham et al.,[9) reported the decomposition of ferrate(VI) is first order ($d[FeO_4^{2-}]/dt = k.\ [FeO_4^{2-}]$)and they calculated the rate constant values at various pH by first order rate law.

$$HFeO_4^- + HFeO_4^- \Leftrightarrow Fe_2O_7^{2-} + H_2O \qquad (1)$$

$$Fe_2O_7^{2-} + 6H^+ + 6H_2O$$
$$\rightarrow Fe_2(OH)_2(H_2O)_8^{4+} + 3/2O_2 \qquad (2)$$

Oxidation of Cyanide

UV-VIS measurements

The UV-Visible data were obtained for analyzing the oxidation of cyanide by Fe(VI) under oxygenated environment at different time intervals. The basic oxidation-reduction reaction involved may be represented below:

$$Fe(VI) + CN^- \rightarrow Fe(III) + CNO \qquad (3)$$

i.e., in presence of Fe(VI) the cyanide is supposed to reduced into cyanate which is 1,000 times less toxic and is often accepted for the end disposal.

The cyanide concentration varied from 0.3 to 15.0 mmol/L were taken in phosphate buffer pH 10 with the initial concentration of Fe(VI) 1.0 mmol/L and the absorbance data were recorded at different time intervals. The change in Fe(VI) concentration with time were shown graphically in Figure 4, which clearly showed

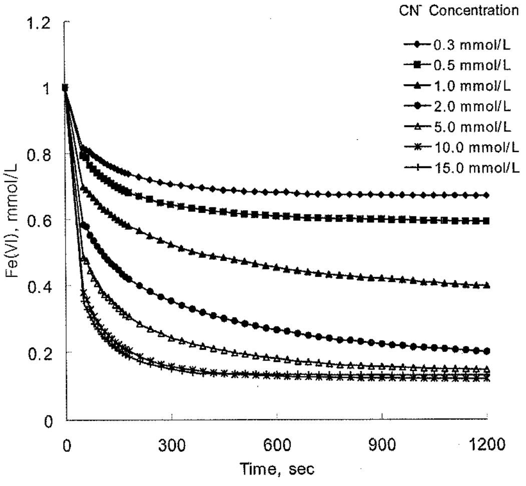

Figure 4. Variation of Fe(VI) concentration as a function of time at various cyanide concentrations.

that within few seconds of contact, a sharp decrease followed by slow decrease in Fe(VI) concentration was observed. Moreover, increase in cyanide concentration the bulk concentration of Fe(VI) decreased i.e., more and more Fe(VI) being consumed for the oxidation of cyanide. However, beyond the cyanide concentration 10.0 mmol/L the change in Fe(VI) concentration is apparently found to be constant. Hence, beyond this, we can assume as the cyanide is in excess.

The rate of the ferrate(VI) reduction in presence of cyanide may be given as:

$$-\frac{d[Fe(VI)]}{dt} = \underset{Self\ Decomposition}{k_1 \cdot [Fe(VI)] \cdot [Fe(VI)]} + \underset{Reaction\ with\ CN^-}{k_2 \cdot [Fe(VI)]^m \cdot [CN^-]^n} \qquad (4)$$

The rate constant k_1 is due to the spontaneous self-decomposition of Fe(VI) and the k_2 is due to the reaction with cyanide. As we already have seen that at pH 10 the rate of the self -decomposition of Fe(VI) was almost negligible in the order of 10^{-3} M sec^{-1}, and also we already made the required correction in absorbance with blank which was very low. Therefore, we can exclude this term.

$$-\frac{d[Fe(VI)]}{dt} = k_2 \cdot [Fe(VI)]^m \cdot [CN^-]^n \qquad (5)$$

Hence, k_2 may infers for overall rate constant for the redox reaction (5). But the results obtained by cyanide probe we can say 1:1 stoichiometry was observed for CN^- oxidation. Hence,

$$-\frac{d[Fe(VI)]}{dt} = k_2 \cdot [Fe(VI)] \cdot [CN^-]^n \qquad (6)$$

$$-\frac{d[Fe(VI)]}{dt} = k \cdot [Fe(VI)] \qquad (7)$$

$$k = k_2 \cdot [CN^-]^n \qquad (8)$$

The pseudo first order rate constant (k) for reaction (7) was obtained and reported in terms of the cyanide concentration in Table 1. It was observed that with the increase in cyanide concentration the rate constant values increases and attains almost a constant value for the cyanide concentration beyond 10 mmol/L. Hence, we assume it as the condition of excess cyanide. Hence, the pseudo first order rate constant may be taken as 6.801×10^{-3} sec^{-1}.

Table 1. Rate constant (k) for the reduction of Fe(VI) obtained for various cyanide concentrations [[Fe(VI)] = 1.0 mmol/L]

CN^- concentration, mmol/L	Rate Constant $\times 10^{-3}$, sec^{-1}
0.33	0.922
0.5	1.844
1.0	1.692
2.0	3.201
5.0	4.770
10.0	6.801
15.0	6.760

Further, the overall rate constant k_2 was optimized as by plotting the k vs cyanide concentration and a reasonable linear relationship was observed with the observed r^2 = 0.946 (cf Figure 5). Hence, this suggests that the 'n' would have the value of 1. The slope of the line could give the overall second order rate constant for the decomposition of Fe(VI) with cyanide and was found to be 0.573 M^{-1} sec^{-1}.

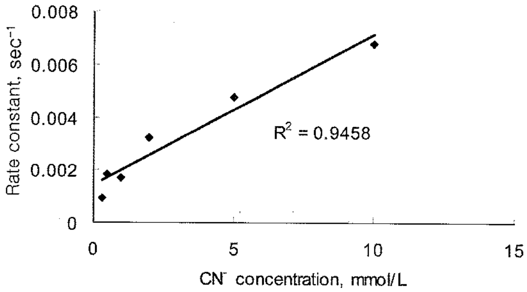

Figure 5. The variation of rate constant for the reduction of Fe(VI) as a function of cyanide concentration.

Cyanide probe measurements

Further the results were also obtained with using the cyanide probe. The various mole ratios of Fe(VI) to cyanide were taken in phosphate buffer at pH 10. The initial and final cyanide concentrations along with the percentage removal were given in Table 2. The results shown in table 2 may indicate for 1:1 stoichiometry as up to ca 1:1 stoichiometry the percent oxidation was almost 100% and beyond that it decreased. Hence, with certain approximations it could be applicable for the oxidation of cyanide with ferrate(VI).

Table 2. The results obtained for various Fe(VI) to cyanide ratios by using cyanide probe [Fe(VI): $1.0x10^{-3}$ mol/L]

Cyanide Concentration (mmol/L)	Ferrate to cyanide ratio			
	1:0.5	1:1.1	1:2.1	1:3.1
Initial	$0.480x10^{-3}$	$1.140x10^{-3}$	$2.073x10^{-3}$	$3.058x10^{-3}$
Final	$1.384x10^{-5*}$	$1.045x10^{-5}$	$1.819x10^{-4}$	$4.539x10^{-4}$
% Oxidation	98.74	99.08	91.22	85.15

* The final concentration achieved within only 50 secs of contact and further the cyanide concentration reaches below the probe detection limit ($8x10^{-6}$ mol/L)

CONCLUSIONS

The ferrate(VI) prepared by the modified wet synthetic process was applied for the oxidation of cyanide as an attempt for cleaner/greener wastewater treatment technologies. The Fe(VI) was found to be very effective for the oxidation of cyanide and it can oxidize the cyanide within few seconds of contact. The data obtained with the decrease in Fe(VI) concentration was employed to calculate the overall rate constant, was found to be 0.573 M^{-1} sec^{-1} and the pseudo first order rate constant $6.801x10^{-3}$ sec^{-1} at the initial concentration of Fe(VI) 1.0 mmol/L.

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