Application of ferrate(VI) in the treatment of industrial wastes containing metal-complexed cyanides: A green treatment

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Abstract

Ferrate(VI) was employed for the oxidation of cyanide (CN) and simultaneous removal of copper or nickel in the mixed/complexed systems of CN-Cu, CN-Ni, or CN-Cu-Ni. The degradation of CN (1.00 mmol/L) and removal of Cu (0.095 mmol/L) were investigated as a function of Fe(VI) doses from 0.3–2.00 mmol/L at pH 10.0. It was found that Fe(VI) could readily oxidize CN and the reduction of Fe(VI) into Fe(III) might serve as a function of Fe(VI) doses from 0.3–2.00 mmol/L at pH 10.0. It was found that Fe(VI) could readily oxidize CN and the reduction of Fe(VI) into Fe(III) might serve as a potential adsorbent, coagulant/foam floatation only can separate and transfer CN from one matrix to another. Various oxidants such as chlorine, hypochlorite, hydrogen peroxide, ozone and etc., are often used to degrade CN (Kitis et al., 2005).

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Introduction

Cyanide (CN) in any form, i.e., free cyanide, cyanide gas or metal-complexed cyanide, poses serious threat to the environment as well to the human being because of its acute and/or chronic toxicity (Boening and Chew, 1999; Deveci et al., 2006; Gijzen et al., 2000; Mudder and Botz, 2004; Pablo et al., 1997). The treatment processes involved for several industrial operations particularly in mining operations, electroplating processes, coal gasification, pharmaceutical attracted public and regulatory attention because they contain great amount of cyanide or associated compounds (Futkawa et al., 1994; Young, 2001; Zagury et al., 2004).

Various physical, chemical, catalytic, photocatalytic, electrolytic, ultrasonic and biological methods have been reported for the removal of cyanide or metal-complexed cyanide in aqueous solutions (Ackil and Mudder, 2003; Augugliaro et al., 1997; Botz, 2001; Mudder et al., 2001a, 2001b; Saterlay et al., 2000; Young and Jordan, 1995). The commonly used methods, such as ion-exchange, adsorption or foam floatation only can separate and transfer CN from one matrix to another. Various oxidants such as chlorine, hypochlorite, hydrogen peroxide, ozone and etc., are often used to degrade CN (Kitis et al., 2005).

However, these chemicals sometimes either ineffective or may release several hazardous byproducts which can affect environment adversely (Beller et al., 1974; Hagg and Hoigne, 1983; Joo et al., 2002; Reckhow et al., 1990; Stevens et al., 1989). For example, the oxidation of CN using HClO/chlorine often generates harmful intermediates along with the aromatic organic chlorides, which are unacceptable if discharged directly to the environment. Therefore, it becomes worth considering to employ certain chemicals that possess comparable cyanide degradation efficiency without generating harmful byproducts.

Ferrate(VI) shows promising behaviour towards the oxidation of several inorganic and organic impurities (Jiang, 2007; Jiang and Lloyd, 2002; Sharma, 2002, 2004; Tiwari et al., 2005) because of its relatively high oxidative capacity (redox potentials of Fe(VI)/Fe(III) couple (E⁰ (FeO₄²⁻/Fe³⁺) and E⁰ (FeO₄²⁻/Fe(OH)₃) are 2.20 and 0.72, respectively at pH 1 and 14). Moreover, the byproducts formed after the reduction of Fe(VI) to Fe(III), is not harmful towards human beings or the environment. Hence, Fe(VI) is to be termed as “green chemical”. In addition, the reduced Fe(III) exists as ferric hydroxide which can be served as a potential adsorbent, coagulant/foam floatation for metal removal (Jiang and Lloyd, 2002; Yngard et al., 2007). Therefore, the application of Fe(VI) in wastewater treatment plays a multifunctional role as not only...
can oxidize impurities in wastewater, but also can form Fe(III) and thus to remove the associated non-degradable impurities, i.e., heavy metals, through the adsorption or coagulation/flocculation process (Ynggard, 2007; Tiwari et al., 2007).

The multifunctional use of Fe(VI) was studied for the treatment of real wastewater obtained from the Sewage Treatments Works of Thames Water, UK and it was reported that Fe(VI) can reduce 50% more colour (Vis<sub>250-400</sub>), 30% more COD and kill 10% more bacteria comparing to aluminium sulphate and ferrous sulphate (Jiang and Panagoulopoulos, 2004). DeLuka et al. (1996) used potassium ferrate(VI) for wastewater treatment, and reported that it can replace several chemicals used for the odour control of sludge, mainly aggressive odours caused by ammonia and sulphides, through the formation of precipitates with iron compounds. The Fe(VI) oxidation process significantly improves the biodegradability of alachlor, an acetanilide herbicide, contained in wastewater (Zhu et al., 2006). It was also reported that Fe(VI) oxidize various synthetic organic compounds viz., benzene, chlorobenzene, allylbenezene, phenol, etc. (Waite and Gilbert, 1978; Bielski et al., 1994). Recently, the composite Fe(VI) with enhanced stability is used for the degradation of active Brilliant Red X-3B in aqueous solutions (Xu et al., 2009).

Ferrate(VI) was fairly effective in killing Escherichia coli, total coliforms and β2 coliphage viruses (Kazma, 1995; Murmann and Robinson, 1974; Schink and Waite, 1980). Cho et al. (2006) reported the novel behaviour of Fe(VI) as a disinfectant. They quantitatively evaluated, modelled the inactivation of E. coli, and reported that the kinetics of E. coli inactivation fitted the Modified Delayed Chick-Watson model well.

Moreover, Fe(VI) was applied for the degradation of the inorganic pollutants viz., ammonia, hydroxylamines, hydrogen sulphide and cyanide (Johnson and Hornstein, 2003; Sharma et al., 1997a, 1997b, 1998a; Tiwari et al., 2007). Extensive study has been carried out for the degradation of CN using Fe(VI) in their single system (Castarramone et al., 2004; Sharma et al., 1997a, 1998a, 1998b; Tiwari et al., 2007). However, the industrial effluents usually contain CN in its complexed form metal-complexed cyanide. For example the electroplating industry effluent contains copper or nickel complexed cyanide. The degradation of such complexed cyanide and simultaneous removal of metal cations from the effluent waters is a concern for environmental engineers. A few studies have been conducted for such mixed systems, the treatment of metal-complexed cyanide using Fe(VI). Zinc-cyanide complex was treated with Fe(VI) in an attempt to deal the gold mining effluent (Ynggard et al., 2007). Cu(I)-cyanide was treated with Fe(VI) and Fe(V) (Sharma et al., 2005). Ynggard et al. (2008) attempted the oxidation of weak-acid dissociable cyanides, Cd(CN)₄²⁻ and Ni(CN)₆³⁻, with ferrate. The kinetics of the dissociation of these weak acid dissociable cyanides was discussed with pH range 9.1–10.5 and temperature 15–45°C. It is suggested that Fe(VI) is effective in removing cyanide in coke oven plant effluent, where organics are also present. The decolplexation of Cu(II)-EDTA was discussed using the Fe(VI) treatment (Tiwari et al., 2008). With an increased interest and a requirement of clean and environment friendly treatment processes, the present investigation deals for the oxidation of cyanide and simultaneous removal of copper or nickel in the mixed systems of cyanide and copper or nickel from aqueous waste solutions.

1 Materials and methods

1.1 Chemicals

Copper sulphate (CuSO₄·5H₂O), and potassium cyanide, guaranteed reagent (GR) were obtained from the Duksan Pure Chem., Co., Ltd., Korea. Nickel nitrate (Ni(NO₃)₂·6H₂O) was obtained from Wako Pure Chem., Japan.

Potassium ferrate was prepared indigenously in the laboratory adopting the reported method (Tiwari et al., 2007) and the purity of the compound was checked using the method described by Lee et al. (2004). The purity of the product was > 98%.

1.2 UV-Visible measurements

The UV-Visible Spectrophotometer, Optizen 2120UV (Mecasys Co., Ltd., Korea) was used to obtain the absorbance data in aqueous solutions, and the purity of the synthesized Fe(VI).

1.3 Measurements with cyanide probe

In order to determine the cyanide concentration, a cyanide probe (Orion Cyanide Electrode 9606, Ionplus annexed with Orion pH meter 720A, USA) was used. The cyanide electrode was calibrated using the standard cyanide solutions at pH 10.0 (already mentioned with the manufacturer of the cyanide probe). Further, the calibrated cyanide probe was used for direct cyanide determination. In case of Cu-CN or Ni-CN system, the cyanide concentration was obtained by the standard EDTA method i.e., first to decomplex the Cu-CN or Ni-CN complex by EDTA at pH 4.0 (adjusted by adding glacial acetic acid and kept the solution at 50°C for 5 min), then raised the solution pH to 13.0 (by adding NaOH). At this pH, free cyanide concentration was obtained using the previously calibrated cyanide probe. In the mixed systems, duplicate samples were prepared for cyanide and copper or nickel determination, respectively. Blank solutions were used either for the cyanide or for the copper or nickel at the specified pH and results were compared accordingly.

The Fe(VI) treated samples were filtered using 0.45 μm syringe filters and then subjected for the determination of copper or nickel concentrations using AAS (Varian Spectra AA-300, USA).

2 Results and discussion

2.1 Cyanide-copper system

2.1.1 Oxidation of cyanide and removal of copper

Our previous study as well as the other reports revealed...
that Fe(VI) is a potential oxidizing reagent for the oxidation of CN (Castarramone et al., 2004; Sharma et al., 1997a; Sharma et al., 2008; Tiwari et al., 2007). Fe(VI) readily oxidized cyanide into cyanate, which is 1000 times less toxic than cyanide, and often being accepted for end disposal.

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\text{Fe(VI)} + \text{CN}^- \rightarrow \text{Fe(III)} + \text{CNO}^-
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In CN-Cu system, the batch experiments were performed to determine the degradation of CN (1.00 mmol/L) and the simultaneous removal of Cu (0.094 mmol/L) in phosphate buffer and NaOH media (both at pH 10.0), with various doses of Fe(VI) (0–2.0 mmol/L). To obtain the alternative of phosphate buffer at high pH, experiments were performed to assess the stability and suitability and the optimum dose of Fe(VI) in two different media.

As shown in Fig. 1, increasing Fe(VI) dosage from 0 to 2.0 mmol/L, significantly enhanced the degradation of CN with decreasing concentration from 1.00 to 0.002 mmol/L. Because the most of the cyanide was being degraded at Fe(VI) dosage 1.0 mmol/L (the final cyanide concentration was 0.03 mmol/L), it was concluded that a 1:1 stoichiometry persist at least for the degradation of cyanide. Similar observation also reported by Sharma et al. (1998b) for the oxidation of CN using Fe(VI). Moreover, it has been also noted that the oxidation of CN was unaffected by medium. Hence, further studies were performed in NaOH medium with an excess of Fe(VI) dose (2.00 mmol/L). On the other hand the removal of Cu which primarily occurs through the coagulation/precipitation which showed only a partial removal at pH 10.0. The NaOH and phosphate buffer media (pH 10.0) caused respectively 31.5% and 21.5% of Cu removal from the Fe(VI) treated samples. These results indicated that copper ions are more stabilized in phosphate buffer than that in NaOH medium, hence, higher removal of copper achieved in the NaOH medium. Further, it was noted that for the same Fe(VI) treated samples, if we raise the solution pH from 10.0 to 13.0 followed by filtering with a 0.45-µm syringe filter and then subjected for the total copper analysis, fairly a good efficiency was achieved as very low concentration of copper remained in the bulk solution i.e., 0.002 mmol/L. Hence, it may be concluded that Fe(VI) first leads to decomplex the metal cyanide complex, followed by the degradation of free cyanide in solution, and at the same time the free copper ions likely to be coagulated/precipitated with Fe(III) as present in the form of Fe(OH)₃. High solution pH will enhance the coagulation/precipitation of free copper ions (Larson and Pugh, 1998). Hence, at pH 13.0 almost 100% copper removal is achieved (Fig. 2).

Similar degradation of cyanide and weakly complexed metal cyanides (i.e., nickel, copper, cadmium and zinc cyanides) was reported by hydrogen peroxide, forming one or more less toxic compounds viz., cyanate. Further, in the presence of excess nitrite and carbonate these cyanates are eventually transformed into nitrate (Mudder et al., 2001a; Monteagudo et al., 2004).

2.1.2 Effect of copper concentration

Study was further extended for various concentrations of Cu (0.094–0.315 mmol/L) at CN 1.00 mmol/L and Fe(VI) 2.0 mmol/L. Solution pH was maintained at 10.0 with NaOH when Fe(VI) treatment was performed (Fig. 3a). After Fe(VI) treatment, solution pH was raised to 13.0 by adding NaOH solution in an attempt to enhance the coagulation/flocculation of Cu (Fig. 3b). The results clearly showed that with increasing copper concentration up to 0.315 mmol/L, the degradation of CN was almost unaffected (99.71%–99.89%) and the removal of Cu was in the range of 95%–99%.

2.1.3 Effect of pH

pH dependence data (pH 10.0, 12.0 and 13.0) were obtained for the degradation of CN (1.00 mmol/L) and removal of Cu (0.094 mmol/L) at Fe(VI) dose 2.00 mmol/L. The Fe(VI) treated samples at different pH values were filtered separately and subjected to analyze the bulk CN and Cu concentrations. The percentage of CN and Cu removal as a function of pH is presented graphically in Fig. 4. It is noted that the degradation of CN was almost unaffected (> 99%) by increasing pH from 10.0–13.0. However, Cu removal was affected greatly. Its removal efficiency was enhanced by increasing solution pH and more than 99% Cu was removed at pH 13.0. This may
be explicable on the basis that at high pH copper ions could significantly coagulated/precipitated in the presence of ferric hydroxide. These results are in accordance with the previous observations described in Section 2.1.1.

### 2.2 Cyanide-nickel system

Study is also conducted for the CN-Ni system. The degradation of CN and simultaneous Ni removal have been assessed as a function of pH in CN (1.00 mmol/L) and Ni (0.170 mmol/L) mixed system at the Fe(VI) dosage of 2.0 mmol/L. Results are shown in Fig. 5. It is noted that with increasing solution pH from 10.0 to 12.0, the degradation of CN decreases from 64.2% to 51.0%, and the removal percentage of Ni decreases from 15.2% to 1.0%. These results suggested that Fe(VI) can degrade partially Ni-CN complex. Therefore, only a partial Ni removal occurs through the coagulation/precipitation process. This may perhaps be ascribed because of the relatively less reactivity of Fe(VI) at higher pH since it possessed less redox potential at higher pH (Lee et al., 2004; Tiwari et al., 2005).

### 2.3 Cyanide-copper-nickel system

Finally, a simulated experiments are planned to treat the industrial wastewater containing CN, Cu and Ni with Fe(VI). The mixture of 1.00 mmol/L CN, 0.100 mmol/L Cu and 0.170 mmol/L Ni was prepared at pH 10.0 and treated with 2.0 mmol/L Fe(VI). The sample was then analyzed for CN using the CN probe following the standard EDTA method. In parallel, the pH of Fe(VI) treated sample was adjusted to 13.0 and then filtered with a 0.45-µm syringe filter. The samples then were subjected for Cu and Ni determination. As shown in Fig. 6, 91.23% of CN was degraded and 98.96% of Cu was removed after the treatment, whereas Ni was removed partly as 36.31%. It inferred that the method is useful for the treatment of waste/effluent waters containing CN, Cu and Ni. These findings are in accordance with our previous results obtained from the treatment of actual effluent waters containing CN, Cu and Ni (Electroplating Industry Waste) (Tiwari et al., 2007).

### 3 Conclusions

Ferrate(VI) was used for the treatment of mixed systems of CN-Cu, CN-Ni and CN-Cu-Ni in an attempt to deal the metal-complexed cyanide wastes. For CN-Cu and CN-Ni system, a rapid and efficient oxidation of CN occurred at pH 10.0 in these mixed systems; almost complete copper removal was achieved relatively at pH 13.0; on the other hand, Ni was only removed partly at pH 10.0, and further decreased when pH increase to 13.0. The similar results were also observed in the system of CN-Cu-Ni, where
a substantive degradation of CN and Cu was achieved treating with Fe(VI), and Ni was removed partly.

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References


