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Ferrate(VI) and ferrate(V) oxidation of cyanide, thiocyanate, and copper(I) cyanide

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Abstract

Cyanide (CN^-), thiocyanate (SCN^-), and copper(I) cyanide ($Cu(CN)_4^{3-}$) are common constituents in the wastes of many industrial processes such as metal finishing and gold mining, and their treatment is required before the safe discharge of effluent. The oxidation of CN^-, SCN^-, and $Cu(CN)_4^{3-}$ by ferrate(VI) ($Fe^{VI}O_4^{2-}$; Fe(VI)) and ferrate(V) ($Fe^{V}O_4^{3-}$; Fe(V)) has been studied using stopped-flow and premix pulse radiolysis techniques. The rate laws for the oxidation of cyanides were found to be first-order with respect to each reactant. The second-order rate constants decreased with increasing pH because the deprotonated species, FeO_4^{2-}, is less reactive than the protonated Fe(VI) species, $HFeO_4^-$. Cyanides react 10^3–10^5 times faster with Fe(V) than with Fe(VI). The Fe(V) reaction with CN^- proceeds by sequential one-electron reductions from Fe(V) to Fe(IV) to Fe(III). However, a two-electron transfer process from Fe(V) to Fe(III) occurs in the reaction of Fe(V) with SCN^- and $Cu(CN)_4^{3-}$. The toxic CN^- species of cyanide wastes is converted into relatively non-toxic cyanate (NCO^-). Results indicate that Fe(VI) is highly efficient in removing cyanides from electroplating rinse water and gold mill effluent.

Keywords: Ferrate(VI); Ferrate(V); Premix pulse radiolysis; Cyanides; Oxidation; Removal

1. Introduction

Cyanide is used or produced in several types of industries that include gas production, metal plating, pharmaceutical, and mining (Young, 2001; Zagury et al., 2004). Speciation of cyanide determines its degree of toxicity, where cyanide exists as free cyanide (HCN, CN^-) and metal-complex species. Metal-complex cyanides are classified as weak-acid dissociables (WADs) and strong-acid dissociables (SADs). WADs are relatively unstable complexes of cyanide with transition metals such as Cd, Cu, Ni, and Zn that dissociate under neutral or mildly acidic conditions. SADs form strong complexes with metals such as Fe, Co, Ag, and Au that are dissociable only under very acidic conditions. Thiocyanate (SCN^-) is considered in its own category although it is a WAD. The free cyanide form is the most toxic form. WADs are less toxic than free cyanide while SADs are relatively non-toxic (Wild et al., 1994; Shirfin et al., 1996).

Various treatment procedures such as physical, adsorption, complexation, and oxidation are known for treating cyanides (Rowley and Otto, 1980; Gurol and Holden, 1988; Beattie and Polyblanc, 1995; Pak and Chang, 1997; Young, 2001; Zagury et al., 2004). The methods other than oxidation give highly concentrated products in which toxic cyanides still exist. Chlorine, hypochlorite, hydrogen peroxide, ozone, sulfur dioxide, and ammonium bisulfite are common oxidants for cyanide destruction. Alkaline chlorination, although adequate, has many disadvantages such as high chemical cost, formation of cyanogens, chloride contamination and incomplete decomposition of some metal cyanide complexes (Young, 2001). Hydrogen peroxide is successful in oxidizing cyanides but it is not effective for SCN^-. Ozone has been studied extensively for the destruction of cyanide (Rowley and Otto, 1980; Gurol and Holden, 1988). The pH of the cyanide solution must be above pH 11 to avoid the formation of hydrocyanic gas.

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However, ozonation becomes less efficient at pH higher than 11 because ozone is decomposed by hydroxide ion. Both sulfur dioxide and bisulfite have been applied to treat cyanide. These procedures are most efficient at pH 9 and lime is added for pH control of the reactions, but this produces gypsum, generating sludge.

Alternate methods, addressing environmental considerations, are needed for the remediation of cyanides in wastewater (Young, 2001). Ferrate(VI) ($Fe^{VI}O_4^{2-}$; Fe(VI)) is a suitable candidate as a new chemical oxidant for the treatment of cyanides. Ferrate(VI) is a strong oxidizing agent, which can be seen from the reduction potentials of reactions (1) and (2) in acidic and alkaline solutions, respectively (Wood, 1958).

$$FeO_4{}^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O \quad E^\circ = +2.20\,V \tag{1}$$

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

The spontaneous reduction of ferrate(VI) in water forms non-toxic by-products, molecular oxygen and iron(III) (Eq. (3)) (Sharma, 2002a), suggesting that ferrate(VI) is an environment-friendly oxidant.

$$2FeO_4{}^{2-} + 5H_2O \rightarrow 2Fe(OH)_3 + \tfrac{3}{2}O_2 + 4OH^- \tag{3}$$

Ferric(III) hydroxide, produced from ferrate(VI), acts as a coagulant for the removal of metals, non-metals, radionuclides, and organics (Potts and Churchwell, 1994; Sharma, 2002a). Ferrate(VI) has been proposed as an alternative to chlorine for the disinfection of water and wastewater since it is also very effective in inactivating bacteria and viruses (Sharma, 2002a, 2007b; Sharma et al., 2005a).

Ferrate(VI) can oxidize a large number of inorganic and organic pollutants in the aquatic environment. Studies have shown that oxidation of nitrogen- and sulfur-containing pollutants by ferrate(VI) can be accomplished in seconds to minutes with the formation of less harmful products (Sharma, 2002a, 2004). Ferrate(VI) also has the potential to oxidize emerging contaminants such as pharmaceuticals, hormones, and endocrine disrupting compounds (Sharma et al., 2006; Sharma, 2007a). Studies of ferrate(VI) remediation of cyanides are presented below, followed by a discussion of the ferrate-cyanide reaction stoichiometries and mechanisms involving both ferrate(VI) and ferrate(V).

2. Cyanide removal

The gold mining and metal finishing industries are among the largest consumers of cyanide due to the high affinity of gold for cyanide. Cyanide is used in more than 85% of the gold mine operations for the extraction of gold from ores, after which the cyanides are released into the environment as effluents and as solid mine tailing. Each year, more than 1 billion tons of gold ore are leached with cyanide. There is an increasing risk to the environment from spills such as those at Baia Mare (Romania), Kumtor (Kyrgyzstan), Omai (Guyana), and Summitville (Colorado) (Boening and Chew, 1999; Beebe, 2001). Effective treatment of effluents must take place in order to achieve a zero discharge level of undesirable contaminants. The metal finishing industry defines the term zero discharge as no measurable cyanide in effluent wastewater and no environmental impact resulting from the discharged wastewater. According to the US EPA, the Drinking Water Quality Standard total cyanide is 0.2 ppm. Comparatively, the Aquatic-Biota Water Standard is 0.05 ppm.

Experiments on the removal of free cyanide from Corpus Christi Army depot rinse water by Fe(VI) were conducted in diluted rinse water (Sharma et al., 1998). The results are shown in Fig. 1A and are compared with cyanide removal by Fe(VI) in deionized water at pH 9.0 (the control). It was found that an excess of 2.5 times the molar amount of

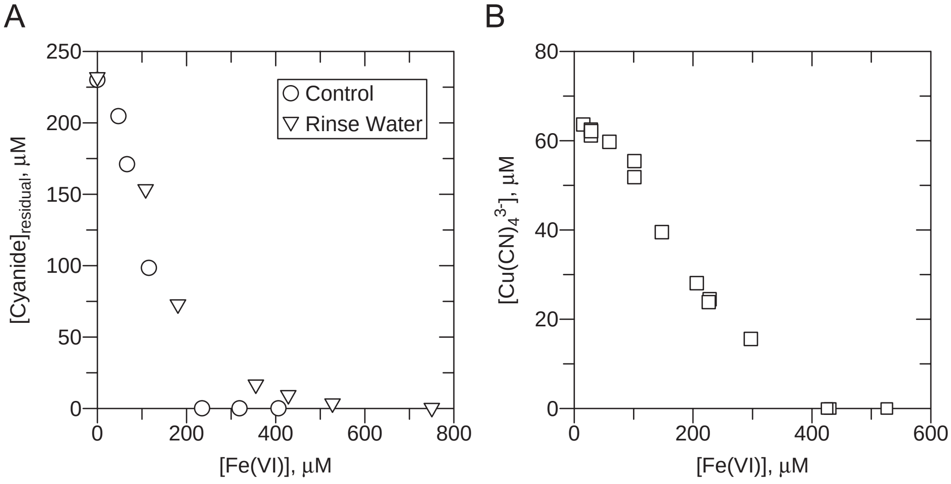

Fig. 1. Removal of cyanide from rinse water, pH 8.6 (A) and gold mine wastewater, pH 9.0 (B). The rinse water was collected from a metal electroplating facility, which usually contains cadmium, copper, iron, and silver in the concentration range varying from 20 to 200 × 10^{-6} M. The control was cyanide in deionized water at pH 9.0 (Sharma et al., 1998). A synthetic gold mine wastewater sample was prepared by adding salts of KSCN, KCN, and $K_3Cu(CN)_4$ to filtered water and adjusting the pH of the sample to 9.1 (Sharma et al., 2005b).