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Ferrate(VI) oxidation of zinc–cyanide complex

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Abstract

Zinc–cyanide complexes are found in gold mining effluents and in metal finishing rinse water. The effect of Zn(II) on the oxidation of cyanide by ferrate(VI) ($Fe^{VI}O_4^{2-}$, Fe(VI)) was thus investigated by studying the kinetics of the reaction of Fe(VI) with cyanide present in a potassium salt of a zinc cyanide complex ($K_2Zn(CN)_4$) and in a mixture of Zn(II) and cyanide solutions as a function of pH (9.0–11.0). The rate-law for the oxidation of $Zn(CN)_4^{2-}$ by Fe(VI) was found to be $-d[Fe(VI)]/dt = k[Fe(VI)][Zn(CN)_4^{2-}]^{0.5}$. The rate constant, k, decreased with an increase in pH. The effect of temperature (15–45 °C) on the oxidation was studied at pH 9.0, which gave an activation energy of 45.7 ± 1.5 kJ mol^{-1}. The cyanide oxidation rate decreased in the presence of the Zn(II) ions. However, Zn(II) ions had no effect on the cyanide removal efficiency by Fe(VI) and the stoichiometry of Fe(VI) to cyanide was approximately 1:1; similar to the stoichiometry in absence of Zn(II) ions. The destruction of cyanide by Fe(VI) resulted in cyanate. The experiments on removal of cyanide from rinse water using Fe(VI) demonstrated complete conversion of cyanide to cyanate.

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1. Introduction

Cyanide was introduced commercially over a century ago and since then it has been used or produced in several types of industry that include metal plating, gold mining, gas production, and pharmaceutical (Young, 2001; Mudder and Botz, 2004; Zagury et al., 2004). Approximately 1.1 million tons of hydrogen cyanide are annually produced worldwide (Mudder and Botz, 2004). Manmade and natural sources are origins of cyanide and several forms of cyanide are present in the aquatic environment (Young, 2001). Cyanide is capable of forming a complex with almost any metal and resulting metal complexes are classified according to the strength of the metal–cyanide bond through the pH at which dissociation happens:

$$M(CN)_x^{y-x} + xH^+ \Longleftrightarrow xHCN(g) + M^{y+} \tag{1}$$

Weak-acid dissociables (WADs) and strong-acid dissociables (SADs) equilibrate with HCN at pH near 4 and 0, respectively. Metal–cyanide complexes of Zn, Cd, and Cu are examples of WADs while complexes of Fe, Co, Ag, and Au are examples of SADs. Speciation of cyanide determines its degree of toxicity.

Some of the environmental risks of cyanide are related to its release from metal mining and finishing facilities. In recent years, a dam failure in Romania produced cyanide and heavy-metal contamination in River Szamos and Tisza, which caused a large-scale fish mortality and effected microscopic and invertebrate organisms (Lakatos et al., 2003). In the gold recovery process in mining, concentrated cyanide solution is added to the ore to give gold cyanide solutions to which zinc is added to extract gold (Eq. (2)).

$$2Au(CN)_2^- + Zn^0 \Longleftrightarrow 2Au^0 + Zn(CN)_4^{2-} \tag{2}$$

Interestingly, a gold SAD-complex is converted into a zinc WAD-complex, thus making the effluent easier to treat. Zinc–cyanide complexes are also found in rinse waters of

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the surface finishing industry using cyanide where Zn electroplating creates a soft, ductile, decorative, and corrosion resistant finish (Chipello and Gal, 1992). 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.

Various treatment procedures such as physical, adsorption, complexation, and oxidation are known for removal of cyanides (Gurol and Holden, 1988; Pak and Chang, 1997; Young, 2001; Zagury et al., 2004). The procedures other than oxidation give high concentrated products in which toxic cyanides still exists. Chlorine, hypochlorite, hydrogen peroxide, ozone, sulfur dioxide, and ammonium bisulfite are common oxidants for cyanide destruction (Young, 2001). All oxidation methods have distinct advantages and disadvantages (Parga and Cocke, 2001) and new processes are still desirable for cyanide destruction. For example, commonly used alkaline chlorination, although adequate, has many disadvantages such as formation of cyanogens, chloride contamination, and incomplete decomposition of some metal cyanide complexes (Young, 2001).

For the last few years, the use of iron in a +6 valence state, ferrate(VI) as $Fe^{VI}O_4^{2-}$ (Fe(VI)) to oxidize pollutants in water has been demonstrated (Jiang and Lloyd, 2002; Sharma, 2004; Lee et al., 2005; Sharma et al., 2005b; Cho et al., 2006; Jiang et al., 2006; Sharma et al., 2006). Fe(VI) has properties such as a high oxidizing power, selectivity, and formation of a non-toxic by-product Fe(III). Fe(VI) is the strongest of all oxidants/disinfectants used for water and wastewater treatment (Jiang and Lloyd, 2002). Moreover, ferric oxide, produced from the treatment, acts as a coagulant for removal of metals, non-metals, and radionuclides (Waite and Gray, 1984; Jiang and Lloyd, 2002). Fe(VI) therefore has a role in cleaner (“greener”) technology for removal of cyanide from wastewater effluents (Sharma, 2002; Licht and Yu, 2005). The work conducted earlier in our laboratory demonstrated that cyanides can be removed by Fe(VI) in seconds to give relatively non-toxic by-products (Sharma et al., 1998; Sharma et al., 2002; Sharma et al., 2005a).

In the present study, the effect of Zn(II) on the removal of cyanide by Fe(VI) was investigated by performing kinetic studies on the rates of oxidation of cyanide present in a potassium salt of zinc cyanide ($K_2Zn(CN)_4$) and in a mixture of Zn(II) and cyanide solutions at different alkaline pH. The effect of the temperature on the kinetics of the oxidation reaction was also determined. The removal of cyanide from the rinse water of a metal electroplating facility by Fe(VI) was also sought.

2. Experimental methods

2.1. Chemicals

All chemicals (Sigma, Aldrich, and Antec) were reagent grade or better and were used without further purification. Potassium zinc cyanide ($K_2Zn(CN)_4$) was purchased from Antec Inc. and used in the form it was received. All solutions were prepared with distilled water that had been passed through an 18 MΩ cm resistivity Milli-Q water purification system. The potassium salt of iron(VI) (K_2FeO_4) was synthesized according to the method of Thompson et al. (1951) and was of high purity (>98%). Fe(VI) solutions were prepared by addition of solid K_2FeO_4 to 0.005 M Na_2HPO_4/0.001 M $Na_2B_4O_7 \cdot 9H_2O$ at pH 9.0, a buffer at which Fe(VI) is most stable. A molar absorption coefficient of $\varepsilon_{510\ \mathrm{nm}} = 1150\ \mathrm{M^{-1}\ cm^{-1}}$ was used to calculate the $[FeO_4^{2-}]$ (Bielski and Thomas, 1987). $K_2Zn(CN)_4$ solutions used in the kinetic studies were prepared by dissolving the solid in 0.02 M Na_2HPO_4 buffer solution and adjusted with $NaOH/H_3PO_4$ to achieve the desired reaction pH.

2.2. Zn(II) effect on the rate

To study the influence of Zn(II) on the rate of the oxidation of cyanide by Fe(VI) at different pH, mixed solutions of cyanide and Zn(II) were prepared in a borate buffer solution. The cyanide stock solution was prepared by adding solid KCN into 0.05 M NaOH while $Zn(NO_3)_2$ salt was added into deionized water to prepare a zinc stock solution. The experiments were carried out by mixing equal volumes of Fe(VI) and zinc–cyanide solutions and concentrations of total cyanide in the mixed solutions were determined at different time intervals. The rate constant for the Fe(VI) oxidation of arsenite is approximately two orders of magnitude higher than that of cyanide (Sharma et al., 1998; Lee et al., 2003), therefore, sodium arsenite ($NaAsO_2$) was used in experiments to stop the reaction between cyanide and Fe(VI).

Cyanide concentrations were determined using Dionex Ion Chromatography (IC): Model ICS 2500. The IC system consisted of an AS7 ion exchange column connected in-line to an electrochemical cell with silver as the working electrode, 0.00 V vs. Ag/AgCl reference. The eluent consisted of 0.5 M NaAc, 0.1 M NaOH, and 0.5% (v/v) ethylenediamine at a flow rate of 1 ml $\mathrm{min^{-1}}$. Concentrations of cyanate, nitrite, and nitrate were determined using Dionex IC: Model ICS 2500. The IC system consisted of an AS16 ion exchange column connected in-line to a Suppressor: ASRS 4 mm conductivity cell. The eluent was KOH, which varied from 2.8 mM to 55 mM in gradient mode at a flow rate of 1 ml $\mathrm{min^{-1}}$.

2.3. Kinetics

$K_2Zn(CN)_4$ solutions used in the kinetic studies were prepared by dissolving the solid in 0.02 M Na_2HPO_4 buffer solution and adjusted with $NaOH/H_3PO_4$ to achieve the desired reaction pH. The kinetics of Fe(VI) reactions with tetracyanozincate(II) ($Zn(CN)_4^{2-}$) was carried out using a stopped-flow spectrophotometer (SX.18 MV, Applied Photophysics, UK) equipped with a photomultiplier detec-

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