Enhanced destruction of Cu(CN)\(_3\)\(^{2-}\) by H\(_2\)O\(_2\) under alkaline conditions in the presence of EDTA/pyrophosphate

Fayuan Chen\(^{a,b}\), Xu Zhao\(^a\), Huijuan Liu\(^a\), Jiuhui Qu\(^a\),*  

\(^a\) Key Laboratory of Aquatic Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China  
\(^b\) University of Chinese Academy of Sciences, Beijing 100085, China

HIGHLIGHTS

- Oxidation of Cu(CN)\(_3\)\(^{2-}\) was enhanced by EDTA and pyrophosphate.  
- The complexation of Cu\(^{3+}\) with EDTA inhibited H\(_2\)O\(_2\) decomposition into \(\text{O}_2\).  
- Cu–pyrophosphate led to more generation of reactive species.

ARTICLE INFO

Article history:  
Received 9 January 2014  
Received in revised form 9 May 2014  
Accepted 10 May 2014  
Available online 16 May 2014

Keywords:  
Metal–cyanide complex  
Hydrogen peroxide  
EDTA  
Pyrophosphate  
Fenton-like reaction

ABSTRACT

Oxidation of Cu(CN)\(_3\)\(^{2-}\) in water by H\(_2\)O\(_2\) is less documented. The present study investigated the effects of pH, H\(_2\)O\(_2\) dose and CN\(^{-}/\text{Cu(I)}\) on oxidation of Cu(CN)\(_3\)\(^{2-}\). Furthermore, oxidation of Cu(CN)\(_3\)\(^{2-}\) by H\(_2\)O\(_2\) was investigated in the presence of ethylenediaminetetraacetate (EDTA) or pyrophosphate. The results indicated that Cu(CN)\(_3\)\(^{2-}\) oxidation was more favored at pH 9.5 and 11.0 than at pH 12.0. With the increase of H\(_2\)O\(_2\) dose, rate of Cu(CN)\(_3\)\(^{2-}\) oxidation was accelerated. Oxidation of Cu(CN)\(_3\)\(^{2-}\) was accelerated with CN\(^{-}/\text{Cu(I)}\) decreasing from 4.0 to 2.8. In the presence of EDTA or pyrophosphate, oxidation of Cu(CN)\(_3\)\(^{2-}\) was significantly enhanced. 4.0 mM cyanide was nearly oxidized by 4.8 mM H\(_2\)O\(_2\) in the presence of 1.0 mM EDTA. According to UV–Visible spectra variation of Cu(CN)\(_3\)\(^{2-}\) solutions, it was found that H\(_2\)O\(_2\) firstly oxidized Cu(CN)\(_3\)\(^{2-}\) to Cu(CN)\(_2\)\(^{+}\). The successive oxidation of cyanide from Cu(CN)\(_3\)\(^{2-}\) led to liberation of Cu(I), Cu(II) was oxidized into Cu(III) with formation of hydroxyl radicals [HO\(^{•}\)] or Cu(II). Cu\(_2\)(OH)\(_2\) was decomposed of into \(\text{O}_2\) in the process. The strong bonding of Cu(II) to EDTA suppressed decomposition of H\(_2\)O\(_2\) into \(\text{O}_2\) and enhanced the effective utilization of H\(_2\)O\(_2\) for cyanide destruction. By contrast, complexation of Cu(II) with pyrophosphate enhanced the catalytic redox reaction (Cu(I)/Cu(II) or Cu(I)/Cu(III)), improving cyanide oxidation. The results provide a possible way to improve treatment of Cu(CN)\(_3\)\(^{2-}\) wastewater by H\(_2\)O\(_2\).

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Cyanide is widely used in the electroplating industry [1] and metallurgical process [2]. Usually, cyanide and copper are present in the effluents simultaneously, and the cyanide species generally include CN\(^{-}\), Cu(CN)\(_2\)\(^{+}\), Cu(CN)\(_3\)\(^{2-}\), and Cu(CN)\(_2\)\(^{2-}\)[3]. All forms of cyanide in wastewater must be adequately treated before being allowed to discharge due to its high toxicity. The cyanides could be removed from wastewater though adsorption [4], coagulation [5] or ion-exchange [6]. However, these processes could generate highly concentrated products in which toxic cyanides still exist, which need additional treatments. By contrast, cyanides could be directly converted into less harmful products by employing oxidation methods, such as ozonation [7], electrochemical oxidation [8,9], photocatalysis [10,11], ferrate oxidation [12,13] and wet oxidation [14]. The most practical method was thought to be alkaline chlorination, but it has many disadvantages such as formation of toxic cyanogens chloride [15] and chloride disinfection by-products [16].

H\(_2\)O\(_2\) as a green chemical oxidant, can address some of the concerns of chlorination in the treatment of cyanides. Oxidation of various cyanide species by H\(_2\)O\(_2\) has been investigated previously. For instance, oxidation of free cyanide by H\(_2\)O\(_2\) was investigated in the presence of Ru/MgO [17], copper-impregnated pumice [18] and copper-impregnated activated carbon [19]. The rate of cyanide removal increased with the rise of initial molar ratio of H\(_2\)O\(_2\) to CN\(^{-}\) and decreased with the increase of pH from 8.0 to 12.0. In
the destruction of cyanide in tailings slurries from low bearing sulfidic gold ores [20], the rate and extent of weak acid dissociable cyanide destruction generally increased with increasing H$_2$O$_2$ doses. The effect of slurry pH on cyanide destruction varied depending upon the doses of copper. Though Beattie and Polynblank[21] have investigated Cu(CN)$_3^{2-}$ oxidation by H$_2$O$_2$, the effects of pH, H$_2$O$_2$ dose and ratio of cyanide to cuprous ion on H$_2$O$_2$ oxidation of Cu(CN)$_3^{2-}$ are still less documented.

It is known that, besides cyanide, EDTA and pyrophosphate are also used in electroplating solutions [22,23]. Generally, cyanide, pyrophosphate and EDTA occurred simultaneously in the waste streams. The occurrence of EDTA or pyrophosphate may affect the cyanide removal. Osathaphan et al. [24,25] investigated the effect of EDTA on cyanide oxidation in an electrochemical process and TiO$_2$ photocatalytic oxidation process. They found that at a molar ratio (EDTA:CN) ranging from 5.2 to 15.7, the electro-oxidation rate of cyanide was increased. Conversely, EDTA retarded the photocatalytic oxidation of cyanide at various molar ratios of EDTA to cyanide (0.1–10.5). Similarly, the removal efficiency of cyanide with ZnO photocatalytic oxidation greatly decreased in the presence of organic compounds (e.g. humic acid, oxalate, EDTA, NTA, phenol) due to the competitive oxidation [26]. To the best of our knowledge, the influence of EDTA and pyrophosphate on the H$_2$O$_2$ oxidation of cyanides has not been reported up to date.

This paper investigated the effects of pH, H$_2$O$_2$ dose, ratio of cyanide to cuprous on oxidation of Cu(CN)$_3^{2-}$ first. Furthermore, oxidation of Cu(CN)$_3^{2-}$ in the presence of EDTA or pyrophosphate was investigated. Their presence both enhanced oxidation of Cu(CN)$_3^{2-}$ by H$_2$O$_2$. The enhanced mechanism was explored based on transformation of cuprous cyanide species, the reduction of H$_2$O$_2$ and reactive species detection.

2. Experimental section

2.1. Chemicals

Sodium cyanide, cuprous cyanide, H$_2$O$_2$ (wt. 30.0%), perchloric acid, sodium hydroxide, EDTA disodium salt, sodium pyrophosphate and tert-butanol (t-BuOH) were all purchased from Sinopharm chemical regent Co., Ltd., China. The reagent 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and benzoquinone (BQ) were purchased from Sigma Chemical Co. All chemicals were used without further purification and all solutions were prepared using freshly prepared Milli-Q water.

Generally, complex cyanides and free cyanide coexisted in electroplating wastewater. In this experiment, we simulated the cyanides in the effluent. Both CN$^-$ and Cu(CN)$_3^{2-}$ concentrations were about 1.0 mM. Cu(CN)$_3^{2-}$ solution was prepared by addition of cuprous cyanide powder to sodium cyanide solutions at a CN$^-$/Cu(1) molar ratio of 4.0:1.0 [27]. The distribution of cuprous cyanide species was calculated with the program Visual MINTEQ 3.0 based on the equilibrium reactions and stability constants (Fig. S1). Other Cu(CN)$_3^{2-}$ solutions with different CN$^-$/Cu(1) molar ratio were prepared similarly. The complex cyanide is the predominant species at the ratio of 3.0:1.0 and 2.8:1.0.

2.2. Experimental procedures

The pH of cyanide solutions was maintained above 9.5 to avoid release of HCN gas [28]. In addition, H$_2$O$_2$ deprotonated and existed as H$_2$O$_2^-$ when the pH of solution was above 12.0 [29]. So the effect of pH on Cu(CN)$_3^{2-}$ oxidation was investigated in the range of 9.5–12.0, adjusted by HClO$_4$ (0.2 M) or NaOH solution (0.2 M).

All experiments were performed in 0.5 L glass beakers, and magnetic stirrer was used to keep the chemicals homogenous. The beaker was covered with aluminum foil and incubated at 25 °C. The reaction started as H$_2$O$_2$ was added into 400 mL Cu(CN)$_3^{2-}$ solution. At pre-set time intervals, sample aliquots were collected for analysis. The samples were dosed with potassium iodide to quench the residual H$_2$O$_2$. Potassium iodide was added in slight excess (i.e., 1.2 times) of the stoichiometric requirements to ensure complete quenching. All the experiments were carried out in triplicate with standard deviations of less than 10%. Each data point represents an average value. For some experiments, EDTA or pyrophosphate (copper-chelating agents) was added before the initiation of the reaction, as well as hydroxyl radical (HO$^-$) scavenger (t-BuOH) and superoxide radical (O$_2^-$) scavenger (BQ).

2.3. Analytical procedures

The total cyanide concentration was determined by colorimetric method after distillation [30]. H$_2$O$_2$ concentration was determined colorimetrically using potassium titanium oxalate solution at a wavelength of 400 nm on a spectrophotometer [31]. The dissolved oxygen (DO) concentration was determined in situ using an oxygen electrode (Model 97-08-99, Orion Research Inc., Beverly, MA).

Transformation of copper species and formation of active radicals were identified with electron spin resonance (ESR) on a Bruker ESR 300E with a microwave bridge (receiver gain, 1 × 10$^5$; modulation amplitude, 2 G; microwave power, 10 mW; modulation frequency, 100 kHz). Since the HO$_2^-$ in water are very unstable and underwent facile disproportionation rather than slow reaction with DMP [32], HO$^-$ was identified with ESR only in the experiment. The samples (100 μL) were collected from the reaction solution at different times. For HO$^-$ measurement, the sample mixed immediately with 20 μL DMPO (0.2 mol L$^{-1}$) to form DMPO–HO$^-$ adduct. The ESR spectra of copper species in solution were obtained at liquid nitrogen temperature 113 K.

UV–Vis spectra of Cu(CN)$_3^{2-}$ solution and the Cu(CN)$_3^{2-}$ solution containing EDTA or pyrophosphate were recorded at different reaction times (Hitachi U3100, Japan).

3. Results and discussions

3.1. Oxidation performance of Cu(CN)$_3^{2-}$ by H$_2$O$_2$

The variation of cyanide concentration with reaction time at various pH values is shown in Fig. 1a. It is observed that cyanide concentration decreased slowly at pH 12.0. After 240 min, cyanide concentration decreased from 4.0 mM to 1.2 mM. By contrast, cyanide concentration decreased much more rapidly at pH 9.5 and 11.0 than at pH 12.0. With the concentration of 4.0 mM H$_2$O$_2$, the residual cyanide concentration was about 1.2 mM at the three pH values. As shown in Fig. 1b, H$_2$O$_2$ decayed slowly at pH 12.0 and was decomposed completely after 240 min. By contrast, H$_2$O$_2$ decayed rapidly at pH 9.5 and 11.0, which was completely decomposed after 55 min and 80 min, respectively. The variation trend of the H$_2$O$_2$ concentration was similar to that of the cyanide concentration.

The oxidation of Cu(CN)$_3^{2-}$ by H$_2$O$_2$ was more effective at lower pH values, which was consistent with free cyanide oxidation in the presence of copper [18,19,33]. It is known that H$_2$O$_2$ was mainly present in the species of HO$_2^-$ at pH 12.0 [29]. The standard redox potential of HO$_2^-$ (E$^\circ$(HO$_2^-$/OH$^-$) 0.88 V/SHE) is lower than that of H$_2$O$_2$ (E$^\circ$(H$_2$O$_2$/H$_2$O) 1.76 V/SHE), which demonstrates a much lower oxidative ability than H$_2$O$_2$ [34]. Then, oxidation of Cu(CN)$_3^{2-}$ with various H$_2$O$_2$ doses was investigated with an initial cyanide concentration of 4.0 mM at pH 11.0.
As shown in Fig. 2a, the cyanide concentration decreased slowly when the H$_2$O$_2$ concentration was 4.0 or 6.0 mM. By contrast, the cyanide concentration decreased sharply when the H$_2$O$_2$ concentration was 12.0 or 18.0 mM. The cyanide was oxidized completely after 15 min with 18.0 mM H$_2$O$_2$. At 15 min, the cyanide concentrations were 3.2, 2.6 and 0.5 mM with the H$_2$O$_2$ concentration of 4.0, 6.0 and 12.0 mM, respectively. These results indicated that the oxidation rate of Cu(CN)$_3^{2-}$/C$_0$ increased significantly when the added H$_2$O$_2$ dose increased from 4.0 to 12.0 mM. As shown in Fig. 2b, H$_2$O$_2$ was decomposed slowly with the concentration of 4.0 mM or 6.0 mM, which was decomposed completely after 75 min and 40 min, respectively. By contrast, H$_2$O$_2$ was decomposed completely after 20 min and 15 min at the concentration of 12.0 mM or 18.0 mM.

With the initial H$_2$O$_2$ concentration of 4.0 mM, 6.0 mM and 12.0 mM, the residual cyanide concentrations were 1.6 mM, 1.3 mM and 0.3 mM, respectively. The oxidation of cyanide was not proportional to the increase of H$_2$O$_2$ concentration. Additionally, it was notable that the decomposition of H$_2$O$_2$ could be

---

Fig. 1. Variations of the cyanide concentrations (a) and the H$_2$O$_2$ concentrations (b) with time at various pHs ([Cu] = 1.0 mM, [CN$^-$] = 4.0 mM, [H$_2$O$_2$] = 4.0 mM).

Fig. 2. Variations of the cyanide concentrations (a) and the H$_2$O$_2$ concentrations (b) with reaction time at various H$_2$O$_2$ dose ([CN$^-$] = 4.0 mM, [CN$^-$]:[Cu] = 4.0: 1.0, pH = 11.0).

Fig. 3. Variations of the cyanide concentrations (a) and the H$_2$O$_2$ concentrations (b) with reaction time at various ratio of CN$^-$ to Cu(I) ([CN$^-$] = 4.0 mM, [H$_2$O$_2$] = 12.0 mM, pH = 11.0).

Fig. 4. Cyanide transformation during the process of Cu(CN)$_3^{2-}$ oxidation ([Cu(CN)$_3^{2-}$] = 1.0 mM, [CN$^-$] = 1.0 mM, [H$_2$O$_2$] = 12.0 mM, pH = 11.0).
divided into the slow decomposition stage and rapid decomposition stage. These results would be discussed and explained in the following section.

In the next step, oxidation of Cu(CN)$_3^{2-}$ under various ratios of CN$^-$ to Cu(I) was investigated with H$_2$O$_2$ concentration of 4.0 mM at pH 11.0. As shown in Fig. 3a, the cyanide concentration decreased more rapidly at the ratio of 3.0 and 2.8 than at the ratio of 4.0. At 15 min, the cyanide concentration decreased from 4.0 mM to 2.1 mM at the ratio of 2.8. The cyanide concentration was 2.2 mM after 25 min at the ratio of 3.0. In the case of the ratio of 4.0, the cyanide concentration was decreased to 1.6 mM after 80 min. In contrast, 0.3 mM free cyanide was oxidized merely. It is concluded that increase of the Cu(I) dose accelerated the oxidation of cyanide.

As shown in Fig. 3b, the decay of H$_2$O$_2$ at the ratio of 4.0 was slower than that at the ratio of 3.0 and 2.8. The H$_2$O$_2$ was decomposed completely at 80 min at the ratio of 4.0. With the ratio of 3.0 and 2.8, the H$_2$O$_2$ was decomposed completely at 25 min and 15 min, respectively. The H$_2$O$_2$ decomposition was accelerated with increase of ratio between Cu(I) and CN$^-$. It is because that H$_2$O$_2$ could be decomposed catalytically by cycle between Cu(I) and Cu(II) [35]. Thus, increase of copper concentration accelerated H$_2$O$_2$ decomposition.

To analyze the pathway of cyanide oxidation with H$_2$O$_2$, intermediates of cyanide oxidation were identified in the course of Cu(CN)$_3^{2-}$ oxidation. As shown in Fig. 4, the cyanate concentration increased with the decrease of cyanide concentration. In the present study, ammonia, nitrite and nitrate were not found. The sum of

![Fig. 5. Oxidation of Cu(CN)$_3^{2-}$ (a) and the H$_2$O$_2$ decomposition (b) in the presence of EDTA ([CN$^-$] = 4.0 mM, [H$_2$O$_2$] = 4.8 mM, pH = 11.0).](image)

![Fig. 6. Oxidation of Cu(CN)$_3^{2-}$ (a) and the H$_2$O$_2$ decomposition (b) in the presence of pyrophosphate ([CN$^-$] = 4.0 mM, [H$_2$O$_2$] = 4.8 mM, pH = 11.0).](image)

![Fig. 7. UV–Vis spectra of Cu(CN)$_3^{2-}$ solution during oxidation process, (a) in the absence of other ligands; (b) in the presence of EDTA (1.0 mM); (c) in the presence of pyrophosphate (5.0 mM) ([CN$^-$] = 4.0 mM, [H$_2$O$_2$] = 4.8 mM, pH = 11.0).](image)
the cyanide concentration and cyanate concentration at different reaction times was found to be nearly equal to the initial cyanide concentration, indicating cyanate was the only oxidized product of cyanide in the experiment.

3.2. Cu(CN)$\textsubscript{3}^2-$ destruction in the presence of EDTA

As shown in Fig. 5a, oxidation of Cu(CN)$_3^{2-}$ was enhanced in the presence of EDTA. When the concentration of EDTA increased from 0 to 1.0 mM, the concentration of residual cyanide decreased obviously. In the presence of 1.0 mM EDTA, the Cu(CN)$_3^{2-}$/C$^0$ could be completely oxidized with 4.8 mM H$_2$O$_2$. By contrast, 18.0 mM H$_2$O$_2$ was required for complete oxidation of cyanide without EDTA (Fig. 2a). Oxidation of Cu(CN)$_3^{2-}$ was not affected in the presence of EDTA before 45 min, but it slowed down after 45 min when the EDTA concentration was increased from 0.5 mM to 2.0 mM.

The variation trend of cyanide was consistent with that of H$_2$O$_2$. As showed in Fig. 5b, the decomposition of H$_2$O$_2$ was not affected in the presence of EDTA before 45 min. However, the decomposition of H$_2$O$_2$ slowed down with the increase of EDTA concentration after 45 min. The H$_2$O$_2$ was decomposed completely until 130 min in the presence of 1.0 mM EDTA. By contrast, in the presence of 2.0 mM EDTA, H$_2$O$_2$ was still present in the solution even after 6.0 h.

3.3. Cu(CN)$_3^{2-}$ destruction in the presence of pyrophosphate

The effect of pyrophosphate on oxidation of Cu(CN)$_3^{2-}$/C$^0$ is illustrated in Fig. 6a. Oxidation of Cu(CN)$_3^{2-}$ was enhanced obviously as the pyrophosphate concentration increased from 0 to 2.0 mM, whereas it was not enhanced significantly as the concentration of pyrophosphate was increased from 2.0 to 5.0 mM. The concentration of residual cyanide was determined to be 0.2 mM as the pyrophosphate concentration was increased to 2.0 mM. These results indicate that oxidation of Cu(CN)$_3^{2-}$ improves slightly if the concentration of pyrophosphate is increased continuously. Before 45 min, the cyanide oxidation was not affected in the presence of pyrophosphate. After that, the presence of pyrophosphate accelerated cyanide oxidation, which was different from the results in the presence of EDTA.

The trend of H$_2$O$_2$ decomposition in the presence of pyrophosphate was similar to that of cyanide oxidation (Fig. 6b). It was notable that the time for H$_2$O$_2$ decomposition was 65 min in the absence of pyrophosphate, which was shortened to 55 min in the presence of 2.0 or 5.0 mM pyrophosphate. The H$_2$O$_2$ was decomposed instantly after 45 min both in the absence and the presence of pyrophosphate. However, the cyanide oxidation was enhanced strongly in the presence of pyrophosphate compared to the results without pyrophosphate. This implied that H$_2$O$_2$ may be converted into other reactive species in the presence of pyrophosphate, which could also oxidize cyanide.

3.4. Characterization of Cu(CN)$_3^{2-}$ destruction with UV–Vis spectrum and ESR spectrum

UV–Vis spectra of Cu(CN)$_3^{2-}$ solution at different reaction time were recorded to explore the evolution of Cu(CN)$_3^{2-}$/C$^0$, as well as
the solutions containing EDTA and pyrophosphate. In addition, we also utilized ESR spectrum to investigate the valence state transformation of copper in the course of Cu(CN)$_2^{2-}$/CO oxidation. In the absence of other ligands (Fig. 7a), two absorption peaks were observed at 208 nm and 238 nm, which were assigned to the absorption of the Cu(CN)$_2^{2-}$/CO$_2$ [21,27]. No obvious change for the absorption peaks at the two wavelengths was observed before 30 min. It is indicated that Cu(CN)$_2^{2-}$/CO was the dominant species in the solution before 30 min. Two new peaks at 223 nm and 234 nm were observed at 45 min instead of the absorption peaks at 238 nm, which was assigned to the absorption of Cu(CN)$_2^{-}$/CO$_2$ [21,36]. These results suggest that the Cu(CN)$_2^{2-}$/CO had been partially transformed to Cu(CN)$_2^{-}$/CO before 45 min Eq. (1). The absorption peaks at 208 nm, 223 nm and 234 nm all decreased at 60 min, and then remained constant with the time, indicating that Cu(CN)$_2^{2-}$/CO and Cu(CN)$_2^{-}$/CO still remained. The Cu(II) signal ($g = 2.265$, $A_{II} = 141$ G, $g = 2.088$) in EPR spectra were observed since 60 min, which was intensified with time (Fig. 8b). Its parameters are close to those observed for a homogeneous Cu(II) complex with EDTA (1:1) of similar structure ($g = 2.321$, $g = 2.040$) [37], which indicates that the Cu(II)–EDTA complex formed in the course of Cu(CN)$_2^{-}$/CO destruction in the presence of EDTA Eq. (4).

$$\text{Cu}^{2+} + \text{EDTA}^4- \rightarrow \text{CuEDTA}^2+$$  \hspace{1cm} (4)

In the presence of pyrophosphate (Fig. 7c), a new absorption peak at 234 nm appeared at 30 min instead of the absorption peak at 238 nm. All the absorption peaks disappeared at 45 min. It implied that Cu(CN)$_2^{2-}$/CO had been transformed to Cu(CN)$_2^{-}$/CO before 30 min, and Cu(CN)$_2^{2-}$/CO and Cu(CN)$_2^{-}$/CO had been destroyed completely before 45 min. The spectrum kept constant and was consistent

\[
\begin{align*}
\text{Cu(CN)}_2^{2-} + \text{H}_2\text{O}_2 & \rightarrow \text{Cu(CN)}_2^{-} + \text{CNO}^- + \text{H}_2\text{O} \\
\text{Cu(CN)}_2^{-} + 2\text{H}_2\text{O}_2 & \rightarrow \text{Cu}^+ + 2\text{CNO}^- + 2\text{H}_2\text{O} \\
\text{Cu}^+ + 2\text{H}_2\text{O}_2 & \rightarrow \text{Cu}^{2+} + \text{HO}^- + \text{OH}^- \\
\end{align*}
\]
with the absorption spectrum of Cu(II)-pyrophosphate solution. In addition, the Cu(II) signal with parameters ($g_{||} = 2.232, A_{||} = 123$ G, $g_{\perp} = 2.069$) in ESR spectra had been observed since 45 min, which intensified with time (Fig. 8c). It is concluded that Cu(II)-pyrophosphate complex formed with the destruction of Cu(CN)$_2$$^-$ Eq. (5).

$$\text{Cu}^{2+} + 2\text{P}_4\text{O}_{10}^{6-} \rightarrow \text{Cu}(\text{P}_4\text{O}_{10}^{4-})_2$$  

(5)

3.5. $\text{H}_2\text{O}_2$ decomposition and involved active radicals with Cu(CN)$_2$$^-$ destruction

$\text{H}_2\text{O}_2$ decomposition and DO change under various conditions are shown in Fig. 9. In the absence of other ligands (Fig. 9a), $\text{H}_2\text{O}_2$ was decomposed slowly before 45 min and DO concentration almost kept constant. After that, the decomposition of $\text{H}_2\text{O}_2$ was accelerated and DO increased instantly. In the presence of EDTA (Fig. 9b), most of $\text{H}_2\text{O}_2$ was decomposed gradually before 125 min. After that, the residual $\text{H}_2\text{O}_2$ was decomposed instantly and DO increased accordingly. In the presence of pyrophosphate (Fig. 9c), the decomposition of $\text{H}_2\text{O}_2$ was slow before 45 min and the DO concentration almost kept constant, whereas it was accelerated and DO increased instantly afterwards. Both of EDTA and pyrophosphate reduced the DO production.

The EPR spin trapping technique was also employed to monitor the active radicals involved in the $\text{H}_2\text{O}_2$ decomposition under various conditions. As shown in Fig. 10a, the signal of hydroxyl radicals adduct was not determined expectedly. In the absence of other ligands (Fig. 10b), the characteristic peaks of DMPO–$\cdot\text{HO}_2$ were observed at 45 min. The intensity of the peaks increased at 50 min, then decreased with time and disappeared at 70 min. By contrast, in the presence of EDTA (Fig. 10c), the DMPO–$\cdot\text{HO}_2$ peaks appeared at 60 min and the intensity of the peaks increased slowly till 120 min. In the presence of pyrophosphate (Fig. 10d), the characteristic peaks of DMPO–$\cdot\text{HO}_2$ were observed at 45 min. The intensity of the peaks at 50 min increased significantly and then decreased with time before its disappearance at 60 min. It is observed that the intensity of the peaks was increased in the presence of pyrophosphate, indicating that the production of $\cdot\text{HO}_2$ was enhanced.

The quench experiment was also performed to identify the role of reactive species for cyanide oxidation in Cu(CN)$_2$$^-$ solution (Fig. 11a), Cu(CN)$_2$$^-$/EDTA (Fig. 11b) and Cu(CN)$_3$$^-$/pyrophosphate system (Fig. 11c). The addition of benzoquinone scavenger for $\cdot\text{O}_2^-$ significantly prohibited cyanide oxidation after 45 min in the Cu(CN)$_2$$^-$ solution and Cu(CN)$_3$$^-$/pyrophosphate system. Whereas the tert-butanol (t-BuOH) scavenger for $\cdot\text{HO}_2$ was added, cyanide oxidation was almost unchanged in the three systems. This is because that $\cdot\text{HO}_2$ or $\cdot\text{O}_2^-$ was generated only when the redox reaction between Cu(I)/Cu(II) and $\text{H}_2\text{O}_2$ was initiated after 45 min Eqs. (3) and (6). Moreover, an alternative oxidant (other than $\cdot\text{HO}_2$) may be generated in the reaction of Cu(II) with $\text{H}_2\text{O}_2$, most likely Cu(III), and this alternative oxidant reacted with cyanide at higher rates than $\cdot\text{HO}_2$ does under the conditions of these experiments Eqs. (7) and (8). $\cdot\text{O}_2^-$ promoted the reduction of Cu(II) to Cu(I) Eq. (9), introducing more Cu(III) formed for cyanide oxidation. This explanation is in agreement with previous observations that, at neutral pH values, Cu(III) was the major oxidant responsible for the inactivation of Escherichia coli and MS2 by the Cu(II)/$\text{H}_2\text{O}_2$ system [38,39].

$$\text{Cu}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{O}_2^- + 2\text{H}^+$$  

(6)

$$\text{Cu}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{3+} + 2\text{OH}^-$$  

(7)

$$\text{Cu}^{3+} + \text{CN}^- + 2\text{OH}^- \rightarrow \text{Cu}^{3+} + \text{NO}_2^- + \text{H}_2\text{O}$$  

(8)

$$\text{Cu}^{2+} + \cdot\text{O}_2^- \rightarrow \text{O}_2 + \text{Cu}^{2+}$$  

(9)

In alkaline medium, superoxo-Cu(II) complex (HO$_2$Cu(OH)$_2$) between Cu(II) and $\text{H}_2\text{O}_2$ was formed in alkaline conditions Eq. (10) besides Cu(OH)$_2$ precipitates Eq. (11) [35]. The HO$_2$Cu(OH)$_2$ was further decomposed into Cu(I) species and O$_2$: in unimolecular due to its low stability Eqs. (12) and (13). The catalytic cycle between Cu(I)/Cu(II) or Cu(I)/Cu(III) species is then propagated by HO$_2$ and O$_2$. In this stage, the decomposition of $\text{H}_2\text{O}_2$ is very rapid. The complexation of Cu(II) with pyrophosphate made more copper species involved in the catalytic cycle between Cu(I)/Cu(II) rather than formation of precipitates Eq. (14), inducing more production of HO$_2^-$ and Cu(II) Eqs. (6) and (7). Thus, the oxidation of Cu(CN)$_2$$^-$ was also enhanced. In the presence of EDTA, however, the strong complexation of Cu(II) with EDTA could prevent any reduction of Cu(II) [39]. Hence, the decomposition of $\text{H}_2\text{O}_2$ into O$_2$ was inhibited in the presence of EDTA. The oxidation of Cu(CN)$_2$$^-$ by $\text{H}_2\text{O}_2$ was enhanced due to the effective utilization of $\text{H}_2\text{O}_2$.

$$\text{Cu}^{2+} + \text{H}_2\text{O}_2 + 3\text{OH}^- \rightarrow \text{HO}_2\text{Cu}(\text{OH})_2 + \text{H}_2\text{O}$$  

(10)

$$\text{Cu}^{2+} + 2\text{OH}^- \rightarrow \text{Cu}(\text{OH})_2$$  

(11)

$$\text{HO}_2\text{Cu}(\text{OH})_2 \rightarrow \text{Cu}(\text{OH})_2 + \text{HO}_2$$  

(12)

$$\text{Cu}(\text{OH})_2 + \text{O}_2 + \text{OH}^- \rightarrow \text{Cu}(\text{OH})_2 + \text{O}_2^- + \text{OH}^-$$  

(13)

$$\text{Cu}(\text{P}_4\text{O}_{10}^{4-})_2 + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^+ + 2\text{P}_4\text{O}_{10}^{6-} + \text{O}_2^- + 2\text{H}^+$$  

(14)
4. Conclusions

(1) Oxidation of Cu(CN)$_3^{2-}$ by H$_2$O$_2$ was favored at pH 9.5 and 11.0, and was accelerated with the increase of H$_2$O$_2$ dose. Oxidation of Cu(CN)$_3^{2-}$ by H$_2$O$_2$ was also accelerated with increased ratio of Cu(I) to CN$^-$. 

(2) Cu(CN)$_2^{2-}$ was converted to Cu(CN)$_2$ firstly. Cu(CN)$_2^{2-}$ was destroyed subsequently with continuous cyanide oxidation. The Fenton-like reaction occurred between liberated Cu(I) and H$_2$O$_2$ with the formation of HO$^.$ and Cu(II). The H$_2$O$_2$ was decomposed into O$_2$ instantly by catalysis of Cu(II).

(3) The presence of both EDTA and pyrophosphate enhanced oxidation of Cu(CN)$_3^{2-}$. The strong bonding of Cu(II) with EDTA inhibited the decomposition into O$_2$. Thus, the oxidation of Cu(CN)$_3^{2-}$ by H$_2$O$_2$ was enhanced due to the effective utilization of H$_2$O$_2$. Conversely, the complexation of Cu(II) with pyrophosphate made more copper species involve in the catalytic cycle between Cu(I)/Cu(II) or Cu(I)/Cu(III) species rather than formation of precipitates, inducing more production of HO$^.$ and Cu(III).

Acknowledgment

This work was supported by the Major Program of the National Natural Science Foundation of China (No. 51290282) and National Natural Science Foundation of China (Nos. 51221892, 51222802).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2014.05.039.

References