Enhancement of electrochemical oxidation of Cu(CN)$_3^{2-}$ by the peroxydisulfate oxidation

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In this work, the peroxydisulfate (PDS/K$_2$S$_2$O$_8$) enhancement of electrochemical oxidation of Cu(CN)$_3^{2-}$ with the RuO$_2$/Ti mesh anode and the stainless steel cathode was investigated. The removal efficiency of cyanide was largely increased with increasing the PDS concentration. When the concentration of K$_2$S$_2$O$_8$ was 1.00 mM and the current density was 14.80 A/m$^2$, the removal efficiency of cyanide was increased from 34.3% to 89.1% at the initial 10 min. The Cu mass distribution onto the anode surface was confirmed by the ESR analysis. It was suggested that Cu(I) reacted with S$_2$O$_8^{2-}$ via a Fenton-like process, leading to the formation of SO$_4^{2-}$ radical. ·OH radical was generated due to the reaction between SO$_4^{2-}$ and OH$^-$/H$_2$O. Therefore, these active radicals and anode oxidation were responsible for cyanide removal.

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1. Introduction

Cyanide-containing wastewater is discharged by various industries, especially in the processes of plating, surface finishing and metallurgy [1,2]. Cyanide is widely used in these industries due to its unique properties [3,4]. Consequently, cyanide-containing wastewater and heavy metals are generated. Various techniques have been employed to treat the cyanide-contaminated effluents. Alkaline chlorination is generally applied to remove the cyanide-containing wastewater. However, this method may generate the toxic cyanogens chloride and the chloride disinfection [5–7]. By contrast, some oxidation techniques have been investigated to remove the cyanide-containing wastewater without harmful products, which mainly include electro-chemical oxidation [8,9], wet oxidation [10], photocatalysis [11,12], ferrate oxidation [13,14] and ozonation [15].

The electrochemical process for removing the cyanide-containing wastewater has been widely investigated [16,17]. The active chlorine species generated via the electrochemical oxidation are efficient for cyanide removal [18,19]. However, the by-product of CNCl is readily generated in the electrochemical oxidation process, which should be treated carefully. In the electrochemical oxidation of copper cyanide complexes, it is reported that copper oxides deposited on the anode occurred, which can enhance the cyanide removal due to its catalytic activity [20].

Peroxydisulfate (PDS) and peroxymonosulfate (PMS) are attracting more and more attention for the degradation of organic pollutants [21,22]. PDS is a popular oxidant in the advanced oxidation processes, because it is cheaper than other oxidants and relatively stable. Persulfates can generate strong sulfate radical by UV, heat, alkaline and transition metals activating [23,24]. Zhang et al. has used the peroxydisulfate for 2, 4-DCP degradation [25], which indicated that peroxydisulfate could be activated by CuO. Moussavi et al. has paid attention to the advanced oxidation processes of VUV and UVC/K$_2$S$_2$O$_8$ for removing cyanide [26].

Herein, the K$_2$S$_2$O$_8$ reagent was used to enhance the electrochemical oxidation for removing Cu(CN)$_3^{2-}$. In this experiment, the effects of current density and K$_2$S$_2$O$_8$ concentration on the removal efficiency of Cu(CN)$_3^{2-}$ were investigated. The electrode surfaces were analyzed by SEM-EDX, XRD and XPS techniques. The generations of hydroxyl and sulfate radicals in the system were confirmed by the ESR technique.

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2. Materials and methods

2.1. Materials

Sodium cyanide, potassium persulfate, sodium hydroxide, sulfuric acid (98% w/w), sodium nitrite, and sodium perchlorate were all purchased from Sinopharm chemical reagent Co., Ltd., China. The reagent 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was purchased from Sigma Chemical Co., Ltd. and stored at −20 °C. All the chemicals were analytically pure. Freshly prepared Milli-Q water was used to prepare the solutions. Cu(CN)\textsubscript{3}\textsuperscript{2−} was prepared by adding the cuprous cyanide powder to cyanide solutions at a molar ratio of CN\textsuperscript{−} to Cu\textsuperscript{+} (3.0:1.0).

2.2. Experimental section

The experiments were carried out in a glass reactor containing 180 mL Cu(CN)\textsubscript{3}\textsuperscript{2−} solutions and the initial concentration of total CN\textsuperscript{−} was 0.90 mM. The sodium perchlorate acted as an electrolyte. The electrochemical system included a direct-current (DC) power supply, an electrolytic cell, a stainless steel cathode, a RuO\textsubscript{2}/Ti mesh anode and a magnetic stirring apparatus. The RuO\textsubscript{2}/Ti electrode was directly connected to the positive electrode of the DC power supply and the stainless steel electrode with the same area was directly connected to the negative electrode of the DC power supply. The electrochemical experiments were carried out at a constant current density, which was controlled by a DC power supply, an electrolytic cell, a stainless steel cathode, a RuO\textsubscript{2}/Ti anode and a magnetic stirring apparatus. The RuO\textsubscript{2}/Ti electrode was directly connected to the positive electrode of the DC power supply. The electrochemical experiments were carried out at a constant current density, which was controlled by a DC power supply (DH1718E-6, Dahua Electronic, Co., Ltd., Beijing, China). The pH of cyanide solutions was kept under alkaline conditions, preventing the release of HCN [27]. The reaction solution was stirred magnetically at a speed of 450 rpm. All the electrochemical experiments were performed at an ambient temperature of 20 ± 2 °C.

2.3. Analysis

The total concentration of CN\textsuperscript{−} was measured by colorimetric method at 610 nm. Cyanate concentration was measured by hydrolyzing cyanate to ammonia at acidic pH (1.5–2.0) and ammonia was measured by UV–vis spectrometer (Hitachi U-3010) at 420 nm. The concentration of Cu ions was determined by a 700 series inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent Technology, U. S. A). The initial pH value of reaction solution was 12.0 and measured by a standard pH-meter (PHI, INC). The generations of active radicals were identified by electron spin resonance (ESR) on a Bruker ESR 300E with a microwave bridge (receiver gain, 1 × 105; modulation amplitude, 2 G; microwave power, 10 mW; modulation frequency, 100 kHz).

3. Results and discussions

3.1. Effect of current density on the removal efficiency of Cu(CN)\textsubscript{3}\textsuperscript{2−}

The effect of the current density on the cyanide removal was investigated in the electrochemical oxidation of Cu(CN)\textsubscript{3}\textsuperscript{2−} process. As shown in Fig. 1, corresponding to the current density of 0 A/m\textsuperscript{2}, 3.70 A/m\textsuperscript{2}, 7.40 A/m\textsuperscript{2}, 14.80 A/m\textsuperscript{2} and 29.60 A/m\textsuperscript{2}, the removal efficiency of CN\textsuperscript{−} are 4.24%, 66.6%, 86.1%, 97.4% and 98.9% after 30 min reaction. The removal efficiency of CN\textsuperscript{−} is increased with the increasing current density. The increased current density would improve the applied electrode potential in the system, which promoted the oxidation efficiency of cyanide. In addition, the high current density would enhance the electrochemical reduction of the copper ions onto the cathode via Eq. (1).

\[
\text{Cu}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cu(s)} \tag{1}
\]

But when the current density was increased from 14.80 A/m\textsuperscript{2} to 29.60 A/m\textsuperscript{2}, the removal efficiency of CN\textsuperscript{−} was remained nearly unchanged. At the high current intensity, secondary reactions occurred easily [28]. With respect to the energy cost, the optimal current density for cyanide removal was selected as 14.80 A/m\textsuperscript{2}.

3.2. Effect of K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} concentration on the removal efficiency of Cu(CN)\textsubscript{3}\textsuperscript{2−}

The effect of initial K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} concentration ranging from 0 to 2.00 mM was investigated in the electrochemical oxidation of Cu(CN)\textsubscript{3}\textsuperscript{2−} process. As shown in Fig. 2, the removal efficiency of Cu(CN)\textsubscript{3}\textsuperscript{2−} is increased significantly with the increasing K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} concentration. When the concentration of K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} is increased from 0 to 1.00 mM, the removal efficiency of CN\textsuperscript{−} is increased markedly from 69.9% to 97.7% at 30 min.

It was clear that the increase of K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} concentration accelerated the degradation of CN\textsuperscript{−} in the electrochemical system. Some metals could be used as K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} activators, such as, Fe (0) [29], Fe (II) [30] and Ag (I) [21], which had advantages of high efficiency without high energy consumption under room temperature conditions. More concentration of K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} would enhance the decomposition of Cu(CN)\textsubscript{3}\textsuperscript{2−}, leading to the release of more Cu (I) ions. As shown in Eq. (2), the increasing concentration of K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} would generate more SO\textsubscript{4}\textsuperscript{−}, which could effectively remove cyanide contaminant.

\[
\text{S}_2\text{O}_5^{2−} + \text{Cu}^+ \rightarrow \text{SO}_4^{2−} + \text{SO}_4^{2−} + \text{Cu}^{2+} \tag{2}
\]

However, when the K2S2O8 concentration is increased from 1.00 mM to 2.00 mM, the removal efficiency of CN\textsuperscript{−} is remained nearly unchanged. Therefore, the optimal K2S2O8 concentration for cyanide removal was 1.00 mM.
In the meantime, the conversion of cyanide was investigated. As shown in Fig. 3, the main product in the cyanide oxidation process is cyanate (CNO\(^{-}\)). In this study, ammonia, nitrite and nitrate are not detected. The sum of the cyanide concentration and cyanate concentration at different reaction time is found to be nearly equal to the initial cyanide concentration, indicating that the main product is CNO\(^{-}\) during the process.

3.3. The Cu mass distribution and balance

The quality of copper ions deposited onto the anode and cathode was dissolved by the dilute nitric acid and then measured by ICP-OES. The concentration of total Cu ions in solution was determined in different reaction time. As shown in Fig. 4(a), the Cu ions concentration in the solution was decreased with the addition of K\(_2\)S\(_2\)O\(_8\) reagent. When the K\(_2\)S\(_2\)O\(_8\) concentration is increased to 1.00 mM, the Cu ions are totally removed within 30 min. In addition, the distribution of Cu species was analyzed at various K\(_2\)S\(_2\)O\(_8\) concentrations after the electrochemical oxidation of Cu(CN)\(_3\)\(^{2-}\). As shown in Fig. 4(b), without the addition of K\(_2\)S\(_2\)O\(_8\), the percentages of Cu (by wt%) deposited onto the anode, in the solution, and deposited onto the cathode are 69.6%, 24.7%, and 5.7%, respectively. With the increase of K\(_2\)S\(_2\)O\(_8\) concentration, the percentage of Cu deposited onto the cathode and in the solution is decreased and the percentage of Cu deposited onto the anode is increased gradually. When the concentration of K\(_2\)S\(_2\)O\(_8\) is 1.00 mM, the percentages of Cu on the RuO\(_2\)/Ti mesh anode are 99.1% and 0.55%, respectively. Thus, it was obvious that the increasing K\(_2\)S\(_2\)O\(_8\) concentration could increase the percentages of Cu deposited onto the anode.

3.4. Analysis of the surface variation of the electrodes

The deposition on the electrodes surface was investigated by SEM-EDX, XRD and XPS. As shown in Fig. 5, there are no copper or copper oxides on the electrodes surface before the electrochemical reaction. After 30 min reaction, copper ions are reduced onto the cathode and copper oxides are generated onto the anode. Meantime, the EDX spectra of the deposition on the electrodes after 30 min reaction were shown in the supporting information.
At 2θ the anode, the pronounced diffraction peaks in the XRD pattern increase the removal efficiency of CN−. Therefore, the generation of CuO on the anode surface could give a preferred orientation. The cubic structure of the Cu2O is not observed in the XRD patterns, indicating the generation of deposition on the electrodes surface contained the Cu element. The deposition on the anode and cathode were further analyzed by the XRD technique. As shown in Fig. 6(a), for the cathode, the pronounced diffraction peaks in the XRD pattern at 2θ of 44.50°, 50.05° and 74.50° are corresponded to (1 1 1), (2 0 0) and (2 2 0) Bragg’s reflections of monoclinic Cu phase in accordance with the standard (JCPDS: 01-085-1326) [31]. As shown in Fig. 6(b), for the anode, the pronounced diffraction peaks in the XRD pattern at 2θ of 32.52°, 35.55°, 38.73°, 53.41°, 68.14°, 72.41° and 75.02° are corresponded to (1 1 0), (−1 1 1), (1 1 1), (0 2 0), (2 2 0), (3 1 1) and (0 0 4) Bragg’s reflections of monoclinic CuO phase in accordance with the standard (JCPDS: 01-085-1326) [32]. The intensity of (1 1 1) peak is much stronger than other peaks, indicating a preferred orientation. The cubic structure of the Cu2O is not observed in the XRD patterns, indicating the generation of deposition onto the anode is CuO.

The value state of the copper deposition on the electrodes was determined by the XPS technique. As shown in Fig. 7(a), according to the XPS spectra of the stainless steel cathode, the Cu2p core level binding energy is observed. The major Cu2p1/2 peaks centers at 952.7 eV confirming the deposition on the anode surface are CuO [34,35]. It has been reported that the CuO deposition on the anode exhibited the catalytic properties for removing CN− [36], because the K2S2O8 reagent was activated by CuO under mild conditions and the activated K2S2O8 showed strong oxidation capacity [25]. Therefore, the generation of CuO on the anode surface could increase the removal efficiency of CN−.

3.5. Involved active species

Sulfate radical, which was generally considered as the oxidant species in the persulfate activation process. The redox potential of SO4− was confirmed as 2.5−3.1 V, while the potential of ‘OH was detected as 2.7 V in acid solution and 1.8 V in neutral solution. Due to the narrow gap of the redox potential between SO4− and ‘OH, the transformation from SO4− to ‘OH occurred via Eqs. (3) and (4) [37,38]. During the process, the OH− ions were consumed and the pH of the solution would be decreased. In order to avoid the release of HCN gas, the initial pH of the solution was maintained at alkaline condition (pH = 12.0).

$$\text{SO}_4^{2-} + \text{OH}^- \rightarrow \text{OH} + \text{SO}_4^{2-}$$  \hspace{1cm} (3)

$$\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{SO}_4^{2-} + \text{H}^+$$  \hspace{1cm} (4)

The formation of SO4− and ‘OH radicals during the Cu(CN)32− oxidation process was checked by the ESR technique. The variation of signal intensity at different reaction time was shown in Fig. 8. The characteristic four peaks of DMPO-‘OH with the intensity of 1:2:2:1 are observed at initial 30 s, indicating the generation of ‘OH radicals [39,40]. And the characteristic six peaks of DMPO-SO4− are observed at 3 min, which is confirmed the generation of the SO4− radicals. In order to analyze the process of K2S2O8 activation, the oxidation reaction was carried out without stirring and the active species generated near the anode, cathode and in the solution were studied by the ESR technique. As shown in the supporting information of Fig. S2, No significant difference of the radical intensity is observed, which indicates that the activation of K2S2O8 is mainly due to the Cu2+ ions.

At the same time, radical quenching experiments were carried out to confirm the role of generated active radicals. The active radical species such as SO4− and ‘OH could react rapidly with the ethanol (EtOH), and ‘OH could react rapidly with the Tert-butanol (TBA). Thus, EtOH acted as the radicals quencher for SO4− and ‘OH...
OH, TBA acted as the radicals quencher for OH. As shown in Fig. 9, the removal efficiency of CN is substantially decreased by 35.2% when the EtOH (500 mM) is added to the system. By contrast, the removal efficiency of CN is only slightly decreased by 18.0% after 30 min reaction when the TBA (500 mM) is added to the system. The results indicated that both OH and SO4 were responsible for the cyanide removal. In addition, the activated K2S2O8 and anode oxidation also had the role for cyanide removal.

4. Conclusions

In this work, the removal efficiency of Cu(CN)3 was largely enhanced with the addition of K2S2O8 reagent. In the cyanide removal process, the K2S2O8 reacted with copper cyanide complexes via a Fenton-like reaction, generating the activated radicals of SO4 and OH, which were responsible for the cyanide removal. At the same time, the increasing K2S2O8 concentration would increase the amount of CuO deposition on the anode surface. The generation of CuO on the anode exhibited the catalytic activities for cyanide removal. By the radical quenching experiments, the combination of anode oxidation and activated radicals was highly effective for cyanide removal. The cyanate was the main oxidation product in this electrochemical system. Therefore, the obtained results provided some valuable information for the treatment of Cu(CN)3 contaminated water.
**Fig. 9.** The removal efficiency of CN\(^-\) with the addition of different concentrations of EtOH and TBA ([EtOH\(]\) = 0.30 mM; [CN\(^-\)] = 0.50 mM; [K\(_2\)S\(_2\)O\(_8\)] = 1.00 mM; current density = 14.80 A/m\(^2\); [NaClO\(_4\)] = 2.00 mM; pH = 12.0).

**Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2017.07.006.

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