Enhancing destruction of copper (I) cyanide and subsequent recovery of Cu (I) by a novel electrochemical system combining activated carbon fiber and stainless steel cathodes

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ABSTRACT

Metal recovery is an attractive strategy for treatment of heavy metal wastewater. Heavy metal cyanide complexes are common pollutants in electroplating or mine industry wastewater, which usually hinder metal recovery due to the high stability of these complexes. A novel electrochemical system with activated carbon fiber and stainless steel combined cathodes was constructed for copper (I) cyanide ($\text{Cu}(\text{CN})_3^{2-}$) destruction and Cu(I) recovery. The destruction of cyanide was significantly improved by combining the stainless steel and activated carbon fiber cathodes due to the enhancement of electro-generated H_2O_2 , which was promoted due to catalysis by copper deposited at the cathodes. Both the destruction of $\text{Cu}(\text{CN})_3^{2-}$ and recovery of Cu(I) at 75 min attained $95.0 \pm 3.0\%$, which were higher than values obtained using stainless steel or activated carbon fiber as individual cathodes. The rate of $\text{Cu}(\text{CN})_3^{2-}$ destruction and Cu(I) recovery increased with increasing pH. The optimal current density was 50 A/m^2 , and higher current density caused more side reactions. $\text{Cu}(\text{CN})_3^{2-}$ was successively transformed into $\text{Cu}(\text{CN})_2^-$, CNO^- and Cu(I), and the liberated Cu(I) was recovered as Cu(0) on the stainless steel and activated carbon fiber electrodes.

1. Introduction

Metal recovery is an attractive strategy for the treatment of metal-laden wastewater, and such recovery provides great economic incentives for pollution control. The copper cyanide complex ($\text{Cu}(\text{CN})_3^{2-}$)

occurs widely in mining and electroplating effluents. The stability of this complex brings challenges to the recovery of Cu(I) ions from effluents.

Recovery of complexed metal ions from wastewater has been studied using many methods. Activated carbon favors adsorption of Cu

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(CN)₂[−] [1,2]. The Cu(I) can be recovered by an activated carbon adsorption and desorption process, followed by cyanide disposal and a Cu(I) deposition or precipitation stage [3]. The metal ions existing in the solution may form a complex with the anions, which would seriously reduce the biosorption of metal ions [4]. Nitrilotriacetic acid anhydride modified ligno-cellulosic material was utilized in a surface chelation and ion exchange chemical process, adsorbing Cd(II) and Pb(II) rapidly [5]. Ion exchange techniques can effectively remove complexes from dilute solution [6,7], with potential issues involved in elution [8]. Wet oxidation has been used to destroy cyanide species rapidly [9,10], with the recovery of heavy metal accomplished by precipitation as the oxide [11].

It has been demonstrated that electrochemical processing is a promising technology applicable for the efficient recovery of complexed metal ions. Electrochemical systems for metal cyanide complex removal can yield two benefits: (1) cyanide is oxidized to harmless cyanate and the metal cyanide complexes are destroyed; (2) the heavy metal can be removed or recovered simultaneously [12]. Szpyrkowicz et al. investigated cyanide oxidation and Cu(I) recovery by a reactor equipped with a stainless steel or Ti/Pt anode, and the performance of the reactor with the Ti/Pt anode was slightly better than that with the SS anode [13]. Flow reactors using Ti/TiO₂/RuO₂ (DSA-type) and graphite electrodes performed well for electro-oxidation of cadmium cyanide complexes and recovery of cadmium in batch recirculating mode [14]. An electrochemical reactor with graphite electrodes was employed for oxidation of cyanide and simultaneous recovery of cadmium in a typical plating rinse effluent. More than 99% of cadmium was recovered on the cathode surface at a cadmium concentration of 50 mg/L [15]. Generally, the electrolytic recovery for metal ions in dilute solutions is limited due to low mass transfer rates. To overcome such problems, many researchers have applied three-dimensional cathodes in electrolytic processes due to their high mass transfer rates [16]. Moreover, electrochemical generation of H₂O₂ on a carbon nano-tube electrode [17] or reticulated vitreous carbon electrode from O₂ reduction [18] can also efficiently oxidize cyanide. Therefore, the application of carbon electrodes in the electrochemical system benefits not only the destruction of Cu(CN)₃^{2−} but also the recovery of Cu(I).

Herein, a novel electrochemical system with two cathode materials, activated carbon fiber (ACF) and stainless steel (SS) coupled with a dimension stable anode (DSA), was constructed to enhance the decomplexation of Cu(CN)₃^{2−} and recovery of Cu(I). The effects of several major parameters including initial pH value, current density, and initial concentration on the Cu(CN)₃^{2−} destruction were evaluated. Lastly, the mechanism and pathway of Cu(CN)₃^{2−} decomplexation and Cu(I) reduction were discussed.

2. Materials and methods

2.1. Chemicals

Cuprous cyanide (CuCN), sodium cyanide (NaCN), perchloric acid (HClO₄), sodium hydroxide (NaOH) and potassium iodide (KI) were all purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals are analytical grade. Cu(CN)₃^{2−} solution was prepared through dissolution of cuprous cyanide in sodium cyanide solution with a molar ratio of Cu(I) to CN[−] of 1.0:3.0 according to a published procedure [19]. The water used for preparing and diluting the solutions was deionized water.

2.2. Configuration and description of the batch electrochemical reactor

The electrochemical system was equipped with a DSA anode with an active area of 35 cm² (70 × 50 mm). ACF and SS with the same active area were used as the #1 cathode and #2 cathode, respectively. The distance between electrodes was 2.0 cm. The electricity was supplied by a direct-current power source, model DH1719A (Dahua Instrument

Corporation of Beijing). The electrodes were arranged in a 600-mL glass beaker. Aluminum foil covered the beaker to prevent photolysis. NaClO₄ solution (0.5 mM) was used as the electrolyte solution. Saturated O₂ was maintained in electrolyte by bubbling compressed oxygen (greater than 99.9% purity) into the solution at atmospheric pressure, starting 30 min before electrolysis. The O₂ flow was kept 0.2 L/min by means of a flow controller placed at the end of the gas line.

2.3. Experiments

To prevent release of hydrocyanic acid (HCN), the pH of the cyanide solution was kept above 9.0 [20]. The pH of the solution was regulated using NaOH or HClO₄. Adsorption and electrochemical treatment experiments in batch mode were conducted in the reactor. The adsorption of Cu(CN)₃^{2−} by ACF was conducted as a control. The solution (400 mL) of Cu(CN)₃^{2−} was put into the reaction cell. The solution was magnetically stirred at 400 rpm to keep the chemicals uniform. 5.0 mL sample was drawn periodically out from the bulk solution for chemical analysis. Sufficient addition of potassium iodide was added to the samples to end the reaction before distillation. The quantity of potassium iodide was 1.3 times the initial H₂O₂ concentration. The samples were filtered before analysis of copper. Once Cu(I) was oxidized into Cu(II), Cu(OH)₂ precipitation took place under alkaline conditions, which would be removed by filtration. The copper in the filtrate was present as the cuprous cyanide complex. All of the experiments were conducted at least twice. The electrodes were taken out and rinsed with distilled water to remove the residual Cu(CN)₃^{2−} on the electrode surface, then dried at room temperature before reuse.

2.4. Analysis method

The pH was measured using a pH electrode connected to a pH analyzer (Orion Research, Inc., Beverly, MA). Total cyanide concentration was measured by a colorimetric method after distillation [21]. Cyanate can be hydrolyzed to produce carbonate and ammonium under acidic conditions, which was analyzed indirectly through ammonia measurement by the Nesslerization method [21]. Copper concentrations were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent Technology). The H₂O₂ concentration in solution was determined colorimetrically at 400 nm using potassium titanium oxalate solution [22]. All analytical measurements were made at least in triplicate, and the standard deviation was found to be below 5% in all cases.

The UV–Visible spectra of Cu(CN)₃^{2−} solutions were recorded at various reaction times for identification of the transformation products of the Cu(I) cyanide complex (Hitachi U3100, Japan). Changes in the morphology of the cathodes were observed using a JSM 6301 scanning electron microscope (SEM). X-ray (EDX) spectroscopy conducted in-situ in the SEM was used to analyze the composition of the electrode surface. A Kratos Axis Ultra X-ray photoelectron spectrometer (XPS) was further used to analyze the changes in the chemical states of elements on the electrode surface. Monochromatic Al K α radiation (225 W, 15 mA, 15 kV) was used as the radiation source. To compensate for charging effects, the binding energies were calibrated using the C1 s hydrocarbon reference peak at 284.80 eV.

3. Results and discussion

3.1. Enhanced destruction of Cu(CN)₃^{2−} and recovery of Cu(I)

The destruction of Cu(CN)₃^{2−} and recovery of Cu(I) by the electrochemical systems with diverse arrangements of anode/cathode (DSA/SS, DSA/ACF, DSA/SS-ACF) were investigated at pH 9.0 and current density of 75 A/m². The adsorption of Cu(CN)₃^{2−} by ACF was also examined as a control one. Fig. 1a illustrates the variation in

Fig. 1. Decay of cyanide concentration (a) and Cu(I) concentration (b), and H₂O₂ concentration in bulk solution (c) as a function of electrolysis time. Operating conditions: initial concentration of $\text{Cu}(\text{CN})_3^{2-}$ was 0.4 mM, current density was 75 A/m², pH was 9.0, Concentration of electrolyte NaClO_4 was 50 mM.

cyanide concentration during the process of electrochemical treatment and ACF adsorption. When SS was used as the individual cathode, the oxidation efficiency of cyanide was about $70.0 \pm 3.0\%$ at 75 min reaction duration. The oxidation efficiency of cyanide rose to $80 \pm 4.1\%$ when the SS cathode was replaced by the ACF cathode. The destruction of cyanide was further improved by combining SS and ACF as the cathodes, and $91.0 \pm 4.9\%$ of cyanide was oxidized. This suggested that the electrochemical reactor with combined ACF and SS cathodes was more effective for destruction of $\text{Cu}(\text{CN})_3^{2-}$. In contrast, only 8% of cyanide was removed by ACF adsorption.

Fig. 1b shows the recovery of Cu(I) by the electrochemical system with diverse anode/cathode arrangements (DSA/SS, DSA/ACF, DSA/SS-ACF). When SS was used as the only cathode, only $38.0 \pm 2.7\%$ of Cu(I) was recovered at 75 min. The recovery efficiency of Cu(I) was increased significantly when the SS cathode was replaced by the ACF cathode, attaining $87.5 \pm 3.1\%$. Combining the SS and ACF cathodes, the recovery efficiency of Cu(I) reached $95.0 \pm 3.0\%$. The activated carbon concentrator cathode increased the concentration of Cu(I) near the electrode surface, which led to the increase in metal recovery efficiency [23]. In the control experiment, ACF without any applied charge had poor adsorption of complexed Cu(I). The isoelectric point of ACF is 6.0–6.7 [24,25]. It is reasonable that under alkaline pH conditions the surface at ACF is negative, which would electrostatically repel the $\text{Cu}(\text{CN})_3^{2-}$.

0.7 mM H₂O₂ was determined in the bulk solution when the ACF was used as the cathode, which showed that H₂O₂ could be

electrochemically generated at the surface of ACF in the presence of O₂ (Fig. 1c). Compared to the ACF cathode alone, the generation of H₂O₂ in the electrochemical system with combined ACF and SS cathodes decreased to 0.5 mM. This is because the current density though the ACF cathode decreased in the combined cathode system. However, the cyanide oxidation was significantly enhanced, and the cyanide was nearly all removed at 75 min. It can be easily observed that only 8% of cyanide was removed via ACF adsorption without any electro-oxidation. Therefore, we can conclude that H₂O₂ generated at the ACF surface in the electrochemical reactor enhanced the destruction of $\text{Cu}(\text{CN})_3^{2-}$. The recovery of Cu(I) corresponded with the cyanide oxidation, which implied that the Cu(I) cannot be recovered until $\text{Cu}(\text{CN})_3^{2-}$ is destroyed. The copper at plate electrode dissolved in the presence of cyanide and formed a cuprous complex, which catalyzed anode oxidation and H₂O₂ oxidation for destruction of the complex [26].

3.2. Effect of key parameters on $\text{Cu}(\text{CN})_3^{2-}$ destruction and Cu(I) recovery

3.2.1. Effect of pH

Fig. 2a shows the decay of cyanide with reaction time at various pH values. It was seen that the oxidation rate of cyanide was accelerated with the increase of pH. At pH 11.0 and 12.0, cyanide was oxidized nearly completely, and $\text{Cu}(\text{CN})_3^{2-}$ was destroyed at 60 min. The direct electrochemical oxidation of cyanide to cyanate in alkaline media occurs with consumption of hydroxide ion [27]. Thus, the higher pH benefited destruction of $\text{Cu}(\text{CN})_3^{2-}$ by the electrochemical method. In addition, Cu(I) oxides formed on the anode surface at pH 12.0, which enhanced the anodic oxidation of cyanide in the electrochemical system [28]. The oxidation of cyanide was faster at pH 9.0 than at pH 10.0 or 11.0, which was not consistent with the above results. As shown in Fig. 2b, the recovery of Cu(I) was also enhanced with the increase of pH. The recovery of Cu(I) was consistent with the oxidation of cyanide. At pH 12.0, 0.4 mM Cu(I) was almost completely recovered at 60 min, while the recovery efficiency of Cu(I) only attained $70.0 \pm 3.6\%$ at pH 9.0. Recovery of copper is strictly related to the preliminary destruction of its complexes with cyanide. The higher pH benefited destruction of $\text{Cu}(\text{CN})_3^{2-}$ by the electrochemical method. Consequently, as expected, the removal of Cu(I) shows a similar pH dependence as cyanide oxidation. As shown in Fig. 2c, the H₂O₂ concentration in bulk solutions at pH 9.0 was higher than that at pH 10.0 and 11.0. Thus, the destruction of $\text{Cu}(\text{CN})_3^{2-}$ occurred at the anode surface in the constructed electrochemical system, with H₂O₂ oxidation in bulk solution being secondary. The H₂O₂ concentration in bulk solution at pH 12.0 was the highest. The consumption of H₂O₂ for cyanide oxidation slowed down at higher pH, leading to the accumulation of H₂O₂.

3.2.2. Effect of current density

We investigated the destruction of $\text{Cu}(\text{CN})_3^{2-}$ by the electrochemical system under various current densities (25 A/m², 50 A/m², 75 A/m² and 100 A/m²). As shown in Fig. 3a, the increase of current density expectedly led to the faster oxidation of cyanide, so that shorter times were needed for attaining $92.1 \pm 2.6\%$ cyanide oxidation at 50 A/m². As the current density increased from 50 A/m² to 75 A/m² or 100 A/m², the oxidation of cyanide slowed down slightly. It is clear that the cyanide oxidation is optimal at the current density of 50 A/m². As shown in Fig. 3b, the recovery of Cu(I) was also optimal with the current density of 50 A/m². With increasing current density from 50 A/m² to 75 A/m² or 100 A/m², the recovery of Cu(I) also slowed down. Higher current density such as 75 A/m² or 100 A/m² did not increase the destruction of $\text{Cu}(\text{CN})_3^{2-}$ and recovery of Cu(I), which can be explained by the enhancement of parasitic side reactions. The reduction of H₂O₂ to H₂O and hydrogen gas evolution occurred at the cathode surface [29]. Higher current density corresponds to higher potential, so reduction of H₂O₂ intensified, as well as evolution of H₂. Similarly, the maximum H₂O₂ concentration was obtained at 50 A/m², i.e., 0.95 mM after electrolysis for 45 min (Fig. 3c).

Fig. 2. Decay of cyanide concentration (a) and Cu(I) concentration (b), and H_2O_2 concentration in bulk solution (c) as a function of electrolysis time under various pHs. Operating conditions: initial concentration of $\text{Cu}(\text{CN})_3^{2-}$ was 0.4 mM, current density was 75 A/m^2 , concentration of electrolyte NaClO_4 was 50 mM, pH were 9.0, 10.0, 11.0 and 12.0, respectively.

3.2.3. Effect of initial concentration

The influence of the initial concentration on $\text{Cu}(\text{CN})_3^{2-}$ destruction and Cu(I) recovery was also studied. The decay of the cyanide concentration is depicted in Fig. 4a. More rapid reduction of cyanide was obtained for the treatment of 0.2 mM $\text{Cu}(\text{CN})_3^{2-}$, and the destruction efficiency attained $92.0 \pm 4.8\%$ after 60 min. With initial concentrations of 0.4 mM and 0.8 mM, $95.0 \pm 2.6\%$ and $90.0 \pm 3.1\%$ of cyanide was oxidized at 75 min, respectively. A longer time for destruction was required as the initial concentration of $\text{Cu}(\text{CN})_3^{2-}$ increased. A similar decay trend with electrolysis time was observed between Cu(I) and cyanide. As shown in Fig. 4b, Cu(I) was almost completely removed at 45 min for an initial concentration of 0.2 mM $\text{Cu}(\text{CN})_3^{2-}$. With the initial concentration increasing to 0.4 and 0.8 mM, the recovery of Cu(I) slowed down, and the recovery efficiency was $85.0 \pm 3.7\%$ and $75.0 \pm 2.3\%$ at 75 min, respectively. The removals of cyanide and Cu(I) were not affected significantly as the initial $\text{Cu}(\text{CN})_3^{2-}$ concentration increased from 0.4 mM to 0.8 mM. This was because the catalysis of $\text{Cu}(\text{CN})_3^{2-}$ destruction by copper was boosted with the increase of initial concentration [30,31]. The maximum H_2O_2 concentration in the solution decreased from 0.6 mM to 0.4 mM as the initial concentration of $\text{Cu}(\text{CN})_3^{2-}$ increased from 0.4 mM to 0.8 mM, which implied that the consumption of H_2O_2 for destruction of $\text{Cu}(\text{CN})_3^{2-}$ increased (Fig. 4c).

Fig. 3. Decay of cyanide concentration (a) and Cu(I) concentration (b), and H_2O_2 concentration in bulk solution (c) as a function of electrolysis time under various current densities. Operating conditions: initial concentration of $\text{Cu}(\text{CN})_3^{2-}$ was 0.4 mM, pH was 9.0, concentration of electrolyte NaClO_4 was 50 mM, current density were 25 A/m^2 , 50 A/m^2 , 75 A/m^2 and 100 A/m^2 , respectively.

3.3. Mechanism of $\text{Cu}(\text{CN})_3^{2-}$ destruction in the electrochemical reactor

Firstly, we used UV–Vis spectra to explore the destruction process of $\text{Cu}(\text{CN})_3^{2-}$ in the electrochemical reactor. Meanwhile, the intermediate and final products of cyanide oxidation were analyzed. The cyanide and copper balances were also checked. The deposition and transformation of copper on the electrode surface were identified by SEM-EDX and XPS.

3.3.1. Transformation of $\text{Cu}(\text{CN})_3^{2-}$ with reaction evolution

As shown in Fig. 5, two absorption bands at 208 nm and 238 nm were observed before the reaction. The assignment of the two bands to absorption by the $\text{Cu}(\text{CN})_3^{2-}$ complex has been reported by previous researchers [19,32]. The two bands declined as the reaction proceeded, and another two peaks at 223 nm and 234 nm were observed starting at 15 min of reaction, which were reported to be the absorption peaks of $\text{Cu}(\text{CN})_2^-$ [32,33]. The above results suggested that $\text{Cu}(\text{CN})_3^{2-}$ had been partially converted into $\text{Cu}(\text{CN})_2^-$ at 15 min. The absorption bands at 208 nm, 223 nm and 234 nm all decreased at 60 min, implying that $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_2^-$ were being destroyed but that some still remained. At 75 min, the absorption bands of both $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_2^-$ disappeared, indicating that the Cu(I) cyanide complex was

Fig. 4. Decay of cyanide concentration (a) and Cu(I) concentration (b), and H_2O_2 concentration in bulk solution (c) as a function of electrolysis time with various initial $Cu(CN)_3^{2-}$ concentration. Operating conditions: pH was 9.0, current density was $75 A/m^2$, concentration of electrolyte $NaClO_4$ was 50 mM, initial $Cu(CN)_3^{2-}$ concentration were 0.2 mM, 0.4 mM and 0.8 mM, respectively.

destroyed completely.

3.3.2. Analysis of product and mass balance

Fig. 6a shows the concentration profiles of cyanide and cyanate at various reaction times. The concentration of cyanate increased as the reaction proceeded. After 75 min, over 95% of the cyanide was oxidized and converted into cyanate. The sum of the cyanide and cyanate concentrations nearly equaled the initial cyanide concentration throughout the experiment. A final yield of cyanide to cyanate of $1.02 \pm 0.03 \text{ mmol } CNO^-/\text{mmol } CN^-$ was obtained from the experimental data (Fig. 6a). This value, which is similar to the maximum theoretical yield (1.00), proves that cyanate is the only product.

This has also been demonstrated by previous studies on cyanide oxidation by electrochemical or H_2O_2 oxidation. Cyanide complexed with copper can be oxidized electrochemically to cyanate with pH in the range of 9.0–12, and cyanate is finally converted to carbonate and nitrogen gas at pH of larger than 12.0 [27]. The copper oxide film was found to be catalytic under very alkaline conditions, capable of electro-

Fig. 5. UV-Visible spectra of $Cu(CN)_3^{2-}$ solution at various reaction time. Operating conditions: initial concentration of $Cu(CN)_3^{2-}$ was 0.4 mM, current density was $75 A/m^2$, pH was 9.0, concentration of electrolyte $NaClO_4$ was 50 mM.

Fig. 6. Concentration profile of cyanide and cyanate (a) and Cu(I) species (b) plotted against time. Operating conditions: initial concentration of $Cu(CN)_3^{2-}$ was 0.4 mM, current density was $75 A/m^2$, pH was 9.0, concentration of electrolyte $NaClO_4$ was 50 mM.

oxidizing cyanate to nitrate [13,34]. The pathway of cyanide oxidation by electrochemical reactor depends on reaction condition, as well as other method like wet oxidation, low temperatures favored the pathway leading to the formation of carbon dioxide and nitrogen,

whereas the formation of formate and ammonia is favored at high temperatures [9].

The copper mass distributions in the electrochemical processes were also investigated. As shown in Fig. 6b, most of the Cu(I) in the solution occurred as $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_2^-$ before 30 min of reaction. The deposition of Cu(0) on the cathodes appeared starting at 30 min. With further decomplexation of $\text{Cu}(\text{CN})_3^{2-}$, the Cu(0) deposited on the ACF cathode surface at 60 min accounted for $87.5 \pm 3.0\%$ of the initial Cu(I) concentration and increased as the reaction proceeded. 7.5% of Cu(I) was deposited on the SS cathode surface. The precipitate in the solution after filtration was a light blue crystalline powder, which was assumed to be $\text{Cu}(\text{OH})_2$. This indicated that the oxidation of liberated Cu(I) into Cu(II) occurred under alkaline conditions with sufficient dissolved oxygen. $\text{Cu}(\text{OH})_2$ in aqueous solution counted for 5% of the copper. It can be concluded that the efficient destruction of $\text{Cu}(\text{CN})_3^{2-}$ was responsible for the high recovery percentage of Cu(I) ions in the electrochemical process.

3.3.3. Observation and identification of copper deposited at the cathode

SEM was employed to characterize the surface morphology and structure of cathode deposits after the reactions. The elemental composition of deposits on the cathode surface was analyzed by SEM-EDX. As shown in Fig. 7, the deposition of copper at the SS and ACF surface was observed after 75 min of electrochemical reaction. Granular deposits of copper can be observed on the ACF cathode surface with a block-like structure. A flocculent structure was observed on the SS cathode surface, and the electrodeposited copper was found to be nonuniform and slightly rough. The copper was accumulated on the SS surface, and that on the ACF was relatively thin and even. The speciation of deposited copper on cathode surfaces was examined by XPS. Fig. 8 shows the high-resolution XPS spectra for the ACF cathode after the reaction. A peak with binding energy of 933.10 eV corresponding to Cu(0) [35] was observed in the XPS spectrum of the ACF sample, which implied that the Cu(I) was recovered as Cu(0) successfully.

Fig. 8. High-resolution Cu 2p 3/2 peak of XPS spectrum at the ACF electrode after treatment. Operating conditions: initial concentration of $\text{Cu}(\text{CN})_3^{2-}$ was 0.4 mM, current density was 75 A/m^2 , pH was 9.0, concentration of electrolyte NaClO_4 was 50 mM.

3.3.4. A proposed reaction mechanism

It has been well recognized that the electrochemical oxidation of copper cyanide complex solutions under alkaline conditions occurs via the following reactions (Eqs. (1)–(3)) [36]. Copper electrodeposition occurs on the cathodes simultaneously with the destruction of $\text{Cu}(\text{CN})_2^-$. In-situ generated H_2O_2 on the ACF cathode surface enhances the destruction of $\text{Cu}(\text{CN})_3^{2-}$ (Eqs. (4)–(6)). The liberated Cu(I) is reduced on at the cathodes as metallic copper (Eq. (7)).

Fig. 7. SEM images and EDX spectra of the deposit on electrode surface after treatment (A) SS electrode and (B) ACF electrode. Operating conditions: initial concentration of $\text{Cu}(\text{CN})_3^{2-}$ was 0.4 mM, current density was 75 A/m^2 , pH was 9.0, concentration of electrolyte NaClO_4 was 50 mM.

3.4. Performance stability of the constructed electrochemical reactor

Repetitive experiments were conducted to investigate the durability of the constructed electrochemical system for destruction of $\text{Cu}(\text{CN})_3^{2-}$ and recovery of Cu(I). The treatment process was repeated four times. As shown in Fig. 9a, the concentration of cyanide after the first cycle decreased by $81.1 \pm 4.5\%$, while it declined by about $97.6 \pm 3.9\%$ at the fourth cycle with reaction time of 60 min. Correspondingly, the concentration of Cu(I) after the first cycle decreased by $84.2 \pm 3.9\%$ after 75 min reaction, and it decreased by about $97.3 \pm 2.7\%$ at the fourth cycle with reaction time of 60 min (Fig. 9b). The efficiency of cyanide oxidation and Cu(I) recovery went up gradually during the four-cycle treatment process, which could have resulted from catalysis of $\text{Cu}(\text{CN})_3^{2-}$ destruction by H_2O_2 oxidation and anode oxidation by copper deposited on the cathode surface. As the dissolution of copper deposited at the cathodes occurred in the presence of cyanide ions, the oxidation of cyanide by H_2O_2 was increased due to the catalysis by

copper [31]. Similar results were also reported in other articles [32,33]. As more copper deposited at the cathode surfaces during the treatment, more $\text{Cu}(\text{CN})_3^{2-}$ was destroyed due to the catalysis of the reaction by copper. Therefore, the electrochemical reactor with ACF-SS combined cathodes is a promising method for destruction of $\text{Cu}(\text{CN})_3^{2-}$ and recovery of Cu(I).

4. Conclusions

In summary, we have demonstrated a novel electrochemical reactor based on the use of ACF and SS cathodes coupled with a DSA anode to destroy $\text{Cu}(\text{CN})_3^{2-}$ and recover Cu(I). The destruction of cyanide was significantly improved by combining the SS and ACF cathodes, and 95% of cyanide was oxidized. The recovery efficiency of Cu(I) attained 95%, which is higher than obtained with the SS or ACF as individual cathodes. The rate of destruction of $\text{Cu}(\text{CN})_3^{2-}$ and recovery of Cu(I) increased with increasing pH in alkaline conditions. The best performance of the electrochemical reactor occurred at current density of 50 A/m^2 . Higher values of current density intensified the side reactions at the electrode surface.

$\text{Cu}(\text{CN})_3^{2-}$ destruction mainly occurred at the DSA anode surface, and H_2O_2 generated at the ACF surface also contributed to $\text{Cu}(\text{CN})_3^{2-}$ destruction. The cyanide was oxidized into cyanate, and the $\text{Cu}(\text{CN})_3^{2-}$ was successively transformed into $\text{Cu}(\text{CN})_2^-$ and Cu(I). The liberated Cu(I) was recovered as Cu(0) on the cathodes, especially the ACF cathode, which accounted for 87.5% of the recovered Cu(I).

In this work a novel electrochemical system was constructed for enhancing the destruction of $\text{Cu}(\text{CN})_3^{2-}$ and recovery of Cu(I) at lab scale. These data can provide a reference for pilot scale electrochemical reactor design parameters, such as current density (50 A/m^2) and hydro retention time (75 min). A pilot study for treating copper cyanide wastewater will be conducted to further optimize the reaction parameters, observe long-term performance and estimate operational cost.

The environment health & safety, water quality, water quantity and power supply will also be considered in engineering stage. The pH of solution was kept above 9.0 to prevent the release of free cyanide. This process can be realized by on-line pH meter and automatic acid adding system in project. Moreover, no by-product was formed in electrochemical oxidation or H_2O_2 oxidation process. In-situ generation of H_2O_2 using such system can avoid the risk of leak in transport and store. The suspended solid particles in the effluent should be removed by pre-filtration or precipitation before feeding into electrochemical reactor. If the wastewater is large, pre-concentration may be applied by nanofiltration or reverse osmosis. The project site should have sufficient power supply.

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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.2017.08.075>.

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Fig. 9. The destruction of $\text{Cu}(\text{CN})_3^{2-}$ (a) and recovery of Cu(I) (b) in the electrochemical system during four runs. Operating conditions: initial concentration of $\text{Cu}(\text{CN})_3^{2-}$ was 0.4 mM , current density was 75 A/m^2 , pH was 9.0, concentration of electrolyte NaClO_4 was 50 mM .

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