



# Cyanide removal with a copper/active carbon fiber Cathode via a combined oxidation of a Fenton-like reaction and *in situ* generated copper oxides at anode



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## ABSTRACT

Cyanide is widely present in electroplating wastewater or metallurgical effluents. In the present study, the electrochemical destruction of cyanide with copper/active carbon fiber (Cu/ACF) composite cathode and Dimensionless Stable Anode (DSA) under alkaline conditions was investigated. Firstly, various cathode materials including stainless steel, ACF, copper plate and Cu/ACF were compared for cyanide removal. Cyanide removal efficiencies by the individual H<sub>2</sub>O<sub>2</sub> oxidation generated using ACF cathode or individual DSAs anodic oxidation using stainless steel cathode were less than 20%. Using Cu/ACF as the cathode, the removal efficiency of cyanide was largely improved compared with other cathodes. At the current density of 50.01 A/m<sup>2</sup> and the geometric area ratio of Cu/ACF=1:2, the concentration of cyanide was lowered from 1.50 to 0.07 mM within 90 minutes. Due to the dissolution of copper plate by the cyanide ions, the concentration of copper ions increased rapidly at first and then decreased with the efficient destruction of cyanide ions. Combined with the SEM-EDX and XPS analysis of the anode surface, it was concluded that the generation of copper oxides occurred at the anode surface, which exhibited catalytic activities for cyanide removal. Meantime, ESR results confirmed the generation of hydroxyl radicals in solution. Hydroxyl radicals generated in the reaction between copper cyanides complex and H<sub>2</sub>O<sub>2</sub> were responsible for the cyanide removal. Once the cyanide removal was completed, part of the copper ions was reduced and deposited onto the cathode and part of the copper ions was deposited onto the anode. Therefore, the next recycle for cyanide removal by copper oxides catalytic oxidation at the anode and the Fenton-like oxidation in the solution began. Cyanate was identified as the only product in this system.

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## 1. Introduction

Cyanides are discharged by various industries, particularly in metallurgical processes, plating and surface finishing [1,2]. Many strategies have been developed to remove cyanides from wastewater including activated carbon adsorption [3,4], coagulation [5] or ion-exchange [6]. These processes can generate highly concentrated products containing toxic cyanides, which need to be further treated. Alkaline chlorination is widely used for the cyanide removal, which will lead to the formation of toxic cyanogens chloride [7] and chloride disinfection by-products [8]. By contrast, cyanides can be directly converted into less harmful products by

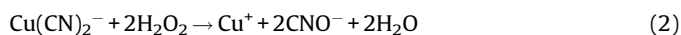
employing oxidation methods, such as ozonation [9], electrochemical oxidation [10,11], photocatalysis [12,13], ferrate oxidation [14,15] and wet oxidation [16].

The electrochemical method was widely investigated for the cyanide and copper cyanide destruction [17,18]. An electrochemical system with stainless-steel anode was generally used for cyanide destruction and copper electrodeposition from dilute wastewater. In the electrochemical removal of copper cyanide complexes, *in situ* deposition of a copper oxyhydroxide film occurred on the anode, which exhibited electrocatalytic properties for the cyanide removal. The cyanide removal efficiency of the electrochemical process depended on the solution pH, applied potential and the type of the cathode and anode materials [11,19]. The electrochemical removal efficiency of individual cyanide was generally limited. However, In the case of copper cyanide complexes degradation, the cyanide removal efficiency increased

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due to the catalytic process induced by the deposited copper oxides at the anode. With respect to the copper recovery, the deposition of copper ions onto the cathode was desired.

$\text{H}_2\text{O}_2$  oxidation of several cyanide species had been investigated recently. The direct oxidation of cyanide by  $\text{H}_2\text{O}_2$  proceeded rather slowly [20]. It was known that the non-selective and highly oxidative hydroxyl radicals were formed in the presence of  $\text{H}_2\text{O}_2$  and ferrous or ferric salts, namely Fenton reaction [21]. With respect to the cyanide oxidation, iron cyanide complexes generated, which were known to be refractory and difficult to be furthermore treated. In the case of copper cyanide complexes, it was found that  $\text{H}_2\text{O}_2$  can oxidize  $\text{Cu}(\text{CN})_3^{2-}$  to  $\text{Cu}(\text{CN})_2^-$ . The successive oxidation of cyanide from  $\text{Cu}(\text{CN})_2^-$  led to the Cu(I) liberation. Cu(I) was oxidized into Cu(II) with the formation of hydroxyl radicals ( $\cdot\text{OH}$ ) [22,23] through Eqs. (1)–(3).



Therefore, it was proposed that a Fenton-like reaction might occur between  $\text{H}_2\text{O}_2$  and  $\text{Cu}(\text{CN})_3^{2-}$ , leading to the efficient removal of cyanide ions [24,25].

In the current work, the combined cathode of copper plate and activated carbon fiber was designed and used to electrochemically destroy the cyanide ions. This paper investigated the effects of initial pH, current density, geometry area ratio of Cu/ACF and stability of the system. Furthermore, the oxidation mechanism was also investigated. By the SEM-EDX and XPS analysis of the anode surface variation, it was concluded that generation of copper oxides occurred at the anode surface, which exhibited catalytic activities for cyanide removal. Meantime, the ESR results confirmed the generation of hydroxyl radicals. The combined action of anode catalysis and hydroxyl radicals oxidation removed cyanide.

## 2. Experimental

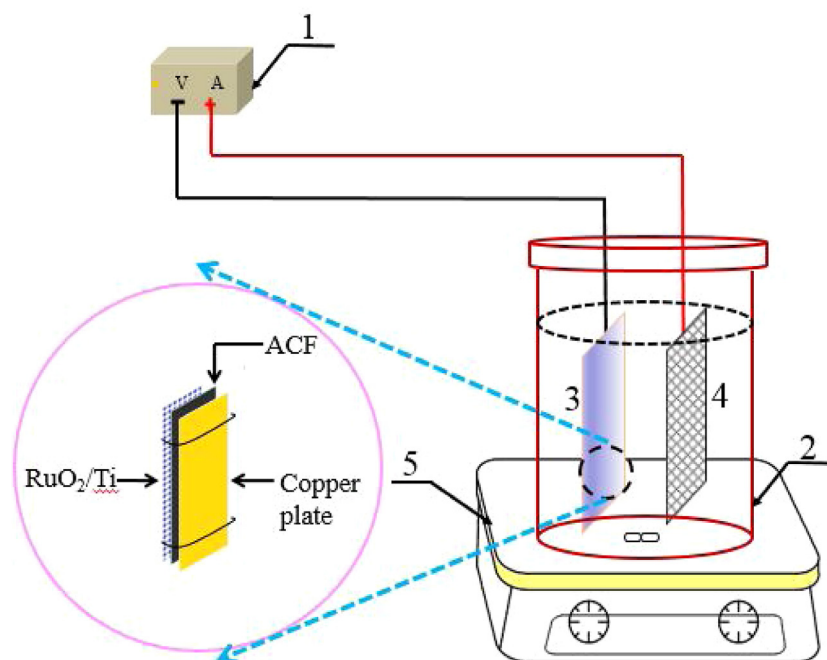
### 2.1. Reagent

Sodium cyanide, hydrogen peroxide (30.0 wt.%), sodium sulfate, hydrogen nitrate and sodium hydroxide were all purchased from Sinopharm chemical reagent Co., Ltd., China. The 5, 5-dimethylpyrroline-N-oxide (DMPO) was purchased from the Sigma chemical corporation and stored at  $-20^\circ\text{C}$ . All chemicals were used without further purification and all solutions were prepared using freshly prepared Milli-Q water.  $\text{RuO}_2/\text{Ti}$  mesh was purchased from Beijing Henglitai Corporation. ACFs were purchased from Nantong Senyou Carbon Fiber Co., Ltd., Nantong, China. A BET specific surface area of the ACFs was  $900\text{--}1000\text{ m}^2\text{ g}^{-1}$  with a thickness of 1–5 mm. The thickness of Copper plate was about  $35\ \mu\text{m}$  (Tianjin Fuchen chemical reagents factory).

### 2.2. Experimental section

The experiments were performed in a glass reactor with 200 mL cyanide solutions. The initial concentration of cyanide ions was 1.5 mM. As shown in Fig. 1,  $\text{RuO}_2/\text{Ti}$  mesh was used as the anode and the various cathode materials including ACF, copper plate were combined with  $\text{RuO}_2/\text{Ti}$  as composite cathode. In this composite cathode, the  $\text{RuO}_2/\text{Ti}$  electrode was directly connected to the negative electrode of direct-current (DC) power, which was equivalent to the electron transferring media. The electrochemical experiments were performed at the constant current mode controlled by a DC power (DH1718E-6, Dahua Electronic, Co., Ltd., Beijing, China). Before using the ACFs, the ACFs were cut into pieces with the size of  $10\text{ cm} \times 20\text{ cm}$  and then kept in boiling water for 1 h to remove soluble salts. After being dried at  $100 \pm 5^\circ\text{C}$  for 6 h, the ACFs were further cut into  $3\text{ cm} \times 5\text{ cm}$  pieces and used as the cathode.

The pH of cyanide solutions was maintained at alkaline conditions to avoid the release of HCN gas [26]. Therefore, the effect of pH on the cyanide oxidation was investigated in the pH range of 10.0–12.0. The pH was adjusted by  $\text{H}_2\text{SO}_4$  (0.2 M) or NaOH



**Fig. 1.** The schematic of the electrochemical reactor: (1) DC power supply; (2) Electrolytic cell; (3) Composite cathode of ACF and Copper plate; (4)  $\text{RuO}_2/\text{Ti}$  mesh anode; (5) Magnetic stirring apparatus.

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