



## Persulfate enhanced photoelectrocatalytic degradation of cyanide using a $\text{CuFe}_2\text{O}_4$ modified graphite felt cathode

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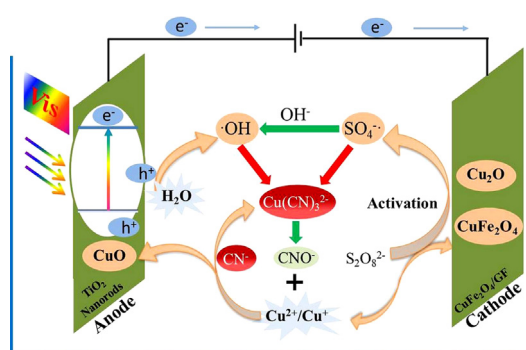
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### HIGHLIGHTS

- Degradation of  $\text{CN}^-$  with  $\text{CuFe}_2\text{O}_4$  cathode was enhanced by persulfate.
- A Fenton-like reaction occurred between persulfate and copper cyanides.
- $\text{OH}^\cdot$  and  $\text{SO}_4^{\cdot-}$  generated were responsible for  $\text{CN}^-$  removal.
- The PEC/PS system showed high efficiency and stability for  $\text{CN}^-$  removal.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

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### ABSTRACT

In order to remove cyanide ( $\text{CN}^-$ ) from wastewater, a photoelectrocatalytic (PEC) system was constructed using  $\text{TiO}_2$  nanorods (NRs) anode and  $\text{CuFe}_2\text{O}_4$  modified graphite felt ( $\text{CuFe}_2\text{O}_4/\text{GF}$ ) cathode. With the addition of persulfate (PS), the performance of PEC for the removal of  $\text{CN}^-$  with an initial concentration of 0.9 mM was increased from 31.10% to 98.21% in 120 min and the pseudo-first-order rate constant was calculated to be  $0.0314 \text{ min}^{-1}$ . The removal rate of  $\text{CN}^-$  was accelerated with the decrease of initial  $\text{CN}^-$  concentration and the increase of PS dose. The optimal bias potential for the removal of  $\text{CN}^-$  and the recovery of Cu was 1.00 V. Results of radical quenching experiments and electron spin resonance analysis suggested that  $\text{OH}^\cdot$  and  $\text{SO}_4^{\cdot-}$  were generated by a Fenton-like process in the PEC/PS system. As proved by the XPS analysis, Cu(II) in  $\text{CuFe}_2\text{O}_4$  cathode was dissolved by  $\text{CN}^-$  into solution and then partially transformed to Cu(I). When  $\text{CN}^-$  was removed, dissolved Cu ions were deposited onto the surface of  $\text{CuFe}_2\text{O}_4$  cathode forming  $\text{Cu}_2\text{O}$ . In addition, the dissolved Cu ions can also be deposited on  $\text{TiO}_2$  photoanode forming  $\text{CuO}$ . Cu(I) ions reacted with PS through a Fenton-like reaction, generating  $\text{SO}_4^{\cdot-}$ , which enhanced the oxidation ability of the PEC/PS system. The results provided a promising way to treat the industrial cyanide effluents efficiently.

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## 1. Introduction

Cyanide containing water is broadly generated in various industrial processes such as electroplating, coking, mineral processing, metal finishing and petrochemical. Because of its high toxicity, cyanide must be adequately removed prior to discharge. Various oxidation processes such as alkaline chlorination [1], anodic oxidation [2,3] and wet oxidation [4] have been studied for the removal of cyanide. The most conventional process that has been used in cyanide oxidation is the alkaline chlorination process, in which  $\text{HOCl}^-$ ,  $\text{OCl}^-$ , or  $\text{ClO}_2$  are used as oxidants. However, the main disadvantages of this process are the slow oxidation rate, low efficiency in the oxidation of cyanide-metal complexes, forming toxic by-product cyanogen chloride and the generation of a large amount of sludge [5,6]. Therefore, the development of a more efficient and cost-effective treatment technology for cyanide removal is desired.

Photocatalysis, especially  $\text{TiO}_2$  based photocatalysis process, has been employed for cyanide removal [7,8]. The photocatalytic removal efficiency of cyanide was more than 90.0% in the presence of  $\text{TiO}_2$ @yeast hybrids under UV-light irradiation [9]. The results showed that cyanide (50 mg/L) was destructed up to 94% in visible light by S, N- $\text{TiO}_2$ /glass micro-bead [10]. Unfortunately,  $\text{TiO}_2$  when applied as a suspension or slurry has to be filtered, making this approach uneconomical and preventing the industrial application of this process for the cyanides elimination. The electrochemical oxidation of cyanide and copper cyanides has been largely investigated. The results indicated that rapid oxidation of cyanide to cyanate was observed with the formation of a black copper oxide film at the anode. However, the overdose copper oxide film will limit the oxidation reaction of cyanide or copper cyanide [11]. Photoelectrocatalytic (PEC) process can achieve a simultaneous decomplexation of copper cyanide complexes and copper recovery by the cathodic reduction process. Copper cyanide complexes were destroyed at the photoanode, and the liberated copper ions were electrodeposited on the cathode. In this process, destruction of copper cyanide mainly occurred near the photoanode with a relatively low efficiency [12]. Therefore, the efforts on enhancing the photoelectrocatalytic efficiency should be made.

To further improve the performance of the PEC system, various oxidizing agents were added into the PEC system. Combining UV irradiation and chemical oxidizing agents, more oxidative radical species, mainly hydroxyl radicals ( $\cdot\text{OH}$ ) are generated, which can be used for oxidizing the cyanide to nontoxic compounds [13–19]. The oxidative radical species can be generated from ozone ( $\text{O}_3/\text{H}_2\text{O}_2$ ,  $\text{O}_3/\text{UV}$ ,  $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$ , and catalytic ozonation) or  $\text{H}_2\text{O}_2$  (Fenton and Fenton-like) catalytic process [20]. The  $\text{O}_3$  based methods usually require sophisticated ozone generation systems, including gas pretreatment unit, ozone generator, cooling system and waste gas destruction system. The removal of Ag-cyanide complexes was 74.1% when a metal-free g- $\text{C}_3\text{N}_4$  photoanode was used in a PEC process assisted by  $\text{H}_2\text{O}_2$  [21]. The  $\text{H}_2\text{O}_2$  based processes require large amount of chemicals for pH adjustment and also lead to the production of a larger amount of sludge. Although the Fenton-like process using supported iron oxides can partially overcome the above mentioned limitations, the efficiency of Fenton-like processes using solid catalysts is still relatively low concerning both  $\text{H}_2\text{O}_2$  utilization rate and reaction time [22].

As an alternative to  $\cdot\text{OH}$  that is used for the degradation of different pollutants, sulfate radical ( $\text{SO}_4^{\cdot-}$ ) is attracting increasing interests because of its high oxidizing ability with a standard oxidation potential of 2.01 V [23–30].  $\text{SO}_4^{\cdot-}$  can be generated from the activation of persulfate (PS) or peroxymonosulfate (PMS) by UV irradiation [31], heating [32], ultrasonic [33] and transition metal catalysts [34]. Among these activation technologies, the activation by transition metal ion or transition metal oxides is widely investigated [35]. A well-crystallized CuO and a spinel copper ferrite ( $\text{CuFe}_2\text{O}_4$ ) were reported to be active in generating  $\text{SO}_4^{\cdot-}$  from PS and PMS. However, high leaching Cu ions in the treated water is a major limitation for industrial

application. In comparison, the leaching of Cu ions from  $\text{CuFe}_2\text{O}_4$  solid phase is efficiently reduced [20].

In our previous work, 96.0% of total cyanide was degraded at a voltage of 2.0 V using titania nanotube electrodes via a PEC process. [36] PEC oxidation of Cu-cyanide complexes was performed and the total cyanide is nearly removed completely with a  $\text{TiO}_2$  nanotube electrode at 2.5 V [37]. The PEC processes mentioned above were intensified by various anodes. In this work, to establish a more efficient and stable system for the cyanide oxidation under visible light irradiation at a low bias potential, we investigated the degradation of cyanide in the PEC/PS system using a  $\text{CuFe}_2\text{O}_4$  modified graphite felt cathode. To achieve the faster electron transfer, one dimensional  $\text{TiO}_2$  NRs electrode material was used as the anode. The effects of operational variables including cyanide concentration, PS dose and bias potential on cyanide degradation were investigated. Furthermore, the leaching of Cu ion was investigated. Five cycles were carried out to evaluate the stability of the PEC system. The kinetic study of cyanide degradation was also performed under different conditions and the possible mechanism of cyanide degradation and Cu ions recovery was discussed. The results obtained in this work provide valuable information for the treatment of industrial cyanide effluents.

## 2. Experimental section

### 2.1. Chemicals

Potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), sodium cyanide (NaCN), sodium hydroxide (NaOH), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), sodium perchlorate ( $\text{NaClO}_4$ ), hydrochloric acid (HCl), ethanol (EtOH) and thiobarbituric acid (TBA), titanium butoxide ( $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ ), polyvinylpyrrolidone (PVP), ethylene glycol ( $(\text{CH}_2\text{OH})_2$ ), copper sulfate ( $\text{CuSO}_4$ ), ferric chloride ( $\text{FeCl}_3$ ), sodium acetate (NaAc) and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) were all purchased from Sinopharm chemical reagent Co. Ltd., China. All chemicals were analytically pure without further purification and all solutions were prepared using freshly deionized water.

### 2.2. Experimental procedures

#### 2.2.1. Preparation of $\text{TiO}_2$ NRs photoanode

In a typical synthesis, deionized water and hydrochloric acid with equal volume (45 mL) were mixed. The mixtures were stirred for 5 min under ambient condition and then 1.5 mL of titanium butoxide was added. After stirring for 15 min, the mixtures were transferred into a stainless steel autoclave with Teflon-lining (150 mL volume). Then a piece of FTO was placed into the autoclave. The hydrothermal synthesis was performed at 150 °C for 5 h in an electric oven. Then the synthesized electrode was washed with deionized water and dried in a vacuum drying oven. Finally, the FTO substrate was calcined in a muffle furnace at 500 °C for 1 h [38].

#### 2.2.2. Preparation of $\text{CuFe}_2\text{O}_4/\text{GF}$ cathode

The GF was degreased with acetone in an ultrasonic bath for 15 min and washed with deionized water prior to use. In a typical experiment, polyvinylpyrrolidone (PVP, 1.0 g) was dissolved in 40 mL ethylene glycol, followed by the addition of 0.4 g  $\text{CuSO}_4$  and 0.8 g  $\text{FeCl}_3$  and 2.46 g NaAc. The mixture was stirred vigorously for 1 h, and then sealed in a 50 mL Teflon-lined stainless-steel autoclave with one piece of GF, which was heated at 200 °C for 8 h. The synthesized electrode was washed with ethanol and deionized water for several times and then dried at 60 °C for 12 h [39].

### 2.3. Analysis and characterization

The total cyanide concentration was determined by colorimetric method after distillation [40]. The concentration of dissolved Cu was determined using 700 series inductively coupled plasma optional

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