Cyanide oxidation by singlet oxygen generated via reaction between H₂O₂ from cathodic reduction and OCl⁻ from anodic oxidation

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1. Introduction

It is known that many waste streams from hydrometallurgical, electroplating, and other operations contain cyanides [1]. These streams are highly toxic and must be treated before being discharged into the environment [2]. Many strategies have been developed to remove cyanides from wastewater including adsorption [3], coagulation [4] and ion-exchange [5]. However, these processes could generate highly concentrated products in which toxic cyanides still exist, which need additional treatments. Recently, removal of cyanide by directly converting it...
into less harmful products via oxidation methods have been reported, which include ozonation [6], electrochemical oxidation [7], photocatalysis [8], ferrate oxidation [9], wet oxidation [10] and alkaline chlorination [11]. Among them, alkaline chlorination is a practical method due to its low operation cost and stable treatment effect. However, this method could generate harmful byproducts (such as chloramines) in the process of treating effluent, which are persistent and toxic to aquatic life. Therefore, finding a safe and effective method for treating cyanide wastewater is urgently demanded.

Electro-chlorination is one of the most cost-effective and widely adopted approaches for disinfection and purification of water [12]. In this method, active chlorine could be generated by passing direct current through electrodes within an electrolytic cell in the presence of salts as electrolytes. In the case of active chlorine, the interest in this oxidant is based on the ubiquitous presence of chloride ions in a certain number of effluents and natural waters, making the involvement of active chlorine during electrochemical treatment possible [13]. In the Electro-chlorination system, Cl

ions could be directly oxidized on anode surface and form molecular chlorine. In the basic solution, molecular chlorine could react with OH

and thus generate ClO

, which is an effective oxidizing agent for cyanide removal [14]. Therefore, cyanide could be removed by the electro-chlorination method. However, the formation of harmful chloride disinfection by-products cannot be avoided in the process of dealing with the cyanide wastewater. Moreover, the oxidation capacity of active chlorine is low at strong alkaline conditions.

Recently, in situ generation of hydrogen peroxide (H2O2) by electrochemical reduction of dissolved oxygen (DO) at cathode in acidic solution is extensively investigated [15]. Activated carbon fiber (ACF) is an attractive carbon material with excellent characteristics of adsorption, conductivity and catalysis [16]. The large surface area makes it attractive as a stable electrode to electro-generate H2O2 by the reduction of O2 on its surface. O2 might be electroreduced easily on the cathode surface and generate more H2O2 than stainless steel cathode [17]. Cyanide can be oxidized by H2O2 into cyanate (OCN

), which is considered much less toxic or into CO3

2- source when the excess of H2O2 is used. However, direct oxidation of cyanide by H2O2 proceeds rather slowly [18] and this process always requires the use of catalysts to increase the cyanide removal efficiency [19].

Singlet oxygen, represented as \( ^1\text{O}_2 \), is an excited form of molecular dioxygen, which includes two different metastable electronic configurations [20]. \( ^1\text{O}_2 \) is a kind of excited species with a very high affinity for electrons captured from compounds in aqueous solutions, like the hydroxyl radicals [21]. \( ^1\text{O}_2 \) is a strong oxidant with standard reduction potential of \( E_0 = 1.52 \text{ V} \) [22]. It is usually produced by photocatalytic activation of dissolved oxygen on metal oxides such as TiO2 and ZnO [23,24]. In addition, many other chemicals such as potassium perchromate [25], triphenyl phosphate [26] and ozonide [27] could also generate \( ^1\text{O}_2 \).

In the current work, an electrochemical system for the cyanide removal with RuO2/Ti mesh as the anode, the ACF as cathode and sodium chloride as electrolytes were established. In this system, cyanide was efficiently destroyed by the combined oxidation process of H2O2 in situ generated by electrochemical cathode reduction and OCl

 in situ generated by anodic oxidation of Cl

. ESR technique confirmed the generation of active radicals of \( ^1\text{O}_2 \), which was responsible for the efficient removal of cyanide. Furthermore, effects of initial pH, current density, electrolyte concentration on the cyanide removal performance and stability of the system were investigated.

2. Materials and methods

2.1. Materials

Cyanide solutions were prepared from NaCN (99%). NaCl, Na2-SO4, NaOH, tertiary butanol (t-BuOH), which were all purchased from Sinopharm chemical regent Co., Ltd., China. 2,2,6,6-Tetramethylpiperidine (TEMP) (98%) was purchased from New Jersey, USA and the 5,5-dimethyl-pyrrolone-N-oxide (DMPO) was purchased from the Sigma chemical corporation. All chemicals were used without further purification and all solutions were prepared using freshly prepared Milli-Q water. RuO2/Ti mesh was purchased from Beijing Hengltai Corporation. Activated carbon fibers (ACFs) were purchased from Nantong Senyou Carbon Fiber Co., Ltd., Nantong, China. The ACFs’ BET specific surface area was 900–1000 m2 g

 with a thickness of 1–5 mm.

2.2. Experimental section

The experiments were performed with 0.2 L cyanide solutions in glass reactor covered with aluminum foil to prevent the contact with light. The initial concentration of cyanide solution was 1.5 mM and the solution was mixed with a magnetic stirrer. As shown in Fig. 1, RuO2/Ti mesh was used as the anode and the ACF used as cathode.

The electrochemical experiments were performed as 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 cm × 20 cm and then kept in boiling water for 1 h to remove dirt and soluble salts. After drying at 100 ± 5 °C for 6 h, the ACFs were further cut into 3 cm × 5 cm for using as the cathode. The effect of pH on cyanide oxidation was investigated under alkaline conditions to avoid the releasing of cyanide. The pH values of the solutions were adjusted by H2SO4 (0.2 M) or NaOH solution (0.2 M). In the experiments, the concentration of cyanide (or cyanate) was measured versus 15 min.

2.3. Analysis

The total cyanide concentration was determined by colorimetric method using UV–vis spectrometer (Hitachi U-3010) at wavelength of 610 nm [28]. Cyanate concentration was determined by hydrolyzing it to ammonia at acidic pH (1.5–2.0) and ammonia was measured by colorimetric method at 420 nm. Ammonia concentration in the solution was also measured before cyanate

Fig. 1. The schematic view of the electrochemical reactor: (1) DC Power supply; (2) Electrolytic cell; (3) ACF cathode; (4) RuO2/Ti anode; (5) Magnetic Stirring Apparatus.
hydrolyzing. The solution was adjusted to pH 12.0 and the pH values were measured by a standard pH-meter (310P-02, Thermo Fisher, U.S.A.). Hydroxyl radical and singlet oxygen were detected by electron spin resonance (ESR) (Bruker ESP-300E). The ACF cathode was checked by scanning electron microscope (SEM) (Model 6700F, Tokyo, Japan). X-ray photoelectron spectra (XPS) was also used to analyze the surface variation of the cathode and anode using a PHI Quantera SXM (PHI-5300/ESCA, ULVAC-PHI, INC).

3. Results and discussions

3.1. Comparison of three systems for cyanide removal

Cyanide removal was studied in the same electrochemical cell with various anode and cathode materials. In A system: using RuO2/Ti as anode and stainless steel as cathode, with sodium chloride as supporting electrolyte media; In B system: using RuO2/Ti as anode and ACF as cathode, with sodium sulfate as supporting electrolyte media; In C system: using RuO2/Ti as anode and ACF as cathode, with sodium chloride as supporting electrolyte media. As shown in Fig. 2(a), the oxidation of cyanide is limited in A system and B system; however, in C system, the cyanide removal rate is the highest. After 30 min, the cyanide removal efficiency is 95%. The generated product of cyanate was identified and measured. As shown in Fig. 2(b), the cyanate concentration is the highest in C system. The variation trend of cyanate concentration is consistent with the cyanide removal rate.

In A system, Cl2 was in situ generated by losing two electron oxidation of Cl– on the anode and it was then converted to hypochlorous acid and hypochlorite via the following reactions (1)–(3) [29]:

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \]  
\[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HClO} + \text{Cl}^- \]

Although the in situ generation of OCl– occurred, the cyanide removal efficiency was low. Many studies had reported the influence of pH on anodic oxidation of organics in chlorine solution. In the lower pH range, the dominant form of active chlorine was hypochlorous acid \( E^0 (\text{HClO}/\text{Cl}_2) = 1.63 \text{ V} \) or \( E^0 (\text{HClO}/\text{Cl}^-) = 1.48 \text{ V} \), which exhibited considerably higher oxidation potential than hypochlorite \( E^0 (\text{OCI}^-/\text{Cl}^-) = 0.89 \text{ V} \) in alkaline media [30]. In our case, removal of cyanide was performed at strong alkaline condition in order to avoid the generation of HCN. Therefore, the oxidation of cyanide by OCl– was limited.

In B system, in situ generation of H2O2 on ACF cathode occurred via the following reaction (4) [31]:

\[ \text{O}_2 + 2e^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 \]  
\[ \text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \]  

The generated H2O2 could be decomposed to HO2 via the reaction (5) when the solution pH was higher than 10.0 [32]. HO2 anions had good stability, but its oxidation potential was lower than H2O2 (oxidation potential \( E^0 = 1.763 \text{ V} \) at pH = 0 and \( E^0 = 0.878 \text{ V} \) at pH = 14). Therefore, it was exhibited that the oxidation of cyanide proceeds was rather slowly in this system.

In C system, the reaction between H2O2 and ClO– may occur, leading to the generation of \({}^1\text{O}_2\) through reaction (6) [33]. Like hydroxyl radicals, \({}^1\text{O}_2\) is a kind of excited species with a very high affinity for electrons captured from compounds in aqueous solutions. Hydroxyl radicals generated in the reaction between copper cyanides complexes and H2O2 were responsible for the cyanide removal [34]. When the \({}^1\text{O}_2\) was generated, the cyanide oxidation reaction proceeded according to the main reaction (7) and the cyanate was the final production. Therefore, it was concluded that the high cyanide removal efficiency was due to the \({}^1\text{O}_2\) oxidation.

\[ \text{OCI}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HCl} + \text{OCN}^- \]  

As shown in Fig. 3(a), the cyanide removal efficiency decreases obviously when N2 is injected in this system. The injected N2 could remove dissolved molecular oxygen in the reaction solution, which inhibited the H2O2 generation. As a result, the generation of \({}^1\text{O}_2\) was also inhibited. Therefore, the cyanide removal efficiency decreased obviously. For some experiments, tertiary butanol (t-BuOH) is known as hydroxyl radicals scavengers, which are used to test the role of hydroxyl radicals [35]. As shown in Fig. 3(a), nearly no effect of t-BuOH addition on the cyanide removal rate. Therefore, it was concluded that the role of active hydroxyl radicals in the decomposition of total cyanide could be ruled out in this system.

The generated active radicals were tested by the electron spin resonance technique. As shown in Fig. 3(b), no signals were observed with the addition of t-BuOH or N2 sparging. By contrast, the signals assigned to \({}^1\text{O}_2\) are observed without addition t-BuOH and N2 sparging [36]. The variation of free radical signal \({}^1\text{O}_2\) was observed in this system: RuO2/Ti as anode and ACF as cathode, with sodium chloride as supporting electrolyte media. As shown in Fig. 3(c), No radical signal is detected in the beginning of this experiment and the signal intensity of \({}^1\text{O}_2\) increases with the reaction going on. When the cyanide is removed completely, the intensity of free radical signal \({}^1\text{O}_2\) remains unchanged.
3.3. The effect of pH on the cyanide removal efficiency

The pH effect on cyanide removal efficiency was investigated. In order to avoid the cyanide volatilization, the pH was selected in the range of 10.0–12.0. As shown in Fig. 4(a), the cyanide removal rate decreases with the pH increasing and the cyanide removal efficiencies reach to nearly the same value after 40 min. However, the concentration of cyanate is not the same after 40 min (Fig. 4(b)). The final cyanate concentration is 1.4 mM at the pH of 12.0, but the cyanate concentrations are 0.4 mM and 0.2 mM at the pH of 11.0 and 10.0, respectively. It can be seen that the pH value influenced the final cyanate concentration.

HCN was predominantly found in water with a pH below approximately 8.5, where volatilization of cyanide occurred [37]. Electric chlorination led to the pH decrease because of the increasing concentration of H⁺ in the reaction process. The final pH of the solution was 5.4 and 8.2 for the initial pH of 10.0 and 11.0 after 60 min reaction. The cyanide would be mainly volatilized in the cyanide removal process, as the result, the oxidation product cyanate concentrations were 0.4 mM and 0.2 mM at the pH of 11.0 and 10.0. Therefore, the toxic cyanide still existed. When the initial pH was 12.0, the cyanide was oxidized by the generated †O₂. Meanwhile, in strong alkaline solution (pH = 12.0), direct oxidation of the cyanide ion at the anode into cyanate ions occurred via the following reaction (8):

$$\text{CN}^- + 2\text{OH}^- \rightarrow \text{CNO}^- + \text{H}_2\text{O} + 2\text{e}^- \quad \text{E}_\text{o} = -0.97 \text{V}$$

It was concluded that high pH favored the oxidation of the cyanide ions into cyanate ions. Therefore, the optimum pH was selected as 12.0.

3.4. Effect of current density on the cyanide removal efficiency

The effect of current density on the cyanide removal efficiency was shown in Fig. 5(a). The cyanide removal efficiency is rather low (15%) with the current density of 4.17 mA/cm². However, the cyanide removal efficiency increases to be approximately 98% at the current density of 8.34 mA/cm². Significantly, the cyanide removal efficiency decreases slightly with the current density of 12.51 mA/cm². As shown in Fig. 5(b), the concentration of cyanate is consistent with the cyanide removal efficiency.

The cell potential was measured as 3.1 V, 4.2 V and 4.6 V for the applied current density of 4.17, 8.34 and 12.51 mA/cm², respectively. When the potential value was higher than 4.3 V, the reduction of O₂ through reaction (9) led to the formation of H₂O₂ instead of H₂O₂ production through reaction (4) [38]. So, the amount of accumulated H₂O₂ decreased in the electrolysis solution at the current density of 12.51 mA/cm². The H₂O₂ concentration had an influence on the generation of †O₂. The amount of in situ generated active chlorine rose almost linearly with the current density [39].
Meanwhile, the higher current density would lead to the higher applied cell potential, which caused the oxidation of water at the anode surface. As a result, the availability of anodic surface for the electro-oxidation of chloride and cyanide was reduced.

\[ \text{O}_2 + 4\text{e}^- + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O} \]  

(9)

The ESR spectra recorded during the electrochemistry process under different current densities were shown in Fig. 5(c). The signal intensity of the \(^1\text{O}_2\) is the highest when the current density is 8.34 mA/cm\(^2\). The current density would influence the generated \(^1\text{O}_2\). According to these results, the current density 8.34 mA/cm\(^2\) was used in this work.

3.5. Effect of electrolyte concentration on the cyanide removal efficiency

Electrolyte concentration had an important effect on the electrochemical processes. In this work, sodium chloride was used as supporting electrolyte to investigate its influence on the cyanide removal efficiency. As shown in Fig. 6(a), the cyanide removal efficiency is clearly proportional to the electrolyte concentration. When the electrolyte concentration reaches a certain value, increasing the sodium chloride concentration has no obvious effect on the cyanide removal efficiency.

At the low concentration of sodium chloride, because of the low electrical conductivity of the solution, higher voltage was required to reach the desired current density. In the beginning of this experiment, the electric voltages measured were 5.1, 4.2 and 2.8 V for the electrolyte concentrations of 0.025, 0.050 and 0.075 M, respectively. As mentioned before, when the potential values was higher...
than 4.3 V, the reduction of O₂ through reaction (9) led to the formation of H₂O₂ instead of H₂O₂. It also accelerated the decomposition of H₂O₂ either on the anode or in the medium directly. Therefore, increasing the sodium chloride concentration from 0.025 M to 0.050 M increased the amount of H₂O₂ generated at the ACF cathode. Meantime, higher concentration of sodium chloride supplied a sufficient amount of Cl⁻ that generated chlorine at the anode, leading to the generation of a large amount of OCI⁻. The reaction between OCI⁻ and H₂O₂ led to the generation of ¹O₂ through reaction (6). But, furthermore increase of sodium chloride concentration had a slight effect on the cyanide removal efficiency. According to these results, the electrolyte concentration of sodium chloride was selected as 0.050 M.

3.6. Stability of the electrochemical system

Stability of the system was studied by the re-use of the same ACF cathode and RuO₂/Ti anode for four successive times. Before each re-use, the ACF cathode was washed with deionized water and dried. As shown in Fig. 7, there is nearly no change in cyanide removal efficiency.

The structure of ACF was analyzed by Scanning Electron Microscope. As shown in Fig. 8, there is also nearly no change in the surface structure of ACF before and after 60 min reaction. ACF is a comparatively modern form of porous carbon material with a number of significant advantages over the more traditional powder or granular forms [40]. The X-ray photoelectron spectra of the ACF cathode and RuO₂/Ti anode are given in Fig. 9. Nearly no change of the major elements of cathode and anode are observed after the reaction. The ACF cathode and RuO₂/Ti anode show good stability, leading to the efficient cyanide removal efficiency.

4. Conclusions

In this work, efficient removal of cyanide in the electrochemical system with RuO₂/Ti as anode and activated carbon fiber as cathode in the presence of sodium chloride was achieved. In this electrochemical system H₂O₂ was in situ generated by the two electron reduction of O₂ on the activated carbon fibers cathode surface and Cl₂ was in situ generated by losing two electron oxidation of Cl⁻ on the anode. As confirmed by ESR analysis, the reaction between H₂O₂ and OCI⁻ resulted in the formation of ¹O₂, which was effective on the oxidation of cyanide. In the process of treating cyanide wastewater by this system, the final pH would decrease due to the generation of hypochlorous acid and hydrochloric acid. In order to avoid the cyanide volatilizing in the form of HCN, the initial pH was selected as 12.0. The cyanide removal efficiency increased by increasing current density up to 8.34 mA/cm², after that the cyanide removal efficiency decreased. The current density would influence the concentration of generated ¹O₂. The cyanide removal efficiency was clearly proportional to the electrolyte concentration. The stability of the electrochemical system was exhibited.

![Fig. 8. Scanning Electron Microscope images of the ACF cathode before and after reaction.](image1)

![Fig. 9. X-ray photoelectron spectra of the ACF cathode (a) and RuO₂/Ti anode (b).](image2)
Acknowledgments

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References