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

Shichao Tian^{a,b}, Yibing Li^b, Xu Zhao^{a,*}

^a Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

^b School of Civil Engineering, Hebei University of Technology, Tianjin 300401, China

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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_2O_2 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^2 and the geometric area ratio of $\text{Cu/ACF}=1:2$, 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_2O_2 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

* Corresponding author at: P.O. Box 2871, 18 Shuangqing Road, Haidian District, Beijing 10085, China. Tel.: +86 010 62849667.

E-mail address: zhaoxu@rcees.ac.cn (X. Zhao).

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.

H_2O_2 oxidation of several cyanide species had been investigated recently. The direct oxidation of cyanide by H_2O_2 proceeded rather slowly [20]. It was known that the non-selective and highly oxidative hydroxyl radicals were formed in the presence of H_2O_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 H_2O_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 H_2O_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°C . All chemicals were used without further purification and all solutions were prepared using freshly prepared Milli-Q water. RuO_2/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 $35\text{ }\mu\text{m}$ (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, RuO_2/Ti mesh was used as the anode and the various cathode materials including ACF, copper plate were combined with RuO_2/Ti as composite cathode. In this composite cathode, the RuO_2/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 H_2SO_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) RuO_2/Ti mesh anode; (5) Magnetic stirring apparatus.

Fig. 2. Effect of various cathode materials on the cyanide removal in the electrochemical process: (a) Removal rate of cyanide; (b) The Cu concentration in the solution with reaction time; and (c) The OCN⁻ concentration and the NH₄⁺ concentration with reaction time ([cyanide] = 1.5 mM; [Cu/ACF] = 1:1; current density = 50.01 A/m²; pH = 12.0).

solution (0.2 M). During all the experiments, the concentration of cyanide (or cyanate) was measured at the given time.

2.3. Analytical procedures

The total cyanide concentration was determined by the colorimetric method at 610 nm after the distillation procedure [27]. Cyanate concentration was determined by hydrolyzing to ammonia at acidic pH (1.5–2.0) and ammonia was measured by UV-vis spectrometer (Hitachi U-3010) at 420 nm. Total Cu ions concentration was measured using a 700 series inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent Technology, U. S. A.). The solution pH value was adjusted to be 12.0 and was measured by a standard pH-meter (310P-02, Thermo Fisher, U.S.A.). Hydroxyl radicals were detected by electron spin resonance (ESR) (Bruker ESP-300E). The deposition on the anode

and the reduction of the dissolved Cu ions in the ACF cathode were checked by scanning electron microscope (SEM, model 6700F, Tokyo, Japan) and energy dispersive x-ray analysis (EDX) (JEOL, 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 discussion

3.1. Comparison of cathode materials for cyanide removal

Various cathode materials including stainless steel, activated carbon fibers, copper plate and the combination of copper plate with ACF (Cu/ACF) are firstly compared for the destruction of cyanide ions in the same electrochemical system under the same

Fig. 3. Effect of pH on the cyanide removal in the electrochemical process: (a) Variations of the removal rate of cyanide; (b) The Cu concentration with reaction time; and (c) Copper distribution in the anode, cathode and in solution ([cyanide] = 1.5 mM, [Cu/ACF] = 1:1, current density = 50.01 A/m²).

Fig. 4. Effect of geometry area ratio of Cu/ACF on the cyanide removal in the electrochemical process: (a) the removal rate of cyanide; (b) The Cu concentration with reaction time; and (c) Copper mass distribution on the anode, cathode and in solution ($[\text{cyanide}] = 1.5 \text{ mM}$, $\text{pH} = 12.0$, current density = 50.01 A/m^2).

experimental conditions. It can be seen from Fig. 2(a), the cyanide removal rate by the stainless steel and activated carbon fibers are limited. With the copper plate cathode, the cyanide removal efficiency can reach up to 50 %. When the Cu/ACF is used as the cathode, it is noticed that the cyanide removal rate is largely increased to be 93 %.

In the case of ACF used as the cathode, *in situ* generation of H_2O_2 could occur. However, When the solution pH was higher than 10.0, the generated H_2O_2 could be decomposed to HO_2^- . HO_2^- anions had good stability, but its oxidation potential was lower than H_2O_2 [28]. Therefore, using ACF as the cathode generating H_2O_2 is limited for the cyanide oxidation. With respect to the stainless steel cathode, individual anodic oxidation occurs, which is also limited for the cyanide oxidation removal. When Cu/ACF is used as the cathode, it is known that H_2O_2 can be *in situ* generated via an

Fig. 5. Effect of current density on the cyanide removal in the electrochemical process: (a) the removal rate of cyanide; (b) The Cu concentration with reaction time; and (c) ESR spectra ($[\text{cyanide}] = 1.5 \text{ mM}$, $[\text{Cu/ACF}] = 1:2$, $\text{pH} = 12.0$).

electroreduction process when ACF is used as cathode with the O_2 injection. In the current case, the O_2 is generated by the anodic oxidation of OH^- . Therefore, in the case of the Cu/ACF cathode, *in situ* generated H_2O_2 may react with the copper cyanide complexes, which increases the cyanide oxidation efficiencies as described in our previous work [29]. Black CuO is observed at the anode surface, which will be carefully analyzed subsequently. It had been reported that the CuO deposited on the anode exhibited

Fig. 6. SEM images of the ACF cathode at various time: (a) 0 min; (b) 15 min; (c) 30 min; (d) 45 min; (e) 60 min; (f) 90 min ([cyanide] = 1.5 mM, pH = 12.0, [Cu/ACF] = 1:2, current density = 50.01 A/m²).

electrocatalytic properties for the cyanide oxidation. At the same time, the reduction of Cu ions in solution occurs at the cathode.

The concentration of the total Cu ions in the reaction solution is measured with the reaction evolution. As shown in Fig. 2(b), within 15 minutes, the Cu ions concentration are largely increased to be as high as 10 mg/L. The copper dissolution and deposition process simultaneously occur. In the beginning, the cyanide contributed to dissolution of copper ions and the dissolution rate was higher than deposition rate in electrode. But with the cyanide removing, the deposition rate in electrode was higher than dissolution rate. When injecting N₂ into the reaction solution to remove dissolved molecular oxygen, the cyanide removal rate is obviously decreased (Fig. 2(a)). But, the liberation of the Cu ions from the copper plate into the reaction solution are not influenced.

In addition, the intermediates are also identified. As shown in Fig. 2(c), cyanide is oxidized to non-toxic cyanate. It is obvious that the combined Cu/ACF is a favorable cathode material for the cyanide removal, which is selected in the following experiments.

3.2. Effect of pH on cyanide removal rate

Effect of pH on the cyanide removal is investigated. In order to avoid the cyanide volatilization, the pH is selected in the range of 10.0–12.0. It can be seen from Fig. 3(a) that there is no obvious difference of the cyanide removal under various pH conditions within the first 15 minutes. After that, an obvious change for the cyanide removal rate is observed. The cyanide removal rate increases with the pH and reaches to the maximum at pH 12.0.

Fig. 7. EDX analysis of the ACF: (a) 0 min; (b) 15 min; (c) 30 min; (d) 45 min; (e) 60 min; (f) 90 min ([cyanide] = 1.5 mM, pH = 12.0, [Cu/ACF] = 1:2, current density = 50.01 A/m²).

Fig. 8. (a) EDX analysis of the anode after 90 minutes; (b) stands for position 1; (c) stands for position 2; and (d) stands for position 3 ([cyanide] = 1.5 mM, pH = 12.0, [Cu/ACF] = 1:2, current density = 50.01 A/m²).

Meantime, the concentration of Cu ions reaches the largest value at 15 minutes. After that, the concentration of Cu ions decreases obviously. When the pH is 12.0, after 60 minutes, the Cu ions concentration reaches the lowest value (Fig. 3(b)). If cyanide in the solution is not completely removed, copper ions could be dissolved by cyanide and form copper cyanide complexes. Therefore, the higher removal rate of cyanide, the lower concentration of Cu ions remained in the solution.

Furthermore, the mass distribution of Cu species in the solution, at the anode and cathode is analyzed at various pH conditions. The amounts of copper ions deposited on the anode and ACF was dissolved by dilute nitric acid and then measured by ICP-OES. As shown in Fig. 3(c), at the initial pH of 10.0, the concentration of Cu ions (by mg/L) deposited onto the anode, in the solution, and deposited onto the cathode are determined to be 0.84, 5.32, and 82.47 mg/L, respectively. With the increasing pH, the Cu amount deposited onto the cathode and in the solution decreases and the Cu amount deposited onto the anode increases gradually. At the initial pH of 12.0, the Cu mass deposited onto the anode and the cathode are determined to be 52.36 and 36.18 mg/L, respectively. Several authors had confirmed that the deposit on the anode was copper oxides, which had catalytic properties towards the cyanide oxidation [17,30]. Therefore, the generation of the

copper oxides at the anode became easy at a high pH condition, which was capable of electro-oxidizing hydroxide to oxygen and cyanide to cyanate [20]. Therefore, the optimum pH is selected to be 12.0.

3.3. Geometric area ratio of Cu/ACF on cyanide removal rate

The effect of geometric area ratio of Cu plate to ACF on the cyanide removal rate is investigated with the area rate of 1:1, 1:2, 1:4. The geometric area of copper plate not only influenced the concentration of CuO deposited on anode but also influenced the concentration of H₂O₂ generated on cathode. As shown in Fig. 4(a), when the geometric area ratio of Cu/ACF is 1:2, the cyanide removal rate is the maximum. Due to the dissolution of copper plate by the cyanide ions, the Cu ions concentration in the solution increases with the geometric area of copper plate at the initial 15 minutes. After 90 minutes, the Cu ions concentration with the various geometric area ratios of Cu/ACF are determined to be lower than 0.2 mg/L (Fig. 4(b)). As shown in Fig. 4(c), the concentration of Cu ions deposited onto the anode are determined to be 56.69, 48.10, and 28.38 mg/L corresponding to the geometric area ratio of Cu plate to ACF 1:1, 1:2, 1:4, respectively. Obviously, the concentration of copper oxide deposited on the anode is the

Fig. 9. (a) XPS spectra of the ACF before and after the electrochemical reaction; (b) XPS Cu2p spectra of the ACF after 90 minutes; (c) XPS spectra of the anode before and after the electrochemical reaction; and (d) Cu2p XPS spectra of the anode after 90 minutes ([cyanide] = 1.5 mM, pH = 12.0, [Cu/ACF] = 1:2, current density = 50.01 A/m²).

maximum with the area ratio of Cu/ACF = 1:1, but the cyanide removal rate is not the highest. Instead, the cyanide removal rate is the highest at the area ratio of Cu/ACF = 1:2.

The cyanide removal is induced by the catalytic oxidation via *in situ* generation of copper oxides on the anode and the Fenton-like oxidation between *in situ* generation H₂O₂ and the copper cyanide complexes. Therefore, the cyanide removal efficiency is related to the concentration of copper oxides amounts deposited on the anode and the H₂O₂ amount. At the area ratio of Cu/ACF = 1:1, the generation amount of H₂O₂ decrease due to the low utilization rate of the dissolved molecular oxygen by the ACF cathode. Therefore, the H₂O₂ would influence the generation of hydroxyl radicals according to the Eqs. (1)–(3). By contrast, at the Cu/ACF area ratio of 1:4, the copper oxides catalyst generated at the anode is minimum as shown in Fig. 4 (c). The deposited copper oxides at the anode are beneficial for the cyanide removal. A small amount of generated copper oxides can lead to a decreased cyanide efficiency. According to these results above, the Cu/ACF with the geometric area ratio of 1:2 is used subsequently.

3.4. Effect of current density on cyanide removal rate

It can be seen from Fig. 5(a) that the removal rate of cyanide ions increases slightly with the increasing current density up to

50.01 A/m². After that, the removal rate of cyanide decreases slightly. The cell potential is measured as 1.6 V, 3.1 V, 4.2 V and 4.6 V for the applied current density of 16.67, 33.34, 50.01 and 66.68 A/m², respectively. At the potential values higher than 4.3 V, the reduction of O₂ through Eq. (4) leads to the formation of H₂O instead of H₂O₂ production through Eq. (5) [31]. So, the amount of accumulated H₂O₂ decreases in the reaction solution at the current density of 66.68 A/m².

Ozcan et al. [32] also reported the same behavior for the H₂O₂ production at the potential value higher than 4.3 V. Also, a high potential should be used in order to get a high current density, which accelerates the H₂O₂ decomposition either on the anode or in the medium directly (Eqs. (6)–(8)). Moreover, the competitive electrode reactions such as the discharge of O₂ and H₂ can inhibit H₂O₂ generation [33].

A similar variation trend for the copper ions concentration in the solution with the current densities is observed in Fig. 5(b). Furthermore, the peak intensity of $\bullet\text{OH}$ radicals also exhibit similar variation (Fig. 5(c)). At the current density of 50.01 A/m², the peak intensity of $\bullet\text{OH}$ is the largest, which can lead to the efficient destruction of copper cyanides.

3.5. XPS and SEM-EDX analysis

The surface variation of the ACF in the cyanide removal process is analyzed by SEM and EDX. As shown in Fig. 6 and Fig. 7, no copper is observed at the surface of the ACF before the electrochemical reaction. In the process of reaction, copper ions reduction occurs onto the cathode. According to the EDX analysis, the proportion of copper in ACF for different time is determined to be 0%, 12.6%, 30.99%, 41.64%, 80.94%, 81.92%, respectively (Fig. 7). Meantime, deposit sediment on the anode after 90 minutes reaction are observed according to the EDX analysis. According to Fig. 8, the major elements on the anode are Cu, Ti, Ru and O.

XPS technique is used to determine the value state of copper deposition on electrode. It has been seen clearly from Fig. 9(a) that the major elements on the ACF before the electrochemical reaction are C and O. After 90 minutes, peaks of Cu appeared on the spectra of ACF. Fig. 9(b) shows the XPS spectra of the Cu2p core level binding energy after 90 minutes oxidation reaction. The major Cu2p_{3/2} peaks centered at 932.9 eV and major Cu2p_{1/2} peaks centered at 955.9 eV are assigned to zero-valent copper. Thus, it is concluded that the copper ions in the reaction solution are reduction onto the cathode by the electrochemical process.

It can be seen clearly from Fig. 9(c) that the major elements on the anode are Ru, Ti, and O, which are consisted with the anode material of RuO₂/Ti mesh. After 90 minutes, Cu peak appears on the anode, which could be ascribed to the generated copper oxides on the anode surface. Fig. 9(d) shows the XPS spectra of the Cu2p core level binding energy after the electrochemical oxidation reaction for 90 minutes. The major Cu2p_{3/2} peaks centered at 933.6 eV and major Cu2p_{1/2} peaks centered at 953.6 eV are assigned to CuO [34,35].

3.6. Stability of the electrochemical system

Stability of the system for the cyanide removal is studied by the repeated use of the same Cu/ACF cathode sample for four successive cycles. Before each cycle, the anode and cathode are washed with deionized water. As shown in Fig. 10(a), in the second cycle, the cyanide removal efficiency decreases slightly comparing with the first cycle. However, it remains nearly constant for the second, third and fourth cycle. The efficiencies of the cyanide removal for each cycle are determined to be 93%, 80%, 76% and 75%, respectively. As shown in Fig. 10(b), the same variation trend of the Cu ions concentration is also observed for the four cycles. Copper ions dissolved from copper plate by cyanide ions resulted in the formation of copper cyanides. When the cyanide was oxidized, the copper ions was generated to copper oxide film deposited on the anode and reduced to zero-valent copper. Therefore, the Cu ions concentration would decrease in Fig. 10(b).

The copper oxide film deposited on the anode is dissolved again when the cyanide concentration is higher than 1 mM, leading to the generation of copper cyanide complexes, which is beneficial for

Fig. 10. (a) The removal rate of cyanide for cycles; (b) The Cu concentration in the solution for cycles ([cyanide] = 1.5 mM, pH = 12.0, [Cu/ACF] = 1:2, current density = 50.01 A/m²).

the cyanide removal. Thus, the system exhibits high stability for cyanide removal and copper recovery.

4. Conclusions

In this work, the efficient removal of cyanide is achieved in the electrochemical process using the composite cathode of Cu/ACF. In the cyanide removal process, the Cu ions are dissolved from the copper plate by the cyanide ions, leading to the formation of copper cyanide complexes. Copper oxides are formed from the copper cyanide complexes oxidation at the anode surface in the electrochemical process, which exhibits catalytic activities for the cyanide removal. H₂O₂ is *in situ* generated by the two electron reduction of O₂ at ACF surface, which reacts with copper cyanide complexes via a Fenton-like reaction, leading to the efficient removal of cyanide ions. Both of the above processes are responsible for the efficient cyanide removal. The recovery and reuse of copper is also achieved via the electrodeposition of metallic copper onto the cathode. This system exhibited high stability for cyanide removal and copper recovery.

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References

- [1] N. Adhoum, L. Monser, Removal of cyanide from aqueous solution using impregnated activated carbon, *Chem. Eng. Process* 41 (2002) 17–21.

- [2] X. Dai, P.L. Breuer, M.I. Jeffrey, Comparison of activated carbon and ion-exchange resins in recovering copper from cyanide leach solutions, *Hydrometallurgy* 101 (2010) 48–57.
- [3] W. Zhang, W. Liu, Y. Lv, B. Li, W. Ying, Enhanced carbon adsorption treatment for removing cyanide from coking plant effluent, *J. Hazard. Mater.* 184 (2010) 135–140.
- [4] A. Behnamfarad, M.M. Salarirad, Equilibrium and kinetic studies on free cyanide adsorption from aqueous solution by activated carbon, *J. Hazard. Mater.* 170 (2009) 127–133.
- [5] G. Moussavi, F. Majidi, M. Farzadkia, The influence of operational parameters on elimination of cyanide from wastewater using the electrocoagulation process, *Desalination* 280 (2011) 127–133.
- [6] A. Gupta, E.F. Johnson, R.H. Schlossel, Investigation into the ion exchange of the cyanide complexes of zinc (2+) cadmium (2+), and copper (1+) ions, *Ind. Eng. Chem. Res.* 26 (1987) 588–594.
- [7] G.E. Eden, B.L. Hampson, A.B. Wheatland, Destruction of cyanide in waste waters by chlorination, *J. Chem. Technol. Biotechnol.* 69 (1950) 244–249.
- [8] X. Yang, C. Shang, Chlorination byproduct formation in the presence of humic acid, model nitrogenous organic compounds, ammonia, and bromide, *Environ. Sci. Technol.* 38 (2004) 4995–5001.
- [9] F. Barriga-Ordóñez, F. Nava-Alonso, A. Uribe-Salas, Cyanide oxidation by ozone in a steady-state flow bubble column, *Miner. Eng.* 19 (2006) 117–122.
- [10] U.B. Oğutveren, E. Toru, S. Kopalal, Removal of cyanide by anodic oxidation for wastewater treatment, *Water Res.* 33 (1999) 1851–1856.
- [11] S.C. Cheng, M. Gattrell, T. Guena, B. MacDougall, The electrochemical oxidation of alkaline copper cyanide solutions, *Electrochim. Acta* 47 (2002) 3245–3256.
- [12] M.A. Barakat, Y.T. Chen, C.P. Huang, Removal of toxic cyanide and Cu (II) ions from water by illuminated TiO₂ catalyst, *Appl. Catal. B* 53 (2004) 13–20.
- [13] M.J. Lopez-Munoz, J. Aguado, R. van Grieken, J. Marugan, Simultaneous photocatalytic reduction of silver and oxidation of cyanide from dicyanoargentate solutions, *Appl. Catal. B* 86 (2009) 53–62.
- [14] V.K. Sharma, W. Rivera, J.O. Smith, Ferrate(VI) oxidation of aqueous cyanide, *Environ. Sci. Technol.* 32 (1998) 2608–2613.
- [15] V.K. Sharma, C.R. Burnett, R.A. Yngard, D.E. Cabelli, Iron (VI) and iron (V) oxidation of copper (I) cyanide, *Environ. Sci. Technol.* 39 (2005) 3849–3854.
- [16] P. Oulego, A. Laca, M. Diaz, Kinetics and pathways of cyanide degradation at high temperatures and pressures, *Environ. Sci. Technol.* 47 (2012) 1542–1549.
- [17] L. Szpyrkowicz, F. Zilio-Grandi, S.N. Kaul, S. Rigoni-Stern, Electrochemical treatment of copper cyanide wastewaters using stainless steel electrodes, *Water Sci. Technol.* 38 (1998) 261–268.
- [18] N. Kuyucak, A. Akcil, Cyanide and removal options from effluents in gold mining and metallurgical processes, *Miner. Eng.* 50 (2013) 13–29.
- [19] L. Szpyrkowicz, G.H. Kelsall, R.M. Souto, F. Ricci, Hydrodynamic effects on the performance of an electrochemical reactor for destruction of copper cyanide-Part 1: *in situ* formation of the electrocatalytic film, *Chem. Eng. Sci.* 60 (2005) 523–533.
- [20] M. Sarla, M. Pandit, D.K. Tyagi, J.C. Kapoor, Oxidation of cyanide in aqueous solution by chemical and photochemical process, *J. Hazard. Mater.* 116 (2004) 49–56.
- [21] N. Kishimoto, Y. Nakamura, M. Kato, H. Otsu, Effect of oxidation-reduction potential on an electrochemical Fenton-type process, *Chem. Eng. J.* 260 (2015) 590–595.
- [22] H.J. Park, T.T. Nguyen, J. Yoon, C. Lee, Role of reactive oxygen species in *Escherichia coli* inactivation by cupric ion, *Environ. Sci. Technol.* 46 (2012) 11299–11304.
- [23] T.T. Nguyen, H.J. Park, J.Y. Kim, H.E. Kim, H. Lee, J. Yoon, C. Lee, Microbial inactivation by cupric ion in combination with H₂O₂: role of reactive oxidants, *Environ. Sci. Technol.* 47 (2013) 13661–13667.
- [24] F.Y. Chen, X. Zhao, H.J. Liu, J.H. Qu, Enhanced destruction of Cu(CN)₃²⁻ by H₂O₂ under alkaline conditions in the presence of EDTA/pyrophosphate, *Chem. Eng. J.* 253 (2014) 478–485.
- [25] G.S. Xia, Y.H. Lua, H.B. Xua, Electrogenation of hydrogen peroxide for electro-Fenton via oxygen reduction using polyacrylonitrile-based carbon fiber brush cathode, *Electrochim. Acta* (2015).
- [26] J.M. Monteagudo, L. Rodriguez, J. Villaseñor, Advanced oxidation processes for destruction of cyanide from thermoelectric power station waste waters, *J. Chem. Technol. Biotechnol.* 79 (2004) 117–125.
- [27] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, 21th ed., APHA, Washington, DC, 2005.
- [28] Z.M. Qiang, J.H. Chang, C.P. Huang, Electrochemical generation of hydrogen peroxide from dissolved in acid solutions, *Water Res.* 36 (2002) 86–94.
- [29] F.Y. Chen, X. Zhao, H.J. Liu, J.H. Qu, Reaction of Cu(CN)₃²⁻ with H₂O₂ in water under alkaline conditions: Cyanide oxidation, Cu⁺/Cu²⁺ catalysis and H₂O₂ decomposition, *Appl. Catal. B* 158 (2014) 85–90.
- [30] L. Szpyrkowicz, S.N. Kaul, E. Molga, M. DeFaveri, Comparison of the performance of a reactor equipped with a Ti/Pt and an SS anode for simultaneous cyanide removal and copper recovery, *Electrochim. Acta* 46 (2000) 381–387.
- [31] A.R. Khataee, M. Safarpour, M. Zarei, S. Aber, Electrochemical generation of H₂O₂ using immobilized carbon nanotubes on graphite electrode fed with air: Investigation of operational parameters, *J. Electroanal. Chem.* 659 (2011) 63–68.
- [32] A. Özcan, Y. Sahina, A. Savas Kopalal, M.A. Oturan, A comparative study on the efficiency of electro-Fenton process in the removal of propanol from water, *Appl. Catal. B* 89 (2009) 620–626.
- [33] I. Yamanaka, T. Hashimoto, R. Ichihashi, K. Otsuka, Direct synthesis of H₂O₂ acid solutions on carbon cathode prepared from activated carbon and vapor-growing-carbon-fiber by a H₂/O₂ fuel cell, *Electrochim. Acta* 53 (2008) 4824–4832.
- [34] P. Ning, J. Qiu, X.Q. Wang, W. Liu, W. Chen, Metal loaded zeolite adsorbents for hydrogen cyanide removal, *J. Environ. Sci.* 25 (2013) 808–814.
- [35] L. Szpyrkowicz, F. Ricci, M.F. Montemor, R.M. Souto, Characterization of the catalytic films formed on stainless steel anodes employed for the electrochemical treatment of cuprocyanide wastewaters, *J. Hazard. Mater.* 119 (2005) 145–152.