Enhancement of electrochemical oxidation of $\text{Cu}(\text{CN})_3^{2-}$ by the peroxydisulfate oxidation

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ARTICLE INFO

Article history:

Received 14 April 2017

Received in revised form 1 July 2017

Accepted 2 July 2017

Available online 4 July 2017

Keywords:

Copper cyanide complexes

Peroxydisulfate

Anodic oxidation

Hydroxyl radical

Sulfate radical

ABSTRACT

In this work, the peroxydisulfate (PDS/ $\text{K}_2\text{S}_2\text{O}_8$) enhancement of electrochemical oxidation of $\text{Cu}(\text{CN})_3^{2-}$ with the RuO_2/Ti mesh anode and the stainless steel cathode was investigated. The removal efficiency of cyanide was largely increased with increasing the PDS concentration. When the concentration of $\text{K}_2\text{S}_2\text{O}_8$ was 1.00 mM and the current density was 14.80 A/m^2 , the removal efficiency of cyanide was increased from 34.3% to 89.1% at the initial 10 min. The Cu mass distribution onto the cathode, in the solution, and onto the anode was investigated. With the increase of $\text{K}_2\text{S}_2\text{O}_8$ concentration, the mass of Cu oxides deposition on the anode surface was increased. Combined with the SEM-EDS, XRD and XPS analysis for the anode surface, it was confirmed that the generation of deposition on the anode surface was CuO . The generation of sulfate and hydroxyl radicals was confirmed by the ESR analysis. It was suggested that Cu(I) reacted with $\text{S}_2\text{O}_8^{2-}$ via a Fenton-like process, leading to the formation of $\text{SO}_4^{\cdot -}$ radical. $\cdot\text{OH}$ radical was generated due to the reaction between $\text{SO}_4^{\cdot -}$ and $\text{OH}^-/\text{H}_2\text{O}$. Therefore, these active radicals and anode oxidation were responsible for cyanide removal.

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1. Introduction

Cyanide-containing wastewater is discharged by various industries, especially in the processes of plating, surface finishing and metallurgy [1,2]. Cyanide is widely used in these industries due to its unique properties [3,4]. Consequently, cyanide-containing wastewater and heavy metals are generated. Various techniques have been employed to treat the cyanide-contaminated effluents. Alkaline chlorination is generally applied to remove the cyanide-containing wastewater. However, this method may generate the toxic cyanogens chloride and the chloride disinfection [5–7]. By contrast, some oxidation techniques have been investigated to remove the cyanide-containing wastewater without harmful products, which mainly include electro-chemical oxidation [8,9], wet oxidation [10], photocatalysis [11,12], ferrate oxidation [13,14] and ozonation [15].

The electrochemical process for removing the cyanide-containing wastewater has been widely investigated [16,17]. The active chlorine species generated via the electrochemical oxidation

are efficient for cyanide removal [18,19]. However, the by-product of CNCl is readily generated in the electrochemical oxidation process, which should be treated carefully. In the electrochemical oxidation of copper cyanide complexes, it is reported that copper oxides deposited on the anode occurred, which can enhance the cyanide removal due to its catalytic activity [20].

Peroxydisulfate (PDS) and peroxymonosulfate (PMS) are attracting more and more attention for the degradation of organic pollutants [21,22]. PDS is a popular oxidant in the advanced oxidation processes, because it is cheaper than other oxidants and relatively stable. Persulfates can generate strong sulfate radical by UV, heat, alkaline and transition metals activating [23,24]. Zhang et al. has used the peroxydisulfate for 2, 4-DCP degradation [25], which indicated that peroxydisulfate could be activated by CuO . Moussavi et al. has paid attention to the advanced oxidation processes of VUV and $\text{UVC/K}_2\text{S}_2\text{O}_8$ for removing cyanide [26].

Herein, the $\text{K}_2\text{S}_2\text{O}_8$ reagent was used to enhance the electrochemical oxidation for removing $\text{Cu}(\text{CN})_3^{2-}$. In this experiment, the effects of current density and $\text{K}_2\text{S}_2\text{O}_8$ concentration on the removal efficiency of $\text{Cu}(\text{CN})_3^{2-}$ were investigated. The electrode surfaces were analyzed by SEM-EDX, XRD and XPS techniques. The generations of hydroxyl and sulfate radicals in the system were confirmed by the ESR technique.

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2. Materials and methods

2.1. Materials

Sodium cyanide, potassium persulfate, sodium hydroxide, sulfuric acid (98% w/w), sodium nitrite, and sodium perchlorate were all purchased from Sinopharm chemical reagent Co., Ltd., China. The reagent 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) was purchased from Sigma Chemical Co., Ltd. and stored at -20°C . All the chemicals were analytically pure. Freshly prepared Milli-Q water was used to prepare the solutions. $\text{Cu}(\text{CN})_3^{2-}$ was prepared by adding the cuprous cyanide powder to cyanide solutions at a molar ratio of CN^- to Cu^+ (3.0:1.0).

2.2. Experimental section

The experiments were carried out in a glass reactor containing 180 mL $\text{Cu}(\text{CN})_3^{2-}$ solutions and the initial concentration of total CN^- was 0.90 mM. The sodium perchlorate acted as an electrolyte. The electrochemical system included a direct-current (DC) power supply, an electrolytic cell, a stainless steel cathode, a RuO_2/Ti mesh anode and a magnetic stirring apparatus. The RuO_2/Ti electrode was directly connected to the positive electrode of the DC power supply and the stainless steel electrode with the same area was directly connected to the negative electrode of the DC power supply. The electrochemical experiments were carried out at a constant current density, which was controlled by a DC power (DH1718E-6, Dahua Electronic, Co., Ltd., Beijing, China). The pH of cyanide solutions was kept under alkaline conditions, preventing the release of HCN [27]. The reaction solution was stirred magnetically at a speed of 450 rpm. All the electrochemical experiments were performed at an ambient temperature of $20 \pm 2^{\circ}\text{C}$.

2.3. Analysis

The total concentration of CN^- was measured by colorimetric method at 610 nm. Cyanate concentration was measured by hydrolyzing cyanate to ammonia at acidic pH (1.5–2.0) and ammonia was measured by UV-vis spectrometer (Hitachi U-3010) at 420 nm. The concentration of Cu ions was determined by a 700 series inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent Technology, U. S. A). The initial pH value of reaction solution was 12.0 and measured by a standard pH-meter (310 P-02, Thermo Fisher, U.S.A.). The deposition on the RuO_2/Ti anode and the stainless steel cathode were analyzed by scanning electron microscope (SEM, model 6700 F, Tokyo, Japan) and energy dispersive X-ray analysis (EDX) (JEOL, Japan). The phase composition of deposition was characterized by X-ray diffraction (XRD) using a diffractometer with Cu $K\alpha$ radiation (D/max-2400, source light at the wavelength (λ) of 0.1541 nm, 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). The generations of active radicals were identified by electron spin resonance (ESR) on a Bruker ESR 300E with a microwave bridge (receiver gain, 1×10^5 ; modulation amplitude, 2 G; microwave power, 10 mW; modulation frequency, 100 kHz).

3. Results and discussions

3.1. Effect of current density on the removal efficiency of $\text{Cu}(\text{CN})_3^{2-}$

The effect of the current density on the cyanide removal was investigated in the electrochemical oxidation of $\text{Cu}(\text{CN})_3^{2-}$ process. As shown in Fig. 1, corresponding to the current density of 0 A/m²,

3.70 A/m², 7.40 A/m², 14.80 A/m² and 29.60 A/m², the removal efficiency of CN^- are 4.24%, 66.6%, 86.1%, 97.4% and 98.9% after 30 min reaction. The removal efficiency of CN^- is increased with the increasing current density. The increased current density would improve the applied electrode potential in the system, which promoted the oxidation efficiency of cyanide. In addition, the high current density would enhance the electrochemical reduction of the copper ions onto the cathode via Eq. (1).

But when the current density was increased from 14.80 A/m² to 29.60 A/m², the removal efficiency of CN^- was remained nearly unchanged. At the high current intensity, secondary reactions occurred easily [28]. With respect to the energy cost, the optimal current density for cyanide removal was selected as 14.80 A/m².

3.2. Effect of $\text{K}_2\text{S}_2\text{O}_8$ concentration on the removal efficiency of $\text{Cu}(\text{CN})_3^{2-}$

The effect of initial $\text{K}_2\text{S}_2\text{O}_8$ concentration ranging from 0 to 2.00 mM was investigated in the electrochemical oxidation of $\text{Cu}(\text{CN})_3^{2-}$ process. As shown in Fig. 2, the removal efficiency of $\text{Cu}(\text{CN})_3^{2-}$ is increased significantly with the increasing $\text{K}_2\text{S}_2\text{O}_8$ concentration. When the concentration of $\text{K}_2\text{S}_2\text{O}_8$ is increased from 0 to 1.00 mM, the removal efficiency of CN^- is increased markedly from 69.9% to 97.7% at 30 min.

It was clear that the increase of $\text{K}_2\text{S}_2\text{O}_8$ concentration accelerated the degradation of CN^- in the electrochemical system. Some metals could be used as $\text{K}_2\text{S}_2\text{O}_8$ activators, such as, Fe (0) [29], Fe (II) [30] and Ag (I) [21], which had advantages of high efficiency without high energy consumption under room temperature condition. More concentration of $\text{K}_2\text{S}_2\text{O}_8$ would enhance the decomposition of $\text{Cu}(\text{CN})_3^{2-}$, leading to the release of more Cu (I) ions. As shown in Eq. (2), the increasing concentration of $\text{K}_2\text{S}_2\text{O}_8$ would generate more $\text{SO}_4^{\cdot -}$, which could effectively remove cyanide contaminant.

However, when the $\text{K}_2\text{S}_2\text{O}_8$ concentration is increased from 1.00 mM to 2.00 mM, the removal efficiency of CN^- is remained nearly unchanged. Therefore, the optimal $\text{K}_2\text{S}_2\text{O}_8$ concentration for cyanide removal was 1.00 mM.

Fig. 1. Effect of current density on the removal efficiency of $\text{Cu}(\text{CN})_3^{2-}$ in the electrochemical oxidation process ($[\text{Cu}(\text{CN})_3^{2-}] = 0.30 \text{ mM}$; $[\text{CN}^-] = 0.90 \text{ mM}$; $[\text{K}_2\text{S}_2\text{O}_8] = 0.75 \text{ mM}$; $[\text{NaClO}_4] = 2.00 \text{ mM}$; $\text{pH} = 12.0$).

Fig. 2. Effect of persulfate concentration on the removal efficiency of $\text{Cu}(\text{CN})_3^{2-}$ in the electrochemical oxidation process ($[\text{Cu}(\text{CN})_3^{2-}] = 0.30 \text{ mM}$; $[\text{CN}^-] = 0.90 \text{ mM}$; current density = 14.80 A/m^2 ; $[\text{NaClO}_4] = 2.00 \text{ mM}$; $\text{pH} = 12.0$).

In the meantime, the conversion of cyanide was investigated. As shown in Fig. 3, the main product in the cyanide oxidation process is cyanate (CNO^-). In this study, ammonia, nitrite and nitrate are not detected. The sum of the cyanide concentration and cyanate concentration at different reaction time is found to be nearly equal to the initial cyanide concentration, indicating that the main product is CNO^- during the process.

3.3. The Cu mass distribution and balance

The quality of copper ions deposited onto the anode and cathode was dissolved by the dilute nitric acid and then measured by ICP-OES. The concentration of total Cu ions in solution was determined in different reaction time. As shown in Fig. 4(a), the Cu ions concentration in the solution was decreased with the addition of $\text{K}_2\text{S}_2\text{O}_8$ reagent. When the $\text{K}_2\text{S}_2\text{O}_8$ concentration is increased to 1.00 mM , the Cu ions are totally removed within 30 min. In addition, the distribution of Cu species was analyzed at various $\text{K}_2\text{S}_2\text{O}_8$ concentrations after the electrochemical oxidation of $\text{Cu}(\text{CN})_3^{2-}$. As shown in Fig. 4(b), without the addition of $\text{K}_2\text{S}_2\text{O}_8$, the percentages of Cu (by wt%) deposited onto the anode, in the solution, and deposited onto the cathode are 69.6%, 24.7%, and 5.7%, respectively.

Fig. 3. Cyanide transformation in the electrochemical oxidation process ($[\text{Cu}(\text{CN})_3^{2-}] = 0.30 \text{ mM}$; $[\text{CN}^-] = 0.90 \text{ mM}$; $[\text{K}_2\text{S}_2\text{O}_8] = 1.00 \text{ mM}$; current density = 14.80 A/m^2 ; $[\text{NaClO}_4] = 2.00 \text{ mM}$; $\text{pH} = 12.0$).

Fig. 4. The variation of Cu concentration and distribution of Cu: (a) The variation of Cu ions concentration in the electrochemical oxidation process; (b) The copper mass balance in the electrochemical oxidation process with different concentrations of $\text{K}_2\text{S}_2\text{O}_8$ ($[\text{Cu}(\text{CN})_3^{2-}] = 0.30 \text{ mM}$; $[\text{CN}^-] = 0.90 \text{ mM}$; current density = 14.80 A/m^2 ; $[\text{NaClO}_4] = 2.00 \text{ mM}$; $\text{pH} = 12.0$).

With the increase of $\text{K}_2\text{S}_2\text{O}_8$ concentration, the percentage of Cu deposited onto the cathode and in the solution is decreased and the percentage of Cu deposited onto the anode is increased gradually. When the concentration of $\text{K}_2\text{S}_2\text{O}_8$ is 1.00 mM , the percentages of Cu deposited onto the anode and the cathode are 99.1% and 0.55%. Corresponding to the $\text{K}_2\text{S}_2\text{O}_8$ concentrations of 0 mM, 0.25 mM, 0.50 mM, 0.75 mM, 1.00 mM and 2.00 mM, the percentages of Cu on the RuO_2/Ti mesh anode are 69.6%, 66.7%, 72.7%, 74.7%, 99.1% and 99.4%, respectively. Thus, it was obvious that the increasing $\text{K}_2\text{S}_2\text{O}_8$ concentration could increase the percentages of Cu deposited onto the anode.

3.4. Analysis of the surface variation of the electrodes

The deposition on the electrodes surface was investigated by SEM-EDX, XRD and XPS. As shown in Fig. 5, there are no copper or copper oxides on the electrodes surface before the electrochemical reaction. After 30 min reaction, copper ions are reduced onto the cathode and copper oxides are generated onto the anode. Meantime, the EDX spectra of the deposition on the electrodes after 30 min reaction were shown in the [supporting information](#).

Fig. 5. SEM analysis of the RuO₂/Ti mesh anode and stainless steel cathode before and after reaction ($[\text{Cu}(\text{CN})_3^{2-}] = 0.30 \text{ mM}$; $[\text{CN}^-] = 0.90 \text{ mM}$; $[\text{K}_2\text{S}_2\text{O}_8] = 1.00 \text{ mM}$; current density: 14.80 A/m^2 ; $[\text{NaClO}_4] = 2.00 \text{ mM}$; $\text{pH} = 12.0$).

(Fig. S1). The EDX spectra results indicated that the major elements on the anode were Cu, O, Ti and Ru. And the major elements on the cathode were Cu, Fe, Mn and Cr. Therefore, it was shown that the deposition on the electrodes surface contained the Cu element.

The deposition on the anode and cathode were further analyzed by the XRD technique. As shown in Fig. 6(a), for the cathode, the pronounced diffraction peaks in the XRD pattern at 2θ of 44.50° , 50.05° and 74.50° are corresponded to (1 1 1), (2 0 0) and (2 2 0) Bragg's reflections of monoclinic Cu phase in accordance with the standard (JCPDS: 01-085-1326) [31]. As shown in Fig. 6(b), for the anode, the pronounced diffraction peaks in the XRD pattern at 2θ of 32.52° , 35.55° , 38.73° , 53.41° , 68.14° , 72.41° and 75.02° are corresponded to (1 1 0), (-1 1 1), (1 1 1), (0 2 0), (2 2 0), (3 1 1) and (0 0 4) Bragg's reflections of monoclinic CuO phase in accordance with the standard (JCPDS: 01-085-1326) [32]. The intensity of (1 1 1) peak is much stronger than other peaks, indicating a preferred orientation. The cubic structure of the Cu₂O is not observed in the XRD patterns, indicating the generation of deposition onto the anode is CuO.

The value state of the copper deposition on the electrodes was determined by the XPS technique. As shown in Fig. 7(a), according to the XPS spectra of the stainless steel cathode, the Cu2p core level binding energy is observed. The major Cu2p_{1/2} peaks centers at 951.4 eV and the major Cu2p_{3/2} peaks centers at 931.4 eV indicating the generation of zero-valent copper, which is indicated that the copper ions are reduced in the electrochemical process [33]. As shown in Fig. 7(b), according to the XPS spectra of the Cu2p core level binding energy appeared on the anode, the major Cu2p_{1/2} peaks centers at 952.7 eV and the major Cu2p_{3/2} peaks centers at 932.7 eV confirming the deposition on the anode surface are CuO [34,35]. It has been reported that the CuO deposition on the anode exhibited the catalytic properties for removing CN⁻ [36], because the K₂S₂O₈ reagent was activated by CuO under mild conditions and the activated K₂S₂O₈ showed strong oxidation capacity [25]. Therefore, the generation of CuO on the anode surface could increase the removal efficiency of CN⁻.

3.5. Involved active species

Sulfate radical, which was generally considered as the oxidant species in the persulfate activation process. The redox potential of $\text{SO}_4^{\cdot-}$ was confirmed as 2.5–3.1 V, while the potential of $\cdot\text{OH}$ was detected as 2.7 V in acid solution and 1.8 V in neutral solution. Due to the narrow gap of the redox potential between $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, the transformation from $\text{SO}_4^{\cdot-}$ to $\cdot\text{OH}$ occurred via Eqs. (3) and (4) [37,38]. During the process, the OH^- ions were consumed and the pH of the solution would be decreased. In order to avoid the release of HCN gas, the initial pH of the solution was maintained at alkaline condition ($\text{pH} = 12.0$).

The formation of $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ radicals during the $\text{Cu}(\text{CN})_3^{2-}$ oxidation process was checked by the ESR technique. The variation of signal intensity at different reaction time was shown in Fig. 8. The characteristic four peaks of DMPO- $\cdot\text{OH}$ with the intensity of 1:2:2:1 are observed at initial 30 s, indicating the generation of $\cdot\text{OH}$ radicals [39,40]. And the characteristic six peaks of DMPO- $\text{SO}_4^{\cdot-}$ are observed at 3 min, which is confirmed the generation of the $\text{SO}_4^{\cdot-}$ radicals. In order to analyze the process of K₂S₂O₈ activation, the oxidation reaction was carried out without stirring and the active species generated near the anode, cathode and in the solution were studied by the ESR technique. As shown in the supporting information of Fig. S2, No significant difference of the radical intensity is observed, which indicates that the activation of K₂S₂O₈ is mainly due to the Cu⁺ ions.

At the same time, radical quenching experiments were carried out to confirm the role of generated active radicals. The active radical species such as $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ could react rapidly with the ethanol (EtOH), and $\cdot\text{OH}$ could react rapidly with the Tert-butanol (TBA). Thus, EtOH acted as the radicals quencher for $\text{SO}_4^{\cdot-}$ and

Fig. 6. XRD patterns of the deposition on the electrodes ($[\text{Cu}(\text{CN})_3]^{2-} = 0.30 \text{ mM}$; $[\text{CN}^-] = 0.90 \text{ mM}$; $[\text{K}_2\text{S}_2\text{O}_8] = 1.00 \text{ mM}$; current density = 14.80 A/m^2 ; $[\text{NaClO}_4] = 2.00 \text{ mM}$; pH = 12.0).

$\cdot\text{OH}$, TBA acted as the radicals quencher for $\cdot\text{OH}$. As shown in Fig. 9, the removal efficiency of CN^- is substantially decreased by 35.2% when the EtOH (500 mM) is added to the system. By contrast, the removal efficiency of CN^- is only slightly decreased by 18.0% after 30 min reaction when the TBA (500 mM) is added to the system. The results indicated that both $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ were responsible for the cyanide removal. In addition, the activated $\text{K}_2\text{S}_2\text{O}_8$ and anode oxidation also had the role for cyanide removal.

4. Conclusions

In this work, the removal efficiency of $\text{Cu}(\text{CN})_3^{2-}$ was largely enhanced with the addition of $\text{K}_2\text{S}_2\text{O}_8$ reagent. In the cyanide removal process, the $\text{K}_2\text{S}_2\text{O}_8$ reacted with copper cyanide complexes via a Fenton-like reaction, generating the activated radicals of $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, which were responsible for the cyanide removal. At the same time, the increasing $\text{K}_2\text{S}_2\text{O}_8$ concentration would increase the amount of CuO deposition on the anode surface. The generation of CuO on the anode exhibited the catalytic activities for cyanide removal. By the radical quenching experiments, the combination of anode oxidation and activated radicals was highly effective for cyanide removal. The cyanate was the main oxidation product in this electrochemical system. Therefore, the obtained results provided some valuable information for the treatment of $\text{Cu}(\text{CN})_3^{2-}$ contaminated water.

Fig. 7. XPS analysis of the deposition on the electrodes: (a) XPS spectra of the deposition on the cathode; (b) XPS spectra of the deposition on the anode ($[\text{Cu}(\text{CN})_3]^{2-} = 0.30 \text{ mM}$; $[\text{CN}^-] = 0.90 \text{ mM}$; $[\text{K}_2\text{S}_2\text{O}_8] = 1.00 \text{ mM}$; current density = 14.80 A/m^2 ; $[\text{NaClO}_4] = 2.00 \text{ mM}$; pH = 12.0).

Fig. 8. ESR signals of $\text{DMPO}\cdot\text{OH}$ and $\text{DMPO}\cdot\text{SO}_4^{\cdot-}$ in the electrochemical oxidation of $\text{Cu}(\text{CN})_3^{2-}$ ($[\text{Cu}(\text{CN})_3]^{2-} = 0.30 \text{ mM}$; $[\text{CN}^-] = 0.90 \text{ mM}$; $[\text{K}_2\text{S}_2\text{O}_8] = 1.00 \text{ mM}$; current density = 14.80 A/m^2 ; $[\text{NaClO}_4] = 2.00 \text{ mM}$; pH = 12.0).

Fig. 9. The removal efficiency of CN^- with the addition of different concentrations of EtOH and TBA ($[\text{Cu}(\text{CN})_2] = 0.30 \text{ mM}$; $[\text{CN}^-] = 0.90 \text{ mM}$; $[\text{K}_2\text{S}_2\text{O}_8] = 1.00 \text{ mM}$; current density = 14.80 A/m^2 ; $[\text{NaClO}_4] = 2.00 \text{ mM}$; $\text{pH} = 12.0$).

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 21377148, 51578532) and the Chinese Academy of Sciences (QYZDB-SSW-DOC018).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.seppur.2017.07.006>.

References

- [1] J. Zhang, L. Liu, Y. Liang, J.Z. Zhou, Y.F. Xu, X.X. Ruan, Y.S. Lu, Z.P. Xu, G.R. Qian, Enhanced precipitation of cyanide from electroplating wastewater via self-assembly of bimetal cyanide complex, *Sep. Purif. Technol.* 150 (2015) 179–185.
- [2] P.D. Vreese, A. Skoczylas, E. Matthijs, J. Franssaer, K. Binnemans, Electrodeposition of copper–zinc alloys from an ionic liquid-like choline acetate electrolyte, *Electrochim. Acta* 108 (2013) 788–794.
- [3] M.A. Barakat, Adsorption behavior of copper and cyanide ions at TiO_2 –solution interface, *J. Colloid Interface Sci.* 291 (2005) 345–352.
- [4] S.C. Tian, Y.B. Li, H.B. Zeng, W. Guan, Y. Wang, X. Zhao, Cyanide oxidation by singlet oxygen generated via reaction between H_2O_2 from cathodic reduction and OCl^- from anodic oxidation, *J. Colloid Interface Sci.* 482 (2016) 205–211.

- [5] 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.
- [6] Y. Zheng, Z.K. Li, X.Y. Wang, X.L. Gao, C.J. Gao, The treatment of cyanide from gold mine effluent by a novel five-compartment electrodialysis, *Electrochim. Acta* 169 (2015) 150–158.
- [7] 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.
- [8] Ü.B. Ögütveren, E. Törü, S. Koparal, Removal of cyanide by anodic oxidation for wastewater treatment, *Water Res.* 33 (1999) 1851–1856.
- [9] S. Pulkka, M. Martikainen, A. Bhatnagar, M. Sillanpää, Electrochemical methods for the removal of anionic contaminants from water – a review, *Sep. Purif. Technol.* 132 (2014) 252–271.
- [10] P. Oulego, A. Laca, M. Diaz, Kinetics and pathways of cyanide degradation at high temperatures and pressures, *Environ. Sci. Technol.* 47 (2013) 1542–1549.
- [11] M.A. Barakat, Y.T. Chen, C.P. Huang, Removal of toxic cyanide and Cu(II) ions from water by illuminated TiO_2 catalyst, *Appl. Catal. B: Environ.* 53 (2004) 13–20.
- [12] M.J. López-Muñoz, J. Aguado, R.V. Grieken, J. Marugán, Simultaneous photocatalytic reduction of silver and oxidation of cyanide from dicyanoargentate solutions, *Appl. Catal. B: Environ.* 86 (2009) 53–62.
- [13] V.K. Sharma, W. Rivera, J.O. Smith, B. O'Brien, Ferrate(VI) oxidation of aqueous cyanide, *Environ. Sci. Technol.* 32 (1998) 2608–2613.
- [14] 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.
- [15] 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.
- [16] 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.
- [17] N. Kuyucak, A. Akcil, Cyanide and removal options from effluents in gold mining and metallurgical processes, *Miner. Eng.* 50–51 (2013) 13–29.
- [18] H.B. Zeng, S.C. Tian, H.F. Liu, B.Y. Chai, X. Zhao, Photo-assisted electrolytic decomplexation of Cu-EDTA and Cu recovery enhanced by H_2O_2 and electro-generated active chlorine, *Chem. Eng. J.* 301 (2016) 371–379.
- [19] F.C. Moreira, R.A.R. Boaventura, E. Brillas, V.J.P. Vilar, Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters, *Appl. Catal. B: Environ.* 202 (2016) 217–261.
- [20] S.C. Tian, Y.B. Li, X. Zhao, 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, *Electrochim. Acta* 180 (2015) 746–755.
- [21] G.P. Anipsitakis, D.D. Dionysiou, Radical generation by the interaction of transition metals with common oxidants, *Environ. Sci. Technol.* 38 (2004) 3705–3712.
- [22] J.K. Du, J.G. Bao, X.Y. Fu, C.H. Lu, S.H. Kim, Facile preparation of S/Fe composites as an effective peroxydisulfate activator for RhB degradation, *Sep. Purif. Technol.* 163 (2016) 145–152.
- [23] Y.Y. Ahn, E.T. Yun, J.W. Seo, C. Lee, S.H. Kim, J.H. Kim, J. Lee, Activation of peroxymonosulfate by surface-loaded noble metal nanoparticles for oxidative degradation of organic compounds, *Environ. Sci. Technol.* 50 (2016) 10187–10197.
- [24] H. Lee, H.I. Kim, S. Weon, W. Choi, Y.S. Hwang, J. Seo, C. Lee, J.H. Kim, Activation of persulfates by graphitized nanodiamonds for removal of organic compounds, *Environ. Sci. Technol.* 50 (2016) 10134–10142.
- [25] T. Zhang, Y. Chen, Y.R. Wang, J.L. Roux, Y. Yang, J.P. Croue, Efficient peroxydisulfate activation process not relying on sulfate radical generation for water pollutant degradation, *Environ. Sci. Technol.* 48 (2014) 5868–5875.
- [26] G. Moussavi, M. Pourakbar, E. Aghayani, S. Shekoohyian, Comparing the efficacy of VUV and UVC/ $\text{S}_2\text{O}_8^{2-}$ advanced oxidation processes for degradation and mineralization of cyanide in wastewater, *Chem. Eng. J.* 294 (2016) 273–280.
- [27] X. Zhao, J.J. Zhang, J.H. Qu, Photoelectrocatalytic Oxidation of Cu-cyanides and Cu-EDTA at TiO_2 nanotube electrode, *Electrochim. Acta* 180 (2015) 129–137.
- [28] C.A. Martinez-Huitle, S. Ferro, Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes, *Chem. Soc. Rev.* 35 (2006) 1324–1340.
- [29] P. Drzewicz, L. Perez-Estrada, A. Alpatova, J.W. Martin, M.G. El-Din, Impact of peroxydisulfate in the presence of zero valent iron on the oxidation of cyclohexanoic acid and naphthenic acids from oil sands process-affected water, *Environ. Sci. Technol.* 46 (2012) 8984–8991.
- [30] S. Rodriguez, L. Vasquez, D. Costa, A. Romero, A. Santos, Oxidation of Orange G by persulfate activated by Fe(II) , Fe(III) and zero valent iron, *ZVI, Chemosphere* 101 (2014) 86–92.
- [31] L.L. Zhang, D.A. Xu, C. Hu, Y.L. Shi, Framework Cu-doped AlPO_4 as an effective Fenton-like catalyst for bisphenol A degradation, *Appl. Catal. B: Environ.* 207 (2017) 9–16.
- [32] S. Lee, U. Kang, G. Piao, S. Kim, D.S. Han, H. Park, Homogeneous photoconversion of seawater uranium using copper and iron mixed-oxide semiconductor electrodes, *Appl. Catal. B: Environ.* 207 (2017) 35–41.
- [33] L.L. Zhang, Y.L. Nie, C. Hu, J.H. Qu, Enhanced Fenton degradation of Rhodamine B over nanoscaled Cu-doped LaTiO_3 perovskite, *Appl. Catal. B: Environ.* 125 (2012) 418–424.
- [34] L.F. Chiang, R.A. Doong, Enhanced photocatalytic degradation of sulfamethoxazole by visible-light-sensitive TiO_2 with low Cu addition, *Sep. Purif. Technol.* 156 (2015) 1003–1010.
- [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.

- [36] L. Szpyrkowicz, S.N. Kaulb, E. Molgac, M. DeFaverid, 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.
- [37] Y. Lei, C.S. Chen, Y.J. Tu, Y.H. Huang, H. Zhang, Heterogeneous degradation of organic pollutants by persulfate activated by CuO-Fe₃O₄: mechanism, stability, effects of pH and bicarbonate ions, *Environ. Sci. Technol.* 49 (2015) 6838–6845.
- [38] Y.H. Guan, J. Ma, X.C. Li, J.Y. Fang, L.W. Chen, Influence of pH on the formation of sulfate and hydroxyl radicals in the UV/peroxymonosulfate system, *Environ. Sci. Technol.* 45 (2011) 9308–9314.
- [39] 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.
- [40] 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: Environ.* 158–159 (2014) 85–90.