Operational conditions of electrochemical oxidation process for removal of cyanide (CN⁻) in real plating wastewater

Xin Zhao^{1a}, Minsik Jang^{1b}, Jin Woo Cho^{2a} and Jae Woo Lee^{*1}

¹Department of Environmental Engineering, college of Science and Technology, Korea University, Republic of Korea ²Department of Environmental, Energy & Geoinformatics, college of Engineering, Sejong University, Republic of Korea

(Received January 11, 2020, Revised January 27, 2020, Accepted February 20, 2020)

Abstract. An electrochemical oxidation process was applied to remove cyanide (CN⁻) from real plating wastewater. CN⁻ removal efficiencies were investigated under various operating factors: current density and electrolyte concentration. Electrolyte concentration positively affected the removal of both CN⁻ and Chemical Oxygen Demand (COD). As the electrolyte concentration increased from 302 to 2,077 mg Cl⁻/L, removal efficiency of CN⁻ and COD increased from 49.07% to 98.30% and from 23.53% to 49.50%, respectively, at 10 mA/cm². Current density affected the removal efficiency in a different way. As current density increased at a fixed electrolyte concentration, CN⁻ removal efficiency increased while COD removal efficiency decreased, this is probably due to lowered current efficiency caused by water electrolysis.

Keywords: electrochemical oxidation; cyanide; current density; electrolyte

1. Introduction

Cyanide (CN⁻) is commonly used in the plating process of gold, silver and copper to improve the efficiency and quality of plating. However, cyanide released from the plating process can react with diverse heavy metals such as the Cu, Ni, Cd, Co, Cr, Fe, Pb and Zn present in the plating wastewater (Botz *et al.* 2005, Dash *et al.* 2009, Johnson, 2015). Discharge of untreated plating wastewater carries harmful pollution to the receiving water bodies and increases environmental damage (Smith & Heath 1979). Therefore, it is necessary to treat this wastewater in order to preserve the aquatic ecosystem.

Various treatment technologies such as alkaline chlorination, biological treatment and iron-cyanide precipitation have been developed for the removal of cyanide from plating wastewater (Botz 2001, Ghosh et al. 1999, Ibrahim et al. 2016, Ly et al. 2017, Mekuto et al. 2016, Yu et al. 2016). Among these technologies, alkaline chlorination is most commonly used due to the simplicity of the process and low costs. However, this particular process requires large amounts of chemicals resulting in fairly high operational costs (Dash et al. 2009). Biological treatment is another cost-effective method to reduce cyanide concentration in wastewater. However, carrying out this biological treatment process effectively is not easy because of the variations in cyanide load depending on the plating process as well as the diverse kinds of bio-toxic substances that can be present in the wastewater (White et al. 2000).

Iron-cyanide precipitation has exhibited relatively good treatment performance but generates a large amount of chemical sludge (Botz 2001).

Electrochemical oxidation has recently gained a huge amount of interest as a promising treatment option along with advances in the technical state of electrodes that have abruptly emerged along with the expansion of the battery industry. This method is considered eco-friendly because it does not use abundant toxic chemicals and does not generate excessive sludge. However, most of these kind of electrochemical oxidation processes have been limited to use with wastewater containing cyanide concentration at 10 - 15% or higher. When the cyanide concentration is lower, the removal efficiency decreases markedly (El-Ghaoui et al. 1982). Since the concentration of cyanide in the plating wastewater can possibly vary in a relatively wide range, it is very important to develop an efficient electrochemical oxidation process for low concentration cyanide. Also, plating wastewater may contain various polluting substances, i.e. heavy metals or organic matters other than cyanide and these co-existing substances can affect electrochemical oxidation performance (Jung et al. 2019, Lee et al. 2016, Li et al. 2019). In case of low concentration of cyanide, electrochemical oxidation treatment might need supportive oxidizing agents. Chloride (Cl⁻) is often used as an electrolyte in electrochemical oxidation process and also plays a role of oxidizing agent by forming chlorine (Cl₂) or hypochlorite (ClO⁻), which is known as an indirect oxidation of CN⁻ (El-Ghaoui et al. 1982, Tian et al. 2016). Therefore, electrolyte concentration is equally important to a major operating factor of current density for oxidation of a low-strengthened cyanide in real plating wastewater.

This study explores a method to treat cyanide (CN⁻) in the real plating wastewater through a lab-scale batch electrochemical oxidation process. Of the various operating

^{*}Corresponding author, Professor

E-mail: jaewoo@korea.ac.kr

^a Ph.D.

^b M.Sc. Student



Fig. 1. Electrochemical oxidation system (a: Ti/RuO₂-IrO₂ electrodes; b: electrode array; c: EO apparatus)

conditions this study specifically focuses on the effects of current density and electrolyte concentration on the removal efficiencies of CN^- and COD in the wastewater.

2. Materials and methods

2.1 Wastewater

The plating wastewater was collected from an electroplating wastewater treatment plant in Namyangju city, Republic of Korea. The amount of plating wastewater generated there is $1,000 - 3,000 \text{ m}^3/\text{day}$, the alkaline chlorination method is usually used for removal of cyanide. The concentrations of CN⁻, Cl⁻ and COD in the wastewater were $47.8\pm6.8 \text{ mg/L}$, $302.3\pm18.7 \text{ mg/L}$ and $440.8\pm65.9 \text{ mg/L}$, respectively.

2.2 Batch electrochemical oxidation process

A 2.5 L rectangular acrylic reactor with a 2.0 L working volume (Fig. 1a) was used for our batch electrochemical oxidation process. An open electrolytic cell module containing double cathodes and anodes was constructed (Fig. 1b), each electrode was coated with Ti/RuO₂-IrO₂ and was specially designed like a mesh-plate in order to enhance mass transfer from the bulk to the electrode surface (Fig.1c). Each electrode cell has a working area of 250.24 cm². The electrolysis current was set to be constant with a DC power supply (EX 100-18, ODA technologies, South Korea). Magnetic stirring at 400 rpm was applied in order to homogenize the wastewater inside the reactor.

Experiments were carried out at room temperature and the solution pH of the water was pre-adjusted to 11 by adding sodium hydroxide in order to minimize the loss of free cyanide at a lower pH. In this study, three different parameters were investigated in order to find the optimal conditions for cyanide removal. Current density was set to 4, 6, 8 and 10 mA/cm². Also, under a fixed current density, electrolyte concentrations were varied from 302 to 2,077 mg Cl⁻/L. Every experiment was conducted for 1 hr and samples were taken every 10 min.

Table 1 Operating conditions of this study.		
	Unit	Value
pН	-	11
Stirring rate	rpm	400
Current density	mA/cm ²	4 / 6 / 8 / 10
Electrolyte conc.	mg/L	302 / 746 / 1,189 / 2,077
Time	min	0 / 10 / 20 / 30 / 40 / 50 / 60



Fig. 2 Effect of current density and electrolyte concentration on removal efficiency of CN⁻

2.3 Analytical methods

The concentration of cyanide (CN^{-}) , chloride (Cl^{-}) and COD were measured by a UV–VIS spectrophotometer (DR 6000, Hach, USA).

2.4 Statistical analysis

Multiple regression analysis was conducted in order to investigate the dependence of the cyanide removal efficiency on three major operating factors: current density (J), electrolyte concentration (E) and reaction time (t). The



Fig. 3. 3-dimensional response surface graph for the CN⁻ removal efficiency as function of current density and electro lyte concentration at a fixed reaction time of 60 min

multiple regression analysis equation can be expressed as follows:

$$R_{CN} = a_1 J + a_2 E + a_3 t \tag{1}$$

where, R_{CN} is the removal efficiency of CN⁻ (%), J is the current density (mA/cm²), E is the electrolyte concentration (mg Cl⁻/L), t is the reaction time (min) while a_1 , a_2 , and a_3 are the fitting parameters. The parameter values and assumptions of the multiple regression equation are subject to uncertainty, i.e. change and error. Thus, a sensitivity analysis was carried out to determine how changes to those factors (i.e. the variables) affect the removal efficiency (Gan *et al.* 2014). Given the determined parameters, each target variable was subject to change from -20 to +20% of its initial value in order to determine their impact on CN⁻ removal efficiency.

3. Results and discussion

3.1 Effect of current density and electrolyte concentration on removal of CN⁻

There are two possible routes of electrolytic oxidation of CN^{-} : direct oxidation and indirect oxidation. When CN^{-} concentration in the wastewater is high >10,000 ppm, direct oxidation of CN^{-} is thought to be dominant through the sequential reactions as follows (Comninellis 1994):

$$MO_{X+1} + CN^- \to MO_X + CNO^- \tag{2}$$

$$MO_{X}(\cdot OH) + CNO^{-} \rightarrow 2MO_{X} + CO_{2} + 0.5N_{2} + H_{2}O + 6e^{-}$$
(3)

However, when the wastewater contained very low CNconcentration and a significant amount of COD, it is presumed that indirect oxidation is dominant. For indirect oxidation, the chloride ion (Cl⁻) added in the form of electrolyte can be mainly used as an oxidizing agent through Eq. 4 - 5 prior to direct oxidation of CN⁻ (Felix-Navarro *et al.* 2011). This means that electrolyte concentration plays as an important a role as current density for enhancing CN⁻ removal. The oxidized form of chloride (Cl⁻), chlorine (Cl₂) or hypochlorite (ClO⁻), might oxidatively degrade COD as well as CN⁻ (El-Ghaoui *et al.* 1982).

$$2Cl^- \to Cl_2 + 2e^- \tag{4}$$

$$Cl_2 + 20H^- \to Cl^- + Cl0^- + H_20$$
 (5)

$$2CN^{-} + 5Cl0^{-} + 2OH^{-} \rightarrow 5Cl^{-} + N_2 + 2CO_3^{2-} + H_2O$$
(6)

Figure 2 shows the effect of current density and electrolyte concentration of Cl⁻ on the removal efficiencies of CN⁻. As the applied current density was increased from 4 to 10 mA/cm², CN⁻ removal efficiency proportionally increased (Fig. 2). It has also been reported that CN⁻ removal in a flow electrochemical reactor is mainly dependent on the current density (Lanza & Bertazzoli 2002). An increase of electrolyte concentration, especially Cl⁻, positively affected the electrochemical oxidation performance resulting in increase in the removal efficiency of CN⁻ as shown in Fig. 2.

In order to demonstrate the effects of current density and electrolyte concentration more clearly, 3-D mesh plots are presented in Fig. 3. Impact of electrolyte concentration and reaction time were more significant than current density. A CN⁻ removal efficiency higher than 90% could be achieved if the current density was greater than 6 mA/cm². However, the required electrolyte concentration for achieving an identical CN⁻ removal efficiency of 90% was at least 1,200 mg Cl⁻/L for 60 min reaction time. Thus, for ensuring satisfactory performance of CN⁻ removal from the plating

219



Fig. 4 Effect of current density and electrolyte concentration on removal efficiency of COD

wastewater used in this study, the optimal current density, electrolyte concentration and reaction time suggested are 6-10 mA/cm², 1,200-2,100 mg Cl⁻/L and 40-60 mins, respectively.

3.2 Electrochemical oxidation of COD and relationship between CN⁻ and COD removal efficiencies

Figure 4 shows the effect of current density and electrolyte concentration of Cl^- on the removal efficiencies of COD. In contrast to CN^- , the removal efficiency of COD tended to slightly decrease with the increase of current density even though the reason for this is not still clear.

In electrochemical oxidation, CN⁻ and COD probably have a competitive relation depending on current density. Removal efficiencies of COD seem to inversely relate to those of CN^- in terms of current density increases (Fig. 5). Excessive current density can adversely affect COD removal due to decreased efficiency (Xu *et al.* 2012). That earlier study described the decrease of current efficiency is associated with the parasitic reaction of water electrolysis on the anode at a high current density. The lowered current efficiency might relate to COD removal but not the decomposition of CN^- . The current efficiency can be directly related to the energy consumption, and thus the optimal combination of current density and electrolyte concentration must be considered carefully in real plating wastewater treatment.

3.3 Multiple regression analysis and sensitivity analysis for cyanide efficiency

Experimental data was analyzed by multiple regression analysis using the IBM SPSS program (Version 22.0). The multi linear regression of CN^- removal efficiency with three variables (i.e., current density, electrolyte concentration and reaction time) is noted in Eq. 1:

$$R_{CN} = 2.117J + 0.020E + 1.181t - 30.369 \tag{7}$$

The adjusted R^2 is 0.948, the *P*-values for the estimated coefficients are 5.036x10⁻⁷, 6.936x10⁻²⁸ and 2.339x10⁻⁴⁹ for a_1 , a_2 , and a_3 . Based on the results of the statistical analysis, Eq. 7 represents the relationship of CN⁻ removal efficiency to the three variables well.

Figure 6 shows the sensitivity of changes in CNremoval efficiency (R_{CN}) depending on the change of the fitting parameter (a_1 , a_2 , and a_3). Absolute values of slopes shown in Fig. 6 can explain the degree to which each factor affects CN⁻ removal efficiency. These, in order, are Reaction time (0.711) > Electrolyte concentration (0.356) > Current density (0.067). The reaction time is a kind of comprehensive factors representing both electrolyte concentration and current input. The reaction time directly affects the electrochemical oxidative removal efficiency of



Fig. 5. The relationship between CN^- and COD removal efficiencies as a function of current density (a: 302 mg Cl⁻/L; b: 746 mg Cl⁻/L; c: 1,189 mg Cl⁻/L; d: 2,077 mg Cl⁻/L)



Fig. 6. Sensitivity of the fitting parameters affecting CNremoval efficiency

 CN^- by increasing both indirect oxidation time for converting electrolyte (Cl⁻) to oxidized forms (Cl⁻ or OCl⁻) and time for direct oxidation of CN^- . According to the results of sensitivity analysis, when the current density is constant, the indirect oxidation reaction can improve the CN^- removal efficiency due to the long reaction time and high electrolyte concentration. Therefore, higher cyanide removal efficiency can be achieved by increasing the reaction time and electrolyte concentration rather than the current density.

4. Conclusion

The effects of current density and electrolyte concentration on removal of CN⁻ and COD were investigated. Electrolyte concentration, especially Cl⁻, dominantly affected the electrochemical removal of both CN⁻ and COD. The increase of current density could improve the electrochemical removal of cyanide but not COD. Statistical analysis indicates that reaction time and electrolyte concentration were the more important factors affecting CN⁻ removal performance.

Acknowledgments

This study was supported by the Korea Ministry of the Environment (MOE) as "Technologies for the Risk Assessment & Management Program (2017000140007)".

References

- Botz, M., Mudder, T. and Akcil, A. (2005), "Cyanide treatment: physical, chemical and biological processes", *Advances in Gold Ore Processing*, Elsevier, Amsterdam, 672-700.
- Botz, M.M. (2001), "Overview of cyanide treatment methods", *Mining Environmental Management*, Mining Journal Ltd., London, United Kingdom, 28-30.
- Comninellis, C. (1994), "Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water

treatment", *Electrochim. Acta*, **39**(11-12), 1857-1862. https://doi.org/10.1016/0013-4686(94)85175-1.

- Dash, R.R., Gaur, A., Balomajumder, C. (2009), "Cyanide in industrial wastewaters and its removal: a review on biotreatment", *J. Hazard. Mater.*, **163**(1), 1-11. https://doi.org/10.1016/j.jhazmat.2008.06.051.
- El-Ghaoui, E., Jansson, R., Moreland, C. (1982), "Application of the trickle tower to problems of pollution control. II. The direct and indirect oxidation of cyanide", *J. Appl. Electrochem.*, **12**(1), 69-73. https://doi.org/10.1007/BF01112066.
- Felix-Navarro, R.M., Wai Lin, S., Violante-Delgadillo, V., Zizumbo-Lopez, A., Perez-Sicairos, S. (2011), "Cyanide degradation by direct and indirect electrochemical oxidation in electro-active support electrolyte aqueous solutions", *J. Mexican Chemical Soc.*, **55**(1), 51-56.
- Gan, Y., Duan, Q., Gong, W., Tong, C., Sun, Y., Chu, W., Ye, A., Miao, C., Di, Z. (2014), "A comprehensive evaluation of various sensitivity analysis methods: A case study with a hydrological model", *Environ. Modell. Softw.*, **51**, 269-285. https://doi.org/10.1016/j.envsoft.2013.09.031.
- Ghosh, R.S., Dzombak, D.A., Luthy, R.G. (1999), "Equilibrium precipitation and dissolution of iron cyanide solids in water", *Environ. Eng. Sci.*, **16**(4), 293-313. https://doi.org/10.1089/ees.1999.16.293.
- Ibrahim, K.K., Syed, M.A., Shukor, M.Y., Ahmad, S.A. (2016), "Biological remediation of cyanide: A review", *BIOTROPIA-The Southeast Asian J. Tropical Biology*, **22**(2), 151-163. http://dx.doi.org/10.11598/btb.2015.22.2.393.
- Johnson, C.A. 2015. "The fate of cyanide in leach wastes at gold mines: An environmental perspective", *Appl. Geochem.*, **57**, 194-205. https://doi.org/10.1016/j.apgeochem.2014.05.023.
- Jung, J., Shin, B., Lee, J.W., Park, K.Y., Won, S., Cho, J. (2019), "Pilot scale membrane separation of plating wastewater by nanofiltration and reverse osmosis", *Membr. Water. Treat.*, 10(3), 239-244. https://doi.org/10.12989/mwt.2019.10.3.239.
- Lanza, M.R., Bertazzoli, R. (2002), "Cyanide oxidation from wastewater in a flow electrochemical reactor", *Ind. Eng. Chem. Res.*, **41**(1), 22-26. https://doi.org/10.1021/ie010363n.
- Lee, C.-G., Song, M.-K., Ryu, J.-C., Park, C., Choi, J.-W., Lee, S.-H. (2016), "Application of carbon foam for heavy metal removal from industrial plating wastewater and toxicity evaluation of the adsorbent", *Chemosphere*, **153**, 1-9. https://doi.org/10.1016/j.chemosphere.2016.03.034.
- Li, T., Xiao, K., Yang, B., Peng, G., Liu, F., Tao, L., Chen, S., Wei, H., Yu, G., Deng, S. (2019), "Recovery of Ni (II) from real electroplating wastewater using fixed-bed resin adsorption and subsequent electrodeposition", *Front. Env. Sci. Eng.*, **13**(6), 91. https://doi.org/10.1007/s11783-019-1175-7.
- Ly, N., Nguyen, T., Zoh, K.-D., Joo, S.-W. (2017), "Interaction between Diethyldithiocarbamate and Cu (II) on Gold in Non-Cyanide Wastewater", *Sensors*, **17**(11), 2628. https://doi.org/10.3390/s17112628.
- Mekuto, L., Ntwampe, S.K., Akcil, A. (2016), "An integrated biological approach for treatment of cyanidation wastewater", *Sci. Total. Environ.*, **571**, 711-720. https://doi.org/10.1016/j.scitotenv.2016.07.040.
- Smith, M.J., Heath, A.G. (1979), "Acute toxicity of copper, chromate, zinc, and cyanide to freshwater fish: effect of different temperatures", *Bull. Environ. Contam. Toxicol.*, 22(1/2). https://doi.org/10.1007/BF02026917.
- Tian, S., Li, Y., Zeng, H., Guan, W., Wang, Y., Zhao, X. (2016), "Cyanide oxidation by singlet oxygen generated via reaction between H2O2 from cathodic reduction and OCI– from anodic oxidation", J. Colloid Interface Sci., 482, 205-211. https://doi.org/10.1016/j.jcis.2016.07.024.
- White, D.M., Pilon, T.A., Woolard, C. (2000), "Biological treatment of cyanide containing wastewater", *Water Res.*, **34**(7),

2105-2109. https://doi.org/10.1016/S0043-1354(99)00362-0.

- Xu, H., Li, A., Feng, L., Cheng, X., Ding, S. (2012), "Destruction of cyanide in aqueous solution by electrochemical oxidation method", J. Electrochem. Sci., 7, 7516-7525.
- wethod", *J. Electrochem. Sci.*, 7, 7516-7525.
 Yu, X., Xu, R., Wei, C., Wu, H. (2016), "Removal of cyanide compounds from coking wastewater by ferrous sulfate: Improvement of biodegradability", *J. Hazard. Mater.*, 302, 468-474. https://doi.org/10.1016/j.jhazmat.2015.10.013.

CC