

Removal of cyanide (CN⁻) in plating wastewater via electro-chemical oxidation

Xin Zhao¹⁾, Minsik Jang²⁾, Jin Woo Cho³⁾, and *Jae Woo Lee⁴⁾

^{1), 2), 4)} *Department of Environmental Engineering, college of Science and Technology,
Korea University, Republic of Korea*

³⁾ *Department of Environmental, Energy & Geoinformatics, college of Engineering,
Sejong University, Republic of Korea*

¹⁾ zhaoxin@korea.ac.kr, ⁴⁾ jaewoo@korea.ac.kr

ABSTRACT

Electrochemical oxidation system was applied to remove the cyanide (CN⁻) in the real plating wastewater. In this study, CN⁻ removal efficiency was investigated under various conditions of operating factors, i.e., current density, electrolyte concentration and reaction time. Electrolyte concentration positively affected the removal of both CN⁻ and 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% at 10 mA/cm². Current density affected the removal efficiency in a different pattern. As current density increased at a fixed electrolyte concentration, CN⁻ removal efficiency increased, while COD removal efficiency decreased probably due to superiority of CN⁻ over other COD matter in the wastewater for direct oxidation.

Keywords: Electrochemical oxidation system, Cyanide, Current density, Electrolyte

1. INTRODUCTION

In the plating process, cyanide (CN⁻) is used in the plating process of gold, silver and copper, to improve the efficiency and quality of plating. However, cyanide released after the plating process reacts with heavy metal ions such as Cu, Ni, Cd, Co, Cr, Fe, Pb and Zn depending on the properties of the plating wastewater (Botz et al., 2005; Dash et al., 2009; Johnson, 2015). Therefore, it must be treated before it is released to aquatic ecosystem.

The electro-chemical oxidation treatment method for cyanide is an efficient and eco-friendly technology because it removes cyanide by using an electron (e⁻). Another advantage is that it can easily handle high concentrations of cyanide. However, most of the electrochemical oxidation processes studied have been limited to wastewater with cyanide concentration of 10 - 15% or more in the wastewater. If the cyanide concentration in the wastewater is low, the removal rate of the cyanide decreases

¹⁾ Research Professor

²⁾ Graduate Student

³⁾ Professor

⁴⁾ Professor, Corresponding author

suddenly (El-Ghaoui et al., 1982). Therefore, it is very important for study of oxidative degradation of low concentration cyanide.

In the present study, lab scale electro-chemical oxidation apparatus was applied to remove the cyanide (CN^-) in the real plating wastewater. The goal of this study was to investigate the effects of current density, electrolyte concentration, and reaction time on removal efficiencies of CN^- and COD.

2. MATERIALS AND METHODS

2.1 Wastewater

The plating wastewater were collected from an electroplating wastewater treatment plant which in Namyangju city, Republic of Korea. The concentration of CN^- , Cl^- , and COD of wastewater were 47.8 ± 6.8 mg/L, 302.3 ± 18.7 mg/L, and 440.8 ± 65.9 mg/L, respectively.

2.2 Batch experiments with electrochemical oxidation system

The batch experiments were carried out in an open electrolytic cell containing double cathodes and anodes (Fig. 1b). $\text{Ti/RuO}_2\text{-IrO}_2$ (Fig.1a) were used as the electrodes which working area was 250.24 cm^2 . The electrolysis of testing solution was performed with an DC power supply (EX 100-18, ODA technologies, South Korea) at constant current density, in square acrylic reactor of 2.5 L capacity (working volume 2 L, Fig. 1c). Homogenization of the electrolysis solution was ensured with a magnetic stirring (400 rpm).

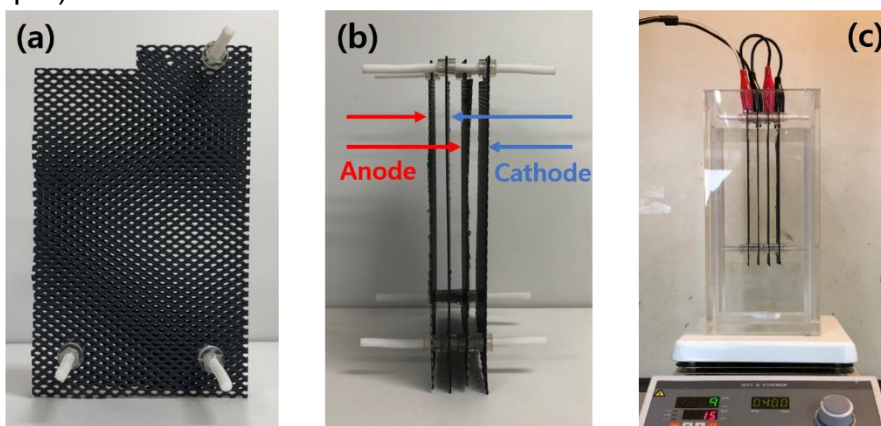


Fig. 1. Electro-chemical oxidation system. (a: $\text{Ti/RuO}_2\text{-IrO}_2$ electrodes; b: electrode array; c: EO apparatus)

Oxidation of plating wastewater was carried out at room temperature and solution pH was adjusted by sodium hydroxide (i.e., $\text{pH}=11$). The oxidation experiments were performed under current-controlled electrolysis conditions, at 4, 6, 8, and 10 mA/cm^2 constant current densities and various electrolyte concentration ranged from 302 to 2,077 mg Cl^-/L .

2.3 Analytical methods

The concentration of cyanide (CN^-), chlorine (Cl^-), and COD were measured by the UV-VIS spectrophotometer (DR 6000, Hach, USA). The analysis methods were shown in Table 1.

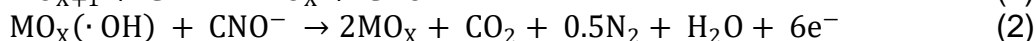
Table 1. Analytical items and methods

Item	Unit	Method	Measurement range (mg/L)	Measurement wavelength (nm)
CN ⁻	mg/L	Pyridine-Pyrazalone	0.002-0.240	612
Cl ⁻	mg/L	Mercuric Thiocyanate	0.1-250	455
COD	mg/L	Potassium Dichromate	3-150	350

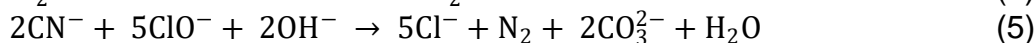
3. RESULTS AND DISCUSSION

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

There were two ways for oxidative degradation of CN⁻, one is direct oxidation and the other is indirect oxidation. CN⁻ could be broken down by direct oxidation without external electrolyte addition in high CN⁻ concentration wastewater (i.e., >10,000 ppm). The reactions for the electrochemical oxidation of CN⁻ as follows:



Electrolyte (i.e., NaCl) were added in solution in order to improve the removal efficiency of CN⁻ in low CN⁻ concentration wastewater. At this point, the CN⁻ could be degraded by indirect oxidation. The detail process can be described as follows (Felix-Navarro et al., 2011):



The CN⁻ concentration of the plating wastewater was not high enough for direct oxidation. Therefore, the applied current density and electrolyte were the main parameters in this study. Tables 2-3 show the effect of current density and NaCl concentration on the removal efficiencies of CN⁻ and COD. The applied current density increased from 4 to 10 mA/cm² resulting, the higher current density the higher CN⁻ removal efficiency (see Table 2). Similar results have been found in the study of cyanide oxidation from wastewater in a flow electrochemical reactor (Lanza & Bertazzoli, 2002). However, the removal efficiency of COD decreased with the increase of the current density (See Table 3). As shown in Tables 2-3, the presence of chloride in the wastewater greatly increased the removal efficiencies of CN⁻ and COD.

CN⁻ reduction degradation occurred, at the same time, a certain amount of COD was removed. Tables 2-3 show the electrochemical removal relationship between CN⁻ and COD. There were competition relations between CN⁻ and COD. And it has nothing to do with the current density and electrolyte concentration. However, considering the energy consumption, the economy and the processing time, the optimal combination of the current density and electrolyte concentration must be considered in the real plating wastewater treatment.

Table 2. CN^- removal efficiency for current density and electrolyte concentrations

Current density (mA/cm^2)	Electrolyte concentrations (mg Cl^-/L)			
	302	746	1,189	2,077
4	36.32	58.98	68.89	87.09
6	43.75	62.09	72.44	92.22
8	47.25	65.12	86.04	95.63
10	49.07	68.30	91.93	98.30

Table 3. COD removal efficiency for current density and electrolyte concentrations

Current density (mA/cm^2)	Electrolyte concentrations (mg Cl^-/L)			
	302	746	1,189	2,077
4	41.00	48.34	52.00	54.81
6	29.41	45.74	46.43	52.08
8	27.63	32.86	45.56	50.00
10	23.53	28.77	42.05	49.50

3.2 Process Optimization

In order to gain a better understanding of the experimental results, the 3-D mesh plots of current density, reaction time, and electrolyte concentration are presented in Fig. 2. Fig. 2a shows the effect of time and electrolyte concentration on CN^- removal efficiency at $10 \text{ mA}/\text{cm}^2$. As can be seen, even if there have enough electrolyte in plating wastewater can be for indirect oxidation of CN^- , but the removal rate of CN^- could not be reached 90% in a short period of time. Fig. 2b shows effect of current density and electrolyte concentration on CN^- removal efficiency at 60 min. Under the condition of sufficient reaction time, higher CN^- removal efficiency can be obtained with the higher the electrolyte concentration within the range of the current density in this study. Fig. 2c shows effect of current density and reaction time on CN^- removal efficiency at $2,077 \text{ mg-Cl}^-/\text{L}$. It is worth nothing that CN^- removal efficiency depends more on the reaction time. We suggest that optimal combination of current density, electrolyte concentration and reaction time is $8\text{-}10 \text{ mA}/\text{cm}^2$, $1,200\text{-}2,100 \text{ mg Cl}^-/\text{L}$, and $40\text{-}60$ mins, respectively.

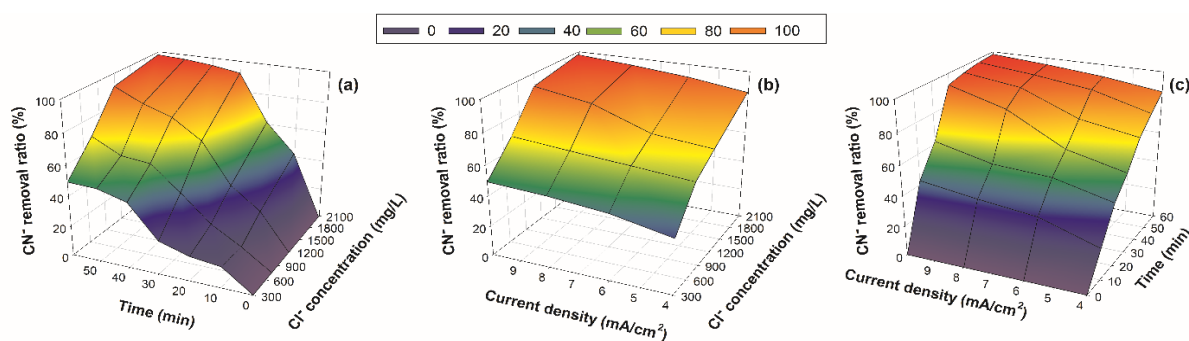


Fig. 2. (a) Effect of time and electrolyte concentration at $10 \text{ mA}/\text{cm}^2$, (b) Effect of current density and electrolyte concentration at 60 min, (c) Effect of current density and time at $2,077 \text{ mg-Cl}^-/\text{L}$.

4. CONCLUSIONS

The effects of current density, electrolyte concentration on removal efficiencies of CN^- and COD were investigated. According to the results, the removal efficiencies of CN^- and COD increased with the increase of the electrolyte concentration and reaction time. The increase of current density could improve the removal rate of cyanide. However, it would reduce the COD removal efficiency. The optimal ranges of the current density, electrolyte concentration, and reaction time were 8-10 mA/cm^2 , 1,200-2,100 mg/L , and 40-60 mins in this study, respectively.

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